Palaeogeography, Palaeoclimatology, Palaeoecology 386 (2013) 23–33

Contents lists available at SciVerse ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Formation of methane-related authigenic carbonates within the bioturbated zone — An example from the upwelling area off Vietnam

Andreas Wetzel *

Geologisch-Paläontologisches Institut, Universität Basel, Bernoullistrasse 32, CH-4056 Basel, Switzerland

ARTICLE INFO

Article history:
Received 7 December 2012
Received in revised form 25 April 2013
Accepted 30 April 2013
Available online 15 May 2013

Keywords:
South China Sea
Methane seep
Authigenic carbonate
Trace fossils

ABSTRACT

In the biologically high-productive area off Vietnam authigenic carbonates formed in the bioturbated zone while methane was oxidized microbially under anaerobic conditions. Open crustacean burrows (*Spongeliomorpha*) connected to the seafloor acted as conduits for methane as suggested by intense cementation of burrow walls having a light C-isotope signature. Although seawater circulated within these open, inhabited tubes, conditions favorable for anaerobic oxidation of methane (AOM) occurred <1 mm away from the tubes. Trace fossils document a gradual stiffening and induration of the material finally reaching hardground condition (indicated by *Trypanites*). Cementation started at several spots that coalesced later to form the nodule. Carbon isotopes indicate a biogenic methane source ($\delta^{13}C_{carb}$ reaching −49 to −40‰ V-PDB), while higher $\delta^{13}C$ values imply mixing with carbon from other sources that is very likely within the bioturbated zone. The cement is generally fine grained (<5 μm); calcite forms about 3/4 of the cement, dolomite about 1/4, and aragonite a minor proportion. High $\delta^{18}O$ values of +5 ± 1‰ reflect the general ^{18}O-enriched isotope signature of the bottom water in South China Sea especially during glacial times, but influence of water released from decaying gas hydrate cannot be excluded. The studied nodule was found on top of a slump that displaced it.

1. Introduction

The South China Sea represents a biologically highly productive area and especially along its margins organic-rich sediments act as carbon sinks (e.g., Wiesner et al., 1996; Liu et al., 2002). Furthermore, the continental margin deposits contain numerous hydrocarbon accumulations (e.g., Fraser et al., 1997; Wu et al., 2005). Consequently, evidence for gas hydrates and methane seeps has been commonly found in the South China Sea (e.g., Chen et al., 2005; Wang et al., 2006). In the northern South China Sea methane seeps and gas hydrates were observed at a considerable number of sites (e.g., Wu et al., 2005; Yang et al., 2006; Han et al., 2008). For the upwelling area off Vietnam such findings are, however, rare in spite of its high productivity and known hydrocarbon resources (e.g., Chen et al., 2005; Wang et al., 2006; Fyhn et al., 2009). In this study the first find of authigenic methane-derived carbonates is reported, that, however, occurs on top of a slump.

In the rock record authigenic carbonates or remains of methanotroph organisms are often the only indication of former presence of methane (e.g., Conti and Fontana, 1999; Pierre and Rouchy, 2004; Campbell, 2006; Bojanowski, 2007). For methane-derived carbonates stable carbon isotopes help to decipher microbially mediated processes during methanogenesis, methane oxidation and mixing with carbon from other sources (e.g., Suess and Whiticar, 1989; Whiticar, 1999; Campbell et al., 2010; Bojanowski, 2012).

Carbonate precipitation induced by methane oxidation may take place from the seafloor to burial depth exceeding hundred meters (e.g., Matsumoto and Matsuhisa, 1986). Within marine sediments large amounts of methane are microbially oxidized under anaerobic conditions (AOM = anaerobic oxidation of methane) by a consortium of methane-oxidizing archaea surrounded by sulfate-reducing bacteria (e.g., Boetius et al., 2000; Knittel and Boetius, 2009, and references therein). During AOM the following net reaction takes place (e.g., Martens and Berner, 1974)

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O.$$

The produced bicarbonate can precipitate as authigenic carbonate (e.g., Ritger et al., 1987; Boetius et al., 2000). It has been invoked that carbonate precipitation is biocatalytically stimulated by extrapolymeric substances (EPS) produced by microbes (e.g., Reitner et al., 2005; Hendry et al., 2006). At methane seeps, authigenic carbonate bodies commonly grow downward within the sediment towards the direction of methane supply or along geochemical interfaces (e.g., Teichert et al., 2005), while degassing and dewatering tubes become cemented and form so-called seepage-associated carbonates (e.g., Greinert et al., 2001; Han et al., 2008). If the methane flux lasts for some time, microbial mediation leads to the formation of carbonate chimneys on the seafloor that may develop to chemoherms (e.g., Teichert et al., 2005). At methane seep sites commonly a specialized fauna related to

* Tel.: +41 61 2673585; fax: +41 61 267 3613.
E-mail address: andreas.wetzel@unibas.ch.

0031-0182/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.palaeo.2013.04.027

methanotroph chemosymbionts establishes (e.g., Campbell, 2006 and references therein).

The studied authigenic carbonates belong to the not often reported case of nodules being formed within the bioturbated zone, and thus deserve detailed investigation (e.g., Greinert et al., 2001; Campbell et al., 2010). On the one hand, the activity of bioturbating organisms extends the oxygenated and sulfate-rich zone downward (e.g., Pischedda et al., 2008), on the other hand, open tubes may act as conduits for methane and enhance its flux to the seafloor. Furthermore, the connection of open burrows to the bottom water induces mixing processes between bicarbonate derived from AOM and those from other sources close to the seafloor and hence, affect the isotopic composition of authigenic carbonates (e.g., Luff et al., 2004). It is the purpose of the present study to combine ichnological observations with geochemical and structural data to better characterize the role of bioturbation at methane seep sites.

2. Regional setting

The South China Sea represents a western marginal sea of the Pacific Ocean, surrounded by the Southeast Asian mainland in the north and west and the islands of Borneo, Palawan, Luzon and Taiwan to the south and the east (Fig. 1). The South China Sea has large shelf regions, such as the Sunda Shelf, and deep basins as between the Philippines and Vietnam.

The only deep connection between the South China Sea and the Pacific Ocean is the Bashi Channel, between Taiwan and Luzon (Philippines), that has a sill depth of ~2600 m (Fig. 1). Oxygenated bottom waters (ca. 2 ml O_2/l; Wyrtki, 1961) are introduced into the South China Sea via that connection (Chao et al., 1996). A uniform water mass occupies the South China Sea between 1500 and 3500 m depth. During interglacial times this water mass exhibited a $\delta^{18}O$ value of ~ +2‰ that might have increased up to ~ +4‰ during glacial times (e.g., Lin, 2003).

The entire region of the South China Sea is under the influence of the monsoon system, during summer, northeasterly directed winds result in strong coastal upwelling at ~10° N (e.g., Tomczak and Godfrey, 1994; Liu et al., 2002; Xie et al., 2003). During November–March the northwest monsoon induces upwelling off northwest Luzon, off the northern Sunda Shelf and in the central South China Sea. Due to upwelling during the high seasons of the monsoon (see above) the particle flux to the seafloor increases by a factor of 3–4; ~70% of the total annual organic matter flux is exported to the deep sea (Wiesner et al., 1996). In the South China Sea there is a strong shift in monsoon regime between glacial and interglacial conditions. Glacial periods are characterized by strong winter monsoon and weak summer monsoon, during interglacial times the situation is reversed like today (Wang et al., 1999).

Although upwelling off Vietnam strengthened during interglacial periods and weakened during glacial times, the organic matter content of bathyal sediments is enlarged during glacial times due to the development of an O_2-minimum layer (Löwemark et al., 2009; Wetzel et al., 2011). Because of upwelling and O_2-minimum zone, the bathyal sediments off Vietnam contain a high amount of organic matter (0.7–1.2% C_{org}; e.g., Wetzel et al., 2011). These conditions in bathyal depth led Wang et al. (2006) to assign this region off southern Vietnam as potential gas-hydrate bearing area.

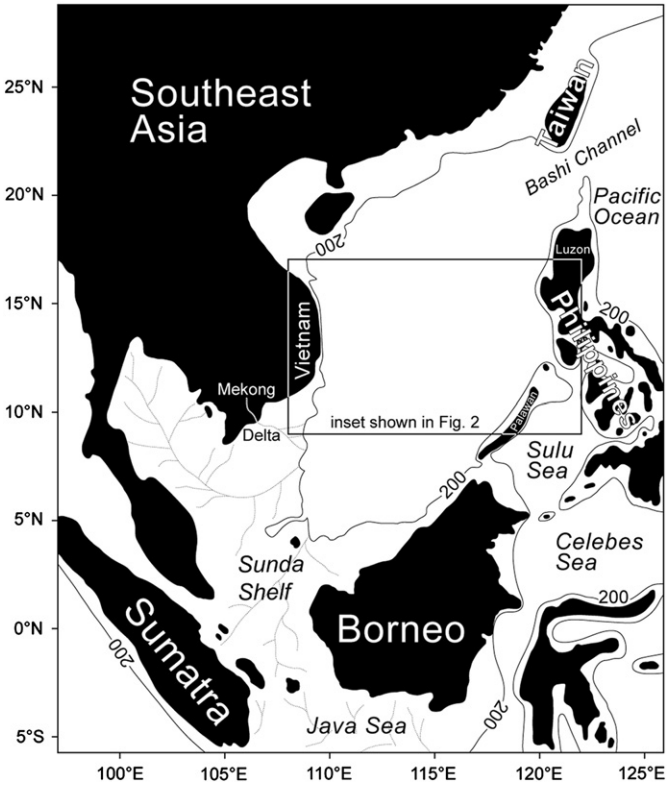

Fig. 1. Location of the study area. Inset represents area shown in Fig. 2.

3. Material and methods

Cores were collected during Cruise 187 of the German research vessel *Sonne* in 2006 (Wiesner et al., 2006). The present study is based on two cores taken at the site SO-187-060 (11°50.097′ N/110° 0.637′ E) in 1864 m water depth (Fig. 2; Table 1). One core is about 9 m long and 12-cm wide and was taken by a gravity corer and the other is 40 cm long and was taken by a 50 × 50 cm^2 box corer.

Description of the cores is based on onboard visual observations, digital camera images, and X-ray radiographs. For X-ray radiography, about 1 cm thick sediment slabs were taken onboard from the spilt core surface directly after opening and sealed to prevent desiccation. The slabs were irradiated at the Academic Center of Radiology of Kiel (Germany) using a Swissray ddR Multi System operated at 40 kV and 100 mA and automatically controlled radiation time.

Trace fossils in cores do not exhibit all characteristics such as surficial or the 3-D architectural morphology, even in serial sections. The taxonomic evaluation of the burrows in this study, therefore, is restricted to the ichnogenus level (e.g., Häntzschel, 1975; Gerard and Bromley, 2008).

Porosity was determined by two methods. Porosity of soft sediment was calculated from micro-resistivity measurements carried out by using Northwest Metasystems equipment. The probe was similar to the system described by Andrews and Bennett (1981). Micro-resistivity measurements were calibrated by using muddy sediments of known porosity. Porosity of cemented sediments was calculated from water loss of a completely water-saturated sample of known volume after drying for 24 h at 110 °C (e.g., Boyce, 1976). To calculate the initial porosity that the sediment has had at the seafloor, the total carbonate volume minus the volume of the pelagic/detrital carbonate was added to the still open porosity.

Shear strength was determined by using a fall-cone penetrometer constructed by Norwegian Geotechnical Institute (Hansbo, 1957). However, the original apparatus was changed in a way that cone with handle was fixed 5″ after release by an automatically closing break.

Bulk powdered sediment samples were put into an Aluminum trail for XRD mineral identification by using a Siemens D 5000 diffractometer. Cu Kα1 radiation was used measuring 0.05 · 2θ steps for 25 min. Minerals were identified by the software package Diffracto plus (EVA and TOPAS) provided by Bruker Analytical X-Ray Systems. Scanning electron microscopic analyses were carried out on dried samples sputtered with Au by using a Philips ESEM 5000 having an elemental