The origin of decoupled carbonate and organic carbon isotope signatures in the early Cambrian (ca. 542–520 Ma) Yangtze platform

Ganqing Jiang a,*, Xinqiang Wang b, Xiaoying Shi b, Shuhai Xiao c, Shihong Zhang b, Jin Dong d

a Department of Geoscience, University of Nevada, Las Vegas, NV 89154-4010, USA
b State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing, 100083, China
c Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China

1. Introduction

Decoupled carbonate and organic carbon isotopes (\(\delta^{13}C_{\text{carb}}\) and \(\delta^{13}C_{\text{org}}\)) from some late Neoproterozoic successions have been interpreted as evidence for the existence of a large oceanic dissolved organic carbon (DOC) reservoir capable of buffering carbon isotopes of organic matter (Fike et al., 2006; McFadden et al., 2008; Rothman et al., 2003). These uncertainties question the causal link between \(\delta^{13}C_{\text{carb}}\) and \(\delta^{13}C_{\text{org}}\). For millions of years from the onset of the Cryogenian glaciations (ca. 720 Ma; Swanson-Hysell et al., 2010) to the latest Ediacaran Period (ca. 560 Ma; Fike et al., 2006; McFadden et al., 2008; Rothman et al., 2003), the early Cambrian (ca. 540–520 Ma) strata record large \(\delta^{13}C_{\text{carb}}\) excursions (e.g., Brasier et al., 1990, 1994, 1996; Ishikawa et al., 2008; Kouchinsky et al., 2007; Maloof et al., 2005, 2010a, 2010b), but existing \(\delta^{13}C_{\text{carb}}\) data show a rather complex picture. Earlier studies reported a negative \(\delta^{13}C_{\text{org}}\) excursion at the Precambrian–Cambrian transition (Banerjee et al., 1997; Kimura and Watanabe, 2001; Knoll et al., 1995; Shen and Schidlowski, 2000) and a weak co-varying \(\delta^{13}C_{\text{carb}}\)–\(\delta^{13}C_{\text{org}}\) trend of Tommotian age (Goldberg et al., 2007; Guo et al., 2007a). Most of these data, however, were obtained from organic-rich shales with only a few paired \(\delta^{13}C_{\text{carb}}\)–\(\delta^{13}C_{\text{org}}\) analyses. More recent studies of the carbonate-rich succession in Morocco showed that decoupled \(\delta^{13}C_{\text{carb}}\) and \(\delta^{13}C_{\text{org}}\) are common in early Cambrian successions (Maloof et al., 2010b), but detailed \(\delta^{13}C_{\text{org}}\) profiles across the
individual δ¹³C_carb excursions and their spatial variability are not yet available. To better understand the temporal and spatial variability of δ¹³C_carb–δ¹²C_organ patterns, in this study we present paired δ¹³C_carb–δ¹²C_organ data of the early Cambrian (ca. 542–520 Ma) strata from the Yangtze platform in South China and compare the early Cambrian δ¹³C_carb–δ¹²C_organ patterns with those from the Ediacaran strata in the same region.

2. Paleogeography and stratigraphy

2.1. Paleogeography

The Ediacaran–Cambrian Yangtze platform development over a late Neoproterozoic rifted continental margin that is inferred to have initiated at the southeastern side of the Yangtze block (Fig. 1A) at ca. 830–820 Ma (Wang and Li, 2003; Zhao et al., 2011). A passive continental margin setting has been inferred for the Ediacaran–Cambrian strata on the basis of stratigraphic pattern, thickness, and the lack of significant igneous activity (Jiang et al., 2003, 2011; Wang and Li, 2003).

During the latest Ediacaran and earliest Cambrian (lower-middle Meishucunian or Nemakit–Daldynian), the Yangtze platform was characterized by predominately carbonate deposits in the northwest and mudstone/shale deposits in the southeast (Fig. 1B; Steiner et al., 2007; Wang, 1985; Zhu et al., 2007). A ‘transitional zone’ characterized by interbedded shale and carbonate deposits is located in northeastern Guizhou, northern Hunan and Hubei provinces (Fig. 1B), representing outer shelf environments of the Yangtze platform. At the end of the middle Meishucunian (after small shelly fossil assemblage 3), the shelf regions of the Yangtze platform was subaerially exposed (Steiner et al., 2007; Zhu et al., 2003), resulting in partial erosion of the earliest Cambrian strata, particularly in the inner shelf regions west of the Yangtze Gorges area (Fig. 1C). Subsequent transgression during the upper Meishucunian (Tommotian) led to deposition of deep-water black shales across the entire Yangtze platform (Fig. 1C). In comparison with the other early Cambrian successions such as those in Morocco (Malof et al., 2005, 2010a, 2010b) and Siberia (e.g., Kouchinsky et al., 2007), the early Cambrian (ca. 542 to 520 Ma) succession in the Yangtze platform are highly condensed and possibly less complete (Fig. 1C).

2.2. Early Cambrian stratigraphy in the Yangtze Gorges area

In the vicinity of the Yangtze Gorges area (Fig. 2A), the late Ediacaran Dengying Formation is overlain by the Yanjiahe Formation (Fig. 2B). The Yanjiahe Formation is composed of sand/chert dolostones in the lower part and interbedded limestone and black shale in the upper part. Thin phosphorite layers (mostly chertified) are present in the lower part and at the top of this unit. The Yanjiahe Formation is overlain by the black shales of the Shuijingtuo Formation (Fig. 1C) in the lower Meishucunian (Tommotian) to deposition of deep-water black shales across the entire Yangtze platform (Fig. 1C). In comparison with the other early Cambrian successions such as those in Morocco (Malof et al., 2005, 2010a, 2010b) and Siberia (e.g., Kouchinsky et al., 2007), the early Cambrian (ca. 542 to 520 Ma) succession in the Yangtze platform are highly condensed and possibly less complete (Fig. 1C).

2.3. Regional stratigraphic correlation

Regional correlation of the early Cambrian (ca. 542–520 Ma) strata in South China is mainly based on small shelly fossils and distinctive marker beds including phosphorite-rich and highly metalliferous black shales (Fig. 1C). Small Shelly Fossil Assemblage Zone 1 (SS1) represented by A. trisulcatus and P. unguliformis and Assemblage Zone 3 (SS3) represented by Watsonella crosbyi are widespread in shelf facies of the Yangtze platform (Steiner et al., 2007; Zhu et al., 2003). Traditionally their appearance was taken as the base of the N–D and Tommotian stages, respectively, but integrated biostratigraphy and carbon isotope chemostratigraphy suggested that the base of the N–D stage (i.e., the Precambrian–Cambrian boundary) would be lower than SS1, most likely coincident with the regional stratigraphic discontinuity at the top of the Dengying Formation (Fig. 1C; Brasier et al., 1990; Goldberg et al., 2007; Ishikawa et al., 2008; Li et al., 2009; Shen and Schidlowski, 2000; Steiner et al., 2007; Zhou et al., 1997; Zhu et al., 2003). Small Shelly Fossil Assemblage Zone 2 (SS2) represented by Paragloborilus subglobosus–P. squamulosa is more restricted to the proximal regions of the Yangtze platform (e.g., eastern Yunnan and Sichuan; Sections 1 and 2 in Fig. 1C) and its biostratigraphic significance is limited (Steiner et al., 2007). In the slope and basin facies, the Precambrian–Cambrian boundary is traditionally defined by the first occurrence of sponge spicules, aided by the presence of phosphorite layers/nodules that are close to the Precambrian–Cambrian boundary. The highly metalliferous black shales with high Ni–Mo concentrations from the Niutitang and Xiaoyanxi formations (Steiner et al., 2007; Lehmann et al., 2007; Wille et al., 2008; Yang et al., 2004) was once considered as close to the Precambrian–Cambrian boundary, but recent radiometric ages of 539.4±2.9 Ma (Compton et al., 2008), 523.2±0.7 Ma (Jiang et al., 2009) and 536±5.5 Ma (Chen et al., 2009) from ash beds below the highly metalliferous black shales indicate that the metalliferous beds are significantly younger than the Precambrian–Cambrian boundary, likely having an early Tommotian age (Fig. 1C).

3. Isotope analysis

Three well-exposed outcrop sections near Yichang and Changyang (Fig. 2A) were sampled at an average spacing of 10–20 cm. Collected samples were cut into two or more chips so that visual and petrographic observations can match the drilling spots. Sample powders (20–50 mg) were drilled from relatively fine-grained dark laminae in cleaned slabs and were then split for carbonate and organic isotope analyses. All isotope values are reported as δ values with reference to the Vienna Pee Dee Belemmite standard (VPDB). Sample preparation and analyses were performed in the Las Vegas Isotope Science (LVIS) Laboratory at the University of Nevada Las Vegas.

For δ¹³C_carb and δ¹⁸O analyses, about 50–200 μg of carbonate powders were reacted with orthophosphoric acid for 10 minutes at 70 °C, using a Kiel IV carbonate device connected to a Finnigan Delta V Plus mass spectrometer via dual-inlet. Analytical reproducibility was better than 0.1‰.
for both $\delta^{13}C_{\text{carb}}$ and $\delta^{18}O$ values, as monitored by NBS-19 and an internal standard.

For organic carbon isotope analysis, aliquots of powdered samples between 5 and 30 mg (depending on TOC content) were decarbonated in silver capsules overnight through acid fumigation (Harris et al., 2001) with concentrated HCl (12 M). After drying, one or more drops of 1 M HCl were added to the capsule to ensure complete carbonate removal. The silver capsules with carbonate-free residue were then neutralized using a stepwise washing process, by which each capsule was immersed in DI water (using 20 mL weighing dishes) for 6 h and then dried at 70 °C for 4 h. This wash and dry process was repeated up to 3 times until pH tests gave a near neutral value ($\geq$6.0). Samples were then dried and wrapped in tin capsules and stored in an oven at 105 °C prior to analysis. Organic carbon isotope were analyzed using an elemental analyzer (EA) coupled with a coniflow interface that automatically transfers carbon dioxide gas into a Finnigan Delta Plus mass spectrometer. USGS-24 (graphite), IAEA-600 (caffeine), and acetanilide (Costech Analytical Technologies) standards were used to monitor the external and internal uncertainty that was better than 0.2‰ for $\delta^{13}C_{\text{org}}$ and 0.1% for TOC. To monitor the reproducibility of organic-rich and organic-poor samples,
duplicates were analyzed for every sixth sample and their reproducibility in $\delta^{13}$C$_{org}$ and TOC was better than 0.5‰ and 0.2%, respectively.

4. Results

4.1. Jiuqunao section

In the Jiuqunao section (loc. 1 in Fig. 2A), a total of 109 samples were analyzed for the 62-m-thick interval that covers stratigraphic units from the uppermost Dengying Formation to the lowermost Shuijingtuo Formation (Fig. 3; Table A1). A negative $\delta^{13}$C$_{carb}$ excursion (CN1) with minimum values down to $\approx -4$‰ covers the lowermost 12 m of the Yanjiahe Formation. The negative to positive shift in $\delta^{13}$C$_{carb}$ occurs right after the phosphorous-cherty shale/limestone that contains abundant Micrhystridium-like acritarchs such as Heliosphaeridium ampliatum (cf. Dong et al., 2009; Yao et al., 2005) and small shelly fossil Anabarites trisulcatus (cf. Steiner et al., 2007). The rest of the Yanjiahe Formation (CP1; Fig. 3) has $\delta^{13}$C$_{carb}$ values mostly within the range of $0$‰ to $+2$‰, with a few down to $-2$‰. The second negative shift in $\delta^{13}$C$_{carb}$ (CN2) occurs at the Yanjiahe–Shuijingtuo transition, with minimum values down to $\approx -4$‰ in limestone layers and concretions of the basal Shuijingtuo Formation. Oxygen isotope values change from $-8$‰ to $-6$‰ in the lower part to $-8 \pm 2$‰ in the upper part of the section, but they do not show covariation with $\delta^{13}$C$_{carb}$ (Fig. 3). Organic carbon isotope ($\delta^{13}$C$_{org}$) values are decoupled from $\delta^{13}$C$_{carb}$ values. At the base of the Yanjiahe Formation, a $2$‰ shift in $\delta^{13}$C$_{org}$ from $-26$‰ to $-28$‰ occurs at the beginning of the negative $\delta^{13}$C$_{carb}$ excursion (CN1), but for the majority of CN1, $\delta^{13}$C$_{org}$ values remain at $-27$‰ to $-28$‰. A large negative shift in $\delta^{13}$C$_{org}$ from $-27$‰ to $-35$‰ occurs at the end of CN1, coincident with the lithological change from cherty dolostone to fossiliferous, phosphorous-cherty shale/limestone. Very stable $\delta^{13}$C$_{org}$ values around $-33$‰ span the rest of the section (CP1 and CN2) and they do not show a covariation with $\delta^{13}$C$_{carb}$ or TOC. The carbonate and organic carbon isotope difference ($\Delta \delta^{13}$C; $\Delta \delta^{13}$C = $\delta^{13}$C$_{carb}$ − $\delta^{13}$C$_{org}$) changes from 28‰ to 24‰ before the top of CN1, to $33 \pm 2$‰ across CP1, and to $-28$‰ at the basal Shuijingtuo Formation (CN2). A clear covariation between $\delta^{13}$C$_{carb}$ and $\Delta \delta^{13}$C is observed throughout the section (Fig. 3).

4.2. Jijiapo section

Samples ($n = 131$) from the 88-m-thick Jijiapo section (loc. 2 in Fig. 2A) covers the uppermost Dengying Formation, the entire Yanjiahe Formation and the lower Shuijingtuo Formation (Fig. 4; Table A1). Two negative $\delta^{13}$C$_{carb}$ excursions (CN1 and CN2) are present at the lower
Yanjiahe Formation and at the Yanjiahe–Shuijingtuo transition, respectively, consistent with those documented from a drilled core adjacent to the section (Ishikawa et al., 2008). However, strongly negative $\delta^{13}$C values down to $-5\%$ reported in Ishikawa et al. (2008) from a 10-cm-thick interval below the Yanjiahe–Shuijingtuo boundary were not observed in this study. Between the two negative $\delta^{13}$C excursions are positive $\delta^{13}$C values mostly from $+2\%$ to $+4\%$ (CP1). Oxygen isotope values are mostly around $-6\%$ in the upper part of the section (EP and CN1) and are around $-8\%$ in the upper part of the section. The $-2\%$ shift in $\delta^{18}$O coincides with the lithological change from dolostone to limestone. No $\delta^{13}$C–$\delta^{18}$O covariance is observed for the entire dataset and across each individual $\delta^{13}$C excursions.

Organic carbon isotope data (n=133) from the Hezi’ao section in Changyang (loc. 3 in Fig. 2A) show two negative $\delta^{13}$C excursions at the lower Yanjiahe and Shuijingtuo formations, respectively (Fig. 5; Table A1). The $\delta^{13}$C excursions at the Dengying–Yanjiahe boundary, a major negative shift down to $-36\%$ associated with the fossiliferous, phosphorous-cherty shale/limestone that contains small shelly fossil Anabarites trisulcatus, very stable $\delta^{13}$C values around $-33\%$ in the upper Yanjiahe Formation, and a $2\%$ increase from $-34\%$ to $-32\%$ in the lower Shuijingtuo Formation. Similar to the other two sections, the $\Delta\delta^{13}$C trend tracks that of $\delta^{13}$Cexcursion at the lower Yanjiahe boundary, and moderate values around $30\%$ across CN2 in the lower Shuijingtuo Formation.

4.3. Hezi’ao section

Carbon isotope data (n=133) from the Hezi’ao section in Changyang (loc. 3 in Fig. 2A) show two negative $\delta^{13}$C excursions at the lower Yanjiahe and Shuijingtuo formations, respectively (Fig. 5; Table A1). The $\delta^{13}$C and $\delta^{18}$O values and trends are similar to those of the Jiujiaonao and Lijiaopo sections (Figs. 3 and 4). Again, $\delta^{13}$Corg is decoupled from $\delta^{13}$Ccarb with a minor negative shift at the Dengying–Yanjiahe boundary, a major negative shift down to $-36\%$ associated with the fossiliferous, phosphorous-cherty shale/limestone that contains small shelly fossil A. trisulcatus, very stable $\delta^{13}$Corg values around $-33\%$ in the upper Yanjiahe Formation, and a $2\%$ increase from $-34\%$ to $-32\%$ in the lower Shuijingtuo Formation. Similar to the other two sections, the $\Delta\delta^{13}$C trend tracks that of $\delta^{13}$Ccarb, with lowest values down to $21\%$ associated with the CN1 $\delta^{13}$Ccarb minimum, maximum values up to $36\%$ across CP1 in the upper Yanjiahe Formation, and moderate values around $30\%$ across CN2 in the lower Shuijingtuo Formation.

4.4. Composite $\delta^{13}$C org–$\delta^{13}$C carb patterns

The overall $\delta^{13}$Ccarb and $\delta^{13}$Corg trends are persistent in the three measured sections, although absolute $\delta^{13}$C values slightly differ due to variable sampling resolution among sections. Composite stratigraphic and carbon isotope data from these sections, normalized to the average thickness of the Yanjiahe and Shuijingtuo formations, provide the following isotope feature (Figs. 6 and 7).
Two negative $\delta^{13}C_{\text{carb}}$ excursions are present in the lower Yanjiahe and lower Shuijingtuo formations, respectively (Fig. 6). The negative $\delta^{13}C_{\text{carb}}$ excursion from the lower Yanjiahe Formation (CN1) has the nadir slightly below the Small Shelly Fossil Assemblage Zone 1 (SS1) that has an early Nemakit–Daldynian (N–D) age. The negative $\delta^{13}C_{\text{carb}}$ excursion from the lower Shuijingtuo Formation (CN2) is associated with Small Shelly Fossil Assemblage Zone 3 (SS3) of early Tommotian age. These $\delta^{13}C_{\text{carb}}$ excursions have been documented from other sections in the Yangtze platform (e.g., Brasier et al., 1990; Goldberg et al., 2007; Ishikawa et al., 2008; Li et al., 2009; Shen and Schidlowski, 2000; Zhou et al., 1997) and have been correlated with those from global successions in Morocco (Maloof et al., 2005, 2010a, 2010b) and Siberia (Brasier et al., 1994; Kaufman et al., 1996; Kouchinsky et al., 2007). The sub-million-year-scale $\delta^{13}C_{\text{carb}}$ excursions documented from Morocco (Maloof et al., 2005, 2010a, 2010b), however, are not well displayed in the studied sections. The upper N–D interval between CN1 and CN2 (CP1 in Fig. 6) has $\delta^{13}C_{\text{carb}}$ values scattered between 0‰ and 4‰, but it is difficult to define discrete $\delta^{13}C_{\text{carb}}$ excursions. The lack of sub-million-year-scale $\delta^{13}C_{\text{carb}}$ excursions in the Yangtze platform is likely due to highly condensed deposition that has obscured the record of short-term carbon cycles.

Oxygen isotopes from the lower part of the sections (EP and CN1) are mostly within the range of $-5$‰ to $-7$‰, while for the upper part of the sections (CP1 and CN2), $\delta^{18}O$ values are 2–3‰ lower, mostly within the range of $-7$‰ to $-10$‰ (Fig. 7A). The 2–3‰ decrease in $\delta^{18}O$ coincides with a lithological change from dolostone to limestone. There is no $\delta^{13}C_{\text{carb}}$–$\delta^{18}O$ covariance across each of the negative $\delta^{13}C_{\text{carb}}$ excursions and for the entire stratigraphic interval (Fig. 7A).

Both CN1 and CN2 show decoupled $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$, but their expressions differ (Fig. 6). The $\delta^{13}C_{\text{org}}$ values across CN1 show a negative shift at the beginning of CN1 (CN1a), an upward increase towards the $\delta^{13}C_{\text{carb}}$ minimum (CN1b), and a large negative shift from $-27$‰ to $-36$‰ followed by a positive shift from $-36$‰ to $-33$‰ at the end of CN1 (CN1c). In contrast, no significant (<2‰) $\delta^{13}C_{\text{org}}$ change is observed across CN2. The most significant change in $\delta^{13}C_{\text{org}}$ at the end of CN1 (CN1c) coincides with an increase in TOC and a lithological change from cherty dolostone to phosphorous-cherty shale/limestone (Figs. 6 and 7B). The stratigraphic interval between CN1 and CN2 (interval CP1) has very stable $\delta^{13}C_{\text{org}}$ values around $-33$‰ and high $\Delta\delta^{13}C$ (>32‰).

There is no covariance between $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ for each of the $\delta^{13}C_{\text{carb}}$ excursions and for the entire stratigraphic interval (Fig. 7C). The $\Delta\delta^{13}C$ profile tracks that of $\delta^{13}C_{\text{carb}}$ (Fig. 6) and there is a clear covariance between $\delta^{13}C_{\text{carb}}$ and $\Delta\delta^{13}C$ for each of the isotope excursions (Fig. 7E). The data points, however, fall into two distinct groups with different slopes and y-axis intercepts in the $\delta^{13}C_{\text{carb}}$–$\Delta\delta^{13}C$ plot (Fig. 7F). Data points from the lower part of the sections (EP + CN1a + CN1b in Fig. 6) have a slope of 0.87 and a y-intercept of $-23.7$‰, while those from the upper part (CN1c + CP1 + CN2 in Fig. 6) show a slope of 0.99 and a y-intercept of $-33.3$‰ (Fig. 7E).
These features are typical of late Neoproterozoic carbonates but they are different from those of the Cenozoic δ¹³C – Δδ¹³C plot that has a slope of 0.2–0.3 and a y-intercept of −6‰ (Rothman et al., 2003).

5. The origin of decoupled carbonate and organic carbon isotopes

The δ¹³C patterns from the early Cambrian strata in the Yangtze Gorges area are similar to those of the late Neoproterozoic in that (1) there is no comparable δ¹³Corg excursions associated with the δ¹³Ccarb excursions (Fig. 6) and (2) there is a strong correlation between δ¹³Ccarb and Δδ¹³C (Fig. 7). These features have been interpreted as resulting from burial diagenetic alteration of δ¹³Ccarb (Derry, 2010a, 2010b) or as evidence for the existence of a large dissolved organic carbon (DOC) reservoir capable of buffering carbon isotopes of oceanic organic matter (Rothman et al., 2003). The diagenetic interpretation emphasizes the δ¹³C – δ¹⁸O covariance through negative δ¹³Ccarb excursions and implies that the negative δ¹³Ccarb excursions from late Neoproterozoic successions are not necessarily globally synchronous. The lack of δ¹³C – δ¹⁸O covariance across the N–D and Tommotian negative δ¹³Ccarb excursions (Fig. 7A) and more importantly, the global occurrence of these δ¹³Ccarb excursions in biostratigraphically correlatable units (Ishikawa et al., 2008; Kouchinsky et al., 2007; Li et al., 2009; Maloof et al., 2010a, 2010b) argue against substantial diagenetic reset of δ¹³Ccarb values. Similarly, the large temporal variations in δ¹³Corg across the N–D δ¹³Ccarb excursion, particularly the co-varying positive shift of δ¹³Ccarb and δ¹³Corg at the end of the N–D δ¹³Ccarb excursion (CN1c in Fig. 6), are difficult to be explained by the isotopic buffering of a large and persistent DOC reservoir in the ocean (cf. Jiang et al., 2010), in which temporal changes in δ¹³Corg would be much less significant or invariant (Fike et al., 2006; McFadden et al., 2008; Rothman et al., 2003; Swanson-Hysell et al., 2010).

5.1. Regional δ¹³Corg Variability

Compilation of existing organic carbon isotope data (Fig. 8) across the Ediacaran–Cambrian transition in South China provides insights on the regional variability of δ¹³Corg in the Yangtze platform. In the inner shelf section of eastern Yunnan Province (Section 1; Fig. 8), co-varying δ¹³Ccarb and δ¹³Corg were reported from the N–D strata, although no paired δ¹³Ccarb–δ¹³Corg data are available (Shen and Schidlowski, 2000). Distal inner shelf (intrashelf lagoon) section in Shatan (Section 2; Fig. 8) has limited N–D strata due to stratigraphic truncation by unconformities and/or stratigraphic condensation. A few δ¹³Corg values reported from the Kuanchuanpu Formation of N–D age are ≤−34‰ (Goldberg et al., 2007; Guo et al., 2007a). It is uncertain if these values are correlatable with those from the upper N–D in the Yangtze Gorges area (Fig. 6). Tommotian strata in this section show co-varying δ¹³Ccarb–δ¹³Corg trends, but Δδ¹³C values are mostly ≥32‰, implying chemoautotrophic biomass contribution (Goldberg et al., 2007). From the slope section in Ganziping (Section 5 in Fig. 8; Chen et al., 2009), a few δ¹³Corg values reported from the Dengying Formation are ≥−28‰, similar to those from the Dengying Formation in the Yangtze Gorges area. Up to 10‰ shift in δ¹³Ccarb occurs at the Ediacaran–
Cambrian transition, coincident with a lithological change from dolostone to siliceous shale and chert. The N–D and Tommotian strata in this section are highly condensed, but δ^13C_{org} values display up to 5‰ temporal variations within N–D strata and remain very stable around −32‰ after the N–D and Tommotian boundary. It is uncertain whether the N–D δ^13C_{org} shift seen in the Yangtze Gorges areas (CN1c in Figs. 6 and 8) should be correlated with the base or the top of the Liuchapo Formation in this section. In the basinal sections at Songtao and Yuanling (Sections 6 and 7 in Fig. 8; Guo et al., 2007a), the uppermost Ediacaran δ^13C_{org} values around −34‰, but a small (−2‰) negative δ^13C_{org} shift is seen at the uppermost Liuchapo Formation. Given the existing age constraints and sample resolution, it is difficult to determine if this negative shift in δ^13C_{org} is time equivalent to the entire N–D δ^13C_{org} excursion (CN1 in Fig. 6) or the uppermost portion of the N–D excursion (CN1c in Fig. 6) in the Yangtze Gorges area. The lower Tommotian strata in the basinal sections have δ^13C_{org} values around −32±1‰, which are similar to those from the outer shelf sections in the Yangtze Gorges area, but they are 1–2‰ higher than those from the inner shelf section (Section 2; Fig. 8). In the Yuanling section (Section 7; Fig. 8), a 5‰ positive δ^13C_{org} ‘excursion’ is present in the upper Tommotian–Atdabanian strata, but its regional correlation and significance need to be clarified in the future because (1) the available age constraints are insufficient to precisely correlate the hosting stratigraphic unit across the basin, and (2) no Tommotian δ^13C_{org} excursion is seen in the other basinal section (Section 6; Fig. 8).

In spite of uncertainties on δ^13C_{org} excursions in deep-water sections that require clarification with additional isotope data of higher stratigraphic resolution and better age constraints, the regional variability in δ^13C_{org} across the shelf-to-basin transect (Fig. 8) is inconsistent with an early Cambrian ocean that was isotopically homogeneous and buffered by a large DOC reservoir. Instead, it indicates that the decoupled δ^13C_{carb}–δ^13C_{org} pattern seen in the Yangtze Gorges area (Figs. 3–6) is a localized phenomenon that may change with paleogeographic settings. In addition, the data also show that during the latest Ediacaran and earliest Cambrian (basal N–D), δ^13C_{org} values from shale- and chert-dominated basinal sections are 8–10‰ lower than those from the carbonate-dominated shelf sections, but more homogeneous δ^13C_{org} values around −33‰ characterize the lower Tommotian strata across the basin.

5.2. Controls on δ^13C_{org}

As have been reviewed in numerous publications (e.g., Ader et al., 2009; Des Marais et al., 1992; Goldberg et al., 2007; Hayes et al., 1983, 1999; Jiang et al., 2010; Kaufman and Knoll, 1995; Maloof et al., 2010b; Young et al., 2008), carbon isotopes of bulk organic matter can be influenced by many factors including carbon isotope fractionation during primary and secondary production, detrital organic carbon input, DOC contribution, post-depositional alteration through diagenesis/metamorphism (e.g., methanogenesis, bio- and thermal degrada-
tion), and hydrocarbon contamination (Fig. 9A). While co-varying δ^13C_{carb} and δ^13C_{org} imply that organic carbon in marine sediments (sedimentary rocks) was mainly derived from primary (photosynthetic) production without substantial post-depositional alteration, decoupled δ^13C_{carb} and δ^13C_{org} have a much less definitive meaning. If organic carbon contribution from one or more of the non-primary sources (secondary production, detrital organic carbon, DOC, post-depositional...
Fig. 7. Cross plots of isotope data from the Yangtze Gorges area. Intervals EP, CN1, CP1, and CN2 match with those in Fig. 6. (A) \( \delta^{13}C_{\text{carb}} \) versus \( \delta^{18}O_{\text{carb}} \). Neither the individual intervals nor the entire data show \( \delta^{13}C_{\text{carb}} \)–\( \delta^{18}O_{\text{carb}} \) covariance. (B) Total organic carbon (TOC) versus \( \delta^{13}C_{\text{org}} \). No clear TOC–\( \delta^{13}C_{\text{org}} \) covariance is observed, except for interval CN1 (\( R^2 = 0.53 \)). (C) \( \delta^{13}C_{\text{carb}} \) versus \( \delta^{13}C_{\text{org}} \). There is no \( \delta^{13}C_{\text{carb}} \)–\( \delta^{13}C_{\text{org}} \) covariance for the individual intervals and for the entire data. (D) \( \delta^{13}C_{\text{org}} \) versus \( \Delta \delta^{13}C \) (\( \Delta \delta^{13}C = \delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}} \)). Except for CN1 (\( R^2 = 0.73 \)), no \( \delta^{13}C_{\text{org}} \)–\( \Delta \delta^{13}C \) covariance is observed for other intervals. (E) Cross plot of \( \delta^{13}C_{\text{carb}} \) versus \( \Delta \delta^{13}C \) for intervals EP+CN1a+CN1b and CN1c+CP1+CN2 (Fig. 6), with a linear fit computed using the reduced major axis method. (F) \( \delta^{13}C_{\text{carb}} \) versus \( \Delta \delta^{13}C \), for intervals EP+CN1a+CN1b and CN1c+CP1+CN2 (Fig. 6), with a linear fit computed using the reduced major axis method.
order or fracturally controlled (Thompson-Rizer, 1993), but they should be localized along lithologically (Chen et al., 2009); 6 constraints). Data source: 1 dissolved organic carbon precursors (Hayes, 2001). Migrating hydrocarbons values may be more negative than those of their particulate and dis- DOC may have experienced multiple recycling, their carbon isotope values (e.g., Clayton, 1991; Hayes et al., 1983; Tocqué et al., 2005). In addition, it has been argued that thermal deg- radation relates to the burial history of sedimentary basins; it may change the absolute δ13Corg values but not the temporal δ13Corg trend (Des Marais et al., 1992). These statements may be true for organic-rich sedimentary rocks, but for organic-poor carbonates, δ13Corg may be more sensitive to diagenesis and thermal maturation. First, assuming that the same amount of 12C-rich carbon were removed during methanogenesis and thermal maturation, the change in δ13C of residual organic matter in organic-poor carbonates may be significantly larger than that in organic-rich shale and carbonates. Second, bio- and thermal degradation of organic matter may lead to the amplification of isotope signature of detrital organic carbon. For both organic-rich and organic-poor sedimentary rocks, there may be a certain amount of detrital organic carbon. Because detrital fossil organic matter is much less reactive compared to fresh photosynthetic organic carbon, diagenesis (e.g., biodegradation and methanogenesis) and thermal maturation would preferentially remove the latter. In organic-rich rocks, removal or altered portion of the primary organic carbon may not substantially change the δ13Corg values, but for

Similarly, methanogenesis releases 13C-depleted methane and results in 13C-enrichment in residual TOC (Irwin et al., 1977; Summons et al., 1998). The degree of 13C-enrichment in TOC through methanogenesis depends on the amount of substrate consumption and can be highly variable in different microbial ecosystems (Bradley et al., 2009; Summons et al., 1998).

It has been frequently reviewed and widely cited that diagenesis and thermal maturation do not substantially alter carbon isotope values of organic matter in sedimentary rocks (e.g., Ader et al., 2009; Bekker et al., 2008; Chen et al., 2009; Malloof et al., 2010b; Young et al., 2008). For rocks metamorphically lower than greens- chist facies, which is most likely the case for the late Neoprotero- zoic–early Cambrian strata in South China (Wang et al., 1993, 2008), 13C-enrichment through bio- and thermal degradation would be in the order of 2–3‰ (e.g., Clayton, 1991; Hayes et al., 1983; Tocqué et al., 2005). In addition, it has been argued that thermal deg- radation relates to the burial history of sedimentary basins; it may change the absolute δ13Corg values but not the temporal δ13Corg trend (Des Marais et al., 1992). These statements may be true for organic-rich sedimentary rocks, but for organic-poor carbonates, δ13Corg may be more sensitive to diagenesis and thermal maturation. First, assuming that the same amount of 12C-rich carbon were removed during methanogenesis and thermal maturation, the change in δ13C of residual organic matter in organic-poor carbonates may be significantly larger than that in organic-rich shale and carbonates. Second, bio- and thermal degradation of organic matter may lead to the amplification of isotope signature of detrital organic carbon. For both organic-rich and organic-poor sedimentary rocks, there may be a certain amount of detrital organic carbon. Because detrital fossil organic matter is much less reactive compared to fresh photosynthetic organic carbon, diagenesis (e.g., biodegradation and methanogenesis) and thermal maturation would preferentially remove the latter. In organic-rich rocks, removal or altered portion of the primary organic carbon may not substantially change the δ13Corg values, but for

overprints) constitutes a significant portion of TOC in sedimentary rocks, decoupled δ13C_carb and δ13C_org values would be expected (Fig. 9A), at least locally.

Carbon isotope signature of non-primary organic matter is strongly dependent on geological settings and placeoenvironmental condi- tions, and thus there is no definitive δ13C value for each category of non-primary organic carbon. However, numerous studies on modern and ancient sedimentary organic matter have provided guidance for qualitatively evaluating the isotope differences between primary and non-primary organic matter. For secondary production, chem- autotrophic organisms use recycled carbon during carbon fixation and their biomass is up to 15% depleted in 13C relative to primary photosynthate (e.g., Conway et al., 1994; Hollander and Smith, 2001). Methanotrophic bacteria assimilate carbon from 13C-depleted methane and their biomass can be 13C-depleted relative to photosyn- thetic organic matter by ~15% to ~40% (Conway et al., 1994; Summons et al., 1994, 1998). Statistic review of paired carbonate and organic carbon isotopes from the geological record suggests that organic matter with Δ13C values ≥32‰ must have involved chemoautotrophic biomass contribution (Hayes et al., 1999). Carbon isotope values of detrital organic carbon should reflect those of the weathering source rocks and, if not following a long-lasting unconfor- mity, may be similar with those of the underlying stratigraphic units. Dissolved organic carbon (DOC) may escape degradation under anox- ic conditions during which small molecules remain as highly aged and slowly cycling components (e.g., Loh et al., 2004). Because aged DOC may have experienced multiple recycling, their carbon isotope values may be more negative than those of their particulate and dis- solved organic carbon precursors (Hayes, 2001). Migrating hydrocarbons have highly variable δ13C values from −21‰ to −33‰ (Whelan and Thompson-Rizer, 1993), but they should be localized along lithologically or fractionally controlled fluid pathways. Thermal maturation of organic matter removes 13C-depleted gases and shifts TOC towards higher δ13C values (e.g., Clayton, 1991; Hayes et al., 1983; Tocqué et al., 2005).

Similarly, methanogenesis releases 13C-depleted methane and results in 13C-enrichment in residual TOC (Irwin et al., 1977; Summons et al., 1998). The degree of 13C-enrichment in TOC through methanogenesis depends on the amount of substrate consumption and can be highly variable in different microbial ecosystems (Bradley et al., 2009; Summons et al., 1998).

It has been frequently reviewed and widely cited that diagenesis and thermal maturation do not substantially alter carbon isotope values of organic matter in sedimentary rocks (e.g., Ader et al., 2009; Bekker et al., 2008; Chen et al., 2009; Malloof et al., 2010b; Young et al., 2008). For rocks metamorphically lower than greens- chist facies, which is most likely the case for the late Neoprotero- zoic–early Cambrian strata in South China (Wang et al., 1993, 2008), 13C-enrichment through bio- and thermal degradation would be in the order of 2–3‰ (e.g., Clayton, 1991; Hayes et al., 1983; Tocqué et al., 2005). In addition, it has been argued that thermal deg- radation relates to the burial history of sedimentary basins; it may change the absolute δ13Corg values but not the temporal δ13Corg trend (Des Marais et al., 1992). These statements may be true for organic-rich sedimentary rocks, but for organic-poor carbonates, δ13Corg may be more sensitive to diagenesis and thermal maturation. First, assuming that the same amount of 12C-rich carbon were removed during methanogenesis and thermal maturation, the change in δ13C of residual organic matter in organic-poor carbonates may be significantly larger than that in organic-rich shale and carbonates. Second, bio- and thermal degradation of organic matter may lead to the amplification of isotope signature of detrital organic carbon. For both organic-rich and organic-poor sedimentary rocks, there may be a certain amount of detrital organic carbon. Because detrital fossil organic matter is much less reactive compared to fresh photosynthetic organic carbon, diagenesis (e.g., biodegradation and methanogenesis) and thermal maturation would preferentially remove the latter. In organic-rich rocks, removal or altered portion of the primary organic carbon may not substantially change the δ13Corg values, but for
organic-poor carbonates, organic carbon from primary production may be largely or completely removed, leaving the less reactive detrital organic carbon as the only organic remains. In this case, $\delta^{13}C_{\text{org}}$ values of organic-poor rocks may record the isotope signature of detrital organic matter rather than photosynthetic organic carbon from the surface ocean.

5.3. The origin of decoupled $\delta^{13}C_{\text{carb}}$–$\delta^{13}C_{\text{org}}$ pattern

The decoupled $\delta^{13}C_{\text{carb}}$–$\delta^{13}C_{\text{org}}$ across the N–D $\delta^{13}C_{\text{carb}}$ excursion (CN1) occurs in organic-poor dolostones that have TOC contents mostly $<0.1\%$ (Fig. 6). As summarized in Fig. 9A, such a carbon isotope pattern implies that the $\delta^{13}C_{\text{org}}$ values across the majority of CN1 may record the isotope signature of non-photosynthetic origin. Among the possible non-photosynthetic organic carbon sources (Fig. 9A), secondary production through chemoautotrophic/methanotrophic biomass contribution commonly results in lower $\delta^{13}C_{\text{org}}$ and higher $\Delta\delta^{13}C$. This is inconsistent with the slight increase of $\delta^{13}C_{\text{org}}$ and decrease of $\Delta\delta^{13}C$ towards the minimum of CN1 (Fig. 9B). The large temporal and spatial variations in $\delta^{13}C_{\text{org}}$ across CN1 (Fig. 8) are also inconsistent with substantial organic carbon contribution from an oceanic DOC reservoir. Hydrocarbon contamination may cause local positive shift in $\delta^{13}C_{\text{org}}$, but it is inconsistent with low TOC contents at the same stratigraphic level in multiple sections (Figs. 3–5), the lack of physical evidence for such an event, and invariable $\delta^{18}O$ values across CN1. The more likely cause of the decoupled $\delta^{13}C_{\text{carb}}$–$\delta^{13}C_{\text{org}}$ from this interval may have resulted from significant chemoautotrophic–methanotrophic biomass contribution.
to bulk organic matter (Hayes et al., 1999) in anoxic–euxinic environments, which may have been pervasive across the Yangtze platform during late N–D and Tommotian times (e.g., Goldberg et al., 2007; Guo et al., 2007b; Lehmann et al., 2007; Wille et al., 2008). Under pervasive anoxia/euxinia, growth of aged DOC at regional or basinal scale, if not globally, would be an expected outcome, adding “buffering” effects to the carbon isotopes of organic matter across the lower Tommotian δ¹³Ccarb excursion (interval D; Fig. 9B).

### 6. Implications for decoupled δ¹³Ccarb–δ¹³Corg from Ediacaran successions

The lower N–D δ¹³Ccarb–δ¹³Corg pattern shows striking similarities to those from the basal (Jiang et al., 2010) and upper (McFadden et al., 2008) Doushantuo Formation of the Ediacaran Period (Fig. 10). In all three cases, decoupled δ¹³Ccarb–δ¹³Corg are seen in organic-poor carbonates (TOC ≤ 0.1%) and coupled δ¹³Ccarb–δ¹³Corg occur in organic-rich black shale and carbonates at the end of the δ¹³Ccarb excursion. The shift from decoupled to coupled δ¹³Ccarb–δ¹³Corg in the upper Doushantuo Formation (McFadden et al., 2008) and Shuram Formation (Fike et al., 2006) was taken as evidence for the terminal oxidation of a unusually large oceanic DOC reservoir, which has been inferred to have existed since the early Cryogenian (Swanson-Hysell et al., 2010). The repetitive occurrences of similar δ¹³Ccarb–δ¹³Corg patterns in Ediacaran–early Cambrian strata are apparently inconsistent with such a simplified oxidation model for late Neoproterozoic oceans. Instead, the strong correlation of δ¹³Corg with lithology and TOC contents suggest that the carbon isotope patterns from three distinct stratigraphic intervals may share the same origin: δ¹³Corg values from organic-poor carbonates mainly record isotopic signature of diagenetically altered or detrital organic carbon, while those from organic-rich shale and carbonates at the end of the δ¹³Ccarb excursion. It does not mean that low TOC carbonates had higher detrital organic carbon content, but implies that organic-poor carbonates had originally low primary/detrital organic carbon ratio, and diagenetic/thermal degradation may have preferentially removed chemically more reactive photosynthetic organic carbon. If this is the case, the decoupled δ¹³Ccarb and δ¹³Corg patterns recorded in low-TOC carbonates of late Neoproterozoic successions (e.g., Fike et al., 2006; McFadden et al., 2008; Swanson-Hysell et al., 2010) should not be taken as evidence for the existence of a large oceanic DOC reservoir capable of buffering the δ¹³C of marine organic carbon.

The concept of a large DOC reservoir, however, still remains intriguing, although its size and causal link with the negative δ¹³Ccarb anomalies require independent evidence. Given the pervasive anoxia in late Neoproterozoic–early Cambrian oceans (Canfield et al., 2008; Goldberg et al., 2007; Lehmann et al., 2007; Li et al., 2010; Wille et al., 2008), high DOC concentration in deep-ocean seawater and marine pore waters would be an expected outcome. In modern anoxic basins such as the Black Sea, anoxic deep waters have an average DOC concentration of 120 μM (Ducklow et al., 2007), 2.6 times that of the deep open ocean (45 μM). In shallow water column close to the chemocline, DOC concentrations are as high as 280 μM, but most of it did not escape bacterial degradation within a few months (Cauwet et al., 2002; Ducklow et al., 2007). With much lower oxygen and sulfate level in late Neoproterozoic–early Cambrian ocean seawater, DOC enrichment of a few times or even tens of times higher than that of the modern ocean is conceivable, particularly in restricted basins with less frequent ventilation through ocean circulation. The early-middle Ediacaran Doushantuo basin in the Yangtze Gorges area might well be one of such basins. Here the lower-middle part of the Doushantuo Formation has high TOC contents (TOC = 1.2 ± 1.0%) but invariable δ¹³Corg values (−29.5 ± 1.0‰; McFadden et al., 2008; Xiao et al., 2012), similar to those of the upper N–D and Tommotian strata (Fig. 6). The invariable δ¹³Corg values from high-TOC black shale and carbonates of the lower-middle Doushantuo Formation could be caused by intensive organic carbon recycling by chemo- and methanotrophs under long-lasting anoxic conditions, but they could also be caused by isotopic “buffering” from highly concentrated DOC in water column and porewater. In fact, the germanium/silica (Ge/Si) ratios from chert nodules of the lower Doushantuo strata in this area do suggest high DOC content in seawater and porewater (Shen et al., 2011). However, the majority of the Ediacaran Doushantuo Formation in the Yangtze Gorges area was deposited from a restricted intrashelf lagoon (Bristow et al., 2009; Jiang et al., 2011); to what extent it records global ocean chemistry is questionable and requires tests in more open-marine settings.

### 7. Conclusions

Paired δ¹³Ccarb–δ¹³Corg analyses of the early Cambrian (ca. 542–520 Ma) strata in the Yangtze Gorges area in South China reveal strongly decoupled δ¹³Ccarb and δ¹³Corg across the lower Nemakit–Daldynian (N–D) and basal Tommotian negative δ¹³Ccarb excursions. Across the N–D δ¹³Ccarb excursion, decoupled δ¹³Ccarb–δ¹³Corg are seen in organic-poor carbonates (TOC ≤ 0.1%), but coupled δ¹³Ccarb–δ¹³Corg occur in organic-rich black shale and carbonates at the end of the δ¹³Ccarb excursion. Across the basal Tommotian δ¹³Ccarb excursion, δ¹³Corg values do not show significant change (≤ 2‰). Regional correlation across a shelf-to-basin transect reveals strong lateral heterogeneity of δ¹³Corg during the early-middle N–D but more homogenized δ¹³Corg values across the basin during the late N–D and Tommotian. The temporal and spatial variations in δ¹³Corg suggest that the decoupled δ¹³Ccarb and δ¹³Corg across the N–D δ¹³Ccarb excursion are localized features resulting from diagenetically altered organic carbon and/or diagenetic amplification of detrital organic carbon isotope signature in organic-poor carbonates. In contrast, decoupled δ¹³Ccarb and δ¹³Corg from the upper N–D and lower Tommotian strata were likely originated from chemoaerotrophic–methanotrophic biomass contribution to organic matter in strongly anoxic/euxinic environments.

The lower N–D δ¹³Ccarb–δ¹³Corg patterns show striking similarities to those from the basal Doushantuo Formation (635 Ma) and upper (ca. 551 Ma) Doushantuo Formation. In all three cases, decoupled δ¹³Ccarb–δ¹³Corg are seen in organic-poor carbonates (TOC ≤ 0.1%) and coupled δ¹³Ccarb–δ¹³Corg occur in organic-rich black shale and carbonates at the end of the δ¹³Ccarb excursion. These similarities suggest that the decoupled δ¹³Ccarb–δ¹³Corg from low-TOC carbonates of Ediacaran–early Cambrian successions recorded isotopic signature of diagenetically altered or detrital organic carbon rather than the isotope buffering from a large dissolved organic carbon (DOC) reservoir. Given the pervasive anoxia/euxinia in Ediacaran–early Cambrian oceans, DOC-rich environments may have been common, but the causal link between the negative δ¹³Ccarb excursions and a large DOC reservoir requires independent evidence other than decoupled δ¹³Ccarb–δ¹³Corg from single sections.

Supplementary materials related to this article can be found online at doi:10.1016/j.epsl.2011.11.018.
A. δ¹³Cₗ and δ¹³C₉₉ pattern at the Precambrian - Cambrian transition

B. δ¹³Cₗ and δ¹³C₉₉ pattern of the upper Doushantuo Formation

C. δ¹³Cₗ and δ¹³C₉₉ pattern at the basal Doushantuo Formation
We thank Dr. M.J. Nicholl for proof reading the manuscript and Drs. Peter deMenocal [Editor], David Fike, and an anonymous reviewer, for their careful review and constructive suggestions that significantly improved the paper. This research was supported by the National Science Foundation (EAR-0745825 and EAR-0745827) and the National Natural Science Foundation of China (40621002). Jiang gratefully acknowledges UNLY Sabbatical Leave support.

Acknowledgements

References


