

Coring and Gas Hydrate-Related Operations During 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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Abstract

This chapter is an illustrated overview of activities related to coring, subsequent sediment analyses, sample preservation, and safety-related issues dealing with the handling and storage of gas hydrate samples at sea. During this cruise, 17 giant piston cores up to 38 meters long, 4 giant box cores up to 10 meters long, and 4 gravity cores up to 9 meters long were recovered along high-resolution seismic reflection transects in widely different geologic environments and in water depths ranging from about 560 to 2,260 meters. Gas hydrate was recovered in three cores at subbottom depths of about 3 to 9 meters, and gas bubbles indicative of gas hydrate dissociation were noticed in a fourth core. Seventeen successful passive heat-flow measurements to subbottom depths of 17 meters were also made at locations near piston-core sites.

Introduction

Gas hydrate, an ice-like crystalline solid containing high concentrations of methane, is a potential energy resource. It is also a potential hazard to hydrocarbon exploration and production, and may influence global climate change. Although the

amount of gas hydrate in the natural environment is inferred to be enormous, little is known about its distribution in shallow sediment or even exactly how it forms. Exploring these and other questions were among the goals of a July 2002 cruise conducted within three continental slope regions of the northern Gulf of Mexico (Tunica Mound, Bush Hill, and the east and west flanks of Mississippi Canyon). The work was supported by the French Polar Institute [Institut Polaire Francais – Paul-Emile Victor (IPEV)] and the U.S. Geological Survey (USGS), and employed a giant piston coring system using the 120.5-meter (m)-long French research vessel (RV) *Marion Dufresne* (fig. 1).



Figure 1. RV *Marion Dufresne* is 120.5 meters in overall length and is 20.6 meters in beam amidships. It has a draft of 6.95 meters and displaces 10,380 tonnes. Coring operations are conducted using the starboard stern A frame.

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Seventeen giant Calypso piston cores of up to 38 m in length (500 m total recovery) and 2 box cores (14 m total recovery) were collected for gas hydrate-related studies (tables 1, 2). The cores were used for study of the potential

distribution of natural gas hydrate using geochemical analyses of pore water (Ussler and Paull, this volume, chapter 8) and gas samples (Lorenson and others, this volume, chapter 9). In addition, physical property (Winters and others, this volume,

Table 1. Core information including location, water depth, recovered core length, and core type.

[ID, identification; deg, degrees; m, meters; PC, piston core; C2 (box), square box core; GHF, gravity core with heat-flow temperature sensors attached; Grav, gravity core without thermal sensors; **, denotes successful determination of geothermal gradient]

Core ID	Latitude (deg)	Longitude (deg)	Site name	Water depth (m)	Core length (m)	PC	C2 (box)	GHF	Grav	Comments
MD02-2535	27.6198	-92.2410	Tunica Mound	605	37.84	*				
MD02-2536GHF-1	27.6198	-92.2410	Tunica Mound	608	8.88			**		
MD02-2536GHF-2	27.6253	-92.2460	Tunica Mound	564	8.88			**		
MD02-2536GHF-3	27.6270	-92.2375	Tunica Mound	585	8.88			**		
MD02-2537	27.6160	-92.2487	Tunica Mound	600	33.58	*				
MD02-2538G	27.6167	-92.2472	Tunica Mound	599	7.76				*	
MD02-2539	27.6397	-92.1922	Tunica Mound	622	31.1	*				
MD02-2540GHF-1	27.6403	-92.1920	Tunica Mound	617	5.65			**		
MD02-2540GHF-2	27.6402	-92.1952	Tunica Mound	620	-			*		
MD02-2541	27.6325	-92.2123	Tunica Mound	615	35.34	*				
MD02-2542GHF	27.6322	-92.2120	Tunica Mound	617	7.7			**		
MD02-2543G	27.6123	-92.2555	Tunica Mound	579	0.15				*	
MD02-2544G	27.6130	-92.2535	Tunica Mound	584	0.1				*	
MD02-2545G	27.6140	-92.2517	Tunica Mound	588	9.27				*	
MD02-2546	27.6157	-92.2470	Tunica Mound	595	31.21	*				
MD02-2547GHF	27.6165	-92.2483	Tunica Mound	607	5.73			**		
MD02-2548	27.6375	-92.1995	Tunica Mound	610	32.92	*				
MD02-2550C2	26.9462	-91.3457	Orca Basin	2,249	9.09		*			
MD02-2553C2	27.1835	-91.4167	Pigmy Basin	2,259	10.03		*			
MD02-2554	27.7833	-91.4990	Bush Hill Basin	602	31.05	*				
MD02-2555	27.7832	-91.4892	Bush Hill Basin	636	35.68	*				
MD02-2556	27.7830	-91.4775	Bush Hill Basin	654	34.25	*				
MD02-2557GHF-1	27.7830	-91.4987	Bush Hill Basin	613	7.59			**		
MD02-2557GHF-2	27.7830	-91.4890	Bush Hill Basin	639	-			**		
MD02-2557GHF-3	27.7828	-91.4805	Bush Hill Basin	659	-			**		
MD02-2559	28.2225	-89.0882	Kane Spur	1,132	33.39	*				
MD02-2560	28.2433	-89.1550	Kane Spur	1,029	28.24	*				
MD02-2561	28.2052	-89.0202	Kane Spur	1,268	28.8	*				
MD02-2562	28.0798	-89.1402	Kane Spur	1,051	26.09	*				
MD02-2563C2	28.1233	-89.1363	MC853 Diapir	1,070	3.86		*			recovered hydrate (gas bubbles)
MD02-2564GHF-1	28.2433	-89.1545	Kane Spur	1,027	7.63			**		
MD02-2564GHF-2	28.2223	-89.0883	Kane Spur	1,261	-			**		
MD02-2564GHF-3	28.2052	-89.0200	Kane Spur	1,269	-			**		

Table 1. Core information including location, water depth, recovered core length, and core type. — Continued

[ID, identification; deg, degrees; m, meters; PC, piston core; C2 (box), square box core; GHF, gravity core with heat-flow temperature sensors attached; Grav, gravity core without thermal sensors; **, denotes successful determination of geothermal gradient]

Core ID	Latitude (deg)	Longitude (deg)	Site name	Water depth (m)	Core length (m)	PC	C2 (box)	GHF	Grav	Comments
MD02-2564GHF-4	28.2070	-89.0200	Kane Spur	1,269	-			**		
MD02-2565	28.1235	-89.1395	MC853 Diapir	1,068	22.5	*				recovered hydrate
MD02-2566	28.1192	-89.1032	Kane Spur	1,186	26.05	*				
MD02-2567	28.1002	-89.0198	Kane Spur	1,318	26.65	*				
MD02-2568GHF-1	28.0790	-89.1400	MC853 Diapir	1,049	6.96			**		
MD02-2568GHF-2	28.0810	-89.1370	MC853 Diapir	1,057	-			**		
MD02-2568GHF-3	28.1193	-89.1030	MC853 Diapir	1,190	-			**		
MD02-2568GHF-4	28.1233	-89.1395	MC853 Diapir	1,068	-			*		
MD02-2568GHF-5	28.1235	-89.1362	MC853 Diapir	1,049	-			*		
MD02-2569	28.1522	-89.4797	Mississippi Canyon	1,032	10.35	*				recovered hydrate
MD02-2570	28.0710	-89.6898	West Mississippi	631	28.35	*				
MD02-2571C2	28.0667	-89.7192	West Mississippi	664	10.38		*			
MD02-2572GHF	28.0710	-89.6897	West Mississippi	628	4.9			**		
MD02-2573GHF	28.1520	-89.4798	Mississippi Canyon	1,027	4.2			*		recovered hydrate
MD02-2574	28.6267	-88.2248	East Mississippi	1,963	32.28	*				

Note: Cores obtained during the cruise that are not listed in this table and cores MD02-2548 in Tunica Mound, MD02-2550C2 in Orca Basin, and MD02-2574 in East Mississippi region are IMAGES/PAGE cores, not dedicated USGS cores.

Table 2. Core and sample list.

[cm, centimeters; m, meters]

Core dimensions:

Box core cross section: 25 cm x 25 cm

Calypso piston core, gravity core, gravity heat-flow core size: 10.1-cm diameter

White opaque PVC liner: 10.1-cm-inside diameter, 11.4-cm-outside diameter

Number of cores recovered:

Calypso piston: 17

Box: 4

Gravity: 4

Gravity heat flow: 21 penetrations at 9 stations produced 17 successful determinations of geothermal gradient

Length of core sediment recovered:

Calypso piston: 500 m

Box: 33 m (approx)

Gravity: 17 m

Gravity heat flow: 57 m

Number of samples acquired:

Pore water: 483

Water content/geotechnical: 1,100 (approx.)

chapter 4) and other measurements have been made on core subsamples. Gravity cores were obtained mainly to acquire heat-flow information (Labails and others, this volume, chapter 6) from sensors attached to the perimeter of the core barrel. Detailed station location maps for each area are located in Appendix B of this report. Chirp seismic-reflection data were acquired at all core sites (this volume, Appendix D).

Nine- and 10-m-long box cores were also collected from Orca and Pigmy Basins, respectively, for studies related to the International Marine Past Global Changes Study (IMAGES) program, and Paleoceanography of the Atlantic and Geochemistry (PAGE) program, and for measuring anthropogenic contaminant input of Holocene age to the northern Gulf of Mexico from the Mississippi River (Flocks and Swarzenski, this volume, chapter 13). In addition, the RV *Marion Dufresne* obtained two cores in Tampa Bay for the USGS Tampa Bay project for climate-history studies. Cores collected for paleoclimate studies as part of the IMAGES and PAGE programs were interspersed with the USGS sites.

Piston and Box Coring Systems

The RV *Marion Dufresne* has an unobstructed starboard main deck that allows the deployment (figs. 2, 3) and recovery (figs. 4–6) of IPEV’s “Calypso” giant piston corer (fig. 7). This piston-coring system, driven by a 6-tonne weight stand (fig. 8), has recently obtained cores as long as 64.5 m. Much longer cores are obtained with piston-coring systems compared to gravity corers because they use a piston (fig. 9) inside the core liner, which theoretically remains near the level of the sea floor during the coring process (fig. 10). The piston creates a vacuum at the sediment surface that helps overcome the

frictional forces between the cored sediment and the internal wall of the barrel liner.

A newly designed 11-m-long box core was also used to recover large (25 centimeter (cm) by 25 cm in cross section) sediment samples from shallow subbottom depths (fig. 11). The box cores were driven into the sea floor by using the same weight stand as the piston corer.



Figure 2. Calypso piston corer about to be pivoted into a vertical position for coring.



Figure 3. Calypso piston corer ready to be lowered. Notice the yellow-colored trigger arm attached to the main cable above the weight stand. The main corer is held in position until a weight suspended from the trigger arm contacts the sea floor. As tension on the trigger arm is reduced, the main corer is released and is driven into the sea floor by the massive weight stand.



Figure 4. Recovery of a Calypso piston corer.



Figure 5. Recovered Calypso piston corer being lowered to the deck.



Figure 6. Recovered Calypso corer ready to be dismantled.

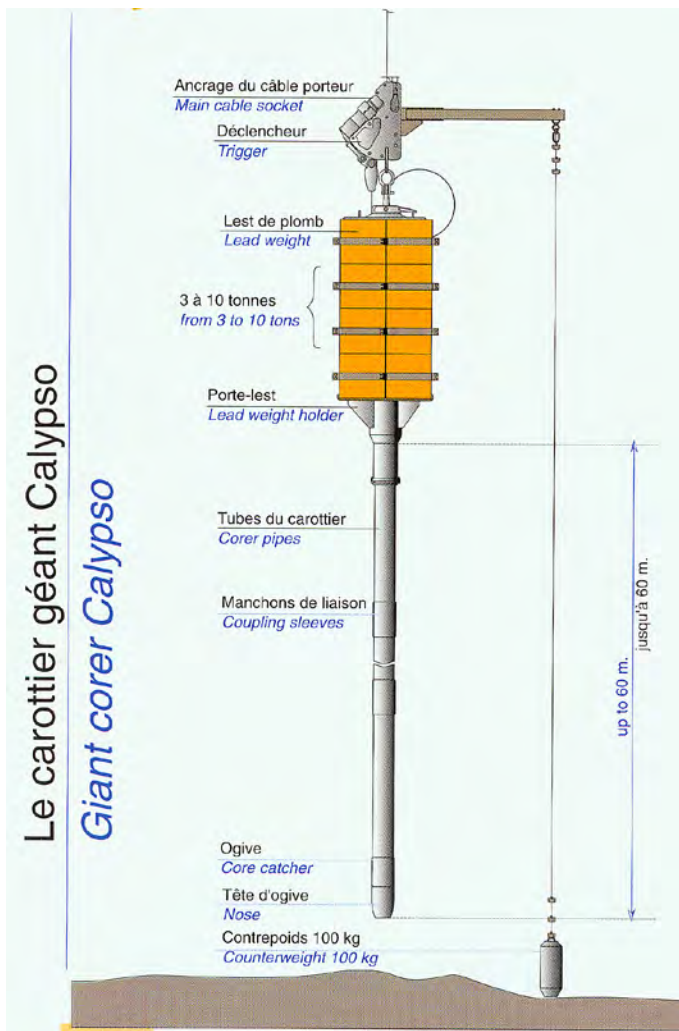


Figure 7. Components of a Calypso giant piston corer (illustration courtesy of Institut Polaire Français – Paul-Emile Victor).



Figure 8. Weight stand used to drive the core barrel into the sea floor.



Figure 9. A critical component of a piston-coring system is the piston that theoretically remains near the level of the sea floor during sediment penetration by the core barrel. The vacuum that develops between the bottom of the piston and the sediment surface helps overcome the frictional forces between the cored sediment and the internal wall of the barrel liner.

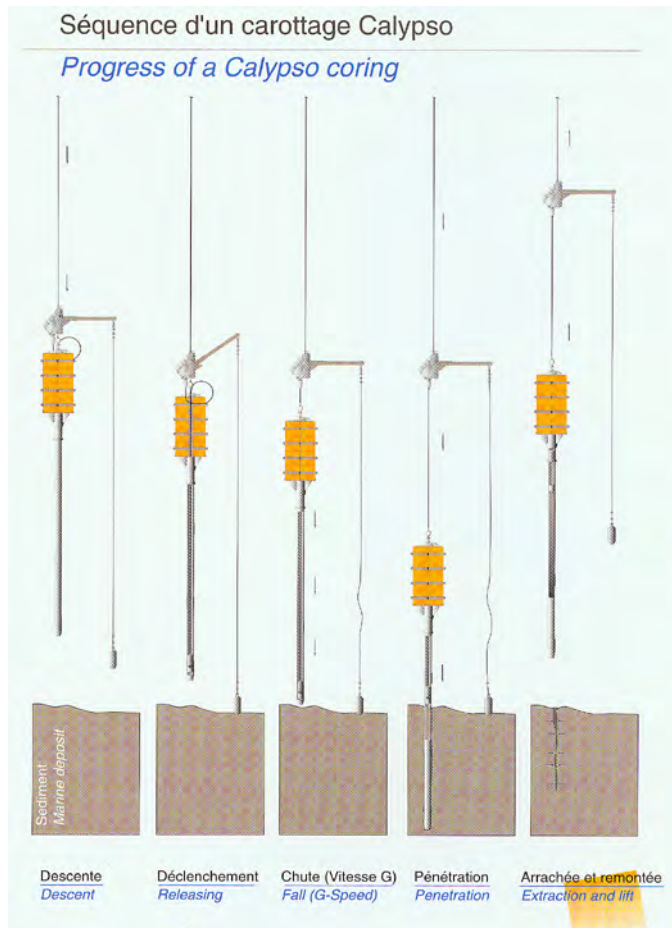


Figure 10. Operation of a Calypso giant piston corer (illustration courtesy of Institut Polaire Français – Paul-Emile Victor).

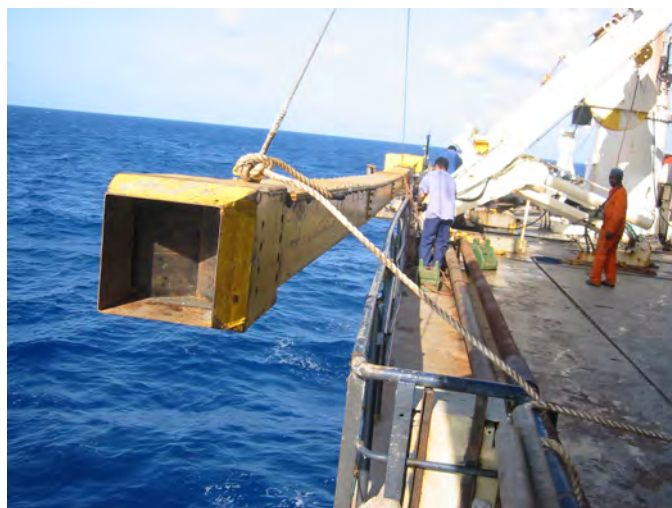


Figure 11. Deployment of a box corer.

Heat-Flow Measurements Using Gravity Corers

Gravity cores (fig. 12) with staggered temperature sensors and recorders (figs. 13–14) were used to determine geothermal gradients to about 17-m-subbottom depth at 17 locations near piston-core sites (table 1). Thermal gradients are important



Figure 12. Gravity core with staggered outrigger heat-flow sensors.

in determining the subbottom extent of gas hydrate stability. Gravity cores obtained during heat-flow measurements supplemented the shallow sediment sections collected at nearby piston-coring sites. Occasionally, multiple heat-flow penetrations were made without changing barrels. A used barrel, containing a sediment core, was slowly towed to another site and dropped, sometimes multiple times. Sediment-related

results from these multiple-dropped cores were treated with caution because of the potential for additional sediment penetration at the base of an existing core. For more information about the heat-flow measurement program and results see Labails and others (this volume, chapter 6).



Figure 13. Installation of a heat-flow sensor onto an outrigger welded to a gravity corer.



Figure 14. Side view of a heat-flow temperature sensor.

Core Handling and Gas Hydrate Recovery

Piston Cores

After Calypso piston cores were brought on deck, a number of procedures were performed sequentially to ensure safe and efficient core processing (fig. 15). To reduce hazards associated with gas overpressures and the presence of toxic gas before general core-related activities began, a small number of scientists used a safety protocol on most of the 17 piston cores recovered for the USGS. As the piston core liner was being removed from the metal core barrel, the liner surface temperature was monitored using an infrared temperature sensor (fig. 16). Holes were drilled at about 1-m

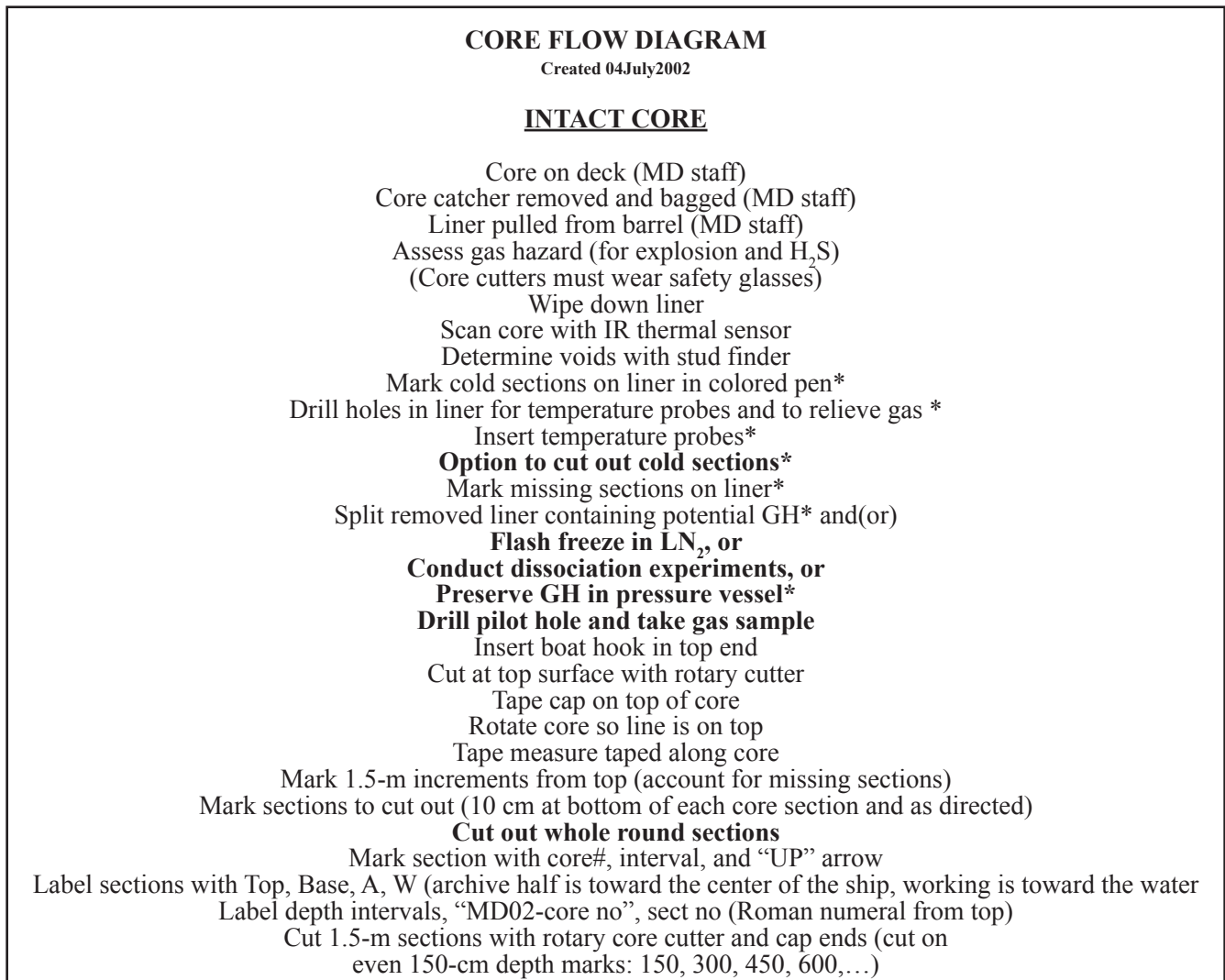


Figure 15. Calypso piston core flow diagram.

Move sections to bench by MST van Place depth labels along longitudinal line for length of core Mark depth intervals Bring to thermal conductivity lab Let temperature equilibrate >4–6 hours Perform thermal conductivity measurements (on whole round sections) Move core to bench by MST van Split section along depth-interval tape	
<u>WORKING HALF</u>	<u>ARCHIVE HALF</u>
Bring to phys props lab Vp, Vs, ER, VS, TV, PP WC, GD, BD Subsampling Cover with Saran wrap Place in heavy plastic sleeve and tape ends Place in labeled D tube Place in reefer on Heliport (Deck F)	Carry to F deck or use lift Scrape core Sedimentologic description (paper form) Photograph core (50 cm per shot) Cover with Saran wrap Spectrophotometry (every ~1–2 cm) MST lab (Main deck) Temp equilibration (for >1 hour) Vp, Mag susc, GRAPE, ER Paleomag U-channel Place in heavy plastic sleeve and tape ends Place in labeled D tube Place in reefer on Heliport (Deck F)

* - As needed
 Subsamples - in **bold**

BD - Bulk density
 ER - Electrical resistivity
 GD - Grain density
 Mag susc - Magnetic susceptibility
 PP - Pocket penetrometer

PV - Pressure vessel
 TV - Torvane
 Vp - P-wave velocity
 Vs - Shear wave velocity
 VS - Vane shear strength

Figure 15 (Continued). Calypso piston core flow diagram.



Figure 16. The surface temperature of the core liner was measured with an infrared sensor after it was removed from the metal core barrel.

spacing to relieve potential hazardous gas pressures (figs. 17, 18) and to collect gas samples (figs. 19, 20) for later isotopic analyses (see Lorenson and others, this volume, chapter 9). Digital temperature probes were inserted into the holes after the gas pressure dissipated (figs. 21, 22) and were monitored to find small thermal anomalies suggestive of gas hydrate dissociation. Much of the recovered sediment was highly gas charged, as evidenced by the abrupt expulsion of sediment (figs. 23, 24) (view video*) and gas (fig. 25) (view video*) from holes drilled in the core liner. On occasion, expanding gas also caused sediment to extrude beyond the core liner after it was cut (figs. 26, 27). Because of the highly toxic nature of hydrogen sulfide gas (table 3), we checked cores and subsamples for its presence (fig. 28) to ensure that safe levels were not exceeded on deck or in the inboard laboratories. A few core subsamples had to be removed from laboratories because hydrogen sulfide (H_2S) may have exceeded the safety threshold. A general note on description of “Hazards Associated with Core Overpressures and Hydrogen Sulfide Gas” is presented at the end of this chapter.

*Video is also accessible at AppendixJ/Winters/Mudworms_gas. Software to view video can be downloaded from <http://www.microsoft.com/downloads> (Windows Media Player) or <http://www.apple.com/downloads> (QuickTime).



Figure 17. Immediately after the PVC core liner is pulled from the metal core barrel the surface temperature was determined with a hand-held infrared thermal sensor.



Figure 18. Holes were drilled in the liner at 1-meter intervals to relieve potential gas overpressures, and a digital thermometer was inserted to record internal sediment temperature.



Figure 19. Gas sample being collected from a hole drilled in a Calypso PVC core liner.



Figure 20. Syringe filled with gas to be later analyzed for isotopic composition.



Figure 21. Thermometers were monitored to determine low thermal anomalies suggestive of gas hydrate dissociation.



Figure 22. Digital thermometers were inserted at 1-meter intervals down core.

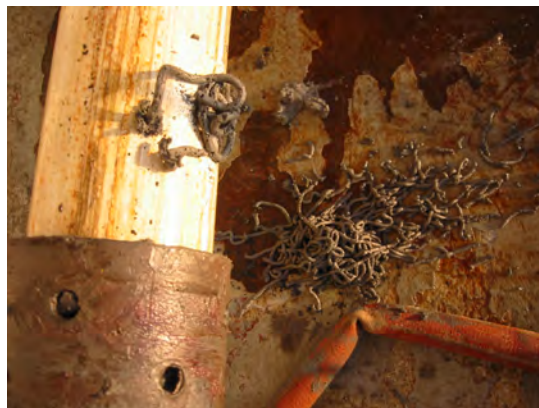


Figure 23. Highly gas-charged sediment resulted in "mud worms" being extruded from holes drilled in the core liner.



Figure 24. Click here to view video* of gas-charged sediment “mud worms” being extruded from holes drilled in the core liner.



Figure 25. Click here to view video* of gas being extruded from holes drilled in the core liner.



Figure 26. Sediment that “self-extruded” because of gas expansion sometimes needed to be collected on a half-round PVC liner.

Table 3. Hydrogen sulfide characteristics.

Concentration in air		Effects
Percent	Parts per million	
0.001	10	Obvious and unpleasant odor; safe for 8 hours exposure.
0.002	20	Safe for 4 hours exposure.
0.01	100	May not be smelled in 3–15 minutes; may sting eyes and throat.
0.02	200	May not be smelled in a very short period of time; stings eyes and throat.
0.05	500	Dizziness; breathing ceases in minutes; need prompt artificial respiration.
0.07	700	Unconsciousness occurs quickly; death will result if not rescued promptly.
0.1	1,000	Unconsciousness occurs nearly immediately; death occurs within minutes.

Note: For more information on hydrogen sulfide safety, see Foss and Julson, 1993, ODP Technical Note 19, Revised H₂S Drilling Contingency Plan, Ocean Drilling Program, College Station, TX.



Figure 27. Occasionally gas expansion caused sediment to self extrude.



Figure 28. Cores and sediment samples were checked for dangerous levels of hydrogen sulfide gas.

*Video is also accessible at AppendixJ/Winters/Mudworms_gas. Software to view video can be downloaded from <http://www.microsoft.com/downloads> (Windows Media Player) or <http://www.apple.com/downloads> (QuickTime).

Following the safety-related procedures, the white PVC core liner was removed from the metal core barrel, labeled, and cut into 1.5-m lengths using a rotary pipe cutter (fig. 29). Whole-round samples, 10-cm to 25-cm long, were cut from



Figure 29. After the PVC core liner was removed from the metal core barrel, it was labeled and cut into 1.5-meter lengths.

the ends of core sections every 1.5 m (fig. 30). Most of the sediment from the whole rounds was placed in two types of squeezers (fig. 31) to obtain pore water for chloride ion, sulfate ion, and methane concentration analyses, performed within a mobile geochemistry van operated by the Monterey Bay Aquarium Research Institute (MBARI) (fig. 32). A total of 483 pore-water samples were obtained during the cruise. Other sediment was frozen for microbiological studies (Hallam and others, this



Figure 30. Whole-round samples, 10-centimeter to 25-centimeter long, were cut from the ends of core sections every 1.5 meters.



Figure 31. Laboratory containing multiple Reeburg-style squeezers to extract pore water from sediment samples.



Figure 32. Pore water samples extracted from sediment were analyzed for the concentration of chloride and sulfate ions in a portable geochemistry van.

volume, chapter 10). The remaining intact whole-round (and split) sections were stored at 4 degrees Celsius ($^{\circ}\text{C}$) (fig. 33) for subsequent shore-based testing, including stress history and other geotechnical studies. Intact whole-round samples were also retained for isotopic gas geochemistry analyses to determine the source of the gas (Lorenson and others, this volume, chapter 9).



Figure 33. Core sections were refrigerated at approximately 4 degrees Celsius during storage.

After whole-round samples were removed on deck, the remaining sections were measured for thermal conductivity (fig. 34) after temperature equalization. Then the cores were split longitudinally (fig. 35). The archive half was brought into the sedimentology lab (fig. 36) where its lithology was described (Bout-Roumazielles and Trentesaux, this volume, chapter 5), color recorded with a spectrophotometer (fig. 37), digitally photographed, and run through a Multi-Sensor Core Logger (MSCL) (fig. 38) for measurement of density, P-wave velocity, magnetic susceptibility, and electrical properties (Bout-Roumazielles and Trentesaux, this volume, chapter 5; Winters and others, this volume, chapter 4).



Figure 36. The archive half of longitudinally-split cores were lithologically described, recorded for color with a spectrophotometer, and digitally photographed in the sedimentology laboratory.



Figure 34. Thermal conductivity measurements were performed on whole-round core sections using a needle probe after the sediment temperature equilibrated.



Figure 37. Sediment color on the archive-half split core was recorded with a spectrophotometer.



Figure 35. The core was longitudinally split after whole-round sections were removed.



Courtesy of
Viviano Bossi/
Univ. Lille

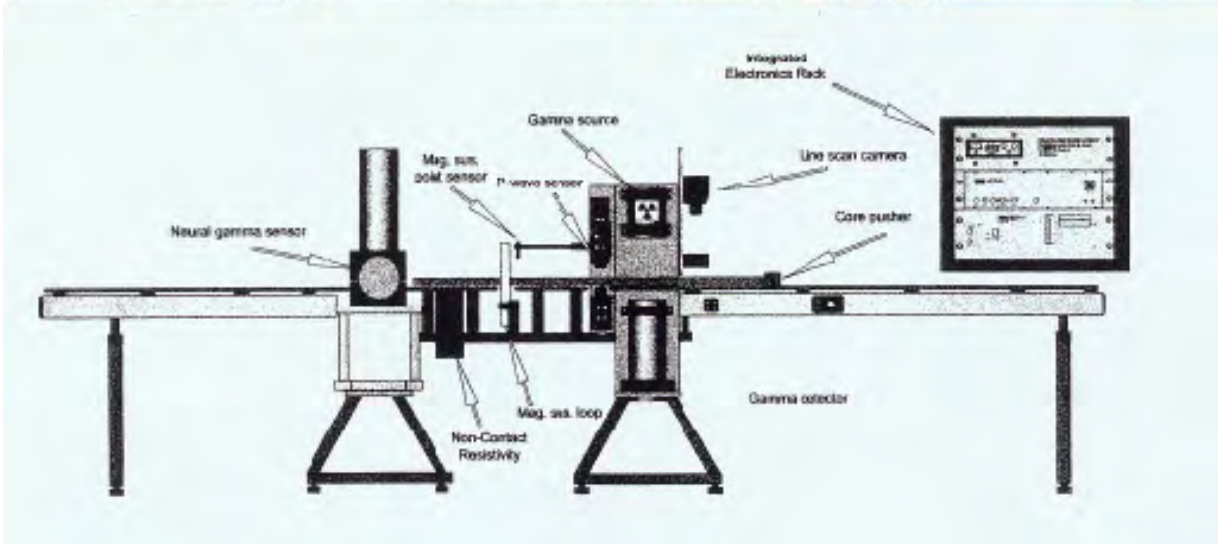


Figure 38. Multi-Sensor Track (MST) used for determining physical properties on a longitudinally-split core section.

The working half of the core was brought into the physical properties laboratory for the determination of electrical resistivity, P-wave velocity, water content, and shear strength by mini-lab vane (fig. 39), torvane (fig. 40), and pocket penetrometer. Approximately 1,100 water-content samples were acquired during the cruise. Post-cruise grain-density and grain-size analyses were conducted in USGS laboratories in Woods Hole, MA (Winters and others, this volume, chapter 4).

The core-barrel length used at each site was determined after viewing seismic records, which are indirectly related to

sea-floor hardness and potential core penetration. Occasionally, core barrels did not achieve optimal penetration. If the length of core barrel remaining above the sea floor after penetration was too long, the barrel would buckle, bend (fig. 41), or even break (figs. 42, 43) due to the force exerted by the mass of the essentially unsupported weight stand. These bent cores were difficult to recover and resulted in extra time being spent to cut the barrels into manageable lengths (fig. 44).



Figure 39. A suite of physical property measurements were made on the working half of the cores. A mini-vane shear machine is located in the foreground.



Figure 40. The working half of the split cores was subsampled for water content and other properties. A Torvane test is being performed in the foreground.



Figure 43. Although most of the core barrel broke during the coring operation, enough strength existed in the remaining barrel and liner to enable retrieval of the core.



Figure 41. Bent core barrels required special handling procedures.



Figure 44. Bent barrels were cut into more manageable lengths after recovery.



Figure 42. The core barrel would actually break if enough stress was placed on it during the coring and recovery process.

Box Cores

Removable panels that covered one side of the box core frame were not pressure tight (fig. 45); thus, the box cores are not likely to become overpressured after recovery. However, the cores were checked for the presence of hydrogen sulfide gas.

After the metal side panels were removed from the IMAGES cores (fig. 46), the sediment surface was scraped (fig. 47), U-channels were pushed into the sediment (fig. 48), and the core was tipped on its side (figs. 49, 50). Archive U-channel

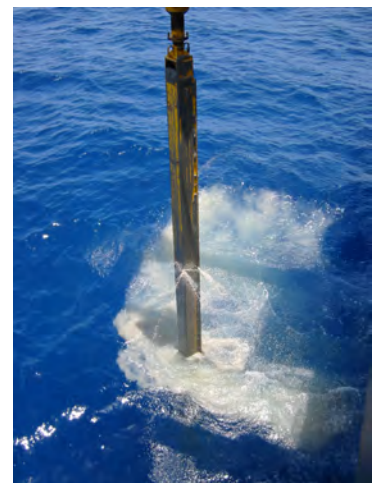


Figure 45. Recovery of a box core. Notice the spray of water exiting between joints in the frame. Unlike Calypso piston cores, box cores could not be overpressured from gas expansion or gas hydrate dissociation.



Figure 46. Top panels being removed from a box corer. Notice the pyramid shape to the recovered sediment at the bottom of the core.



Figure 47. Sediment surface being scraped to enhance interpretation of stratigraphic features.

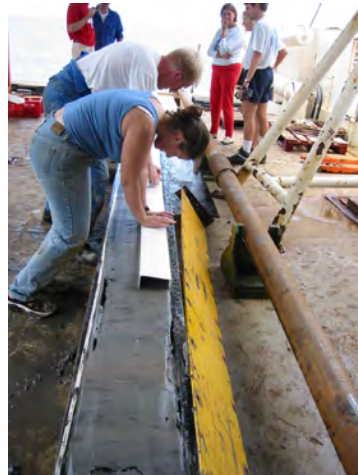


Figure 48. U-channels being pushed into a box core.



Figure 49. A box core about to be tipped onto its side.

cores were removed (fig. 51) and processed in the sedimentology lab. Working U-channel cores were sampled for paleoclimate and other analyses. Sediment remaining in the corer was subsampled for various studies (fig. 52), including physical properties and pore-water geochemistry (fig. 53). Strength was also determined using a pocket penetrometer. Dedicated gas hydrate box cores were not tipped on their side during subsampling. As with piston cores, sediment temperature was measured using digital-reading probes (fig. 54). Hydrocarbon presence was noticed in some box cores (figs. 55–58).



Figure 51. Removal of a U-channel from a box core.

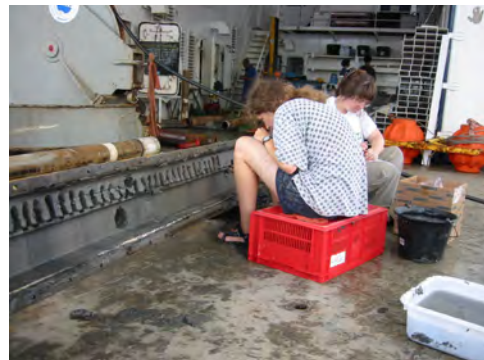


Figure 52. Subsampling a box core. After removal of U-channel samples.



Figure 50. A box core on its side. Notice the styfoam plug at the top of the core used to stabilize the soft sediment surface.



Figure 53. Sediment from a box core being placed into a sample holder that will be used to squeeze pore water from the sediment pore spaces.



Figure 54. A dedicated USGS box core being subsampled. Sediment in the foreground is being placed into a pore water sample holder. This core, MD02-2563C2, located on a large diapir in the MC853 lease area, was saturated with liquid hydrocarbons.



Figure 57. The hydrocarbons had a sticky consistency that did not allow easy removal from surfaces.



Figure 55. Hydrocarbons recovered in box core MD02-2563C2.



Figure 58. Hydrocarbons recovered in box core MD02-2563C2. Notice the pen tip in the lower right corner of the photograph.



Figure 56. Hydrocarbons recovered in box core MD02-2563C2. Notice the filament-like, viscous nature of the hydrocarbons.

Gas Hydrate Recovery

A hand-held infrared camera was used to measure surface core-liner temperatures during extrusion from the metal core barrel. A decrease in temperature, resulting from the endothermic cooling caused by gas hydrate dissociation, typically is the first indication of the presence of hydrate. In order to retrieve samples of gas hydrate, short sections were cut out of the cores at locations of temperature anomalies (fig. 59). For example, in core MD02-2565, typical liner temperatures of 23 to 24 °C were measured. However, temperatures between 10 and 19 °C were observed proximal to gas hydrate occurrences. A thermometer inserted into the hydrate-containing sediment layer displayed an internal temperature of 4 °C. Temperatures recorded on the liner surface for core MD02-2569 typically ranged from 23 to 24 °C, except near gas hydrate-bearing zones, which had liner-surface temperatures of 19 to 21 °C.

Gas hydrate was recovered in three different cores at a maximum subbottom depth of about 8.2 m. The gas



Figure 59. Removal of core sections containing gas hydrate was based on low sediment liner surface or internal sediment temperature anomalies. Samples were immediately placed in the liquid nitrogen Dewar shown next to the core.

hydrate in core MD02-2565 was disseminated within fine-grained sediment and was associated with the presence of nearby hydrocarbons, whereas the gas hydrate recovered in core MD02-2569 consisted of massive veins that filled the entire cross section of the core liner (figs. 60, 61). Those pieces typically were at least 2 cm thick. This implies that we



Figure 60. Gas hydrate chunks recovered from Calypso giant piston core MD02-2569. The sediment clinging to the gas hydrate was washed away with water from the bottle.



Figure 61. Gas hydrate chunks recovered from Calypso giant piston core MD02-2569.

cored continuous layers of gas hydrate of some unknown lateral extent. Hydrate samples recovered from cores were preserved in liquid nitrogen (fig. 62) or in a freezer kept at a temperature of -80°C for post-cruise, shore-based laboratory testing.



Figure 62. Recovered hydrate samples were preserved in liquid nitrogen.

The generation of gas caused by hydrate dissociation was spectacularly demonstrated when the upper several meters of core MD02-2565 blew vertically out the end of the core barrel as the weight stand was removed, flew at least 10 m into the air, and landed in the waters next to the ship. The gas hydrate remained on the surface of the water because of its low density and floated away as it dissociated.

The recovered cores are currently available for further scientific study upon application to the Integrated Ocean Drilling Program at Texas A&M University in College Station, TX.

Summary

During this cruise, 17 giant piston cores (as much as 38-m long), 4 giant box cores (4 to 10-m long), and 4 gravity cores were recovered in widely different geologic environments in water depths ranging from about 560 to 2,260 m. The cores were used to predict the regional distribution of natural gas hydrate using geochemical analyses of pore water and gas samples. Physical properties and a host of other measurements were also obtained from at-sea and shore-based analyses. Gravity cores, instrumented with temperature-sensing outriggers, were attempted at 21 different sites adjacent to piston-core locations. From those penetrations, 17 successful determinations of geothermal gradient were obtained.

Gas hydrate was recovered in three cores at subbottom depths of about 3 to 9 m, and gas bubbles indicative of gas hydrate dissociation were noticed in a fourth core. Safety protocols to relieve potential sediment overpressures and to monitor hazardous gas concentrations were implemented on cores that could potentially contain gas hydrate.

Box cores from Orca and Pigmy Basins were collected for measuring anthropogenic contaminant input of Holocene age to the northern Gulf of Mexico from the Mississippi River. Cores collected for paleoclimate studies were interspersed with the USGS sites as part of the IMAGES and PAGE programs.

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programs. The IMAGES program is an international effort to understand the mechanisms and consequences of climatic changes using the oceanic sedimentary record.

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The U.S. Minerals Management Service provided information used to determine core locations and avoid existing sea-floor infrastructure.

The Integrated Ocean Drilling Program provided facilities to store and archive recovered cores.

Metadata from the cruise, including navigation, personnel, and core locations, are available on the Internet at the USGS Web site <http://walrus.wr.usgs.gov/infobank/d/d102gm/html/d-1-02-gm.meta.html>.

A Note on the Hazards Associated with Core Overpressures and Hydrogen Sulfide Gas: Safety Procedure Applied During RV *Marion Dufresne* Giant Piston Coring Operations

Some unusual hazards can be associated with cores collected from gas and gas hydrate-rich environments. These include problems associated with generating very elevated gas pressures and with the release of hydrogen sulfide, a highly poisonous gas.

1. Pressure problems: The exsolution of gas from pore water within the core liners can produce highly pressurized gas pockets. As the pressure builds, various things can happen. In some cases, gas pockets have caused material to shoot violently out of the end of the core liner. The Ocean Drilling Program (ODP) has had some sections of core liner explode on the deck and shoot fragments of the liner several meters away.
2. Hydrogen sulfide: Some sea-floor gas seeps are known to be associated with high concentrations of dissolved hydrogen sulfide, which will escape from the cores when they depressurize at the surface. Hydrogen sulfide is an extremely poisonous gas. Exposure to hydrogen sulfide at even modest levels can be fatal to humans. In small concentrations, the hydrogen sulfide smells like “rotten eggs.” However, as the concentration increases, humans are no longer able to smell it. Thus, people are in most danger when they no longer smell hydrogen sulfide. Hydrogen sulfide is also a heavy gas; it settles into low areas; therefore, closed areas and areas on the lower decks of the ship are sites of greatest danger.

During this cruise, we will be coring in environments that are very similar to those in which other groups have experienced these problems.

Procedures:

1. Initial assessment of core gas hazards will be made by USGS watch leaders and IMAGES watch chiefs. Treat the core barrel and core liner like the barrel of a gun and never stand in its “fire path.” The people inspecting the cores initially should wear eye protection. Holes may be drilled in the liner to release gas pressure. Please stay 10 m from the exposed core liner until the watch chiefs give an “all clear.”
2. If initial contact with the core indicates a strong scent of hydrogen sulfide on deck, the deck chiefs will commence a sulfide caution.
 - A. First step is to close off all the companionways and vents that could allow the sulfide to enter from the coring deck. Signs should be posted on the main companionways to indicate that they are closed to traffic. People should only use companionways on the upper decks.
 - B. The bridge should be notified and, if possible, head into the wind and make enough way to generate a breeze.
 - C. In a severe case, the bridge will announce that a gas hazard exists and request that all personnel seek refuge outside and as high as possible. Two areas are recommended, forward on the bow and on the helicopter deck. It could take several hours for the gas to vent from the core. Please stay outside and upwind until the bridge announces that it is “all clear.”