Reducing microenvironments promote incorporation of magnesium ions into authigenic carbonate forming at methane seeps: Constraints for dolomite formation

YANG LU*,†, XIN YANG*, ZHIYONG LIN*,‡, XIAOMING SUN*,‡§, YIPING YANG¶**, and JÖRN PECKMANN†*

*School of Marine Sciences, Sun Yat-sen University, Guangzhou, 510006, China
†Institute für Geologie, Centrum für Erdsystemforschung und Nachhaltigkeit, Universität Hamburg, Hamburg, 20146, Germany (E-mail: joern.peckmann@uni-hamburg.de)
‡Guangdong Provincial Key Laboratory of Marine Resources and Coastal Engineering, Guangzhou, 510006, China
§School of Earth Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, China
¶CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
**CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China

Associate Editor – Hairuo Qing

ABSTRACT

In part composed of Mg calcite and dolomite with a nearly continuous spectrum of MgCO$_3$ contents, carbonates forming at marine methane seeps are ideal candidates to study the formation of early diagenetic dolomite at surface conditions. Laboratory experiments, modelling and the co-variation of mineralogical and geochemical attributes of seep carbonates suggest that sulphide locally released from sulphate-driven anaerobic oxidation of methane drives catalytic dolomite formation at seeps. Direct comparison of the concentration of dissolved sulphide with the MgCO$_3$ content of seep carbonate could test this hypothesis. Although the concentration of sulphide during precipitation of carbonate cannot be determined, sedimentary fabrics probably had an effect on local sulphide concentration. Carbonates from the seabed of the Shenhu seepage area of the South China Sea reveal longitudinal, winding and branched fabrics with a width of 400 to 700 μm, interpreted to represent burrows piercing semi-consolidated sediment. The abandoned burrows were infilled with fine-grained sediment, which was subsequently cemented by microcrystalline dolomite and Mg calcite. The degree of cation ordering of dolomite in burrow infills and host sediment is similar, indicating coeval dolomite formation. The Mg/Ca mole ratios of carbonate minerals are lower in burrow infills than in the surrounding sedimentary matrix. Similarly, $\delta^{13}$C values tend to be higher for burrow infills (from −41 to −33‰) than for the matrix (from −43 to −38‰), suggesting stronger seawater influence on pore waters in the burrows. More reducing microenvironments of the sedimentary matrix supposedly came along with higher concentrations of dissolved sulphide, which allowed more Mg$^{2+}$ ions to enter the crystal lattice and led to more catalytic dolomite formation in the host sediment. The distribution of MgCO$_3$ contents and $\delta^{13}$C values in the authigenic Shenhu carbonates reinforces the hypothesis that sulphide release by sulphate-driven anaerobic oxidation of methane is a key factor in the formation of dolomite at seeps.
Keywords Bioturbation, burrows, dolomite formation, sedimentary fabrics, seep carbonates, South China Sea.

INTRODUCTION

Modern early diagenetic dolomite is forming in environments including but not limited to sab-khas, lagoons, mixing zones, reducing marine sediments and alkaline lakes (Kastner, 1984; Burns et al., 2000; Mazzullo, 2000; Roberts et al., 2010; Pettrash et al., 2017; Feng et al., 2018; McCormack et al., 2018). However, direct formation of stoichiometric and ordered dolomite using supersaturated solutions was never observed in laboratory experiments at surface conditions (Lippmann, 1973; Land, 1998; Burns et al., 2000; Machel, 2004; Gregg et al., 2015). The formation process is impeded by: (i) the higher dehydration energy required for Mg$^{2+}$ ions than for Ca$^{2+}$ ions, which prevents the incorporation of Mg into carbonates; and (ii) the intrinsic barrier obstructing direct ordering of Mg in the crystal lattice (Lippmann, 1973; Davis et al., 2000; de Leeuw & Parker, 2001; Higgins & He, 2005; Hu et al., 2005; Xu et al., 2013). The following factors, able to overcome the above barriers, have been put forward: (i) high Mg/Ca ratios and high concentrations of dissolved carbonate; (ii) high pH and high alkalinity (Lippmann, 1973; Hardie, 1987; Compton, 1988; Slaughter & Hill, 1991; Burns et al., 2000; Mazzullo, 2000; Warren, 2000; McKenzie & Vasconcelos, 2009; Sanchez-Roman et al., 2009); (iii) extracellular polymeric substances (EPS) acting as a template for Ca$^{2+}$ and Mg$^{2+}$ ions (Van Lith et al., 2003; Bontognali et al., 2008; Bontognali et al., 2010; Pettrash et al., 2017); (vi) oscillating pH or saturation conditions (Deelman, 2011); and (v) low and approaching equilibrium supersaturation conditions allowing for slow formation of ordered dolomite (Hu et al., 2005).

However, these factors are probably insufficient to drive the formation of abundant authigenic dolomite in the shallow subsurface at marine methane seeps. The pore waters of seepage-affected sediments are characterized by high alkalinity and high concentration of dissolved sulphide as a consequence of sulphate-driven anaerobic oxidation of methane (SD-AOM), a biogeochemical process performed by a consortium of methane-oxidizing archaea and sulphate-reducing bacteria (Boetius et al., 2000):

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$$

The resultant bicarbonate-rich pore waters together with Ca$^{2+}$ and Mg$^{2+}$ ions derived from seawater cause the precipitation of aragonite, low-Mg calcite (LMC), high-Mg calcite (HMC) and dolomite at seeps (Ferrell & Aharon, 1994; Roberts & Aharon, 1994; Roberts et al., 2010; Feng et al., 2018; Lu et al., 2018), while dissolved sulphide tends to combine with iron to form iron sulphide minerals that transfer into authigenic pyrite (Jørgensen et al., 2004; Lin et al., 2017, 2018). Formerly, close to complete sulphate consumption by SD-AOM was considered to be the main factor favouring dolomite formation at seeps (e.g. Magalhães et al., 2012), based on the concept that high sulphate concentrations impede dolomite formation (Burton, 1993). Some early studies, however, had already suggested that high concentration of sulphate, as found in seawater, does not necessarily inhibit dolomite formation (Hardie, 1987; Brady et al., 1996). More recent experiments and modelling indicated that dissolved sulphide and EPS promote the dehydration of Mg$^{2+}$ ions, favouring Mg incorporation into the carbonate lattice and resulting in the precipitation of very high-Mg calcite (VHMC), which can subsequently transform into dolomite by cation ordering (Gaines, 1974; Reeder, 1981; Zhang et al., 2012a,b; Shen et al., 2014, 2015; Zhang et al., 2015). Evidence of this formation pathway has also been reported for seep dolomite, comparing microstructures and lattice parameters, rare earth element (REE) patterns and carbon stable isotope compositions (Lu et al., 2018).

To support the catalytic effect of dissolved sulphide on dolomite formation at seeps, a positive correlation of MgCO$_3$ contents of carbonate minerals, the proportion of dolomite among carbonate minerals making up seep deposits and the former local sulphide concentration needs to be established. The mineralogical and geochemical characteristics of carbonate minerals can be analysed at high resolution, whereas the former concentration of the purported catalyst for high-Mg calcite and dolomite formation – dissolved hydrogen sulphide – cannot be determined from the mineral
product (i.e. seep carbonate). Nevertheless, the covariation between the content and isotopic composition of carbonate associated sulphate, the isotopic composition of chromium reducible sulphur and Ce anomalies on the one hand, and the MgCO$_3$ contents of carbonate minerals on the other hand, suggested that dolomite exclusively forms under strongly reducing conditions in closed microenvironments at seeps (Lu et al., 2018; Tong et al., 2019). Some sedimentary fabrics such as fractures, borings and burrows promote the establishment of more open conditions due to seawater ingress into sedimentary environments (Aller, 1982; Aller & Aller, 1992; Pedley, 1992; Wallmann et al., 1997; Zorn et al., 2006; Suess, 2010; Wetzel, 2013). In seep-affected sediments, infiltration of oxidizing seawater along such pathways will inhibit high-Mg calcite and dolomite formation by sulphide catalysis. Consequently, the degree of sediment reworking and associated seawater ingress should be reflected in the mineralogical composition of seep carbonates. To test the sulphide catalysis hypothesis, this study compares two sedimentary fabrics of seep carbonate from the South China Sea. Both fabrics were lithified during early diagenesis by cementation of sediment by methane-derived, microcrystalline high-Mg calcite and dolomite. The first fabric represents the largely undisturbed host sediment, the second fabric is interpreted to represent the infill of burrows produced by seep biota.

**GEOLOGICAL SETTING**

The South China Sea is the largest marginal basin of the western Pacific Ocean. Its northern margin is characterized by the Xisha trough extending for nearly 900 km to south-east Taiwan. Its average water depth is approximately 2000 m. Seamounts, sea knolls and Cenozoic sedimentary basins are widely developed on the seafloor (Huang et al., 2008). The northern margin of the South China Sea is characterized by the Xisha trough extending for nearly 900 km to south-east Taiwan. Its average water depth is approximately 2000 m. Seamounts, sea knolls and Cenozoic sedimentary basins are widely developed on the seafloor (Huang et al., 2008). The northern margin of the South China Sea has been subsided since the Oligocene, resulting in a sedimentation rate of more than 150 m Ma$^{-1}$. Large amounts of organic matter-rich sediments accumulated, causing widespread gas formation. Several gas reservoirs are known and have been explored (Huang et al., 2008). The Shenhua area is located in the centre of the northern margin (Fig. 1). It is known for its ubiquitous pockmarks, normal faults, mud diapirs and mud volcanoes, connecting deep sedimentary strata with the seafloor (Hou et al., 2008; Sun et al., 2012a,b; Li et al., 2013), and facilitating the establishment of methane seeps and the formation of gas hydrates; the latter were sampled for the first time in 2007 (Zhang et al., 2007; Liu et al., 2012). Extensive and long-lasting supply of methane in the Shenhua area favoured the formation of abundant and widespread seep carbonates (Ge et al., 2015; Lu et al., 2015), having formed between approximately 330 to 150 ka (Tong et al., 2013).

**SAMPLES AND METHODS**

Three pieces of seep carbonates were dredged from site HS4 of the Shenhua area in 2004 at a water depth of 350 m (Fig. 1). The samples – referred to as 4-1, 4-2 and 4-3 – are irregular in shape (Fig. 2A). Three to four thin sections were made from each sample to document sedimentary fabrics with an optical microscope. Sample 4-3 (Fig. 2A) was selected for a more detailed study (see below); one part of it, referred to as 4-3a (Fig. 2A), was cut off and five continuous slices were produced (Fig. 2B) to analyse the change of sedimentary fabrics on the scale of several millimetres. Selected thin sections were carbon coated and analysed in backscatter mode with a Zeiss field emission-scanning electron microscope (FE-SEM; Zeiss Microscopy, Jena, Germany) at 15 kV, School of Earth Science and Engineering, Sun Yat-sen University (SYSU). Mineralogical compositions of the sedimentary matrix and burrow infills were analysed with X-ray diffraction (XRD) and transmission electron microscopy (TEM). Selected areas of slices 3 and 5 (Fig. 2B) were cut into smaller, approximately 1 × 1 cm$^2$ slices and attached to the sample stage of a Rigaku Rapid II X-ray diffraction system (Mo Kα radiation; Rigaku, Tokyo, Japan) operated at 50 kV and 30 mA, School of Marine Sciences, SYSU. Points to be analysed were aligned to the X-ray beam (ca 100 µm in size), allowing the slices to be rotated for the widest possible angle range. Diffraction signals were collected by the image plate and converted into 20-intensity profiles with the 2DP software. Major mineral phases and their semi-quantitative contents were identified and calculated with the PDFX2 software (Rigaku). Selected boundaries between the two fabrics in slices 3 and 5 were mounted through the centre of copper grids and ion milled with a Gatan PIPS II (Gatan Inc., Pleasanton, CA, USA) at 8 kV, Instrumental Analysis & Research Center (IARC) of SYSU to obtain nanometre-thick foils.
for both fabrics. Then, sample grids were carbon coated and analysed with a Thermo Scientific Talos F200S transmission electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) at 200 kV, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

To compare MgCO$_3$ contents of carbonate minerals, more than 220 point analyses on the selected areas of slices 1 to 5 of sample 4-3a were made by electron probe microanalysis (EPMA) with a JEOL JXA-8800R (JEOL Limited, Tokyo, Japan) at 20 kV with a beam size of 1 μm, IARC of SYSU. Only results agreeing with pure carbonate composition were selected for this study. Grid points for which Mg/Ca mole ratios were calculated were converted into contour maps with the ioGAS software.

About 1 mg powder of burrow infill and nearby sedimentary matrix were micro-milled with a Reliontron MSS VI system (Reliontron Industries LLC, Bedford, MA, USA) and analysed with a Thermo Gasbench II connected to a Thermo Scientific 253 Plus at 9.5 kV and vacuum of $6 \times 10^{-7}$ mBar, School of Marine Sciences, SYSU for carbon and oxygen stable isotope compositions. The sample pre-treatment procedure followed the method in Lu et al. (2018). The isotopic values are denoted in the δ-notation (‰) relative to the Vienna PeeDee Belemnite (V-PDB) standard. The standard deviation was better than ±0.1‰.

**RESULTS**

**Characteristics of inferred burrow infills**

Although not readily apparent on the polished surface of hand samples (Fig. 2A), the fabric interpreted to represent burrow infill can be identified in thin sections under transmitted light (Fig. 2B). Burrow infills stand out from the sedimentary matrix, which is more transparent under transmitted light. They appear on all five continuous thin sections of sample 4-3a, suggesting that the burrows penetrated much of the...
sediment (Fig. 2B). Infilled burrows are round or elliptical, depending on cross-cutting relationships. Some of the burrows are in the shape of twisted or branched pipes or more irregular patches (Figs 2B and 3). Burrow infills either cluster in some areas of the rock (Fig. 2B) or are distributed over the whole thin section (Fig. 3). In one thin section of sample 4-3, the axes of pipes and more irregular patches reveal a preferred orientation (Fig. 3B). Overall, 255 patches with the burrow infill fabric have been identified in the thin sections of samples 4-1 to 4-3.

The widths of burrows range from 400 to 700 μm (Fig. 4). Microscope and SEM observations revealed that the boundary between sedimentary matrix and burrow infill is smooth (Figs 3 and 5). Burrow infills are composed of microcrystalline carbonate crystals with some fine grains of quartz, feldspar and minor skeletal carbonate, whereas the surrounding sedimentary matrix is represented by coarser grains of quartz, feldspar and abundant skeletal carbonate cemented by microcrystalline carbonate crystals (Figs 2, 3 and 5). Given that the patches of fine-

Fig. 2. Seep carbonates from site HS4 (A), including samples 4-1 (1), 4-2 (2), 4-3 (3) and 4-3a (4), the latter cut off from 4-3. Sample 4-3a was selected for the production of five continuous thin sections (B), corresponding to thin sections ‘1’ to ‘5’. Textures interpreted to represent burrows are highlighted by white dashed lines.
grained microfabric are distributed in a matrix of coarser-grained sediment, the formation of the fine-grained microfabric post-dates the deposition of the latter. No particles from the sedimentary matrix are truncated at the transition to the fine-grained microfabric. Together with the irregular shape of the fine-grained microfabric, this observation renders an interpretation as borings unlikely, supporting the interpretation that the fine-grained microfabric represents infilled burrows.

**Mineralogical composition**

*In situ* XRD results reveal that the main mineral phases in both fabrics – sedimentary matrix and burrow infills – are calcite, Mg calcite, dolomite, quartz, feldspar and illite (Fig. 6). Dolomite is
the major carbonate phase accompanied by some calcite and Mg calcite (Table 1). The $d_{104}$ values of Mg calcite and dolomite vary between $3.030\,\text{Å}$ and $2.930\,\text{Å}$ and from $2.922\,\text{Å}$ to $2.911\,\text{Å}$, respectively (Table 1). TEM observations revealed that the carbonate crystals are anhedral to sub-euhedral with a size of approximately 1 $\mu$m. Illite occurs as fine grains in both fabrics (Fig. 7). Near stoichiometric ordered dolomite with similar MgCO$_3$ and CaCO$_3$ contents and intense ordering reflections including (00.3) as well as weakly ordered dolomite with slightly lower MgCO$_3$ contents and only weak ordering reflections have been detected in both fabrics (Fig. 7). Near stoichiometric ordered dolomite contains approximately 50 mol% MgCO$_3$ with most Ca$^{2+}$ and Mg$^{2+}$ cations located in the respective Ca and Mg layers normal to the c-axis, whereas in weakly ordered dolomite, Ca and Mg layers reveal a greater degree of cation disorder. Although similar mineral inventories typify both fabrics, some differences in relative contents are apparent. Ratios between carbonate and silicate contents are higher in burrow infills than in the sedimentary matrix (Table 1), agreeing with microscopical observations. Ratios of Mg calcite to dolomite contents are lower in the sedimentary matrix than in the burrow infills (Fig. 8).

**Carbonate Mg/Ca ratios**

For slices 1 to 4 of sample 4-3a, the carbonate Mg/Ca mole ratios tend to be higher in the sedimentary matrix than in the burrow infills, varying from 0.5 to 0.8 and 0.3 to 0.6, respectively (Fig. 9A to D). However, for slice 5, ratios are similar for the two fabrics and the mean and median values are slightly higher for the burrow infills (Fig. 9E). Nevertheless, taken together, the data show a clear trend with lower Mg/Ca ratios in the burrow infills (Fig. 9F). Contour maps show a similar trend, with lower Mg/Ca mole ratios for burrow infills than for the sedimentary matrix (Fig. 10).

**Carbon and oxygen isotope compositions**

The $\delta^{13}C$ values of the two sedimentary fabrics are exclusively negative, ranging from $-45.3$ to $-31.2\%$, while the $\delta^{18}O$ values vary between $-1.1\%$ and $2.4\%$ (Table 2). A negative correlation between $\delta^{13}C$ and $\delta^{18}O$ values is apparent (Fig. 11A). Overall, the $\delta^{13}C$ values of the sedimentary matrix are lower than those of burrow infills, falling between $-45.3\%$ and $-34.9\%$ and $-43.4\%$ and $-31.2\%$, respectively (Fig. 11A). At small scale, the $\delta^{13}C$ values of burrow infill carbonate are also higher than those of the carbonate of the directly adjacent sedimentary matrix (Fig. 11B to D).

**INTERPRETATION AND DISCUSSION**

**Sedimentary fabrics and sequence of early diagenetic events**

The exclusively negative $\delta^{13}C$ values lower than $-31.2\%$ confirm that the authigenic dolomite and Mg calcite cementing both burrow infills and sedimentary matrix are methane-derived carbonates. Methane-derived carbonates forming at marine seeps are characterized by a range of sedimentary fabrics, which are mostly of low to moderate specificity for the local chemo synthesis-based environment. Micritic microclots (Peckmann et al., 2002), nodules (Peckmann et al., 1999; Adachi et al., 2004) and in situ brecciation (Hikida et al., 2003; Peckmann et al., 2003) are common fabrics of seep limestones. Metazoans contribute to the formation of sedimentary microfabrics and mesofabrics by the production trace fossils like faecal pellets (Senowbari-Daryan et al., 2007) and by taphonomic mineralization processes associated with body fossils, including worm tubes (Goedert et al., 2000; Haas et al., 2009). Because of the local chemo synthesis-based food web, methane seeps are oases of life in the deep-sea.
supporting high abundance and low diversity communities of metazoan benthos (e.g. Suess, 2010; Joye, 2020). Some of the endemic benthos like bivalves and crustaceans cause extensive bioturbation of the sediment at seeps (Peckmann et al., 2007; Kiel, 2010; Wetzel, 2013; Wiese et al., 2015; Zwicker et al., 2015; Kiel et al., 2016). Potential trace makers include infaunal, chemosymbiotic bivalves (Seike et al., 2012; Blouet et al., 2021) and decapod crustaceans; the latter are common in different chemosynthesis-based environments including methane seeps (Chevaldonné & Olu, 1996; Martin & Haney, 2005).

The irregular, fine-grained microfabric piercing the sedimentary matrix of the Shenhu seep carbonates is best explained to represent infilled burrows. The roundish contacts between the fine-grained microfabric and the host sediment and the lack of truncation excludes in situ brecciation. Likewise, the fine-grained microfabric does not result from boring into lithified seep carbonate (cf. Byers & Stasko, 1978), since no particles of the sedimentary matrix are truncated. Similarly, excavations resulting from bioerosion tend to be more regular in shape than the fine-grained microfabric of the Shenhu carbonates (cf. Golubic et al., 1975; Wisshak et al., 2005). The fine-grained microfabric of the Shenhu carbonates, interpreted to reflect infilled burrows, resembles dolomite-filled burrows from a Devonian succession of bedded limestone.

Fig. 5. Scanning electron microscope images of burrow infills (BI) and the surrounding primary sedimentary matrix in thin sections 1 (A) and (B), and 2 (C) and (D). Burrows are delineated by yellow dashed lines. Close-up images of the sharp transition (yellow dashed lines) between the two types of fabrics in thin sections 4 (E) and 2 (F). Note that no particles are truncated and that the infill is finer grained than the host sedimentary matrix.

© 2021 The Authors. Sedimentology published by John Wiley & Sons Ltd on behalf of International Association of Sedimentologists. Sedimentology, 68, 2945–2964
According to morphology and size, the undiagnosed, locally branching backfilled burrows resemble *Chondrites* (cf. Bromley & Ekdale, 1984). Based on thin section observations alone, the ichnotaxon cannot be identified, although an assignment to *Chondrites* would be consistent with bathymetry. *Chondrites* are typified by a branched burrow system, penetrating anoxic sediments that are rich in hydrocarbons or hydrogen sulphide (Savrda & Bottjer, 1989; Uchman & Wetzel, 2012). This ichnofossil is found in multiple environments including marine shelves, yet the trace maker is of unknown taxonomic affinity (Bromley & Ekdale, 1984; Buatois & Gabriela Mángano, 2011). The typical width of burrows ranges from 0.1 to 10 mm (Bromley & Ekdale, 1984). Burrows are kept open by their inhabitants, possibly obtaining energy from chemosymbiosis (Buatois & Gabriela Mángano, 2011; Uchman & Wetzel, 2012). Branching in *Chondrites* cannot be satisfactorily explained by deposit feeding, possibly representing sulphide mining by a chemosymbiotic worm-like animal (Seilacher, 1990; Fu, 1991). After the unknown endobenthic animal abandoned its edifice, burrows are passively filled with sediment (Bromley & Ekdale, 1984).

---

**Fig. 6.** *In situ* X-ray diffraction profiles of the sedimentary matrix and burrow infills from thin sections (ThS) 3 and 5 and peaks of identified minerals. The (10.1) peak of quartz and the (10.4) peaks of carbonate minerals are magnified and compared with the (10.4) peaks of ideal calcite and dolomite on the right panel. The areas for low-Mg calcite (LMC), high-Mg calcite (HMC) and dolomite are highlighted in grey according to Lu et al. (2015). 1 = LMC, 2 = HMC, 3 = dolomite (upper right).
Table 1. Relative semiquantitative contents (wt% = weight%) of major phases calculated from X-ray diffraction profiles, $d_{104}$ values of detected Ca-Mg carbonates, and content ratios of carbonates versus silicates particles and Mg-calcite versus dolomite of burrow infills and sedimentary matrix.

| Location        | Sample | Quartz (wt%) | Feldspar | Illite | Calcite | LMC | HMC | Dol | $d_{104}$ Cal (Å) | $d_{104}$ LMC (Å) | $d_{104}$ HMC (Å) | $d_{104}$ Dol (Å) | Carb/silic | Mg Cal/Dol |
|-----------------|--------|--------------|----------|--------|---------|-----|-----|-----|------------------|------------------|------------------|------------------|-------------|------------|
| Burrow infills  | 3-A-1  | 18.0         | 1.9      | 8.0    | n.d.    | 14.0| 15.0| 43.0| n.d.             | 3.021            | 2.949            | 2.913            | 3.62        | 0.67       |
|                 | 3-A-2  | 12.0         | 11.0     | 8.0    | 14.0    | n.d. | 11.0| 45.0| 3.035            | n.d.             | 2.970            | 2.922            | 3.04        | 0.24       |
|                 | 3-A-3  | 25.0         | 5.8      | 6.2    | n.d.    | 12.0| 20.0| 31.0| n.d.             | 3.019            | 2.945            | 2.913            | 2.05        | 1.03       |
|                 | 3-A-4  | 16.0         | 2.4      | 4.8    | n.d.    | 13.0| 21.0| 42.0| n.d.             | 3.030            | 2.966            | 2.915            | 4.13        | 0.81       |
|                 | 5-A-1  | 5.7          | 3.5      | 9.7    | n.d.    | 17.0| 21.0| 44.0| n.d.             | 3.029            | 2.933            | 2.913            | 8.91        | 0.86       |
|                 | 5-A-1-2| 14.1         | 1.8      | 5.6    | n.d.    | 8.6  | 28.0| 42.0| n.d.             | 3.026            | 2.933            | 2.916            | 4.94        | 0.87       |
|                 | 5-A-1-3| 10.0         | 0.1      | 8.1    | n.d.    | 12.6| 27.0| 42.0| n.d.             | 3.021            | 2.93              | 2.913            | 8.08        | 0.94       |
|                 | 5-A-2  | 14.5         | 0.1      | 7.9    | 14.0    | n.d. | 10.5| 53.0| 3.034            | n.d.             | 2.932            | 2.913            | 5.31        | 0.20       |
|                 | 5-A-2-2| 8.6          | 0.4      | 6.8    | n.d.    | 9.7  | 29.0| 46.0| n.d.             | 3.024            | 2.937            | 2.913            | 9.41        | 0.84       |
| Sedimentary matrix | 3-B-1  | 8.3          | 4.0      | 5.5    | n.d.    | 10.0| 16.0| 56.0| n.d.             | 3.012            | 2.955            | 2.915            | 6.67        | 0.46       |
|                 | 3-B-2  | 21.2         | 20.0     | 4.6    | n.d.    | 10.4| 18.0| 26.0| n.d.             | 3.021            | 2.945            | 2.911            | 1.32        | 1.09       |
|                 | 3-B-3  | 26.0         | 2.9      | 2.6    | 18.0    | n.d. | 12.0| 39.0| 3.035            | n.d.             | 2.981            | 2.917            | 2.39        | 0.31       |
|                 | 3-B-4  | 16.0         | 10.4     | 1.1    | 8.8     | n.d. | 16.0| 48.0| 3.035            | n.d.             | 2.959            | 2.914            | 2.76        | 0.33       |
|                 | 5-A-3  | 22.0         | 13.0     | 6.0    | n.d.    | 4.4  | 17.0| 37.0| n.d.             | 3.028            | 2.937            | 2.920            | 1.67        | 0.58       |
|                 | 5-A-4  | 22.9         | 1.8      | 20.8   | 8.6     | n.d. | 13.0| 33.0| 3.035            | n.d.             | 2.941            | 2.921            | 2.21        | 0.39       |
|                 | 5-A-5  | 17.9         | 5.3      | 7.3    | n.d.    | 6.0  | 7.5 | 56.0| n.d.             | 3.025            | 2.934            | 2.912            | 3.00        | 0.24       |

LMC, low-Mg calcite; HMC, high-Mg calcite; Dol, dolomite; Cal, calcite; Carb, Cal + LMC + HMC + Dol; Silic, quartz + feldspar; Mg-calcite, LMC + HMC; n.d., not detected.
Since at least some of the burrows stayed open for long enough to be filled later on by fine-grained sediment, the host sediment probably was semi-lithified by the precipitation of methane-derived microcrystalline carbonate when burrowing commenced. After the open burrows were finally infilled by fine-grained sediment, the latter was subsequently also cemented by methane-derived microcrystalline carbonate. This sequence of events reveals that seepage activity must have lasted long enough for the detrital burrow infill still to be cemented by authigenic carbonate. Irrespective of our interpretation of the nature of the fine-grained microfabric dispersed within the sedimentary matrix of the Shenhu carbonates, the paragenetic sequence reveals that the development of the former was post-dating the latter. Yet, mineralogical arguments discussed below will lead to the conclusion that not much time had passed between: (i) partial lithification of the host sediment; (ii) burrowing activity; (iii) infilling of formerly open burrows; and (iv) cementation of the burrow infill.

**Carbonate mineralogy and microenvironment**

The XRD results revealed that the Shenhu seep carbonates are a mixture of Mg calcite and dolomite. Their $d_{104}$ values vary from 3.030 to 2.930 Å and 2.922 to 2.911 Å, respectively (Table 1), deviating from those of standard carbonates.

---

**Fig. 7.** Transmission electron microscope (TEM) images of dolomites in sedimentary matrix (A) and (B), and burrow infills (C) and (D) of thin sections 3 (A) and (C) and 5 (B) and (D). The insets are energy-dispersive X-ray spectroscopy profiles and electron diffraction patterns at [010] zone axis. Minor illite is indicated by the yellow arrow in (B).

© 2021 The Authors. *Sedimentology* published by John Wiley & Sons Ltd on behalf of International Association of Sedimentologists. *Sedimentology*, 68, 2945–2964
calcite and dolomite (3.035 Å and 2.885 Å; Graf, 1961; Markgraf & Reeder, 1985). Because the $d_{104}$ value has an empirical negative relationship with the MgCO$_3$ mole percentage (Goldsmith et al., 1961; Reeder & Sheppard, 1984; Zhang et al., 2010), such varying $d_{104}$ values indicate changing mole percent of MgCO$_3$ in Mg calcite and dolomite. On the other hand, both calcite and dolomite, despite differences in space group symmetry, display similar superstructures (Gregg et al., 2015). The structures are composed of alternating layers of carbonate ions and cations normal to the c-axis. The cation layers in calcite are all occupied by Ca$^{2+}$, while those in dolomite are represented by alternating Ca$^{2+}$ and Mg$^{2+}$ layers (Graf, 1961; Markgraf & Reeder, 1985). Consequently, the mixture of Mg calcites and dolomites in the Shenhu seep carbonates can be considered as carbonate minerals with various MgCO$_3$ contents and similar structures. When such mineral contains high enough MgCO$_3$ and develops an ordered structure, it is dolomite. The content ratios of Mg calcite/dolomite are higher in burrow infills than in surrounding matrix (Fig. 8) and EPMA results

![Box charts of relative content ratios of Mg calcite versus dolomite of microcrystalline carbonates of the sedimentary matrix and burrow infills. Data ranges, median values, mean values and outlier data are illustrated in the same way as in Fig. 4.](image)

**Fig. 8.** Box charts of relative content ratios of Mg calcite versus dolomite of microcrystalline carbonates of the sedimentary matrix and burrow infills. Data ranges, median values, mean values and outlier data are illustrated in the same way as in Fig. 4.

![Box charts of Mg/Ca mole ratios of microcrystalline carbonates of the sedimentary matrix and burrow infills in thin sections 1 to 5 (A) to (E) and the integration of all the data from the five slices (F). Data ranges, median values, mean values and outlier data are illustrated in the same way as in Fig. 4.](image)

**Fig. 9.** Box charts of Mg/Ca mole ratios of microcrystalline carbonates of the sedimentary matrix and burrow infills in thin sections 1 to 5 (A) to (E) and the integration of all the data from the five slices (F). Data ranges, median values, mean values and outlier data are illustrated in the same way as in Fig. 4.
confirmed that the seep carbonate minerals in burrow infills contain less MgCO$_3$ than those in the surrounding host sediment (Figs 9 and 10).

The formation of authigenic carbonates in burrows and in the host sediment at the Shenhu seep was probably influenced by variable redox conditions in different microenvironments. The open burrows will have necessarily been flushed by oxygenated seawater (Aller, 1982; Aller & Aller, 1992; Wetzel, 2013; Zorn et al., 2006); residual molecular oxygen or other electron acceptors deriving from this ingress of seawater probably contributed to the decrease of SD-AOM-derived hydrogen sulphide when the burrows were successively filled by sediment, which was progressively cemented by methane-derived carbonate. The matrix of the host sediment on the other hand, representing a sediment buffered system, was necessarily dominated by reducing pore water affected by methane seepage. The carbon stable isotope compositions of carbonate minerals of the burrow infills and the sedimentary matrix can be used to assess this hypothesis. The carbon sources of seep carbonates include methane ($\delta^{13}$C < $-40\%$), oil ($\delta^{13}$C between ca $-20\%$ and $-30\%$), sedimentary organic matter ($\delta^{13}$C ca $-25\%$) and seawater dissolved inorganic carbon (DIC; $\delta^{13}$C ca 0$\%$; Campbell, 2006). No oil has been observed in the Shenhu study area. Since $\delta^{13}$C values of the Shenhu carbonates are lower than $-31.2\%$, methane must have been a major carbon source in addition to residual pore water DIC. The $\delta^{13}$C values of burrow infills are higher than those of

Table 2. Carbon and oxygen stable isotope compositions of burrow infills and sedimentary matrix.

| Location      | Sample | $\delta^{13}$C$_{\text{v.pdb}}$ (%) | $\delta^{18}$O$_{\text{v.pdb}}$ (%) |
|---------------|--------|-------------------------------|---------------------------------|
| Burrow infills| 3-1    | $-31.2$                        | 0.6                             |
|               | 3-2    | $-33.7$                        | $-0.4$                         |
|               | 3-3    | $-38.5$                        | 1.2                             |
|               | 3-4    | $-36.1$                        | 0.0                             |
|               | 3-5    | $-42.2$                        | 1.9                             |
|               | 5-1    | $-33.1$                        | $-0.3$                         |
|               | 5-2    | $-40.6$                        | 0.8                             |
|               | 5-3    | $-41.8$                        | 2.0                             |
|               | 5-4    | $-43.4$                        | 2.4                             |
|               | 5-5    | $-32.8$                        | $-1.1$                         |
| Sedimentary   | 3-6    | $-37.6$                        | 2.2                             |
| matrix        | 3-7    | $-37.2$                        | $-0.2$                         |
|               | 3-8    | $-43.5$                        | 2.1                             |
|               | 3-9    | $-45.3$                        | 2.4                             |
|               | 5-6    | $-42.6$                        | 2.4                             |
|               | 5-7    | $-43.9$                        | 2.4                             |
|               | 5-8    | $-35.7$                        | 1.1                             |
|               | 5-9    | $-34.9$                        | 0.9                             |

© 2021 The Authors. Sedimentology published by John Wiley & Sons Ltd on behalf of International Association of Sedimentologists, Sedimentology, 68, 2945–2964

Fig. 10. Scanning electron microscope images of selected burrow infills (BI) in thin section 1 (A) and (C) and corresponding Mg/Ca contour maps (B) and (D).
the carbonate cementing the host sediment, indicating more influence of seawater on the precipitation of the carbonate cementing burrow infills. Because the burrow infills contain much less skeletal carbonate than the surrounding host sediment (see Fig. 3), the obtained δ^{13}C values will underestimate the real difference in the carbon isotopic compositions; skeletal carbonate has an isotopic composition close to that of seawater DIC (Swart, 2015). Moreover, the δ^{13}C values of dolomite are theoretically 1‰ higher than those of LMC precipitating from the same fluid (Swart, 2015). Yet, the δ^{13}C values of the matrix with more dolomite and more skeletal carbonate are instead lower than those of the burrow infills. Consequently, the higher δ^{13}C values of the authigenic carbonate cementing the burrow infills are best explained by a higher contribution of seawater DIC in a more open environment.

If the formation of carbonate minerals in the two sedimentary fabrics would have been separated by a long period of time, a comparison of the microenvironment of carbonate formation would be problematic. The observation made with TEM, however, eliminates this concern. Dolomite with high and low degrees of cation ordering has been identified in both sedimentary fabrics (Fig. 7). Ordering of seep dolomites needs time at surface conditions. Older seep dolomite (ca 330 ka to ca 150 ka; Tong et al., 2013) has been found to be more ordered than younger seep dolomite (ca 30 ka; Han et al., 2014; Lu et al., 2018). In the Shenhu samples, the overall degrees of cation order of dolomite are similar, implying a short time gap between carbonate precipitation, and subsequent alteration in both host sediment and burrow infills.

**Implications for dolomite formation at seeps**

Although both the product of early diagenesis during a period of active seepage, the authigenic carbonate minerals cementing the

---

**Fig. 11.** (A) Plots of δ^{18}O versus δ^{13}C (in per mill versus V-PDB) of sedimentary matrix and burrow infills (BI) and *in situ* δ^{13}C values in slices 3 (B) and (C) and 5 (D).
sedimentary matrix and burrow infills show different contents of MgCO₃ and reflect different proportions of dolomite. This pattern is best explained by the existence of different microenvironments. Within burrows, organic matter remains will favour heterotrophic bacteria including sulphate-reducing bacteria (Byers & Stasko, 1978; Gunatilaka et al., 1987; Gingras et al., 2004; Rameil, 2008), possibly inducing local formation of dolomite. Interestingly, Corlett & Jones (2012) described dolomite-filled burrows from a Devonian succession of bedded limestone, interpreted as deep ramp deposits. In contrast to burrows filled by calcite found closer to the palaeo-shoreline, the dolomite-filled burrows were suggested to reflect more reducing conditions in an environment shaped by organoclastic sulphate reduction at greater water depth (Corlett & Jones, 2012). These observations agree with a key role of the redox potential of sedimentary environments in early diagenetic dolomite formation.

The composition of pore waters at seeps is influenced to different degrees by oxidizing seawater and reducing pore water affected by seepage. Burrows are more open to seawater than the sedimentary matrix (Pedley, 1992; Zorn et al., 2006). The inflow of seawater into burrows will also introduce dissolved sulphate, which was once considered as an inhibitor of dolomite formation (Baker & Kastner, 1981). However, neither field observation nor laboratory experiments support the inhibition effect (Hardie, 1987; Brady et al., 1996; Zhang et al., 2012a). One of the kinetic barriers in dolomite formation is the difference in hydration energy between Ca²⁺ and Mg²⁺ ions (de Leeuw & Parker, 2001; Higgins & He, 2005; Hu et al., 2005). In situ monitoring on the surface of growing calcite or dolomite crystals revealed that only few Mg²⁺ ions are incorporated into newly formed layers, not resulting in stoichiometric dolomite but increasing solubility and impeding further formation of dolomite (Davis et al., 2000; Leeuw & Parker, 2001; de Leeuw, 2002; Higgins & He, 2005; Fenter et al., 2007; Berninger et al., 2017).

Such a kinetic barrier can be overcome by catalysis. Experiments and modelling results have demonstrated that dissolved sulphide and microbial EPS enhance dehydration of Mg²⁺...
ions, promoting the formation of VHMC (Zhang et al., 2012a,b; Shen et al., 2014, 2015; Zhang et al., 2015), and VHMC may subsequently transform into dolomite by cation ordering facilitated by successive stages of recrystallization (Nordeng & Sibley, 1994; Kaczmarek & Sibley, 2014; Gregg et al., 2015). Experiments revealed that the MgCO₃ content of VHMC is positively correlated with the concentration of the catalyst (Zhang et al., 2012a,b). This scenario also agrees with the negative correlation between δ¹³C and δ¹⁸O values of Shenhu seep carbonates (Fig. 11A). Microenvironments shaped by SD-AOM are typified by high concentrations of ¹³C-depleted carbonate species and dissolved sulphide. Upon carbonate precipitation in a fluid with the same δ¹⁸O value and temperature, higher MgCO₃ contents of Mg calcite will correspond with higher δ¹⁸O values (Friedman & O’Neil, 1977). Thus, with increasing influence of SD-AOM on calcite precipitation: (i) higher MgCO₃ contents; (ii) lower δ¹³C values; and (iii) higher δ¹⁸O will result. Consequently, when the first stage microcrystalline carbonate minerals precipitated in the pore space of the sedimentary matrix of the Shenhu seep carbonates, high concentrations of dissolved sulphide occurred in the sediment buffered, largely closed environment, catalysing the formation of Mg calcite with high MgCO₃ contents (Fig. 12A). Later on, a second stage of carbonate minerals precipitated in burrow infills that were still affected by the previous ingress of oxygenated seawater, resulting in less reducing conditions than in the surrounding host sediment. The MgCO₃ contents of the authigenic carbonates forming in the burrow infills were consequently lower than in the sedimentary matrix due to a lesser effect of sulphide catalysis in a more oxidizing environment (Fig. 12B). After precipitation, the mineralogy of the authigenic carbonates evolved by cation ordering, resulting in Mg calcite and dolomite with different degrees of ordering.

CONCLUSIONS

In methane-seep environments with their steep geochemical gradients, sedimentary fabrics influence the mineralogy of newly forming authigenic minerals by sustaining different redox conditions. Seep carbonates from the Shenhu area, South China Sea, contain abundant patches of fine-grained sediment dispersed in the coarser sedimentary matrix. These patches of fine-grained sediment are interpreted as formerly open burrows, which were later filled by fine-grained detritus. Microcrystalline methane-derived carbonate – high-Mg calcite and dolomite – cemented both the sedimentary matrix and the burrow infills, with cementation of burrow infills post-dating cementation of the host sediment. Yet, similar degrees of cation ordering of dolomite in both matrix and burrows indicate that only little time elapsed between carbonate authigenesis in the two sedimentary fabrics. Higher δ¹³C values of burrow infills agree with a stronger influence of oxidizing, dissolved inorganic carbon-rich seawater within the burrows than in the host sediment. Correspondingly, MgCO₃ contents of high-Mg calcite and dolomite and the proportions of dolomite are lower in burrow infills. This covariation indicates that the catalytic effect of sulphide released from sulphate-driven anaerobic oxidation of methane was weaker in the infilled burrows after preceding seawater ingress, resulting in the precipitation of very high-Mg calcite (VHMC) with lower MgCO₃ content than in the host sediment. Finally, cation ordering transformed VHMC in both fabrics into Mg calcite and dolomite. This study documents that sedimentary fabrics may provide the means to disentangle the effect of different redox conditions on mineral authigenesis in ancient sedimentary environments, and reinforces the hypothesis that sulphide catalysis is the key driver of dolomite formation at methane seeps.

ACKNOWLEDGEMENTS

This work benefited from the financial support of the Natural Science Foundation of China (Nos 41606063, 41806049, 41876038, 91128101), the open fund of Key Laboratory of Marine Mineral Resources, Ministry of Land and Resources (No. KLMMR-2015-B-02), the National Key Research and Development Program of China (2018YFC0310004) and the Guangdong Special Fund for Economic Development (Marine Economy, GDME-2018D001). Yang Lu gratefully acknowledges the support of K. C. Wong Education Foundation, DAAD, and Guangzhou Elite Project (No. JY201223). We thank Martin Zuschin for comments on bioturbation. Insightful comments by Editor Alexander Brasier, Associate Editor Hairoo Qing, Murray Gingras, Jay M. Gregg and Adrian Immenhauser helped to improve the manuscript and are greatly appreciated. Open Access funding enabled and organized by Projekt DEAL.
DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article and are also available from the corresponding author upon reasonable request.

REFERENCES

Adachi, N., Ezaki, Y. and Liu, J. (2004) The fabrics and origins of peloids immediately after the end-Permian extinction, Guizhou Province, South China. Sed. Geol., 164, 161–178.

Aller, R.C. (1982) The effects of macrobenthos on chemical properties of marine sediment and overlying water. In: Animal-Sediment Relations. Topics in Geobiology (Eds McCall, P.L. and Tevesz, M.J.S.), pp. 100. Springer, Boston, MA.

Aller, R.C. and Aller, J.Y. (1992) meiofauna and solute transport in marine muds. Limnol. Oceanogr., 37, 1018–1033.

Baker, P.A. and Blouet, J.P. (1993) Controls on marine carbonate cement and International Association of Sedimentologists, Boetius, A.

Chevaldonné, P. and Ou, K. (1996) Occurrence of anomuran crabs (Crustacea: Decapoda) in hydrothermal vent and cold-seep communities: a review. Proc. Biol. Soc. Wash., 109, 286–298.

Compton, J.S. (1988) Degree of supersaturation and precipitation of organogenic dolomite. Geology, 16, 318–321.

Corlett, H.J. and Jones, B. (2012) Petrographic and geochemical contrasts between calcite- and dolomite-filled burrows in the Middle Devonian Lonely Bay Formation, Northwest Territories, Canada: Implications for dolomite formation in Paleozoic burrows. J. Sed. Res., 82, 648–663.

Davis, K.J., Dove, P.M. and De Yoreo, J.J. (2000) The role of Mg$^+$ as an impurity in calcite growth. Science, 290, 1134–1137.

Deelman, J.C. (2011) Low-temperature formation of dolomite and magnesite. Version 2.3. 515 pp. http://www.jcdeelman.org/dolomite/bookprospectus.html

Feng, D., Qiu, J., Hu, Y., Peckmann, J., Guan, H., Tong, H., Chen, C., Chen, J., Gong, S., Li, N. and Chen, D. (2018) Cold seep systems in the South China Sea: An overview. J. Asian Earth Sci., 168, 3–16.

Fenter, P., Zhang, Z., Park, C., Sturchio, N.C., Hu, X. and Higgins, S.R. (2007) Structure and reactivity of the dolomite (104)-water interface: New insights into the dolomite problem. Geochim. Cosmochim. Ac., 71, 566–579.

Ferrell, R.E. and Aharon, P. (1994) Mineral assemblages occurring around hydrocarbon vents in the northern Gulf of Mexico. Geo-Mar. Lett., 14, 74–80.

Friedman, I. and O’Neil, J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In: Data of Geochemistry (Ed. Fleischer, M.), 6th edn, pp. 440–KK. U.S. Government Printing Office, Washington, D.C.

Fu, S. (1991) Funktion, Verhalten und Einteilung fucider und lophocheniider Lebensspuren. Courier Forschungs-Institut Senckenberg, 135, 1–79.

Gaines, A.M. (1974) Protodolomite synthesis at 100°C and atmospheric pressure. Science, 183, 518–520.

Ge, L., Jiang, S., Blumenberg, M. and Reitner, J. (2015) Lipid biomarkers and their specific carbon isotopic compositions of cold seep carbonates from the South China Sea. Mar. Petrol. Geol., 66, 501–510.

Gingras, M.K., Pemberton, S.G., Muelenbachs, K. and Machel, H. (2004) Conceptual models for burrow-related, selective dolomitization with textural and isotopic evidence from the Tyndall Stone, Canada. Geobiology, 2, 21–30.

Goedert, J.L., Peckmann, J. and Reitner, J. (2000) Worm tubes in an allochthonous cold-seep carbonate from lower Oligocene rocks of western Washington. J. Paleontol., 74, 992–999.

Goldsmith, J.R., Graf, D.L. and Heard, H.C. (1961) Lattice constants of the calcium-magnesium carbonates. Am. Mineral., 46, 453–457.

Golubic, S., Perkins, R.D. and Lukas, K.J. (1975) Boring microorganisms and microborings in carbonate substrates. In: The Study of Trace Fossils (Ed. Frey, R.W.), pp. 229–259. Springer, Berlin.
Hikida, H. and Higgins, S.R. (1987) Dolomitization: A critical view of some
Han, X. Jørgensen, B.B. Huang, Y. Hu, X. Kiel, S. (2010) The fossil record of vent and seep mollusks.
Hao, X. Suess, E. Liebetrau, V. Eisenhauer, A. and Huang, Y. (2014) Past methane release events and environmental conditions at the upper continental slope of the South China Sea: Constraints by seep carbonates. Int. J. Earth Sci., 103, 1873–1887.
Hardie, L.A. (1987) Dolomitization: A critical view of some current views. J. Sed. Petrol., 57, 166–183.
Higgins, S.R. and He, X.M. (2005) Self-limiting growth on dolomite: Experimental observations with in situ atomic force microscopy. Geochim. Cosmochim. Ac., 69, 2005–2009.
Hikida, H. Suzuki, S. Togo, Y. and Ijiri, A. (2003) An exceptionally well-preserved fossil seep community from the Cretaceous Yezo Group in the Nakagawa area, Hokkaido, norther Japan. Palaeontol. Res., 7, 329–342.
Hou, D. Pang, X., Xiao, J., Zhang, J., Shi, H., Wang, J., Shu, Y. and Zu, J. (2008) Geological and geochemical evidence on the identification of natural gas migration through fault system, Baiyun Sag, Pearl River Mouth basin, China. Earth Sci. Front., 15, 81–87.
Hu, X. Grossie, D.A. and Higgins, S.R. (2005) Growth and dissolution kinetics at the dolomite-water interface: An in-situ scanning probe microscopy study. Am. Mineral., 90, 963–968.
Huang, Y. Suess, E. and Wu, N. (2008) Methane and Gas Hydrate Geology in the Northern Slope of the South China Sea. Special Report for Sino-German Cooperative SO-177 Cruise. Geological Publishing House, Beijing, 197 pp. (in Chinese).
Jørgensen, B.B., Böttcher, M.E., Löschen, H., Neretin, L.N. and Volkov, I.I. (2004) Anaerobic methane oxidation and a deep H₂S sink generate isotopically heavy sulfides in Black Sea sediments. Geochim. Cosmochim. Ac., 68, 2095–2118.
Joye, S.B. (2020) The geology and biogeochemistry of hydrocarbon seeps. Annu. Rev. Earth Pl. Sc., 48, 205–231.
Kaczmarek, S.E. and Sibley, D.F. (2014) Direct physical evidence of dolomite recrystallization. Sedimentology, 61, 1862–1882.
Kastner, M. (1984) Control of dolomite formation. Nature, 311, 410–411.
Kiel, S. (2010) The fossil record of vent and seep mollusks. In: The Vent and Seep Biota (Ed. Kiel, S.), pp. 255–278. Springer, Heidelberg.
Kiel, S., Amano, K. and Jenkins, R.G. (2016) Predation scar frequencies in chemosymbiotic bivalves at an Oligocene seep deposit and their potential relation to inferred sulfide tolerances. Palaeoecogr. Palaeoecol., 453, 139–145.
Kuechler, R.R., Birgel, D., Kiel, S., Freiwald, A., Goedert, J.L., Thiel, V. and Peckmann, J. (2012) Miocene methanederived carbonates from southwestern Washington, USA and a model for silification at seeps. Lethaia, 45, 259–273.
Land, I.S. (1998) Failure to precipitate dolomite at 25 °C from dilute solution despite 1000-fold oversaturation after 32 years. J. Res. Geochem., 361–369.
de Leeuw, N.H. (2002) Molecular dynamics simulations of the growth inhibiting effect of Fe²⁺, Mg²⁺, Cd²⁺, and Sr²⁺ on calcite crystal growth. J. Phys. Chem. B, 106, 5241–5249.
de Leeuw, N.H. and Parker, S.C. (2001) Surface-water interactions in the dolomite problem. Phys. Chem. Chem. Phys., 3, 3217–3221.
Li, L., Lei, X., Zhang, X. and Sha, Z. (2013) Gas hydrate and associated free gas in the Dongsha area of northern South China Sea. Mar. Petrol. Geol., 39, 92–101.
Lin, Z., Sun, X., Strauss, H., Lu, Y., Gong, J., Xu, L., Lu, H., Teichert, B.M.A. and Peckmann, J. (2017) Multiple sulfur isotope constraints on sulfate-driven anaerobic oxidation of methane: Evidence from authigenic pyrite in seepage areas of the South China Sea. Geochim. Cosmochim. Ac., 211, 153–173.
Lin, Z., Sun, X., Strauss, H., Lu, Y., Böttcher, M.E., Teichert, B.M.A., Gong, J., Xu, L., Liang, J., Lu, H. and Peckmann, J. (2018) Multiple sulfur isotope evidence for the origin of elemental sulfur in an iron-dominated gas hydrate-bearing sedimentary environment. Mar. Geol., 403, 271–284.
Lippmann, F. (1973) Sedimentary Carbonate Minerals. Springer-Verlag, Berlin and New York, 229 pp.
Liu, C., Ye, Y., Meng, Q., He, X., Lu, H., Zhang, J., Liu, J. and Yang, S. (2012) The characteristics of gas hydrates recovered from Shenhu area in the South China Sea. Mar. Geol., 307–310, 22–27.
Lu, Y., Sun, X., Lin, Z., Xu, L., Gong, J. and Lu, H. (2015) Cold seep status archived in authigenic carbonates: Mineralogical and isotopic evidence from Northern South China Sea. Deep-Sea Res. Pt. II, 122, 95–105.
Lu, Y., Sun, X., Xu, H., Konishi, H., Lin, Z., Xu, L., Chen, T., Hao, X., Lu, H. and Peckmann, J. (2018) Formation of dolomite catalyzed by sulfate-driven anaerobic oxidation of methane: Mineralogical and geochemical evidence from the northern South China Sea. Am. Mineral., 103, 720–734.
Machel, H.G. (2004) Concepts and models of dolomitization: A critical reappraisal. In: The Geometry and Petrogenesis of Dolomite Hydrocarbon Reservoirs (Eds Braithwaite, C.J.R., Rizzi, G. and Darke, G.), Geological Society, London, Special Publications, 235, 7–63.
Magalhães, V.H., Pinheiro, L.M., Ivanov, M.K., Kozlova, E., Blinova, V., Kolганova, J., Vasconcelos, C., McKenzie, J.A., Bernasco, S.M., Kopf, A.J., Díaz-del-Río, V., Javier González, F. and Somozano, L. (2012) Formation processes of methane-derived authigenic carbonates from the Gulf of Cadiz. Sed. Geol., 243, 155–168.
Markgraf, S.A. and Reeder, R.J. (1985) High-temperature structure refinements of calcite and magnesite. Am. Mineral., 70, 590–600.
Martin, J.W. and Haney, T.A. (2005) Decapod crustaceans from hydrothermal vents and cold seeps: a review through 2005. Zool. J. Linn. Soc., 145, 445–522.
Mazzullo, S.J. (2000) Organogenic dolomitization in peritidal carbonate successions. Ph.D. dissertation, University of California, Santa Barbara.
McCormack, J., Bontognali, T.R.R., Immenhauser, A. and Kwiecien, O. (2018) Controls on cyclic formation of Quaternary early diagenetic dolomite. Geophys. Res. Lett., 45, 3625–3634.
McKenzie, J.A. and Vasconcelos, C. (2009) Dolomite mountains and the origin of the dolomite rock of which they mainly consist: Historical developments and new perspectives. *Sedimentology*, 56, 205–219.

Nordeng, S.H. and Sibbey, D.F. (1994) Dolomite stoichiometry and Ostwald step rule. *Geochim. Cosmochim. Ac.*, 58, 191–196.

Peckmann, J., Goedert, J.L., Thiel, V., Michaelis, W. and Reitner, J. (2002) A comprehensive approach to the study of methane-seep deposits from the Lincoln Creek Formation, western Washington State, USA. *Sedimentology*, 49, 855–873.

Peckmann, J., Goedert, J.L., Heinrichs, T., Hoefs, J. and Reitner, J. (2003) The Late Eocene ‘Whiskey Creek’ methane-seep deposit (western Washington State) – Part II: Petrology, stable isotopes, and biogeochemistry. *Facies*, 48, 241–254.

Peckmann, J., Senowbari-Daryan, B., Birgel, D. and Goedert, J. (2007) The crustacean ichnofossil *Palaxius* associated with callianassid body fossils in an Eocene methane-seep limestone, Humptulips Formation, Olympic Peninsula, Washington. *Lethaia*, 40, 273–280.

Peckmann, J., Thiel, V., Michaelis, W., Clari, P., Gaillard, C., Martire, L. and Reitner, J. (1999) Cold seep deposits of Beauvoisin (Oxfordian; southeastern France) and Marmorito (Miocene; northern Italy): microbially induced authigenic carbonates. *Int. J. Earth Sci.*, 88, 60–70–87.

Pedley, M. (1992) Bio-retexturing: early diagenetic fabric modifications in outer-ramp settings — a case study from the Oligo-Miocene of the Central Mediterranean. *Sediment. Geol.*, 79, 173–188.

Petras, D.A., Bialik, O.M., Bontognali, T.R.R., Vasconcelos, C., Roberts, J.A., McKenzie, J.A. and Konhauser, K.O. (2017) Microbially catalyzed dolomite formation: From near-surface to burial. *Earth-Sci. Rev.*, 171, 558–582.

Rameil, N. (2008) Early diagenetic dolomitization and dedolomitization of Late Jurassic and earliest Cretaceous platform carbonates: A case study from the Jura Mountains (NW Switzerland, E France). *Sediment. Geol.*, 212, 70–85.

Rieder, R. (1981) Electron optical investigation of sedimentary dolomites. *Contrub. Mineral. Petrol.*, 76, 148–157.

Reeder, R.J. and Sheppard, C.E. (1984) Variation of lattice-parameters in some sedimentary dolomites. *Am. Mineral.*, 69, 520–527.

Roberts, H.H. and Aharon, P. (1994) Hydrocarbon-derived carbonate buildups of the northern Gulf of Mexico continental slope: A review of submersible investigations. *Geo-Mar. Lett.*, 14, 135–148.

Roberts, H.H., Feng, D. and Joyce, S.B. (2010) Cold-seep carbonates of the middle and lower continental slope, northern Gulf of Mexico. *Deep-Sea Res. Pt. II*, 57, 2040–2054.

Sanchez-Roman, M., McKenzie, J.A., Wagener, A.D.R., Rivadeneyra, M.A. and Vasconcelos, C. (2009) Presence of sulfate does not inhibit low-temperature dolomite precipitation. *Earth Planet. Sci. Lett.*, 285, 131–139.

Savvda, C.E. and Bottjer, D.J. (1989) Anatomy and implications of bioturbated beds in “black shale” sequences: Examples from the Jurassic Posidonienschiefere (southern Germany). *Palaios*, 4, 330–342.

Seike, J., Jenkins, R.G., Watanabe, H., Nomaki, H. and Sato, K. (2012) Novel use of burrow casting as a research tool in deep-sea ecology. *Biol. Lett.*, 8, 648–651.

Seilacher, A. (1990) Aberrations in bivalve evolution related to photo- and chemoosymbiosis. *Hist. Biol.*, 3, 289–311.

Senowbari-Daryan, B., Gaillard, C. and Peckmann, J. (2007) Crustacean microfossilites from Jurassic (Oxfordian) hydrocarbon-seep deposits of Beauvoisin, southeastern France. *Facies*, 53, 229–238.

Shen, Z., Liu, Y., Brown, P.E., Szulufarska, I. and Xu, H. (2014) Modeling the effect of dissolved hydrogen sulfide on Mg$^{2+}$-water complex on dolomite 104 surfaces. *J. Phys. Chem. C.*, 118, 15716–15722.

Shen, Z., Szulufarska, I., Brown, P.E. and Xu, H. (2015) Investigation of the role of polysaccharide in the dolomite growth at low temperature by using atomic simulations. *Langmuir*, 31, 10435–10442.

Slaughter, M. and Hill, R.J. (1991) The influence of organic-matter in organogenic dolomitization. *J. Sed. Petroli.*, 61, 296–303.

Suess, E. (2010) Marine cold seeps. In: *Handbook of Hydrocarbon and Lipid Microbiology* (Ed. Timmis, K.N.), pp. 187–203. Springer-Verlag, Berlin Heidelberg.

Sun, Q., Wu, S., Cartwright, J. and Dong, D. (2012) Shallow gas and focused fluid flow systems in the Pearl River Mouth Basin, northern South China Sea. *Mar. Geol.*, 315–318, 1–14.

Suzuki, Y., Wu, S., Dong, D., Lüdmann, T. and Gong, Y. (2012) Gas hydrates associated with gas chimneys in fine-grained sediments of the northern South China Sea. *Mar. Geol.*, 311–314, 32–40.

Swart, P.K. (2015) The geochemistry of carbonate diagenesis: The past, present and future. *Sedimentology*, 62, 1233–1304.

Tong, H., Feng, D., Cheng, H., Yang, S., Wang, H., Min, A.G., Edwards, R.L., Chen, Z. and Chen, D. (2013) Authigenic carbonates from seeps on the northern continental slope of the South China Sea: New insights into fluid sources and geochemistry. *Mar. Petrol. Geol.*, 43, 260–271.

Tong, H., Feng, D., Peckmann, J., Roberts, H.H., Chen, L., Bian, Y. and Chen, D. (2019) Environments favoring dolomite formation at cold seeps: A case study from the Gulf of Mexico. *Chem. Geol.*, 518, 9–18.

Uchman, A. and Wetzel, A. (2012) Deep-sea fans. In: *Trace Fossils as Indicators of Sedimentary Environments* (Eds Knaust, D. and Bromley, R.), *Developments in Sedimentology*, 64, 643–671.

Van Lith, Y., Warthmann, R., Vasconcelos, C. and McKenzie, J.A. (2003) Sulphate-reducing bacteria induce low-temperature Ca-dolomite and high Mg-calcite formation. *Geobiology*, 1, 71–79.

Wallmann, K., Linke, P., Suess, E., Bohrmann, G., Sahling, H., Schlüter, M., Dähnhall, A., Lammers, S., Greinert, J. and von Mirbach, N. (1997) Quantifying fluid flow, solute mixing, and biogeochemical turnover at cold vents of the eastern Aeulitot subduction zone. *Geochim. Cosmochim. Ac.*, 61, 5209–5219.

Warren, J. (2000) Dolomite: Occurrence, evolution and economically important associations. *Earth-Sci. Rev.*, 52, 1–81.

Wetzel, A. (2013) Formation of methane-related authigenic carbonates within the bioturbated zone — An example from the upwelling area off Vietnam. *Palaeogeogr. Palaeocl.* *386*, 23–33.

Wiese, F., Kiel, S., Pack, A., Walliser, E.O. and Agirrezabala, L.M. (2015) The beast burrowed, the fluid followed - Crustacean burrows as methane conduits. *Mar. Petrol. Geol.*, 66, 631–640.

Wissmak, M., Gektidis, M., Freiwald, A. and Lundåv, T. (2005) Bioerosion along a bathymetric gradient in a cold-
temperate setting (Kosterfjord, SW Sweden): An experimental study. *Facies*, 51, 93–117.

Xu, J., Yan, C., Zhang, F.F., Konishi, H., Xu, H.F. and Teng, H.H. (2013) Testing the cation-hydration effect on the crystallization of Ca-Mg-CO\(_3\) systems. *Proc. Natl. Acad. Sci. USA*, 110, 17750–17755.

Zhang, F., Xu, H., Konishi, H. and Roden, E.E. (2010) A relationship between \(d_{104}\) value and composition in the calcite-disordered dolomite solid-solution series. *Am. Mineral.*, 95, 1650–1656.

Zhang, F., Xu, H., Konishi, H., Kemp, J.M., Roden, E.E. and Shen, Z. (2012a) Dissolved sulfide-catalyzed precipitation of disordered dolomite: Implications for the formation mechanism of sedimentary dolomite. *Geochim. Cosmochim. Ac.*, 97, 148–165.

Zhang, F., Xu, H., Shelobolina, E.S. and Roden, E.E. (2012b) Polysaccharide-catalyzed nucleation and growth of disordered dolomite: A potential precursor of sedimentary dolomite. *Am. Mineral.*, 97, 556–567.

Zhang, F., Xu, H., Shelobolina, E.S., Konishi, H., Converse, B., Shen, Z. and Roden, E.E. (2015) The catalytic effect of bound extracellular polymeric substances excreted by anaerobic microorganisms on Ca-Mg carbonate precipitation: Implications for the "dolomite problem". *Am. Mineral.*, 100, 483–494.

Zhang, H., Yang, S., Wu, N., Su, X., Holland, M., Schultheiss, P., Rose, K., Butler, H., Humphrey, G. and GMGS-I Science Team (2007) Successful and surprising results for China’s first gas hydrate drilling expedition. *Fire in the Ice*, 7, 6–9.

Zorn, M.E., Lalonde, S.V., Gingras, M.K., Pemberton, S.G. and Konhauser, K.O. (2006) Microscale oxygen distribution in various invertebrate burrow walls. *Geobiology*, 4, 137–145.

Zwicker, J., Smrzka, D., Gier, S., Goedert, J.L. and Peckmann, J. (2015) Mineralized conduits are part of the uppermost plumbing system of Oligocene methane-seep deposits, Washington State (USA). *Mar. Petrol. Geol.*, 66, 616–630.

Manuscript received 2 February 2021; revision accepted 24 June 2021