Marine Geology 268 (2010) 129–136

Contents lists available at ScienceDirect

Marine Geology

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

Patterns of carbonate authigenesis at the Kouilou pockmarks on the Congo deep-sea fan

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ARTICLE INFO

Article history:
Received 13 August 2008
Received in revised form 14 August 2009
Accepted 31 October 2009
Available online 10 November 2009

Communicated by G.J. de Lange

Keywords:
methane seeps
carbonates
pockmarks
gas hydrates
biomarkers
stable isotopes
Congo fan

ABSTRACT

Different types of seep carbonates were recovered from the 'Kouilou pockmarks' on the Congo deep-sea fan in approximately 3100 m water depth. The carbonate aggregates are represented by pyritiferous nodules, crusts and slabs, tubes, and filled molds. The latter are interpreted to represent casts of former burrows of bivalves and holothurians. The nodules consisting of high-Mg-calcite apparently formed deeper within the sediments than the predominantly aragonitic crusts and slabs. Nodule formation was caused by anaerobic oxidation of methane dominantly involving archaea of the phylogenetic ANME-1 group, whereas aragonitic crusts resulted from the activity of archaea of the ANME-2 cluster. Evidence for this correlation is based on the distribution of specific biomarkers in the two types of carbonate aggregates, showing higher hydroxyarchaeol to archaeol ratios in the crusts as opposed to nodules. Formation of crusts closer to the seafloor than nodules is indicated by higher carbonate contents of crusts, probably reflecting higher porosities of the host sediment during carbonate formation. This finding is supported by lower $\delta^{18}O$ values of crusts, agreeing with precipitation from pore waters similar in composition to seawater. The aragonitic mineralogy of the crusts is also in accord with precipitation from sulfate-rich pore waters similar to seawater. Moreover, the interpretation regarding the relative depth of formation of crusts and nodules agrees with the commonly observed pattern that ANME-1 archaea tend to occur deeper in the sediment than members of the ANME-2 group. Methane represents the predominant carbon source of all carbonates ($\delta^{13}C$ values as low as −58.9‰ V-PDB) and the encrusted archaeal biomarkers ($\delta^{13}C$ values as low as −140‰ V-PDB). Oxygen isotope values of some nodular carbonates, ranging from +3.9 to +5.1‰ V-PDB, are too high for precipitation in equilibrium with seawater, probably reflecting the destabilization of gas hydrates, which are particularly abundant at the Kouilou pockmarks.

1. Introduction

Hydrocarbon seepage in marine sediments is a frequently observed phenomenon in marine settings (Judd and Hovland, 2009, and references therein). The anaerobic oxidation of methane (AOM), conjointly operated by consortia of methane-oxidizing archaea and sulfate-reducing bacteria, is the key biogeochemical process at methane seeps (e.g., Boetius et al., 2000). This process leads to (1) an increase of carbonate alkalinity, inducing the precipitation of carbonate minerals, and (2) the generation of sulfide, which is the substrate for sulfide-oxidizing microorganisms at the sediment–water interface of seeps. Seep carbonates provide an excellent archive of past seepage and environmental parameters (Ritger et al., 1987; Bohrmann et al., 1998; Aloisi et al., 2000; Peckmann et al., 2001; Mazzini et al., 2004; Naehr et al., 2007; Gontharet et al., 2007). Low $\delta^{13}C$ values identify methane as the dominant carbon source of seep carbonates (e.g., Peckmann and Thiel, 2004). Furthermore, biomarker data agree with the hypothesis of archaea and sulfate-reducing bacteria causing the precipitation of authigenic carbonates (Peckmann et al., 1999; Thiel et al., 1999; Elvert et al., 2000; Pancost et al., 2001; Pape et al., 2005; Bouloubassi et al., 2006). The composition of AOM communities seems to vary in response to changing environmental conditions including flux rates of methane and redox conditions (Blumenberg et al., 2004; Nauhaus et al., 2005), which also can cause different mineralogies of carbonate precipitates (Reitner et al., 2005a).

Here we describe different types of authigenic carbonates from the seepage area of the Kouilou pockmarks on the Congo deep-sea fan, applying petrography, mineralogy, as well as stable isotope and biomarker analyses. We use the obtained data to constrain the conditions under which carbonate formation occurred and estimate the relative depth of formation of the different types of carbonate aggregates.

2. Geological setting

An area with several pockmarks was identified by seismic and echo-sounding profiling in approximate 3100 m water depth on the

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0025-3227/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.margeo.2009.10.027

Congo deep-sea fan during cruises M47/3 and M56 with RV Meteor (Fig. 1). The setting of these pockmarks has been recently described in detail by Sahling et al. (2008). Briefly, the so-called 'Kouilou pockmarks' range from several tens to hundreds of meters in diameter and a few to tens of meters in depth. They include three large individual pockmarks, namely 'Worm Hole', 'Hydrate Hole', and 'Black Hole'. These pockmarks are characterized by columnar zones of seismic blanking generated by focused fluid migration and strong subsurface reflectors, which represent gas hydrate and carbonate deposits (Spiess et al., 2006; Sahling et al., 2008).

In the Early Aptian up to 1000 m thick salt-deposits accumulated, which were subsequently buried by black shales and bituminous sandstones during anoxic conditions in the Late Aptian (Uenzelmann-Neben, 1998). The seepage of methane-bearing fluids is probably caused by the remobilization of hydrocarbons from the Late Aptian black shales migrating through salt-diapirs (Emery et al., 1975). However, there is also evidence for an alternative origin of fluids from buried channel-levee systems of ancient turbidity currents (Gay et al., 2006).

3. Methods

A total of 34 carbonate samples from 3 gravity cores (GC) and 6 TV-guided grabs (TVG) were selected for detailed analyses after visual examination. Samples were preferentially taken from TV-grab stations (GeoB 8203-1, 8207-1, 8212-1, 8212-2, 8212-3, Hydrate Hole; and 8208-2, Worm Hole; see Fig. 1 for locations). Four samples were taken from gravity cores GeoB 8211-1, 8211-2 (Hydrate Hole) and 8205-2 (Black Hole). The samples, which are stored in the Department of Earth Sciences, Bremen, were examined and categorized according to their shape and macroscopic features. Afterwards, the samples were cut into sections for sub-sampling, thin section preparation, X-ray powder diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), stable carbon and oxygen isotope measurements, and biomarker analyses.

Qualitative and semi-quantitative mineralogical composition of the samples was analyzed by XRD measurements using a Philips PW 1820 instrument (CoKα) at the Alfred-Wegener-Institute in Bremerhaven. The samples were ground with an agate mortar and pestle, mixed with an internal standard (α-Al_2O_3), homogenized with ethanol and prepared as random oriented powder slides. Scans were run between 20° to 60° at a scanning speed of 0.01° 2θ steps. Semi-quantitative abundances of different carbonate minerals were determined using standard calibration curves of different mineral mixtures (precision ± 3 wt.%). The shift in the d (104) calcite peak was used to determine the $MgCO_3$ content of Mg-calcite according to Lumsden (1979). Thin sections were stained with a mixture of potassium ferricyanide and alizarin red dissolved in 0.1% HCl, or Feigl's solution and examined with a petrographic microscope under transmitted light. A LEO 1530 Gemini field emission-scanning electron microscope (FE-SEM) with an energy-dispersive X-ray spectrographic analyzer (EDX) was used for micro-fabric analysis and phase identification (Earth Science Department, University of Göttingen).

Samples for stable carbon and oxygen isotope analyses were obtained by using a hand-held micro drill. The sample powders were treated with 100% phosphoric acid at 75 °C in an online carbonate preparation line (Carbo-Kiel-single sample acid bath) connected to a Finnigan Mat 251 mass spectrometer. All isotope values are expressed

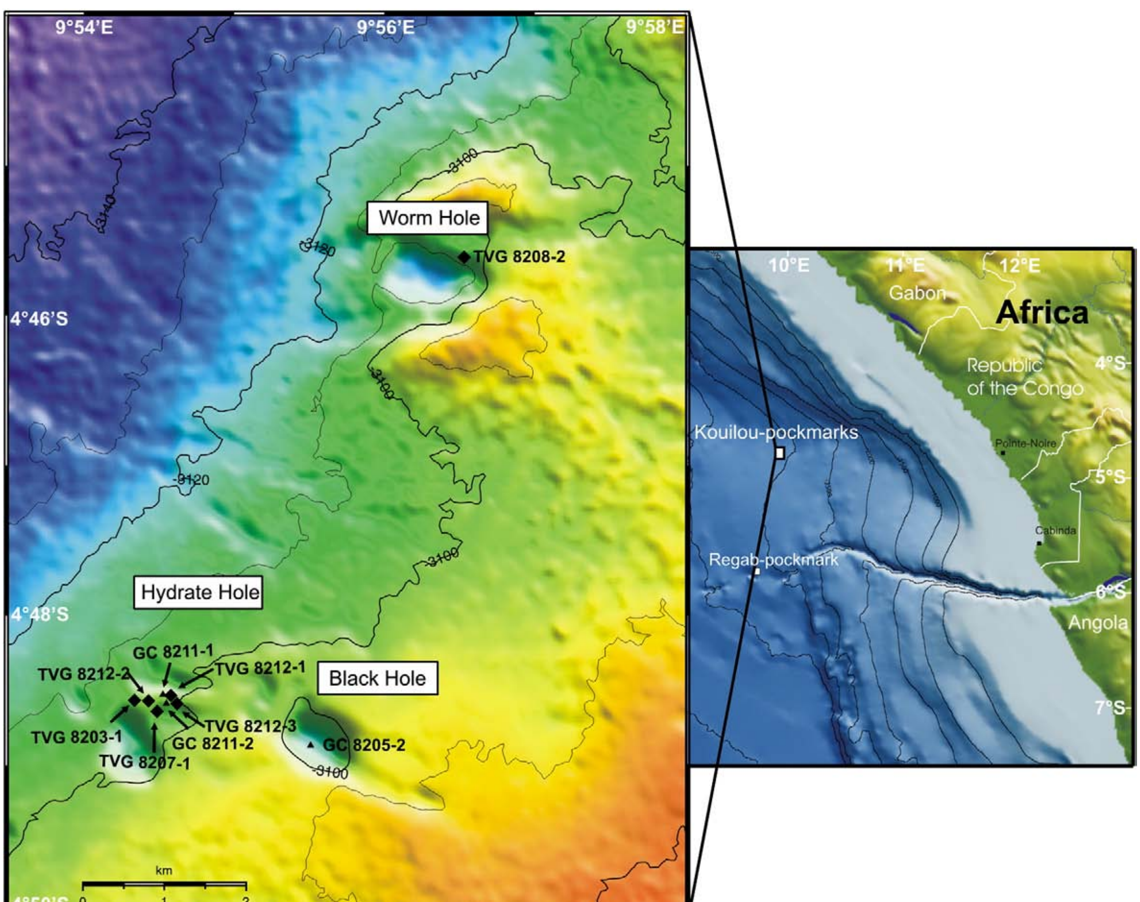

Fig. 1. Right: map of the south-west African continental margin, the Congo River estuary, the Congo Canyon, and the Regab and Kouilou pockmarks; modified after Sahling et al. (2008). Left: detailed map showing the position of the Kouilou pockmarks named "Worm Hole", "Black Hole" and "Hydrate Hole". Symbols indicate sampling positions during RV METEOR Cruise M56 (triangles = gravity cores, diamonds = TV-guided grabs).