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Characteristics of hydrocarbons in sediment core samples from the northern **Okinawa** Trough

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ABSTRACT

Sediment core samples from the northern Okinawa Trough (OT) were analyzed to determine abundances and distributions of hydrocarbons by gas chromatography-mass spectrometer (GC-MS). The results show that the n-alkanes in this sediment core conform to a bimodal distribution, and exhibit an odd-to-even predominance of high molecular weights compared to an even-to-odd predominance in low molecular weight n-alkanes with maxima at C_{16} and C_{18} . The concentrations of bitumen, alkanes and polyaromatic hydrocarbons (PAHs) were higher in samples S10-07 than all others. Three maturity parameters as well as the ratios between parent phenanthrenes (Ps) and methylphenanthrenes (MPs) in samples S10-07 and S10-17 were higher. The distribution and composition of hydrocarbons in sample S10-07 suggest that one, or several, undetected hydrothermal fields may be present in the region of this sediment core. Results also suggest that volcanism may be the main reason for the observed distribution and composition of hydrocarbons in S10-17 sample.

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Although the study of hydrocarbons in geology dates back several centuries (Lein et al., 2003; Simoneit et al., 2004), the discovery of hydrothermal activity has provided a new impetus for further investigations of the nature of organic matter (OM) in the environment (Lein et al., 2003; Simoneit et al., 2004; Peng et al., 2011). Following the discovery of hydrothermal petroleum in 1978 in the Guaymas Basin, Gulf of California (Simoneit et al., 1979), a number of researchers began to study seafloor OM in hydrothermal settings at localities including the Okinawa Trough (OT) (Zhang et al., 2001), the Escanaba Trough on the southern Gorda Ridge (Kvenvolden et al., 1986), the middle vallev of the Juan de Fuca Ridge (Simoneit, 1994), the Red Sea (Simoneit et al., 1987; Michaelis et al., 1990), the Andaman Basin (Chernova et al., 2001; Venkatesan et al., 2003), the Kairei hydrothermal field on the central Indian Ridge (Peng et al., 2011; Li et al., 2011, 2012), the Rainbow vent field (Lein et al., 2003; Simoneit et al., 2004; Konn et al., 2009; Shulga et al., 2010), the Lost City (Proskurowski et al., 2008; Konn et al., 2009; Shulga et al., 2010; Bradley and Summons, 2010), Broken Spur (Shulga et al., 2010), Ashadze (Morgunova et al., 2012), and Logatchev hydrothermal fields (Peng et al., 2011; Li et al., 2011, 2012), as well as on the northern Mid-Atlantic Ridge, and in the Arctic Ocean

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(Petrova et al., 2010). A number of researchers have also explored the origin and evolution of OM in hydrothermal environments using simulation experiments (McCollom and Seewald, 2007; Konn et al., 2011).

The OT, which extends from southwest of Kyushu Island, Japan, to the Lanyang Plain in northeastern Taiwan, is a back-arc basin separating the continental shelf of the East China Sea from the Ryukyu arc (Sibuet et al., 1998; Dou et al., 2010a, b, 2012, 2015, 2016). Since the discovery of hydrothermal activity in the OT in 1984 (KIMURA et al., 1986), a number of hydrothermal fields have been discovered in this region, including the new Tang Yin hydrothermal field (122°34′E, 25°4′N; 1206 m), identified in 2014 in the southern OT (Zeng, 2015). Hydrothermal fields in the OT are mainly distributed in central and southern sections; just a handful of suspected fields are thought to exist in the northern OT (Zhai et al., 2001). Volcanoes are also widely developed in the northern OT, and their influence is widespread across this region (Zeng, 2011).

In this study, we measured the abundance and distribution of hydrocarbons in samples from a sediment core collected from the northern OT, comparing the results from different layers. Our goal was to reveal the main hydrocarbon source within the sediment core, identify responses in sediments to seafloor hydrothermal activity and volcanism, and assess the possibility of hydrothermal activity in the northern OT.

The 340-cm long HOBAB1-S10 core was collected in 2013 at a water depth of 986 m from the northern OT (29°29'N, 128°11'E) (Fig. 1) by the Institute of Oceanology, Chinese Academy of Sciences. The core was split

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Fig. 1. Sample collection sites in the northern OT. Of these, site ES1 and ES2 are inferred hydrothermal fields (Zhai et al., 2001).

lengthwise and logged in detail by visual examination; the lithology is characterized by the continuous deposition of silty clay that changes color along the length of the core. This clay is greyish-green between 0 cm and 50 cm, dark gray between 50 cm and 135 cm, dark green between 125 cm and 260 cm, and gray between 260 cm and 340 cm. When we sampled between 120 cm and 135 cm, we noticed a smell of rotten eggs.

We used 17 bulk samples (labeled with Arab numerals from top-tobottom) taken at 20-cm intervals for OM abundance and distribution measurements. Approximately 200 g of sediment from each sample was placed into a dry acid-cleaned glass beaker, and dried at 40 °C for 48 h. Dried sediment was then powdered with an agate mortar into 100 meshes and dried again for 24 h.

Extraction and analysis of fatty acids were performed at the Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences. To do this, bitumen was extracted using a Soxhlet extractor with chloroform for 72 h, while n-hexane was used to remove asphaltene and to solubilize OM. Soluble OM was then separated using column chromatography (i.e., a silica-gel 60 with an internal diameter (i.d.) of 15 mm and a length of 35 mm), while aliphatic and aromatic compound fractions were analyzed using gas chromatography-mass spectrometry (GC-MS). This system consists of a 6890 N GC analyzer with a 30 m DB-5MS fused silica capillary column (i.d.: 0.2 mm; film thickness: 0.2 µm), filled with He carrier gas. The GC temperature program comprised injection at 80 °C, followed by 2 min of constant temperature, gradual temperature change from 80 °C to 290 °C at increments of 4 °C per minute, and then another 20 min of constant temperature. The MS system (5973 N) was an EI model operated at 70 eV.

We measured the abundance and distribution of OM in 17 sediment samples using GC-MS. Hydrocarbon compositions are listed in Table 1.

Measured CB in sediment core samples ranged between 77.61 μ g/g and 155.12 μ g/g (Table 1), with the highest seen in sample S10-7 (Fig. 2). Indeed, CB values in these samples are higher than those

reported from sediment cores from the Middle Valley hydrothermal field along the Juan de Fuca Ridge (Rushdi and Simoneit, 2002a), from the Escanaba Trough on the southern Gorda Ridge (Rushdi and Simoneit, 2002b), and from hydrothermal sediments in the Kairei hydrothermal field on the central Indian Ridge and the Logatchev hydrothermal field along the northern Mid-Atlantic Ridge (Peng et al., 2011).

Measured CA ranged between $7.77 \times 10^{-3} \,\mu\text{g/g}$ and $5.24 \,\mu\text{g/g}$ (Table 2). Recorded values were highest in samples S10-07 and S10-08, and their lengths ranged between C₁₃ and C₃₅. The n-alkanes in our samples conform to a bimodal distribution (Fig. 3), while the carbon preference

Tab	21
Нус	ocarbon compositions of sediment core samples.

Sample	Layer (cm)	Weight of sample (g)	Concentration of bitumen (µg/g)	Concentration of alkanes (µg/g)	Concentration of PAHs (µg/g)
S10-01	0-20	84	117.74	46.67	0.95
S10-02	21-40	96.5	103.94	43.63	1.79
S10-03	41-60	97.5	109.64	45.54	0.65
S10-04	61-80	98	101.02	46.84	2.01
S10-05	81-100	96	113.33	49.90	1.58
S10-06	101-120	99	127.58	52.12	2.06
S10-07	121-140	104.5	155.12	68.13	2.95
S10-08	141-160	99	92.93	47.58	0.91
S10-09	161-180	101.5	94.98	42.27	1.09
S10-10	181-200	101	92.57	49.70	1.30
S10-11	201-220	98	91.94	42.65	1.29
S10-12	221-240	102	83.14	40.39	1.56
S10-13	241-260	103.3	84.22	37.95	0.59
S10-14	261-280	104.5	93.68	37.61	0.64
S10-15	281-300	104.5	77.61	33.40	1.75
S10-16	301-320	106.8	90.82	42.23	3.69
S10-17	321-340	115	82.96	35.30	3.80

Abbreviation: PAHs, Polyaromatic hydrocarbons.

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