

Characterization of Northern California Petroleum by stable carbon isotopes [paper edition]

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U.S. DEPARTMENT OF THE INTERIOR U.S. GEOLOGICAL SURVEY

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Introduction

The purpose of this study is to characterize natural occurrences of petroleum at the surface and in the subsurface within northern California in order to define and map petroleum systems for U.S. Geological Survey energy resource assessments. Furthermore, the chemical characterization and mapping of natural petroleum occurrences could also be used to discriminate natural occurrences from accidental oil spills during the activities of extraction or transportation of petroleum. Samples include petroleum from exploratory well tests, producing fields, natural seeps, and oil-stained rocks, and condensates from gas wells. Most of the sample localities are in northern California but a few samples from central and southern California are included for comparison (table 1). Even though other analyses were performed, only stable carbon isotope (δ^{13} C) data are presented here for brevity and because δ^{13} C values are one of the most discriminating characteristics of California petroleum.

Magoon and others (1995) identified four hydrocarbon types in northern California based on stable carbon isotopic compositions of 16 oil and 6 condensate samples (figure 1). Stanley and others (1996) presented additional data and focused on the oil types found in the San Francisco Bay area of northern California. Lillis and Stanley (1999) identified three oil types (two Miocene and one Eocene) in the La Honda basin (northern California) and presented oilsource rock correlations for each oil type. This report redefines and subdivides the petroleum types based on the isotope data from these studies as well as from new data.

Methods

For oil-stained rocks, the oil was extracted from the rock sample by soaking the sample in chloroform for about one hour at room temperature. Filtered extracts were vacuum evaporated to about 3 milliliters (ml) using a rotary evaporator with moderate vacuum and water bath temperature of about 35° C, and transferred to a volumetric flask for a gravimetric determination of concentration. An aliquot of known concentration was placed in a vial and the volume was reduced to approximately 1 ml in a stream of nitrogen gas at room temperature. About 2 ml of iso-octane was added and mixed with a vortex mixer on low speed, and gently evaporated in a stream of nitrogen gas to about 1 ml. The iso-octane addition and evaporation step was repeated at least three times until the chloroform was completely displaced by iso-octane precipitating the asphaltene fraction of the oil out of solution. The asphaltenes were removed by filtration and the remaining solution (maltene fraction) was gently evaporated in a stream of nitrogen to about 1 ml in preparation for column chromatography.

For petroleum samples, about 50 milligrams of oil sample was mixed with about 2 milliliters (ml) iso-octane (1:40 weight/volume ratio) with a vortex mixer on low speed. The asphaltene fraction of the oil precipitated out of solution and was removed by filtration. The maltene fraction (prepared from both oil-stained rocks and from petroleum samples) was separated into saturated hydrocarbon, aromatic hydrocarbon, and resin fractions by column chromatography using alumina/silica columns and elution solvents of increasing polarity (iso-octane, benzene, and benzene-methanol). Elution solvents and light hydrocarbons (less than C₁₅) were removed from each fraction by evaporation using a nitrogen gas stream under a fume hood or a rotary vacuum evaporator.

Stable carbon isotope ratios were determined for the C_{15} + saturated and aromatic hydrocarbon fractions, and in a few cases, the entire oil sample. Two methods were utilized that are believed to have comparable results. Prior to 1997 all isotope measurements were determined by placing an aliquot of each sample in a quartz tube with cupric oxide and a silver strip. The tubes were sealed under a vacuum and combusted at 840° C for 4 hours. The evolved CO₂ was collected in a liquid nitrogen trap, and further purification and dehydration of the gas was accomplished by cryogenic distillation under vacuum. Carbon isotope ratios of the CO₂ were measured on a Finnigan MAT 251 dual-inlet isotope ratio mass spectrometer. During 1997 a change in instrumentation occurred and during the transition both old and new methods were used. After 1997 all samples were analyzed with a Carlo Erba elemental analyzer (EA) interfaced with a Micromass Optima continuous-flow isotope ratio mass spectrometer (IRMS). Sample aliquots were heated to approximately 1800°C in the EA quartz combustion tube filled with oxygen. The evolved CO₂ passed through chromium oxide (to complete oxidation), copper granules (reducing agent), and anhydrone (to remove water) before being swept into the IRMS with a helium carrier gas. The results are expressed in the delta (δ) notation that represents the deviation of the ${}^{13}C/{}^{12}C$ ratio in parts per thousand (per mil, or ‰) relative to the Peedee belemnite (PDB) standard.

Results and Discussion

Results of the stable carbon isotopic analyses (δ^{13} C) are listed on table 1 and shown on figure 2 along with a line proposed by Sofer (1984) that separates waxy oils from non-waxy oils. Waxy oils are usually derived from terrigenous organic matter, whereas non-waxy oils are usually derived from marine organic matter. Nearly all of the samples plot on the marine side of the Sofer line (figure 2). Polygonal boundaries that are roughly parallel to the Sofer line trend are placed around data groups (table 2). Unclassified samples are individually labeled on figure 2.

Classification of condensate samples into oil types using the δ^{13} C values of the C₁₅+ hydrocarbon fractions is problematic for two reasons. First, condensates are predominately composed of volatile hydrocarbons and the C₁₅+ fraction of the saturated and aromatic hydrocarbons constitutes only a small weight percentage of the total sample. Thus, the C₁₅+ stable carbon isotope values of condensates are not as representative as are the values for normal crude oil. Second, the saturate/aromatic hydrocarbon ratio is usually so high (greater than 10) that the C₁₅+ aromatic fraction weight is too small to measure the δ^{13} C value. In many cases, column chromatography was not performed and the isotope measurement was made on the C₁₅+ whole oil. In addition to these methodology problems, there is some question as to whether condensates should be compared with crude oils; that is, condensates are not crude oils but rather are the minor liquid fraction that condenses out of gas during natural gas production. For these reasons, the condensates are classified as separate groups.

Cretaceous (K) Oil Group

K1 Subgroup

The K1 samples were collected from the Wilbur Springs area east of Clear Lake and include several oil seeps and an oil sample from an exploratory well. Although the source is unknown, K1 oils are speculated to be derived from Cretaceous source rocks based on the age of the rocks in which the oil is found (Early Cretaceous). Furthermore, Peabody (1990) found that petroleum from the Wilbur Springs quicksilver district has a chemical composition compatible with the Tithonian to Valanginian Stony Creek Formation as their primary source. Magoon and others (1995, 1996) considered oil samples from the Arbuckle and Bunker gas fields (Oils 26-28, table 1) to be part of this group, but are here classified with K4 oils discussed below. The

McLaughlin Mine (Oil 103) and Rathbun (Oil 105) seeps are isotopically heavier than the other K1 seeps, possibly due to mixing of Miocene with Cretaceous sources.

K2 Subgroup

Many of the mercury deposits of the California Coast Ranges have small quantities of oil, solid bitumen, and hydrocarbon minerals that are genetically associated with the mercury ore (Bailey, 1959; Peabody, 1990, 1993; Peabody and Einaudi, 1992). The K2 samples are oils genetically associated with mercury deposits and have an isotopic composition similar to the other Cretaceous oils. However, three samples associated with mercury ore are isotopically distinct from the K2 subgroup: (1) the oil in vugs of the mercury ore from the Mirabel Mine (Oil 107), (2) the curtisite sample (a hydrocarbon mineral) from the Mirabel Mine (Oil 108), and (3) an oil-coated silica gel in mercury-bearing silica-carbonate rock from near the Helen mine (Oil 109).

K3 and K4 Subgroups

The K3 and K4 samples are liquid hydrocarbons produced from gas fields along the west side of the Sacramento basin. The K3 samples are clear to straw-yellow liquids with insufficient C_{15} + aromatic hydrocarbons to measure $\delta^{13}C$ values, whereas the K4 samples are yellow, red, and brown liquids and have measurable $\delta^{13}C$ aromatic hydrocarbon values. All of K3 and some of K4 samples are assumed to be condensates based on their light color, high saturated/aromatic hydrocarbon ratio (greater than 10) and their origin from gas fields. The K4 samples from Arbuckle, Bunker, and Winters gas fields have a darker color and lower saturated/aromatic hydrocarbon ratio (less than 8) and are reported to be oils; the Winters gas field has had minor oil production (California Division of Oil and Gas, 1983). The K3 and K4 samples are speculated to be derived from Cretaceous source rocks based on their intimate association with natural gas accumulations that, in turn, are believed to be derived from Cretaceous source rocks (Magoon and others, 1994). Although K4 and K1 samples have an association with gas production. Sherman Island (Oil 106) and Concord (Oil 101) gas field condensate samples are located in the same area (west side of Sacramento basin) as the K3 and K4 samples, but are isotopically distinct possibly due to mixing of Eocene and Cretaceous sources.

Eocene Oil Group

The Eocene oil group includes crude oil samples from three northern California oil fields: Brentwood, Livermore, and Oil Creek. Several oils analyzed from central and southern California fall into the Eocene group, including samples from Coalinga, North Antelope Hills, and Antelope Hills oil fields. These oils are believed to be derived from Eocene source rocks based on similar isotopic composition with other proposed Eocene oils in California (Sofer, 1984; Kornacki and McNeil, 1996) and based on oil-source rock correlation studies (Peters and others, 1994; Lillis and Stanley, 1999). The produced oil from Cymric field (Oil 102) is probably a mixture of Eocene and Miocene oils based on correlations of other Cymric oils to either Eocene or Miocene sources (Peters and others, 1994).

Miocene Oil Group

M1 Subgroup

The M1 oil group consists of four crude oils from the Half Moon Bay field, San Mateo County. Lillis and Stanley (1999) show that the source of these oils is the lower Miocene Lambert Shale, and that these oils are isotopically heavier than oils derived from middle and upper Miocene source rocks. Similarly, oils from lower Miocene source rocks in central

California are isotopically heavier than the middle and upper Miocene Monterey oils (Kornacki, 1988; Lillis, 1988; Lillis, 1994; Peters and others, 1994; Kornacki, 1996).

M2 Subgroup

The M2 oil group includes oil seeps and stains from Marin, Mendocino, Santa Cruz and San Mateo Counties and most of the northern California oil field samples including Petrolia, Petaluma, Pinole Point, La Honda, South La Honda and Sargent fields (table 1). Nearly all oils analyzed from central and southern California oil fields fall into the M2 group, including South Belridge, Edison, Hollister, King City, San Ardo, Kern Front, and portions of Antelope Hills. Magoon and others (1995) defined the Miocene oil group boundaries with saturated hydrocarbons being -22.9 \pm 0.6‰ and the aromatic hydrocarbons being -22.1 \pm 0.5‰ (figure 1). We redefine the boundaries as shown on figure 2 and listed in table 2. These oils are likely derived from middle and upper Miocene marine source rocks (mostly Monterey Formation but also including some other units) based on similar isotopic composition with other Miocene oils in California (Magoon and Isaacs, 1983; Sofer, 1984; Crain and others, 1985; Curiale and others, 1985; Orr, 1986; Zumberge, 1987; Kornacki, 1988; Lillis, 1988; Lundell and Gordon, 1988; Sofer, 1988; Jeffrey, and others, 1991; Lillis, 1994; Peters and others, 1994; Kornacki, 1996).

M3 Subgroup

Two condensate samples from the Tompkins Hill gas field are classified as a separate subgroup (M3) because of their distinct isotopic composition, although we consider them to be genetically related to the Petrolia oils (subgroup M2). We speculate that the Tompkins Hill condensate δ^{13} C saturated hydrocarbon values are lower (isotopically lighter) because the source rock has higher amounts of Miocene vascular plants and/or pre-Miocene organic matter. However, the δ^{13} C aromatic hydrocarbon values may be lower due to low sample weights. The composition of the oil from Table Bluff gas field (Oil 110) is suspiciously different from the Tompkins Hill condensates although both fields share the same stratigraphy and producing formation and are in close proximity (less than 5 miles). The Table Bluff sample was donated from the Chevron oil collection and we speculate that the sample may be mislabeled.

M4 Subgroup

The M4 samples are mudstones and sandstones with a kerosene odor (the so-called "stink muds") exposed in the sea cliffs in the False Cape and Bear River areas of Humboldt County. Gas chromatography and δ^{13} C hydrocarbon data suggest that these oils are genetically related to the Tompkins Hill (M3) and Petrolia oils (M2). However, most of these samples plot farther from the Sofer line than the other Miocene oils. This shift is possibly due to low aromatic hydrocarbon sample weights that may yield lower the δ^{13} C aromatic hydrocarbon values. Because these "stink muds" are an unusual sample type and have slightly different isotopic characteristics, they are excluded from the Miocene boundary box. Sample 104 is compositionally distinct from all other oil-stained rocks collected in Humboldt County (M4 oils), and may be derived from sources older than Miocene.

Conclusions

Naturally occurring petroleum in northern California can be classified into Cretaceous, Eocene, or Miocene oil groups based on δ^{13} C hydrocarbon composition. Cretaceous subgroups include oil seeps from the Wilbur Springs area (K1), oil associated with mercury deposits (K2), and condensates and oils associated with natural gas production (K3 and K4). Miocene subgroups include lower Miocene oils (M1), middle and upper Miocene oils (M2), Tompkins Hill condensate (M3), and Humboldt County oil seeps (M4).

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Table 1. Stable carbon isotope composition of crude oils, oil seeps and oil-stained rocks from northern and central California

1	\$1¢		Sample Identification	API Number	Comments ^a	Latitude	Longitude	SecTwnRng	County	Deput or Ellev	Producing Formation/Zone	Formation Age	Sats*			Sample Donator	Information Source
		seep - Culver Ranch seep - Gibson Gusher	Culver Ranch AJ-0997 Gibson Gusher 2		Heavily biodegraded. Heavily biodegraded.	39.05149 39.05231	-122.40040 -122.41023	22-14N-5W 21-14N-5W	Colusa Colusa		Knowille	Lower Cretaceous Lower Cretaceous	-25.85 -26.31	-24.87 -24.57		Elison & Mackevett Reynolds, Sarge	LL-5 LL-5. Fm-7. Age-7
	3 1	seep - Gibson Gusher	Gibson Gusher AJ-0996		Severely biodegraded.	39.05231	-122.41023	21-14N-5W	Colusa		Knowile	Lower Cretaceous	-26.31	-24.57		Elison & Mackevett	LL-5, Fm-7, Age-7 LL-5, Fm-7, Age-7
		seep - Salt Creek	Salt Creek AJ-0999		Heavily biodegraded.	39.10261	-122.33649	31-15N-4W	Colusa			Upper Cretaceous		-26.05		Elison & Mackevett	LL-5
		seep - Thompson	Thompson Seep AJ-0995		Heavily biodegraded.	39.15731	-122.34898	7-15N-4W	Colusa				-26.47	-25.56		Elison & Mackevett	LL-5
		seep - Thompson wildcat well	Thompson Seep 2 Amalgamated 1	04011002530000	Heavily biodegraded. Drill stem test. Aromatics degraded.	39.15731 39.03119	-122.34898 -122.40415	7-15N-4W 27-14N-5W	Colusa Colusa		Knowile	Lower Cretaceous	-26.62 -26.96	-25.64 -25.78		Reynolds, Sarge Reynolds, Sarge	LL-5 LL-2
	63	widcat well	Amalgamated 1 Amalgamated AJ-0998	04011002530000	Drill stem test. Aromatics degraded. Drill stem test. Aromatics degraded.	39.03119	-122.40415	27-14N-5W 27-14N-5W	Colusa		Knowle	Lower Cretaceous	-26.95	-25.78		Elison & Mackevett	LL-2 LL-2
	0 I	seep - Abbott Mine	Abbott Seep	04011002530000	Severely biodegraded.	39.03119	-122.40415	32-14N-5W	Lake		Knowine	Lower Cretaceous	-26.81	-25.24		Reynolds, Sarge	LL-2 LL-5
	10 1	stain - Contact mine	Contact mine		Oil extract from silica carbonate Hg ore.	38,75917	-122.76333	5-10N-8W	Sonoma	Elev. 2920			.27.21	-24.22		Lillis & others (USGS)	11.5
2		stain - Culver Baer mine	Culver Baer mine		Oil-filled vugs in silica carbonate Hg ore.	38.78069	-122.81883	24-11N-9W	Sonoma				-26.70	-24.02		Lillis & others (USGS)	LL-5
2 .	12 :	stain - Helen mine stain - New Almaden Mine	Helen mine New Almaden Mine		Oil extract in silica carbonate Hg ore. Oil extract from mecury mine ore.	38.74111 37.18083	-122.69944 -121.84389	1-10N-8W 3-9S-1E	Lake Santa Clara	Elev. 2640	Franciscan	Jurassic-Cretaceous	-26.22 -26.58	nd -24.34		Lillis & others (USGS) 0 Stanley, Rick (USGS)	LL-5 LL-5
		stain - New Almaden Mine Dutch Slough (Bethel Island)	New Almaden Mine TransAmer, Development 3	04013001000101		37.18083	-121.84389 -121.64919	3-98-1E 21,2N-3E	Contra Costa	7520,7580	Franciscan Martinez/First Massive sand	Jurassic-Cretaceous Paleocene	-26.58			5 Reed, Gary (Amer.Expl.Co)	11.2
		Knightsen	Cecchini 1-32. RD 2		Condensate. Deep pool S. of Dutch Slough field.	37.97117	-121.67057	32-2N-3E	Contra Costa	8767-8873	Mokelumne River/3rd Massive	Upper Cretaceous	nd	nd -	26.76	Hector, Scott (Baker Oil & Gas)	LL-2
	16 1	Lindsey Slough	Kroutch 16-1	04095209310000	Condensate.	38.18652	-121.75010	16-4N-2E	Solano	5738-5752	Capay/Margaret Hamilton sand	Eccene	nd		26.29	Hector, Scott (Baker Oil & Gas)	LL4
		Maine Prairie	Liberty Farms 1	04095201290000	Condensate.	38.29078	-121.71157	11-5N-2E 27.6N-2E	Solano	6163-6165	H&T send	Upper Cretaceous	-27.00	nd		Chevron	LL-2, STR-2
		Maine Prairie Pleasant Creek	WZU 3 (Edward Wineman 2) Shell-Pleasant Creek Unit 5-1	04095001560001	Condensate. Moderately degraded. Condensate. Moderately degraded.	38.33738 38.54603	-121.73071 -122.00356	27-6N-2E 17-8N-1W	Solano Yolo	4755-4795	Basal Capay	Eccene	-25.76 -25.28	nd		Chevron	LL-2, API-2, STR-2 LL-2, API-2, STR-2, SmID 2
		Rio Vista (East Midland)	RVGU 12	04067000490000	Moderately degraded condensate. Formerly Brannon Island 3.	38.14835	-122.00356	33-4N-3E	Sacramento	4450-4495	Mokelumne River/Midland sand	Linner Cretanenus	-20-20 nd		25.90 .25.3	8 Amerada Hess	LL-2, API-2, STR-2, SHID 2 LL-2
3 3	21 I	Rio Vista (East Midland)	RVGU 137	04067000640000	Condensate, Well formerly Kuhn Community 3.	38.12064	-121.66852	8-3N-3E	Sacramento	5290-5390	Capav/Margaret Hamilton sand	Eccene	nd	nd	26.27 -26.0	7 Amerada Hess	LL-2
		Rio Vista (West Midland)	RVGU 158 (2 Twitchell Fee)		Condensate. Mildly degraded.	38.10930	-121.66224	17-3N-3E	Sacramento	5049-5115	Capay/Margaret Hamilton sand	Eccene	-26.30	nd		Amerada Hess	LL-2
		Rio Vista (West Midland)	Trigueiro 4	04095208620000		38.16744	-121.70349	25-4N-2E	Solano	9562-9638	Mokelumne Rivet/Peterson	Upper Cretaceous	nd		28.07 -28.0	2 Amerada Hess	LL-1
	24	Suisun Bay W. Thornton-Walnut Grove	Suisun Community 7 Maherto 1	04095004080000	Condensate.	38.13972 38.22059	-121.99284	5-3N-1W	Solano Sacramento	4405-4470	Domengine	Eccene	-26.07	nd nd		Chevron	LL-2, API-2, STR-2 LL-2, API-2, STR-2, Field-3
		W. Thormon-Warnut Grove Arbuckle	Maberto 1 Marsh 1		Condensate. Heavily biodegraded oil from gas field.	38.22059 39.00498	-121.44265	4-4N-5E 4-13N-2W	Colusa	6363-6381	Forbes/ F Zone sand	Cretaceous		-25.96		Revnolds, Sarge	LL-2, API-2, STR-2, Field-3 LL-2
		Bunker	O'Keele 1	04095205810100	Midly degraded oil from gas field.	38.36390	-121.78449	17-6N-2E	Solano	6702-6718	Molelumne River	Upper Cretaceous	-26.59	-25.13		Boyd, Richard (Capitol Oil)	LL-2
4 3	28 1	Bunker	O'Keele 1	04095205810000	Mildly degraded oil from gas field.	38.36390	-121.78449	17-6N-2E	Solano	6700-6730	Mokelumne Rivet/Lower sand	Upper Cretaceous	-26.61	-25.29		MacKevett, Nat	LL-2
	29 1	Kirby Hill	Wagenet 2	04095000780000	Condensate.	38.16997	-121.91100	19-4N-1E	Solano	5398-5650	Martinez	Paleocene	-26.57	-25.42		Chevron	LL-2, STR-2
4 3		Ryer Island Winters	Ryar 3 McCune 1	04095200300000	Condensate. Mildly degraded.	38.07681 38.49065	-122.01122 -121.88715	30-3N-1W 32-8N-1E	Solano Solano	4300-5000 5576-5585	Nortonville/Domengine Winters/McCune?	Eccene	-26.55 -26.73	-24.53 -25.14		Haglund, Dave (Shell) Haglund, Dave (Shell)	LL-2 LL-2
4		Winters	McCune 1 McCune 1	04035207160000	Condensate(?) Midly degraded. Condensate(?) Midly degraded.	38,49065	-121.88715 -121.88715	32-8N-1E 32-8N-1E	Solano	5576-5585 5600-5600	Winters/McCune? Winters	Upper Cretaceous		-25.14		Haglund, Dave (Shell) Chevron	LL-2 11-2
		Winters	Winters Unit 4-1 (?)	04095004910000	Condensate, Well ID uncertain, Moderately degraded.	38.53123	-121.89718	19-8N-1E	Solano	4845-4885	Winters/McCune sand	Upper Cretaceous	-26.44	-27.12		Chevron	SampID-4, LL-2, API-2, STR-2,
	34	Antelope Hills	Hopkins A 56X	04029134410000	Moderately biodegraded.	35.53185	-119.85739	31-27S-20E	Kern	2045-2132	Point of Rocks sandstone	Upper Eccene	-29.20	-28.93		MacKevett, Nat	шл
	35	Antelope Hills Antelope Hills North	Hopkins A 62X Fussel Fee 2.14	04029134430000	Moderately biodegraded	35.53974	-119.85468	31-27S-20E	Kern	2412-2429	Phacoides sand Phacoides sand	Lower Miccene	-29.06	-28.14		MacKevett, Nat MacKevett, Nat	11.4 11.4
		Antelope Hills, North Brentwood (East area)		04030015870000 04013000750202	Moderately biodegraded.	35.57393 37.93694	-119.90219 -121.74488	14-278-19E 15-1N-2E	Kern Contra Costa	1560-1636 4100-4200	Phacoides sand Mokelumne River/3rd Massive	Lower Miocene Upper Cretaceous	-28.43 -29.40	-27.75		MacKevett, Nat Reed, Gary (Amer.Expl.Co)	LL-1 LL-2
	38 1	Brentwood (East area) Coalinga	Ginochio 1 Fee 122-13D		Heavily biodegraded. Mixed light saturated hydrocarbons.	37.93694 36.18475	-121.74488 -120.39792		Eresno	+100-4200	Temblor sand	Mocene		-27.46		Peters, Ken (Chevron)	LL-2 LL-2
	39 1	Livermore	Nissen 3	04001200120000	Mildly biodegraded.	37.69359	-121.68289	7-38-3E	Alameda	1410-1420	Cierbo/Greenville sand	Upper Miccene	-28.37	-27.20		Reed, Gary (Amer.Expl.Co)	LL-2
Ε.	40 I	Livermore	Schenone 1	04001200440000	Mildly biodegraded.	37.69519	-121.68423	6-3S-3E	Alameda	1500-1510	Cierbo/Greenville sand	Upper Miccene	-28.34	-27.21		Reed, Gary (Amer.Expl.Co)	LL-2
	41 (Oil Creek	Costa 7-A	04081200200000		37.23927	-122.16484	14-8S-3W	San Mateo	1940-2040	Butano/Costa	Eccene		-27.51		Haglund, Dave (Shell)	LL-2
	42 I 43 I	Half Moon Bay (Verde) Half Moon Bay (Verde)	Cowell 1 (Wilshire) Cowell Estate 3 (Zia Oli Corp.)		Deepest well in field - TD 7982 ft. Operator now Midcoast Oil LTD, Partnership.	37.39722 37.39650	-122.40471 -122.40228	21-6S-5W 22-6S-5W	San Mateo San Mateo	1373-2724 1732-2242	Purisima Purisima	Pliccene Pliccene		-21.60 -21.35		Chevron	LL-2, API-2, DE-3, Fm-3, Age-3 SampID-4, LL-API-2, DE-3, Fm-
		Half Moon Bay (Verde) Half Moon Bay (Verde)	DeBenedetti 1	04081200430000	Operator now Midcoast Oil LTD. Partnership.	37.39650	-122.40228	22-68-5W 21-68-5W	San Mateo San Mateo	1/32-2242	Purisima	Pliccene	-22.25	-21.35		Chevron	SampiD-4, LL-API-2, DE-3, Fm- LL-2, DE-3, Fm-3, Age-3
		Half Moon Bay area	Cowell 1 (Mid-St Consolidated)	04081000900000	Northwest of Verde producing area of field.	37.42199	-122.43236	8-6S-5W	San Mateo					-21.10		Chevron	SampID-4, LL-API-2, STR-2
2 4	46	Antelope Hills	Phippen 18	04029618790000	Moderately biodegraded.	35.51158	-119.84815	8-28S-20E	Kern	2295-2460	Button Bed (IB) sand	Middle Miccene	-22.99	-22.34		MacKevett, Nat	LL-1
		Belridge, South	Sec 13 88-A	04029297650000	Moderately biodegraded.	35.48505	-119.76203	13-28S-20E	Kern	0-1500	Etchegoin/Gusher	Pliocene		-22.22		Peters, Ken (Chevron)	Field-2, LL-1, API-1
12 4	48 1	Edison Half Moon Bay (Purisima Ck.)	Ryan Brown 4B	04029065460000	Heavily biodegraded.	35.37200 37.41511	-118.86729 -122.39804	28-29S-29E 15-6S-5W	Kern San Mateo	710	Chanac Purisima	Pliccene Pliccene		-22.73		Peters, Ken (Chevron)	LL-1, API-1
		Half Moon Bay (Pursima Ck.) Hollister- Flint Hills area	Layne 2 (John Tedesco) Justo 1		Petrolex Inc operator.	37.41511 36.86477	-122.39804	15-68-5W 28-128-5E	San Mateo San Benito	/10	Etchegoin (?)	Pliccene Pliccene (?)	-23.67	-23.08		Haglund, Dave (Shell) Chevron	Field-2, LL-2, API-2, STR-2, Fm-
		Kern Front	Fee 10-11	04029106620000	Heavily biodegraded.	35 45659	-119.04887	27.285.27F	Kern		Chanac	Pliocene	-23.37	-22.52		Peters, Ken (Chevron)	LL-1, API-1
12 5	52 I	King City	BCB Doud 4-32	04053009970000	Heavily biodegraded.	36.15286	-121.12717	32-20S-8E	Monterey	2000	Monterey/Thorup zone	Miocene	-22.99	-22.43		Abel, Pat (CDOGG)	LL-2
		La Honda	Lane Union Oil 4		Well name formerly Neaves Union Lane 4.	37.32188	-122.31536	17-78-4W	San Mateo	1800-2277	Butano/Costa	Eccene	-23.14	-22.19		Chevron	SampID-2, LL-2, DE-3, Fm-3, Ap
		La Honda, South	Neaves Union Burns 8	04081000610000	Moderately biodegraded. Producing formation is informal name.	37.30524	-122.29546	21-78-4W 21-78-4W	San Mateo	1358-1468	Burns sand	Lower Miccene		-21.86		Haglund, Dave (Shell)	LL-2, Age-7
		La Honda, South Petaluma	Neaves-Burns took bottoou oil in NE1/4 of roo 30.	04007000080000	Well # unknown, location center of sec 21. Heavily biodegraded. Specific well unknown use Petakima Community 5/2 location	37.3076	-122.3042 -122.55575	21-78-4W 30-5N-6W	San Mateo Soooma	920 avn	Burns sand (?) Petaluma	Lower Miocene (?) Plincene	-22.84	-22.49		Chevron Magoon Les (USGS)	Field-4, LL-5, Fm-3
		Petrolia	Hidden Valley 1	04023200270000		40.37421	-122.00075	21-18-2W	Humboldt	1185-1363	Franciscan		-23.51	-22.56		McLaughlin, Robert (USGS)	LL-2 LL-6
12		Petrolia	Hidden Valley 1	04023200270000	Well shut in.	40.37421	-124.29039	21-1S-2W	Humboldt	1185-1363	Franciscan	Eccene to Cretaceous	-23.30	-23.31		Lillis & others (USGS)	LL-6
		Petrolia	Shelby Woods 1	04023000970000	Well shut in.	40.37369	-124.28996	21-1S-2W	Humboldt	700-1394	Franciscan			-23.28		Lillis & others (USGS)	LL-6
12 1		Petrolia Petrolia	Shelby Woods 1 Whitchurch 1A	04023000970000	Chevron sample collection. Sample 1 of 3. Well shut in.	40.37369 40.37596	-124.28996 -124.28962	21-18-2W 16-18-2W	Humboldt	1365-1394	Franciscan	Eccene to Cretaceous Eccene to Cretaceous	-23.31	-23.19 -23.18		Chevron Lillis & others (USGS)	SampID-4, LL-6, Fm-7, Age-7 LL-6
12 1	62 1	Petrolia	Whitchurch 1A	04023200650000	Sample 3 of 3. Well shut in.	40.37596	-124.28962	16-15-2W	Humboldt	726-760 726-760	Franciscan Franciscan		-23.37	-23.10		Lillis & others (USGS)	11.6
12 1		Pinole Point	Bethlehem 1	04013200430000		37,99988	-122.34032	19-2N-4W	Contra Costa	6400	Neroly fower zone	Upper Miccene	-22.36	-21.53		Terlesco Larry (Chevron)	LL-2
		San Ardo	Alexander 23	04053206600000	Heavily biodegraded.	35.94882	-120.81090	8-23S-11E	Monterey		Monterey/Aurignac sand	Miocene	-23.38	-22.74		Abel, Pat (CDOGG)	LL-2
		San Ardo	Hambey 46-18		Heavily biodegraded.	35.93439	-120.82957	18-23S-11E	Monterey	2300	Monterey/Lombardi sand	Miocene	-23.40	-22.21		Abel, Pat (CDOGG)	LL-2
12 1	66 1 67 1	Sargent Sargent	10 (no lease name)	04085000370000	Moderately biodegraded. Well formerly named McMillan M-1, Heavily biodegraded.	36.93113 36.92974	-121.58987 -121.58528	36-11S-3E 36-11S-3E	Santa Clara Santa Clara		Etchegoin (?) Etchegoin (?)	Pliccene (?) Pliccene (?)	-24.26 -24.52	-23.57 -23.93		Chevron	LL-2, API-2, Fm-7, Age-7
		Sargent	tank battery oil	04085200330000	Moderately biodegraded. Specific well known, use Sargent #2.	36.92974	-121.58663	36-118-3E	Santa Clara	600 avg	Etchegoin (?)	Pliccene (?)	-24.52	-23.93		Abel. Pat (CDOGG)	LL-2, SampID-7, DE-7, Fm-7, Age-
	69 :	seep - Tarwater Creek	Tarwater Creek Seep	04003200300000	Severely biodegraded.	37.26823	-122.23937	6-8S-3W	San Mateo		Purisima	Pliccene		-21.88		Magoon & Lorenson (USGS)	LL-5, Fm-8, Age-8
12 3	70 :	stain - Majors Creek	Majors Creek		Oil-stained sandstone. Severely biodegraded.	36.98278	-122.14216	12-11S-3W	Santa Cruz	Elev. 160	Santa Cruz Mudstone	Mocene		-22.10		Lillis, Paul (USGS)	LL-5
12 3	71 :	stain - Majors Creek area	98SM-1 Point Quarry		Bituminous sandstone. Projected SecTwnRng.	37.00681	-122.10889	6-11S-2W	Santa Cruz	Elev. 880	Santa Cruz Mudstone	Miocene		-22.05		Stanley, Rick (USGS)	LL-5
12 1		stain - Majors Creek area stain - Majors Creek area	985M-2 Point Quarry 985M-3 Coast Road		Asphalt in fractured mudstone. Projected SecTwnRng. Asphalt in fractured dolomite concretion. Projected SecTwnRng.	37.00681	-122.10889 -122.14750	6-11S-2W	Santa Cruz Santa Cruz	Elev. 880 Elev. 120	Santa Cruz Mudstone Santa Cruz Mudstone	Miccene Miccene	-23.05 -22.91	-22.06 -22.69		Stanley, Rick (USGS) Stanley, Rick (USGS)	LL-5 LL-5
12 1		stain - Majors Creek area stain - Majors Creek area	98SM-3 Coast Road 98SM-4 Back Ranch Rd		Asphalt in fractured dolomite concretion. Projected SecTwnRng. Bituminous sandstone. Projected SecTwnRng.	36.98417 36.99042	-122.14750 -122.13722	11-11S-3W 12-11S-3W	Santa Cruz Santa Cruz	Elev. 120 Elev. 520	Santa Cruz Mudstone Santa Cruz Mudstone	Miccene Miccene		-22.69		Stanley, Rick (USGS) Stanley, Rick (USGS)	LL-5
12 3	75 :	stain - Majors Creek area	98SM-5 Hwy 1/Back Ranch Rd		Bituminous sandstone. Projected SecTwnRng.	36.98292	-122.14222	12-11S-3W	Santa Cruz	Elev. 160	Santa Cruz Mudstone	Mocene	-22.85	-22.10		Stanley, Rick (USGS)	LL-5
12 1	76 :	stain - Yellow Bank Creek	985M-6 Yellow Bank Creek		OIP-stained sandstone. Projected SecTwnRng.	36.99139	-122.16806	10-11S-3W	Santa Cruz	Elev. 20	Santa Cruz Mudstone	Miocene	-24.01	-23.26		Stanley, Rick (USGS)	LL-5
		stain - Point Arena	Point Arena Cove		Oil-stained sandstone. Severely biodegraded.	38.91639	-123.71139	11-12N-17W	Mendocino	Elev. 25	Point Arena Formation	Mocene	-23.40	-22.70		Stanley, Rick (USGS)	LL-5
		stain - Point Montara stain - Pt Reyes	CS -1 PR-1 Palomarin Beach		Oll-stained sandstone. Severely biodegraded. Sandstone dike, 7cm, visible oil, strong HC odor.	37.53733 37.92638	-122.51767 -122.73667	33-4S-6W ##-1N-8W	San Mateo Marin	Elev. 25	marine terrace Santa Cruz Mudstone	Pleistocene Miocene	-21.35 -22.54	-20.57 -22.37		Stevens, Cal (San Jose State) Stanley, Rick (USGS)	LL-5
	/3/ 1 80 -	stain - Pt Reyes stain - Pt Reyes	PR-1 Palomarin Beach PR-2 Palomarin Beach		Sandstone dike, 7cm, visible oil, strong HC odor. Sandstone dike, 18in , visible oil.	37.92638	-122.73667 -122.73750	##-1N-8W ##-1N-8W	Marin Marin	Elev. 20 Elev. 20	Santa Cruz Mudstone Santa Cruz Mudstone	Mocene Mocene		-22.37		Stanley, Rick (USGS) Stanley, Rick (USGS)	LL-6 LL-6
12 1	81 :	stain - Pt Reyes	PR-3 Palomarin Beach		Thin ""hraided" sandstone dike visible	37.92694	-122.73806	##-1N-8W	Marin	Elev. 20	Santa Cruz Mudstone	Mocene	-22.55	-22.29		Stanley, Rick (USGS)	LL-6
12 1	82 :	stain - Pt Reyes	PR-4 Palomarin Beach		Sandstone dike, visible oil, HC odor.	37.92917	-122.74167	##-1N-8W	Marin	Elev. 20	Santa Cruz Mudstone	Mocene	-22.72	-22.20		Stanley, Rick (USGS)	LL-6
		stain - Pt Reyes	PR-6 Wildcat Beach		Sandstone sill or bed, visible oil, HC odor.	37.95278	-122.78236	##-1N-8W	Marin	Elev. 20	Santa Cruz Mudstone	Mocene	-23.17	-22.50		Stanley, Rick (USGS)	LL-6
12 1	84 : or	stain - Pt Reyes stain - Pt Reyes	PR-7 Wildcat Beach PR-8 Wildcat Beach		Sandstone sill or bed, visible oil, HC odor. Sandstone sill or bed, visible oil, HC odor.	37.95569	-122.78319 -122.78403	##-1N-8W ##-1N-8W	Marin Marin	Elev. 20 Elev. 20	Santa Cruz Mudstone Santa Cruz Mudstone	Mocene Mocene	-23.08	-22.41		Stanley, Rick (USGS) Stanley, Rick (USGS)	LL-6
12 1	60 1 86 4	stain - Pt Reyes stain - Pt Reyes	PR-8 Wildcat Beach PR-9 Wildcat Beach		Sandstone sill or bed, visible oil, HC odor. Sandstone sill or bed with visible oil.	37.95778 37.96125	-122.78403 -122.78625	##-1N-8W ##-1N-8W	Marin Marin	Elev. 20 Elev. 20	Santa Cruz Mudstone Santa Cruz Mudstone	Mocene Miocene	-22.90 -22.93	-22.52		Stanley, Rick (USGS) Stanley, Rick (USGS)	LL-6 LL-6
12 1	87 :	stain - Pt Reyes	PR-27 Wildcat Beach		Sandstone, oil-stained.	37.97500	-122.79500	36-2N-9W	Marin	Elev. 20	Monterey Formation	Miocene	-23.15	-22.37		Lillis & Stanley (USGS)	LL-5
12 1	88 1	unnamed field	Dr. Peck's well		Production from Dr. Peck's well.Heavily biodegraded.	37.24514	-121.95832	10-8S-1W	Santa Clara	125(?)	Monterey (?)	Mocene	-23.65	-23.14	-23.3	2 Stanley, Rick (USGS)	LL-5
12 1	89 1	wildcat well	Etter 1	04023000540000		40.24844	-124.13554	36-2S-1W	Humboldt	1800-1900	Franciscan (?)	Eccene to Cretaceous	-23.30	-22.87		Chevron	LL-2, Fm-7, Age-7
		wildcat well Tomokios Hill	Pearson USL 1-B Holmes Fureka 16		Indian Valley area east of San Ardo field. Conferente Arromatic data questionable	36.04636	-120.63676 -124.16260	1-228-12E 22-3N-1W	Monterey Humboldt	1982-1997 3908-4422	Rin Dell	Middle Pliocene	-23.82	-23.11		Chevron Hanlund Dave (Shell)	LL-2 11-2
		Tompkins Hill Tompkins Hill	Holmes Eureka 16 tank battery oli	04023000450000	Condensate. Aromatic data questionable. Condensate, specific well unknown, use sec22 location.	40.63436 40.63	-124.16260 -124.16	22-3N-1W 22-3N-1W	Humboldt	3:308-4422	NO Del	Model Miccene	-24.06 -24.28	-24.37		Haglund, Dave (Shell) Lorenson, Thomas (USGS)	LL-2 LL-2
й <u>з</u>		seep - Bear River	97PGL-22		Sandstone, oil stained, HC odor.	40.63	-124.40306	22-1N-3W	Humboldt	Elev. 20			-24.06	-24.51		Lillis & others (USGS)	LL-2 LL-6
14 3	94 :	seep - Bear River	97PGL-23		Fractured rock, 2 oil stains/seeps about 6 ft apart.	40.44667	-124.40472	27-1N-3W	Humboldt	Elev. 20			-24.76	-23.24		Lillis & others (USGS)	LL-6
		seep - False Cape	97PGL-10		Limestone, Oil stained vugs, HC odor.	40.50361	-124.38583	3-1N-3W	Humboldt	Elev. 20			-22.36	-22.87		Lillis & others (USGS)	LL-6
		seep - False Cape	97PGL-7		Sandstone, HC odor.	40.51556	-124.38250	35-2N-3W	Humboldt	Elev. 20				-23.42		Lillis & others (USGS)	LL-6
	97 :	seep - False Cape seep - False Cape	97PGL-3 97PGL-4		Mudstone, HC odor. Sandstone, w oil stained veins, HC odor.	40.52444 40.52144	-124.37611 -124.37909	26-2N-3W 26-2N-3W	Humboldt Humboldt	Elev. 20 Elev. 20			-24.10 -23.41	-26.05		Lillis & others (USGS) Lillis & others (USGS)	LL-6 LL-6
<u> </u>		seep - False Cape seep - False Cape	97PGL-4 97PGL-5		Sandstone, w oil stained veins, HC odor. Sandstone, HC odor.	40.52144 40.51922	-124.3/909 -124.38149	26-2N-3W 26-2N-3W	Humboldt	Elev. 20 Elev. 20			-23.41	-24.44		Lilis & others (USGS) Lilis & others (USGS)	LL-6
14 1 14 1		seep - False Cape seep - False Cape	97PGL-6		Sandstone, HC odor.	40.51922	-124.38149	35-2N-3W	Humboldt	Elev. 20 Elev. 20				-24.25		Lillis & others (USGS)	LL-6
Č i	01 0	Concord	Boylan 1	04013000900000		38.00334	-122.02547	24-2N-2W	Contra Costa	2936-3044	F1 zone	Upper Cretaceous	-28.13	-26.00		Chevron	LL-2
C 1	02 0	Cymric	Sauer Dough 25	04029746080000		35.38320	-119.68833	23-29S-21E	Kern		Phacoides sand	Miocene	-25.26	-24.07		Peters, Ken (Chevron)	LL4
		seep - McLaughlin Mine	McLaughlin Gold Mine		Heavily biodegraded. Located in NE NE of sec 1.	38.83556	-122.35974	1-11N-5W	Napa	Elev. 1590	volcanic rock - brecciated zone	Pleistocene		-23.91		Enderlin, Dean (Homestake Mine)	
		seep - Oil Creek north	97PGL-2		Sandstone, black, HC odor.	40.52528	-124.37556	26-2N-3W	Humboldt	Elev. 20		1 C	-27.91	-26.82		Lillis & others (USGS)	LL-6
		seep - Rathbun Sherman Island	Rathbun AJ-1000 Signal-Upham 1	04067002560000	Severely biodegraded.	39.01970 38.07804	-122.37758 -121.72989	35-14N-5W 27-3N-2E	Colusa Sacramento	6300	Martinez/Anderson	Lower Cretaceous	-25.18 -28.22	-24.07 -25.56		Elison & Mackevett Haglund, Dave (Shell)	LL-5
2 1	105	Sherman Island stain - Mirabel mine	Signal-Upham 1 Mirabel mine	04067002560000	Condensate. Oli-filled yugs in silica carbonate Hg ore.	38.07804 38.69917	-121.72989 -122.59611	27-3N-2E 23-10N-7W	Sacramento	6300 Elev. 1360	martini/2/Anderson	managoene	-28.22 -24.50			Haglund, Dave (Shell) Lillis & others (USGS)	LL-2 LL-5
: 1	108	stain - Mirabel mine stain - Mirabel mine	Mrabel mine Mrabel mine curtisite		Cultisite - hydrocarbon mineral.	38.69917	-122.59611	23-10N-7W 23-10N-7W	Lake	Elev. 1360 Elev. 1360			-24.50 nd	-23.17 nd	-23 1	3 Lillis & others (USGS)	LL-5 LL-5
		stain - near Helen mine	unnamed mine "Paul's mine"		Oil-coated nel in silica carbonate Hn ore	38 73944	-122.69778	1-10N-8W	Lake	Elev. 2640			-25.10	.25 59	2.0.1	Lillis & others (USGS)	LL-5
c 1	09 :	stain - near Helen mine															
C 1	10	stain - near Helen mine Table Bluff (?) water well	Leon-Oro-Blanco T-1 (?) Granny Creek H2O	04023000190000	Questionable sample identification. Near confluence w/ Mattole River, Possible distillate.	40.66742 40.26229	-124.21832 -124.19300	6-3N-1W 28-2S-1W	Humboldt	4800-4810			-25.74 -27.30	-24.84		Chevron Lillis & Lorenson (USGS)	LL-2

a Comments by writton. Biodegradation interpretation based on unpublished gas chromatography data: Mid – aduras concentration law or not detected Modularia asguid, propendity & earphicity photometry photometry photometry and biological asguid and assumed as a strategical asguid asguid asguid asguid asguid asguid Biological asguid write as based on MOZ 2 datam. 4 Production Depth or Outcog Execution I had. 5 Production Depth or Outcog Execution I had. 5 Production Depth or Outcog Execution I had. 1 Production Depth or Outcog Execution I had.

Data Type LL = laftude and longitude API = API Number DE = Depth Elevation Fm = Producing Formation.Zone Age = Formation.Age SampID = Sample Identification STR = SecTwnRng

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Table 2. Stable carbon isotope boundaries of petroleum types from northern and centralCalifornia. Values refer to corners of boxes shown on figure 2.

Boundary for Cretaceous	-25.70 -24.90
	-26.80 -23.70
	-27.90 -24.90
	-27.00 -26.40
Boundary for Eocene	-27.70 -27.47
	-28.60 -26.46
	-30.00 -28.00
	-29.20 -29.12
Boundary for Miocene	-21.20 -20.60
	-22.00 -20.00
	-24.80 -24.00
	-24.30 -24.70

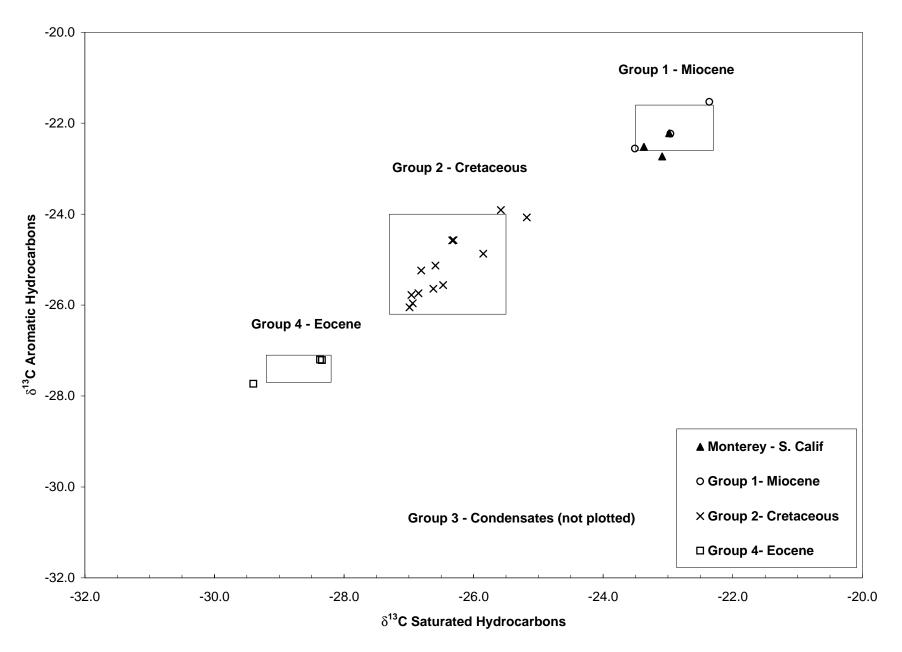


Figure 1. Hydrocarbon types in northern California (after Magoon and others, 1995)

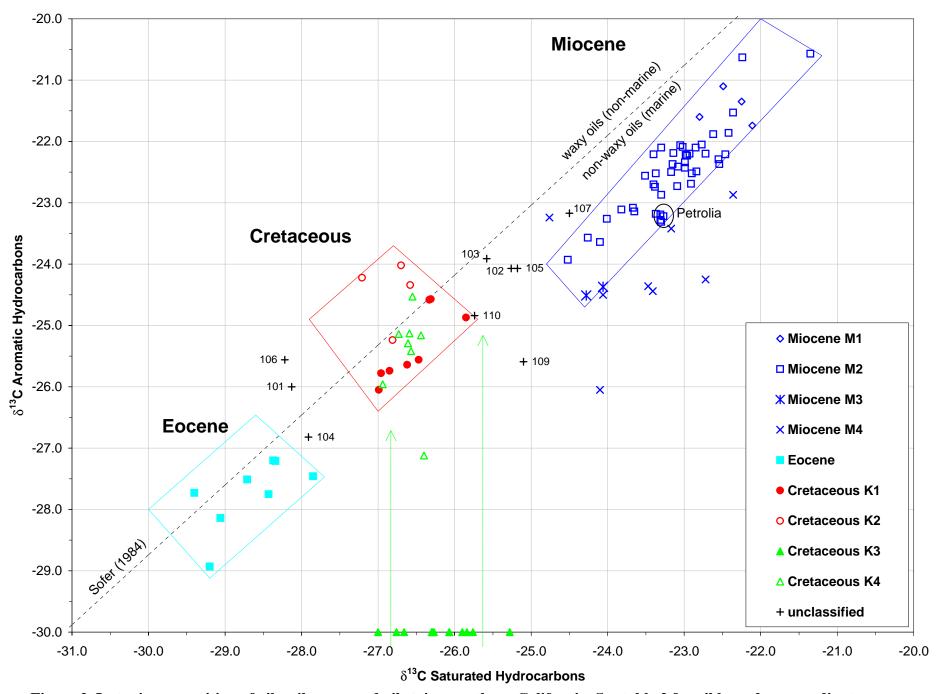


Figure 2. Isotopic composition of oils, oil seeps, and oil stains, northern California. See table 2 for oil boundary coordinates.