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## **Authigenic carbonates in the sediments of Goa offshore basin, western continental margin of India**

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**Euhedral crystals (~1 mm) of authigenic carbonates are identified in 5 m long sediment cores collected from the western continental margin of India in water depths between 2665 and 3070 m. Low-Mg calcite and aragonite are the dominant authigenic minerals while high-Mg calcite, dolomite and siderite occur in minor amounts. Morphological evidences such as euhedral carbonate crystals and slender radiating aragonite crystals suggest that they are formed authigenically in the sediment column. The  $\delta^{13}\text{C}$  values of the authigenic carbonates range between 0.63‰ and –8.12‰, and is attributed to the contribution of isotopically light carbon derived from the oxidation of sedimentary organic matter in the surficial sub-oxic Fe reduction and the bacterial sulphate reduction zone during early diagenesis. Mineralogy, morphology and stable carbon isotope signatures of authigenic carbonates and the occurrence of pyrite framboids and octahedral crystals and the evaluation of pore-fluid chemis-**

**try are not indicative of enhanced methane flux. They argue against a precipitation of carbonates due to anaerobic oxidation of methane and refute the possible connection of methane gas from the shallow gas-charged sediments to the observed carbonates.**

**Keywords:** Authigenic carbonates, euhedral crystals, methane flux, sediment core.

AUTHIGENIC carbonates are indirect indicators of high methane flux regions which are common in areas overlying gas hydrate deposits in various geological settings<sup>1–4</sup>. A variety of authigenic carbonates have been observed at numerous locations adjacent to gas seepages and pore fluid venting<sup>2,5</sup> as individual slabs, thinly lithified pavements, vertical pillars, mushroom-like structures, microbial mats, dispersed crystal aggregates, carbonate build-ups and as micro-concretions<sup>1</sup>. Precipitation and consequent preservation of authigenic carbonates is mainly due to increase in pore water bicarbonate [ $\text{HCO}_3^-$ ] ion concentration due to anaerobic oxidation of methane (AOM) from the gas hydrate system and concomitant sulphate reduction process in the sediment sequence<sup>1,6–9</sup>. Authigenic carbonates can also be formed due to degradation of organic matter during early diagenesis<sup>3,5,10</sup>. These processes increase pore water alkalinity by the production of bicarbonate [ $\text{HCO}_3^-$ ] thus favouring precipitation of authigenic carbonate minerals in the shallow subsurface<sup>1,7</sup>. Determining which of the above two processes is responsible for the authigenic carbonate precipitation is essential, as it provides definite evidence for high methane fluxes either due to localized diagenetic processes or due to the presence of gas hydrates beneath<sup>11–13</sup>. Goa offshore basin is characterized by shallow gas charged sediments and several gas escape features<sup>14</sup>. Geophysical studies in the Goa offshore basin, west coast of India revealed the presence mud diapirs<sup>15,16</sup> and bottom simulating reflectors (BSRs) and vent-like features representing gas escape features from the seafloor<sup>17,18</sup>. In the northern Indian Ocean occurrences of methane-derived authigenic carbonates are reported from the Krishna–Godavari basin, eastern continental margins of India<sup>19,20</sup> and Makran accretionary prism off Pakistan<sup>3,4,21</sup> in the Arabian Sea. Recent drilling work carried out on-board JOIDES Resolution Leg-3A (ref. 22) confirmed the presence of massive authigenic carbonate nodules/concretions<sup>23</sup> along with more than 100 m thick accumulation of gas hydrates in the Krishna–Godavari offshore basin, and fully developed gas hydrate system in the Mahanadi offshore area, Bay of Bengal<sup>22,24,25</sup>.

Since occurrence of authigenic carbonates can help decipher the source of gas seepages in an area<sup>11,13,19,20,23,26</sup>, we undertook a study of authigenic carbonates from the sediments of Goa offshore basin characterized by shallow gas charged sediments<sup>14,27</sup>. In the present study, we report the occurrence of dispersed authigenic carbonates in

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sedimentary cores from the Goa offshore basin (western continental margin of India) and discuss their origin based on their mineralogy, morphology and stable carbon isotopes signatures.

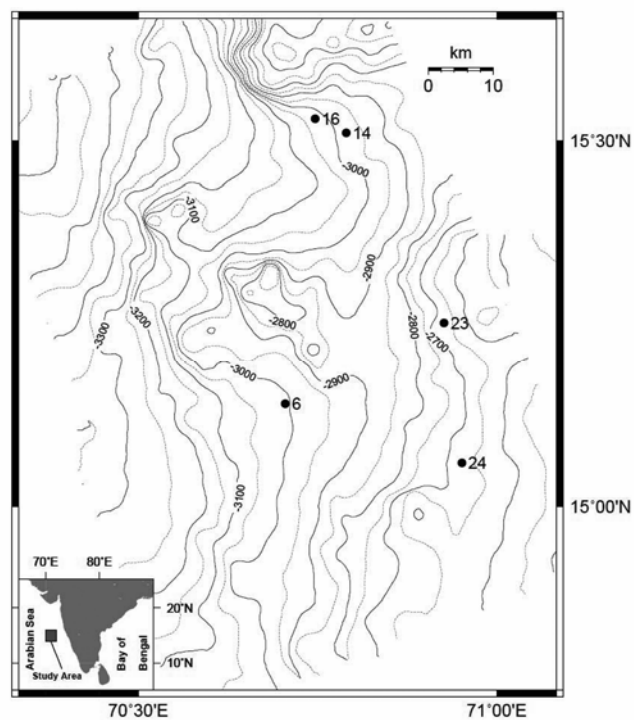
The western continental margin of India is a passive margin and characterized by: (i) NW–SE trending shelf more than 200 km wide in the north and about 50 km in the south near Cape Comorin; (ii) a straight outer edge limited by 200 m isobaths; (iii) a narrow continental slope bounded by 200 and 2000 m isobaths; (iv) deep sedimentary basins, viz. western Arabian Basin, eastern Arabian Basin, Kori–Komorin Basin and Kerala–Konkan Basin, and (v) several structural features such as Chagos–Laccadive Ridge, Laxmi Ridge and Pratap Ridge (east of Chagos–Laccadive Ridge). Geographically Goa offshore (eastern Arabian Basin) lies between the eastern end of Laxmi–Laccadive Ridge and the adjacent western continental slope of India<sup>28–30</sup>. The depth in this basin ranges from 1800 to 3600 m. Approximately 2.9 km thick sediments overlie the basement. The Indus River is the primary source of detrital sediment to this region. Average sedimentation rate in this region is 2–6 cm/kYr over last 100 kYr (ref. 31). Sediment cores selected for the present study are shown in Figure 1. The study area in the eastern Arabian Sea has oxic bottom waters (2665–3210 m) and overlain by the well-established oxygen minimum zone (OMZ) in the mid-depths (200–1500 m)<sup>32</sup>. The occurrence of gas-charged sediments and the presence of BSRs (possible gas hydrate horizons) have been detected along the western continental margin of India based on shallow seismic records<sup>14,15,17,18</sup>.

Based on the preliminary geophysical observations representing possible gas escape features<sup>14,17,30,33</sup>, gravity cores of 5–5.4 m long were collected from Goa offshore basin, west coast of India (Figure 1). Details of core locations are provided in Table 1. Sub-samples were collected at 50 cm intervals within 15–20 min after opening the core and were transferred to an on-board laboratory for pore water extraction using a temperature-controlled centrifuge (Heraeus-Biofuge). Pore waters in 25 ml airtight bottles were stored in refrigerators at –18°C for onshore analyses of  $\text{SO}_4^{2-}$  concentration using Dionex ion-chromatograph, DX-600I. The degassing system<sup>34</sup> was used for methane extraction from the sediment samples. Methane content was determined with a Carlo-Erba model CE-8000 TOP gas chromatograph. The total organic carbon (TOC) was estimated by chromic acid oxidation method<sup>30,35</sup>.

Dried and disaggregated sediment samples were first examined under a binocular (Nikon, SMZ-1500) to determine their original size, morphology and depth of maximum carbonate abundance (Table 1). From the zones of maximum abundance, 10 g of sediment sample was sieved using 63  $\mu\text{m}$  mesh and the number of carbonate grains was counted from the coarse fraction to estimate their relative abundance (Table 1). Some selected grains

were examined under scanning electron microscope (JEOL-JSM 5800 LV1) for morphological studies. The mineralogy of hand-picked carbonate samples was determined by X-ray diffraction (XRD) analyses using a Philips PW1840 diffractometer at National Institute of Oceanography, Goa. The XRD samples were scanned from  $24^\circ$  to  $59^\circ 2\theta$  at a low scan speed of  $0.02^\circ \theta/\text{s}$ . Stable oxygen ( $\delta^{18}\text{O}$ ) and carbon ( $\delta^{13}\text{C}$ ) isotopic measurements of hand-picked carbonate grains from these levels were carried out using a Delta<sup>Plus</sup> Advantage Isotope Ratio Mass Spectrometer (IRMS) coupled with a Kiel IV automatic carbonate device. Samples were reacted with saturated orthophosphoric acid at  $\sim 70^\circ\text{C}$  in a vacuum system and the  $\text{CO}_2$  evolved was analysed using the mass spectrometer at the National Geophysical Research Institute, Hyderabad. Isotopic compositions were reported in  $\delta$  notation as per mil deviation from Viena Pee Dee Belemnite (VPDB) standard. Analytical precision was better than 0.1‰ for  $\delta^{18}\text{O}$  and 0.05‰ for  $\delta^{13}\text{C}$ . Replicate measurements were performed in each sample to ensure reproducibility. Calibration to the VPDB standard was achieved by repeated measurements of NBS-19 and NBS-18 standards.

Sediment cores studied (GC 06, 14, 16, 23 and 24) showed moderate yellowish-brown colour sediments in the top 50 cm, while 50 cm to core bottom exhibited homogeneous greyish-olive colour. The difference in colour of the sediments could most probably be due to relatively more active diagenetic nature of the shallow



**Figure 1.** Bathymetric map of the study area in the Goa offshore basin. Double circles indicate gravity core locations.

**Table 1.** Location of sediment cores, water depth, core length and authigenic carbonate sampling depth, carbonate abundance, carbonate mineralogy, and carbon and oxygen isotope compositions (isotopic compositions are in per mil relative to VPDB) and down-core distribution of total organic carbon (TOC), CaCO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, CH<sub>4</sub>, at the top, middle and bottom sections of the cores

Station ID	Location	Water depth (m)	Core length (m)	Carbonate sampling depth (cm)	Carbonate abundance (g)	Carbonate mineralogy	$\delta^{13}\text{C}$ CaCO <sub>3</sub> (‰ VPDB)	$\delta^{18}\text{O}$ CaCO <sub>3</sub> (‰ VPDB)	Core depth (cm)	TOC (wt %)	CaCO <sub>3</sub> (wt%)	SO <sub>4</sub> <sup>2-</sup> ion (mM)	CH <sub>4</sub> (nM)
GC-06	Lat. 15.14°N Long. 70.70°E	3070	5.1	248–250	0.76	Low-Mg calcite	-0.63	-0.22	2.5 249 499	0.31 0.66 0.55	65.5 34.13 43.33	18.1 19.4 13.25	1.66 0.68 10.88
GC-14	Lat. 15.51°N Long. 70.79°E	2980	5.2	0–5	0.62	Aragonite	-7.42	2.6	2.5 267.2 517.2	0.38 0.72 0.69	65.53 44.27 42.8	25.85 24.12 14.68	5.25 11.25 13.23
GC-16	Lat. 15.53°N Long. 70.74°E	3035	5.4	40–45	0.73	Aragonite	-8.12	2.1	2.5 297.5 547.5	0.45 2.17 0.62	62.79 49.5 43.6	28.45 25.08 24.1	0.45 3.29 0.64
GC-23	Lat. 15.25°N Long. 70.92°E	2665	5.0	100–105	1.36	Low-Mg calcite	0.2	-1.04	2.5 252.5 500	0.38 0.45 0.48	65.04 40.13 52.48	27.83 26.92 12.75	2.29 1.98 8.17
GC-24	Lat. 15.05°N Long. 70.95°E	2673	5.4	390–395	0.97	Low-Mg calcite	0.2	-1.09	2.5 242.5 542.5	0.38 0.48 0.48	58.87 42.28 40.59	27.33 27.25 23.49	2.4 4.93 9.62



**Figure 2.** Authigenic carbonate precipitates. *a*, Low-Mg calcite aggregates occurring in the sediments. *b*, High-Mg calcite precipitates in the pore spaces.

sediments at the sediment–water interface. Sub-rounded authigenic carbonate grains of  $\sim 10\ \mu\text{m}$  to 1 mm diameter were present in all the samples (Figure 2). High concentrations of calcareous grains were noticed at depth intervals of 248–250 cm in GC-06, 0–5 cm in GC-14, 40–45 cm in GC-16, 100–105 cm in GC-23 and 390–395 cm in GC-24 (Table 1). The relative weight abundance of authigenic carbonate was maximum in GC-23 and minimum in GC-14, i.e. 1.36 and 0.67 g respectively, in the  $> 63\ \mu\text{m}$  fraction. The horizons of carbonate accumulation zones do not show any inhomogeneities/hiatuses.

XRD showed that the carbonates consist mainly of low-Mg calcite (LMC) and aragonite with minor amounts of high-Mg calcite (HMC), dolomite and siderites (Table 1). The carbonate precipitates were characterized by prominent euhedral calcite crystals (Figure 3 *a*), cylindrical-shaped HMC crystals and dumbbell-shaped globular masses of HMC (Figure 3 *d*). HMC mainly occurred as foraminifera tests and pore-fillings (Figure 2 *b*), as well as individual aggregates, while LMC occurred predominantly as cementing material. Aragonite was primarily associated with skeletal matter and occurred as individual aragonite needles or a cluster of needles (Figure 3 *b*) and occasionally as dense palisade fabric on the surface of skeletal matter. Nucleations of aragonite around lithogenic grains have been observed. HMC sometimes occurred as clusters on the skeletal matter (Figure 3 *d*). Pyrite framboids and octahedral crystals were also noticed (Figure 3 *c*).

Sulphate, methane and TOC data at the top, middle and bottom sections of the cores are presented in Table 1. The sulphate concentration can be seen decreasing slightly with depth in all the studied locations. The methane concentration varied from 0.45–5.25 nM (top) to 11.25 nM (middle) and 0.64–13.23 nM (bottom). The  $\text{CaCO}_3$  content

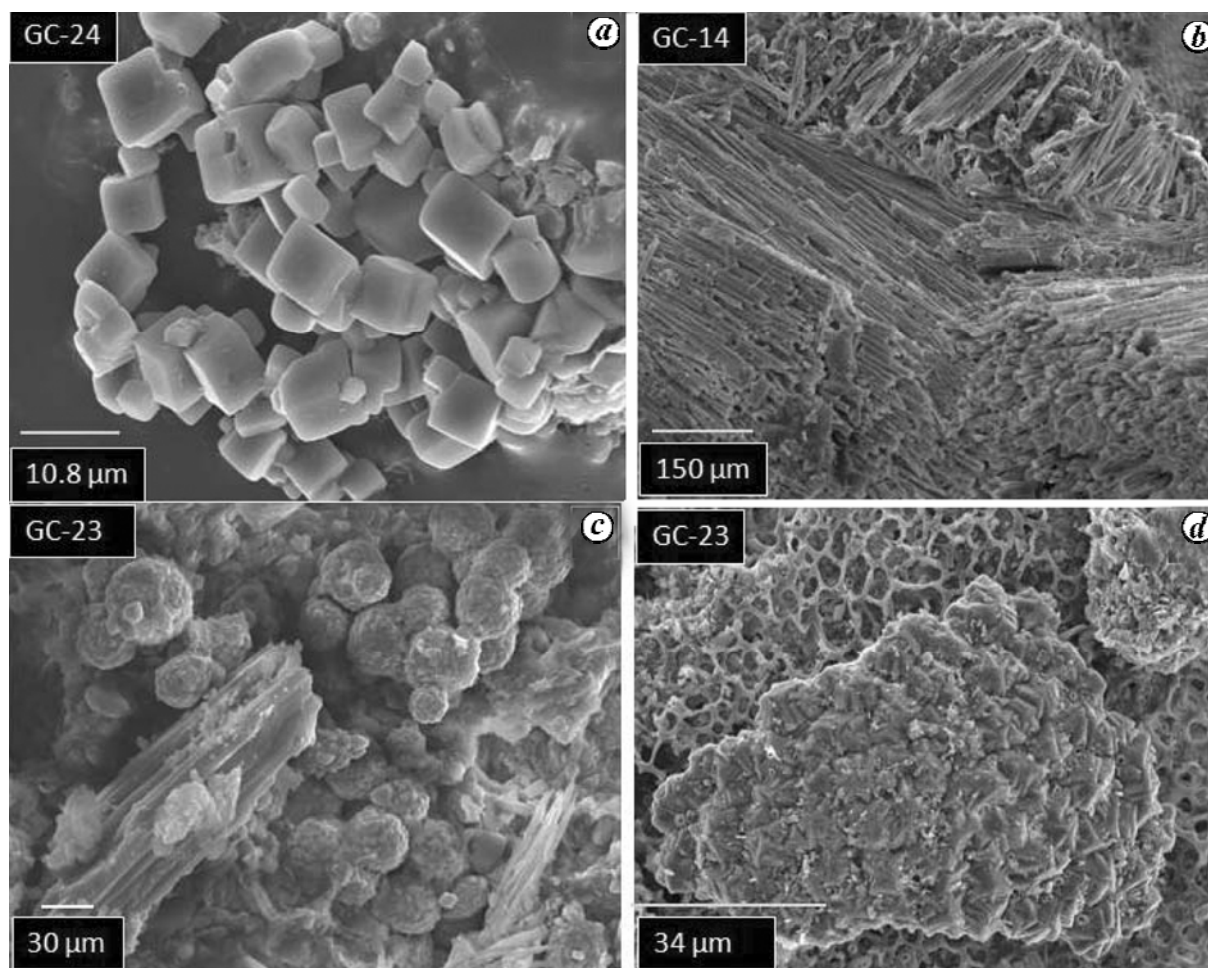
of the sediments ranged from 33.6% to 69.9% and TOC varied from 0.21% to 0.86%. The porosity of the sediments was around 57%, while dissolved oxygen of the near bottom waters was in the range of 81–150  $\mu\text{M}$  (ref. 30).

Carbonates were present throughout the core. However, due to insufficient sample quantities, one representative sample (maximum carbonate depth) from each of the five studied cores has been analysed for carbon and oxygen isotope ratios; the  $\delta^{13}\text{C}$  values of the authigenic carbonates ranged between  $-0.63\text{‰}$  VPDB and  $-8.12\text{‰}$  VPDB and the  $\delta^{18}\text{O}$  values ranged from  $-0.22\text{‰}$  VPDB to  $+2.6\text{‰}$  VPDB (Table 1).

Precipitation and consequent preservation of authigenic carbonates is mainly due to increase in bicarbonate [ $\text{HCO}_3^-$ ] ion concentration in the pore waters. This bicarbonate ion is derived either by (i) coupled AOM and sulphate reduction<sup>6,9,36,37</sup> or (ii) organic matter oxidation by sulphate or iron reduction<sup>38</sup>. These authigenic carbonates provide definite evidence of methane source and in most cases served as a proxy to identify regions of high methane flux and the associated AOM process across the globe in various geological settings<sup>11–13</sup>, including the northern Indian Ocean<sup>19,22</sup>.

AOM needs sulphate, methane and anoxic conditions and the methane required for AOM does not need to be provided by hydrates. There could be a source of shallow methane from the gas-charged sediments reported in the study area<sup>14,27,33</sup> or could be due to the oxidation of organic matter. The occurrence of pyrite framboids and octahedral crystals (Figure 3 *c*) indicates reduction of ferric iron ( $\text{Fe}^{3+}$ ), mediated by organic carbon<sup>39</sup>.

To evaluate the diagenetic aspects of the authigenic carbonates, we briefly describe the limited pore water data below. The average sea water  $\text{SO}_4^{2-}$  value is about 28.8 mM (ref. 40). The observed  $\text{SO}_4^{2-}$  concentrations in



**Figure 3.** Scanning electron photomicrographs. *a*, Euhedral calcite crystals with rhombic texture within carbonates and clay matrix from anaerobic sediments. *b*, Stubby aragonite needles. *c*, Cluster of pyrite framboids and octahedral crystals. *d*, A chunk of high-Mg calcite crystals occurring in the tests.

the study area were low and showed significant change with depth in cores 06, 14 and 23 (Table 1). This reduction could be due to microbial degradation of organic matter at the sediment–water interface. At the sediment–water interface microbes create microenvironments where sulphate reduction could have generated sufficient bicarbonate to stimulate authigenic carbonate precipitation<sup>41–43</sup>. Similarly, the observed CH<sub>4</sub> concentration (Table 1) does not show an appreciable increase with depth, indicating that the contribution of CH<sub>4</sub> from the shallow gas-charged sediments to authigenic carbonate formation is negligible. Background CH<sub>4</sub> concentrations were in the 2–3 nM range<sup>44</sup>.

Further, the  $\delta^{13}\text{C}$  values of the aragonite in cores 14 and 16 were relatively more negative (–7‰ to –8‰) than low-Mg calcites in the cores 06, 23 and 24 (0.2‰ to –0.63‰; Table 1), and the values close to zero suggest that they have formed at the sediment–water interface, where small amounts of <sup>12</sup>C-rich biogenic CO<sub>2</sub> were mixed to the marine bicarbonate dissolved in the pore water<sup>7,9</sup>. Depleted  $\delta^{13}\text{C}$  values in samples from cores 14 and 16 were probably due to a contribution of isotopi-

cally light CO<sub>2</sub> derived from the oxidation of sedimentary organic matter in the surficial sub-oxic Fe reduction and the bacterial sulphate reduction zone during early diagenesis as observed in the Gulf of California<sup>45,46</sup>.

Authigenic carbonates formed due to AOM have more negative  $\delta^{13}\text{C}$  values for both biogenic (–110‰ to –60‰) and thermogenic methane (–50‰ to –20‰) and are characterized by highly depleted carbon isotopic compositions<sup>23,29,47–53</sup>, whereas dispersed authigenic carbonates formed due to microbial degradation of organic matter have less negative  $\delta^{13}\text{C}$  values (–20‰ and –15‰)<sup>46,47,49</sup>. The formation of carbonate aggregates due to microbial oxidation of organic matter takes place with varying intensity in majority of the reduced Quaternary sediments on shelves and continental slopes of the oceans<sup>38,54</sup>, and in marginal and intercontinental seas<sup>7</sup>. Such authigenic carbonates are characterized by widely variable mineralogy and isotopic composition with relatively low  $\delta^{13}\text{C}$  values (–3.6‰ to –15.6‰)<sup>54</sup>.

The oxygen isotopic composition of authigenic carbonates is a function of sea water/pore water temperature and mineralogy, which affect oxygen isotope fractionation.

The change in the sediment column temperature regime in the upper 1–2 m may not drastically change. However, increased temperature gradient beyond 10 m was noticed in the deep sediment cores drilled during Leg-1 on-board JOIDES Resolution during NGHP-01 expedition in the Indian margins<sup>22</sup>. Assuming that the pore water temperature at 1–2 m sediment depth is similar to that of the sea water (4.5°C at 1400–1500 m), the calculated  $\delta^{18}\text{O}$  of aragonite showed 0.8‰ depletion relative to the measured value (at sea water  $\delta^{18}\text{O} = 0.0\text{‰}$  SMOW). Similarly, for calcite the calculated  $\delta^{18}\text{O}$  was 0.6–1.2‰ depleted relative to the measured value. Variable  $\delta^{18}\text{O}$  enrichment in methane-derived carbonates has been reported<sup>7,9</sup> and can be attributed to  $\delta^{18}\text{O}$  enrichment in the formational water itself, assuming carbonate crystallization in equilibrium with the formational water.

Evidences such as size of carbonate crystals, their mineralogy, morphology and stable carbon isotopic compositions and pore water  $\text{SO}_4^{2-}$  and  $\text{CH}_4$  values in the study area collectively suggest that these carbonate aggregates are purely diagenetic in origin and not related to AOM as seen in the Krishna–Godavari basin, eastern continental margins<sup>19,23,47</sup>.

Dispersed authigenic carbonates have been reported from five sediment cores from Goa offshore region central continental margin of western India between water depths 2665 and 3070 m. Morphological evidences such as euhedral carbonate crystals, slender radiating aragonite crystals and  $\delta^{13}\text{C}$  values suggest that these carbonates were formed authigenically. The  $\delta^{13}\text{C}$  values of the authigenic carbonates ranged between  $-0.63\text{‰}$  and  $-8.12\text{‰}$ , which is attributed to a contribution of isotopically light  $\text{CO}_2$  derived from the oxidation of sedimentary organic matter in the surficial sub-oxic Fe reduction and the bacterial sulphate reduction zone during early diagenesis.

Although the presence of gas-charged sediments and subsurface gas-escape features in and around the study area has been inferred from shallow seismic studies and possible occurrence of gas hydrates by BSRs, mineralogy, morphology and stable carbon isotope signatures of authigenic carbonates and evaluation of pore-fluid chemistry are not indicative of enhanced methane flux in the region. They argue against a precipitation of carbonates due to AOM and refute the possible connection of methane from the shallow gas-charged sediments to the observed carbonates or suspected BSRs. The recent drilling carried by JOIDES Resolution (NGHP-Leg1) in the study area rules out the occurrence of BSRs due to gas hydrates and supports our contention. Further studies are in progress for a comprehensive understanding of the process involved.

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