Authigenic carbonates from an active cold seep of the northern South China Sea: New insights into fluid sources and past seepage activity

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ABSTRACT

Site F (also named Formosa ridge) represents the most vigorous cold seep on the northern South China Sea continental slope. In order to constrain the fluid sources and intensities of seepage, we investigated the petrography, mineralogy, stable carbon and oxygen isotopic compositions, element geochemistry and radiocarbon dating of authigenic carbonate rocks retrieved from the seafloor. Carbonate rocks mainly occurred as crusts, nodules, and nodular masses incorporated in carbonate breccias. The carbonates were comprised mainly of high-Mg calcite and aragonite. The δ^{13}C of authigenic carbonate varied from $-55.3‰$ to $-34.3‰$ (mean: $-48.5‰$; $n=47$) vs. V-PDB, suggesting biogenic methane is the dominant carbon source fuelling the system. The $\delta^{18}O_{Carbonate}$ values were from $+3.6‰$ to $+4.8‰$ (mean: $+3.9‰$; $n=47$). The observed ^{18}O-enrichment in relation to calculated equilibrium values in the carbonates probably reflects dissolution of gas hydrates. Combination of seafloor observations and the obtained AMS ^{14}C ages suggest that (1) initiation of methane seepage from at least 10.6 ka ago; (2) environmental conditions may have been favorable for enhanced fluid seepage around 6 ka BP and (3) relatively low intensity of seepage from 2 ka BP till today.

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1. Introduction

Hydrocarbon seepage is common in marine settings worldwide (e.g. Campbell, 2006; Judd and Hovland, 2007; Boetius and Wenzhöfer, 2013). Anaerobic oxidation of methane (AOM) is the key process at seeps (Boetius et al., 2000). A direct consequence of AOM is the precipitation of authigenic carbonate minerals (Hinrichs et al., 1999; Suess, 2014). Such carbonate, thus provides an excellent archive of past seepage activity and associated environmental parameters (e.g. Bayon et al., 2009, 2013; Peckmann et al., 2009; Feng et al., 2010, 2014; Han et al., 2014).

Seep carbonates are known to have a wide range of mineralogical as well as carbon and oxygen isotopic compositions (e.g. Ritger et al., 1987; Peckmann et al., 2001; Peckmann and Thiel, 2004; Naehr et al., 2007; Roberts and Aharon, 1994; Campbell et al., 2010; Roberts et al., 2010; Pierre et al., 2012, 2014). The dominance of high-Mg calcite (HMC), aragonite and other less common minerals such as low-Mg calcite, dolomite, and others has been documented by various authors (e.g. Roberts and Aharon, 1994; Aloisi et al., 2000; Peckmann et al., 2001; Peckmann and Thiel,

2004; Greinert et al., 2001; Naehr et al., 2007). δ^{13}C and δ^{18}O of seep carbonates provide information pertaining to the composition and temperature of fluids from which carbonates precipitated (e.g. Naehr et al., 2000, 2007; Peckmann and Thiel, 2004; Han et al., 2014). Moreover, seep-related authigenic minerals provide an important geological archive, as they represent one of the few permanent records of an otherwise ephemeral and perhaps changing fluid flow regime (Mazzini et al., 2004, 2006; Roberts et al., 2010; Crémière et al., 2013).

Recent studies indicate that the physical, chemical, and biological processes at seeps can change significantly with time (e.g. Greinert, 2008; Roberts, 2001; Solomon et al., 2008; Schneider von Deimling et al., 2011), and such temporal variability can be expressed by the difference in geochemical and mineralogical signatures of the associated authigenic carbonates (e.g. Bayon et al., 2009; Feng et al., 2010, 2014; Birgel et al., 2011; Naehr et al., 2007; Peckmann et al., 2001, 2009; Pierre et al., 2012, 2014; and many others). Most cold seeps have their specific lifetimes and cyclicities, which might be controlled by factors such as the exhaustion of hydrocarbon sources and shift of pressure gradients between pore water and hydraulic pressure of seawater (Aharon et al., 1997; Teichert et al., 2003). Therefore, defining the time integrated variation of seepage dynamics is critical to understand the nature of seeps and accordingly, provides insights into factors that influence the seepage.

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On northern continental slope of the South China Sea (SCS), authigenic carbonates have been recovered from over 30 seep sites, such as Site 1, Site 2, and Site 3 (Fig. 1). Constant research on these carbonates since 10 years ago had produced an impressive body of literatures (e.g. Chen et al., 2005; Suess, 2005; Han et al., 2008, 2014; Ge et al., 2010; Guan et al., 2013; Tong et al., 2013 and many others). However, a common feature of these seeps is that they are not active recently (at least since 11.5 ka BP; Tong et al., 2013; Han et al., 2014) except Site 3, which is still weakly active based on methane concentration profiles of the water column (Suess, 2005). The 2013 deep submergence vehicle (DSV) Jiaolong dives were designed to fill the data gap between inactive and active seeps. Our study area, Site F (also named Formosa Ridge, 22°06.922N; 119°17.130E; Fig. 1) represents the most vigorous cold seep known on the northern SCS continental slope. The motivation of this study is to (1) provide the insights into fluid sources and (2) evaluate the dynamics of seepage over the course of carbonate formation.

2. Site characteristics and sampling

During Dayang 31 cruise in summer 2013, DSV Jiaolong was used to conduct seafloor observation and sampling at Site F on continental slope of the South China Sea (SCS; Fig. 1). The geologic setting of this site has been described in detail by Liu et al. (2008). Briefly, underneath the southern summit of the site, seismic profiles identify a well-developed bottom simulating reflections (BSR) and a clear vertical migration pathway from the deep subsurface to the ocean bottom (Liu et al., 2008). The NNW-SSE trending Site F is the result of canyon erosion in the north, west, and east (SONNE Cruise Report SO227 TAIFLUX, 2013). The northern summit of the site has water depth about 1100 m while the southern one has a water depth of ~1120 m.

3. Materials and methods

Authigenic carbonates from Site F were collected using DSV Jiaolong in 2013 (Table 1). Carbonate samples were obtained from mound-like buildups, crusts on the seafloor and nodules in the subsurface

sediment (< 50 cm). These samples were described, photographed, and subsequently stored at room temperature for sectioning, subsampling, and analysis. Water depth at the site was approximately 1120 m and the bottom water temperature was typically around 3.5 °C.

Semiquantitative mineralogy of the bulk samples was determined by X-ray diffraction (XRD; Rigaku DXR 3000) at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG, CAS). Sample preparation and measurements were described by Tong et al. (2013). Calcite with less than 5 mol% $MgCO_3$ is considered as low-Mg calcite (LMC), whereas calcite with 5–20 mol% $MgCO_3$ is referred to as high-Mg calcite (HMC; Burton and Walter, 1991). Carbonate phases with 30–40 mol% $MgCO_3$ are classified as protodolomite (Naehr et al., 2007). Petrographic observations of thin sections were made with an optical microscope.

Powder samples for $\delta^{13}C$ and $\delta^{18}O$ analyses were taken from the surfaces of polished slabs using a dental drill. The analyses were conducted using a Gasbench II-Delta V Advantage mass spectrometer at the Third Institute of Oceanography, State Oceanic Administration. The CO_2 was liberated by reacting with 100% phosphoric acid at 90 °C. Results were reported in permil (‰) using standard δ notation relative to the Vienna-Pee Dee Belemnite (V-PDB). Precision was on the order of 0.1‰ (2σ) for both $\delta^{13}C$ and $\delta^{18}O$ values.

About 50 mg of powdered samples were weighed to determine rare earth element (REE) and trace element contents in authigenic minerals. The samples were leached by an ultra-pure solution of 5% acetic acid for 2 h to separate carbonate mineral and residue phases. The obtained solutions were centrifuged immediately after carbonate dissolution, and then evaporated on a hotplate until dry (Hu et al., 2014). Finally, the samples were dissolved in 3% HNO_3 spiked with an internal Rh standard (10 ppb) for REE analysis. The abundances of REE and trace element in the carbonate samples were determined by Perkin–Elmer Sciex ELAN 6000 ICP–MS at Institute of Geochemistry, CAS. Certified reference materials (GSR-1 and OU-6) were used for quality control. Precision and accuracy were both better than 5%. In this paper, $Ce/Ce^* = 3Ce_N/(2La_N + Nd_N)$, where N refers to normalization of concentration against the Post Archean Australian Shale (PAAS; McLennan, 1989).

The AMS ^{14}C measurements were made on shell fragments. Seven samples were shell fragments cemented by matrix of the carbonates while the other two samples were dead mussel shells scattered in
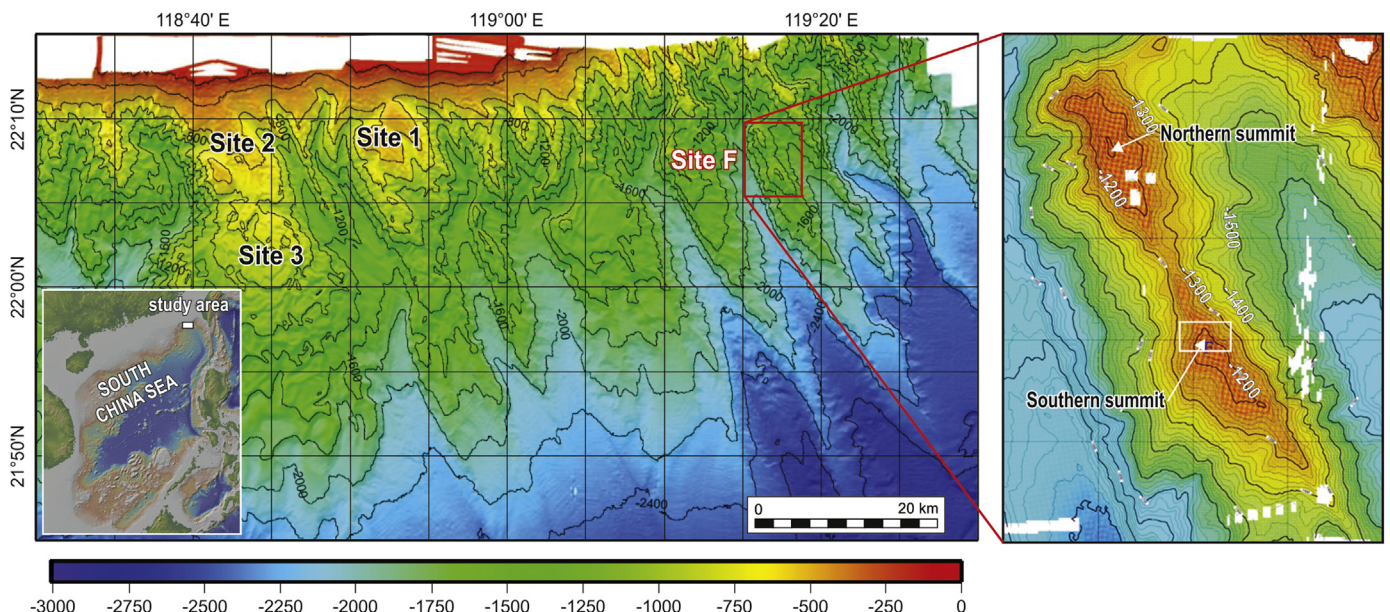

Fig. 1. Location of seep carbonates on the northeastern continental slope of the South China Sea (after Han et al., 2014). The main observation and sampling site (Site F) is delimited by the white box. Bathymetry map on the right courtesy of Prof. Chi-Yue Huang (National Cheng Kung University).