U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

Rock-Eval pyrolysis and vitrinite reflectance results from outcrop samples of the Rincon Shale (lower Miocene) collected at the Tajiguas Landfill, Santa Barbara County, California

by

Richard G. Stanley[1], Zenon C. Valin[1], and Mark J. Pawlewicz[2]

U.S. Geological Survey

Open-File Report 92-571

[1]Menlo Park, California 94025 [2]Denver, Colorado 80225

1992

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ABSTRACT

The lower Miocene Rincon Shale is exposed in scattered, generally poor outcrops in the Santa Ynez and Topatopa Mountains, and is widespread in the subsurface in the petroliferous offshore Santa Barbara Channel and onshore Ventura basin. In this region, the Rincon is as much as 760 m thick and consists mainly of mudstone, shale, and dolomite that record deposition in bathyal marine environments. We measured a stratigraphic section of the Rincon in unusually fresh and continuous exposures in excavations at the Tajiguas Landfill, about 40 km west of Santa Barbara. Fifty-one samples from this section were analyzed using Rock-Eval pyrolysis and vitrinite reflectance. Total organic carbon in these samples ranges from 0.21 to 5.71 weight percent and averages about 2.66 weight percent, suggesting that the Rincon has good to very good potential as a source of hydrocarbons. A modified van Krevelen diagram and a plot of hydrogen index (HI) versus Rock-Eval T_{max} show that most kerogens in our Rincon samples are oil- and gas-prone types II and III. Vitrinite in these samples is too sparse to be of value in determining thermal maturity, but values of Rock-Eval T_{max} are less than 432 °C, indicating that the samples are thermally immature with respect to the oil window.

Organic-rich strata within the Rincon Shale, while thermally immature at the Tajiguas Landfill, are likely sources of oil and gas in areas of the Santa Barbara Channel and onshore Ventura basin where the Rincon has been buried as deep as the oil window. However, further geochemical studies (for example, oil-source rock correlations) are needed to establish whether the Rincon has actually generated hydrocarbons in commercially significant amounts.

INTRODUCTION

The offshore Santa Barbara Channel and adjacent onshore Ventura basin are an important petroleum-producing region in coastal southern California (fig. 1). Most of the oil and gas is produced from reservoirs in sandstones and fractured fine-grained rocks of Tertiary age (Curran and others, 1971; Nagle and Parker, 1971; Keller, 1988; California Division of Oil and Gas, 1991). However, little public information is available about petroleum source rocks in this region, which are believed to include organic-rich strata ranging in age from Cretaceous to Pliocene (Keller, 1988).

The lower Miocene Rincon Shale has long been recognized as a possible source of hydrocarbons (e.g., Curran and others, 1971, p. 201; Nagle and Parker, 1971, p. 267; Edwards, 1972, p. 46; Link and Dibblee, 1988, p. 29), but little has been published on the organic geochemistry of this unit. The purpose of this report is to present the results of a reconnaissance study, using Rock-Eval pyrolysis and vitrinite reflectance, of the petroleum source potential and thermal maturity of 51 samples collected from the Rincon Shale in a measured stratigraphic section at the Tajiguas Landfill, about 40 km west of Santa Barbara (figs. 1, 2, 3). Our data show that mudstone, shale,

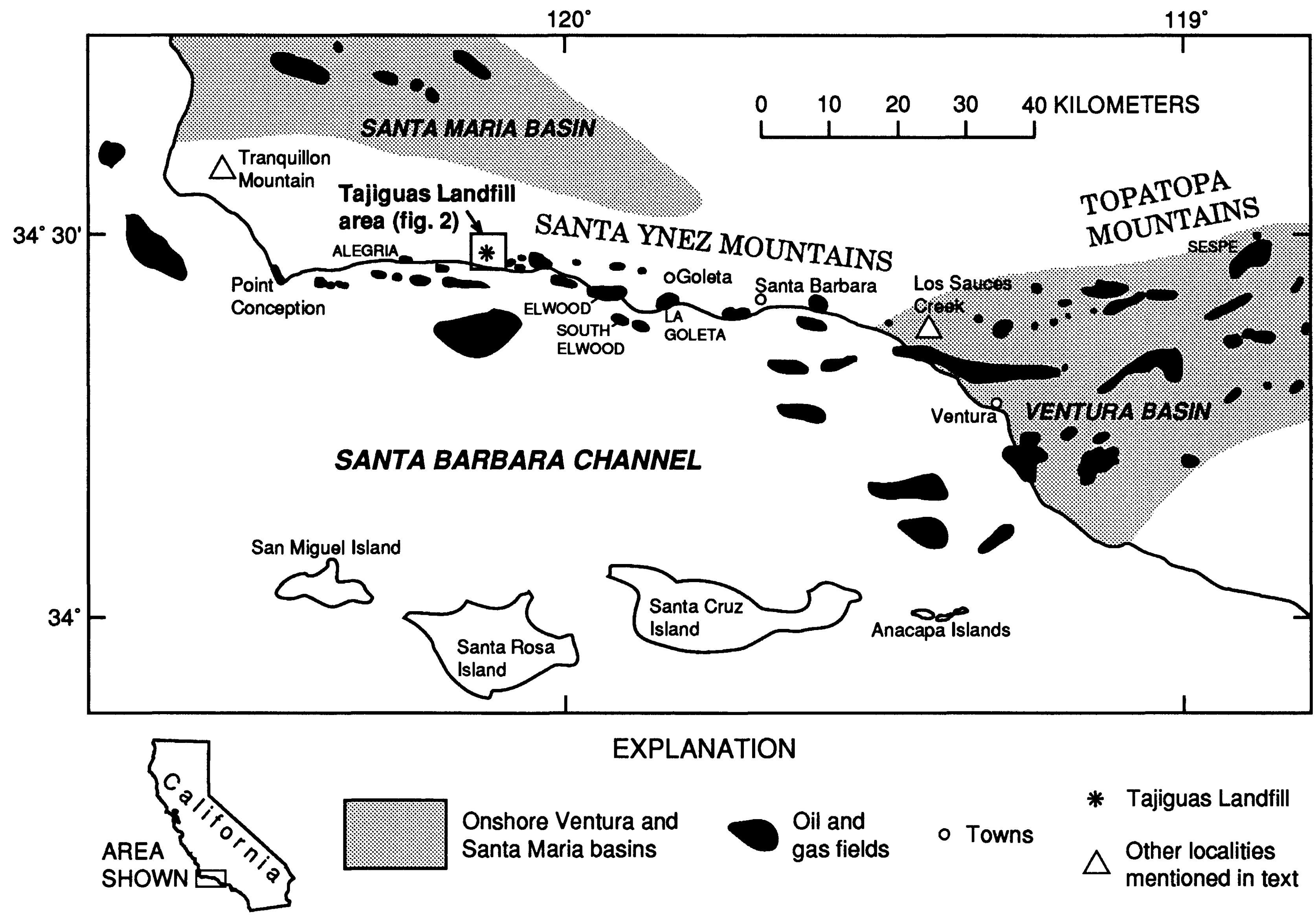

Figure 1. Map showing location of Tajiguas Landfill and other features mentioned in the text.

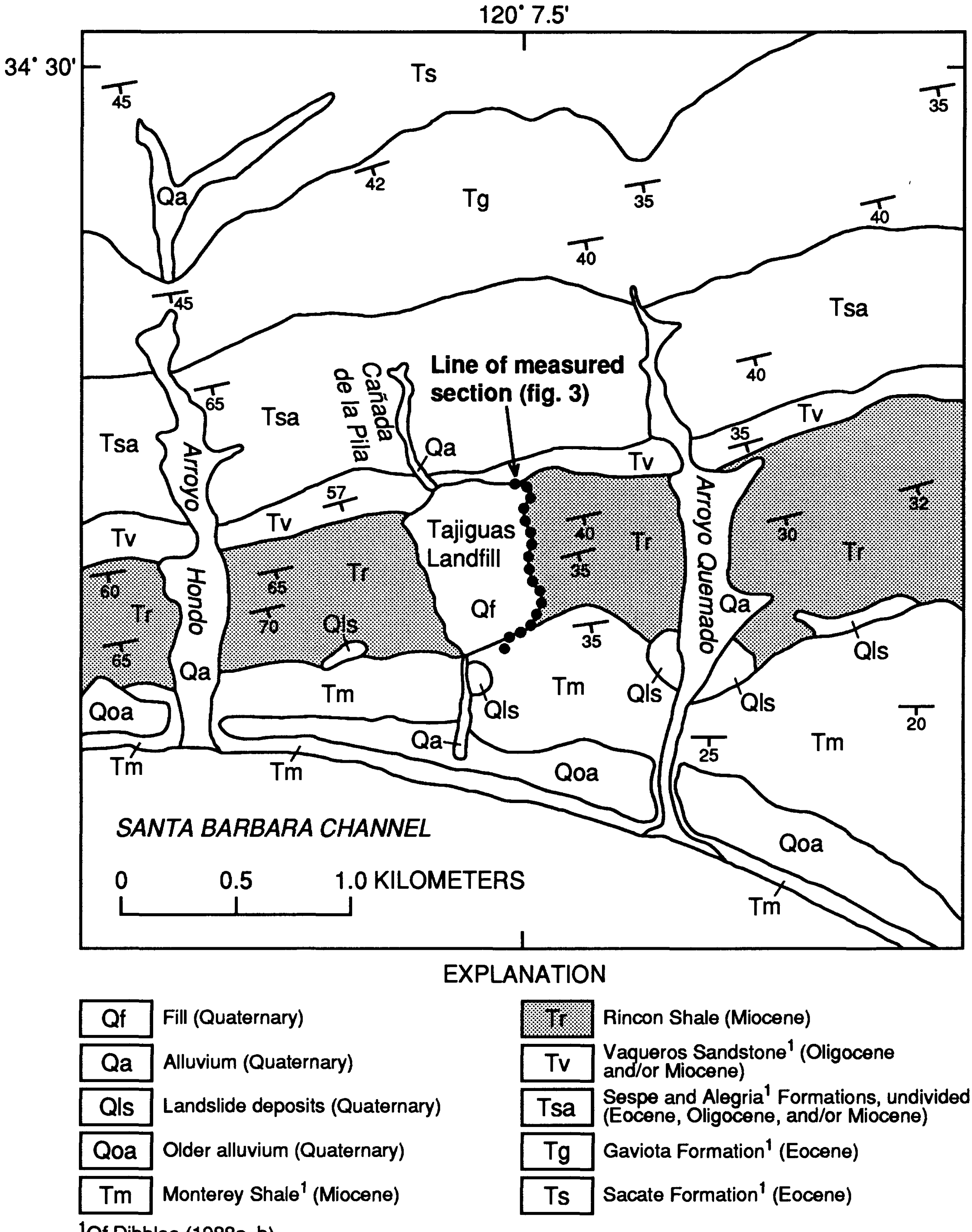

Figure 2. Geologic sketch map of the Tajiguas Landfill area (modified from Dibblee, 1988a, b), showing location of the measured stratigraphic section in fig. 3.

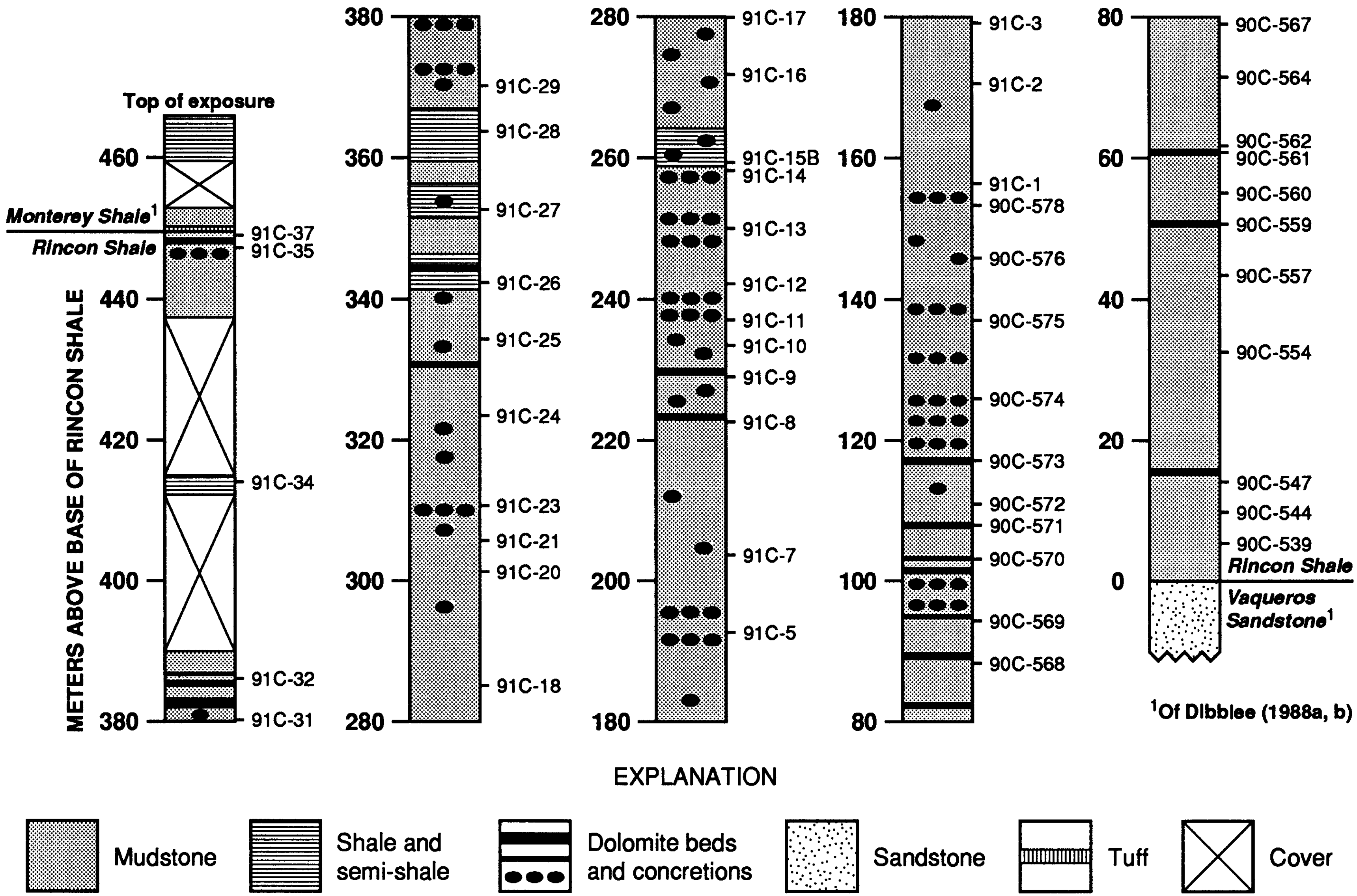

Figure 3. Generalized measured stratigraphic section of the Rincon Shale at the Tajiguas Landfill, showing sample sites. See fig. 2 for location.

and dolomite in the Rincon are possible sources of both oil and gas, but are thermally immature with respect to the oil window in the area sampled.

The Tajiguas Landfill is operated by the County of Santa Barbara, and is located along the east side of Cañada de la Pila in the Gaviota and Tajiguas 7.5-minute quadrangles. Bulldozer excavations at the landfill created unusually fresh and continuous exposures of the Rincon Shale, which we measured and sampled during September, 1990, and June, 1991. Subsequently, however, many of these exposures were covered by household garbage and other fill materials.

REGIONAL STRATIGRAPHIC SETTING

The Rincon Shale is exposed in discontinuous, generally poor outcrops in the Santa Ynez and Topatopa Mountains, and also has been penetrated by numerous wells in the onshore Ventura basin and offshore Santa Barbara Channel (fig. 1). The Rincon consists primarily of mudstone, with minor dolomite, siliceous shale, and sandstone (Dibblee, 1966; Edwards, 1971, 1972). In places, the Rincon is as thick as 760 m (Vedder and others, 1969, p. 3; Curran and others, 1971, p. 201).

The name "Rincon Shale" is the current preferred usage of the U.S. Geological Survey for this unit in the region between Goleta and Point Conception (J.R. Le Compte, U.S. Geological Survey, oral communication, 1992); this area includes the Tajiguas Landfill (fig. 1). The name "Rincon Shale" has been used by many authors, including Woodring (1932, pl. 2), Upson (1951), Bandy and Kolpack (1963), Weaver (1965a, b), Dibblee (1966, 1988a, 1988b), Vedder and others (1969), Nagle and Parker (1971), Isaacs (1981, 1983), and Ogle and others (1987). However, the same rocks in the same area also have been called the Rincon Formation by Kerr (1931), Kew (1932, p. 50), Carson (1965), Edwards (1971, 1972), Patet (1972), Finger (1983), Arends and Blake (1986), Huddleston and others (1986), DePaolo and Finger (1991), and Pinkerton (1991); "Temblor clay shale" by Cushman and Laiming (1931); the Temblor Shale by Swayze (1943); "Temblor" claystone by Hill (1943); the Rincon Mudstone by Bramlette (1946, pl. 2); and the Rincon Claystone by Dibblee (1950, 1988c). The type section is along Los Sauces Creek, about 67 km east of the Tajiguas Landfill (fig. 1; Kerr, 1931; Keroher, 1966, p. 3277).

The Rincon Shale was deposited at bathyal depths in an elongate trough whose axis was nearly coincident with the present-day coastline (Edwards, 1971, 1972). Paleomagnetic data suggest that the basin axis, now oriented east-west, may have been north-south prior to clockwise tectonic rotation of about 90° (Hornafius, 1985; Pinkerton, 1991) beginning about 17.7 Ma (Stanley and others, 1992). The depositional setting of the Rincon is unclear, and probably varied from place to place; environments suggested for the Rincon in the Santa Barbara coastal area include slope (Ingle, 1980), basin floor (Finger, 1983), and bank-top (Hornafius, 1991). Paleobathymetric analyses of benthic foraminiferal assemblages in the lower part of the Rincon in the area of its type locality, and at the Tajiguas Landfill, indicate rapid bathymetric deepening from water depths of less than 100 m (represented by shallow-marine sandstones of the Vaqueros Formation) to bathyal depths greater than 2,000 m (Finger, 1983; Pinkerton, 1991). The rate and magnitude of the deepening indicate rapid tectonic subsidence (Ingle, 1980; Finger, 1983; Pinkerton, 1991; Pinkerton and Rigsby, 1991), perhaps associated with an episode of regional extension or transtension related to a change in plate motions in the circum-Pacific area (Stanley, 1988).

Fractured shale reservoirs in the Rincon Shale produce oil in the Alegria field (Weaver, 1965a, p. 5) and Sespe field (Nagle and Parker, 1971, p. 269); oil and gas in the onshore and offshore areas of the Elwood field (Hill, 1943, p. 380; Dryden and others, 1968, p. 140; California Division of Oil and Gas, 1991, p. 655); and gas in the La Goleta field (Swayze, 1943, p. 384). Sandstone interbeds in the Rincon Shale are reservoirs of petroleum locally in the Ventura basin (Nagle and Parker, 1971, p. 267) and in the South Elwood offshore field (Curran and others, 1971, p. 201; Taylor, 1976, p. 27; California Division of Oil and Gas, 1991, p. 659). Published cross-sections from many onshore and offshore fields (California Division of Oil and Gas, 1991) suggest that the Rincon is an important seal for petroleum accumulations that occur in sandstone reservoirs within the underlying Vaqueros.

THE TAJIGUAS LANDFILL SECTION

In the Tajiguas Landfill section (fig. 3), the Rincon Shale conformably overlies the Vaqueros Sandstone of Dibblee (1988a, b); the contact is gradational over a few centimeters from fine sandstone upward to siltstone and mudstone. New data indicate that the Rincon Shale in the Tajiguas Landfill section is entirely of early Miocene age (Saucesian benthic foraminiferal stage of Kleinpell, 1938, 1980) on the basis of benthic and planktic foraminifers and calcareous nannofossils (Mary Lou Cotton and Mark Filewicz, Unocal Corporation, oral and written communications, 1991, 1992). Several previous investigations, however, concluded that the lower part of the Rincon along the Santa Barbara coast may fall within the Zemorrian benthic foraminiferal stage of Kleinpell (1938, 1980), and may be as old as late Oligocene (e.g., Kleinpell and Weaver, 1963; Edwards, 1972; Isaacs, 1981, 1983; Finger, 1983; Huddleston and others, 1986; Pinkerton, 1991). According to Mary Lou Cotton (written communication, 1992), new evidence suggests that the conclusions of these previous investigations were probably the result of an original miscorrelation by Kleinpell (1938).

The Rincon is conformably overlain by the Miocene Monterey Shale of Dibblee (1988a, 1988b). According to Dibblee (1966, p. 46), the basal part of the Monterey in this area is a soft white tuff (commonly referred to by the term "bentonite"). At the Tajiguas Landfill, the tuff is weathered, poorly exposed, apparently felsic, and about 70 cm thick. This tuff may have originated from the same eruptive center and may be the same age as a welded tuff yielding an $^{40}Ar/^{39}Ar$ age of 17.79 ± 0.10 Ma (Stanley and others, 1991) in the Tranquillon Volcanics of Dibblee (1950) on Tranquillon Mountain, about 42 km west of the Tajiguas Landfill (fig. 1). In the Tajiguas Landfill section, the lower part of the Monterey is of early Miocene age (Saucesian and

Relizian benthic foraminiferal stages of Kleinpell, 1938 and 1980) on the basis of microfossils (Edwards, 1972; Pinkerton, 1991).

At the Tajiguas Landfill, the Rincon Shale is 449 m thick and consists mainly of mudstone with subordinate semi-shale, siliceous shale, and dolomite. The mudstone is generally gray brown to dark chocolate brown on fresh surfaces, and weathers white to shades of grayish-, orangish-, and reddish- brown. In places, yellow jarosite, a weathering product, is common along fractures. Most of the mudstone is hard and displays chippy to spheroidal weathering. The mudstone is bioturbated to apparently massive and crudely stratified. Where visible, stratification is marked by (1) subtle variations in texture, color, and weathering; (2) by tabular dolomite concretions; and (3) by laterally persistent zones of spheroidal to ellipsoidal dolomite concretions. The mudstones display varying reactions to dilute hydrochloric acid (HCl); in this report, mudstones with vigorous to weak reactions to HCl are referred to as calcareous, while mudstones with no reaction to HCl are called noncalcareous. Fossil foraminifers and fish fragments (scales, bones, and teeth) are commonly observed on freshly broken surfaces. A shark's tooth collected about 184.5 m above the base of the Rincon was identified by J.D. Stewart (Natural History Museum of Los Angeles County, written communication, 1991) as belonging to the genus *Carcharhinus*, a group of voracious predators.

The term "semi-shale," an unconventional lithologic name used in this report, refers to mudstone that displays weak fissility parallel to stratification. At the Tajiguas Landfill, semi-shale is commonly more resistant to weathering than nonfissile mudstone, and in places exhibits a distinctive shiny luster on weathered surfaces in bright sunlight. Stratigraphically, semi-shale occurs in the uppermost 108 m of the Rincon Shale at the Tajiguas Landfill.

Siliceous shale is present in the uppermost 50 m of the Rincon Shale at the Tajiguas Landfill. It exhibits well-developed fissility and porcelaneous luster, and is more resistant to weathering than mudstone and semi-shale. The siliceous shale is noncalcareous, hard, and brittle; it is mainly thin to medium bedded, and in places is laminated on a millimeter scale. Fish scales and bones are abundant. The siliceous shale is dark brown on fresh surfaces, and weathers white to reddish brown.

Dolomite is present through nearly the entire stratigraphic interval of the Rincon Shale at the Tajiguas Landfill, but is most abundant beginning about 94 m above the base of the Rincon. Dolomite occurs as (1) tabular beds up to 50 cm thick; (2) scattered individual spheroids and ellipsoids up to 150 cm thick and 130 cm across; and (3) laterally persistent zones of many such spheroids and ellipsoids. The dolomite is generally aphanitic, with abundant fish scales and bones; gray-brown to yellow-brown on fresh surfaces; hard and brittle; orange-weathering; and more resistant to weathering than the surrounding mudstone and shale. Sparse vascular plant fragments were noted in sample 90C-561, about 60.3 m above the base of the Rincon.

Interbeds of sandstone and bentonite within the Rincon Shale have been reported from several localities in the Santa Barbara-Ventura coastal area (Carson, 1965, p. 39; Dibblee, 1966, p. 43; Curran and others, 1971, p. 201; Edwards, 1971, p. 207 and p. 216-219; Edwards, 1972, p. 47) but were not observed by us in the Tajiguas Landfill section. Offshore in the Santa Barbara Channel, blueschist-bearing turbidite sandstones in the Rincon are thicker to the south, and apparently were derived from that direction (Hornafius, 1991, p. 895-897).

METHODS

Fifty-one rock samples were collected from the Rincon Shale in bulldozer excavations at the Tajiguas Landfill. The stratigraphic positions of the samples were measured by tape and compass traverse. Samples of rock were taken from about 20 to 50 cm back from the outcrop faces in order to obtain the freshest available material. All 51 samples were analyzed using a Rock-Eval II pyroanalyzer, and 15 of these were examined for vitrinite reflectance, in the laboratories of the U.S. Geological Survey, Branch of Petroleum Geology, in Denver, Colorado. The results of the Rock-Eval pyrolysis and vitrinite reflectance analyses are shown in tables 1, 2, and 3.

Rock-Eval pyrolysis is a widely used method of rapidly evaluating the quality and thermal maturity of prospective petroleum source rocks (Espitalié and others, 1977, 1984; Clementz and others, 1979; Tissot and Welte, 1984; Peters, 1986). The procedure mimics, in some respects, the natural hydrocarbon-generation processes which occur at much slower rates within the earth when sediments containing kerogen (sedimentary organic matter) are buried progressively deeper and subjected to higher temperatures (Waples, 1985). Pulverized samples of rock are held at 250 °C for 3 minutes (the "isothermal period"), then gradually heated from 250 °C to 600 °C at 25 °C per minute in an oxygen-free atmosphere, causing the release of water, carbon dioxide, and hydrocarbons from the rock. Several parameters are measured automatically by the Rock-Eval apparatus (table 1). The quantity S1 is the amount of hydrocarbons (HC), measured in milligrams HC per gram of rock, that is released upon initial heating to 250 °C; this quantity includes the bitumen (free organic compounds, including gas and oil) already present in the rock. The quantity S2 (also measured in milligrams HC per gram of rock) is the amount of hydrocarbons generated by pyrolytic degradation (or "cracking") of the remaining organic matter in the rock and is an indicator of the potential of the rock to generate additional oil and gas. T_{max} is the temperature--generally about 400 °C to 500 °C--at which S2 is at a maximum and is regarded as a rough indicator of thermal maturity. S3 is the amount of carbon dioxide (in milligrams of CO_2 per gram of rock) generated during pyrolysis, and is thought to be related to the amount of oxygen in the pyrolyzed organic matter. Additional Rock-Eval parameters include the total organic carbon (TOC) in weight percent; the hydrogen index (HI), defined as the product 100(S2/TOC); the oxygen index (OI), defined as the product 100(S3/TOC); and the production index (PI), defined as the ratio S1/(S1 + S2).

Table 1. Rock-Eval pyrolysis data from the Rincon Shale in the Tajiguas Landfill section. T_{max} values for samples with S2 less than 0.2 mg HC/g rock were rejected as unreliable, following Peters (1986)

[Rock-Eval parameters are discussed in the text. mdst = mudstone, calc = calcareous, noncalc = noncalcareous, sh = shale]

Sample number	Meters above base[1]	Rock type	Sample weight (mg)	TOC (weight percent)	S1 (mg HC/ g rock)	S2 mg HC/ g rock)	S3 (mg CO_2/ g rock)	S2/S3	PI (S1/ S1+S2)	HI	OI	T_{max} (°C)
91C-37	448.99	mdst--calc	193.8	0.32	0.01	0.23	0.54	0.42	0.04	71	168	425
91C-35	447.34	mdst--noncalc	185.4	.21	.01	.10	.48	.20	.10	47	228	
91C-34	413.87	siliceous sh	147.3	1.36	.01	.57	2.44	.23	.02	41	179	430
91C-32	385.23	mdst--noncalc	210.0	.49	0	.12	1.61	.07	0	24	328	
91C-31	380.07	mdst--noncalc	24.6	2.65	0	4.84	1.83	2.56	0	182	68	427
91C-29	369.97	mdst--noncalc	28.7	3.39	.13	8.78	2.22	3.95	.01	258	65	423
91C-28	363.38	semi-shale	21.1	2.37	.04	6.68	2.36	2.83	.01	281	99	425
91C-27	352.40	mdst--noncalc	27.7	2.68	.03	7.22	2.34	3.08	0	269	87	430
91C-26	342.45	semi-shale	24.5	3.10	.04	5.83	2.73	2.13	.01	188	88	426
91C-25	334.27	mdst--noncalc	25.5	4.31	.03	12.94	3.09	4.18	0	300	71	426
91C-24	323.34	mdst--calc	19.4	2.90	.05	6.90	2.62	2.63	.01	237	90	431
91C-23	310.97	mdst--noncalc	24.0	3.02	.08	7.91	2.16	3.66	.01	261	71	429
91C-21	305.68	mdst--calc	34.6	3.09	.05	11.44	2.34	4.88	0	370	75	429
91C-20	301.19	mdst--noncalc	40.9	3.54	.07	12.61	2.22	5.68	.01	356	62	425
91C-18	285.03	mdst--noncalc	29.0	4.72	.06	14.20	2.93	4.84	0	300	62	420
91C-17	279.95	mdst--noncalc	57.4	3.75	.05	13.79	2.12	6.50	0	367	56	417
91C-16	270.92	mdst--noncalc	67.2	3.65	.05	11.07	2.70	4.10	0	303	73	425
91C-15B	259.00	semi-shale	150.0	2.36	.04	6.56	1.30	5.04	.01	277	55	409
91C-14	257.03	mdst--noncalc	46.3	3.15	.08	11.31	1.90	5.95	.01	359	60	422
91C-13	249.29	mdst--noncalc	30.7	2.96	.06	10.87	1.79	6.07	.01	367	60	424
91C-12	241.67	mdst--noncalc	22.7	2.88	.08	9.69	1.71	5.66	.01	336	59	428
91C-11	236.39	mdst--noncalc	35.0	3.89	.05	12.00	2.80	4.28	0	308	71	425
91C-10	232.99	mdst--noncalc	50.3	3.50	.05	12.32	2.00	6.16	0	352	57	422
91C-9	228.74	mdst--noncalc	70.1	3.61	.07	13.80	1.71	8.07	.01	382	47	419
91C-8	222.20	mdst--noncalc	40.5	2.97	.04	11.35	1.92	5.91	0	382	64	429

Table 1. Continued

Sample number	Meters above base[1]	Rock type	Sample weight (mg)	TOC (weight percent)	S1 (mg HC/ g rock)	S2 mg HC/ g rock)	S3 (mg CO_2/ g rock)	S2/S3	PI (S1/ S1+S2)	HI	OI	T_{max} (°C)
91C-7	203.79	mdst--noncalc	32.7	2.62	.03	7.38	2.40	3.07	0	281	91	428
91C-5	192.50	mdst--noncalc	41.4	3.14	.07	12.17	2.12	5.74	.01	387	67	423
91C-3	178.29	mdst--noncalc	47.9	3.69	.06	13.36	1.98	6.74	0	362	53	420
91C-2	169.98	mdst--noncalc	39.1	2.22	.02	6.24	1.99	3.13	0	281	89	432
91C-1	156.77	mdst--noncalc	71.1	2.93	.04	9.90	1.50	6.60	0	337	51	418
90C-578	152.76	mdst--noncalc	86.2	3.20	.06	11.04	1.48	7.45	.01	345	46	424
90C-576	145.31	dolomite	52.2	3.00	.07	10.03	1.60	6.26	.01	334	53	427
90C-575	136.52	mdst--noncalc	51.0	3.09	.09	10.66	1.78	5.98	.01	344	57	426
90C-574	125.47	mdst--calc	24.4	2.74	.08	9.01	2.50	3.60	.01	328	91	427
90C-573	116.52	dolomite	236.0	.70	.02	2.06	.62	3.32	.01	294	88	418
90C-572	110.57	mdst--calc	36.8	4.54	.10	20.21	2.33	8.67	0	445	51	420
90C-571	107.23	dolomite	221.4	1.21	.03	3.32	.77	4.31	.01	274	63	416
90C-570	102.74	dolomite	209.0	.73	.01	1.57	.68	2.30	.01	215	93	419
90C-569	94.05	mdst--calc	37.2	5.71	.13	25.80	2.68	9.62	.01	451	46	418
90C-568	88.05	mdst--calc	41.4	3.55	.14	14.39	2.10	6.85	.01	405	59	421
90C-567	78.88	mdst--calc	49.5	3.55	.08	12.84	1.55	8.28	.01	361	43	425
90C-564	71.16	mdst--calc	72.9	2.72	.09	8.44	1.30	6.49	.01	310	47	428
90C-562	61.38	mdst--calc	41.6	2.62	.04	8.12	1.53	5.30	0	309	58	432
90C-561	60.30	dolomite	139.5	1.74	.05	4.61	.75	6.14	.01	264	43	424
90C-560	54.93	mdst--noncalc	114.8	1.70	.02	4.11	.62	6.62	0	241	36	430
90C-559	50.28	dolomite	167.3	.70	0	.92	.41	2.24	0	131	58	428
90C-557	43.07	mdst--calc	105.1	1.49	.04	3.27	.56	5.83	.01	219	37	430
90C-554	32.47	mdst--calc	96.2	2.06	.06	5.94	.81	7.33	.01	288	39	426
90C-547	13.99	mdst--calc	136.4	1.45	.03	3.13	.67	4.67	.01	215	46	429
90C-544	9.73	mdst--calc	109.9	1.55	.03	4.04	.48	8.41	.01	260	30	431
90C-539	5.21	mdst--calc	84.5	2.06	.08	6.72	.67	10.02	.01	326	32	426

[1] Above base of Rincon Shale at the Tajiguas Landfill.

Table 2. Summary of Rock-Eval pyrolysis data from the Rincon Shale at the Tajiguas Landfill

Subset	Number of samples analyzed	TOC (wt. pct.)	S1 (mg HC/ g rock)	S2 (mg HC/ g rock)	S3 (mg HC/ g rock)	S2/S3	PI	HI	OI	T_{max} (°C)
All samples	51									
minimum		0.21	0	0.10	0.41	0.07	0	24	30	409
maximum		5.71	.14	25.80	3.09	10.02	.10	451	328	432
mean		2.66	.05	8.48	1.72	4.99	.01	287	75	425
Mudstone--calcareous	15									
minimum		.32	.01	.23	.48	.42	0	71	30	418
maximum		5.71	.14	25.80	2.68	10.02	.04	451	168	432
mean		2.69	.07	9.37	1.51	6.20	.01	306	61	427
Mudstone--noncalcareous	26									
minimum		.21	0	.10	.48	.07	0	24	36	417
maximum		4.72	.13	14.20	3.09	8.07	.10	387	328	432
mean		3.00	.05	9.61	1.98	4.86	.10	297	80	425
Dolomite	6									
minimum		.70	0	.92	.41	2.24	0	131	43	416
maximum		3.00	.07	10.03	1.60	6.26	.01	334	93	428
mean		1.35	.03	3.75	.81	4.10	.01	252	66	422
Semishale	3									
minimum		2.36	.04	5.83	1.30	2.13	.01	188	55	409
maximum		3.10	.04	6.68	2.73	5.04	.01	281	99	426
mean		2.61	.04	6.36	2.13	3.33	.01	249	81	420
Siliceous shale	1									
minimum		1.36	.01	.57	2.44	.23	.02	41	179	430
maximum		1.36	.01	.57	2.44	.23	.02	41	179	430
mean		1.36	.01	.57	2.44	.23	.02	41	179	430

Table 3. Vitrinite reflectance (R_o) data from the Rincon Shale at the Tajiguas Landfill

Sample number	Number of measurements	Range of R_o (percent)	Mean R_o (percent)	Standard deviation	Remarks
91C-37	7	0.61-1.18	0.91	0.20	All measurements on recycled vitrinite. No bitumen observed.
91C-34	5	0.59-0.67	.62	.04	Poor sample. Very small particles, with some signs of weathering.
91C-28	4	0.22-0.29	.25	.03	Measured particles may be bitumen rather than vitrinite.
91C-24					Poor sample. Some small, globular, structureless particles may be bitumen.
91C-20					No vitrinite.
91C-18	11	0.22-0.33	.29	.03	Fair sample. Most material degraded or too small to measure; some higher rank recycled material.
91C-9	2	0.23-0.26	.24	.02	Poor sample. Organic material sparse, and either degraded or too small to measure. Some higher rank recycled material.
91C-7					Poor sample. Organic material sparse, and either degraded or too small to measure. All very low rank except for some higher rank recycled material.
91C-3					No vitrinite.
91C-1	9	0.17-0.28	.23	.03	Poor sample. Organic material sparse; includes some inertinite, and recycled vitrinite. Measured particles may be bitumen rather than vitrinite.
90C-574	3	0.21-0.28	.24	.03	Measured particles may be bitumen rather than vitrinite.
90C-570					Poor sample. Material sparse and too small to measure; includes apparently recycled vitrinite with R_o about 0.8%.
90C-567					Material too sparse to measure; some particles with very low R_o.
90C-561	12	0.18-0.28	.24	.03	Poor sample. Organic particles sparse and very small; include inertinite, recycled vitrinite. Measured particles may be bitumen rather than vitrinite.
90C-539					Poor sample. Organic particles sparse, mostly very small, and degraded; mostly very low rank except for some higher rank recycled particles.

Vitrinite reflectance (R_o) is a common method of determining thermal maturity and is obtained by measuring the percentage of light reflected by vitrinite, a type of kerogen formed from woody terrestrial plant material (Tissot and Welte, 1984; Waples, 1985). Higher values of vitrinite reflectance correspond to higher levels of thermal maturity. The maturation of vitrinite is directly related to maximum burial temperature and is irreversible (Barker and Pawlewicz, 1986).

QUANTITY OF ORGANIC MATTER

The quantity of organic matter in the samples is indicated by the TOC (total organic carbon, in weight percent) and the quantities S1 and S2. The TOC of samples from the Rincon Shale ranges from 0.21 to 5.71 weight percent with a mean of 2.66 weight percent (tables 1 and 2). Out of 51 samples, 45 exhibit values of TOC greater than 1 weight percent, and therefore have good to very good source rock generative potential (table 4).

Only 3 of the 51 samples show TOC values less than 0.5 weight percent (table 1), which generally is regarded as the lower limit for potential source rocks of petroleum (Tissot and Welte, 1984). We attribute these low values to oxidation of organic matter during weathering because all 3 samples (samples 91C-32, 91C-35, and 91C-37 in table 1 and fig. 3) were collected from near the margin of the freshly-excavated part of the exposure at the Tajiguas Landfill, where the rocks were noticeably more weathered than in the rest of the section. Previous studies have shown that TOC can be significantly reduced by oxidation of organic matter during outcrop weathering (Leythaeuser, 1973; Clayton and Swetland, 1978; Peters, 1986; Stanley, 1987).

The ranges of TOC values for all rock types represented in our samples--including calcareous and noncalcareous mudstone, dolomite, semi-shale, and siliceous shale--show significant overlap (table 2), suggesting that there is little if any correlation between lithology and organic content in our samples. However, this preliminary conclusion should be viewed with caution because of the small number of samples of dolomite, semi-shale, and siliceous shale that were examined.

Values of S1 are quite low in our samples, averaging about 0.05 (table 2), indicating that the samples contain very little bitumen (free organic compounds, including gas and oil). The most likely reason for this is that the rocks have never generated bitumen because they are thermally immature, as discussed later in this report. In addition, the very low S1 suggests that no hydrocarbons have migrated into the Rincon Shale in the Tajiguas Landfill area from other hydrocarbon source beds. It is possible that small amounts of highly volatile organic compounds were originally present in the samples but were lost to the atmosphere during transport from the field to the laboratory. Low values of S1 also can be caused by adsorption onto clay minerals of the hydrocarbons produced during pyrolysis (Peters, 1986).

Table 4. Geochemical parameters describing source rock generative potential, from Peters (1986)

Potential	TOC (weight %)	S1 (mg HC/g rock)	S2 (mg HC/g rock)
Poor	0-0.5	0-0.5	0-2.5
Fair	0.5-1.0	0.5-1.0	2.5-5.0
Good	1.0-2.0	1.0-2.0	5.0-10.0
Very good	2.0+	2.0+	10.0+

Table 5. Geochemical parameters describing type of hydrocarbon generated, from Peters (1986)

Type	Hydrogen Index (HI)	S2/S3
Gas	0-150	0-3
Gas and oil	150-300	3-5
Oil	300+	5+

Table 6. Geochemical parameters describing level of thermal maturation, from Peters (1986)

Maturation	Production Index (PI)[1] [S1/(S1 + S2)]	T_{max}[1] (° C)	Vitrinite reflectance (percent R_o)
Top oil window	ca. 0.1	ca. 435-445	ca. 0.6
Bottom oil window	ca. 0.4	ca. 470	ca. 1.4

[1] T_{max} and PI are crude measurements of thermal maturation and are partly dependent on other factors, including the type of organic matter (Peters, 1986).

Values of S2 in our samples range from 0.1 to 25.8, averaging about 8.48 (table 2). Thirty-seven of the samples show values of S2 greater than 5 (table 1), indicating good to very good source rock generative potential (table 4). The anomalously low values of S2 (less than 0.5) in 3 samples near the top of our measured section (samples 91C-32, 91C-35, and 91C-37 in table 1 and fig. 3) may reflect oxidation of organic matter during outcrop weathering.

TYPES OF ORGANIC MATTER

Plots of hydrogen index (HI) versus oxygen index (OI) on a modified van Krevelen diagram (fig. 4) show that most of the samples are intermediate between types II and III, but a few are intermediate between types III and IV. Similar results are indicated on a plot of hydrogen index versus T_{max} (fig. 5). Type II kerogens are generally considered to be potential sources of oil, while type III kerogens are sources mainly of gas (Tissot and Welte, 1984; Peters, 1986). Type IV kerogens are generally regarded as inert, with little or no hydrocarbon source potential (Peters, 1986).

Twenty-one of the samples exhibit values of hydrogen index (HI) greater than 300 and S2/S3 greater than 5, suggesting that these rocks are oil-prone (tables 1 and 5). Most of the remaining samples are both oil- and gas-prone. Only 5 samples show HI values less than 150 and S2/S3 less than 3 (table 1). However, these results should be viewed with caution because both HI and S2/S3 can be reduced by oxidation of organic matter during outcrop weathering (Peters, 1986). Therefore, the unweathered rocks of the Rincon Shale in the subsurface may be more oil-prone than is suggested by the Rock-Eval data from our surface samples.

Four of the samples (91C-32, 91C-34, 91C-35, and 91C-37) plot as intermediate between types III and IV on the modified van Krevelen diagram (fig. 4) and also show oxygen index (OI) values greater than 150. Such values are unusually high (Katz, 1983), and can be caused by oxidation of organic matter in the samples during outcrop weathering (Peters, 1986; Stanley, 1987).

Elevated values of oxygen index (OI) also can be caused by generation of carbon dioxide during pyrolysis by thermal degradation of carbonate minerals such as calcite, dolomite, and siderite (Katz, 1983; Peters, 1986). None of our samples were treated with acid to remove carbonate before pyrolysis, so the impact of thermal degradation of carbonate on our results is uncertain. However, such effects probably weren't very great, because values of OI of our dolomite samples (range 43 to 93, mean 66) are not noticeably higher than those of other rock types (tables 1 and 2).

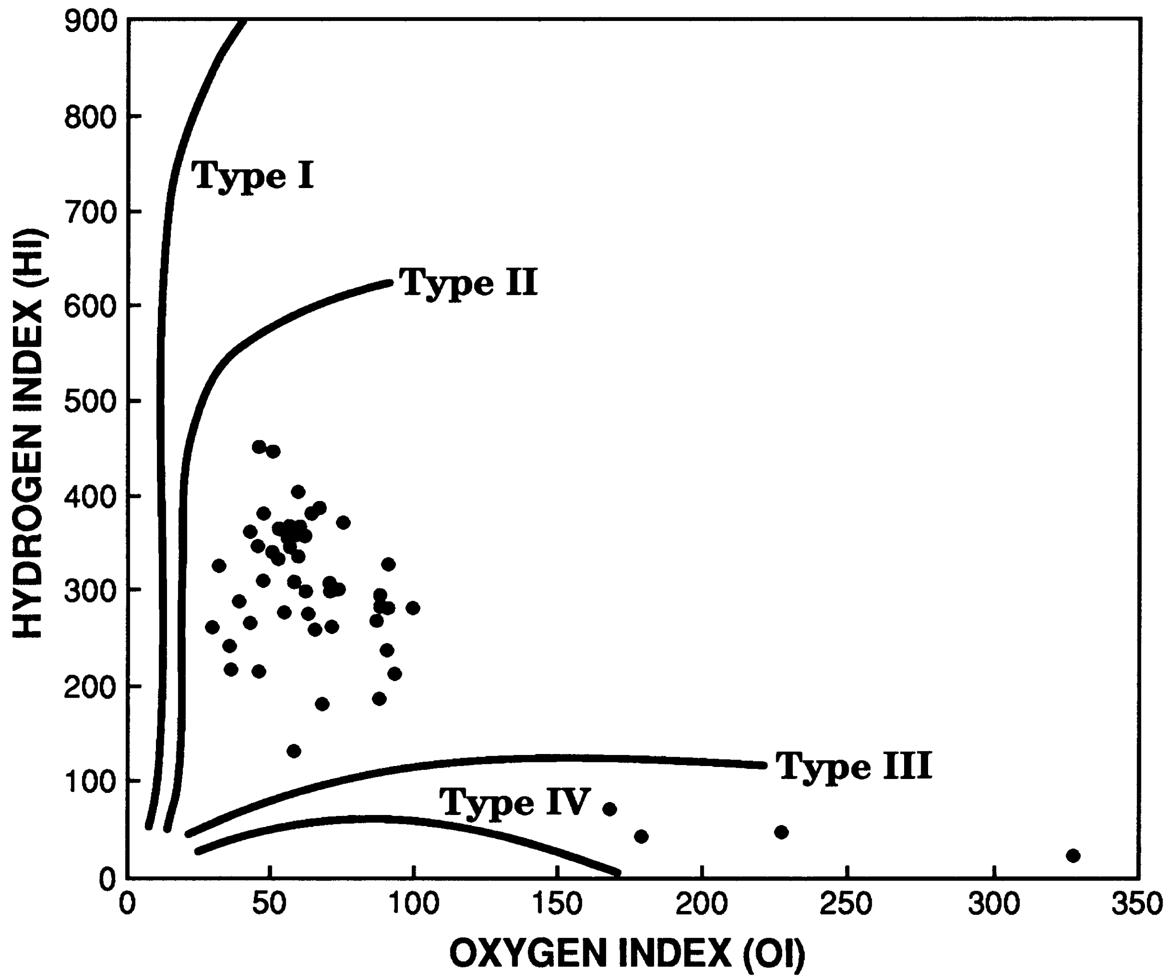

Figure 4. Modified van Krevelen diagram (Peters, 1986) showing idealized kerogen types (solid lines) and results for samples of the Rincon Shale at the Tajiguas Landfill (dots). Most samples are intermediate between types II and III. Type I and type II kerogens are oil-prone, type III kerogens are gas-prone, and type IV kerogens are inert (Peters, 1986).

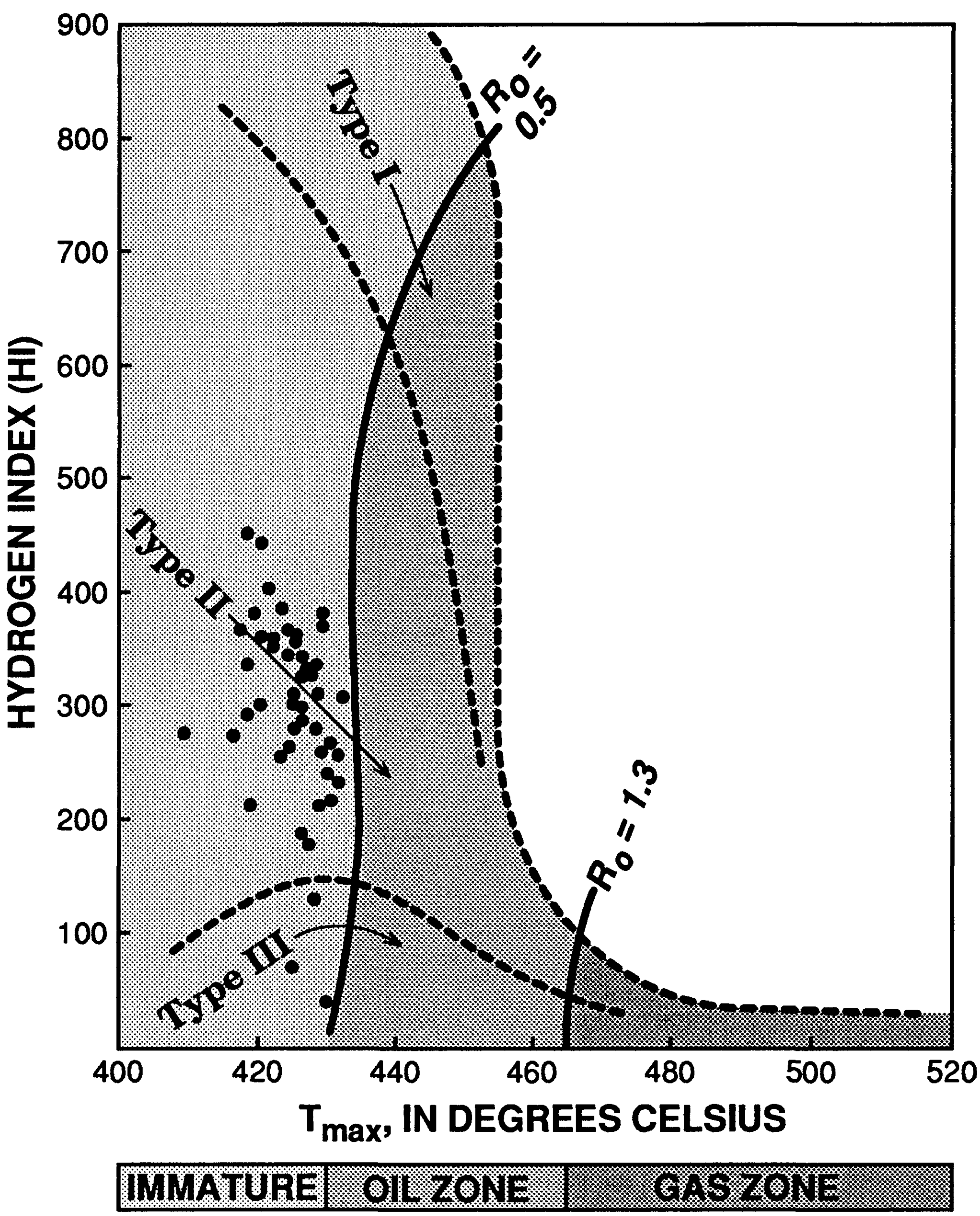

Figure 5. Hydrogen index versus T_{max} (Espitalié and others, 1984), showing idealized kerogen types (fields separated by dashed lines), lines of equal vitrinite reflectance, or R_o (solid lines), and results for samples of the Rincon Shale at the Tajiguas Landfill (dots). All samples are thermally immature with respect to the oil zone, or oil window. In this figure, the boundaries of the oil window in terms of vitrinite reflectance (R_o) and T_{max} are according to Espitalié and others (1984) and differ slightly from those shown in table 6, which are from Peters (1986).

THERMAL MATURITY

All of the samples exhibit T_{max} less than 432 °C (table 1), suggesting that these rocks are thermally immature with respect to the oil window (table 6).

All but one of the 51 samples analyzed show values of PI less than 0.1, suggesting that they are thermally immature (table 6). The single exception, sample 91C-35, has a PI of 0.1; however, this value is probably not reliable due to oxidation of organic matter by outcrop weathering, which is suggested by the anomalously high OI, low TOC, and low S1 of this sample (table 1).

Fifteen samples were processed and examined for vitrinite reflectance (table 3), but the results provide no useful information on thermal maturity. Vitrinite particles are absent from some samples, and sparse in the rest. Where present, the particles are very small. Much of the vitrinite shows strong signs of weathering and/or transport, and probably is recycled. Many samples contain organic material that has a very low reflectance and may be either vitrinite of low rank, or solid bitumen (table 3).

SUMMARY AND CONCLUSIONS

The results of Rock-Eval pyrolysis of outcrop samples collected from the Tajiguas Landfill suggest that the Rincon Shale is a potential source of petroleum. TOC values in our samples average 2.66 weight percent, and range as high as 5.71 weight percent. Kerogens in most of our samples are oil- and gas-prone types II and III (figs. 4, 5). For comparison, the Miocene Monterey Formation of the Santa Barbara-Ventura coastal area and Santa Maria basin exhibits values of organic carbon averaging about 5 weight percent and ranging as high as 23 weight percent in individual beds (Isaacs and Petersen, 1987, p. 91). Kerogens in the Monterey are mostly oil- and gas-prone types II and III, and of mixed marine algal and terrestrial origin (Isaacs and Petersen, 1987, p. 94).

Our conclusions are generally in agreement with a previous Rock-Eval study of the Rincon Shale by Frizzell and Claypool (1983), who analyzed eight samples of the Rincon from outcrops in the Topatopa Mountains (fig. 1). Frizzell and Claypool's data are shown in table 7. The best of their samples exhibit high values of TOC (up to 2.52 weight percent), high S2/S3 (as much as 30.31), high HI (up to 1,102), and low T_{max} (up to 428 °C), indicating that the Rincon in the Topatopa Mountains is a potential source of oil and gas but is thermally immature.

In a study of cuttings from a well in the South Elwood field area, Isaacs and others (1990) analyzed 35 samples from the Rincon Shale and reported organic carbon contents ranging from 1.98 to 4.00 weight percent, with a mean of 2.7 weight percent. These results fall within the range of the TOC values from our outcrop samples, which vary from 0.21 to 5.71 weight percent and average 2.66 weight percent (tables 1 and 2). As noted earlier in this report, the lower TOC values of some of our samples

Table 7. Rock-Eval pyrolysis data from the Rincon Shale in the Topatopa Mountains (Frizzell and Claypool, 1983). T_{max} values for samples with S2 less than 0.2 mg HC/g rock are not reported here because they are unreliable, according to Peters (1986)

[Rock-Eval parameters are discussed in the text]

Map number[1]	Sample number[1]	TOC (weight percent)	S1 (mg HC/ g rock)	S2 mg HC/ g rock)	S3 (mg CO_2/ g rock)	S2/S3	PI (S1/ S1+S2)	HI	OI	T_{max} (°C)
2	VF-81C-287	0.16	0.02	.08	.46	0.17	.17	50	288	
3	VF-81C-288	.75	.20	2.65	.22	12.05	.07	353	29	428
4	VF-81C-310	.13	.02	.39	.26	1.50	.04	300	200	428
5	VF-81C-313	.75	.06	1.44	.55	2.62	.04	192	73	434
6	VF-81C-966	2.40	.28	13.12	.57	23.02	.02	547	24	409
7	VF-81C-970	1.32	.49	14.55	.48	30.31	.03	1102	37	411
8	VF-81C-973	2.52	.31	14.57	.58	25.12	.02	578	23	413
35	VF-80C-603	1.60	.03	0.00	1.42	0.00	1.00	0	89	

[1] Of Frizzell and Claypool (1983).

are from rocks that were recognized as weathered at the time of sampling. In a study of strata in a tunnel beneath the Santa Ynez Mountains near Santa Barbara, Bandy and Kolpack (1963) analyzed 22 samples from the Rincon Shale and found organic carbon contents ranging from 0.05 to 3.61 weight percent and averaging 1.26 weight percent; these values are generally lower than those from both the South Elwood field and the Tajiguas Landfill. We caution that the organic carbon results reported from the tunnel, South Elwood field, and Tajiguas Landfill were obtained by different laboratories using different analytical methods, and may not be directly comparable (Dembicki, 1984). However, the relatively high average values of organic carbon reported from both surface and subsurface samples strongly suggest that the Rincon is indeed a potential source of hydrocarbons.

Available thermal maturity data, discussed earlier in this report, indicate that the Rincon Shale is immature with respect to the oil window in the Tajiguas Landfill area and Topatopa Mountains. However, elsewhere in the offshore Santa Barbara Channel and onshore Ventura basin, organic-rich strata in the Rincon may have been buried as deep as the oil window, and may have generated significant quantities of hydrocarbons. Structural cross-sections suggest that lower Miocene rocks, including the Rincon, have been buried to depths greater than 6,000 m in the central parts of the Ventura basin and Santa Barbara Channel (Nagle and Parker, 1971, p. 282-284; Curran and others, 1971, p. 206). The likely importance of the Rincon as a source of petroleum should be further investigated by geohistory analysis, and by regional organic geochemical studies using methods such as kerogen elemental composition and oil-source rock correlation (e.g., Tissot and Welte, 1984, and references therein).

ACKNOWLEDGMENTS

We thank Cathy Rigsby for introducing us to the Tajiguas Landfill section; Ted Clark of EMCON Associates and Chris Wilson of the County of Santa Barbara for providing access to the property and a map of the landfill; John Pinkerton for providing a copy of his thesis; and Mary Lou Cotton and Mark Filewicz of Unocal Corporation for paleontological analyses and many helpful discussions. An informal review of geologic names was provided by J.R. Le Compte, and helpful technical reviews of the manuscript were done by Kenneth J. Bird and Leslie B. Magoon.

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