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Organic matter in surface sediments from the Gulf of Mexico and South China Sea: Compositions, distributions and sources

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ABSTRACT

Sediments from the Gulf of Mexico (GOM) and the South China Sea (SCS) were analyzed. The low δ^{13} C values of pentamethylicosane (PMIs) and fatty acids (−81.3 to −85.2‰) were found in only the S-1 sample collected from the GOM, indicating that methanogenic archaea associated with gas hydrate formation contributed to the sediment organic matter. Principle component analysis of fatty acids suggested that similar microbial biomass was found in the S-1, S-9, O-3 and O-5 samples. However, a comparison of the alkanes, fatty acids, and alcohols indicated that the percentage of *n*-alkan-2-ols in the S-1 sample from the GOM was the highest, while *n*-alkanes and *n*-fatty acids were the highest percentages in other samples from the GOM and SCS. This finding suggests that microbial species or the oxidation/reduction environment of the sample site of S-1 were different from those of the other samples. The present study provides a basis for detecting gas hydrate sites on the seafloor of the SCS.

1. Introduction

Lipid compounds often contain the basic skeletal structure and functional group details of their original source (Venkatesan, 1988). Hence, lipids have been widely used as tracers to characterize the nature and distribution of organic matter in sediment (Carreira et al., 2010).

The investigation of lipid compositions in modern sediments in the field of gas venting and gas hydrates can provide information about their biological origins. Abundant gas hydrates have been found in the sediments associated with natural gas venting and at cold hydrocarbon seeps in the Gulf of Mexico (GOM) (Brooks et al., 1986; Roberts and Carney, 1997; Sassen et al., 1994). Some reports investigated the geological setting for structure II gas hydrates in GC184, GC185, 234, MC853, and AT42 (Alexei and Sassen, 2003). Specifically, many researchers studied the origins of hopane, sterane, and archaeal lipid biomarkers (isoprenoid hydrocarbons such as glycerol dialkyl glycerol tetraethers and 2,6,10,15,19-pentamethylicosane (PMI), fatty acids and alkanols) in sediments from the GOM. Furthermore, the isotopic values of some biomarkers, such as PMIs, fatty acids, and alcohols, were analyzed. It has been found that biomarkers with low isotopic values (between −70‰ and −120‰) carried signatures of gas hydrate formation in the anaerobic methane oxidation process in the GOM (Elvert et al., 2000; Zhang et al., 2002, 2003; Zhou et al., 2014). The studies provide direct evidence for estimating gas hydrate formation.

The tropical South China Sea (SCS), the largest marginal sea of the western Pacific, is characterized by the occurrence of both passive and active continental margins and high sedimentation rates (Taylor and Hayes, 1983). In 2013, gas hydrates were found in the shallow subsurface by a drilling program (Zhang et al., 2014). Cold-seepage related features, such as acoustic plume, acoustic void, and mud volcanoes, were identified in the study area (Liu et al., 2015). Extensive studies have investigated the possibility of gas hydrate occurrence from cold-seep carbonates in cold-seep sites (Lu et al., 2015) and have found that the pore water geochemistry of the shallow sediments was linked to the presence of deeply buried gas hydrates in the SCS (Ye et al., 2016). However, there is little information on the archaeal lipid biomarkers in sediments from the SCS. Hence, it is necessary to determine whether gas hydrates exist in the SCS by comparing the organic compound distributions in the sediments with those from the GOM, where the presence of gas hydrates on the seafloor has been confirmed.

The present study objective is to compare the distribution, composition, source, and sedimentary environment of organic matter, including *n*-alkanes, isoprenoid hydrocarbons, fatty acids and alcohols (including *n*-alkanols, *n*-alkan-2-ols and sterols), from the GOM to those of organic

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Table 1
Samples description and total extracts of soluble organic matter (SOM) and fractional composition of SOM. Al = aliphatic; Ar = aromatic; Pol = Polar.

Locations	Samples	Sites	Description	Longitude and latitude	Total extracts (mg/g)	Ali (%)	Aro (%)	Pol (%)
Gulf of Mexico	S-1	GC238	Hydrate mud	27°44.4453′N, 91°03.0470′W	0.50	9.68	16.13	74.19
	S-7	GC527	Black bacterial mats, cold seep	No details	0.90	9.43	11.00	79.56
	S-8	EW1001	Black bacterial mats	No details	1.00	14.67	15.89	69.44
	S-9	EW1001	Black bacterial mats, cold seep	27°57.6861′N, 90°23.5377′W	1.00	7.76	14.02	78.22
	S-10	EW1001	Black bacterial mats	27°57.6861′N, 90°23.5377′W	3.10	54.15	19.66	26.19
	S-11	EW1001	Black bacterial mats	27°57.6861′N, 90°23.5377′W	4.20	50.44	21.54	28.02
South China Sea	O-1	No	No	110.99.28N, 12. 07315 W	1.27	6.10	3.08	90.82
	O-2	No	No	110.3897N, 11.2064W	1.13	6.14	12.22	81.63
	O-3	No	No	109.7304N, 10.25765W	2.82	9.45	7.07	83.46
	O-4	No	No	115.1115N, 6.492917W	2.90	15.52	10.34	74.14
	O-5	No	No	114.4919N, 6.696917W	1.20	8.33	2.78	88.89
	O-6	No	No	112.3231N, 18.4031W	1.43	3.09	3.09	93.82
	O-10	No	No	115.6004N, 8.133783W	1.12	3.57	10.71	85.72
	O-11	No	No	114.0235N, 6.979733W	2.0	5.00	5.00	90.00
	O-13	No	No	111.50528N, 5.78706667W	1.64	2.15	3.23	94.62

matter from the SCS. Based on the sediments sampled from gas hydrate sites in the GOM, some biomarkers associated with gas hydrate formation and methane seeps are investigated to explore the similarities and differences between the sedimentary environments of the GOM and SCS. The biomarkers have provided another important piece of evidence supporting gas hydrate formation. These results will help us to investigate whether there are gas hydrates in the SCS based on the organic geochemistry data. Although only a few samples were analyzed, this paper provides useful information for an analysis of the sediment characteristics.

2. Samples and experimental procedures

2.1. Sample collection

The sediment samples were collected in 2002 by Johnson-Sea-Link from the Green Canyon (GC) protraction area. One gas hydrate site (GC238), a hydrocarbon cold-seep site (GC527), and EW1001 in the GOM were sampled. The water salinity at the sea floor was approximately 35‰. Samples were collected using a Van Veen grab sampler. Detailed sample descriptions and locations from the GOM are listed in Table 1 and Fig. 1. Sediment core samples from the SCS were taken in November of 2003, and the sampling locations are listed in Table 1 and Fig. 1. A stainless steel static gravity corer (8 cm i.d.) was used to minimize the disturbance of the surface sediment layer.

The sediments were stored in aluminum boxes and then transported to the laboratory, where they were stored below 0 °C in a refrigerator for further treatment and analysis.

2.2. Lipids extraction

The sediment samples from the GOM were air-dried in a desiccator and stirred until they were homogenized. A 15 g sample of the homogenized sediment was subjected to Soxhlet extraction for 72 h using a 9:1 mixture of dichloromethane/methanol. Activated copper turnings were used to remove elemental sulfur during the extraction. The total extracts were dried with anhydrous Na_2SO_4 before filtration to remove the insoluble particles and copper turnings. Following volumetric quantification, the solvent extract was concentrated to approximately 3 ml using a rotary evaporator (35 °C). Subsequently, the total extract was dissolved in hexane to precipitate asphaltene. After removing the asphaltene by filtration, the remaining extract was subjected to column chromatography and divided into aliphatic, aromatic, and polar fractions. The resulting aliphatic and aromatic fractions were quantified volumetrically, while the asphaltene and polar fraction were air-dried for quantification.

2.3. Separation of lipid classes

The maltene fraction was separated into three fractions using column chromatography: the aliphatic fraction was eluted with *n*-hexane; the aromatic fraction was eluted with n-hexane/DCM 6:4; and the polar fraction was eluted with DCM/methanol 5:5 + methanol. The aliphatic and aromatic fractions were concentrated to 2 ml by rotary evaporation while the polar fraction was dried with high purity N_2- for quantification. The polar fraction was then saponified overnight with 6% KOH-methanol at room temperature. The corresponding neutral and fatty acid fractions were successively recovered with hexane, the latter after acidification to pH 1.0 with concentrated HCl. The neutral fraction was fractioned using column chromatography on alumina over silica gel. The neutral lipids were separated into ketones/esters and alcohols. The fatty acid, ketone/ester, and alcohol compounds were converted to their silyl ethers by treatment with BSTFA prior to instrumental analysis (Barbe et al., 1989).

2.4. Derivatization and analysis

The aliphatic hydrocarbon fraction was further analyzed using an HP 6890 series II gas chromatography interfaced with an HP 5972 mass selective detector using electron impact mode (70 eV). The temperature of the MS detector was 180 °C, and the mass scan ranged from *m/z* 50 to *m/z* 550. A J & W DB-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used, with helium as the carrier gas at a constant flow rate of 1.2 ml/min. The temperatures of the injector and FID detector were 290 and 300 °C, respectively. The oven temperature was initially held at 80 °C for 5 min and then increased at a rate of 3 °C /min to 290 °C and maintained for 30 min.

2.5. Stable carbon analysis

The carbon isotopic analysis of the aliphatic and fatty acid compounds was performed on an Isoprime gas chromatography-isotopic ratio mass spectrometer. A DB-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used. The injector was set to splitless mode at 290 °C, and helium was used as the carrier gas. The oven temperature was initially set to 80 °C, increased to 140 °C at a rate of 10 °C/min, then programmed to 290 °C at a rate of 6 °C/min and held for 15 min. For the isotopic analysis of the branched and cyclic alkanes, an AT-5 capillary column (50 m × 0.32 mm × 0.3 μm) was used. The oven temperature was initially set to 80 °C, increased to 245 °C at a rate of 1 °C/min, and then increased to 290 °C at a rate of 10 °C/min. The standard carbon isotope gas was calibrated using the NS22 crude oil standard provided by the IAEA, and the isotopic error of the parallel analysis was less than 0.5‰.