Formation of carbonate pipes in the northern Okinawa Trough linked to strong sulfate exhaustion and iron supply

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Abstract

The microbial anaerobic oxidation of methane (AOM), a key biogeochemical process that consumes substantial amounts of methane produced in seafloor sediments, can lead to the formation of carbonate deposits at or beneath the sea floor. Although Fe oxide-driven AOM has been identified in cold seep sediments, the exact mode by which it may influence the formation of carbonate deposits remains poorly understood. Here, we characterize the morphology, petrology and geochemistry of a methane-derived Fe-rich carbonate pipe in the northern Okinawa Trough (OT). We detect abundant authigenic pyrites, as well as widespread trace Fe, within microbial mat-like carbonate veins in the pipe. The in situ $\delta^{34}$S values of these pyrites range from $-3.9$ to $31.6$‰ (VCDT), suggesting a strong consumption of seawater sulfate by sulfate-driven AOM at the bottom of sulfate reduction zone. The positive $\delta^{56}$Fe values of pyrite and notable enrichment of Fe in the OT pipe concurrently indicate that the pyrites are primarily derived from Fe oxides in deep sediments. We propose that the Fe-rich carbonate pipe formed at the bottom of sulfate reduction zone, below which Fe-driven AOM, rather than Fe-oxide reduction coupled to organic matter degradation, might be responsible for the abundantly available Fe$^{2+}$ in the fluids from which pyrites precipitated. The Fe-rich carbonate pipe described in this study probably represents the first fossil example of carbonate deposits linked to Fe-driven AOM. Because Fe-rich carbonate deposits have also been found at other cold seeps worldwide, we infer that similar processes may play an essential role in biogeochemical cycling of sub-seafloor methane and Fe at continental margins.

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1. INTRODUCTION

Fluid venting at cold seeps has been widely recognized in various tectonic settings at continental margins in both modern marine environment and throughout the geological record (Michaelis et al., 2002; Peckmann and Thiel, 2004; Campbell, 2006; Knittel and Boetius, 2009; Roberts et al., 2010). The inherent nature of seeps is that fluid flow intensity is highly variable both spatially and temporally (Peckmann et al., 2009; Haas et al., 2010; Nöthen and Kasten, 2011; Feng et al., 2016). A dominant reduced chemical component of cold seep fluids is dissolved or free methane. The microbial anaerobic oxidation of methane...
(AOM) typically occurs in anoxic sub-surface sediments at cold seeps, consuming substantial amounts of methane produced in seafloor environments (Reeburgh, 2007; Knittel and Boetius, 2009; House et al., 2009; Milucka et al., 2012; Wankel et al., 2012; Feng et al., 2016). To date, AOM has been widely observed in different cold seep environments at continental margins (Alperin et al., 1988; Martens et al., 1999; Díaz-del-Río et al., 2003; Inagaki et al., 2006; Holler et al., 2011; Maignien et al., 2013; Lin et al., 2016b). Although AOM is often thought of as a sulfate-driven process (Milucka et al., 2012), it is coupled, either directly or indirectly, to a larger variety of oxidants (e.g., Fe oxide, Mn oxide, nitrate and nitrite) than previously thought (Raghoebarsing et al., 2006; Beal et al., 2009; Ettwig et al., 2010; Wankel et al., 2012; Egger et al., 2015; Scheller et al., 2016). Laboratory incubations and field investigations have demonstrated that Fe oxide-driven AOM may indeed occur in freshwater, brackish and cold seep sedimentary environments (Adler et al., 2011; Sivan et al., 2011, 2014; Nordi et al., 2013; Segarra et al., 2013; Slomp et al., 2013).

In cold seep sedimentary systems, AOM results in an increased alkalinity level in pore waters, commonly leading to the precipitation of authigenic carbonates and the formation of carbonate deposits including carbonate crust, pipes and chimneys within sediments or at the seafloor (Peckmann et al., 2001; Díaz-del-Río et al., 2003; Bayon et al., 2013). These carbonate deposits, to a certain extent, can act as a valuable archive of seepage activity and environmental conditions (Peckmann and Thiel, 2004; Bayon et al., 2009, 2013; Birgel et al., 2011; Feng et al., 2014; Han et al., 2014). Previous studies on trace and major elements, stable isotopes, lipid biomarkers and biogenic fabrics of seep carbonates have shown a diversity of seep carbonate deposits in mineralogy and geochemistry (Thiel et al., 1999; Peckmann et al., 2001; Peckmann and Thiel, 2004; Chen et al., 2007; Bayon et al., 2013; Ge et al., 2015; Sun et al., 2015; Lin et al., 2016a,b). However, the exact mode by which different AOM processes (e.g., Fe oxide-driven AOM and sulfate-driven AOM) may influence the mineralogy and geochemistry of seep carbonate deposits still remains insufficiently understood.

Recently, Sun et al. (2015) reported that Fe-rich carbonate deposits associated with cold seep activities are widely found in the northern OT. The authors inferred that Fe-driven AOM probably occurs during the formation of Fe-rich carbonate deposits, simply based on a complementary relationship between the content distributions of goethite and carbonate in the samples. To demonstrate the validity of this hypothesis, however, further robust evidence from high-resolution data are inevitably required. Here, we use a combination of nano-scale secondary ion mass spectrometry (NanoSIMS) ion mapping, NanoSIMS in situ sulfur isotopic analyses, multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) analyses and synchrotron-based soft X-ray absorption near edge structure (XANES) analyses to elucidate the origin of S and Fe in a Fe-rich carbonate pipe collected from the northern OT. The data obtained in this study provide unique insights into the formation of Fe-rich carbonate pipe linked to Fe oxide-driven AOM within deep-sea sediments at cold seeps.

2. MATERIALS AND METHODS

2.1. Geological setting and sampling site

Okinawa Trough (OT), located at the eastern edge of the East China Sea (ECS), is an extension back-arc basin that forms as a result of the subduction of the Philippine Sea plate beneath the Eurasian plate at the Ryukyu Trench (Fig. 1a). The strike direction of the northern OT is nearly NNE-SSW, whereas it is NE-SW in the middle and E-W to the south. A previous study on profiles perpendicular to the OT has shown that the OT has a typical U-shape, indicating abundant sedimentary supply from the ECS continental shelf (Wu et al., 2014). The thickness of sediments in the northern section of the OT is up to 8 km, due to a huge supply of terrigenous matter from the Yangtze and Yellow Rivers (Sibuet et al., 1987; Wu et al., 2014). Topographically, submarine canyons, fans and turbidite deposits have extensively developed on the western slope of the northern OT.

Abundant Fe-rich carbonate pipes were recovered by geological dredging in an olistostrome zone on the west slope of the northern OT during the integrated environmental and geological expedition of R/V KexueYihao in July to August 2013 (Fig. 1). The sampling site is located at the head of a small-scale submarine canyon that incises the western slope of the northern OT (Fig. 1a). These Fe-rich carbonate pipes have likely been excavated on the sea floor by sediment winnowing, erosion by bottom currents, or sediment instability, similar to those found in other cold seep environments (Merinero et al., 2012; Han et al., 2013). In addition to Fe-rich carbonate pipes, abundant Fe-rich carbonate crusts, concretions and various mollusk shells (vesicomyids and lucinids), along with other animals, were also recovered during this cruise (Sun et al., 2015). A bottom-simulating reflection in this area has been identified through a high-resolution multi-channel seismic survey, reflecting the possible presence of a natural gas hydrate reservoir with an average depth of over 600 m beneath the sea floor (Sun et al., 2015). The local geology of the OT has been described in detail elsewhere (Wu et al., 2014; Sun et al., 2015).

2.2. Methods

2.2.1. Computerized X-ray tomography

Computerized X-ray tomography (CT) measurements were performed on a GE Light Speed VCT instrument to determine the inner structure of the carbonate pipe. The instrument was operated at 140 kV, with a 10 mA current and 1.5 s exposures. CT images were computerized by the reconstruction of the distribution function of the linear attenuation coefficient.

2.2.2. Light microscopy

Light microscopy analysis was performed on the polished thin sections of the Fe-rich carbonate pipe in the marine chemistry lab at the School of Ocean and Earth Science in Tongji University, China. Pyrite aggregations were located within the thin sections by using light microscopy.
Specimens at the top of the thin section were selected for NanoSIMS and photographed using a Leica DM4500P Polarizing Light Microscope.

2.2.3. Conventional geochemical techniques

X-ray diffraction (XRD) analyses were performed on a D/max-2600PC X-ray diffractometer (Rigaku Corporation) at 40 kV and 100 mA. Prior to the analysis, small pieces of the carbonate pipe were freeze-dried under anoxic conditions to avoid oxidation during drying and then thoroughly ground using a pestle and mortar. The major elements were measured using a Shimadzu XRF-1800 X-ray fluorescence spectrometer (XRF) operated at 40 kV and 95 mA after the fusion of 0.1 g of sample material with 3.6 g of dilithium tetraborate at 1050 °C for 16 min. To determine the trace and rare earth elements, the samples were dissolved using a solution of HNO₃ + HF diluted in 2% HNO₃ and then characterized using a Thermo VG-X7 inductively coupled plasma mass spectrometer. The stable carbon isotope compositions were determined using dual-inlet isotopic ratio mass spectrometry (IsoPrime), following the procedure described in Liu et al. (2002). The CO₂ was liberated by reacting with 100% H₃PO₄ at 70 °C for mass spectrometric isotopic analysis. The isotopic compositions are reported in conventional delta (δ) units relative to the Vienna Pee Dee Belemnite reference (VPDB). The reactive organic carbon contents of the sediments around Fe-rich carbonate pipes were measured using a spectrophotometer, following the procedure described in Lefroy et al. (1993). Separate sediment samples containing ~15 mg C were tumbled for 1 h in 25 mL of 333 mM KMnO₄. The oxidation of organic matter was determined at 565 nm by measuring the change in KMnO₄ concentration, and the data are reported in mg C g sediments⁻¹.

2.2.4. NanoSIMS ion mapping

Elemental mapping was performed on the polished 30-μm-thick thin sections using a Cameca NanoSIMS 50L (CAMECA, Paris, France) at the Institute of Geology and Geophysics, Chinese Academy of Sciences, following the procedure described in Peng et al. (2016). The NanoSIMS is capable of imaging at a sub-50 nm lateral resolution for negatively charged secondary ions and at a lateral resolution of approximately 200 nm for positively charged secondary ions. To remove the conductive coating (Au) and the contaminants that were generated during
pretreatment, each region of interest was pre-sputtered with a 150 pA beam current and an ion dose of \( N = 5 \times 10^{16} \) ions/cm\(^2\). In the multi-collection mode, negative secondary ions \({}^{12}\mathrm{C}^-\), \({}^{16}\mathrm{O}^-\), \({}^{12}\mathrm{C}^{-14}\mathrm{N}^-\), \({}^{28}\mathrm{Si}^-\), \({}^{31}\mathrm{P}^-\), \({}^{32}\mathrm{S}^-\), \({}^{34}\mathrm{S}^-\), \({}^{23}\mathrm{Al}^{16}\mathrm{O}^-\), \({}^{23}\mathrm{Na}^{16}\mathrm{O}^-\), \({}^{55}\mathrm{Mn}^{16}\mathrm{O}^-\), and \({}^{56}\mathrm{Fe}^{16}\mathrm{O}_2^-\) were sputtered from the sample surface using a Cs\(^+\) primary beam with \( \sim 2.5 \) pA intensity. All of the images referred to in this paper are 256 \( \times \) 256 pixels, recorded in \( \sim 30 \) min.

2.2.5. Synchrotron-based XANES analyses

The focused-ion-beam (FIB) cross-sections of the carbonate pipe were prepared for the synchrotron-based soft X-ray absorption measurements using the FEI Quanta 3D scanning electron microscopy/focused-ion beam instrument (Wirth, 2004). All Synchrotron-based soft X-ray absorption measurements were performed on the Shanghai Synchrotron Radiation Facility at beam line BL08U1A, following the procedure described in Peng et al. (2015). The spatial distribution of Fe was determined by transmission mode dual energy (TMDE) analysis. The X-ray absorption near-edge structure (XANES) of Fe was obtained by total electron yield (TEY) analyses for powder samples at the Fe L\(_{2,3}\) edge or by scanning an area of interest (30 nm \( \times \) 30 nm) from 703.0 to 730.0 eV with an energy increment of 0.2 eV for the FIB sections. Five reference Fe compounds (vivianite, magnetite, pyrite, goethite and FePO\(_4\)) were used to fit the spectra of samples.

2.2.6. In situ NanoSIMS sulfur isotopic analyses

In situ sulfur isotopic analyses were performed using a Cameca NanoSIMS 50L instrument following the procedure described in Zhang et al. (2014). Each area of 40 \( \times \) 40 \( \mu \)m\(^2\) or 30 \( \times \) 30 \( \mu \)m\(^2\) was first pre-sputtered with a primary beam of \( \sim 1 \) nA for \( \sim 2 \) min to remove the coating and to implant enough Cs\(^+\) (>10\(^{17}\) ions per cm\(^2\)) into the sample surface to stabilize the yield of secondary ions and sulfur isotope ratio. The ion images of each pre-sputtered region were acquired to exactly select interesting grains for sulfur isotopic analyses. The more abundant \( ^{32}\)S isotopes were detected using a Faraday Cup (FC) and the less abundant \( ^{34}\)S isotopes were detected using an electron multiplier (EM). Using the widths of the entrance slit (30 mm), aperture slit (350 mm) and exit slit (90 mm), a mass resolution of \( \text{M}/\Delta \text{M} = 7000 \) was achieved to eliminate potential interference from other ions or molecules that were extremely close in mass to the ions of interest. The instrument then automatically analyzed all of the selected grains by rastering the primary beam over each pre-set area (e.g., 2 \( \times \) 2 \( \mu \)m\(^2\)) of the grains. Each sulfur isotopic analysis consisted of four blocks of 40 measurement cycles of \( \sim 8 \) s each. Fe isotope data are reported in standard \( \delta \)-notation (in units of per mil, \( \%e \)) relative to the international IRMM-014 Fe standard:

\[
\delta^{56}\text{Fe} = \left[ \left\{ ^{56}\text{Fe} / ^{56}\text{Fe}_{\text{IRMM-014}} \right\} - 1 \right] \times 1000
\]

where \( x \) refers to mass 56 or 57. The long-term external reproducibility is better than \( \pm 0.049\%e \) (2SD) for \( \delta^{56}\text{Fe} \) measurements and \( \pm 0.064\%e \) (2SD) for \( \delta^{57}\text{Fe} \) measurements.

3. RESULTS

3.1. Mineralogical and geochemical characterization

The pipe studied here is composed of quartz, K-feldspar, plagioclase, pyrite, goethite and microcrystalline cements, mainly high Mg calcite and dolomite based on X-ray diffraction analysis. We collected data for nine oxides (Al\(_2\)O\(_3\), CaO, MgO, Fe\(_2\)O\(_3\)(T), MnO, K\(_2\)O, Na\(_2\)O, TiO\(_2\) and P\(_2\)O\(_5\)) and 37 elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Nb, Rb, Sr, Y, Zr, Nb, Pb, Cs, Ba, Hf, Th, U, and 14 rare earth elements) in the eight subsamples by using a combination of ICP-MS and XRF (Table 1). The composition of the pipe is characterized by a high content of Fe\(_2\)O\(_3\) (4.09–4.63%), Al\(_2\)O\(_3\) (9.95–10.92%), P\(_2\)O\(_5\) (4.09–4.63%), CaO (10.95–11.05%), MgO (5.93–6.12%), K\(_2\)O (1.95–2.00%), and Na\(_2\)O (1.95–2.00%).
slight Ce anomalies (Ce/Ce* = 0.96–0.99) and negative Eu anomalies (Eu/Eu* = 0.63–0.67) – suggest that the pipe was formed in either a hypoxic or anoxic environment (Díaz-del-Río et al., 2013). The reactive organic carbon contents (9.20–12.60%), SiO₂ (30.0–35.8%) and CaO (16.56–23.47%), indicating that the pipe consists of much detrital material. In addition, the high total rare earth elements content (ΣREE = 113.12 ppm – 180.24 ppm; average = 144.73 ppm) and similar distribution patterns– depleted heavy REEs relative to light REEs (Pr/Yb = 4.74–5.68), slight Ce anomalies (Ce/Ce* = 0.96–0.99) and negative Eu anomalies (Eu/Eu* = 0.63–0.67) – suggest that the pipe was formed in either a hypoxic or anoxic environment (De Baar et al., 1988; Tribouillard et al., 2012; Feng et al., 2013). The δ³¹Ce values of the carbonates (Table A1), ranging from −6.29‰ to −25.84‰ (average = −13.95‰, VPDB), are generally higher than those of the typical seep carbonates, indicating that their possible source is from methanogenic zone (Díaz-del-Río et al., 2003; Peckmann and Thiel, 2004; Roberts et al., 2010; Tong et al., 2013). The reactive organic carbon contents of the sediments around Fe-rich carbonate pipes range from 0.49% to 0.52% (average = 0.5%; Table A2).

### 3.2. NanoSIMS ion mapping and XANES spectra

Light microscope observations show reddish microbial mat-like carbonate veins cementing a large number of detrital minerals in the pipe (Fig. 2 and Fig. A1). Abundant dark spheroids formed in the veins, most of which vary in diameter from ~0.8 to 25 μm. We used NanoSIMS with the smallest primary beam spot (~50 nm in diameter) to acquire the elemental distribution in the pipe (Fig. 3 and Figs. A2–A5). The high-resolution elemental mapping images show that Fe (measured as ⁵⁶Fe³¹O₂) is distinctly enriched in the exterior of the spheroids, and S is mainly enriched in the interior of the spheroids, suggesting that they are frambooidal pyrites coated by a thin layer of Fe

<table>
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<th>Sample ID</th>
<th>Li (ppm)</th>
<th>Be</th>
<th>Sc</th>
<th>V</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Rb</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
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<td>9.03</td>
<td>89.03</td>
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<td>10.97</td>
<td>32.72</td>
<td>24.06</td>
<td>68.64</td>
<td>89.62</td>
<td>1256.59</td>
<td>16.11</td>
<td>98.88</td>
<td>5.96</td>
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<td>1.32</td>
<td>8.26</td>
<td>79.75</td>
<td>53.05</td>
<td>11.64</td>
<td>32.38</td>
<td>19.89</td>
<td>64.54</td>
<td>84.11</td>
<td>1051.67</td>
<td>19.48</td>
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<td>18.1</td>
<td>98.88</td>
<td>10.98</td>
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</table>

### Table 1

**Chemical compositions of Fe-rich carbonate chimney in the northern Okinawa Trough.**

<table>
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<tr>
<th>Sample ID</th>
<th>Al₂O₃ (wt%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃(T)</th>
<th>K₂O</th>
<th>MgO</th>
<th>SO₃</th>
<th>MnO</th>
<th>Na₂O</th>
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<td>1.71</td>
<td>12.6</td>
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<td>0.14</td>
<td>2.01</td>
<td>12.34</td>
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*Ce/Ce* = 2EuN/(SmN + GdN).
oxides (Fig. 3a, b). The C distribution is consistent with that of Ca, providing a glimpse of the authigenic carbonates that cement detrital minerals in the pipe (Figs. A2 and A3). The distributions of Si and Al are distinctly different from those of C and Fe (Fig. 3a, b and Figs. A2, A3 and A5), reflecting the presence of quartz and feldspar in the pipe, respectively. These detrital minerals commonly exhibit irregular morphologies with sharp edges, implying that they originate from sediments (Zhao et al., 2011; Sun et al., 2015).

NanoSIMS was also employed to detect the distribution of trace Fe in carbonate veins of the pipe (Fig. 3c). Minor amounts of widely scattered Fe were distinctly identified in the microbial mat-like carbonate veins, consistent with the result from synchrotron-based soft X-ray TMDE analysis (Fig. 4). This finding implies that Fe probably originated from seep fluid and that it co-precipitated with carbonate during the pipe formation. The Fe L_{2,3}-edge XANES spectra of the powder carbonate samples are similar in shape to those of Fe^{3+} minerals (e.g., goethite), reflecting that the whole pipe underwent a high degree of oxidation after the initial formation (Fig. 4c). The oxidation process likely results from the exposure to oxygenated seawater caused by turbidity currents (Naehr et al., 2007; Han et al., 2013). However, the XANES spectra collected from the focused-ion-beam cross-sections are characterized by a major peak at 708.7 eV, showing that Fe^{2+} still exists in the local area of the carbonate veins and spheroids (Fig. 4). The Fe^{2+} in the carbonates might bind with reduced sulfur species to form pyrites or their precursors (e.g., FeS), as indicated by the fact that trace S, as well as trace Fe, are widely detected in the carbonate veins (Fig. 3c).

3.3. In situ S isotope composition

In this study, the average $\delta^{34}S$ count rate for 16 accepted analyses of the standard was $1.81 \times 10^{5}$ counts/s (for a total of $2.72 \times 10^{7}$ counts/analysis), and the average $\delta^{34}S$ count rate for 21 accepted analyses of the pyrite aggregations was $1.75 \times 10^{5}$ counts/s (for a total of $2.63 \times 10^{7}$ counts/analysis), indicating the suitability of the standard sample.
and a good accuracy for these measurements. The $\delta^{34}S$ values ranged from $-3.9 \pm 0.5 \permil$ to $31.6 \pm 0.5 \permil$ VCDT (average = $16.4 \permil$, $n = 45$), showing a notable enrichment of $^{34}S$ in pyrites (Fig. 5 and Table A3).

3.4. Fe isotope composition of pyrites

Hand-picked pyrites within carbonate pipe analyzed here had positive $\delta^{56}Fe$ values ($0.501 \pm 0.029 \permil$ and $0.220 \pm 0.029 \permil$; Table 2), showing an enrichment of $^{56}Fe$ in pyrites.

4. DISCUSSION

High-resolution NanoSIMS mappings (Fig. 3a, b) imply that pyrites within carbonate pipe form first, and Fe oxides are secondary minerals produced via oxidation of pyrites in a later stage, dissimilar from previous observation on the absence of pyrite (Sun et al., 2015). This hypothesis is also supported by the Fe L$_{2,3}$-edge XANES spectra of powder carbonate samples. These pipes, after their initial formation within sediments, are thus thought to be exposed on the sea floor by sediment winnowing, erosion by bottom currents, or sediment instability (Naehr et al., 2007; Han et al., 2013). These events could have extensively occurred in the geological past in the study area, considering that it is located in an olistostrome zone that is a non-steady-state depositional system (Zhao et al., 2011; Wu et al., 2014).

4.1. Origin of S in pyrites within the OT pipe

Previous studies have shown that pyrites associated with methane seepage generally show an increase in $\delta^{34}S$ values with depth at the cold seep site (Wang et al., 2008; Lin et al., 2016a,b) and that the concentration of seawater sulfate may be responsible for the sulfur isotope fractionation imposed by bacterial sulfate reduction between the initial sulfate and the produced sulfides (Canfield et al., 2000; Habicht et al., 2002). The $\delta^{34}S$ values in this study imply that the S in pyrites is not derived from the $^{34}S$-depleted $H_2S$ of the uppermost sediment layers (Clvert et al., 1996) but is instead derived from either anoxic bottom water or a sulfate minimum zone characterized by lower sulfate concentration and high $\delta^{34}S$ values (Shen et al., 2008).
Sea (Cl vert et al., 1996; Peckmann et al., 2001; Jørgensen et al., 2004), Blake Ridge sediments (Borowski et al., 2013), Shenhu seep sediments in South China Sea (Lin et al., 2016a,b) and sedimentary rocks formed throughout the last 2–3 billion years of Earth's history (Canfield and Raiswell, 1999). Variations in the δ 34S values on a nanometer to micrometer scale in the individual pyrite aggregates of the OT pipe are consistent with the Rayleigh fractionation of S isotopes, which most likely results from sulfate-reducing bacteria utilizing small, residual pools of 34S-enriched seawater sulfate in microenvironments (Kohn et al., 1998; Peckmann and Thiel, 2004; Lin et al., 2016b).

Although both diagenetic organiclastic sulfate reduction and sulfate-driven AOM can consume large amounts of sulfate in sediments, the positive δ 34S values of pyrites in seepage areas have been interpreted to potentially derive from extensive sulfate-driven AOM occurring at sulfate reduction zone (Jørgensen et al., 2004; Neretin et al., 2004; Peketi et al., 2012; Borowski et al., 2013; Wang et al., 2015; Lin et al., 2016a,b). Jørgensen et al. (2004) proposed a compelling model for explaining how sulfate-driven AOM combined with a deep H 2S sink leads to 34S-enriched pyrites in deep sediments. Peketi et al. (2012) noted that the past sulfate-driven AOM activity could be recorded in 34S-enriched sulfide minerals. Borowski et al. (2013) observed that δ 34S values of bulk sulfide minerals tend to be more enriched in 34S at and below sulfate reduction zone and thus postulated that large 34S enrichments within sulfide minerals is a consequence of high proportions of sulfate-driven-AOM. Lin et al. (2016b) used secondary ion mass spectroscopy for in situ δ 34S values of pyrites to identify that the highly positive δ 34S values of pyrites result from near to complete exhaustion of dissolved sulfate via AOM at the bottom of sulfate reduction zone in the seepage area.

Generally, available sulfate is preferentially utilized via sulfate-driven AOM provided that methane is present, although organiclastic sulfate reduction is energetically more favorable than sulfate-driven AOM (Kasten and Jørgensen, 2000; Borowski et al., 2013; Antler et al., 2014; Lin et al., 2016a,b). As Lin et al. (2016b) identified, the upward methane flux resulting from underlying gas hydrates in the study area (Sun et al., 2015) would consume most of the sulfate within sulfate reduction zone, potentially limiting early diagenetic organiclastic sulfate reduction. Therefore, the highly positive δ 34S values of pyrites in the OT pipe probably reflect an early incursion of seawater followed by the near-complete consumption of seawater sulfate via sulfate-driven AOM in the bottom of sulfate reduction zone (Sivan et al., 2011; Borowski et al., 2013; Antler et al., 2015; Lin et al., 2016b).

4.2. Origin of Fe in pyrites within the OT pipe

It was generally thought that the reactive Fe oxides in marine sediments react with the H 2S derived from microbial sulfate reduction, leading to the formation of pyrites...
in sediments and carbonate (Berner, 1984). The formation of pyrites produced by these processes, however, is limited by the availability of reactive Fe oxides. As such, the pyrite in seep carbonates or uppermost sediments commonly shows consistently low, negative $\delta^{34}S$ values due to the low detrital Fe fluxes (Formolo and Lyons, 2013). Thus, the $^{34}S$-enriched $\delta^{34}S$ values for pyrite, along with the notable enrichment of Fe in Fe-rich carbonate pipe, indicate that pyrite did not form in a Fe-limited environment. Using the elemental mapping of NanoSIMS and TMDE, we identified a distinctly widespread distribution of minor amounts of Fe in microbial mat-like carbonate veins (Fig. 3c and Fig. 4), strongly indicating the co-precipitation of Fe with carbonate from seep fluids. We propose that migration of seep fluids might provide the available dissolved Fe$^{2+}$ to react with the H$_2$S derived from microbial sulfate reduction, leading to the precipitation of pyrites and their precursors in carbonates of the pipe. The supply of dissolved Fe$^{2+}$ from seep fluids is also supported by the directional arrangement of pyrites, probably indicating the flowing direction of seep fluids (Fig. A1). In addition, this is also indicated by the fact that pyrites typically embed within the microbial mat-like matrices of authigenic carbonates that precipitate from seep fluids, in contrast to the distribution of detrital minerals that indicate a sedimentary source (Fig. 3a).

Fe may have two possible sources in the study area. One is from the dissolved Fe$^{2+}$ of hydrothermal vents and the other is from the input of Fe oxides in deep sediments. The hand-picked pyrites analyzed here yielded positive $\delta^{56}$Fe values (Table 2), implying that Fe$^{2+}$ of pyrites is primarily derived from Fe oxides in deep sediments (Canfield, 1989; Wolfe et al., 2016). Previous studies have shown that turbidites can contribute to high input of Fe oxides and rapid burial of reactive Fe oxides below sulfate reduction zone in deep sediments (Riedinger et al., 2014). These events could have extensively occurred in the geological past in the study area, considering that it is located in an olistostrome zone that is a non-steady-state depositional system (Riedinger et al., 2014; Egger et al., 2015). However, it can’t be neglected that high input of Fe oxides may also origin from ferruginous sediments associated with hydrothermal activities which are widespread in OT (Zhao et al., 2011; Wu et al., 2014).

The Fe-oxides could be reduced via two possible pathways within deep sediments in the study area, i.e. Fe-oxide reduction coupled to organic matter degradation (Fe-driven OMD) or Fe-oxide reduction coupled to anaerobic oxidation of methane (Fe-driven AOM). The former may be one of the oldest forms of respiration where Fe$^{3+}$ acts as an electron acceptor (Vargas et al., 1998); however, this pathway could be largely limited by the poor availability and reactivity of the residual total organic matter within deep sediments (Sivan et al., 2011; Riedinger et al., 2014). Reactive organic carbon contents of the sediments around Fe-rich carbonate pipes show very low values (~0.5 wt%), also indicating that Fe-driven OMD might be largely limited in the study area.

Table 2
Iron isotopic compositions of pyrites in the carbonate pipe.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\delta^{56}$Fe (%)</th>
<th>$\pm$2SD (%)</th>
<th>$\delta^{57/54}$Fe (%)</th>
<th>$\pm$2SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>0.501</td>
<td>0.029</td>
<td>0.744</td>
<td>0.052</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.220</td>
<td>0.029</td>
<td>0.300</td>
<td>0.052</td>
</tr>
</tbody>
</table>
We propose that Fe-driven AOM might be the most plausible pathway responsible for the high dissolved Fe$^{2+}$ within deep sediments. A basic prerequisite for the occurrence of Fe-driven AOM is the concurrent presence of porewater CH$_4$ and abundant reducible Fe-oxides in sulfate-poor systems (Sivan et al., 2011; Riedinger et al., 2014). In this study, the highly positive $\delta^{34}$S values of pyrites clearly indicate that seawater sulfate was almost consumed within deep sediments where the Fe-rich carbonate pipe formed (Jørgensen et al., 2004; Sivan et al., 2011; Borowski et al., 2013; Lin et al., 2016b). The abundant reactive Fe oxides probably derived from turbidites in the north OT can act as electron acceptors for the biological oxidation of CH$_4$ released from the sub-seafloor hydrocarbon reservoir that already exists in the study area (März et al., 2008; Riedinger et al., 2014; Egger et al., 2015; Sun et al., 2015; Scheller et al., 2016). Available evidences obtained in this study strongly imply that the basic conditions for Fe-driven AOM have been developed within deep sediments in the northern OT sedimentary system. Similar Fe-driven AOM has been recently discovered in different sedimentary environments, such as brackish coastal sediments (Egger et al., 2015), Argentine Basin sediments (Riedinger et al., 2014), coastal freshwater and brackish wetland sediments (Segarra et al., 2013), Lake Kinneret sediments (Sivan et al., 2011) and marine anoxic sediments (Beal et al., 2009). High dissolved Fe$^{2+}$ concentration produced via Fe-driven AOM below the sulfate/methane transition could lead to an inverse zoning within deep sediments, different from the zoning in normal sedimentary systems where the zone of microbial iron reduction is commonly above the zone of microbial sulfate reduction (Riedinger et al., 2014; Egger et al., 2015).

4.3. Potential model for the formation of Fe-rich carbonate pipe

The co-occurrence of the highly positive pyrite $\delta^{34}$S values, positive pyrite $\delta^{56}$Fe values and notable enrichment of Fe in the northern OT pipe provides insights into the formation of Fe-rich carbonate precipitates influenced by both sulfate-driven AOM and Fe oxide-driven AOM within deep sediments at cold seep (Fig. 6). The highly positive $\delta^{34}$S values of pyrites reflect that the Fe-rich carbonate pipe forms via sulfate-driven AOM at the bottom of sulfate reduction zone where sulfate is almost consumed (Jørgensen et al., 2004; Lin et al., 2016b). This sulfate-driven AOM process results in an increased alkalinity level in pore waters, leading to the precipitation of carbonates in and around the seep fluid conduits (Peckmann and Thiel, 2004; Borowski et al., 2013; Lin et al., 2016b). Meanwhile, Fe-driven AOM occurs below the pipe formation zone where seawater sulfate is completely consumed, owing to concurrent presence of CH$_4$ and abundant reducible Fe-oxides in this zone (Beal et al., 2009; House et al., 2009; Sivan et al., 2011; Riedinger et al., 2014; Egger et al., 2015; Scheller et al., 2016). A large amount of dissolved Fe$^{2+}$ produced via Fe-driven AOM might migrate upward with seep fluids.

![Fig. 6. Formation model of Fe-rich carbonate pipes linked to Fe-driven AOM. At the bottom of sulfate reduction zone, sulfate-driven AOM provides the available HCO$_3^-$ and heavy isotopic HS$^-$ for the precipitation of carbonates and pyrites in the pipe. Below sulfate reduction zone, Fe-driven AOM generates Fe$^{2+}$ that migrates upwards with the seep fluids to react with the H$_2$S at the bottom of sulfate reduction zone, leading to the precipitation of pyrites in the pipe.](image)
When Fe$^{2+}$ reaches the bottom of sulfate reduction zone, it reacts with H$_2$S derived from sulfate-driven AOM, leading to the precipitation of pyrites (or their precursors) in the carbonate matrix. This model proposed above might be valid for the formation of Fe-rich carbonate precipitates in similar methane seep systems characterized by organic matter-poor and iron oxides-rich conditions. To further demonstrate the validity of this model, more geochemical studies of Fe and S speciation within sediments in the study area are needed in the future.

5. IMPLICATIONS AND CONCLUSIONS

The formation of Fe-rich carbonate pipe in the northern OT is driven by both sulfate-driven AOM and Fe oxide-driven AOM that may act as a double biological barrier to prevent the emission of seep methane into the overlying water column. Although Fe oxide-driven AOM was proposed to have the potential to act as a CH$_4$-removal mode at cold seeps (Beal et al., 2009), direct evidence from the geological record is lacking. Hence, the Fe-rich carbonate pipe formed in the northern OT probably represents a first fossil example of carbonate deposits linked to Fe-driven AOM. To date, similar Fe-rich carbonate precipitates have also been identified in other cold seep environments worldwide, such as the South China Sea (Tong et al., 2013; Han et al., 2013) and the Gulf of Cadiz (Diaz-del-Rio et al., 2003; Merinero et al., 2012). This implies that Fe oxide-driven AOM may be widespread within deep sediments in cold seep environments where the input of Fe oxides is high, and thus may play an essential role in biogeochemical cycling of sub-surface methane and Fe at continental margins.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2017.02.010.

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