Reports

Venting of Carbon Dioxide–Rich Fluid and Hydrate Formation in Mid-Okinawa Trough Backarc Basin

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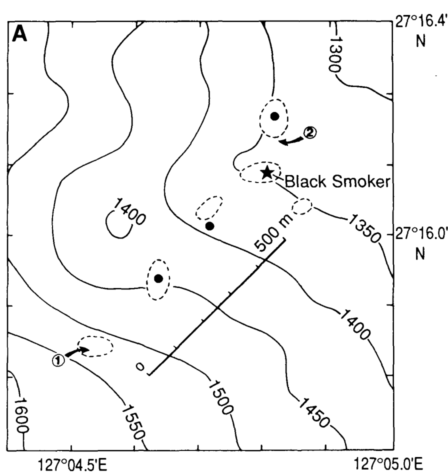
Carbon dioxide–rich fluid bubbles, containing approximately 86 percent CO_2, 3 percent H_2S, and 11 percent residual gas ($CH_4 + H_2$), were observed to emerge from the sea floor at 1335- to 1550-m depth in the JADE hydrothermal field, mid-Okinawa Trough. Upon contact with seawater at 3.8°C, gas hydrate immediately formed on the surface of the bubbles and these hydrates coalesced to form pipes standing on the sediments. Chemical composition and carbon, sulfur, and helium isotopic ratios indicate that the CO_2-rich fluid was derived from the same magmatic source as dissolved gases in 320°C hydrothermal solution emitted from a nearby black smoker chimney. The CO_2-rich fluid phase may be separated by subsurface boiling of hydrothermal solutions or by leaching of CO_2-rich fluid inclusion during post-eruption interaction between pore water and volcanogenic sediments.

ALTHOUGH VOLCANIC GASES ARE known to carry with them valuable chemical information on the genesis and evolution of magma, their juvenile nature is often modified by contamination, boiling, and dispersion during shallow subaerial eruption. Recent study has shown that volcanic rocks and hydrothermal solutions at the mid-ocean ridge (MOR) spreading axes are much less altered and thus contain more information on volatile magmatic components than the terrestrial counterparts; therefore, search for a "gas window" into the deep earth has been extended to the backarc basins around the Japanese Islands. The JADE hydrothermal field was found in 1988 along the northeastern slope of the Izena Cauldron in the mid-Okinawa Trough Backarc Basin (Fig. 1) (*1*). The 1000 m by 200 m field is composed of active and inactive sulfide-sulfate chimneys and mounds at a depth of 1300 to 1550 m below sea level (Fig. 1) (*2*). One "black smoker" chimney has been found, and it emits a solution, together with suspended sulfide particulates at 320°C (the highest temperature in this field), while clear solutions of up to 220°C are emitted from other chimneys and mounds (*2, 3*).

The black smoker solution contains 200 mM CO_2, 12.4 mM H_2S, and 14.8 mM $CH_4 + H_2$ per kilogram of water, a gas content that is about 50 to 100 times that of submarine hydrothermal solutions found at MORs (*3*). The JADE fluid is also highly enriched in K and Li; it has the highest K content (72 mM) so far reported for submarine hydrothermal solutions (*3*). The gas- and K-rich nature of the JADE fluid is typical of hydrothermal fluids formed by reaction between seawater and acid to intermediate volcanic rocks (*3*) and contrasts with the gas-poor, Ca-rich nature of MOR fluids, which result from interaction between seawater and basalt. In accord with those relations, the volcanic rocks recovered from the field consist of dacitic lava and pumice (*4*).

During extensive submersible study of the area made in 1989 bubbles were observed emerging out from the sea floor of active hydrothermal sites. Furthermore, when sulfide ores and sediments taken by the submersible from active sites were brought to depths shallower than about 300 m, they often evolved quantities of bubbles. In order to determine the composition and origin of these bubbles, we collected them, observed their phase change during the ascent of the submersible, and analyzed their chemical and isotopic compositions. These analyses reveal that CO_2-rich fluids were venting at the sea floor of the JADE hydrothermal field and forming hydrates. Gas hydrates of methane and some higher hydrocarbons



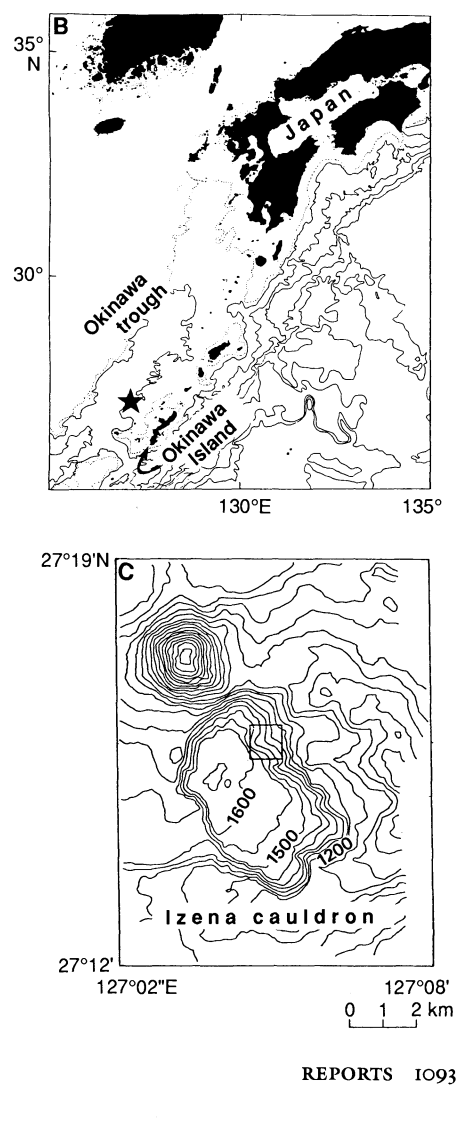


Fig. 1. Map showing the vent locality of CO_2-rich fluid and hot water in the JADE hydrothermal area (**A**). Contours are in meters. Areas of hot water discharge with and without active chimneys and mounds are enclosed by dashed line with and without solid circle. Site 1 (arrow) is location of samples 424-M and 424-RV4; site 2 is bubbling site shown in Fig. 2. (**B**) Locality of Izena Cauldron (shown by star) relative to Okinawa Island. (**C**) Seabeam map of Izena Cauldron [modified from (*4*)] with a square area indicating the JADE hydrothermal field shown in (A).

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have been recovered from marine (5) as well as terrestrial sediments (6–8) under high-pressure, low-temperature environments. The presence of CO_2 hydrates has also been predicted in organic-rich marine sediments (9) but was not previously observed.

Bubbling was confirmed at two sites (Fig. 1), where it occurred within subcircular yellowish white alteration zones 2 to 5 m in diameter. Bubbles emerged out intermittently but freely (site 1, Fig. 1) or when sediment was disturbed by a temperature probe or a corer (site 2). The bubbles showed peculiar behavior upon emergence into seawater from sediment; they often formed a translucent elongated conical pipe ~10 cm long and 1 cm in top diameter, the narrower bottom end of which appeared to be stuck in the sediment, and through which bubbles continued to emerge into seawater. When bubbling momentarily ceased, the translucent horn-shaped pipe was left standing on the sediment for ~1 s (Fig. 2A), and then bubbling either resumed from its top (Fig. 2, B and C) or more often the whole pipe was carried away (Fig. 2D). Then, another bubbling cycle started from the same spot.

We collected bubbles into a 30-cm-long plexiglass cylinder with a 6-cm internal diameter and a closed upper end by holding it upright over a freely bubbling hole at 1550-m depth (site 1, Fig. 1). The transparent bubbles that entered into the cylinder immediately became translucent milky white and resembled a "cluster of grapes" without uniting into a larger bubble (Fig. 3A). When one-third of the cylinder was filled, we closed the bottom end with an O-ring–sealed cap driven by an elastic band. The cylinder was held in front of a window of the submersible and phase changes of the trapped bubbles were observed and video-recorded during our return to the surface (Fig. 3, A to C).

Table 1. Compositions (in percent by volume) and stable isotopic ratios of the gas left in the plexiglass cylinder (424-M) and that evolved from sediment collected by the submersible (424-RV4) at the JADE hydrothermal field (15, 16). Both samples are from the site 1 (Fig. 1). Black smoker is the data of dissolved gas in black smoker solution (3).

Sample	Compositions			Isotopic ratios			
	CO_2	H_2S	R-gas*	$\delta^{13}CO_2$	$\delta^{13}CH_4$ (per mil)†	$\delta^{34}S$	$^3He/^4He$ (R/R_a)‡
424-M	86 ± 5	3	11 ± 1	−5.0	−36	+8.0	6.6
424-RV4	92 ± 1	4.4	4 ± 1	−4.8		+7.2	5.8
Black smoker	91.1 ± 1	5.5	3.5	−4.8	−40	+7.3	6.5

*Residual gas after removal of CO_2 and H_2S; CH_4 and H_2 are the main components. The presence of CH_4 was confirmed but H_2 was not analyzed. †Stable isotopic ratios are expressed in per mil deviation from PDB (C) and from Canon Diablo troilite (S) standards. ‡Ratio to the $^3He/^4He$ ratio of atmospheric helium (1.4×10^{-6}).

The first sign of change appeared at a depth of about 730 m; the "grapes" became unstable and a fluid phase appeared to coexist with collapsed bubbles, giving rise to a "sherbet-like" appearance at 650 m (Fig. 3B). Droplets, probably of fluid, were seen to rise, slowly at first but increasingly more rapidly as water depth decreased, through the sherbet layer to the top of the cylinder. Meanwhile, many white tubes about 5 mm in diameter, resembling "macaroni," started to grow downward from the bottom of the sherbet layer. The cluster of "macaroni" remained to a depth of 360 m (Fig. 3C), where they rapidly thinned out as gas bubbles started to escape into water through the bottom cap. Vigorous bubbling continued to surface, where only a gas was left in the cylinder. These changes are schematically plotted in Fig. 4 along the temperature-depth profile that was followed by the ascending submersible.

The chemical compositions of the gas phase left in the cylinder (Sample 424-M, Table 1) indicates that the "bubbles" are CO_2-rich liquid with minor H_2S, CH_4, and H_2. Evolved gas from the sediment sample (424-RV4, Table 1) has a similar composition, and thus such fluid appears to be widely trapped in the surface sediment. On the basis of these data and the stability fields of the CO_2-H_2O system (Fig. 4), we suggest that the cluster of globules that were observed at depth in the plexiglass cylinder (grapes) developed because a hydrate film formed on each bubble surface and prevented further coalition of bubbles into larger ones, as well as further migration of water into the CO_2-rich liquid globules. The hydrate must have been a mixture of CO_2 (mostly), CH_4, and H_2S. The presence of these additional components would have shifted the stability field from that of pure CO_2 hydrate (7); however, such effects are not significant and are not considered in Fig. 4. The CO_2-rich fluid inside each globule seemed to have diffused out slowly into seawater in the lower half of the cylinder and, when the gas concentration reached saturation, gas hydrate again started to precipitate, growing into the macaroni. With decreasing water depth, the expansion of the CO_2-rich fluid is greater than that of seawater and hydrate. Destruction of the cluster of grapes and appearance of the sherbet at 650-m water depth (Fig. 3B) may have occurred when such expansion broke the hydrate envelope.

Similarly, the translucent milky white pipes that formed on the sediment surface (Fig. 2) where bubbling was observed can be ascribed to the formation of CO_2-rich gas hydrate at the boundary of the emerging CO_2-rich fluid and seawater. At the white alteration zone where bubbles emerged, the

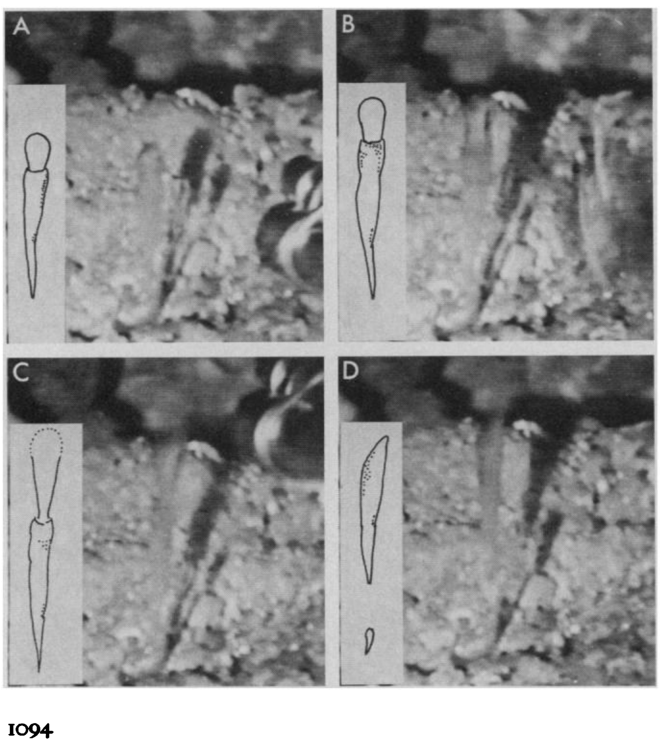

Fig. 2. Photos showing a gas hydrate pipe standing on a 1333-m-deep sea floor (site 2, Fig. 1A) at the JADE hydrothermal field (**A**) and a CO_2-rich fluid bubble which grew on (**B**) and nearly left from the top of the pipe (**C**); the whole pipe finally drifted away (**D**). Note shadows of pipes projected on sea floor at its right. These shadows indicate the presence of another shorter pipe beside the longer one. The longer pipe is approximately 10 cm long.

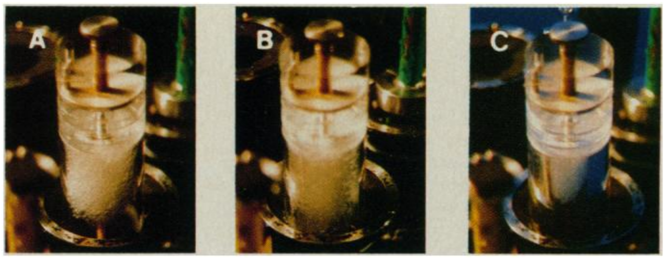

Fig. 3. Photos showing variation of CO_2-rich bubbles from site 1 entrapped in the plexiglass cylinder of 7-cm outside diameter held at the front side of the sample basket of "Shinkai 2000" during its ascent to surface. Translucent milky white color indicates that the bubbles are covered by hydrate envelope. Approximate water depths are 1550 m (**A**), 600 m (**B**), and 360 m (**C**).

temperature gradient in the sediment is high, approximately 0.8°C/cm (*10*); here a temperature of 10°C, the equilibrium temperature for CO_2 hydrate formation (Fig. 4), would be reached at about 8 cm below the surface. Therefore, CO_2-rich fluid must be liquid below that depth. When it emerges out into cold bottom seawater (3.8°C), hydrate immediately forms on its surface and grows upward forming a pipe until the fluid breaks the top and emerges into water as bubbles (Fig. 5).

The chemical compositions and the C, S, and He isotopic ratios all indicate that the CO_2-rich fluid has the same magmatic origin as the nearby black smoker fluid (Table 1). However, the concentration of CO_2 in the hydrothermal solution [200 mM per kilogram of water or 0.34 mol percent (*3*)] is much less than the saturation concentration in water under 140 atm [2.6 and 1.8 mol percent CO_2 at 25° and 100°C, respectively (*11*)]. Therefore, the CO_2-rich fluid cannot form simply by separation during cooling of the present JADE hydrothermal fluid. The effect of salt on CO_2 solubility (*12*) is not large enough to allow saturation of CO_2.

Two mechanisms are conceivable that could lead to separation of the CO_2-rich fluid phase. First, during a volcanic cycle, the upward CO_2 flux from the magma chamber would significantly fluctuate; fractional crystallization in the magma chamber or intrusion of new magma at a shallower depth may cause a sharp increase in the concentration of CO_2 in hydrothermal solution. Furthermore, the boiling point of seawater at the water depth of the black smoker chimney (1335 m) is 335°C (*13*), only 15°C greater than the measured temperature of the hydrothermal solution. The boiling point would be closer to the observed temperature if the effect of dissolved CO_2 is taken into account (*14*). Therefore, if recent volcanic activity was more intense than at present and the hydrothermal solution attained a higher temperature, it could have undergone subsurface boiling and produced a vapor phase with a sufficiently high CO_2 content to form a separate CO_2-rich fluid upon cooling (*14*). Evidence for such subsurface boiling and segregation of vapor-derived CO_2-rich solution has been found at Axial Volcano, Juan de Fuca Ridge (*14*).

Second, unlike subaerial volcanic rocks, submarine volcanic rocks may retain in vesicles a substantial amount of the volatiles contained in erupted magma because of the hydrostatic confining pressure. The CO_2-rich fluid retained in the vesicles could be released into pore water as a result of posteruption hydrothermal alteration. Under appropriate conditions and water to rock ratios, pore water could be saturated with CO_2. This effect would lead to separation and accumulation of a CO_2-rich fluid in the volcaniclastic sediments. Direct transport of CO_2 from magma chamber is assumed in the first model, whereas posteruptive water-rock interaction is required in the second. Criteria for the choice between the two could come from study of the fluid inclusion in the lava and pumice of this area.

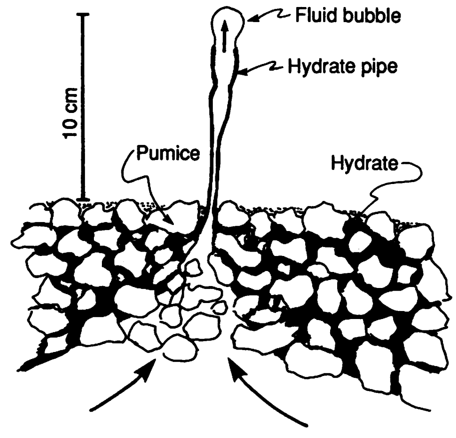

Fig. 5. Schematic cross section of a hydrate pipe standing on a hydrate-sealed sediment. The pipe was traced after the one in Fig. 2B. If a local increase in heat flow elevates the 10°C isotherm so that its apex reaches the surface, CO_2-rich fluid can vent into bottom seawater. Above the isotherm, the pore space is filled with hydrate (black), while underneath it, CO_2-rich fluid accumulates, probably with CO_2-saturated seawater. Arrows indicate flow direction.

Regardless of the formation mechanism, the segregated two-phase mixture of CO_2- and H_2O-rich fluids would migrate upward, driven by buoyancy, through fissures and cracks in the consolidated sedimentary cover or through porous volcaniclastic sediments. When these fluids reach a horizon where the temperature is less than 10°C, hydrate would immediately form and fill interstices of sediments (Fig. 5). A hydrate seal thus formed would work as an effective barrier against upward migration and dispersion of the CO_2-rich fluid into bottom seawater and thereby enhance accumulation of CO_2-rich fluid at shallow depth. When the hydrate seal is raptured, perhaps because of change in hydrothermal activity and elevation of the 10°C isotherm, fluid could begin to leak into bottom seawater (Fig. 5). This model is in accordance with the observation that the bubbling of the CO_2-rich fluid was associated with areas of high heat flow (*10*).

Important questions that arise from these

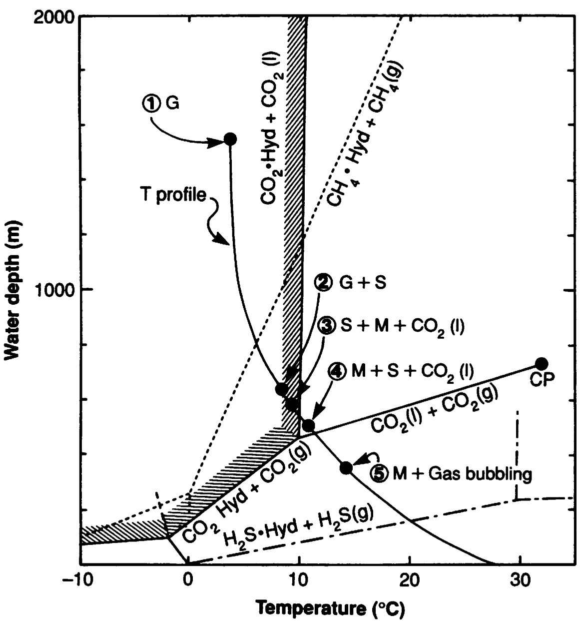

Fig. 4. Phase changes of CO_2-rich fluids (sample 424-M, Table 1) along the depth-temperature profile in the water column above the JADE hydrothermal field, superimposed on the stability field diagrams of hydrate (Hyd) of CO_2 [solid line, after (*17*)], CH_4 [dashed line, after (*17*)], and H_2S [dash-dotted line, after (*7*)]. The stability field of CO_2-hydrate is marked by shaded boundary. G, Grapes; S, Sherbet; M, Macaroni; CP, critical point of CO_2. See text for further explanation.

observations are: (i) what is the extent and distribution of the CO_2-rich fluid and hydrate within the JADE field in relation to those of hydrothermal vents, (ii) what is the effect on the geochemical and biological processes associated with hydrothermal venting, (iii) do they occur at other submarine arc and backarc volcanoes, and (iv) is the carbon flux from these submarine volcanoes important relative to the global carbon flux?

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15. The gas samples were shaken, on board the tendership *Natsushima*, successively with 1 M Zn-acetate solution and a saturated $Ba(OH)_2$ solution and the volume changes were ascribed to formation of H_2S and CO_2, respectively. The residual gas was combusted with CuO at 800°C. The CO_2 produced was used to estimate CH_4 in the residual gas. The ZnS, $BaCO_3$, and CO_2 that formed during these procedures were used to measure the stable isotopic ratios of H_2S, CO_2, and CH_4, respectively. The He isotopic ratios were measured on the residual gases (*16*).
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18. We thank all the scientists, pilots, and operation team members of "Shinkai 2000" who were involved in this project and the captain and crew of the tendership *Natsushima*. We also thank K. Marumo and M. Kimura, who first found the bubbling phenomena and gave us detailed information on it, and H. Hotta. Technical assistance by K. Hasegawa and N. Sueda is greatly appreciated. This study was supported in part by the Grant in Aid for Scientific Study from the Ministry of Education, Sciences and Culture, Nos. 60430010 and 01549468, to H.S. and T.G.

24 January 1990; accepted 22 March 1990

Chemosynthetic Mussels at a Brine-Filled Pockmark in the Northern Gulf of Mexico

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A large (540 square meters) bed of *Bathymodiolus* n. sp. (Mytilidae: Bivalvia) rings a pool of hypersaline (121.35 practical salinity units) brine at a water depth of 650 meters on the continental slope south of Louisiana. The anoxic brine (dissolved oxygen ≤0.17 milliliters per liter) contains high concentrations of methane, which nourishes methanotrophic symbionts in the mussels. The brine, which originates from a salt-cored diapir that penetrates to within 500 meters of the sea floor, fills a depression that was evidently excavated by escaping gas. The spatial continuity of the mussel bed indicates that the brine level has remained fairly constant; however, demographic differences between the inner and outer parts of the bed record small fluctuations.

THE VIOLENT ESCAPE OF GAS through surface sediment often forms sea floor pockmarks (*1*) or craters (*2*). During a submarine survey of the continental slope, northern Gulf of Mexico, we found pockmarks that were filled with hypersaline brine. These features are evidently a consequence of salt tectonism in a hydrocarbon province. One of the pockmarks, brine pool NR-1, was ringed by a large bed of *Bathymodiolus* n. sp., a mussel (*3*) that possesses methanotrophic symbionts (*4*). This discovery signals that the potential habitat for *Bathymodiolus* n. sp. on the slope may be greater than previously thought and demonstrates that chemosynthetic fauna, already known for their tolerance of toxic sulfides (*5*) and aromatic compounds (*6*), also tolerate hypersaline conditions.

Tectonic deformation of the Louann Salt, a Jurassic evaporite deposit, has created

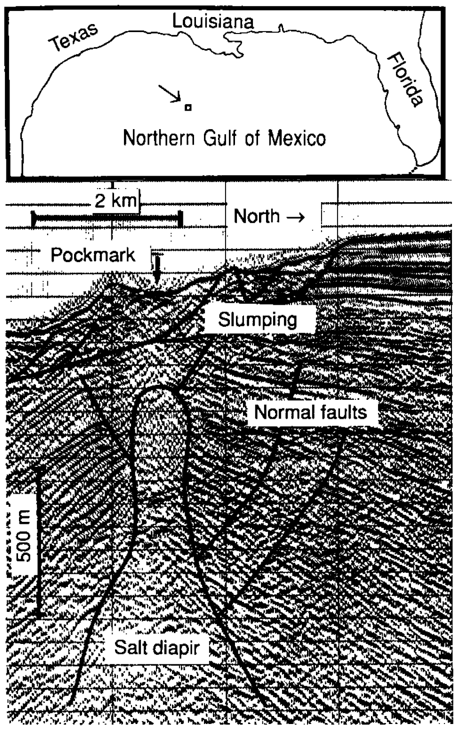

Fig. 1. Two dimensionally processed, common-depth-point (CDP) seismic data showing a north-south transect of the pockmark. Inset map shows its general location in the northern Gulf of Mexico. [Data provided courtesy of Halliburton Geophysical Services, Inc.]

much structural complexity in the northern Gulf of Mexico (*7*); common features include salt diapirs and growth faults. The faults provide a conduit for natural hydrocarbon seepage (*8–10*), which is recognized as a widespread phenomenon on the Louisiana slope (*11*). Large chemosynthetic communities, which have been reported at oil and gas seeps in water depths of 500 to 900 m (*12*), are biological consequences of hydrocarbon seepage.

Because many salt diapirs penetrate recent sedimentary strata, sea floor brine seepage is also thought to be a common phenomenon in the Gulf of Mexico (*7*), but only a few actual seeps have been documented. Brine that originates from the Louann Salt has been found in a shallow (~25 cm deep) pool on the Texas shelf (*13*) and in a large (90 km^2) basin (*14*) on the lower Louisiana slope; both features are filled from the side by drainage from salt deposits located above. Brine that originates from saline aquifers in the Florida-Bahama platform saturates surface sediments at the abyssal base of the Florida escarpment (*15*). Reduced compounds associated with this brine nourish chemosynthetic communities that include a second species of mussel (*16, 17*).

Brine pool NR-1 was found (*18*) approximately 285 km southwest of the Mississippi Delta (27°43'24"N, 91°16'30"W) near the

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