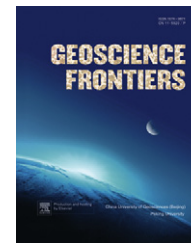


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RESEARCH PAPER

Acidolysis hydrocarbon characteristics and significance of sediment samples from the ODP drilling legs of gas hydrate

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Acidolysis hydrocarbon methane carbon isotopes;
Geochemical characteristics

Abstract To study on the significance and basis of acidolysis index to China marine gas hydrate exploring, since 2006, 111 samples derived from Leg 164 and 204 of the Ocean Drilling Program (ODP) were analyzed in the experiment center of China Petroleum Exploration Research Institute to obtain data on acidolysis hydrocarbon index and methane carbon isotopes by the gas chromatography (GC) of PE AutoSystem XL and isotope mass spectrometer (IRMS) of Finnigan MAT251. Through these, we study the reliability of the acidolysis method and characterize the gas hydrate potential. The results show that the acidolysis hydrocarbon index has a stable correspondence with the Gas Hydrate Stability Zone (GHSZ) in the ODP, and that there are clear abnormal signs in shallow samples that might reliably reflect the existence of authigenic carbonate caused by hydrocarbon migration from bottom hydrate. We therefore propose that the ability to characterize the acidolysis hydrocarbon is crucial to submarine gas hydrate exploration in China.

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1. Introduction

Gas hydrate is an ice-like crystalline compound in which hydrocarbon gases, mainly methane, and water are trapped in a cage-like structure. Gas hydrates mainly occur in permafrost and seafloor sediments below 300 mbsf (meters below seafloor), the environment is characterized by low temperature, high pressure and adequate gas sources. Considering the global attention to clean energy, substantial gas hydrate reserves assume prime importance (Sun et al., 2004b, 2007; Jin et al., 2006). At present, over 100 regions over the world have been identified with gas hydrate reserves (including the gas hydrate found in the Shenhu



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area of Nankai in 2007). Submarine gas hydrates account for about 90% of earth's total hydrate sources. Therefore, seeking an effective exploratory method for gas hydrate in China is important for economic development of the country.

The exploration for gas hydrate involves a multidisciplinary approach, integrating information from geology, geophysics, geochemistry and other branches. Geological information provides an overall direction for exploration of sources and accumulation model. Geophysical data provide the signal for their occurrence, such as Bottom Simulated Reflector (BSR), Blank Zone (BZ) and Amplitude Versus Offset/Angle (AVO or AVA). Geochemical data can function as a useful tracer of gas hydrate (Zhu et al., 2001; Jiang et al., 2002; Wang et al., 2002; Zhang et al., 2003; Chen et al., 2004; Sun et al., 2004a).

Countries like the United States, Japan and Canada, where intensive exploration is going on for gas hydrates, basically rely on drilling data. The Ocean Drilling Program (ODP) (Pimmel and Claypool, 2001) conducted Leg 164 (Paull et al., 1996) in 1996 on the Blake Plateau, and Leg 204 (Tréhu et al., 2003a) in 2002 in the east Pacific Hydrate Ridge west of Oregon, as an international platform for studying gas hydrates. The geological, geophysical, geochemical data that emerged from the above legs have greatly aided in improving the technology of gas hydrate exploration and research. Furthermore, the drilling during the legs provides researchers with precious samples for geochemical studies.

Samples obtained in ODP drill cores permit evaluation of potential exploration targets by direct measurement of hydrocarbon concentration in free gas, absorbed gas, dissolved gas and ions in water. The detection and measurement of hydrocarbon gases is a tool that, when combined with theoretical models of formation, can be of significant value in the search for Gas Hydrate Stability Zones (GHSZs). Three different methods commonly have been used for analyses of hydrate related hydrocarbons. These are the headspace (HS), Vacutainer (VAC) and Pressure Coring System (PCS) methods. The three methods yield different concentration of hydrocarbons. For example, the methane concentration in the GHSZ of ODP Leg 204 shows the following characteristics. The methane concentration

by the HS is about 10^3 – 10^4 ppmV, the VAC method yields about 10^5 – 10^6 ppmV, and for the PCS method, about 10^5 – 10^6 ppmV (Tréhu et al., 2003c). The hydrocarbon gases collected by the three methods used in the ODP project are mainly the free gas in the voids or the weakly-absorbed hydrocarbon in the surface of sediments. The exploration for marine gas hydrate in China is still in the initial stage, and all the methods can not be applied presently for exploration associated with Chinese projects. For several decades in China, the acidolysis method on shallow sediments rather than the HS method has been used for gas hydrate exploration. However a direct connection between acidolysis results and GHSZ or its geological generation has yet been firmly established. Also the indication and genetic analysis on gas hydrate by acidolysis data and its carbon isotope are still uncertain. To solve these problems, we need to study the corresponding relationship between the acidolysis hydrocarbon, carbon isotopic composition, and gas hydrate.

The 111 samples used in this study are from the hydrate existence intervals of specific drilling sites along ODP legs 164 and 204 since 1996. The samples were obtained from the ODP sample libraries in the University of Bremen, Germany and Texas A&M University, USA. The samples are from five holes (A, B, C, D, E, mainly Hole A and E) of Site 996 and Hole C of Site 1250. Site 996 of Leg 164 and Site 1250 of Leg 204 both encountered gas hydrates. Acidolysis and gas chromatography of hydrocarbons and carbon isotopic analyses of methane were conducted to obtain geochemical data used for comparison with that of the ODP.

2. Samples districts' geology and analytical methods

2.1. Geology of ODP legs on gas hydrate

2.1.1. Leg 164

ODP Leg 164 focused on the content and distribution of gas hydrate below the seafloor. The prospecting zone (Fig. 1) is on top of the Blake Diapir of the upper Blake zone located in the

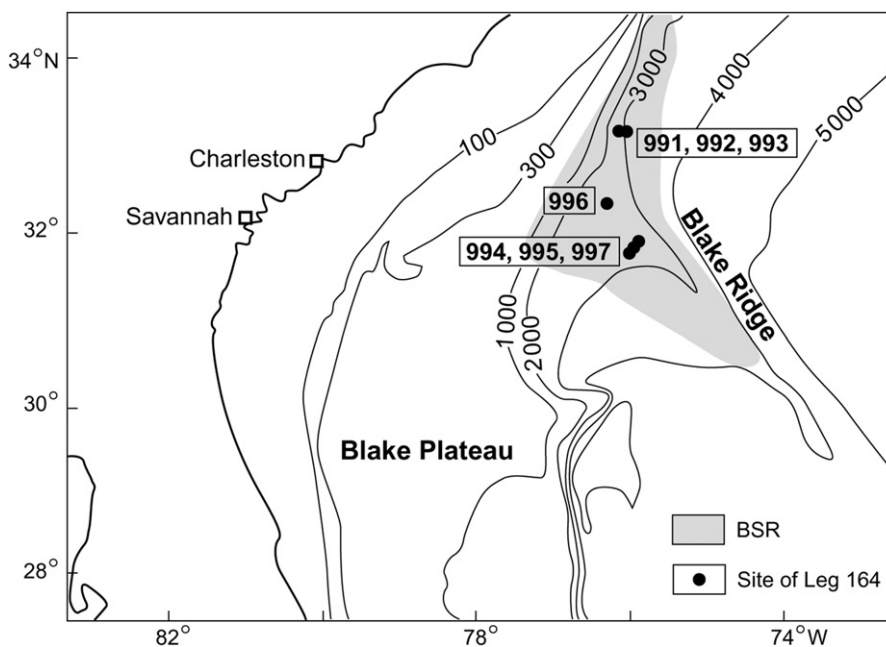


Figure 1 The sites of Leg 164 (from Leg 164 shipboard reports).

continental ridge of Atlantic. The leg operated in November, 1995. The leg has seven sites, Site 991, 992, 993, 994, 995, 996 and 997 (Fig. 1). Exploration at Sites 994, 995 and 996 revealed that the sediments at 200–450 mbsf contain at least 1% gas hydrate, with some solid tumor-like hydrate also existing (Paull et al., 1996). With regard to the amount of gas hydrate samples recovered, Site 996 is the most important site in this leg. The water depth is 2169.6 m, and the penetration depth is about 63.0 mbsf.

2.1.2. Leg 204

ODP Leg 204 focused on the biogeochemical factors controlling the distribution and concentration of gas hydrates in the accretionary margin setting. It sailed south of Hydrate Ridge in the Cascadia of the Oregon continental margin (Fig. 2B). The Hydrate Ridge is a 25-km long and 15-km wide ridge in the Cascadia accretionary complex (Fig. 2A, shadow area), formed as the Juan de Fuca plate subducts obliquely beneath North America. Leg 204 was established in July 2002. The amount of gas hydrate samples recovered in this leg is more than those obtained from other DSDP and ODP legs in the last 20 years, including Leg 164.

Nine sites were drilled in this leg from the top to the slope basin in the south peak of the Hydrate Ridge (Fig. 3), representing different tectonic positions of the anticline and slope basin formed by the tectonic uplift. The water depth is about 70–1000 m, and the drilling depth which was about 500 m at the most penetrated into the top of the accretionary complex.

Site 1250 is important in studying gas hydrate, and the water depth is ~792 m. There are gas hydrates at depths of 1.4–6.5, 81.5, 86.7 and 100.2 mbsf in this site. The samples have 55%–98% methane by testing the free gas composition (Tréhu et al., 2003b). Both Site 164-996 and Site 204-1250, contain abundant hydrate samples.

2.2. Analytical methods of samples

Hydrocarbon is the material basis of forming gas hydrate, and a series of physical and chemical changes take place during the process of upward migration. The hydrocarbons in the sediments mainly exist as (1) free hydrocarbon gas in sediment voids, (2) weakly-absorbed hydrocarbon on the surface of sediments, (3) dissolved hydrocarbon as micro-bubbles in the pore water of sediments, (4) hydrocarbon absorbed by clay minerals and organism in the sediments and (5) entrapped hydrocarbon in the form of being entrapped in the secondary minerals (e.g., carbonate mineral) and their cements (Zhu et al., 2008). The fourth is strongly-absorbed hydrocarbon that can be extracted by heating and also known as pyrolysis-desorbed hydrocarbon. The hydrocarbon of the fifth kind can be extracted by acidolysis method and therefore is referred to as acidolysis hydrocarbon. The acidolysis hydrocarbon index has a high reproducibility and proven effectiveness in onshore oil-gas geochemical exploration in China (Zhao and Sun, 2004; Miao et al., 2005).

The three methods (HS, VAC and PCS) used in the ODP geochemical exploration test mainly the free gas and weakly-absorbed hydrocarbon. In this study we use pyrolysis and acidolysis (Sun, 2007) method to get the hydrocarbon concentration. The details are as follows: we first deal with the samples in the vacuum by heating (60 °C) and dilute HCl (1:6) to release the gas, then filter them with removal of HCl and CO₂ by an alkaline agent (300 g/L), and collect the residual gas for species analyses by the GC of PE AutoSystem XL and IRMS of Finnigan MAT251. All the samples are tested by the experiment center of China Petroleum Exploration

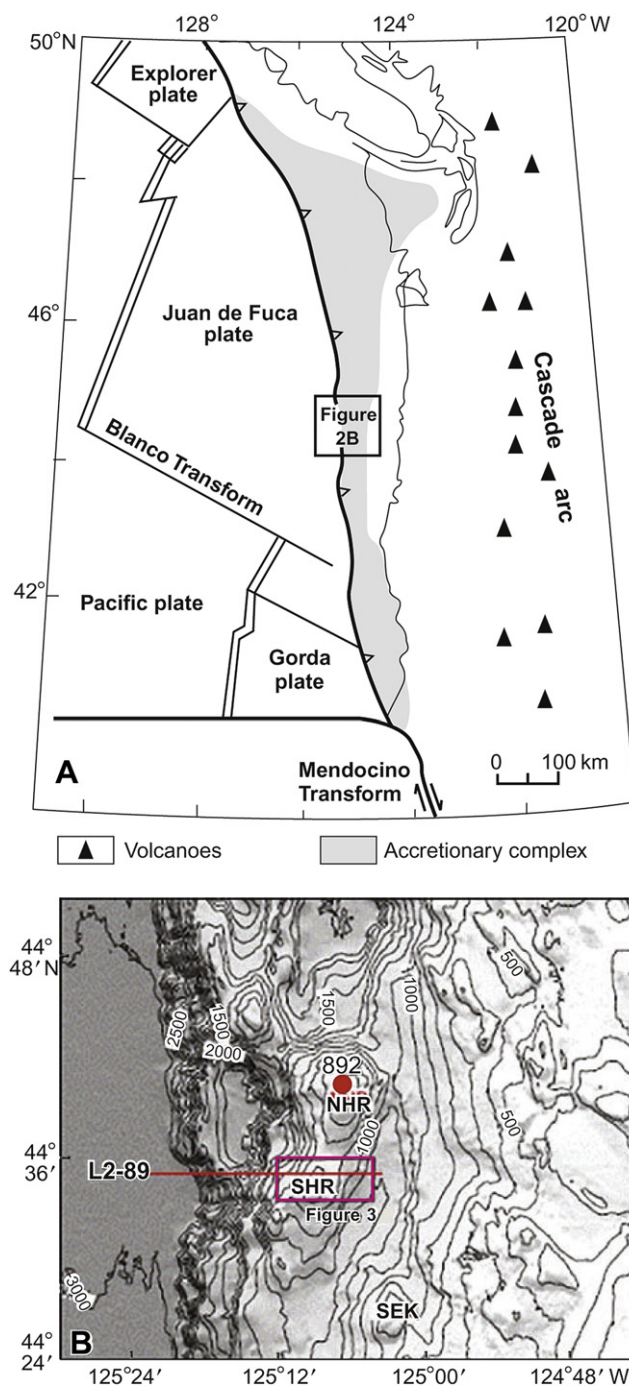


Figure 2 The location of Leg 204 (from Leg 204 shipboard reports). NHR: North hydrate ridge; SHR: South hydrate ridge; SEK: Southeast Knoll; L2-89: seismic line; 892: ODP Site 892.

Research Institute to get the acidolysis index and methane carbon isotope. Some testing samples were randomly set up, and when the analytical relative errors of GC values were below 5% and of IRMS values were below 3‰, the data were thought to be useful.

2.3. Unit conversion of acidolysis hydrocarbon index

The acidolysis index of the ODP samples is determined in units of $\mu\text{L}/\text{kg}$. The values determined have been converted from $\mu\text{L}/\text{kg}$ to

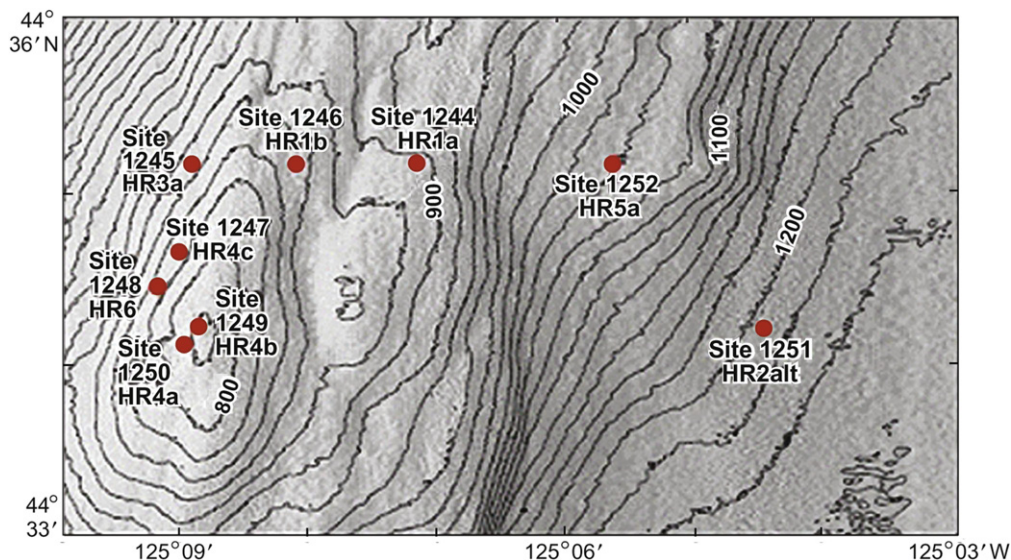


Figure 3 The nine drilling sites of Leg 204 (from Leg 204 shipboard reports). Proposed site HR: precruise designation.

ppmV in order to facilitate direct comparison with values reported in the ODP Initial Reports (Paull et al., 1996; Tréhu et al., 2003a). Conversion of units was done as follows.

1 $\mu\text{L}/\text{kg}$ stands for 1 kg samples having 1 μL gas; 1 ppmV stands for 1 L samples having 1 μL gas. We need to, therefore, equate the volume in the form of L in 1 kg samples.

Gas volume in 1 $\mu\text{L}/\text{kg}$ samples = void volume in 1 kg samples – water volume in voids of 1 L samples.

The sample density is expressed in a (g/cm^3), the porosity is b (%), and the moisture is c (%), so

$$\text{Void volume in 1 kg samples} = \frac{1000 \text{ g}}{a \text{ g}/\text{cm}^3} \times b = \frac{1000b}{a} \text{ cm}^3$$

Assuming the water volume in the voids of 1 L samples is x , the density of water is $1.0 \text{ g}/\text{cm}^3$, so $c = \frac{x}{1000 - x}$, and we can

$$\text{get } x = \frac{1000c}{1+c} \text{ cm}^3. \text{ Therefore, Gas volume in 1 kg samples} = \frac{1000b}{a} - \frac{1000c}{1+c} = 1000 \left(\frac{b}{a} - \frac{c}{1+c} \right) \text{ cm}^3.$$

So we can transfer $\mu\text{L}/\text{kg}$ to ppmV as follow:

$$\frac{1 \mu\text{L}}{\text{kg}} = \frac{1 \mu\text{L}}{1000 \left(\frac{b}{a} - \frac{c}{1+c} \right) \text{ cm}^3} = \frac{1 \mu\text{L}}{\frac{b}{a} - \frac{c}{1+c}} = \frac{1}{\frac{b}{a} - \frac{c}{1+c}} \text{ ppmV}$$

Table 1 The data of HS, acidolysis hydrocarbon and hydrate distribution in the Hole 1250C, ODP 204.

Core section	Depth (ppmV)	HS C ₁ (ppmV)	HS Methane coefficient (C ₁ /C ₂ ⁺)/100	Acidolysis C ₁ (ppmV)	Acidolysis Methane coefficient (C ₁ /C ₂ ⁺)/100	Acidolysis $\delta^{13}\text{C}_1$ (‰, PDB)	Hydrate existence interval	Method
1H-1	1.20	12019.0	8.8	No sample			▲	HS
2H-CC	5.06	7271.0	7.8	No sample			▲	HS
3H-3	17.00	16942.0	16.4	4656.0	0.66			HS, acidolysis
4H-4	27.60	34893.0	59.1	4344.0	0.70			HS, acidolysis
5H-1	33.74			7530.0	1.24	–55.6		Acidolysis
5H-3	35.98	13115.0	62.5	8541.0	1.00		▲	HS, acidolysis
6H-3	44.77	9654.0		3142.0	0.26			HS, acidolysis
7H-6	58.50	10442.0	15.6	4874.0	1.07			HS, acidolysis
10H-3	75.46	15818.0	23.6	6614.0	0.96			HS, acidolysis
11H-1	83.41			9022.0	1.72			Acidolysis
11H-3	85.41	13918.0	15.3	9280.0	1.20		▲	HS, acidolysis
12H-2	92.65	12874.0	14.8	7215.0	1.31			HS, acidolysis
13H-3	103.39	17293.0	6.8	10711.0	2.18			HS, acidolysis
14H-3	114.00	13276.0	3.2	5512.0	0.93		BSR	HS, acidolysis
15H-2	121.86	12111.0	4.4	7412.0	1.59			HS, acidolysis
17H-3	135.00	12894.0	4.3	10630.0	1.15			HS, acidolysis
17H-4	136.70			10865.0	1.46	–48.43		Acidolysis
19X-3	141.50	11271.0	6.0	7216.0	0.71			HS, acidolysis

Table 2 The data of HS, acidolysis hydrocarbon and hydrate distribution in the Hole 996A and E, ODP 164.

Core section	Depth (mbsf)	HS C ₁ (ppmV)	HS methane coefficient (C ₁ /C ₂ ⁺)/100	Acidolysis C ₁ (ppmV)	Acidolysis methane coefficient (C ₁ /C ₂ ⁺)/100	Acidolysis δ ¹³ C ₁ (‰, PDB)	Hydrate existence interval	Method
A-1-1	0.34			4345.0	0.28	−52.20	▲	Acidolysis
A-1H-2	0.90	8540.0	8.63	11534.0	0.26	−42.29	▲	HS, Acidolysis
A-2H-1	8.50	6810.0	11.40	6749.0	0.19	−47.64		HS, Acidolysis
A-3X-1	10.06	4510.0	11.30	8237.0	0.22	−47.35		HS, Acidolysis
A-8H-3	49.83	820.0	3.01	4688.0	0.15	−49.65	▲	HS, Acidolysis
A-8-4W	50.43			2967.0	0.12	−48.91	▲	Acidolysis
A-9H-2	59.43	10980.0	3.81	4226.0	0.11	−50.56	▲	HS, Acidolysis
E-1-1	0.85			4459.0	0.19	−40.59		Acidolysis
E-1-2	1.89	30.7		17873.0	0.21	−42.12		HS, Acidolysis
E-2H-4	8.60	30800.0	11.80	15341.0	0.25	−39.54		HS, Acidolysis
E-4H-3	25.40	6550.0	13.30	20405.0	0.19	−43.60	▲	HS, Acidolysis
E-5-2W	33.03	6650.0	12.60	9771.0	0.12	−38.79		Acidolysis
E-6X-4	42.20	13300.0	10.10				▲	HS
E-6-2W	43.51			3537.0	0.16	−54.66	▲	Acidolysis
E-7H-4	51.80	9220.0	9.80	3284.0	0.12	−48.86	▲	HS, Acidolysis

3. Results and geochemical characteristics of the acidolysis hydrocarbon of ODP sediment samples

3.1. Data and geochemical characteristics of the acidolysis hydrocarbon in the Hole 1250C, Leg 204

ODP Leg 204 drilled nine sites on the south of the Hydrate Ridge. Site 1250 is important in studying gas hydrate, and here six holes were drilled and 17 hydrate samples were collected, among which seven samples came from the Hole C. We analyzed 44 samples from Hole 1250C by the acidolysis method. ODP reports indicate the hydrocarbon analysis is mainly performed by the HS method. Therefore we have converted our acidolysis units to ppmV. Table 1 reports the converted acidolysis data for those samples for which ODP HS data are available. Table 2 likewise reports data for samples from Hole 996A of ODP Leg 164. Table 3 shows the acidolysis index characteristics.

Fig. 4 shows the methane concentration with depth profile. In the background area (with no hydrate finding), the normal acidolysis methane concentration is about 169.67 μL/kg (taking NaiHai for example by calculating almost all the data can be collected) while the average acidolysis methane concentration here is 7347.75 ppmV (661.1 μL/kg). We can see that the methane concentration has clear geochemical abnormality, and relative to the background area, the methane concentration has the characteristics of high abundance, high abnormality, high contrast and high dispersion.

The characteristic coefficient of the HS are all over 100, especially coefficient of some samples from hydrate area are greater than 1000, which indicates that the methane is mainly biogenic from the traditional standard (Wang et al., 2008) and the methane of Site 204–1250 is generated mainly from bacteria. The acidolysis methane coefficients are approximately 100, suggesting the methane is of mixed causes or sources. This means the hydrocarbon is both from the methane caused by permeation and adsorption and from protogenic hydrocarbon. These are the reason for the differences of HS and acidolysis concentration.

Through the acidolysis methane concentration is one magnitude lower than of HS, the two curves of HS and acidolysis have the similar trend which can be seen in the “Methane Concentration–Depth” figure (Fig. 4). In the hydrate area, the acidolysis methane has clear high peak while the HS abnormality is a little upward. Below the BSR, gas peak is more clear, especially the acidolysis hydrocarbon, and from the methane coefficient we can tell that these may be caused by the increase of free gas, like the ethane.

3.2. Data and geochemical characteristics of acidolysis hydrocarbon in Hole 996A and E, Leg 164

Compared to Hole 1250C of ODP Leg 204, the Hole 164-996A and E have mainly shallow hydrate depth, generally within 50 mbsf. The acidolysis and HS data of 15 samples from different depth are showed in Table 2. Also carbon isotope values of

Table 3 The geochemical characteristics of methane concentration by the HS and acidolysis method.

Leg/Site	Hole	Method	Min (ppmV)	Max (ppmV)	Average (ppmV)	Standard deviation	Contrast	Methane coefficient
204/1250	C	HS	7271.00	34893.00	14252.73	6290.20	2.45	3.20–62.50
		Acidolysis	3142.00	10865.00	7347.75	2401.00	1.47	0.26–2.18
164/996	A	HS	820.00	10980.00	6332.00	3.60	1.73	3.00–11.40
		Acidolysis	2967.00	11534.00	6106.00	0.06	1.89	0.11–0.28
	E	HS	30.70	30800.00	11091.80	1.37	2.70	9.80–13.30
		Acidolysis	3284.00	20405.00	10667.00	0.04	1.91	0.12–0.25

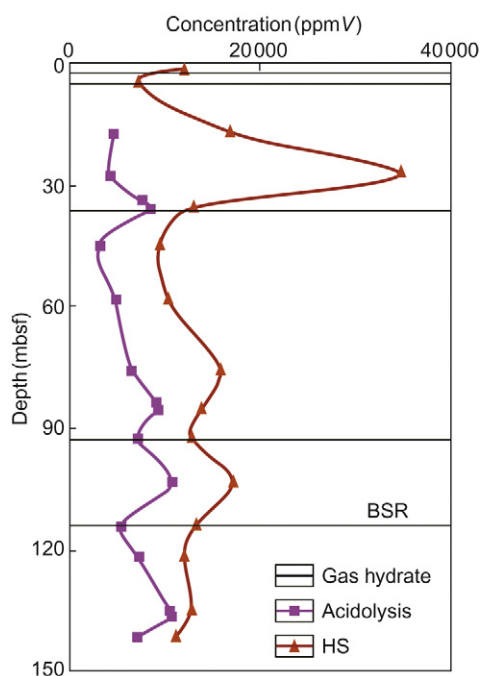


Figure 4 The HS, acidolysis hydrocarbon and hydrate distribution in the Hole 1250C, Leg 204.

acidolysis methane are showed in Fig. 5. The acidolysis and HS index characteristics of the Hole A and E can be seen from the Table 3.

In the most shallow samples, the methane concentration determined by acidolysis is significantly greater than that determined by HS, and the low methane coefficient points to the methane being mainly thermogenic. Therefore infer that this enhanced methane concentration is related to the authigenic carbonate, caused by anaerobic methane oxidation in the hydrate existence area (Yang et al., 2009). We suggest that the enhanced methane detected by acidolysis reflects the development degree of authigenic carbonate, and indicates indirectly the existence of GHSZ below.

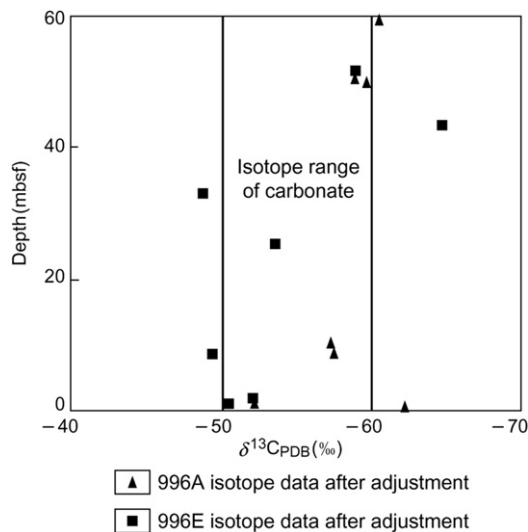


Figure 5 The acidolysis carbon isotope distribution after adjustment in the Hole 996A, E of the Leg 204.

The Fig. 5 shows the $\delta^{13}\text{C}$ of acidolysis methane in Hole A and E. From the Table 2 we can see that the $\delta^{13}\text{C}_1$ (PDB) is about -40% to -50% . Compared with the HS carbon isotope, the methane extracted after acidolysis would occur fractionation when under isotope testing, which make the carbon heavier (Wang et al., 2008), the data should be adjusted by 10% (Pu et al., 2009). Mi and Li (2010) have brought up that the $\delta^{13}\text{C}_1$ (PDB) of the authigenic carbonate caused by cold seeps is around -50% to -60% . After adjudication, the acidolysis isotope of Site 996 is mainly in this range, which is consistent with the shallow acidolysis abnormality being related to the GHSZ.

4. Conclusions

- (1) Gas concentrations determined by acidolysis and HS have different values because the two methods test different hydrocarbon phases. At sampling depths without hydrate, results by both methods have the characteristics of high abundance, high contrast and high dispersion. The methane concentration versus depth trends are similar, and they can indicate the existence of hydrate.
- (2) The acidolysis and HS methane concentration of the holes in the paper are mainly of the same magnitude while the values are different. The HS test measures mainly the free gas, and the acidolysis method test determines mainly the absorbed hydrocarbon on the surface of sediments and entrapped hydrocarbon within the lattice of the secondary altered minerals. The free gas provides more information but is readily influenced by microbe etc. and thus polluted (Cheng et al., 2003). The absorbed and entrapped hydrocarbons are more stable. Especially in the shallow regions of gas hydrate occurrence, hydrocarbon is important to the exploration and evaluation of hydrate since it is formed afterwards.
- (3) At ODP Site 204-1250, the methane coefficient of the HS and methane carbon isotope distribution of the acidolysis hydrocarbon can reflect that the methane is generated mainly by bacteria. The acidolysis hydrocarbon are both from the methane caused by permeation and adsorption and protogenic hydrocarbon. This is the cause of the relatively low values of acidolysis methane coefficients.
- (4) Because China geochemical exploration for gas hydrate mainly tests samples from shallow sediments, it is important to have a clear, shallow methane abnormality to indicate the hydrate below. The acidolysis methane geochemistry and carbon isotope distribution of the Hole 164-996A and E show that the geochemical characteristics of acidolysis index can be in evaluating the potential GHSZ below and studying on authigenic carbonate development caused by methane seepage.

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