41. ORGANIC GEOCHEMISTRY OF SEDIMENTS FROM LEG 135 (LAU BASIN) AND OF AN OIL SEEP (TONGA)[1]

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ABSTRACT

The average total organic carbon (TOC) content obtained after Rock-Eval/TOC analysis of 156 sediment samples from the eight sites cored during Leg 135 is 0.05%. Hence, the TOC content of Leg 135 sediments is extremely low. The organic matter that is present in these samples is probably mostly reworked and oxidized material. Ten sediment samples were selected for extraction and analysis by gas chromatography and gas chromatography–mass spectrometry. Very low amounts of extractable hydrocarbons were obtained and some aspects of the biomarker distributions suggest that these hydrocarbons are not representative of the organic matter indigenous to the samples.

A sample of an oil seep from Pili, Tongatapu was also analyzed. The seep is a biodegraded, mature oil that shows many characteristics in common with previously published analyses of oil seeps from Tongatapu. Biomarker evidence indicates that its source is a mature, marine carbonate of probable Late Cretaceous–Early Tertiary age. The source rock responsible for the Tongatapu oil seeps remains unknown.

INTRODUCTION

Previous work on the petroleum geochemistry of Tonga and the surrounding area was initiated because of the occurrence of oil seeps on Tongatapu. These were found in shallow holes at several locations in vuggy coral limestone of Pleistocene to Holocene age (Maung et al., 1981; Sandstrom and Philp, 1984; Sandstrom, 1985). Detailed geochemical analyses of five oil seeps from two different locations indicated that they were moderately to severely biodegraded, mature crude oils that probably had the same source (Sandstrom and Philp, 1984; Sandstrom, 1985). However, the suspicion that the oil seeps could be anthropogenic pollutants was not completely ruled out by these authors.

Attempts to identify possible source rocks for these seeps have been unsuccessful. Buchbinder and Halley (1985) reported the total organic carbon (TOC) contents of eight samples collected from outcrop and boreholes on Tongatapu and 'Eua. The best of these samples had a TOC content of 0.42% whereas the rest were below 0.25%. When the sample with the highest TOC content was analyzed by Rock-Eval, it produced no S_2 peak indicating that it had no hydrocarbon potential. Sandstrom (1985) reported the TOC contents of eight dredge samples recovered during a cruise of the southern Tonga Platform by the *S.P. Lee*. The highest TOC content of these samples was 0.04%. Microscopic observations of kerogen isolates indicated that most of the organic matter was terrestrially derived.

This paper presents the results obtained from organic geochemical analyses of sediment samples cored during Ocean Drilling Program (ODP) Leg 135 from the western Lau Basin, Tonga Ridge, and Tonga Forearc (Fig. 1), and of an oil seep from Tongatapu.

EXPERIMENTAL METHODS

An aliquot of each Leg 135 sample received was dried and powdered for Rock-Eval/TOC analysis. The instrument used was a Delsi Rock-Eval II pyrolysis unit equipped with a total organic carbon (TOC) analysis module. This instrument permits rapid determination of the amount, type, and maturity of organic matter in rock samples of about 100 mg. Briefly, this pyrolysis technique involves a microprocessor-controlled temperature program that causes the release of

hydrocarbons and CO_2 in a stream of helium. The amount of hydrocarbons is determined by a flame ionization detector (FID), whereas for CO_2 a thermal conductivity detector (TCD) is employed. Table 1 contains the standard measured Rock-Eval parameters (Espitalié et al., 1977, 1985) as well as several derived parameters:

TOC = total organic carbon reported as the weight percent of the whole rock;

S_1 = hydrocarbon evolved (distilled or thermovaporized) at 300°C (mg hydrocarbon/g rock);

S_2 = hydrocarbon evolved during heating at 25°C/min between 300°C and 600°C (mg hydrocarbon/g rock);

S_3 = organic carbon dioxide evolved at 300°C and up to 390°C (mg CO_2/g rock);

$PI = S_1/(S_1 + S_2)$

T_{max} = the temperature (°C) at the top of the S_2 peak;

HI = hydrogen index, which is $(100 \times S_2)/TOC$ (mg HC/g TOC); and

OI = oxygen index, which is $(100 \times S_3)/TOC$ (mg CO_2/g TOC).

Ten samples were selected for more detailed geochemical analysis based on the Rock-Eval/TOC results and, because of the low TOC contents of the samples, on the quantity of sample available. Hence, there was a tendency to choose samples from shallow depths from which pore waters had been squeezed as these were the largest samples available. The samples were pulverized and then extracted for 24 hr in Soxhlet apparatus using azeotropic chloroform:methanol (87:13). These extracts and the oil seep sample were deasphalted using n-pentane before fractionation. The deasphalted fractions were fractionated using open-column chromatography (three-fourths activated alumina and one-fourth activated silica gel with an adsorbent:sample mass ratio of 100:1). Saturates were recovered by eluting with 3.5 mL of pentane/g of adsorbent. Aromatics were recovered by eluting with 4.0 mL of 50:50 pentane-dichloromethane/g of absorbent, and the resins were recovered with 4.0 mL/g methanol.

The oil seep gasoline-range hydrocarbons were analyzed using an OI Corporation 4660A Purge and Trap connected to a Hewlett-Packard 5890A Gas Chromatograph fitted with a 50-m, 0.31-i.d. DB-1 fused silica column.

Gas chromatograms of the saturate fractions were acquired on a Varian 3700 FID gas chromatograph (GC) using a 30-m DB-1 column with a temperature program of 60°–300°C at 6°C/min. Gas chromatography–mass spectrometry (GC–MS) data were collected using a VG 70SQ hybrid MS-MS (100 μA trap current and 70 eV ionization

Table 1. Results of Rock-Eval/TOC analyses of Leg 135 cored sediment samples.

Core, section, interval (cm)	Depth (mbsf)	TOC	S_1	S_2	S_3	PI	T_{max}	HI	OI
135-834A-									
1H-3, 102–103	4.02	0.02	0.06	0.03	3.70	0.67	0	150	18500
1H-4, 140–150	5.90	0.02	0.02	0.07	1.53	0.22	365	350	7650
2H-3, 75–76	11.35	0.01	0.03	0.02	2.46	0.60	379	200	24600
2H-4, 140–150	13.50	0.02	0	0.01	2.06	0	0	50	10300
3H-2, 60–61	19.20	0.01	0.02	0.01	2.64	1	445	100	26400
3H-4, 140–150	23.00	0.01	0	0.01	2.29	0	0	100	22900
4H-4, 73–74	31.83	0.08	0.02	0.70	2.37	0.03	443	875	2963
4H-4, 140–150	32.50	0.02	0	0.01	2.14	0	0	50	10700
5H-4, 73–74	41.33	0.07	0	0.01	2.73	0	0	14	3900
5H-4, 140–150	42.00	0.03	0	0.01	2.95	0	0	33	9833
6H-2, 75–76	47.85	0.03	0	0.01	2.47	0	0	33	8233
6H-4, 140–150	51.50	0.01	0	0.01	2.09	0	0	100	20900
7H-6, 81–82	63.41	0.02	0	0.01	1.37	0	0	50	6850
8H-1, 96–97	65.56	0.46	0.01	0.02	2.99	0.33	0	4	650
9H-2, 109–111	76.69	0.08	0	0.01	2.79	0	0	13	3488
9H-4, 140–150	80.00	0.03	0.01	0.03	4.36	0.25	449	100	14533
10X-1, 81–82	84.41	0.09	0.02	0.01	2.59	0.67	0	11	2878
11X-1, 79–80	93.99	0.03	0.12	0.11	2.83	0.52	382	367	9433
12X-1, 140–150	104.30	0.04	0	0.01	2.08	0	0	25	5200
12X-2, 53–54	104.93	0.07	0	0.01	2.78	0	0	14	3971
16X-1, 140–150	133.30	0.01	0	0.01	0.07	0	0	100	700
135-835A-									
1H-4, 140–150	5.90	0.04	0	0.01	3.21	0	0	25	8025
1H-5, 30–31	6.30	0.03	0.07	0.05	2.86	0.58	310	167	9533
2H-2, 69–70	11.69	0.04	0.01	0	2.82	1.00	0	0	7050
2H-4, 50–51	14.50	0.05	0.03	0	3.38	1.00	0	0	6760
2H-4, 140–150	15.40	0.02	0	0.01	1.97	0	0	50	9850
2H-5, 27–34	15.77	0.05	0	0.01	3.13	0	0	20	6260
3H-4, 140–150	24.90	0.02	0	0.01	2.21	0	0	50	11050
4H-2, 73–74	30.73	0.03	0	0.01	2.19	0	0	33	7300
4H-4, 140–150	34.40	0.01	0	0.01	1.97	0	0	100	19700
5H-2, 104–105	40.54	0.04	0.05	0.03	2.61	0.63	302	75	6525
6H-2, 71–72	49.71	0.05	0.01	0.02	2.74	0.33	365	40	5480
6H-4, 140–150	53.40	0.01	0	0.01	1.73	0	0	100	17300
6H-7, 19–20	56.69	0.06	0.02	0.01	3.14	0.67	304	17	5233
7H-2, 93–94	59.43	0.03	0.01	0	2.75	1.00	0	0	9167
7H-7, 54–55	66.54	0.10	0.01	0.01	3.13	0.50	337	10	3130
8H-2, 72–73	68.72	0.03	0.01	0	2.88	1.00	0	0	9600
8H-4, 140–150	72.40	0.03	0	0.01	2.65	0	0	33	8833
9H-2, 78–79	78.28	0.07	0.01	0	2.61	1.00	0	0	3729
10H-2, 66–67	87.66	0.04	0.01	0.02	2.75	0.33	310	50	6875
10H-4, 67–68	90.67	0.10	0.01	0.02	3.17	0.50	310	20	3170
10H-4, 140–150	91.40	0.01	0	0.01	0.01	0	0	100	100
11H-6, 70–71	103.20	0.06	0.02	0.01	3.18	0.67	0	17	5300
12H-2, 69–70	106.69	0.05	0.01	0	3.12	1.00	0	0	6240
12H-4, 140–150	110.40	0.04	0	0.01	2.29	0	0	25	5725
12H-6, 69–70	112.69	0.04	0.02	0	3.44	1.00	0	0	8600
13H-6, 91–92	122.69	0.08	0.03	0.01	3.20	0.75	407	13	4000
14H-4, 92–99	128.92	0.04	0	0.01	2.68	0	0	25	6700
14H-4, 140–150	129.40	0.04	0	0.01	2.63	0	0	25	6575
14H-6, 47–48	131.47	0.04	0.03	0	3.86	1.00	0	0	9650
15H-3, 61–62	136.23	0.09	0.02	0	3.72	1.00	0	0	4133
16H-2, 69–71	144.69	0.17	0.07	0	3.94	1.00	0	0	2318
16H-6, 140–150	151.35	0.06	0	0.01	2.43	0	0	17	4050
17H-1, 74–75	152.74	0.05	0.01	0	2.79	1.00	0	0	5580
135-836A-									
1H-1, 57–58	0.57	0.02	0.07	0.09	2.60	0.44	367	450	13000
2H-1, 62–63	1.82	0.04	0.20	0.19	2.13	0.51	369	475	5325
2H-3, 63–64	4.83	0.03	0.01	0.01	3.18	0.50	445	33	10600
2H-4, 140–150	7.10	0.07	0	0.01	2.44	0	348	14	3486
2H-6, 71–72	9.41	0.03	0.01	0.01	2.65	0.50	445	33	8833
3H-5, 20–21	16.78	0.01	0.03	0.02	2.39	0.60	427	200	23900
3H-5, 140–150	17.98	0.02	0	0.01	1.88	0	412	50	9400
3H-6, 69–70	18.77	0.03	0.06	0.08	2.69	0.43	459	267	8967
135-837A-									
1H-3, 69–70	3.69	0.03	0.11	0.16	2.39	0.41	365	533	7967
1H-3, 140–150	4.40	0.04	0	0.01	2.78	0	0	25	6950
1H-4, 78–79	5.28	0.01	0	0.01	0.01	0	343	100	100
2H-4, 140–150	13.90	0.03	0	0.01	2.55	0	0	33	8500
3H-4, 140–150	23.40	0.02	0	0.01	2.76	0	0	50	13800
4H-4, 140–150	32.90	0.02	0.02	0.32	0.23	0.06	0	1600	1150
4H-5, 81–82	33.72	0.01	0.02	0.03	2.76	0.40	370	300	27600
6H-5, 140–150	53.40	0.06	0	0.02	3.26	0	373	33	5433

Table 1 (continued).

Core, section, interval (cm)	Depth (mbsf)	TOC	S_1	S_2	S_3	PI	T_{max}	HI	OI
135-837A-									
8H-2, 86–87	67.36	0.04	0.14	0.14	3.26	0.50	372	350	8150
8H-4, 140–150	70.90	0.05	0.01	0.01	2.90	0.50	310	20	5800
9H-4, 63–64	79.63	0.05	0.04	0.04	3.31	0.50	449	80	6620
135-838A-									
2H-4, 140–150	9.60	0.02	0	0.01	2.82	0	353	50	14100
3H-4, 140–150	19.10	0.01	0	0.01	2.27	0	0	100	22700
4H-4, 140–150	28.60	0.03	0.01	0.04	3.27	0.20	388	133	10900
8H-4, 140–150	66.60	0.02	0	0.04	2.32	0	401	200	11600
135-839A-									
1H-2, 140–150	2.90	0.01	0	0.04	1.42	0	431	400	14200
1H-3, 69–70	3.69	0.03	0	0.01	3.54	0	0	33	11800
2H-4, 140–150	10.40	0.02	0	0.01	2.52	0	530	50	12600
3H-4, 140–150	19.90	0.03	0.04	0.37	0.31	0.10	0	1233	1033
6H-4, 140–150	48.40	0.01	0.04	0.19	0.58	0.17	0	1900	5800
8H-4, 140–150	67.40	0.02	0.03	0.23	0.46	0.12	0	1150	2300
4H-5, 140–150	30.90	0.02	0	0.01	2.18	0	0	50	10900
10H-5, 140–150	87.90	0.05	0.03	0.06	2.66	0.33	310	120	5320
135-840A-									
1H-3, 55–56	3.60	0.01	0.05	0.06	0.56	0.45	339	600	5600
135-840B-									
1X-1, 13–14	0.13	0.05	0.14	0.18	1.31	0.44	390	360	2620
4X-CC, 12–13	28.52	0.01	0.06	0.05	0.76	0.55	310	500	7600
9X-CC, 4–5	76.44	0.03	0.13	0.10	0.72	0.57	376	333	2400
10X-1, 12–13	86.22	0.02	0.08	0.07	0.71	0.53	310	350	3550
11X-2, 70–71	97.90	0.02	0.15	0.09	0.71	0.63	348	450	3550
12X-4, 104–105	109.52	0.02	0.06	0.01	0.91	0.86	310	50	4550
12X-4, 140–150	109.88	0.01	0.01	0	1.12	1.00	0	0	11200
13X-2, 140–150	118.00	0.01	0	0.01	1.21	0	0	100	12100
15X-CC, 0–1	134.40	0.05	0.19	0.17	0.76	0.53	413	340	1520
22X-CC, 7–8	201.77	0.06	0.21	0.12	1.03	0.64	394	200	1717
29X-1, 13–14	269.53	0.14	0.28	0.18	1.19	0.61	378	129	850
31X-1, 44–45	289.24	0.03	0.08	0.06	0.86	0.57	330	200	2867
35X-1, 18–19	327.68	0.04	0.06	0.07	0.52	0.46	309	175	1300
38X-1, 124–125	348.34	0.03	0.05	0.03	0.57	0.63	309	100	1900
39X-1, 18–23	356.98	0.01	0	0.02	0.74	0	310	200	7400
42X-3, 8–10	388.88	0.03	0.02	0.02	0.59	0.50	309	66	1966
49X-1, 68–69	453.08	0.09	0.11	0.11	1.49	0.22	376	122	1656
51X-5, 44–45	478.14	0.05	0.12	0.10	0.61	0.22	310	200	1220
53X-4, 59–60	496.09	0.04	0.08	0.07	1.10	0.57	347	175	2750
56X-2, 56–57	522.22	0.07	0.12	0.09	1.27	0.57	421	129	1814
135-840C-									
1H-2, 127–128	40.77	0.01	0.07	0.05	0.74	0.58	349	500	7400
3H-2, 126–136	59.76	0.01	0.01	0.03	0.42	0.25	392	300	4200
4H-2, 103–104	69.03	0.03	0.05	0.06	0.56	0.45	357	200	1867
4H-4, 140–150	72.40	0.01	0.01	0.01	0.74	0.50	310	100	7400
5H-1, 139–147	125.39	0.07	0	0.03	0.47	0	341	43	671
6H-4, 52–53	139.02	0.02	0.05	0.02	0.88	0.71	449	100	4400
7H-2, 143–150	144.78	0.01	0	0.01	0.30	0	0	100	3000
10H-1, 52–53	172.02	0.02	0.07	0.07	0.50	0.50	367	350	2500
135-841A-									
1H-1, 88–89	0.88	0.13	0.19	1.05	0.22	0.15	0	808	169
1H-4, 140–150	5.90	0.03	0.04	0.33	0.26	0.11	582	1100	867
1H-5, 80–81	6.80	0.14	0.25	1.01	0.21	0.20	0	721	150
2H-4, 15–16	13.15	0.24	0.50	1.01	0.21	0.33	0	421	88
2H-4, 140–150	14.40	0.08	0.17	0.48	0.07	0.26	475	600	88
3H-3, 82–83	21.82	0.24	0.67	1.92	0.11	0.26	0	800	46
3H-4, 140–150	23.90	0.18	0.48	1.75	0.01	0.22	498	972	6
4H-3, 76–77	31.26	0.28	0.88	2.38	0.06	0.27	521	850	21
4H-4, 140–150	33.40	0.06	0.26	0.58	0.01	0.31	530	967	17
6H-2, 9–10	48.09	0.18	0.62	1.16	0.01	0.35	586	644	6
6H-4, 140–150	52.40	0.08	0.12	0.96	0.01	0.11	506	1200	13
8H-3, 140–150	69.90	0.02	0.04	0.20	0.21	0.17	0	1000	1050
15X-1, 62–63	130.22	0.11	0.20	0.33	0.54	0.38	532	300	491
21X-1, 80–81	177.70	0.12	0.16	0.41	0.36	0.28	551	342	300
135-841B-									
2R-1, 47–48	170.27	0.09	0.12	0.19	0.30	0.39	0	211	333
2R-1, 142–150	171.22	0.04	0.03	0.06	1.03	0.33	336	150	2575
5R-1, 152–150	200.12	0.06	0.03	0.07	0.61	0.30	331	117	1017
8R-1, 75–85	228.45	0.02	0.02	0.03	0.43	0.40	395	150	2150

Table 1 (continued).

Core, section, interval (cm)	Depth (mbsf)	TOC	S_1	S_2	S_3	PI	T_{max}	HI	OI
135-841B-									
11R-1, 61–74	257.31	0.02	0.01	0.11	0.33	0.08	593	550	1650
15R-1, 135–150	296.25	0.02	0	0.02	0.02	0	352	100	100
18R-2, 77–95	325.77	0.01	0.01	0.12	0.01	0.08	403	1200	100
21R-1, 12–32	352.22	0.01	0	0.12	0.07	0	434	1200	700
29R-1, 130–150	430.40	0.01	0	0.02	0.03	0	401	200	300
32R-1, 104–105	459.14	0.08	0.07	0.08	0.56	0.47	371	100	700
33R-1, 8–9	467.88	0.07	0.13	0.06	0.19	0.68	326	86	271
35R-3, 125–126	491.39	0.03	0.04	0	0.15	1	0	0	500
37R-3, 0–13	509.27	0.01	0	0.01	0.09	0	0	100	900
40R-2, 8–20	536.81	0.01	0	0.05	0.10	0	367	500	1000
40R-3, 35–36	537.08	0.11	0.20	0.06	0.43	0.77	364	55	391
42R-3, 0–9	557.30	0.01	0	0.01	0.58	0	0	100	5800
45R-1, 6–8	583.36	0.01	0.11	0.04	0.77	0.73	400	400	7700
46R-1, 71–73	593.61	0.06	0.06	0.07	0.64	0.46	363	117	1067
46R-2, 12–13	594.52	0.08	0.05	0.06	0.61	0.45	349	75	763
46R-2, 72–73	595.12	0.05	0.03	0.01	0.39	0.75	310	20	780
46R-2, 111–112	595.51	0.06	0	0.02	0.41	0	310	33	683
46R-3, 8–10	595.94	0.06	0.05	0.05	0.42	0.50	349	83	700
46R-CC, 14–15	596.37	0.10	0.10	0.16	0.68	0.38	400	160	680
47R-1, 143–144	604.03	0.13	0.15	0.09	0.46	0.63	310	69	354
51R-3, 0–19	642.80	0.03	0.07	0.41	0.01	0.15	490	1367	33
53R-1, 132–150	661.92	0.01	0.02	0.18	0.01	0.10	380	1800	100
54R-3, 65–66	673.85	0.01	0.04	0.19	0.01	0.17	464	1900	100
62R-1, 130–150	748.50	0.01	0	0.13	0.03	0	447	1300	300

Notes: Derived parameters (T_{max}, HI, and OI) are suspect because of the low TOC and high $CaCO_3$ concentrations of the sediments. TOC = total organic carbon as weight percent of the whole rock; S_1 = hydrocarbon evolved (distilled or thermovaporitized) at 300°C (mg HC/g rock); S_2 = hydrocarbon evolved during heating at 25°C/min between 300° and 600°C (mg HC/g rock); S_3 = organic carbon dioxide evolved at 300°C and up to 390°C (mg CO_2/g rock); PI = $S_1/(S_1 + S_2)$; T_{max} = temperature (°C) at the top of the S_2 peak; HI = hydrogen index ($100 \times S_2$)/TOC (mg HC/g TOC); and OI = oxygen index ($100 \times S_3$)/TOC (mgO_2/g TOC).

voltage) under the control of a VG 11-250 data system. The gas chromatograph was fitted with a 25-m DB-5 column that was coupled directly to the ion source and temperature programmed from 50° to 310°C at 4°C/min. The high-resolution, multiple ion detection (MID) experiments monitored the following ions: m/z 177.1638, 191.1794, 217.1950, 218.2028, 231.2106, and 259.2262 for the saturate fraction and m/z 231.1170 for the triaromatic steroids in the aromatic fraction. Full scan data, for peak identification by comparison of mass spectra, were obtained for the seep sample by scanning from m/z 650 to 50 at 1 s/decade. Sterane and hopane distributions in the oil seep sample were also examined using Collision Activated Decomposition MS-MS as described by Fowler and Brooks (1990).

ROCK-EVAL/TOC ANALYSES OF LEG 135 SAMPLES

Organic carbon determinations given in the individual site chapters of the Leg 135 *Initial Reports* volume (Parson, Hawkins, Allan, et al., 1992) were obtained indirectly as the difference between total carbon and inorganic carbon values. The Rock-Eval instrument on the *JOIDES Resolution* was only operational for the last two sites drilled (840 and 841) and even then the TOC module was not functioning. Therefore, it was considered desirable to conduct Rock-Eval/TOC analyses on Leg 135 samples despite the unpromising organic geochemical results obtained on board the *JOIDES Resolution* (Parson, Hawkins, Allan, et al., 1992).

Sediment samples, from all eight sites cored during Leg 135 (Fig. 1), were analyzed by Rock-Eval/TOC analysis. Six of these sites were drilled in the Lau Basin backarc region (Sites 834–839), one on the Tongan Platform (Site 840), and one in the Tonga forearc region on the arc-trench slope (Site 841). The samples selected for analysis were either those sampled for carbonate and CNS analysis, or were a portion of the interstitial water squeezecake. These represent a biased

sample set, as lithologies likely to have no organic carbon content were not selected (i.e., volcaniclastic intervals).

The results of the Rock-Eval/TOC analyses are given in Table 1. Parameters used in the table are defined in the "Experimental Methods" section (this chapter). As evident from the summary in Figure 2, the TOC contents of the Leg 135 samples are extremely low. Only one sample, from a depth of 65.56 m in Hole 834A, has a TOC content greater than 0.3%. The average TOC content of the 156 samples is 0.05%. As there was a tendency to avoid picking samples for organic geochemical analyses that were obviously predominately volcaniclastic, these values overestimate the average TOC content of the sediments recovered during Leg 135. In comparison, the organic carbon contents of 148 samples analyzed on board the *JOIDES Resolution*, using the NCS analyzer to obtain total carbon and then subtracting the inorganic carbon value, was 0.14%. Values up to 0.67% were obtained from this latter method. Hence, for a similar sample set, lower values were obtained from the Rock-Eval instrument at the Institute of Sedimentary and Petroleum Geology.

It should be emphasized that the Rock-Eval instrument is not designed for the analysis of samples with such low TOC contents; therefore, the results are not strictly accurate. Sources of errors inherent in the shipboard method will also be accentuated by samples that are very lean in organic carbon. Regardless of the absolute values, the results from both methods indicate that the organic carbon contents of the sediments recovered during Leg 135 are extremely low. This is in agreement with the results reported by previous workers who have analyzed sediments from this area. Buchbinder and Halley (1985) reported a TOC range from 0.09% to 0.42% for ten samples, with an average of 0.16%; on the other hand, Sandstrom (1985) found a TOC range from 0.018% to 0.04%, with an average of 0.025%, for the eight samples he analyzed.

As the TOC contents and the S_2 and S_3 values are extremely low for all samples, the derived HI and OI values are questionable and
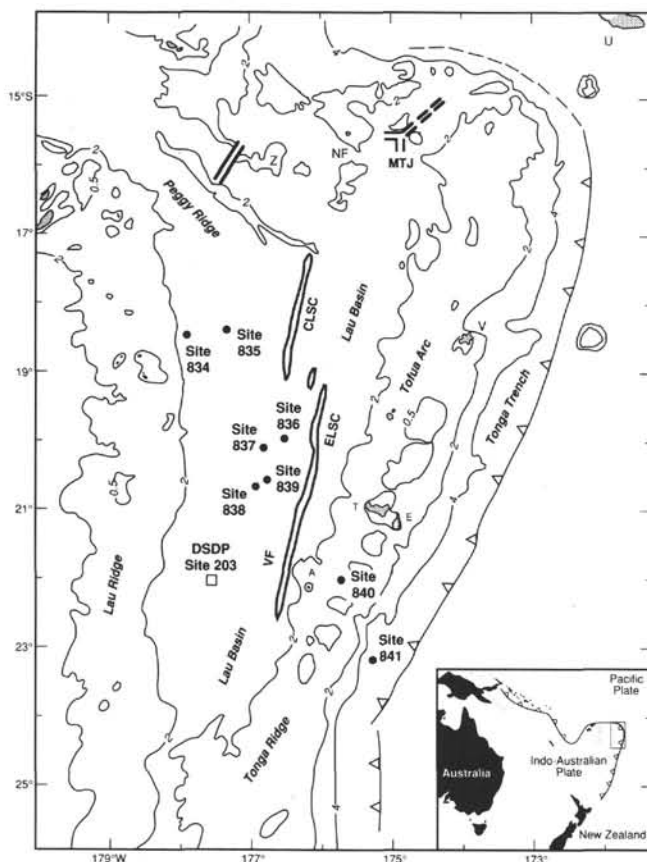
Figure 1. Location of sites cored during Leg 135. Water depths in kilometers. Tongan Islands indicated are Tongatapu (T), 'Eua (E), 'Ata (A), Vava'u (V), NF = Niuafo'ou, and U = Upolu.
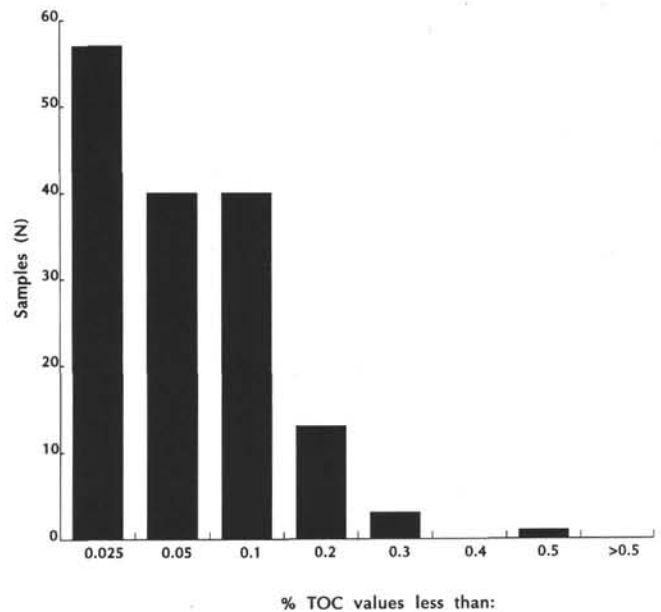

Figure 2. Histogram showing total organic carbon (TOC) contents of Leg 135 sediment samples.

is evident from the lack of any consistency or trend in T_{max} values for any of the holes. However, the values for all these parameters are given in Table 1 for completeness.

It is not unexpected that open-ocean sediments with a large volcaniclastic contribution such as those cored during Leg 135 should have low TOC contents. Primary productivity in the upper waters of the open ocean is low (e.g., Tissot and Welte, 1984, p. 24), and efficient scavenging by organisms or oxidation in the water column means that sediments deposited in such areas normally contain a low abundance of organic carbon (e.g., Hunt, 1979, p. 104). The addition of volcaniclastic sediments further dilutes this carbon, which is, in any case, mostly inertinite with no metabolic value for bacteria. The lack of enough carbon for the sulfate-reducing bacteria to metabolize is possibly the reason why sulfate levels at the Leg 135 sites show little change with depth and also why methane was not detected above background levels in any of the head-space samples taken during Leg 135 (Parson, Hawkins, Allan, et al., 1992). Hence, two of the diagenetic stages that are generally observed in marine sediments, sulfate reduction and methanogenesis (Curtis, 1987), do not occur in Leg 135 sediments, which should have important consequences for the diagenesis of inorganic species.

probably meaningless. This is illustrated by the extremely high OI values given in Table 1, which are a function of the combination of a low TOC content and a possible contribution to the S_3 peak from carbonate (cf. Katz, 1983; Snowdon and Meyers, 1992). The very high HI values displayed by some samples are not related to an input of algal organic matter. They occur because of "small but multiplicative analytical errors in the TOC and S_2 measurements" (Snowdon and Meyers, 1992) in these very low TOC samples. Also, no sample gave a large enough S_2 peak for the T_{max} value to be considered a reliable indicator of the thermal maturity of the organic matter. This

Table 2. Data from extraction, fractionation, and gas chromatographic analysis for ten Leg 135 sediment samples and Pili oil seep.

Core, section, interval (cm)	Depth (mbsf)	TOC (%)	Extract yield (mg/g orgC)	HC yield (mg/g orgC)	HC (%)	R + A (%)	Saturate (%)	Aromatic (%)	pr/ph	pr/nC$_{17}$	nC$_{17}$/nC$_{27}$
135-834A-1H-4, 140–150	5.90	0.03	2.7	0.2	7.41	74.07	3.70	3.70	0.65	0.91	0.50
135-835A-1H-4, 140–150	5.90	0.05	3.7	0.6	16.22	73.00	5.41	10.81	0.75	0.63	3.06
135-836A-2H-4, 140–150	7.10	0.02	3.8	0.4	10.53	81.58	5.26	5.26	0.75	1.21	1.55
135-837A-4H-4, 140–150	32.90	0.02	3.6	0.3	8.33	72.22	2.78	5.56	0.57	ND	ND
135-839A-3H-4, 140–150	19.90	0.04	5.5	0.7	12.73	70.91	5.45	7.27	0.60	0.88	ND
135-840C-5H-1, 139–147	125.39	0.07	2.9	0.4	13.79	65.52	6.90	6.90	0.80	2.06	ND
135-841A-2H-4, 140–150	14.40	0.09	3.1	0.2	6.45	83.87	3.23	3.23	0.71	2.16	2.40
135-841A-3H-4, 140–150	23.90	0.07	3.7	0.5	13.51	56.76	5.41	8.11	0.61	0.67	2.27
135-841A-4H-4, 140–150	33.40	0.03	2.8	0.4	14.29	67.86	3.57	10.71	0.62	1.44	1.42
135-841A-6H-4, 140–150	52.40	0.05	2.9	0.5	17.24	79.31	6.90	10.34	0.64	1.04	0.07
Pili oil seep					81.24	17.72	34.56	46.80	0.85		

Notes: TOC = total organic carbon as weight percent of the whole rock; HC = percentage of hydrocarbons in total extract; R + A = percentage of resins and asphaltenes in total extract; pr/ph = pristane/phytane; pr/nC$_{17}$ = pristane/n-heptadecane; and C$_{17}$/C$_{27}$ = n-heptadecane/n-heptacosane. ND = not determined because compounds present in such low concentrations.
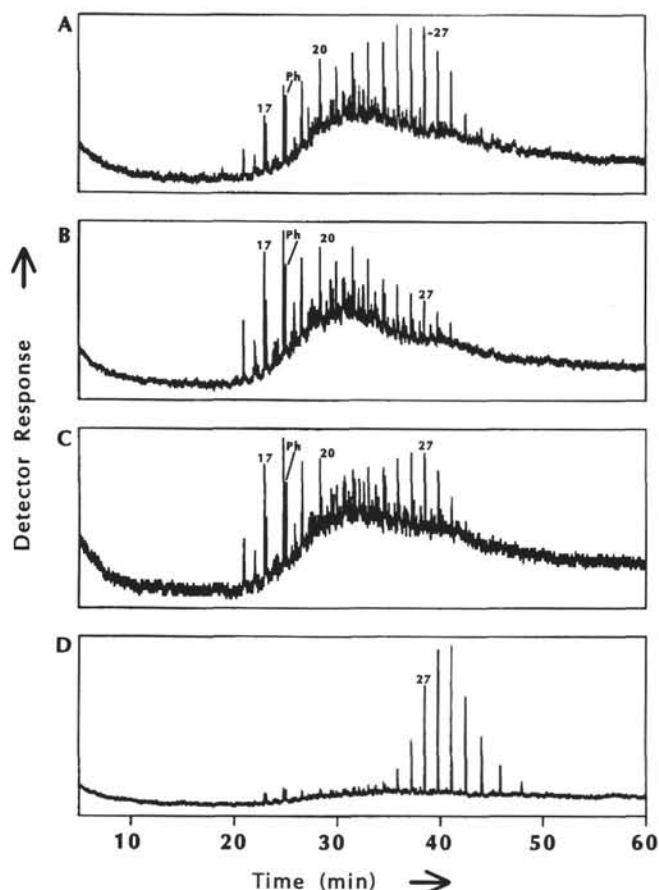
Figure 3. Representative saturate fraction gas chromatograms of Leg 135 samples. **A.** Sample 135-834A-1H-4 (5.9 mbsf). **B.** Sample 135-835A-1H-4 (5.9 mbsf). **C.** Sample 135-840C-5H-1 (125.39 mbsf). **D.** Sample 135-841A-6H-4 (52.4 mbsf). The numbers 17, 20, and 27 represent the C_{17}, C_{20}, and C_{27} n-alkanes, and Ph = phytane.

HYDROCARBON ANALYSES OF LEG 135 SEDIMENTS

Ten samples were selected for extraction and analysis of their saturate fractions using the criteria and methodology outlined in the "Experimental Methods" section (this chapter). As indicated by the extract and hydrocarbon yields (Table 2), the amounts of total extractable organic matter and hydrocarbons obtained from these samples were extremely small. Only 0.1–0.3 mg of saturate hydrocarbons were obtained from powdered rock samples ranging from 7.8 to 17.17 g. These are such low amounts that the possibility of contamination must be considered very great.

The saturate fraction gas chromatograms (SFGCs) display a low signal-to-noise ratio (Fig. 3). The n-alkanes are the predominant peaks in all the SFGCs, with the acyclic isoprenoids (e.g., pristane and phytane) also present in high relative abundance in most samples (Table 2, pr/nC_{17}). Some SFGCs show a predominance of the C_{15}–C_{20} and others a predominance of the C_{20+} n-alkanes (Table 2, nC_{17}/nC_{27}), implying that some samples have received mostly marine organic and others mostly terrestrial organic matter (Tissot and Welte, 1984). All the samples have low pristane/phytane ratios that could, for example, suggest anoxic conditions of deposition (Didyk et al., 1978); however, as evident from the SFGCs (Fig. 3), this is more likely a result of evaporative losses during the workup of such small amounts.

The terpane and sterane distributions were examined by GC–MS–MID (Figs. 4–5). Several aspects of the distributions of these compounds exist that suggest they are not representative of the organic
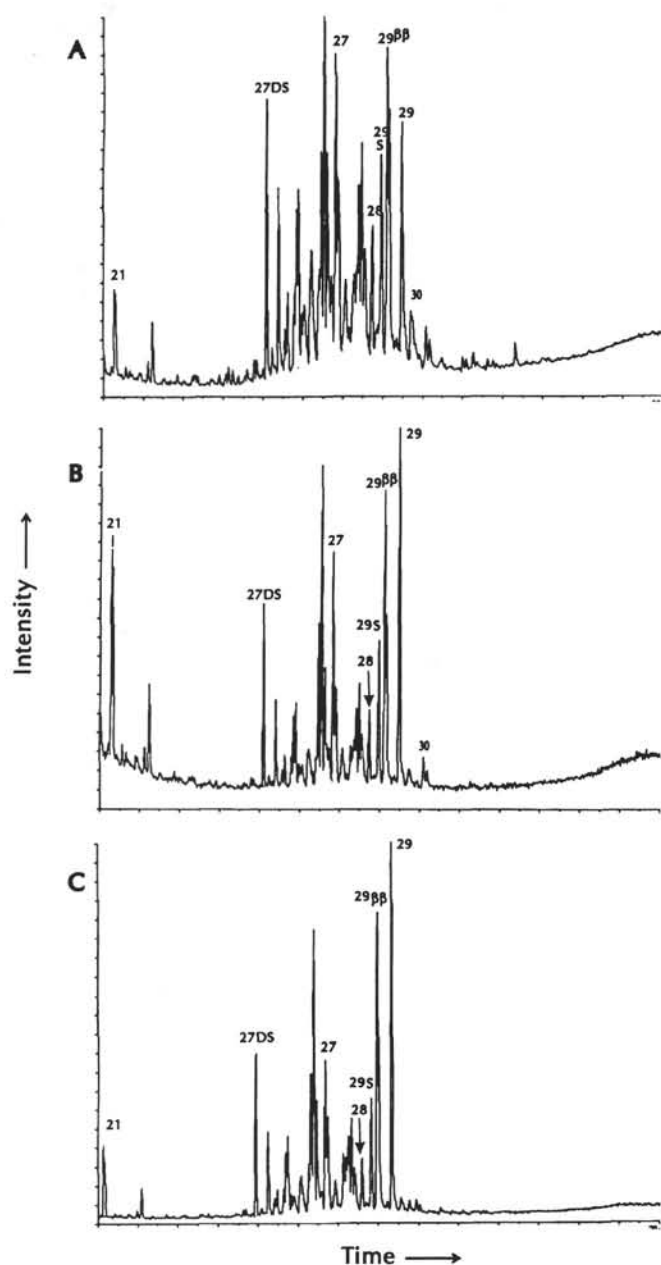

Figure 4. Representative m/z 217 mass fragmentograms showing the distributions of steranes in Leg 135 samples. **A.** Sample 135-834A-1H-4 (5.9 mbsf). **B.** Sample 135-840C-5H-1 (125.39 mbsf). **C.** Sample 135-841A-6H-4 (52.4 mbsf). The numbers 27, 28, and 29 represent the C_{27}, C_{28}, and C_{29} $5\alpha(H),14\alpha(H),17\alpha(H)$-20R steranes; 29S represents the C_{29} $5\alpha(H),14\alpha(H),17\alpha(H)$-20S sterane; $29\beta\beta$ represents the C_{29} $5\alpha(H),14\beta(H),17\beta(H)$ steranes; 27DS is the C_{27} $13\beta(H),17\alpha(H)$-20S diasterane; and 21 and 30 are the C_{21} and C_{30} steranes, respectively.

matter of these samples and are contamination. The maturity of the samples, as indicated by biomarker maturation parameters (e.g., Mackenzie, 1984), is much greater than would be expected for their depth (e.g., the following ratios in Table 3: 20S to 20R $5\alpha(H),14\alpha(H)$, $17\alpha(H)$ steranes, $5\alpha(H),14\beta(H),17\beta(H)$ to $5\alpha(H),14\alpha(H),17\alpha(H)$ steranes, $17\alpha(H),21\beta(H)$-hopane/$17\beta(H),21\alpha(H)$-moretane, and the C_{32} $17\alpha(H),21\beta(H)$ 22S and 22R hopanes). These ratios imply that most of the samples are marginally mature with respect to hydrocarbon generation, although their present depths range only from 5.9 to 125.39 mbsf. Also, these and other parameters that are normally thought to be
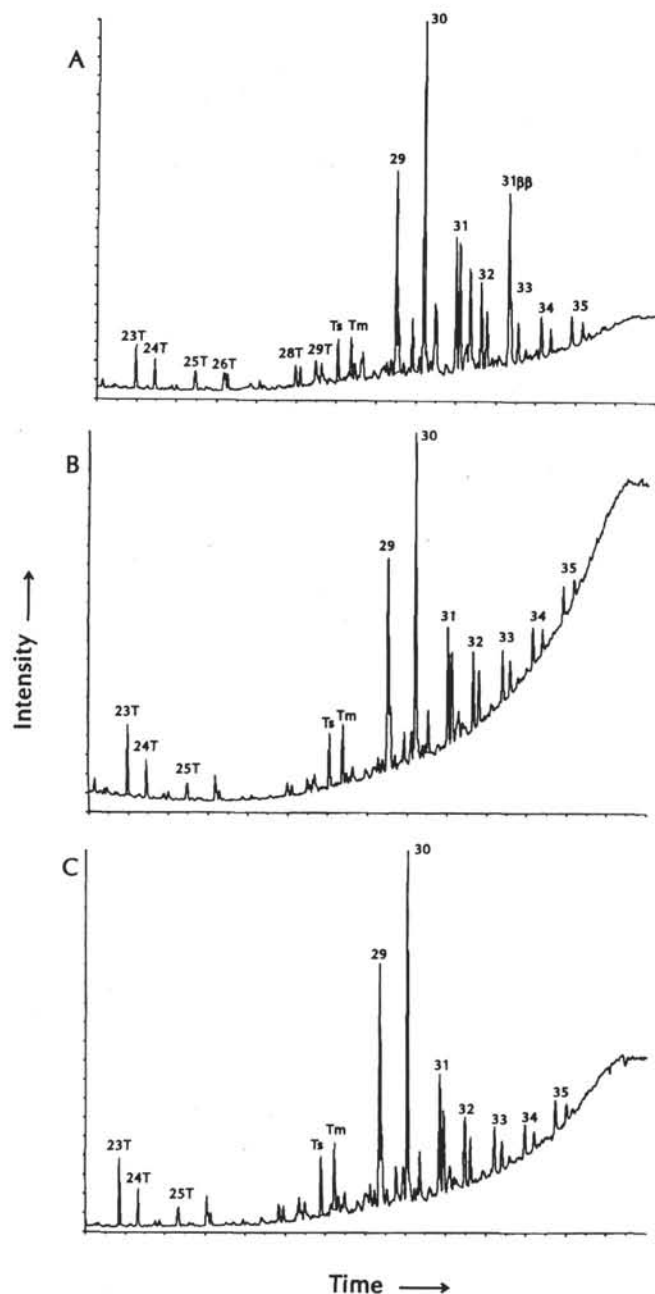
Figure 5. Representative m/z 191 fragmentograms showing the distributions of terpanes in Leg 135 samples. **A.** Sample 135-834A-1H-4 (5.9 mbsf). **B.** Sample 135-840C-5H-1 (125.39 mbsf). **C.** Sample 135-841A-6H-4 (52.4 mbsf). The labels 23T–29T represent the C_{23}–C_{29} tricyclic terpanes; 29–35 are the C_{29}–C_{35} 17α(H)-hopanes; Ts is 18α(H)-trisnorhopane; Tm is 17α(H)-trisnorhopane; and 31$\beta\beta$ is C_{31} 17β(H),21β(H)-homohopane.

more source dependent (e.g., ratio of C_{27}:C_{28}:C_{29} steranes, ratio of diasteranes to regular steranes, Ts/Tm, etc.; Table 3), suggest that all the samples had a contribution from a similar mix of organic material, regardless of site or stratigraphic horizon. Some differences are present between the samples, such as the sterane distribution of the sample from a depth of 52.4 mbsf, in Hole 841A (Fig. 4C), which has significantly lower C_{29} S/R and C_{21}/C_{29} sterane ratios (Table 3), and the hopane distribution of the sample from 5.9 mbsf, in Hole 834A, which has higher amounts of 17β(H),21α(H)-moretanes and 17β(H),21β(H)-hopanes compared with other samples (Fig. 5A; hopane/moretane in Table 3). In the case of this latter sample, its hopane distribution indi-
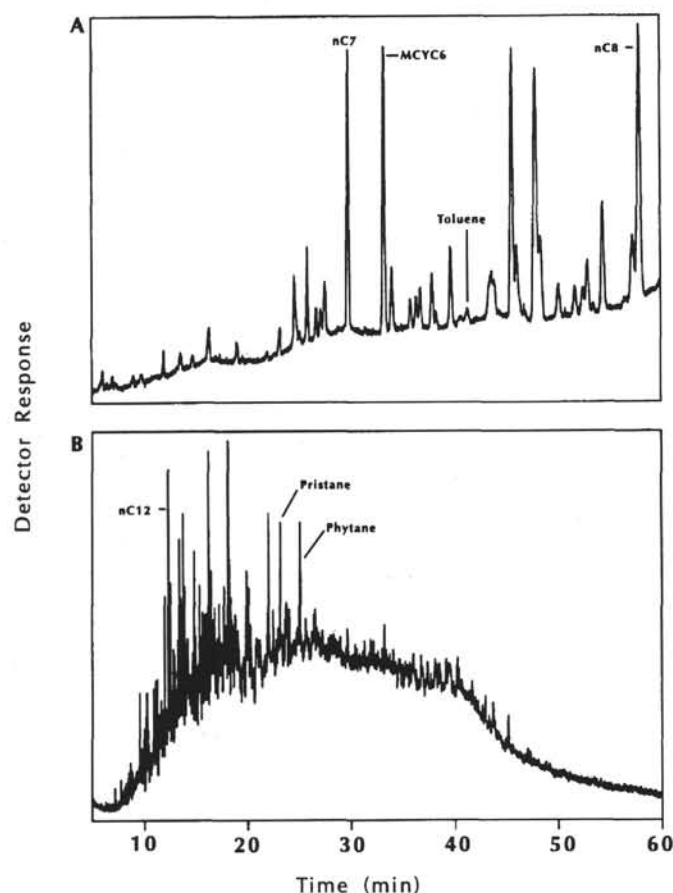

Figure 6. **A.** Gasoline range (C_6–C_8) chromatogram of Pili oil seep sample. MCYC6 is methylcyclohexane. **B.** Saturate fraction gas chromatogram of Pili oil seep sample.

cates that it is the least mature, whereas its sterane distribution suggests that it is the most mature of the samples. The variations in the m/z 191 and 217 fragmentograms may be because indigenous hydrocarbons do in fact comprise a portion of the extracted saturate hydrocarbon fraction of some samples. Biomarkers are present in such low concentrations in these samples that the level of contamination would not need to be very great for their distributions to have been affected.

GEOCHEMISTRY OF PILI OIL SEEP

A sample of an oil seep from Tongatapu was obtained from Sione Soakai of the Ministry of Lands, Surveys and Natural Resources, Tonga. The results of an analysis of this sample were compared with the results obtained from samples collected and analyzed in the early 1980s (Sandstrom and Philp, 1984; Sandstrom, 1985) and used to suggest the nature of source of the seeps.

The sample analyzed here originated from Pili, in the southern outskirts of Nuku'alofa, Tongatapu. It arrived in a jar ($\approx$ 0.5 liter) as a mass of oil floating on water (ratio of oil:water $\approx$ 1:1). A minor amount of vegetable matter was also in the jar.

The sample consisted mostly of hydrocarbons with aromatics predominating over saturates (Table 2). The high proportion of hydrocarbons suggests that this is a migrated oil. The five samples from Hofoa and Fasi analyzed by Sandstrom and Philp (1985) contained much lower amounts of hydrocarbons (20.7%–40.9% vs. 81.24%), possibly because they were more biodegraded. The ratio of saturates to aromatics (0.74) falls into the upper part of the range of values reported by Sandstrom and Philp (1984).

Table 3. Sterane and terpane biomarker ratios for ten Leg 135 sediment samples and Pili oil seep.

Core, section, interval (cm)	Depth (mbsf)	C_{29} S/R[a]	C_{29} αββ/ αββ+ααα[b]	C_{27} D/R[c]	C_{21}/C_{29}[d]	C_{27}[e]	C_{28}[e]	C_{29}[e]	29/30[f]	Ts/Tmg[g]	C_{30} αβ/βα[h]	C_{32} S/S+R[i]	C_{23}/C_{30}[j]
135-834A-1H-4, 140–150	5.90	0.85	0.57	1.09	0.40	30	26	44	0.57	1.13	5.22	1.59	0.13
135-835A-1H-4, 140–150	5.90	0.51	0.48	0.88	0.68	30	17	53	0.68	0.85	7.82	1.50	0.23
135-836A-2H-4, 140–150	7.10	0.57	0.50	0.89	0.53	31	20	49	0.69	0.95	8.75	1.50	0.19
135-837A-4H-4, 140–150	32.90	0.53	0.49	1.00	0.52	30	22	48	0.74	0.92	7.32	1.55	0.19
135-839A-3H-4, 140–150	19.90	0.54	0.50	0.93	0.53	30	20	50	0.69	1.00	11.00	1.43	0.20
135-840C-5H-1, 139–147	125.39	0.40	0.48	0.85	0.64	29	16	55	0.65	0.88	10.80	1.48	0.22
135-841A-1H-4, 140–150	14.40	0.47	0.46	0.71	0.77	32	22	46	0.67	0.88	6.85	1.38	0.29
135-841A-3H-4, 140–150	23.90	0.53	0.48	0.99	0.68	30	21	49	0.65	0.96	7.82	1.60	0.21
135-841A-4H-4, 140–150	33.40	0.44	0.48	0.93	0.58	38	16	46	0.68	0.89	8.41	1.24	0.27
135-841A-6H-4, 140–150	52.40	0.30	0.48	1.12	0.20	32	18	50	0.69	0.85	7.72	1.47	0.19
Pili oil seep		0.97	0.61	0.59	1.50	36	32	32	0.88	0.55	14.90	1.49	0.82

Notes: Results for Pili samples are from GC-MS-MS, which gave similar values to the GC-MS-MID analysis except for the C_{27}:C_{28}:C_{29} 5α(H),14α(H),17α(H)20R ratio, which is different from the ratio of 5α(H),14β(H),17β(H) steranes obtained from the m/z 218 fragmentograms. The C_{27}:C_{28}:C_{29} 5α(H),14α(H),17α(H)20R ratio for the Pili oil seep determined by GC-MS-MS analysis is 44:26:30.

[a] 5α(H),14α(H),17α(H) 20S/5α(H),14α(H),17α(H) 20R-C_{29} sterane.
[b] 5α(H),14β(H),17β(H)/5α(H),14β(H),17β(H)+5α(H),14α(H)17α(H) C_{29} steranes.
[c] 13β(H),17α(H) 20S-diacholestane/5α(H),14α(H),17α(H) 20R–cholestane.
[d] C_{21} sterane/5α(H),14α(H),17α(H) 20R-C_{29} sterane.
[e] Normalized proportion of C_{27}:C_{28}:C_{29} 5α(H),14β(H),17β(H) steranes from m/z 218 fragmentograms.
[f] 17α(H)-norhopane/17α(H)-hopane.
[g] 18α(H)-trisnorhopane/17α(H)-trisnorhopane.
[h] 17α(H)-hopane/17β(H)-moretane.
[i] 22S/22S+22R 17α(H)-bishomohopanes.
[j] C_{23} tricyclic terpane/17α(H)-hopane.

The gasoline-range hydrocarbons of the Pili sample (Fig. 6A) are dominated by n-alkanes and cyclic compounds. Aromatics such as benzene and toluene are present in very low amounts, suggesting that this sample has been affected by water-washing. The chromatogram has lower than normal amounts of C_6 relative to C_7 hydrocarbons, presumably because of the preferential loss of lighter compounds before or during transportation.

The Pili oil seep SFGC consists of a large hump of unresolved compounds with some discrete peaks superimposed, including the C_{14}–C_{20} acyclic isoprenoids (Fig. 6B). This is consistent with the sample having undergone moderate biodegradation (Volkman et al., 1983). The SFGC appears to show the presence of the C_{12} and C_{13} n-alkanes. The occurrence of these compounds and the C_6–C_8 n-alkanes in the gasoline-range fraction implies that mixing of biodegraded hydrocarbons and light unbiodegraded hydrocarbons has occurred. This suggests that the seep is presently active with the addition of hydrocarbons from a more mature source to those previously generated and subsequently biodegraded. Alternately, the source rock may be of similar maturity at present, but preferential migration of lighter hydrocarbons is occurring to the site of the seep.

The saturate hydrocarbons were analyzed by three different GC–MS techniques: GC–MS–MID to look at the distributions of steranes and terpanes, GC–MS–MS to look at the distributions of some of these compounds with greater specificity, and GC–MS in full scan mode to look at the distribution of other compound classes and to obtain mass spectra for the identification of certain peaks. In addition, the distribution of triaromatic steranes was monitored. No evidence was obtained from any of these analyses that the biomarkers had been affected by biodegradation. For example, the 25-norhopanes reported by Sandstrom and Philp (1984) in their seep samples were not detected in the Pili sample.

The steranes (Fig. 7A and Table 3) show a mature distribution, with the ratios of the 20S and 20R 5α(H),14α(H),17α(H) steranes and the 5α(H),14β(H),17β(H) to 5α(H),14α(H),17α(H) steranes near their equilibrium values (Mackenzie, 1984). A low abundance of diasteranes relative to the regular steranes, as displayed by this sample, is normally shown by carbonates and their derived oils (McKirdy et al., 1983). The relative abundance of the C_{27}:C_{28}:C_{29} regular steranes suggests a Cretaceous- to Tertiary-aged source rock (Grantham and Wakefield, 1988). This is also indicated by the ratio of C_{27} to C_{28} triaromatic

steranes ([26R + 27S] – 26S/28S = 2.06; Fig. 7C), which also show a trend through geological time (P.W. Brooks, pers. comm., 1992). Other steroidal compounds identified in this sample are C_{30} regular steranes and C_{28}–C_{30} 4-methylsteranes with the C_{30} members having a dinosterol-derived skeleton. The presence of these compounds indicates a contribution from dinoflagellates and other marine algae to the organic matter of the source rock (Summons et al., 1987; Moldowan et al., 1990). The C_{27}–C_{29} tricyclic compounds that show a major fragment ion of m/z 219 and are thought to be derived from steroidal compounds (Jiang et al., 1990) were also detected.

The m/z 191 mass fragmentogram of the Pili oil seep shows a mature distribution of the 17α(H)-hopanes (Fig. 7B). Tricyclic terpanes are also present in high abundance. The relatively low Ts/Tm ratio (Table 3) is further evidence of a probable carbonate source for these hydrocarbons (McKirdy et al., 1983). Also detected were the C_{29} and C_{30} 8,14-secohopanes and the C_{28} 28,30-bisnorhopane. A small peak with the correct retention time for 18α-oleanane was detected by both GC–MS (Fig. 7B) and GC–MS–MS (using the m/z 412→191 transition) methods. This peak was not in high enough abundance to obtain a mass spectrum good enough to confirm this identification. If oleanane is present, then a minor contribution from Late Cretaceous–Tertiary higher land plant material to the organic matter of the source rock is indicated (Moldowan et al., 1991). It is unlikely that the oleanane originated from the plant material in the jar with the oil sample. This is because a degree of thermal maturation is required to form oleanane from its precursors (ten Haven and Rullkötter, 1988).

Other classes of compounds identified within the oil seep were regular head-to-tail acyclic isoprenoids up to C_{40}, C_{12}–C_{20} n-alkylcyclohexanes, and bicyclic alkanes with the drimane skeleton (Alexander et al., 1984). None of these compounds have a specific biological precursor.

DISCUSSION AND CONCLUSIONS ON THE ORIGIN OF TONGATAPU OIL SEEPS

The m/z 191 and 217 mass fragmentograms of the Pili sample (Fig. 7) show a close resemblance to those of the less degraded samples from Fasi and Hofoa published by Sandstrom and Philp (1984). The only difference is that their samples have a higher abundance of tricyclic terpanes relative to 17α(H)-hopane than the Pili sample. This

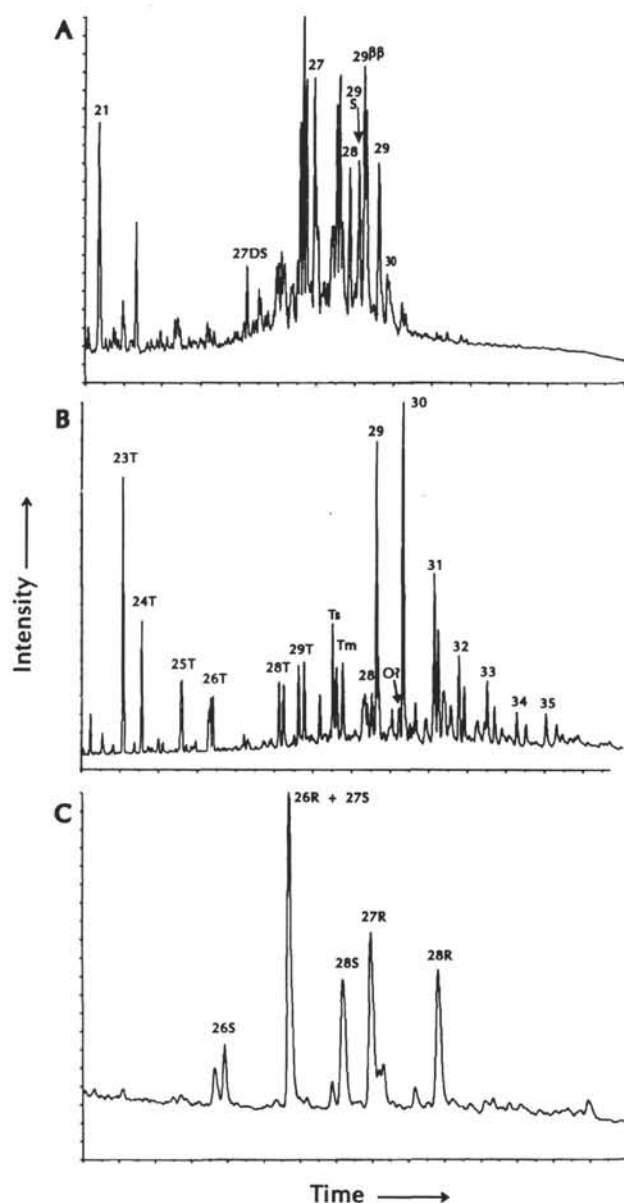
A
21
27DS
27
29ββ
29
S
28
29
30
B
23T
24T
25T
26T
28T
29T
Ts
Tm
28
O?
29
30
31
32
33
34
35
C
26R + 27S
26S
28S
27R
28R
Intensity ⟶
Time ⟶

Figure 7. Mass fragmentograms showing distributions of biomarkers in Pili oil seep sample. **A.** The m/z 217 fragmentogram showing sterane distribution. **B.** The m/z 191 fragmentogram showing terpane distribution (28 is bisnorhopane). **C.** The m/z 231 fragmentogram showing triaromatic sterane distribution. The annotation for Figures 7A and 7B is as for Figures 4 and 5 except for O? in Figure 7B, which indicates the peak that is possibly 18α-oleanane. For Figure 7C, the numbers 26, 27, and 28 are the carbon numbers of the triaromatic steranes, with S and R referring to the stereochemistry of the C20 position.

would be expected because even the less degraded samples analyzed by Sandstrom and Philp (1984) were more severely biodegraded than the Pili oil seep.

The Pili sample was collected during 1991, whereas the samples analyzed by Sandstrom and Philp (1984) were collected during 1982. The close similarity between the geochemical signatures of samples collected from different locations and 9 yr apart is strong evidence against these seeps having an anthropogenic origin. Hence, it is likely that they have been generated from a mature source rock in the vicinity of Tongatapu and migrated into their present location where they have been moderately biodegraded. Geochemical evidence suggests that the source rock is a marine carbonate of probable Cretaceous–Early Tertiary age. As this is not unreasonable for this geological setting, it is additional evidence for the hydrocarbons to have been derived from a local source. The presence of light hydrocarbons that are not biodegraded suggests either that the seep is active, with the source rock still generating hydrocarbons, or that there has been some contamination by lighter hydrocarbons.

The source of the Tongatapu oil seeps remains to be discovered. The results from the Rock-Eval/TOC analysis of Leg 135 samples and the data published by previous workers (Buchbinder and Halley, 1985; Sandstrom, 1985) do not indicate any potential source rocks in the vicinity of Tonga that could possibly be responsible for the seeps on Tongatapu. Eocene limestones equivalent to those exposed on 'Eua and possibly related to those drilled on the Tongan forearc at Site 841 (Unit V, 549.1–605.0 mbsf; Parson, Hawkins, Allan, et al., 1992, pp. 625–628) are thought to be the most likely source (Gatliff, 1990). However, the lithologic features of the Eocene sediments recovered from Hole 841B do not appear to indicate anoxic bottom waters during deposition and consequently do not seem favorable for the development of source rock facies. This is evident from the low TOC contents of these sediments.

ACKNOWLEDGMENTS

I thank Ross Stewart, Sneh Achal, and Marg Northcott for their excellent technical assistance, and the Geological Survey of Canada and the Ocean Drilling Program for the opportunity to be a shipboard scientist on Leg 135. This is Geological Survey of Canada Contribution No. 16992.

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[*] Abbreviations for names of organizations and publication titles in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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