

Data report: elemental, isotopic, and Rock-Eval compositions of bulk sediments from Hole U1357A in the Adélie Basin, Antarctica¹

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Abstract

We examined the elemental (total nitrogen, total organic carbon, and C/N), isotopic ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{org}}$), and Rock-Eval pyrolysis (S_2 , S_3 , hydrogen index, oxygen index, and T_{max}) compositions of bulk marine sediments from Hole U1357A in the Adélie Basin, Antarctica, to assess the organic geochemical characteristics and vertical variations in the late Holocene diatomaceous-dominated sediments. Pyrolysis parameters indicate that most of the organic materials are immature and in the Type II stage, indicative of a marine source. In contrast, the results from a conventional cross-plot of $\delta^{13}\text{C}_{\text{org}}$ vs. total organic carbon/total nitrogen indicate organic materials that originated as freshwater organic carbon, not marine organic carbon. Given that ^{13}C -depleted phytoplankton are dominant in diatomaceous ooze-rich sediments of the Adélie Basin, the apparent dominance of freshwater organic matter is likely attributable to the extremely low $\delta^{13}\text{C}_{\text{org}}$ (‰) values in the bulk sediments.

Introduction

Operations in Expedition 318 Hole U1357A in the Adélie Basin, located on the Antarctic continental shelf off the Wilkes Land margin, led to the recovery of a long core of Holocene diatomaceous ooze-dominated sediment. The aim of this expedition was to develop the first annually resolved time series of Holocene oceanographic and climatic variability (see the “Expedition 318 summary” chapter [Expedition 318 Scientists, 2011]). Reconstruction of coastal environmental change in the Holocene has traditionally been achieved using a combination of biological and physical indicators (e.g., pollen, diatoms, foraminifers, and sediment grain size). In addition to these traditional indicators in Holocene sediments, organic geochemical proxies such as total organic carbon (TOC), C/N, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{15}\text{N}_{\text{org}}$ have also been used to reconstruct oceanographic processes and to understand the origin of the organic materials in these sediments (Lamb et al., 2006; Jacot Des Combes et al., 2008). Rock-Eval pyrolysis is the most basic organic geochemical analysis of sedimentary organic matter, providing valuable parameters, including S_1 , S_2 , and S_3 peaks, hydrogen index (HI), oxygen index (OI), and T_{max} to aid discrimination of the type and maturity of the organic matter. Here, we report several results from organic geochemical analyses

¹Kong, G.S., and Dunbar, R.B., 2014. Data report: elemental, isotopic, and Rock-Eval compositions of bulk sediments from Hole U1357A in the Adélie Basin, Antarctica. In Escutia, C., Brinkhuis, H., Klaus, A., and the Expedition 318 Scientists, *Proc. IODP, 318*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.318.201.2014

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of the diatomaceous ooze sampled from the Adélie Basin that are vital for understanding the characteristics of the organic matter and identifying the decadal changes in surface productivity during the late Holocene.

Methods

A total of 276 geochemical samples were collected from Hole U1357A at 20 cm intervals. The depth of the sampled cores ranges from 0 to 54.35 m. After being freeze-dried for 48 h, all samples were powdered and homogenized using a ball mill. Rock-Eval pyrolysis was performed on powdered bulk samples using the Rock-Eval VI instrument to obtain several valuable indicators, including S_1 , S_2 , HI, OI, and T_{max} . The Rock-Eval pyrolysis method consists of a programmed heating cycle of a small sample (~100 mg) in an inert atmosphere (helium). The pyrolysis oven temperature program was as follows. For 3 min, the oven is kept isothermally at 300°C and the free hydrocarbons are volatilized and measured as the S_1 peak (detected by flame ionization detector [FID]). The temperature is then increased from 300° to 550°C (at 25°C/min). This is the phase of volatilization of very heavy hydrocarbons compounds (> C_{40}) and cracking of nonvolatile organic matter. The hydrocarbons released from this thermal cracking are measured as the S_2 peak (by FID). The temperature at which S_2 reaches its maximum depends on the nature and maturity of the kerogen and is called T_{max} . The CO_2 emitted from the cracking of kerogen is trapped in the temperature range 300°–390°C. The trap is heated, and CO_2 is released and detected by a thermal conductivity detector (TCD) during the cooling of the pyrolysis oven, giving the S_3 peak (Pimmel and Claypool, 2001). When these components are normalized to the TOC content, the S_2 peak gives the HI ($S_2 \times 100/TOC$) and S_3 gives the OI ($S_3 \times 100/TOC$) (Tissot and Welte, 1984; Peters, 1986).

Residual powdered bulk samples were subsampled to make carbonate-free samples. They were treated with 3 N HCl, diluted to pH 7, dried, and powdered again to remove carbonates. TOC, total nitrogen (TN), and stable isotopes of carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N_{org}$) in the organic matter were determined using a continuous-flow stable isotope ratio mass spectrometer (IRMS; IsoPrime-EA, Micromass, UK) linked with a CN analyzer (NA Series 2, CE Instruments, Italy) at Seoul National University (Korea). Carbon and nitrogen isotopic compositions ($\delta^{13}C_{org}$ and $\delta^{15}N_{org}$) were calculated using the relation

$$\delta^{13}C_{org} \text{ or } \delta^{15}N_{org} (\text{‰}) = [(R_{sample}/R_{standard}) - 1] \times 1000,$$

where R is the ratio of $^{13}C/^{12}C$ or $^{15}N/^{14}N$, with a Pee Dee belemnite (PDB) standard for carbon and an atmospheric N_2 standard for nitrogen. Precision of $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ measurements was checked against reference materials procured from the International Atomic Energy Agency. For $\delta^{13}C_{org}$ (RM 8542: Glucose ANU, $-10.47\text{‰} \pm 0.13\text{‰}$) and $\delta^{15}N_{org}$ (RM 8548: IAEA-N2 $+20.3\text{‰} \pm 0.2\text{‰}$), uncertainties in the measurements were less than 0.1‰ and 0.2‰, respectively.

Results

The TOC content measured from the Rock-Eval pyrolysis ranges from 1.20 to 2.16 wt% with an average of 1.67 wt%, whereas the TOC content from the IRMS ranges from 1.06 to 1.86 wt% with an average of 1.44 wt%. The vertical discrepancy in the TOC contents between these two methods is on average 0.22 wt%, yet both TOC values are higher than those reported from other regions in the Antarctic Peninsula (Khim et al., 2002). TOC contents usually depend on sediment grain size in marine environments, with a negative correlation between TOC and mean grain size. The TN content varies between 0.16 and 0.35 wt%, with the lowest values observed at a depth of 20.94 meters below seafloor (mbsf). TN contents vertically covary with TOC contents, except at 17–21 and 45–50 mbsf. C/N ratios range from 4.70 to 9.36, with an average value of 6.62 (Table T1; Fig. F1). C/N ratios <10 generally represent the marine environment, whereas values >15 indicate a freshwater environment (Stein et al., 1994). Crosta and Shemesh (2002) report that the C/N ratio of diatom-bound organic matter varies between 3 and 11 in the Southern Ocean.

The $\delta^{13}C_{org}$ ratio varies from -28.33‰ to -21.81‰ , with an average of -26.23‰ . Values display an overall constant vertical trend, except for a distinct excursion in the uppermost part of the core. The vertical variation in the $\delta^{13}C_{org}$ ratio is similar to that seen in Core JPC17B from the Adélie Drift (average = 26.6‰ ; Costa et al., 2007). The $\delta^{13}C_{org}$ value is also used as a common proxy for the origin of organic matter. If measured $\delta^{13}C_{org}$ values lie in the range -24‰ to -27‰ , they indicate a dominance of terrigenous organic matter in the sediment. In contrast, if the values are less than -24‰ , the organic matter is thought to be derived from the marine environment (Ruttenberg and Goñi, 1997). The $\delta^{15}N_{org}$ ratio ranges from 2.44‰ to 12.37‰, exhibiting a gradual upcore

decrease in value with the lowest value occurring at the core top (Table T1; Fig. F1). In general, the $\delta^{15}\text{N}_{\text{org}}$ ratio of terrigenous organic matter ranges widely from -5‰ to 18‰ , with an average of 3‰ , and the C/N ratio of marine organic matter varies from 7 to 10 (Peters et al., 1978; Schoeninger and DeNiro, 1984). In addition, a vertical change in $\delta^{15}\text{N}_{\text{org}}$ is related to consumption of nutrient nitrate (Jacot Des Combes et al., 2008).

Of the pyrolysis parameters measured during this analysis, S_2 values varies between 2.75 and 6.98 mg hydrocarbon (HC)/g rock, with an average of 4.53 mg HC/g rock, whereas S_3 values range from 1.48 to 4.99 mg CO_2 /g rock, with an average of 2.43 mg CO_2 /g rock. S_2 values increase slightly upcore. HI and OI values are 232–440 mg HC/g TOC and 100–299 mg CO_2 /TOC, respectively. The vertical variation of HI is negatively correlated with the OI along the entire sample depth. High HI values are dominant shallower than 12.34 mbsf after an abrupt decrease in values between 16.37 and 12.34 mbsf (Table T1; Fig. F1). A HI value of <100 mg HC/g TOC in marine sediment implies that the TOC is mainly made up of terrigenous organic matter, whereas a HI value between 200 and 400 mg HC/g TOC indicates marine organic matter (Tissot and Welte, 1984). T_{max} values were observed to be between 384° and 429°C along the entire sampled depth. T_{max} provides an estimate of the organic matter thermal maturity, with values $<435^\circ\text{C}$ indicative of immaturity, relative to that of the petroleum generation process (Espitalié et al., 1977; Peters, 1986). Thus, the measured values indicate that most of the organic matter is thermally immature (Table T1).

Correlations of the pyrolysis parameters (HI, OI, S_2 , and TOC) measured from the Rock-Eval pyrolysis give useful information that can help to elucidate the origin of the organic matter (Type I, Type II, or Type III) through a modified van Krevelen diagram (HI vs. OI) and cross-plot (S_2 vs. TOC). Here, Type I is indicative of organic matter with a lacustrine origin, Type II represents the dominance of marine organic matter, and Type III indicates organic matter with a terrigenous origin (Espitalié et al., 1985). As shown in the modified van Krevelen diagram (Fig. F2A), most of the 276 sample points plot in the Type II area, except for some excursions to Type I, implying that the organic matter primarily originated from a marine source, likely attributed to the surface primary productivity.

Cross-plots of S_2 vs. TOC show that S_2 values are strongly correlated with TOC values ($r^2 > 0.98$), having an inclination of 3.13 (Fig. F2B). This means that

the organic matter contains $>30\%$ hydrocarbon that can undergo pyrolysis. It also shows that the high organic carbon content, ranging from 1 to 2 wt%, belongs to Type II, as shown in the van Krevelen diagram.

In the coastal environment where organic matter sources are mixed, typical ranges of $\delta^{13}\text{C}_{\text{org}}$ values and the C/N ratios can be used to classify the sources of organic matter. Terrestrial plants (C3) using the Calvin photosynthetic pathway have $\delta^{13}\text{C}_{\text{org}}$ values between -32‰ and -21‰ , whereas C4 plants utilizing the Hatch-Slack photosynthetic pathway have $\delta^{13}\text{C}_{\text{org}}$ values ranging from -17‰ to -9‰ (Deines, 1980). Terrestrial vegetation normally has C/N ratios >12 (Prahl et al., 1980). The $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios for marine particulate organic carbon (POC) are limited to -24‰ to -18‰ and 5 to 10, respectively, whereas the $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios for freshwater POC vary from -33‰ to -25‰ and 4 to 10, respectively (Lamb et al., 2006).

As shown in Figure F3, most of the data points measured from Hole U1357A were classified as freshwater algae. The results seem to indicate that the organic matter is strongly affected by freshwater algae rather than marine algae. However, the extremely low $\delta^{13}\text{C}_{\text{org}}$ values observed here are related to a general ^{13}C depletion in phytoplankton in Southern Ocean surface waters. It is also known that $\delta^{13}\text{C}_{\text{org}}$ values across the Antarctic and Southern Ocean can range from -25‰ to 30‰ (Gibson et al., 1999).

Acknowledgments

This study used samples provided by the Integrated Ocean Drilling Program (IODP) and was supported by the study on Korea Integrated Ocean Drilling Program of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Land, Transport and Maritime Affairs of Korea.

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Initial receipt: 28 February 2013

Acceptance: 24 July 2014

Publication: 14 October 2014

MS 318-201

Figure F1. Variations in the Rock-Eval pyrolysis, elemental analysis, and stable isotopes plotted against core depth, Hole U1357A. R = rock, HI = hydrogen index, TOC = total organic carbon, OI = oxygen index, TC = total carbon, TN = total nitrogen.

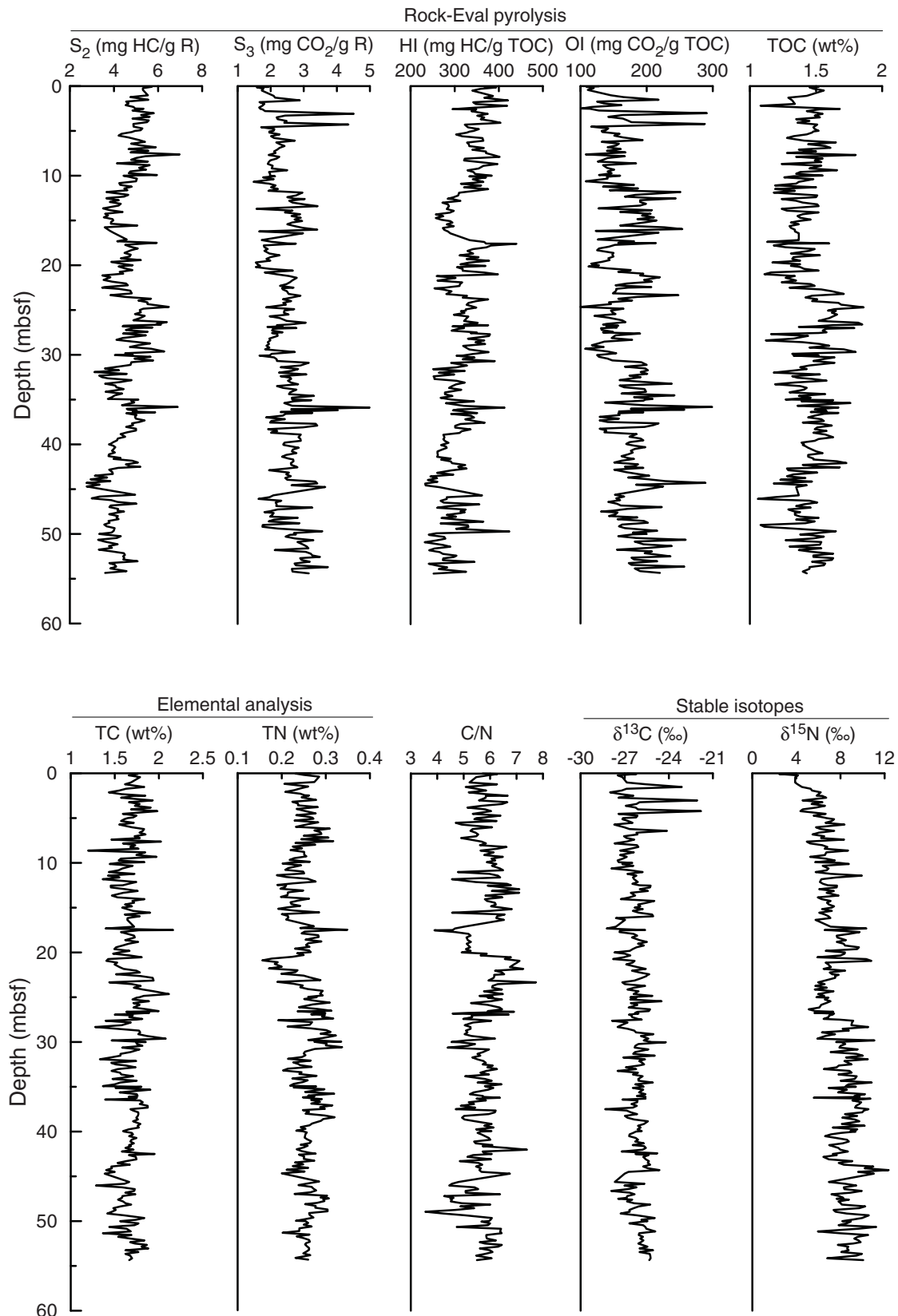


Figure F2. Pyrolysis parameters, Hole U1357A. **A.** Modified van Krevelen-type diagram. **B.** Cross-plot for S_2 vs. TOC. HI = hydrogen index, TOC = total organic carbon, R = rock.

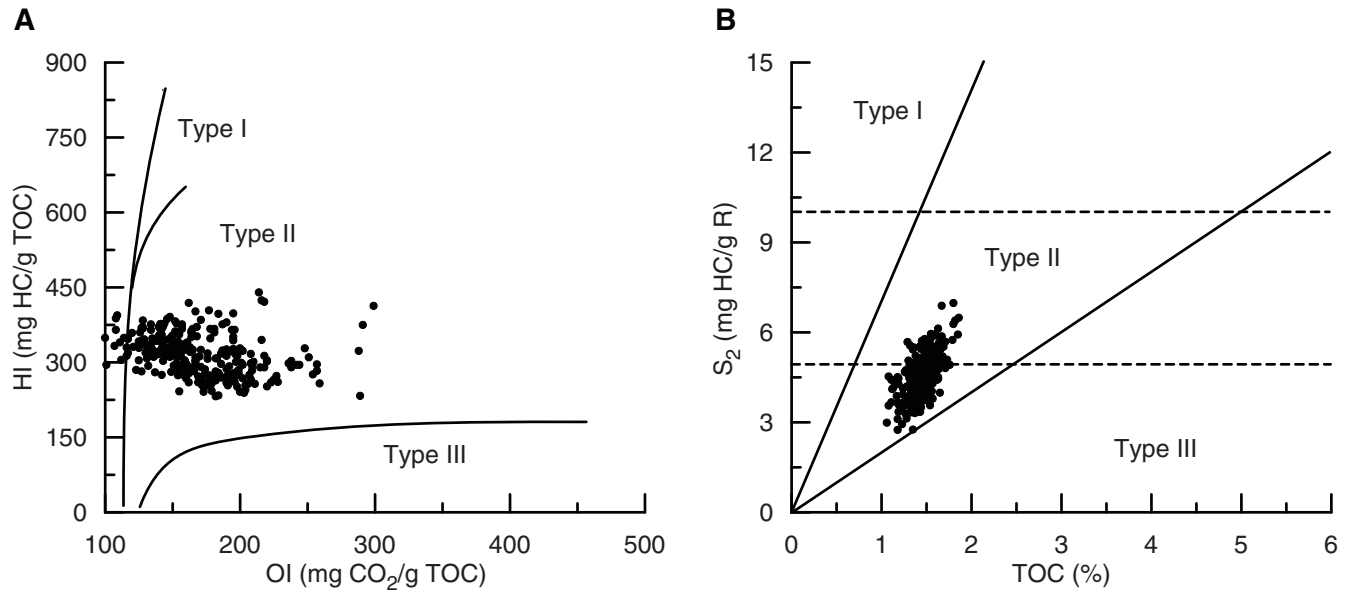


Figure F3. Correlation between $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios (after Lamb et al., 2006). POC = particulate organic carbon.

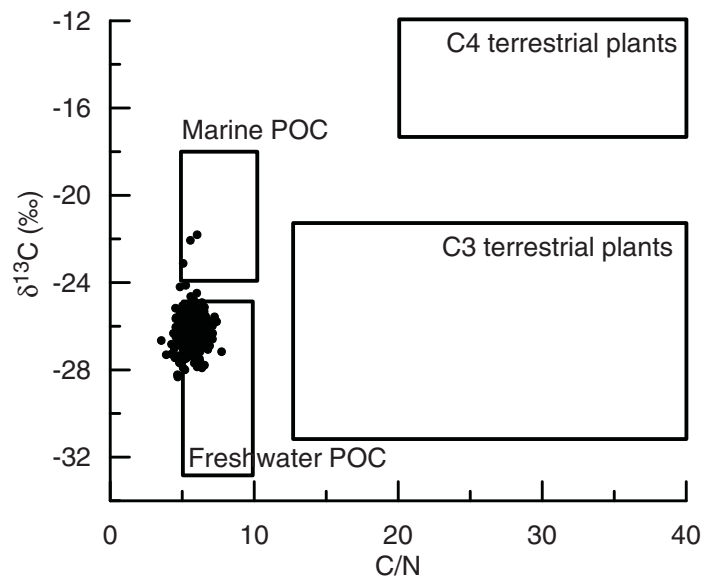


Table T1. Organic geochemical compositions of bulk sediments, Hole U1357A. (Continued on next four pages.)

Core, section, interval (cm)	Depth (mbsf)	Rock-Eval pyrolysis						Major elements			Isotopes	
		S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (wt%)	TOC (wt%)	TN (wt%)	C/N ratio	δ ¹³ C (‰)	δ ¹⁵ N (‰)
318-U1357A-												
1H, 1-2	0.035	5.59	1.94	410	368	128	1.52	1.76	0.27	6.62	-26.84	3.97
1H, 1-6	0.075	5.72	1.58	411	394	109	1.45	1.76	0.23	7.61	-26.21	2.44
1H, 1-22	0.23	5.31	1.78	408	359	120	1.48	1.66	0.25	6.64	-27.48	4.15
1H, 1-42	0.43	5.31	1.73	397	340	111	1.56	1.79	0.29	6.27	-27.16	3.89
1H, 1 102	1.03	5.54	2.09	408	387	146	1.43	1.68	0.27	6.14	-26.86	3.88
1H, 1 122	1.23	4.74	2.13	411	367	165	1.29	1.62	0.21	7.84	-25.56	4.11
1H, 2-2	1.53	5.56	2.88	425	421	218	1.32	1.83	0.26	7.05	-23.12	4.50
1H, 2-22	1.73	4.55	1.66	395	342	125	1.33	1.63	0.24	6.70	-26.88	5.30
1H, 2-42	1.93	4.66	1.81	396	348	135	1.34	1.55	0.23	6.76	-27.21	5.42
1H, 2-62	2.13	4.53	1.75	392	419	162	1.08	1.43	0.21	6.89	-28.00	6.21
1H, 2-82	2.33	4.89	1.65	394	347	117	1.41	1.58	0.24	6.51	-27.25	6.01
1H, 2-99	2.5	4.95	1.69	424	295	101	1.68	1.85	0.25	7.33	-26.41	5.84
1H, 2 102	2.53	5.34	1.75	395	349	114	1.53	1.72	0.26	6.55	-26.66	6.34
1H, 2 122	2.73	4.84	1.83	393	338	128	1.43	1.57	0.25	6.41	-27.43	6.71
1H, 3-2	3.03	5.81	4.51	424	375	291	1.55	1.93	0.28	6.94	-22.07	4.56
1H, 3-22	3.23	5.23	2.44	392	351	164	1.49	1.66	0.22	7.42	-25.99	6.36
1H, 3-42	3.43	5.62	2.18	392	367	142	1.53	1.78	0.24	7.52	-26.20	5.38
1H, 3-62	3.63	4.84	2.21	397	359	164	1.35	1.73	0.24	7.29	-26.93	6.60
1H, 3-82	3.83	5.58	2.48	419	385	171	1.45	1.91	0.28	6.77	-26.26	5.77
1H, 3 102	4.03	5.50	2.41	425	404	177	1.36	1.68	0.23	7.20	-26.10	4.58
1H, 3 122	4.23	4.88	4.35	424	323	288	1.51	1.98	0.25	7.94	-21.81	4.36
1H, 4-2	4.53	4.89	1.71	397	330	116	1.48	1.59	0.28	5.74	-27.43	6.66
1H, 4-22	4.73	5.29	2.11	391	355	142	1.49	1.75	0.23	7.49	-26.13	5.56
1H, 4-42	4.93	5.21	2.09	392	343	138	1.52	1.71	0.26	6.50	-26.22	6.48
1H, 4-50	5.01	4.95	1.96	399	334	132	1.48	1.65	0.27	6.10	-27.12	6.73
1H, 4-62	5.13	4.81	1.96	391	327	133	1.47	1.61	0.27	5.91	-27.16	7.42
1H, 4-82	5.33	4.34	2.27	390	303	159	1.43	1.57	0.23	6.86	-26.77	7.22
1H, 4 102	5.53	4.21	2.01	394	317	151	1.33	1.72	0.28	6.06	-26.47	6.64
1H, 4 122	5.73	4.65	2.10	394	363	164	1.28	1.55	0.26	5.96	-27.72	8.37
1H, 5-2	6.03	5.15	2.73	400	365	194	1.41	1.70	0.23	7.31	-27.04	5.77
1H, 5-22	6.23	5.41	2.17	395	328	132	1.65	1.83	0.31	5.93	-26.67	6.19
1H, 5-42	6.43	4.78	2.28	407	332	158	1.44	1.82	0.27	6.64	-24.13	7.43
1H, 5-62	6.63	5.23	2.42	396	333	154	1.57	1.78	0.29	6.18	-26.21	6.04
1H, 5-82	6.83	5.90	2.27	390	366	141	1.61	1.85	0.29	6.38	-26.13	5.46
1H, 5 102	7.03	4.66	2.20	388	340	161	1.37	1.73	0.25	6.90	-27.05	6.53
1H, 5 122	7.23	5.56	2.10	388	371	140	1.5	1.78	0.31	5.83	-26.87	6.23
1H, 5 140	7.41	4.75	2.15	384	371	168	1.28	1.46	0.24	5.99	-26.35	8.33
2H, 1-2	7.63	6.98	1.94	400	388	108	1.8	2.03	0.32	6.39	-26.89	4.94
2H, 1-22	7.83	5.43	2.26	395	402	167	1.35	1.59	0.23	6.89	-27.69	5.24
2H, 1-42	8.03	5.00	2.18	398	323	141	1.55	1.73	0.28	6.28	-26.16	6.35
2H, 1-62	8.23	4.78	1.99	394	321	134	1.49	1.68	0.23	7.44	-26.07	6.81
2H, 1-82	8.43	5.54	1.94	395	360	126	1.54	1.77	0.25	7.19	-26.62	6.57
2H, 1 102	8.63	4.13	1.91	390	397	184	1.24	1.20	0.22	5.45	-27.31	8.69
2H, 1 122	8.83	5.62	2.06	395	365	134	1.54	1.85	0.25	7.35	-26.38	6.71
2H, 2-2	9.13	5.14	2.03	395	354	140	1.45	1.75	0.25	6.95	-27.32	6.60
2H, 2-22	9.33	5.46	2.50	395	329	151	1.66	1.97	0.26	7.71	-26.86	5.25
2H, 2-42	9.53	4.74	1.95	393	343	141	1.38	1.57	0.23	6.89	-27.12	6.64
2H, 2-62	9.73	4.67	1.98	398	346	147	1.35	1.54	0.22	7.08	-27.49	7.49
2H, 2-82	9.93	5.95	1.98	395	384	128	1.55	1.84	0.26	6.96	-27.41	5.70
2H, 2-90	10.01	4.43	2.13	388	333	160	1.33	1.54	0.22	6.95	-26.49	7.91
2H, 2-102	10.13	4.68	1.77	391	371	140	1.26	1.44	0.20	7.14	-27.17	8.76
2H, 2-122	10.33	5.04	2.09	391	341	141	1.48	1.70	0.24	6.98	-26.41	6.38
2H, 3-2	10.63	5.00	1.48	407	365	108	1.37	1.59	0.22	7.38	-27.91	6.92
2H, 3-22	10.83	4.24	1.95	391	314	144	1.35	1.54	0.21	7.42	-26.61	6.75
2H, 3-42	11.03	4.28	2.15	398	360	181	1.19	1.43	0.25	5.75	-25.78	5.74
2H, 3-62	11.23	4.81	2.01	413	321	134	1.5	1.72	0.25	6.86	-26.82	7.14
2H, 3-82	11.43	4.47	2.22	395	376	187	1.19	1.42	0.19	7.52	-26.21	9.94
2H, 3-102	11.63	4.61	1.93	414	344	144	1.34	1.55	0.21	7.40	-26.44	7.62
2H, 3-122	11.83	3.66	2.96	392	310	251	1.18	1.36	0.26	5.26	-26.36	6.26
2H, 4-2	12.14	4.65	2.77	411	308	183	1.51	1.74	0.28	6.30	-26.11	6.13
2H, 4-22	12.34	4.46	2.50	409	297	167	1.5	1.66	0.23	7.32	-26.48	6.41
2H, 4-39	12.51	3.66	2.70	413	284	209	1.29	1.59	0.19	8.37	-26.00	6.85
2H, 4-42	12.54	3.66	3.03	393	295	244	1.24	1.45	0.21	6.92	-25.24	7.69
2H, 4-62	12.74	4.22	2.56	411	313	190	1.35	1.46	0.21	7.00	-25.28	7.65

Table T1 continued. (Continued on next page.)

Core, section, interval (cm)	Depth (mbsf)	Rock-Eval pyrolysis						Major elements			Isotopes	
		S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (wt%)	TOC (wt%)	TN (wt%)	C/N ratio	δ ¹³ C (‰)	δ ¹⁵ N (‰)
2H, 4-82	12.94	3.81	2.66	420	272	190	1.4	1.62	0.20	8.23	-25.98	6.07
2H, 4-102	13.14	4.31	3.01	395	285	199	1.51	1.76	0.25	7.07	-25.42	7.40
2H, 4-122	13.34	4.21	3.42	411	287	190	1.52	1.60	0.21	7.47	-26.59	6.74
2H, 5-2	13.65	3.50	1.57	425	282	127	1.24	1.47	0.21	6.89	-26.29	7.83
2H, 5-22	13.85	3.81	2.66	407	298	208	1.28	1.53	0.20	7.74	-26.67	5.94
2H, 5-42	14.05	4.39	2.43	414	289	160	1.52	1.84	0.26	7.01	-27.27	6.28
2H, 5-62	14.25	3.60	2.89	423	257	206	1.4	1.70	0.24	7.14	-24.99	7.11
2H, 5-82	14.45	3.73	2.63	419	274	193	1.36	1.72	0.22	7.82	-25.50	6.77
2H, 5-102	14.65	3.54	2.91	406	257	211	1.38	1.62	0.22	7.27	-26.09	6.95
2H, 5-122	14.85	3.94	2.72	419	270	186	1.46	1.70	0.24	7.01	-25.94	7.42
2H, 5-138	15.01	3.97	2.95	410	290	215	1.37	1.58	0.21	7.43	-26.33	7.20
2H, 6-2	15.17	3.87	2.65	419	295	202	1.31	1.64	0.19	8.54	-25.77	6.32
2H, 6-22	15.37	3.86	2.50	413	282	182	1.37	1.71	0.23	7.49	-26.45	7.22
2H, 6-42	15.57	5.06	2.72	409	298	160	1.3	1.90	0.29	6.67	-26.04	6.07
2H, 6-62	15.77	3.58	2.97	418	273	227	1.31	1.61	0.20	8.07	-25.13	6.58
2H, 6-82	15.97	3.70	3.41	422	276	254	1.34	1.78	0.21	8.33	-25.06	6.91
2H, 6-102	16.17	3.82	1.65	426	285	123	1.34	1.65	0.22	7.65	-27.60	7.09
2H, 6-122	16.37	3.97	2.98	401	290	218	1.37	1.64	0.21	7.82	-26.98	5.73
3H, 1-2	17.13	4.58	1.73	413	334	126	1.37	1.72	0.27	6.30	-27.60	7.11
3H, 1-22	17.33	4.15	2.04	386	367	181	1.13	1.40	0.24	5.77	-28.23	10.35
3H, 1-40	17.51	5.94	2.51	424	371	157	1.6	2.16	0.35	6.19	-25.61	6.56
3H, 1-42	17.53	5.68	2.76	393	440	214	1.29	1.77	0.33	5.36	-27.31	7.15
3H, 1-62	17.73	4.51	1.79	396	382	152	1.18	1.57	0.25	6.23	-27.36	9.74
3H, 1-82	17.93	4.73	1.81	392	372	143	1.27	1.64	0.25	6.71	-26.40	8.81
3H, 1-102	18.13	5.08	1.91	393	341	128	1.49	1.72	0.28	6.07	-26.15	7.65
3H, 1-122	18.33	4.77	1.81	408	329	125	1.45	1.73	0.28	6.08	-26.51	7.71
3H, 2-2	18.63	4.48	1.96	396	342	150	1.31	1.62	0.25	6.37	-25.99	8.50
3H, 2-22	18.83	4.76	2.27	420	311	148	1.53	1.77	0.29	6.09	-25.49	7.67
3H, 2-42	19.03	4.71	2.00	412	354	150	1.33	1.66	0.26	6.38	-26.10	8.28
3H, 2-62	19.23	4.31	1.87	390	327	142	1.32	1.59	0.26	6.23	-25.70	8.41
3H, 2-82	19.43	5.22	1.99	395	378	144	1.38	1.52	0.26	5.76	-26.20	9.68
3H, 2-102	19.63	3.88	1.55	409	332	132	1.17	1.50	0.23	6.50	-26.46	9.51
3H, 2-122	19.83	4.32	1.60	413	313	116	1.38	1.67	0.26	6.37	-26.66	6.66
3H, 2-140	20.01	4.85	1.68	391	370	128	1.31	1.55	0.27	5.82	-27.70	8.41
3H, 3-2	20.14	4.21	1.55	418	305	112	1.38	1.48	0.24	6.30	-27.00	8.38
3H, 3-22	20.34	4.48	1.97	408	318	140	1.41	1.67	0.25	6.69	-26.62	8.00
3H, 3-42	20.54	4.84	2.67	396	318	176	1.52	1.81	0.22	8.06	-27.07	5.90
3H, 3-62	20.74	4.26	1.82	386	367	157	1.16	1.43	0.18	8.05	-27.79	10.33
3H, 3-82	20.94	4.42	2.17	387	398	195	1.11	1.40	0.16	9.00	-26.33	10.81
3H, 3-102	21.14	3.47	2.55	409	259	190	1.34	1.53	0.19	8.00	-26.47	6.65
3H, 3-122	21.34	3.84	2.79	384	302	220	1.27	1.50	0.18	8.14	-26.90	6.89
3H, 4-2	21.64	3.53	2.65	425	261	196	1.35	1.55	0.20	7.77	-26.14	7.14
3H, 4-22	21.84	3.93	2.58	423	317	208	1.24	1.60	0.17	9.36	-25.57	6.47
3H, 4-42	22.04	4.55	2.48	386	312	170	1.46	1.75	0.24	7.40	-26.51	8.43
3H, 4-62	22.24	4.63	2.28	418	311	153	1.49	1.79	0.23	7.73	-25.99	7.02
3H, 4-82	22.44	3.57	2.69	409	275	207	1.3	1.51	0.20	7.61	-25.33	7.25
3H, 4-89	22.51	3.46	2.34	421	254	172	1.36	1.61	0.22	7.29	-25.46	7.84
3H, 4-102	22.64	4.22	2.37	422	274	154	1.54	1.80	0.25	7.18	-25.52	7.51
3H, 4-122	22.84	4.74	2.49	419	293	154	1.62	1.93	0.26	7.31	-25.82	7.52
3H, 5-2	23.14	4.81	2.54	417	281	149	1.71	1.94	0.29	6.74	-26.34	6.60
3H, 5-22	23.34	3.84	2.90	386	328	248	1.47	1.44	0.19	7.56	-27.17	5.97
3H, 5-42	23.54	4.52	2.64	392	318	186	1.42	1.70	0.23	7.51	-26.99	6.57
3H, 5-62	23.74	5.68	2.37	394	376	157	1.51	1.80	0.25	7.24	-25.61	5.71
3H, 5-82	23.94	5.11	2.62	415	348	178	1.47	1.72	0.24	7.09	-26.36	6.76
3H, 5-102	24.14	5.52	2.38	398	331	143	1.67	1.82	0.26	7.02	-26.82	5.66
3H, 5-122	24.34	5.52	2.46	421	327	146	1.69	1.94	0.29	6.63	-26.06	7.37
3H, 6-2	24.65	6.49	1.86	425	349	100	1.86	2.12	0.29	7.37	-26.40	5.97
3H, 6-22	24.85	5.33	2.71	417	325	165	1.64	1.83	0.29	6.24	-25.12	6.53
3H, 6-38	25.01	5.17	2.42	404	325	152	1.59	1.78	0.26	6.85	-26.62	5.82
3H, 6-42	25.05	5.18	2.41	419	314	146	1.65	1.75	0.28	6.26	-26.21	6.91
3H, 6-62	25.25	5.22	2.40	411	322	148	1.62	1.70	0.25	6.78	-26.63	6.58
3H, 6-82	25.45	4.95	2.54	423	298	153	1.66	1.89	0.28	6.84	-24.49	7.10
3H, 6-102	25.65	5.40	1.97	407	331	121	1.63	1.71	0.31	5.54	-26.59	6.70
3H, 6-122	25.85	5.23	2.28	418	327	142	1.6	1.78	0.27	6.58	-26.14	6.25
3H, 7-2	26.16	4.88	2.48	414	321	163	1.52	1.71	0.24	7.16	-26.73	6.09
3H, 7-22	26.36	6.40	3.06	393	352	168	1.82	1.87	0.28	6.62	-25.28	5.11
3H, 7-42	26.56	5.93	2.57	421	321	139	1.85	2.00	0.31	6.38	-25.36	5.73

Table T1 continued. (Continued on next page.)

Core, section, interval (cm)	Depth (mbsf)	Rock-Eval pyrolysis						Major elements			Isotopes	
		S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (wt%)	TOC (wt%)	TN (wt%)	C/N ratio	δ ¹³ C (‰)	δ ¹⁵ N (‰)
3H, 7-62	26.63	6.13	2.19	406	376	134	1.63	1.63	0.24	6.91	-26.13	7.35
3H, 7-82	26.76	4.43	2.36	420	295	157	1.5	1.89	0.29	6.52	-26.30	5.63
4H, 1-2	26.83	4.39	1.90	409	320	139	1.37	1.74	0.30	5.82	-26.06	7.42
4H, 1-22	26.96	5.75	2.78	393	321	155	1.79	1.50	0.27	5.62	-26.72	7.28
4H, 1-42	27.03	4.86	2.07	405	308	131	1.58	1.70	0.30	5.72	-26.55	6.98
4H, 1-62	27.23	4.54	2.04	409	293	132	1.55	1.66	0.29	5.72	-26.50	6.91
4H, 1-82	27.43	5.53	2.36	411	350	149	1.58	1.81	0.32	5.72	-26.10	6.47
4H, 1-90	27.51	5.11	2.04	416	336	134	1.52	1.75	0.28	6.30	-25.84	7.91
4H, 1-102	27.63	4.41	2.20	390	380	190	1.16	1.40	0.19	7.27	-27.87	9.16
4H, 1-122	27.83	5.45	2.21	387	378	153	1.44	1.68	0.27	6.25	-26.81	9.05
4H, 2-2	28.13	4.39	1.96	396	330	147	1.33	1.58	0.26	5.98	-27.24	8.99
4H, 2-22	28.33	4.11	1.99	388	367	178	1.12	1.28	0.21	6.00	-27.49	10.52
4H, 2-42	28.53	4.86	1.91	407	347	136	1.4	1.53	0.27	5.75	-26.80	8.19
4H, 2-62	28.73	5.64	1.95	393	369	127	1.53	1.78	0.30	5.90	-26.35	8.76
4H, 2-82	28.93	5.10	1.87	423	319	117	1.6	1.79	0.31	5.75	-26.24	6.31
4H, 2-102	29.13	4.72	1.96	421	326	135	1.45	1.77	0.29	6.14	-25.05	7.51
4H, 2-122	29.33	5.69	1.83	413	333	107	1.71	1.86	0.32	5.76	-25.90	6.63
4H, 3-2	29.63	6.28	2.73	410	377	141	1.8	2.08	0.29	7.14	-25.39	5.90
4H, 3-22	29.83	4.51	2.03	409	342	154	1.32	1.46	0.26	5.63	-25.71	11.08
4H, 3-40	30.01	4.85	1.97	424	319	130	1.52	1.85	0.34	5.53	-25.18	7.60
4H, 3-42	30.03	4.04	1.66	426	304	125	1.33	1.74	0.27	6.36	-24.20	8.10
4H, 3-62	30.23	5.66	2.10	414	345	128	1.64	1.75	0.30	5.79	-26.07	8.44
4H, 3-82	30.43	4.93	2.18	410	318	141	1.55	1.81	0.30	6.04	-26.28	8.01
4H, 3-102	30.63	5.78	2.19	412	391	148	1.48	1.58	0.34	4.70	-26.33	7.90
4H, 3-122	30.83	4.79	3.15	424	292	192	1.64	1.78	0.28	6.48	-25.39	9.57
4H, 4-2	31.13	4.75	2.90	411	328	200	1.45	1.68	0.25	6.63	-26.30	7.11
4H, 4-22	31.33	4.18	2.30	412	303	167	1.38	1.57	0.25	6.26	-26.43	9.46
4H, 4-42	31.53	3.59	2.83	424	251	198	1.43	1.56	0.25	6.16	-24.96	10.03
4H, 4-62	31.73	4.23	2.64	420	323	202	1.31	1.45	0.25	5.91	-27.10	8.50
4H, 4-82	31.93	3.11	2.25	424	264	191	1.18	1.33	0.21	6.22	-25.62	10.48
4H, 4-102	32.13	4.58	3.08	414	299	201	1.53	1.74	0.27	6.55	-26.02	8.36
4H, 4-122	32.33	3.33	2.30	424	252	174	1.32	1.46	0.23	6.46	-25.80	8.70
4H, 4-140	32.51	3.46	2.60	424	254	191	1.36	1.51	0.24	6.35	-25.68	9.01
4H, 5-2	32.63	3.73	2.62	416	254	178	1.47	1.63	0.24	6.75	-26.04	7.85
4H, 5-22	32.83	4.80	2.52	424	304	159	1.58	1.74	0.27	6.48	-26.92	7.65
4H, 5-42	33.03	4.33	2.61	427	323	195	1.34	1.53	0.21	7.17	-26.22	6.49
4H, 5-62	33.23	3.60	2.83	427	303	238	1.19	1.46	0.20	7.21	-27.49	8.82
4H, 5-82	33.43	4.06	2.19	425	294	159	1.38	1.56	0.25	6.37	-26.10	9.02
4H, 5-102	33.63	4.11	2.37	423	287	166	1.43	1.57	0.24	6.55	-26.44	7.82
4H, 5-122	33.83	4.44	2.78	423	315	197	1.41	1.71	0.28	6.13	-25.78	9.47
4H, 6-2	34.13	3.62	2.59	424	278	199	1.3	1.48	0.22	6.58	-26.08	9.29
4H, 6-22	34.33	4.37	2.55	423	278	162	1.57	1.75	0.26	6.75	-26.06	8.01
4H, 6-42	34.53	4.04	3.31	427	295	242	1.37	1.56	0.25	6.30	-25.09	10.84
4H, 6-62	34.73	3.91	2.64	424	268	181	1.46	1.50	0.23	6.61	-26.28	8.73
4H, 6-82	34.93	3.72	2.65	421	293	209	1.27	1.37	0.22	6.23	-25.76	8.48
4H, 6-90	35.01	5.11	3.23	424	313	198	1.63	1.80	0.28	6.48	-25.72	9.40
4H, 6-102	35.13	4.78	2.71	422	344	195	1.39	1.51	0.23	6.65	-26.45	6.92
4H, 6-122	35.33	4.92	2.41	427	280	137	1.76	1.90	0.30	6.41	-25.74	8.59
4H, 7-2	35.63	4.36	2.65	425	321	195	1.36	1.56	0.25	6.15	-26.03	7.78
4H, 7-22	35.83	6.89	4.99	420	413	299	1.67	1.75	0.32	5.49	-25.59	10.23
4H, 7-42	36.03	4.58	2.62	423	307	176	1.49	1.76	0.26	6.77	-26.18	9.28
4H, 7-62	36.13	4.64	4.03	423	296	257	1.57	1.66	0.27	6.05	-25.58	9.74
4H, 7-82	36.23	5.03	2.96	424	318	187	1.58	1.75	0.25	7.06	-25.65	5.57
5H, 1-2	36.33	4.85	2.30	409	332	158	1.46	1.72	0.27	6.48	-25.58	10.72
5H, 1-22	36.43	5.87	3.26	409	351	195	1.67	1.39	0.29	4.78	-27.16	9.69
5H, 1-42	36.53	4.56	2.45	422	292	157	1.56	1.79	0.27	6.69	-26.13	9.08
5H, 1-62	36.73	5.02	2.37	417	337	159	1.49	1.82	0.29	6.33	-26.15	9.88
5H, 1-82	36.93	4.95	1.86	412	344	129	1.44	1.78	0.27	6.68	-26.54	9.71
5H, 1-102	37.13	4.99	2.43	422	324	158	1.54	1.87	0.32	5.95	-26.18	9.41
5H, 1-122	37.33	5.39	2.02	424	346	129	1.56	1.88	0.29	6.53	-26.44	9.32
5H, 1-140	37.51	5.15	1.98	415	368	141	1.4	1.68	0.30	5.63	-28.33	10.54
5H, 2-2	37.65	4.82	3.36	425	313	218	1.54	1.71	0.25	6.88	-26.87	10.12
5H, 2-22	37.85	4.87	3.41	426	301	210	1.62	1.77	0.26	6.74	-26.59	9.98
5H, 2-42	38.05	4.55	2.97	426	301	197	1.51	1.77	0.25	6.96	-26.15	8.41
5H, 2-62	38.25	5.00	1.92	423	336	129	1.49	1.76	0.30	5.93	-26.99	9.51
5H, 2-82	38.45	5.00	2.20	414	316	139	1.58	1.74	0.32	5.45	-26.82	8.16
5H, 2-102	38.65	4.60	2.01	423	311	136	1.48	1.76	0.29	6.00	-26.36	9.30

Table T1 continued. (Continued on next page.)

Core, section, interval (cm)	Depth (mbsf)	Rock-Eval pyrolysis						Major elements			Isotopes	
		S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (wt%)	TOC (wt%)	TN (wt%)	C/N ratio	δ ¹³ C (‰)	δ ¹⁵ N (‰)
5H, 2-122	38.85	4.30	2.91	426	274	185	1.57	1.71	0.29	5.91	-25.42	9.72
5H, 3-2	39.15	4.51	2.84	420	277	174	1.63	1.79	0.27	6.66	-25.69	8.12
5H, 3-22	39.35	4.17	2.90	421	274	191	1.52	1.76	0.26	6.69	-26.10	10.20
5H, 3-42	39.55	4.14	2.91	421	278	195	1.49	1.77	0.24	7.30	-25.92	7.30
5H, 3-62	39.75	3.97	2.42	419	286	174	1.39	1.66	0.25	6.53	-26.13	9.52
5H, 3-82	39.95	3.84	2.38	424	272	169	1.41	1.59	0.23	6.84	-25.84	8.90
5H, 3-88	40.01	3.77	2.39	424	269	171	1.4	1.61	0.25	6.48	-26.24	9.37
5H, 3-102	40.15	3.97	2.59	424	280	182	1.42	1.69	0.26	6.59	-26.43	8.05
5H, 4-2	40.32	4.06	2.85	424	282	198	1.44	1.71	0.25	6.72	-26.67	7.13
5H, 4-22	40.52	3.99	2.67	422	271	182	1.47	1.66	0.25	6.57	-26.70	6.60
5H, 4-42	40.72	3.91	2.64	427	261	176	1.5	1.75	0.25	6.93	-26.25	7.60
5H, 4-62	40.92	4.04	2.78	425	261	179	1.55	1.69	0.26	6.55	-26.09	8.59
5H, 4-82	41.12	3.77	2.47	424	262	172	1.44	1.68	0.27	6.28	-26.29	8.76
5H, 4-102	41.32	3.75	2.34	426	260	162	1.44	1.72	0.26	6.50	-25.70	8.20
5H, 4-122	41.52	4.30	2.53	423	291	171	1.48	1.66	0.24	6.84	-26.46	6.97
5H, 5-2	41.63	3.98	2.68	427	269	181	1.48	1.68	0.26	6.50	-25.68	7.27
5H, 5-22	41.83	4.83	2.69	424	291	162	1.66	1.62	0.25	6.48	-25.56	7.81
5H, 5-42	42.03	5.09	2.61	426	294	151	1.73	1.71	0.23	7.32	-25.79	7.99
5H, 5-62	42.23	4.54	2.62	421	324	187	1.4	1.58	0.25	6.45	-27.21	8.68
5H, 5-82	42.43	4.72	2.78	423	308	182	1.53	1.80	0.26	6.81	-24.78	7.73
5H, 5-90	42.51	5.20	2.81	418	310	167	1.68	1.95	0.28	7.05	-26.27	7.30
5H, 5-102	42.63	4.19	2.50	426	327	195	1.28	1.66	0.24	6.95	-25.37	7.67
5H, 5-122	42.83	3.78	1.95	414	293	151	1.29	1.74	0.25	6.92	-25.74	6.45
5H, 6-2	43.1	3.93	2.55	425	260	169	1.51	1.75	0.25	6.98	-25.57	6.94
5H, 6-22	43.3	3.95	2.47	426	297	186	1.33	1.63	0.27	5.95	-25.35	9.08
5H, 6-42	43.5	3.13	2.61	424	245	204	1.28	1.53	0.23	6.66	-25.44	7.84
5H, 6-62	43.7	3.69	2.44	427	260	172	1.42	1.67	0.25	6.71	-25.27	8.30
5H, 6-82	43.9	2.94	2.50	423	239	203	1.23	1.46	0.23	6.49	-25.75	10.98
5H, 6-102	44.1	3.84	3.35	424	261	228	1.47	1.47	0.26	5.65	-25.42	10.20
5H, 7-2	44.31	2.75	3.41	428	233	289	1.18	1.40	0.21	6.64	-24.64	12.37
5H, 7-22	44.51	3.35	2.63	425	234	184	1.43	1.50	0.25	5.95	-26.75	9.60
5H, 7-42	44.71	2.76	3.65	423	265	225	1.35	1.39	0.20	6.93	-27.01	11.03
6H, 1-2	45.63	4.96	2.08	423	362	152	1.37	1.66	0.29	5.84	-27.68	6.94
6H, 1-22	45.83	3.35	1.97	423	282	166	1.19	1.61	0.26	6.17	-25.66	8.41
6H, 1-42	46.03	2.99	1.63	420	282	154	1.06	1.29	0.24	5.41	-27.02	9.43
6H, 1-62	46.23	3.88	2.32	419	268	160	1.45	1.58	0.27	5.91	-26.20	8.30
6H, 1-82	46.43	4.16	2.15	420	275	142	1.51	1.73	0.27	6.35	-26.79	8.36
6H, 1-102	46.63	5.02	2.18	407	356	155	1.41	1.72	0.28	6.19	-27.92	9.93
6H, 1-122	46.83	3.85	2.17	419	285	161	1.35	1.62	0.27	6.09	-26.66	8.91
6H, 2-2	47.01	3.79	3.26	426	260	223	1.46	1.73	0.23	7.57	-26.33	7.18
6H, 2-22	47.21	4.19	2.21	414	325	171	1.29	1.59	0.30	5.23	-26.83	7.89
6H, 2-42	47.41	4.16	1.98	414	313	149	1.33	1.58	0.29	5.49	-26.87	8.25
6H, 2-52	47.51	4.46	1.81	411	323	131	1.38	1.56	0.31	5.07	-27.45	7.64
6H, 2-62	47.61	4.19	2.09	410	313	156	1.34	1.54	0.29	5.22	-26.49	8.77
6H, 2-82	47.81	3.78	2.05	417	282	153	1.34	1.59	0.30	5.37	-26.85	7.82
6H, 2-102	48.01	4.18	1.98	417	303	143	1.38	1.62	0.28	5.79	-26.37	8.02
6H, 3-2	48.15	4.11	2.82	423	270	186	1.52	1.69	0.25	6.67	-25.26	8.11
6H, 3-22	48.35	4.21	2.10	423	312	156	1.35	1.57	0.28	5.66	-26.04	10.25
6H, 3-42	48.55	3.75	1.94	415	365	196	1.49	1.48	0.28	5.37	-26.38	9.71
6H, 3-62	48.75	3.80	2.87	415	268	202	1.42	1.51	0.30	4.97	-26.69	7.37
6H, 3-82	48.95	3.56	1.76	413	330	163	1.08	1.47	0.30	4.83	-26.66	7.55
6H, 3-102	49.15	3.67	1.75	413	331	158	1.11	1.42	0.26	5.40	-27.28	8.56
6H, 3-122	49.35	4.03	2.22	419	303	167	1.33	1.60	0.26	6.10	-26.17	10.57
6H, 4-2	49.65	3.99	3.56	428	424	216	1.65	1.84	0.27	6.75	-24.96	9.97
6H, 4-22	49.85	3.89	2.70	421	258	179	1.51	1.74	0.25	6.93	-25.87	8.99
6H, 4-38	50.01	3.33	2.76	421	241	200	1.38	1.56	0.23	6.73	-25.45	8.16
6H, 4-42	50.05	3.50	2.58	421	243	179	1.44	1.59	0.25	6.28	-25.75	8.94
6H, 4-62	50.25	4.31	2.45	420	276	157	1.56	1.77	0.26	6.80	-26.69	8.55
6H, 4-82	50.45	4.13	2.73	421	279	184	1.48	1.72	0.25	6.90	-25.75	7.83
6H, 4-102	50.65	3.28	3.29	422	258	259	1.27	1.44	0.27	5.37	-25.60	11.24
6H, 4-122	50.85	3.57	2.81	420	232	182	1.54	1.64	0.24	6.81	-25.53	9.59
6H, 5-2	51.15	4.17	2.99	423	273	195	1.53	1.68	0.24	7.01	-24.92	5.95
6H, 5-22	51.35	3.77	3.09	423	290	238	1.3	1.37	0.20	6.76	-26.02	7.96
6H, 5-42	51.55	3.91	3.14	426	254	204	1.54	1.69	0.26	6.42	-26.05	10.51
6H, 5-62	51.75	3.31	2.12	422	242	155	1.37	1.54	0.23	6.57	-25.76	9.56
6H, 5-82	51.95	3.91	3.06	424	266	208	1.47	1.68	0.25	6.72	-25.95	9.25
6H, 5-102	52.15	4.45	3.21	423	273	197	1.63	1.84	0.26	7.01	-25.73	9.64

Table T1 continued.

Core, section, interval (cm)	Depth (mbsf)	Rock-Eval pyrolysis						Major elements			Isotopes	
		S ₂ (mg HC/g rock)	S ₃ (mg CO ₂ /g rock)	T _{max} (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (wt%)	TOC (wt%)	TN (wt%)	C/N ratio	δ ¹³ C (‰)	δ ¹⁵ N (‰)
6H, 5-122	52.35	4.50	3.26	422	304	220	1.48	1.67	0.26	6.34	-25.90	9.83
6H, 5-138	52.51	4.41	3.49	410	298	236	1.48	1.73	0.26	6.78	-26.08	9.15
6H, 6-2	52.65	4.47	2.89	423	274	177	1.63	1.87	0.25	7.37	-25.82	7.76
6H, 6-22	52.85	4.42	2.93	423	273	181	1.62	1.80	0.26	7.02	-25.45	8.71
6H, 6-42	53.05	5.07	3.18	423	345	216	1.47	1.88	0.26	7.18	-25.99	8.60
6H, 6-62	53.25	3.79	2.72	424	241	173	1.57	1.62	0.26	6.19	-25.07	8.74
6H, 6-82	53.45	4.04	2.76	423	259	177	1.56	1.77	0.26	6.91	-25.99	8.07
6H, 6-102	53.65	4.10	3.73	423	283	257	1.45	1.62	0.25	6.51	-25.30	9.95
6H, 6-122	53.85	3.83	2.64	425	264	182	1.45	1.68	0.27	6.32	-25.26	9.45
6H, 7-2	54.15	4.57	2.66	429	326	190	1.4	1.70	0.23	7.35	-25.24	6.79
6H, 7-22	54.35	3.60	3.15	424	252	220	1.43	1.66	0.26	6.40	-25.33	10.06

HC = hydrocarbon, HI = hydrogen index, OI = oxygen index, TOC = total organic carbon, TN = total nitrogen.