Environmental Redox Changes of the Ancient Sea in the Yangtze Area during the Ordo-Silurian Transition

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Abstract: Extensive organic-matter (OM) rich facies (black shales) occur in the Ordo-Silurian boundary successions in the Yangtze area, South China. To investigate the redox changes of the Yangtze Sea during the Ordo-Silurian transition, two OM sections (Wangjiawan in Yichang, Hubei Province, and Sanjianguan in Zhangjiajie, Hunan Province) straddling the Ordo-Silurian boundary are studied. The measurements finished in this study include contents of the total organic carbon (TOC), pyrite sulphur, and different species of Fe, including dithionite-extractable Fe (FeD), pyrite Fe (FeP), HCl-extractable Fe (FeH), and total Fe (FeT), in black shales, as well as other redox proxies, such as the S/C ratio, the ratio between highly reactive Fe (FeH = FeD + FeP) and FeT, and the FeD/FeT ratio, known as the degree of pyritization (DOP). In the Wangjiawan section, the Middle Ashgill sediments have high FeH/FeT ratios (0.20–0.77; avg. 0.45), high DOP values (0.21–0.72; avg. 0.54), and a relatively constant sulfur content independent of the organic carbon content. By the contrast, the mid-early Hirnantian deposits generally have low FeH/FeT ratios (0.10–0.35; avg. 0.21), low DOP values (0.11–0.40; avg. 0.28), and S/C values are clustering on the normal marine value (S/C = 0.36). The late Hirnantian and early Rhuddanian deposits, similar to those of the Middle Ashgill deposits, are characterized by high FeH/FeT ratios (0.32–0.49; avg. 0.41), high DOP values (0.46–0.68; avg. 0.53) and fairly constant sulfur contents. These data suggest the occurrences of marine anoxia on the Yangtze Sea shelf during intervals of the Mid Ashgill, Late Hirnantian and Early Rhuddanian, and ventilated and oxygenated marine conditions during the mid-early Hirnantian time. The mid-early Hirnantian ventilated event was concomitant with the global glacial period, likely resulted from the glacio-eustatic sea-level fall and subsequent circulation of cold, dense oxygenated waters upon the shelf seabed. Accordingly, the abrupt change from oxygenated to anoxic marine waters from the late Hirnantian and the early Rhuddanian were resulted from the post-glacial rise of eustatic sea level. Combined with the data from Sanjianguan section near the subemergent highland, salinity stratification of water columns are strongly evidenced by very low S/C ratios (0.00–0.08, avg. 0.02), low FeH/FeT ratios (0.10–0.37, avg. 0.27), low DOP values (0.01–0.27, avg. 0.10), and TOC contents (0.72%–4.27%, avg. 2.55%). Under this circumstance, the anoxic water columns could have formed beneath the halocline, above which desalinized waters formed. In the Wangjiawan section, TOC contents are generally high (0.94–9.32%, avg. 4.44%), but low (0.35%–2.12%, avg. 1.29%) in the mid-early Hirnantian that is coincident with the oceanic oxic stage, together with relation of the organic contents to the stratal thickness, suggesting that the accumulation of the organic matter was mainly controlled by the oxygen levels of the water columns; on the other hand, productivity and depositional rate may also have played a role in the organic accumulation and preservation.

Key words: oceanic anoxia, water column stratification, Fe-S geochemistry, organic carbon, Late Ordovician, Early Silurian, Yangtze Sea, South China

1 Introduction

Organic Matter (OM) rich black shales deposited in marine environments are considered as the most important source rocks of the hydrocarbon and sources of massive sulphides, evaporites and other economic mineral deposits. Therefore, understanding their origins is important for the
exploration of hydrocarbon and other mineral deposits. Schlanger and Jenkyns (1976) proposed that the globally distributed OM black shales were formed by the Oceanic Anoxic Events (OAEs); however, there are still many controversies over the origins of OM-rich black shale successions. Other researchers (Federsen and Calvert, 1990; Calvert et al., 1992; Calvert and Pedersen, 1992; Guo et al., 2006), however, proposed that the accumulation of OM-rich sediments is mainly controlled by bioproductivity, rather than by the anoxia.

The Ashgill to Rhuddanian is one of the well-studied stratigraphic successions in China, from which the biotic mass extinction and recovery were well documented (Wang et al., 1993; Wang et al., 1997). Organic-rich black shales also extensively deposited across the Ordovician-Silurian successions in the Yangtze Sea and elsewhere over the world. The Ordovician-Silurian organic-rich black shales of the Yangtze Sea have been studied extensively in terms of depositional environments, stratigraphy, and tectonics, but no unambiguous conclusion on the depositional mechanism has been reached (Chen, 1984; Zhang et al., 2000). Ma et al. (2004) proposed that extensive black shales formed in response to foreland basin subsidence associated with the Caledonian Orogeny. Other researchers proposed eustatic global sea-level rise and sediment starvation as a major factor for the deposition of black shales in Yangtze area (Zhang et al., 2000; Chen et al., 2004; Yang et al., 2007).

This study aims to unravel the relation of ocean oxic-anoxic changes to the accumulation of organic matters in black shales. To investigate the redox and bioproductivity changes of the Yangtze Sea during the Ordovician transition, the organic carbon content (TOC), pyrite sulfur content, and Fe species—including dithionite-extractable Fe (Fe(DT)), pyrite Fe(FeP), HCl-extractable Fe(FeHCl), as well as total Fe(FeT), are measured, from which S/C ratios (Berner, 1984; Lenventhal, 1987), FeHCl/FeT ratios (Calvert and Karlin, 1991; Geritse, 1999), FeDT/FeP ratios (Raiswell and Canfield, 1998) and DOP values (Raiswell and Berner, 1985; Shen et al., 2002) are further used to constrain the anoxic conditions.

2 Geological Setting

South China block appeared to have been as a distinct plate from the mid-Paleozoic, but was still attached to the margins of Gondwana during the Late Ordovician to Early Silurian (Metcalfe, 1994). The Yangtze Platform, a part of the South China block during the Ordovician-Silurian transition, was covered by a broad epeiric sea bordered to the deeper marginal sea southeast, which was probably connected to the open oceans (Wang et al., 1993). As the sea level dropped, uplifts expanded and coalesced, leading the Yangtze Platform to be largely isolated from the open sea (Fig. 1) (Mu et al., 1981; Chen, 1984).

In this study, two outcrop organic-rich sections across the Ordovician-Silurian boundary are chosen, they are the Wangjiawan section in Yichang, Hubei Province and the Sanjianguan section in Zhangjiajie, Hunan Province. The Wangjiawan section, located at a relatively deep environment, is the recommended type section for the
Ordo-Silurian boundary in China, in which the biozones were well established (see Fig. 2; Mu et al., 1986; Wang et al., 1993). In this section, the Lingxiang micritic limestone is overlain by Wufeng black shale (5.3 m thick), which is overlaid by the Kuanyinchiao muddy shelly limestone horizontally (0.2 m thick). Going upwards, the Longmachi brown–black shales with thin sandstone beds (650.5 m thick) occur. The Sanjiaoguan section, palaeogeographically close to the subemergent height (Fig. 1), deposited in a relatively shallow depositional setting, thereby the Kuanyinchiao Formation was absent (Fig. 3).

3 Samples and Analytical Methods

Thirty-six samples collected from a ca. 6.0 m thick sequence in the Wangjiawan section and twenty-three samples from a ca. 5.8 m thick sequence in Sanjiaoguan section have been provided for the present study. All samples, pulverized to <200 mesh sizes, were split in several parts for organic carbon content, pyrite sulfur and iron species analyzed. Organic carbon analyses were determined by the combustion method of Krom and Berner (1983). In this method, one subsample is analyzed for total (inorganic plus organic) carbon (by combustion) and another is analyzed for inorganic carbon (by acid evaporation-gravimetry). The difference represents the organic carbon. The relative precision of TOC analysis is better than 1%.

Various iron extraction methods were used to characterize the reactivity of the sedimentary iron toward sulfide. Thus, sediments were extracted with dithionite (Canfield, 1989), which removes iron oxide/oxyhydroxide phases (lepidocrocite, ferrhydrite, goethite, and hematite).
Fig. 3. Concentrations of pyrite sulfur, Fe\textsubscript{308}/Fe\textsubscript{T} ratios and DOP data for the Sanjiaguan section. Some graptolite stratigraphy is uncertain. Symbols names as in Fig. 2.

but only relatively small amounts of Fe from iron silicates (Shen et al., 2002). For this extraction a buffered solution was prepared from 58.8 g/L tri-sodium citrate dihydrate (C\textsubscript{6}H\textsubscript{5}Na\textsubscript{2}O\textsubscript{7}·2H\textsubscript{2}O) and 20 mL/L acetic acid. Individual extractions were carried out using 10 mL buffer mixed with approx 0.2 g sample, and finally approx 0.5 g sodium dithionite was added. Reproducibility of replicate analyses was generally better than 4% (Canfield, 1989; Raiswell et al., 1994; Shen et al., 2002). Dithionite-extractable iron is termed Fe\textsubscript{D}.

Abundances of HCl-leachable iron were determined following the method outlined by Berner (1970) and Leventhal and Taylor (1990). A 1 mol HCl solution was prepared and 0.1 g of sediment reacted with 10 mL of acid for 24 hr. The precision of the analysis is generally <7% of the reported values. The iron removed with cold HCl is termed Fe\textsubscript{H}. The concentrations of dithionite-extractable and HCl-extractable iron were determined by atomic absorption using an air-acetylene flame.

Total reducible sulfur (TRS, mostly pyrite) was extracted by the Cr-reduction method of Canfield et al. (1986). Precisely weighed powered sample reacts with CrCl\textsubscript{3} to extracted sulfur as H\textsubscript{2}S under a stream of purified nitrogen gas. The liberated H\textsubscript{2}S quantitatively precipitates as ZnS in a zinc-acetate solution, then converts to Ag\textsubscript{2}S by adding a silver-nitrate solution. The Ag\textsubscript{2}S precipitate is
quantitatively filtrated, dried in an oven, and weighed precisely. The content of pyrite sulfur is thus determined gravimetrically, and the amount of Fe bound in pyrite (Fe\textsubscript{py}) was calculated with a molar Fe:S ratio of 1.2 (Shen et al., 2002). Finally, total iron content (Fe\textsubscript{T}) is analyzed using an automatic X-ray fluorescence spectrometer (XRF-1500) using fusion glasses made from a mixture of sample powders and flux (Li\textsubscript{3}B\textsubscript{4}O\textsubscript{6}) in the proportion of 1:5. The precision of the analysis is generally <5% of the reported total iron values.

In this study, several parameters (C/S, Fe\textsubscript{total}/S, Fe\textsubscript{Fe}/Fe\textsubscript{T} and DOP) were used to characterize the anoxic conditions under which the black shales deposited. Quantitatively, highly reactive iron (Fe\textsubscript{RX}) is equivalent to the iron already formed into pyrite (Fe\textsubscript{py}) plus the iron remaining in the sediment that could still be incorporated into pyrite during continued early diagenesis (Fe\textsubscript{D}) (Shen et al., 2002). Therefore, Fe\textsubscript{RX} = Fe\textsubscript{py} + Fe\textsubscript{D}. The degree of pyritization (DOP) is defined as DOP = Fe\textsubscript{py}/(Fe\textsubscript{py} + Fe\textsubscript{D}) (Raiswell et al., 1988).

4 Results and Discussion

4.1 Organic carbon-sulfur relationships

TOC values of the samples from the Wangjiawan section generally vary from 0.35% to 9.32% (avg. 3.72%); but those from the mid-lower Hirnantian have lower TOC values (avg. 1.29%). Abundance of pyrite sulfur is variable, but is generally lower than 1.0% throughout the entire sequence. The S/C ratios of the samples from the mid-lower Hirnantian are ~0.36, those from other intervals are consistently low (<0.36). It is noted that there is no covariance between the TOC and sulfur contents, except for the positive correlation between the samples from the mid-lower Hirnantian (Fig. 4).

The TOC and pyrite sulfur contents in black shales from the Sanjiaguan section vary from 0.37% to 4.27%, from 0.01% to 0.21%, respectively. Sulfur contents are fairly consistent and independent of the TOC variations (Figs. 3 and 4). The S/C ratios of black shales are very low (0.00-0.10, avg. 0.02).

The Organic carbon-sulfur (C-S) relationship is a quick method that commonly used to assess the oxygen level of bottom waters (Hofmann et al., 2000). This method is based on the covariance of organic carbon and sulfide sulfur, which results from the metabolism of organic carbon and consecutive reduction of sulfate by sulfate reducing bacteria to form hydrogen sulfides that reacts with iron to form pyrite in the sediments (Leventhal, 1987). Berner (1984) proposed that sediments deposited underoxic marine conditions generally yield S/C ratio of 0.36. In this case, the S/C ratios in the mid-early Hirnantian samples thus point to the oxygenated bottom waters under which the marine sediments deposited. Euxinic environments are either characterized by S/C ratios higher than 0.36 with positive intercepts on the S-axis in S-C plots (Leventhal, 1983; Berner, 1984), or by a fairly constant sulfur content independent of the organic carbon content (Hofmann et al., 2000). The latter case occurs mainly in euxinic environments where sulfur fixation via pyrite formation is limited by the availability of reactive iron, hence, pyrite precipitate ceases after the reactive iron is exhausted (Raiswell and Berner, 1985; Dean and Arthur, 1989). Samples from the mud ashgill, late Hirnantian and Early Rhuddanian, although yield fairly low S/C ratios, have a fairly constant sulfur content independent of the organic carbon content, this is probably a reflection of prevalence of euxinic bottom water and iron-limitation conditions.

S/C ratios of black shales from Sanjiaguan section are substantially lower than 0.36 (Fig. 4). These data are rather similar to those from the modern fresh water lake sediments (Berner and Raiswell, 1984), suggesting a desalination of surface water columns there. Based on geochemical analysis of the Wufeng shales in the northwestern Yangtze
area, Cheng and Wang (1991) provided samples of local low salinity water deposit. In the light of the S/C ratio method, they analyze four samples from the upper Wufeng Formation at Fucheng, southern Shanxi. Similar as our results, all ratios for the samples fall into the region, which is lower than normal marine sediments. Another sample dealing with salinity analysis is from the west corner of the Yangtze area at Hongya and Hanyuan given by Feng et al. (1993). They investigated the synthetic index of palaeosalinity by using the ratios of magnesium to aluminum, strontium to barium, and the amount of chlorine. They concluded that there were two desalination events in this area at mid Ashgill (D.complexus zone) and Hirnantian.

### 4.2 Sulfur-iron relationships

In the Wangjiawan section, pyrite sulfur content is linearly related to the concentration of reactive Fe in the mid Ashgill, the late Hirnantian and early Rhuddanian sediments (regression $r^2 = 0.68$); the regression line has a slope that is slightly lower than that for the ideal pyrite (Fig. 5). By comparison, sediments in the Sanjiaguang section show a different relationship between pyrite sulfur and reactive Fe. The regression line for this group of the samples has an intercept on the Fe$_{oxy}$-axis (Fig. 5).

If all the iron ions were reactive, the S/Fe$_{oxy}$ ratio would be constant at 1.15, a signature of stoichiometric pyrite. If all the iron ions were not reactive, the constant S/Fe$_{oxy}$ ratio would be less than 1.15 that is proportional to the amount of unreactive iron (Dean and Arthur, 1989). The pattern of the relatively constant S/Fe$_{oxy}$ ratios in the Wangjiawan section, along with little or no correlation between organic carbon and sulfur contents discussed above, suggesting an iron-limited system in anoxic water columns during the mid Ashgill, late Hirnantian and early Rhuddanian intervals.

Similar iron-limited anoxic environments were reported by Dean and Arthur (1989), Arthur and Sageman (1994) and Hofmann et al. (2000). All of the examples reported by these authors are characterized by iron-limited pyrite formation and high amounts of organic matter still preserved in the sediments. The high amount organic matter suggests that continued sulfate reduction beyond the point at which most reactive iron was exhausted and mineralized as pyrite (Hofmann et al., 2000).

Gerdes (1999) documented that SO$_4^{2-}$ concentration in the water column exerts an important control on the Fe/S ratio. The degree of sulfidation of Fe can be determined mainly by the diffusional flux of SO$_4^{2-}$, which in turn depends partly on the SO$_4^{2-}$ concentration in bottom water. In the Sanjiaguang section, all samples have very low pyrite sulfur values, likely resulting from the oxic environments with low sulfate concentrations in water columns, so that an intercept on the Fe$_{oxy}$-axis of S/Fe$_{oxy}$ regression line is produced by the presence of a large fraction of acid-soluble iron, probably in the form of oxyhydroxides (Calvert and Karlin, 1991).

### 4.3 Fe species

The present data of the various iron species from the Wangjiawan section are summarized in Figs. 2 and 5 and Fig. 6, respectively, together with some other information that will be of help in discussing their significance. Samples from the Middle Ashgill, late Hirnantian and early Rhuddanian deposits are characterized by high Fe$_{oxy}$/Fe$_T$ (0.32–0.77, avg. 0.44) and DOP (0.46–0.72, avg. 0.55) values except for two samples with low Fe$_{oxy}$/Fe$_T$ (0.2 and 0.29) and DOP (0.21 and 0.41) values. By contrast, samples from the mid-early Hirnantian deposits yield low Fe$_{oxy}$/Fe$_T$ (0.1–0.35, avg. 0.21) and DOP (0.11–0.40, avg. 0.28).

The data of various iron species from Sanjiaguang section are summarized in Figs. 3, 5 and 6, respectively. All samples have low Fe$_{oxy}$/Fe$_T$ (0.1–0.37, avg. 0.27) and DOP (0.01–0.27, avg. 0.10) (Fig. 3).

The relationship between highly reactive iron (Fe$_{oxy}$) and
total iron (Fe$_{\text{Tot}}$) provides a potentially important indication of ancient depositional conditions (Raiswell and Canfield, 1998). Sediments deposited under oxygenated water columns have Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios do not exceed 0.38. By contrast, sediments deposited in euxinic water columns have Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios typically exceeding 0.38 (Raiswell and Canfield, 1998; Shen et al., 2003). In the Wangiawan section, most samples from the Middle Ashgill (only except for two samples) are dominated by high Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios (0.38-0.77, avg. 0.50), indicating that the Yangtze Sea was generally under the euxinic condition, but water columns might have been oxygenated in short-term interval due to the fluctuation of O$_2$/H$_2$S interface (Fig. 2). Those samples from the mid-early Hirnantian interval are dominated by low Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios (0.1-0.35, avg. 0.21), indicating oxic bottom waters environment similar to the modern normal marine environments. The high Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios (0.38-0.49, avg. 0.42) from the late Hirnantian and early Rhuddanian black shales, excepted for one low value of 0.32, suggest a persistent euxinic depositional environment. In the Sanjiang section, the Fe$_{\text{Tot}}$/Fe$_{\text{T}}$ ratios (0.1-0.37, avg. 0.27) indicate full oxygenated depositional environments (Fig. 3).

The degree of pyritization (DOP) has also been calibrated as a paleoenvironmental indicator of bottom water oxygenation (Raiswell et al., 1988). Values of DOP that <0.45 are generally found for the sediments depositing from oxic bottom water, whereas values that >0.45 are found for the sediments depositing in very low bottom water oxygen or under euxinic conditions (Raiswell et al., 1988; Shen et al., 2002). In Wangiawan section, high DOP values as stated above indicate that sediments from the late Hirnantian and early Rhuddanian formations deposited in a predominantly euxinic depositional environment, however, the water column was at least partly oxygenated during the mid Ashgill. During the Hirnantian interval, the water column was full oxygenated. In the Sanjiang section, the low values of DOP (Fig. 3) show that deposition took place in aerobic waters (full oxygenated water). The DOP is genetically related to the Fe$_{\text{T}}$/Fe$_{\text{T}}$ ratio. This is because high DOP values, as often reported in euxinic environments, require an enhanced deposition of Fe$_{\text{T}}$ compared to oxic bottom water settings (Canfield et al., 1996; Shen et al., 2002). Direct comparison between DOP and Fe$_{\text{T}}$/Fe$_{\text{T}}$ values provides a highly concordant picture; most samples from the middle Ashgill, upper Hirnantian and lower Rhuddanian strata plot together in a quadrant defined by Fe$_{\text{T}}$/Fe$_{\text{T}}$ >0.38 and DOP >0.45. These samples are all distinctive from the quadrant containing the samples from the Sanjiang section and the Hirnantian interval of the Wangiawan section, which deposited under oxic conditions (Fig. 6). One sample with high DOP value but low concentration of Fe$_{\text{T}}$ from the early Rhuddanian interval is an exception (Fig. 6). However, taken as a whole, both DOP values and the Fe$_{\text{T}}$ contents of the middle Ashgill, late Hirnantian and early Rhuddanian samples clearly indicate a euxinic environment in which they deposited.

4.4 Paleo-redox conditions

Geochemical parameters used as paleo-oxygenation indices, combined with other sedimentary and biotic indicators, can reveal changes in oxidation state of the ocean-floor waters throughout the intervals studied. The occurrences of well laminated, graptoleite-bearing black shales in the mid Ashgill, upper Hirnantian and lower Rhuddanian, by themselves, indicate an anoxic/dysoxic depositional environment. Chen et al. (2004) documented that the calcareous Kuanynchiao Formation (lower-mid Hirnantian) is an extensively-burrowed biotlastic horizon with abundant fragments of brachiopods, trilobites, crinoids, and minor terrigeneous admixtures. These features point to an agitated environment influenced by current activities. Well-developed benthic faunas in this Formation are a clear indicator of oxygenated seafloor (Fig. 7a). Wang et al. (1993) interpreted a greater diversity of benthic fauna in the Hirnantian interval in the eastern part of the Yangtze Platform as reflecting an increase of ventilation in that area. By contrast, the overlying Lungmachi Formation (lower Rhuddanian) has pelagic organism, such as sponge spicules (Fig. 7b), and that indicates an anoxic environment; the underlying Wufeng Formation (Ashgill) has poor benthic faunas, and shows an oxygen-deficient environment.

Concentrations of redox-sensitive trace elements have been used as proxies to reconstruct the oxygenation level in Yangtze Sea. Zhang et al. (2000) revealed the sharp change of redox-sensitive elements through the Ord-Silurian
transition and interpreted the changes of oxidation state in the ocean-floor waters. Wang et al. (1992) interpreted the increased concentrations of As, Sb and U in the eastern portions of the Yangtze Sea, at Jixian as representing reducing conditions at the base of the *persculptus* zone, coincide with the disappearance of benthic faunas at the base of the Lungmachi Formation as the sea level rose and the seafloor became anoxic.

Fig. 7. (a) Brochiopod dominated benthic assemblages from the early-mid Hirnantian; (b) spongia spicule from the early Rhuddanian; both at Wangjiawan section, Yichang, Hubei Province.

Our geochemical results discussed above show a consistent scenario for the regional distribution of anoxia at the Ordovician and Silurian transition in the Yangtze Sea. The development of anoxic conditions occurred mainly in the deep water column during the middle Ashgill, late Hirnantian and early Rhuddanian intervals (Wangjiawan section). Anoxic bottom water conditions are indicated by high TOC and relative constant pyrite sulfur content (Fig. 4). Pyrite precipitate was limited by the availability of the reactive iron at these intervals as indicated by a constant Fe/S ratio (Fig. 5). The presence of anoxic deep water column is further substantiated by the ratio between highly reactive Fe (Fe_{org}) and total Fe (Fe_{T}) and the degree of pyritization (DOP). The relatively high DOP values and the poor correlation between DOP and organic carbon concentrations in the Wangjiawan section also suggest that pyrite formation in this anoxic environment is limited by insufficient Fe (Fig. 8). Minute difference of the deposition environment among the mid Ashgill, the late Hirnantian and the early Rhuddanian existed. In the middle Ashgill interval, sediment deposition took place in the environments that fluctuate between oxygenated and anoxic bottom waters. However, in the late Hirnantian and the early Rhuddanian intervals, all sediment depositions took place in an anoxic environment.

In the Sanjiaguan section, anoxic environment did not develop. As discussed above, S/C ratios in the sediments of the Sanjiaguan section display the relationships typically for the sedimentary environments where sulfate is insufficient. The presence of the low sulfate water column is further substantiated by the ratio of Fe_{org}/Fe_{T} and DOP values of the Sanjiaguan section. Low Fe_{org}/Fe_{T} and DOP values suggest that iron has not been the limiting factor in the sedimentary pyrite formation. The content of organic carbon reaches values of up to 4.27%, indicating that pyrite formation is not limited by the availability of organic matter. Analogous to Phanerozoic conditions, these values could be indicative for low sulphate environment (Berner, 1984), where a proportionally higher percentage of organic carbon is preserved in the sediment instead of being consumed during sulphate reduction. In the case of Yangtze Sea, the sediments of the Sanjiaguan section were formed...
under bottom water conditions similar to brackish water, however, the sediments of the Wangjiawan section were formed under bottom water conditions similar to normal marine environments. This would imply that a sulphate gradient existed from the “shallow” water areas (Sanjiaoguan section, which is close to the subemergent high) to the “deep” water areas (Wangjiawan section) of the Yangtze Sea. The factors which caused low concentrations of sulphate in the “shallow” waters are: 1. The Yangtze Sea was nearly enclosed and fresh water entered the Yangtze Sea from the surrounding land (Chen et al., 1987); 2. The obvious climate zone caused by the great ice cover in South Pole resulted in abundant rainfall in the Yangtze area (Cheng and Wang, 1991).

In sum, the present data provided strong evidence for the change of depositional environment (Fig. 9). The stagnant environments of the Yangtze Sea during the Ashgill might have been caused by its semi-isolated location (Chen et al., 2004). A stagnant ocean implies strong density stratification in non-glacial times (Wilde and Berry, 1984). On the other hand, abundant fresh water entered the Yangtze basin during the Ashgill to form an upper water layer with lower salinity. It would also have increased the salinity between different water layers, strengthening anoxic conditions in the base of the Yangtze Sea (Chen et al., 2004). As a result, an upper oxic and low sulfate water column and a lower anoxic and normal sulfate water column developed. During the early-mid Hirnantian interval, glacial cooling is likely to have resulted in the drop of the sea level and the oxygenation of the ocean floor, disrupting the previously stable, anoxic bottom waters circulation of cold, dense oxygen-rich water to the seabed, followed by re-establishment of the stagnant and anoxic environment as the temperature rose, post-glaciation (Zhang et al., 2000).

4.5 Controls on the accumulation of organic matter

Factors controlling the accumulation of marine organic matter mainly include sedimentation rates, productivity and oxygenation level of the water column (Hofmann et al., 2000). It should be noted, however, these factors are not independent variables, but are related to each other (Tyson, 1995). In the Wangjiawan section, the TOC content is low in the sediments from the mid-lower Hirnantian horizon, which deposited during the eustatic sea-level fall, so that the organic matter was likely mostly degraded in ventilated water columns. The increase of TOC content in black shales from the upper Hirnantian and lower Rhuddanian was temporally concomitant with the post-glacial rise of the sea level and subsequently the abrupt change from oxic to anoxic conditions, so that accumulation of organic matter-rich sediments was mainly controlled by water column oxygenation levels. It is worthwhile to note that the black shales from Normalograptus persculptus zone, which apparently deposited under a euxinic setting as stated above, contain a significantly high amount of marine organic matter (6.65-
7.72%, avg. 7.43%), further supporting the importance of oceanic anoxia in organic accumulation and preservation. On the other hand, the anoxia may have enhanced the primary productivity in the *Normalograptus persculptus*, either by upwelling of nutrient-rich waters or by increased nutrient delivering from the continent (Wang et al., 1997; Joachimski et al., 2001; Chen et al., 2005). It is further noteworthy that the Wangjiawan section experienced higher sedimentation rates than the Sanjauguan section did during the mid Ashgill interval, which can be indicated by a greater thickness of time-equivalent strata. Higher sedimentation rates imply shorter residence times at the sediment/water interface, and a faster burial rate of organic matter through the post-depositional diagenetic stages, which are favorable to protect the organic matter from decomposition, thereby enhance the overall preservation potential (Hofmann et al., 2000). In summary, the accumulation of organic matter-rich sediments in the Yangtze Sea was mainly controlled by water column oxygenation levels, probably with the help of the productivity and the sedimentation rate.

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