

13. GEOCHEMICAL AND STABLE ISOTOPIC COMPOSITIONS OF PORE FLUIDS AND AUTHIGENIC SIDERITE CONCRETIONS FROM SITE 1146, ODP LEG 184: IMPLICATIONS FOR GAS HYDRATE¹

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ABSTRACT

Bottom-simulating reflectors were observed beneath the southeastern slope of the Dongsha Islands in the South China Sea, raising the potential for the presence of gas hydrate in the area. We have analyzed the chemical and isotopic compositions of interstitial water, headspace gas, and authigenic siderite concretions from Site 1146. Geochemical anomalies, including a slight decrease of chlorine concentration in interstitial water, substantial increase of methane concentration in headspace gas, and ¹⁸O enrichment in the authigenic siderite concretion below 400 meters below seafloor are probably caused by the decomposition of gas hydrate. The low-chlorine pore fluids contain higher molecular-weight hydrocarbons and probably migrate to Site 1146 along faults or bedded planes.

INTRODUCTION

Gas hydrate is a crystalline substance in which many of the cavities in the H₂O lattice contain low molecular weight gases (mostly methane) under conditions of moderate to high pressure and low temperature (Sloan, 1990). The total amount of methane in gas hydrate is

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thought to be very large, perhaps as much as 10^{19} g of methane carbon (Kvenvolden, 1993). Gas hydrate is a potentially important fossil fuel resource, can affect global climate, and plays a role in submarine geohazards (Kvenvolden, 1988a, 1988b).

Currently, the presence of gas hydrate in deep-sea sediments can be detected mainly based on the presence of a bottom-simulating reflector (BSR) on seismic profiles, which corresponds to the base of the gas hydrate stability zone (GHSZ). In addition, the bulk and isotopic composition of pore fluids and authigenic carbonates are useful evidence for the presence of gas hydrate in sediments. In this chapter, we describe the chemical and isotopic composition of interstitial water, headspace gas, and authigenic siderite recovered from Site 1146 of Ocean Drilling Program (ODP) Leg 184 and discuss the possible relationships between these geochemical anomalies and the presence of gas hydrate.

GEOLOGICAL SETTING

The South China Sea is the largest marginal sea in the western Pacific, and it is well known for its abundant oil and gas reserves. A broad and wide continental slope 210,000 km² in area extends to the northern parts of the South China Sea, and it is a good site for gas hydrate formation and conservation (Zhu et al., 2001). Furthermore, BSRs have been found on the northern slope (Fig. F1) (Yao, 1998; Chi et al., 1998; Song et al., 2001; Zhang and Chen, 2000; Chow et al., 2000).

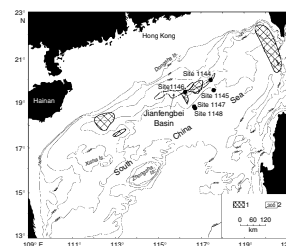
Site 1146 is located at 19°27.40'N, 116°16.3'E at a water depth of 2092 m within a small rift basin (Jianfengbei Basin) on the southern slope of the Dongsha Islands (Fig. F1) (Wang et al., 2000). Three holes (Holes 1146A, 1146B, and 1146C) drilled at Site 1146 penetrated to the maximum depths of 607, 245.1, and 603.5 meters below seafloor (mbsf), respectively, and ended in lower Miocene, Pliocene, and lower Miocene sediments, respectively, with a maximum basal age of ~19 Ma (Shipboard Scientific Party, 2000b). Hole 1146C is ~30 m east of Hole 1146A.

SAMPLING AND METHODS

We asked the Shipboard Scientific Party of ODP Leg 184 to take 35 interstitial water samples and 29 headspace gas samples from Site 1146 for our shore-based laboratory. More than 400 sediment samples were also collected from Site 1146.

We analyzed 24 interstitial water samples from Hole 1146A, with a frequency of one per 10 m between 0 and 75 mbsf and one per 29 m between 75 and 506 mbsf. We also measured 11 samples from Hole 1146C, with a frequency of one per 19 m between 406 and 598 mbsf. Interstitial water was extracted with a titanium squeezer from whole-round sections 5–10 cm long, which were cut immediately after core retrieval on deck. Water samples were placed into plastic syringes and filtered through 0.45- μ m Gelman polysulfone disposable filters and then stored in heat-sealed acid-washed glass vials for shore-based analyses (Wang et al., 2000). The concentrations of sodium (Na⁺), calcium (Ca²⁺), lithium (Li⁺), chloride (Cl⁻), and sulfate (SO₄²⁻) were measured post-cruise for all interstitial water samples, and isotopic compositions of oxygen and hydrogen were measured on 18 samples. The concentrations of Na⁺ and Ca²⁺ were measured by inductively coupled plasma-atomic emission spectrometry, with an analytical precision of 3%, and Li⁺ con-

F1. Leg 184 drill site locations, p. 10.



centrations were measured by inductively coupled plasma–mass spectrometry, with an analytical precision of 3%. The Cl^- concentration was measured by volumetric methods, and SO_4^{2-} concentration was measured by turbidimetry. Isotopic compositions of hydrogen and oxygen were determined by the standard CO_2 equilibrium method, using a Finnegan MAT-251 mass spectrometer with an analytical precision of 2‰ for hydrogen and 0.2‰ for oxygen. We also analyzed 13 headspace samples collected from Hole 1146A, with a frequency of one per 19 m between 342.6 and 592.1 mbsf and 16 samples collected from Hole 1146C, with a frequency of one per 19 m between 406.5 and 482.8 mbsf and one per 9.6 m between 482.8 and 598.3 mbsf. As soon as cores arrived on deck, a sediment sample of 5 cm^3 was collected using a borer tool, the sample was placed in a 21.5- cm^3 glass serum vial, and the vial was sealed on deck (Wang et al., 2000). After the samples arrived in the shore-based laboratory, the headspace gas was extracted following the standard headspace sampling method. The compositions of methane (C_1), ethane (C_2), propane (C_3), isobutene ($i\text{-C}_4$), n -butane ($n\text{-C}_4$), isopentane ($i\text{-C}_5$), and n -pentane ($n\text{-C}_5$) were analyzed for all samples using a SQ-203 gas chromatograph, and the carbon isotopic composition of methane was measured for nine samples with a Finnegan MAT-251 mass spectrometer. The mineralogical compositions of two authigenic carbonate concretions from sediments were identified by X-ray diffraction (XRD). The oxygen and carbon isotopic compositions of siderite were measured using a MAT-251-EM mass spectrometer. Samples were treated at 50°C with 100% phosphoric acid for 4 days. The isotopic compositions are expressed in the conventional δ notation relative to the Peedee belemnite (PDB) reference. The analytical precision is 0.2‰ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

GEOCHEMISTRY OF INTERSTITIAL WATER

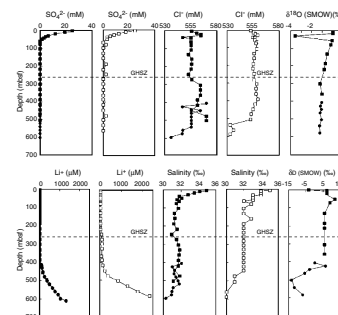
Chemical and isotopic compositions of interstitial water are given in Table T1. However, the results of chemical compositions from Hole 1146A essentially confirm those of the Leg 184 shipboard geochemists (Shipboard Scientific Party, 2000b) (Table T1; Fig. F2). SO_4^{2-} concentration is highest near the surface, with a maximum of 25 mM at 2.95 mbsf, a value similar to that of seawater. It decreases rapidly downhole to reach 0 mM at 65.35 mbsf, which indicates that sulfate reduction is completed at this depth. Below the zone of sulfate reduction, it remains 0 mM until the base of the hole (Table T1; Fig. F2).

Cl^- concentrations at Site 1146 are relatively constant above 540.41 mbsf, ranging from 547 to 570 mM, which are values similar to that of seawater. Below 540.41 mbsf, Cl^- begins to decrease, with values of 547 mM at 559.7 and 579.0 mbsf and a minimum value of 536 mM at 598.20 mbsf (~3.6% dilution) (Fig. F2). A similar result was obtained by the Leg 184 Shipboard Scientific Party (Shipboard Scientific Party, 2000b).

Li^+ is very low, with a value of 23 μM near the surface, and then increases slowly downhole to 44 μM at 361.7 mbsf, a value similar to that of seawater. Downward, Li^+ increases sharply from 179 μM at 390.5 mbsf to a maximum value of 1337 μM at the base of the hole (598.2 mbsf) (Fig. F2). A similar increase was obtained by the Leg 184 shipboard geochemists, but they found the maximum value was up to 2390 μM (Shipboard Scientific Party, 2000b) (Table T1; Fig. F2).

T1. Chemical and isotopic compositions of interstitial water, Site 1146, p. 14.

F2. Chemical and isotopic composition of interstitial water, Holes 1146A and 1146C, p. 11.



Na⁺ concentrations are relatively constant above 521.1 mbsf, ranging from 432 to 452 mM. Below 521.1 mbsf, Na⁺ begins to decrease with depth to a minimum value of 407 mM. Ca²⁺ concentrations are 16.7 mM near the surface and decrease quickly to a minimum value of 2.6 mM at 65.35 mbsf, in correspondence with sulfate reduction. Ca²⁺ increases slowly downhole to a maximum of 23.8 mM at the base of the hole.

Interstitial water salinities decrease rapidly from 35‰ at 2.95 mbsf to 32‰ at 36.85 mbsf. Further downhole, they remain relatively constant in the range of 31‰–32‰ between 36.85 and 579 mbsf and then decrease to 30‰ at the base of the hole (Fig. F2).

The δ¹⁸O values of the interstitial water from Site 1146 decrease slowly with depth, in the range from 0.2‰ to –1.30‰ standard mean ocean water (SMOW), except for an anomalously lower value of –3.7‰ at 27.35 mbsf (Table T1; Fig. F2). The δD values are relatively constant between 8.35 and 361.7 mbsf, ranging from –1‰ to 3‰ SMOW and begin to decrease slowly with a minimum value of –14‰ below 406.4 mbsf (Fig. F2). The δ¹⁸O and δD values of interstitial water are typical of seawater stored in sediments, with no freshwater contribution.

GEOCHEMISTRY OF HEADSPACE GAS

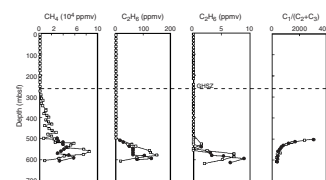
Unfortunately, the hydrocarbon gas concentrations of the headspace gas samples obtained in the shore-based laboratory were lower than those measured in the shipboard laboratory (Shipboard Scientific Party, 2000b), presumably because gas escaped from the sediments during sampling, transportation, and storage. The results of shipboard analyses are, therefore, used to discuss the hydrocarbon anomalies at Site 1146. Methane concentrations are relatively low (<30 parts per million by volume [ppmv]) and constant above 217.2 mbsf in Hole 1146A. Below this depth, the concentrations rise sharply, reaching 1,000 ppmv at 284.7 mbsf; 10,000 ppmv at 390.6 mbsf; and a maximum of 85,000 ppmv at 563.2 mbsf and then decrease slightly down to the base of the hole (Fig. F3). C₂H₆ was first detected at 505.7 mbsf and reached a maximum concentration (155 ppmv) at 572.8 mbsf (Fig. F3). C₃H₈ was first detected at 534.4 mbsf and reached a maximum concentration (7 ppmv) at 572.8 mbsf (Fig. F3). The resulting C₁/(C₂+C₃) ratio rapidly decreased from 2460 ppmv at 505.7 mbsf to 345 ppmv at the bottom of the hole (Fig. F3). A very similar pattern was observed in the lower 100 m at Hole 1146C, and the concentrations of methane, ethane, and propane reached the maximum values of 56,987, 130, and 9 ppmv at 588.7 mbsf, respectively (Shipboard Scientific Party, 2000b).

The δ¹³C values of CH₄ from nine headspace gas samples range from –37.8‰ to –24.0‰, relative to PDB. The two values from Hole 1146A are significantly higher (–24.0‰ and –26.4‰) than all the values from Hole 1146C (–31.3‰ to –37.8‰ (Table T2), which is probably closer to the faults and where more thermogenic gas was trapped.

AUTHIGENIC SIDERITE

Fortunately, some concretions composed of microcrystalline carbonate minerals (1 cm × 4 cm) were observed at the bottom of Holes 1146A and 1146C. Two brownish concretions were collected from Samples 184-1146C-63X-7, 8–10 cm (602.88 mbsf), and 184-1146A-64X-7, 8–10

F3. Concentrations of C₁, C₂, and C₃ and molecular ratios of hydrocarbons in headspace gas, Holes 1146A and 1146C, p. 12.



T2. Concentration of hydrocarbon and isotopic composition of methane, Site 1146, p. 15.

cm (606.28 mbsf), in the greenish lower Miocene sediments. XRD analyses indicate that the concretions are predominantly composed of siderite, with a small amount of rhodochrosite. The $\delta^{13}\text{C}$ values of those two siderite concretions are -5.9‰ and -5.2‰ PDB, and $\delta^{18}\text{O}$ values are 2.5‰ and 2.4‰ PDB, respectively. Thus, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in these siderite concretions are similar to those of authigenic carbonates from Blake Ridge (Matsumoto, 1989; Pierre et al., 2000; Rodriguez et al., 2000), Cascadia (Bohrmann et al., 1998), and Guatemala Basin (Morad and Al-Aasm, 1997).

DISCUSSION

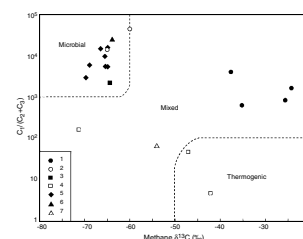
The chemical and isotopic compositions of pore fluids from Site 1146 show that the interstitial water and headspace gas between 0 and 400 mbsf are of a marine origin. Below 400 mbsf, a slight decrease in chlorine concentrations and a sharp increase in lithium concentrations correspond to a considerable increase in methane concentration and the presence of ethane and propane in the headspace gas samples. In particular, chlorine concentrations begin to decrease, whereas methane, ethane, and propane concentrations reach the maximum values at ~ 560 mbsf.

Possible explanations for the low-chlorine anomalies include phase transformations of minerals (e.g., dewatering of clay minerals and opal/quartz transformation), dissociation of gas hydrates, migration of diluted liquids from other places, and influx of meteoric water from the nearby continent or from deeper waters. Phase transformation in clay minerals was not observed at 560 mbsf from the shipboard XRD data (Shipboard Scientific Party, 2000b). Dewatering of clay minerals and opal/quartz transformation cannot explain the increase in the hydrocarbon concentrations. Influx of continental meteoric waters can be excluded, judging from the oxygen and hydrogen isotopic compositions of interstitial waters at Site 1146.

High methane contents might originate from in situ microbial methanogenesis, migration from a deep thermogenic gas reservoir, or dissociation of gas hydrate. The $\delta^{13}\text{C}$ values of methane and $\text{C}_1/(\text{C}_2+\text{C}_3)$ ratios show that gas below 400 mbsf is composed of thermogenic gas or mixed gas rather than microbial gas (Fig. F4) (Wiese and Kvenvolden, 1993).

It is well known that the crystallization of gas hydrate excludes ions of dissolved salts from the crystal structure (Hesse and Harrison, 1981). When gas hydrate decomposes, it releases freshwater into the pore space and decreases the salinity of interstitial water. In this case, the concentrations of chlorine and sodium slightly decrease. During this process, a large amount of hydrocarbon is also released into the pore space, which would lead to increased methane, ethane, and propane concentrations. Therefore, the most likely explanation for these geochemical anomalies at Site 1146 is decomposition of gas hydrates, which dilutes pore water and increases methane levels. The bottom boundary of the gas GHSZ is predicted to be ~ 268 mbsf at Site 1146 based on the thermal gradient of $59^\circ\text{C}/\text{km}$ and a bottom-water temperature of 2.9°C (Shipboard Scientific Party, 2000b). It is, therefore, impossible that the geochemical anomalies at 560 mbsf (Site 1146) are caused by in situ decomposition of gas hydrate. More likely, pore fluids with low salinity and high hydrocarbon concentrations were released from decomposition of nearby gas hydrate and migrated laterally to Site

F4. Molecular ratios of hydrocarbons vs. methane in headspace gas, Site 1146, p. 13.



1146 through faults or bedded planes. However, migration of pore fluids with high hydrocarbon contents and low salinity from deeper levels cannot be excluded. Preliminary results of testing by the Shipboard Scientific Party indicate that reflector T₂ at 430 mbsf (Site 1146) is equivalent to the middle/upper Miocene boundary. Reflector T₄ at 520–530 mbsf, near the middle/lower Miocene boundary, could be linked with a fault extending to ~1 nmi north-northwest of Site 1146 (Shipboard Scientific Party, 2000a, 2000b). The pore fluids with low salinity and high hydrocarbons from decomposition of gas hydrate could thus migrate laterally to Site 1146 along reflector T₂ or T₄ and the linked fault. Authigenic siderite is commonly associated with gas hydrate-bearing sediments (Matsumoto, 1989), and authigenic rhodochrosite concretions related to the dissociation of gas hydrate were also detected at Site 503 of the Deep Sea Drilling Project Leg 68 in the Guatemala Basin (Morad and Al-Aasm, 1997). Authigenic carbonates with high $\delta^{18}\text{O}$ values have been discovered in nearly all gas hydrate sites, indicating that carbonate formation was related to the decomposition of gas hydrate, which releases water enriched in $\delta^{18}\text{O}$ (Davidson et al., 1983). Therefore, $\delta^{18}\text{O}$ enrichment in the authigenic siderite concretions at Site 1146 is probably the result of gas hydrate decomposition. Furthermore, the low $\delta^{13}\text{C}$ values of these carbonates indicate that the occurrence of CO₂ was not produced by in situ bacterial fermentation.

BSRs have been found near Site 1146 (Fig. F1) and at Site 1144 (Song et al., 2001). The multichannel seismic survey of Guangzhou Marine Geological Survey in 2001 again proved that BSRs are present in the areas near Site 1146 (Huang, unpubl. data). Furthermore, a relatively thin sulfate reduction zone and linear sulfate gradient may indicate gas hydrate (Borowski et al., 1996, 1999). The sulfate reduction zone is ~11 m at Site 1144 (Wang et al., 2000) and ~65 m at Site 1146, and the sulfate gradient is linear through the sulfate reduction zone. Gas hydrate could, therefore, be present in the areas near Site 1146.

CONCLUSIONS

Chemical and isotopic measurements of interstitial water and headspace gas samples, together with XRD and isotope studies of siderite concretions from Site 1146 have shown the following:

1. The interstitial water above 400 mbsf trapped in the sediments has a typical seawater composition. The increase of lithium below 400 mbsf and a slight decrease of chlorine below 560 mbsf indicate the contribution of other fluids migrated from elsewhere.
2. Anomalously high methane concentrations (with a maximum of 85,000 ppmv at 563.2 mbsf) were detected in headspace gas below 400 mbsf, together with the presence of ethane and propane below 500 mbsf with peak values at 572 mbsf. The carbon isotopic composition of methane and molecular ratios (C₁/C₂+C₃) indicate that the hydrocarbon is thermogenic gas or mixed gas.
3. Authigenic siderite concretions with high $\delta^{18}\text{O}$ values, found at ~600 mbsf, are probably related to the decomposition of gas hydrate. Their carbon isotopic compositions indicate that they have no relation with bacterial fermentation.

4. All these results suggest that a pore fluid with high hydrocarbon and low chlorine concentrations was probably produced by decomposition of gas hydrate near the area and migrated to Site 1146 along faults or bedded planes.

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Figure F1. ODP Leg 184 drill site locations, with respect to the regional BSRs on the northern part of the South China Sea. 1 = regional BSRs based on Zhang and Chen (2000), Chi et al. (1998), and Chow et al. (2000). 2 = bathymetry in meters. Is. = island.

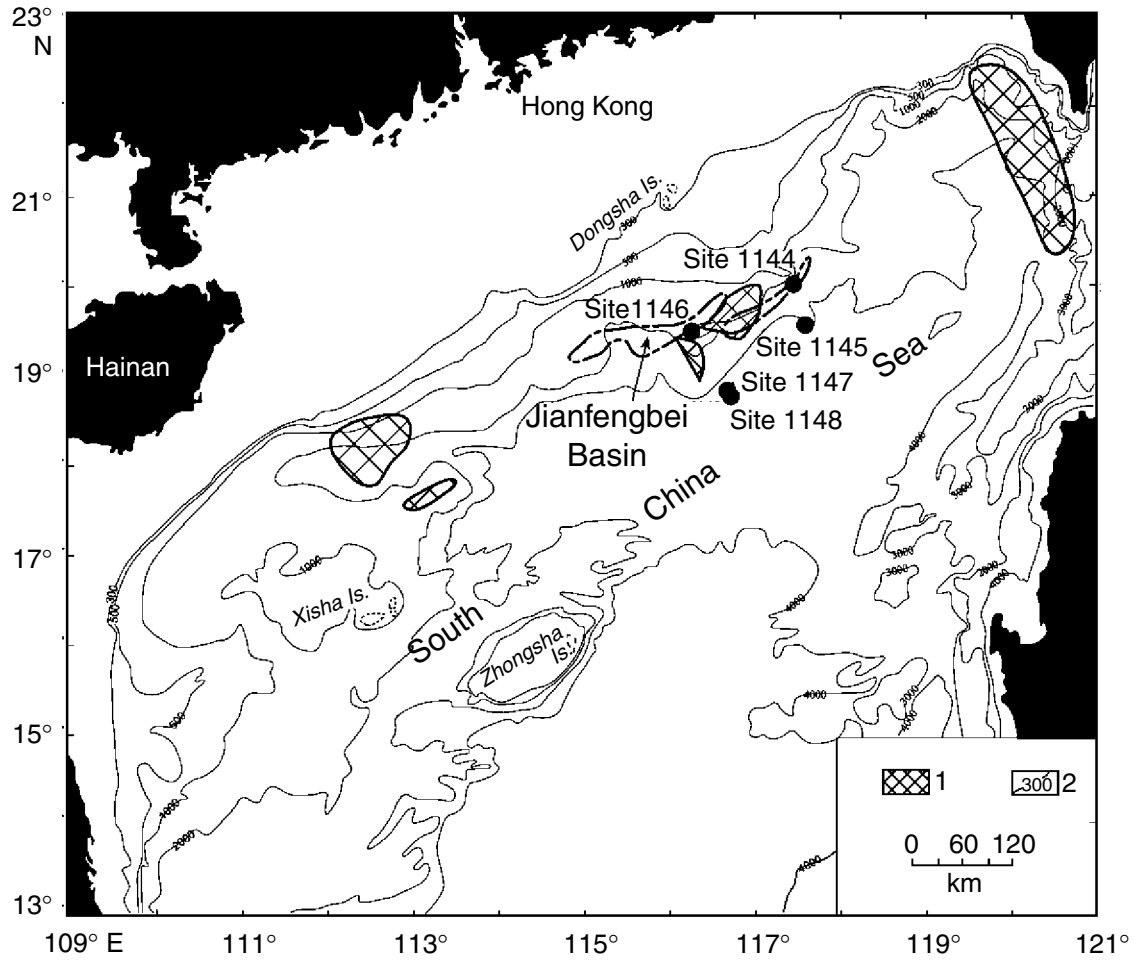


Figure F2. Chemical and isotopic composition of interstitial water from Holes 1146A (solid squares) and 1146C (solid circles). Open squares = results of Leg 184 shipboard geochemical analysis from Hole 1146A (Shipboard Scientific Party, 2000b). SMOW = standard mean ocean water. GHSZ = gas hydrate stability zone.

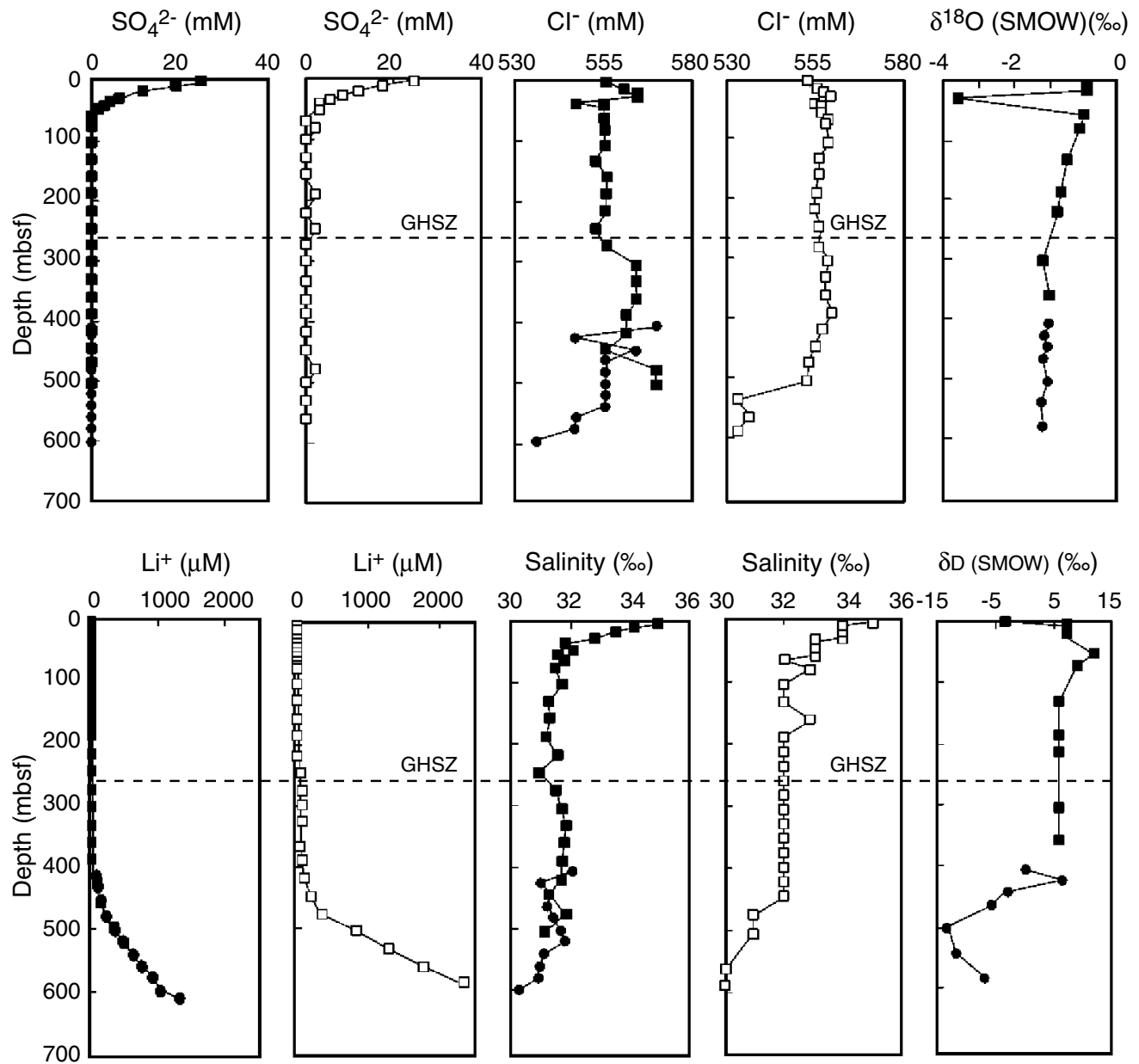


Figure F3. Concentrations of methane, ethane, and propane and molecular ratios of hydrocarbon from headspace gas at Holes 1146A (open squares) and 1146C (open circles). Data are from Shipboard Scientific Party (2000b) Dotted line = inferred base of gas hydrate stability zone (GHSZ).

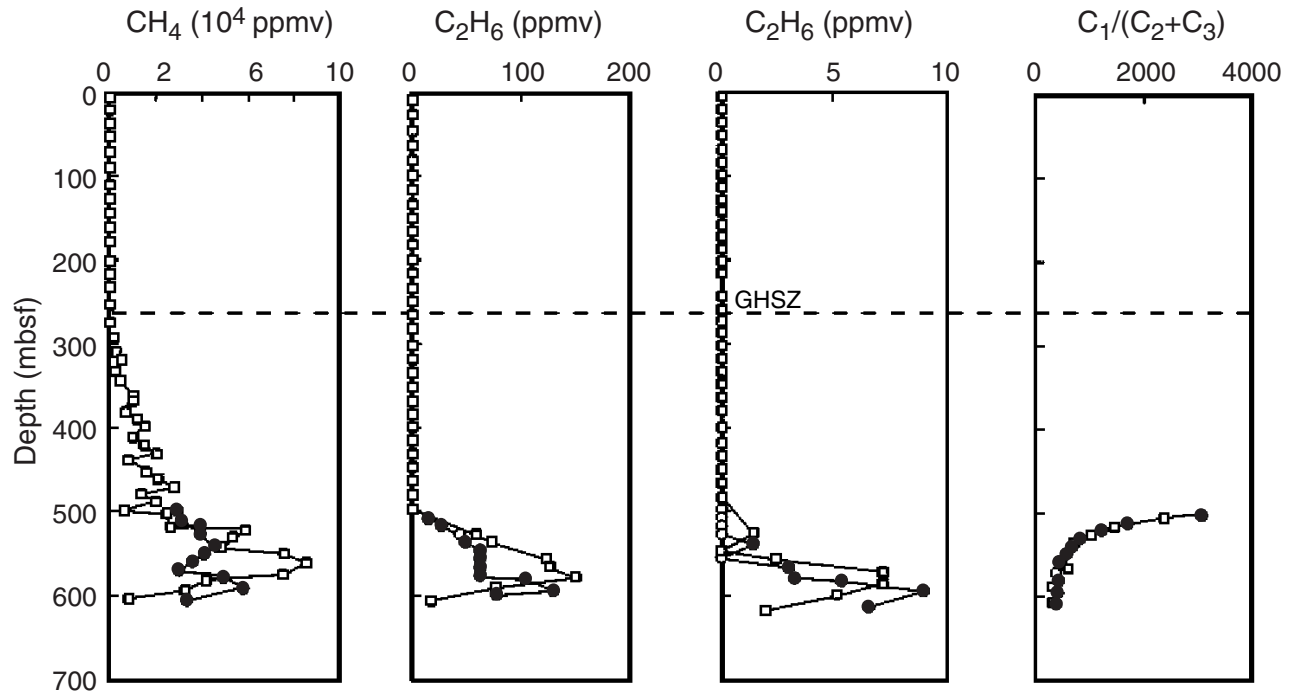


Table T1. Chemical and isotopic compositions of interstitial water, Site 1146.

Piece	Depth (mbsf)	Ca ²⁺ (mM)		Na ⁺ (mM)		Li ⁺ (μM)		Cl ⁻ (mM)		SO ₄ ²⁻ (mM)		Salinity (‰)		δD (SMOW) (‰)	δ ¹⁸ O (SMOW) (‰)
		Shore	Shipboard	Shore	Shipboard	Shore	Shipboard	Shore	Shipboard	Shore	Shipboard	Shore	Shipboard		
184-1146A-															
1	2.98	16.7	10.2	448	460	23	24	556	553	25	24	35	35	-7	0.1
2	8.38	6.0	7.2	448	471	19	21	561	556	19	18	34	34	0	0.2
3	17.88	3.7	4.7	452	473	22	22	564	557	12	11	34	34	0	0.2
4	27.38	3.1	4.2	448	480	23	23	564	559	6	7	33	34	0	-3.7
5	36.88	2.8	4.2	448	474	23	24	547	555	4	5	32	33		
6	46.38	2.7	4.1	452	474	27	27	556	557	2	2	32	33		
7	55.88	2.6	4.1	439	479	29	31	556	557	1	2	32	33	3	0.1
8	65.38	2.6	3.8	448	472	35	34	556	559	0	0	32	32		
9	74.88	3.0	4	439	477	35	37	556	558	0	1	30	13	31	-0.1
12	103.38	3.5	4.6	452	475	37	39	556	559	0	0	32	32		
15	131.85	3.5	4.7	443	474	30	32	553	556	0	0	31	32	-1	-0.5
18	160.35	3.6	4.7	443	478	28	31	556	556	0	0	31	33		
21	188.85	4.2	5	439	476	29	35	556	555	0	1	31	32	-1	-0.7
24	217.15	5.5	6	452	474	32	43	556	555	0	0	32	32	-1	-0.8
27	246.15	4.0	6.8	435	476	34	48	553	557	0	1	31	32		
30	275.05	8.1	8.1	448	474	31	51	556	556	0	0	31	32		
33	303.95	9.1	9	443	476	33	55	564	559	0	0	32	32	-1	-1.2
36	332.85	9.8	9.5	448	475	35	61	564	558	0	0	32	32		
39	361.75	10.0	9.8	443	474	44	71	564	558	0	0	32	32	-1	-1.1
42	390.55	11.0	10.6	443	473	65	97	561	560	0	0	32	32		
45	419.35	11.9	11.4	443	470	104	143	561	557	0	0	32	32		
48	448.13	12.9	12.5	433	469	179	232	556	555	0	0	31	32		
51	476.83	14.5	13.9	432	469	291	353	570	553	0	1	32	31		
54	505.63	15.7	15.1	405	458	463	855	570	553	0	0	31	31		
57	534.33		18.3				1320		533	0					
60	563.15		18.4		445		1770		537	0		30			
63	591.95		21.3				2390		533			30			
184-1146C-															
43	406.40	11.1		443		86		570		0		32		-5	-1.1
45	425.60	12.2		443		119		547		0		31		-1	-1.2
47	444.60	12.0		430		169		564		0		31		-7	-1.1
49	463.90	14.1		435		215		556		0		31		-9	-1.2
51	482.70	14.6		439		313		556		0		31			
53	501.90	16.2		443		403		556		0		32		-14	-1.1
55	521.10	18.7		448		545		556		0		32			
57	540.41	18.7		420		693		556		0		31		-13	-1.3
59	559.70	20.5		424		880		547		0		31			
61	579.00	22.1		421		1022		547		0		31		-10	-1.3
63	598.20	23.8		407		1337		536		0		30			

Notes: "Shore" columns are the results of shore-based laboratory analyses. "Shipboard" columns are the results of Leg 184 shipboard chemistry analyses (Shipboard Scientific Party, 2000a). SMOW = standard mean ocean water.

Table T2. Isotopic composition of methane and concentrations of hydrocarbons, Site 1146.

Hole	Depth (mbsf)	Methane (ppmv)	Ethane (ppmv)	Propane (ppmv)	C ₁ /(C ₂ +C ₃)	δ ¹³ C ₁ (PDB) (‰)
184-1146A-						
	515.3	23,595*	16*	ND*	1,475	-24.0
	534.4	53,093*	72*	1.1*	726	-26.4
184-1146C-						
	406.5	4,776	ND			
	425.7	9,712	ND	ND		-37.7
	444.7	2,714	ND	ND		-33.3
	464.0	6,570	ND	ND		-37.7
	482.8	10,295	ND	ND		-34.4
	502.0	24,802*	8*	ND*	3,100	-37.8
	559.8	34,114*	67*	2.6*	490	-35.5

Notes: * = Shipboard Scientific Party (2000a). ND = not detectable.
PDB = Peedee belemnite.