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GEOCHEMICAL ANALYSIS OF POTASH MINE SEEP OILS, COLLAPSED BRECCIA PIPE OIL SHOWS AND SELECTED CRUDE OILS, EDDY COUNTY, NEW MEXICO

by

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ABSTRACT

Oil shows, in the form of oil stains and bleeding oil, in core samples from two breccia pipes, Hills A and C, Eddy County, New Mexico, and seepage oils in a potash mine near Hill C breccia pipe are geochemically similar. The geochemical similarities strongly suggest that they belong to the same family of oils and were derived from similar sources.

The oils are relatively high in sulfur (0.89 to 1.23 percent), rich in hydrocarbons (average 82 percent), relatively high in saturated hydrocarbon/aromatic hydrocarbon ratios (average 2.9), and based on analysis of seep oils alone, have a low API gravity (average 19.4°). The oils are for the most part severely biodegraded as attested by the loss of n-paraffin molecules.

Geochemical comparison of seven crude oils collected in the vicinity of the breccia pipes indicates that the Yates oils are the likely source of the above family of oils. Six barrels of crude oil that were dumped into a potash exploration borehole near Hill C breccia pipe, to release stuck casing, are considered an unlikely source of the breccia pipe and mine seep oils. Volumetric and hydrodynamic constraints make it highly improbable that such a small volume of "dumped" oil could migrate over distances ranging from about 600 feet to 2.5 miles to the sites of the oil shows.

INTRODUCTION

Numerous geologic, geophysical, and hydrologic studies are being carried out in the Carlsbad area of Eddy County, southeastern New Mexico, by the U.S. Geological Survey on behalf of the Department of Energy. The area is being considered for an underground storage facility for radioactive waste. One of these studies concerns breccia pipes, nearly cylindrical collapsed-type features, filled with fractured rock, silt, sand, and mud. Two of these breccia pipe features (Fig. 1), Hills A and C, about 2.5 miles apart, and about 20 miles northeast of Carlsbad, have been drilled and cored in an attempt to reconstruct the geologic history of their formation. Rocks were found to have been displaced downward in Hill A as much as about 1,100 ft and in Hill C as much as 350 ft.

Traces of oil in the form of oil stains and bleeding oil were observed in core samples retrieved from drill holes WIPP-31 (Hill A breccia pipe) and WIPP-16 (Hill C breccia pipe) at depths of 1,629 and 1,281 ft, respectively. The WIPP-16 core sample is from a displaced block of the Rustler Formation; the other core sample is from a displaced block of either the Rustler or the Salado Formation, both of which are Late Permian in age (Fig. 2). Both of the samples are a few hundred feet below their normal stratigraphic horizons. The breccia pipes occur over the buried Capitan reef just north of the Delaware Basin (Fig. 1).

Substantially greater amounts of oil were also discovered in an active oil seep, about 140 ft east of the boundary of Hill C breccia pipe, along a fault zone in salt and potash deposits of the Salado Formation in the Mississippi Chemical Corporation (MCC) potash mine (Fig. 3). At the time when the oil seep was first encountered in 1975, at least five gallons of oil were recovered. Bleeding and dripping oil along the fault plane has continued to date but at a much reduced rate. The oil seep, at a depth of 1,164 ft beneath the surface, is also located about 600 ft north of a plugged and abandoned potash exploration borehole (U.S. B & C 184; Fig. 3) drilled about 1950. This latter borehole is singled out because about six barrels of crude oil were dumped into the hole to facilitate release of stuck casing. One of the problems that evolved and one that needs to be resolved is whether this "dumped oil" migrated north and northwestward and acted as the source of the mine seep oil and breccia pipe oil shows.

Representative samples of oil-stained breccia pipe cores (Nos. 11, 12) and mine seep oils (Nos. 10, 10A, and MC, Table 1) were collected for geochemical analysis to determine the nature of the oils, their relation to one another, and their possible sources.

In addition, seven crude oil samples (Nos. 1-9, Table 2), (six Permian and one Pennsylvanian in age) were collected from nearby oil fields. They were submitted for analysis to determine, by means of oil-to-oil correlation, their likelihood as a possible source for the breccia pipe and mine seep oils. One drill cuttings sample (No. 218, Table 2), of the Bone Spring Limestone of Early Permian age was also included to determine whether the Bone Spring might be the ultimate source of the breccia pipe and seep oils. Other studies (J. A. Williams, 1977; oral commun., 1981) have shown that the Bone Spring Limestone is the likely source of many of the Permian oils in the Delaware Basin and Northwest Shelf.

ACKNOWLEDGMENTS

We thank James Walls, vice-president and general manager of Mississippi Chemical Corporation, Eddy County, New Mexico, for his generous assistance and cooperation and for allowing us access to the oil source in the mine. We thank C. W. McCroskey, chief chemist of the Corporation, for supplying us with a sample of the oil taken when the oil was first encountered in 1975. Thanks are also due to James Brasfield, USGS, Artesia, N. Mex., who was responsible for collecting crude oil samples from producing wells.

ANALYTICAL PROCEDURES

Deasphaltening and silica gel chromatography were used to characterize the gross chemical composition of the crude and extracted oils. Heptane was initially used to precipitate out the heavy asphaltene fraction. The successive silica-gel column elutants--heptane, benzene, and benzene-methanol (1:1)--gave rise to the saturated hydrocarbon, aromatic hydrocarbon, and resins fractions, respectively. The fraction of "amount lost" is attributed predominantly to lower molecular weight hydrocarbons ($<C_{12}$) lost by evaporation during the removal of the elutant solvents and to a much lesser degree to heavier hydrocarbons retained on the silica gel column. In general, higher "amount lost" values are correlative with higher API gravities and indicate relatively greater amounts of lower molecular weight hydrocarbons in the oils.

Gas chromatographic analysis, a method for characterizing molecular distributions of volatile organic chemical compounds, was limited to only the saturated hydrocarbon fraction. These molecular distributions can be used as "fingerprints" for identifying and correlating crude oils and crude oil/source rock combinations. Analyses were made on a Varian 2800 gas chromatograph using a 1.8 m x 2 mm I.D. glass column packed with 3% SE-30 on 100/120 Mesh Gas Chrom Q. Column temperature was 80°C at injection (injector temperature at 300°C) and was programmed to rise 12°C/-min for 10 minutes, then 10°C/min for 10 minutes to a final temperature of 300°C, which was then held for another six minutes.

RESULTS AND DISCUSSION

Mine Seep Oils

Geochemical analyses, including gas chromatography and carbon isotope ratios for the three mine seep oil samples, collected in three different spot locations underground all within 100 ft of each other (Fig. 3) and at different times from the MCC potash mine, are essentially identical, indicating that they were derived from a common source (Table 3, Figs. 4, 5, 6). The oils are heavy (average API gravity, 19.4°, relatively rich in sulfur (average 1.1 percent), rich in total hydrocarbon content (average 88 percent), and moderately high in the ratio of saturated hydrocarbons to aromatic hydrocarbons (sat/arom ratio) (average 2.8). The hydrocarbon richness and relatively high sat/arom ratios strongly suggest that the source of the seep oils was from a mature oil or mature source rock. Immature oils or extracts, on the other hand, would be characterized by a much higher percentage of nonhydrocarbons, i.e., resins and asphaltenes (>50 percent), and by a lower sat/arom ratio (generally <1.0). Leakage or secondary migration from an underlying oil accumulation is considered the most viable explanation for the seep oil, although expulsion and primary migration from an underlying source rock, or migration of "dumped oil" from the nearby potash exploration borehole are alternative hypotheses that must be considered.

Gas chromatographic analysis indicates that the seep oils were subjected to biodegradation (Fig. 4,5). Biodegradation or bacterial alteration is indicated by the absence of normal-paraffin hydrocarbon molecules, which are selectively consumed by bacteria in the presence of oxygenated waters (Winters and Williams, 1969; Milner and others, 1977). If the n-paraffins were present, they would be readily recognized as distinct peaks or spikes distributed in a regularly spaced pattern above the hump that consists of branched and cyclic hydrocarbons (naphthenes). Removal of these n-paraffins is strongly suggested when comparison is made of saturated hydrocarbon distributions of samples 10, 10A, and MC with those of mature-looking crude oil samples from the lower Bell Canyon and older rocks, where regularly spaced n-paraffin peaks are present and apparently very slightly or not at all affected by biodegradation (Figs. 4-7 and 12-16).

Breccia Pipe "Oils"

The chemical composition of the two breccia pipe "oil shows", hereafter simply referred to as "oils", are also, in general, similar to one another (Table 3 and Figs. 4, 8, 9), indicating that they were probably derived from a common source or from similar sources. Some variability in molecular distributions, however, is present, but this is attributed mainly to differing degrees of biodegradation. That biodegradation is a viable cause for the observed differences in the oils is supported by similar hydrocarbon molecular variations attributed to microbiological alterations in other petroliferous areas. As an example, Figure 18 shows dramatic compositional variations in the hydrocarbon distribution patterns of reservoired oil within the Bell Creek field, Powder River Basin, Montana (Winters and Williams, 1969). These variations are attributed to microbiological degradation. Another example of apparent microbiological alteration is illustrated in Figure 19 (Winters and Williams, 1969). Comparison of two oils, believed derived from the same source in an area of North Africa, shows that one of the oils has undergone extensive loss of n-paraffins while the other oil is still intact.

In this study, gas chromatographic analysis clearly shows that the WIPP-16 breccia pipe oil has undergone more intense biodegradation (with all the n-paraffins removed) than the WIPP-31 oil where only partial removal of the n-paraffins has occurred (Figs. 8, 9). This explains, in part, the relatively lower amount of saturated hydrocarbon content in the WIPP-16 oil (46.8 percent) as against the higher amount (65.2 percent) in the WIPP-31 oil (Table 3).

It is interesting to note that the removal of n-paraffins from the WIPP-16 oil not only results in a lower saturated hydrocarbon content but also gives rise to a gross chemical composition that is very similar to that of the Bone Spring rock extract (Table 3), but this apparent correlation is purely fortuitous and not supported by other evidence. The Bone Springs extract has a full complement of n-paraffins. The coincidentally similar gross compositions actually argue against genetic association, because migration effects, due in large part to adsorption-desorption phenomena, especially for long distance vertical migration through varying lithologies, almost invariably show that the composition of crude oil, with respect to a solvent extract of the presumed source rock, is enriched in saturated hydrocarbons and depleted in high molecular weight compounds (resins and asphaltenes) (Tissot and Welte, 1978, p. 290). Conversely, source rock extracts are depleted in saturated hydrocarbons and enriched in resins and asphaltenes. Such is not the case for the WIPP-16 oil and Bone Spring rock extract.

In addition to similarities of molecular distributions, the breccia pipe oils are also similar to the mine seep oils in having a relatively high sulfur content (average 1.1 percent), relatively high total hydrocarbon content (average 74.2 percent), and a moderately high sat/arom ratio (average 3.1).

In summary, comparison of the breccia pipe oils with the mine seep oils in terms of gross chemical parameters (Table 3) and in molecular distributions (Figs. 5-9) strongly suggests that they belong to the same family of oils and hence are derived from similar sources.

Possible Oil Source: Crude Oils

In considering a possible source for the above family of oils, geochemical comparisons were made with seven representative crude oils (Nos. 1-9) collected from nearby oil fields. Assuming that the above oil shows were derived from leakage of underlying oil accumulations, it appears that the most likely source for the above oils is from the oils reservoired in the Yates Formation or from the same source rocks that produced the Yates oils. The Yates oils are stratigraphically the closest to the above family of oils (Figs. 2 and 4), have similar overall chemical composition (Table 3), somewhat comparable gas chromatographic fingerprints (Figs. 4-11), and nearly identical API gravities as the mine seep oils (Table 3). One graphic representation indicating the close relationship of the Yates oils to the oil shows is demonstrated in Figure 20 where the API gravities are plotted against the sat/arom ratios, one of the key bulk chemical parameters. In addition, of the seven crude oils analyzed in this study, the two Yates oils are the only ones that show any appreciable amount of microbiological degradation, again suggesting some genetic affinity to the oil shows. We theorize that prior to oil leakage from the reservoir, the Yates oils had already undergone a certain degree of biodegradation (Figs. 10, 11) probably within the reservoir at the oil-water contact. Subsequent to leakage, the oils were further biodegraded either during migration or at the depositional sites as the oils came in contact with meteoric waters charged with oxygen and bacteria.

It is interesting to point out that the two Yates oils collected from the same stratigraphic unit but from two different localities also show significant differences in compositions that are attributable to differences in microbiological alterations. These differences are comparable to those seen for the two breccia pipe oils determined in this study and for those observed in the Bell Creek oils (Fig. 18) and in the North African oils (Fig. 19) determined in outside studies. The Yates crude oil (No. 7, Fig. 10) which shows signs of a greater degree of biodegradation (lesser amounts of n-paraffins) also has a relatively lower amount of saturated hydrocarbons (54.6 percent) when compared to the No. 1 oil (64.2 percent, Fig. 11). These compositional variations might also account for some of the variations observed in the breccia pipe and mine seep oils, assuming, of course, that the Yates oils are indeed the source oils.

Carbon Isotope Analyses

Carbon isotope analyses measure the abundance ratios of two stable isotopes ^{13} and ^{12}C in natural carbonaceous materials relative to the ^{13}C/^{12}C ratio of the traditional standard, the Peedee Belemnite (PDB), a Cretaceous belemnite from the Peedee Formation of South Carolina. The difference between isotope ratios of the sample and the standard is normally expressed in terms of a "delta" value, δ^{13}C (in units of parts per thousand, ^{o}/oo) which is defined as follows:

$$\delta^{13}C\ {}^{o}/oo = \left(\frac{{}^{13}C/{}^{12}C_{\text{sample}} - {}^{13}C/{}^{12}C_{\text{PDB}}}{{}^{13}C/{}^{12}C_{\text{PDB}}} \right) \times 1000$$

The $^{13}C/^{12}C$ ratio is dependent on the original source of the carbon in the sample and on the isotopic fractionation which has taken place in the formation of the sample. Carbon isotope ratios, therefore, are unique measurements and can be used as a tool in characterizing and correlating geologic materials. For example, oils derived from the same source or similar sources should have similar isotope ratios. Conversely, oils derived from decidedly different source materials, should show, for the most part, significant deviations in isotope ratios.

In determining the source of the mine seep and breccia pipe oils, isotope analyses of the saturated hydrocarbon and aromatic hydrocarbon fractions showed that the average $\delta^{13}C$ values (per mil) for the Yates oils (-28.2 and -28.2, respectively) are comparable to those of the mine seep oils (average, -28.2, -28.4) and breccia pipe oils (average, -28.3, -28.2) (Table 3). Although the data indicate that the Yates oils are similar to and hence a possible source of the seep and breccia oils, the data are unfortunately not conclusive. The reason for this is that the carbon isotope ratios for the other Permian oils (Table 3) also have similar values, all within a few tenths of a part per mil. Consequently, from the standpoint of carbon isotope analyses alone, the immediate source of the seep and breccia oils cannot be pinpointed. On the other hand, the Pennsylvanian crude oil has significantly different $\delta^{13}C$ values (-27.2, -26.7) and hence is judged not to be a source of the mine seep and breccia pipe oils.

Possible Oil Source: Exploration Borehole "Dumped" Oil

In the following discussion, consideration is also given to the "dumped oil" in the exploration borehole as a possible source of the mine seep and breccia pipe oils. This, of course, can only be entertained if the dumped oil were a Yates oil which previously has been identified as the likely source. If any other stratigraphically deeper oil were used, each of which has been shown to be compositionally mismatched with the mine seep oils, it would seem that the borehole oil would have to be automatically disqualified as a possible source.

Assuming, however, that the borehole oil was a Yates oil, the chances of its being the source of the mine seep and breccia pipe oils are still rated highly improbable for several reasons.

Before delving into the reasons, certain facts must be established or reiterated.

1) In about 1950, six barrels of crude oil were injected (probably under pressure) into the potash exploration borehole (U.S. B & C 184; TD, 1,233 ft) to help release the stuck steel casing (TD, approx. 800 ft) which extended beneath some of the porous beds of the Rustler Formation and into about 110 ft of the generally impervious dissolution zone at the top of the Salado Formation. It is assumed that a bridge plug was set intact immediately below the bottom of the casing to prevent the oil from merely filling part of the open hole, thus rendering the oil's purpose ineffective. Whatever the reasons, the efforts to dislodge and retrieve the casing were unsuccessful.

Although the specific details are not known, it seems reasonable to assume that a) some, if not most, of the oil remained within the casing, b) some of the oil that was forced upward from the bottom of the casing through the annulus was in contact (for the first 110 ft) only with the impervious dissolution beds at the top of the Salado Formation thus being restricted from any long distance migration, and c) the remainder of the oil, if any at all, that was forced upward beyond the first 110 ft, penetrated and saturated all porous rock units of the lower part of the Rustler Formation.

2) Owing to the fact that no water was observed along the fault plane where the seep oil was encountered in the mine, the oil (if indeed it did migrate this far) had to migrate through a porous and permeable rock unit more or less as a continuous oil phase without the aid of flowing ground water. Also, if ground water had been the medium of transport and was actively flowing for an appreciable time in the immediate geologic past, then there should have been some evidence of dissolution of the soluble halite and potash deposits at or near the fault plane where the oil seepage occurs. However, no such evidence has been demonstrated. Furthermore, according to Brokaw and others (1972), the prevailing direction of water movement in transmissive zones above the Salado Formation is to the south and southwest - nearly opposite to what would be required if water were to transport the oil north and northwest from the borehole to the mine seep and breccia pipe areas.

With the above facts in mind, it seems highly unlikely for a portion of six barrels of oil to have escaped from the immediate environs of the borehole and to have migrated in a continuous oil phase, (or for that matter in solution or as globules in flowing ground water against the prevailing hydrodynamic gradient) over a distance of 2.5 miles and to have exsolved or "settled out" of solution at more or less comparable depths of 1164 ft (mine seep), 1281 ft (Hill C breccia pipe) and 1629 ft (Hill A breccia pipe) without any traces of oil discovered in the overlying rocks. Furthermore, if we were to take every drop of oil that was forced down the borehole, concentrate it and let it migrate in continuous oil phase radially (i.e. equally in all directions away from the borehole) through only a one-foot porous and permeable zone, then for a rock unit with 10 percent porosity, calculations (see Appendix) show that the oil can migrate only about 10.5 ft away from the borehole. For a transmissive one-foot bed with 5 percent porosity the oil could migrate only a distance of about 15 feet.

In summary, the above considerations strongly suggest that the borehole oil is not the source of the WIPP-31 and WIPP-16 breccia pipe oils nor of the mine seep oils which are located about 2.5 miles, 1,400 ft, and 600 ft, respectively, north and northwest of the borehole.

SUMMARY AND CONCLUSIONS

Geochemical analyses have shown that the mine seep and breccia pipe oils of Eddy County, New Mexico have similar compositions based on gross chemical characteristics, hydrocarbon molecular distributions, and stable carbon isotope ratios. Such similarities indicate that they are genetically related, (i.e. belonging to the same family of oils), and probably derived from a common source or similar sources. The compositional variations that are apparent are largely due to differences in degree of microbiological degradation.

From geologic considerations, the oil "dumped" into the potash exploration borehole (drilled about 1950 in the vicinity of one of the collapsed breccia pipes) is ruled out as a source of 1) the mine seep oils discovered along a fault in the MCC potash mine, about 600 ft from the borehole and 2) the breccia pipe oils at Hills A and C approximately 2.5 miles and 1,400 ft respectively, from the borehole.

Geochemical analysis and oil-to-oil correlation of seven crude oil samples collected from oil fields in the vicinity of the breccia pipes, indicate that the Yates oils are the likely source of the breccia pipe and mine seep oils.

The breccia pipe and mine seep oils were probably emplaced at their present sites during or sometime after the brecciation, fracturing, and faulting of rocks in response to the dissolution of the Capitan Limestone, a reef facies, and subsequent caving of the overlying rocks. Partial leakage from disrupted Yates oil reservoirs probably accounts for the above oil shows.

The presence of significant amounts of seepage oil (in excess of 5 gallons) in the MCC mine might be a reflection of leakage from commercial accumulations of oil in the Yates Formation in the vicinity of the mine. Such oil shows should warrant further petroleum exploration. Necessary precautions could be taken to insure that such exploration did not interfere with the potash mining.

REFERENCES

Brokaw, A. L., Jones, C. L., Cooley, M. E., and Hays, W. H., 1972, Geology and hydrology of the Carlsbad Potash Area, Eddy and Lea Counties, New Mexico: U.S. Geological Survey Open-File Report No. 1793, 86p, 19 figs., 6 tables.

Milner, C. W. D., Rogers, M. A., and Evans, C. R., 1977, Petroleum transformations in reservoirs: Journal of Geochemical Exploration, v. 7, p. 101-153.

Tissot, B. P. and Welte, D. H., 1978, Petroleum formation and occurrence: Springer-Verlag, New York, 538 p.

Williams, J. A., 1977, Characterization of oil types in the Permian Basin: Preprint of paper presented at Southwest Section Mtg., American Association of Petroleum Geologists, Abilene, Texas, March 7, 1977.

Winters, J. C. and Williams, J. A., 1969, Microbiological alteration of crude oil in the reservoir: in Symposium, Petroleum Transformations in Geologic Environments, American Chemical Society, Division of Petroleum Chemistry, Sept. 7-12, 1969, New York, N.Y., Paper PETR 86, p. E22-E31.

Table 1. - Location of mine seep and breccia pipe oil samples, Eddy County, New Mexico.

Sample No.	Location
Mine Seep Oils	
10	MCC mine, 16-L drift, about 140 ft from boundary of breccia pipe (Hill C), collected 1980.
10A	MCC mine, 15-L drift, about 140 ft from boundary of breccia pipe (Hill C), collected 1980.
MC	MCC mine, 16-L drift, about 140 ft from boundary of breccia pipe (Hill C), collected 1975.
Breccia Pipe Oils	
11	Drillhole Wipp-31, Hill A, Sec. 35, T.20S., R.30E.
12	Drillhole Wipp-16, Hill C, Sec. 5, T.21S, R.30E.

Table 2. -- Well name, field name (if any), location, and name and age of formation from which crude oil and drill cuttings samples were taken. [Crude oil samples collected in 1980 by James Brasfield, USGS, Artesia, N. Mex., and R. P. Snyder, USGS, Denver, Colo.; cuttings sample provided by Jack Williams, Amoco Production Company, Tulsa, Okla.].

Sample No. Crude Oils	Description
1	Gulf Fed. Lease, Hudson and Hudson; Dos Hermanos field; Sec. 33, T.20S., R.30E., Eddy Co., N.M.; Yates Fm.; Permian.
	Meadco Properties Ltd., Hudson Fed. #2; wildcat; Sec. 4, T.21S, R.29E, Eddy Co., N.M.; Cherry Canyon or basal Bell Canyon Fm.; Permian.
3	Perry R. Bass, Fed. Cobb #1; field unknown; Sec. 23, T.20S, R.31E., Eddy Co., N.M.; lower Brushy Canyon Fm.; Permian.
4	Perry R. Bass - Big Eddy #7; undesignated field; Sec. 19, T.20S, R.31E., Eddy Co., N.M.; Pennsylvanian.
5	Perry R. Bass - Big Eddy #58; Indian Flats Delaware field; Sec. 35, T.21S., R28E., Eddy Co., N.M.; lower Bell Canyon Fm.; Permian.
7	Barber Oil Co., #3 Colgazier "O"; Dos Hermanos field; Sec. 20, T.20S, R.30E., Eddy Co., N.M.; Yates Fm.; Permian.
9	Yates Pet. Co., #1 Fed. GN; Indian Flats field; Sec. 27, T.21S., R.28E., Eddy Co., N.M.; lower Bell Canyon Fm.; Permian.
Cuttings	
218	Bass - N. Custer Mountain; Sec. 28, T.23S., R.35E., Lea Co., N.M.; Bone Spring Ls.; Permian.

Table 3. Geochemical analyses of potash mine seep oils, collapsed breccia pipe oils, and selected crude oils, Eddy County, New Mexico.

						SILICA GEL CHROMATOGRAPHIC FRACTIONS AS PERCENT OF TOTAL SAMPLE						$\delta^{13}C$ o/oo (PDB)	
SPL. NO.	TYPE OF SAMPLE	DEPTH (Ft)	FORMATION OR LOCALITY	API GRAVITY	S %	SAT HC %	AROM HC %	RESINS %	ASPHALTENES %	AMOUNT LOST %	SAT/AROM RATIO	SAT HC	AROM HC
10	Mine seep oil	1164	MCC mine	18.9	1.14	64.8	22.1	6.8	1.4	4.9	2.9	-28.2	-28.3
10A	Mine seep oil	1164	MCC mine	20.0	1.23	64.2	23.4	6.9	1.0	4.5	2.7	-28.2	-28.5
MC	Mine seep oil	1164	MCC mine	19.1	.96	65.8	22.7	5.9	1.5	4.1	2.9	ND	ND
12	Breccia pipe oil	1281	WIPP-16	ND	.89	46.8	18.3	15.2	10.1	9.6	2.6	-28.1±.1	27.9±.5
11	Breccia pipe oil	1629	WIPP-31	ND	1.16	65.2	18.0	10.1	3.8	2.9	3.6	-28.5±.1	28.4±.3
7	Crude oil	1475-1480	Yates	20.0	2.08	54.6	27.9	4.8	4.2	8.5	2.0	-28.4	-28.2
1	Crude oil	1646-1702	Yates	25.3	0.58	64.2	20.4	3.5	.1	11.8	3.2	-28.1	-28.1
5	Crude oil	3544-3553	L. Bell Canyon	43.2	.13	52.3	9.2	1.1	.1	37.3	5.7	-28.2	-28.4
9	Crude oil	3660-3687	L. Bell Canyon	37.8	.31	55.7	9.9	1.2	.2	33.0	5.6	ND	ND
2	Crude oil	4008-4190	Cherry Canyon or basal Bell Canyon	38.3	.46	58.2	9.7	1.3	.1	30.7	6.0	-28.2	-28.2
3	Crude oil	7003-7035	L. Brushy Canyon	41.9	.12	57.2	9.1	1.3	.1	32.3	6.3	-28.0	-28.0
4	Crude oil	12656-12948	Pennsylvanian	49.0	.03	48.5	1.5	.3	.1	49.6	31.6	-27.2	-26.7
218	Cuttings	8790-8900	Bone Spring	ND	ND	49.8	19.7	15.1	5.8	9.6	2.5	ND	ND

ND = not determined; S = sulfur; Sat HC = saturated hydrocarbons; arom HC = aromatic hydrocarbons; sat/arom ratio = saturated hydrocarbon/aromatic hydrocarbon ratio.

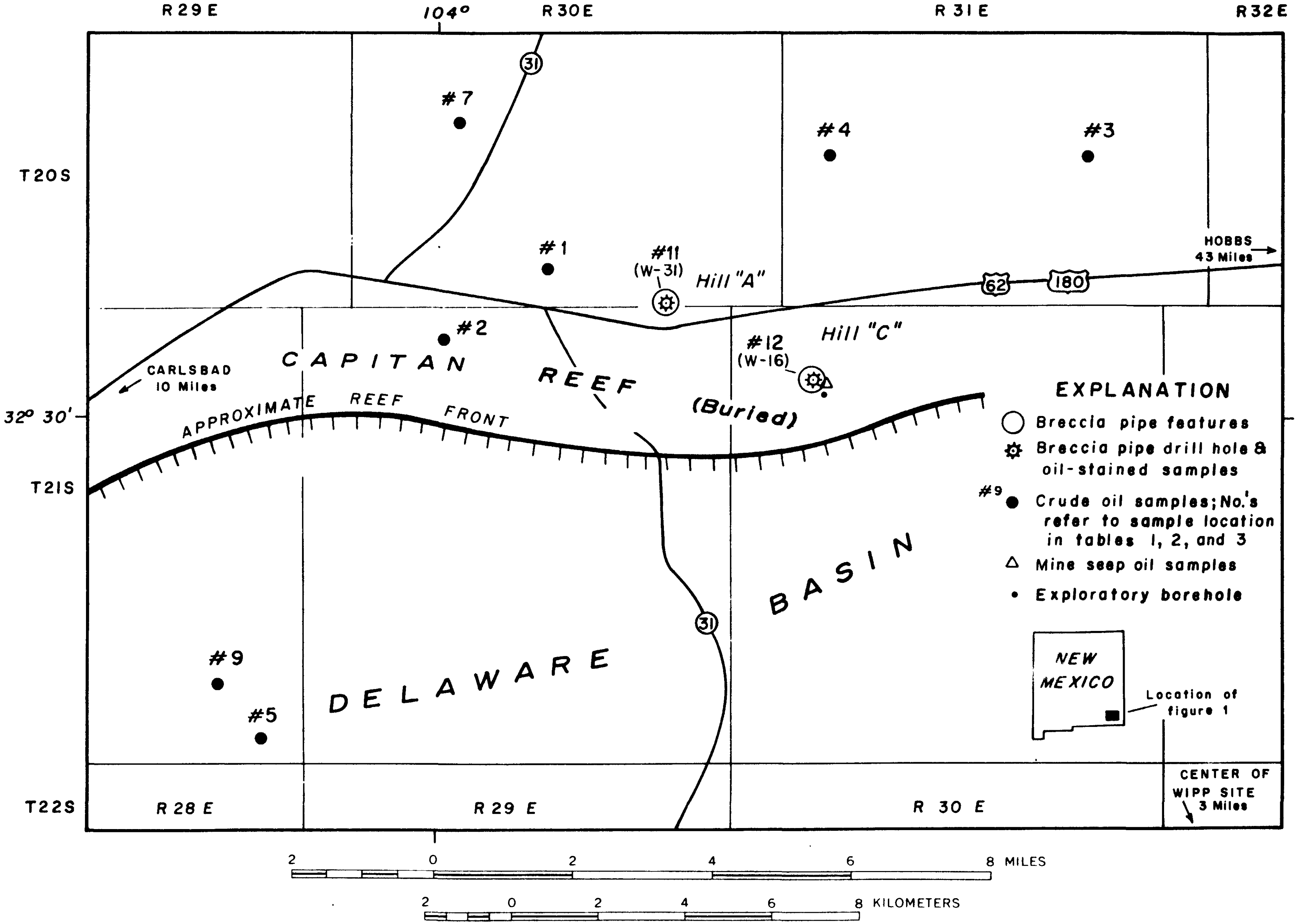

Figure 1.--Location of breccia pipe features, breccia pipe, mine seep, and crude oil samples, and approximate Capitan reef front in Eddy County, New Mexico. [Sample No. 218 not in area of map; W-16 and W-31 are drill holes at breccia pipe features.]

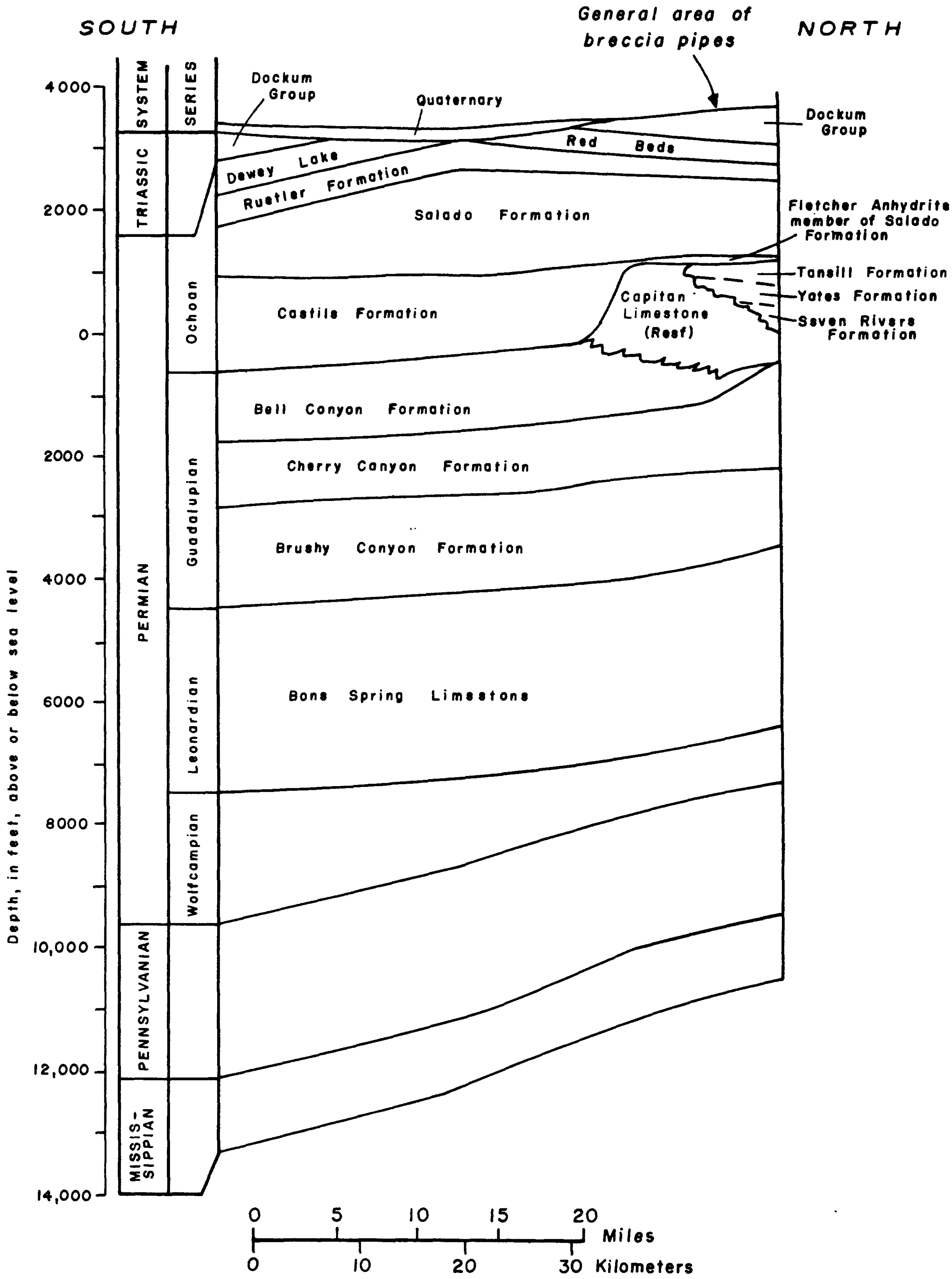

Figure 2.--Generalized geologic cross section across breccia pipe area, Eddy County, New Mexico (modified from Brokaw and others, 1972).

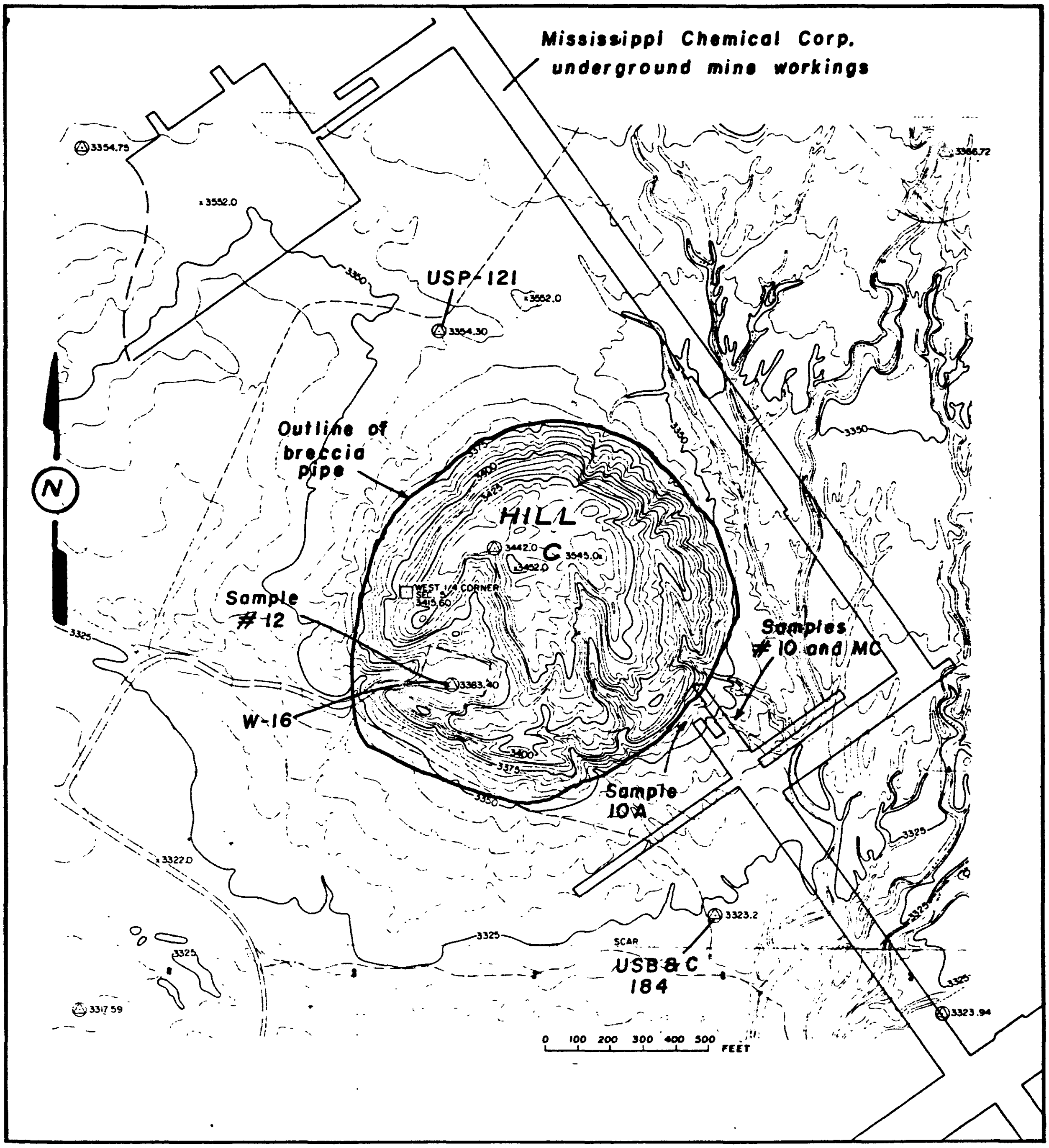

Figure 3.--Enlarged map of Hill C breccia pipe area showing drill holes, mine workings, and oil sample locations.

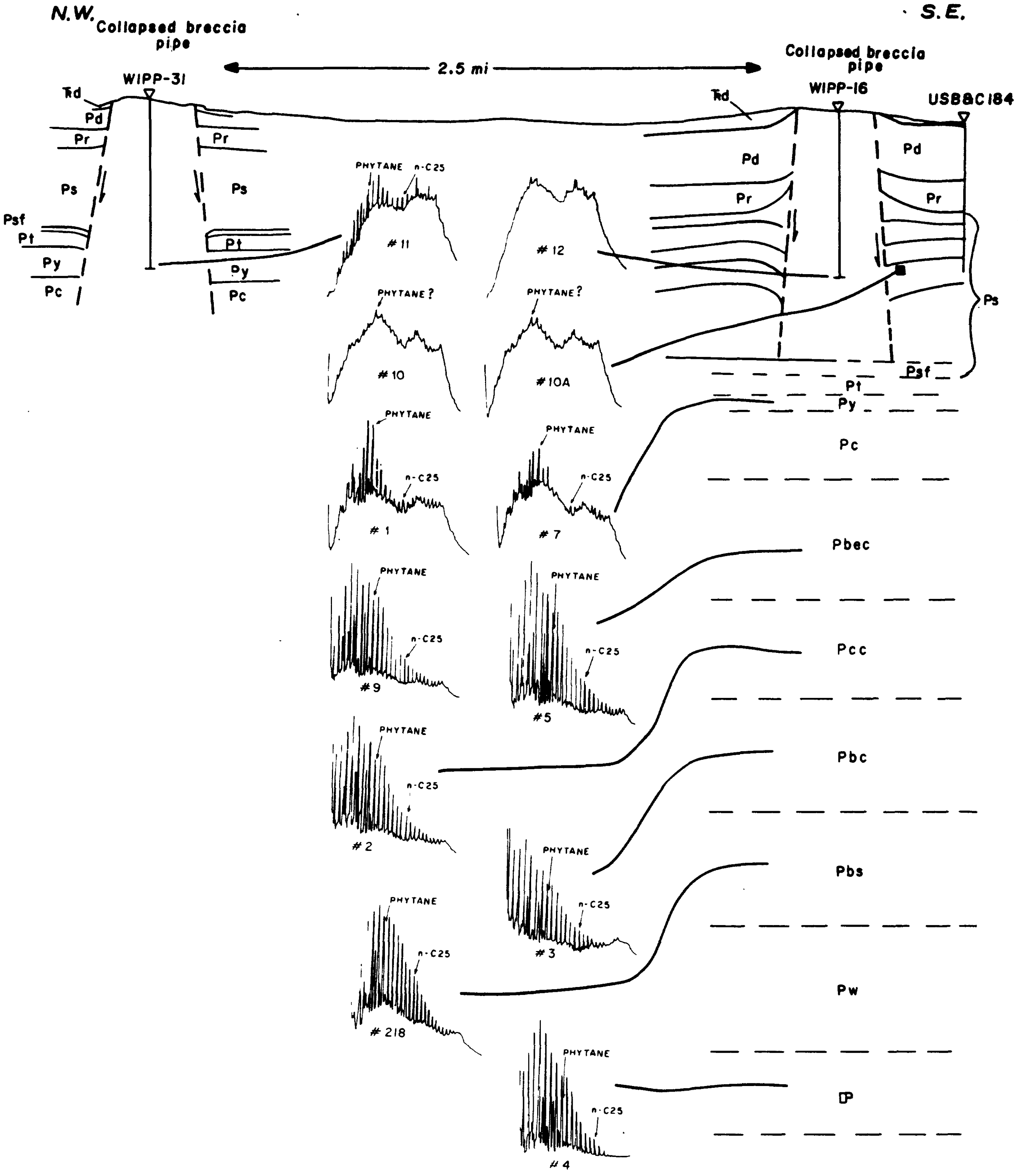

Figure 4 - Diagrammatic cross section of breccia pipe features and generalized stratigraphic section below Salado Fm. showing gas chromatograms of C_{15+} saturated hydrocarbon distributions of mine seep, breccia pipe, and selected crude oils. Caption continued on next page.

EXPLANATION

TRIASSIC	TRd	Dockum Group
PERMIAN	Pd	Dewey Lake Red Beds
	Pr	Rustler Formation
	Ps	Salado Formation
		Marker beds
	Psf	Fletcher Anhydrite Member(on reef)
	Pt	Tansill Formation
	Py	Yates Formation
	Pc	Capitan Limestone
	Pbec	Bell Canyon Formation
	Pcc	Cherry Canyon Formation
	Pbc	Brushy Canyon Formation
	Pbs	Bone Spring Limestone
	Pw	Wolfcampian
	IP	Pennsylvanian

Figure 4 - Cont'd. Gas chromatograms (GC) are identified by sample numbers indicated below each chromatogram. Enlargements of GC's are illustrated in Figures 5-17. GC column conditions are described under analytical procedures.

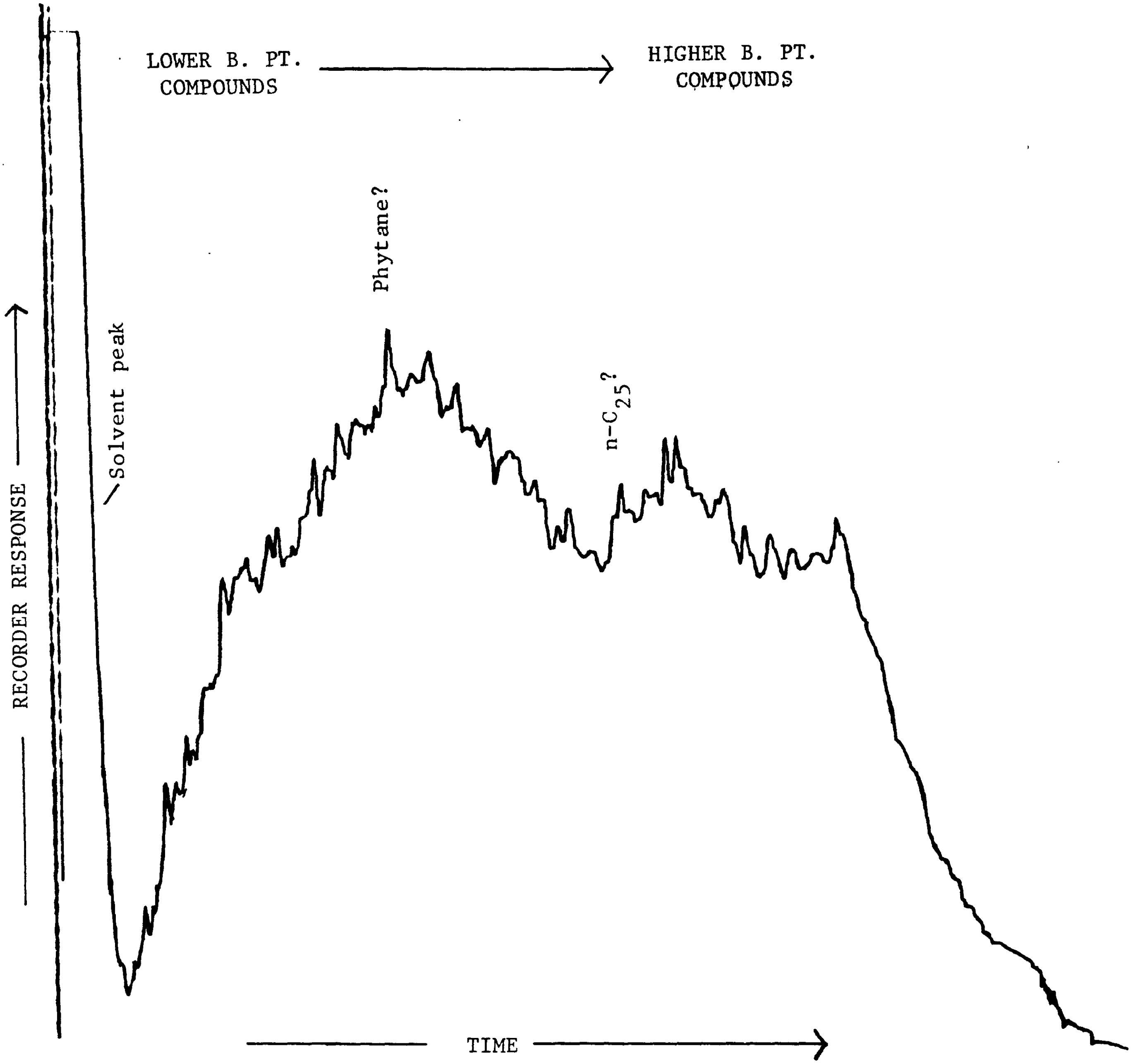

Figure 5. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of potash mine seep oil No. 10. For location of oil sample see Figure 3 and Table 1. The n-paraffin molecules have been removed apparently by microbiologic degradation. The unresolved envelope consists predominantly of naphthenes (cyclic hydrocarbons) and subordinately of branched-chain hydrocarbons. In order to determine the approximate molecular weight distribution of the unresolved saturated hydrocarbons, the approximate positions of phytane and pentacosane (n-C_{25}) are shown. Phytane is a 20-carbon isoprenoid or branched-chain hydrocarbon that is directly related to a specific biologic precursor, and pentacosane is a normal or straight-chain hydrocarbon that has 25 carbon atoms. Gas chromatographic column conditions are given in the text under analytical procedures.

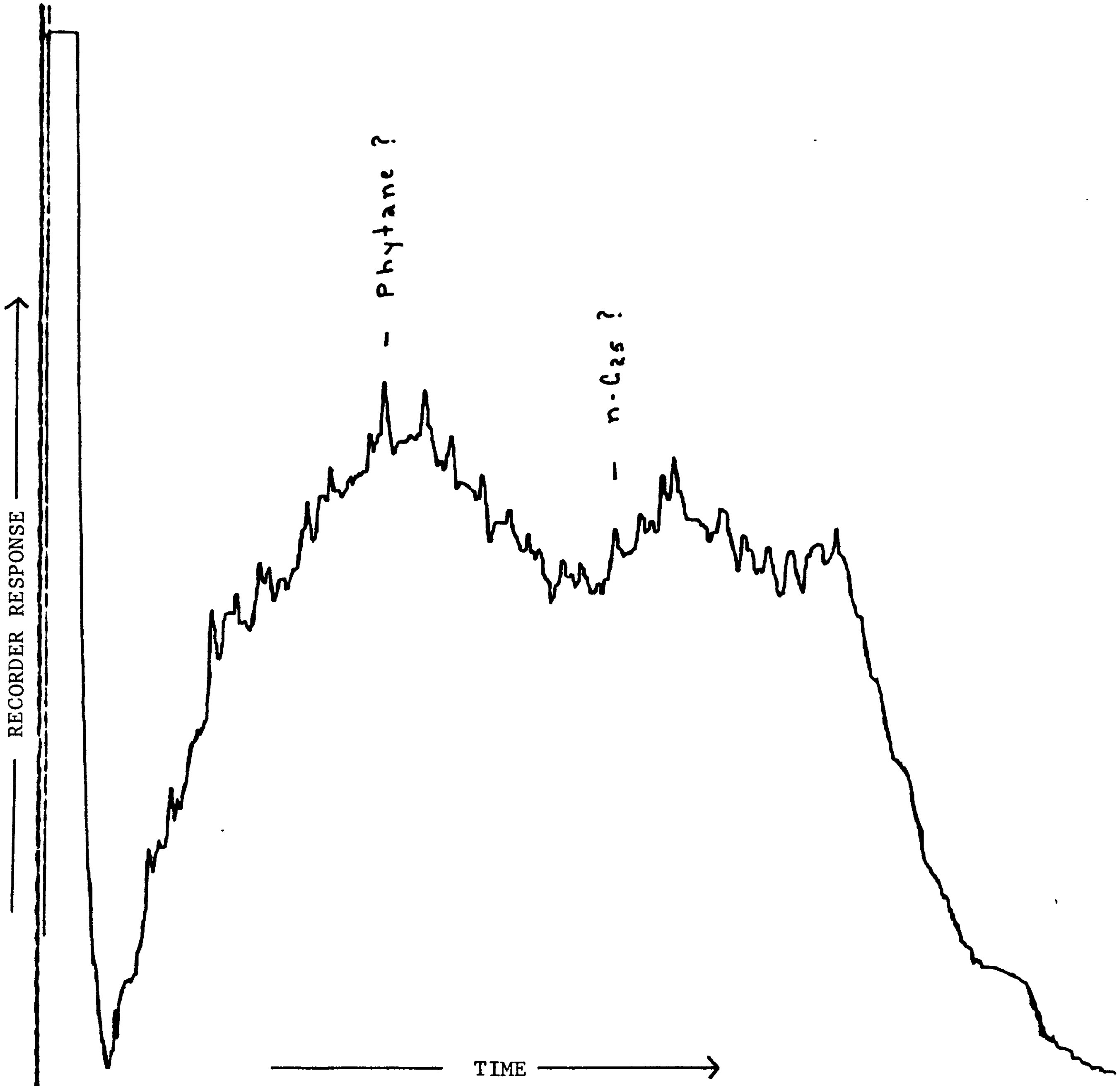

Figure 6. Gas chromatogram (GC) of C_{15+} saturated hydrocarbon fraction of potash mine seep oil No. 10A. The GC fingerprint is essentially identical to that of Figure 5. See caption in Figure 5 for other pertinent information.

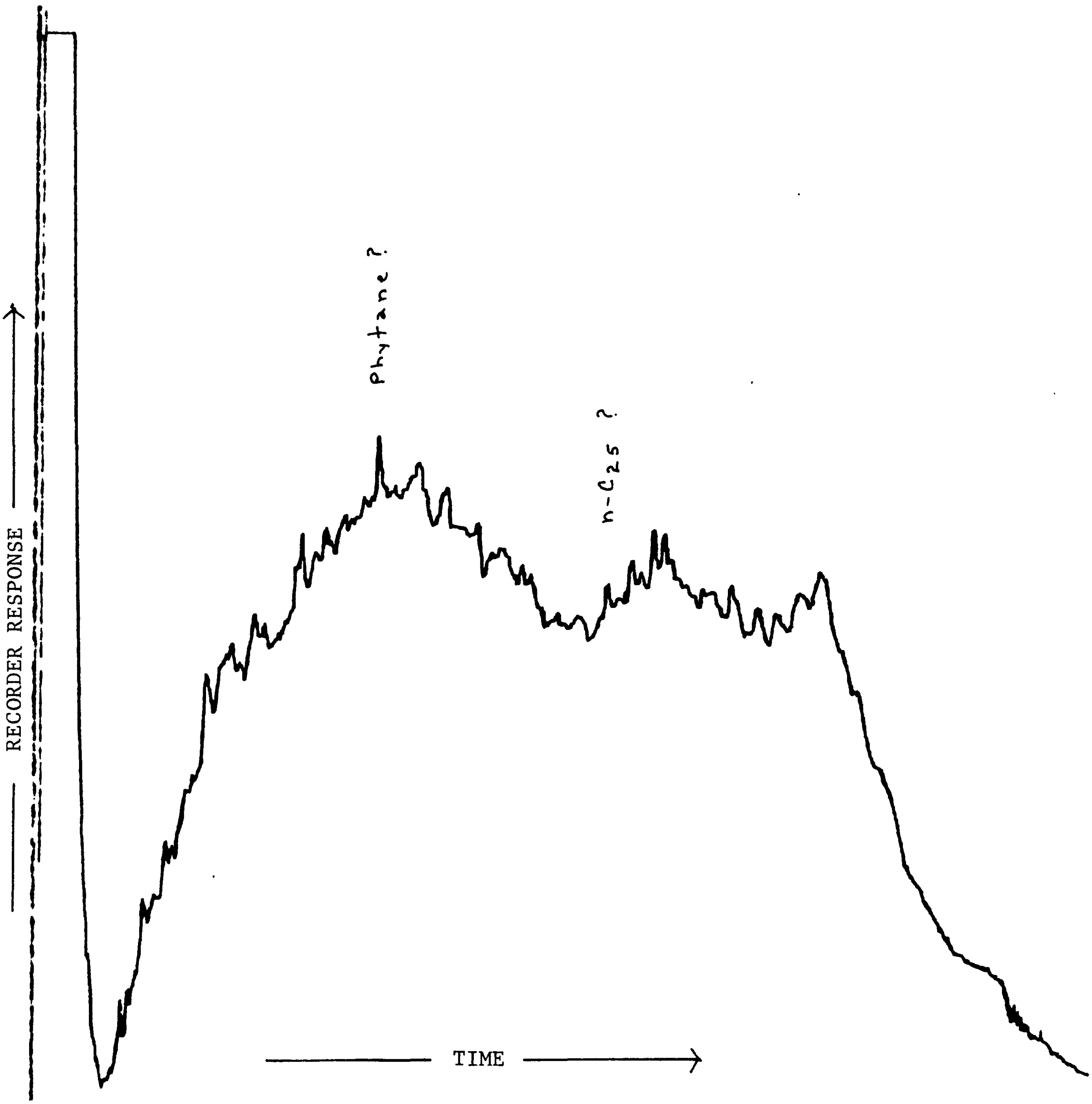

Figure 7. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of potash mine seep oil No. MC. The GC fingerprint is essentially identical to those of Figures 5 and 6. See caption in Figure 5 for other pertinent information.

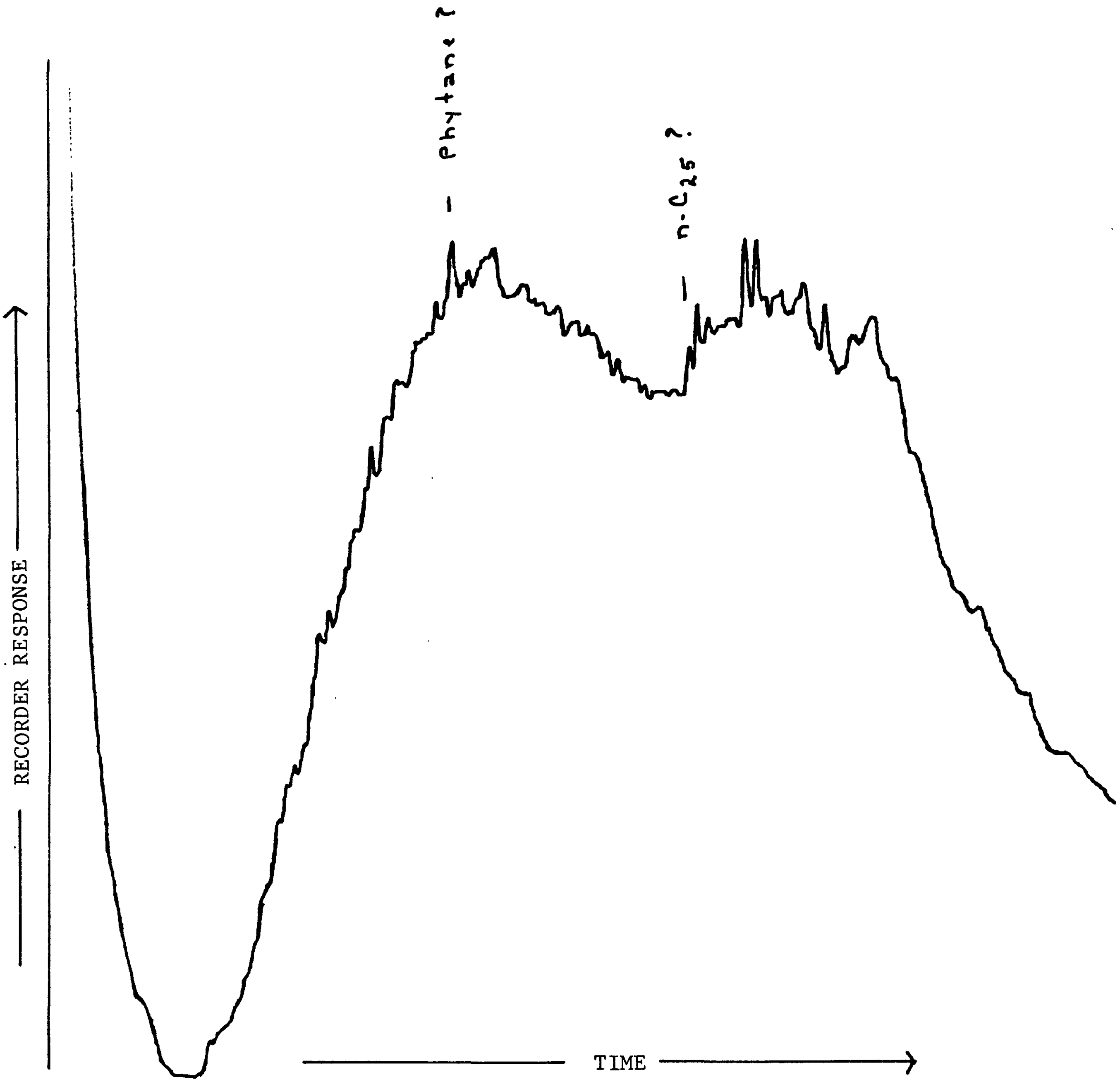

Figure 8. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of breccia pipe oil No. 12 obtained from the WIPP No. 16 borehole. See Table 1 and Figure 3 for location of sample. The GC fingerprint is very similar to those of the mine seep oils (Figs. 5, 6, and 7). Again, the absence of n-paraffins is attributed to biodegradation. See Figure 5 for other pertinent information.

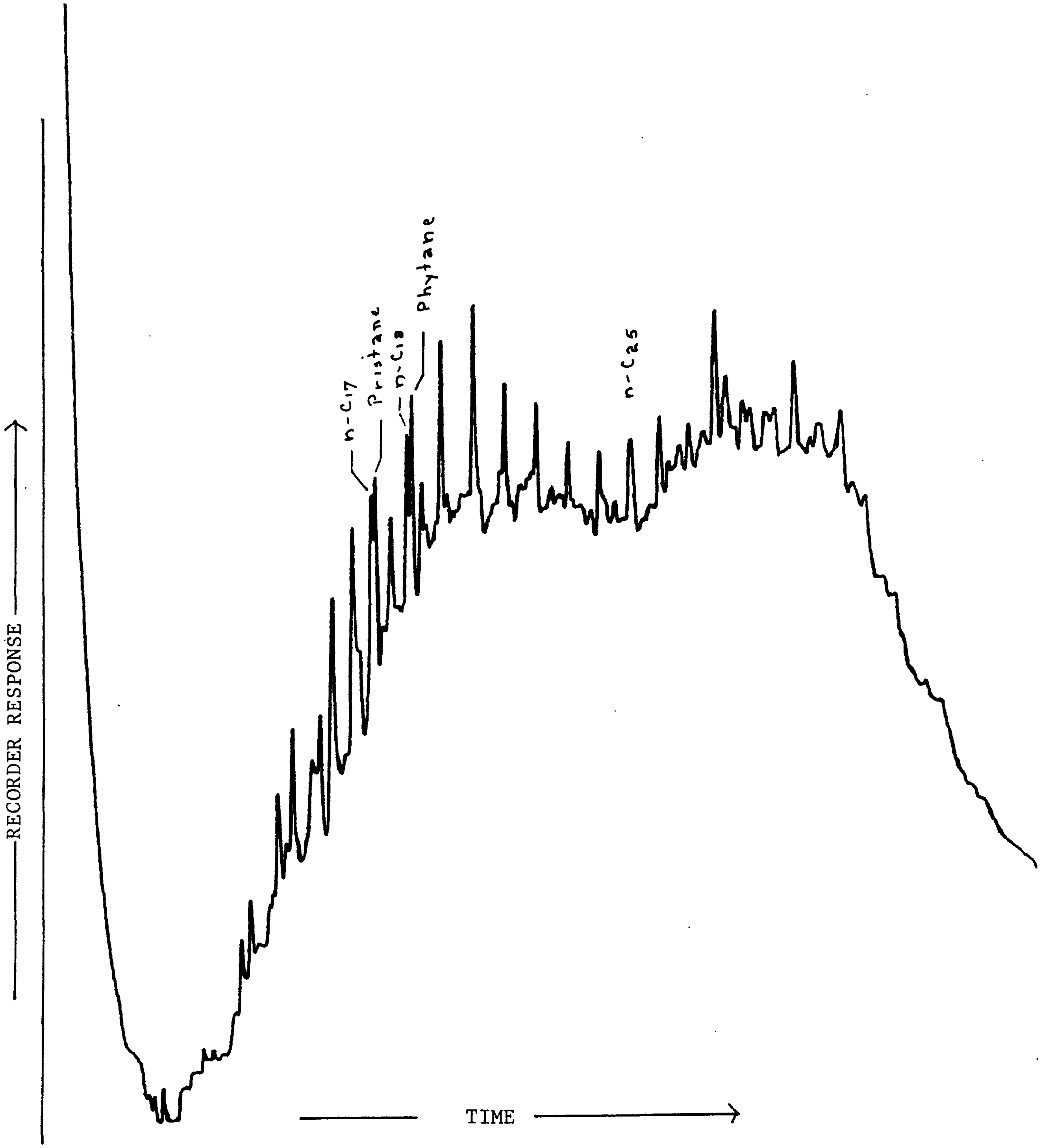

Figure 9. Gas chromatogram of saturated hydrocarbon fraction of breccia pipe oil No. 11 obtained from the WIPP No. 31 borehole. See Table 1 and Figure 1 for location of sample. This breccia pipe oil appears less biodegraded than the other breccia pipe oil (No. 12, Fig. 8). Note that the series of n-paraffin and branched paraffin peaks (including pristane and phytane), below about n-C_{25}, are still projecting above the hump. Pristane, a 19-carbon branched paraffin, like phytane, is considered a biologic marker compound since it is derived from a distinct biologic precursor. See analytical procedures for chromatographic column conditions.

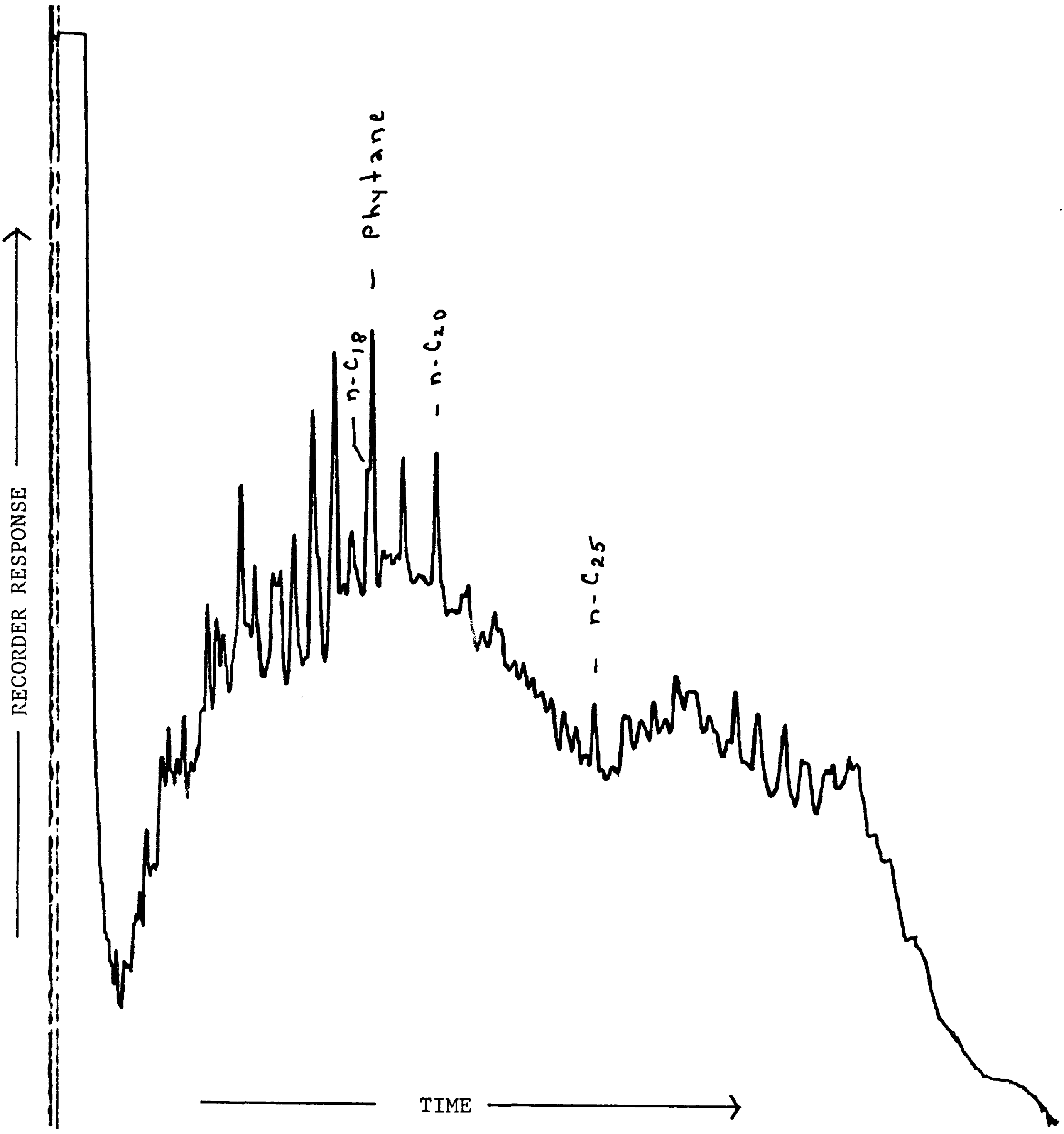

Figure 10. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of Yates crude oil No. 7. See Table 2 and Figure 1 for location of sample. This oil is also considered to have undergone biodegradation as indicated by the disappearance of a significant portion of the n-paraffin distribution above n-C_{20}, especially in the region n-C_{20} to n-C_{25}. See analytical procedures for column conditions.

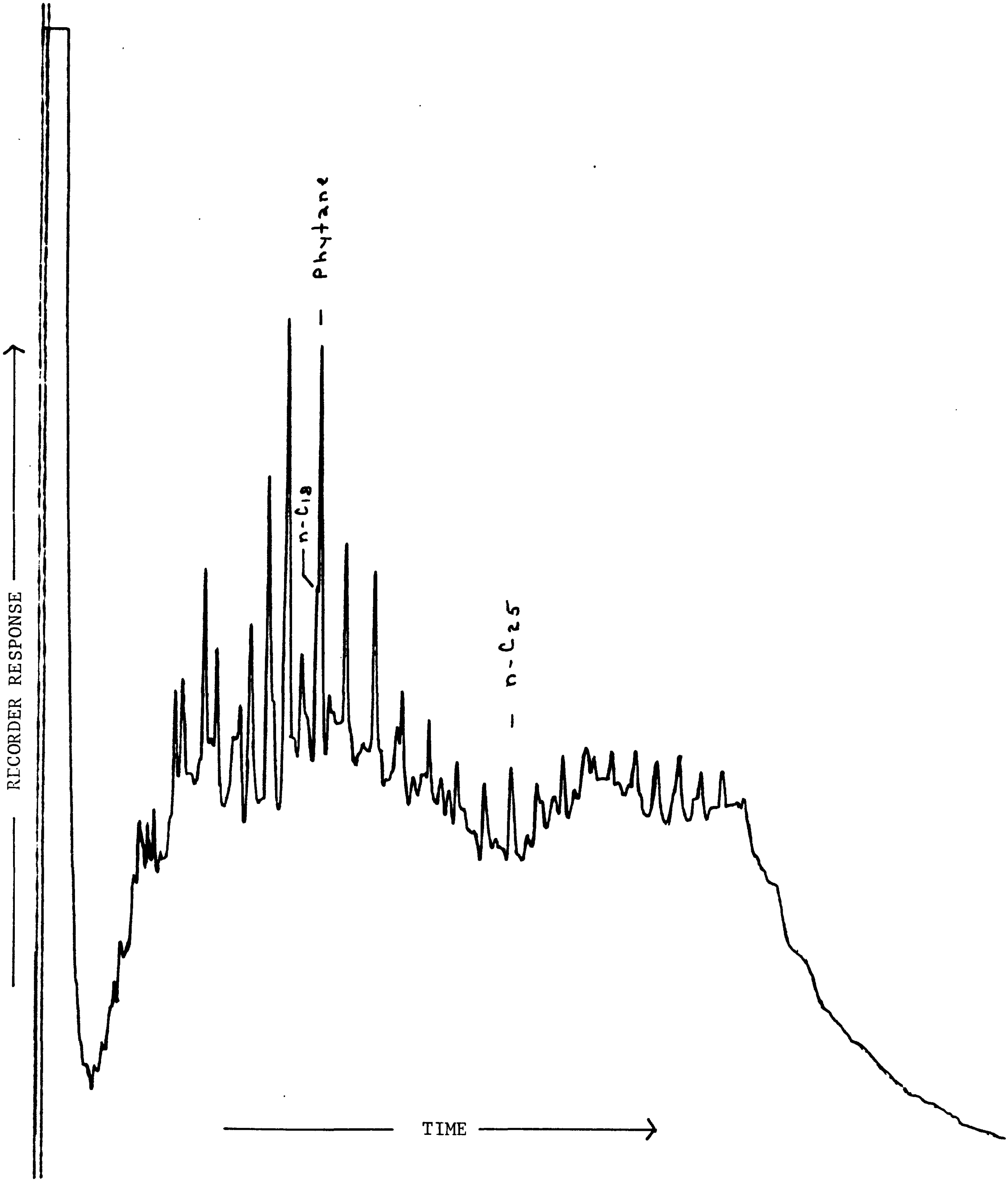

Figure 11. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of Yates crude oil No. 1. See Table 2 and Figure 1 for location of sample. This oil also shows signs of biodegradation but slightly less than that of Yates No. 7 oil (Fig. 10). See analytical procedures for column conditions.

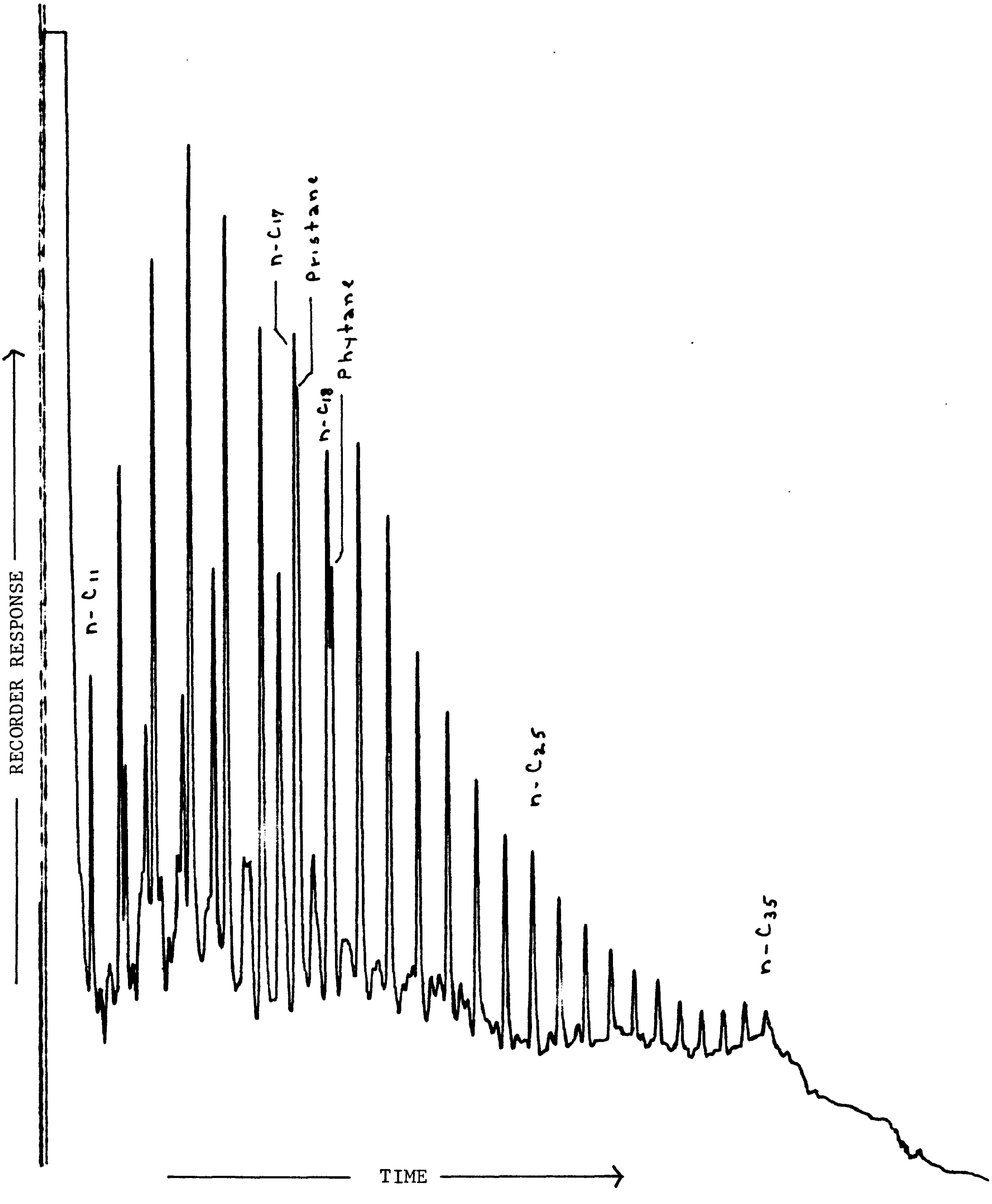

Figure 12. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of lower Bell Canyon crude oil No. 5. See Table 2 and Figure 1 for location of sample. This chromatogram shows the full complement of prominent n-paraffin peaks ranging from about n-C_{11} to n-C_{35}, with no obvious signs of microbiological alteration. See analytical procedures for column conditions.

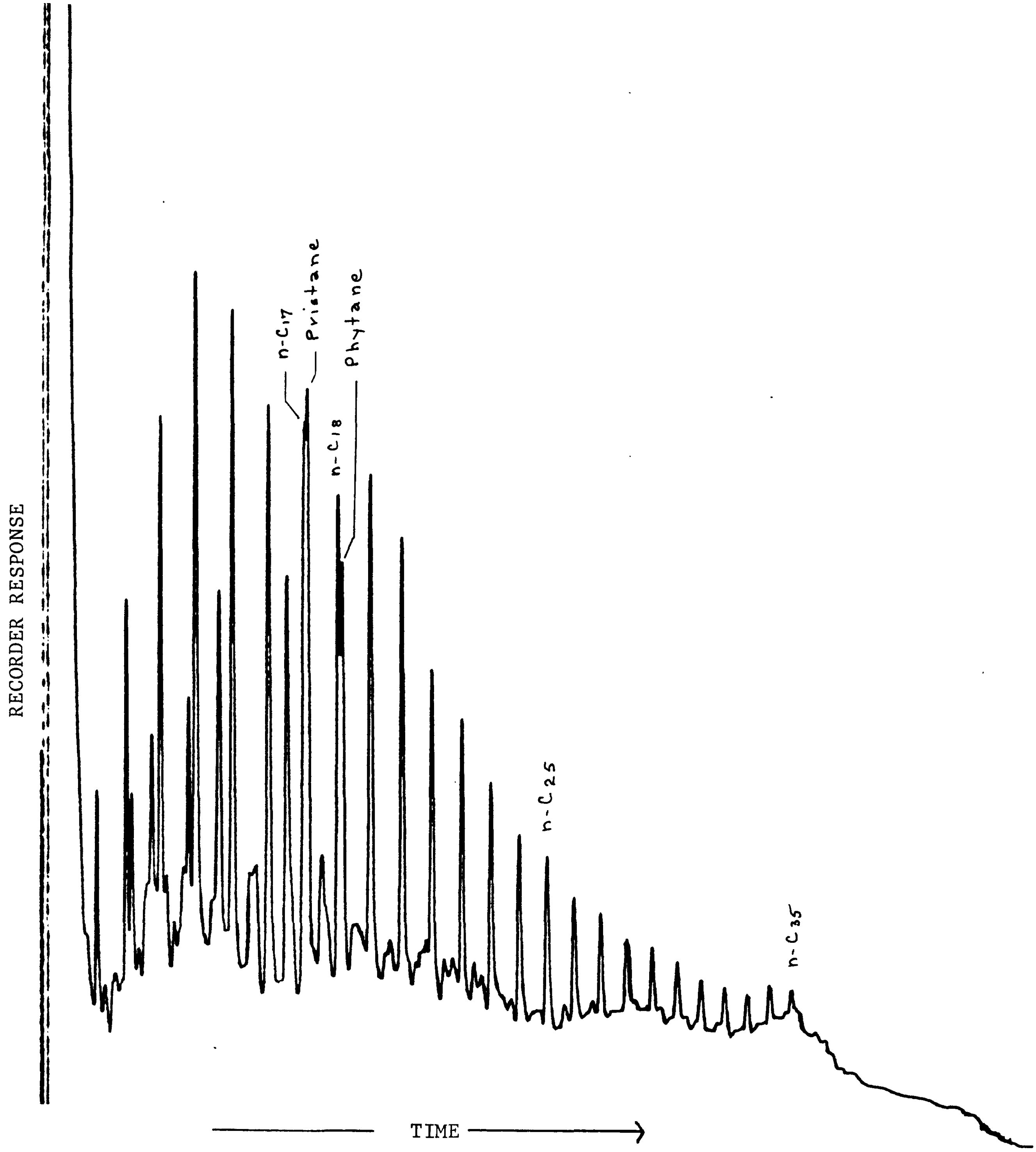

Figure 13. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of lower Bell Canyon crude oil No. 9. See Table 2 and Figure 1 for location of sample. The distribution of saturated hydrocarbons is nearly identical to that of the No. 5 oil in Figure 12 with one minor exception. The No. 9 oil has a slightly lower n-C_{17}/pristane ratio than the No. 5 oil. The similarity of molecular distributions as well as gross chemical characteristics indicates that these two oils (No. 9 and No. 5) were derived from the same sequence of source rocks. See analytical procedures for column conditions.

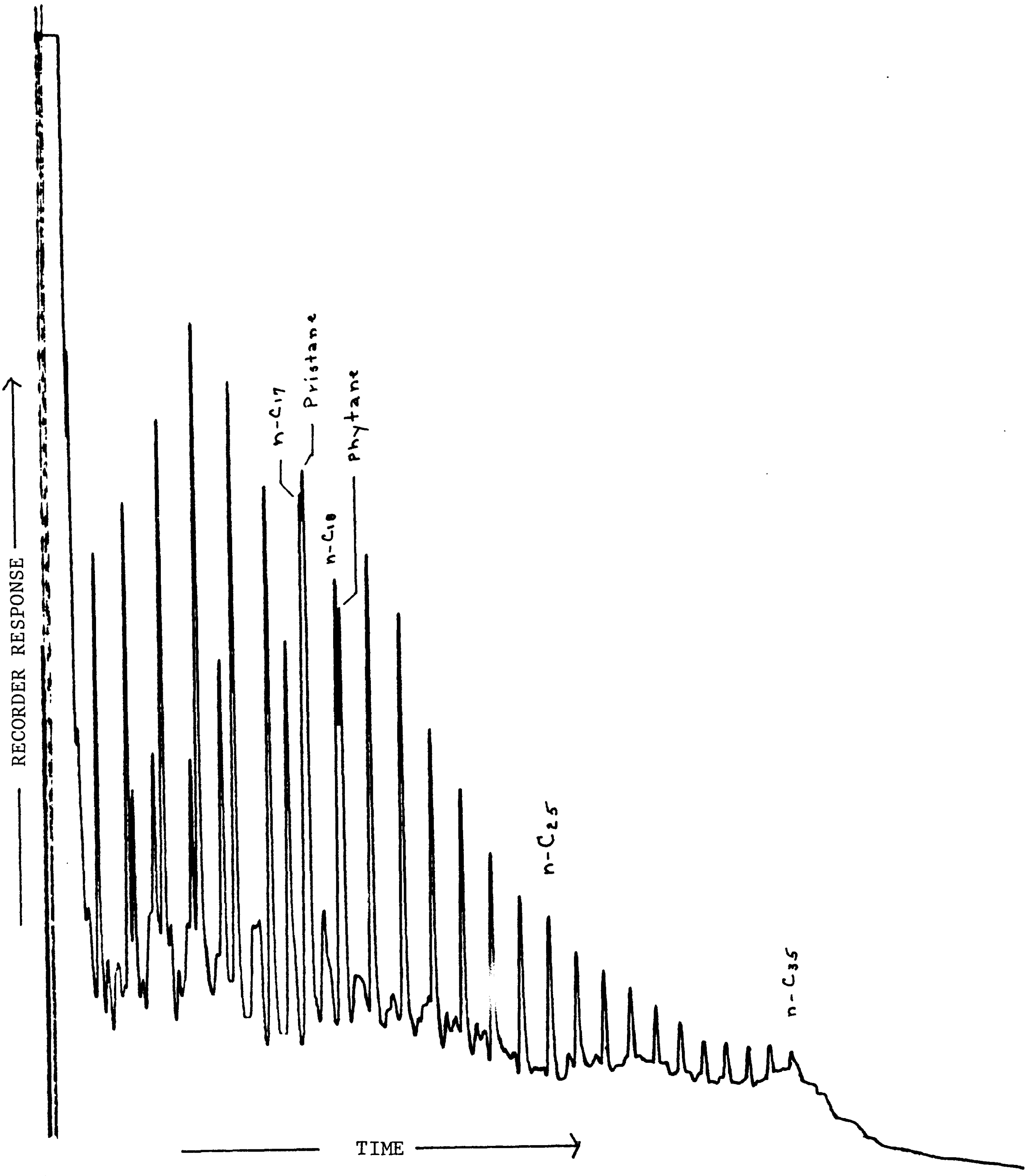

Figure 14. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of Cherry Canyon or basal Bell Canyon crude oil No. 2. See Table 2 and Figure 1 for location of sample. This chromatogram is essentially identical to that of the No. 9 oil (Fig. 13) and quite similar to the No. 5 oil (Fig. 12) indicating that all three oils belong to the same family of oils and hence were derived from the same or a similar source rock sequence. See analytical procedures for column conditions.

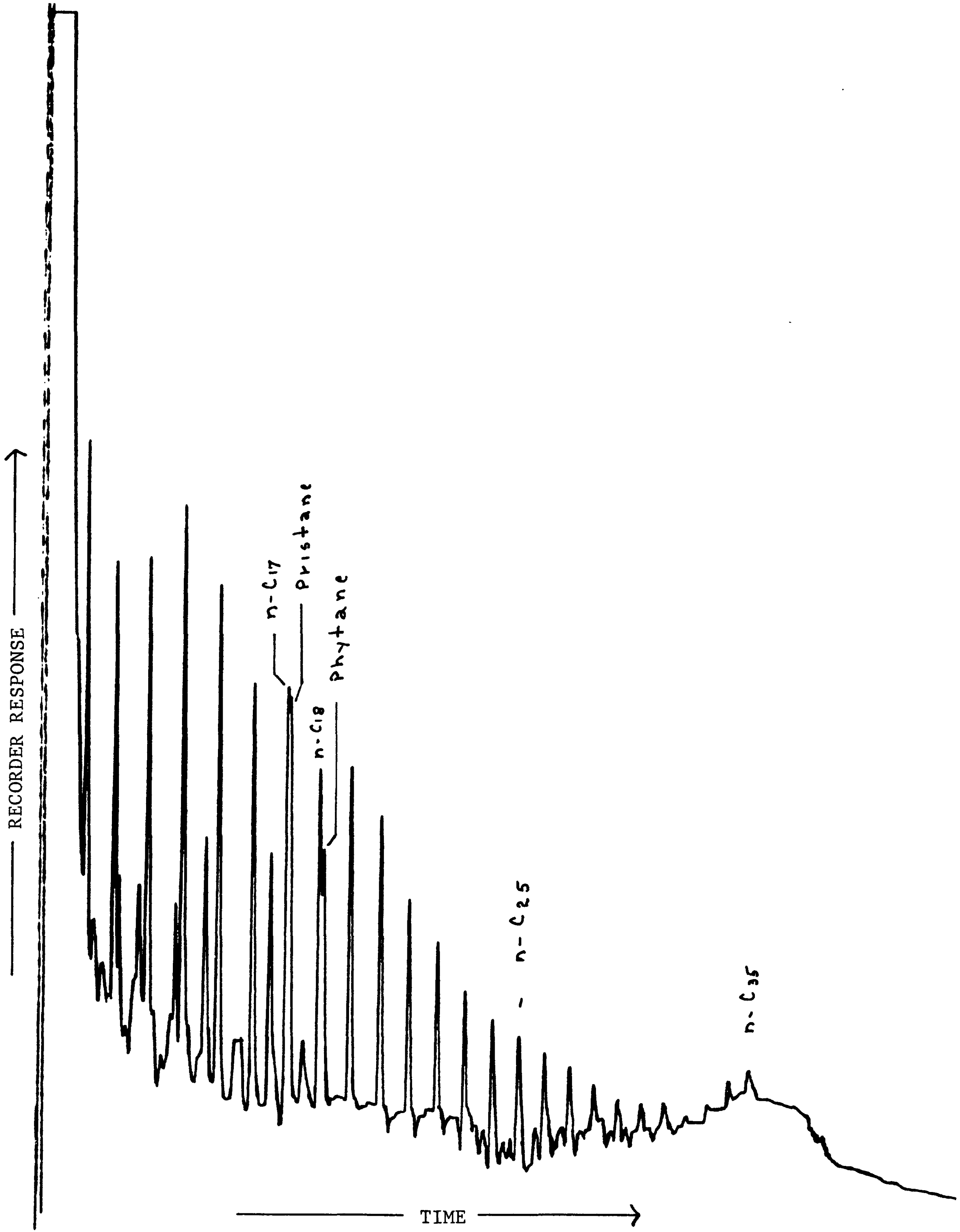

Figure 15. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of lower Brushy Canyon crude oil No. 3. See Table 2 and Figure 1 for location of sample. The distribution of saturated hydrocarbons as well as the gross chemical composition (Table 3) indicate that this oil belongs to the same family of oils as the Bell Canyon crude oils (Figs. 12, 13, 14). See analytical procedures for column conditions.

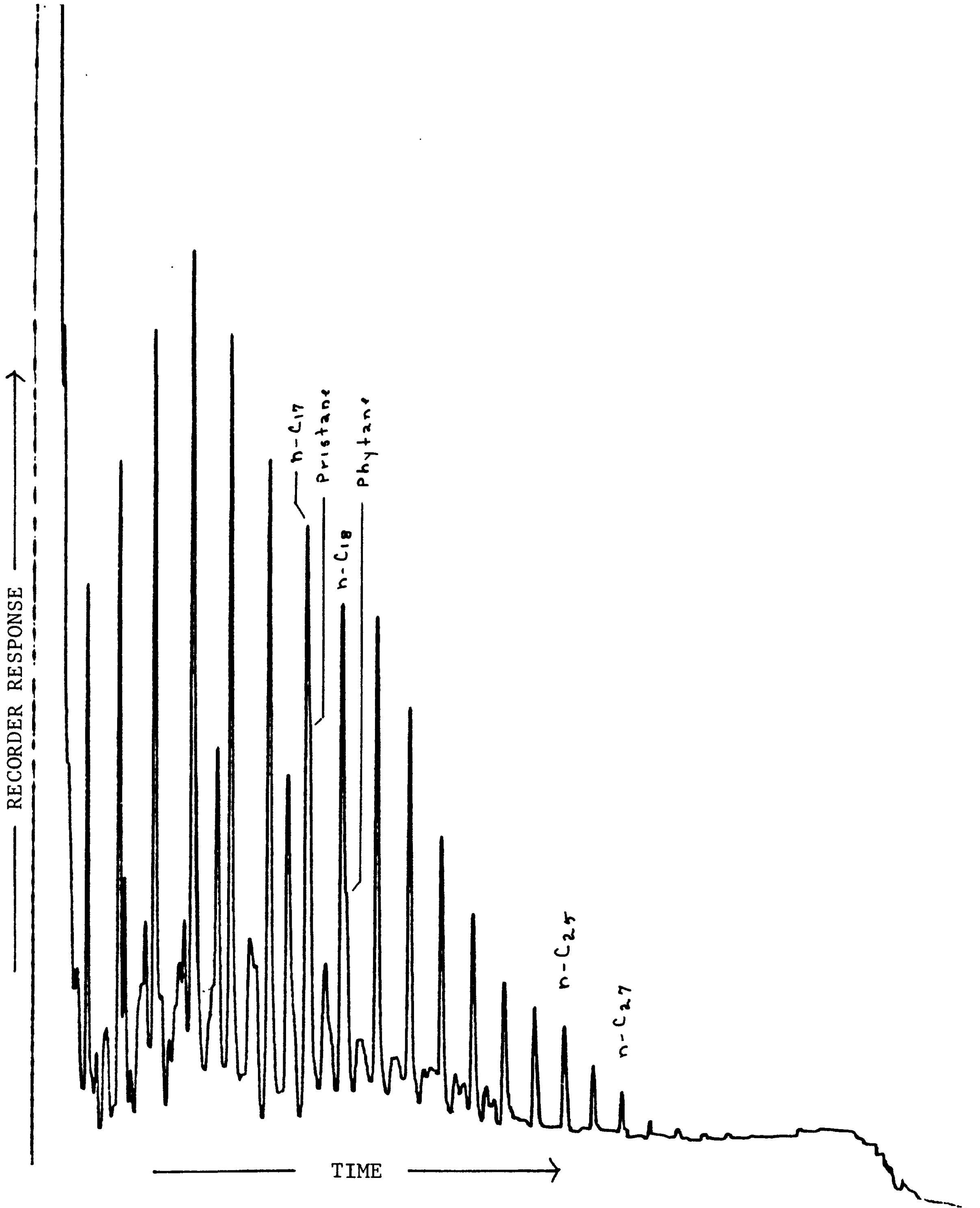

Figure 16. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of Pennsylvanian crude oil No. 4. See Table 2 and Figure 1 for location of sample. Comparable to the four Permian oils (Figs. 12, 13, 14, 15), this Pennsylvanian oil also has a full complement of n-paraffins devoid of any apparent biodegradation but it differs from them in several respects. (1) The range of n-paraffins (that have any appreciable concentration) extends only to n-C_{27} whereas in the 4 Permian oils the range extends to n-C_{35}. (2) The amounts of pristane and phytane relative to n-C_{17} and n-C_{18}, respectively, are much less in the Pennsylvanian oil compared to the Permian oils. (3) Although not reported in this study, molecular sieve analyses show that the isoprenoid distribution of the Pennsylvanian oil is quite different than that of the Permian oils. The above data coupled with carbon isotope and gross chemical analyses (Table 3) strongly indicate that the Pennsylvanian oil is not related to the Permian oils and consequently was derived from a different rock source. See analytical procedures for column conditions.

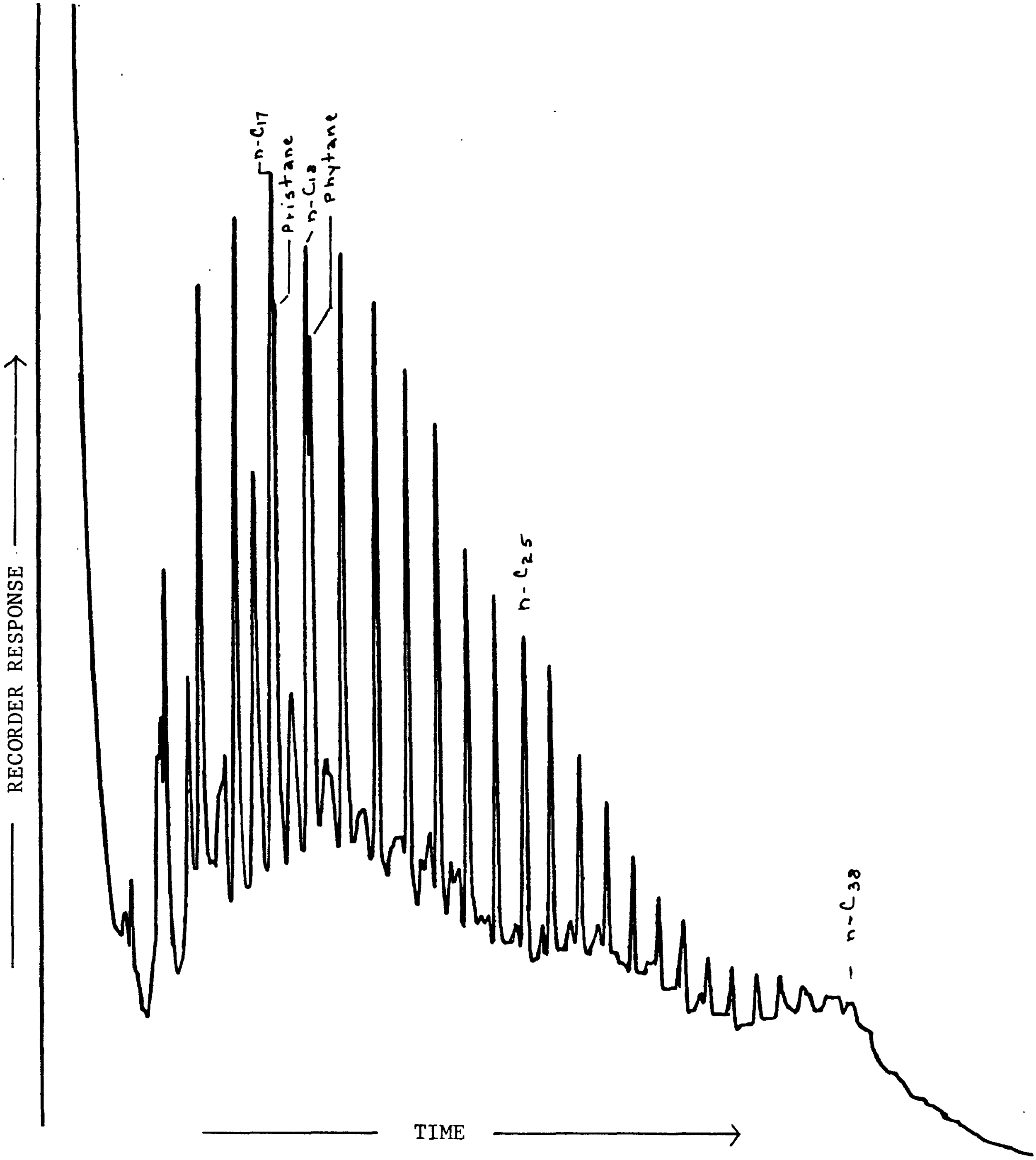

Figure 17. Gas chromatogram of C_{15+} saturated hydrocarbon fraction of a chloroform extract of rock cuttings (No. 218) from the Bone Spring Limestone. See Table 2 for location of sample. The overall character of the saturated hydrocarbon distribution coupled with its stratigraphic position indicates that the Bone Spring may be the source of the four Permian oils shown in Figure 12, 13, 14, and 15. Whether it is also the ultimate source of the Yates, breccia pipe, and mine seep oils has yet to be determined. More detailed and sophisticated oil-to-oil correlation analyses have to be made to ascertain this possibility. See analytical procedures for column conditions.

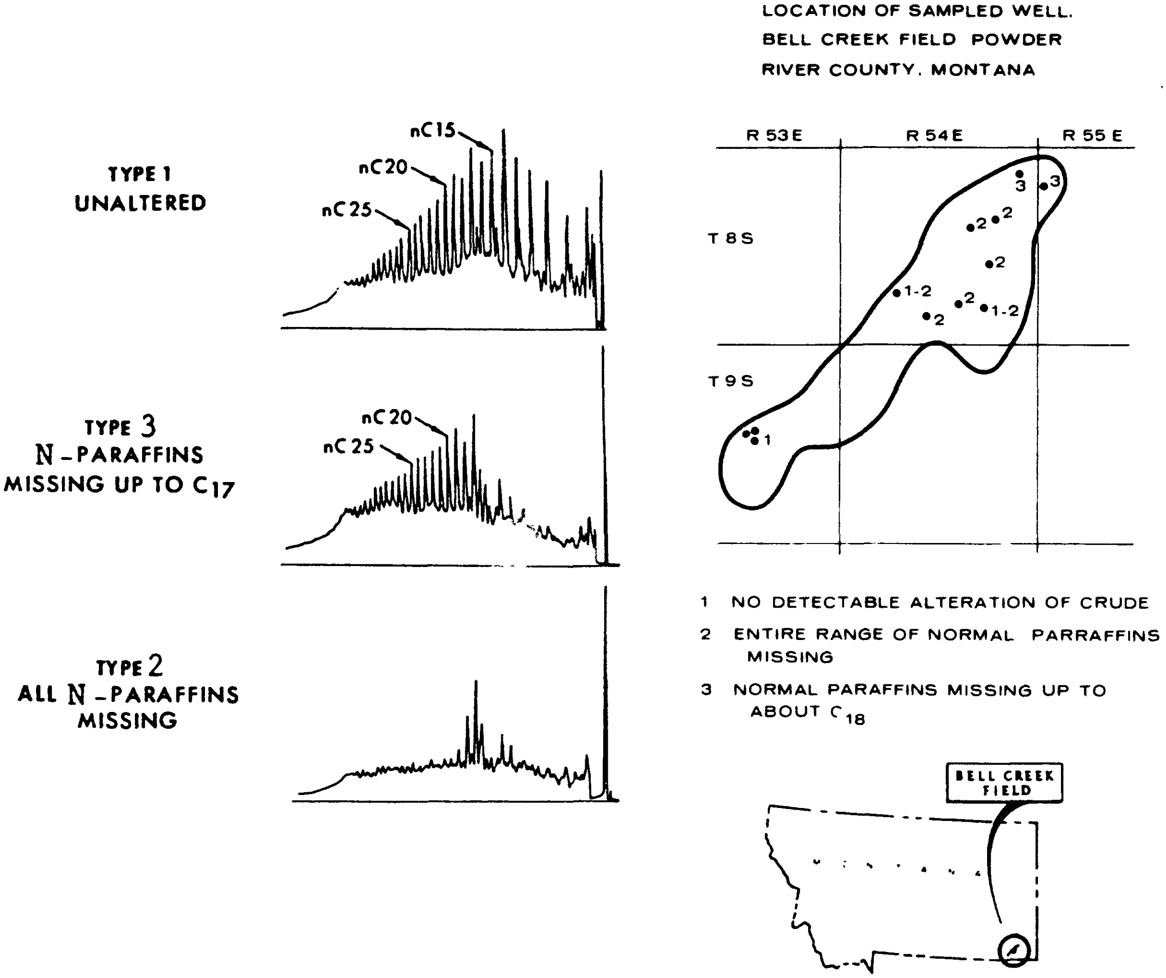

Figure 18 - Gas chromatograms of saturated hydrocarbon fractions of oils from Bell Creek Field, Montana, showing different degrees of microbiological alteration. Type 1 to the southwest is least altered; type 3 in the extreme northeast part of the field is partially altered with n-paraffins missing up to n-C_{17}. The most altered are the type 2 oils which occur in the central and north central part of the field (modified from Winters and Williams, 1969).

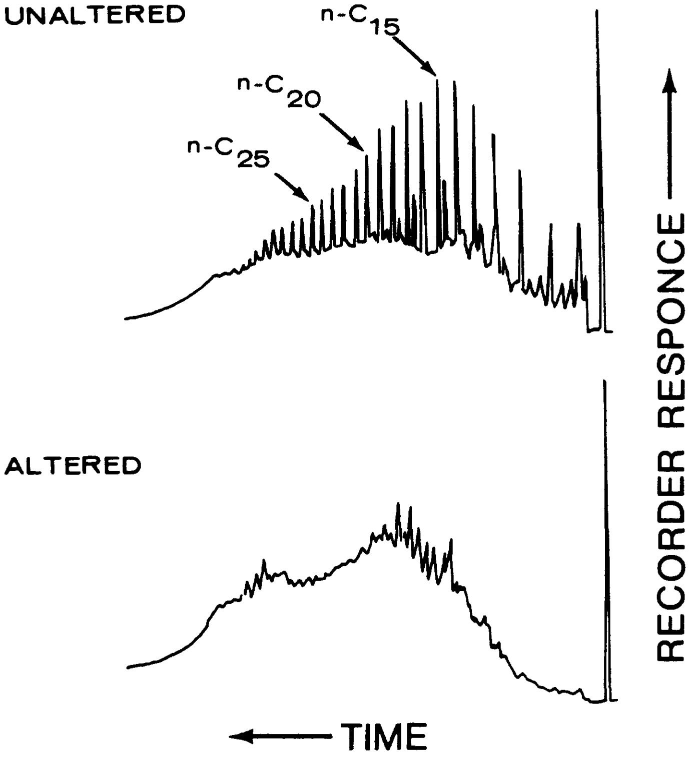

Figure 19 - Gas chromatograms of saturated hydrocarbon fractions of altered and unaltered oils from North Africa. Both oils are believed to be derived from the same source (after Winters and Williams, 1969). Note that the overall shape of the altered oil is more or less similar to that of the mine seep oils (Figs. 5 and 6), suggesting that both biodegraded oils underwent similar degrees of biodegradation at least with respect to the removal of n-paraffins.

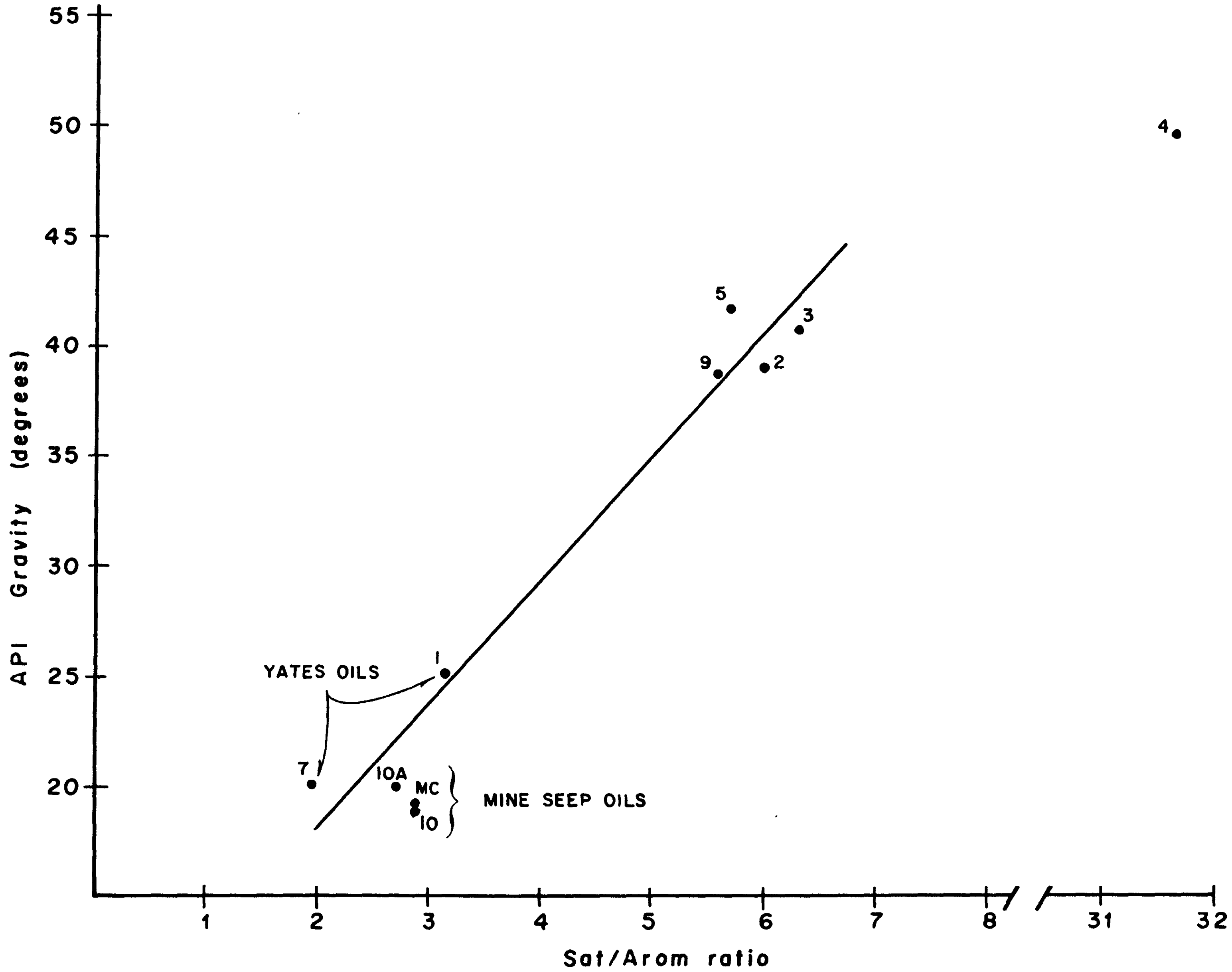

Figure 20 - Plot of API gravity versus saturated hydrocarbon/aromatic hydrocarbon (Sat/Arom) ratios showing relationship of mine seep oils to Yates crude oils in Eddy County, New Mexico. (Key to sample numbers in Table 3).

APPENDIX

6 bbl (0.95 m^3) of oil could fill

9.5 m^3 of rock at 10% porosity

or 19.0 m^3 of rock at 5% porosity.

If this volume of rock were a cylinder 0.3 m (1 ft) in height (h) that represents an oil-filled rock volume eminating radially from a borehole, then the radius or furthest extent of the oil-filled rock porosity is given by the formula:

$$r = \sqrt{\frac{V}{\pi h}}$$

for 10% porosity

$$r = \sqrt{\frac{9.5\ m^3}{\pi \times 0.3\ m}} = 3.2\ m$$ (10.4 ft or approx. 10.5 ft)

for 5% porosity

$$r = \sqrt{\frac{19\ m^3}{\pi \times 0.3\ m}} = 4.5\ m$$ (14.7 ft or approx 15 ft)