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THE PORPHYRIN MATURITY PARAMETER AS AN INDICATOR OF OIL MATURITY AND THE ONSET OF OIL GENERATION IN THE CRETACEOUS SLATER RIVER FORMATION, FORT NORMAN AREA, NORTHWEST TERRITORIES

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CHEVRON CANADA RESOURCES

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Abstract

Rock Eval pyrolysis data from twelve wells in the area of Fort Norman, NWT indicate that the radioactive shale zone of the Cretaceous Slater River Formation is a very good, oil-prone source rock. Thermal maturity increases to the southwest of the study area and oil generation begins at low pyrolysis Tmax values because of the high sulphur content of the kerogen. High-performance liquid chromatographic porphyrin analyses were run on five Slater River extracts from the Brackett C-21, Tate J-65, Little Bear L-21, East Mackay I-55 and Stewart B-30 wells. The porphyrin maturity parameter demonstrates that the Slater River zone in these wells has reached the onset of oil generation.

Biomarker distributions were used by previous workers to correlate the oil recovered from the Cambrian-Ordovician Franklin Mountain Formation in the East Mackay B-45 well to the radioactive shale zone of the Slater River Formation as the source. The biomarker ratios for the B-45 oil indicated a low level of maturity, corresponding more or less to the onset of oil generation. The porphyrin maturity parameter (PMP) also indicates that the maturity level of the B-45 oil is low, corresponding to the onset of oil generation, and is similar to the maturity of the overlying source rocks. The PMP results support local generation and accumulation of the B-45 oil with limited migration.

Introduction

The Fort Norman area in the Northwest Territories (Figure 1) has nearly two kilometres of Upper Cretaceous to Eocene sandstones and shales within the Brackett Basin. Clastic sediment, both marine and non-marine, was derived primarily from the Cordilleran orogeny to the southwest and, originally, likely covered the entire Mackenzie Corridor. However, because of subsequent uplift and erosion, the Brackett Basin is one of the few areas in the corridor where this section is preserved.

In this area, the Keele Arch was emergent prior to Cretaceous sedimentation and was progressively onlapped by the marine shales of the Arctic Red (Albian) and Slater River (Cenomanian to Coniacian) Formations (Figure 2). The arch was completely buried during deposition of the marine, shallowing upward to non-marine, sandstones of the Little Bear Formation (Santonian to Campanian). The Little Bear was overlain by the marine shales of the East Fork Formation (Campanian to Maastrichtian) and the non-marine sandstones, conglomerates and volcanics of the Summit Creek Formation (Paleocene to Eocene) (after Yorath and Cook, 1981; Williams, 1989).

The East Mackay B-45 well (64°44'9"N, 125°38'18"W) tested 558m of 20.4° API oil, 168m of water and 30m of oil cut mud from the Cambrian-Ordovician Franklin Mountain Formation. Feinstein et al. (1988) correlated this oil to the unconformably overlying, organic rich, Cretaceous Slater River radioactive shale zone as the source. Rock Eval pyrolysis data and High Performance Liquid Chromatographic (HPLC) analysis of vanadylporphyrins were used to evaluate the maturities of the Slater River radioactive zone and the East Mackay B-45 oil.

Experimental

Well cuttings from the Slater River radioactive zone and an aliquot of the B-45 oil were obtained from the Institute of Sedimentary and Petroleum Geology. The cuttings were pulverized with a mortar and pestle and analyzed by a Rock Eval II (TOC) pyroanalyzer. Pyrolysis procedures are described by Peters (1986).

Five pulverized composite Slater River samples, one from each of the Brackett C-21, Tate J-65, Little Bear L-21, East Mackay I-55 and Stewart B-30 wells (see Figures 1 and 2), were extracted using methylene chloride. The bitumen was chromatographed on active II alumina and eluted with methylene chloride to provide a polar fraction which included vanadylporphyrins (Sundararaman, 1985 and Sundararaman et al., 1988). The polar fraction was purified with propane-sulphonic acid bonded silica and eluted with toluene:hexane (1:1). The HPLC analysis used a 65 cm Hypersil C_{18} column with a flow rate of 0.8 ml/min and a solvent system of 47.5% methanol, 47.5% acetonitrile and 5% water.

Results and Discussion

The Rock Eval pyrolysis results for the Slater River radioactive zone are listed in Table 1. Peters (1986) geochemical parameters describing source rock generative potential and type of hydrocarbons generated are listed in Tables 2 and 3. The Slater River radioactive zone is a very good, oil-prone source rock. The Slater River extracts contain predominantly vanadyl porphyrins and have low Ni/(Ni+VO) ratios, indicating that the formation was deposited in an anoxic marine environment where vanadium was in the correct oxidation state (VO^{2+}) for complexation with porphyrins (Table 4). The anoxic conditions allowed the preservation of organic matter. Source rocks deposited in suboxic

marine or lacustrine environments have high Ni/(Ni+VO) ratios because vanadium oxidizes to the V^{V} and V^{VI} species and cannot be incorporated into porphyrins (Table 5). These environments favour the formation of nickel porphyrins (Sundararaman and Boreham, 1991, Sundararaman et al., 1992).

The average Tmax value for the Slater River zone in each of the twelve wells is mapped in Figure 1. Thermal maturity increases to the southwest and the Tmax values are lower than expected because of the high sulphur content of the kerogen. The Slater River extracts from the Tate J-65 and Little Bear L-21 wells have respective sulphur contents of 3.7% and 4.9% and the B-45 oil has a sulphur content of 2.0% (Table 4). Orr (1986), who examined Monterey oils in the Santa Maria basin, states that "high sulphur kerogens appear to generate oil at significantly lower thermal exposures" because "preferential cleavage at weak sulphur linkages tends to produce larger fragments, leading to high initial amounts of asphaltenes, resins, and sulphur-rich aromatics together with smaller amounts of saturated hydrocarbons". The average production indices for the Slater River radioactive zone are mapped in Figure 1 and range from 0.04 to 0.21. Peters (1986) states that the top of the oil window, or birthline, occurs at a production index of approximately 0.1.

The onset of oil generation in the Slater River radioactive zone was also assessed using the Porphyrin Maturity Parameter ($PMP=C_{28}E/(C_{28}E+C_{32}D)$ where $C_{28}E$ is an ETIO porphyrin and $C_{32}D$ is a DPEP porphyrin (Figure 3, a-e). Porphyrins are derived from chlorophylls and bacteriochlorophylls and were the first biological marker compounds identified in fossil fuels. PMP increases with maturity as the concentration of C_{28} ETIO porphyrins changes relative to the C_{32} DPEP porphyrins (Sundararaman et al., 1988). A PMP less than 0.2 indicates immaturity (Aizenshtat and Sundararaman, 1989).

HPLCs of vanadylporphyrins for the Slater River extracts from the Brackett C-21, Tate J-65, Little Bear L-21, East Mackay I-55 and Stewart B-30 wells are shown in Figure 3, a-e. The C_{32} DPEP porphyrins predominate over the C_{28} ETIO porphyrins. The C-21 extract has a PMP of 0.00, indicating that the Slater River radioactive zone is immature in the northeast part of the study area (Table 4, Figure 1). The PMPs for the J-65, L-21, I-55 and B-30 extracts range from 0.22 to 0.41 indicating that oil generation has begun in the southwest part of the study area even though the Tmax values for these wells only range from 418 to 425°C.

Feinstein et al. (1988) correlated the B-45 oil to the Slater River Formation as the source using the terpane and sterane distributions, which are respectively obtained from the GC-MS m/z 191 and m/z 217 mass fragmentograms. The (22S/22R)C_{32}-hopane and (20S/20R)C_{29}-sterane isomerization ratios indicated that the maturity of the B-45 oil corresponded more or less to the onset of oil generation. The maturity distribution of the Slater River shale and the direct source/reservoir contact suggested local hydrocarbon generation and accumulation with limited migration (Feinstein et al., 1988). The B-45 oil has a PMP of 0.24 (Figure 3f) which corresponds to the onset of oil generation and is similar to the PMP of 0.38 for the Slater River radioactive zone in the offsetting East Mackay I-55 well (Table 4 and Figure 3d). The PMP results support the hypothesis of local hydrocarbon generation and accumulation with limited migration.

Acknowledgements

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MacNabb. The pyrolysis data were plotted by E. Truscott. Sample extraction was done by J. Dyer and the HPLC of vanadylporphyrins was run by R. Stewart. Chevron Canada Resources is gratefully acknowledged for providing the resources necessary to complete this project.

References

Aizenshtat, Z. and Sundararaman, 1989, Maturation trend in oils and asphalts of the Jordan Rift: Utilization of detailed vanadylporphyrin analysis. Geochim. et Cosmochim. Acta vol. 53, pp 3158-3188.

Feinstein, S., Brooks, P.W., Fowler, M.G., Snowdon, L.R. and Williams, G.K., 1988, Families of oils and source rocks in the central Mackenzie Corridor: A geochemical oil-oil and oil-source rock correlation. CSPG Memoir 15, pp 543-552.

Orr, W.L., 1986, Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils. Adv. in Org. Geochem. vol. 10, pp 499-516.

Peters, K.E., 1986, Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bull. vol. 70, no. 3, pp 318-329.

Sundararaman, P., 1985, High-performance liquid chromatography of vanadyl porphyrins. Anal. Chem. vol. 57, pp 2204-2206.

Sundararaman, P., Biggs, W.R., Reynolds, J.G. and Fetzer, J.C., 1988, Vanadylporphyrins, indicators of kerogen breakdown and generation of petroleum. Geochim. et Cosmochim. Acta vol. 52, pp 2337-2341.

Sundararaman, P. and Boreham, C.J., 1991, Vanadyl 3-nor C_{30} DPEP: Indicator of depositional environment of a lacustrine sediment. Geochim. et Cosmochim. Acta vol. 55, pp 389-395.

Sundararaman, P., Schoell, M., Littke, R., Baker, D., Leythaeuser, D. and Rullkötter, J., 1992, Depositional environment of Toarcian shales from northern Germany as monitored by porphyrins. submitted to Geochim. et Cosmochim. Acta for publication.

Yorath, C.J. and Cook, D.G., 1981. Cretaceous and Tertiary stratigraphy and paleogeography, Northern Interior Plains, District of Mackenzie. GSC Memoir 398. 76 p.

Williams, G.K., 1989, Tectonic evolution of the Fort Norman area, Mackenzie Corridor, NWT. GSC Open File 2045.

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Table 1: Rock Eval II (TOC) Pyrolysis Data

Depth	%TOC	S1	S2	HI	Tmax	PI
Brackett C-21 65°10'N 125°05'W						
920m	5.49	1.33	29.83	543	405	0.04
930m	5.16	0.90	19.96	386	408	0.04
940m	4.48	0.79	18.90	421	407	0.04
950m	5.58	1.03	24.87	445	405	0.04
960m	5.04	0.87	15.70	311	405	0.05
East Mackay I-55 64°45'N 125°38'W						
1320m	3.89	0.51	9.64	248	421	0.05
1325m	3.94	0.55	12.65	321	419	0.04
1330m	4.87	1.15	23.79	489	420	0.05
1335m	3.61	0.54	12.01	333	418	0.04
1340m	3.63	0.61	15.16	418	419	0.04
1345m	2.54	0.26	3.92	154	424	0.06
1350m	1.76	0.27	2.84	161	426	0.09
1355m	3.96	0.35	7.73	195	425	0.04
1360m	1.45	0.31	2.37	163	424	0.12
Keele R I-01 64°21'N 125°00'W						
3570ft	2.24	0.47	4.63	207	424	0.09
3580ft	4.28	1.18	15.04	351	421	0.07
3590ft	5.48	2.48	24.57	448	423	0.09
3600ft	4.70	2.97	25.18	536	429	0.11
3610ft	4.37	2.51	20.97	480	426	0.11
3620ft	1.63	0.32	3.61	221	428	0.08
3630ft	1.56	0.47	3.05	196	430	0.13
Keele R L-04 64°24'N 125°02'W						
2180ft	4.85	1.63	19.86	409	415	0.08
2190ft	6.88	2.67	35.00	509	415	0.07
2200ft	8.96	3.00	41.64	465	417	0.07
2210ft	8.77	3.61	44.82	511	421	0.07
2220ft	7.12	2.67	36.72	516	420	0.07
2230ft	1.99	0.73	6.17	310	421	0.11
2240ft	2.63	1.28	13.88	528	419	0.08
2250ft	1.91	1.00	6.91	362	423	0.13
2260ft	1.87	0.89	7.20	385	423	0.11
2270ft	1.60	0.68	5.02	314	423	0.12
2280ft	1.64	0.75	5.07	309	424	0.13
2290ft	3.12	0.89	13.63	437	421	0.06

Table 1: Rock Eval II (TOC) Pyrolysis Data

Depth	%TOC	S1	S2	HI	Tmax	PI
Keele S A–28 64°07'N 125°04'W						
3820ft	0.89	0.26	1.16	130	441	0.18
3840ft	0.95	0.22	0.94	98	439	0.19
3850ft	0.99	0.16	0.95	95	432	0.15
3860ft	1.54	0.25	2.40	155	428	0.09
3870ft	1.32	0.21	1.84	139	431	0.10
Keele S E–19 64°08'N 125°04'W						
780m	1.48	0.19	1.20	81	421	0.14
810m	1.74	0.33	2.22	128	423	0.13
840m	2.67	4.33	8.22	308	418	0.35
Kialo B–62 65°11'N 125°27'W						
335m	6.15	0.88	25.21	409	405	0.03
340m	3.15	0.95	13.39	425	406	0.07
345m	2.73	0.51	9.33	341	410	0.05
350m	1.83	0.33	6.22	339	411	0.05
Little Bear L–21 64°41'N 125°50'W						
1363m	4.43	1.00	12.21	276	422	0.08
1370m	5.71	1.98	23.20	406	423	0.08
1375m	7.52	3.02	32.53	433	421	0.08
1380m	5.46	1.97	22.36	410	423	0.08
1395m	5.05	1.68	21.88	433	426	0.07
1410m	3.53	1.04	10.36	293	425	0.09
1425m	2.88	0.69	6.91	240	427	0.09
Redstone P–78 64°08'N 124°28'W						
1150ft	1.49	0.23	2.27	152	423	0.09
1160ft	1.30	0.27	1.89	145	422	0.12

Table 1: Rock Eval II (TOC) Pyrolysis Data

Depth	%TOC	S1	S2	HI	Tmax	PI
Stewart B–30 64°19'N 125°04'W						
5300ft	1.64	0.34	4.18	254	431	0.08
5310ft	1.96	0.52	4.87	248	427	0.10
5320ft	2.92	1.09	11.88	406	426	0.08
5330ft	4.16	1.48	19.54	469	425	0.07
5340ft	4.44	1.70	20.73	466	424	0.08
5360ft	4.63	1.49	20.53	443	425	0.07
5380ft	4.10	1.34	18.22	444	425	0.07
5400ft	3.80	1.64	18.97	499	428	0.08
5420ft	2.43	0.99	12.03	495	425	0.08
5440ft	2.11	0.56	6.70	317	427	0.08
Tate J–65 64°25'N 125°27'W						
5560ft	1.46	0.21	2.02	138	422	0.09
5580ft	1.87	0.32	3.12	167	422	0.09
5600ft	5.04	1.47	21.91	435	418	0.06
5620ft	7.17	2.68	39.08	545	417	0.06
5640ft	6.57	2.51	35.82	545	418	0.07
5660ft	3.31	0.72	12.94	391	417	0.05
5680ft	3.37	0.89	15.68	465	420	0.05
5700ft	4.49	1.34	24.01	535	418	0.05
5720ft	5.24	1.77	31.00	592	420	0.05
5740ft	3.59	0.75	15.61	435	419	0.05
Windy Island A–53 64°52'N 125°39'W						
940m	6.63	1.12	25.93	391	414	0.04
945m	7.54	1.49	31.06	411	413	0.05
950m	7.10	1.32	30.84	434	413	0.04
955m	4.30	0.70	17.14	398	412	0.04
960m	4.73	0.76	19.53	412	412	0.04
965m	4.18	0.81	20.64	493	413	0.04
970m	2.97	0.43	11.64	391	415	0.04
975m	2.39	0.33	9.69	405	415	0.03

Table 2: Geochemical Parameters Describing Source Rock Generative Potential (Peters, 1986)

Quantity	TOC (wt %)	S1	S2
Poor	0–0.5	0–0.5	0–2.5
Fair	0.5–1	0.5–1	2.5–5
Good	1–2	1–2	5–10
Very Good	2+	2+	10+

S1=mg HC/g rock
S2=mg HC/g rock

Table 3: Geochemical Parameters Describing Type of Hydrocarbon Generated (Peters, 1986)

Type	HI (mg HC/g C org)*	S2/S3*
Gas	0–150	0–3
Gas and Oil	150–300	3–5
Oil	300+	5+

* Assumes a level of thermal maturation equivalent to Ro=0.6%

Table 4: Maturity Parameters for the Slater River Extracts and the B-45 Oil

Well	Sample Depth	%S	Tmax	PI	Ni/(Ni+VO)	PMP
Brackett C-21	920–960m		406	0.04	0.00	0.00
Tate J-65	5600–5640'	3.7	418	0.06	0.04	0.22
Little Bear L-21	1370–1395m	4.9	423	0.08	0.00	0.22
East Mackay I-55	1325–1340m		419	0.04	0.00	0.38
Stewart B-30	5320–5380'		425	0.07	0.00	0.41
East Mackay B-45	3990–4042'	2.0			0.20	0.24

Table 5: Porphyrin Parameters Describing Source Rock Maturity and Depositional Environment

	PMP		Ni/(Ni+VO)
Immature	0–0.2	Anoxic	0–0.2
Early Oil Generation	0.2–1.0	Suboxic	0.2–1.0
Peak Oil Generation	1.0		

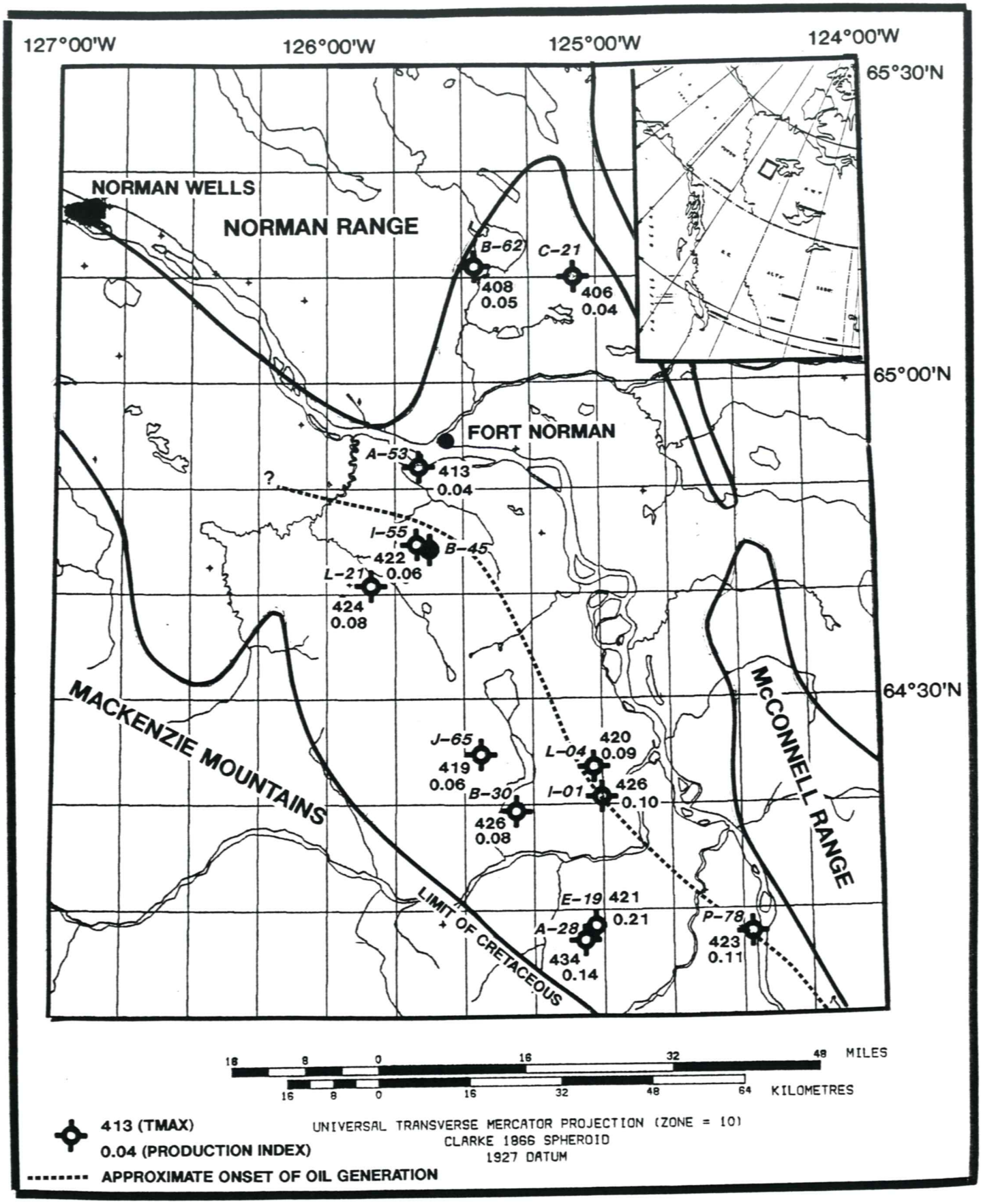


Figure 1: Thermal Maturity Map (Tmax) on the Slater River Radioactive Zone

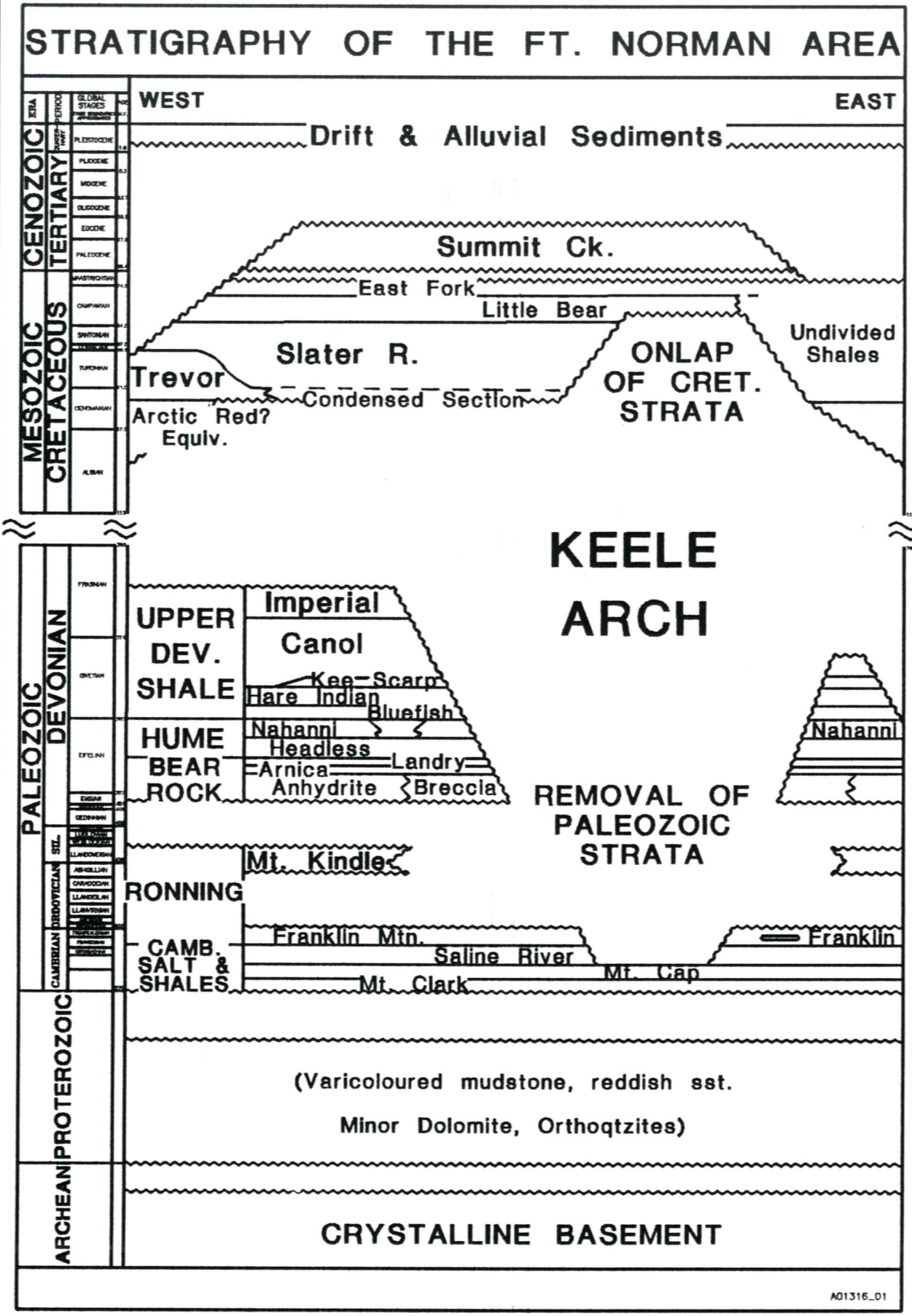
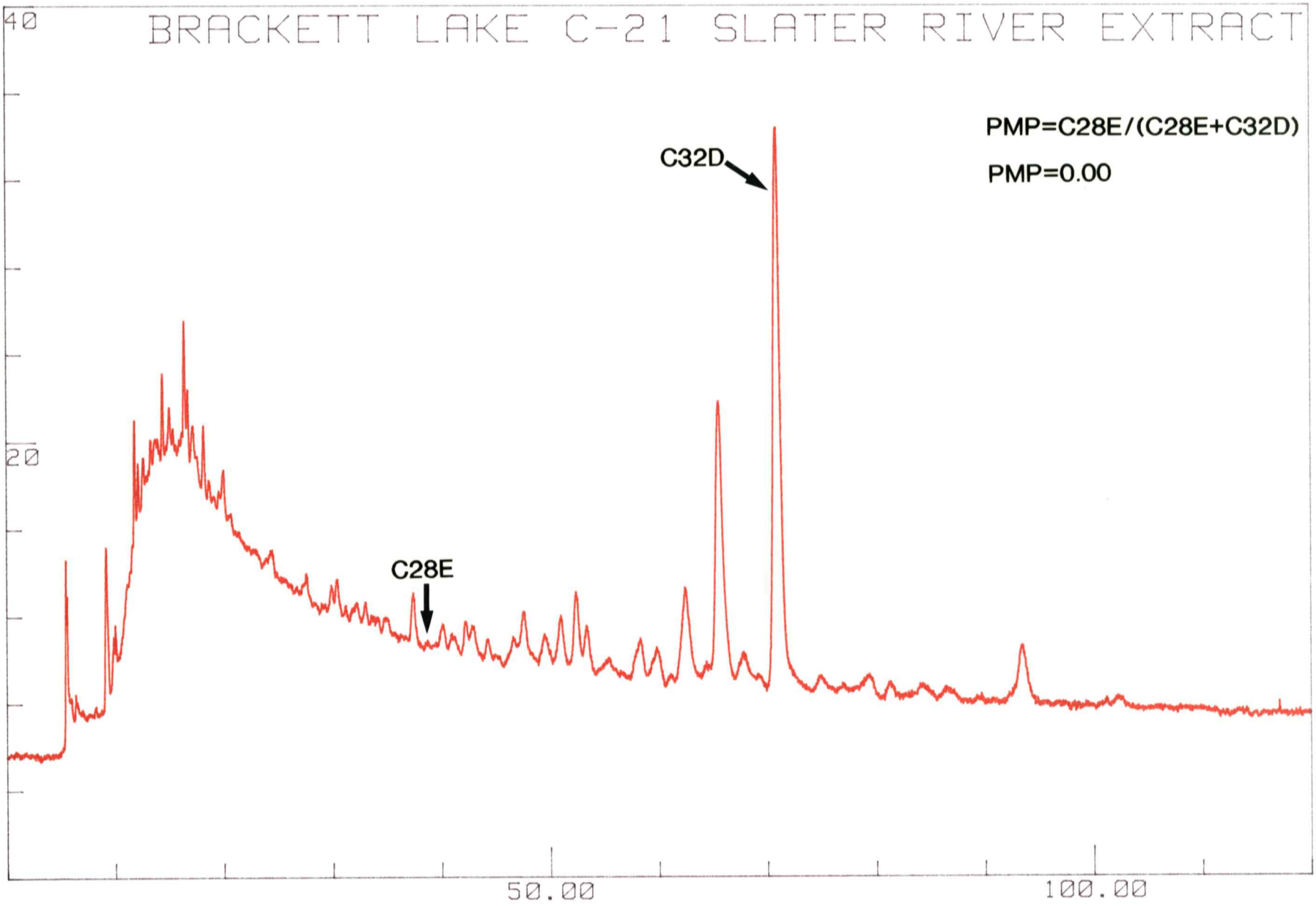

STRATIGRAPHY OF THE FT. NORMAN AREA
WEST
EAST
Drift & Alluvial Sediments
CENOZOIC
MESOZOIC
TERTIARY
CRETACEOUS
Summit Ck.
East Fork
Little Bear
Slater R.
Trevor
Condensed Section
ONLAP OF CRET. STRATA
Undivided Shales
Arctic Red? Equiv.
KEELE ARCH
PALEOZOIC
DEVONIAN
UPPER DEV. SHALE
Imperial
Canol
Kee Scarp
Hare Indian
Bluefish
HUME
Nahanni
Headless
BEAR ROCK
Arnica
Landry
Anhydrite
Breccia
Nahanni
REMOVAL OF PALEOZOIC STRATA
Mt. Kindle
RONNING
CAMB. SALT & SHALES
Franklin Mtn.
Saline River
Mt. Clark
Mt. Cap
Franklin
PROTEROZOIC
(Varicoloured mudstone, reddish sst.
Minor Dolomite, Orthoqtzites)
ARCHEAN
CRYSTALLINE BASEMENT
A01316_01

Figure 2


BRACKETT LAKE C-21 SLATER RIVER EXTRACT
40
20
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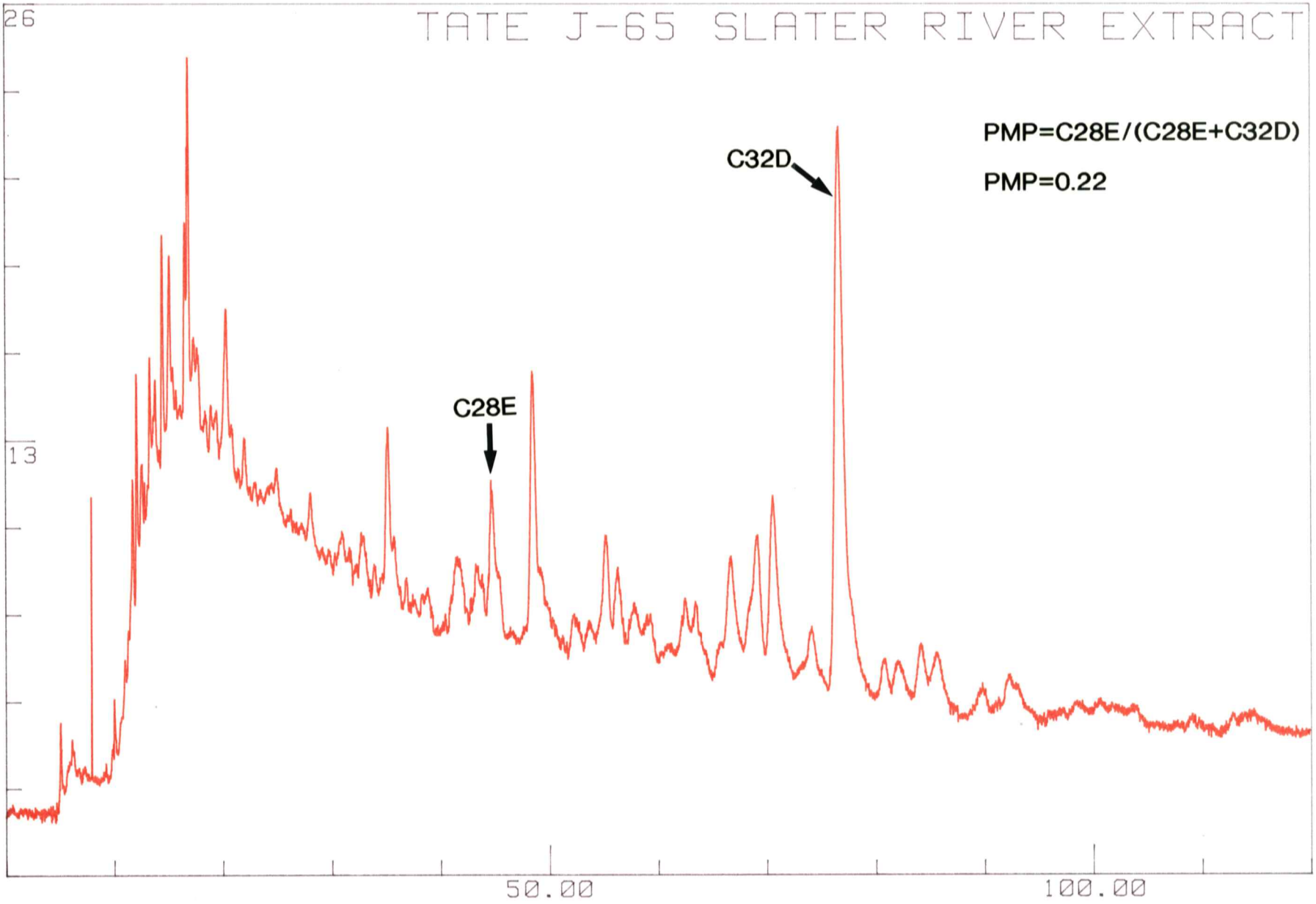
PMP=0.00
C32D
C28E
50.00
100.00

Figure 3a


TATE J-65 SLATER RIVER EXTRACT
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13
C32D
C28E
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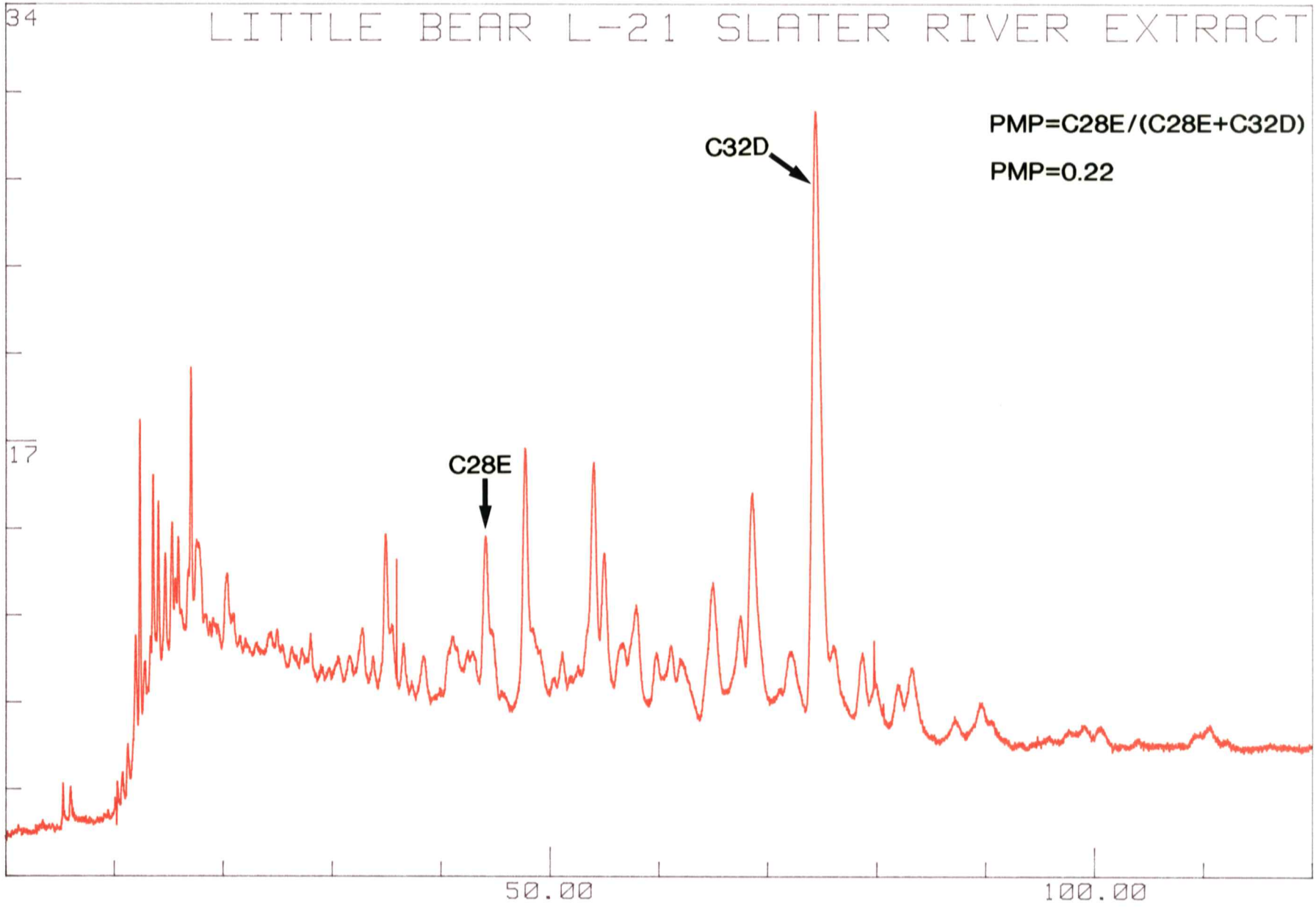
PMP=0.22
50.00
100.00

Figure 3b


34
LITTLE BEAR L-21 SLATER RIVER EXTRACT
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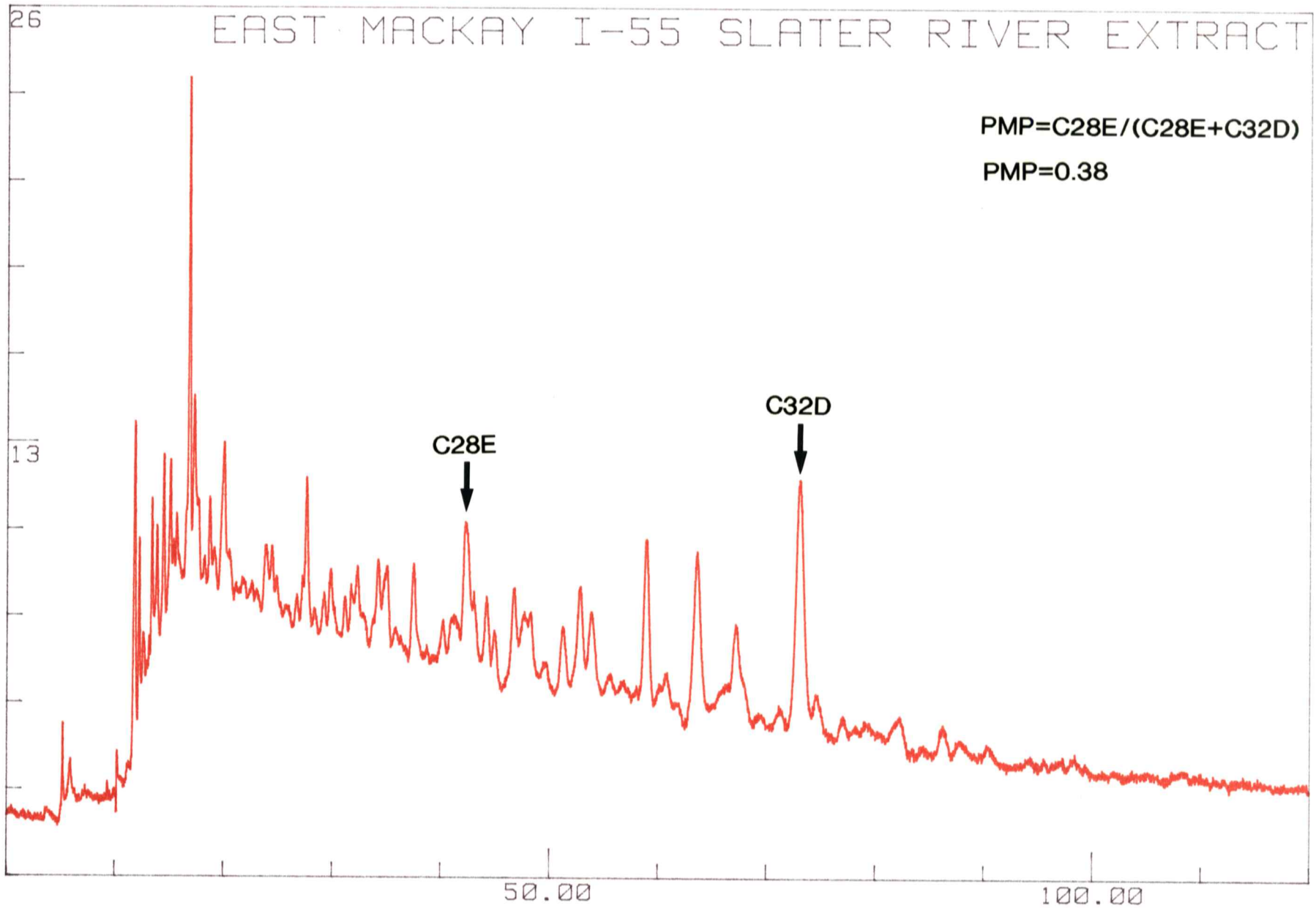
PMP=0.22
C32D
C28E
17
50.00
100.00

Figure 3c


EAST MACKAY I-55 SLATER RIVER EXTRACT
26
13
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PMP=0.38
C28E
C32D
50.00
100.00

Figure 3d

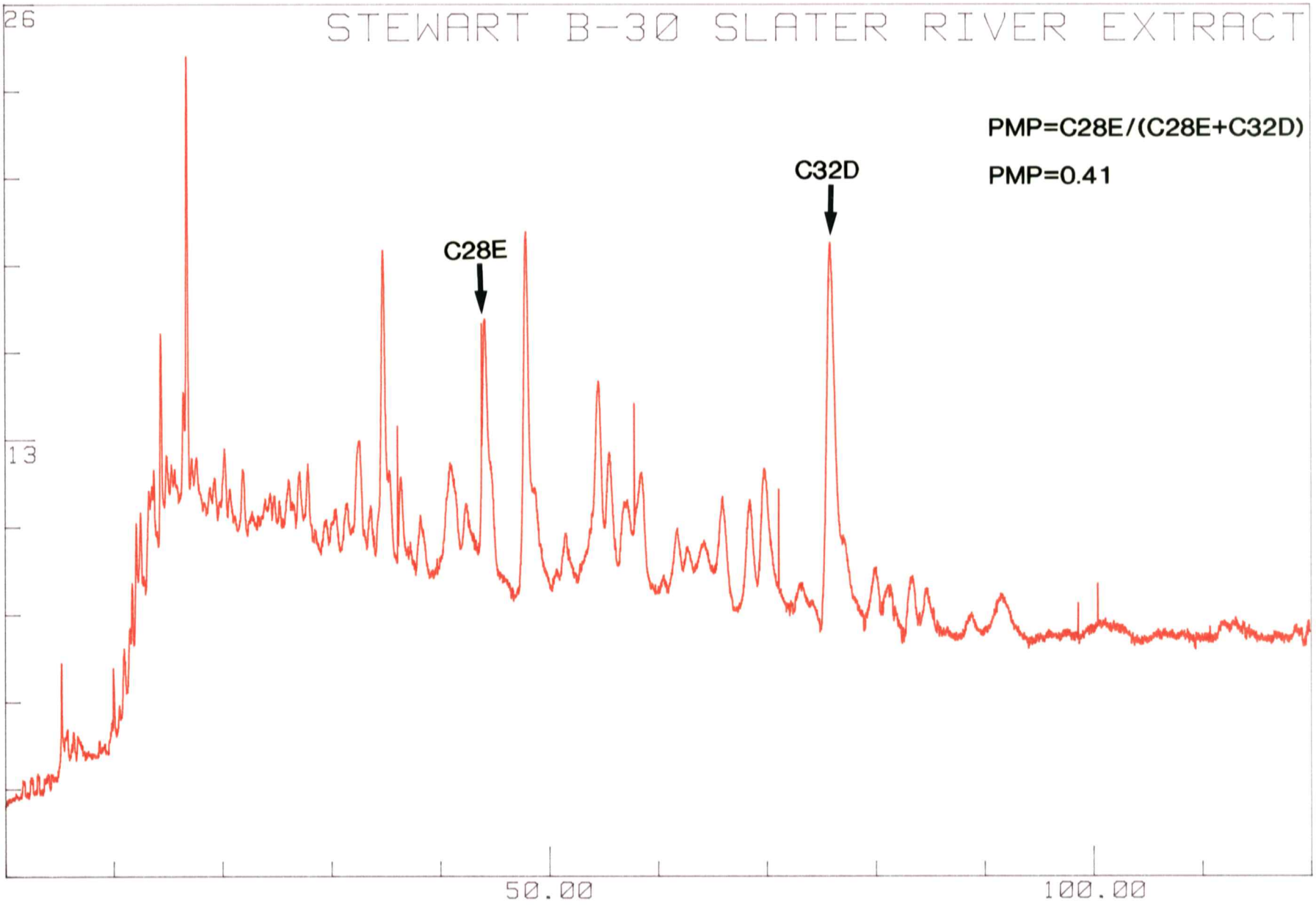
STEWART B-30 SLATER RIVER EXTRACT
26
13
C28E
C32D
PMP=C28E/(C28E+C32D)
PMP=0.41
50.00
100.00

Figure 3e

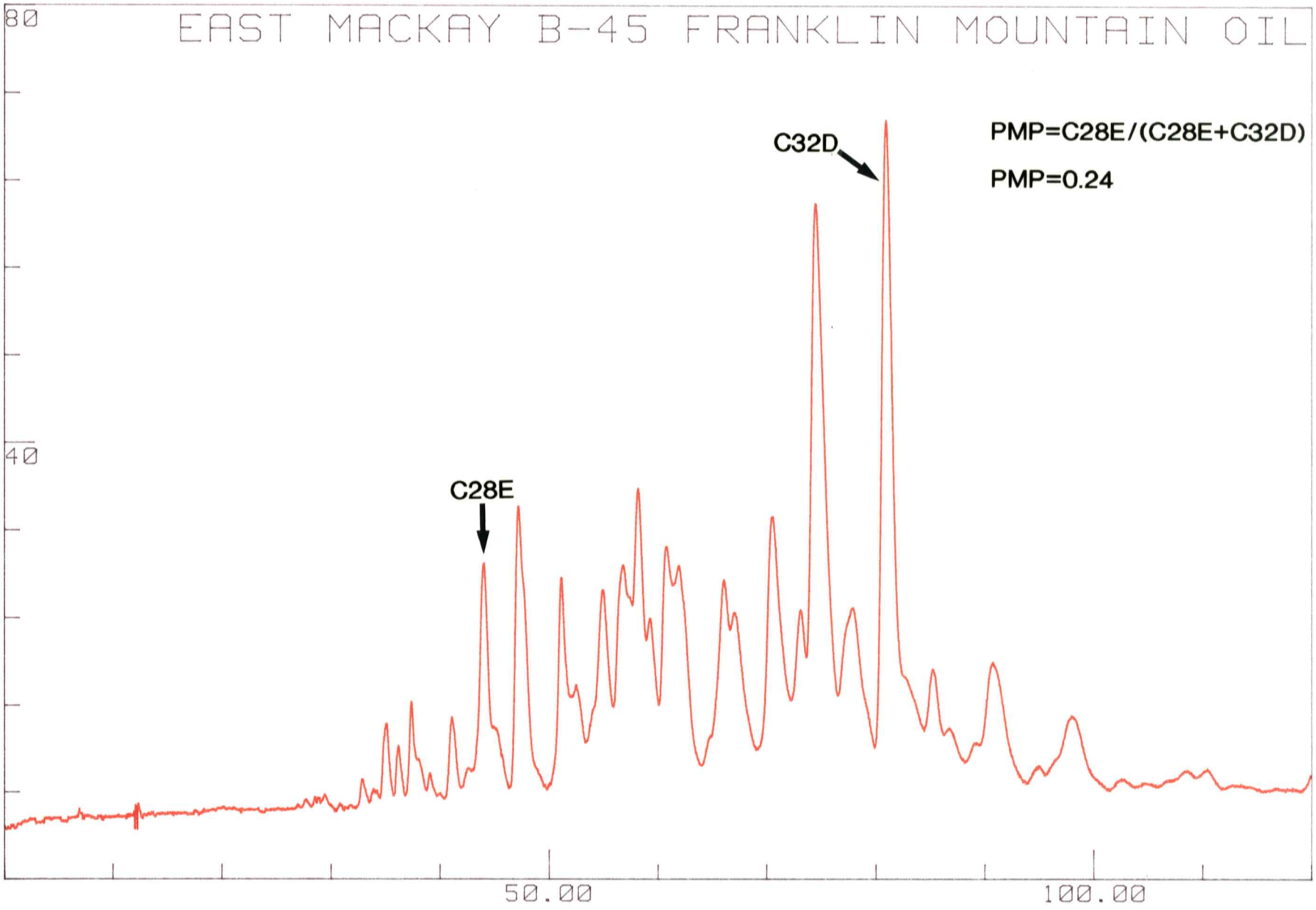
EAST MACKAY B-45 FRANKLIN MOUNTAIN OIL
80
40
C32D
C28E
PMP=C28E/(C28E+C32D)
PMP=0.24
50.00
100.00

Figure 3f