Geochemistry and sedimentology of the Lower Silurian Longmaxi mudstone in southwestern China: implications for depositional controls on organic matter accumulation

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ABSTRACT

Spatial and temporal changes of lithofacies and abundance of organic matter in mudstones control distribution of prospective unconventional petroleum reservoirs in a sedimentary basin. Lithofacies characterization is an essential prerequisite to understanding of organic matter accumulation, depositional processes and water column chemistry. This research combines geochemical analyses and detailed sedimentologic observations in order to investigate the depositional controls on organic matter abundance in the prolific black mudstone of the Long-1 Member of the Lower Silurian Longmaxi Formation in southwestern China.

Six primary lithofacies deposited at variable marine water depths and under differing water column chemistry were identified from a 83 m long core based on microscopic observations of sediment texture and structure, and biota, and analyses of total organic carbon (TOC) content, mineralogy, and trace element abundances. Our results show that TOC content is well correlated to biogenic quartz content and the non-detrital components of V, U, Mo, Ni and Cu, suggesting the accumulation of organic matter in the studied mudstone was controlled by high paleoproductivity and anoxic water conditions. The good correlations also suggest that the abundant organic matter was produced by algal blooms, which are typically associated with radiolarian thrive because of the symbiotic relationship between algal and radiolarian. The low Mo/TOC ratios of the three lithofacies formed in deep, anoxic environments were

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4 similar to the ratios of modern sediments deposited in anoxic-euxinic environments,
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6 suggesting moderate basin restriction during deposition. The mudstone in the lower
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8 Longmaxi Formation may be part of the globally abundant organic-rich mudstones of
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10 Early Silurian age, whose depositional mechanism have yet to be fully explored.
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15 The distribution of lithofacies in the studied interval shows an overall trend from
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17 deep water to shallow water depositional environments. We developed a detailed
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19 depositional model to interpret the evolution of depositional environments of the
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21 lower Longmaxi Formation. This study provides an example to how better
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23 characterize unconventional hydrocarbon systems through coupling of rigorous
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25 geochemical and sedimentological analysis.
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34 **Keywords:** mudstone; lithofacies; paleoproductivity; Longmaxi Formation;
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42 **1. Introduction**

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45 Mudstones with high TOC (>1.0 wt.%) and high hydrocarbon yield upon
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47 pyrolysis are good source rocks (e.g., Bissada, 1982; Katz, 2005). Although such
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49 source rocks have very low porosity and permeability, they are in certain cases
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51 prolific unconventional reservoirs because hydraulic fracturing and horizontal drilling
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53 have made commercial hydrocarbon production from such rocks feasible (e.g., Hao et
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al., 2013; Tan et al., 2014; Camp et al., 2016). Rock texture, composition, organic carbon type and amount are often heterogeneously distributed throughout each mudstone unit, making geologic characterization of unconventional reservoirs a requirement that has to be part of each evaluation of gas capacity, optimization of well designs, and stimulation strategy (Bowker, 2007; Hickey and Henk, 2007; Ross and Bustin, 2008; Chen et al, 2011; Guo, 2013; Hart et al., 2013; Romero-Sarmiento et al, 2013; Sondergeld et al., 2013; Tan et al, 2014).

Depositional processes, productivity, and bottom water redox conditions have a profound control on the basin-wide distribution of lithofacies as well as the amount and quality of organic matter (e.g., Pedersen, 1985; Wignall, 1989; Macquaker, 1994; Macquaker et al., 2010; Bowker, 2007; Hickey and Henk, 2007; Loucks and Ruppel, 2007; Schieber et al., 2007; Könitzer et al., 2014). Recent advances using microscopic techniques have allowed significant progress in understanding mudstone heterogeneity and the underlying depositional processes that form fine-grained sedimentary rocks. For example, studies about major gas shale plays in North America, including the Barnett Shale in the Fort Worth Basin and the Marcellus Shale in the Appalachian Basin, have demonstrated that mudstone lithofacies can be well characterized based on mineralogy composition, rock texture, and organic matter content, and are crucial for effective placement of lateral wells and choice of proppant material (e.g., Jarvie et al., 2007; Hickey and Henk, 2007; Loucks and Ruppel, 2007;

Abouelresh and Slatt, 2012; Wang and Carr, 2013). The combination of geochemical and sedimentologic approaches not only brings understanding to paleoproductivity and water chemistry conditions, but also unravels the relationships among organic matter accumulation, depositional processes and water column chemistry (e.g., Jiang et al., 2013; Könitzer et al., 2014).

The Lower Silurian black mudstone of the Longmaxi Formation is encountered throughout the upper Yangtze craton in southwestern China (Fig. 1). The Longmaxi Formation has long been known to be the principal source rock for conventional carbonate petroleum reservoirs of the Carboniferous Huanglong Formation and the Early Permian Qixia and Maokou formations (Zhang et al., 2011). The formation has recently become a target for exploration and development of unconventional shale gas. In the Sichuan Basin, the formation is 229-673 m thick (Chen et al., 2011), and the formation is thermally mature with a measured vitrinite reflectance ($R_0\%$) varying from 1.5% in most parts of the basin to 3.5% in the Fulin-Shizhu area, the eastern Sichuan Basin and the Dazhou-Wanxian area in the northeastern Sichuan Basin (Wang et al., 2009; Liu et al., 2013; Wu et al., 2013). The lower Longmaxi Formation is the most prolific shale interval with a stable gas production rate greater than 60000 m³ per day in some wells in Fulin County. Previous studies of the Longmaxi Formation focused mainly on understanding the mechanisms of gas maturation and accumulation by characterizing the regional structure, sedimentation patterns, and the

micro-pore structures, with the aim of making quantitative gas content predictions (e.g., Su et al., 2007; Yan et al., 2008; Zhang et al., 2011; Guo, 2013; Guo and Liu, 2013; Jiang et al., 2013; Liu et al., 2013; Chen, 2014; Guo et al, 2014; Guo and Zhang, 2014; Yan et al, 2014). A paleoenvironmental description and lithologic framework of the Lower Silurian strata within the Sichuan Basin has been presented elsewhere (e.g., Zhao, 1984; Chen et al, 1998; Wen et al, 2002; Wan and Xu, 2003; Guo et al, 2004; Wang et al, 2008; Jiang et al., 2013). A recent study of the Longmaxi Formation in the southeastern Sichuan Basin has documented sequence stratigraphic control on mudstone heterogeneity (Chen et al., 2015). However, as one of the most important source rocks and unconventional reservoirs in China and a prime example for a Lower Paleozoic deep shelf succession deposited during a worldwide marine transgression after the Early Silurian melting of Gondwana glaciation (Mu et al., 1981; Wang and Mo, 1995; Chen et al., 2004; Guo, 2013; Guo and Zhang, 2014; Yan et al., 2015; Yang et al., 2016), a detailed depositional model that explains the influences of depositional processes and water column conditions on organic matter accumulation in the prolific lower Longmaxi Formation is still lacking.

In this study, we characterize the mudstone-dominated lower Longmaxi Formation in a 83 m long, continuous vertical core from the JY1 Well in Fulin County, which is located in the center of the upper Yangtze craton (Fig. 1). We combine geochemical and sedimentological data collected from closely-spaced shale samples.

Our geochemical analyses include TOC weight percentage, mineralogy compositions based on X-ray diffraction (XRD) analysis, and trace element index. Our sedimentologic study is based on microscopic observations of mineralogy, rock texture and structure, biota, and degree of bioturbation. The new data and lithofacies interpretation are used to develop a depositional evolution model of the lower Longmaxi Formation and understand the depositional controls on organic matter abundance.

2. Geologic setting and stratigraphy

The Sichuan Basin developed on the Precambrian metamorphic basement of the upper Yangtze craton (Zhang et al., 2012a) (Fig. 1 A). The accumulation of basinal, Lower Paleozoic strata was significantly influenced by several important tectonic events during the Sinian to Silurian, including the late Sinian Tongwan movements, the Early Cambrian Xingkai movements, the Late Cambrian Yunan movements, and the Late Ordovician to Late Silurian Kwangsian movements (Tong, 1985; Chen et al., 2013). By the Early Silurian, the tectonics had formed several Kwangsian paleohighs surrounding the Sichuan Basin, including the Chuanzhong uplift in the west, the Xuefeng uplift in the east, and the Qianzhong uplift in the south of the basin (Wang and Mo, 1995; Chen et al., 2006) (Fig. 1 A).

The Lower Silurian Longmaxi Formation is widespread in the Sichuan Basin,

and pinches out toward the Chuanzhong uplift (Guo, 2013; Guo and Zhang, 2014). The formation is dominantly composed of mudstones that were deposited during a major marine transgression after the Early Silurian global glacial ablation (e.g., Mu et al., 1981; Wang and Mo, 1995; Chen et al., 2004). In Fulin County, the Longmaxi Formation is conformably overlain by the Silurian Xiaoheba Formation and is underlain by the Ordovician Wufeng Formation (Guo and Liu, 2013) (Fig. 1 B). The Longmaxi Formation is divided into three members which are, from bottom to top, including the Long-1 Member, which is composed of black mudstone and argillaceous siltstone; the Long-2 Member, which consists of light gray argillaceous siltstone and fine-grained sandstone; and the Long-3 Member dominated by gray mudstone (Chen, 2014). The Long-1 Member is the major gas-bearing interval in the Longmaxi Formation and the focus of this study (Fig. 1).

3. Methods

This study integrates the observations of sedimentary structure and texture, and chemical and biogenic features in core and thin sections of a 83 m long drill core from the JY1 Well, which was drilled by China Petroleum and Chemical Corporation in November, 2012 (Guo and Zhang, 2014). XRD analysis of 80 samples, TOC analysis of 93 samples, and trace element analysis of 88 samples were included to characterize the mudstone lithofacies and assist with the interpretations of depositional

environments. Samples used for these analyses were freshly cut after removing weathered surface of the core.

Thirty-five representative thin sections were manufactured using standard techniques employed for petrographic analysis. Nine thin sections were highly polished by using a Gatan Model 697, Ilion II Broad Beam Argon Milling System. Standard thin section observations were made using an Axio Imager A2m polarizing microscope. A JSM-6700F Field Emission Scanning Electron Microscopy (FE-SEM) was used to identify and analyze the size distribution of pyrite framboids from polished thin sections. Only the pyrite framboids with a primary texture (i.e. uniform microcrystals and abundant intercrystal nanopores) were measured and more than 50 measurements were taken from each thin section to ensure reliability and comparability (cf. Wei et al., 2012).

Mudstone is referred to as a dark gray to black fine-grained sedimentary rock if it contains more than 50% grains in the mud-sized fraction, and siltstone is referred to as a sedimentary rock if it contains more than 50% grains in the silt-size fraction (Lazar et al., 2015). Our sedimentologic descriptions include identifications of fresh color, grain size, sedimentary structures, presence and type of bioclasts, degree of bioturbation, presence and size of pyrite framboids, presence of fractures and concretions, and abundance and orientation of graptolites by following the guidelines in Lazar et al. (2015).

Samples used for trace element analyses were ground in an agate mill down to a grain size smaller than 75 μm . Samples used for XRD analysis were ground to less than 40 μm using an agate mortar to thoroughly disperse minerals. No chemical pre-treatment was employed and the powdered samples were oven-dried at 40°C for 2 days prior to analysis. XRD measurements were performed at the National Research Center for Geoanalysis (NRCGA) Laboratory using a Panalytical X'Pert PRO MPD X-ray diffractometer. Powdered samples were scanned using Cu K- α radiation, automatic divergent and antiscatter slits, and a secondary graphite monochromator with a scintillation counter. The generator settings were 40 kV and 40 mA. Samples were scanned from 5° to 90° with a step size of 0.02°. The resultant diffraction patterns were transferred to ICDD/Jade 9 software with Rietveld refinement to match diffraction peaks with standard minerals in its database. The software carried out several iterations until the best solution was achieved (Bruner et al., 2015). Weight percentage of each mineral type was determined by relative peak height. Whole-rock trace element analyses were conducted using a GBC OptiMass 9500 ICP-TOF-MS at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan. The samples were digested in Teflon bombs with a mixture of HNO_3 and HF before analysis. The digestion procedures are described in Liu et al. (2008). Analytical precision and accuracy were evaluated by duplicate analyses of samples and five international reference standards (AGV-2, BCR-2,

BHVO-2, GSR-5 and GSR-6). The analytical precisions are better than $\pm 5\%$ for U, V, Mo, Ni, Cu. Weight percentage of TOC was analyzed using a LECO CS-200 carbon/sulfur analyzer at the Experimental Geology Research Center of the Wuxi Research Institute of Petroleum Geology, SINOPEC. The precision of the TOC analyses is better than $\pm 0.5\%$ based on repeated analyses of an internal standard.

4. Principles of trace element proxies

Redox and productivity proxies were adopted to infer the water redox condition and marine productivity during the deposition of the Long-1 Member. This research particularly focuses on uranium (U), vanadium (V), molybdenum (Mo), nickel (Ni) and copper (Cu). U, V and Mo are good paleoredox proxies and Ni and Cu are good paleoproductivity proxies (Algeo and Maynard, 2004; Algeo and Lyons, 2006; Algeo and Rowe, 2012). In oxidizing environments, uranium is converted to soluble uranyl (U^{6+}) carbonate, which is readily removed in solution, whereas under anoxic conditions, uranium is reduced and fixed as U^{4+} in sediments (Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993). Therefore, anoxic-nonsulfidic sediments are typically more uranium-enriched than oxic ones. Vanadium presents as V^{5+} in vanadate oxyanions (HVO_4^{2-} and $\text{H}_2\text{VO}_4^{2-}$) in oxic environments, but as V^{4+} and forms vanadyl ion (VO^{2+}) in hydroxyl species ($\text{VO}(\text{OH})_3^-$) or insoluble hydroxide ($\text{VO}(\text{OH})_2$) under mildly reducing conditions (Algeo and Maynard, 2004; Tribovillard

et al., 2006). In marine environments, the V^{4+} ionic species may be deposited in sediments by surface adsorption processes or by the formation of organometallic ligands (Emerson and Huested, 1991; Morford and Emerson, 1999). Under strongly reducing conditions, free H_2S presented in the water column causes vanadium to be further reduced to V^{3+} , which can be taken up by geoporphyrins or be precipitated as solid oxide V_2O_3 or hydroxide $V(OH)_3$ phase (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). Molybdenum primarily presents as molybdate (MoO_4^{2-}) in oxic conditions (Emerson and Huested, 1991; Algeo and Maynard, 2004). In anoxic sediments, molybdate may be released from organic matter through decay by sulfate-reducing bacteria, but molybdenum is mostly deposited as organic thiomolybdates ($MoO_xS_{4-x}^{2-}$) or MoS_4^{2-} when thiomolybdates are further reduced (e.g., Emerson and Huested, 1991; Algeo and Maynard, 2004). Owing to a general enrichment of TOC in marine sediments deposited under anoxic conditions, high molybdenum concentration in sediments have been widely used to indicate restricted depositional conditions (e.g., Meyers et al., 2005; Algeo and Lyons, 2006; Tribouillard et al., 2006; Hammes and Frébourg, 2012). Nickel and copper are delivered to the sea floor mainly in association with organic matter and retained within the sediments, even if the initial organic matter is partially or completely degraded (Nameroff et al., 2002, 2004; Piper and Perkins, 2004).

Terrigenously derived U, V, Mo, Ni, and Cu must be removed in order to restore

the paleoproductivity levels and paleoredox conditions (Algeo and Maynard, 2004; Tribovillard et al., 2006; Chen et al., 2012). Because titanium (Ti) is an indicator of terrigenous sources, it is often employed as a reference element to exclude the detrital contribution of other elements (Timothy and Calvert, 1998; Murray and Leinen, 1996; Ma et al., 2008; Chen et al., 2012). The contents of the non-detrital component of each element is calculated as:

$$\text{Element}_{\text{xs}} = \text{Element}_{\text{total}} - \text{Ti}_{\text{total}} \times (\text{Element}/\text{Ti})_{\text{PAAS}}$$

$\text{Element}_{\text{xs}}$ and $\text{Element}_{\text{total}}$ are the content of non-detrital origin of an element and the total content of the element in a sample, respectively. $(\text{Element}/\text{Ti})_{\text{PAAS}}$ is the content ratio of the element to Ti in Post-Archean Australia Shales (PAAS) (Nance and Taylor, 1976; Taylor and McLennan, 1985).

5. Analytical results

Thin-section examination and XRD analysis show that all the lithologies of the Long-1 Member are primarily composed of quartz, feldspar, carbonate, and clay minerals (Figs. 2 and 3; Table 1; Appendix A). Pyrite is commonly observed in thin sections as framboid, authigenic crystal, and cement. Quartz grains are dominantly of silt size and the diameters are mostly of 63-80 μm . Quartz abundances range from 18 wt.% to 57 wt.%, while clay mineral contents vary between 20 wt.% and 63 wt.% (Fig. 2). Clay minerals consist primarily of illite and mixed-layer of illite/smectite (I/S)

with minor amounts of chlorite. Quartz content decreases upward, whereas clay content increases upward in the Long-1 Member (Fig. 3). Carbonate minerals include both calcite and dolomite, and the content is less than 34 wt.% with an average of 10 wt.% (Fig. 2). The mudstone contains 0.6 wt.%-4.8 wt.% TOC, and TOC is positively correlated with the quartz content (Fig. 4). In the bottom 31 m of the Long-1 Member the TOC content decreases upwards, with overall TOC content being above 2.5 wt.% (Fig. 3).

Statistics of framboid size distributions, including mean, standard deviation, skewness, and maximum framboid diameter, are listed in Table 2. The mean framboid diameters range from 3.5 μm to 7.3 μm . The maximum diameter is less than 13 μm . Box-and-whisker plots are used to describe the variations of size distributions of framboids in our sedimentary succession following previous studies (e.g., Wilkin et al., 1997; Zhou and Jiang, 2009; Tian et al., 2014). The general trends of the V_{xs} , U_{xs} , Mo_{xs} , Cu_{xs} , and Ni_{xs} values are similar to TOC (Fig. 5), and these values are positively correlated to TOC (Fig. 6). The bottom 31 m of the Long-1 Member has the highest V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values and these values decrease upward. The middle 25 m have relatively low and nearly constant V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values. However, the same elements decrease in value within the upper 27 m.

6. Lithofacies and lithofacies assemblages

We subdivide the Long-1 Member of the JY 1 core into six lithofacies based on sedimentary structure and texture, mineralogy, biota, TOC content, and trace element proxies. The average mineral composition and TOC content of each lithofacies are summarized in Table 1.

6.1 Siliceous mudstone (lithofacies 1)

Black siliceous mudstone is the predominant lithofacies within the lower Long-1 Member (Fig. 3). This lithofacies consists of faintly to well laminated mudstone and abundant nonoriented graptolites (Fig. 7 A-C). The grain size is fine mud. The lamination is generally parallel and continuous, and the bedding surfaces are planar and perfectly smooth. Pyrite is present in pyrite laminae (Fig. 7 A), pyrite-filled sponge spicules and radiolarians (Fig. 7 D-E), and small pyrite framboids generally less than 4 μm in mean diameter (Fig. 5, 7 F). Skeletal grains are commonly observed, but no signs of bioturbation are found in this lithofacies. The skeletal grains include mostly radiolarians and some sponge spicules, locally filled by silica or pyrite (Fig. 7 A-C). This lithofacies contains abundant quartz, averaging 46 wt.%. Quartz occurs mostly as rounded microcrystalline grains, and few as angular to subrounded monocrystalline grains (Fig. 7 G). Carbonate content is low with an average of 8 wt.%. Carbonate is present mainly as calcite and dolomite cement with minor amounts of non-skeletal grains scattered within clay matrix. Clay minerals make up 34 wt.% of the mineral content (Fig. 2). This lithofacies has the

highest TOC, averaging 3.8 wt.%, compared to the other five lithofacies (Fig. 2). The V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values are high, and the average values are 152.4 ppm, 13.0 ppm, 34.4 ppm, 67.9 ppm, and 27.6 ppm, respectively (Fig. 5).

6.2 Siliceous clay-rich mudstone (lithofacies 2)

Dark-gray to black siliceous clay-rich mudstone is restricted mainly to the upper part of the lower Long-1 Member and the lower part of the upper Long-1 Member (Fig. 3). The grain size of this lithofacies ranges between fine and medium mud. This mudstone is similar to the siliceous mudstone (lithofacies 1) in many aspects, including abundant small framboids pyrites with a mean diameter of 4-5 μm , presences of nonoriented graptolites, no signs of bioturbation, skeletal fragments of radiolarians and sponge spicules, and low feldspar, calcite and dolomite contents (Fig. 2). This lithofacies is different from the siliceous mudstone (lithofacies 1) in that this lithofacies contains faintly to well laminated clay-rich and detrital quartz-rich mudstone, many horizontal fractures filled by calcite (Fig. 8 A, B), and silty lenses (Fig. 8 C). The lamination is generally continuous, planar and parallel in hand specimen, and continuous, parallel to wavy-parallel laminae are also documented by microscopic observations (Fig. 8 A, B). The silty lenses are generally 100-500 μm thick, and have clear outlines with prominent tapered ends. Some lens greater than 300 μm thick comprise several individual lenses that are grouped together (Fig. 8 D). This lithofacies also contains less abundant graptolites, a higher amount of

clay (45 wt.%), and a lower amount of quartz (33 wt.%) than the siliceous mudstone lithofacies (Fig. 2). The quartz grains are dominantly microcrystalline with a small amount of angular to subrounded, monocrystalline quartz grains of very fine silt size scattered within an organic-rich clay matrix (Fig. 8 D). Carbonate is present mainly as calcite and dolomite cement. The average TOC of this lithofacies is 2.6 wt.%. The V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values are lower than those of the siliceous mudstone (lithofacies 1), and are 118.5 ppm, 8.5 ppm, 20.9 ppm, 47.8 ppm, and 28.4 ppm, respectively (Fig. 5).

6.3 Silty-shaly interlaminated mudstone (lithofacies 3)

Dark to light gray silty-shaly interlaminated mudstone is the predominant lithofacies within the middle Long-1 Member, and occurs occasionally in the upper Long-1 Member (Fig. 3). The grain size of this lithofacies varies from medium to coarse mud. The lithofacies is organized into 0.5- to 10-mm-thick laminae and beds of structureless clay-rich mudstones intercalated with 0.2- to 8-mm-thick laminae and beds of normally graded siltstone (Fig. 9 A). The siltstone laminae have erosional or sharp bases and generally vary laterally in thickness (Fig. 9 A, B). The silt-size grains are predominantly angular to subrounded monocrystalline quartz grains. This lithofacies contains oriented graptolites (Fig. 9 C) and few radiolarians, sponge spicules. Fecal strings can be observed in several parts of this lithofacies. These fecal strings are generally characterized by irregular tube-like structures that cut across and

disrupt some beddings, and sometimes follow bedding surfaces and are U-shaped (Fig. 9 D, E). Most of these fecal strings are 0.25-0.45 mm in diameter, and are preferentially filled with material that is similar in composition to the host sediment. These fecal strings are referred to as *Phycosiphon incertum* (cf. Wetzel and Uchman, 1998a; Egenhoff and Fishman, 2013). This lithofacies is sparsely to moderately bioturbated, with a bioturbation index between 2 and 3 (cf. Lazar et al., 2015). Carbonate is present mainly as calcite and dolomite cement. Authigenic pyrite are observed in this lithofacies and have diameters ranging between 8 μm and 300 μm (Fig. 9 B, F). The mean diameter of pyrite framboid presented in this lithofacies is larger than 7.0 μm (Fig. 9 F). The average TOC of this lithofacies is 1.6 wt.%, and the V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values are of 63.7 ppm, 5.2 ppm, 9.7 ppm, 26.5 ppm, and 9.7 ppm, respectively (Fig. 5).

6.4 Siliceous-dolomitic mudstone (lithofacies 4)

Dark gray siliceous-dolomitic mudstone occurs as thin beds in the lower and upper Long-1 Member (Fig. 3). The grain size of this lithofacies varies from fine to medium mud. This lithofacies is faintly laminated, and the laminae are 100-200 μm thick, mostly even, and to a lesser extent wavy (Fig. 9 G). Dolomite content of this lithofacies is in the range of 13 wt.%-31 wt.% (Fig. 2). Quartz and dolomite grains are present as microcrystalline crystals of very fine silt size. Dolomite also occurs as dolomitization of detrital grains (Fig. 9 H). Abundant small pyrite framboids with a

mean diameter of 3.5 μm are present in this lithofacies. Skeletal grains of radiolarians and sponge spicules are commonly observed, and both have a microcrystalline quartz shell and are locally replaced by dolomite or pyrite. The V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} , and Cu_{xs} values are high, of 107.3 ppm, 13.5 ppm, 28.6 ppm, 48.9 ppm, and 23.1 ppm, respectively. The mean TOC is 2.9 wt.%. These values are similar to those of the siliceous clay-rich mudstone (lithofacies 3).

6.5 Clay-rich mudstone (lithofacies 5)

Light gray clay-rich mudstone (Fig. 10 A-E) occurs in the upper part of the upper Long-1 Member (Fig. 3). The grain size of this lithofacies is medium to coarse mud. This lithofacies rarely contains any graptolite debris, but abundant burrows and fecal strings in thin sections (Fig. 10 B, D, E). Burrows typically constitute unbranched, lenticular-shaped and horizontal, and have shape margin that are readily distinguished from the surrounding rock based on color and sediment fill (Fig. 10 B). This type of burrow is referred to as *Planolites* (e.g., Wetzel and Uchman, 1998a; Zonneveld et al. 2010; Egenhoff and Fishman, 2013). Most of the burrows are 0.22- to 1.6-mm across and generally less than 0.15 mm in height, and contain mainly clay with minor amount of fine-grained siliceous grains and organics (Fig. 10 B). Fecal strings of *Phycosiphon incertum* are 0.2-0.8 mm in diameter, and are preferentially filled with material that is similar in composition to the host sediment (Fig. 10 D, E). These fecal strings are generally characterized by irregular tube-like structures that cut across and

disrupt most of beddings and retain a vertical to subvertical component and can also change direction. This lithofacies is moderately to strongly bioturbated with bioturbation index varying between 3 to 4 (cf. Lazar et al., 2015). This lithofacies is rich in clay, averaging ~57 wt.% (Fig. 2). Quartz grains are mainly silt-sized, monocrystalline, and subrounded to angular in shape (Fig. 10 C). Carbonate content is very low, occurring mostly as fracture fillings and concretions (Fig. 10 F). Individual concretions are ellipsoidal or irregularly shaped, and range from 4 cm to 15 cm in diameter (Fig. 10 G). The fractures are irregular and occur in the matrix as well as in the concretions. The lithofacies has the largest mean framboid diameter among all the studied lithofacies. TOC in this lithofacies is low, with an average of 1.4 wt.%. The V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values are also low, and are 57.0 ppm, 5.0 ppm, 9.9 ppm, 19.7 ppm, and 8.9 ppm, respectively.

6.6 Dolomitic- siliceous mudstone (lithofacies 6)

Light gray dolomitic mudstone occurs as thin beds mainly in the middle and upper Long-1 Member, and occasionally in the lower Long-1 Member (Fig. 3). The grain size of this lithofacies is fine to medium mud. This lithofacies contains less than 24 wt.% quartz and more than 23 wt.% dolomite (Fig. 2). The quartz grains are monocrystalline, and of very-fine silt size. The dolomite occurs as rhombohedral grains with diameters of 3-10 μm (Fig. 11 A, B). This lithofacies has a low content of calcite which is only presents as cement. This lithofacies also contains abundant

Phycosiphon incertum, which have tube diameters generally less than 1 mm, and obscure the bed continuity (Fig. 11 C, D). The bioturbation index in this lithofacies varies between 3 and 4 (cf. Lazar et al., 2015). This lithofacies has low TOC, with an average of 1.5 wt.%, and low V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} and Cu_{xs} values of 39.1 ppm, 4.7 ppm, 8.1 ppm, 13.4 ppm, and 10.4 ppm, respectively.

6.7 Lithofacies assemblages

According to the overall trend of lithofacies distribution within in the core, and changes of TOC and geochemical proxies, we divide the Long-1 Member of the Longmaxi Formation into three lithofacies assemblages (Fig. 3). The siliceous mudstone-dominated lithofacies assemblage (LA 1) occurs in the bottom 31 m of the core, and contains predominantly siliceous mudstones (lithofacies 1) and thin beds of siliceous clay-rich mudstone (lithofacies 2), siliceous-dolomitic mudstone (lithofacies 4), and dolomitic-siliceous mudstone (lithofacies 6). The bed thickness of the siliceous mudstone (lithofacies 1) increases upwards, reaching a maximum of 6.5 m near the top of the assemblage. This assemblage has the highest TOC content, with an average of 3.4 wt.%. The silty-shaly interlaminated mudstone-dominated lithofacies assemblage (LA 2) occurs in the central 25 m of the core, and includes predominantly silty-shaly interlaminated mudstones (lithofacies 3) and some thin beds of siliceous clay-rich mudstone (lithofacies 2) and dolomitic-siliceous mudstone (lithofacies 6). This assemblage has low TOC values, in the range of 1.3 wt.%-2.2 wt.%. The

clay-rich mudstone-dominated lithofacies assemblage (LA 3) occurs in the top 27 m of the core, and includes predominantly clay-rich mudstones (lithofacies 5), and some thin beds of siliceous clay-rich mudstone (lithofacies 2), dolomitic- siliceous mudstone (lithofacies 6), silty-shaly interlaminated mudstone (lithofacies 3), and siliceous-dolomitic mudstone (lithofacies 4). TOC in this assemblage decreases upward from ~2.8 wt.% to 0.6 wt.%.

7. Discussion

7.1 Interpretation of depositional processes

7.1.1 Siliceous mudstone (lithofacies 1)

The presence of good lamination and fine sediment grain size suggest that the siliceous mudstone was deposited predominantly by suspension sedimentation (Loucks and Ruppel, 2007; Abouelresh and Slatt, 2012). Microcrystalline quartz within the shale is most likely formed as a diagenetic product of opal from radiolarians and sponges (Bowker, 2003; Papazis, 2005; Fishman et al., 2015; Camp et al., 2016). Angular-subrounded monocrystalline quartz is generally from terrigenous sources (Zuffa et al., 1980; Underwood et al., 2005; Liang et al., 2012; Marsaglia and Nolasco, 2016), and most likely represent eolian input during deposition (cf. Egenhoff and Fishman, 2013). Biogenic quartz is a major component of this lithofacies and is far more abundant than detrital quartz, suggesting high productivity of the ocean water, and the depositional setting is deep and far from terrigenous input (Fishman et al., 2015). The absence of bioturbation in this

lithofacies indicates highly dysoxic to anoxic conditions that were hostile to benthic life (Egenhoff and Fishman, 2013). The enrichment of U_{xs} , V_{xs} and Mo_{xs} reflect euxinic conditions at the sediment-water interface or in the water column (Algeo and Maynard, 2004; Tribovillard et al., 2004, 2006). Due to the high Mo enrichment in this lithofacies, bottom-water conditions were most likely sulfidic (Torres et al., 1996; Tribovillard et al., 2004; 2006). High Ni_{xs} and Cu_{xs} values indicate relatively high paleoproductivity because the two elements were delivered to the sea floor mainly in association with organic matter (Algeo and Maynard, 2004; Tribovillard et al., 2006). The size range of pyrite framboids has been used as a key to understand the redox state of the water column chemistry (Wilkin et al., 1996, 1997; Bond et al., 2004; Loucks and Ruppel, 2007). The high abundance of very small pyrite framboids with a mean diameter lower than 4 μm indicates the water column, at least for some periods, was euxinic or anoxic. A crossplot of mean framboid size versus standard deviation is shown in Fig. 12 for the purpose of paleoredox interpretation (cf. Wilkin et al., 1996; Zhou and Jiang, 2009; Tian et al., 2014). Three samples of this lithofacies fall within the anoxic field, indicating persistently oxygen-poor conditions in the bottom water. The interpretation of an anoxic-euxinic seafloor is additionally supported by elevated TOC values, which suggest that the flux of organic matter outpaced the degradation of organic matter by microbial community (Loucks and Ruppel, 2007). Therefore, we suggest that the siliceous mudstone (lithofacies 1) was deposited in euxinic-anoxic

deep water within the oxygen minimum zone, and the paleoproductivity was relatively high in surface waters above the zone.

7.1.2 Siliceous clay-rich mudstone (lithofacies 2)

The presence of detrital quartz-rich laminae suggests a somewhat higher terrigenous detrital influx, and a more dynamic seafloor energy regime. The silty lenses most closely resemble examples found in the Proterozoic Rampur Shale in India, and the Mississippian Edale Shale Group in England, which were previously considered as clasts (Schieber et al., 2007; Könitzer et al., 2014). Imbricated lenses or aggregates of lenses were deposited in areas of low flow velocity (Schieber et al., 2010) or were bundled while in the bed load and deposited once they exceeded a critical weight to be maintained in motion (Könitzer et al., 2014). Two samples of this lithofacies fall within the anoxic field on a crossplot of mean framboid size versus standard deviation (Fig. 12). The interpretation of anoxic water column condition is also supported by the absence of bioturbation in this lithofacies. The depositional environment of siliceous clay-rich mudstone is interpreted as the top part of the oxygen minimum zone, which has most likely been the inner shelf near storm-wave base. The apparent abrupt change to shallower water depth is most likely the result of a sea-level drop, which may have promoted oxygenated bottom waters with low TOC and U_{xs} (McManus et al., 2005; Tribovillard et al., 2006). Therefore, we infer the siliceous clay-rich mudstone (lithofacies 2) was deposited under euxinic to anoxic

condition in somewhat shallower water depth than the siliceous mudstone (lithofacies 1).

7.1.3 Silty-shaly interlaminated mudstone (lithofacies 3)

Abundant detrital quartz suggests a higher terrigenous input compared to the preceding two lithofacies. The presence of *Phycosiphon incertum* is interpreted to reflect possibly highly oxygenated conditions on the seafloor and in at least the upper few millimeters of the deposited sediments throughout much of this facies (Wetzel and Uchman, 1998a, b; Egenhoff and Fishman, 2013). Two samples of this lithofacies fall within the dysoxic-oxic field on the crossplot of mean framboid size versus standard deviation (Fig. 12). The interpretation of a somewhat oxygenated water column condition is consistent with the observation of sparse to moderate bioturbation in this lithofacies. The orientation of graptolites and erosional contacts (Fig. 9B, C) indicate the presence of erosive currents during deposition (O'Brian, 1996). The repetitive nature of siltstone and mudstone laminae suggests periodic high-energy depositional events followed by periods of low-energy deposition (Singh, 2008; Egenhoff and Fishman, 2013). During high-energy events such as storms, currents scoured irregular erosional surfaces into mud-rich substrates and deposited siltstone laminae in the low-energy flow (Egenhoff and Fishman, 2013). The siltstone laminae with variable thickness and erosional bottom contacts are most likely the product of discontinuous sediment accumulation by bedload transport (Macquaker et al., 2010;

Egenhoff and Fishman, 2013; Lazar, 2015). The silt-size quartz grains likely were concentrated by storm-induced currents through bedload transport, and such currents generally slow down farther basinward (Egenhoff and Fishman, 2013). Interlaminated mudstone and siltstone have been previously interpreted as storm deposits in a number of studies (e.g., Schieber, 1989, 1999; Ghadeer and Macquaker, 2012; Harazim and McIlroy, 2015), without the presence of characteristic traction-induced structures typically produced by storms, such as hummocky cross-stratification (Aigner and Reineck 1982; Schieber 1990; Könitzer et al., 2014). Storms may have caused resuspension of near shore silt and mud, and these diluted suspensions were likely transported by offshore-directed underflows depositing graded silt and mud below storm wave base (Pedersen, 1985; Wignall, 1989; Cattaneo et al., 2003; Kwon et al., 2006). It is possible that dilute offshore-directed density flows or even turbidity currents were an important sediment transport mechanism to the siltstones, and the lack of Bouma sequences suggests sediment deposition occurred at great distances from the sediment source (Mulder and Alexander, 2001; Loucks and Ruppel, 2007). Dysoxic-oxic conditions and low productivity represented by the low values of V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} , Cu_{xs} , and TOC (Fig. 5) suggest that the ocean water in which this lithofacies was deposited was not deep, and those low values do not support the interpretation of distal density or turbidity flows. Therefore, we suggest that the silty-shaly interlaminated mudstone (lithofacies 3) was deposited in dysoxic-oxic,

relatively shallow water below storm wave base.

7.1.4 Siliceous-dolomitic mudstone (lithofacies 4)

Continuous, wavy-parallel to discontinuous, wavy-nonparallel lamination implies sediment reworking by wave activity (Lazar et al., 2015). Very small pyrite framboids with a mean diameter smaller than 4 μm indicates that the water column was euxinic or anoxic, which is supported by one sample of this lithofacies falls within the anoxic field on the crossplot of mean framboid size versus standard deviation (Fig. 12), and the absence of bioturbation. The depositional environment is similar to that of the siliceous clay-rich mudstone (lithofacies 2) and siliceous mudstone (lithofacies 1), and is within the oxygen minimum zone. The prominent microcrystalline dolomite grains most likely replaced lime-mud and scattered skeletal grains in the sediment during early diagenesis (cf. Hickey and Henk, 2007). Dolomite replacement occurs predominantly in restricted marine or in the intertidal-supratidal zone where freshwater is mixed with saline seawater or where seawater is forced upward and downward through the sediment when sea-level fluctuates (Folk and Land, 1975; Carballo et al., 1987). The dolomitization in this lithofacies may have occurred during early diagenesis when sea-level significantly dropped. Therefore, we consider that the siliceous-dolomitic mudstone (lithofacies 4) was deposited in restricted water column with anoxic bottom water condition and the surface water had rather high paleoproductivity.

7.1.5 Clay-rich mudstone (lithofacies 5)

This lithofacies was most likely deposited below fair-weather wave base because of the fine sediment grain size and lack of sedimentary structures formed by waves. The ellipsoidal or irregular carbonate concretions and fractures with calcite fillings in this lithofacies were formed during early diagenesis when the sediment was exposed to meteoric water during the subsequent sea-level drop, and were compacted during burial (Woodland, 1984; Lash and Blood, 2004; Dong et al., 2008). The presence of abundant *Phycosiphon incertum* and *Planolites* argues for not anoxic and possibly highly oxygenated seafloor conditions (Wetzel and Uchman, 1998a, b; Egenhoff and Fishman, 2013). The presence of large pyrite framboids, and the relationship between mean framboid size and standard deviation (Fig. 12) also suggest that the clay-rich mudstone (lithofacies 5) was deposited in more oxygenated seafloor conditions than the silty-shaly interlaminated mudstone (lithofacies 3). The low TOC and Ti-normalized trace element abundances further suggest that this lithofacies was deposited under relatively high oxic bottom water conditions and the paleoproductivity in the surface water was rather low. Therefore, depositional paleowater depth of clay-rich mudstone (lithofacies 5) must have been shallower than that of silty-shaly interlaminated mudstone (lithofacies 3) given the intensity of bioturbation and possibility of exposure to meteoric water during sea-level drops are higher for clay-rich mudstone (lithofacies 5).

7.1.6 Dolomitic- siliceous mudstone (lithofacies 6)

The dolomite rhombs, similar to the ones in the siliceous-dolomitic mudstone lithofacies, are products of early diagenesis. Depositional paleowater depth of the dolomitic-siliceous mudstone (lithofacies 6) should be below fair-weather wave base and is similar to that of the clay-rich mudstone (lithofacies 5). The presence of abundant *Phycosiphon incertum*, intense bioturbation, and the low TOC and Ti-normalized trace element abundances suggest that this lithofacies was deposited in shallow and oxic bottom water where the depositional energy and paleoproductivity were low.

7.2 Depositional model

The overall trend of the lithofacies assemblage shows a general change from anoxic deep-water environment to oxic shallow water environment based on the integration of rock description and geochemical trends for each lithofacies assemblage. Here we propose a model that explains the depositional processes of the Long-1 Member in the studied core. The model is also compatible with other interpretations of depositional environment in the much broader eastern Sichuan Basin (Fig. 13).

During the Early Paleozoic, the Yangtze platform was at low latitudes and the climate was tropical and subtropical. Glacial ablation during the Early Silurian caused rapid sea-level rise (Wilde et al., 1996; Chen et al., 2004), and marine upwelling

based on carbon isotope studies (Lü et al., 2004, Young et al., 2008, Chen et al., 2012). The early stage deposition of the Long-1 Member must have occurred during a sea-level highstand (Fig. 13 A). Marine upwelling provided rich nutrients to surface water and promoted blooms of radiolarians and algae, which caused high productivity in the surface water, and enrichment of biogenic silica and TOC when the suspended sediments settled gradually in deep euxinic and anoxic water (Caplan and Bustin, 2001; Kametaka et al., 2005; Lazurus, 2005; Loucks and Ruppel, 2007; Chen et al., 2012). Previous studies suggested that most of the upper Yangtze platform was covered by an epicontinental marine shelf of the upper Yangtze Sea during the Early Paleozoic (Tan et al., 2014), and the shelf became a restricted marine basin when the surrounding paleohighs were uplifted during the Early Silurian (Mu et al., 1981; Chen et al., 1987; Wang and Mo, 1995; Chen et al., 2004; 2006). The water depth of the marine basin was estimated to be 50-450 m based on the presence of different species of radiolaria, graptolite, brachiopod and sponge spicule, and Cerium anomaly (He, 2002; He et al., 2002). A recent study by Jiang et al. (2013) suggested that the depositional environment of the lower Longmaxi Shale may have been located below shelf depth, and occurred in outer shelf and bathyal plain environments. Our study shows that the deposition of the lower Long-1 Member in Fulin County was below storm wave base and within the oxygen minimum zone with a depth generally greater than ~200 m. Our interpretations are based on a lithofacies study that better clarifies

the water depths at which the prolific Long-1 Member was deposited compared to previous studies. At the end of this early stage deposition, sea-level began to fall when siliceous clay-rich mudstone (lithofacies 2) was deposited in the upper part of the lower Long-1 Member (Fig. 5). The magnitude of sea-level drop was small, <50 m, and the studied area remained the top part of the oxygen minimum zone, but became closer to the shoreline.

During the middle stage, storm-induced bottom currents and bedload transport frequently brought large amounts of terrigenous quartz grains (Fig. 9A, B, D, E) into the study area and the upper Yangtze Sea became relatively unrestricted. This coincided with a sea-level fall and the study site was most likely located above the oxygen minimum zone (Fig. 13 B). The depositional setting during this time was slightly below storm-wave base because the silty laminae in the silty-shaly interlaminated mudstone (lithofacies 3) represent distal storm deposits. Deposition continued during this lowstand until the end of the middle stage.

A marine transgression occurred at the initiation of the late stage of the Long-1 Member (Fig. 5), and sea-level rose to approximately its pre-highstand position. Change to lithofacies assemblage suggests the basin returned to be restricted again. Associated with this sea-level rise, the depositional setting in the study area changed back to anoxic conditions. At the end of this transgression, sea-level began to fall when the clay-rich mudstone (lithofacies 5) was deposited in the upper part of the

Long-1 Member and the study area remained between fair-weather wave base and storm wave base when sea-level dropped (Fig. 13 C). During marine lowstands, limited amount of nutrients would be available to marine biota, and marine communities were restricted to nutrient recycling (Könitzer et al., 2014), thus the paleoproductivity must have been low. The reduced fluxes of organic matter to the seafloor due to low primary productivity likely decreased the consumption of dissolved oxygen in water column, promoting establishment of oxic water conditions and further debasing preservation potential of organic matter (Loutit et al., 1988).

7.3 Mechanisms of TOC enrichment in the Long-1 Member

High organic matter content in mudstone may result from a high rate of terrigenous organic matter supply or marine organic matter production, enhanced preservation under anoxic conditions or due to limited degradation, or some combination of these factors (Demailson and Moore, 1980; Bohacs et al., 2005; Katz, 2005). The organic matter in the Long-1 Member is regarded as predominantly marine-derived for three reasons. First, the studied mudstone is highly siliceous with quartz grains being predominantly biogenic (Fig. 7D-E, 7G). The quartz content correlates well with the TOC values (Fig. 4), and the biogenic quartz-rich siliceous mudstone-dominated lithofacies assemblage (LA 1) has the highest amount of TOC. Taken together, this suggests that the production of organic matter in the Long-1

Member is related to the production of biogenic quartz. Siliceous organisms are mostly radiolarians and sponge spicules (Fig. 7D-E). Previous research demonstrates that radiolarian blooms can cause simultaneous enrichment of biogenic quartz and total organic carbon (DeMaster, 1981; Heinze et al., 2003; Xiang et al., 2013). Secondly, the Ni_{xs} and Cu_{xs} values, as good marine paleoproductivity proxies, are well correlated with TOC (cf. Harazim et al., 2015) (Fig. 6), suggesting that the organic matter was mainly produced in the ocean. Guo (2013) studied microscopic constituents of the organic matter assemblage in the Long-1 Member, and concluded that the organic matter is predominantly composed of amorphous alginite and sapropel (type I kerogen), which typically form in anoxic marine or lacustrine paleoenvironments (Fig. 4 in Guo, 2013).

We suggest that the high algae productivity is an important contributor to the organic matter in the Long-1 Member. Studies in modern marine environments show that spherical radiolarians contain large numbers of autoeciousness algae inside their tests by supplying living space and nutrition for the algae, while the algae are used as food by the radiolarians, thus forming a symbiotic dependence (Caron et al., 1995; Dennett et al., 2002; Wei et al., 2015). Studies in modern marine environments also demonstrate that the autoeciousness algae inside radiolarian contribute a large part to overall marine primary productivity in the photic zone (Anderson et al., 1989; Caron et al., 1995; Dennett et al., 2002; Lazarus et al., 2006, 2008). The algae usually sink to

the ocean bottom along with the radiolarians and are preserved in sediment after the radiolarians die (Dennett et al, 2002). Despite the presence of siliceous sponges in the studied interval, their contribution to bulk TOC is considered to be small given their low abundance (Xiang et al., 2013).

The organic matter enrichment in the Long-1 Member is also a result of enhanced preservation potential under anoxic conditions. As paleoredox proxies, the V_{xs} and U_{xs} values are well correlated with TOC (Fig. 6), suggesting that the preservation of the organic matter in the Long-1 Member was strongly influenced by paleoredox conditions of the water. TOC values are the lowest in the silty-shaly interlaminated mudstone-dominated lithofacies assemblage (LA 2) and the top of the clay-rich mudstone-dominated lithofacies assemblage (LA 3). The dominant lithofacies in these assemblages were deposited in oxic water conditions suggesting a high oxygen availability in shallow water, which in turn should not favor the preservation of organic matter (cf. Burdige, 2007). Adsorption of carbon compounds onto clay mineral surfaces favors burial and preservation of organic matter (Kennedy et al., 2002), which may also cause organic matter enrichment. However, the TOC of the clay-rich mudstone (lithofacies 5) and siliceous clay-rich mudstone (lithofacies 2) are low, while the clay contents are high (Figs. 2, 3), suggesting that adsorption to clay mineral surfaces may not influence the organic matter accumulation in the studied interval.

7.4 Mo–TOC constraints on Early Silurian hydrography

The ratio of redox sensitive trace metals such as Mo to TOC has been previously used to investigate metal replenishment and basin restriction, with low Mo/TOC (ppm/wt.%) ratio indicating strongly restricted conditions (Algeo and Lyons, 2006). This approach to hydrographic analysis is applicable only to anoxic environments exhibiting some degree of water mass restriction (Algeo and Lyons, 2006; Algeo and Rowe, 2012). A crossplot for Mo versus TOC in the siliceous mudstone (lithofacies 1), siliceous clay-rich mudstone (lithofacies 2) and siliceous-dolomitic mudstone (lithofacies 4) that were deposited in anoxic environments shows a linear trend (Fig. 14). The average Mo/TOC ratio of the three lithofacies is similar to the ratios of sediments in the Framvaren Fjord and the Cariaco Basin, which were deposited in anoxic and euxinic environments (Algeo and Rowe, 2012). The ratio, however, is larger than the ratios of the Black Sea sediment and the Barnett Shale in the Fort Worth Basin in U.S.A., both of which were deposited in stratified shallow ocean basins (Algeo and Rowe, 2012). The ratio of the three lithofacies in the Long-1 Member is smaller than that of the sediment deposited in the Saanich Inlet, which is reported to be anoxic during most time of the year, but oxic during late summer and early fall (Zaikova et al., 2010). These comparisons suggest that the upper Yangtze Sea was stratified and at least intermittently anoxic during the Early Silurian, but not

as severely restricted as the Black Sea or the Fort Worth Basin. The restriction may have resulted from the isolation of the upper Yangtze Sea from the open oceans by surrounding tectonic barriers formed by the Kwangsi orogeny (Chen et al., 2013). This inference is consistent with previous studies that suggest that the upper Yangtze Sea, which was covering most of the upper Yangtze platform during the Early Paleozoic, was an epicontinental sea surrounded by paleohighs (Mu et al., 1981; Chen et al., 1987; Wang and Mo, 1995; Chen et al., 2004; 2006; Tan et al., 2014).

In addition to the local tectonic configuration, the Early Silurian basin hydrography may favor high productivity of organic matter. Many organic-rich, marine mudstones were deposited globally during the Early Silurian, such as in northern Africa and Arabia, northern and western Europe, and southwestern China (e.g., Leggett, 1980; Dabard and Paris, 1986; Thickpenny and Leggett, 1987; Lüning et al., 2000). The global abundance of organic-rich mudstone of Early Silurian age in general may be influenced by the combination of three factors. Firstly, intense upwelling along continental shelf margins caused by winds may have triggered high productivity and enhanced oxygen-deficiency in the ocean (Lüning et al., 2000). Secondly, a rapid marine transgression associated with warm climatic conditions during the Early Silurian flooded continental margins and many glacially formed paleodepressions (Schandelmeier, 1988). Wind-driven vertical circulation may have promoted the development of a stable thermocline, which placed bottom waters in

deep shelf areas below the level of recycling and subsequently triggered anoxic conditions (Leggett, 1980; Thickpenny and Leggett, 1987). Finally, atmospheric oxygen pressure was generally low during the Early Paleozoic (Berner, 1994), which may have caused low dissolved oxygen in ocean water and intensified anoxic conditions. The mudstone in the lower Longmaxi Formation may only be part of the globally abundant organic-rich mudstone of Early Silurian age, and the formation mechanism is yet to be fully explored.

8. Conclusions

The prolific mudstones of the Lower Silurian Long-1 Member of the Longmaxi Formation in the Sichuan Basin, southwestern China have been studied to understand lithofacies variability and underlying reasons for enhanced organic matter accumulation. We identified six lithofacies that were deposited at different water depths and proximity to shoreline and under different degree of basin stratification. Our results show that biogenic quartz is abundant, and TOC are well correlated to quartz content and non-detrital trace element proxies (V_{xs} , U_{xs} , Ni_{xs} and Cu_{xs}), suggesting the enrichment of organic matter in the Long-1 Member was controlled by changing paleoproductivity and bottom water redox conditions in a periodically stratified marine basin. We suggest synchronous enrichment of biogenic quartz and TOC were caused by algae blooms.

Three of the lithofacies, including the siliceous mudstone (lithofacies 1), siliceous

clay-rich mudstone (lithofacies 2), and siliceous-dolomitic mudstone (lithofacies 4), have an average TOC larger than 2.6 wt.% and high non-detrital trace element abundances, suggesting they were deposited in variable depths of stratified, deep, euxinic-anoxic water with high paleoproductivity. The low Mo/TOC ratios of the three lithofacies suggest that the marine basin was moderately restricted by surrounding paleohighs. The other three lithofacies, including the silty-shaly interlaminated mudstone (lithofacies 3), clay-rich mudstone (lithofacies 5), and dolomitic-siliceous mudstone (lithofacies 6), have an average TOC less than 1.6 wt.% and low trace element abundances, suggesting they were deposited in variable depths of shallow, oxic water with low paleoproductivity. Based on the association of different lithofacies, we divided the Long-1 Member into three lithofacies assemblages. We then developed a depositional model to explain the evolution of the deposition environments of the Long-1 Member.

This study presents a case study showing that combination of rigorous geochemical analyses and sedimentologic observations is a powerful approach to interpret the depositional environments of apparently homogenous mudstone successions and allow the identification of the depositional controls on organic matter accumulation in Paleozoic sedimentary basins in China and elsewhere.

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Figure captions

Figure 1. (A) Isopach map showing distribution of the Long-1 Member of the Longmaxi Formation and location of the studied core (JY1 Well) in the upper Yangtze

Craton. EF represents the location of the cross section in Fig. 13. (B) Stratigraphic column of the Longmaxi Formation and the gamma-ray log of the JY1 Well. Modified from Guo (2013), Guo and Zhang (2014).

Figure 2. Ternary diagram showing the mineralogy compositions of the six lithofacies in the Long-1 Member.

Figure 3. Lithofacies log, mineral content, and TOC of the Long-1 Member in the JY1 Well.

Figure 4. Linear correlation between TOC and quartz content of the Long-1 Member in the JY1 Well.

Figure 5. Plots showing framboid-size variations; general trends of the V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} , and Cu_{xs} values and TOC; and inferred sea-level changes based on the interpretation of lithofacies in the Long-1 Member in the JY1 Well. Framboid-size variations are displayed in box-and-whisker plot, which shows the first and third quartiles at the ends of the box, the mean as a vertical line inside of the box, and the maximum and minimum at the ends of the whiskers.

Figure 6. Linear correlations between TOC and the V_{xs} , U_{xs} , Mo_{xs} , Ni_{xs} , and Cu_{xs} values of the Long-1 Member in the JY1 Well.

Figure 7. Characteristic sedimentologic observations of the siliceous mudstone (lithofacies 1) (A-G). (A) Core photograph at 2387.8 m showing faint to good lamination and abundant pyrite laminae (arrows). (B) Core photograph at 2387.8 m showing nonoriented graptolite. (C) Thin-section photograph at 2397.1 m showing faint lamination. (D) Thin-section photograph at 2390.0 m showing pyrite-filled sponge spicules (arrows). (E) Thin-section photograph at 2389.3 m showing pyrite-filled radiolarians (arrows) and silica-filled radiolarians (white arrows). (F) SEM image of very small pyrite framboids at 2399.0 m. (G) SEM image at 2399.0 m showing many microcrystalline quartz grains (arrows) and intergranular pores (white arrows).

Figure 8. Characteristic sedimentologic observations of the siliceous clay-rich mudstone (lithofacies 2) (A-D). (A) Core photograph at 2381.4 m showing siliceous clay-rich mudstone with continuous, planar lamination, and many horizontal fractures filled with calcite (arrows). (B) Thin-section photograph at 2406.16 m showing interlaminated clay-rich laminae (double-sided arrow) and detrital quartz-rich laminae. (C) Core photograph at 2348.4 m showing silt lenses within a clay matrix (arrows).

(D) Thin-section photograph at 2337.27 m showing lenticular fabric. Some lenses appear to be imbricated and in larger aggregates (outlined in yellow). Fine silt-sized quartz (arrows) scattered in a clay- rich matrix.

Figure 9. Characteristic sedimentologic observations of the silty-shaly interlaminated mudstone (lithofacies 3) (A-F), and siliceous-dolomitic mudstone (lithofacies 4) (G-H). (A) Core photograph at 2368.5 m showing interlaminated silty (light gray) and shaley (black) laminae in lithofacies 3. White dashed lines separate four depositional cycles. The abundance of silty lamina increases upward in each cycle. (B) Thin-section photograph at 2366.7 m showing siltstone laminae with variable thickness, erosional base (dashed lines), and some large authigenic pyrite (circled) in lithofacies 3. (C) Core photograph at 2368.5 m showing oriented graptolites in lithofacies 3. Arrow points to orientation. (D) Thin-section photograph at 2373.52 m showing examples of *Phycosiphon incertum* that disrupt lamina continuity. (E) Sketch map superimposed on the photomicrograph of D showing the vertical and subvertical components of some *Phycosiphon incertum* and their dissection to laminae. (F) SEM image of relatively large pyrite framboids (diameter = 9 μm) (white arrow) and authigenic pyrite (yellow arrow) at 2376.1 m. (G) Thin-section photograph at 2403.6 m showing faint planar to wavy laminations and detrital quartz grains of silt-very fine sand size within an organic-rich clay matrix in lithofacies 4. (H) Thin-section

photograph at 2402.55 m showing dolomitization of detrital grains (arrow) in lithofacies 4.

Figure 10. Characteristic sedimentologic observations of the clay-rich mudstone (lithofacies 5) (A-G). (A) Core photograph at 2332.5 m showing light gray clay-rich mudstone with massive bedding. (B) Thin-section photograph at 2330.46 m showing horizontal, *Planolites* burrows (surrounded by dash lines). Note that the burrow fill is lighter in color than the surrounding mudstone. (C) Thin-section photograph at 2340.82 m showing silt-size quartz that are angular to subrounded. (D) Thin-section photograph at 2334.62 m showing example of *Phycosiphon incertum* that disrupt lamina continuity. (E) Sketch map superimposed on the photomicrograph in D showing the vertical and subvertical components of some *Phycosiphon incertum* and their dissection to laminae. (F) Core photograph at 2341.5 m showing fractures filled by calcite. (G) Core photograph at 2341.3 m showing an irregularly shaped calcareous concretion with fractures filled by calcite and pyrite.

Figure 11. Characteristic sedimentologic observations of the dolomitic-siliceous mudstone (lithofacies 6) (A-D). (A) Thin-section photograph at 2335.08 m showing abundant very fine silt size dolomite grains (arrows) embedded in a clayey matrix. (B) Thin-section photograph at 2335.08 m showing rhombohedral dolomitic crystals

(arrows) with diameters of 3-10 μm . (C) Thin-section photograph at 2335.08 m showing examples of *Phycosiphon incertum*. (D) Sketch map superimposed on the photomicrograph in C.

Figure 12. Crossplot of mean framboid size versus standard deviation of the Long-1 Member. Framboid size data are in Table 2.

Figure 13. Depositional model showing the depositional processes of the Long-1 Member at variable water depths. The location of cross section EF is shown in Fig. 1A. Note here the cross section does not extend to other paleohighs surrounding the marine basin.

Figure 14. Comparison of Mo-TOC relationship between the results of this study and those of modern anoxic silled-basin environments and the Fort Worth Basin. The Mo-TOC regression lines are from Rowe et al. (2008) and Algeo and Rowe (2012). Note that all Mo/TOC ratios reported here are in units of 10^{-4} , equivalent to ppm/wt.%.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

A) Siliceous mudstone-dominated lithofacies assemblage

B) Silty-shaly interlaminated mudstone-dominated lithofacies assemblage

C) Clay-rich mudstone-dominated lithofacies assemblage

Figure 14

Table 1

Table 1. Lithofacies and their average mineral compositions and TOC wt.% in the Long-1 Membe

Quantity of samples	Lithofacies	Average mineral content (wt.%)						TOC (wt.%)
		Quartz	Feldspar	Calcite	Dolomite	Clay mineral	Pyrite	
21 XRD, 23 TOC	Siliceous mudstone	46	8	4	4	34	4	3.8
14 XRD, 16 TOC	Siliceous-clayey mudstone	33	10	4	4	45	4	2.6
22 XRD, 27 TOC	Silty-shaly interlaminated mudstone	33	12	5	5	43	2	1.6
5 XRD, 5 TOC	Siliceous-dolomitic mudstone	37	8	4	21	27	3	2.9
12 XRD, 13 TOC	Clayey mudstone	30	8	2	2	57	1	1.4
6 XRD, 9 TOC	Dolomitic mudstone	24	9	3	23	39	2	1.5

Table 2**Table 2.** Statistics of the pyrite framboid size distribution in the Long-1 Member

Depth (m)	Lithofacies	Mean (μm)	Standard deviation	Skewness	MFD (μm)	Numbers measured
2334.8	Clay-rich mudstone	7.3	2.7	0.3	13	58
2343.1	Siliceous-dolomitic mudstone	3.5	1.4	0.4	7	52
2348.8	Siliceous clay-rich mudstone	4.2	1.3	0.5	8	54
2356.2	Silty-shaly	7.0	2.3	0.6	12	58
2376.1	interlaminated mudstone	7.2	2.2	0.7	12	57
2384.0	Siliceous clay-rich mudstone	4.6	1.4	0.3	8	53
2388.6		3.6	1.1	0.2	6	51
2399.0	Siliceous mudstone	3.8	1	0.4	6	52
2406.2		3.5	1.2	0.4	7	85

MFD: maximum framboid diameter.