

## Original Article

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# Sedimentology and chemostratigraphy of the terminal Ediacaran Dengying Formation at the Gaojiashan section, South China

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**Abstract**

The terminal Ediacaran Dengying Formation (*c.* 551.1–538.8 Ma) in South China is one of two successions where Ediacara-type macrofossils are preserved in carbonate facies along with skeletal fossils and bilaterian animal traces. Given the remarkable thickness of carbonate-bearing strata deposited in less than 12.3 million years, the Dengying Formation holds the potential for construction of a relatively continuous chemostratigraphic profile for the terminal Ediacaran Period. In this study, a detailed sedimentological and chemostratigraphic ( $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{18}\text{O}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{34}\text{S}_{\text{pyrite}}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) investigation was conducted on the Dengying Formation at the Gaojiashan section, Ningqiang County of southern Shaanxi Province, South China. Sedimentological results reveal an overall shallow-marine depositional environment. Carbonate breccia, void-filling botryoidal precipitates and aragonite crystal fans are common in the Algal Dolomite Member of the Dengying Formation, suggesting that peritidal facies were repeatedly karstified. The timing of karstification was likely early, probably soon after the deposition of the dolomite sediments. The presence of authigenic aragonite cements suggests high alkalinity in the terminal Ediacaran ocean. Geochemical analysis of micro-drilled samples shows that distinct compositions are registered in different carbonate phases, which should be considered when constructing chemostratigraphic profiles representative of true temporal variations in seawater chemistry. Integrated chemostratigraphic data suggest enhanced burial of organic carbon and pyrite, and the occurrence of extensive marine anoxia (at least in the Gaojiashan Member). Rapid basinal subsidence and carbonate accumulation during a time of elevated seawater alkalinity and increased rates of pyrite burial may have facilitated the evolutionary innovation of early biomineralizing metazoans.

**1. Introduction**

The Ediacaran Period (*c.* 635.2–538.8 Ma) witnessed the first rise of macroscopic, mobile and biomineralizing animal life in Earth's history (Narbonne *et al.* 2012; Xiao *et al.* 2016). Ediacara-type macrofossils are primarily preserved as soft-bodied impressions in fine-grained siliciclastic rocks (Narbonne, 2005). However, these lithologies offer limited opportunities for palaeoenvironmental analysis using geochemical tools. Two rare Ediacara-type macrofossil assemblages have thus far been found in well-preserved marine carbonate successions: the Khatyspyt Formation in Arctic Siberia (Fedonkin, 1990; Knoll *et al.* 1995; Grazhdankin *et al.* 2008; Rogov *et al.* 2012, 2013a,b, 2015; Nagovitsin *et al.* 2015; Cui *et al.* 2016a) and the middle Dengying Formation (Gaojiashan or Shibantan members) in South China (Sun, 1986; Xiao *et al.* 2005; Chen *et al.* 2014, 2018; Cui *et al.* 2016b; Mason *et al.* 2017; Shen *et al.* 2017). Insofar as both exhibit extraordinary fossils with exceptional preservation, these Lagerstätten provide unique windows into terminal Ediacaran ecosystems.

One of the foci of ongoing research in the Ediacaran Period is to better understand the biogeochemical conditions that may have affected the evolutionary transition of the earliest metazoans. In this regard, the terminal Ediacaran Dengying Formation at the Gaojiashan section (referred to as the DYF@GJS hereafter) can offer key insights (see details in Section 2). Although the bio- and chemostratigraphy of the DYF@GJS has been previously studied (Meyer *et al.* 2012;

Cai *et al.* 2014, 2019; Cui *et al.* 2016b), no complete and integrated chemostratigraphic profiles have ever been published for the entire DYF@GJS.

In this study, we conducted a high-resolution chemostratigraphic investigation of the 631.5 m thick DYF@GJS, including the Algal Dolomite and Beiwan members that we have not investigated in detail in previous studies (Figs 1–12), in order to (1) complete its chemostratigraphic profile (Fig. 13) based on our earlier publication (H. Cui, unpub. Ph.D. thesis, Univ. Maryland, 2015; Cui *et al.* 2016b); (2) evaluate the impact of diagenesis on various lithofacies preserved in the succession; (3) better constrain the environmental context of the carbonate platform; and (4) explore the potential causal link between palaeoenvironmental change and early animal biomineralization during the terminal Ediacaran Period.

## 2. Significance the Dengying Formation

The Dengying Formation in the studied region has a number of features that may aid in a better understanding of the terminal Ediacaran ecosystems, which are summarized below.

### 2.a. Biomineralizing animal fossils and trace fossils

The Gaojiashan Member of the middle Dengying Formation hosts the Gaojiashan biota, including the earliest biomineralizing animal fossils *Cloudina* and *Sinotubulites* (Hua *et al.* 2007; Cai *et al.* 2010, 2011, 2013, 2014, 2015, 2017), other calcareous fossils such as *Protolagena* (Cai *et al.* 2010), non-biomineralizing tubular fossils such as *Shaanxilithes*, *Gaojiashania* and *Conotubus* (Cai *et al.* 2010), as well as trace fossils made by mobile bilaterian animals (Lin *et al.* 1986; Zhang, 1986; Ding *et al.* 1992). *Cloudina* and *Sinotubulites* also extend into the overlying Beiwan Member at the Gaojiashan and nearby Lijiagou sections (Cai *et al.* 2010). The first appearance datum (FAD) of biomineralizing animals has been regarded as a key datum for the definition of the Terminal Ediacaran Stage (Xiao *et al.* 2016; G. M. Narbonne, unpub. data, Terminal Ediacaran Stage Working Group, results of the first ballot, July 2018).

### 2.b. Chemostratigraphy

The dominance of well-preserved carbonates in the thick Dengying Formation enables global correlations via chemostratigraphy. For example, the carbonate carbon isotope ( $\delta^{13}\text{C}_{\text{carb}}$ ) profile reveals a positive excursion in the Gaojiashan Member of the Dengying Formation (Cui *et al.* 2016b), which is likely correlative with a similar magnitude excursion in the basal Khatyspyt Formation in Siberia (Cui *et al.* 2016a). In addition, large isotopic fluctuations in nitrogen ( $\delta^{15}\text{N}$ ), pyrite sulfur ( $\delta^{34}\text{S}_{\text{pyrite}}$ ) and uranium ( $\delta^{238}\text{U}$ ) isotopes have been documented from the Gaojiashan Member of the DYF@GJS (Fig. 13) (Guo *et al.* 2012; A. Gamper, unpub. Ph.D. dissertation, Freie Universität Berlin, 2014; Zhang *et al.* 2014a, 2018; H. Cui, unpub. Ph.D. thesis, Univ. Maryland, 2015; Cui *et al.* 2016b). Individually or in unison, these secular stable isotope variations provide potential markers for chemostratigraphic correlations.

### 2.c. Ediacara-type macrofossils

The DYF@GJS has not yet yielded soft-bodied Ediacara-type macrofossils. However, Ediacara-type fossils such as *Pteridinium*, *Rangea*, *Charniodiscus*, *Hiemalora* and many others have been

found in the equivalent Shibantan Member of the Dengying Formation in the Yangtze Gorges area (Sun, 1986; Xiao *et al.* 2005; Shen *et al.* 2009, 2017; Chen *et al.* 2014; Mason *et al.* 2017).

### 2.d. Age constraints

Based on a U–Pb zircon age of  $551.1 \pm 0.7$  Ma from a volcanic ash layer at the Doushantuo–Dengying boundary in the Yangtze Gorges area (Condon *et al.* 2005), and a new radiometric constraint of 538.8 Ma from Namibia (Linnemann *et al.* 2019) for the Ediacaran–Cambrian boundary, the Dengying Formation represents the last 12.3 million years of the Ediacaran Period. In addition, a youngest detrital zircon age of  $548 \pm 8$  Ma (interpreted as the maximum possible depositional age) was reported from the lower Gaojiashan Member of the DYF@GJS (Cui *et al.* 2016b), which is consistent with the previously published geochronological framework in this region.

### 2.e. Accessibility

The DYF@GJS is located near the Gaojiashan village in southern Shaanxi Province of South China (Fig. 1), which is easily accessed with field vehicles. From the major city of Hanzhong the drive is ~75 km on the Jingkun Highway (G5) to Hujiaba Town, where the vehicles can continue on for an additional 5 km on unpaved road to the base of the section at the Huangjia Mountain.

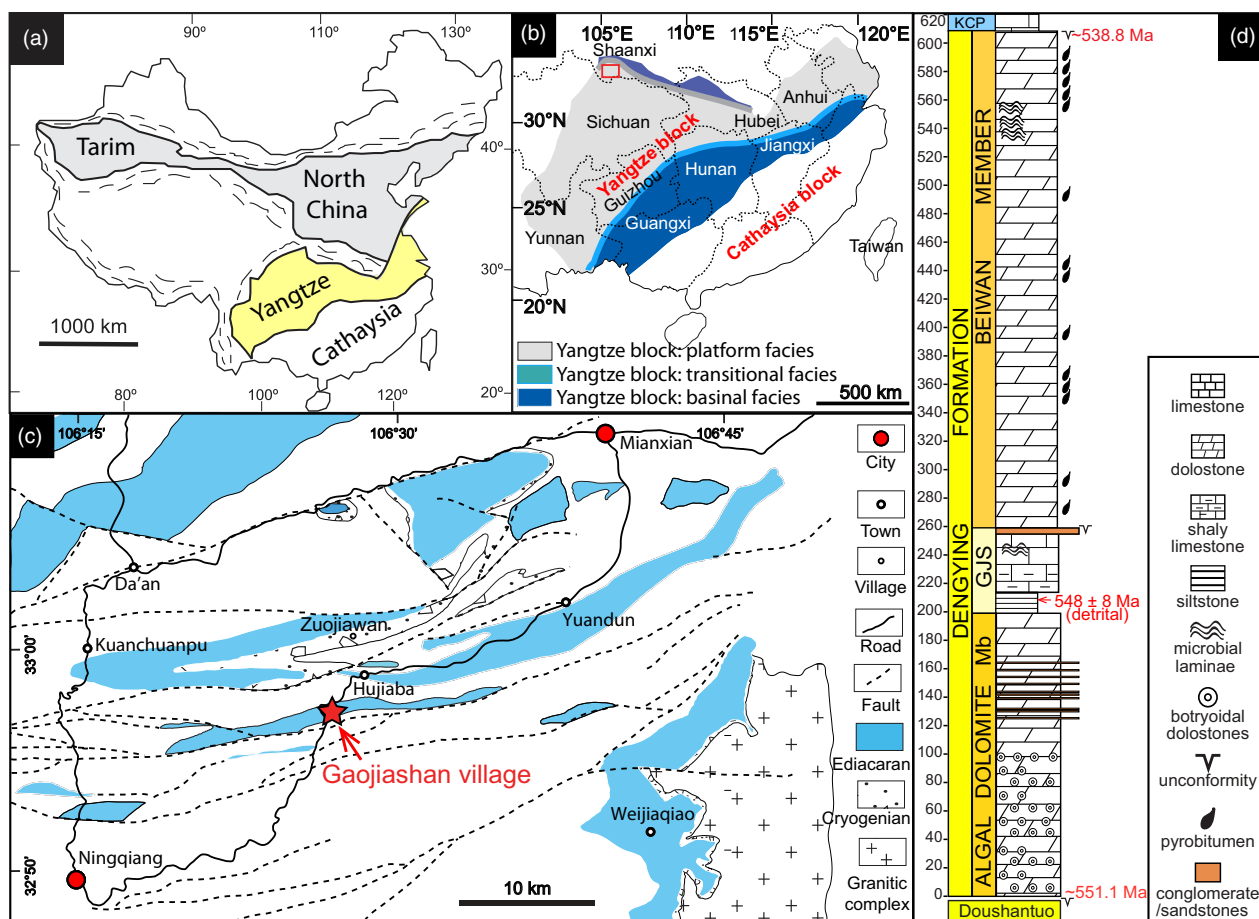
In summary, we regard that the Dengying Formation in South China offers a clear window through which to view the terminal Ediacaran Period. This study builds upon an earlier study (Fig. 13) (H. Cui, unpub. Ph.D. thesis, Univ. Maryland, 2015; Cui *et al.* 2016b) and aims at obtaining high-resolution integrative chemostratigraphic profiles of  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{18}\text{O}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{pyrite}}$  throughout the formation.

## 3. Geologic settings

The DYF@GJS is geographically located near the Gaojiashan village in southern Shaanxi Province of South China, and palaeogeographically is part of the northwestern Yangtze Block (Fig. 1a–c). It should be noted that the word ‘Gaojiashan’ has been used to refer to both the locality (e.g. Gaojiashan village, the Gaojiashan section, DYF@GJS) and the stratigraphic unit (i.e. the Gaojiashan Member).

Stratigraphically, the Dengying Formation (c. 551.1–538.8 Ma) is sandwiched between the Ediacaran Doushantuo Formation (c. 635–551 Ma) and the basal Cambrian Kuanchuanpu Formation (Fig. 1d) (Zhu *et al.* 2007; Jiang *et al.* 2011). The Dengying Formation in the studied region is typically subdivided into three members including, in ascending order, the Algal Dolomite (dolostones), the Gaojiashan (limestones and calcareous siltstones) and the Beiwan (dolostones). These three members are generally correlated with the Hamajing, Shibantan and Baimatuo members, respectively, in the Yangtze Gorges area of South China (Zhou & Xiao, 2007; Zhu *et al.* 2007; Duda *et al.* 2015).

The DYF@GJS is at least 631.5 m in thickness, with the Algal Dolomite Member measured from 0 to 202 m, the Gaojiashan Member from 202 to 257 m and the Beiwan Member from 257 to 631.5 m (Fig. 1d). The basal Algal Dolomite Member, and hence the Doushantuo–Dengying boundary, is faulted out, indicating that the Dengying Formation is probably thicker than the measured thickness of 631.5 m. The Beiwan Member of the DYF@GJS is overlain by limestones of the Kuanchuanpu Formation and then shales of the Guojiaba Formation. The



**Fig. 1.** (Colour online) Simplified tectonic map, geological map, litho- and chemostratigraphy of the terminal Ediacaran Dengying Formation at the Gaojiashan section, South China. (a) Tectonic framework of China, with the Yangtze Craton highlighted in yellow. (b) Ediacaran depositional environments on the Yangtze Craton (Jiang *et al.* 2007). Rectangle showing the location of the Ningqiang area in the northwestern margin of the Yangtze Platform. (c) Geological map of the Gaojiashan area in southern Shaanxi Province, modified after Cai *et al.* (2014). Red star indicates the studied section at Gaojiashan village, Niqiang county, Hanzhong city, southern Shaanxi Province. (d) Simplified stratigraphy of the Dengying Formation at Gaojiashan (Cui *et al.* 2016b). Sources of age data: Condon *et al.* (2005); Cui *et al.* (2016b); Linnemann *et al.* (2019). Abbreviations: GJS – Gaojiashan Member; KCP – Kuanchuanpu Formation.

Kuanchuanpu Formation in southern Shaanxi Province and northeastern Sichuan Province contains basal Cambrian small shelly fossils (Steiner *et al.* 2004) and the oldest known priapulid-like and kinorhynch-like scalidophoran animals (Liu *et al.* 2014b; Zhang *et al.* 2015; Han *et al.* 2017).

#### 4. Analytical methods

In total 270 rock samples were continuously collected at high stratigraphic resolution from exposed outcrops of the DYF@GJS for systematic sedimentological and chemostratigraphic investigation. These included 45 samples from the Algal Dolomite Member, 113 samples from the Gaojiashan Member (35 samples collected during the 2009 field season and 78 samples collected during the 2014 field season) and 112 samples from the Beiwang Member. Samples were analysed for carbonate carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ) and oxygen ( $\delta^{18}\text{O}_{\text{carb}}$ ) isotopes, organic carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ ), strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and sulfur isotopes ( $\delta^{34}\text{S}$ ) of total sulfur in acidified residues. Sample preparation (including sample cutting, crushing, acidification and leaching) and geochemical analyses were conducted using standard operation procedures (e.g. Cui *et al.* 2015, 2018a) in the Department of Geology, University of Maryland.

#### 4.a. Fabric-specific sampling strategy using micro-drills

Many samples in the Dengying Formation comprise multiple generations of diagenetic textures, which likely record isotopic signatures reflecting different sources of alkalinity. To better evaluate the impact of diagenesis on bulk rock carbonate compositions, micro-drilling was guided by petrographic fabrics so that different phases (e.g. cements, intraclasts, micritic matrix, crystal fans, microbial laminae, carbonate veins, nodules, vug fills) were sampled separately on polished slabs using a micro-drilling apparatus, in order to characterize the isotopic signatures of different stages of diagenesis. For chemostratigraphic purposes, powders for carbonate carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ), oxygen ( $\delta^{18}\text{O}_{\text{carb}}$ ) and strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotope analyses were only sampled from the least-altered and least-recrystallized phases in order to minimize the impact of post-depositional processes on geochemical signals.

#### 4.b. Carbon and oxygen isotope analysis

Carbonate carbon and oxygen isotopes were measured by continuous flow isotope ratio mass spectrometry in the University of Maryland Palaeoclimate Laboratory using a refined method for the analysis and correction of carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ) and oxygen

( $\delta^{18}\text{O}_{\text{carb}}$ ) isotopic compositions of 100  $\mu\text{g}$  carbonate samples (Spötl, 2011; Evans *et al.* 2016). Up to 180 samples loaded into 3.7 ml Labco Exetainer vials and sealed with Labco septa were flushed with 99.999 % helium and manually acidified with 103% phosphoric acid at 60 °C. The  $\text{CO}_2$  analyte gas was isolated via gas chromatography, and water was removed using a Nafion trap prior to admission into an Elementar Isoprime stable isotope mass spectrometer fitted with a continuous flow interface. Data were corrected via automated MATLAB scripting on the Vienna Pee Dee Belemnite and LSVEC Lithium Carbonate (VPDB–LSVEC) scale (Coplen *et al.* 2006) using periodic in-run measurement of international reference carbonate materials and/or in-house standard carbonates, from which empirical corrections for signal amplitude, sequential drift and one or two-point mean corrections were applied. Precision for both isotopes is routinely better than 0.1 ‰ (Evans *et al.* 2016).

#### 4.c. Organic carbon and pyrite sulfur isotope analyses

The organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) and total sulfur ( $\delta^{34}\text{S}_{\text{TS}}$ ) isotope compositions were measured by combustion of the decalcified residues to  $\text{CO}_2$  or  $\text{SO}_2$  with a Eurovector elemental analyser in-line with a second Elementar Isoprime isotope ratio mass spectrometer. Around 15 g of bulk crushed sample was acidified with 3 M HCl to achieve quantitative removal of carbonates. These acidified residues were washed with ultra-pure Milli-Q (18M $\Omega$ ) water, centrifuged, decanted and dried. The residues were packed into folded tin cups for combustion (0.1 to 0.3 mg of  $\text{V}_2\text{O}_5$  were added to the sulfur samples to aid in combustion), and released  $\text{CO}_2$  and  $\text{SO}_2$  were used for the analysis of  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{TS}}$ , respectively. Owing to the negligible amount of organic sulfur in the acidified residues, the dominant sulfur species is pyrite. Thus,  $\delta^{34}\text{S}_{\text{TS}}$  values are regarded as a proxy for pyrite sulfur isotope compositions ( $\delta^{34}\text{S}_{\text{pyrite}}$ ). Uncertainties for carbon and sulfur isotope measurements determined by multiple analyses of standard materials during analytical sessions are better than 0.1 ‰ and 0.3 ‰, respectively.

#### 4.d. Strontium isotope analysis

For strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) analysis, only limestone samples from the Gaojiashan Member were selected for extraction and measurement. Micro-drilled powders (*c.* 10 mg) were leached three times in 0.2 M ammonium acetate (pH  $\sim$ 8.2) to remove exchangeable Sr from non-carbonate minerals, and then rinsed three times with Milli-Q water. The leached powder was centrifuged, decanted and acidified with doubly distilled 0.5 M acetic acid overnight to remove strontium from the carbonate crystal structure. The supernatant was centrifuged to remove insoluble residues, and then decanted, dried and subsequently dissolved in 200  $\mu\text{l}$  of 3 M  $\text{HNO}_3$ . Strontium separation by cation exchange was carried out using small polyethylene columns containing  $\sim$ 10 mm of Eichrom<sup>®</sup> Sr specific resin. The column was rinsed with 400  $\mu\text{l}$  of 3 M  $\text{HNO}_3$  before the dissolved sample was loaded onto the column. After loading, the sample was sequentially eluted with 200  $\mu\text{l}$  of 3 M  $\text{HNO}_3$ , 600  $\mu\text{l}$  of 7 M  $\text{HNO}_3$  and 100  $\mu\text{l}$  of 3 M  $\text{HNO}_3$  to remove the Ca, Rb and rare earth element fractions; the Sr fraction adsorbs strongly to the resin in an acidic environment. The Sr fraction was removed by elution with  $\sim$ 800  $\mu\text{l}$  of 0.05 M  $\text{HNO}_3$  and the resultant eluate was collected and dried. Approximately 200–300 ng of the dried sample was transferred onto a degassed and pre-baked ( $\sim$ 4.2 A under high vacuum) high purity Re filament with 0.7  $\mu\text{l}$  of  $\text{Ta}_2\text{O}_5$  activator. Filaments were transferred to a sample carousel, heated

under vacuum ( $\sim$ 10<sup>-7</sup> to 10<sup>-8</sup> atm) to a temperature of between 1450 °C and 1650 °C, and analysed when a stable signal ( $>$ 1.0 V) was detected on the mass 88 ion beam. The measurements were conducted on a VG Sector 54 thermal ionization mass spectrometer in the TIMS facility of the University of Maryland Geochemistry Laboratories. Approximately 100  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were collected for each sample. The data have been corrected for fractionation using the standard value  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . The fraction of  $^{87}\text{Sr}$  resulting from *in situ* decay from  $^{87}\text{Rb}$  was removed by measurement of rubidium abundance at mass 85. Repeated analyses of the NBS SRM987 standard yielded an average value of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 0.000011$  ( $2\sigma$ ) during the analytical window.

## 5. Sedimentology of the Dengying Formation

Sedimentological observations of the DYF@GJS can provide direct palaeoenvironmental context for the depositional basin. Various lithofacies with distinct sedimentary textures can be identified in each of the three members of the DYF@GJS, which are summarized below.

### 5.a. Lithofacies of the Algal Dolomite Member

The Algal Dolomite Member (0–202 m of the DYF@GJS) is dominated by bedded dolostones (including thrombolites) with abundant karstification textures (e.g. botryoidal dolostones, carbonate breccias, authigenic carbonate crystal fans) and other post-depositional alteration (e.g. saddle dolomite cements).

#### 5.a.1. Botryoidal dolostones

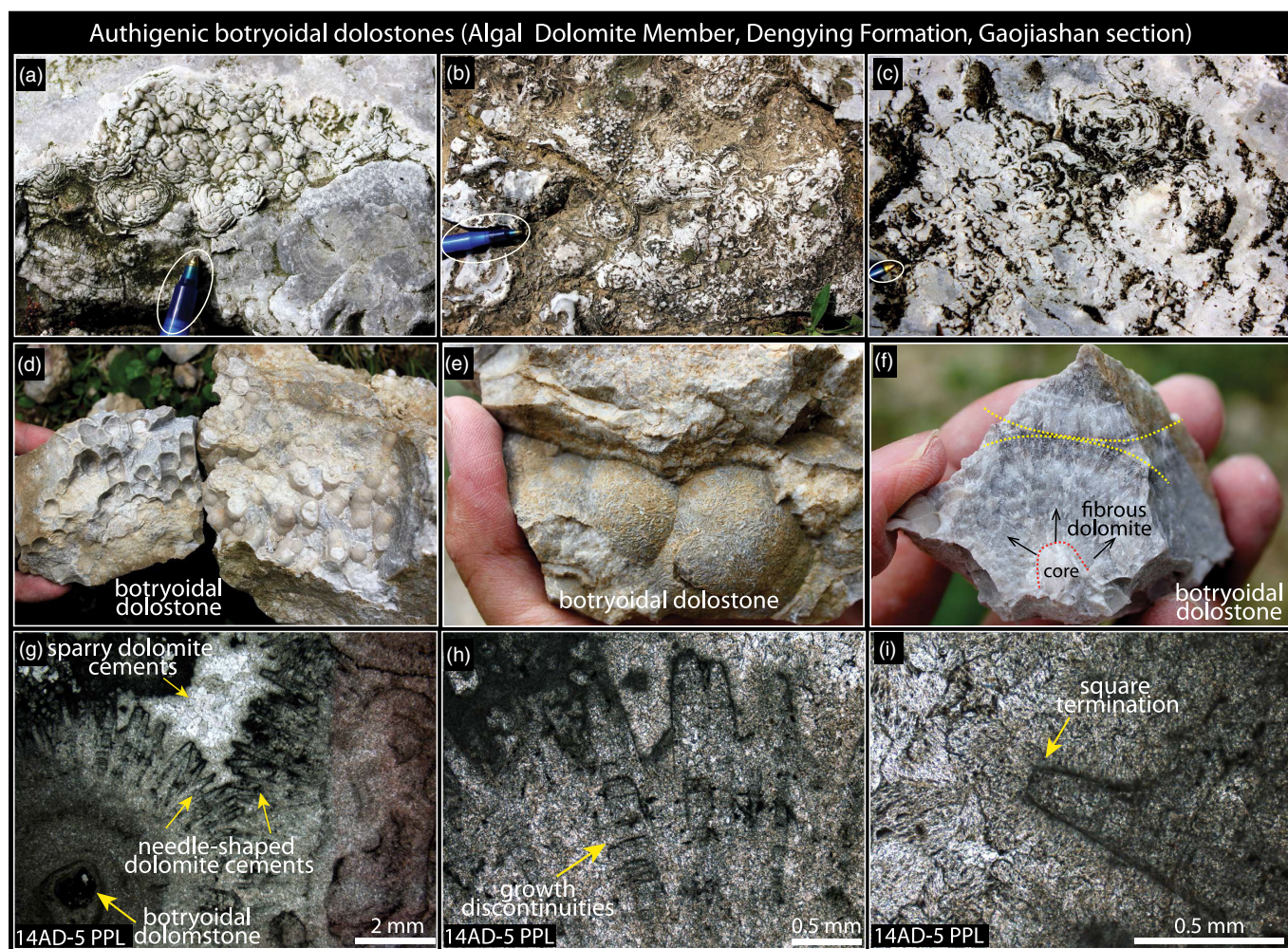
Diagnostic karst carbonates are abundant in the outcrop, including void-filling botryoidal dolostone (Fig. 2) and karst breccia (Fig. 3). Botryoidal dolostone typically shows concentric layers around a core of millimetre to centimetre scale, suggesting centrifugal precipitation (Fig. 2f, g). Based on their distinct textures, including growth discontinuities and square crystal terminations (Fig. 2g–i), it is likely that they were initially aragonite in mineralogy, and were subsequently replaced by calcite and dolomite (e.g. Ginsburg & James, 1976; Aissaoui, 1985; Sandberg, 1985). The occurrences of botryoidal aragonites are typically parallel with the primary bedding.

#### 5.a.2. Carbonate breccias

Closely associated with botryoidal dolostones, carbonate breccia is abundant in the Algal Dolomite Member (Fig. 3a–c). Isopachous cements in the botryoidal dolostone were broken into centimetre-sized breccia and were then cemented after final deposition (Fig. 3). Some primary pores between the carbonate breccias are still not yet fully cemented (Fig. 3b). Petrographic observations reveal that these carbonate breccias are mostly composed of isopachous cements growing on dolomite intraclasts or botryoidal dolostone (Fig. 3d–f).

#### 5.a.3. Authigenic carbonate crystal fans

Distinct authigenic crystal fans of centimetre size have been found in the Algal Dolomite Member (Fig. 4). These crystal fans were initially misidentified as algal fossils in previous studies (Cao & Zhao, 1978a,b), and then re-interpreted as inorganic carbonate precipitates (Cai *et al.* 2010). The sharp square crystal terminations and growth discontinuities within the crystal fan (Fig. 4d, e, h, i) suggest that these authigenic cements were initially aragonite in



**Fig. 2.** (Colour online) Field and microscopic views of the authigenic botryoidal dolostones that are typical in the lower half of the Algal Dolomite Member of the Dengying Formation at the Gaojiashan section. (a–c) Outcrops showing distinct botryoidal textures with concentric lamina. Pen for scale. (d, e) Hand samples showing the distinct botryoidal texture. Note the part and counterpart in (d). (f) Fresh fracture surface showing radial fabrics diverging from the core. (g) Microscopic images of the authigenic botryoidal dolomite showing needle-shaped crystals with growth discontinuities and square terminations. Note the needle-shaped crystals as the first-stage cements and the sparry dolomite as the second-stage cements. (h, i) Magnified views of the needle-shaped crystals with discontinuities and square terminations, indicating original aragonite mineralogy. PPL – plane polarized light.

mineralogy (e.g. Mazzullo & Cys, 1979; Mazzullo, 1980; Sandberg, 1985; Corsetti *et al.* 2004; Pruss *et al.* 2008; Loyd *et al.* 2013) and then converted to dolomite (no fizz in acid test) (Aissaoui, 1985; Lin *et al.* 2015; Peng *et al.* 2017).

#### 5.a.4. Thrombolites

Thrombolites with a distinct clotted texture are abundant in the Algal Dolomite Member (Figs 4b, 5a–c). The occurrence of thrombolites in the Dengying Formation (Fang *et al.* 2003; Li *et al.* 2013b; Liu *et al.* 2015; Wang *et al.* 2016; Chen *et al.* 2017; Luo *et al.* 2017; Wen *et al.* 2017), along with other Ediacaran occurrences in the Ara Group of Oman (Grotzinger *et al.* 2000, 2005; Grotzinger & Al-Rawahi, 2014) and the Blueflower Formation in the Mackenzie Mountains of Northwestern Canada (Aitken & Narbonne, 1989), suggests that thrombolites were abundant in Ediacaran shallow-marine environments.

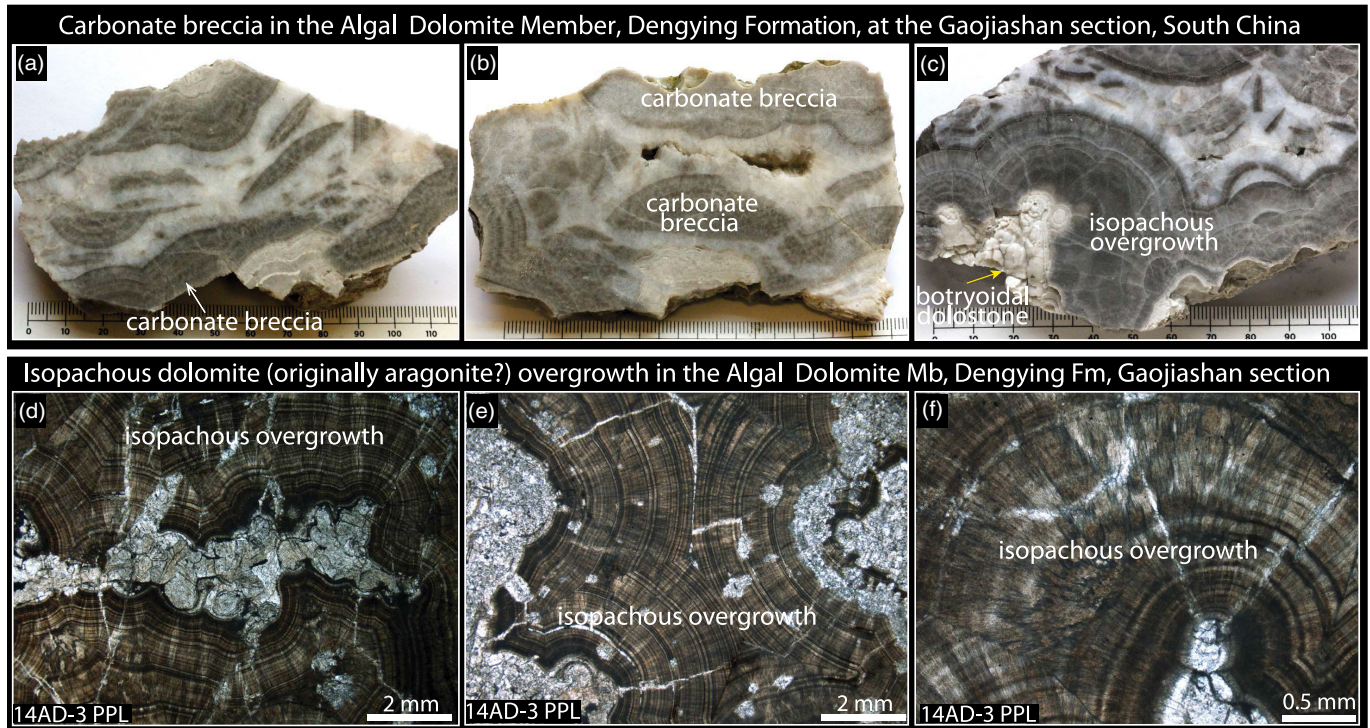
#### 5.a.5. Saddle dolomite cements

Petrographic observations reveal that many late-stage void-filling cements are composed of large saddle dolomite crystals, which are

characterized by a distinct cleavage and sweeping extinction under cross-polarized light (Fig. 5d–f). These saddle dolomite cements are typically interpreted as precipitates from hydrothermal fluids during deep burial (Davies & Smith, 2006; Shi *et al.* 2013; Liu *et al.* 2014a; Zhu *et al.* 2014a), thus should be avoided in chemostratigraphic studies.

#### 5.b. Lithofacies of the Gaojiashan Member

The fossiliferous Gaojiashan Member (202–257 m of the DYF@GJS) is 55 m in thickness, including a siltstone interval in the lower part, repetitious siltstone–mudstone–limestone facies with crinkly and microbially laminated limestone in the middle part, and a coarse sandstone/conglomerate interval at the top (Fig. 6) (Cai *et al.* 2010; Cui *et al.* 2016b). Sedimentological observations suggest that the Gaojiashan Member was mainly deposited in a subtidal marine setting between the fair weather and storm wave bases. Limestones with abundant microbial laminae (Fig. 6d–h) and intraclasts in this member (Fig. 6i) suggest sediment reworking by episodic storm events (Cai *et al.* 2010).



**Fig. 3.** (Colour online) Field samples and microscopic views of the carbonate breccia and isopachous overgrowth that are typical in the lower half of the Algal Dolomite Member of the Dengying Formation at the Gaojiashan section. (a–c) Karst breccia cemented by carbonates in the vugs between breccias. Scale in millimetres. (d–f) Petrographic images of sample 14AD-3, showing isopachous void-filling carbonate cements with concentric textures (brown colour) surrounding coarse dolomite sediments (white colour). PPL – plane polarized light.

#### 5.b.1. Bedded siltstones or silty limestones (lower Gaojiashan Member, 202–222 m of the DYF@GJS)

The lower Gaojiashan Member is mainly composed of thinly bedded siltstones or silty limestones without cross-bedding textures, suggesting a relatively deep environment. The enigmatic body fossil *Shaanxilithes ningqiangensis* is found in the siltstone facies of this member (Meyer *et al.* 2012).

#### 5.b.2. Bedded limestones or silty limestones (middle Gaojiashan Member, 222–254 m of the DYF@GJS)

The middle Gaojiashan Member contains *Conotubus hemiannulatus* and *Gaojiashania cyclus* preserved in thin, normally graded calcisiltite-siltstone beds interpreted as distal event deposits (Cai *et al.* 2010). Further up section, the first appearance of the biomineralizing animal *Cloudina* occurs in intraclastic limestone facies c. 40 m above the base of the Gaojiashan Member (Fig. 7a–f) (Hua *et al.* 2007; Cai *et al.* 2010). Notably, *Cloudina* fossils at the DYF@GJS are typically associated with microbial laminae (Cai *et al.* 2014). Similar observations have also been made in the Nama Group of Namibia (Grotzinger & James, 2000; Adams *et al.* 2004; Grotzinger *et al.* 2005), the Byng Formation of the Miette Group in British Columbia (Hofmann & Mountjoy, 2001), the Tamengo Formation of the Corumbá Group in Southwest Brazil (Becker-Kerber *et al.* 2017) and the Itapucumi Group in Paraguay (Warren *et al.* 2011), where intimate associations of *Cloudina* with microbialites have also been reported.

#### 5.b.3. Gypsum (middle Gaojiashan Member, 251.5 m of the DYF@GJS)

It is notable that a distinct gypsum (now replaced by calcite) horizon (c. 20–30 mm in thickness) occurs within the limestone

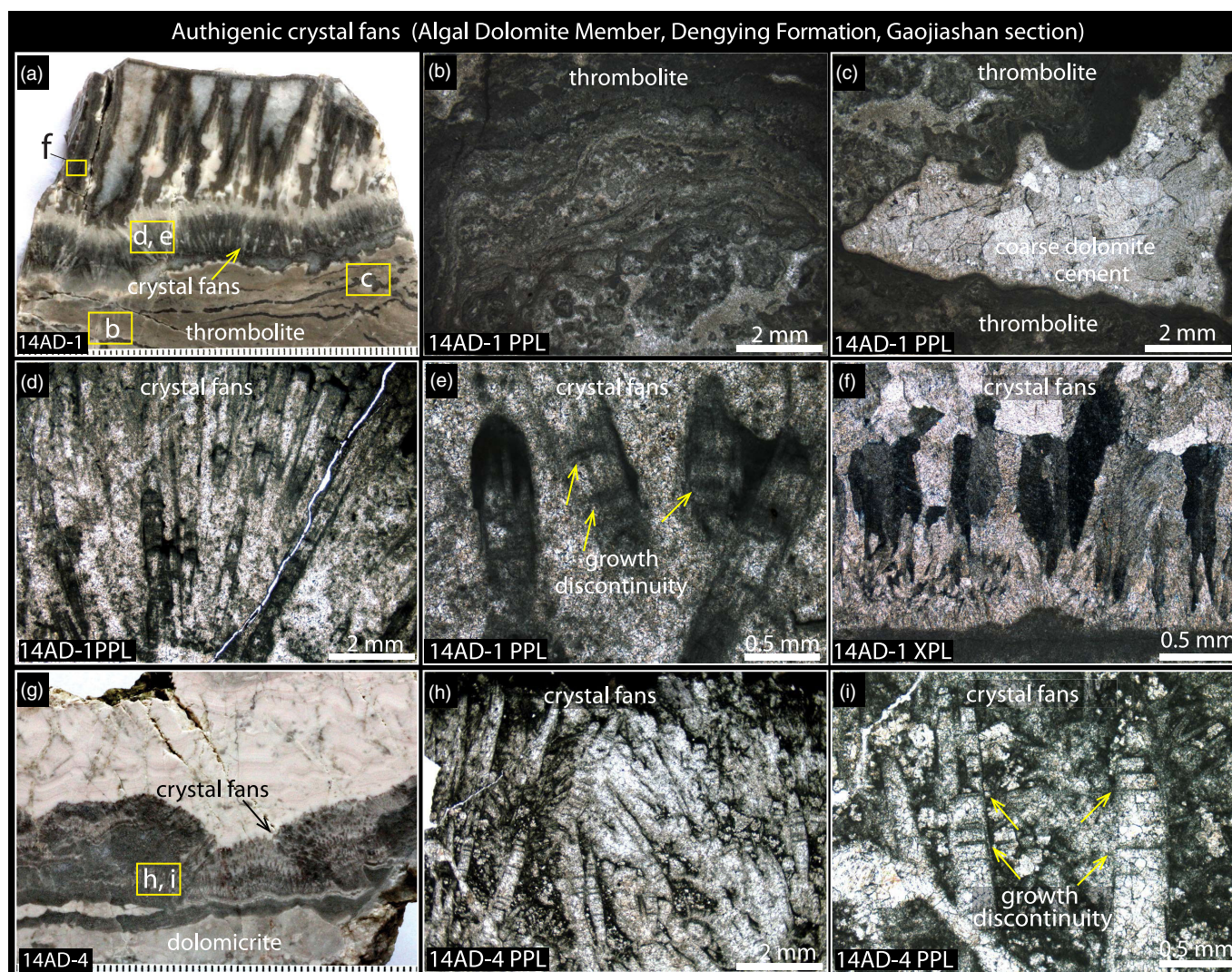
interval 5.5 m below the conglomerate and sandstone interval of the upper Gaojiashan Member (Fig. 7g–i). In this layer, calcite pseudomorphs with distinct gypsum crystal shapes suggest the dissolution and replacement of pre-existing gypsum. This gypsum layer, along with sedimentary structures indicative of shallow-water depositional environments, suggests an evaporative environment with high concentrations of seawater sulfate. The presence of gypsum in the DYF@GJS is also consistent with published sedimentological observations in other localities across the Yangtze Block, where evaporites, including halite, gypsum and anhydrite, have also been widely reported from the Dengying Formation (Xi, 1987; Siegmund & Erdtmann, 1994; Meng *et al.* 2011; Lu *et al.* 2013; Duda *et al.* 2015; Liu *et al.* 2015; Luo *et al.* 2017).

#### 5.b.4. Sandstones and conglomerates (upper Gaojiashan Member, 254–257 m of the DYF@GJS)

A distinct interval of coarse sandstones and conglomerates occurs in the uppermost Gaojiashan Member, suggesting an increasingly shallower depositional environment. This conglomerate and sandstone interval is dominated by pure quartz grains in the DYF@GJS, and shows large-scale cross-bedding in the nearby Shiziya section (Cai *et al.* 2010).

#### 5.c. Lithofacies of the Beiwan Member

The Beiwan Member (257–631.5 m of the DYF@GJS) is dominated by thick-bedded dolostones with void-filling bitumen (Fig. 8). At the outcrop scale, bitumen-rich layers can be parallel to or cross-cut the primary bedding. Petrographic observations in thin-sections (Fig. 8) reveal that the pores in the Beiwan dolostones are often surrounded by quartz rims (Fig. 8e, f, h, i, k), suggesting



**Fig. 4.** (Colour online) Hand samples and microscopic views of the thrombolite and authigenic aragonite (now dolomite) crystal fans that are typical in the lower half of the Algal Dolomite Member of the Dengying Formation at the Gaojiashan section. (a) Sample slab 14AD-1, showing thrombolite sediments in the lower part and two generations of crystal fans in the middle and upper parts, respectively. Scale in millimetres. (b, c) Magnified views of thrombolitic texture in labelled rectangles in (a). Note the coarse dolomite cements within a large void in the thrombolitic dolomite matrix. (d, e) Authigenic crystal fans in labelled rectangles in (a). Note the crystals with growth discontinuities (arrows). Although the entire rocks have been dolomitized, the relic fabrics of the original aragonite crystals are retained. (f) Divergent fabrics of dolomite crystals with sweeping extinction under cross-polarized light in labelled rectangles in (a). (g) Dolostone slab 14AD-4 with crystal fans growing above dolomitic sediments. Scale in millimetres. (h, i) Magnified views of crystal fans in labelled rectangles in (g), showing growth discontinuities (arrows in (i)) within the aragonite crystals. PPL – plane polarized light; XPL – cross-polarized light.

that silicification in low pH conditions may have promoted the dissolution of primary dolostones and contributed to the genesis of secondary porosity. These secondary pores or vugs consequently facilitated oil migration that resulted in the infilling of bitumen in the voids.

#### 5.d. A synthetic depositional model

Based on the above sedimentological observations, the deposition of the DYF@GJS can be divided into multiple stages as described below (Fig. 9).

##### 5.d.1. Stage 1 (Algal Dolomite Member)

The Algal Dolomite Member of the Dengying Formation was rapidly deposited in a relatively warm peritidal environment (Fig. 9a). In light of the repeating occurrences of botryoidal carbonates in parallel with the primary bedding, sea levels were likely low and

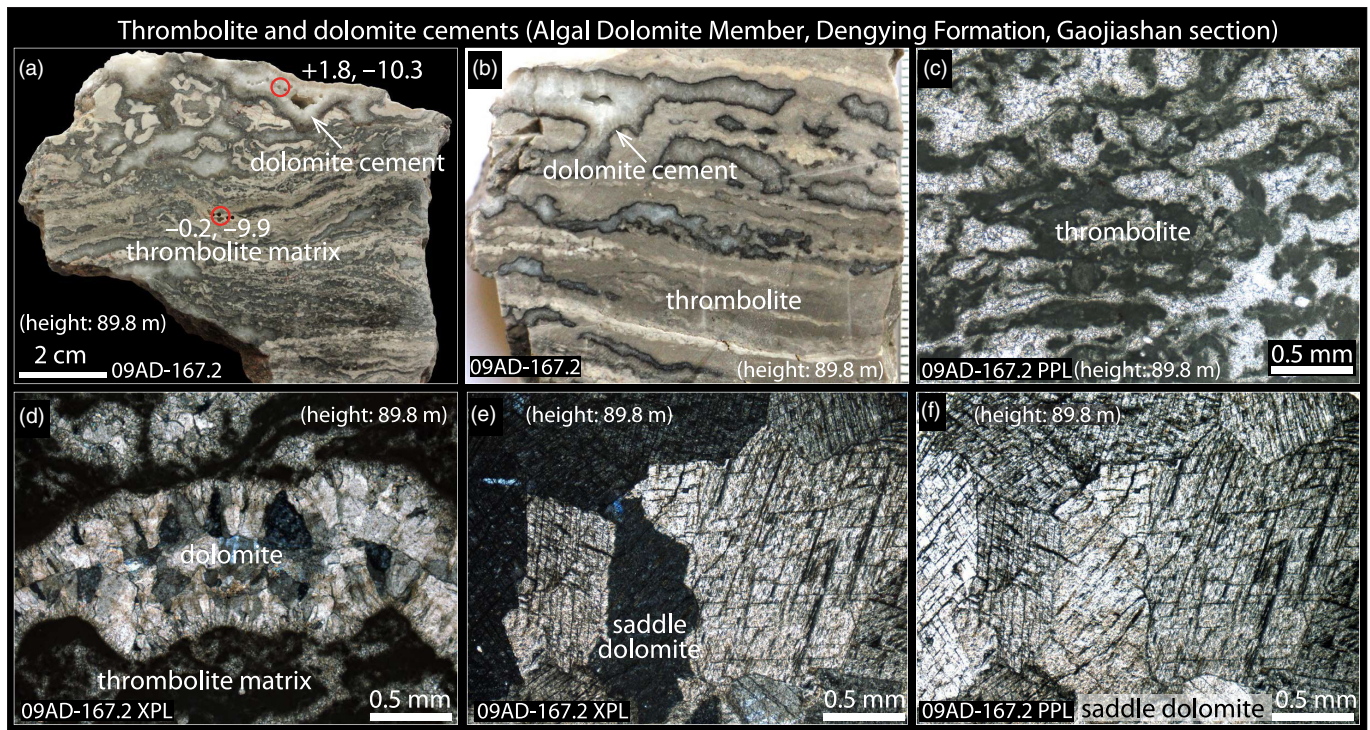
the carbonate deposits were subject to frequent subaerial exposure, so that syn-depositional or very early post-depositional karstification occurred repeatedly. The void-filling authigenic aragonite cements and crystal fans in this formation may have formed penecontemporaneously with sedimentation when sea level fluctuated and the carbonate sediments were repeatedly exposed and submerged.

##### 5.d.2. Stage 2 (lower Gaojiashan Member)

The lower Gaojiashan Member represents deposition below storm wave base, as evidenced by the thinly bedded siltstone and silty limestones in this unit.

##### 5.d.3. Stage 3 (middle and upper Gaojiashan Member)

Deposition mostly occurred in an environment above the storm wave base (Cai *et al.* 2010) (Fig. 9b). Towards the upper



**Fig. 5.** (Colour online) Thrombolitic dolostone and void-filling hydrothermal dolomite cements in the Algal Dolomite Member, Dengying Formation, at the Gaojiashan section. Sample 09AD-167.2 from a stratigraphic height of 89.8 m in Figure 12. (a, b) Dolostone slabs showing thrombolitic dolomite matrix with vug-filling dolomite cements. Fabric-specific  $\delta^{13}\text{C}$  (left) and  $\delta^{18}\text{O}$  (right) data are provided in (a). Scale in (b) in millimetres. (c) A magnified view of the thrombolitic dolomite matrix under plane-polarized light. (d) A magnified view of coarse dolomite cements in the thrombolitic dolomite matrix under cross-polarized light. (e, f) Magnified views of hydrothermal saddle dolomites with two distinct sets of cleavages and sweeping extinction. PPL – plane polarized light; XPL – cross-polarized light.

Gaojiashan Member, the relative sea level dropped progressively, leading to the deposition of gypsum, carbonate intraclasts, and conglomerate and sandstones.

#### 5.d.4. Stage 4 (Beiwán Member)

The Beiwán Member represents another period of carbonate deposition in a peritidal environment with a high sedimentation rate (Fig. 9c).

The overall shallowing trend from the Gaojiashan to the Beiwán Member may have been controlled by regional tectonic uplift (Xue et al. 2001; Wang et al. 2014a; Zhu et al. 2014b, 2015; Li et al. 2015; Yang et al. 2017). The repeated karstification of the Algal Dolomite Member, on the other hand, may be related to minor sea level fluctuations in a peritidal environment.

## 6. Geochemical results of the Dengying Formation

### 6.a. Fabric-specific $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data

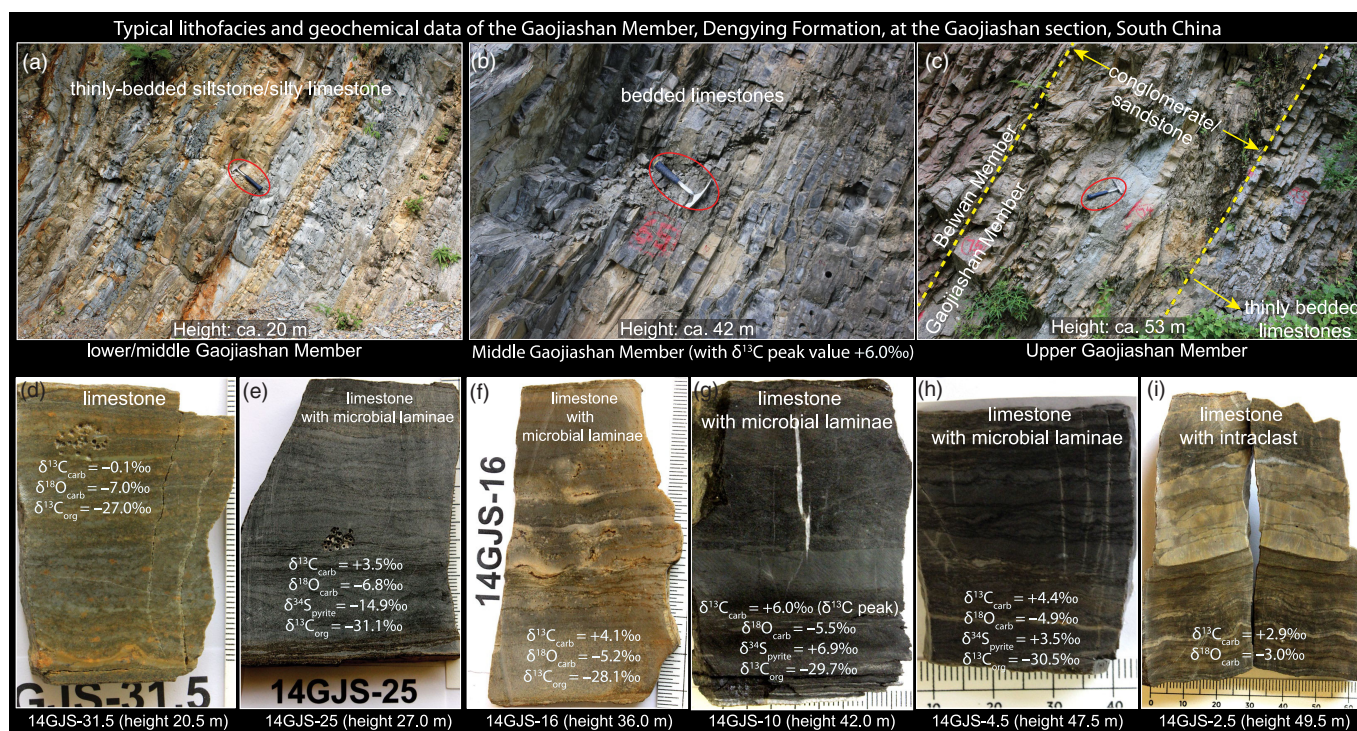
Samples in the dolostone-dominated Algal Dolomite Member and Beiwán Member typically show complex textures, including a dolomicrite matrix, large aragonite (now dolomite) crystal fans and void-filling aragonite (now dolomite) or quartz cements. Fabric-specific geochemical analysis via micro-drilling shows different isotopic signatures among individual phases (Fig. 10). It is notable that the aragonite (now dolomite) crystal fans record the highest  $\delta^{18}\text{O}_{\text{carb}}$  values ( $-0.9\text{‰}$  in Fig. 10a and  $-1.8\text{‰}$  in Fig. 10c) among the data measured from the micro-drilled carbonates. In contrast, late-stage hydrothermal saddle dolomite cements typically show the lowest  $\delta^{18}\text{O}_{\text{carb}}$  values ( $-10.3\text{‰}$  in Fig. 10a).

During the field investigation, multiple calcite-filled vugs and veins were found in the limestone intervals of the upper Gaojiashan Member (1–2 m below the conglomerate/sandstone interval) (Fig. 11a–c). Both the calcite veins and micritic limestone host rock were micro-drilled and analysed for  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  compositions (Fig. 11d–g). The data show that the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values measured from the calcite vugs and veins are consistently lower than those of the limestone host rock.

### 6.b. Chemostratigraphic profiles of the Dengying Formation

For chemostratigraphic purposes, only data measured from the least-altered micritic carbonate matrix were compiled when constructing the chemostratigraphic profiles (Figs 12, 13). Carbonate percentages (carbonate wt %) of the DYF@GJS are mostly  $>90\%$  except for a few siltstone intervals in the Gaojiashan Member (Fig. 12a). The  $\delta^{13}\text{C}_{\text{carb}}$  profile of the DYF@GJS shows a positive excursion (up to  $+6\text{‰}$ ) in the Gaojiashan Member (Figs 12b, 13b) and two broad positive excursions (up to  $+4\text{‰}$ ) in the Algal Dolomite Member and Beiwán Member, respectively (Figs 12b, 14a). The  $\delta^{18}\text{O}_{\text{carb}}$  data for the DYF@GJS mostly range between  $-5\text{‰}$  and  $0\text{‰}$ , with the exception of the Gaojiashan Member (down to c.  $-8\text{‰}$ ; Fig. 13b), the uppermost Beiwán Member and the Kuanchuanpu Member (Fig. 12b). The organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) data for the DYF@GJS mostly range between  $-30\text{‰}$  and  $-25\text{‰}$ , with more negative values (down to c.  $-35\text{‰}$ ) in the Gaojiashan and the Kuanchuanpu members (Figs 12c, 13c). Calculated values of carbon isotope fractionation ( $\Delta\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) between the carbonate carbon and organic carbon of the DYF@GJS mostly range between  $+25\text{‰}$





**Fig. 6.** (Colour online) Typical lithofacies and geochemical data of the Gaojiashan Member, Dengying Formation, at the Gaojiashan section, South China. Stratigraphic height numbers represent the distance above the Algal Dolomite/Gaojiashan boundary. (a) Thinly bedded siltstones and silty limestones in the lower/middle transition of the Gaojiashan Member. (b) Dark-coloured thin-bedded limestones in the middle Gaojiashan Member that records a  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion of up to +6 ‰ (Cui *et al.* 2016b). (c) A conglomerate/sandstone interval in the upper Gaojiashan Member. Hammer for scale is 33 cm long. (d–i) Photographs of freshly cut slabs of samples from the Gaojiashan Member with microbial laminae and intraclasts. These slabs represent (d) greenish grey dolostone, (e–h) limestones with microbial laminae, and (i) intraclastic limestone. The numbers in the sample IDs represent distance (in metres) below the conglomerate interval in the upper Gaojiashan Member; for example, sample 14GJS-10 is 10 m below the conglomerate interval in the Gaojiashan Member. The  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values of micro-drilled carbonate powders are marked on the slab. The  $\delta^{34}\text{S}_{\text{pyrite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values of each slab were analysed from bulk acidified residues.

and +35 ‰, with higher values in the Gaojiashan Member and some horizons of the Beiwán Member (Fig. 12d).

Given the potential impact of dolomitization,  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis of the DYF@GJS was only conducted for selected limestone samples from the Gaojiashan Member. Considering that  $^{87}\text{Sr}/^{86}\text{Sr}$  values in carbonates typically increase during burial diagenesis owing to the influence of Rb-rich fluids (Banner, 1995; Jacobsen & Kaufman, 1999), the lowest value likely better represents the primary seawater signals (e.g. Li *et al.* 2013a). In this study, the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  value is 0.7084 measured from the limestone sample 09GJS-11 (collected at the stratigraphic height of 246 m in the DYF@GJS; Figs 12, 13), which is consistent with the published  $^{87}\text{Sr}/^{86}\text{Sr}$  data (c. 0.7084) measured from the equivalent Shibantan Member in the Yangtze Gorges area (Fig. 14b) (Jiang *et al.* 2007).

Pyrite sulfur isotope ( $\delta^{34}\text{S}_{\text{pyrite}}$ , measured from acidified residues) data for the DYF@GJS show positive values ranging between +10 ‰ and +40 ‰ through most of the section, except for two remarkable negative anomalies (down to –30 ‰) in the siltstone and silty limestone intervals of the middle and lower Gaojiashan Member (Figs 12e, 13f). The  $\delta^{34}\text{S}_{\text{CAS}}$  data for carbonate-associated sulfate (CAS) have only been analysed for the Gaojiashan Member and have been published previously (Cui *et al.* 2016b).

## 7. Discussion

### 7.a. Timing of the karstification event

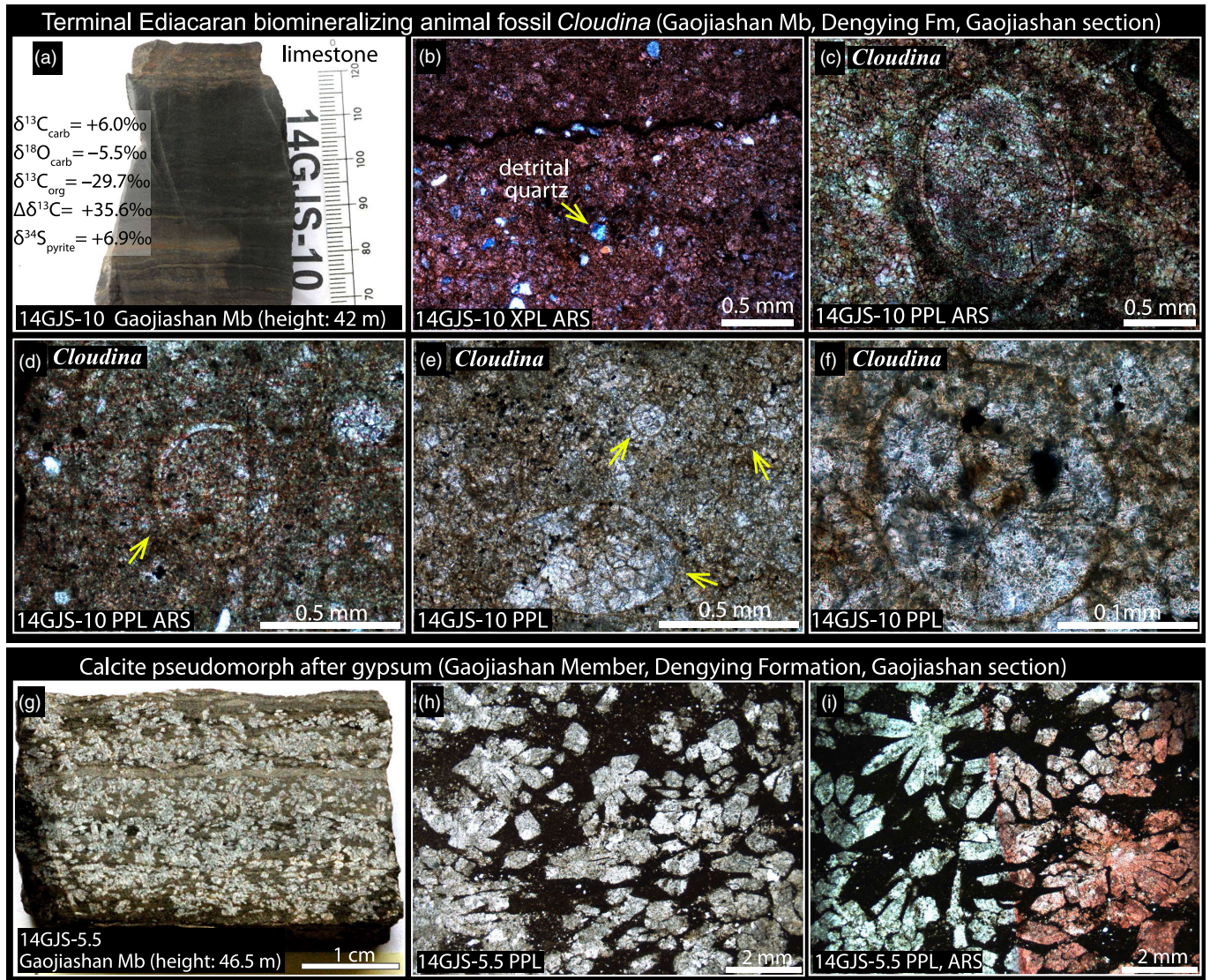
The bedded dolostones in the Algal Dolomite Member are mostly composed of dolomitic matrix and multiple stages of void-filling

carbonate cements (Figs 4, 5). The dolomitic matrix is very fine grained, therefore likely formed as primary precipitates in seawater or during very early diagenesis in a dolomitic ocean (Tucker, 1982, 1983; Lei & Zhu, 1992; Wang & Xiang, 1999; Corsetti *et al.* 2006). Notably, the Algal Dolomite Member of the DYF@GJS shows abundant karstification textures. The occurrence of botryoidal dolostones, carbonate breccia and distinct carbonate crystal fans in this member suggests pervasive karstification followed by void-filling carbonate authigenesis (Figs 2–4, 10).

Field investigations reveal that the karstification textures in the DYF@GJS are restricted to the lower half of the Algal Dolomite Member, with botryoidal aragonites in parallel with the primary bedding. Based on the stratigraphic relationship, the karstification events of the Algal Dolomite Member should have occurred relatively early, probably penecontemporaneously with the deposition of dolomite sediments in response to sea level fluctuations in a peritidal environment. Sea levels may have been subject to frequent fluctuations so that early karstification could occur repeatedly.

### 7.b. Origin of the authigenic aragonite cements

Although the authigenic carbonates in the Algal Dolomite Member of the DYF@GJS have already been completely dolomitized, diagnostic textures that suggest an original aragonite mineralogy are retained. Supporting evidence includes large carbonate crystal fans with discontinuities and square terminations, botryoidal carbonates and fibrous isopachous cements (Figs 4, 10), which are all distinct from typical dolomite cements formed during post-depositional diagenesis (Purser *et al.* 2009; Tucker, 2009).



**Fig. 7.** (Colour online) Fossils and gypsum pseudomorphs in the Gaojiashan Member, Dengying Formation, at the Gaojiashan section. (a) Limestone slab 14GJS-10 (collected at 42 m in Fig. 13) with the terminal Ediacaran fossil *Cloudina*. (b) Thin-section of 14GJS-10 stained by Alizarin Red S, confirming its limestone lithology. Note abundant detrital quartz in this sample (arrow). (c–f) Transverse cross-sections of *Cloudina* (arrows) in thin-sections of the sample 14GJS-10. (g) Rock slab of sample 14GJS-5.5 (collected at 46.5 m in Fig. 13), showing calcite pseudomorphs after gypsum in the Gaojiashan Member. (h, i) Magnified views of the calcite pseudomorphs after gypsum rosettes. The right half of image (i) shows a red colour after being stained by Alizarin Red S, confirming the calcite composition of the pseudomorphs. PPL – plane polarized light; XPL – cross-polarized light; ARS – stained by Alizarin Red S.

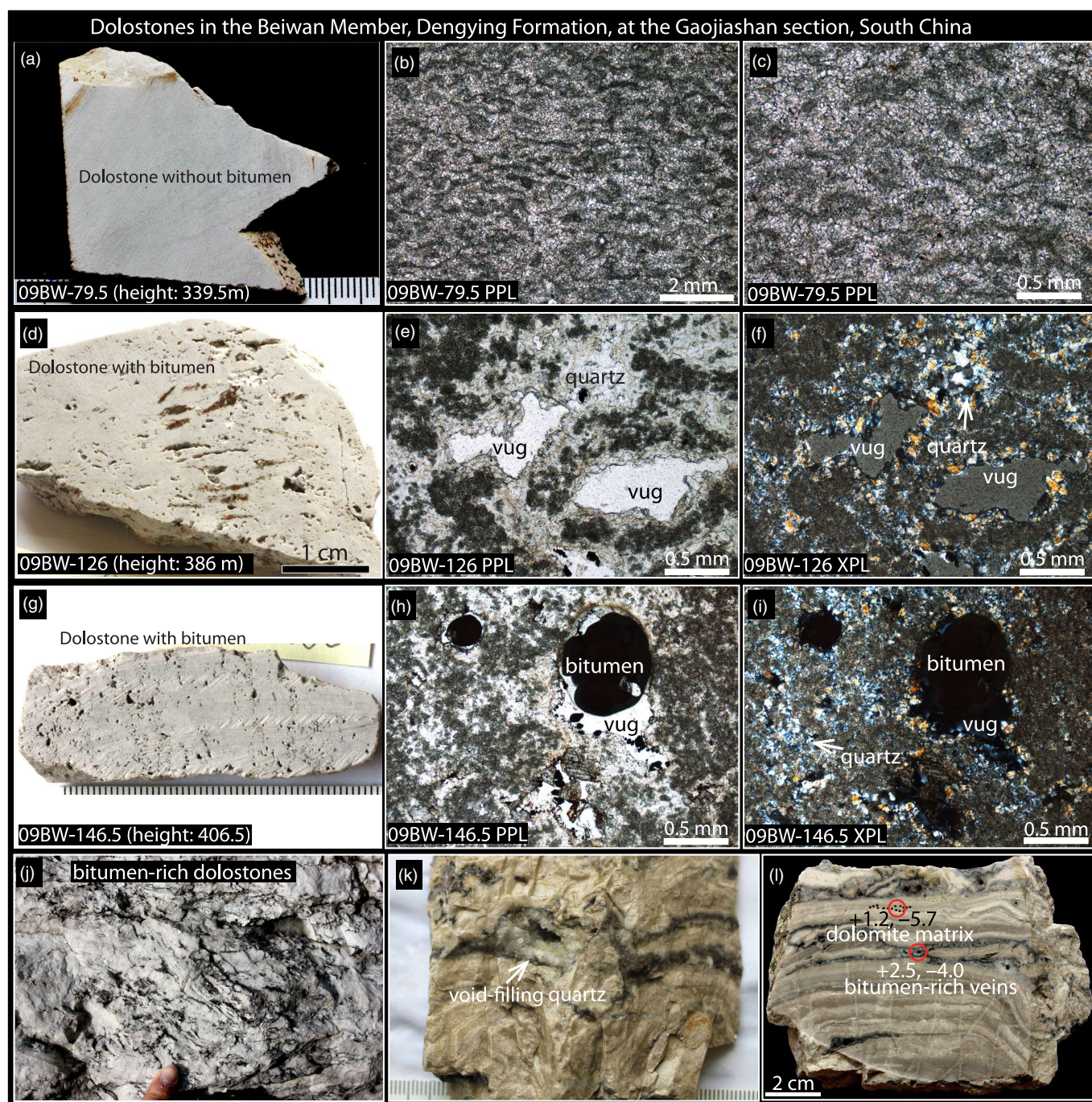
The origin of the authigenic aragonites in the Algal Dolomite Member remains debated. In geological records, botryoidal aragonites of both marine origin (Ginsburg & James, 1976; Mazzullo & Cys, 1979; Aissaoui, 1985; Jiang *et al.* 2006a) and non-marine origin (Mazzullo, 1980; Aissaoui, 1985) have been reported. Proposed interpretations for the Dengying aragonites include primary syn-depositional seafloor precipitates (Zhang, 1980; Cao, 2002; Zhang *et al.* 2014b; Lin *et al.* 2015; Peng *et al.* 2017), authigenic carbonates formed in meteoric waters (Wang *et al.* 2010; Shi *et al.* 2011), authigenic carbonates formed in marine environments (Si *et al.* 2014; Hao *et al.* 2015; Mou *et al.* 2015; Tan *et al.* 2015) and late authigenic carbonates formed during burial diagenesis (Wang *et al.* 2000).

Based on multiple lines of evidence, an early authigenic marine origin for the Dengying aragonites is preferred in this study. First, the botryoidal aragonites in the Dengying

Formation are mostly void-filling, distributed mostly in parallel with the primary sedimentary bedding. Therefore, a syn-depositional origin, instead of a syn-genetic (in water columns) origin, is more likely.

Second, fabric-specific  $\delta^{18}\text{O}_{\text{carb}}$  values of different carbonate phases reveal that the authigenic aragonite crystal fans show higher  $\delta^{18}\text{O}_{\text{carb}}$  values than the host dolostones (Fig. 10a, c). Considering that meteoric waters typically have much lower  $\delta^{18}\text{O}$  signals than seawater (Knauth & Kennedy, 2009; Bishop *et al.* 2014; Oehlert & Swart, 2014), the impact by meteoric waters on these authigenic cements should be minimized. Therefore, an evaporitic marine origin, instead of a karst-related meteoric water origin, is more likely.

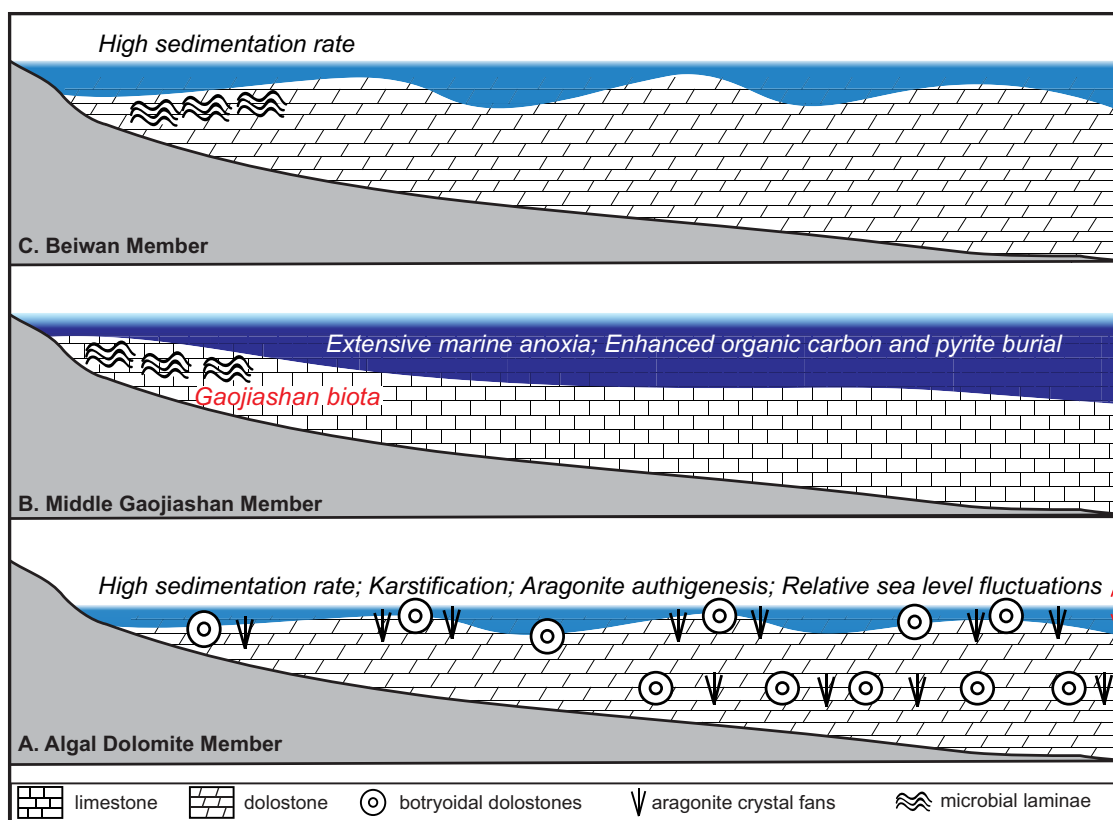
Third, published studies show that the late Ediacaran botryoidal aragonites in the Dengying Formation (Zhang *et al.* 2014b; Lin *et al.* 2015; Mou *et al.* 2015; Peng *et al.* 2017),



**Fig. 8.** (Colour online) Petrographic observations of dolostones in the Beiwai Member, Dengying Formation, at the Gaojiashan section. (a–c) Slab and petrographic photographs of sample 09BW-79.5 (collected at 339.5 m in Fig. 12) showing dolomitic texture with abundant algal fabrics (?). (d–f) Slab and petrographic photographs of sample 09BW-126 (collected at 386 m in Fig. 12) showing dolostone with vugs and quartz cements. (g–i) Slab and petrographic photographs of sample 09BW-146.5 (collected at 406.5 m in Fig. 12). Note the vugs with bitumen in (h) and (i), and the quartz cements (arrows) in (f) and (i) under cross-polarized light. (j) Outcrop photograph showing dolostones (white) with abundant bitumen (black). (k, l) Photographs of hand samples showing bitumen in dissolution vugs. Note the void-filling quartz (arrow) in (k). Micro-drilling geochemical  $\delta^{13}\text{C}$  (left) and  $\delta^{18}\text{O}$  (right) data are provided in (l). PPL – plane polarized light; XPL – cross-polarized light.

as well as correlative strata in the Nama Group of Namibia (Grant *et al.* 1991), typically show dull or non-luminescent colour under cathodoluminescence (CL), which is consistent with marine carbonates, instead of late-diagenetic carbonates that typically show bright CL colours. In addition, aragonite is unstable in meteoric or late-diagenetic fluids, so it is not likely that these aragonite cements formed through late-diagenetic processes.

Taken together, based on sedimentological and geochemical results, the botryoidal aragonite textures, aragonite crystal fans and karstification features in the Algal Dolomite Member of the DYF@GJS were formed during frequent sea level fluctuations and repeated exposure and submergence in a peritidal environment. Thus, although the botryoidal aragonite textures and aragonite crystal fans are technically early post-depositional in origin, they still appear to record seawater signals.



**Fig. 9.** (Colour online) A depositional model of the terminal Ediacaran Dengying Formation based on studies of the Gaojiashan section. See main text for a detailed discussion.

### 7.c. A high-alkalinity ocean in the terminal Ediacaran Period

If our interpretation of these authigenic aragonite (now dolomite) cements is correct, then the ocean chemistry may have witnessed the occurrence of a high-alkalinity ocean during the terminal Ediacaran Period. The existence of a high-alkalinity ocean at that time is consistent with the sedimentological observations that authigenic aragonites have also been found in the correlative terminal Ediacaran strata in Namibia (Grant, 1990; Grant *et al.* 1991; Grotzinger *et al.* 2000, 2005; Wood *et al.* 2002; Hall *et al.* 2013; Penny *et al.* 2014; Wood, 2016) and the Siberia Platforms (Wood *et al.* 2017b).

Supporting evidence for a high-alkalinity ocean in the terminal Ediacaran Period also comes from the strontium concentration data. Published geochemical data show elevated concentrations of strontium in the carbonates of the Dengying Formation in South China (Fig. 13g) (Sawaki *et al.* 2010; Cui *et al.* 2016b) and the Nama Group of Namibia (Grant *et al.* 1991; Ries *et al.* 2009). Considering that strontium has a crystal ionic radius larger than that of  $\text{Ca}^{2+}$  and thus prefers the more open octahedral crystal structure of aragonite over the smaller hexagonal structure of calcite (Wray & Daniels, 1957; Lorens, 1981), the precipitation of aragonites in a high-alkalinity ocean during deposition could account for the enrichment of strontium concentrations in marine carbonates during the late Ediacaran Period.

Taken together, it is likely that a high-alkalinity ocean occurred in the late Ediacaran Period. This inferred high-alkalinity ocean is evidenced by the authigenic aragonites in the Algal Dolomite Member and high Sr concentrations in the Gaojiashan Member of the Dengying Formation.

### 7.d. Evaluating the impact of authigenesis

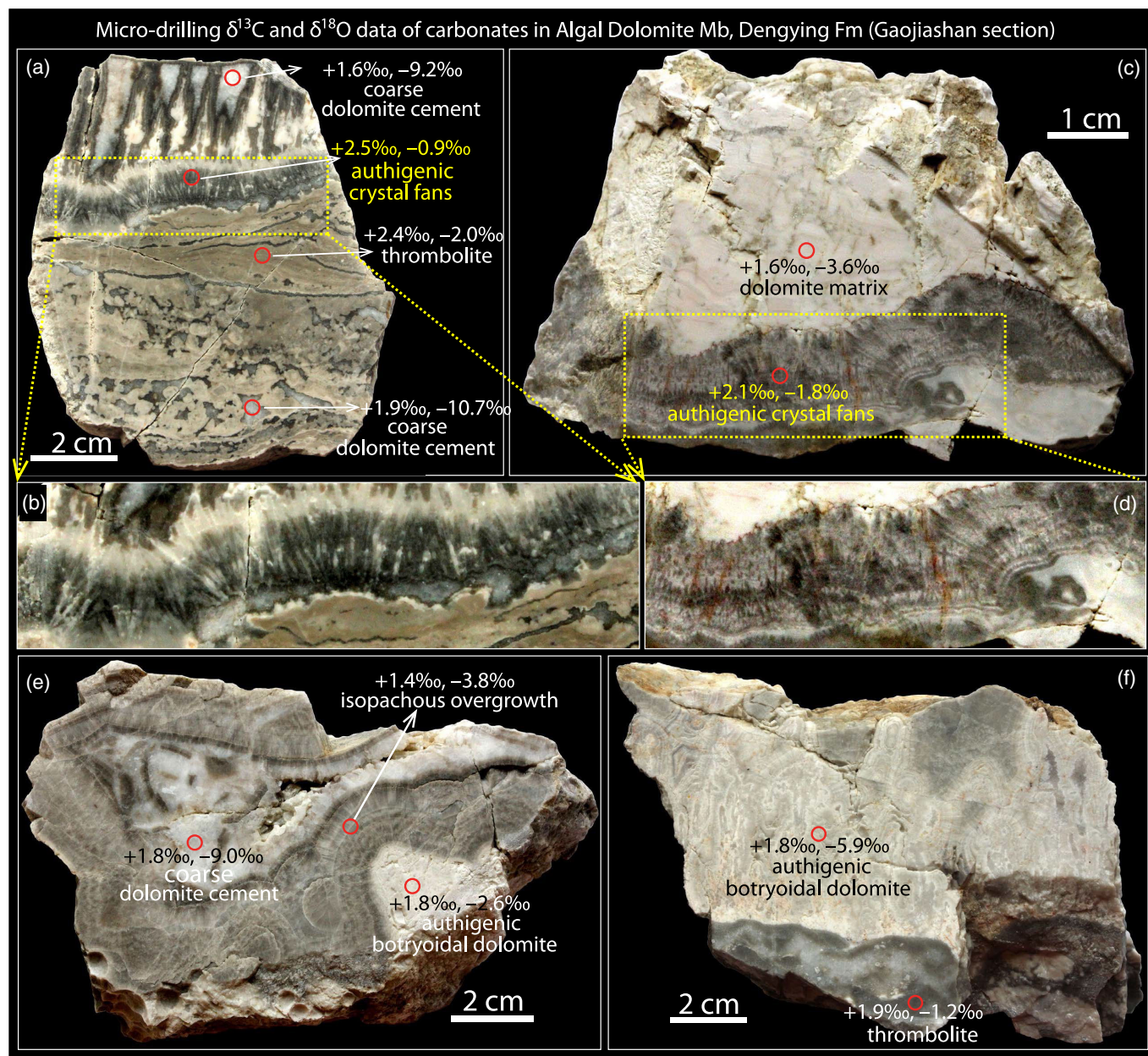
Given the significant heterogeneity of carbonates in the studied samples, fabric-specific  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  analysis of different phases and textures of the DYF@GJS was adopted as the sampling strategy. Guided by detailed sedimentological observations, we evaluated the impact of authigenesis for each of the three members.

#### 7.d.1. Authigenesis of the Algal Dolomite Member

Authigenic aragonite (now dolomite) crystal fans from the Algal Dolomite Member have been investigated for  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values by micro-drilling analysis (Fig. 10). The  $\delta^{18}\text{O}_{\text{carb}}$  values of the dolomitized crystal fans ( $-0.9\text{‰}$  in Fig. 10a and  $-1.8\text{‰}$  in Fig. 10c) are notably enriched in  $^{18}\text{O}$  compared with other carbonate phases, suggesting high-alkalinity evaporative conditions during precipitation (Ufnar *et al.* 2008; Gomez *et al.* 2014; Guo & Chafetz, 2014; Horton *et al.* 2015; Leleu *et al.* 2016). On the contrary, isotope data for the late carbonate cements, particularly the hydrothermal saddle dolomite, show much lower  $\delta^{18}\text{O}_{\text{carb}}$  values (c.  $-10\text{‰}$ ) than early crystal fans and dolomitic matrix, which is consistent with a high-temperature origin during deep burial. Similar observations of hydrothermal dolomite in the Dengying Formation in the Sichuan Basin (Shi *et al.* 2013; Liu *et al.* 2014a; Jiang *et al.* 2016) suggest that the occurrence of saddle dolomite in the Dengying Formation may result from a basin-scale geothermal event during deep burial.

#### 7.d.2. Authigenesis of the Gaojiashan Member

Multiple calcite-filled vugs and veins were found in the limestone intervals of the upper Gaojiashan Member (1–2 m below the



**Fig. 10.** (Colour online) Carbonate  $\delta^{13}\text{C}$  (left) and  $\delta^{18}\text{O}$  (right) values of micro-drilled samples from the Algal Dolomite Member, Dengying Formation, at the Gaojiashan section. (a–d) Freshly cut dolostone slabs showing authigenic crystal fans. (a) and (b) also illustrated in Figure 4a–f; (c) and (d) also illustrated in Figure 4g–i. Although all samples have been dolomitized, relic fabrics of aragonite are retained. (e, f) Freshly cut dolostone slabs showing thrombolite matrix, botryoidal dolomite, isopachous cements and late-stage dolomite cements. Note the relatively high  $\delta^{18}\text{O}_{\text{carb}}$  values in the aragonite crystal fans (-0.9‰ in (a) and -1.8‰ in (c)) and the relatively low  $\delta^{18}\text{O}_{\text{carb}}$  values in the late-stage coarse dolomite cements (-9.2‰ in (a) and -9.0‰ in (e)).

conglomerate/sandstone interval) (Fig. 11a–c). We micro-drilled and analysed the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values of both the calcite veins and micritic limestone phases in order to evaluate the impact of diagenesis (Fig. 11d–g). The  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values of the calcite veins show more negative values compared with the host limestone rocks (Fig. 11). Two interpretations could possibly explain this observation: (1) these calcite veins may be early authigenic carbonates formed by microbial sulfate reduction in pore waters (e.g. Campbell *et al.* 2002; Jiang *et al.* 2003, 2006a,b; Schrag *et al.* 2013; Zhou *et al.* 2016; Cui *et al.* 2017a), or (2) these calcite veins may result from intrusions of late-diagenetic fluids (e.g. Bristow *et al.* 2011; Lin *et al.* 2011). Based on the sharp contact

between these white calcite phases and the host carbonates, which sometimes cut across the primary sedimentary bedding, a late diagenetic origin for these calcite phases is preferred in this study.

Recently, largely based on a newly discovered  $\delta^{13}\text{C}_{\text{carb}}$  negative excursion in the upper Gaojiashan Member, Gamper *et al.* (2015) placed the Ediacaran–Cambrian boundary in the middle Dengying Formation. However, it should be noted that this  $\delta^{13}\text{C}_{\text{carb}}$  negative excursion occurs in the conglomerate/sandstone interval of the uppermost Gaojiashan Member, which more likely reflects late-diagenetic signals instead of primary seawater signals. Therefore, Gamper *et al.*'s (2015) placement of the Ediacaran–Cambrian boundary should be treated with caution. Our observation of

late-diagenetic calcite veins with negative  $\delta^{13}\text{C}_{\text{carb}}$  values around this interval casts doubt on the fidelity of the proposed  $\delta^{13}\text{C}_{\text{carb}}$  negative excursion and its relationship with the Ediacaran–Cambrian boundary.

### 7.d.3. Authigenesis of the Beiwang Member

Bitumen-bearing dolostones in the Beiwang Member have also been tested to evaluate the impact of bitumen on the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values. Potential oxidation of the bitumen may have caused a significant decrease in  $\delta^{13}\text{C}_{\text{carb}}$  values (e.g. Bristow *et al.* 2011). However, no strongly negative  $\delta^{13}\text{C}_{\text{carb}}$  values have been found in the bitumen-bearing samples (Fig. 81), suggesting little impact of bitumen on the  $\delta^{13}\text{C}_{\text{carb}}$  compositions. That being said, it is notable that the  $\delta^{13}\text{C}_{\text{org}}$  data in the Beiwang Member show large variations (Fig. 12c), which may be caused by the influence of bitumen in the dolostone samples.

In summary, the texture-specific micro-drilling method employed in this study demonstrates that coupled petrographic and isotope analysis is an informative tool for the evaluation of diagenetic influences in chemostratigraphic studies. Late-diagenetic signatures should be identified and treated with caution in palaeoenvironmental interpretations.

### 7.e. Biogeochemical carbon cycles

The chemostratigraphic  $\delta^{13}\text{C}_{\text{carb}}$  profile of the DYF@GJS shows a positive excursion of up to +6 ‰ in the Gaojiashan Member (Figs 1d, 12b, 13b). Comparisons of the  $\delta^{13}\text{C}_{\text{carb}}$  profile with other Dengying or equivalent sections at regional and global scales show both similarities and differences (Fig. 14). In the Yangtze Block, similar  $\delta^{13}\text{C}_{\text{carb}}$  positive excursions have also been reported from correlative Ediacaran sections at Shipai (Jiang *et al.* 2007), Jiulongwan (Wang *et al.* 2014b), Lianghekou (Chen *et al.* 2015), Lianghong (Wang *et al.* 2012) and Huajipo (Zhang *et al.* 2004) (Fig. 14). The difference in the chemostratigraphic  $\delta^{13}\text{C}_{\text{carb}}$  profiles of these sections may result from a difference in local redox conditions, sedimentation rates, stratigraphic hiatus or sampling resolutions. Regardless, most of the sections show a  $\delta^{13}\text{C}_{\text{carb}}$  excursion of up to +6 ‰.

Viewed at a global scale, the finding of a  $\delta^{13}\text{C}_{\text{carb}}$  excursion of up to +6 ‰ in the Dengying Formation is also consistent with published chemostratigraphic profiles of the roughly correlative terminal Ediacaran strata in Namibia (Saylor *et al.* 1998; Wood *et al.* 2015; Tostevin *et al.* 2017) and Arctic Siberia (Knoll *et al.* 1995; Pelechaty *et al.* 1996b; Cui *et al.* 2016a; Vishnevskaya *et al.* 2017) where  $\delta^{13}\text{C}_{\text{carb}}$  positive excursions with similar magnitude (up to +6 ‰) have also been reported.

Two hypotheses may be able to explain this  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion. First, canonical models of the global carbon cycle suggests that  $\delta^{13}\text{C}_{\text{carb}}$  positive anomalies likely result from an enhanced organic carbon burial rate because organic carbon is strongly enriched in  $^{12}\text{C}$  (Broecker, 1970; Hayes *et al.* 1999). Alternatively, a  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion can also result from the mixing of high  $\delta^{13}\text{C}_{\text{carb}}$  authigenic carbonates during early diagenesis. This is possible if residual carbon after fermentation (methanogenesis) led to the formation of authigenic carbonates (Claypool & Kaplan, 1974; Irwin *et al.* 1977; Talbot & Kelts, 1986; Meister *et al.* 2007; Wehrmann *et al.* 2011; Birgel *et al.* 2015; Pierre *et al.* 2016). Such processes may have been particularly prevalent in the Precambrian ocean where the seawater was mostly anoxic and therefore may promote authigenic carbonate precipitation on the seafloor (Higgins *et al.* 2009; Schrag *et al.* 2013).

Based on multiple lines of evidence, we prefer the former hypothesis (i.e. enhanced organic carbon burial) for this  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion. First, no extremely high or low  $\delta^{13}\text{C}_{\text{carb}}$  signals that are indicative of the existence of methane have been found based on our detailed geochemical analysis of micro-drilled samples. Therefore, there is no supporting evidence for the occurrence of methane generation or oxidation in the DYF@GJS. Second, the presence of a gypsum layer near the height of the  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion in the middle Gaojiashan Member of the DYF@GJS suggests that the sulfate concentration was high during the  $\delta^{13}\text{C}_{\text{carb}}$  excursion. Considering that methanogens are typically outcompeted for substrates (e.g. lactate and acetate) by sulfate reducers in sulfate-rich environments (Jørgensen & Kasten, 2006), methanogenesis would not have played a considerable role in generating this  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion. Third, the recent investigations of N and U isotopes (Fig. 13) suggest that extensive oceanic anoxia occurred during the late Ediacaran Period (Wei *et al.* 2018; Zhang *et al.* 2018). This oceanic anoxia event may have promoted organic carbon burial and led to the  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion.

In summary, a  $\delta^{13}\text{C}_{\text{carb}}$  excursion up to +6 ‰ has been found in the Dengying Formation and many other correlative terminal Ediacaran sections. Based on multiple lines of evidence, we regard that enhanced organic carbon burial may have caused this excursion.

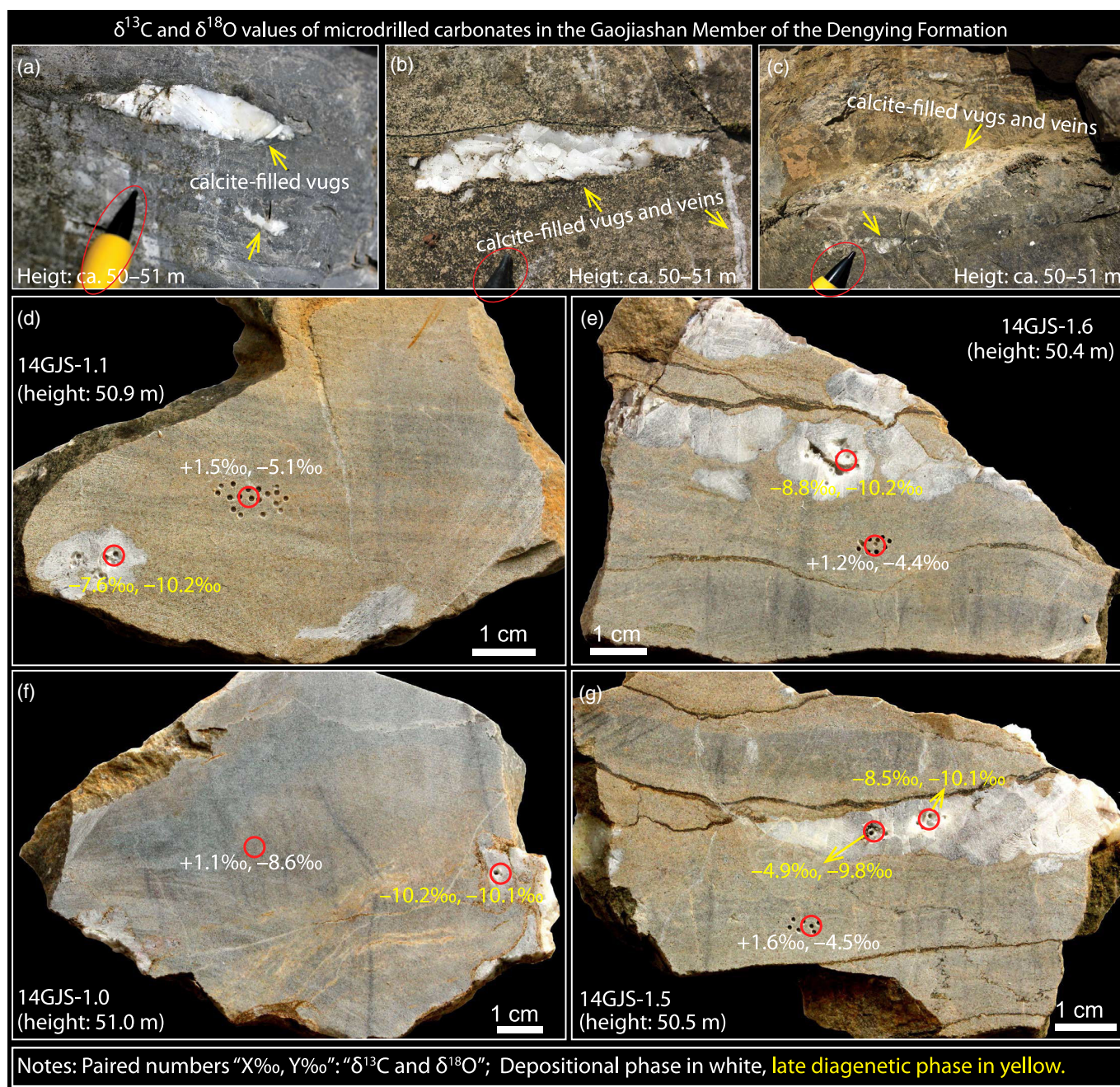
### 7.f. Biogeochemical sulfur cycles

Sulfur isotope chemostratigraphy of the DYF@GJS shows overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values ranging between +20 ‰ and +30 ‰ through most of the section, except for two episodes of anomalous negative excursions down to c. –30 ‰ in the lower and middle Gaojiashan Member (Figs 12e, 13f). The occurrence of highly positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values in the terminal Ediacaran strata has also been reported from the roughly equivalent strata in Oman (Fike & Grotzinger, 2008), Namibia (Ries *et al.* 2009; Tostevin *et al.* 2017), Arctic Siberia (Cui *et al.* 2016a) and Newfoundland (Canfield *et al.* 2007; Hantsoo *et al.* 2018), suggesting a global phenomenon. The origin of the low  $\delta^{34}\text{S}_{\text{pyrite}}$  signals in the Gaojiashan Member has been fully discussed in our earlier paper (Cui *et al.* 2016b); we will mainly focus on the overall high  $\delta^{34}\text{S}_{\text{pyrite}}$  signals below.

Four hypotheses can be proposed to explain the overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  signals in the studied section. They are discussed below.

#### 7.f.1. Thermochemical sulfate reduction (TSR)

The high  $\delta^{34}\text{S}_{\text{pyrite}}$  values may result from Rayleigh fractionations during thermochemical sulfate reduction (TSR) of hydrothermal fluids in post-depositional processes. Such a scenario has recently been proposed for the Cryogenian Datangpo Formation, where extremely high  $\delta^{34}\text{S}_{\text{pyrite}}$  values (up to +70 ‰) have been found (Cui *et al.* 2017b, 2018b,c). However, our field observations revealed no clear evidence for a significant impact by hydrothermal fluids. Moreover, assuming a seawater  $\delta^{34}\text{S}_{\text{sulfate}}$  value of +40 ‰ for the late Ediacaran ocean based on gypsum or CAS analyses (Fike & Grotzinger, 2008; K. D. Bergmann, unpub. Ph.D. thesis, California Institute of Technology, 2013; Cui *et al.* 2016b), these  $\delta^{34}\text{S}_{\text{pyrite}}$  values, though positive, can still be explained by microbial sulfate reduction with normal (rather than reversed) fractionations (i.e.  $\Delta^{34}\text{S}_{\text{sulfate-pyrite}} = \delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{pyrite}} > 0$ ). Therefore, a TSR origin for the overall high  $\delta^{34}\text{S}_{\text{pyrite}}$  values in the DYF@GJS is not preferred in this study.



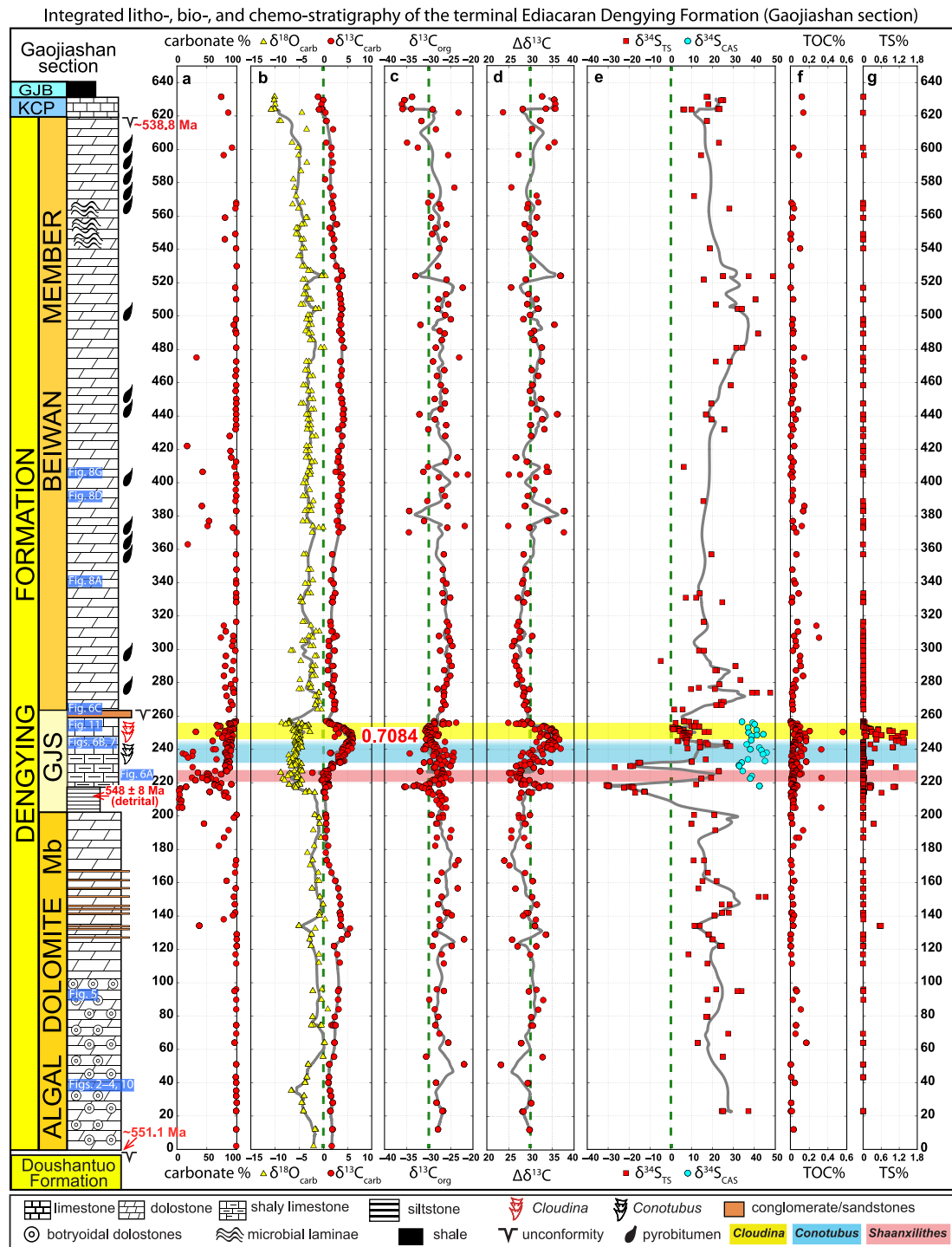
**Fig. 11.** (Colour online) Carbonate  $\delta^{13}\text{C}$  (left) and  $\delta^{18}\text{O}$  (right) values of micro-drilled samples from the Gaojiashan Member, Dengying Formation, at the Gaojiashan section. (a–c) Calcite-filled vugs and veins (arrows) at c. 50–51 m in Figure 13. Pencil for scale. (d–g) Carbonate  $\delta^{13}\text{C}$  (left) and  $\delta^{18}\text{O}$  (right) values of micro-drilled samples from the Gaojiashan Member. Note that the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (in yellow) of the vug-filling calcite are consistently lower than those (in white) measured from the host carbonate rocks. Numbers in sample IDs represent distance (in metres) below the conglomerate/sandstone interval of the upper Gaojiashan Member. The stratigraphic height values in (d–g) represent the distance above the Gaojiashan/Algal Dolomite boundary.

### 7.f.2. Low sulfate concentrations of seawater

The positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values may reflect limited S isotope fractionation in seawaters with very low concentrations of sulfate (Habicht *et al.* 2002; Loyd *et al.* 2012). However, given the presence of gypsum in the Dengying Formation across the Yangtze Platform and the overall shallow and evaporative environments inferred from the lithofacies, seawater sulfate concentration should not be a limiting factor for microbial sulfate reduction. Therefore, this hypothesis is not favoured here.

### 7.f.3. Higher proportions of pyrite burial

The overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  signals in the late Ediacaran Period may be caused by enhanced rates of pyrite burial. This scenario has been proposed based on an earlier study of the terminal Ediacaran strata in Oman (Fike & Grotzinger, 2008). More recent studies of the Dengying Formation have shown notably high  $\delta^{15}\text{N}$  signals and low  $\delta^{238}\text{U}$  signals (Fig. 13) indicative of a significant ocean anoxic event with enhanced denitrification and U removal from the ocean into the sediments (A. Gamper, unpub. Ph.D.



**Fig. 12.** (Colour online) Integrated litho-, bio- and chemostratigraphy of the terminal Ediacaran Dengying Formation at the Gaojiashan section. Geochemical profiles show (a) carbonate contents, (b) carbonate carbon isotopes ( $\delta^{13}\text{C}_{\text{carb}}$ , ‰ VPDB), carbonate oxygen isotopes ( $\delta^{18}\text{O}_{\text{carb}}$ , ‰ VPDB), (c) organic carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ , ‰ VPDB), (d) carbon isotope fractionations ( $\Delta\delta^{13}\text{C}_{\text{carb-org}}$ ), (e) pyrite sulfur isotopes ( $\delta^{34}\text{S}_{\text{TS}}$ , ‰ VCDT), carbonate-associated sulfate (CAS) sulfur isotopes ( $\delta^{34}\text{S}_{\text{CAS}}$ , ‰ VCDT), (f) total organic carbon content (TOC) and (g) total sulfur content (TS, dominated by pyrite with trace amount of organic S) of acidified residues. The grey lines represent the five-point running average of the chemostratigraphic data. The lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  value (0.7084) measured from a limestone sample in the Gaojiashan Member is also marked in the  $\delta^{13}\text{C}_{\text{carb}}$  profile (at 246 m in stratigraphic height). The stratigraphic positions of some figures have been marked on the lithology column. Note that  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  data plotted here and in Figures 13, 14 only include micro-drilled samples of the least-altered micritic carbonate matrix, whereas  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{TS}}$  data were measured from bulk samples after a complete acidification of carbonates. TS and TOC data are generally low owing to significant carbonate dilutions. Source of the detrital zircon age: Cui *et al.* (2016b). Abbreviations: GJS – Gaojiashan Member; KCP – Kuanchuanpu Formation; GJB – Guojiaba Formation. See online Supplementary Material Table S1 for complete data.

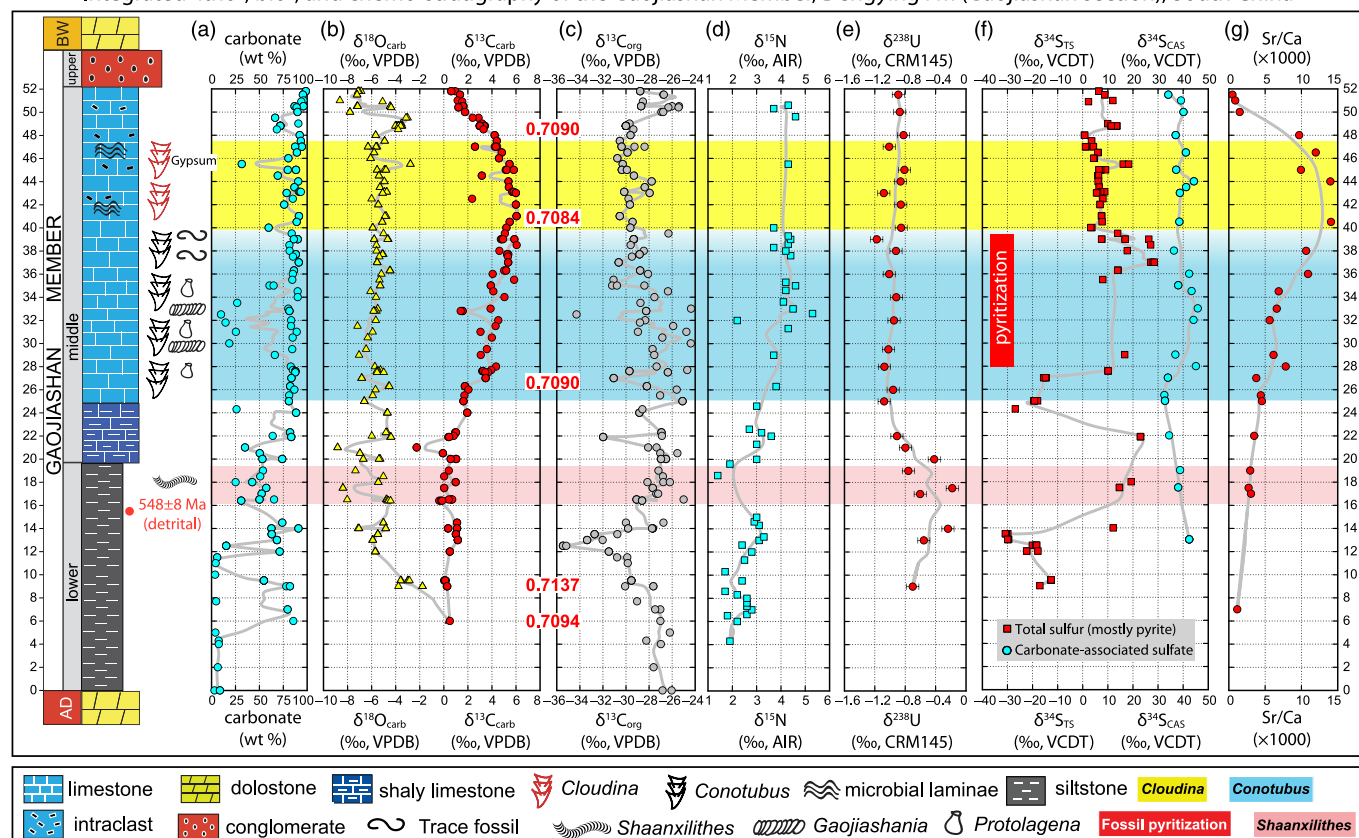
dissertation, Freie Universität Berlin, 2014; Wei *et al.* 2018; Zhang *et al.* 2018). This inferred ocean anoxic event at that time may have promoted organic carbon and pyrite burial, leading to the high  $\delta^{34}\text{S}_{\text{pyrite}}$  signals.

#### 7.f.4. High sedimentation rates

It is also possible that enhanced sedimentation rates may have contributed to the overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  signals in the studied section. It has been found that higher sedimentation rate could cause higher



## Integrated litho-, bio-, and chemo-stratigraphy of the Gaojiashan Member, Dengying Fm (Gaojiashan section), South China



**Fig. 13.** (Colour online) Integrated litho-, bio- and chemostratigraphy of the Gaojiashan Member of the middle Dengying Formation at the Gaojiashan section. Geochemical profiles show (a) carbonate contents (wt %), (b) carbonate carbon isotopes ( $\delta^{13}\text{C}_{\text{carb}}$ , ‰ VPDB), carbonate oxygen isotopes ( $\delta^{18}\text{O}_{\text{carb}}$ , ‰ VPDB), (c) organic carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ , ‰ VPDB), (d) nitrogen isotopes ( $\delta^{15}\text{N}$ , ‰ AIR), (e) uranium isotopes ( $\delta^{238}\text{U}$ , ‰ CRM145), (f) sulfur isotopes ( $\delta^{34}\text{S}_{\text{TS}}$ , ‰ VCDT) of total sulfur (TS, dominated by pyrite with trace amount of organic S) after a complete acidification of carbonates, carbonate-associated sulfate (CAS) sulfur isotopes ( $\delta^{34}\text{S}_{\text{CAS}}$ , ‰ VCDT), and (g) Sr and Ca concentration (in ppm) ratios (Sr/Ca). Grey lines represent the three-point running average of the chemostratigraphic data.  $^{87}\text{Sr}/^{86}\text{Sr}$  values measured from limestone beds or limestone nodules in the Gaojiashan Member are also marked along the  $\delta^{13}\text{C}_{\text{carb}}$  profile. Data sources:  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{34}\text{S}$ , Sr/Ca data (H. Cui, unpub. Ph.D. thesis, Univ. Maryland, 2015; Cui *et al.* 2016b),  $^{87}\text{Sr}/^{86}\text{Sr}$  values (this study),  $\delta^{15}\text{N}$  data (A. Gampner, unpub. Ph.D. dissertation, Freie Universität Berlin, 2014),  $\delta^{238}\text{U}$  data (Zhang *et al.* 2018). Modified from Cui *et al.* (2016b). AD – Algal Dolomite Member; BW – Beiwan Member.

$\delta^{34}\text{S}_{\text{pyrite}}$  in marine sediments (Pasquier *et al.* 2017; Liu *et al.* 2019). Although karstification may have eroded the Algal Dolomite Member, compared with the well-studied Doushantuo Formation in the Yangtze Block (Zhou & Xiao, 2007; Zhu *et al.* 2007, 2013; McFadden *et al.* 2008; Jiang *et al.* 2011; Cui *et al.* 2015), the Dengying Formation is remarkably thick (Fig. 15). The general thickness of the Doushantuo Formation (c. 635.2–551.1 Ma) is <300 m in thickness for over 80 million years (Condon *et al.* 2005; Zhou & Xiao, 2007; Zhu *et al.* 2007), while the studied DYF@GJS (c. 551.1–538.8 Ma) is >630 m in thickness for only ~12.3 million years (Fig. 15). Given the exceptionally high sedimentation rate of the Dengying Formation compared with the underlying Doushantuo Formation, it is likely that high sedimentation rate may have also played a role in generating the positive  $\delta^{34}\text{S}_{\text{pyrite}}$  signals.

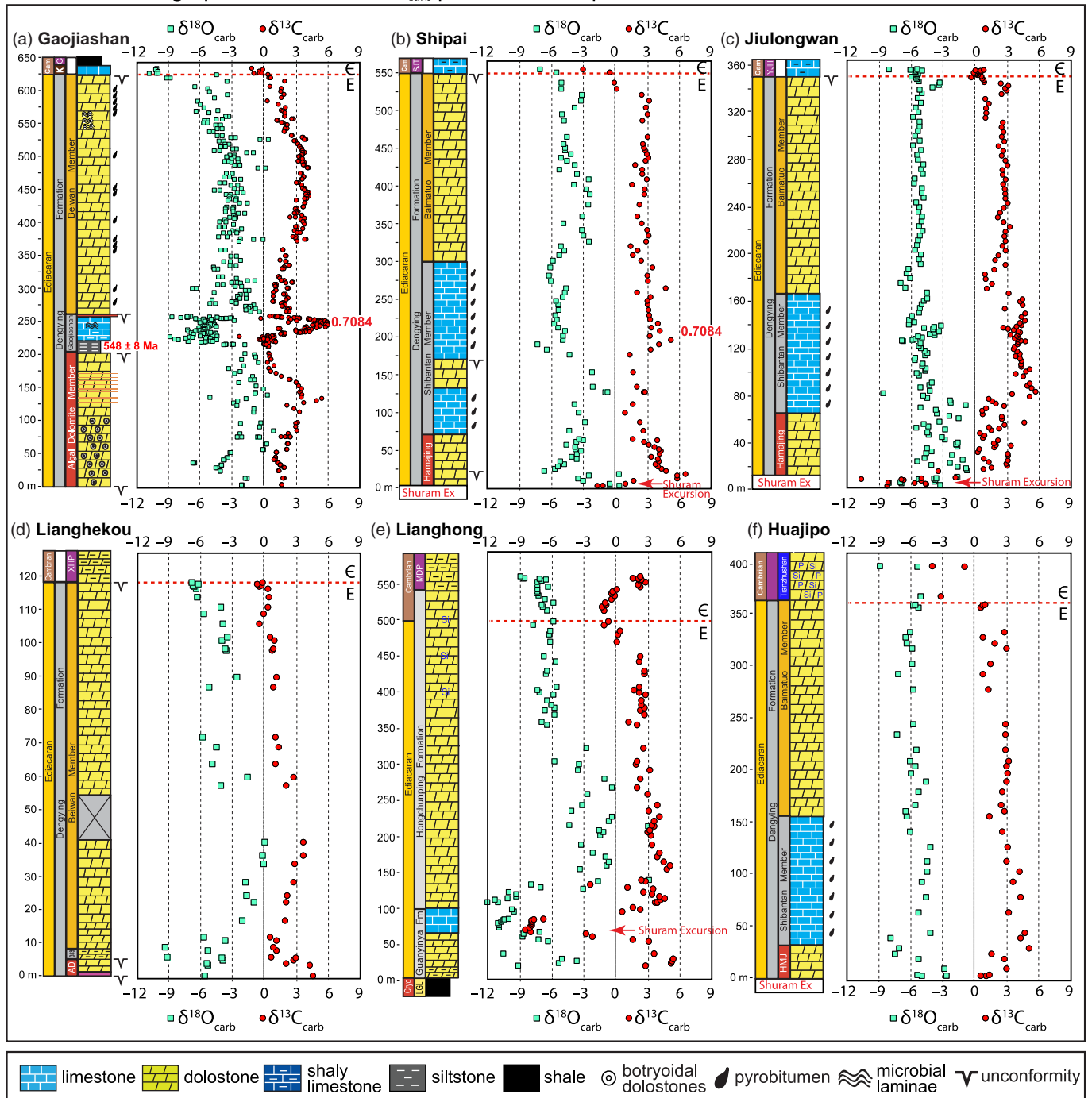
Taken together, based on multiple lines of sedimentological and geochemical evidence, we regard that enhanced rates of pyrite burial may be the main cause of the overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values. High sedimentation rates may have also contributed to the high  $\delta^{34}\text{S}_{\text{pyrite}}$  values, but more information is needed to specifically test this hypothesis.

### 7.g. Implications for early metazoan evolution

The contrasting thickness between the Dengying Formation and the underlying Doushantuo Formation can provide useful insights

into the changing environment. This sharp contrast suggests that the depositional environment during the late Ediacaran Period has been subject to significant change, which is possibly characterized by overall shallower water depth, higher alkalinity and higher accommodation space. Such conditions are suitable for continuous production and accumulation of marine carbonates.

Sedimentological observations suggest that the karstification events of shallow carbonate platforms may be widespread in the late Ediacaran Period. Notably, similar karstification textures of carbonate breccia, aragonite crystal fans and botryoidal aragonites have also been found from other correlative sections, including the other Dengying sections in South China (Zhang, 1980; Cao & Xue, 1983; Siegmund & Erdtmann, 1994; Xiang *et al.* 2001; Wang *et al.* 2010, 2012; Shi *et al.* 2011; Liu *et al.* 2012; Mo *et al.* 2013; Zhang *et al.* 2014b; Lin *et al.* 2015; Mou *et al.* 2015; Lian *et al.* 2016, 2017), the Qigebulake Formation in the Tarim basin in Northwestern China (Qian *et al.* 2017), the Buah Formation in Oman (Gorin *et al.* 1982; Cozzi & Al-Siyabi, 2004; K. D. Bergmann, unpub. Ph.D. thesis, California Institute of Technology, 2013), the K3 and K4 units of the Katakaturuk Dolomite succession in Arctic Alaska (Macdonald *et al.* 2009) and the Turkut Formation in the Siberia Platform (Knoll *et al.* 1995; Pelechaty *et al.* 1996a; Nagovitsin *et al.* 2015; Rogov *et al.* 2015; Cui *et al.* 2016a). These observations suggest widespread karstification of shallow carbonate platforms on a global scale.

Chemostratigraphic  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  profiles of multiple terminal Ediacaran sections in South China

**Fig. 14.** (Colour online) Chemostratigraphic  $\delta^{13}\text{C}_{\text{carb}}$  (‰, VPDB) and  $\delta^{18}\text{O}_{\text{carb}}$  (‰, VPDB) profiles of multiple terminal Ediacaran sections in South China. Data sources: (a) Gaojiashan section (this study); (b) Shipai section (Jiang *et al.* 2007); (c) Jiulongwan section (Wang *et al.* 2014b); (d) Lianghekou section (Chen *et al.* 2015); (e) Lianghong section (Wang *et al.* 2012); (f) Huajipo section (Zhang *et al.* 2004). Source of the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7084): Gaojiashan section (this study) and Shipai section (Jiang *et al.* 2007). Abbreviations: AD – Algal Dolomite Member; Cam – Cambrian;  $\epsilon$  – Crogenian Period; E – Ediacaran; G – Guojiaba Formation; GJS – Gaojiashan Member; HMJ – Hamajing Member; K – Kuanchuanpu Formation; LGL – Lieguli Formation; MDP – Maidiping Formation; SJT – Shuijingtuo Formation; Shuram Ex – Shuram Excursion; XHP – Xihaoing Member; YJH – Yanjiahe Formation.

The overall shallow-marine environment may be caused by regional tectonic uplift in the depositional basin (Xue *et al.* 2001; Wang *et al.* 2014a; Zhu *et al.* 2014b; Li *et al.* 2015; Zhu *et al.* 2015; Yang *et al.* 2017). The extensive karstification of shallow carbonate platforms during the late Ediacaran Period was probably

triggered by fluctuations of relative sea level at that time. This scenario is in agreement with an overall increase in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  and decrease in seawater Nd isotopes through the Proterozoic–Phanerozoic transition (Halverson *et al.* 2007, 2010; Peters & Gaines, 2012; Cox *et al.* 2016). The break-up of the Rodinia




the composition of the earliest biominerals of early animals. It is likely that the high concentration of alkalinity and nutrient influx in the ocean may have caused the supersaturation of marine carbonates and facilitated early animal biomineralization in this critical period (Zhuravlev & Wood, 2008; Peters & Gaines, 2012; Cui *et al.* 2016b; Wood *et al.* 2017a).

## 8. Conclusions

An integrated sedimentological and chemostratigraphic study was conducted for the terminal Ediacaran Dengying Formation at the Gaojiashan section (DYF@GJS), Ningqiang County of southern Shaanxi Province, South China. Multiple types of lithofacies and diagenesis have been identified and summarized based on detailed field observations, petrographic studies and isotope measurements of micro-drilled spots.

- (1) The DYF@GJS was deposited in a largely shallow-marine platform with dynamic sea level changes and overall high accommodation space, though the lower Gaojiashan Member may represent a temporarily deeper and more anoxic environment. Sedimentological evidence suggests that extensive karstification of shallow-marine platforms occurred soon after the deposition of the lower part of the Algal Dolomite Member.
- (2) We propose that the finding of authigenic aragonites in the Algal Dolomite Member may have significant implications on the Ediacaran ocean chemistry. The micro-drilling  $\delta^{18}\text{O}_{\text{carb}}$  data for the authigenic aragonites (now dolomites) suggest that meteoric waters had little impact on the genesis of these authigenic aragonites. Instead, the Dengying authigenic aragonites may have formed in marine environments during repeated sea level fluctuations in a peritidal environment, which resulted in karstification features being formed during subaerial exposure, followed by void-filling aragonite botryoids being formed during submergence. These Dengying authigenic aragonites reflect the existence of a high-alkalinity ocean at that time.
- (3) Geochemical analysis of micro-drilled samples reveals different compositions among depositional, early authigenic and late-diagenetic components. The post-depositional phases should be excluded when constructing chemostratigraphic profiles.
- (4) Chemostratigraphic data show a  $\delta^{13}\text{C}_{\text{carb}}$  positive excursion (up to +6 ‰) in the Gaojiashan Member and overall positive  $\delta^{34}\text{S}_{\text{pyrite}}$  values in most of the Dengying Formation. Based on multiple lines of sedimentological and geochemical evidence, enhanced burial of organic matter and pyrite in shallower environments is proposed for the studied basin. High concentrations of seawater alkalinity and nutrients may have facilitated the evolutionary innovation of early metazoan biomineralization.

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1017/S0016756819000293>

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