

Geophysical Research Letters

RESEARCH LETTER

10.1029/2019GL085643

Key Points:

- U/Th dating of seep carbonates from a gas hydrate-bearing sediment drill core provides constraints on the timing of methane seepage
- Carbonates precipitated from ^{18}O -enriched pore fluids derived from methane hydrate dissociation
- Methane hydrate dissociation occurred during sea-level highstand (MIS 5e) possibly induced by increasing bottom-water temperatures

Supporting Information:

- Data Set S1

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Citation:

Chen, F., Wang, X., Li, N., Cao, J., Bayon, G., Peckmann, J., et al. (2019). Gas hydrate dissociation during sea-level highstand inferred from U/Th dating of seep carbonate from the South China Sea. *Geophysical Research Letters*, 46, 13,928–13,938. <https://doi.org/10.1029/2019GL085643>

Received 3 OCT 2019

Accepted 19 NOV 2019

Accepted article online 26 NOV 2019

Published online 6 DEC 2019

Fang Chen and Xudong Wang should be regarded as joint first authors.

Gas Hydrate Dissociation During Sea-Level Highstand Inferred From U/Th Dating of Seep Carbonate From the South China Sea

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Abstract Gas hydrates represent a huge reservoir of methane in marine sediments, prone to dissociation in response to environmental changes. There is consensus that past events of gas hydrate dissociation in the marine environment mainly occurred during periods of low sea level. Here, we report geochemical data for 2-m-thick layers of seep carbonate collected from a hydrate-bearing drill core from ~800-m water depth in the northern South China Sea. The aragonite-rich carbonates reveal positive $\delta^{18}\text{O}$ values, confirming a genetic link with gas hydrate dissociation. Uranium-thorium dating of seep carbonates indicates that gas hydrates at the study site dissociated between 133,300 and 112,700 years BP, hence coinciding with the Last Interglacial (MIS 5e) sea-level highstand. We put forward the concept that a climate-driven increase in temperature was responsible for a period of pronounced gas hydrate dissociation.

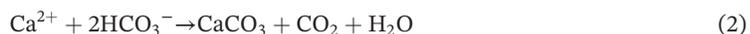
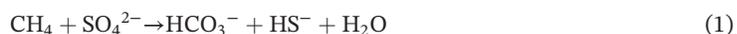
Plain Language Summary The gas hydrate reservoir is a dynamically changing system extremely susceptible to variations of seafloor temperature and pressure. Therefore, gas hydrate dissociation and subsequent methane seepage frequently occur during times of global climate change, especially during sea-level lowstands with reduced seabed pressure. However, this conclusion was mainly based on dating of seep carbonates sampled from the seabed. As a consequence, one cannot exclude that previous results have been compromised by a sampling bias since seafloor samples are easier to collect. Authigenic seep carbonates from drill cores represent a continuous record of gas hydrate dynamics. Our uranium-thorium dating of seep carbonate from drill cores provides a unique example of the effects of temperature and pressure on the stability of the hydrate system in the Dongsha area, northern South China Sea (SCS), during the last interglacial stage (MIS 5e, about 130,000 years BP). Representing the most similar and most contemporary analog to the current interglacial, the study of a methane release event in the SCS during MIS 5e will shed light on the expected trend of methane release events in the future, while providing insight into the response of low-latitude oceans to climate change.

1. Introduction

Due to abundant supply of sedimentary organic matter and subsequent diagenetic transformation, large quantities of methane are encountered at continental margins worldwide (Suess, 2014). Acting as a potential source of methane for fluid seepage, gas hydrate forms under favorable conditions of low temperature and high pressure along continental margins. Methane-rich fluids migrate toward the seabed along faults or fractures when gas hydrate becomes unstable, which can eventually cause prolonged seepage (Campbell, 2006). The current estimation of the global gas hydrate reservoir remains elusive, with the estimated total volume of methane in marine hydrate layers ranging from 200 to 3,000,000 trillion cubic meters at standard

temperature and pressure; the most commonly cited estimate is 20,000 trillion cubic meters (Boswell & Collett, 2011). Consequently, there is no doubt that gas hydrates play a major role in the oceanic carbon cycle.

One important characteristic of the oceanic gas hydrate reservoir is its sensitivity to environmental change (Karstens et al., 2018; Ruppel, 2011; Ruppel & Kessler, 2017), with possible impact on slope stability and global climate. Specifically, the dissociation of gas hydrate in marine sediments is primarily driven by changes in temperature, pressure, methane supply, and/or salinity (Dickens & Quinby-Hunt, 1994; Riboulot et al., 2018). Once methane is released from gas hydrates, it can be transported toward the seafloor and the water column and sometimes even to the atmosphere (Clark et al., 2010; Hovland et al., 1993; Padilla et al., 2019). However, a substantial fraction of methane is consumed through microbial activity in marine sediments. At seeps, the coupled activity of anaerobic methane-oxidizing archaea and associated sulfate-reducing bacteria in shallow subseafloor environments drives the anaerobic oxidation of methane (equation (1)), which results in the formation of authigenic carbonates (equation (2); Roberts & Aharon, 1994; Peckmann et al., 2001). Such carbonates represent excellent archives to investigate past relationships between hydrate dissociation events and environmental changes.



Among the geochemical tools that are commonly applied to seep carbonates, carbon, and oxygen stable isotopes can provide information on the source of methane-rich fluids and formation environments (Naehr et al., 2007; Peckmann et al., 2001). Since anaerobic oxidation of methane comes along with strong ^{13}C depletion, the most prominent characteristic of seep carbonates is their highly negative $\delta^{13}\text{C}$ composition (Peckmann & Thiel, 2004; Suess, 2018). Instead, the oxygen isotopic composition of seep carbonates usually reflects ambient temperature, carbonate mineral phase, and/or the ^{18}O composition of the fluids from which carbonates have precipitated. In particular, in hydrate-bearing sediments seep carbonates usually display positive ^{18}O values, reflecting the fact that gas hydrate dissociation typically releases ^{18}O -enriched water (Aloisi et al., 2000; Bohrmann et al., 1998).

Methane seeps are dynamic systems with long lifetimes and periodicities that result from the combination of various factors including sedimentation rate, hydrocarbon supply, bottom-water temperature, and seabed pressure (Bayon et al., 2009; Bayon et al., 2015; Tong et al., 2013). Constraints on the parameters controlling seepage activity and gas hydrate dynamics can be obtained by dating seep carbonates. While the utility of radiocarbon dating is limited due to the incorporation of methane-derived fossil carbon upon carbonate precipitation (Aharon et al., 1997), uranium-thorium (U-Th) dating of carbonate offers a unique chronometer to assess the timing and duration of methane seepage on relatively long timescales up to approximately 500,000 years (Teichert et al., 2003; Bayon et al., 2009; Bayon et al., 2015; Feng et al., 2010; Cr mi re et al., 2013; Cr mi re, Lepland, Chand, Sahy, Condon, et al., 2016; Tong et al., 2013; Himmler et al., 2019). In particular, dating of seep carbonates from hydrate-bearing drill cores can be used to investigate past gas hydrate dynamics throughout the Late Quaternary. However, to the best of our knowledge, only two studies have reported U-Th carbonate chronologies for long drill cores (Himmler et al., 2019; Liebetrau et al., 2014). It has been previously argued that past hydrate dissociation events mostly coincided with sea-level lowstands, hence suggesting that hydrostatic pressure was the most important factor controlling gas hydrate stability. However, this study including U-Th dating of seep carbonates from a ~100-m-long core drilled at the northern South China Sea (SCS) margin demonstrates that gas hydrate dissociation can also occur during sea-level highstands, providing new insight into the relationship of oceanic hydrate reservoirs and environmental change.

2. Materials and Methods

Sedimentary strata were cored during the second Guangzhou Marine Geological Survey gas hydrate expedition (GMGS2) in 2013 (Figure 1; Zhang et al., 2015). Five cores were obtained from site GMGS2-08 (water depth: ~800 m), referred to as core B (0–6 meters below the seafloor; mbsf), core C (0–22 mbsf), core G (20–28 mbsf), core E (58–70 mbsf), and core F (58–94 mbsf; Figure 2; Chen et al., 2016). Carbonate nodules and bivalve shells were abundant in cores B, C, E, and F. Two continuous seep carbonate layers were

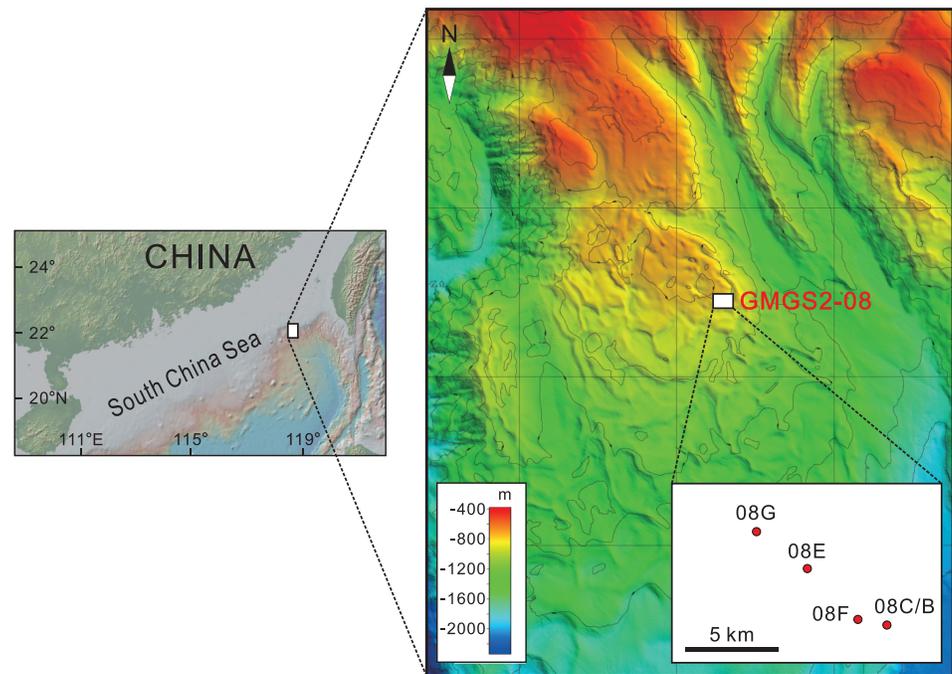


Figure 1. Maps showing the study region, the GMGS2-08 drilling site, and drill cores (08B, 08C, 08E, 08F, and 08G) on the northern continental slope of the South China Sea (modified from Chen et al., 2016).

identified in core F at 58.95–59.46 mbsf (08F-1M) and 61.52–62.55 mbsf (08F-2M). Seep carbonates and bivalve shells were sampled from core sections as whole samples and loose gravels (Figure 2). Samples were washed with deionized water and air dried prior to onshore investigation. Detailed information on the GMGS2 cruise and sampling can be found elsewhere (Chen et al., 2016; Zhang et al., 2015).

For X-ray diffraction (Rigaku D/MAX 2500PC Diffractometer), samples were crushed into powder using an agate mortar and pestle. Carbonate samples for carbon and oxygen stable isotopes obtained with a hand-held microdrill were analysed with a GasBench II preparation line connected to a Thermo Finnigan MAT253 mass spectrometer (Thermo Scientific, USA). All analyses were performed in the laboratory of the Guangzhou Marine Geological Survey (see supporting information for details).

U/Th dating was carried out on 10–25-mg microdrilled carbonate samples from the two carbonate layers of core F and a crust from core E (Figure 3 and supporting information S1). Nodules were discarded because of the presence of abundant detrital sediment (cf. Bayon et al., 2009). Whenever possible, both the microcrystalline carbonate matrix and early diagenetic cements were collected from the same sample. The microcrystalline matrix usually represents initial seepage-related precipitation, whereas cavity-filling cement typically reflects a later stage (Feng et al., 2010). Two subsamples with evident growth direction patterns were chosen for growth rate determination. Measurements were made on a multi-collector inductively coupled plasma mass spectrometer (Thermo-Finnigan Neptune) at Xi'an Jiaotong University. Analytical protocols for the separation and purification of U and Th from carbonates and instrument dispositions are the same as those to Edwards et al. (1987), Shen et al. (2012), and Cheng et al. (2013).

3. Results

3.1. Mineral and Stable Isotope Compositions of Seep Carbonates

The carbonate content of samples varies between 68.3% and 100% (mean: 90.3%). Carbonates are mainly composed of aragonite (mostly >90 wt%) with minor amounts of calcite (Table S1). The $\delta^{13}\text{C}$ values show little variation between -52.9‰ and -47.2‰ (08F-1M) and from -54.1‰ to -40.5‰ (08F-2M) in the two carbonate layers, respectively, with corresponding mean values ($\pm 1\sigma$) of $-49.9 \pm 2.1\text{‰}$ ($N = 10$) and

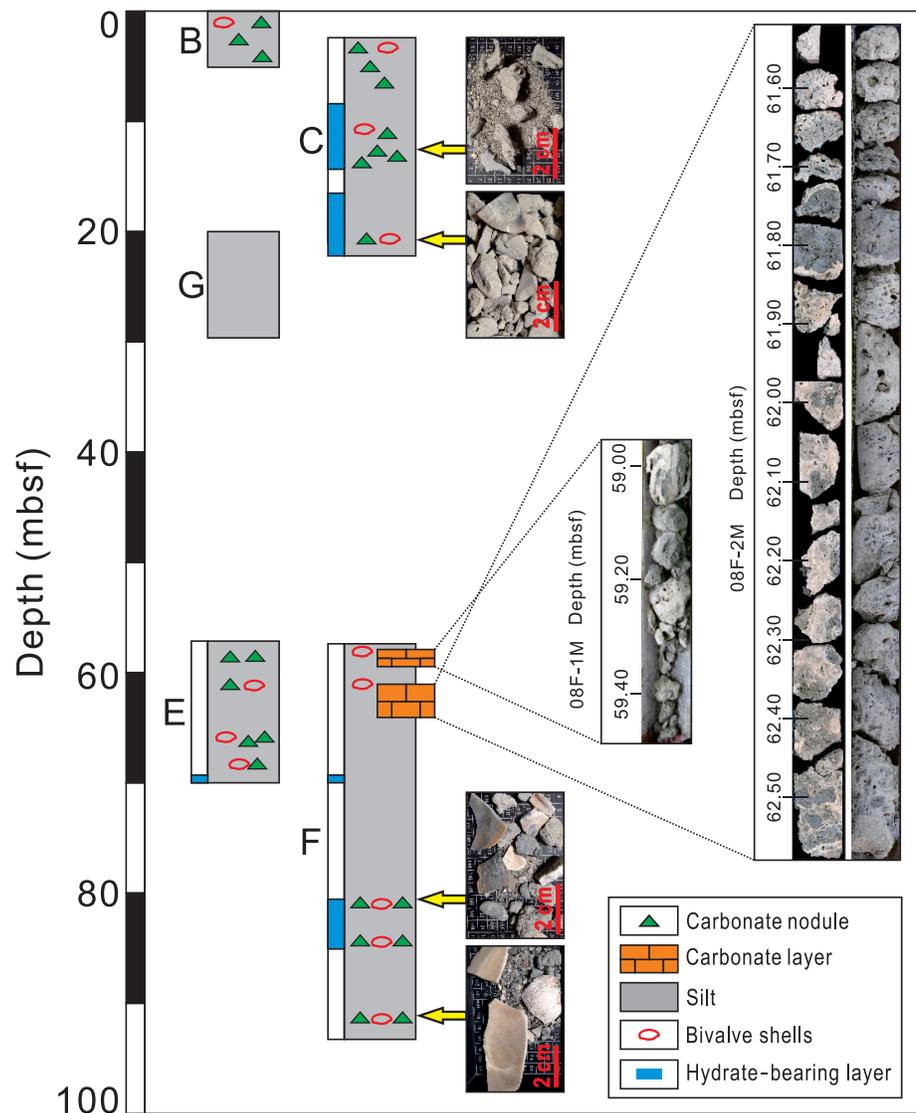


Figure 2. Distribution of sediment cores 08B, 08C, 08E, 08F, and 08G at the GMGS2-08 site.

– $46.6 \pm 3.8\text{‰}$ ($N = 35$). The $\delta^{18}\text{O}$ values for 08F-1M and 08F-2M carbonates fall between 2.9‰ and 3.8‰ ($3.2 \pm 0.3\text{‰}$; $N = 10$) and 3.0‰ to 4.2‰ ($3.6 \pm 0.3\text{‰}$; $N = 35$), respectively (Table S2; Figure S2).

3.2. Carbonate U-Th Ages

The U-Th dating results of seep carbonates are shown in Table S3 and Figure 4. A total of five dates was obtained for microcrystalline matrix samples ($133,100 \pm 7,800$ – $128,300 \pm 14,400$ years BP) and 36 dates for carbonate cements ($133,300 \pm 500$ – $112,700 \pm 400$ years BP), hence yielding a similar age distribution, although matrix samples were typically $\sim 3,000$ – $4,000$ years older than associated cements from the same sample. One carbonate crust (depth: 61.0–61.1 mbsf) from hole 08E yielded a U-Th age of $130,800 \pm 500$ years BP.

4. Discussion

4.1. Seep Carbonates at Site GMGS2 Record the Dissociation of Gas Hydrate

The expected equilibrium oxygen isotopic composition of aragonite can be calculated using the oxygen isotope fractionation equation of the aragonite-water system of Kim et al. (2007):

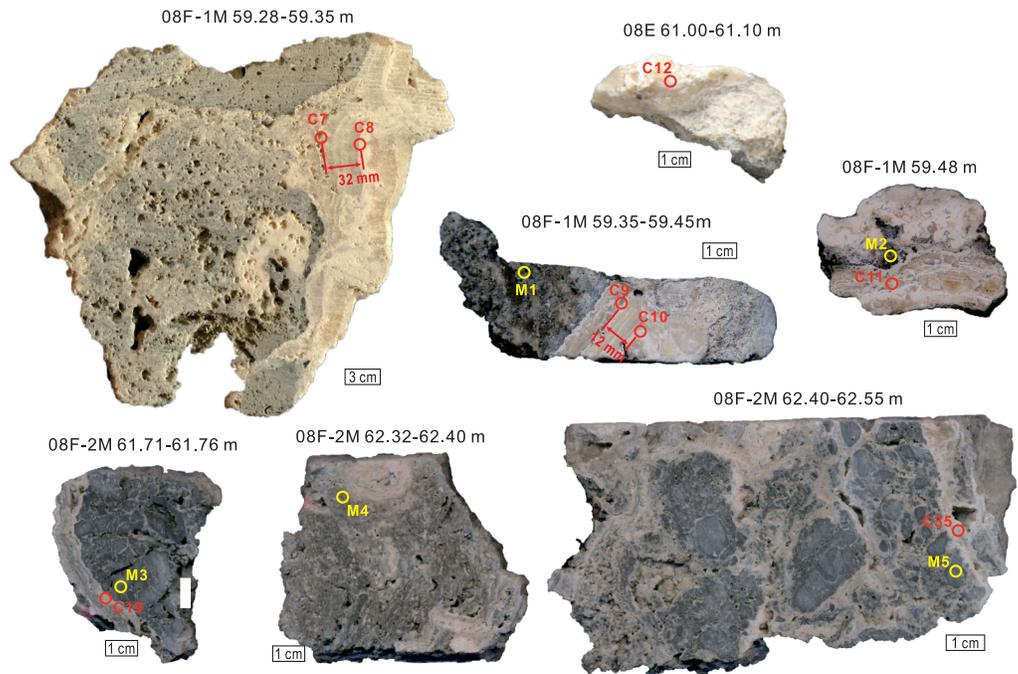


Figure 3. Selected seep carbonates from core 8F with U/Th sample locations. The depths (meters below the seafloor) of samples are indicated above the images.

$$10^3 \ln \alpha_{\text{ara.-water}} = 17.88 \times 10^3 / T - 31.14, \quad (3)$$

$$\delta^{18}\text{O}_{\text{VPDB}} = 0.97006 \times \delta^{18}\text{O}_{\text{VSMOW}} - 29.94, \quad (4)$$

(Friedman & O'Neil, 1977)

$$\alpha_{\text{mineral-water}} = (\delta^{18}\text{O}_{\text{mineral}} + 1000) / (\delta^{18}\text{O}_{\text{water}} + 1000), \quad (5)$$

where the present bottom-water temperature (T) is 5.4 °C (278.55 K; Han et al., 2014; Yang, Shi, et al., 2018), and the $\delta^{18}\text{O}_{\text{water}}$ value is -0.3‰ Vienna Standard Mean Ocean Water (VSMOW) (Zhu et al., 2003; Feng & Chen, 2015). The calculated theoretical equilibrium $\delta^{18}\text{O}$ value is 2.4‰ Vienna Pee Dee Belemnite (VPDB). The equilibrium $\delta^{18}\text{O}$ value is consequently about 1.0‰ lower than the measured $\delta^{18}\text{O}$ values, pointing at a source of ^{18}O -enriched fluids during carbonate precipitation. While ^{18}O -rich fluids may derive from different processes including clay mineral dehydration (Hesse, 2003), gas hydrate dissociation represents the most probable cause of ^{18}O enrichment for the studied seep carbonates (cf. Hesse & Harrison, 1981; Sha et al., 2015; Ussler & Paull, 1995; Zhang et al., 2015). The circumstance that samples from the deeper 08F-2M layer yielded higher $\delta^{18}\text{O}$ values than samples from the shallower 08F-1M layer may suggest a greater contribution of hydrate water in the former. Similar to what has been put forward in previous studies to account for the presence of massive authigenic carbonate layers in the sedimentary record at cold seeps (Bayon et al., 2015; Berndt et al., 2014; Crémière, Lepland, Chand, Sahy, Kirsimäe, et al., 2016; Ketzer et al., 2018; Suess et al., 1999), our data strongly suggest that the formation of GMGS2 carbonate layers was the consequence of gas hydrate dissociation. This hypothesis is supported by the predominance of aragonite, indicative of high methane flux with the sulfate-methane transition zone located close to the seafloor (Burton, 1993; Luff & Wallmann, 2003). The occurrence of bivalve shells in adjacent strata (Figure 2) is in accord with such interpretation, indicating active methane seepage and the presence of chemosynthesis-based seep communities at that time.

4.2. Estimating Past Methane Flux Caused by Gas Hydrate Dissociation

Any attempt to quantify the total amount of methane released during an episode of gas hydrate dissociation is challenging, and we only aim at providing a back-of-the-envelope estimate of the total methane flux

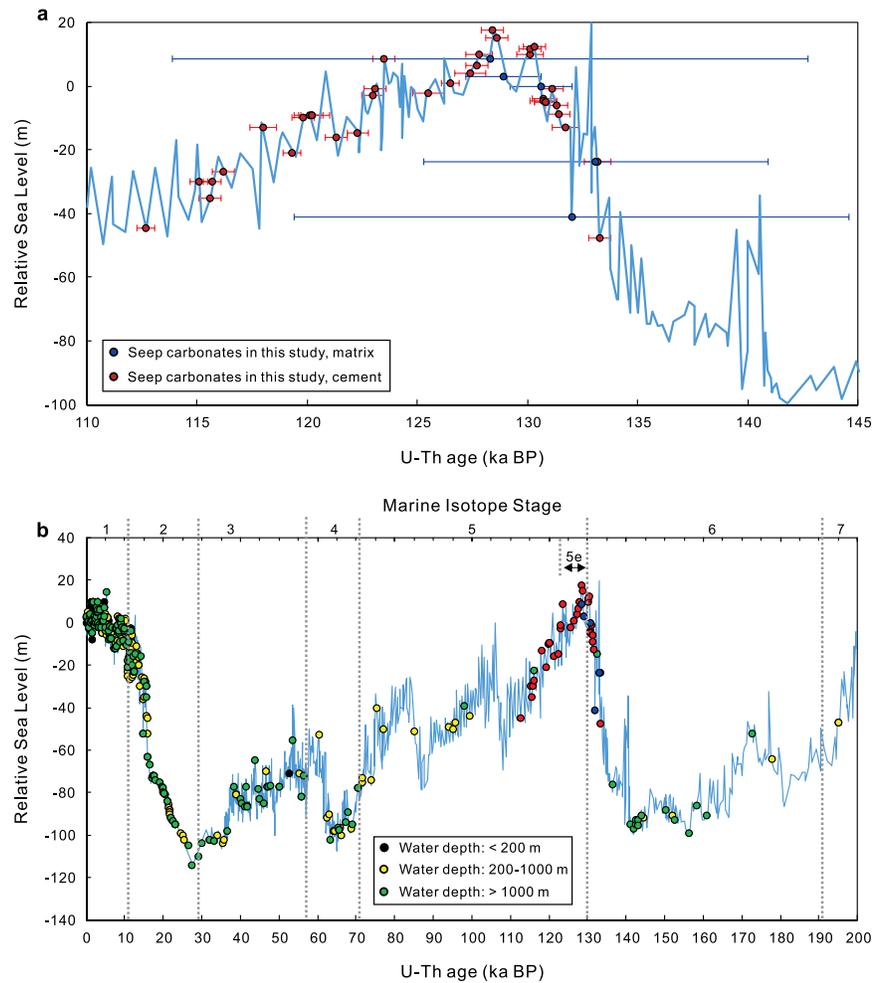


Figure 4. Timing of seep carbonate formation (U-Th ages) versus global sea-level changes. Sea-level curve from Rohling et al. (2009). (a) Seep carbonates in this study. (b) Previously reported seep carbonates grouped by water depth (black, yellow, and green circles; see Table S4 for detail) and seep carbonates in this study (red and blue circles; Table S3). Samples from water depths greater than 1,000 m (Aharon et al., 1997; Bayon et al., 2009; Bayon, Loncke, et al., 2009; Bayon et al., 2013, 2015; Çağatay et al., 2018; Crémière et al., 2013; Feng et al., 2010; Himmler et al., 2015, 2019; Kutterolf et al., 2008; Lalou et al., 1992; Liebetrau et al., 2010, 2014; Mazumdar et al., 2009; Prouty et al., 2016; Watanabe et al., 2008) represent sites with a weak link between hydrostatic pressure and hydrate dissociation, whereas samples from water depths less than 200 m represent sites where hydrate dissociation was not involved (Aharon et al., 1997; Crémière, Lepland, Chand, Sahy, Kirsimäe, et al., 2016; Feng et al., 2010). Samples from water depths between 200 and 1,000 m represent sites with a possible link between hydrostatic pressure and hydrate dissociation (Çağatay et al., 2018; Crémière et al., 2013; Han et al., 2014; Himmler et al., 2016; Liebetrau et al., 2010, 2014; Mazzini et al., 2017; Prouty et al., 2016; Ruffine et al., 2013; Teichert et al., 2003; Tong et al., 2013; Yang, Chu, et al., 2018). Note that the Norwegian margin was glaciated during the last Ice Age. The lowstand consequently corresponds to a time of hydrate accumulation due to pressure exerted by the grounded Scandinavian Ice Sheet and not hydrate dissociation (Crémière, Lepland, Chand, Sahy, Condon, et al., 2016; Sauer et al., 2017).

associated with the destabilization of gas hydrate layers. Using a simple model, we calculate methane flux as follows:

1. gas hydrate is estimated to cover an area of about 55 km² today (Zhang et al., 2015).
2. we consider a three-layer gas hydrate deposit (50 m thick in total), including a shallow (9.0–23.0 mbsf), middle (58.0–63.0 mbsf), and deep part (66.0–94.0 mbsf).
3. the average gas hydrate saturation estimated from pore water freshening analysis ranges from 45% to 55% of the total pore space (Zhang et al., 2015; we use 50% for calculation);
4. 1 m³ of natural gas hydrate contains 164 m³ of methane;

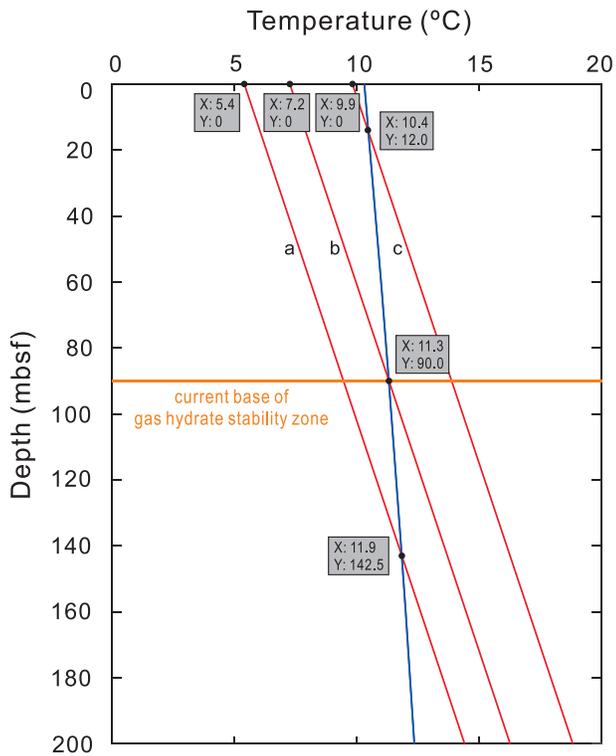


Figure 5. Depth-temperature phase diagram of the gas hydrate stability zone. The geothermal gradient (0.045 K/m) is from Wang et al. (2016). The blue line represents the border line of the gas hydrate stability zone; the orange line represents the current base of gas hydrate stability zone; the red lines a, b, and c represent the seafloor temperatures of 5.4, 7.2, and 9.9 °C, respectively.

5. $1 \text{ m}^3 \text{ CH}_4 = 44.64 \text{ mol CH}_4$; and
6. previous studies indicated that a temperature increase of 4 °C results in a 30% thinning of the gas hydrate stability zone (Milkov & Sassen, 2003). Therefore, the total amount of methane equals $55 \times 10^6 \times 50 \times 50\% \times 164 \times 44.64 \times 30\% = 3 \times 10^{10} \text{ mol}$, corresponding to an average methane flux of about $26 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{year}$.

This estimate is similar to an estimate made for Blake Ridge ($\sim 10 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{year}$; Dickens, 2001) but significantly lower than estimates made for Hydrate Ridge (up to $300 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{year}$; Torres et al., 2002) and the Gulf of Mexico (up to $2,000 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{year}$; Solomon et al., 2009). The spatial heterogeneity and episodic changes in seep activity typically hamper attempts to upscale fluid flux to larger areas (Ruppel & Kessler, 2017). However, seep carbonates collected from drill cores above hydrate reservoirs have the potential to facilitate the reconstruction of the chronologies of past methane emissions, providing valuable constraints on the local and global drivers of long-term seepage from subsurface methane reservoirs (cf. Himmler et al., 2019).

4.3. Gas Hydrate Dissociation During Sea-Level Highstands

Calculated U-Th ages of GMGS2 seep carbonates indicate that the inferred hydrate dissociation event and associated seepage activity occurred between $133,300 \pm 500$ – $112,700 \pm 400$ years BP, a period of time that fully encompasses the last interglacial period. This timing of enhanced methane seepage at the northern SCS margin is consistent with biostratigraphic constraints using foraminifera (Zhang et al., 2015), which provided an estimated age of 120,000 years BP for the same sediment horizon at 67.90 mbsf. The similar ages of sediment and associated authigenic carbonates also agree with carbonate precipitation taking place close to the sediment-seawater interface. A variety of factors, including bottom-

water temperature, hydrostatic pressure, thermal gradients in the sediment, and pore water salinity, control the stability of gas hydrate (Milkov & Sassen, 2001). Since there is no evidence for volcanic or hydrothermal activity in the study area and other factors potentially favoring gas hydrate dissociation are not apparent, it is very likely that dissociation was induced by changes in bottom-water temperature.

During MIS 5e, the most recent interglacial period, sea level and temperature were even higher than today (Polyak et al., 2018). During the transition from the glacial to the interglacial period, sea-level rise was accompanied by a gradual temperature increase of bottom waters (Rohling et al., 2014). For example, the glacial-interglacial increase of bottom-water temperature in the Atlantic Ocean was 3–4 °C (Cutler et al., 2003; Dwyer et al., 1995; Labeyrie et al., 1987; Martin et al., 2002). Based on the Mg/Ca ratio in ostracods, Dwyer et al. (1995) even suggested that the increase of bottom-water temperature was 4.5 °C during the last two 100,000-year glacial-interglacial cycles. To the best of our knowledge, no record of bottom-water temperature during the MIS 5e exists for the SCS, but a similar increase of temperature had likely occurred.

To this end, we simulate the dynamic changes of gas hydrate reservoirs in the northern SCS in the context of inferred elevated temperatures (cf. Sloan & Koh, 2008). It becomes apparent that the base of the gas hydrate stability zone is 142.5 mbsf at current bottom-water temperature (red line a, Figure 5), which is deeper than the actual depth at present (~ 90 mbsf, Zhang et al., 2015); the gas hydrate is thus currently stable. However, gas hydrate at 90 mbsf would become unstable if the bottom-water temperature exceeds 7.2 °C (red line b, Figure 5). Such elevated bottom-water temperature is very likely for MIS 5e (Tachikawa et al., 2009; Visser et al., 2003). Simulating a possible maximum bottom-water temperature of 9.9 °C during MIS 5e (cf. Dwyer et al., 1995) would result in the base of the gas hydrate stability zone being up to 12 mbsf (red line c, Figure 5), hence resulting in the dissociation of almost all gas hydrates in the sediment column.

The increase in bottom-water temperature during MIS 5e was to some extent hysteretic compared to surface seawater and atmospheric temperatures, which may explain why seepage activity did not already occur at the onset of the transition from glacial to interglacial (i.e., the lowest sea level at 135,000 years; Figure 4b). While the impact of bottom-water temperature change on the gas hydrate reservoir is expected to be mitigated due to hysteresis, this effect should be small (less than a few millennia) compared to the relatively long period of sustained fluid seepage inferred from our U-Th data (about 21,000 years long). Indeed, it has been argued that it takes 700–2,000 years for seawater to circulate within the seabed (Gebbie & Huybers, 2012; Primeau, 2005). Similarly, a recent study suggested that for most of the deep Pacific, 800–1,400 years are required for an efficient transmission of a temperature change (Gebbie & Huybers, 2019).

Dickens et al. (1995) were the first to suggest a putative link between temperature rise and hydrate dissociation when explaining the global carbon isotope excursion (2–3‰) during the Paleocene-Eocene thermal maximum. While the causal relationship between hydrate dissociation and the Paleocene-Eocene thermal maximum remains speculative (Dickens, 2011), the effect of elevated temperature on hydrate stability is unquestionable (Berndt et al., 2014; Cardoso & Cartwright, 2016; Hornbach et al., 2004; Kennett, 2000; Ménot & Bard, 2010). A number of studies have attempted to show that the stability of gas hydrates is more sensitive to temperature variations than to pressure. Temperature sensitivity is particularly pronounced in the Arctic and other shallow seas, where an increase in water temperature of only 1 °C may induce methane release from the seabed, while seawater of the deeper ocean (>1,000 m) seems relatively insensitive to temperature change on short timescales (Biastoch et al., 2011; Buffett & Archer, 2004; Mienert et al., 2005; Reagan & Moridis, 2007; Westbrook et al., 2009). Since the study area in the SCS is relatively shallow (~800-m water depth), gas hydrate dissociation and methane release were likely caused by rising temperatures during MIS 5e.

5. Conclusions and Outlook

Our work not only confirms that the formation of seep carbonate in the northern SCS is inextricably linked to gas hydrate but also provides, for the first time, evidence for extensive seep activity during the sea-level highstand associated with MIS 5e. Research on methane release during MIS 5e remains scarce due to the lack of suitable carbonate samples for dating. As a consequence, further research on buried seep carbonates collected through drilling will be required in the future to refine our understanding on the driving factors of gas hydrate dissociation on long timescales. At the same time, we must admit that our current estimates of total methane fluxes during past hydrate dissociation events are still inaccurate, and the mechanisms controlling seepage activity are only imperfectly understood. In order to test our hypothesis, the use of "clumped isotopes" in future studies could help to constrain bottom-water temperature during precipitation of seep carbonates. Although their application to seep carbonates may be complicated by kinetic isotope effects (Lloyd et al., 2016), future assessment of the role of temperature in gas hydrate dynamics should include this methodology (Zhang et al., 2019). Overall, our research elucidates an unexpected relationship between seepage activity and climate change during MIS 5e, contributing to a better understanding of the interdependence of climate change and the stability of gas hydrate reservoirs.

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Acknowledgments

We thank the crew and scientists of the research vessel during the GMGS2 gas hydrate drilling expedition. Yuncheng Cao (Shanghai Ocean University) is acknowledged for assistance during preparation of the gas hydrate phase diagram. This research was supported by the NSF of China (Grants 41776066, 41773091, 41730528, and 41888101) and the Qingdao National Laboratory for Marine Science and Technology (Grant QNLM2016ORP0204). Xudong Wang acknowledges the China Scholarship Council for supporting a research visit to IFREMER. Data sets for this research are available in the following in-text data citation references: supporting information, Mendeley Data, and V3 (<https://doi.org/10.17632/nkdd44zcyk.3>). This article benefited from insightful comments of three anonymous reviewers.

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