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Cold seep status archived in authigenic carbonates: Mineralogical and isotopic evidence from Northern South China Sea

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ABSTRACT

Cold-seep carbonates are precipitated under high alkalinity conditions created by the anaerobic oxidation of methane in cold-seep sites. Multiple Ca–Mg-carbonate phases are identified, including aragonite, low-Mg calcite (LMC), high-Mg calcite (HMC), protodolomite, and dolomite. These phases result from different conditions that are related with cold-seep activities. Here, we report on the relationship between the Ca–Mg-carbonate phases and the cold-seep status. Authigenic carbonates were sampled from northern slope of South China Sea. Carbon isotopic compositions of samples from Shenhu area are lower than $-40‰$, indicating methane-derived carbon. The $\delta^{13}C$ values of samples from Southwest (SW) Taiwan area range from $\sim-30‰$ to $\sim-20‰$, which is the result of the mixture of methane carbon and seawater carbon. Carbonate phases were identified according to the composition and structure results. Samples from Shenhu area are composed of protodolomite and HMC. Three zones were discovered from the center to the rim of the cross-section of the tube-like sample from SW Taiwan area. From the external to the internal zones, the carbonate phases are HMC; LMC and protodolomite; HMC, respectively. The intensity of superstructure reflections of the protodolomite from Shenhu area is stronger than that from SW Taiwan area, indicating higher $MgCO_3$ content. Based on the formation conditions of Ca–Mg-carbonates from LMC to dolomite, those with higher $MgCO_3$ content are formed in more active cold-seep environment. According to the distribution of carbonate phases in each sample, the cold seep flux was high in Shenhu area and was sustained for a long time. By contrast, the flux in SW Taiwan area was relatively low and not stable. It once became higher, but finally returned to low.

1. Introduction

Cold seep, a kind of low-temperature and hydrocarbon-containing fluid, has been discovered on the seafloor along the continental margins (Johnson et al., 2003; Ritger et al., 1987; Suess, 2010). In most cases, the major component of hydrocarbon is methane, which is accumulated into gas hydrates under appropriate pressure and temperature conditions. Gas hydrate is considered to be a potential energy source in the future (Makogon et al., 2007). Methane oxidizing archaea and sulfate reducing bacteria that assemble around cold seep sites operate a life-supporting process called anaerobic oxidation of methane (AOM) (Boetius et al., 2000), which is expressed as follows:

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

Sulfate and methane are converted into sulfide and bicarbonate. Sulfide is the energy source for a large number of communities associated with cold seep (Boetius and Suess, 2004), while the large amount of bicarbonate induces the precipitation of a considerable quantity of authigenic cold-seep carbonates in the sediments near cold seep sites.

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Cold-seep carbonates consist of multiple Ca–Mg-carbonate phases. Aragonite, LMC, HMC, protodolomite, dolomite, and ankerite have been reported in cold seep or gas hydrate sites, such as the Gulf of Cadiz (Magalhães et al., 2012; Merinero Palomares et al., 2012; Stadnitskaia et al., 2008; Vanneste et al., 2012), Gulf of Mexico (Birgel et al., 2011; Canet et al., 2006; Chen et al., 2007; Feng et al., 2014a; Ferrell and Aharon, 1994; Mansour and Sassen, 2011; Naehr et al., 2009; Roberts et al., 2010), Cascadia margin (Greinert et al., 2001; Kulm and Suess, 1990; Ritger et al., 1987; Teichert et al., 2005a, 2005b), Norwegian Sea (Hovland et al., 2005; Mazzini et al., 2006), St. Lawrence Estuary (Lavoie et al., 2010), Japan Sea (Nehza et al., 2012), Black Sea (Bahr et al., 2010; Peckmann et al., 2001), Gulf of Guinea (Haas et al., 2010), Mediterranean Sea (Aloisi et al., 2000; Cangemi et al., 2010), Monterey Bay (Stakes et al., 1999), Ryukyu Island (Takeuchi et al., 2007), and South China Sea (SCS) (Chen et al., 2005, 2006; Ge et al., 2010; Han et al., 2008, 2013; Lu et al., 2010; Tong et al., 2013; Wang et al., 2014, 2012). In the cold seep area of Hydrate Ridge, two zones of carbonate phases have been identified: (1) the aragonite- and HMC-rich zone, located near the seafloor, and (2) the HMC- and (proto) dolomite-rich zone, which is at a certain depth in the sediments (Greinert et al., 2001). The mineralogy of Ca–Mg-carbonates is controlled by the conditions in cold seep environment, such as degree of supersaturation, content of Ca^{2+} and Mg^{2+}, sulfate and phosphate concentration, temperature, partial pressure of CO_2, biological activities, hydrocarbon flux, and the efficiency of AOM (Aloisi et al., 2000; Feng and Roberts, 2010; Mansour and Sassen, 2011; Peckmann et al., 2001; Roberts et al., 2010). The precipitation of aragonite is favored under conditions with supersaturation of bicarbonate, high Mg/Ca ratio, and elevated sulfate concentration (Aloisi et al., 2000; Peckmann et al., 2001). From LMC, HMC to dolomite, the formation conditions are required to be high alkalinity and increasingly lower sulfate content (Aloisi et al., 2000; Chen et al., 2006; Feng et al., 2014b; Naehr et al., 2009; Peckmann et al., 2001; Roberts et al., 2010). In addition, dolomite formation may also be mediated by microbes (Feng and Roberts, 2010; Magalhães et al., 2012; Roberts et al., 2010).

Some information of cold seep has been uncovered from the morphology, geochemistry, and biomarkers of cold-seep carbonates. When at high flux, cold seep flows into the bottom water, inducing the precipitation of chimney-like carbonates. On the other hand, cold seep at low flux results in massive carbonates cementing sediments (Kulm and Suess, 1990). Different stages of cold seep activity are indicated by multiple cementation of aragonite and magnesian calcite (Mansour and Sassen, 2011; Peckmann et al., 2001; Roberts et al., 2010; Teichert et al., 2005a). The changing redox conditions and fluid compositions are revealed by the results of rare earth elements and some other trace elements, showing various cold seep activity and in situ microbial effect (Birgel et al., 2011; Feng et al., 2010, 2009, 2013; Ge et al., 2010; Himmler et al., 2010; Hu et al., 2014; Rongemaille et al., 2011; Wang et al., 2014). The carbon source and $\delta^{18}O$ of the pore water can be deduced from the carbon and oxygen isotopic compositions of the related authigenic carbonates (Bohrmann et al., 1998; Naehr et al., 2007; Stakes et al., 1999). Seawater or deep source origin of cold seep fluids is recorded in the Sr isotopic compositions (Ge and Jiang, 2013; Greinert et al., 2002; Peckmann et al., 2001; Rongemaille et al., 2011). U/Th dating results provide the age of cold seep activity (Bayon et al., 2009; Teichert et al., 2003; Tong et al., 2013). The species of archaea and bacteria that thrive in the cold seep sites are indicated by the biomarkers in the cold-seep carbonates (Birgel et al., 2011; Feng et al., 2014a; Ge et al., 2011, 2015; Naehr et al., 2009).

Gas hydrates were discovered on northern slope of SCS (Liu et al., 2015, 2012; Song et al., 2014). Authigenic carbonates from SCS were studied in order to reveal the characteristics of cold seep that is significant to evaluate the quantity of released methane and the gas hydrate deposit. Aragonite, HMC, protodolomite, ankerite, and siderite were identified (Chen et al., 2005, 2006; Ge et al., 2010; Han et al., 2008, 2013; Lu et al., 2010). The formation of dolomite may be transferred from HMC with high $MgCO_3$ content (Han et al., 2008). These authigenic carbonates are methane-derived indicated by carbon isotopic compositions (Chen et al., 2005, 2006). Trace element and calcium isotope results show that they were rapidly precipitated in anoxic environment of cold seep (Ge et al., 2010; Wang et al., 2014, 2012). Some of them were precipitated in the fluid originated from gas hydrate dissolution (Han et al., 2013), which was happened during sea-level lowstands (Tong et al., 2013).

Cold-seep carbonates are archives of cold seep and AOM processes (Aloisi et al., 2000; Magalhães et al., 2012; Peckmann et al., 2001; Roberts and Aharon, 1994; Roberts et al., 2010; Stakes et al., 1999; Suess, 2010). Although some characteristics of cold seep have been uncovered, few features that indicate the intensity and the endurance time of cold seep have been discovered. From aragonite to dolomite, the $MgCO_3$ content rises and the structure changes. The various compositions and structures of carbonate phases are the results of precipitation conditions, which are related with cold seep status. In this study, we report the mineralogical and C–O isotope results of cold-seep carbonates from Shenhu area and SW Taiwan area on northern slope of SCS. The specific Ca–Mg-carbonate phases are identified. Based on the formation mechanisms of different phases from previous works, we try to make an initial study on the connection between the Ca–Mg-carbonate mineralogy and cold seep status.

2. Materials and methods

Samples were collected from two areas on northern slope of the SCS, namely: (from west to east) Shenhu (site HS4 and site HS4a) and SW Taiwan (site HD314) (Fig. 1). Tow net sampling operations were completed by the ship HAI YANG SI HAO from the Guangzhou Marine Geological Survey in 2003 for SW Taiwan area and in 2004 for Shenhu area. The water depths of the sampling sites are 350 m and 400 m, respectively. Samples were cleaned with distilled water and dried under room temperature. Thin sections were made in the specimen factory affiliated with the Beijing Geological Museum.

Carbonates from HS4 and HS4a are in irregular shapes. Evident tube features were developed in some samples from HS4 (Fig. 2A). Color zoning is observed on the polished surfaces. Some parts are gray with disseminated brown or yellow components, while other parts are brown. These two zones are set as the I and O zones, respectively (Fig. 2B–D).

The sample from SW Taiwan is concrete and only a few bioclasts are observed on the yellow surface (Fig. 2E). Channels were developed near the center of cross section (Fig. 2F). From the central part to the rim of the sample, the cross section is divided into three zones: Y, I, and O (Fig. 2F). Y zone is the yellow component highlighted by the dash line in Fig.2F. I zone is the gray component. O zone is the rim or the surface of the sample (Fig. 2F).

2.1. Scanning electron microscopy (SEM) analysis

Some parts from I zone were cut into small tablets for SEM analysis. The surfaces to be studied were carefully polished and coated with carbon. The samples were analyzed by using the JEOL JSM-6330F field-emission scanning electron microscope with an operation voltage of 15 kV. Then, the studied surfaces were etched by concentrated hydrochloric acid for less than 30 s. The etched