

Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks

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Abstract—Amorphous kerogens from Phanerozoic sedimentary rocks may be divided into two groups on the basis of their $\delta^{13}\text{C}$ values. *h*-amorphous kerogens have isotopic values in the range of -24 to -20 per mil, and *l*-amorphous kerogens have isotopic values in the range of -35 to -26 per mil. The occurrence of amorphous kerogens in the intermediate isotopic range from one rock unit in the data set suggests a weak continuum may exist between these two groups. Phytoplankton and, to a lesser extent, zooplankton and bacteria are considered to be the precursors for both kerogen types. A plausible explanation for this dichotomy may be found in the source of CO_2 utilized by phytoplankton, which is considered to be controlled by environmental factors. *h*-amorphous kerogens are expected to occur in silled basins that are overlain by expansive well-circulated deep (>500 m) water, where the prevailing source of carbon in the photic zone is atmospheric-derived CO_2 . Conversely, *l*-amorphous kerogens are expected to occur in restricted basins that are overlain by stratified shallow (<200 m) water, where the prevailing source of carbon in the photic zone may be organic-derived CO_2 .

INTRODUCTION

STRUCTURELESS MASSES of insoluble sedimentary organic matter in sedimentary rocks are referred to as amorphous kerogen (STAPLIN, 1969; BURGESS, 1974). In spite of its common occurrence and importance as a source of petroleum, the origin of this kerogen type is poorly understood. Phytoplankton and, to a lesser extent, zooplankton and bacteria are usually considered precursors of amorphous kerogens (STAPLIN, 1969; BURGESS, 1974; TISSOT and WELTE, 1978, p. 437). This deduction is based primarily on the common occurrence of amorphous kerogens in marine sedimentary rocks and the prolific biomass generated by plankton in modern marine environments. Amorphous kerogens usually plot on the modified van Krevelen diagram (TISSOT *et al.*, 1974) as Type-I or Type-II kerogen, but some have also been reported on or near the Type-III kerogen trend (DURAND and MONIN, 1980, p. 131; POWELL *et al.*, 1982; SUZUKI, 1984). This wide spread in composition and the influence of thermal maturation and oxidation on elemental compositions, hinders this type of analysis in elucidating the origin of amorphous kerogens. Stable carbon isotopes offer a more promising approach because of their sensitivity to type of precursor (SACKETT and THOMPSON, 1963; NEWMAN *et al.*, 1973; SHULTZ and CALDER, 1976; HEDGES and PARKER, 1976; GEARING *et al.*, 1977; STUERMER *et al.*, 1978; RASHID and REINSON, 1979), and their constancy through early diagenesis (GEARING *et al.*, 1984) and thermal maturation prior to metamorphism (WICKMAN, 1953; LANDERGREN, 1955; GAVELIN, 1957; BAKER and CLAYPOOL, 1970; MCKIRDY and POWELL, 1974; HOEFS and FREY, 1976). The objectives of this study are to examine the stable-carbon isotope distributions of amorphous kerogens from Phanerozoic sedimentary rocks and discuss their implication on the origin of this kerogen type.

METHODS AND RESULTS

Kerogen isolation

Isolation of kerogen from its inorganic matrix involves a series of acid treatments and a heavy-liquid separation. Approximately 500 ml of dilute HCl (18%) is slowly poured into an 800-ml plastic beaker containing 25–75 g of pulverized rock. This thoroughly stirred mixture is placed in a warm-water bath ($\sim 50^\circ\text{C}$) for two hours. Most of the spent solution is siphoned off the settled residue with a peristaltic pump. Five hundred milliliters of deionized (ASTM Type III) water are thoroughly mixed with the residue and centrifuged at 1500 rpm for 10 minutes. The resulting clear solution is carefully decanted and 500 ml of HF (52%) are slowly added to the remaining residue. After the effervescence of the mixture subsides, the beaker is placed in a warm-water bath ($\sim 50^\circ\text{C}$) for three hours, followed by 15 hours at room temperature. Most of the spent acid is siphoned off the settled residue, which is resuspended in 500 ml of deionized water and centrifuged at 1500 rpm for 10 minutes. The water is decanted and this residue is transferred to a 100-ml centrifuge tube. Three-quarters of the tube is filled with concentrated HCl (36.5–38.0%) and thoroughly mixed with the residue. The tube is placed in a boiling-water bath for one hour. After the tubes have cooled and the residue settles, the spent acid is siphoned off. Deionized water is added to the residue and centrifuged at 1500 rpm for 10 minutes. The water is decanted and this rinse procedure is repeated two additional times. Following the final decanting, a zinc-bromide solution, adjusted to a density of 2.1 g/cm^3 , is thoroughly mixed with the residue. Centrifuging this suspension at 2000 rpm for 20 minutes usually results in an organic supernatant residue. This is transferred by spatula to an 800-ml plastic beaker containing approximately 15 ml of dilute HCl (18%). Five hundred ml of deionized water are added and then centrifuged at 1500 rpm for 10 minutes. The water is decanted and this rinse procedure is repeated two additional times. After the final decanting, the residue is rinsed into a Buchner filtering funnel with a hardened fine-porosity filter (Whatman 50). The residue is dried in a vacuum oven at 50°C for 18 hours before being extracted with a benzene-methanol mixture (60:40 wt%) in a Soxhlet apparatus for 24 to 72 hours. This final residue is considered kerogen and is dried in a vacuum oven at 50°C for 24 hours.

Visual analysis

Visual analysis is a descriptive microscopic assessment of kerogen dispersed in clear plastic casting resin on a glass slide. Transmitted and reflected light are used to illuminate the kerogen with a Leitz MPV2 microscope at magnifications ranging from 600 to 800 \times . In transmitted light, amorphous kerogen is defined by its irregular and diffuse outline (Fig. 1-a, -c, -e), which is maintained at all levels of thermal maturation. Internally its texture may be frothy, granular, or fluffy, with colors ranging from translucent yellow or reddish brown at low levels of maturity to an opaque black at high levels of maturity. The angular sharp outline of structured kerogen makes it readily distinguishable from amorphous kerogens at low and high levels of maturity. Structured kerogen is used

here purely as a descriptive term and includes vitrinites, inertinites, and exinites. Reflected light is also employed to insure that amorphous kerogens are not embedded with large quantities of structured kerogen (Fig. 1-d, -f). Transmitted light alone will not always reveal such mixtures, and erroneous interpretations on the amount of amorphous kerogen present may occur.

Although subdivisions of this kerogen type have been proposed (MASRAN and POCOCCO, 1981; VENKATACHALA, 1981), their limited use to low levels of thermal maturity makes them unapplicable for this study. The samples used in this study have greater than 85 vol% of amorphous kerogen and range from low to high levels of thermal maturity. A listing and description of the rock units from which these kerogens were isolated are given in Table 1. It should *not* be implied from

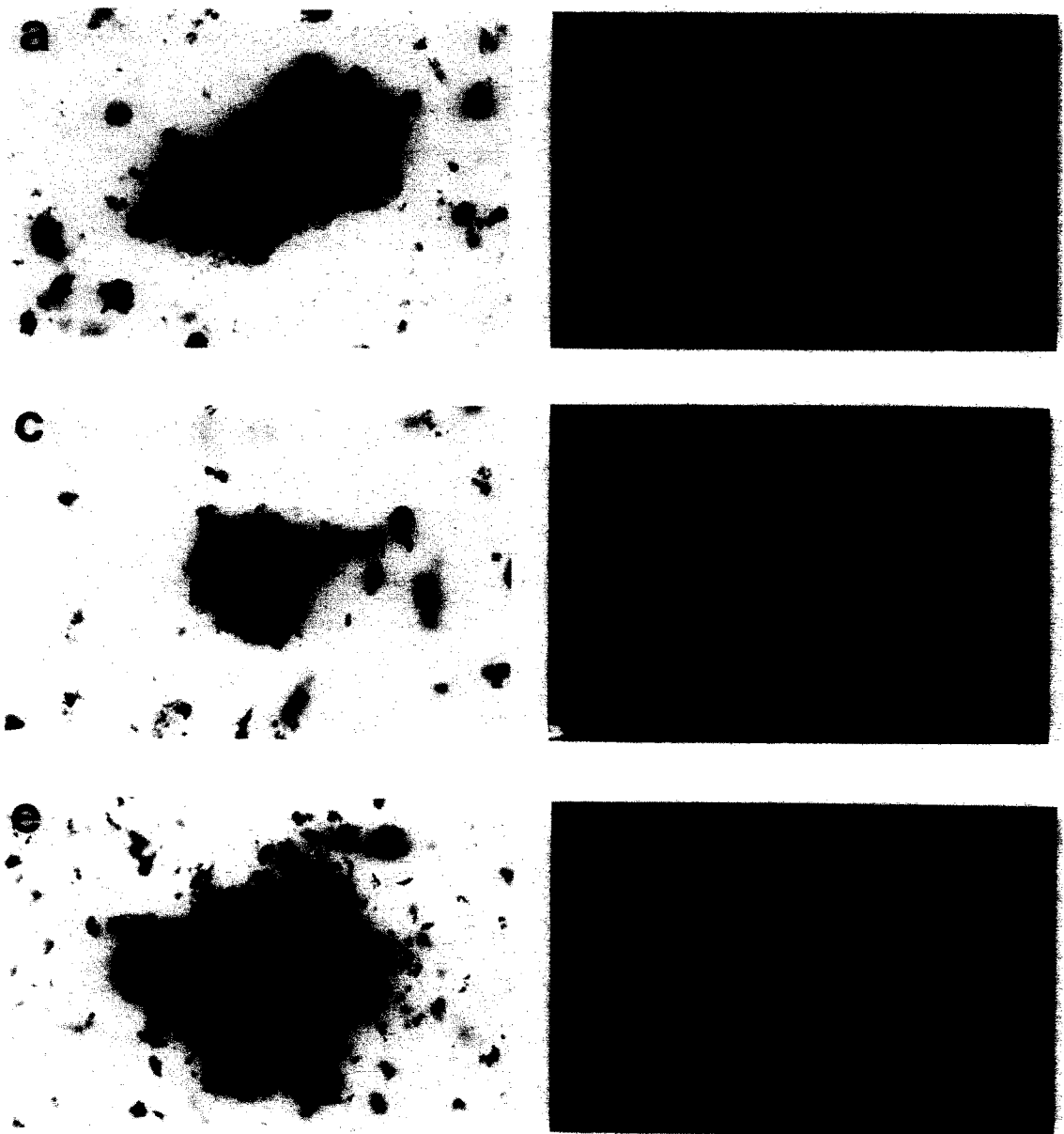


FIG. 1. Photomicrographs of immature amorphous kerogen from the Monterey Formation under transmitted light (a) and reflected light (b); mixture of amorphous and structured (labeled s) kerogens from the Mowry Shale under transmitted light (c) and reflected light (d); and overmature amorphous kerogen from the Alum Shale under transmitted light (e) and reflected light (f). The basal length of each photomicrograph is equal to 160 μm .

TABLE 1. DESCRIPTION OF ROCK UNITS FROM WHICH AMORPHOUS KEROGENS WERE ISOLATED AND THEIR $\delta^{13}\text{C}$ VALUES (PER MILL VS. PDB)

No.	Rock Unit*	Age	Locations	$\delta^{13}\text{C}$ of Amorphous Kerogens	
				Mean	Std. Dev.
1	Marlstones (N=1)	Pliocene	Box Elder Co., UT	-30.7	—
2	Peace Valley Fm. (N=2)	Pliocene	Los Angeles Co., CA	-26.6	0.4
3	Sesquoc Fm. (N=1)	Pliocene	Santa Barbra Co., CA	-21.3	—
4	Carbonates (N=1)	Pliocene-Miocene	Offshore Sicily	-21.8	—
5	Solfifera Fm. (N=3)	Miocene	Onshore Sicily	-22.9	0.8
6	Monterey Fm.				
	(a) Siliceous Beds (N=64)	Miocene	Santa Barbra Co. Los Angeles Co., San Luis Obispo Co., CA	-22.1	1.0
	(b) Calcareous Beds (N=64)	Miocene	Ventura Co., Los Angeles Co., Orange Co., Santa Barbra Co., San Luis Obispo Co., CA	-22.4	1.0
7	Shale Cuttings (N=1)	Miocene	Matagorda Island Area, Offshore TX	-27.2	—
8	Rincon Sh. (N=4)	Miocene	Santa Barbra Co., CA	-21.6	0.3
9	Poul Creek Fm. (N=2)	Mio.-Oligocene	Bearing Glacier Co., AK	-23.4	0.8
10	Maemoh Fm. (N=4)	Oligocene	Mae Sot Area, Thailand	-27.6	1.7
11	Kreyenhagen Sh. (N=12)	Olig.-Eocene	Kings Co., Fresno Co., CA	-28.1	0.4
12	Elko Fm. (N=1)	Eocene	Elko Co. NV	-26.4	—
13	Cozy Dell Fm. (N=1)	Eocene	Santa Barbra Co., CA	-28.6	—
14	Green River Fm.				
	(a) Wilkins Peak (N=15)	Eocene	Sweetwater Co., WY	-30.2	2.0
	(b) Tipton (N=5)	Eocene	Sweetwater Co., WY	-32.3	1.1
	(c) Parachute Ck., (N=13)	Eocene	Uintah Co., Duchesne Co., UT	-28.8	1.6
15	Midway Shale (N=2)	Paleocene	East Baton Rouge Parish, LA	-25.1	0.3
16	Morocco Oil Shale (N=1)	Cretaceous	Timahdite, Morocco	-28.3	—
17	Turonian Shale (N=5)	Cretaceous	North Slope, AK	-27.4	0.5
18	Greenhorn Fm. (N=1)	Cretaceous	McCone Co., MT	-27.5	—
19	Napo Fm. (N=1)	Cretaceous	Rio Misahualli, Ecuador	-26.7	—
20	Neocomian Shale (N=6)	Cretaceous	North Slope, AK	-27.4	0.1
21	Kimmeridge Clay (N=6)	Jurassic	Dorset Coast, England	-21.8	0.3
22	Kimmeridgian Shale (N=1)	Jurassic	North Sea, U.K.	-28.3	—
23	Jurassic Shale (N=2)	Jurassic	Tarim Basin, Western China	-32.3	0.1
24	Mufara Fm. (N=2)	Triassic	Onshore Sicily	-27.2	1.1
25	Streppenosa Sh. (N=1)	Triassic	Onshore Sicily	-26.9	—
26	Phosphoria Fm.				
	(a) Retort Sh. (N=12)	Permian	Fremont Co., Lincoln Co., WY; Beaverhead Co., Powell Co., MT	-29.3	0.6
	(b) Meade Peak (N=21)	Permian	Lincoln Co., WY; Bingham Co., Bear Lake Co., ID	-28.8	0.6
27	Kupferschiefer (N=1)	Permian	North Sea, U.K.	-27.0	—
28	Copacabana Fm. (N=1)	Permian	Palos Blancos, Bolivia	-30.5	—
29	Admire Fm. (N=1)	Permian	Cheyenne Co., NE	-26.9	—
30	Marmaton Fm. (N=2)	Pennsylvanian	Lincoln Co., CO	-27.4	0.2
31	Paradox Fm. (N=3)	Pennsylvanian	Montrose Co., Mesa Co., CO	-29.0	1.0
32	Tyler Fm. (N=1)	Pennsylvanian	McCone Co., MT	-27.7	—
33	Heath Fm. (N=1)	Mississippian	McCone Co., MT	-29.8	—
34	Doughnut Fm. (N=1)	Mississippian	Moffat Co., CO	-26.7	—
35	Stanley Sh. (N=5)	Mississippian	Murray Co., OK	-28.7	1.5
36	St. Louis Ls. (N=1)	Mississippian	Hardin Co., IL	-29.0	—
37	L. Oil Shale Gp. (N=10)	Carboniferous	West Lothian, Scotland	-30.6	1.5
38	Sycamore Ls. (N=1)	Mississippian	Murray Co., OK	-29.8	—
39	Bakken Sh. (N=2)	Miss.-Devonian	Dunn Co., Williams Co., ND	-28.8	0.4
40	Grassy Ck., Fm. (N=5)	Miss.-Devonian	Pike Co., MO; Hardin Co., Union Co., Effingham Co., IL	-28.9	0.9
41	New Albany Sh. (N=19)	Miss.-Devonian	Powell Co., Nelson Co., Bullitt Co., Rowan Co., Jefferson Co., KY; Clark Co., Jennings Co., IN	-29.2	0.5
42	Woodford Sh. (N=11)	Miss.-Devonian	Carter Co., Murray Co., OK	-30.3	0.5
43	Chattanooga Sh. (N=24)	Miss.-Devonian	Cumberland Co., KY; DeKalb Co., Giles Co., Chreatham Co., TN; Etowah Co., AL; Cherokee Co., OK; Chattooga Co., Walker Co., GA	-28.7	1.0
44	Ark. Novaculite (N=8)	Miss.-Devonian	Pulaski Co., Garland Co., Hot Springs Co., Montgomery Co., AR; Atoka Co., OK	-28.9	1.8
45	Woodruff Fm. (N=5)	Devonian	Elko Co., NV	-29.4	0.5
46	Gothlandian Sh. (N=4)	Silurian	Medenine Permit, Tunisia	-29.1	1.1
47	Maquoketa Fm. (N=3)	Ordovician	Newton Co., IN; Waubesa Co., KS	-29.3	0.3
48	Polk Ck. Sh. (N=2)	Ordovician	Yell Co., Pulaski Co., AR	-26.7	0.4
49	Athens Sh. (N=4)	Ordovician	Shelby Co., AL	-30.2	0.4
50	Big Fork Chert (N=3)	Ordovician	Latimer Co., OK; Pulaski Co., AR	-28.4	1.2
51	Vinini Fm. (N=5)	Ordovician	Eureka Co., NV	-29.6	0.3
52	Womble Sh. (N=4)	Ordovician	Atoka Co., OK; Montgomery Co., AR	-28.3	0.5
53	Alum Sh. (N=10)	Cambrian	Oslo, Norway; Gotland, Oland, Sweden	-28.3	1.0
54	Conasauga Gp. (N=3)	Cambrian	Murray Co., GA	-21.8	0.7

*N = number of samples

this table that the listed rock units are typically rich in amorphous kerogen. Only those samples bearing more than 85 vol% amorphous kerogen are included and these are not always representative of the entire rock unit. A good example of this is the Kimmeridge Clay along the Dorset Coast of England. The majority of shales at this location contain an abundance of structured kerogen. The only samples used in this study that contain an abundance of amorphous kerogen are from the limestone ledge and oil shale intervals.

Stable carbon isotopes

Analyses were performed at Amoco Production Company Research Center (APRC) on a Nuclide RMS-2 ratio mass spectrometer and at Coastal Sciences Laboratories Incorporated (CSL) on a Micromass 602E mass spectrometer. Both laboratories employed similar cryogenic trapping methods for

CO_2 purification, and only differed significantly in their combustion procedures. APRC combusted kerogens with oxygen at 1200°C for 15 minutes in an RF induction furnace, while CSL combusted kerogens with cupric oxide at 590°C for 60 minutes in a muffle furnace. In spite of this procedural difference, a comparative study showed that the values obtained from CSL were within the ± 0.3 per mil standard error of the values obtained from APRC. $^{13}\text{C}/^{12}\text{C}$ ratios are expressed as per mil (‰) deviations from the $^{13}\text{C}/^{12}\text{C}$ ratio of the Chicago PDB standard ($\delta^{13}\text{C}$).

$\delta^{13}\text{C}$ values are summarized in Table 1 and shown graphically in Fig. 2. This data set for Phanerozoic sedimentary rocks shows two distinct groups. Those in the isotopically heavy group range from -20 to -24 per mil and are referred to as *h*-amorphous kerogens,

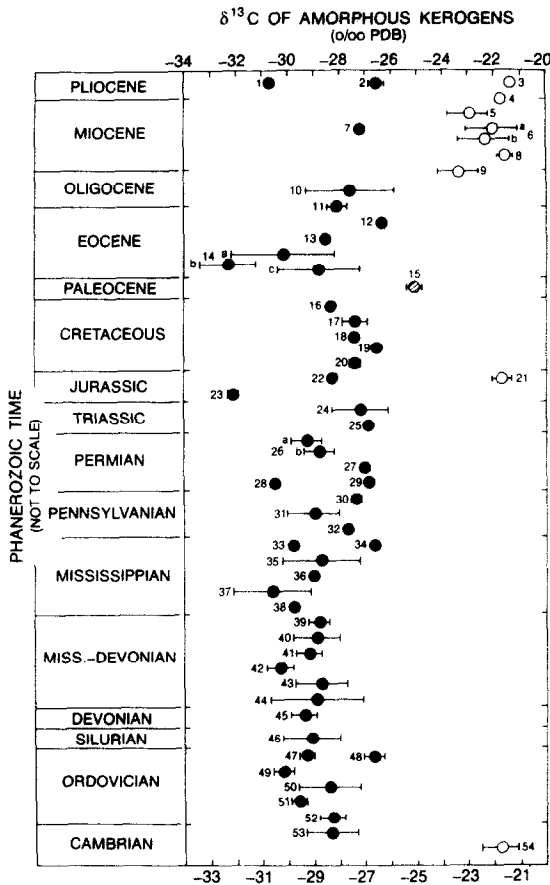


FIG. 2. Mean and standard deviation of stable carbon isotopes of *h*-amorphous kerogens (●) and *l*-amorphous kerogens (○) from Phanerozoic rock units. Numbers correspond to those listed for the rock units in Table 1.

while those in the isotopically light group have a larger range from -26 to -35 per mil and are referred to as *l*-amorphous kerogens. The range of $\delta^{13}\text{C}$ values separating these two groups is typical for structured kerogens derived from vascular plants employing the C_3 cycle (SACKETT and THOMPSON, 1963; DEGENS, 1969; HEDGES and PARKER, 1976; GEARING *et al.*, 1977; NISSENBAUM and KAPLAN, 1972; LEWAN, 1980). In this data set, only the amorphous kerogens from the Midway Shale fell within this intermediate range. This suggests either a continuum exists between the two groups or that some amorphous kerogens may be derived from highly degraded vascular plant debris.

DISCUSSION

The prevalence of *h*-amorphous kerogens in the Neogene period and the similar isotopically heavy values for organic matter derived from plankton in modern ocean sediments, allure evolution of plankton communities as a possible cause of the $\delta^{13}\text{C}$ dichotomy. Unfortunately, the abrupt change at the base of the Neogene period and the sporadic occurrence of *h*-amorphous kerogens in the Jurassic and Cambrian indicate that factors other than geological time are important. It should also be noted that a similar dichot-

omy in $\delta^{13}\text{C}$ values of organic matter has been observed in the Precambrian Gunflint Iron Formation (BAR-GHOORN *et al.*, 1977). Thermal maturation is also an unlikely cause of the $\delta^{13}\text{C}$ dichotomy in kerogens. Several studies of the natural system show no significant change in $\delta^{13}\text{C}$ values of kerogens until metamorphic conditions are encountered (WICKMAN, 1953; LANDERGREN, 1955; GAVELIN, 1957; BAKER and CLAYPOOL, 1970; MCKIRDY and POWELL, 1974; HOEFS and FREY, 1976). Major changes at high-grade metamorphism occur when carbonates in a host rock experience isotopic exchange with associated kerogens (VALLEY and O'NEIL, 1981; ESQUEVIN and SOURISSE, 1982). Laboratory pyrolysis of kerogen in modern sediment (ISHIWATARI *et al.*, 1978) and in ancient sedimentary rock (LEWAN, 1983) verifies the stability of their $\delta^{13}\text{C}$ values under premetamorphic conditions. With evolution and thermal maturation unlikely causes of the dichotomy, four other possible causes are discussed in more detail. These include variations in plankton species, atmospheric CO_2 concentrations, selective preservation, and CO_2 sources. It should be emphasized that the cause or causes of the dichotomy may have changed through geological time, and one unique cause may not be universally applicable.

Plankton species

A major portion of the planktonic biomass in oceans is comprised of phytoplankton (BORDOVSKIY, 1965), which are usually considered the primary precursor of amorphous kerogens. Phytoplankton are the food source for accompanying zooplankton within planktonic communities. Field and experimental observations indicate that the $\delta^{13}\text{C}$ values of zooplankton are the same or within one per mil of their phytoplankton *ingesta* (SACKETT *et al.*, 1965; DEGENS *et al.*, 1968a; DENIRO and EPSTEIN, 1978; GEARING *et al.*, 1984). $\delta^{13}\text{C}$ values of plankton in modern oceans usually range from -18 to -24 per mil, with the exception of -26 to -31 per mil values for plankton in Antarctic waters (SACKETT *et al.*, 1965; FONTUGNE and DUPLESSY, 1981). Although this isotopic dichotomy in plankton of modern oceans is an attractive analogy for the ancient dichotomy, the factors responsible for this modern difference in isotopic values are poorly understood.

Temperature alone does not appear to be a major control on isotopic fractionation by phytoplankton (DEGENS *et al.*, 1968b; WONG and SACKETT, 1978; RAU *et al.*, 1982), but at temperatures below 15°C particular species may become significantly enriched in ^{12}C (WONG and SACKETT, 1978; FONTUGNE and DUPLESSY, 1981). SACKETT (1986) advocates that particular species in the cold Antarctic waters are responsible for the ^{12}C enrichment of the plankton. These particular species have not yet been identified, but SACKETT (1986) advocates diatoms in general as being responsible. This is not supported by the dominance of *h*-amorphous kerogens in the diatomite-rich rocks and diatomites of the Monterey Formation (rock unit 6a) and Sesquoc Formation (rock unit 3). Isotopic

fractionation by the diatom *Skeletonema costatum* has been shown to be strongly temperature dependent, but its cosmopolitan distribution (CUPP, 1943, p. 43; GUILLARD and KILHAM, 1977) with a tropical to temperate water preference (HARGRAVES, 1968, p. 92) makes its significance in Antarctic waters dubious. Based on the study by RAU *et al.* (1982), an abundance of these particular unidentified species would be limited to Antarctic waters due to the lack of ^{12}C enriched plankton in Arctic waters. In spite of the lack of specifics on species, it remains difficult to invoke this explanation for the modern dichotomy as an analogy for the ancient dichotomy. Such an attempt would suggest that the *l*-amorphous kerogens, which dominate the Phanerozoic, were derived from isotopically temperature-dependent species that populated cold waters ($<15^\circ\text{C}$). The wide variations in climate and ocean conditions throughout the Phanerozoic make this explanation unlikely.

Atmospheric CO_2 concentrations

It has been observed that there is a significant increase in isotopic fractionation of carbon during photosynthesis as the concentration of available CO_2 increases. Laboratory experiments by DEGENS *et al.* (1968b) showed that $\delta^{13}\text{C}$ values of phytoplankton are enriched in ^{12}C by 9 per mil when grown in CO_2 concentrations ten times greater than those in modern oceans. Field observations by ESTEP (1984) also verified this phenomenon for thermophilic algae and bacteria in hydrothermal environments. Several geochemical models for the Phanerozoic have suggested variations in the concentration of atmospheric CO_2 (MACKENZIE and PIGOTT, 1981) and concentrations one order of magnitude greater than those of present day have been suggested (BUDYKO and RONO, 1979).

ARTHUR *et al.* (1985) suggest that the isotopically lighter organic carbon in Cretaceous rocks compared to modern marine sediments is in part the result of higher concentrations of CO_2 in the Cretaceous atmosphere. Although there appears to be a consensus that atmospheric CO_2 concentrations were higher in the Cretaceous, BERNER *et al.* (1983) have demonstrated that the magnitude of these concentrations remains debatable. The coexistence of *h*- and *l*-amorphous kerogens in the Neogene (Fig. 2, Rock Units 1 through 8), Kimmeridgian (Fig. 2, Rock Units 21 and 23), and Ordovician (HATCH *et al.*, 1985; and Fig. 2, Rock Units 47 through 52) indicate that atmospheric CO_2 concentrations in the Phanerozoic were not high enough (ten times present day concentrations) to cause the isotopic dichotomy of amorphous kerogens.

This conclusion is also supported by the $\delta^{13}\text{C}$ values of Phanerozoic humic coals, which should reflect the response of vascular land plants to changes in atmospheric CO_2 concentrations. Laboratory experiments by PARK and EPSTEIN (1960) indicate $\delta^{13}\text{C}$ values of vascular land plants are enriched in ^{12}C by approximately 4 per mil when grown in CO_2 concentrations ten times higher than modern atmospheric concentra-

tions. Examination of $\delta^{13}\text{C}$ values compiled on humic coals and plant debris in sedimentary rocks through the Phanerozoic by DEGENS (1969, Fig. 8), LEWAN (1980, Fig. 2.6), and SCHOELL (1984, Fig. 1) shows no ^{12}C enrichment relative to modern C_3 vascular plants.

Selective preservation

The composition of planktonic organisms (*i.e.*, phytoplankton, zooplankton, and bacteria) may be discussed in terms of three chemical groups: (1) proteins, (2) carbohydrates, and (3) lipids. All three of these chemical groups are highly susceptible to bacterial degradation under aerobic conditions, but the lipids are considered more resistant to bacterial degradation under anaerobic conditions (ZOBELL, 1946; R. E. KALLIO, pers. commun.). BREGER (1960, 1977) has suggested that kerogens may be the result of selective preservation of lipids from decomposed plankton. This has been supported in part by studies involving stable carbon isotopes (ISHIWATARI and MACHIHARA, 1983) and nuclear magnetic resonance spectroscopy (HATCHER *et al.*, 1983; SPIKER and HATCHER, 1984). DEGENS *et al.* (1968a) reported that lipids of marine plankton are usually enriched in ^{12}C by 8 to 10 per mil relative to the carbohydrates and proteins. In spite of this potential difference, SPIKER *et al.* (1986) have shown that only a 4 per mil enrichment of ^{12}C occurs in algal remains under optimum anaerobic conditions. Although selective preservation may account for some of the $\delta^{13}\text{C}$ variations observed in Fig. 2, it does not appear to be a significant factor in explaining the dichotomy.

Another consideration is that condensation of carbohydrates and proteins into polymeric complexes may enhance the preservation of these liable constituents. These complexes are referred to as melanoidins and are the result of the Maillard reaction (MCWEENEY *et al.*, 1974). LARTER and DOUGLAS (1980) have provided experimental data supporting the concept that melanoidins bind lipids into high-molecular weight complexes, which may later develop into humic acids (HOERING, 1973) or amorphous kerogens (WELTE, 1974). Incorporation of carbohydrates and proteins into a kerogen by this process would suggest that *h*-amorphous kerogens contain a significantly greater amount of melanoidins in their matrix than *l*-amorphous kerogens. This interpretation is severely hampered by the experimental work of Drozdova (as cited by GALIMOV, 1980), which shows that melanoidins are enriched in ^{12}C by 10 per mil relative to the carbohydrates from which they formed. Therefore, melanoidins would have isotopic compositions in the range of *l*-amorphous kerogens and are not likely to be a discrimination factor in the dichotomy.

Plankton suspended in the euphotic zone of water columns have thus far been considered the primary source of both types of amorphous kerogens. Chemoautotrophic bacteria in sediments below the euphotic zone have been considered to be a major source of organic matter in some marine sediments (KEPKAY

et al., 1979). In particular, colorless H₂S-oxidizing bacteria of the family *Beggiatoaceae* have been proposed to be the source of organic matter in some laminated-siliceous rocks of the Monterey Formation (WILLIAMS, 1984). The exclusion of this precursor from settling time through a water column prior to burial in sediment may enhance the preservation of carbohydrates and result in the formation of *h*-amorphous kerogens. This suggests that the precursor for *l*-amorphous kerogens is plankton, while the precursor for *h*-amorphous kerogen is bacterial mats. Although organic matter in some lithologies of the Monterey Formation may have been sourced by bacterial mats, the uniform $\delta^{13}\text{C}$ values of kerogens throughout the Monterey Formation regardless of facies, sulfur content, degree of lamination, and organic richness suggests that bacterial mats are not responsible for the isotopic dichotomy.

CO₂ sources

Variations in the $\delta^{13}\text{C}$ values of the dissolved CO₂ metabolized by phytoplankton during photosynthesis offers another explanation for the isotopic dichotomy in amorphous kerogens. Dissolved CO₂ in isotopic equilibrium with the atmosphere is the primary source of carbon for phytoplankton in modern oceans (DEUSER *et al.*, 1968). The $\delta^{13}\text{C}$ value of this CO₂ ranges from -12.0 per mil at 0°C to -8.4 per mil at 30°C as a result of its isotopic equilibration with HCO₃⁻ (MOOK *et al.*, 1974). These values are considered to be essentially constant throughout the Phanerozoic based on the similar $\delta^{13}\text{C}$ values of marine limestones from this eon (KEITH and WEBER, 1964; WEBER, 1967; GALIMOV *et al.*, 1975; VEIZER and HOEFS, 1976). Although dissolved CO₂ in equilibrium with the atmosphere is the primary source of carbon in the deep (>500 m) well-circulated oceans at the present, an organic source of CO₂ may have been more prevalent in the shallow (<200 m) restricted epicontinental seas in the past. Anaerobic and aerobic bacterial decomposition of organic matter in a water or sediment column may provide a source of CO₂ with $\delta^{13}\text{C}$ values as low as -22 per mil (OANA and DEEVEY, 1960). The effect of this organic-derived CO₂ on the $\delta^{13}\text{C}$ value of phytoplankton would depend on its degree of dilution with atmospheric-derived CO₂ in the photic zone of a water column. In deep (>500 m) expansive oceans, the effect of organic-derived CO₂ on the $\delta^{13}\text{C}$ value of phytoplankton would be negligible due to its diffusion through a long and well-mixed water column. As observed by DEUSER (1970a) in the Black Sea, the CO₂ in the lower portion of the water column is enriched in ¹²C by 7 per mil due to the input of CO₂ from anaerobic decay of organic matter. This enrichment is gradually diluted upward in the long water column (2000 m) with atmospheric-derived CO₂. Within the photic zone, only atmospheric-derived CO₂ appears to be present and the mean $\delta^{13}\text{C}$ value of the phytoplankton is -23 per mil (DEUSER, 1970b). Conversely, in shallow (<200 m) restricted epicontinental seas, the effect of organic-derived CO₂ on the $\delta^{13}\text{C}$ value of phy-

toplankton could be appreciable due to its diffusion through a short and stagnant water column. This is observed in stratified lakes where the dissolved CO₂ in the photic zone may be enriched in ¹²C by 7 to 13 per mil (MCKENZIE, 1982) and the $\delta^{13}\text{C}$ value of the phytoplankton may be as high as -35.5 per mil (OANA and DEEVEY, 1960).

This suggests that *h*-amorphous kerogens are derived from phytoplankton growing in photic zones of deep (>500 m) expansive oceans where the major carbon source is atmospheric-derived CO₂. Conversely, *l*-amorphous kerogens are derived from phytoplankton growing in the photic zone of shallow (<200 m) restricted epicontinental seas where the carbon source is dominated by organic-derived CO₂. In addition to CO₂ derived directly from the microbial decay of organic matter, oxidation of methane derived from bacterial decay of organic matter, as described by SCHOELL and WELLMER (1981) may also provide an isotopically light source of CO₂. The relatively narrow range of $\delta^{13}\text{C}$ values for *h*-amorphous kerogens would be expected from an essentially fixed atmospheric-derived CO₂ source, while the relatively wide range of $\delta^{13}\text{C}$ values for *l*-amorphous kerogens would be expected from an organic-derived CO₂ source that may vary in amount and isotopic composition.

Although it is beyond the scope of this study to evaluate each of the rock units in Table 1 in terms of depositional setting, a terse comparison of the Monterey Formation with Devonian-Mississippian black shales of the central lowland states is supportive of this interpretation. Deposition of the Monterey Formation is considered to have occurred in deep-water (>1000 m, INGLE, 1981) silled basins, marginal to the continent with a common overlying water body open to the Pacific Ocean (BRAMLETTE, 1946; PISCOTTO and GARRISON, 1981). The carbon source for phytoplankton under these conditions would be primarily atmospheric-derived CO₂, and the occurrence of *h*-amorphous kerogen throughout the Monterey Formation supports this interpretation. Conversely, deposition of the Devonian-Mississippian black shales of the central lowland states is considered to have occurred in a shallow (<200 m) restricted epicontinental sea with a well-developed anaerobic water column (RICH, 1951; CONANT and SWANSON, 1961; LINEBACK, 1968; PROVO, 1977). The carbon source for phytoplankton under these conditions would include appreciable quantities of organic-derived CO₂, and the occurrence of *l*-amorphous kerogen throughout the New Albany Shale and Chattanooga Shale supports this interpretation.

Use of organic-derived CO₂ in the photic zone of stratified lakes as an analogy for shallow restricted epicontinental seas is encouraged by the exclusive occurrence of *l*-amorphous kerogens in the documented lacustrine rock units of this study (*i.e.*, Peace Valley beds, LINK and OSBORNE, 1978; Mae Moh shales, SHERWOOD *et al.*, 1984; Elko shale, SOLOMON *et al.*, 1979; Green River Formation, BRADLEY, 1964; and Scottish Lower Oil Shale Group, GREENSMITH, 1968). The

most ^{12}C -enriched kerogens shown in Fig. 2 are from oil-shale bearing facies of the Green River Formation, which were formed in shallow-water lacustrine environments (EUGSTER and SURDAM, 1973; BRADLEY, 1973; ROBINSON, 1979). The importance of water depth in determining the effectiveness of organic-derived CO_2 is also encouraged in part by the organic matter of the Gunflint Iron Formation, which has been reported to be isotopically light (-25 to -30 per mil) in the shallow water facies and heavy (-15 to -20 per mil) in the deepwater facies (BARGHOORN *et al.*, 1977).

CONCLUSIONS

$\delta^{13}\text{C}$ values of amorphous kerogens from Phanerozoic sedimentary rocks show a distinct dichotomy. One group is referred to as *h*-amorphous kerogens which have values ranging from -20 to -24 per mil. The other group is referred to as *l*-amorphous kerogens, which have values ranging from -26 to -35 per mil. Kerogens from one rock unit in this data base showed intermediate values and suggest that a weak continuum between the two groups may exist. The occurrence of *l*- and *h*-amorphous kerogens in some rock units of equivalent geological age suggests that evolution of planktonic communities and changes in atmospheric CO_2 concentrations are not viable explanations for the dichotomy. Some isotopic variation in the kerogens may be attributed to selective preservation during anaerobic bacterial degradation and differences in planktonic species with changing water temperatures, but these do not appear to be of primary importance in explaining the dichotomy. The most durable explanation considered here involves the sources of CO_2 utilized by phytoplankton. Phytoplankton residing in environments that are dominated by atmospheric-derived CO_2 result in *h*-amorphous kerogens, while those residing in environments that are dominated by organic-derived CO_2 result in *l*-amorphous kerogens. *h*-amorphous kerogens are expected to occur in silled basins that are overlain by expansive well-circulated deep (>500 m) water, where the prevailing source of carbon in the photic zone is atmospheric-derived CO_2 . Conversely, *l*-amorphous kerogens are expected to occur in restricted basins that are overlain by stratified shallow (<200 m) water, where the prevailing source of carbon in the photic zone may be organic-derived CO_2 . This latter situation has been observed in stratified lakes, which may provide a good analogy for shallow restricted epicontinental seas of the Phanerozoic.

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