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Research paper

Formation of methane-related authigenic carbonates in a highly dynamic biogeochemical system in the Krishna–Godavari Basin, Bay of Bengal

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ABSTRACT

We report the abundant occurrence of authigenic Fe-rich carbonate, high Mg-calcite (HMC) and low Mg-calcite from 11 cores recovered from the Krishna–Godavari Basin (K–G Basin), Bay of Bengal. The cores were collected as part of the Indian gas hydrate exploration program on board R/V *Marion Dufresne* (MD-161: May, 2007) in different environments, including mounds (mud diapirs), mass flows, and hemipelagic sediments over a range of water depths from 647 to 2079 m. Authigenic carbonates range in size from 1 mm to 12 cm and display various morphologies like roundish or platy (micro-) nodules and tube-like forms. From the cores, 173 carbonate samples have been investigated for their depth distribution, mineralogy, geochemical and stable isotopic composition. The stable carbon isotopic composition of 46 out of 88 measured carbonate samples are around −50‰ which allows the differentiation into methane-related carbonates (HMC), especially at Sites 8 and 15, but also in low abundance at Sites 1, 5, 9 and 12. Results indicate that the carbonates at Site 8 and 15 represent paleo methane seepage locations. The Fe-rich carbonates occur abundantly at many sites in the K–G Basin. Their varying carbon isotopic composition indicates that probably not only sulfate reduction through organic matter degradation but also methanogenesis are the responsible processes for their formation.

1. Introduction

Methane-derived authigenic carbonates are witnesses of diffuse to vigorous, focused methane flux in regions where also gas hydrates often occur (e.g. Han and Suess, 1989; Hovland et al., 1987; Mazzini et al., 2006; Teichert and Bohrmann, 2005; von Rad et al., 1996). These authigenic carbonates occur in many different morphologies like slabs, nodules, pavements, build-ups, chemoherms, bioturbation casts, and tubes or as dispersed crystals ranging in size from millimeter to tens of meters. The precipitation of authigenic carbonates is mainly linked to the microbial reduction of sulfate either via organic matter (equation (1)) or anaerobic methane oxidation (equation (2)).

$$2CH_2O + SO_4^{2-} \Leftrightarrow 2HCO_3^- + H_2S \quad (1)$$

$$CH_4 + SO_4^{2-} \Leftrightarrow HCO_3^- + HS^- + H_2O \quad (2)$$

During both biogeochemical processes bicarbonate [HCO_3^-] is being produced and thus pore water alkalinity increases. This will lead together with seawater calcium to the precipitation of authigenic carbonate minerals (equation (3)).

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O \quad (3)$$

It is important to determine which of the above processes (equations (1) and (2)) are responsible for authigenic carbonate formation because the process reveals valuable information about the biogeochemical environment of carbonate formation and possibly advection of methane-rich fluids. Since authigenic carbonates are not only witnesses of ongoing methane seepage but

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also paleo seepage activity, they are usually the only remnants with which paleo methane seepage can be reconstructed (Mazumdar et al., 2009; Peckmann et al., 2009; Teichert et al., 2003). In addition, the morphologies of the authigenic carbonates can give an indication about the relative fluid flux rate. Focused fluid flow will rather lead to carbonate build-ups like chemoherms while diffusive fluid flow leads to disseminated carbonate cements and finally carbonate pavements (e.g. Naehr et al., 2007; Suess, 2014; Teichert et al., 2005).

In the northern Indian Ocean, occurrences of methane-derived authigenic carbonates are reported from the Krishna–Godavari (K–G) Basin along the Eastern Continental Margins of India (ECMI) (Kocherla et al., 2006; Mazumdar et al., 2009) and from the Makran accretionary prism off Pakistan in the Arabian Sea (von Rad et al., 1996; von Rad et al., 2000; Klauda and Sandler, 2005). The continental slope region of the K–G Basin is one of the promising petroliferous basins of India and the recent drilling and coring carried out during the National Gas Hydrate Program Expedition 01 (NGHP-01) in 2006 (Collett et al., 2008) confirmed the presence of massive authigenic carbonate precipitates (Teichert et al., 2014) along with more than 100 m thick accumulation of gas hydrates in the K–G Basin (Collett et al., 2008, 2014; Dewangan et al., 2010; Kumar et al., 2014; Ramana et al., 2007, 2009).

During the R/V *Marion Dufresne* cruise (MD-161, May 2007) 17 sediment cores of various lengths (25–35 m long) were recovered from geological settings, including mud diapirs, mass flows, and hemipelagic sediments over a range of water depths (647–2079 m) in the K–G Basin (Table 1). This cruise was part of the gas hydrate research program at the National Institute of Oceanography, Goa, with the objective to characterize sediments and diagenetic minerals with respect to their value as recorders of methane-rich fluid advection and accompanying gas hydrate formation. In this study, we present a unique data set from 11 cores in the K–G Basin that provide a deep insight into the history of biogeochemical processes within the sediments. The proximity of the cores records the high variability of different processes within short distances.

2. Geological setting

The study area in the K–G Basin lies in the middle of Eastern continental Margins of India (ECMI) which is a pericratonic rift basin (Rao, 2001) that evolved after the breakup of Gondwanaland around 130 Ma years ago (Powell et al., 1988; Scotese et al., 1988; Ramana et al., 1994). Onshore extension of K–G Basin is ~28,000 km^2 and its offshore extension is ~145,000 km^2 (Ojha and Dubey, 2006). Much of the detrital influx into the K–G Basin is brought by the two major river systems: Krishna and Godavari Rivers. The sediment thickness ranges from 3 to 5 km in onshore region to ~8 km in the offshore portion of the basin (Prabhakar and Zutshi, 1993; Basti, 2007) with several cycles of deposition, ranging in age from late Carboniferous to Pleistocene. The sediment in the study area consists of silty clay with negligible amount of sand (Kocherla et al., 2006). The dominant clay fraction is smectite with low abundances of illite and kaolinite and very little chlorite (Phillips et al., 2014).

In the K–G Basin, widespread presence of gas hydrate is manifested in the multi-channel seismic data in the form of bottom simulating reflectors (BSRs). Drilling and coring in the K–G Basin has confirmed the presence of gas hydrate (Collett et al., 2008). Several acoustic features related to fluid and/or gas migration have been reported in the shallow subsurface (Dewangan et al., 2010; Ramana et al., 2007, 2009) suggesting active migration of methane in the study area. The geological and geochemical analyses of long sediment cores, acquired on-board the R/V *Marion Dufresne*, have confirmed paleo-methane seepage in the study area (Mazumdar et al., 2009). Slumping/sliding of slope sediments, associated with fluid and/or gas migration, has led to mass transport deposits in the K–G offshore basin (Ramprasad et al., 2011). Several bathymetric mounds formed due to shale tectonics are heavily faulted and show acoustic signatures of fluid and/or gas migration through the fault system (Dewangan et al., 2010). The analysis of available geophysical datasets such as multi-channel seismic, high resolution seismic, sub-bottom profiler, and multibeam bathymetry has divided the study area into distinct depositional environments, including mid-slope mini basins, in the north-east and south-west directions, bathymetric mounds, toe-thrust sedimentary ridges, and deep oceanic basin (Dewangan et al., 2010; Ramana et al., 2007, 2009; Ramprasad et al., 2011).

Total organic carbon (TOC) content of the sediments in the K–G Basin is mainly from terrestrial sources supplied by the Krishna and Godavari rivers. The terrestrial source is also indicated by studies on the provenance of the sediments with the main source being the Deccan basalts (Phillips et al., 2014). The high terrestrial fluxes and sedimentation rates and the consequently rapid burial have resulted in a high preservation of TOC in the K–G Basin sediments (Johnson et al., 2014).

Table 1
Locations, water depth, core length, sulfate–methane transition zone (SMTZ) of sediment cores from R/V *Marion Dufresne* cruise MD-161.

Site	Latitude N	Longitude E	Water depth (m)	Core length (m)	Approx. SMTZ depth[a] (m)
17	16 03.6300 N	82 01.2900 E	790	30.0	24.9
18	17 26.3106 N	83 49.9501 E	1691	32.0	12
19	18 59.1092 N	85 41.1669 E	1480	39.1	11.21
20	18 47.3600 N	85 36.4400 E	1866	50.1	17.17
21	19 05.3872 N	85 35.9960 E	986	36.4	19.65
22	19 09.0000 N	85 46.3900 E	1365	32.4	15
23	19 06.2500 N	85 50.1500 E	1600	38.6	17.25
24	19 03.4825 N	85 45.8415 E	1578	31.9	16.89
25	19 01.8100 N	85 38.3498 E	1429	39.2	24.06
26	19 13.9900 N	85 37.4699 E	414	34.2	11.21
27	18 57.3600 N	85 43.4400 E	1691	36.1	18.62

[a] Based on pore water geochemistry by Mazumdar et al. (2009).

3. Samples and methods

A total of 11 long cores with lengths between 20 and 34 m were recovered over a water depth range of 790–2079 m (Table 1, Fig. 1). The cores were retrieved during R/V *Marion Dufresne* cruise (MD-161, May 2007) in the K–G Basin using a Giant Calypso piston corer. On-board analysis of sediment cores revealed that the main lithology is nannofossil-bearing clay with silty beds with a high terrigenous organic carbon content. A total of 173 authigenic carbonates were subsampled from the sediment cores (Table 2). The shallowest carbonate sample is from 3.4 mbsf (meters below seafloor) and the deepest is from 29 mbsf (Fig. 2). The authigenic carbonate show different colors from greyish, to yellowish and brownish shadings. They are either semi-lithified or hard and completely lithified. The morphologies are variable (Fig. 3). Roundish or platy nodules (0.1–12 cm) or micro-nodules (<0.1 cm) are very common followed by tube-like forms (Fig. 3). Samples were washed with water to remove the salts and then washed in an ultrasonic bath for 15 min. Finally they were dried and powdered with an agate mortar and pestle for further analyses.

Bulk mineralogy of all carbonate precipitates was determined by X-ray diffraction (XRD) on randomly oriented samples using a Regaku X-ray diffractometer (Ultima-IV). All samples were run from 25 to 35 °2θ at 1°/min scan speed using CuKα radiation (λ = 1.541838Å) at the National Institute of Oceanography, Goa,