Integrated chemostratigraphy of the Doushantu Formation at the northern Xiaofenghe section (Yangtze Gorges, South China) and its implication for Ediacaran stratigraphic correlation and ocean redox models

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The Ediacaran Doushantu Formation in the Yangtze Gorges of South China plays an important role in our understanding of biologic evolution, global correlation, and ocean redox conditions, because of the availability of high-resolution paleontological and geochemical data and numerous radiometric dates. However, integrated study has been focused on the Jiulongwan section that was largely deposited below wave base in a restricted shelf lagoon (Jiang et al., 2011; Zhu et al., 2011). Studies of shallower water successions are lacking, and this presents a challenge to test Ediacaran stratigraphic correlation and ocean redox models. To fill this knowledge gap, we conducted a high-resolution integrated study of the Doushantu Formation at the northern Xiaofenghe (NXF) section approximately 35 km to the northeast and paleogeographically up-dip of the Jiulongwan section. With the exception of the basal 20 m, NXF sediments were deposited above normal wave base. Integrated biostratigraphic and chemostratigraphic data indicate that the 140 m thick NXF section correlates with the lower Doushantu Formation (Member I and much of Member II); i.e., the lower ca. 70 m of the formation) at Jiulongwan. Geochemical data from NXF and other Doushantu sections indicate that euxinic conditions may have been limited to a shelf lagoon (represented by the Jiulongwan section) that was restricted between the proximal inner shelf and a distal shelf margin shoal complex, at least during early Doushantu time following the deposition of the Doushantu cap dolostone. Further integrated studies are necessary to test whether euxinic conditions existed in open marine shelves in South China and elsewhere during the Ediacaran Period.

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1. Introduction

The Doushantu Formation (ca. 635–551 Ma) on the Yangtze Craton of South China has played an important role in our understanding of Ediacaran stratigraphic correlation, biological evolution, and ocean redox history (Xiao et al., 1998; Jiang et al., 2007; Zhou et al., 2007; Zhu et al., 2007, 2011; McFadden et al., 2008, 2009; Li et al., 2010; Liu et al., 2011). Current models of Ediacaran stratigraphic correlation in South China are based upon biot stratigraphic, chemostratigraphic, and geochronological data from the Yangtze Gorges area, particularly the Jiulongwan and other sections on the southern limb of the Huangling anticline (Condon et al., 2005; McFadden et al., 2008; Yin et al., 2011). In the area around Jiulongwan, the Doushantu Formation has been sampled at high resolution by several research groups, in both outcrop and drill core, and has been analyzed using a combination of micropaleontological and geochemical tools (Jiang et al., 2007; McFadden et al., 2008, 2009; Sawaki et al., 2010; Liu et al., 2011; Yin et al., 2011; Zhu et al., 2011). However, the Doushantu Formation is characterized by significant facies and thickness variations on the shelf (McFadden et al., 2009; Jiang et al., 2011), and it is complicated by the presence of allochthonous olistostromes in upper slope environments (Vernhet et al., 2006; Vernhet and Reijmer, 2010). Furthermore, Doushantu fossil occurrences are subject to
Fig. 1. Geological maps, localities, and stratigraphic correlations. (A) Map showing location of the Yangtze, Cathaysia, North China, and Tarim blocks in China. (B) A generalized paleogeographic map of the Yangtze Craton during the early Ediacaran Period (Jiang et al., 2011). Rectangle at Yichang marks the Huangling anticline. Localities (Baokang, Lantian, Longe, Minle, Weng’an, and Zhongling) mentioned in text are marked. (C) Geological map of the Huangling anticline. Localities (Jiulongwan = JLW, Tianjiayuanzi = TJYZ, northern Xiaofenghe = NXF, southern Xiaofenghe = SXF, and Zhangcunping) are marked. Note that the location of Xiaofenghe and Zhangcunping were incorrectly marked in previous publications, including Zhou et al. (2007), Zhu et al. (2007, 2011), McFadden et al. (2009), Jiang et al. (2011), and Yin et al. (2011). (D–F) Possible correlation between Doushantuo Formation in the Yangtze Gorges area (e.g., Jiulongwan section) and in shallower facies (e.g., Weng’an section), highlighting the implications for the biostratigraphic division of acanthomorph assemblages. (D) Correlation proposed by Zhu et al. (2007, 2011), in which Tianzhushania spinosa is restricted to the lower assemblage. (E) Correlation proposed by Zhou et al. (2007), in which Tianzhushania spinosa extends to the upper assemblage. (F) Alternative correlation, in which potentially three assemblages can be recognized in the Doushantuo Formation. $\delta^{13}$C curves, radiometric ages, and exposure surfaces are omitted in (E)–(F) for clarity. NT: Nantuo Formation; DV: Dengying Formation.
paleoenvironmental and taphonomic biases (Zhou et al., 2007). As a result, fine-scale litho- and biostratigraphic correlation of the Doushantuo Formation at the regional scale is not always straightforward. The difficulty is exacerbated by the condensed nature of the Doushantuo Formation: ~84 million years of geological history is recorded in ~200 m of sedimentary rocks, possibly with multiple biotures. It is therefore important to test biostratigraphic models derived from one area through integrated analysis of high-resolution stratigraphic data from others. Similarly, geochemical models derived from the Jiulongwan section also need to be tested against new data from other sections. For example, Li et al. (2010) proposed a stratified redox model for the Doushantuo basin that consists of an oxice surface layer, a thin ferruginous layer at the chemocline, a euxinic wedge, and a ferruginous deep ocean. This model was based on elemental and isotopic data from the Jiulongwan section, the Zhongling section (then interpreted to have been deposited in the outer shelf on a ramp-like platform; see Fig. 1B for section location), and two poorly sampled sections at Minle and Longe representing slope and basinal facies. This model makes certain predictions about the ocean redox conditions in the onshore part of the basin, but these predictions cannot be tested without high-resolution data from the Doushantuo Formation deposited in shallow-water environments.

To address the need for high-resolution, integrated data from a shallow-water inner shelf environment, we investigated the northern Xiaofenghe (NXF) section. This section was chosen because (1) detailed micropaleontological studies have already been published (Yin et al., 2007; McFadden et al., 2009), (2) the micropaleontological sample horizons were marked on the outcrop so that geochemical data can be precisely integrated with paleontological data, and (3) according to current basin architecture reconstruction (Jiang et al., 2011), this section is about 35 km up-dip from the Jiulongwan section, allowing an exploration of paleoenvironmental conditions in shallower parts of the Yangtze Craton. Here we present carbonate carbon, organic carbon, pyrite sulfur, carbonate associated sulfate sulfur, and strontium isotopic data from the NXF section to address basinwide correlations (Jiang et al., 2011) and test predictions of the stratified redox model (Li et al., 2010).

2. Geological background and review of previous stratigraphic work

2.1. Physical stratigraphy and radiometric age constraints

Neoproterozoic successions in South China developed on a south–southeast facing (present-day position) passive margin on the Yangtze Craton during the breakup of Rodinia about ~830–750 Ma (Wang and Li, 2003; Zhao et al., 2011). The Cryogenian glacial and interglacial successions (750–635 Ma) record a rift-drift transition (jiang et al., 2003a), and subsequent deposition of the early Ediacaran Doushantuo Formation (635–551 Ma) occurred in marginal marine environments and focused on topographic lows created by block faulting during the development of the Nanhua Rift System (Cao et al., 1989; Wang and Li, 2003; Vennhet, 2007). As a result, the Doushantuo Formation shows significant variations in facies and thickness (Zhu et al., 2007, 2011; Jiang et al., 2011); its thickness ranges from 40 m at Weng’an to ~300 m at Zhongling (see Fig. 1B for locations). The Yangtze Platform eventually evolved into an open shelf extending to a deepwater basin during the deposition of the late Ediacaran Dengying Formation (551–542 Ma) and its deepwater equivalent Liuchapo Formation, which are overlain by basal Cambrian chert, phosphorite, and shale (Dong et al., 2008, 2009; Ishikawa et al., 2008).

Although the Doushantuo Formation outcrops widely in South China, previous work has been centered on the Yangtze Gorges area, where the well exposed Jialulongwan section on the southern limb of the Huangling anticline is among the most extensively studied (Fig. 1). In the Yangtze Gorges area, the Doushantuo Formation can be more than 200 m thick and generally it has been subdivided into four lithostratigraphic members (e.g., Zhao et al., 1988; McFadden et al., 2008, 2009). Member I is a 5-m-thick cap dolostone characterized by abundant sheet cracks, tepee structures, macropeloids, and barite fans (jiang et al., 2006). Member II (~80 m thick) is characterized by alternating organic-rich calcareous shale and shaley dolostone beds with abundant pea-sized fossiliferous chert nodules (Xiao et al., 2010). The boundary between Member II and Member III is transitional at the Jialulongwan section, but has been correlated with a mid-Doushantuo exposure surface in several shallow-water sections (e.g., Weng’an and Zhangcuping; see Fig. 1 for location) (Zhou and Xiao, 2007). This correlation that has been challenged by more recent studies (Yin et al., 2009, 2011; Liu et al., 2011; Zhu et al., 2011). Member III (~60 m thick) consists of massive and laminated cherty dolostone overlain by interbedded lime mudstone and dolomititic mudstone. Member IV (~10 m thick) is composed of black organic-rich calcareous shale, siliceous shale, or mudstone. The four-fold division of the Doushantuo Formation, however, is not easily applicable to sections beyond the Yangtze Gorges area.

Three depositional cycles (sequences) are recognized in the Doushantuo Formation in the Yangtze Gorges area (Zhu et al., 2007; McFadden et al., 2008). The boundary between the first two cycles is marked by a mid-Doushantuo exposure surface in shallow-water sections elsewhere in the Yangtze Craton, such as the Weng’an and Zhangcuping sections (Liu et al., 2009b; McFadden et al., 2009; Jiang et al., 2011; Zhu et al., 2011). In the Yangtze Gorges area, however, no easily recognizable exposure surfaces have been identified, and various authors have correlated the mid-Doushantuo exposure surface at Weng’an with a lithofacies change near the Members II–III boundary (Zhou and Xiao, 2007; McFadden et al., 2009; Jiang et al., 2011) or with a Member II horizon where a carbonate unit is overlain by black shale with chert and phosphatic nodules (Zhu et al., 2007, 2011). The third cycle starts at a major lithofacies change at the Members III–IV boundary and is terminated by a widespread karst surface in the Hamajing Member of the Dengying Formation (Zhu et al., 2007), although Zhu et al. (2011) have recently discovered “a 30 cm thick interval of silty shale” in Member III at the Jialulongwan section and interpreted this silty shale “to mark a sequence boundary” and the beginning of the third cycle. These uncertainties highlight the challenge in identifying cycles or sequences in the Yangtze Gorges area where exposure surfaces are poorly developed.

The depositional environment of the Doushantuo Formation in the Yangtze Gorges area is a matter of debate. The abundance of saponitic smectite and unusually low concentration of redox-sensitive elements (Mo, U, V) in the lower Doushantuo Formation in the Yangtze Gorges area has been interpreted as evidence for deposition in alkaline lacustrine environments (Bristow et al., 2009). This view, however, is at odds with the spatial continuity of the Doushantuo Formation across much of the Yangtze Craton, the marine affinity of Doushantuo fossil assemblages, and the similarity of Doushantuo lithostratigraphic and chronostratigraphic trends with Ediacaran successions beyond the Yangtze Gorges area (jiang et al., 2003a, 2007; Kaufman et al., 2006; Zhou and Xiao, 2007; Zhou et al., 2007). Recent analysis of facies variations favors the interpretation that the Doushantuo Formation (with the exception of the cap dolostone) at Jialulongwan was deposited in a restricted shelf lagoon (Adler et al., 2009; Vennhet and Reijmer, 2010; Jiang et al., 2011).

Several radiometric dates constrain the depositional age of the Doushantuo Formation. A U–Pb zircon age from the Cryogenian Nantuo Formation (636.4 ± 4.9 Ma) (Zhang et al., 2008) places a maximum age constrain on the Doushantuo Formation.
On the southern limb of the Huangling anticline, zircon U–Pb TIMS ages have been reported from Member I cap dolostone (635.2 ± 0.6 Ma), lower Member II (632.5 ± 0.5 Ma), and uppermost Member IV (551.1 ± 0.7 Ma) (Condon et al., 2005). Two Re–Os ages of 598 ± 16 Ma (Kendall et al., 2009) and 593 ± 17 Ma (Zhu et al., 2010) have been reported from the Member IV black shale at Jiulongwan, although Kendall et al. (2009) cautioned the interpretation of their Re–Os age because of possible heterogeneity of the black shale samples.

Additionally, Liu et al. (2009b) reported a zircon U–Pb SHRIMP age of 614 ± 7.6 Ma from an ash bed in the Doushantuo Formation at the Zhangcunping section on the northeastern limb of the Huangling anticline, about 60 km to the northeast of Jiulongwan. This ash bed was collected within a dolostone that overlies the lower Doushantuo black shale but underlies the mid-Doushantuo exposure surface. Finally, a Pb–Pb age of 599 ± 4 Ma (Barford et al., 2002) has been reported from the upper Doushantuo phosphorite at Weng’an, above the mid-Doushantuo exposure surface. These two ages constrain the mid-Doushantuo exposure surface between 614 ± 7.6 Ma and 599 ± 4 Ma.

2.2. Chemostatigraphy

The chemostatigraphy of the Doushantuo Formation in the Yangtze Gorges area has been the focus of intensive investigation. Several sections on the southern limb of the Huangling anticline, including the Jiulongwan section, show nearly identical δ13C_carbon profiles (Jiang et al., 2007; Zhou and Xiao, 2007; McFadden et al., 2008; Sawaki et al., 2010). The cap dolostone of Member I is characterized by a negative δ13C_carbon excursion (EN1) down to around −4‰, with localized occurrence of extremely negative δ13C_carbon values as low as −48‰ (Jiang et al., 2003b; Wang et al., 2008; Zhou et al., 2010). Member II is characterized by a positive δ13C_carbon excursion (EP1) with values up to +5‰. One or two negative δ13C_carbon excursions have been reported punctuating EP1 at Tianjiayuani (Chu et al., 2003) and Jiulongwan (Sawaki et al., 2010; Zhu et al., 2011). We are uncertain whether such sporadic occurrences of negative δ13C_carbon values are of secular or diagenetic origin. Zhu et al. (2007, 2011), however, believe that these negative δ13C_carbon values have chemostatigraphic significance and they have named this negative excursion WANCE (=Weng’an negative carbon isotope excursion). WANCE at Weng’an occurs at the mid-Doushantuo exposure surface. As discussed above, the correlation between Weng’an and the Yangtze Gorges area is ambiguous: some correlate the mid-Doushantuo exposure surface at Weng’an with the Members II–III boundary in the Yangtze Gorges area (Zhou and Xiao, 2007) and thus WANCE at Weng’an would be equivalent to EN2 in the Yangtze Gorges area, whereas others correlate this exposure surface with a horizon within Member II in the Yangtze Gorges area (Zhu et al., 2007, 2011), implying a negative δ13C_carbon excursion within EP1. Even if one accepts the latter correlation, among the 11 Doushantuo sections where WANCE has been identified by Zhu et al. (2007, 2011), only three actually have negative δ13C_carbon values at WANCE (three data points at Weng’an, one at Xiangdangping, and two at Jiulongwan by Sawaki et al., 2010; the latter two are essentially the same section). At all the other sections, WANCE is represented by positive δ13C_carbon values. Thus, it remains to be tested whether WANCE is a truly negative excursion of chemostatigraphic significance or just a kink within EP1.

A more consistent negative δ13C_carbon excursion (EN2, down to −7‰ and perhaps −9‰) occurs at the Members II–III boundary in the Yangtze Gorges area (Jiang et al., 2007; Sawaki et al., 2010; Yin et al., 2011; Zhu et al., 2011), followed by another positive δ13C_carbon excursion (EP2) in dolostone of lower Member III. Carbonates of upper Member III and carbonate nodules in Member IV are characterized by a strongly negative δ13C_carbon excursion (EN3) with values as low as −10‰. The overall δ13C_carbon chemostatigraphic profile has been corroborated in multiple sections in the southern Huangling anticline although local variations exist (Condon et al., 2005; Jiang et al., 2007; McFadden et al., 2008; Lu et al., 2009; Yin et al., 2009, 2011; Sawaki et al., 2010; Zhu et al., 2011). Beyond the southern Huangling anticline, δ13C_carbon profiles of the Doushantuo Formation at the Zhangcunping and Weng’an sections, as well as sections of the equivalent Lantian Formation in southern Anhui Province, are broadly similar to those near Jiulongwan (Zhou, 1997; Zhou and Xiao, 2007; Zhu et al., 2007; Zhao and Zheng, 2010; Yuan et al., 2011), but precise chemostatigraphic correlation is insecure because of the lack of independent stratigraphic markers. Major departure from the Jiulongwan profile has been described in deep-water slope and basinal sections, and these have been interpreted as evidence for major geochemical gradients in Ediacaran seawater (Jiang et al., 2007).

2.3. Biostratigraphy

The biostratigraphy of the Doushantuo Formation in South China, and particularly in the Yangtze Gorges area, has similarly been a focus of previous studies (McFadden et al., 2009; Yin et al., 2009, 2011; Liu et al., 2011). Combining biostratigraphic data from multiple sections in the Yangtze Gorges area, McFadden et al. (2009) recognized two possible acritarch biozones. The lower is dominated by the species Tianzhusania spinosa, whereas the upper is characterized by greater species evenness and includes abundant occurrence of Eritractaspheira rigidata, T. spinosa, Eotylopopalla dactylos, Meghystrichosphaeridium “perfectum”, and Tanarium conoides. Yin et al. (2009, 2011) also recognized two assemblages in the Doushantuo Formation in the Yangtze Gorges area, with the lower assemblage dominated by the genus Tianzhusania whereas the upper devoid of Tianzhusania but dominated by leiospheres, diverse acanthomorphs, and the tubular fossil Sinocylocyclosis guizhouensis. Similarly, Liu et al. (2011) recognized two assemblages in the Doushantuo Formation (the lower T. spinosa assemblage and the upper Tanarium anozaos–T. conoides assemblage) and they also regarded that “the genus Tianzhusania does not extend into the upper assemblage”. Thus, these studies differ in whether Tianzhusania and T. spinosa extend to the upper biozone. This discrepancy is a result of difference in methodology and stratigraphic correlation (see Fig. 1D–F for an example). First, McFadden et al.’s (2009) method was aimed at quantitatively testing whether the lower and upper biozones – which are recognized independent of biostratigraphic data, but on the basis of sequence stratigraphic and chemostatigraphic correlation – are taxonomically distinct. As emphasized by McFadden et al. (2009), their method was not designed to locate the optimal boundary between the two biozones. In contrast, Yin et al. (2009, 2011) started off defining the two assemblages by the presence/absence of Tianzhusania, which may introduce circularity because the stratigraphic and environmental ranges of Tianzhusania has not been independently tested before it is used to define biostratigraphic units. Thus, because McFadden et al. (2009) divided their biozones based on depositional cycles and chemostatigraphic features whereas Yin et al. (2009, 2011) separated their assemblages based on the presence/absence of Tianzhusania, the exact biozone or assemblage boundaries may be different between the two studies. Second, although McFadden et al. (2009), Yin et al. (2009, 2011), and Liu et al. (2011) all claimed that the two biozones/assemblages occur in lithostratigraphic units Members II and III and are associated with EP1 and EP2, respectively, the correlation of these lithostratigraphic units and chemostatigraphic features beyond the Yangtze Gorges area is different between these studies, resulting in different conclusions with regard to the stratigraphic range.
of Tianzhushania. This pertains to the Weng’an and Zhangcunping sections, where acanthomorphs (including Tianzhushania and T. spinosa) occur in the upper Doushantu Formation above a mid-Doushantu exposure surface (Xiao and Knoll, 1999; McFadden et al., 2009; Chen et al., 2010; Liu et al., 2011). McFadden et al. (2009) correlated this exposure surface (and the associated negative δ13C_carb excursion at Weng’an) with the Ill/Ill boundary (and associated EN2) at Jiujiangwan on the basis of cyclostratigraphy and chemoostratigraphy, thus placing the Tianzhushania fossils from Weng’an and Zhangcunping acritarchs in their upper biozone (Fig. 1E). In contrast, partly driven by the assumption that Tianzhushania is restricted to their lower assemblage, Yin et al. (2009, 2011) and Liu et al. (2011) followed Zhu et al.’s (2007, 2011) WANCE concept and correlated the mid-Doushantu exposure surface at Weng’an and Zhangcunping with a poorly defined horizon in middle Member II at Jiujiangwan, thus permitting the Tianzhushania fossils from Weng’an and Zhangcunping acritarchs to be correlated with the upper EP1 or the upper part of the lower assemblage (Fig. 1D).

The biostratigraphic division proposed by Yin et al. (2009, 2011) and Liu et al. (2011) is appealing because of its simplicity: the presence/absence of a single genus (Tianzhushania) defines the two assemblages. However, one needs to consider taphonomic and environmental biases, as well as uncertainties in stratigraphic correlation, when testing the biostratigraphic model proposed by Yin et al. (2009, 2011) and Liu et al. (2011). Certainly, at Jiujiangwan and perhaps in the Yangtze Gorges area, Tianzhushania and T. spinosa are absent from Member III (McFadden et al., 2009; Liu et al., 2011). But a more important question is whether the Tianzhushania-bearing strata above the mid-Doushantu exposure surface at Weng’an, Zhangcunping, and Baokang (Xiao and Knoll, 2000; Yin et al., 2004; Zhou et al., 2007; McFadden et al., 2009; Chen et al., 2010) can all be unambiguously correlated with Member II at Jiujiangwan. As discussed above, correlation of these sections based on sequence stratigraphic and chemoostratigraphic data is indeed ambiguous. Furthermore, different taxa may have conflicting stratigraphic ranges at different sections due to environmental and taphonomic biases (Zhou et al., 2007). As an example, Yin et al. (2009) claimed that S. guizhouensis first appears in their upper assemblage; however, this taxon has so far been known only from the Weng’an biota (indeed first appearing right above the mid-Doushantu exposure surface) and Member III in the Yangtze Gorges area (Xiao et al., 2000; Liu et al., 2008, 2009a). Yin et al.’s (2009) claim about S. guizhouensis would actually support a correlation of the Tianzhushania-bearing Weng’an biota with their upper, not the lower, assemblage in the Yangtze Gorges area. Indeed, this correlation can better explain the taxonomic difference between the Weng’an biota and the lower assemblage in the Yangtze Gorges area: the latter is dominated by T. spinosa whereas the former is not. Finally, even if one accepts Zhu et al.’s (2007, 2011) WANCE and sequence boundaries, the Tianzhushania-bearing Weng’an and Zhangcunping biotas are restricted to Zhu et al.’s sequence 2, whereas the Tianzhushania-dominated lower assemblage in the Yangtze Gorges area (e.g., Jiujiangwan, Tianjiaoyunzi, and Wangfenggang) is mostly if not entirely restricted to Zhu et al.’s sequence 1 (Liu et al., 2011). Thus, it is possible to envision three Doushantu assemblages when all evidence is considered (Fig. 1F): a lower assemblage dominated by T. spinosa (e.g., Member II in the Yangtze Gorges area), a middle assemblage where T. spinosa is still present but become less abundant (e.g., upper Doushantu at Weng’an), and an upper assemblage without T. spinosa (e.g., the upper assemblage of Liu et al., 2011). For now, we readily accept that the lower Doushantu biocenosis is dominated by the species Tianzhushania (McFadden et al., 2009). If in the future it is confirmed that Tianzhushania exclusively occurs in the lower Doushantu Formation (Yin et al., 2009, 2011), our favored chronostratigraphic correlation of the NFX section to the lower Doushantu at Jiujiangwan would be further strengthened by the dominance of Tianzhushania at NFX.

3. Methods

The NFX section is located at 30°56.693′N, 111°13.988′E (Fig. 1). It is the same as the lower ~135 m of the Xiaofenghe section in Yin et al. (2007) and Zhu et al. (2007), the lower ~140 m of the Xiaofenghe section in Jiang et al. (2011), and the northern hillside Xiaofenghe section of Zhu et al. (2011). The Xiaofenghe stratocolumns in Yin et al. (2007, 2011), Liu et al. (2011), and Jiang et al. (2011) represent composite sections consisting of the NFX and SXF (southern Xiaofenghe section, 30°55.945′N, 111°13.266′E, Fig. 1), although splicing of these two sections is not straightforward. Because of the splicing problem, there are major inconsistencies in published stratigraphic thickness of the composite Xiaofenghe section, ranging from <100 m (Vernhet and Reijmer, 2010) to >200 m (Zhu et al., 2011). To avoid this problem and the stratigraphic repetitions resulting from modern landslides at the SXF section (Jiang et al., 2011), we focused here only on the NFX section, which was carefully measured and sampled at sub-meter scale (ca. 0.5 m intervals) for petrographic, palaeontological, and geochemical analysis.

Petrographic thin sections were made for each sample and were examined under a transmitted light microscope. Thin section examination allowed us to quantitatively estimate the mineralogical (e.g., calcite, dolomite, silica, quartz, phosphate, and clay) and petrological compositions (e.g., mudstone, wackestone, packstone, and grainstone). These data, along with sedimentary structures observed from field investigation, are plotted as three separate columns in the stratigraphic log (Fig. 2). All chert-phosphatic nodules in thin sections were thoroughly examined for microfossils (McFadden et al., 2009).

For δ13C_carb and δ18O_carb analysis, powders were micro-drilled from the finest-grained portions of polished slabs determined by petrographic observation of corresponding thin sections. Approximately 100 μg of carbonate powder was reacted for 10 min at 90°C with anhydrous H3PO4 in a Multiprep inlet system connected to a GV Isoprime dual inlet mass spectrometer. Isotopic results are expressed in the standard δ notation as per mil (‰) deviation from V-PDB. Uncertainties determined by multiple measurements of NBS-19 were better than 0.05‰ (1σ) for both C and O isotopes. Total organic carbon content (TOC) and δ13C_org were determined following procedures described by Kaufman et al. (2007). Approximately 1 g of whole rock powder was weighed and then quantitatively digested with 6 M HCl. Residues were washed with deionized water, centrifuged, isolated, dried, and weighed to determine abundance of carbonate in the samples. TOC abundance (wt% of rock powder) was calculated from measured abundance of carbon in the residues quantified by an elemental analyzer (EA) relative to the urea standard. Isotope abundances were determined on a continuous flow GV Isoprobe mass spectrometer. δ13C_org values are reported as per mil (‰) deviation from V-PDB. Uncertainties based on multiple extraction and analyses of a standard carbonate are better than 0.15‰ (1σ) for TOC and 0.3‰ (1σ) for δ13C_org.

Disseminated pyrite concentrations and δ34S_py were analyzed using both combustion and chromium reduction methods (Canfield et al., 1986). For pyrite-rich samples, decalcified residues were subjected to direct EA combustion. For pyrite-poor samples, powdered samples were reacted with 50 ml of 1 M CrCl2 and 20 ml of 10 M HCl in an N2 atmosphere. H2S produced from pyrite reduction by CrCl2 was bubbled through a 1 M silver nitrate trap and precipitated as Ag2S. The Ag2S was centrifuged, washed, dried, and weighed. Pyrite sulfur isotope and concentrations were determined by EA combustion at 1030°C on a continuous flow GV Isoprime mass

spectrometer. 100–500 µg of decalcified residue (for direct combustion samples) or 100 µg Ag₂S (for chromium reduction samples) was dropped into a quartz reaction tube packed with quartz chips and elemental copper for quantitative oxidation and O₂ resorption. Water was removed from combustion products with a 10-cm magnesium perchlorate trap, and SO₂ was separated from other gases with a 0.8 m PTFE GC column packed with Porapak 50–80 mesh heated at 90 °C. Pyrite concentrations were calculated from SO₂ yields and reported as wt% pyrite. δ³⁴S_{py} values are reported as per mil (‰) deviation from V-CDT. Uncertainties determined from multiple analyses of NBS 127 interspersed with the samples are better than 0.3‰ (1σ) for concentration and 0.3‰ (1σ) for isotope composition.

Extraction of CAS was conducted using techniques modified from Burdett et al. (1989), Gellatly and Lyons (2005), and Shen et al. (2008). Roughly 100 g of sample was leached with 10% NaCl solution, washed, dried, powdered, and weighed. Dried powders were treated with 30% hydrogen peroxide for 48 h to remove disseminated pyrite and organically bound sulfur that could potentially contaminate CAS extractions. Leached powders were quantitatively dissolved in 3 M HCl and insoluble residues were separated from the supernatant by gravity filtration through 8 µm Whatman filters. Total volume of supernatant was measured, and 10 ml of 0.1 M BaCl₂ was added to 40 ml of supernatant to precipitate barite. The precipitates were then centrifuged, washed, dried, and weighed.

CAS concentrations were calculated from ICP–AES (inductively coupled plasma atomic emission spectrometer) analysis of small aliquots of the leached solutions at Virginia Tech Soil Testing Laboratory. CAS concentrations were calculated from sulfur abundances and reported as ppm SO₄²⁻ in carbonate, with uncertainties better than 5%. Barite precipitates were combusted with a Eurovector EA and ³⁴S/³²S ratios were determined using a continuous flow GV Isoprime mass spectrometer. δ³⁴S_{CAS} values are reported as per mil (‰) deviation from V-CDT. Uncertainties determined from multiple analyses of NBS 127 are better than 0.3‰ (1σ).

For strontium isotope analyses, micro-drilled carbonate powders (ca. 5 mg) were repeatedly leached (3×) with ultrapure 0.2 M ammonium acetate (pH ~ 8.2) to remove exchangeable Sr from non-carbonate minerals (Montañez et al., 1996) and then treated with ultrapure 0.5 M acetic acid for 12 h. The supernatant was separated from insoluble residues by centrifugation, decanted, dried, and
subsequently dissolved with 200 μl of 3 M HNO₃. Small polyethylene columns were prepared with quartz wool and ~1 cm of Sr spec resin and washed with 400 μl of 3 M HNO₃. After loading, the sample was sequentially eluted with 3 M HNO₃ (200 μl), 7 M HNO₃ (600 μl) and 3 M HNO₃ (100 μl) to primarily remove Ca and Rb, and then 400 μl of 0.05 M HNO₃ was passed through the column to collect the Sr fraction. The samples were then dried and loaded with 0.7 μl of T₀a onto a Re filament for analysis in a VG Sector 54 thermal ionization mass spectrometer at the University of Maryland. Sr beams of 0.5 V on mass 88 were obtained at temperatures between 1450°C and 1650°C allowing for at least 75 stable ratios. Repeated analysis of NBS 987 during the analytical session yielded an average value of 0.710238 ± 0.000006 (1σ).

4. Lithostratigraphy

Overall, the NXF section (Fig. 2) contains greater abundances of carbonate, phosphatic clasts, silt and sand, but less shale than the Jiulongwan section. An important marker bed of the Doushantuo Formation, the basal Doushantuo cap dolostone (Member I), is present at the NXF section and overlies diamicite of the Cryogene Nantuoy Formation. The cap dolostone at NXF is very similar to Ediacaran cap dolostones described elsewhere in South China: it is a 3.9 m thick massive-bedded microlaminated dolomitic, with peloids, abundant tepee-like structures (Fig. 3A), and quartz-filled sheet cracks (Fig. 3B–D). The crest of the tepee-like structures strikes at 90–110°, consistent with measurements taken at Jiulongwan. The upper part of the cap dolostone becomes thinner–bedded, more limy, and partially silicified. The cap dolostone passes into a 20-m thick organic-rich shale interbedded with fine-grained phosphatic siltstone (Fig. 3E). Phosphatic grains are silt to fine sand-size, subangular to rounded, well sorted, and occur in thin lenses and layers 1–3 cm thick. Small wave ripples were observed at the base of this unit around 41 m above the formation. Thin dolostone interbeds also occur locally and contain abundant pea-size chert nodules. The phosphatic component increases upsection from around 10% at the base of the unit to greater than 50% near the top. In outcrop, the phosphatic lenses increase in density and thickness up to 5–7 cm thick.

Overlying the siltstone is a thick unit composed of cherty dolomitic mudstone and wackestone (25–106 m). Dolostones are locally argillaceous, thin to medium bedded, and contain minor to moderate amounts of quartz and phosphate grains (Fig. 3F). Chert nodules (Fig. 4A and B) are 1–5 cm in diameter, spheroidal to oblong in shape and oriented parallel to bedding. Chert nodules contain abundant acritarchs (Fig. 4C–E) and phosphatic grains. The abundance of phosphatic grains increases upsection, although it is lower than the underlying phosphatic siltstone. A sharp lithofacies change occurs at ~96 m, where phosphatic–dolomitic wackestone–packstone gives way to dolomitic mudstone and then lime mudstone that dominate the rest of the section (96–140 m); this change may represent a flooding surface. The uppermost part of the NXF section (106–140 m) was measured along a satellite section offset from the main section. Splicing of this satellite section with the main section resulted in an approximate 5 m discrepancy between our stratigraphic thickness measurements and those published in Yin et al. (2007) and Zhu et al. (2007, 2011). This unit is characterized by massive limestone with thin (possibly microbial) laminations interbedded with argillaceous limestone. Cherts in this unit are oblong to banded, and contain well preserved acritarchs (Fig. 4F–H).

The upper NXF section is not exposed above 140 m in the study area. Others (e.g., Yin et al., 2007; Zhu et al., 2007, 2011) continued their stratigraphic measurements up to the Doushantuo–Dengying boundary along the SXF section, which is complicated by many faults/landslides and is inappropriate for high-resolution chronostratigraphic sampling. Yin et al. (2007) and Zhu et al. (2007) placed a black shale unit in the uppermost Doushantuo Formation in their SXF stratocolumns, which were adopted by McFadden et al. (2009). This black shale unit would be regarded as equivalent to Doushantuo Member IV recognized at the Jiulongwan section. However, we were unable to verify this black shale unit at SXF (see also Zhu et al., 2011). Instead, the Doushantuo–Dengying boundary at SXF is represented by the transition from Doushantuo oolitic grainstone/packstone to Dengying cherty dolostone with dissolution structures. It is possible that this black shale unit is missing because of bedding–parallel faults, but it is more likely that a facies change led to the disappearance of the black shale in shallow water environments such as at the Weng’an section (Zhou et al., 2005; Jiang et al., 2011).

Comparison between the NXF and Jiulongwan section suggests that the former is dominated by dolomitic phosphatic wackestone and packstone whereas the latter by argillaceous mudstone, which is consistent with the paleobathymetric inference that the NXF section was more proximal than the Jiulongwan section (Jiang et al., 2011). Although the Nantuoy–Doushantuo boundary is unambiguously identifiable at NXF, the three sedimentary cycles are not easily recognizable because the exposure surfaces are poorly developed. Sequence boundaries or erosional surfaces have been marked on Xiaofenghe stratocolumns at ~57 m (Fig. 2 in Yin et al., 2011; Liu et al., 2011), ~62 m (Fig. 3 in Yin et al., 2011), ~74 m (Jiang et al., 2011), and ~88 m (Yin et al., 2007; Zhu et al., 2007, 2011). These surfaces are all based on a single possible erosional surface identified at SXF and correlated to SXF strata, and the variation in stratigraphic height is an indication of the difficulty in splicing the NSF and SXF sections. Our stratigraphic analysis of NXF identifies a possible flooding surface at ~96 m. However, no erosional unconformity has been identified at NXF (see also Zhu et al., 2011). Similarly, because of the absence of the black shale unit in the uppermost Doushantuo Formation, the surface separating the second and third cycles is also ambiguous at Xiaofenghe. From the lithostratigraphic and chronostratigraphic point of view, the cap carbonate and overlying organic-rich mudstone/siltstone and phosphatic wackestone/packstone (0–96 m) could be equivalent to the first cycle (Members I and II) at Jiulongwan, whereas the dolomitic mudstone and overlying limestone (96–140 m) equivalent to dolostone and overlying ribbon rocks of the second cycle or Member III at Jiulongwan (Fig. 5; see also Jiang et al., 2011). Alternatively, Zhu et al. (2007, 2011) propose that the sequence boundary at ~88 m in SXF could be correlated with a horizon within Member II at Jiulongwan, implying that much if not all of the NXF section is equivalent to Member II at Jiulongwan. The biostratigraphic and chronostratigraphic data, reported below, indicate that the entire NXF section is more likely correlative to the lower Doushantuo, consistent with Zhu et al.’s (2011) correlation. This correlation indicates that lithostratigraphic differences between the upper NXF and its potential correlative at Jiulongwan could be related to facies changes between the inner shelf lagoon and nearshore subtidal carbonates (Jiang et al., 2011).

5. Biostratigraphy

Acritarch biostratigraphy of the Doushantuo Formation at Xiaofenghe has been previously published (Yin et al., 2007; McFadden et al., 2009). Yin et al. (2007) presented acritarch occurrence data from the lower Doushantuo Formation at NXF and upper Doushantuo Formation at SXF. As discussed above, McFadden et al. (2009) and Yin et al. (2009, 2011) recognized two potential acritarch biozones in the Doushantuo Formation. Although there are some differences between the two studies, both recognized
that the lower biozone is dominated by Tianzhushania, particularly T. spinosa. The dominance of T. spinosa in the NXF section (McFadden et al., 2009; Yin et al., 2009), from ~35 m to ~110 m (Figs. 4C–H and 5), indicates a biostratigraphic assignment to the lower biozone and correlation to the lower Doushantuo Formation at Jiulongwan.

6. Chemostratigraphy and correlation with the Jiulongwan section

Chemostratigraphic data are presented in Table S1 (see Supplemental Online Material) and plotted in Fig. 6. The data show several important features that are useful in correlation with the Jiulongwan section. First, the $\delta^{13}$C$_{org}$ profile is remarkably constant around $-28.8\%$ over the section, despite $\delta^{13}$C$_{carb}$ variation up to $10\%$o, resulting in a strong correlation between $\delta^{13}$C$_{carb}$ and $\Delta^{13}$C$_{org}$ (Fig. 7A). Second, the $\delta^{13}$C$_{carb}$ profile can be divided into three segments: (1) the cap dolostone (0–4 m), characterized by negative values around $-3\%$o; (2) the overlying 31 m strata (4–35 m), where $\delta^{13}$C$_{carb}$ values hover around $0\%$o (with three exceptions, $-9.6\%$o at 25.5 m, $-6.4\%$o at 29.2 m, and $+3.9\%$o at 26.0 m); and (3) the rest of the section (35–140 m) with positive values mostly around $+5\%$o to $+6\%$o. This profile is similar to previously reported $\delta^{13}$C$_{carb}$ data from NXF (Liu et al., 2011; Yin et al., 2011; Zhu et al., 2011). Third, $\Delta^{34}$S$_{py}$ values are all positive and vary between $+14.2\%$o and $+32.6\%$o. $\delta^{34}$S$_{CAS}$ values are also positive with irregular variation between $+6.6\%$o and $+39.1\%$o. $\Delta^{34}$S$_{CAS}$-py varies from $-6.1\%$o to $16\%$o. The variability in some intervals likely reflects diagenetic processes, although if only $\Delta^{34}$S$_{py}$ values of pyrite-rich samples (those with $>2$ mg Ag$_2$S yield from chromium reduction extraction) are considered, sample-to-sample stratigraphic scattering in $\Delta^{34}$S$_{py}$ and $\Delta^{34}$S$_{CAS}$-py is reduced (Fig. 6). Finally, $^{87}$Sr/$^{86}$Sr values of limestone samples range between 0.7079 and 0.7081.

There has been extensive discussion on the diagenetic alteration of Proterozoic carbon, sulfur, and strontium isotope signatures (Kaufman and Knoll, 1995; Lyons et al., 2004; Gellatly and Lyons, 2005; Halverson et al., 2007; Marenco et al., 2008; Shen et al., 2008, 2011; Knauth and Kennedy, 2009; Derry, 2010; Halverson et al., 2010). We interpret the $\delta^{13}$C and $\Delta^{34}$S of the NXF section as representing mainly primary signatures. This interpretation is
supported by the well defined stratigraphic trends (particularly in $\delta^{13}$C$_{\text{carb}}$ and $\delta^{13}$C$_{\text{org}}$) and regional consistency in the Yangtze Gorges area (when compared with the Jiu-longwan section). Furthermore, there is very little correlation between $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ data from NXF (Fig. 7B), and these data plot outside the meteoric diagenetic trend (Knauth and Kennedy, 2009); at least $\delta^{13}$C$_{\text{carb}}$ data from 35 to 104 m are not strongly altered by meteoric diagenesis, although the primary origin of a few negative $\delta^{13}$C$_{\text{carb}}$ values at 25–30 m may be questioned because of the large sample-to-sample variation (i.e., stratigraphic inconsistency). NXF pyrite is mostly disseminated and likely of authigenic origin. Even so, the ultimate source of sulfur for pyrite precipitation came from marine sulfate. The highly positive $\delta^{34}$S$_{\text{py}}$ values from the NXF section are similar to those reported from other Ediacaran successions (Shen et al., 2008, 2011; Ries et al., 2009) and may reflect unique marine geochemistry of Ediacaran oceans. The strong sample-to-sample variation in $\delta^{34}$S$_{\text{CAS}}$ and $\delta^{18}$O$_{\text{carb}}$ time series likely reflects variable degrees of alteration, although the range of sulfate
S isotope compositions may also reflect the low sulfate availability in Ediacaran oceans (McFadden et al., 2008). $^{87}$Sr/$^{86}$Sr ratios are susceptible to diagentic processes such as dolomitization and influence of detrital sediments. Thus, we deem that the $^{87}$Sr/$^{86}$Sr ratios from limestone samples more faithfully reflect the depositional values.

Consistent with the biostratigraphic match between sections, chemostratigraphic profiles from NXF show similarities to those from the lower Doushantuo Formation at Jiulongwan. Carbon isotope trends of the NXF section can be readily correlated with those from the lower Doushantuo Formation (Members I and II) at Jiulongwan (McFadden et al., 2008). $\delta^{13}$C$_{\text{Carb}}$ trends are nearly identical between the two sections. The negative $\delta^{13}$C$_{\text{Carb}}$ excursion in the cap dolomite and the positive excursion at 35–140 m can be matched with, respectively, EN1 in Doushantuo Member I and EP1 identified in Doushantuo Member II. $\delta^{13}$C$_{\text{Carb}}$ values at 5–35 m are also similar to the average $\delta^{13}$C$_{\text{Carb}}$ values in lower Member II at Jiulongwan and other sections on the southern limb of the Huangling anticline despite local variations (Jiang et al., 2007; Zhou and Xiao, 2007; Zhu et al., 2007, 2011; McFadden et al., 2008; Yin et al., 2009, 2011; Sawaki et al., 2010). The negative $\delta^{13}$C$_{\text{Carb}}$ excursion at 25–30 m in the NXF section is only defined by two data points and could represent diagentic alteration, although they may be correlated with a brief negative $\delta^{13}$C$_{\text{Carb}}$ excursion, also defined by one or two data points, recovered from the lower Doushantuo Formation (around 58 m from the base) in a drill core near Jiulongwan (Sawaki et al., 2010) and an equivalent horizon at Tianjiayuanzi in the Yangtze Gorges area (Chu et al., 2003; Zhou and Xiao, 2007). At the present, we are inclined to interpret these negative values as diagentic artifacts with little chemostratigraphic significance.

$\delta^{34}$S$_{\text{py}}$ values at NXF are unusually positive, again similar to values from the lower Doushantuo Formation at Jiulongwan, although $\delta^{34}$S$_{\text{py}}$ and $\delta^{34}$S$_{\text{CAS}}$ profiles at NXF show more consistent stratigraphic trends and less stratigraphic scattering than the lower Doushantuo Formation at the Jiulongwan section. The NXF section also has higher $\delta^{24}$S$_{\text{py}}$ values but lower $\delta^{34}$S$_{\text{CAS}}$ values, resulting in
Fig. 6. Chemostratigraphic profiles of the NXF section. In the $\delta^{13}$C$_{org}$ and $\Delta^{34}$S$_{CAS-py}$ profiles, solid symbols represent samples with $>2$ mg Ag$_2$S yield in CRS extraction (roughly equivalent to $>0.02\%$ pyrite). In the $^{87}$Sr/$^{86}$Sr profile, solid and empty symbols represent limestone and dolostone samples, respectively.
lower $^{34}$S$_{CAS-py}$ values relative to the lower Doushantu Formation at Jiulongwan. From a chemostratigraphic point of view, it is important to note that the prominent decrease in both $^{34}$S$_{py}$ and $^{34}$S$_{CAS}$ observed in the upper Doushantu Formation at Jiulongwan (arrows in Fig. 8) (McFadden et al., 2008; Li et al., 2010) is not seen at NXF, further strengthening the view that only the lower Doushantu Formation is represented at NXF.

As a critical test of these regional correlations, we evaluated variations in strontium isotope signatures in limestone samples throughout the NXF section. Previous studies (Yang et al., 1999; Jiang et al., 2007; Sawaki et al., 2010) revealed a strong isotopic contrast between lower and upper Doushantu Formation limestones at multiple sections in the Yangtze Gorges area. $^{87}$Sr/$^{86}$Sr values of best-preserved samples rise from ca. 0.7078 to 0.7089 from the bottom to top of the formation (Fig. 8), a transition consistent with data derived from other Ediacaran successions (Shields and Veizer, 2002; Halverson et al., 2010). This rise cannot be explained by an upsection increase in the content of clays that contain more radiogenic Sr, because overall the lower Doushantu is more argillaceous than the upper Doushantu and the highest $^{87}$Sr/$^{86}$Sr values are found in Member III limestone with little clay (McFadden et al., 2008; Sawaki et al., 2010). Our analyses (Figs. 6 and 8) of limestone samples near the top NXF section are consistently low (ranging from 0.7079 to 0.7081). Matched with the trend defined by high Sr-content limestone samples from previous studies (including core samples analyzed by Sawaki et al., 2010), the upper NXF samples are clearly equivalent to those in the lower Jiulongwan strata, further supporting our correlation.

The established isotopic contrasts between the lower and upper Doushantu Formation at Jiulongwan are striking. The upper interval contains a carbon isotope anomaly (EN3) known globally as the Shuram event, named after a long-lived negative carbon isotope excursion to values near $–10\%$ in drill core from Oman (Burns and Matter, 1993; Le Guerroue et al., 2006; Le Guerroue and Cozzi, 2010; Bergmann et al., 2011; Grotzinger et al., 2011; Verdel et al., 2011). This biogeochemical anomaly is recorded in upper Member III and Member IV of the Doushantu Formation, and stratigraphic data from these intervals also record simultaneous depletion of $^{34}$S in both sulfides and sulfates (McFadden et al., 2008). Neither these significant anomalies,
Fig. 8.
Table 1

Statistics of chemostratigraphic data from Doushantuo strata representing the $\delta^{13}$C$_{\text{carb}}$ feature EP1 at NXF (this study) and Jiulongwan (Jiang et al., 2007; McFadden et al., 2008; Li et al., 2010). Statistics of $^{87}$Sr/$^{86}$Sr data at Jiulongwan also includes data from Tianjiayuansi (Yang et al., 1999) and a drill core near Jiuangwan (Sawaki et al., 2010).

<table>
<thead>
<tr>
<th></th>
<th>NXF (34–140 m)</th>
<th>Jiulongwan (25.7–66 m) (Jiang et al., 2007; McFadden et al., 2008)</th>
<th>Jiulongwan (29–65 m) (Li et al., 2010)</th>
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<tr>
<td></td>
<td>(this study)</td>
<td></td>
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</tr>
<tr>
<td>TOC (wt%)</td>
<td>0.58 ± 0.39 (n = 163)</td>
<td>1.44 ± 0.81 (n = 52)</td>
<td>0.87 ± 0.21 (n = 9)</td>
</tr>
<tr>
<td>Pyrite (wt%)</td>
<td>0.03 ± 0.04 (n = 44)</td>
<td>0.79 ± 1.08 (n = 40)</td>
<td>1.22 ± 0.70 (n = 6)</td>
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<tr>
<td>$S_{\text{py}}$</td>
<td>0.04 ± 0.02 (n = 42)</td>
<td>0.3 ± 0.4 (n = 41)</td>
<td>0.6 ± 0.6 (n = 9)</td>
</tr>
<tr>
<td>CAS (ppm)</td>
<td>310 ± 557 (n = 159)</td>
<td>591 ± 710 (n = 50)</td>
<td>131 ± 133 (n = 18)</td>
</tr>
<tr>
<td>$\delta^{13}$C$_{\text{carb}}$ (%)</td>
<td>−28.8 ± 0.6 (n = 163)</td>
<td>−29.8 ± 0.4 (n = 52)</td>
<td>−29.9 ± 0.3 (n = 20)</td>
</tr>
<tr>
<td>$\delta^{13}$C$_{\text{org}}$ (%)</td>
<td>5.5 ± 1.3 (n = 161)</td>
<td>4.8 ± 1.2 (n = 68)</td>
<td>4.0 ± 1.9 (n = 20)</td>
</tr>
<tr>
<td>$\Delta^{13}$C$_{\text{sub-redox}}$</td>
<td>34.2 ± 1.3 (n = 155)</td>
<td>35.5 ± 0.7 (n = 17)</td>
<td>33.8 ± 2.0 (n = 20)</td>
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<tr>
<td>$\delta^{13}$S$_{\text{carb}}$ (%)</td>
<td>24.6 ± 3.2 (n = 44)</td>
<td>18.3 ± 9.0 (n = 40)</td>
<td>7.0 ± 9.2 (n = 9)</td>
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<tr>
<td>$\delta^{13}$S$_{\text{carb}}$ (%)</td>
<td>28.8 ± 4.5 (n = 110)</td>
<td>32.5 ± 9.9 (n = 36)</td>
<td>38.0 ± 5.8 (n = 18)</td>
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<tr>
<td>$\Delta^{13}$S$_{\text{carb}}$ (%)</td>
<td>3.3 ± 4.2 (n = 27)</td>
<td>12.7 ± 9.0 (n = 25)</td>
<td>28.9 ± 8.0 (n = 9)</td>
</tr>
<tr>
<td>$^{87}$Sr/$^{86}$Sr</td>
<td>0.708004 ± 0.000071 (n = 5)</td>
<td></td>
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</table>

Fig. 9. Paleographic reconstruction (A; box diagram modified from Jiang et al., 2011) and stratified redox ocean model (B; cross section modified from Li et al., 2010), with the approximate location of Doushantuo sections marked on the diagrams. In this model, euxinia is restricted to the shelf lagoon. It remains uncertain whether euxinia extends the open shelf and to deep oceans.

nor the high $^{87}$Sr/$^{86}$Sr values, are recorded in samples from NXF. Thus, chemostratigraphic and biostratigraphic data indicate that the 140-m-thick NXF section is correlated with the ~70-m-thick lower Doushantuo Formation at Jiuangwan (highlighted in Fig. 8), implying that the sedimentation rate at NXF was about twice that at Jiuangwan, probably because NXF was closer to a carbonate factory and detrital sediment sources. This correlation also suggests that the lithostratigraphic similarity between the dolostone–limestone unit (96–140 m) at NXF and Member III at Jiuangwan does not imply chronostratigraphic equivalency.

Fig. 8. Comparison of chemostratigraphic profiles of the NXF and Jiuangwan sections, with proposed chemostratigraphic correlation (yellow shading). To facilitate comparison, corresponding chemostratigraphic profiles are plotted at the same scale. Highly radiogenic $^{87}$Sr/$^{86}$Sr values (0.709–0.713) from the cap carbonate at a drill core near Jiuangwan were regarded as altered values (Sawaki et al., 2010) and are omitted from the Jiuangwan $^{87}$Sr/$^{86}$Sr profile. $^{87}$Sr/$^{86}$Sr data from the Tianjiayuansi (see Fig. 1C for location) (Yang et al., 1999) are scaled to the thickness of the Jiuangwan section based on $\delta^{13}$C chemostratigraphic correlation (Zhou and Xiao, 2007). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
7. Test of Ediacaran ocean redox models

Li et al. (2010) proposed a stratified redox model for the Doushantuo basin. In this model, the Doushantuo basin consisted of anoxic surface ocean that was underlain by a thin ferruginous layer, a wedge of euxinic water resting on an open shelf, and a deep ferruginous ocean. This model was derived from geochemical data from successions deposited in bathymetrically deep basinal ferruginous setting (Zhongling, Minle, and Longe sections) and intermediate-depth euxinic setting (Jiulongwan section). However, geochemical data from the Minle and Longe sections were sparse, and no data from proximal shallow facies were available. Further, the Zhongling section, previously interpreted to have accumulated on a distal ramp (Li et al., 2010), is now reinterpreted as sedimentation on the lagoonal side of a shelf margin shoal complex (Jiang et al., 2011; Zhu et al., 2011). This reinterpretation of the basin architecture has implications for the stratified redox model.

Importantly, the basin architecture reinterpretation and our data from NXF indicate that both the NXF and Zhongling sections may have been deposited beneath non-euxinic (oxic or ferruginous) waters in shallower environments surrounding a deeper euxinic lagoon, which developed shortly after the deposition of the Doushantuo cap dolostone (Jiang et al., 2011). The interpretation that the NXF sediments appear to have been deposited in non-euxinic waters is supported by their lower TOC and pyrite contents (Table 1) and lower S_{pyrite}/C_{org} ratios as compared with the lower Doushantuo Formation at Jiulongwan (Fig. 7C), although this interpretation needs to be further tested by iron speciation data from NXF. A non-euxinic environment for the NXF section is consistent with predictions of the Li et al. model. However, the euxinic condition at Jiulongwan spatially bracketed by non-euxinic conditions at NXF (this study) and Zhongling (Li et al., 2010) can alternatively be interpreted in the framework of a recent basin architecture reconstruction (Jiang et al., 2011); euxinia developed in a restricted lagoon and may have come and gone in the Ediacaran Period (Fig. 9). This restricted euxinic lagoon is different in geometry from the euxinic wedge that rested on an open shelf (Li et al., 2010). More high-resolution chemos stratigraphic data are needed to test whether euxinia also occurred in shelf margin and whether the global ocean was stratified with ferruginous/euxinic deep waters belowoxic surface waters.

In detail, some of the chemostратigraphic differences between NXF and Jiulongwan can also be explained in the framework of the basin architecture presented by Jiang et al. (2011). First, although the NXF section and lower Doushantuo Formation at Jiulongwan have remarkably invariant δ^{13}C_{org} profiles, the δ^{13}C_{org} values are slightly greater at NXF than at Jiulongwan (Table 1). This subtle difference may indicate that photosynthesis had a greater contribution to organic production at the non-euxinic NXF section, whereas microbial recycling of aged organic carbon played a greater role in euxinic conditions at Jiulongwan (Fike et al., 2006; McFadden et al., 2008). This interpretation is also consistent with slightly greater δ^{13}C_{carb}, δ^{34}S_{py}, and δ^{34}S_{CAS} profiles at Jiulongwan than NXF (Fig. 8; Table 1). The most likely cause of this difference is short-term perturbations related to sea-level and chemocline fluctuations, which affected the remineralization of deep-water DOC through bacterial sulfate reduction (Rothman et al., 2003; Li et al., 2010); the Jiulongwan section located at or just below the chemocline would have been more affected by such fluctuations than the NXF section located persistently above the chemocline. Finally, the smaller Δ^{34}S_{CAS-py} values at NXF as compared with the Jiulongwan section (Table 1) can be readily explained by authigenic pyrite formation at NXF (vs syntgenetic pyrite formation at Jiulongwan) where diffusion of seawater sulfate to pore waters limited the isotopic fractionation between sulfate and pyrite.

8. Conclusion

This study highlights the necessity of integrating basin architecture, biostatigraphy, and chemostatigraphy when correlating Ediacaran strata and reconstructing environmental changes in Earth’s distant past. Our biostatigraphic and chemostatigraphic data highlight the potential of acanthomorph acritarchs and carbonate carbon isotope values in Ediacaran correlation (Moczydlowska, 2005; Willman and Moczydlowska, 2008; Vorob’eva et al., 2009; McFadden et al., 2009; Liu et al., 2011; Sergeev et al., 2011; Zhu et al., 2011), and they show that only lower Doushantuo Formation is represented at the NXF section. A positive identification of the upper Doushantuo Formation at the SXF section remains to be verified by integrated stratigraphic data. Geochemical data indicate that the NXF sediments were laid down in non-euxinic waters. Considered with published basin architecture reconstruction (Jiang et al., 2011; Zhu et al., 2011), the new data is consistent with euxinia in a shelf lagoon bracketed by non-euxinic waters in the inner shelf (e.g., NXF) and outer shelf margin (e.g., Zhongling), at least during the early Doushantuo time following the deposition of the cap dolostone. More data are needed to further test whether a euxinic wedge, which appears to be an emerging feature in the redox structures of late Archean to early Neoproterozoic oceans (Reinhard et al., 2009; Johnston et al., 2010; Kendall et al., 2010; Poulton et al., 2010; Poulton and Canfield, 2011), also characterizes the Ediacaran oceans; and if so, whether the Eudicaran euxinic lens or wedge was controlled by oceanic factors such as a sulfate gradient (Li et al., 2010), paleogeographic factors such as basin restriction (Jiang et al., 2011), or a combination of both. Such a test requires geochemical data from Ediacaran successions beyond the Yangtze Gorges area and beyond South China.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.precamres.2011.10.021.

References


