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Carbon isotope systematics of individual hydrocarbons in hydrothermal petroleum from Middle Valley, Northeastern Pacific Ocean

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Abstract

Individual aliphatic hydrocarbons in samples of bulk hydrothermal petroleum from Middle Valley (ODP Site 858) were submitted to compound specific isotope analysis to trace their origins. The C isotope compositions of the *n*-alkanes and isoprenoid hydrocarbons [means *n*-alkanes: -30.1 ± 1.01 (858A), -28.3 ± 1.7 (858C) and -24.8 ± 1.4 (858D)‰; isoprenoids: -26.0 ± 2.7 (858C) and -27.9 ± 0.4 (858D)‰, respectively] reflect mixed marine and terrestrial organic matter sources. Biphytane from thermophiles has a $\delta^{13}\text{C}$ value of -21.0 ‰.

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1. Introduction

Hydrothermal vent systems at sediment covered ridges are of interest to petroleum geochemists because they are natural laboratories where active petroleum generation (hydrous pyrolysis of immature organic matter), expulsion and migration can be studied (Simoneit and Lonsdale, 1982; Simoneit, 1993; Kvenvolden et al., 1986, 1987). The provenance of the source organic matter may be primarily marine (e.g. Guaymas Basin, Simoneit and Schoell, 1995), terrigenous (e.g., Escanaba Trough, Kvenvolden and Simoneit, 1990) or mixed from both sources (e.g., Middle Valley, Simoneit, 1994; Simoneit et al., 1992). The C isotopic compositions of the bulk organic matter or those of individual compounds can further define the origins of the source organic matter. Results of compound specific isotope analyses (CSIA) are presented here for the hydrocarbons

of 3 samples of hydrothermal petroleum from Middle Valley, northeastern Pacific Ocean (Fig. 1).

2. Experimental

2.1. Samples and extraction

Hydrothermal petroleum was derived from sediment samples of drill cores from Site 858 on Leg 139 of the Ocean Drilling Program. Samples were extracted with a methylene chloride and methanol mixture (3:1) by ultrasonic agitation of solvent aliquots with a bulk sample. The extracts were concentrated, asphaltene precipitated by addition of excess hexane and the clear supernatants were reconcentrated and analyzed for the C isotope composition.

2.2. Instrumental analysis

Compound Specific Isotope Analyses (CSIA) of C by online gas chromatography–combustion–isotope ratio mass spectrometry were conducted on the total extract fractions. The CSIA were performed on a modified version

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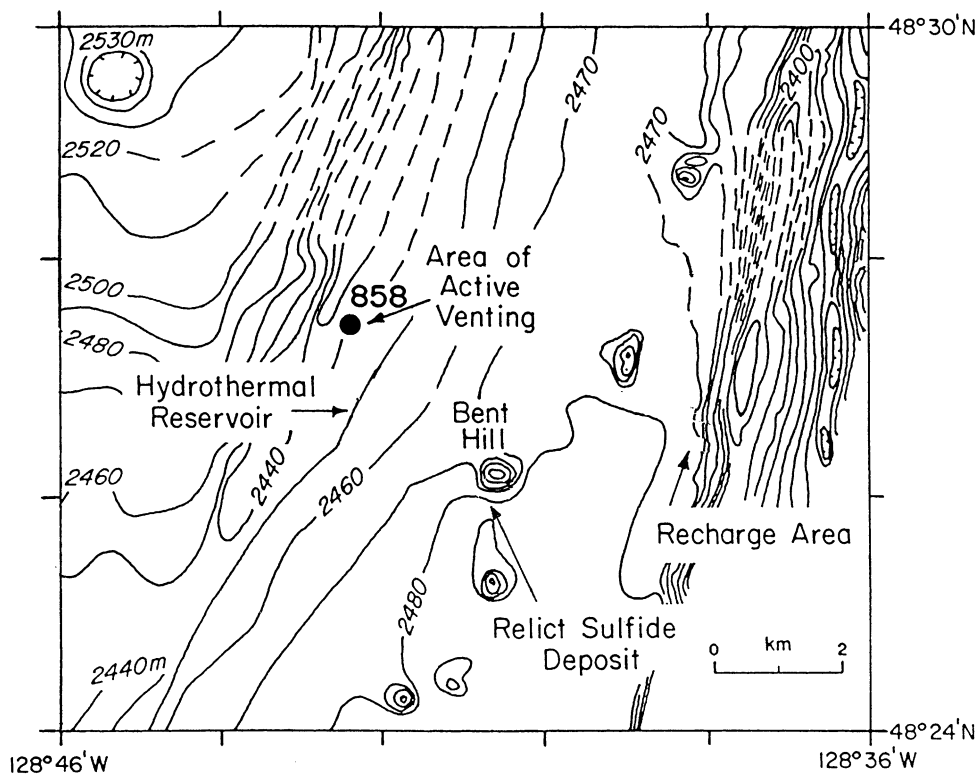


Fig. 1. Location and index map for the sample sites in Middle Valley (adapted from Simoneit, 1994).

of a Finnigan GC–C–MS system (Hayes et al., 1988, 1990; Schoell et al., 1992). The data system was ISO-DAT version 4.0. The gas flow and the combustion interface were completely rebuilt for better resolution of complex mixtures with closely eluting peaks. A VALCO 4-way valve was installed at the end of the GC-column, but within the GC oven, for easier diversion of gas flows. The oven is a quartz capillary (0.1 mm i.d.) with a CuO wire insert and uses a combustion temperature of 850 °C. The GC conditions were as follows: Column, Hewlett-Packard Ultra 1 (50 m×0.31 mm i.d., 0.5 µm stationary phase, cross linked methyl silicone); carrier gas, He (1.5 ml/min); temperature program, 3°/min from 60 to 320 °C, and 20 min hold at 320 °C. The standard was CO₂ injected during analysis through the changeover valve of the mass spectrometer with or without sample background. The reproducibility of isotope values from different background corrections performed on one run alone is ±0.5‰ (1σ standard deviation). The C isotopic compositions of individual compounds were calculated relative to the CO₂ standard and are reported in the usual delta notation vs. the PDB standard. The reproducibilities (expressed as standard deviation) in Table 1 are from 2–3 repeat analyses and range between ±0.0 and ±5.6‰, indicating that factors other than data reduction procedures affect the reproducibility (e.g. peak intensity, UCM/bleed and incomplete peak resolution).

3. Results and discussion

The results of CSIA for normal and isoprenoid hydrocarbons are given in Table 1. The *n*-alkane data for the hydrothermal petroleum range from C₁₅ to C₃₄ and the gas chromatograms for samples 858A-1H-1, 149–150 and 858C-2H-CC are shown in the site report (Figs. 44A and 45A, respectively in Davis et al., 1992) and sample 858D-3P-1 has a similar GC trace as shown for sample 858D-4H-2 (Fig. 2F in Simoneit, 1994). The CPI values [calculated over the C ranges from C₂₄ to C₃₄ (Cooper and Bray, 1963) and C₂₅ to C₃₃ (Marzi et al., 1993)] for the *n*-alkanes are <1, the uncommon even to odd predominance (Table 1).

The δ¹³C values of the *n*-alkanes in the hydrothermal petroleum samples range from –22.6 to –32.4‰ (vs. PDB), and the data are plotted in Fig. 2. In general the data fit within or close to the 1σ error of the overall mean of –29.0±1.3‰ for samples 858A-1H-1 and 858C-2H-CC and are typical isotope ratios for terrestrial organic matter. The δ¹³C values for the odd *n*-alkanes (C₂₉, C₃₁, C₃₃) are significantly lighter than the mean for sample 858C-2H-CC, supporting their origin from terrestrial plant waxes. The mean for sample 858D-3P-1 is –24.8±1.4‰, significantly heavier and indicating a more marine organic matter origin. The trend to less negative values (heavier) with decreasing C

Table 1
Stable C isotope data for individual hydrocarbons in hydrothermal petroleum from Middle Valley, NE Pacific

Compound	Composition	Samples $\delta^{13}\text{C}$ (‰, vs. PDB) ^a		
		858A-1H-1, 149–150	858C-2H-CC	858D-3P-1
<i>n-Alkanes</i>				
Pentadecane	C ₁₅ H ₃₂		–22.6	–28.6
Hexadecane	C ₁₆ H ₃₄		–28.5±0.1	–24.2±0.6
Heptadecane	C ₁₇ H ₃₆		–26.7±0.7	–25.0±0.3
Octadecane	C ₁₈ H ₃₈		–28.2±0.2	–24.9±0.2
Nonadecane	C ₁₉ H ₄₀	–30.8	–28.0±3.6	–23.4±0.1
Eicosane	C ₂₀ H ₄₂	–28.9	–28.5±0.4	–23.8±2.4
Heneicosane	C ₂₁ H ₄₄	–30.2±1.0	–28.5±0.3	–23.1±0.3
Docosane	C ₂₂ H ₄₆	–28.5±5.6	–26.8±0.9	–23.6±1.3
Tricosane	C ₂₃ H ₄₈	–30.1±0.6	–27.1±0.2	–23.8±2.9
Tetracosane	C ₂₄ H ₅₀	–30.6±5.5	–27.0±0.4	–24.2±0.6
Pentacosane	C ₂₅ H ₅₂	–29.4±0.7	–28.6±1.3	–25.6±0.6
Hexacosane	C ₂₆ H ₅₄	–29.8±0.2	–28.1±0.3	–24.6±2.8
Heptacosane	C ₂₇ H ₅₆	–30.0±0.7	–28.2±0.9	–27.7±0.1
Octacosane	C ₂₈ H ₅₈	–28.5±0.8	–29.1±0.4	–22.6
Nonacosane	C ₂₉ H ₆₀	–30.6±1.0	–31.8±2.0	–26.5
Triacontane	C ₃₀ H ₆₂	–31.1±4.2	–27.7±1.5	
Hentriacontane	C ₃₁ H ₆₄	–31.8±2.8	–30.8±1.8	
Dotriacontane	C ₃₂ H ₆₆	–29.7	–27.0±0.0	
Tritriacontane	C ₃₃ H ₆₈	–32.2	–32.4±1.1	
Tetracontane	C ₃₄ H ₇₀		–31.3	
Mean (C ₁₅ –C ₃₄)		–30.1±1.0‰	–28.3±1.7‰	–24.8±1.4
CPI (C ₂₆ –C ₃₄)		0.68	0.46	0.88
<i>Isoprenoids</i>				
Norpristane	C ₁₈ H ₃₈		–23.3±5.0	–21.4±0.8
Pristane	C ₁₉ H ₄₀		–27.6±0.1	–26.3±0.6
Phytane	C ₂₀ H ₄₂		–27.1±0.3	–35.9±1.3
Mean			–26.0±2.7	–27.9±0.4
3,7,11,15,18,22,26,30-Octamethyldotriacontane	C ₄₀ H ₈₂		–21.0±0.9	

^a Standard deviation is for $n=2-3$.

number may also indicate an increasing contribution of marine derived organic matter to the lower molecular weight *n*-alkanes or alternatively may be the inherent characteristic isotope signature observed for deltaic oils (Chung et al., 1994). The greatest $\delta^{13}\text{C}$ deviations in each sample are observed for the lowest and highest homologs of the *n*-alkane series. This deviation is probably due to the low *n*-alkane concentrations as was discussed in the case of similar samples from Escanaba Trough (Simoneit et al., 1997) and Guaymas Basin (Simoneit and Schoell, 1995). The differences in the means of the 3 samples (Table 1) are significant, however, the overall mean value ($-27.8\pm 1.3\text{‰}$) is in the same range as the mean for the Escanaba Trough hydrothermal petroleum (-27.5‰ , Table 2).

The isoprenoid alkanes (C₁₈–C₂₀) of these samples have a $\delta^{13}\text{C}$ range from -21.4 to -35.9‰ , with an overall mean of $-27.0\pm 5.2\text{‰}$ (Tables 1 and 2). These values are similar as the *n*-alkanes but more variable and may reflect various inputs of organic matter from

marine sources or alternatively represent the inherent organic matter character as described by Chung et al. (1994). The $\delta^{13}\text{C}$ value of the C₄₀ isoprenoid (3,7,11,15,18,22,26,30-octamethyldotriacontane, biphytane) is $-21.0\pm 0.9\text{‰}$ for sample 858C-2H-CC. This compound has been reported as a major lipid component bound in membranes of thermophilic bacteria and is found as the hydrocarbon in some petroleum (e.g. DeRosa et al., 1980; Moldowan and Seifert, 1979; Petrov et al., 1990).

A comparison of the mean isotope values with those reported for hydrothermal petroleum samples from Guaymas Basin is also given in Table 2. The mean isotopic composition of the *n*-alkanes from Middle Valley is 4.7‰ lighter than that for Guaymas Basin and the difference for the isoprenoid alkanes is similar in magnitude (5.4‰). Thus, these two locales are distinguishable based on the molecular and compound specific isotope compositions, whereas the Escanaba Trough samples are similar to those from Middle Valley.

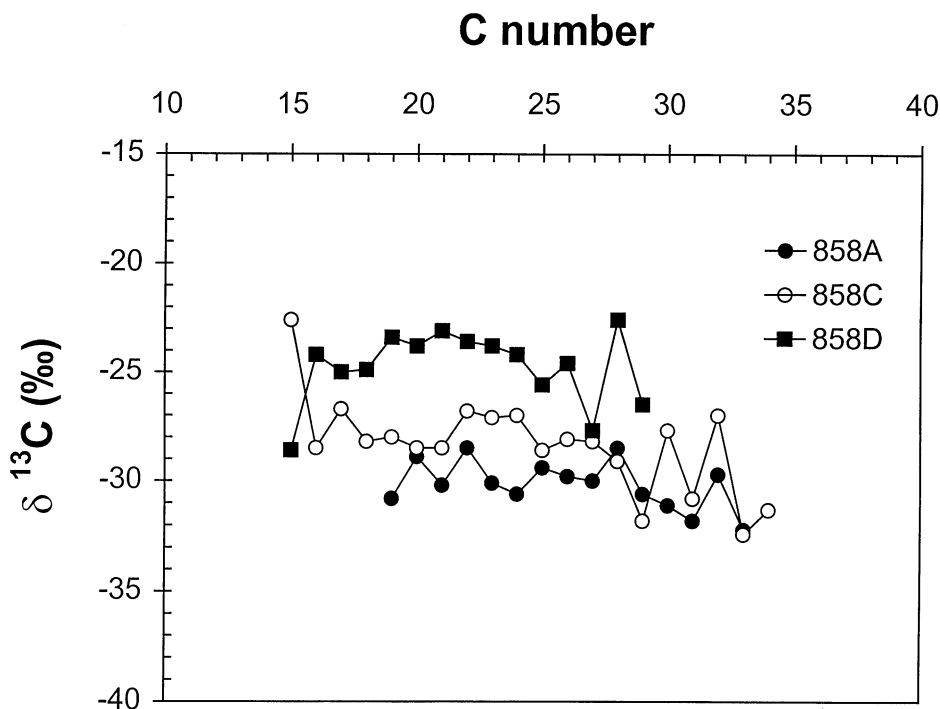


Fig. 2. Plots of $\delta^{13}\text{C}$ vs. C number for the *n*-alkanes in the hydrothermal petroleum from Middle Valley.

Table 2

Overview of carbon isotope data for Middle Valley, Escanaba Trough and Guaymas Basin

Organic matter type	$\delta^{13}\text{C}$ (overall mean, ‰ vs. PDB)	Number of samples (<i>n</i>)
<i>Middle Valley (ODP 139)</i>		
<i>n</i> -Alkanes, CSIA		
Holes 858A and 858C	-29.0 ± 1.3	5
Hole 858D (condensate)	-24.8 ± 1.4	2
All samples	-27.8 ± 1.3	
Isoprenoid alkanes, CSIA	-27.0 ± 5.2	4
<i>Escanaba Trough^a</i>		
<i>n</i> -Alkanes, CSIA		
	-27.5 ± 1.3	3
Isoprenoid alkanes, CSIA	-25.6 ± 0.6	3
PAH, CSIA	-24.7 ± 0.6	2
Bulk oil	-24.8	1
<i>Guaymas Basin, Gulf of California^b</i>		
<i>n</i> -Alkanes, CSIA		
	-23.1 ± 0.9	5
Isoprenoid alkanes, CSIA	-21.6 ± 1.0	5
PAH, CSIA	-21.2 ± 0.6	2
Bulk oil	-22.5 ± 1.1	10

^a Data from Simoneit et al. (1997).

^b Data from Simoneit and Schoell (1995).

4. Conclusion

The C isotope compositions of individual alkanes have been determined in sediment extracts from the Middle Valley hydrothermal system. The data support a dominant origin from terrestrial organic matter with a significant admixed and variable marine component.

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