# 32. GAS HYDRATES OF THE PERUVIAN OUTER CONTINENTAL MARGIN<sup>1</sup>

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### ABSTRACT

Gas hydrates were recovered during coring by Ocean Drilling Program (ODP) Leg 112 at Sites 685 and 688 on the Peruvian outer continental margin at latitudes of  $9^{\circ}$  and  $11.5^{\circ}$ S, where water depths are 5070 and 3820 m, respectively. In addition, nearby Sites 682 and 683 yielded compelling evidence that gas hydrates are present, but gas hydrates were not directly observed there. Anomalous acoustic reflectors, known as bottom-simulating reflectors (BSRs), on marine seismic profiles from the region also provided inferential evidence that gas hydrates are present. Geothermal gradients of about 43 and  $49^{\circ}$ C/km were calculated on the basis of relations between depths to BSRs, bottom-water temperatures, and the pressure-temperature stability field of gas hydrates.

Geochemical studies revealed that methane concentrations increase rapidly with depth after pore-water sulfate concentrations have been depleted. The relationship between methane and sulfate suggests that microbial processes account for the generation of methane, and the relationship between the carbon isotopic composition of methane and dissolved carbon dioxide supports this suggestion. We believe that decreasing chlorinity in pore water from squeezed sediment at the four sites results mainly from the decomposition of gas hydrates and is a dilution artifact observed as a result of the squeezing procedure. Maximum chlorinity values at or near the surface result from excess salt that comes from the formation of gas hydrates composed of freshwater. Record alkalinity attests to the intensity of diagenetic processes and has significant effects on salinity profiles at these sites.

Gas hydrates were recovered at 99 and 166 meters below the seafloor (mbsf) at Site 685, and at 141 mbsf at Site 688 in Pleistocene diatomaceous mud. Methane constitutes more than 99% of the hydrocarbon gas mixture in the gas hydrates. The volumetric ratio of methane to water in the sample from Site 685 is 100, indicating that the sampled gas hydrate is either undersaturated with respect to methane or had partially decomposed during core recovery or both. The discovery of gas hydrates in lower slope deposits of the Peruvian outer continental margin extends our knowledge of gas-hydrate formation and occurrence in the Circum-Pacific region.

### INTRODUCTION

During Ocean Drilling Program (ODP) Leg 112, the paleoenvironmental history of upwelling regimes and the tectonic evolution of the Peruvian continental margin were investigated. Drilling provided core samples ranging in age from Eocene to Holocene that reflect both the tectonic influence on the sedimentary record since establishment of the present margin and the initiation of the modern coastal upwelling system (von Huene et al., 1987). Together, the tectonic and paleoenvironmental factors created conditions on the Peruvian outer continental margin conducive to the development of gas hydrates, which are solid substances that occupy the sediment pore space and are made up of rigid frameworks of water molecules in which natural gas has been trapped and condensed. Gas hydrates form under specific pressure-temperature conditions that are met in oceanic sediment at depths up to about 1,100 meters below the seafloor (mbsf), where water depths exceed 300 to 500 m (Kvenvolden and McMenamin, 1980).

During Leg 112, organic-rich sediments with up to 12% organic carbon were cored at 10 sites on the continental margin of Peru (Fig. 1). Pressure-temperature conditions are conducive to the formation of gas hydrates at only four of these sites (682, 683, 685, and 688). Evidence for gas hydrates was found at all four deep-water sites, and gas hydrates were recovered at two of them (685 and 688). Here we describe the geological evidence for gas hydrates in lower slope sediments

offshore Peru and our organic and inorganic geochemical observations about sediment gases, pore waters, and recovered gas hydrates.

#### **GEOLOGIC SETTING**

Four ODP sites exhibiting evidence for gas hydrates were drilled in lower slope deposits of the outer continental margin offshore Peru near latitudes of 9° and 11°S, at water depths ranging from 3,071 to 5,070 m (Fig. 1). At Site 682 (3,788 m water depth), 437 m of Pleistocene to middle Eocene sediment was cored. These sedimentary strata are composed mainly of biosiliceous ooze and mud grading downward to diatomaceous mudstone, siltstone, and sandstone. At Site 683 (3,071 m water depth), the sedimentary strata, cored to a depth of 488 m, span the same age range as Site 682. The Neogene lithology at Site 683 is dominated by diatomaceous mud and mudstone grading downward to more silty, and eventually, sandy lithologies composed of turbiditic debris and volcanic glass. The core taken at Site 685 (5,070 m water depth) consists of 468 m of Pleistocene to late Miocene sedimentary strata composed of diatomaceous mud grading to mudstone, which is variably calcareous. Sedimentary breccias and sand are found near the bottom of the hole. Coring at Site 688 (3,820 m water depth) recovered sediment to a depth of 770 mbsf reflecting progressively deeper water sedimentation from early Eocene to Pleistocene time. Downhole, the lithology consists of bioturbated diatomaceous mud and includes terrigeous turbidites underlain by laminated sediments composed of diatomite and mudstone. Calcareous mudstones, siltstones, and sandstones that include terrigenous debris are found in the lower part of the hole.

## GEOPHYSICS

The identification of gas hydrates in oceanic sediment has been based mainly on the appearance of an anomalous acous-

<sup>&</sup>lt;sup>1</sup> Suess, E., von Huene, R., et al., 1990, Proc. ODP Sci. Results, 112: College Station, Texas (Ocean Drilling Program).

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Figure 1. Location of drill sites for ODP Leg 112. Sites producing evidence for gas hydrates are shown as filled squares. Bathymetric contour interval is 1,000 m.

tic reflector that approximately parallels the seafloor on marine seismic-reflection profiles (Shipley et al., 1979). This bottom-simulating reflector (BSR) is thought to result from a velocity contrast between overlying, higher-velocity sediment containing gas hydrates and underlying, lower-velocity sediment possibly containing free gas. This contrast in velocities often produces large reflection coefficients and reversed polarities relative to the seafloor reflector. The depth of this anomalous reflector generally correlates with the theoretical pressure-temperature-dependent depth for the base of the gas-hydrate stability zone. Thus, besides approximately paralleling the seafloor, the gas-hydrate-caused BSR should also increase in subbottom depth with increasing water depth (that is, with increasing pressure). In addition, the depth of the BSR can, in theory, be used to estimate geothermal gradients within gas-hydrate zones because of the pressure-temperature dependency of gas-hydrate formation (Shipley et al., 1979; Yamano et al., 1982). BSRs attributed to gas hydrates were observed on marine seismic-reflection profiles from at least 19 locations along continental margins of the world (Kvenvolden and Barnard, 1983), including the continental margin of Peru.

Offshore Peru, BSRs, inferred to indicate the base of gas hydrates, were observed on most seismic-reflection profiles obtained over the landward slope of the Peru-Chile Trench (Shepard, 1979). Between latitudes of about 5° and 7°S, these BSRs occur at depths of between about 350 and 570 mbsf, where water depths range from 800 to 3,200 m. On a multichannel seismic-reflection profile across the outer continental margin of central Peru at a latitude of 9°S, a discontinuous BSR was observed (von Huene et al., 1985). Figure 2 shows a segment of this seismic profile with a clearly defined BSR.

ODP Sites 682, 683, 685, and 688 were purposely located to avoid BSRs because of the possible hazards that could result from drilling through a gas-hydrate-bearing zone. However,



Figure 2. Segment of multichannel seismic profile showing a bottomsimulating reflector (BSR) attributed to the base of the gas-hydrate stability zone. Data from von Huene et al. (1985).

BSRs were observed on seismic profiles through three of the sites (682, 685, and 688) at a minimum distance of 2.5 km from the holes (Suess, von Huene et al., 1988). There was no geophysical evidence for gas hydrates at Site 683.

On a seismic-reflection profile through Site 682, a welldefined BSR was observed at 0.58 s (two-way traveltime) about 8 km seaward of the site. This BSR, located at a depth of 477 mbsf (assumed seismic velocity of 1,645 m/s), is believed to correspond to the base of the gas-hydrate stability zone. Using methods modified after Shipley et al. (1979) and Yamano et al. (1982), we determined by means of an enlarged version of the phase diagram of Fig. 3 that the geothermal gradient at this site is about 49°C/km, where the bottom-water temperature is 1.7°C (Fig. 3). Because no seismic evidence existed for a BSR near Site 683, a measured geothermal gradient of 43°C/km and a bottom-water temperature of 1.8°C was used to estimate a BSR depth of 529 mbsf. At Site 685, a BSR shows on a seismic profile at a depth of 0.68 s, or 612 mbsf (assumed velocity of 1,800 m/s), about 4.6 km seaward of the site. We calculated a geothermal gradient here of about 43°C/km (Fig. 3) using a bottomwater temperature of 1.5°C. A BSR was observed on seismic profiles about 2.5 km seaward of Site 688. The depth of this reflector, which occurs at 0.52 s or about 473 mbsf, and a bottom-water temperature of 1.7°C were used to calculate a geothermal gradient at this site of about 50°C/km (Fig. 3). Thus, the geothermal gradient for deep-water, continental slope sediment of the Peru margin near latitude 9°S (Sites 683 and 685) is 43°C/km, and near latitude 11°S (Sites 682 and 688) averages 49.5 °C/km, based on calculations from the occurrences of gas hydrates. These values are similar to those determined by Yamano and Uyeda (this volume) from heat- flow studies in this area.

### GAS CHEMISTRY

The composition of hydrocarbon gases released from sediment cores after recovery was determined at each of the four sites. Details of the gas analyses are given in the individual site chapters (Suess, von Huene et al., 1988). Gases were collected with Vacutainers by sampling, through the core liner or through the end caps, the gas voids that formed in the sediment during core recovery. Gas voids were first observed in cores taken at about 30 mbsf at Sites 683, 685, and 688; at Site 682, gas voids first formed at 106 mbsf. Gases also were extracted from sediment samples using a headspace technique modified from Kvenvolden and Redden (1980). With this



Figure 3. Phase diagram showing the region of methane hydrate stability; the phase boundary is for a pure-methane/pure-water system (Kvenvolden and McMenamin, 1980) and is based on information from Katz et al. (1959). Within this region, the pressure and temperature conditions at the four deep-water sites are given as are the geothermal gradients, determined by the methods modified from Shipley et al. (1979) and Yamano et al. (1982).

technique, an approximate measure of the amount of residual gas in the sediment after degassing during core recovery can be obtained. Gas analyses showed that methane constitutes more than 99% of the hydrocarbon gas mixture in all samples; other hydrocarbon gases, such as ethane and propane, are present in parts per million concentrations. Carbon dioxide was probably an important component of the total gas mixtures at all sites, but it was measured only at Site 688 where a maximum concentration of 42.4% was noted (Suess, von Huene, et al., 1988). The carbon dioxide was probably present as bicarbonate in the subsurface and outgassed as carbon dioxide when cores were recovered.

Concentrations of residual methane extracted from sediment increase rapidly with depth and reach a maximum value of about 100,000 microliters of methane per liter of wet sediment ( $\mu$ L/L) within the first 25 m of sediment at Sites 683, 685, and 688 and at about 77 mbsf at Site 682 (Fig. 4); methane concentrations are reported in microliters per liter of wet sediment ( $\mu$ L/L). These units are nonconventional, but expedient and express the amount of methane extracted from a core sample. Below the depths of maximum concentrations, methane concentrations remain high, exceeding 1,000  $\mu$ L/L and often 10,000  $\mu$ L/L. These residual methane values are similar to those found at gas-hydrate-bearing sites on the Blake Outer Ridge and near the Middle America Trench (Kvenvolden, 1985). A concentration of 100,000 µL/L may represent the maximum residual methane that can be recovered using the headspace extraction technique.



Figure 4. Profiles of methane and sulfate concentrations with depth at Sites 682, 683, 685, and 688, ODP Leg 112, Peruvian outer continental margin, Pacific Ocean.

The carbon isotopic composition of methane collected in Vacutainers was determined at the four sites (G. E. Claypool and A. K. Vuletich, written comm., 1987). The earliest encountered methane that could be sampled with Vacutainers has carbon isotopic values of about -79 to -73 % [relative to the Peedee Belemnite standard (PDB)]. With increasing depth, the carbon compositions become heavier and level off in the range of -65 to -55 % (Fig. 5).

### PORE-WATER CHEMISTRY

Interstitial water, squeezed mechanically from core samples at the four deep-water sites, was analyzed onboard the ship for several inorganic geochemical parameters (Suess, von Huene et al., 1988) The most important of these, relative to the study of gas hydrates, are sulfate, chlorinity, salinity, and alkalinity. In addition, the carbon isotopic composition of carbon dioxide dissolved in the interstitial water was determined at a shorebased laboratory (G. E. Claypool and A. K. Vuletich, written comm., 1987).

The profiles of interstitial-water sulfate concentration with depth at all four sites show a rapid depletion below the surface that reaches fairly constant values between 0 and 4 mmol. Further work by Kastner et al. (this volume) has shown that the sulfate values larger than 0 mmol are likely the result of seawater contamination of the samples. Minimum concentrations begin at about 16 and 18 mbsf at Sites 683 and 685, respectively, whereas minimum concentrations begin at 70 and 30 mbsf at Sites 682 and 688, respectively.

The rapid depletion of sulfate concentrations in the pore water correlates inversely with concentrations of residual methane, i.e., the methane measured by the headspace technique (Fig. 4). Our results strongly support the microbial sulfate reduction-methane generation model of Claypool and Kaplan (1974). The rapid increase of methane in sediment with



Figure 5. Profiles of  $\delta^{13}$ C of methane and carbon dioxide with depth at Sites 682, 683, 685, and 688 ODP Leg 112, Peruvian outer continental margin, Pacific Ocean (G.E. Claypool and A.K. Vuletich, written comm., 1987).

depth is a result of the complete removal of sulfate by sulfatereducing bacteria, thereby promoting methanogenesis, which is inhibited in the presence of sulfate ions.

Chlorinity and salinity in the pore water squeezed from sediment generally decrease with depth at all four sites (Fig. 6). We believe that these decreasing concentrations are derived, to a large extent, from the decomposition of gas hydrates, which should be composed of pure water. Chloride concentrations were measured on mixtures composed of *in-situ* pore water and decomposed gas-hydrate water. Thus a progressive dilution artifact is produced in the interstitial water that can be squeezed from the sediment at increasing depths. In theory, an *in-situ* pore-water sampler should be able to acquire water that does not show the dilution artifact, but *in-situ* pore-water samples acquired at sites with gas hydrates all showed the dilution effect to some extent. This dilution effect was discussed previously by Hesse and Harrison (1981) and has been observed at sites where gas hydrates were recovered, for example, at the Blake Outer Ridge (Kvenvolden and Barnard, 1983) and the Middle America Trench (Harrison et al., 1982; Kvenvolden and McDonald, 1985; Hesse et al., 1985).

Within the upper 100 m of cored sediment, a small but distinct maximum interrupts the general trend of decreasing chlorinity with depth at all four sites. At Sites 682 and 688, these chlorinity values exceed that of seawater (559 mM). We



Figure 6. Profiles of chlorinity, salinity, and alkalinity with depth at Sites 682, 683, 685, and 688, ODP Leg 112, Peruvian outer continental margin, Pacific Ocean.

believe that these chlorinity values most probably reflect a part of the salt that must be excluded from the water that forms the gas hydrates, because this gas hydrate water is fresh, as discussed later. Thus, during the formation of gas hydrates, the excluded salts diffuse to the seafloor and give rise to the maxima in chlorinity profiles measured from interstitial water, as we observed.

Salinity profiles for Sites 682 and 683 are generally parallel to chlorinity profiles and show a decrease with depth (Fig. 6). However, salinity and chlorinity profiles for Sites 685 and 688 are not parallel (Fig. 6). The reason for the difference is that salinity profiles are significantly affected by alkalinity, and record-high alkalinity values were observed at Sites 685 and 688 (Fig. 6). Previous alkalinity records in oceanic sediment were recorded from inner slope sediment of the Middle America Trench (Harrison et al., 1982). High alkalinities result from the intensity of the geochemical processes taking place in these sediments and are preserved or maintained by high sedimentation rates. Carbonate precipitation in response to reduction of carbon dioxide to methane is one reaction that results in the observed alkalinity decrease with depth.

The carbon isotopic composition of carbon dioxide dissolved in the interstitial water changes from about 0 % at the sediment-water interface to about -8 to -20 % at the depth where sulfate is essentially depleted (G. E. Claypool and

Core:	685A-18X-8	688A-15X-7	688A-15X-7	688A-15X-7
Sample:	1	Α	В	С
Depth (mbsf):	165.6	141.0	141.0	141.0
Age:	Pleistocene	Pleistocene	Pleistocene	Pleistocene
Lithology:	Diatomaceous Mud	Diatomaceous Mud	Diatomaceous Mud	Diatomaceous Mud
Equilibrium pressure (psig):	383	85	95	-
Equilibrium temperature (°C):	25	25.4	21.5	
Composition of gas:				
Methane (%)	95	91.5	91.5	
Ethane (ppm)	39	22	22	1.0000
Propane (ppm)	28		-	
Air, CO <sub>2</sub> (%)	5	8	8	-
Volume of methane (cm <sup>3</sup> , STP):	587	147	162	-
Volume of water (mdm <sup>3</sup> ):	5.89	11.3	6.2	-
Ratio of methane/water:	100	13	26	-
Weight of sediment (g):	1.25	2.5	3.1	-
Composition of water:				
Salinity (g/kg)	4.0	7.8	20.0	11.8
Alkalinity (mM)	17.93			-
Chlorinity (mM)	51.4	90.6	232.3	136.6
Sulfate (mM)		0	0	_
Isotopic composition:				
$\delta^{13}$ C methane (%, PDB)	<sup>a</sup> -65.0	<sup>a</sup> -59.6		
$\delta^{18}$ O water (‰, SMOW)	nd	+1.8		
δD water (‰, SMOW)	+19.3	+17.6		
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a work at alcount offic oned decomposition of gub nitures notin offic ate	Table 1.	Results	from	controlled	decomp	osition o	of gas	hydrates	from	ODP	Leg	112	
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<sup>a</sup>G. E. Claypool, written comm. (1987).

nd = not determined; - = not measured.

A. K. Vuletich, written comm., 1987). After the initiation of methanogenesis, the carbon isotopic composition of the dissolved carbon dioxide rapidly shifts from negative values to about +10 to +20 % as isotopically lighter methane forms from the carbon dioxide (Fig. 5). The methane formed at any time is about 65 to 80 % lighter than the carbon dioxide pool from which it has been generated.

#### GAS HYDRATES

Samples of gas hydrates were recovered from cores at Sites 685 and 688 in diatomaceous mud of Pleistocene age within 200 m of the seafloor. Gas hydrates were observed in two cores at Site 685 at depths of 99 and 166 mbsf. Core recovery was disturbed by rapid gas expansion that often forcibly ejected core from the core liners. At the first occurrence (99 mbsf), a few small pieces (each about 1 cm<sup>3</sup> in size) of dark gray gas hydrate were noticed. At 166 mbsf, two pieces of dark gray gas hydrate (18 and 1 cm<sup>3</sup>) were found in the core. These samples looked like partially rounded pieces of mudstone, but closer examination showed bubbling foam on the edges and coldness to the touch. The samples were placed in special pressure vessels (Kvenvolden et al., 1984). The gas hydrates decomposed within the vessel, and geochemical analyses were obtained on the released gas and water; results are summarized in Table 1. These results augment those made previously on gas hydrates recovered from sediment of outer continental margins, for example, from the Blake Outer Ridge (Kvenvolden and Barnard, 1983), the Middle America Trench Kvenvolden and McDonald, 1985), and the Gulf of Mexico (Brooks et al., 1984; Pflaum et al., 1986).

Fully saturated methane hydrate has a formula,  $CH_4 \cdot 5.75$  H<sub>2</sub>O, which means that upon decomposition one can expect a volumetric ratio of methane to water of about 164 (Davidson et al., 1978). The gas-hydrate sample from Site 685 has a volumetric ratio of 100, which indicates either partial decomposition during core recovery or undersaturation or both. The water, recovered from the gas hydrate, should be pure (devoid of salts), but in our sample it contains some seawater as indicated by a salinity of 4.0 g/kg, about 11% that of seawater, and a chlorinity of 51.4 mM, about 9% that of seawater.

chlorinity of the gas-hydrate water (51.4 mM) contrasts with a chlorinity of 541 mM of the nearby pore water squeezed from sediment of the same core. The higher value is 96.8% of seawater chlorinity (559 mM). The almost freshwater composition of this gas hydrate sample explains the lowered salinity and chlorinity measured in pore waters squeezed from sediment containing gas hydrates.

Gas hydrates were recovered from a core at about 141 mbsf at Site 688. These samples were composed of a mixture of gas hydrate and dark- gravish black mud (Fig. 7). Four samples were designated A through D. Samples A and B were confined in pressure vessels, as mentioned earlier; sample C was allowed to decompose in an open beaker so that a large sample of gas-hydrate water could be obtained. Sample D was placed in a special container for long-term storage (Sloan, 1985); however, the seals failed and the sample was lost. Shipboard results for Samples A through C (given in Table 1) suggest that the gas hydrates recovered at Site 688 underwent significant decomposition before the measurements were made. For example, the volumetric ratios of methane to water were only 13 and 26, values significantly smaller than those obtained from the Site 685 sample. The salinity and chlorinity values also indicate that the samples were contaminated with some seawater.

For the gas hydrate samples from Sites 685 and 688, we assume that the chloride concentrations indicate the amount of *in-situ* interstitial water that is mixed with pure gas-hydrate water. Thus, on the basis of an interstitial water chloride concentration of approximately 530 mM, which is found within the depth range of these two gas-hydrate samples (Kastner et al., this volume), we calculate that the amount of admixed interstitial water is 10 and 17% in the gas-hydrate water from Sites 685 and 688, respectively. This information is useful in interpreting the  $\delta^{18}$ O and  $\delta$ D values that have been measured on these samples (Table 1).

In order to extrapolate the  $\delta^{18}$ O and  $\delta$ D values of the measured gas-hydrate water to the end-member values of the original, *in-situ* gas hydrates, the  $\delta^{18}$ O and  $\delta$ D values of the admixed interstitial waters must be known; however, no such data are as yet available for Site 685, and there is minimal information from Site 688. Nevertheless, on the basis of



1 cm

Figure 7. Gas hydrate recovered from Core 112-688A-15X-7 at 141 mbsf, ODP Leg 112, Peruvian outer continental margin, Pacific Ocean.

oxygen and hydrogen isotopic compositions measured on interstitial water from two other locations on the slope (Sites 682 and 683) (Kastner et al., this volume) and on interstitial water from a deep sample (688E-3R-4, 140-150) for which  $\delta^{18}O$ = -1.20 % and  $\delta D$  = -8.5 % (relative to standard mean ocean water [SMOW]), the inferred interstitial water isotope values that are used for extrapolations to the end-member values of the original gas hydrate are:

and

$$\delta D = -3.0 \%$$

 $\delta^{18}O = -1.2 \%$ 

Accordingly, the  $\delta^{18}$ O value of the *in-situ* gas-hydrate sample 688A-15X-7 would be +2-4 ‰, and the D value would be +21.8 ‰. For gas hydrate sample 685A-18X-8, the  $\delta^{18}$ O value was not yet determined because of the extremely small sample size and the special precautions needed for analysis; however, the end-member  $\delta^{18}$ O value for this sample was calculated to be +2.04 ‰ based on a chloride concentration of 51.4 mM and an assumed pure gas hydrate  $\delta^{18}$ O value of +2.1.8 ‰, identical to the value calculated for Sample is +21.8 ‰, identical to the value calculated for Sample 688A-15X-7. In all of these calculations, a single step isotope fractionation was assumed.

The analogy between the water of gas hydrates and the water of ice was suggested by Trofimuk et al. (1974). The oxygen isotopic fractionation factor for the ice-water system determined experimentally by direct freezing ranges between 1.0031 and 1.0027 (Craig and Hom, 1968; O'Neil, 1968; Suzuki and Kimura, 1973). According to Craig and Hom (1968), who studied the formation of sea ice, the fractionation factor is 1.0027. The  $\delta^{18}$ O enrichment of a gas hydrate system was determined experimentally by Davidson et al. (1983), who report an  $\alpha$  value of 1.0026. Our extrapolated value of +2.4 % is very close to the experimental ones, being only 0.2 or 0.3 % lighter than the results of Davidson et al. (1983) or of Craig and Hom (1968), respectively.

The original interstitial water from which gas hydrates formed must have had oxygen and hydrogen isotopic compositions lighter than in standard mean ocean water (SMOW). Indeed, the  $\delta^{18}$ O value of south and equatorial Pacific deep waters is -0.17 % (Craig and Gordon, 1965). The  $\delta^{18}$ O value of ice that forms from these bottom waters should be +2.5%[using the fractionation factor of Craig and Hom (1968)] or +2.4 % [using the fractionation factor of Davidson et al. (1983)] Our calculated value of +2.4 ‰ suggests that isotopically light residual interstitial water from gas hydrate formations had little or no influence on the isotopic values of our two gas-hydrate samples. The theoretical hydrogen isotopic fractionation factor for the ice-water system is 1.0192 + 0.002(Weston, 1955), and the experimental results range from 1.0235 to 1.0195 (Merlivat and Nief, 1967; Craig and Hom, 1968; O'Neil, 1968; Arnason, 1969). Our extrapolated value of +21.8 % falls within this range.

Although only a few small samples of gas hydrates were recovered at Sites 685 and 688, gas hydrates probably are present in much of the sediment column between depths of about 20 mbsf and the base of the gas-hydrate stability zone at about 612 mbsf at Site 685 and at about 500 mbsf at Site 688. Gas hydrates probably are also present at Sites 682 and 683. The likely reason that more gas hydrates were not observed is because they are unstable at shipboard conditions and are destroyed during the coring and recovery process. Only rarely do natural gas hydrates survive long enough to be analyzed.

### DISCUSSION

The Peruvian outer continental margin provides a setting particularly conducive to the formation of gas hydrates. A well-developed coastal upwelling regime, active since the Miocene, coincides with the subduction of the Nazca Plate, resulting in organic-rich sedimentary facies in lower slope deposits at depths where gas hydrates are stable. Organic carbon content of sediments at the four sites is usually high and reaches as much as 8% (Suess, von Huene et al., 1988). Centers of upwelling generate oxygen-deficient waters that enhance the preservation of organic matter (Reimers and Suess, 1983; Suess et al., 1987), and microbially-mediated decomposition of this organic matter ultimately leads to the generation of methane, mainly from the reduction of carbon dioxide (Claypool and Kaplan, 1974). When the amount of methane approximates its solubility in water, gas hydrates will form if specific pressure and temperature conditions in the sediment are met. (See Fig. 3 for the pressure-temperature field in which methane hydrate is stable.)

The first evidence that gas hydrates might be found in lower slope sediments of the Peruvian outer continental margin came from marine geophysical surveys in which seismic-reflection profiles, oriented perpendicular to the coast, show well-defined BRSs at depths near the base of the zone of gas-hydrate stability (Shepard, 1979; von Huene et al., 1985). Although BSRs may also be caused by certain diagenetic conditions in sediment (Kvenvolden and Cooper, 1987), the recovery of gas hydrates from sediment of the Peruvian outer continental margin strongly supports the inference that the BSRs here are due to the presence of gas hydrates.

As drilling progressed at each of these deep-water sites, it became apparent that the sediment contained high concentrations of gas manifested not only in the disrupted condition of the recovered cores but also in the gas analyses. Within the first 100 m of sediment at each site, residual methane concentrations reached about 100,000 µL/L of wet sediment, an upper limit found previously at other gas-hydrate-bearing sites (Kvenvolden, 1985). This upper limit is equal to a concentration of about 6 mM in the pore water assuming a porosity of 75% and using 4 mM as the solubility of methane in water at 1 atm and 20°C. Associated with the presence of significant amounts of methane was the depletion in pore-water sulfate concentrations (Fig. 4). This evidence for the microbial reduction of sulfate to sulfide preceding the microbial reduction of carbon dioxide to methane follows the generally accepted model of Claypool and Kaplan (1974). The relation between the carbon isotopic compositions of methane and dissolved carbon dioxide (Fig. 5) provides strong evidence that this methane is of shallow microbial origin, rather than of deeper thermal origin. Clearly, the dissolved carbon dioxide is linked to microbial processes occurring in the sediment.

Pore-water chloride concentrations indicated that gas hydrates should be present at these four sites because of the general trend of decreasing chlorinity with depth (Fig. 6). Such decreases may also result from mineral dehydration, membrane filtration, and dewatering of subducting sediment (Kastner et al., this volume). The chlorinity profiles of the

Peruvian outer continental margin can best be explained as mainly caused by the presence of gas hydrates, especially in light of all the other evidence for gas hydrates at these sites. If the negative gradients of chlorinity observed at all of these lower slope sites are due only to dilution by fresh water released from the dissociation of gas hydrates, the dilution near the bottom of the holes at Sites 682, 683, 685, and 688 is 10%, 9%, 3%, and 10%, respectively. These results suggest that a comparable proportion of the sediment volume could be occupied by gas hydrates. Perhaps most important in the chlorinity profiles is the slightly higher chloride concentrations noted at or near the seafloor. We believe that these concentrations represent a part of the excess salt that must be present as a result of the formation of gas hydrates, the water of which is fresh. Thus, as gas hydrates form, excess salt diffuses upward into the seawater. These chlorinity profiles (Fig. 6) are the first to be used to interpret the fate of the excess salt resulting from gas-hydrate formation.

The gas-hydrate samples from Sites 685 and 688 were found in dark diatomaceous mud of Pleistocene age (Fig. 7). These sediments show extremely high alkalinity values (Fig. 6), which reflect that intense diagenetic processes are taking place during rapid sedimentation and lead to the formation of dolomites and calcites. Alkalinity values at these sites exceed the maximum values observed previously in inner-slope sediment of the Middle America Trench (Harrison et al., 1982; Hesse et al., 1985). The recovered gas hydrates occur in very fine-grained sediment (mud), in contrast to previous observation, where gas hydrates appeared to occupy the pore spaces of coarser-grained lithologies (Shipley and Didyk, 1982; Harrison and Curiale, 1982; Kvenvoiden and McDonald, 1985).

At Site 688, the base of the gas hydrate was inferred to be at 473 mbsf, based on the depth of a nearby BSR on a marine seismic profile through the site. The total depth of the hole at Site 688 was 770 mbsf. This means that drilling penetrated the base of the zone of gas hydrate stability where high concentrations of free gas may be expected. No obvious, anomalously large gas accumulations were present, at least as recorded in the recovered cores (Suess, von Huene et al., 1988). The penetration, without incident, of this boundary at the inferred base of gas hydrate indicates that drilling through this boundary does not pose a safety problem at carefully selected sites.

#### SUMMARY

The recovery of samples of gas hydrates in sediments of the outer continental margin offshore Peru provides strong evidence that BSRs, often observed on marine seismic records from this region, are, indeed, indicative of gas-hydrate occurrence. Geothermal gradients, calculated on the basis of relations between depths to BSRs, bottom-water temperatures, and the pressure temperature stability field of gas hydrates, are similar to gradients determined from heat-flow studies. These similar results provide additional evidence that BSRs in this region mark the base of the zone in which gas hydrates are stable. Apparently gas hydrates are common and widespread in the outer continental margin of Peru.

The molecular composition of hydrocarbon gases, the carbon isotopic compositions of methane and carbon dioxide, and the pore-water chemistry all indicate that microbial processes are responsible for the methane that formed the gas hydrates. Organic carbon contents of up to 8% indicate a rich supply of organic matter for methanogenesis. Salts were excluded from water during gas-hydrate formation, and this water underwent oxygen and hydrogen isotopic fractionation similar to the fractionation that occurs during the formation of ice. The geochemical details of these gas hydrates and their associated sediments have yielded information which will be applicable to the study of gas hydrates that will be found in future explorations.

#### ACKNOWLEDGMENTS

We especially appreciate the cooperation and help of the ODP chemistry technicians, Katie Sigler-Tauxe and Matt Mefferd, and senior marine technician, Brad Julson, who provided the critical shipboard support for this work. We also thank Dr. J. Wehlan for oxygen and hydrogen analyses on four samples, and T. Frank for preparation of figures. This work could not have been accomplished without the skill and dedication of the operations and drilling crews of the *JOIDES Resolution*. A part of this work was supported by a USSAC grant to M.K.

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Date of initial receipt : 1 August 1988 Date of acceptance: 11 April 1989 Ms 112B-147