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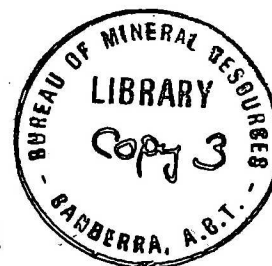
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METAMORPHIC ALTERATION OF CARBON ISOTOPIC  
COMPOSITION IN ANCIENT SEDIMENTARY ORGANIC  
MATTER: NEW EVIDENCE FROM THE PRECAMBRIAN  
AND CAMBRIAN OF AUSTRALIA

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# ABSTRACT

Insoluble organic matter (kerogen) was isolated from a suite of 23 marine shales and carbonates of Early Proterozoic to Middle Cambrian age from Australia. The stable carbon isotopic composition,  $\delta C_{PDB}^{13}$ , of the organic matter appears to vary with late diagenetic or incipient metamorphic rank as given by hydrogen to carbon atomic ratio. Geochemical maturation of the kerogen beyond a rank equivalent to 84-86% carbon results in progressive enrichment of the residual organic matter in  $C^{13}$ . Hence low rank (unmetamorphosed) organic matter is isotopically lighter ( $\delta C_{PDB}^{13}$  range = -18.6 to -31.3 per mil, mean = -28.0 per mil) than that of higher rank ( $\delta C_{PDB}^{13}$  range = -10.8 to -28.2 per mil, mean = -21.6 per mil). Kerogens from two Precambrian evaporitic sediments are isotopically heavier than normal marine organic matter of similar rank.

## INTRODUCTION

Uptake and fixation of  $\text{CO}_2$  during photosynthesis leads to fractionation between  $\text{C}^{12}$  and  $\text{C}^{13}$  such that the resultant organic matter is richer in the lighter isotope than the inorganic carbon reservoir (Degens, 1969). Thus the discovery of isotopically light carbonaceous material in rocks as old as 3300 m.y. is consistent with the idea that photosynthetic microbiota evolved very early in Precambrian time (Hoefs and Schidlowski, 1967; Hoering, 1967a,b; Schopf and others, 1971; Oehler and others, 1972). Hitherto, the stable carbon isotopic composition<sup>1</sup> of

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1. Usually expressed in terms of  $\delta\text{C}^{13}$  per mil, defined as:

$$\left[ \frac{\text{C}^{13}/\text{C}^{12} \text{ sample}}{\text{C}^{13}/\text{C}^{12} \text{ standard}} - 1 \right] \cdot 1000$$

The Chicago PDB standard was used in this study.

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insoluble organic matter (kerogen) dispersed in ancient sedimentary rocks has been regarded as one of the most reliable geochemical indicators of contemporaneous autotrophic biological activity (Schopf, 1970; McKirdy, 1974). Being particulate and insoluble, kerogen is thought to be less susceptible to post-lithification contamination by younger materials than are other chemical fossils such as hydrocarbons, fatty acids, porphyrins, and amino acids (Hoering, 1967 a,b). Furthermore its stable carbon isotopic composition is apparently



resistant to substantial modification by diagenetic and incipient metamorphic processes (Wickman, 1953; Gavelin, 1957; Degens, 1969; Hoefs, 1973). Oehler and others (1972) consider post-depositional alteration unlikely to have caused the anomalously heavy isotopic composition (mean  $\delta C_{PDB}^{13} = -16.5$  per mil) of organic carbon in cherts of the Theespruit Formation from the lower Onverwacht Group, Swaziland Sequence, South Africa. Brooks and others (1973) disagree with this interpretation; <sup>they</sup> maintain that the discrepancy between the high  $\delta C_{PDB}^{13}$  values reported for the insoluble organic matter of the Theespruit cherts and those for kerogens from formations higher in the Swaziland Sequence (generally less than -25 per mil) is attributable to the more intense thermal alteration of the former. Their contrary view is based largely on the isotopic data of Silverman (1964) which indicate that evolution of low molecular weight hydrocarbons enriched in  $C^{12}$  during thermal maturation of crude oil precursor compounds leads to a slight increase in  $C^{13}/C^{12}$  ratio for the gasoline and asphaltene fractions of the resultant petroleum.

Support for the opinion that metamorphism can, indeed, lead to some enrichment of  $C^{13}$  in kerogen is provided by the work of Barker and Friedman (1969) on the isotopic composition of carbonaceous matter in pelites from the Precambrian Uncompahgre Formation, Colorado. Metamorphosed schists containing less than 1% organic carbon had  $\delta C_{PDB}^{13}$  values of -23 to -28 per mil, whereas

less metamorphosed carbonaceous slates and phyllites (1-6% organic C) gave  $\delta C_{PDB}^{13}$  values of -29 to -31 per mil. In addition, Baker and Claypool (1970) found the total organic carbon of two metamorphosed Phanerozoic shales, each from within approximately 30 m of an igneous contact, to have  $\delta C^{13}$  values 12 to 18 per mil higher than their less metamorphosed equivalents.

So far, however, isotopic studies of insoluble organic matter in Precambrian and younger sediments have lacked suitable compositional or structural data which would permit the kerogen itself (as distinct from the host rock) to be classified according to its degree of diagenetic or metamorphic alteration. We have recently established (McKirdy, 1971; McKirdy and others, 1974) that kerogens derived from marine algal and bacterial detritus may be ranked metamorphically on the basis of their hydrogen to carbon atomic ratio (H/C). In the present study,  $\delta C_{PDB}^{13}$  values for a suite of such kerogens of varying rank from Precambrian and Cambrian formations across Australia (Table 1) have been determined to further investigate the effect of late diagenesis and incipient metamorphism on the stable carbon isotopic composition of particulate organic matter in ancient sediments.

#### METHODS

Samples of unweathered rock were ground to minus 200 mesh in a Siebtechnik mill and their

TABLE 1. ROCK SAMPLES AND ANALYTICAL DATA

Sample no.	Formation name	Marine lithofacies	Location	Estimated age (m.y.)	$\delta C_{PDB}^{13}$ (per mil)	$\frac{H}{C}$
160	Que River Beds	Shale	Tullah, Tas.	520 (late ME)	-23.8	0.20*
50	Inca Formation	Limestone	Duchess, Qld.	530 (early ME)	-30.8*	0.71*
60	Beetle Creek Formation	Limestone	Duchess, Qld.	530 (early ME)	-31.3*	0.87*
40	Moodlatana Formation	Dolomitic lst.	Red Hill Well, S.A.	535 (early ME)	-29.2*	0.67*
11	Emu Bay Shale	Shale	Kangaroo Is., S.A.	545 (late EE)	-28.4*	0.48*
130	Heatherdale Shale	Shale	Sellick Beach, S.A.	560 (EE)	-25.4*	0.19*
70	Parara Limestone	Argillaceous lst.	Stansbury, S.A.	565 (early EE)	-28.7*	0.50*
32	Wilkawillina Limestone	Archaeocyathal lst.	Brachina Gorge, S.A.	565 (early EE)	-28.6*	0.53*
3	Brachina Formation	Shale	Angepena Hill, S.A.	600-700	-27.9	0.15*
TM 9			Melrose, S.A.		-18.8	0.11
TM 10			Kapunda, S.A.		-14.7	0.06
TM 12	Tindelpina Shale Mbr.,		Spring Creek, S.A.		-23.8	0.14
TM 16	Tapley Hill Formation	Shale	Spring Creek, S.A.	700	-22.9	0.15
TM 17			Darlington, S.A.		-23.4	0.18
TM 19			Willouran Hill, S.A.		-24.2	0.25
TM 20			Waukaringa, S.A.		-17.5	0.09
MC 26	Gillen Mbr., Bitter Springs Formation	Anhydritic dol.	Mount Charlotte, N.T.	900	-18.6	0.73*
S 405	Skillogalee Dolomite	Stromatolitic dol.	Depot Creek, S.A.	1000	-10.8	0.10*
2	Kyalla Mbr., McMinn Formation	Calcareous sh.	Urapunga, N.T.	1400	-30.2	1.17*
110	Urquhart Shale	Dol. siliceous sh.	Mount Isa, Qld.	1500	-28.2	0.13*
150	Marimo Slate	Shale	Marimo, Qld.	1500	-25.8	0.05*
170	H.Y.C. Pyritic Shale Mbr., Barney Creek Formation	Dolomitic shale	McArthur River, N.T.	1600	-26.6	0.64
182	Golden Dyke Formation	Dolomitic shale	Rum Jungle, N.T.	1800 - 2000	-15.8	0.04

\* Data from McKirdy (1971)

soluble bitumen removed by exhaustive extraction with benzene/methanol in Soxhlet apparatus. Digestion of the residual powder in acid - dilute HCl to remove carbonates, and concentrated HF/HCl (5:1) to destroy silicates - was followed by treatment with sodium borohydride to remove pyrite (McIver, 1967). Finally a 'sink-float' technique was employed to separate the kerogen from acid-resistant mineral grains (e.g. rutile, zircon, tourmaline). This involved dispersion of the concentrate in chloroform, sonication, brief centrifuging at low speed, and decantation, the whole procedure being repeated until no further kerogen remained in suspension upon centrifugation. The initial solvent extraction step was omitted in the case of the Tindelpina Shale samples. Instead, the kerogen concentrates were extracted ultrasonically with chloroform. After drying, the remaining kerogen (a fine brown to black powder) was analysed for carbon and hydrogen (by the CSIRO Microanalytical Service, Melbourne, Victoria) and for  $\delta C_{PDB}^{13}$  (by Geochron Laboratories, Cambridge, Massachusetts). The isotopic data quoted in Table 1 for the Cambrian limestones are  $\delta C_{PDB}^{13}$  values of the total organic fraction (TOF) as determined by Oehler and others (1972).

#### RESULTS AND DISCUSSION

The marine shales (0.3 - 5.5% organic C) and carbonates (0.02 - 0.17% organic C) from which kerogens were isolated (Table 1) range in age from Early Proterozoic (ca. 1900 m.y.) to late Middle

Cambrian (ca. 520 m.y.). No obvious secular trend in  $\delta C_{PDB}^{13}$  is evident over this 1400 m.y. interval (Fig. 1). Three quarters of the  $\delta C_{PDB}^{13}$  values fall between -22 and -32 per mil, well within the established range of -20 to -40 per mil for biogenic organic carbon preserved in sedimentary rocks (Degens, 1969). Of greater significance, however, are the six kerogens for which  $\delta C_{PDB}^{13}$  is less than -20 per mil.

A possible cause of this isotopic variation becomes apparent when  $\delta C_{PDB}^{13}$  for each kerogen is plotted against its rank as given by H/C atomic ratio (Fig. 2). With increasing kerogen rank (decreasing H/C ratio), there is a marked increase in corresponding  $\delta C_{PDB}^{13}$  value. The fourteen kerogens of higher rank (H/C < 0.3) are isotopically heavier ( $\delta C_{PDB}^{13}$  range = -10.8 to -28.2 per mil, mean = -21.6 per mil) than the <sup>nine</sup> kerogens ~~nine~~ of lower rank (H/C > 0.4;  $\delta C_{PDB}^{13}$  range = -18.6 to -31.3 per mil, mean = -28.0 per mil). The threshold between low rank (unmetamorphosed) and high rank (metamorphosed) kerogen is equivalent to a dry, ash-free carbon content of 84-86%.

Although our suite of rocks as a whole lacks the stratigraphic and lithologic control which is a feature of the study by Oehler and others (1972) of cherts from the Swaziland Sequence, the seven Tindelpina Shale samples (Table 1) do satisfy both criteria. Moreover, the kerogens from these shales display an appreciable spread in  $\delta C_{PDB}^{13}$  (-24.2 to -14.7 per mil) which

corresponds to an independently established increase in regional metamorphic grade (McKirdy and others, 1974).

Kerogen H/C atomic ratio shows a good correlation with crystallinity of the clay mineral illite (Kubler, 1968) in the sediments used in this study (McKirdy and Powell, unpublished results). The illite crystallinity measurements made by us indicate that the rocks straddle the anchizone (Dunoyer de Segonzac, 1970) of regional metamorphism, despite their generally unmetamorphosed appearance in hand specimen and thin section. It is possible therefore that geochemical maturation (analogous to coalification) during late diagenesis and incipient metamorphism has resulted in progressive enrichment of the residual carbonaceous matter in the  $C^{13}$  isotope. This is in agreement with isotopic data summarized by Degens (1969, fig. 20) which showed that organic matter from 'unmetamorphosed' Precambrian sediments (16 samples, median  $\delta C_{PDB}^{13} = -33$  per mil) was distinctly lighter than that from 'metamorphosed' sediments of Precambrian age (86 samples, median  $\delta C_{PDB}^{13} = -24$  per mil).

Experimental isotopic studies of the thermal degradation of simple organic compounds have demonstrated that  $C^{12} - C^{12}$  bonds rupture more frequently (depending on bond type, temperature and reaction time) than do  $C^{13} - C^{12}$  bonds because of the lower dissociation energy of the former (Sacket and others, 1970). As an example of this kinetic

isotope effect, Silverman (1964) found that methane and homologues generated during thermal cracking of a crude oil were enriched in  $C^{12}$  by up to 10 per mil relative to the residual higher boiling fractions. As Silverman (1964, p. 100) has pointed out, this loss of low molecular weight hydrocarbons from more complex petroleum constituents is a dehydrogenation process whereby unsaturated hydrocarbons would also form as by-products. The fragmentation, ring closure, and polymerization of these unstable intermediates could ultimately lead to the formation of aromatic hydrocarbons and asphaltenes. In accord with this maturation hypothesis, the  $C^{13}$  content of both compound types in petroleum is slightly but consistently higher than that of the whole crude (Silverman, 1964; Silverman and Epstein, 1958).

Methane and other hydrocarbon gases are generated during the later diagenesis and incipient metamorphism of kerogen (McIver, 1967; Tissot and others, 1974). Thus the same isotope effect noticed in petroleum maturation may be expected to operate during kerogen degradation. Sackett and others (1970) showed that methane depleted in  $C^{13}$  relative to the parent organic material resulted from the pyrolysis at  $500^{\circ}C$  of samples of the Posidonian shale kerogen (Jurassic, Germany) and the Fleming coal (Pennsylvanian, Kansas), although the degree of depletion was some 13 per mil greater in the case of the kerogen-derived methane. This possibly indicates weaker terminal carbon-carbon bonds in the kerogen than in the

coal. Similarly, gas (predominantly methane) absorbed in German coal seams may be as much as 47 per mil lighter than the coal itself (Colombo and others, 1970).

Whether this isotopic disproportionation process is also capable of increasing the  $\delta C^{13}$  value of the residual organic matter by 10-15 per mil in algal kerogens above a rank equivalent to  $H/C = 0.3$  (Fig. 2), is not yet clear. Admittedly, studies of coals by Wickman (1953) and Colombo and others (1970) failed to detect any significant variation in  $C^{13}/C^{12}$  ratio with increasing rank. However, closer examination of their data reveals the rank of nearly all their samples to be lower than that ( $H/C = 0.3$ ) at which the postulated maturation effect starts to become evident. Furthermore, the difference in chemical structure and composition between most coals (algal types, e.g. torbanite, excepted) and algal-derived kerogens (such as those in the present study) may be expected to influence their isotopic behaviour during metamorphism. The latter are more aliphatic and hydrogen-rich, even at relatively high rank; their longer and more prolific alkyl groups impart a greater potential for the generation of isotopically light methane during thermal maturation (cf. Sackett and others, 1970, p. 44; Colombo and others, 1970, p. 3) and, consequently, for  $C^{13}$  enrichment in the mature kerogen.



Two of the kerogens analysed (viz. MC 26 and S 405) appear to be anomalously enriched in  $C^{13}$  for their rank. Both were isolated from dolomites which are inferred to be of primary or penecontemporaneous shallow marine origin. Rock sample MC 26 comes from the lower part of the Gillen Member, Bitter Springs Formation, in the Mount Charlotte No. 1 well, Northern Territory. The unit comprises a sequence of anhydritic dolomite with subordinate beds of sandstone, siltstone, shale, halite, and gypsum (Wells and others, 1970). Dark <sup>possible</sup> cryptalgal laminae occur throughout the dolomite. A columnar stromatolite, Tungussia erecta, forms a biostrome near the base of the member at two known localities (Walter, 1972). The environment represented is one of evaporitic sedimentation in local barred basins of a shallow sea. The second sample, S 405, was taken from a specimen of the stromatolite, Baicalia burra, found in the Skillogalee Dolomite at Depot Creek, South Australia. The formation at this locality contains mud cracks and interbeds of magnesite conglomerate, suggesting deposition in a near-shore lagoon on a wide carbonate-depositing shelf that was subject to frequent exposure and erosion (Preiss, 1973). Thus, the depositional environment in each case was probably more highly stressed (viz. higher temperature, higher pH, lower concentration of dissolved  $CO_2$ ) than if normal marine conditions had prevailed. Under such circumstances it is also reasonable to assume a slower growth rate for the mat builders (blue-green and green algae, bacteria) and other organisms.

contributing organic matter to the sediments. As recent experiments with marine phytoplankton have shown (Degens and others, 1968; Degens, 1969), these conditions would favour low carbon isotopic fractionation relative to the inorganic carbon source during algal photosynthesis. We wish to suggest, therefore, that because of significant differences in pH, water temperature, CO<sub>2</sub> concentration, and possibly also growth rate of precursor organisms, the kerogens from the two evaporitic rocks studied were originally isotopically heavier than the organic matter deposited in synchronous, deeper-water marine sediments. Behrens and Frishman (1971) have described a similar situation in Baffin Bay, Texas, where Holocene organic carbon in lagoonal (inter - or supratidal) blue-green algal mats is enriched in C<sup>13</sup> by some 4 per mil compared to the organic matter preserved in marine muds of the bay.

Finally, we suggest that the results of our investigation may be pertinent to the problem of the isotopically-heavy reduced carbon in sediments of the lower Onverwacht Group, South Africa. We have recently commenced an examination of the insoluble organic matter in a collection of laminated black cherts from the Onverwacht Group, kindly provided by Dr. A.Y. Glikson (Bureau of Mineral Resources, Geology and Geophysics, Canberra). The H/C atomic ratios (range = 0.03 - 0.08, mean = 0.05) determined for kerogens isolated from seven samples of Theespruit chert (0.20 - 0.68% organic C) from three separate

localities along the Komati River in the type area (Viljoen and Viljoen, 1969), place them well over the threshold (Fig. 2) at which isotopic modification begins. By contrast, four cherts (0.11 - 0.13% organic C) from the Hooggenoeg Formation, upper Onverwacht Group, yielded kerogens with H/C atomic ratios an order of magnitude higher (range = 0.41 - 0.69, mean = 0.53). Because of its lower rank (H/C > 0.4) the Hooggenoeg organic carbon would not be expected to have sustained any appreciable metamorphic alteration to its isotopic composition, as is borne out by the results of Oehler and others (1972, fig. 2). If, as now appears feasible, isotopic alteration resulting from thermal effects of burial, regional, or contact metamorphism has occurred in the reduced carbon of the Theespruit Formation, then the anomalously high  $\delta C^{13}$  values reported by Oehler and others (1972) may be at least partly due to post-depositional alteration. Consequently, it seems to us that the usefulness of kerogen  $\delta C^{13}$  data in future palaeobiological studies will be greatly enhanced when the corresponding H/C atomic ratios are also known. Combined  $\delta C^{13}$  and H/C analyses may well afford a means of distinguishing original isotopic differences in ancient organic matter from those acquired during diagenesis.

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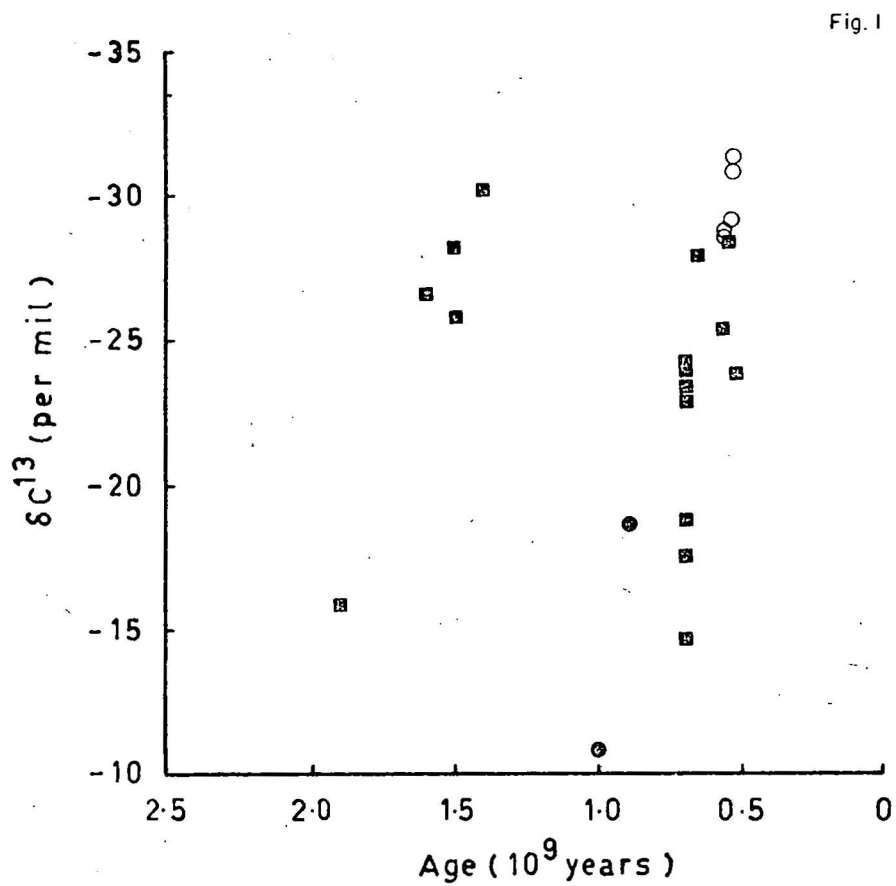
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FIGURE CAPTIONS

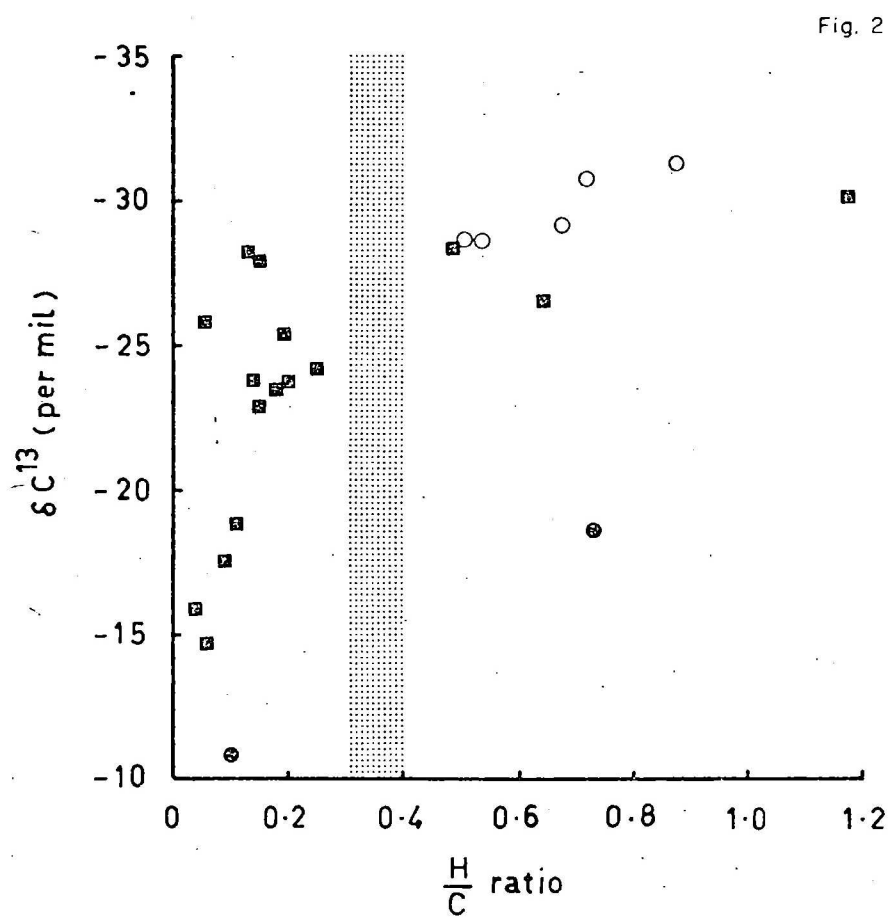
FIG. 1 Relationship between stable carbon isotopic composition and age of sedimentary organic matter. Closed squares = shale kerogen; closed circles = carbonate kerogen; open circles = carbonate total organic fraction.

FIG. 2 Relationship between stable carbon isotopic composition and rank of sedimentary organic matter. Symbols as for Fig. 1. Stippled zone represents threshold of metamorphic influence on  $\delta C_{PDB}^{13}$ .



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