27. TIME-TEMPERATURE HISTORIES OF KEROGEN AND MINERAL AMMONIA FROM LEG 139 (MIDDLE VALLEY) SEDIMENTS¹

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ABSTRACT

Sediments from four Ocean Drilling Program sites in the Middle Valley Hydrothermal area were analyzed for thermal maturity by solid-state ¹³C nuclear magnetic resonance (¹³C NMR) and thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR). General trends matched those found from vitrinite reflectance (R_o) profiles indicating increases in thermal maturity from 200 to 400 m in Hole 857C and from 0 to 300 m in Hole 858A. Holes 858B, 858D, and 858C all showed high maturities in samples shallower than 50 mbsf via both ¹³C NMR and TG-FTIR. Some samples showed relatively high maturities via these two techniques but relatively low R_o values, suggesting that thermal alteration is reflected more rapidly via ¹³C NMR and TG-FTIR than by vitrinite reflectance in these hydrothermal systems. The TG-FTIR analyses showed strong nitrogen depletion and alteration of the nitrogen-containing material in samples exposed to higher temperatures.

For Hole 857C, maximum temperature exposures estimated from the vitrinite reflectance data using R_o/maximum temperature calibrations of Barker (1983) and Barker and Pawlewicz (1986) are less than 30°C at depths shallower than 47 m, 200° to 225°C at 378 m and 256° to >270°C at 433 m. These values closely match present-day temperatures of <30°C, 210° to 225°C, and 260°C, respectively, for the same intervals as measured by downhole temperature and δ^{18} O. Maximum temperature exposures for other Leg 139 samples for which downhole measurements were not available were estimated to be in the range of <20° to 40°C for Sample 139-855C-1R-2, 141–144 cm at 2.91 m; <20° to 70°C for Sample 139-856A-2H-4, 86–101 cm at 8.06 m; and 260° to >280°C for Sample 139-856A-13X-2, 143–149 cm at 108.23 m.

At the bottom of geothermally cold Hole 855C, preferential biodegradation of aliphatic portions of kerogen by aerobic microorganisms, activated by a flow of oxygenated cold seawater from basement, is postulated to be responsible for the absence of aliphatic and the predominance of aromatic carbon atoms detected by ¹³C NMR. Vitrinite reflectance measurements show this section to be immature.

INTRODUCTION

Many sediments obtained during drilling of the Middle Valley hydrothermal area are very similar to each other (Davis, Mottl, Fisher, et al., 1992) but have been subjected to a wide variety of thermal and hydrothermal regimes. These sediments provided an excellent opportunity to compare various methods of measuring or estimating thermal maturity. This contribution describes measurement of thermal alterations to sediment kerogen as determined by solid-state 13C nuclear magnetic resonance (13C NMR) and a new pyrolysis technique, thermogravimetric Fourier transform infrared analysis (TG-FTIR) (Whelan et al., 1988 and 1990) compared with vitrinite reflectance (R_o) profiles (Mao et al., this volume). Initial results of the TG-FTIR technique are described with respect to alterations to mineral nitrogen from the hydrothermal system. The NMR, TG-FTIR, and %Ro data are all compared to direct temperature measurements (Davis and Wang, this volume; Davis, Mottl, Fisher, et al., 1992). In addition, estimates of maximum temperature exposure are carried out by using calibrations of %Ro vs. maximum temperature from various laboratories.

METHODS

Elemental analyses on whole-rock samples were carried out aboard ship using a Carlo Erba CHNS analyzer (Davis, Mottl, Fisher, et al., 1992, p. 76). Precise measurements were obtained on these low total organic carbon (TOC) rocks (Davis, Mottl, Fisher, et al., 1992, p. 76). Additional shore-based analyses were carried out using a Perkin-Elmer CHN analyzer and the method of Krom and Berner (1983). Because TOC values were relatively constant within a particular core, values from an adjacent section (generally within 3 m) were used in a few cases where insufficient sample was available to make the measurement on the sample used for other measurements, as indicated in Table 1.

TG-FTIR measurements were carried out on whole rocks as described in Whelan et al., 1988 and 1990.

Kerogen isolation was carried out by treatment of powdered whole rock, first with 6N HCl and then with HF as described in Durand and Nicaise (1980).

Vitrinite reflectance and thermal alteration (TAI) measurements were carried out as described in Mao et al., this volume.

Solid-state NMR measurements were made using a Chemagnetics CMX 100/200 solids NMR spectrometer. These measurements were carried out on isolated kerogens in most cases.

An attempt was also made to carry out measurements on whole rocks with a large-diameter probe. However, because of the organiclean nature of the rocks, no signal was obtained above background.

For the kerogen measurements, carbon aromaticity measurements were made at a ¹³C frequency of 25 MHz using the technique of cross polarization (CP) with magic-angle spinning (MAS) and high-power decoupling. A 9.5-mm diameter zirconia bullet spinner was used. Spinning rates were between 3.5 and 4 kHz. Other instrumental parameters were a 90R pulse width of 5.1 ms, a contact time of 1 ms, and a pulse delay of 1 s. A 50 Hz exponential multiplier was applied to the free induction decay of each ¹³C spectrum before integration. These parameters are typical for CP/MAS measurements on these types of materials (Miknis et al., 1982; Wilson et al., 1991). The number of transients varied between 43,200 and 64,800 counts because of the low levels of total organic carbon (TOC) in many of the kerogen concentrates.

Concerns about the accuracy of the carbon aromaticity measurements have been discussed (Snape et al., 1989), including the use of a single contact time for determining carbon aromaticities. Aliphatic and aromatic carbons are known to cross polarize at different rates; therefore a single contact time may not give representative aromatici-

¹ Mottl, M.J., Davis, E.E., Fisher, A.T., and Slack, J.F. (Eds.), 1994. Proc. ODP, Sci. Results, 139: College Station, TX (Ocean Drilling Program).

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Fable 1. Summary	y of TG-FTIR,	NMR, TOC, and	%Ro data for	Leg 139.
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				R _o Equiv	R	TG-FTIR						
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Core, section,	Depth	NMR	% (TAD	%	T _{max} NH ₃ (1)	T _{max} NH ₃ (2)	Wt% NH	Wt % NH ₃	TmaxCH4	T _{max} CH4	TOC
	interval (cm)	(mosr)	Ta	(1AI)	(vit refie)	°C, min	°C, max	5(10+)	(EA)	(mm)	(max)	(%)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-855A-	25/253	1980 market	12020					9			0.000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1R-2, 141–144	2.91	0.56	0.3	0.1210.01	504	647	0.060	0.06	765	765	0.5a
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	5K-2, 157-140	19.47		0.5	0.42±0.04	594	647	0.009	0.00	705	705	0.5
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-855C-								0.0268			0.111
	11R-2, 10–13	96.20	NM	0.38	0.43±0.03				0.026			0.11
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-856A-								1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	35322-5	101010	1210134
214:5, 137-140 100.77 0.44 0.99 >2.58 2.11±0.29 ND ND ND 0.092 ^m ND ND ND 0.15 139.558-8 11X-1, 102-106 74.52 NM 0.038 ^d ND ND 0.15 139.557A- 114.2, 102-106 74.52 0.53 0.2 0.2660, 10 ND ND ND ND ND ND 0.045 559 783 0.51 144.4, 137-140 27.77 0.51 0.2 0.3840.04 ND ND ND ND ND ND 0.045 559 783 0.51 0.51 39.557C 664 0.63 0.6420.10 ND ND ND ND ND ND 0.067 358 775 0.44 138.2, 105-109 155.5 0.61 ND ND ND 0.017 ND ND 0.017 ND 0.017 ND 0.017 0.44 ND 0.017 0.44 ND	2H-4, 86-101	8.06	12012	0.4	0.37±0.10	ND	ND	ND	0.09 ^a	ND	ND	0.24 ^a
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2H-5, 137-140 13X-2 143-149	108.23	0.44	>2.58	2 11+0 20	ND	ND	ND	0.160	ND	ND	0.49
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	157-2, 145-145	100.20	0.9	~4.30	2.1120.27	ND .	ND	nD	0.072	1465	110	0.10
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-856B-	74.22	100						0.0268	NID	NID	0.228
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	11X-1, 102–108	14.32	NM						0.036	ND	ND	0.32
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-857A-							1-11-12	triviteant?	100.000	20228	201221
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1H-2, 95-109	4.35	0.53	0.2	0.26±0.10	592	640	0.073	0.045	559	783	0.51
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	4H-4, 137-140 6H A 137-140	21.11	0.51	0.2	0.38 ± 0.04 0.37±0.00	ND	ND	ND	ND	ND	ND	0.49 0.37 ^a
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9H-1, 110-116	70.50	0.63	0.38	0.41+0.04b	ND	ND	ND	ND	ND	ND	0.45
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		10.00	0.00	0.45	0.1120.01	110	112	110	1.00	1.155		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	139-857C-	00 22	0.56	0.28	0.62+0.10	ND	NID	NID	0.0608	ND	ND	0.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	13R-2, 105-109	155.65	0.50	0.56	0.0210.10 ND	575	575	0.065	0.069	538	775	0.44
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	14R-2, 37-43	164.67	0.65	0.01	nD.	210	010	0.005	0.049 ^a	220	110	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16R-1, 0-2	182.20	1.000	0.61 ^b	ND	ND	ND	ND	0.017	ND	ND	0.17
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	17R-2, 126-130	194.66		0.61	0.67±0.14	579	661	0.028	ND	530	803	ND
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19R-1, 74–78	212.04	0.67	0.78b	0.7±0.120	626	626	0.037	0.023	512	749-792	0.22"
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25R-1, 5-8 25R 1 80 03	249.95	NM	0.69~	$0.75\pm0.10^{\circ}$	6.30	630	0.041	0.045	501	780	0.48
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23R-1, 89-93 28R-2, 27-30	209.09		0.58	1.10+0.16	615	615	0.054	0.042	581	791	0.36
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	31R-1, 111-115	323.81		1.1 to 1.2 ^b	1.2±0.15 ^b	611	611	0.075	0.041	622	791	0.39
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35R-3, 67-71	344.97	NM		h			0.046 ^a				0.37 ^a
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	41R-3, 66-71	378.56	0.91	ND	1.7 ± 0.12^{0}	631	631	0.06	0.069	522	829	0.28
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	53R-1, 27-30	433.07		>2.58	>2.48±.019°	652	652	0.025	0.02	330	812	0.27
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	139-857D-	772 //		ND	ND	ND	NID	0	0.001	562 000	562.000	0.12
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	21K-1, 140–148	115.00		ND	ND	ND	ND	0	0.001	302-900	302-900	0.15
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	139-858A-				100000000000000				0.053			0.70
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1H-1, 93–95	0.93		0.2	0.43±.09				0.053			0.69
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2H-1, 42-44 2H-3, 141-145	6.81	0.46	0.3					0.052 ND			ND
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2H-5, 6-10	8.46	0.40	0.38					ND			ND
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3H-4, 68-72	17.08			0.52±0.04				0.032^{a}			0.27^{a}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6H-3, 105-107	44.45			1.24±.10				0.036 ^a			0.32^{a}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7H-3, 27-30	53.17	NM	0.00					ND			ND
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	/H-3, /2-/5	55.62	0.05	0.98					0.039			0.16
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19X-1, 32-34	149.59	0.95	1.16	1.67+16				ND .			ND
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21X-1, 110-113	169.70	0.95	1.10	1.072.10				0.014*			0.17 ^a
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24X-1, 54-56	198.14		2.58	2.61±.20				0.036 ^a	12/24/2	10000	0.32^{a}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32X-1, 14–15	274.64	0.97	>2.58	2.61±0.20 ⁰	714	714	0.0071	0.015	549	809	0.2"
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	139-858B-											
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1H-3, 101-104	4.01		0.3	0.45±.03	591	656	0.0036	0.04 ^a	762-855	762-855	0.51 ^a
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1H-4, 147–150	5.97	0.71	0.45		ND	ND	ND	0.051 ^a	ND	ND	0.49^{a}
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	IH-CC 5H 2 127 140	7.20	NINA	a seb	0.52±0.08	ND	ND	ND 0.0020	0.033~	ND 506: 572	ND 708	0.26
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	511-5, 157-140	28.27	INIM	>2.38	ND	ND	ND	0.0029	0	500, 572	190	0.09
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	139-858C-	12.425	0.000	a ab	a tara b	1222				000 545		1.02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1H-1, 2–17	0.02	NM	0.30	0.45±0.06	423	623	0.18	0.1	327-542	743	1.02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2H-1, 1-15 5H-1, 150, 52	3.51	NM	0.38	0.49±0.0/°	590	645	0.0044	0.04	369-605	730_881	0.5a
139-858D- 0.072 ^a 0.86 ^a 1H-1, 0-30 0.00 NM 0.033 ^a 0.34 ^a 2H-3, 137-141 13.67 NM 0.033 ^a 0.34 ^a 4H-3, 137-140 23.12 0.84 0.03 ^a 0.25a	7H-2, 5–7	43.05	0.97	>2.58b	1.54±0.16	ND	ND	0	0.013 ^a	447-607	742; 834	0.22 ^a
1.59-558D- 0.072 ^a 0.86 ^a 1H-1, 0-30 0.00 NM 0.033 ^a 0.34 ^a 2H-3, 137-140 23.12 0.84 0.03 ^a 0.25a	120.0500	2 - 2 - 4 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5	1.7.7.5.1					1.175	000000000	and the set of the set	5. YEAR (1977)	
2H-3, 137-141 13,67 NM 0.03 ^a 0.34 ^a 4H-3, 137-140 23,12 0.84 0.03 ^a 0.25a	139-858D- 1H-1 0-30	0.00	NM						0.072 ^a			0.86 ^a
4H-3, 137–140 23.12 0.84 0.03 ^a 0.25a	2H-3, 137-141	13.67	NM						0.033 ^a			0.34 ^a
	4H-3, 137-140	23.12	0.84						0.03 ^a			0.25a

Notes: ND = no data and NM = not able to measure.

^a Estimated from adjacent samples (Davis, Mottl, Fisher, et al., 1992)

^b Extrapolated from surrounding samples (Mao et al., this volume)

ties. However, Wilson et al. (1991) compared aromaticities for coaly source rocks from the Brent group (North Sea). The contact times were varied between 10 ms and 8 ms and signal intensities were calculated by curve fitting. In all but one case, the aromaticities agreed within experimental error. They concluded that CP/MAS ¹³C NMR aromaticity made at a 1 ms contact time could be used with confidence. Thus, a 1-ms contact time was utilized in this work.

All spectra were manually phased and integrated using the instrument's dedicated computer software. Because of the low levels of carbon in the kerogens and the large number of transients required to obtain a spectrum, some broad signals from the NMR probe were also recorded. Consequently, a probe background spectrum was sub-tracted from each kerogen spectrum prior to integration.

The carbon aromaticity measurements were integrated over the range from 360 ppm to -160 ppm. This large range was required to include any contributions from spinning side bands in the aromaticity measurements. The region between 340 ppm and 90 ppm was considered the aromatic region, and included unresolved contributions from



Figure 1. A. Location of Middle Valley hydrothermal area studied during Leg 139. B. Locations of holes drilled during Leg 139 in Middle Valley. At the time of drilling, active venting was occurring at Site 858.

any carbonyl carbons in the region 165 ppm to 210 ppm which might be present. The region between 90 and -20 ppm was considered the aliphatic carbon region. The integrated intensity between -20 ppm and -80 ppm was added to the aromatic carbon integral.

DESCRIPTION OF SAMPLES

The location of the sites from which samples were recovered for this work are shown in Figure 1. TOC was low (Table 1), ranging from a maximum of about 0.5% to values of less than 0.1% in deeper and more hydrothermally altered sediments (Davis, Mottl, Fisher, et al., 1992).

Site 855

Site 855 was drilled to determine the nature of seawater recharge outside the area of hydrothermal upflow. Pore-water geochemical data confirm that cold, recharging seawater permeates the basement at this site. The chemical changes observed in the fluid, sediment, and basalt are associated with low-temperature biogenic reactions and seafloor weathering (Davis, Mottl, Fisher, et al., 1992).

Site 856

Site 856 was drilled into a fossil hydrothermal upflow zone. Hole 856A was drilled at the center of a 400-m diameter hill of sediment which has been uplifted 50 m above the surrounding turbidite-filled valley floor during the Holocene. Indications of former hydrothermal activity include growth of authigenic carbonate nodules; precipitation and subsequent dissolution of anhydrite; alteration of mafic minerals and plagioclase feldspar; formation of pyrite, albite, and chlorite; and the presence of a massive sulfide deposit at the site.

Site 857

Site 857 was located 1.6 km south of the zone of active venting (Fig. 1). Four holes were drilled into this high-temperature hydrothermal reservoir (heat flow 0.8 W/m²) outside the area of active hydrothermal flow. The deepest hole penetrated 471 m of sediment and metasedimentary rock and 467 m of diabasic sills interlayered with metasedimentary rock. The thermal structure of the upper part of the sediment is conductive to about the depth of the sheeted sill complex beginning at 470 m. A zone between 200 m and 400 m depth shows sodium depletion in pore water and strong sodium metasomatism in the sediments which, together with strong concentration gradients in the composition of pore fluid, require lateral flow of hydrothermal fluid in this zone. Mass balance constraints further suggest that many volumes of pore water have flushed through this zone. The sill-sediment complex below 470 m appears to be isothermal at approximately 275°C (as determined by direct temperature measurements; Davis and Wang, this volume), the temperature of the active hydrothermal vent area at Site 858, 1.6 km to the north.

Site 858

Site 858 drilling defined the temperature structure in and around the hydrothermal upflow zone of the Dead Dog vent field (Fig. 1). The thermal anomaly associated with the active vents is highly localized and appears to be nearly isothermal at the temperature of the vents (275°C) from a shallow depth down to basement. Thermal induration and hydrothermal alteration of the sediment are similar to that found at Site 857, but occur at shallower depth in accordance with the higher temperature. Near-surface gradients in pore-fluid and hydrocarbon composition are interpreted to be maintained by lateral flow of hydrothermal structure.



Figure 2. Solid state ¹³C nuclear magnetic resonance spectra of Leg 139 kerogens with sub-bottom depths indicated. **A.** Holes 855C, 856A, and 858D. **B.** Holes 857A and 857C. **C.** Holes 858A, 858B, and 858C.

mal fluid. A carbonate- and silica-cemented zone at about 20 to 30 mbsf was encountered and interpreted to be associated with near-surface lateral flow of hydrothermal fluid (Davis, Mottl, Fisher, et al., 1992).

Hole 858B was drilled at the base of one of the hydrothermal mounds within 20 m of an active 265°C vent. Magnesium-rich smectite, anhydrite, and pyrite occur at shallow depth in this hole. The larger-scale control on the location of the hydrothermal upflow zone was established by deeper drilling at Holes 858A, 858F, and 858G. Hole 858A, on the flank of the venting area, was drilled to a depth of 333 m and did not encounter basaltic rock. Hole 858F, in the core of the vent area, encountered basalt pillows and massive flows from 258 m to the bottom of the hole at 433 m. These flows occur more than 200 m higher in the sedimentary section than sills drilled at Site 857. Seismic reflection profiles show that this volcanic high is very narrow, consistent with the absence of igneous rock in Hole 858A, less than 200 m west.

RESULTS

Nuclear Magnetic Resonance Data

Nuclear magnetic resonance data are presented in Figures 2-4 and in Tables 1-3. The upfield signal above 90 ppm is considered to be the aliphatic carbon region and the downfield region below 90 ppm the aromatic carbon region (see "Methods" section, this chapter). With increasing temperature and maturity, the aliphatic signal disappears while the aromatic signal remains the same or increases. This relationship is expressed quantitatively by f'a, termed the aromaticity, which is the ratio of aromatic to aliphatic plus aromatic carbon atoms. As geothermal temperature or maturity of the kerogen increases, f'a approaches its theoretical maximum value of 1. In Figure 2, this change is observed as the progressive disappearance of the upfield aliphatic signal and the relative enhancement of the lower field aromatic signal. For example, a strong aliphatic signal is observed in Sample 139-855C-1R-2, 141-144 cm (2.91 m), which has not been heated (f'a = 0.56), while only a weak aromatic and no aliphatic signal is observed for Sample 855C-11R-2, 10-13 cm (96.20 m). Due to the weakness of the kerogen signal relative to background, it was not possible to calculate f'a for the latter sample. A similar change is observable between Samples 857A-1H-2, 95-109 cm (4.35 m) and 857C-41R-3, 66-71 cm (378.6 m), where the downhole temperature also increases by about 200°C in the deeper sample (Davis, Mottl, and Fisher, et al., 1992).

Three samples from Site 856 were analyzed (Fig. 2a); however f'a could only be measured for two of these: a shallow immature sample,



Figure 2 (continued).

856A-2H-5, 137–140 cm (10.07 m), with f'a = 0.44, and 856A-13X-2, 143–149 cm (108.23 m) with a high maturity f'a of 0.9. The vitrinite reflectances within the same intervals were $R_o = 0.4\%$ (immature) and 2.1 ± 0.29% (highly mature), respectively (Table 1).

Sample 856B-11X-1, 102–108 cm (74.32 m) in Fig. 2a is typical of many kerogens analyzed in this work which gave only a broad noisy band in the aromatic region and could not be integrated to give an f'a value. Other examples of this problem, which arose for some samples at all four sites, include 855C-11R-2, 10–13 cm (96.20 m, Fig. 2a) which we believe did not undergo geothermal heating in the past (Mao et al., this volume); 857C-23R-1, 5–8 cm (249.95 m); and surface intervals in both Holes 858C and 858D (Figs. 2c and 2a, respectively).

In these samples, it seems likely that paramagnetic impurities (such as iron and other metal sulfides) intimately associated with the kerogen and not removed during acid treatment during the isolation process may be responsible for degradation and broadening of the NMR signal. The problem may be aggravated by the low amounts of kerogen in the deeper sections and the admixing of significant sulfide minerals, which are almost impossible to remove without also destroying the kerogen (Durand and Nicaise, 1980). For a number of the Leg 139 kerogens, particularly those from deeper sections of Site 857 and from many Site 858 samples, a large amount of grey, presumably sulfidic residue remained after acid treatment rather than the black or brown/black residue typical of isolated kerogens.

Curiously, in some holes, the NMR signal becomes relatively strong and well resolved below these ¹³C "wipe-out" areas. Loss of TOC was not responsible, since levels were approximately the same in samples showing and not showing the NMR "wipe-out" (Table 1). Two examples are: (1) two noisy surface samples (858D-1H-1, 0-30 cm, 0.00 m; and 858D-2H-3, 137-141 cm, 13.67 m) compared with a much better resolved deeper sample, 858D-4H-3, 137-140 cm (23.12 m) (Fig. 2a); and (2) Sample 857C-23R-1, 5-8 cm (249.95 m) which shows only a weak and noisy 13C NMR spectrum while the deeper and hotter 857C-41R-3, 66-71 cm (378.56 m) shows a much less noisy and better resolved aromatic region (Fig. 2b). Neither the degree of kerogen thermal alteration nor the amount of TOC seem to show any correlation with this weakening and broadening of the ¹³C NMR signal. Likewise, on the basis of the shipboard core descriptions (Davis, Mottl, Fisher, et al., 1992), there seems to be no obvious association between the NMR signal broadening and the presence of any particular mineral.

Because of the problems in isolating kerogen in some samples, an attempt was made to measure the NMR carbon signal in HCl treated whole-rock samples using a large-diameter probe. However, even in immature surface samples containing relatively high abundances of TOC for this sample set (1%-1.5%), no signal significantly above background noise could be obtained.



Figure 2 (continued).

At Site 857, a progressive increase in maturity with depth occurs (Fig. 3) which is reflected in an increasing f'a and %R_o with increasing depth and temperature. Shallow samples from 4 to 90 m show typical immature f'a values of 0.44 to 0.64. In contrast, Sample 857C-41R-3, 66–71 cm (378.56 m) has a much higher f'a value (0.91) and higher R_o (1.7% ± 0.12%; Table 1). A large increase in f'a occurs between 200 and 400 m, consistent with the postulated past hydrothermal flow through this section (Davis, Mottl, Fisher, et al., 1992).

For Hole 858A, all f'a values that could be measured were high (0.95), from 149 to 275 m (Fig. 4; Table 1). The high f'a values are consistent with the high vitrinite reflectance values (1.5% at 150 m, increasing to >2.5% below 250 m; Fig. 4; Mao et al, this volume). High f'a values were also observed for all samples measured from Holes 858B, 858C, and 858D (Fig. 4, depths all less than 50 m), consistent with the active hydrothermal flow that was occurring at this site. Note Sample 858-1H-4, 147-150 cm (5.97 m) from the area of active hydrothermal flow has a high f'a value (0.71), but a relatively low Ro value (0.45%, a value just below the beginning of the oil window; Table 1). This discrepancy between f'a and Ro is consistent with the very rapid heating this sample has undergone due to presentday active hydrothermal venting. The more rapid response of f'a to rapid heating pulses, compared with vitrinite reflectance, was previously noted by Dennis et al. (1982) and is shown by the change in slope in the correlation line between the two parameters in Fig. 8.

TG-FTIR Data

TG-FTIR data are shown in Table 1, Figures 3 through 7, and Figures 3 and 4 for Sites 857 and 858 respectively. TG-FTIR analyses of selected samples from Holes 855A, 857A and 857B, and 858A, 858B, and 858C reveal the evolution of abundant NH₃ during pyrolysis of bulk sediment samples. Whelan et al. (1988) suggest that the temperature of maximum NH3 generation (Tmax) may be a useful indicator of both thermal maturity of sediments and the source of the NH3 within sediments, particularly for relatively organic lean sediments such as those from Middle Valley. Specifically, they suggest that increasing thermal maturity results in increasing T_{max} for NH₃. Furthermore, recent data suggest that N in organic matter (kerogen) is thermally released during pyrolysis at lower temperatures than N in inorganic minerals (Whelan et al., 1988 and unpubl. data). In support of this idea, isolated kerogens produced only one peak at relatively low temperature (about 350° to 420°C) while minerals containing little or no organic matter, such as organic-lean, iron-rich "red bed" samples, produce only one weak high-temperature peak with a T_{max}NH₃ > about 600°C (Whelan, unpubl. data).

TG-FTIR profiles for many of the relatively shallow samples from Middle Valley were characterized by two distinct maxima for the T_{max} of NH₃ (labeled T_{max} NH₃(1) and T_{max} NH₃(2) in Table 1) while others were characterized by a single well-defined peak. In analogy to previous results, the low-temperature peak is postulated to reflect NH₃ derived predominantly from organic matter while the second peak may reveal the presence of a more thermally resistant pool of N, possibly associated with inorganic phases. However, in samples characterized by a single NH₃ peak where a combination of organic and inorganic sources may be contributing, it is impossible to distinguish the source of N solely on the basis of T_{max} values. Research is in progress on samples subjected to chemical leaching to better define the types of nitrogen in each pyrolysis peak for various kinds of sediments and rocks.

Table 1 and Figures 3 and 4 reflect T_{max} values for NH₃ in Middle Valley sediments from Sites 857 and 858 as a function of depth. Examination of Figure 3 and Table 1 reveals a systematic increase in both $T_{max}NH_3$ values with increasing depth at Site 857. For Hole 858A, one measurement was also obtained for a high $T_{max}NH_3$ value from near the bottom of Hole 858A (Fig. 4 and Table 1), consistent with the high maturities registered by $\%R_o$ and f'a values in the same interval and suggestive of a $T_{max} NH_3$ profile similar to that of Hole 857C. In Hole 858C, an abrupt increase in $T_{max} NH_3$ occurs below the surface, consistent with the increases in the vitrinite reflectance and NMR f'a values in the same interval (Fig. 4). The profile of $T_{max} NH_3$ values with depth is somewhat erratic for Hole 858C, possibly because of narrow zones of lateral or localized hydrothermal flow.



Figure 3. TG-FTIR data for Site 857.



Figure 4. TG-FTIR data for Site 858.

The fraction of total nitrogen in the sediment represented by ammonia can also be obtained using the TG-FTIR technique. For the Leg 139 sediments, the weight percent (wt%) of nitrogen in the sediments as measured by elemental analyses shows a correlation with weight lost as NH₃ as measured by TG-FTIR (Fig. 6). In fact, the NH₃ values measured by TG-FTIR are either equal to or slightly lower than the total nitrogen values as determined from elemental analysis, showing that most of the nitrogen in the sediments must be in the form of reduced nitrogen, i.e., as ammonia or ammonium or as organic amino groups. The wt% of pyrolyzable ammonia in these sediments also generally decreases with increased geothermal heating (Figs. 3 and 4). For example, the surface Samples 855A-3R-2, 137-140 cm (19.47 m) and 857A-1H-2, 95-109 cm (4.35 m), which have not been heated, give 0.069% and 0.045% NH3, respectively, while Sample 858B-1H-3, 101-104 cm (4.01 m) and 858B-5H-3, 137-140 cm (28.27 m), which have been exposed to strong geothermal heating, show 0.0036 and 0 wt% ammonia, respectively. A steeply decreasing trend of weight percent of ammonia with depth and increased geothermal heating can also be observed for Hole 858C (Fig. 4 and Table 1).

 $T_{max}NH_3(1)$ is plotted vs. R_o for all Leg 139 samples measured to date in Figure 5. $T_{max}NH_3$ generally increases with increasing R_o , but the data show considerable scatter. We suggest that changes in the minerals admixed with the kerogens may be responsible for the scatter. Previously, it has been found that $T_{max}NH_3$ increases with increasing maturation, but that the intercepts of the lines are very dependent on the specific minerals present (Whelan et al., unpubl. data).

In addition to ammonia, methane evolution was monitored during the TG-FTIR analysis of these sediment samples. The T_{max} of CH₄ generation from isolated kerogens was previously found to show an excellent correlation with maturity over a wide maturity range (Whelan et al., 1990). For Middle Valley sediments, evolution of CH₄ from wholerock samples (rather than kerogens) occurred continuously during progressive heating of the sample, resulting in broad complex CH₄ generation curves. Unfortunately, the T_{max} for CH₄ from these rocks did not vary systematically with depth or any other maturation dependent parameter (Fig. 7), although there does appear to be a general increase with R_o at higher maturities. Part of the scatter is probably produced by mineral matrix effects in these low TOC samples. Measurements on isolated kerogens, which eliminate this problem (Whelan et al., 1990), have not yet been carried out.

No longer-chain hydrocarbons (tars, paraffins, etc.) were observed during pyrolysis of these rock samples. Similar results have been observed previously with low TOC samples where amounts and T_{max} values of "tar" (i.e., the sum of hydrocarbons larger than methane) and methane were obtainable only on isolated kerogens and not on wholerock samples (Whelan et al., 1988 and 1990). Work is in progress to carry out TG-FTIR measurements on isolated kerogens from Leg 139 samples.



Figure 5. TG-FTIR data for Leg 139: Tmax NH3 vs. vitrinite reflectance (%Ro).

DISCUSSION

Source of Nitrogen in Leg 139 Sediments

Increasing TmaxNH3(1) for NH3 from 423° to 714°C with increasing thermal maturity is consistent with derivation of the ammonia nitrogen from pyrolytic degradation of organic matter. The degradation of organic matter is a function of both time and temperature, although at Middle Valley, temperature may be the dominant variable owing to the geologically young age of the sediments and the high temperatures associated with basaltic volcanism at mid-ocean ridges. During progressive maturation of sediments, the weakest bonds within the organic matter are broken first. Liquid and gaseous alteration products are removed and residual solid material becomes increasingly resistant to thermal degradation, which in turn is reflected by higher Tmax for NH3 during pyrolysis. For example, the extremely low Tmax value for NH3 of the shallowest sample from Hole 858C, which was essentially collected at the seafloor, probably reflects a high abundance of nitrogen as proteinaceous material not yet destroyed by diagenetic and hydrothermal processes. Because proteinaceous material is easily degraded by heating, maximum NH3 evolution occurs at relatively low temperatures. The majority of organic N in deeper samples, however, is likely increasingly contained in various NSO compounds in generated bitumen and kerogen components. As these become increasingly bound into the residual kerogen and mineral matrix via heterocyclic groups and crosslinking, resistance to thermal degradation and consequently maximum NH3 generation occurs at higher temperatures.

 $T_{max}NH_3(2)$ also shows increasing T_{max} values with increasing maturity (Fig. 3), suggesting that a significant portion of this nitrogen, as well, may be derived from organic matter. Similar arguments may apply to sediment samples characterized by only a single NH₃ peak, where an increasing T_{max} with increasing maturation is also observed. Alternatively, the increases in $T_{max}NH_3$ could also represent the increasing proportion of minerals with increased stability under pyrolysis conditions in the more mature sections. Such an alteration might explain the maximum in $T_{max}NH_3(2)$ observed from 200 to 300 mbsf in Hole 857C (Fig. 3), a zone highly influenced by lateral hydrothermal flow (Davis, Mottl, Fisher, et al., 1992).

Relationship of NMR and Vitrinite Reflectance Data to Geothermal Temperature

NMR f'a values correlate reasonably well with vitrinite reflectance values (Fig. 8) and the Leg 139 points lie fairly close to the correlation line previously defined for basaltic intrusions into Creta-

Core, section,	Depth	%Ro		Estimated present geothermal	Past maximum temperatures	Estimated from Barker	Estimated from Barker	Estimated from Sweeney an Burnham (1990) Heating rat		ey and ng rate
interval (cm) (mbsf)	(mbsf)	osf) (composite)	f'a	temperatures	(¹⁸ O)	(1983)	and Pawlewicz (1986)	1°C/1000 yr	10°C/yr	5°C/m.y.
139-855C-										
1R-2, 141-144	2.91	0.3	0.56			<20	40	75	150	50
139-856A-										
2H-4, 86-101	8.06	0.4	0.63			<20	70	110	180	75
13X-2, 143-149	108.23	>2.58	0.9			261	>280	>260	>360	>220
139-857A-										
1H-2, 95-109	4.35	0.2	0.53	<30	<30	<20		30	90	20
4H-4, 137-140	27.77	0.2	0.51	<30	<30	<20		30	90	20
6H-4, 137-140	46.77	0.38	0.64	60	30	<20	30	100	175	70
9H-1, 110-116	70.50	0.42	0.63	70		<20	50	120	190	80
139-857C-										
6R-2, 62-64	88.32	0.4 to 0.6	0.56	65	40	20	70 to 90	110 to 150	180 to 225	75 to 110
41R-3, 66-71	378.56	1.7	0.91	225	210	200	225	240	325	190
53R-1, 27-30	433.07	>2.5	ND	260	260	256	>270	>260	>360	>220
139-858B-										
1H-3, 101-104	4.01	0.3 to 0.45	0.71	40		<20	<20 to 60	75 to 130	150 to 200	50 to 90

Table 2. Maximum past temperatures of Leg 139 samples based on NMR f'a and %Ro values compared with data of Barker (1983), Barker and Pawlewicz (1986), and Sweeney and Burnham (1990).

Notes: ND = not determined; $\Re R_o$ (composite)s from both TAI and vitrinite reflectance (see text). Estimated present geothermal temperatures taken from Davis et al. (this volume) and Davis, Mottl, Fisher, et al., (1992). Past temperatures from Boni et al. and Baker et al. (both in this volume). Estimates from Barker (1983) were determined by means of regression equation $R_m = 0.435e^{(0.00683T)}$.

Table 3. Estimate of maximum temperature of Leg 139 samples, based on R_0 -T calibrations other than those in Table 2.

		%R _o (composite)	NMR ťa	Estimated temperatures (T, °C, see text)					
Core, section, interval (cm)				F	From Bostik (1971)				
				Field data; T estimated from:		Laboratory heating data; T estimated from:		T estimated from:	
	Depth (m)			%R _o (composite)	fa	%R _o (composite)	f'a	%R _o (composite)	
139-855A-									
1R-2, 141—144	2.91	0.3	0.56	100	125	≈300	300	30	
139-856A-									
2H-4, 86-101	8.06	0.4	0.63	125	145	301	325	45	
13X-2, 143-149	108.23	>2.58	0.9	>475	400	500	490	>145	
139-857A-									
1H-2, 95-109	4.35	0.2	0.53	50	115	300	305	<30	
6H-4, 137-140	46.77	0.38	0.64	120	150	335	325	=40	
9H-1, 110-116	70.50	0.42	0.63	125	145	330	320	=50	
139-857C-									
6R-2, 62-64	88.32	0.4 to 0.6	0.56	120 to 200	125	305	300	45 to 60	
41R-3, 66-71	378.56	1.7	0.91	375	400	520	495	123	
53R-1, 27-30	433.07	>2.5	ND	>440	ND	ND	ND		
139-858B-									
1H-3, 101-104	4.01	0.3 to 0.45	0.71	98 to 135	250	350	360	30 to 45	

Notes: %R_o (composite) from Table 1. ND = not determined.

ceous sapropelic organic-rich South Atlantic sediments recovered on DSDP Leg 41 (Dennis et al., 1982; Peters et al., 1978).

Two types of R_o values were used for the " $\Re R_o$ (composite)" axis in Figs. 3, 4, and 8 in order to obtain reliable R_o values in all maturity ranges. In Tables 1–3, " R_o % (vit refle)" in Table 1 was obtained by measuring reflectance of the vitrinite maceral; " R_o equiv" was calculated from thermal alteration indices (TAI) on spores (Mao et al., this volume). At low R_o values, below $R_o = 0.4\%$, a R_o calculated from TAI is more reliable while direct measurement of R_o gives a better indication of maturity at $R_o > 0.4\%$ (Jones and Edison, 1979).

NMR f'a values are generally low (<0.6) for immature Leg 139 samples ($R_0 < 0.5\%$), such as those from shallow sections of Holes 855A and 857A (Tables 1–3). The NMR f'a values increase to typical high-maturity values of about 0.9 in Sample 857C-41R-1, 66–71 cm

(378.56 m), which also has a relatively high R_o value of $1.7 \pm 0.19\%$, typical of kerogens beyond the oil window in the gas condensate and starting into the dry gas window (Mao et al., this volume).

It is interesting that Sample 855C-11R-2, 10–13 cm from near the bottom of Hole 855C (96.20 m) shows predominantly a broad and weak aromatic NMR signal (Fig. 2a) even though there is no evidence of geothermal heating ($R_o = 0.4\%$, Table 1; Mao et al., this volume). We postulate that the low abundance of aliphatic carbon atoms in this interval may be due to cold recharging seawater flowing into this section from the basement rocks below. Such a flow of oxygenated water, which may also contain microbial nutrients, would allow any aerobic bacteria present either in the water or the sediments to degrade the residual organic matter. Previous research has shown that microorganisms in deep sediments as old as 110,000 yr can be reactivated



Figure 6. Wt% of NH₃ from TG-FTIR plotted vs. the same measurement made via elemental analysis (EA).



Figure 7. TG-FTIR data for Leg 139: T_{max} methane vs. percent vitrinite reflectance (% R_{p}).

if proper nutrients are provided (Whelan et al., 1986). In addition, microbial degradation in sediments preferentially destroys the aliphatic over the aromatic part of kerogen (Tarafa et al., 1987).

Because of the reasonably good correlation between f'a and Ro in the combined plot for the Leg 41 and Leg 139 samples (Fig. 8), an attempt was made to estimate the maximum temperature exposure of Leg 139 kerogens by comparison to Ro and f'a values from the Leg 41 samples (Dennis et al., 1982). The results are shown in Table 3. Two different sets of temperatures are shown, one derived from laboratory heating experiments of Leg 41 kerogens (listed as "laboratory" in Table 3) and the other derived from "field data," using estimated well temperatures from Peters et al. (1978) and Bostik (1971). For comparison, estimated present geothermal temperatures are shown in Table 2, based on downhole temperature measurements (Davis, Mottl, and Fisher, et al., 1992) and modeling by Davis and Wang (this volume) and maximum past temperatures as estimated from δ^{18} O measurements (Boni et al., this volume; Baker et al., this volume). Both of the estimated maximum well temperatures based on the Leg 41 calibrations (Table 3) are much higher than the present-day measured values (Table 2). In fact, the maximum temperature exposures estimated from the Leg 41 heating experiments, in the range of 300°C even for immature surface samples (e.g., Samples 855C-1R-2, 141–144 cm, $R_o = 0.3\%$, and 857A-1H-2, 95–109 cm, $R_o = 0.2\%$;



Figure 8. NMR aromaticity, f'a vs. vitrinite reflectance ($%R_o$), Leg 41 and Leg 139 samples. The two lines represent the correlation lines for the Leg 41 well samples (from Dennis et al., 1982).

Table 3), seem geologically unreasonable. The calculated temperatures estimated from the Leg 41 well calibration set are lower (Table 3), but still seem high, particularly for the immature samples.

We propose that the maximum temperature exposures derived from both sets of the Leg 41 data (Table 3) are too high and that other R_o vs. maximum temperature calibration sets of Barker (1983), Barker and Pawlewicz (1986) and Sweeney and Burnham (1990) provide more realistic estimates of maximum heating of the Leg 139 samples, as shown in Table 2 and discussed below.

Several researchers have discussed the problem of using laboratory heating experiments as a calibration for estimating maximum geologic temperatures, even for hydrothermal systems where geologic heating times are relatively short (Barker, 1983 and 1991; Barker and Pawlewicz, 1986; Sweeney and Burnham, 1990). Barker postulates, based on earlier work of Hood et al. (1975), that the time the sample spends within 15°C of its maximum temperature is the critical parameter in setting the vitrinite reflectance values and that this time is relatively short even for slowly buried sediments. However, if heating times are very short, as is the case in laboratory heating experiments, then the kerogen has insufficient time to react and produce a steady-state Ro value characteristic of that particular temperature. With somewhat longer reaction times, such as those in hydrothermal systems that heat at an average rate of about 1°C/1000 yr (Barker, 1983; 1991), the kerogen vitrinite reaction does have time to reach its stable state at a specific temperature. In addition, Barker and Pawlewicz (1986) have shown that heating times longer than the critical required amount at a particular temperature have no further influence in changing the vitrinite reflectance value beyond the scatter from the initial R, and well temperature measurements. Therefore, they postulated that vitrinite reflectance is an excellent indicator of maximum temperature exposure in cases where Ro values and downhole temperature measurements of both the sample and the calibration data sets are well constrained.

Sweeney and Burnham (1990 and references cited) have developed a method for calculating vitrinite reflectance values which they show to be applicable to a variety of geologic systems, including the hydrothermal systems discussed by Barker (1983; 1991). They conclude that temperature is generally more important than time, but that both have an influence and that time is particularly important in cases with short heating times.

The maximum temperature exposures for the Leg 139 samples were estimated using calibration data of Barker (1983), Barker and Pawlewicz (1986) and Sweeney and Burnham (1990) and are compared to the Leg 139 present-day temperature measurements in Table 2. In all cases, except for that utilizing the very high heating rate

(10°C/yr) from Sweeney and Burnham (1990) the estimated past maximum temperatures are close to the estimated present-day values. The two sets of values from Barker utilize very different kerogen types. Barker (1983) uses data from several liquid-dominated hydrothermal systems with both Ro and temperature measurements coming from Barker's laboratory; Barker and Pawlewicz (1986) develop the R_o/temperature correlation from a data set with much more scatter, which includes a wide variety of literature data on humic kerogens covering many wells and heating rates. The latter calibration set gives an excellent match to the present-day temperatures estimated for the Leg 139 samples in spite of the considerable scatter in the Barker and Pawlewicz (1986) plot due to the measurements being collected from many different laboratories. Using the Barker (1983) and Barker and Pawlewicz (1986) calibrations, maximum temperature exposures of Samples 855A-1R-2, 141-144 cm (2.91 m), 856A-2H-4, 86-101 cm (8.06 m), and 856A-13X-2, 143-149 cm (108.23 m), where downhole temperature information is not available, can be estimated to have been 40°C, 70°C, and >280°C, respectively.

Data of Sweeney and Burnham (1990) do not give as good a match to present-day temperatures. In particular, maximum temperatures calculated for the 46 to 88 m intervals of Holes 857A and 857C using the higher heating rates (1°C/1000 yr, and 10°C/yr) are considerably higher than present-day measured values. In addition, the highest heating rate calibration curve of Sweeney and Burnham gives maximum temperatures that appear to be too high for the immature Hole 857A surface samples. Of the three different heating rates from Sweeney and Burnham (1990) used in Table 2, the slowest of 5°C/m.y. reproduces the present-day Leg 139 temperatures best for all except the deepest and hottest Leg 139 samples. However, on the basis of data in Davis and Wang (this volume) and Davis, Mottl, Fisher, et al. (1992), the Sweeney and Burnham (1990) curve for the more rapid heating rates of at least 1°C/1000 m are closer to the actual average geothermal gradient of about 2.24°C/1000 m measured for Hole 857C, suggesting that in the past, several intervals have been hotter than they are at the present time.

None of the sediments examined in this work, with the possible exception of those at Site 856, were older than Pleistocene, so that heating times are short on a geologic time scale. Davis and Wang (this volume) estimate that Site 857 sediments were heated at close to their current temperature maximum of 280°C for most of the past 125,000 yr, giving a heating rate at this site of 2.24°C/1000 yr. In the active shallower hydrothermal system at Site 858, maximum temperature is estimated to be about the same as deeper values for Site 857, except that hydrothermal fluids are currently penetrating very close to the ocean floor so that heating times for some intervals are probably very short, perhaps less than 10 years.

Maximum temperatures were also estimated from data in Bostick (1971), but appear to be too low in comparison with present-day measurements (Table 3).

Humic kerogen and hydrothermal well data have been used to replicate present-day temperatures of Leg 139 samples, as shown in Table 2. The excellent match suggests why the temperature estimates using the Leg 41 kerogen Ro and f'a values of Dennis et al. (1982) are probably too high. Part of the problem may be discrepancies in heating rates, with the Leg 41 kerogens being heated much more rapidly by an igneous intrusion, compared with the Leg 139 samples, which were heated more slowly by the underlying hydrothermal system. In addition, maturation rates of the very different kerogen types are being compared. Leg 41 kerogens typically are sapropelic and organic rich; Leg 139 sediments contain lower amounts of typically more oxidized type III kerogens (Mao et al., this volume). For the NMR data, this means that the initial starting NMR f'a value for the Leg 41 values is much lower than for Leg 139 samples (0.2 compared to 0.5). Also, the hydrogen-rich liptinitic nature of the Leg 41 samples may be suppressing and artificially lowering their vitrinite reflectance values (Walker et al., 1983). Similar suppression would not be expected for the less hydrogen-rich Leg 139 Ro values, so that using Leg 41 as a calibration



Figure 9. Schematic diagram showing how calibration line of R_o vs. temperature using suppressed vitrinite values (e.g., sapropelic kerogens such as those from Leg 41) would cause overestimates of maximum well temperatures when applied to nonsuppressed (i.e., more humic) kerogens, such as those recovered on Leg 139.

set could produce artificially high calculated maximum temperatures for Leg 139 kerogens, as shown in Figure 9.

CONCLUSIONS

1. At Site 857, a progressive increase in maturity with depth to 379 m is reflected by increasing ¹³C NMR aromaticity values (f'a) along with an increase in %R_o and downhole temperature. Shallow samples from 4 to 90 m show typically immature f'a values of 0.5 to 0.64 while Sample 857C-41R-3, 66–71 cm at 378.56 m has a typical high maturity f'a value of 0.91. A large increase in f'a occurs between 200 and 379 m, consistent with the postulated past hydrothermal flow through this section.

2. At Site 858, only high maturity f'a values (>0.9) occurred below 150 m in Hole 858A, consistent with the high vitrinite reflectance values (>1.5) in the same interval. High f'a values are also observed for shallow sections (<50 mbsf) of Holes 858B, 858D, and 858C, consistent with active hydrothermal flow in these holes.

3. NMR f'a values correlate reasonably well with vitrinite reflectance values and the Leg 139 points lie fairly close to the correlation line previously defined for basaltic intrusions into Cretaceous sapropelic organic-rich South Atlantic sediments recovered on DSDP Leg 41. However, maximum temperatures estimated for Leg 139 samples using the Leg 41 temperature/f'a/R_o data as a calibration are much higher than present-day temperatures and seem geologically unreasonable. We postulate that the problem arises from the very different kerogen types present in organic-lean sediments from Leg 139 vs. organic-rich sapropelic sediments present at Leg 41 in the Southeast Atlantic. A second problem may be introduced by using laboratory heating experiments as a calibration for estimating maximum geologic temperatures, even for hydrothermal systems where geologic heating times are relatively short.

4. Other R_o vs. maximum temperature calibration sets of Barker (1983), Barker and Pawlewicz (1986) and Sweeney and Burnham (1990) provide estimates of maximum heating of the Leg 139 samples: for Hole 857C, less than 30°C at depths shallower than 47 m; 200° to 225°C at 378 m; and 256° to >270°C at 433 m. These values closely match present-day downhole measured temperatures of <30°C, 210° to 225°C, and 260°C, respectively. Maximum temperature exposures for other Leg 139 samples for which downhole measurements were not available were estimated to be in the range of <20° to 40°C for 855C-1R-2 at 2.91 m; <20° to 70°C for 856A-2H-4 at 8.06 m; and 261° to >280°C for Sample 856A-13X-2 at 108.23 m.

5. TG-FTIR profiles for several Middle Valley rocks were characterized by two distinct temperature maxima for maximum evolution of ammonia, TmaxNH3(1) and TmaxNH3(2). In some cases, the two peaks overlapped to produce a single well-defined peak. We postulate that the low-temperature peak reflects NH3 derived predominantly from organic matter, while the second peak may reflect the presence of a more thermally resistant pool of N, possibly associated with inorganic phases, as well as associated organic matter. Both TmaxNH3 values showed a general increase with increasing thermal maturity and maximum temperature exposure. Simultaneously, the total wt% of ammonia in the rocks decreased. We postulate that scatter in the TmaxNH3 trends is caused by changes in the mineral matrix. Specifically, the presence of an increasing proportion of more thermally stable minerals might explain the maxima in T_{max}NH₃(2) profiles observed from 200 to 300 mbsf in Hole 857C, a zone influenced by lateral hydrothermal flow.

6. For Hole 857C, T_{max} for NH₃ increases from 575°C at 154.6 m to 652°C at 433.0 m, consistent with a substantial increase in thermal maturity within this interval, as is also reflected in both the vitrinite reflectance and ¹³C NMR f'a values. Hole 858C shows a similar trend for T_{max} NH₃(1), but with the gradient increasing much more steeply. One measurement was also obtained from near the bottom of Hole 858A, showing a high T_{max} NH₃ value, consistent with the high maturities registered by %R_o and f'a values.

7. The wt% of nitrogen in the sediments as measured by elemental analyses shows an excellent correlation with weight lost as NH_3 as measured by TG-FTIR. Comparison of the TG-FTIR and elemental analysis data suggests that most of the nitrogen in these sediments is present as reduced nitrogen (i.e., as ammonia or ammonium or as organic amino groups), and is increasingly incorporated into kerogen heterocyclic compounds or the mineral matrix at higher maturities.

8. T_{max} for CH₄ from whole rocks did not vary systematically with maturation, although there does appear to be a general increase with R_o at higher maturities (R_o>1%). No longer-chain hydrocarbons ("tars") were observed during pyrolysis of these relatively organic lean-rock samples (TOC generally <0.5 to 1%).

9. We postulate that the low abundance of aliphatic relative to aromatic carbon atoms in kerogens isolated from geothermally cold Hole 855C is caused by the flow of cold recharging oxygenated seawater into this section, which causes preferential biodegradation of aliphatic parts of the kerogen by aerobic bacteria.

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