

Methane-Derived Authigenic Carbonates from the IMAGES VIII/PAGE 127 Gas Hydrate and Paleoclimate Cruise on the RV *Marion Dufresne* in the Gulf of Mexico, 2–18 July 2002

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Methane-derived authigenic carbonates from the IMAGES VIII/PAGE 127 gas hydrate and paleoclimate cruise on the RV Marion Dufresne in the Gulf of Mexico, 2–18 July 2002; chapter 14 in Winters, W.J., Lorenson, T.D., and Paull, C.K., eds., 2007, Initial report of the IMAGES VIII/PAGE 127 gas hydrate and paleoclimate cruise on the RV Marion Dufresne in the Gulf of Mexico, 2–18 July 2002: U.S. Geological Survey Open-File Report 2004–1358.

Abstract

Authigenic carbonates were sampled in piston cores collected from the Tunica Mound and the Mississippi Canyon areas on the continental slope of the northern Gulf of Mexico during a cruise conducted on the RV *Marion Dufresne* in July 2002. Carbonates are present as hardgrounds, porous crusts, concretions or nodules, and shell fragments with or without carbonate cements. The carbonate samples recovered during the cruise occurred at gas-venting sites, which likely overlie gas hydrate-bearing sediments. Electron microprobe, X-ray diffraction (XRD), and thin-section investigations indicate that these carbonates are high magnesium calcite (6–21 mole (mol %) MgCO_3), with a significant presence of framboidal pyrite. All carbonates are depleted in ^{13}C ($\delta^{13}\text{C} = -61.9$ to -31.5 parts per thousand (‰) Peedee Belemnite (PDB)), indicating that the carbon is derived mainly from anaerobic methane oxidation (AMO). Age estimates based on ^{14}C dating of shell fragments and on regional sedimentation rates indicate that these authigenic carbonates formed within the last 1,000 years in the Mississippi Canyon region and within the last 5,500 years at Tunica Mound. The oxygen isotopic composition of carbonates ranges from +3.4 to +5.9‰ PDB. Oxygen isotopic compositions and Mg^{2+} contents of the carbonates, in conjunction with current in situ temperatures of bottom

seawater and sediment, indicate that some of these carbonates (especially from cores associated with underlying massive gas hydrates) precipitated in or near equilibrium with present bottom-water conditions. On the other hand, those carbonates more enriched in ^{18}O are interpreted to have precipitated from ^{18}O -rich fluids, which are thought to have been derived from dissociation of gas hydrates. The dissociation of gas hydrates in the northern Gulf of Mexico within the last 5,500 years may be caused by nearby salt movement and related brines.

Introduction

The co-occurrence of authigenic carbonates and gas venting has been documented at many gas hydrate sites (for example, the Blake Ridge (Naehr and others, 2000); the Cascadia Margin (Bohrmann and others, 1998); the Gulf of Mexico (Sassen and others, 2004)). In these areas, the carbon in the carbonates was mainly derived from methane. Thus, carbonate precipitation may be related to the decomposition of gas hydrates.

Determining the age of authigenic carbonate is difficult. Some researchers hypothesize that gas hydrate-related authigenic carbonates formed during the last glacial maximum (LGM) (Bohrmann and others, 1998; Aloisi and others, 2000). This interpretation, however, assumes that the lowered sea level during the Pleistocene epoch reduced pressure on the ocean margins and triggered gas hydrate dissociation.

Because ^{14}C datable shell fragments were mixed with some sampled authigenic carbonates in the northern Gulf of Mexico (GOM), some chronological control is available that

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helps constrain the time of formation of these authigenic carbonates. High-resolution seismic profiles across the core sites and regionally well-known sedimentation rates (Coleman and others, 1983; Rowan and Weimer, 1998) also help constrain the time of carbonate formation.

Geochemical data are presented for carbonates recovered from piston cores obtained from the northern Gulf of Mexico (fig. 1). Core information, including water depths and locations, is presented in Appendix A. The data document variations in the carbon and oxygen isotopes, chemical compositions, mineralogy, and the timing of the carbonate precipitation. The carbon isotopic values suggest carbonate carbon is derived from anaerobic oxidation of methane. The variations in oxygen isotopes together with other geochemical proxies provide evidence for the relations between authigenic carbonate and gas hydrates.

Geological Background and Sampling

The northern Gulf of Mexico is a passive continental margin characterized by more than 10 kilometers (km) of sediments of Mesozoic-Cenozoic age, which are well-suited for the generation and accumulation of large oil and gas reservoirs. The extensive salt deposits and salt thrusts within this margin provide an excellent environment for both hydrocarbon accumulation and migration (Sassen and others, 1994). During the Late Triassic period, rifting of the Gulf of Mexico led to the formation of many subbasins; these basins were then floored by thick salt (Louanne/Werner formations) during Middle Jurassic marine incursions (Salvador, 1987) and formed the main structural features of the northern Gulf of Mexico. Since the Cenozoic era, the long history of ongoing salt diapirism has resulted in structural deformation, faulting, fracturing, and sediment slumping, all of which provide conduits for upward seepage of gaseous and liquid hydrocarbons. Authigenic carbonate minerals and gas hydrates on the

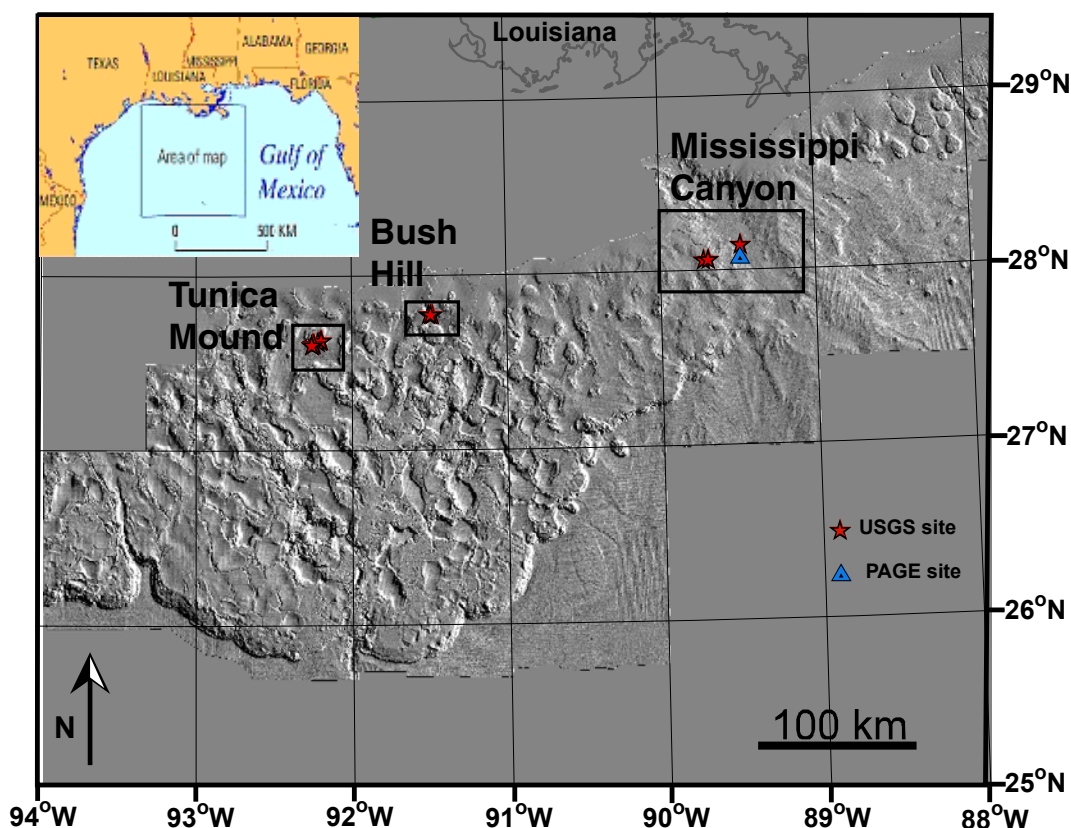


Figure 1. Coring locations of carbonates and pore water in the northern Gulf of Mexico during the July 2002 RV *Marion Dufresne* Cruise (MD-02). Carbonates were recovered from two areas—the Tunica Mound and the Mississippi Canyon.

sea floor and within sediments are the cumulative products of these extensive hydrocarbon seeps (for example, Brooks and others, 1984; Roberts and Aharon, 1994). Authigenic carbonates are so pervasive in the northern GOM that carbonate mounds and hydrate-related hills may exceed a kilometer in diameter (Neurauter and Roberts, 1992). These authigenic carbonates may cap gas hydrate-bearing strata and provide a temporal record of hydrocarbon seeps.

During July 2002, the research vessel (RV) *Marion Dufresne* was used to investigate the occurrence and distribution of gas hydrate in the shallow subsurface of the northern Gulf of Mexico (fig. 1). A giant Calypso piston corer was used to obtain sediment samples up to 38 meters (m) in length (Winters and others, this volume, chapter 3). Authigenic carbonates were recovered between 0 and 27 meters below the sea floor (mbsf) in sediments from several different geological environments: (1) on or near sea-floor sediments on the crest of a salt diapir at Tunica Mound (cores MD02-2543G, 2544G, 2545G), (2) in shallow subbottom sediment over a gas chimney (MD02-2570, 2571C2) west of the Mississippi Canyon, (3) near a salt diapir at Tunica Mound (MD02-2546), and (4) in sediment associated with gas hydrates (MD02-2569 and MD02-2573GHF) on the floor of the Mississippi Canyon (figs. 2–3). Prior to this cruise, carbonate samples typically were recovered in the Gulf of Mexico only from near-surface

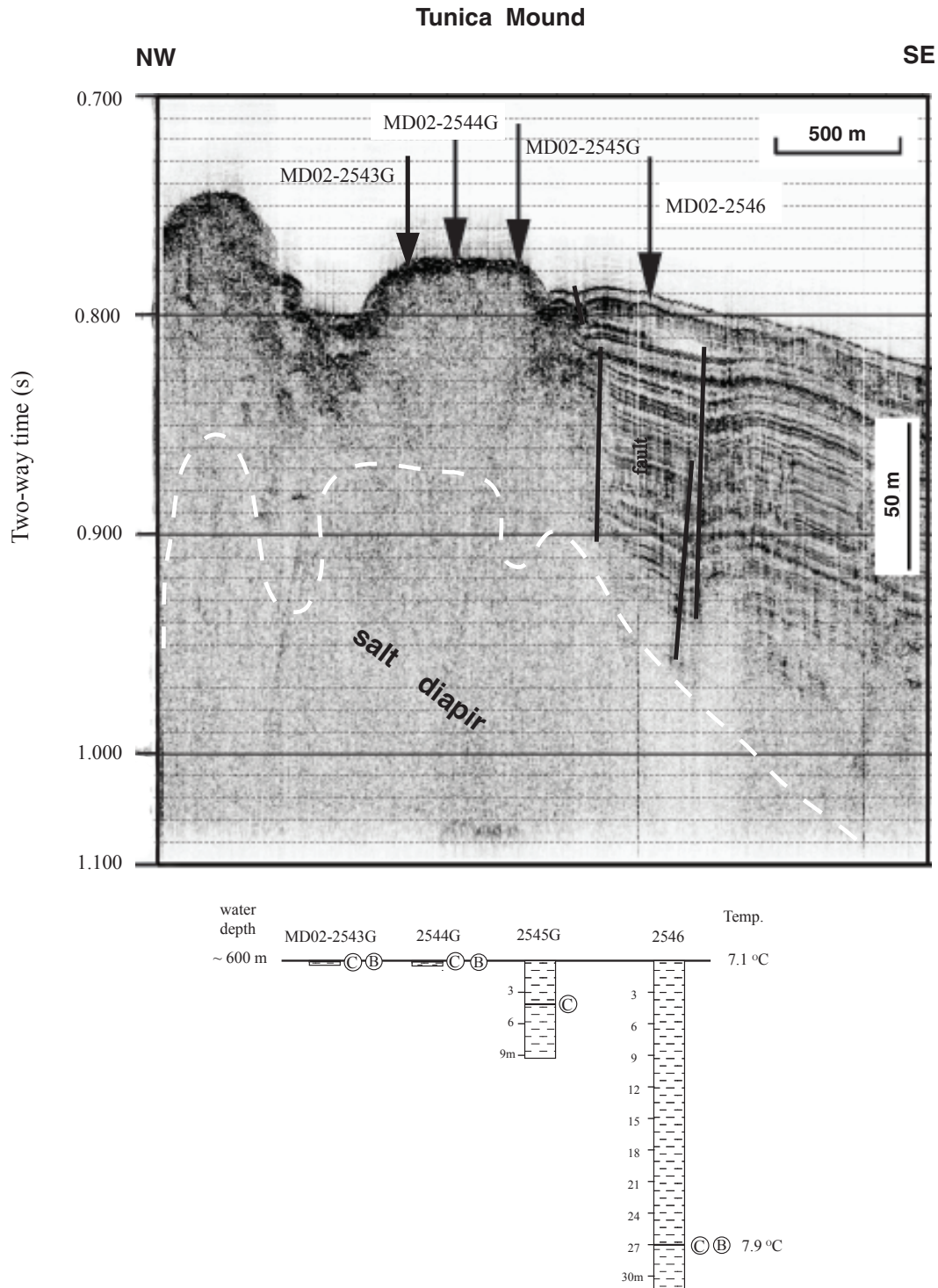


Figure 2. Upper: Seismic profile oriented northwest–southeast across the Tunica Mound sea-floor area of Garden Bank Block 386 on the upper continental slope. Locations of cores containing carbonates are indicated with arrows. Note the underlying salt diapir and the well-defined faults, which function as conduits for gas and fluids to migrate to the sea floor. This has created a variety of vent-related features. Lower: Graphic logs showing the lithology and distribution of carbonates in cores (C = carbonate nodules/crusts/hardgrounds; B = bivalves shell fragments).

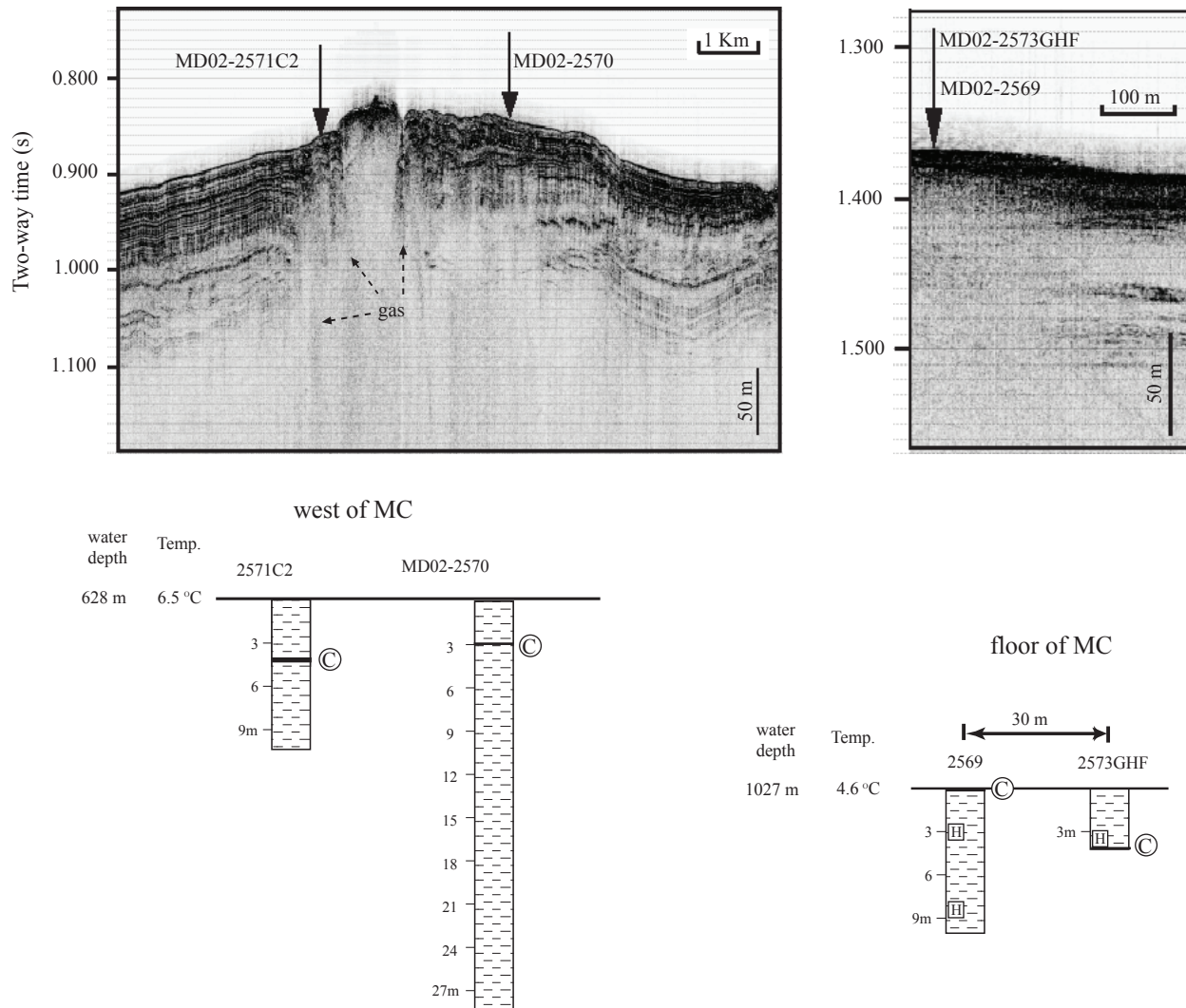


Figure 3. Upper: Seismic profile oriented northwest–southeast across a site west of the Mississippi Canyon (MC) and in the central MC sea-floor area. Locations of cores containing carbonates are indicated with arrows. Lower: Graphic logs showing lithology and distribution of carbonates in cores (C = carbonate nodules/crusts/hardgrounds; H = gas hydrates).

sediment by using submersibles (Roberts and Aharon, 1994; Aharon and others, 1997).

Methods

The carbonates (number of samples (n) = 25) in hand samples were petrographically and geochemically examined. Bulk mineralogy (n = 35) was determined on pressed powder mounts by using a Mac Science MXP3 Powder X-ray Diffractometer (XRD) at the University of Tokyo. The XRD patterns were obtained from 0° to $40^\circ 2\theta$ at a scanning speed of $2^\circ 2\theta/\text{min}$. The weight percentages of minerals were estimated using the peak weights (Müller, 1967) with an estimated error of $\pm 5\%$. Carbon-coated, polished thin sections were made from selected authigenic carbonates and examined by electron

microprobe analyses by using a JEOL Superprobe 733 – II to provide detailed chemical compositions of calcite. In addition, concentrations of Ca, Mg, Mn, Fe, Sr, and Ba were determined. The analytical precision is 1% for Ca, 2% for Mg, 4% for Mn and Fe, and 9% for Sr and Ba.

Oxygen and carbon isotope compositions (n = 34) were measured on the same set of samples by XRD. Carbon dioxide gas was produced by reaction with 100-% phosphoric acid at 25°C for 24 hours, and the purified CO_2 gas was analyzed using a Finnigan MAT 252 Mass Spectrometer at the University of Tokyo. The isotopic compositions are given relative to the Peedee Belemnite (PDB) reference, with a precision of $\pm 0.2\%$ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

Pore waters for stable oxygen isotope analyses were collected by squeezing 10-centimeter (cm) long, whole-round core sections at about 3-m intervals (Ussler and Paull, this

volume, chapter 8). Oxygen isotopic compositions of 155 pore-water samples were determined using the $\text{H}_2\text{O}-\text{CO}_2$ equilibration method (Epstein and Mayeda, 1953). The resulting CO_2 was purified and collected by cryogenic transfer. Stable oxygen isotope ratios of CO_2 also were measured on a Finnigan MAT 252 mass spectrometer at the University of Tokyo. Oxygen isotope measurements on the pore waters are reported in standard delta notation (δ) with respect to Standard Mean Ocean Water (SMOW). The cumulative (vacuum line and mass spectrometer) accuracy and precision of oxygen isotopic measurements are $\pm 0.2\text{‰}$ and $\pm 0.06\text{‰}$, respectively.

The ^{14}C measurements were made on shell fragments with and without carbonate cements ($n = 2$) in core MD02-2543G. To remove contaminants, each shell fragment was carefully stripped of adhering sediments under a microscope, repeatedly placed into deionized water in an ultrasonic bath, and leached using 1 molar (M) HCl. The washing was finished with a final rinsing with deionized water, and the sample was dried in a desiccator in a vacuum line. Under vacuum, the shell was reacted with phosphoric acid, and the evolved CO_2 was reduced to obtain graphite targets prepared following the method described by Miyairi and others (2004). The ^{14}C concentration was measured using accelerator mass spectrometry (AMS) in a Pelletron 5UD Tandem accelerator at the Research Center for Nuclear Science and Technology, University of Tokyo. The analytical precision was $\pm 0.5\%$. The age was calculated as years before present (BP, years from A.D. 1950), and errors are expressed as ± 1 standard deviation (σ).

Results

Occurrence of Authigenic Carbonates

Authigenic carbonates were collected at the Tunica Mound in cores MD02-2543G, 2544G, 2545G, and 2546 with water depths ranging between 579 and 595 m. The geothermal gradient at these sites was 29 degrees Celsius per kilometer ($^\circ\text{C}/\text{km}$), with a bottom-water temperature of $7.1\text{ }^\circ\text{C}$ at these sites (Labails, this volume, chapter 6). Seismic profiles of this site (fig. 2) show that Tunica Mound is underlain by a large salt diapir. The authigenic carbonates were found at the top of core MD02-2543G and occurred as broken pieces of hardgrounds, with or without carbonate-cemented shell fragments being present (fig. 3). Carbonates recovered from core MD02-2544G consisted of porous crusts with noncemented shell fragments (fig. 4) on the sea floor. One large, hard and irregularly shaped concretion was obtained at 4.25 mbsf in core MD02-2545G (fig. 4). A semi-consolidated concretion, with a small cemented shell fragment was at ~ 27 mbsf in core MD02-2546. This was the deepest concretion recovered during the cruise (fig. 4). No gas hydrates were found or inferred to have existed in any of the cores collected at the Tunica

Mound (Paull and others, 2005); however, this area is characterized with gas venting.

Authigenic carbonates also were recovered from two cores (MD02-2569 and 2573GHF) on the floor of the Mississippi Canyon in a gas hydrate area at water depths of 1,032 and 1,027 m, respectively, and bottom-water temperature of $4.6\text{ }^\circ\text{C}$ (fig. 3). Both cores were observed to contain gas hydrates. Carbonates in MD02-2569 occurred as irregular hard nodules in sediments just below the sea floor, underlain by two layers of massive gas hydrates (fig. 3). One layer occurred at ~ 3 mbsf, as a chunk of gas hydrate filling the entire 10-cm diameter core liner (fig. 5). Carbonates in core MD02-2573GHF were found coexisting with small pieces of gas hydrate, distributed as porous concretions in irregular shapes (fig. 5).

The authigenic carbonates recovered in cores MD02-2570 and 2571C2 are near a gas chimney west of the Mississippi Canyon (fig. 3) in 631 and 664 m of water. Bottom-water temperature is $6.5\text{ }^\circ\text{C}$, and a geothermal gradient of $36\text{ }^\circ\text{C}/\text{km}$ (Labails and others, this volume, chapter 6) is present in the area. In core MD02-2570, round semi-consolidated carbonate nodules were obtained at ~ 3 mbsf; whereas, the carbonates in core MD02-2571C2 were ~ 35 cm thick and occurred as semi-consolidated nodules and slabs. One ~ 2 -cm-thick carbonate slab has a round hole of ~ 0.5 cm in diameter, which may be a conduit for gas venting (fig. 5).

In summary, most of the authigenic carbonate samples occurred on the sea floor or in shallow sediments (that is, ≤ 5 mbsf) surrounding gas vents, except for one sample obtained at ~ 27 mbsf in core MD02-2546.

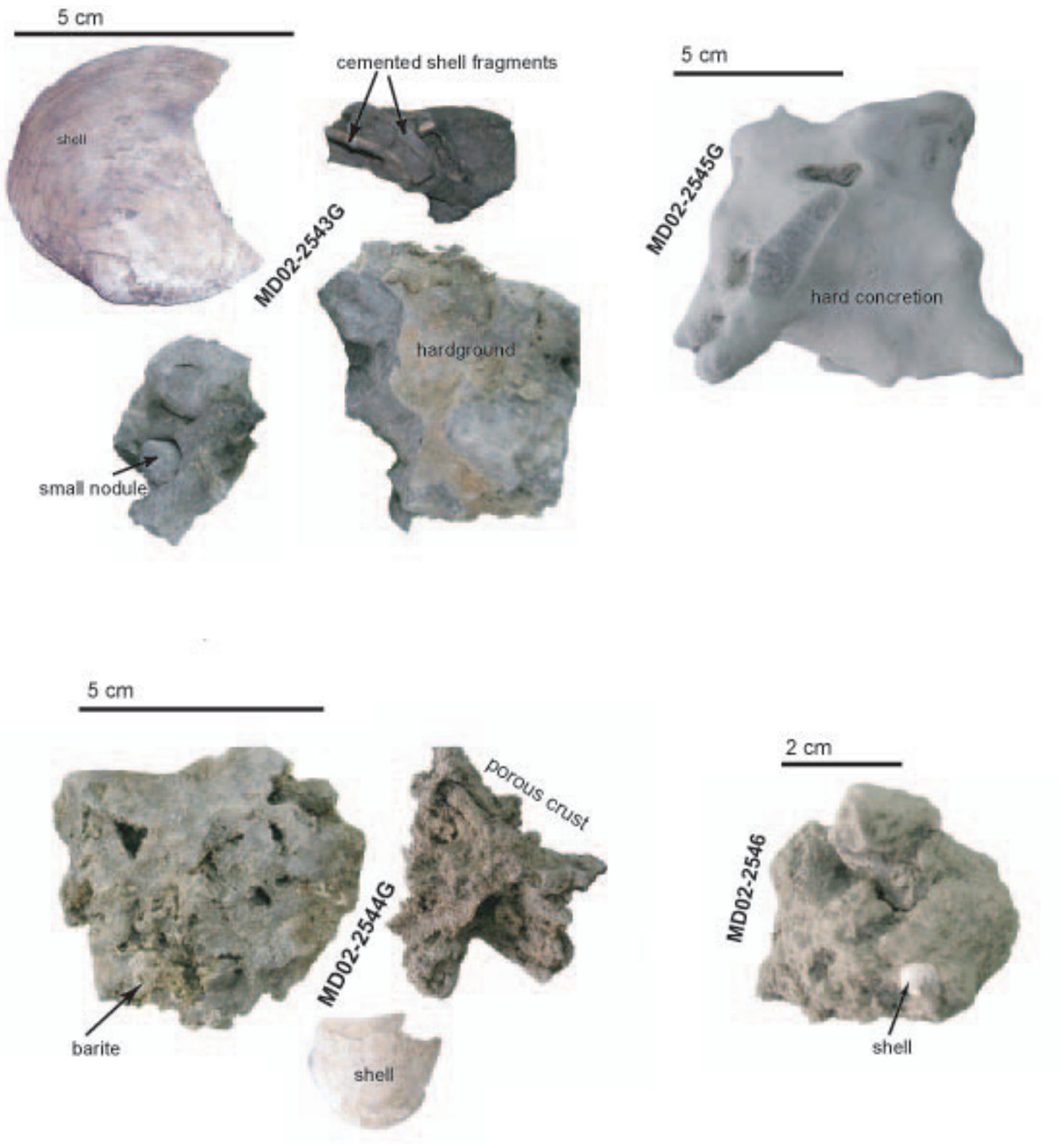


Figure 4. Specimens of carbonates in piston cores from the Tunica Mound in the northern Gulf of Mexico.

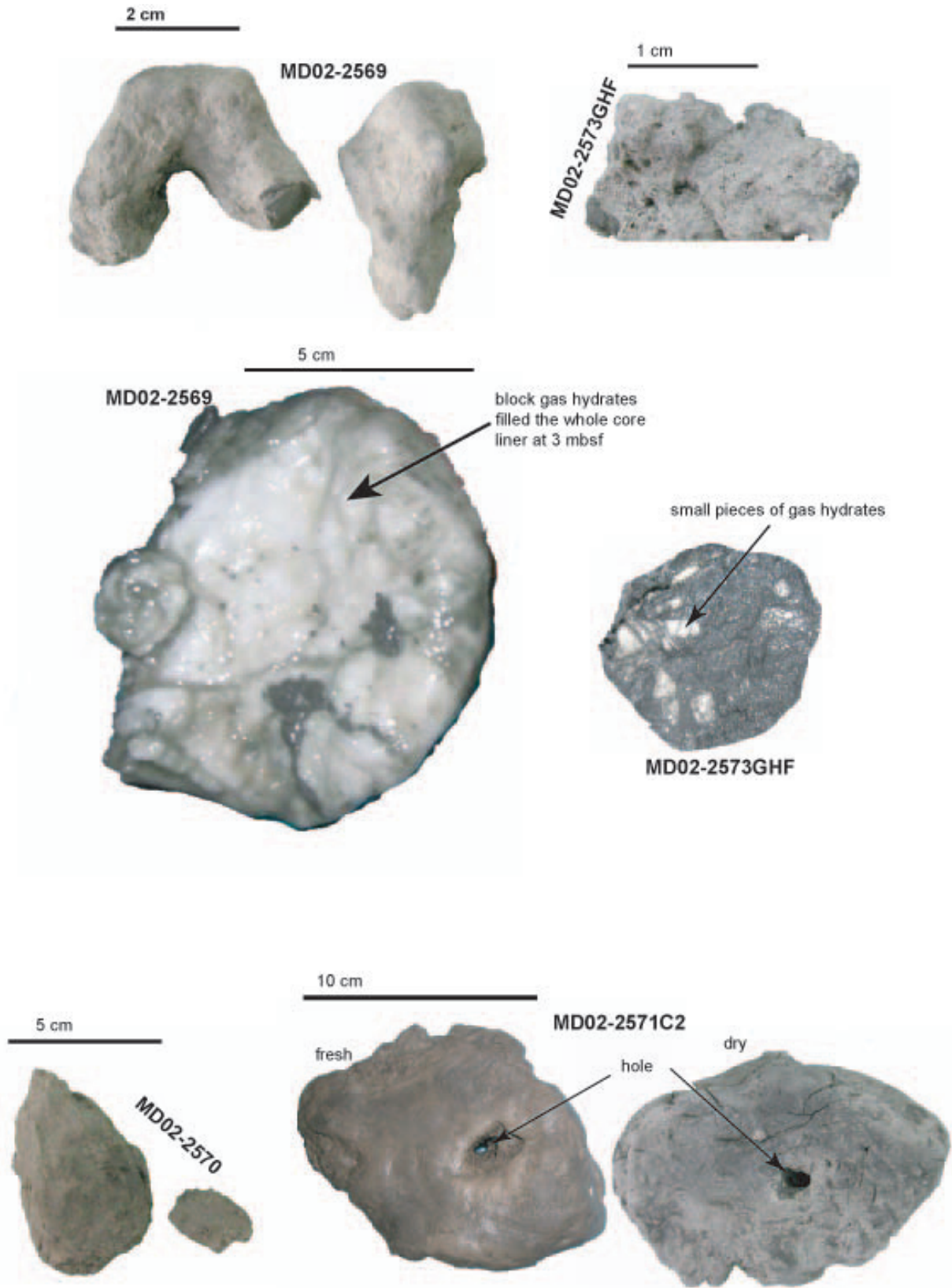


Figure 5. Specimens of carbonates from piston cores from the Mississippi Canyon in the northern Gulf of Mexico. A sample from core MD02-2571C2 has a hole that is probably a gas conduit for the upward migration of methane. Specimens of gas hydrates were recovered in cores MD02-2569 and 2573 (photographs provided by W. Winters and T. Lorenson, respectively).

Petrography and Mineralogy

Observations of thin sections showed that the predominant micritic authigenic carbonates were developed within fine-grained clastic sediments. Silt-sized quartz grains, foraminifera (mostly planktonic), bivalve shell fragments, and framboidal pyrites were noted as well as numerous cavities. The cavities were cemented with micritic carbonates, organic matter, and some framboidal pyrites. Barite was identified ($\leq 5\%$) in only one sample (MD02-2544G) (fig. 6).

Thirty-one authigenic carbonates and one bivalve shell were analyzed by XRD. The samples are composed primarily of calcite and quartz with subordinate amounts of dolomites

and pyrites. Calcite content ranges from 41 weight percent (wt%) to 94 wt%, with a mean of 73 wt%. Differences in mineralogy by area are not obvious among crust, hardground and nodules.

The position of the major diffraction peak $d(104)$ of calcite varies between 2.978 and 3.014 angstroms (\AA ; fig. 7). The shift of $d(104)$ values away from that of stoichiometric calcite (3.035 \AA) is caused by substitution of Mg^{2+} for Ca^{2+} , as well as by other divalent ions. Most calcites centered around 2.998 \AA , indicating a MgCO_3 content of approximately 12 molar percent (mol%) based on the standard calibration curves from Müller (1967). However, two extreme values of calcite $d(104)$ were measured, which indicate that MgCO_3 content in the calcite ranges from 6 mol% to 20 mol%.

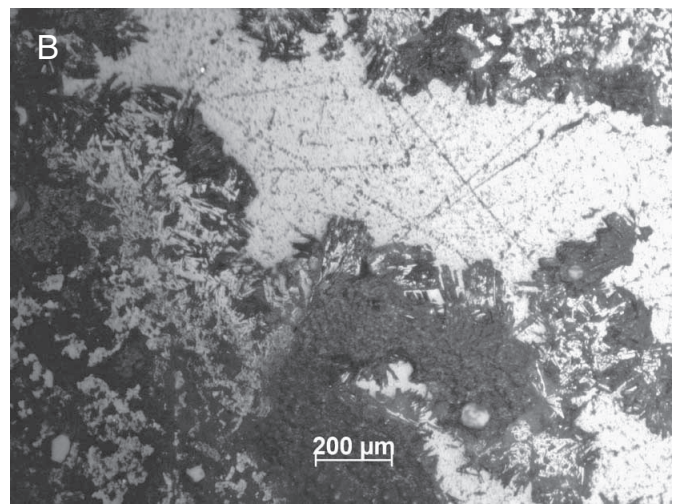
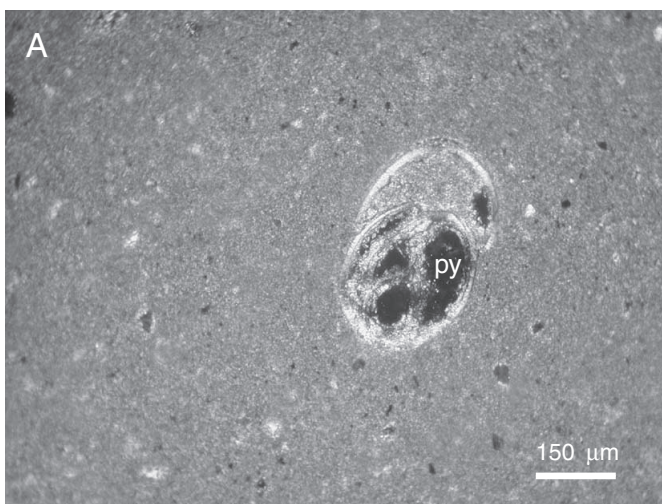


Figure 6. Thin-section photomicrographs of carbonates. (A) Micritic carbonates developed within silt-sized quartz grains (shining spots), framboidal pyrite (py) formed inside the cavities of forams (polarized light, sample MD02-2543G hardground). (B) Bladed crystals of barite developed within the cavities around micritic calcites (polarized light, sample MD02-2544G porous nodule).

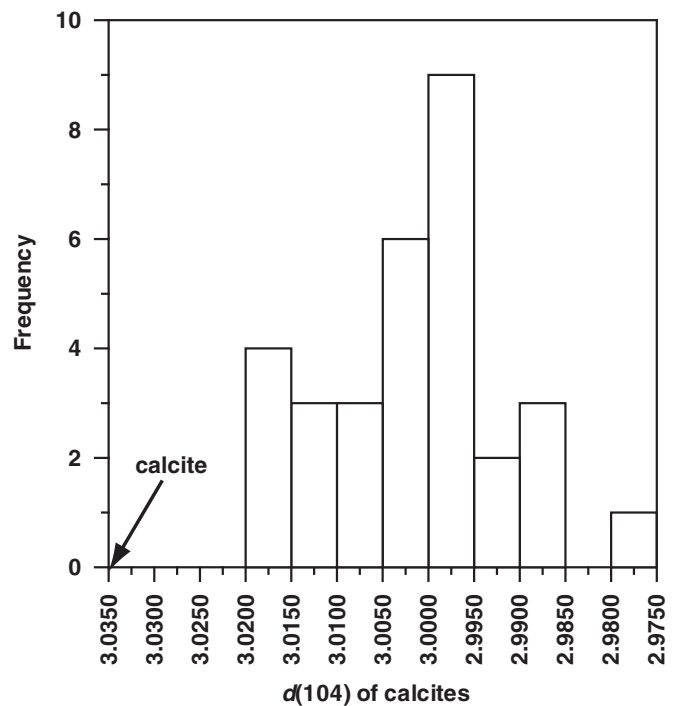


Figure 7. Distribution of $d(104)$ values for calcite of 31 authigenic carbonates.

Geochemistry

Chemical Compositions of Calcite

Seventeen authigenic carbonate samples were measured by electron microprobe. The data indicate that all carbonates are high magnesium calcite, with 6 to 21 mol% Mg^{2+} (table 1), which are consistent with the shifts of $d(104)$ determined by XRD analysis. These carbonates also contain minor amounts of FeO and MnO (table 1), which indicate carbonates have precipitated in reducing environments.

Stable Carbon and Oxygen Isotopic Compositions of Carbonates

Stable isotopes of carbon and oxygen were measured on 23 bulk authigenic carbonate samples and on 11 micro drilled samples from carbonate nodules in cores MD02-2545G, MD02-2569, and MD02-2571C2 A20-25cm (table 2). Except for a shell fragment ($\delta^{13}C_c = -3.1\text{‰}$), all the carbonates are extremely depleted in ^{13}C , with $\delta^{13}C_c$ values ranging from -35.8 to -61.9‰ . The oxygen isotopes of carbonates ($\delta^{18}O_c$) range from $+3.4$ to $+5.9\text{‰}$ (table 2; fig. 8).

Table 1. Chemical compositions of calcite in authigenic carbonates analyzed by electron microprobe analysis.

Core no.	Molar percent					Point no.	Sample no.
	Calcium	Magnesium	Iron	Manganese	Strontium		
MD02-2543G	89.3 (42.7–100)	10.0 (0.0–55.2)	0.6 (0.0–17.9)	0.0 (0.0–3.4)	0.1 (0.0–2.1)	840	5
MD02-2544G	93.6 (79.9–100)	6.1 (0.0–19.6)	0.2 (0.0–11.3)	0.0 (0.0–0.3)	0.0 (0.0–0.5)	521	3
MD02-2545G	89.6 (52.6–100)	9.5 (0.0–46.8)	0.9 (0.0–7.7)	0.0 (0.0–0.3)	0.0 (0.0–0.3)	74	1
MD02-2546	77.6 (71.0–84.7)	21.3 (15.3–25.3)	1.1 (0.0–4.5)	0.0 (0.0–0.0)	0.0 (0.0–0.0)	47	1
MD02-2569	83.0 (50.2–100)	16.6 (0.0–49.3)	0.3 (0.0–0.6)	0.0 (0.0–0.6)	0.0 (0.0–0.4)	179	2
MD02-2573GHF	83.5 (54.2–99.2)	15.8 (0.8–45.6)	0.6 (0.0–4.7)	0.0 (0.0–0.4)	0.1 (0.0–0.3)	50	1
MD02-2570	80.9 (51.7–100)	18.2 (0.0–48.1)	0.8 (0.0–2.4)	0.0 (0.0–0.5)	0.0 (0.0–0.3)	193	3
MD02-2571C2	83.7 (50.6–100)	15.3 (0.0–49.4)	1.0 (0.0–6.0)	0.1 (0.0–1.5)	0.0 (0.0–0.4)	123	1

Note: Data shown in average (range); point no., number of points; sample no., number of thin sections.

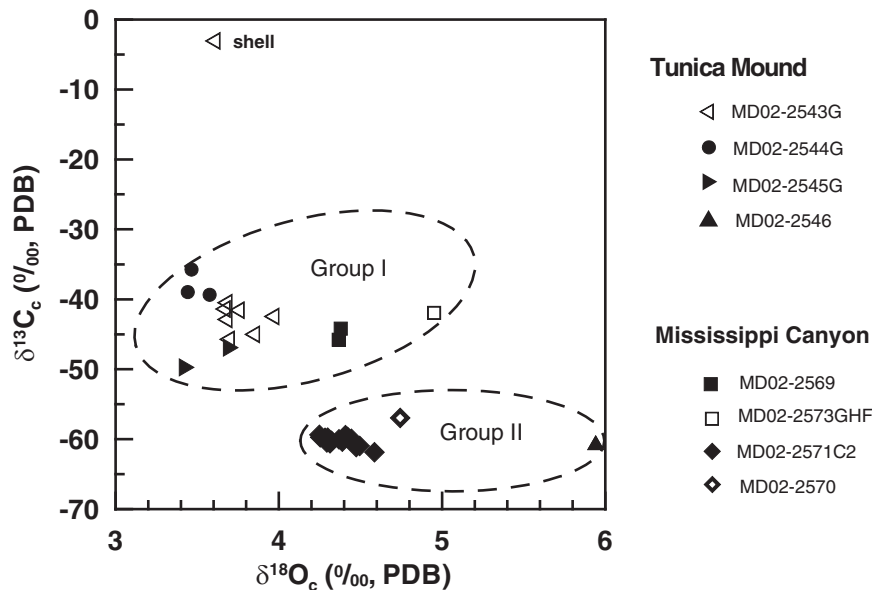


Figure 8. Carbon and oxygen isotopic compositions of carbonates.

Table 2. Geological setting and results of isotopic and Mg²⁺ contents of carbonates, $\delta^{18}\text{O}$ values of interstitial water sampled from the upper 6 meters of sediment cores, and calculated carbonate precipitated water oxygen isotopes.

[m, meters; mbsf, meters below sea floor; $\delta^{13}\text{C}_c$, the stable carbon isotope of carbonate; PDB, Peedee Belemnite; $\delta^{18}\text{O}_c$, the stable oxygen isotope of carbonate; Mg, magnesium; mol%, molar percent; Bottom water temperature, measured bottom water temperature (Labails and others, 2007); °C, degrees Celsius; Temperature, assumed carbonate precipitated temperature; $\delta^{18}\text{C}_{w(\text{cal})}$, calculated carbonate precipitated water oxygen isotope; SMOW, standard mean ocean water]

Core no.	Water depth (m)	Depth (mbsf)	Location structure	$\delta^{13}\text{C}_c$ (PDB)	$\delta^{18}\text{O}_c$ (PDB)	Mg (mol%)	Bottom water temperature (°C)	Temperature (°C)	$\delta^{18}\text{O}_{w(\text{cal})}$ (SMOW)
Tunica Mound									
MD02-2543G C.C. TOP hardground	579	0.03	over salt diapir	-42.9	3.7	11	7.1	7.1	1.0
MD02-2543G C.C. TOP porous crust	579	0.03	over salt diapir	-42.5	4.0				
MD02-2543G C.C. TOP small nodule	579	0.03	over salt diapir	-45.7	3.7				
MD02-2543G C.C. TOP hardground with the small nodule	579	0.03	over salt diapir	-40.5	3.7				
MD-02-2543G C.C. TOP shell cements	579	0.03	over salt diapir	-41.4	3.7	9	7.1	7.1	1.1
MD02-2543G C.C. TOP shell	579	0.03	over salt diapir	-3.1	3.6	0	7.1	7.1	0.7
MD02-2543G C.C. A	579	0.15	over salt diapir	-45.0	3.8				
MD02-2543G C.C. C	579	0.15	over salt diapir	-41.6	3.7	10	7.1	7.1	1.1
Mississippi Canyon									
MD02-2544G C.C. A	584	0.1	over salt diapir	-39.0	3.4	7	7.1	7.1	0.9
MD02-2544G C.C. A porous crust	584	0.1	over salt diapir	-39.4	3.6				
MD02-2544G C. C. B	584	0.1	over salt diapir	-35.8	3.5	6	7.1	7.1	1.0
MD02-2545 inner rim	588	4.23	over salt diapir	-49.7	3.4				
MD02-2545 outer rim	588	4.23	over salt diapir	-46.9	3.7				
MD02-2545	588	4.23	over salt diapir	-48.3	3.6	10	7.1	7.1	1.0
MD02-2546	595	26.95	near salt diapir	-60.8	5.9	21	7.1	7.1	2.5
MD02-2546	595	26.95	near salt diapir	-60.8	5.9	21	7.1	7.9	2.7
Mississippi Canyon									
MD02-2569 inner rim	1,032	0.03	over salt diapir	-45.8	4.4				
MD02-2569 outer rim	1,032	0.03	over salt diapir	-44.2	4.4				
MD02-2569	1,032	0.03	over salt diapir	-45.0	4.4	17	4.6	4.6	0.7
MD02-2573 GHF	1,027	4.2	over salt diapir	-41.9	5.0	16	4.6	4.6	1.3
MD02-2570	631	2.95	gas chimney	-57.0	4.7	18	6.5	6.5	1.4
MD02-2571C2 A 0–5 cm	664	4.28	gas chimney	-61.1	4.5				
MD02-2571C2 A 5–10 cm	664	4.34	gas chimney	-60.0	4.4				
MD02-2571C2 A ~10 cm	664	4.37	gas chimney	-59.7	4.4				
MD02-2571C2 440 cm	664	4.4	gas chimney	-61.9	4.6				
MD02-2571C2 A 10–15 cm	664	4.4	gas chimney	-59.4	4.4				

Table 2. Geological setting and results of isotopic and Mg²⁺ contents of carbonates, $\delta^{18}\text{O}$ values of interstitial water sampled from the upper 6 meters of sediment cores, and calculated carbonate precipitated water oxygen isotopes. — Continued

[m, meters; mbsf, meters below sea floor; $\delta^{13}\text{C}_c$, the stable carbon isotope of carbonate; PDB, Peedee Belemnite; $\delta^{18}\text{O}_c$, the stable oxygen isotope of carbonate; Mg, magnesium; mol%, molar percent; Bottom water temperature, measured bottom water temperature (Labails and others, 2007); °C, degrees Celsius; Temperature, assumed carbonate precipitated temperature; $\delta^{18}\text{O}_{w(\text{cal})}$, calculated carbonate precipitated water oxygen isotope; SMOW, standard mean ocean water]

Core no.	Water depth (m)	Depth (mbsf)	Location structure	$\delta^{13}\text{C}_c$ (PDB)	$\delta^{18}\text{O}_c$ (PDB)	Mg (mol%)	Bottom water temperature (°C)	Temperature (°C)	$\delta^{18}\text{O}_{w(\text{cal})}$ (SMOW)
MD02-2571C2 A 15–20 cm	664	4.46	gas chimney	−59.9	4.4	15	6.5	6.5	1.3
MD02-2571C2 A 20–25 cm #1	664	4.52	gas chimney	−60.4	4.4				
MD02-2571C2 A 20–25 cm #2	664	4.52	gas chimney						
MD02-2571C2 A 20–25 cm #3	664	4.52	gas chimney	−60.5	4.3				
MD02-2571C2 A 20–25 cm #4	664	4.52	gas chimney	−59.8	4.3				
MD02-2571C2 A 20–25 cm #5	664	4.52	gas chimney	−60.6	4.3				
MD02-2571C2 A 20–25 cm #6	664	4.52	gas chimney	−59.7	4.3				
MD02-2571C2 A 20–25 cm #7	664	4.52	gas chimney	−59.8	4.3				
MD02-2571C2 A 20–25 cm #8	664	4.52	gas chimney	−61.0	4.5				
MD02-2571C2 A 25–30 cm	664	4.58	gas chimney	−59.4	4.2				

Stable Oxygen Isotopic Compositions of Interstitial Water

Because all sampled carbonates occurred within the upper 5 m of sediment (except for core MD02-2546), the stable oxygen isotopic values of interstitial water ($\delta^{18}\text{O}_{\text{IW}}$) from the upper 6 m of sediment were accounted for in this study. These $\delta^{18}\text{O}_{\text{IW}}$ values remain almost constant with depth for the upper 6 m in each core, and most of the values ($n = 30$ of 34) range from +0.7‰ to +1.0‰, with a mean of +0.8‰. Thus, we can regard these $\delta^{18}\text{O}_{\text{IW}}$ values as reflecting the regional bottom seawater oxygen isotope ($\delta^{18}\text{O}_{\text{sw}}$), except for four samples in core MD02-2543G, which have values ranging from −0.6‰ to −0.4‰. These four samples may be out of place because they came from the upper 0.15 m of a core with a bent barrel. The negative $\delta^{18}\text{O}_{\text{IW}}$ values may have been caused by diagenetic reactions at low temperatures with the underlying patchy tephra in the core. Because the carbonates in core MD02-2543G were just below the sea floor, we will assume $\delta^{18}\text{O}_{\text{IW}}$ values of these carbonates are the same as the regional $\delta^{18}\text{O}_{\text{sw}}$.

There was no interstitial water available for $\delta^{18}\text{O}$ analysis in cores MD02-2544G, 2573GHF, and 2571C2 because of the lack of sediment recovery. The carbonates in these cores occurred within 5 mbsf, thus we assume that $\delta^{18}\text{O}_{\text{IW}}$ values of the host sediment are the same as the regional $\delta^{18}\text{O}_{\text{sw}}$ values. The $\delta^{18}\text{O}_{\text{IW}}$ value of the pore water sampled from the same horizon that contained the carbonates at ~27 mbsf in core MD02-2546 is +1.3‰.

¹⁴C Ages of Shells

Results of ¹⁴C analyses show that a shell and carbonate-cemented shell in core MD02-2543G have $\Delta^{14}\text{C} = -361.1 \pm 4.7\%$ ($\delta^{13}\text{C} = -3.1\%$), and $\Delta^{14}\text{C} = -499.5 \pm 5.0\%$, respectively. Based on the conventional ¹⁴C age calculation (Stuiver and Polach, 1977), these two shells may have ages of 3,600 ± 60 years BP and 5,560 ± 80 years BP, respectively.

Discussion

Carbon Isotopic Variations of Carbonates

The sources of carbon in the pore fluids in the Gulf of Mexico include: (1) methane ($\delta^{13}\text{C} = -120$ to -30%), (2) oil fractions ($\delta^{13}\text{C} = -25$ to -28%) (Aharon and others, 1997), (3) sedimentary organic matter ($\delta^{13}\text{C} = -25\%$ on average), (4) marine biogenic carbonate ($\delta^{13}\text{C} = \sim 0\%$), and (5) seawater CO_3^{2-} with a $\delta^{13}\text{C}$ value of $\delta^{13}\text{C} = 0 \pm 3\%$ (Anderson and Arthur, 1983).

In order to identify the carbon source and the carbonate-forming mechanism for the authigenic carbonates, carbon isotope analyses were carried out on the same subsamples, which also were analyzed mineralogically. Because carbonate carbon isotope values (from -35.8 to -61.9%) are lower than those found in any known carbon source other than methane, this is an indication that methane is the major carbon source of the carbonates. Supporting this conclusion is the occurrence of framboidal pyrite in these carbonates, which requires

anoxic conditions to form. Thus, these carbonates probably were formed near conditions of anaerobic methane oxidation (AMO) by sulfate reduction. One of the effects of AMO is to generate HCO_3^- and to increase the alkalinity of the pore fluids, which contributes to the precipitation of authigenic carbonates. Moreover, the addition of methane carbon to the pore fluid dissolved inorganic carbon (DIC) pool, which decreases the $\delta^{13}\text{C}$ value of the DIC, may result in authigenic carbonates with low $\delta^{13}\text{C}$ values (Paull and others, 1992; Greinert and others, 2001). In contrast, the carbon isotope values of the shells are much higher (-3.1‰), suggesting that the carbon came mainly from seawater bicarbonate.

Two general mechanisms generate methane in the marine environment: microbial methane formed by CO_2 -reduction and thermogenic-methane generated during organic matter maturation (Bernard and others, 1978; Whiticar, 1999). The $\delta^{13}\text{C}$ values of microbial methane typically are $<-60\text{‰}$. Conversely, thermogenic methane with the $\delta^{13}\text{C}$ values typically are $>-50\text{‰}$ (Bernard and others, 1978).

According to the $\delta^{13}\text{C}_c$ values of -35.8 to -61.9‰ , carbonates can be classified into two groups: Group I ($\delta^{13}\text{C}_c = -35.8$ to -49.7‰) and Group II ($\delta^{13}\text{C}_c = -59.4$ to -61.9‰) (fig. 8). Group I carbonates were found in Tunica Mound cores MD02-2543G, 2544G, and 2545G but not in core MD02-2546, and in both cores (MD02-2569 and 2573GHF) containing gas hydrates from the floor of the Mississippi Canyon. At Tunica Mound, carbonate $\delta^{13}\text{C}_c$ values range from -35.8 to -49.7‰ with a mean of -42.6‰ . At the floor of the Mississippi Canyon, the carbonate $\delta^{13}\text{C}_c$ values are in a tight range of -41.9 to -45.8‰ with a mean of -44.0‰ . Group II carbonates were recognized in both cores (MD02-2570 and 2571C2) near a gas chimney west of the Mississippi Canyon and a core (MD02-2546) on the flank of Tunica Mound. The carbonate $\delta^{13}\text{C}$ values range from -59.4 to -61.9‰ , with an average of -60.3‰ .

The distinction in the carbon isotopic values in groups I (-35.8 to -49.7‰) and II (-59.4 to -61.9‰) may reflect the variation in the source of the methane carbon, particularly if the carbon comes from thermogenic or microbial sources. The group II values clearly indicate that microbial methane carbon dominates in the DIC pool from which the carbonates precipitated. However, the group I carbonates may be coming from either primarily thermogenic methane sources or may indicate more dilution of the DIC pool with carbon from other sources; for example, microbial methane carbon diluted by seawater DIC, or a mixture of microbial and thermogenic methane carbon. Localized conduits, for example faults and fractures, caused by salt movement from the migration of thermogenic hydrocarbons from great depth in the sedimentary section to the sea floor are common in the Gulf of Mexico (fig. 2, for example).

Ages of Carbonates

The age of the authigenic carbonates can be estimated from known regional sedimentation rates and/or ^{14}C measurements of associated shells.

Tunica Mound: Carbonates at Tunica Mound are from Garden Banks Block 386 (GB 386), and in this area the sedimentation rate is 7 to 11 meters per thousand years (m/k.y.) for the upper sedimentary section (Rowan and Weimer, 1998; Cooper and Hart, 2003). The carbonates in core MD02-2546 occurred at about 27 mbsf in the stratified sediments inferred from the seismic profile (fig. 2). If constant sedimentation rates are assumed, this suggests the nodule is only 4,000 years old.

Carbonates recovered from cores MD02-2543G, 2544G, and 2545G occurred on the top of Tunica Mound. Because erosion is occurring here, the sedimentation rates cannot be used to determine the sediment ages. Fortunately, shell fragments were also recovered together with these carbonates (fig. 3). The ^{14}C measurements of the shell and carbonate-cemented shell in core MD02-2543G yielded ages of $3,600 \pm 60$ years BP and $5,560 \pm 80$ years BP, respectively. These calculated ages suggest the carbonate-cemented shell is about 2,000 years older than the shell without cements. Because the top of Tunica Mound is believed to be eroding, shells of different ages may be in close proximity. Moreover, the apparently older carbonate-cemented shell may have survived longer because it was protected from erosion due to the carbonate-cemented cover. Authigenic carbonates from other cores (MD02-2544G and 2545G) are very near the location of MD02-2543G (on top of Tunica Mound). Thus, they are likely to be of similar ages (younger than 5,500 years).

Mississippi Canyon: The authigenic carbonates in the Mississippi Canyon occurred from the sea floor to 4.6 mbsf in stratified sediments interpreted from seismic profiles (fig. 2); therefore, we can use the known sedimentation rates to constrain the ages of the authigenic carbonates in these sediments. The average sedimentation rates at the upper slope of the Mississippi Canyon are 15 to 20 m/k.y. because of sediment instabilities during the last 20 ka (Coleman and others, 1983). Because the carbonate concretions in the sediment cannot be older than the sediment deposits, the carbonates probably precipitated in recent times (less than 1,000 years ago).

In summary, all the authigenic carbonates collected during this cruise precipitated very recently—less than 5,500 years in the Tunica Mound and less than 1,000 years ago in the Mississippi Canyon region.

Oxygen Isotopic Variations of Carbonates and Gas Hydrate Dissociation

The oxygen isotopic composition of any particular sample of authigenic carbonate is controlled by a combination of factors, including (1) sample mineralogy and chemistry,

(2) temperature of carbonate precipitation, and (3) pore-fluid isotopic composition (Anderson and Arthur, 1983). To investigate if the analyzed $\delta^{18}\text{O}$ values of the carbonates are in equilibrium with ambient waters and to determine the factors that are critical to the $\delta^{18}\text{O}$ of the authigenic carbonates, the following oxygen isotope fraction equations were used:

Magnesium calcite: $1000\ln\alpha = 2.78 * (10^6/T^2) - 2.89 + 0.06 * \text{mol \% MgCO}_3$ (Friedman and O'Neil, 1977); and

Aragonite: $t = 19.9 - 4.34 * [\delta^{18}\text{O}_{\text{arag (PDB)}} - \delta^{18}\text{O}_{\text{w (SMOW)}}]$ (Hudson and Anderson 1989).

In these equations:

$$\alpha = \frac{1030.91 + 1.03091 * d^{18}\text{O}_{\text{c (PDB)}}}{1000 + d^{18}\text{O}_{\text{w (SMOW)}}$$

representing the oxygen isotope fractionation between the carbonate and the water in which it precipitated;

T is the absolute temperature (K); and
t is the Celsius temperature (°C).

According to ^{14}C dating and sedimentation rates, authigenic carbonates collected during this cruise have precipitated within the last few thousand years; therefore, influence of the last glacial-interglacial cycles on bottom seawater temperatures and oxygen isotopes can be ignored. Thus, present in situ bottom-seawater temperatures are similar to those at which these authigenic carbonates were precipitated.

Because the authigenic carbonates were precipitated in non-eroded sediment, we estimated the temperature at which these carbonates were precipitated according to the heat-flow data measured by Labails and others (this volume, chapter 6). Using these temperatures, the $\delta^{18}\text{O}_{\text{w}}$ of the water in equilibrium with these carbonates was calculated.

Tunica Mound: Because bivalves live on the sea floor, we assumed that they formed at current bottom-water temperature. The $\delta^{18}\text{O}$ of water for the formation of shell material in core MD02-2543G was calculated to be +0.7‰, using a present bottom-seawater temperature of 7.1 °C. This is in agreement with the measured regional $\delta^{18}\text{O}_{\text{sw}}$ (fig. 9).

Erosion is believed to have caused the carbonates in cores MD02-2543G and 2544G to be exposed at the sea floor. We assumed that the present bottom-water temperature of 7.1 °C represents the temperature at which these carbonates were formed. The theoretical $\delta^{18}\text{O}_{\text{w}}$ values for these carbonates at the Tunica Mound were calculated from +0.9 to +1.1‰, close to the measured present regional $\delta^{18}\text{O}_{\text{sw}}$ (fig. 9). Therefore, it is reasonable to infer that these carbonates from Tunica Mound precipitated in or near isotopic equilibrium with present regional bottom water, and this also confirms that carbonates in cores MD02-2543G, 2544G, and 2545G have originally

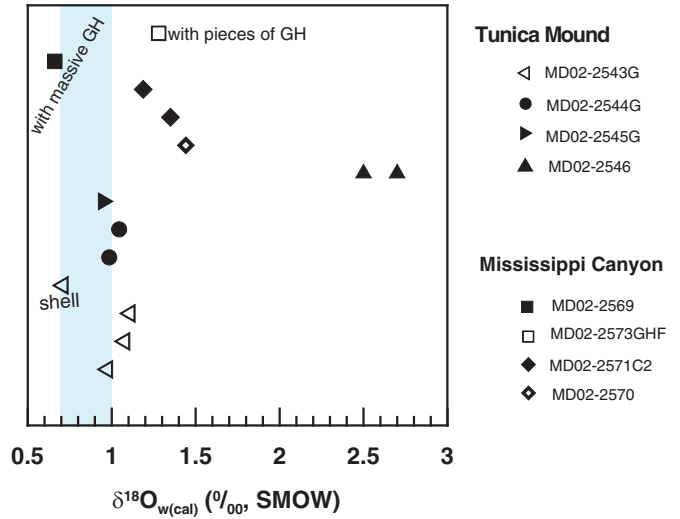


Figure 9. Calculated carbonate precipitated water oxygen isotopes. The blue shaded area represents present bottom-water oxygen isotopes (+0.7 to +1.0‰). There is no specific vertical scale.

precipitated in very recent times in the shallow subbottom sediment.

For the carbonate nodule in core MD02-2546, we assumed that the nodule was precipitated in the sediments not deeper than the present subbottom depth (~27 mbsf). Therefore, the nodule precipitated between the present bottom-seawater temperature of 7.1 °C and a subsurface temperature of 7.9 °C (which was estimated from heat-flow data). Then the calculated $\delta^{18}\text{O}_{\text{w}}$ values for carbonate in core MD02-2546 are from +2.7 to +2.5‰, which are much higher than those of the present observed pore water (+1.3‰) or the present bottom water (+0.7‰) (fig. 9).

Mississippi Canyon: Authigenic carbonates in core MD02-2569 present in shallow sea-floor sediment are underlain by two horizons of massive gas hydrate at 3 and 6 mbsf, respectively. The bottom-water temperature of 4.6 °C suggests carbonates precipitated from water with an oxygen isotope composition of +0.7‰, which is in agreement with present $\delta^{18}\text{O}_{\text{sw}}$ (fig. 9). Therefore, carbonate in core MD02-2569 precipitated in or near isotopic equilibrium with present regional bottom water.

The carbonates in core MD02-2573GHF coexisted with pieces of gas hydrate at 4.2 mbsf. Because a geothermal gradient was not determined at that site because of a bent core barrel, we assumed the nodule precipitated at a bottom-water temperature of 4.6 °C. The carbonates were calculated to have precipitated from water of much heavier oxygen isotope $\delta^{18}\text{O}_{\text{w}} = +1.3‰$ (fig. 9; table 2); however, core MD02-2573 is only 30 m away from core MD02-2569.

Authigenic carbonates in cores MD02-2570 and MD02-2571C2 occurred at 2.95 and ~4.4 mbsf in the sediments, respectively, with a bottom-water temperature of 6.5 °C and

a geothermal gradient of 36 °C/km. The calculated in situ temperature of the carbonate-bearing sediments are all 6.6 °C. There is only a negligible 0.1 °C difference from present bottom-water temperature. Assuming a bottom-water temperature of 6.5 °C as the precipitation temperature of these carbonates, the calculated $\delta^{18}\text{O}_w$ for the precipitated carbonates are +1.3 and +1.4‰, respectively. These values are heavier than the present $\delta^{18}\text{O}_{sw}$ values (fig. 9).

In summary, the calculated $\delta^{18}\text{O}_w$ values for authigenic carbonates in cores MD02-2546, 2573GHF, 2570, and 2571C2 are from +1.3 to 2.7‰, which are +0.5 to +1.9‰ higher than present $\delta^{18}\text{O}$ values of in situ bottom water or pore water in the northern Gulf of Mexico. The possible sources for the ^{18}O -enriched water are (1) LGM (Last Glacial Maximum) northern Atlantic bottom seawater ($\delta^{18}\text{O} \sim +1.7$ to +1.8‰) (Schrag and others, 2002), (2) deep-seated fossil brines ($\delta^{18}\text{O} > +3.0$ ‰) (Gat, 1996), and (3) fluids from gas hydrates dissociation ($\delta^{18}\text{O} \sim +2.9$ ‰) (for example, Hesse and Harrison, 1981; Matsumoto, 1989).

The first option can be ruled out because the authigenic carbonates precipitated in very recent time —younger than 5,500 years ago. The bottom-seawater $\delta^{18}\text{O}_{sw}$ cannot be affected by the LGM bottom seawater oxygen isotope fractionation and should be the same as the present measured values (+0.7 to +1.0‰). As for the second possibility, some of the pore-water samples contained anomalously high Cl⁻ concentrations (1,000 millimoles (mM) to 2,161 mM) (Ussler and Paull, this volume, chapter 8). However, their $\delta^{18}\text{O}_{pw}$ values vary from -0.9 to +1.3‰, which indicates that high salinity pore waters do not carry water with an isotopic composition that is distinctive from seawater. These anomalously high pore-water salinities are not derived from deep-seated brines but are from the simple dissolution of salts. Therefore, deep-seated fossil brines with heavy $\delta^{18}\text{O}$ values can also be excluded as the source of the ^{18}O -enriched water.

^{18}O -enriched carbonates that may be related to gas hydrate dissociation have been reported for a number of cold seep environments worldwide (for example, Matsumoto, 1989; Aloisi and others, 2000; Naehr and others, 2000; Pierre and others, 2000; Greinert and others, 2001). During the formation of gas hydrates from interstitial water, the water containing heavier oxygen isotopes is preferentially incorporated into the gas hydrate structure (Davidson and others, 1983; Matsumoto, 2000). Therefore, gas hydrate decomposition liberates ^{18}O -enriched water molecules, which can contribute between 1 and 2.9‰ to the ^{18}O enrichment of the interstitial waters (Hesse and Harrison, 1981).

Formation and decomposition of gas hydrates are observed to be ongoing in the northern GOM (Milkov and Sassen, 2003). This evidence leads us to conclude that dissociation of pre-existing gas hydrate must have provided the ^{18}O -enriched water incorporated into the anomalously heavy ^{18}O in carbonates in core MD02-2546 at the Tunica Mound, in core MD02-2573GHF where carbonates coexisted with pieces of gas hydrates, and in cores MD02-2570 and 2571C2 at the Mississippi Canyon region. Group II carbonates in cores

MD02-2546, 2570, and 2571C2 were derived from microbial methane. Thus, all these carbonates are related to the dissociation of gas hydrate.

During the last 5,500 years, it is not possible that bottom seawater temperature increased or the sea level dropped to trigger the dissociation of gas hydrates associated with cores MD02-2546, 2573GHF, 2570, and 2571C2. The northern Gulf of Mexico, however, is characterized by ongoing salt diapirism since the Cenozoic era. The salt movement has caused uplift of sediment layers and faulting and fracturing of sediments, which led to (1) a decrease in geo-pressures of the associated gas hydrate-hosting sediment horizons and (2) an increase in pore-water salinity of nearby gas hydrate-bearing sediments. As a consequence, decomposition of gas hydrates was triggered in the associated sediment horizons. The seismic profile across the Tunica Mound (fig. 2) clearly shows a large, shallow salt diapir existing near core MD02-2546. The Cl⁻ concentrations of core MD02-2569, which is just 30 m from core MD02-2573GHF, indicate that a salt diapir underlies this core also (Ussler and Paull, this volume, chapter 8). The seismic profile across core MD02-2570 and 2571C2 (fig. 4) shows gas chimneys in the sediment, which may also have been caused by the upward migration of underlying salt. Thus, we can conclude that nearby salt movement probably caused the dissociation of gas hydrate associated with these cores.

Summary and Conclusions

Carbonates sampled from various subbottom depths in sediments at the Tunica Mound and the Mississippi Canyon region in the northern Gulf of Mexico are dominated by authigenic, micritic high magnesium calcite. The $\delta^{13}\text{C}$ values of carbonates indicate that these authigenic carbonates precipitated from DIC produced by microbially mediated anaerobic oxidation of methane.

The $\delta^{18}\text{O}$ values indicate that some carbonates, including those from core MD02-2569 (with underlying massive gas hydrate), precipitated in or near equilibrium with present bottom-water temperature. Others, from core MD02-2573GHF (with underlying small pieces of gas hydrates) for example, precipitated from ^{18}O -enriched fluids caused by the decomposition of gas hydrates away from present bottom-water and pore-water equilibrium. That is, some authigenic carbonates at cold seeps in the northern Gulf of Mexico are derived from the dissociation of gas hydrates, but others are probably only associated with methane venting from deep hydrocarbon gases. The dissociation of gas hydrates in the northern Gulf of Mexico within the last 5,500 years probably was caused by salt migration.

Authigenic carbonates recorded the history of fluxes from gas hydrates in the Gulf of Mexico. Procedures used during this study on authigenic carbonates can also be used in other geologic settings, such as the Nankai Trough.

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