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**D. Des Marais: CARBON ISOTOPE GEOCHEMISTRY  
AND GEOBIOLOGY**

The Earth's carbon cycle involves crustal reservoirs that include atmospheric CO<sub>2</sub>, oceanic inorganic and organic carbon, carbon in sedimentary organic matter such as that in shales, sedimentary carbonate, and igneous rocks. There also seems to be a relatively low but nontrivial rate of exchange between the carbon reservoir in the Earth's mantle and crustal carbon.

Certain processes moving carbon between these reservoirs are isotopically selective. Photosynthetic carbon fixation produces organic matter which can be between 0.3 and 3 percent depleted in <sup>13</sup>C relative to sources of inorganic carbon (Degens, 1969; Deines, 1980). This preference for <sup>12</sup>C is principally due to catalysis in the first step of carbon dioxide fixation (e.g., the Calvin cycle enzyme ribulose biphosphate carboxylase; Estep, 1978). The amount of fractionation is often attenuated by processes which transport inorganic carbon to cellular cytoplasm (e.g., O'Leary, 1981). The respiration of organic carbon is also associated with a discrimination against <sup>13</sup>C. The carbon dioxide produced is typically depleted between 0 and 1.2 percent in <sup>13</sup>C relative to the organic carbon source (De Niro, 1977; Kaplan and Rittenberg, 1964).

The organic carbon buried in sediments can be isotopically fractionated by sulfate reduction (Fuchs, 1979). Work in our laboratory has shown that even fermentation can produce striking discrimination against the <sup>13</sup>C isotope.

More deeply buried organic carbon becomes progressively more reduced by thermal decomposition. If this carbon is heated to several hundred degrees Celsius, it can be converted to graphite. The <sup>13</sup>C content of this residual organic matter changes very little until its elemental carbon to hydrogen ratio falls below 0.2 (Schopf, 1983). Below 0.2 the residual carbon becomes more <sup>13</sup>C-enriched. Because the <sup>13</sup>C value of sedimentary carbon is so well preserved, we are assured that the <sup>13</sup>C values in the better preserved sedimentary rocks as old as 3.5 billion years reflect ancient microbial processes.

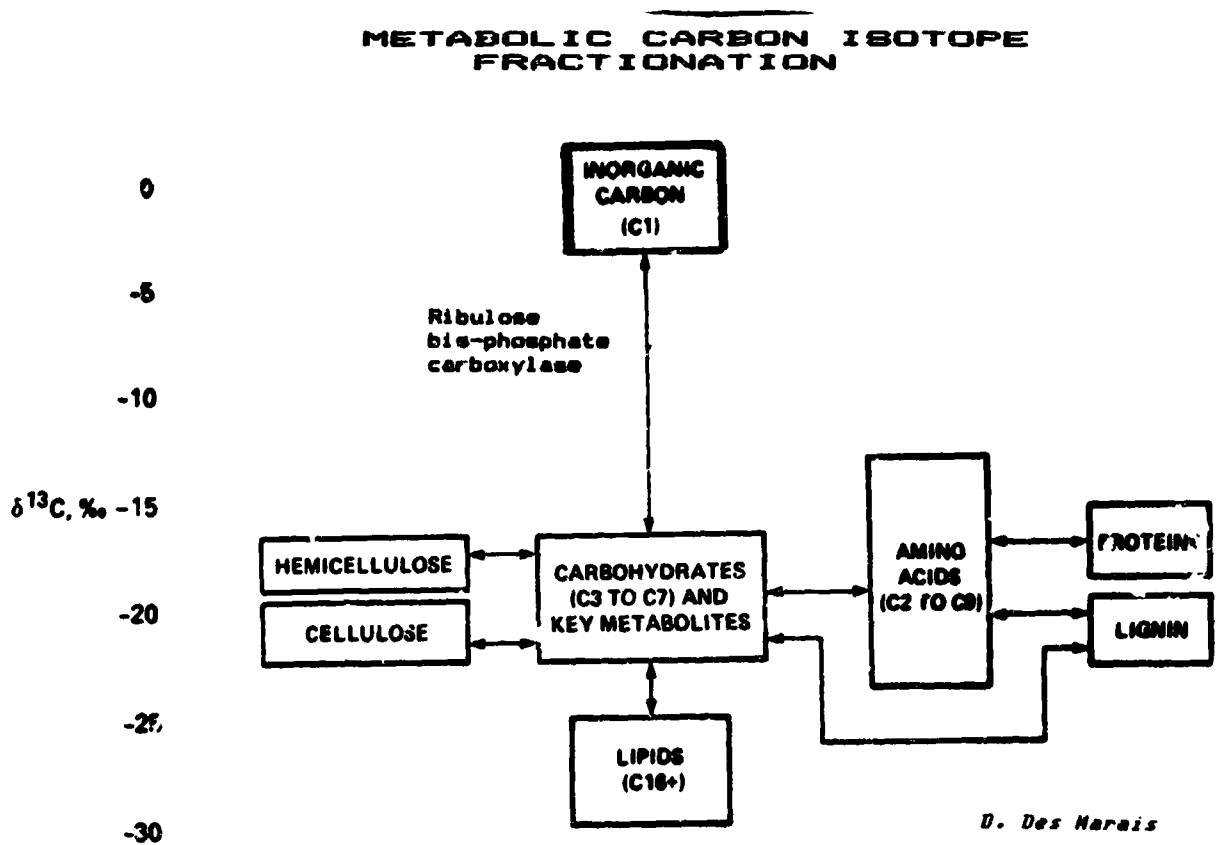
Carbon issuing from the midocean ridges is about 0.6 percent depleted in <sup>13</sup>C relative to marine carbonates, and about 2 percent enriched in <sup>13</sup>C relative to sedimentary organic carbon (Des Marais and Moore, 1984). This midocean ridge carbon represents the largest single carbon flux from the mantle, and its isotopic composition is the same as the average of all the crustal reservoirs. The crust/mantle exchange of carbon was more intense during the early Precambrian Eon and, very likely, the crust had a larger carbon inventory then than now (see Des Marais' article in Sundquist and Broeker, 1984).

Carbon isotope fractionation values have been used to understand the history of the biosphere. For example, plankton analyses confirmed that marine extinctions at the end of the Cretaceous period were indeed severe (see Hsu's article in Sundquist and Broecker, 1984). Variations in the isotopic compositions of carbonates and evaporitic sulfates during the Paleozoic might reflect the relative abundances of euxinic (anoxic) marine environments and organic deposits from terrestrial flora (Berner and Raiswell, 1983). The carbon isotopic composition of Precambrian sediments suggest that the enzyme ribulose biphosphate carboxylase has existed for perhaps 3.5 billion years (Schopf, 1983). Future work in our laboratory seeks to elucidate the relationship between the carbon isotopic composition of stromatolites, atmospheric CO<sub>2</sub>, and oxygen inventories.

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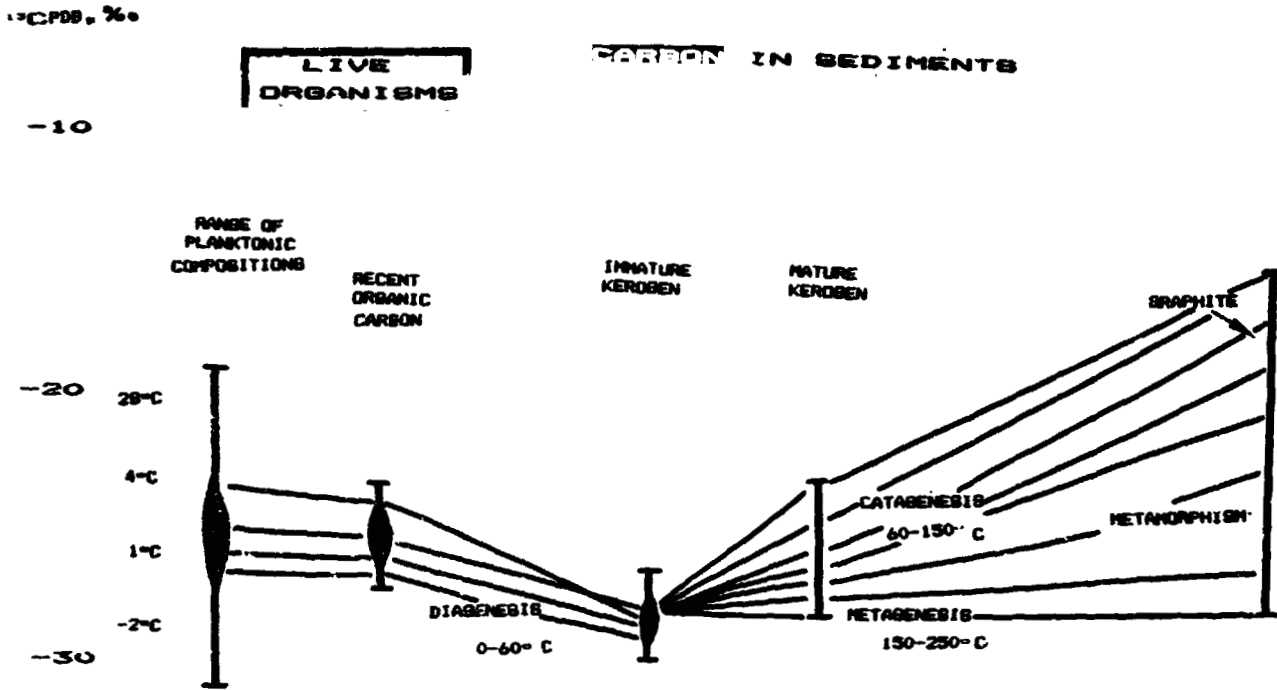
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Figure I-3. Metabolic carbon isotope values for classes of biological compounds as determined by mass spectrometry.



**CARBON ISOTOPE FRACTIONATION  
VALUES IN LIVE ORGANISMS  
AND SEDIMENTS**

Summary of the range of values



**PROCESSING OF SEDIMENTARY CARBON**

modified from Hayes, J.N., et al., 1983 in Schopf,  
*The Earth's Earliest Biosphere*

Figure I-4. Carbon isotope fractionation values in live organisms and sediments. The  $\delta^{13}\text{C}$  values are a function of temperature in live marine organisms, and these values are altered by temperature alteration in sediments.

# EARTH'S ISOTOPIC CARBON CYCLE

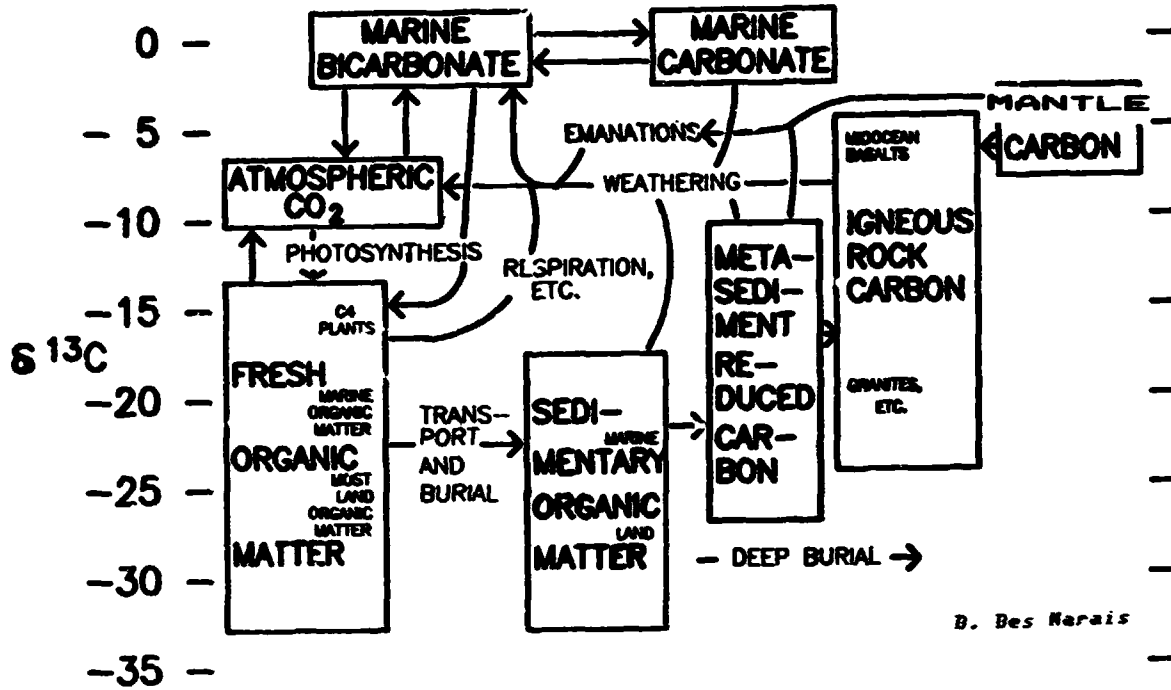
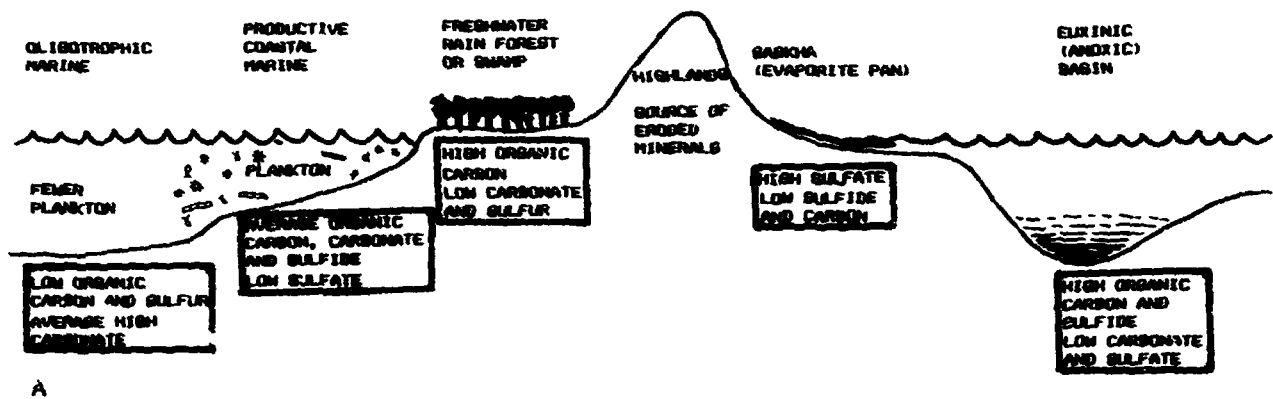


Figure I-5. Carbon isotopic fractionation ranges for extant carbon samples from terrestrial sources. Delta  $^{13}\text{C}$  scale at left, boxes represent major reservoirs, arrows represent major processes that transport and convert the carbon between the reservoirs.

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ENVIRONMENTS FOR THE DEPOSITION  
OF CARBON AND SULFUR



A

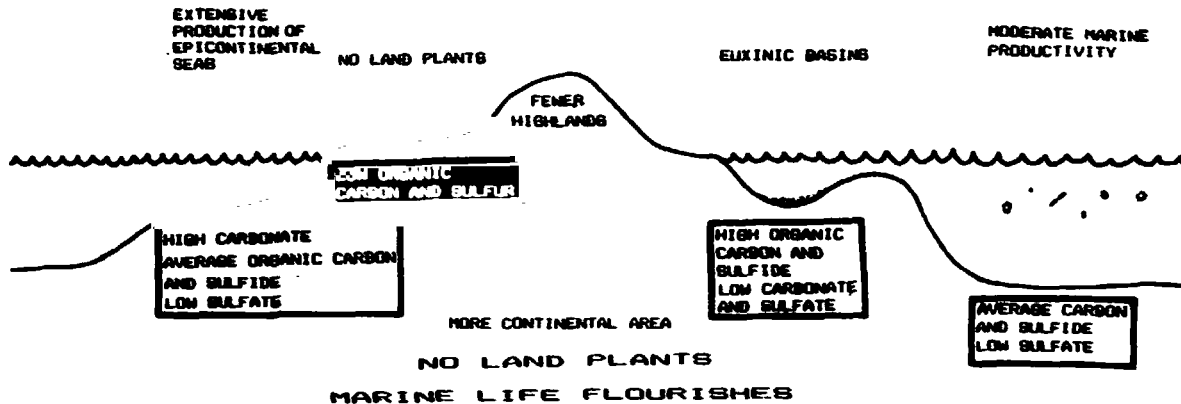
Des Meris based on hypothesis  
of Berner and Raiswell, 1983

Figure I-6. Reconstruction of the extent of depositional environments based on carbon and sulfur isotope fractionation measurements from ancient sedimentary rocks.

- A. Major extant environments where sulfur and carbon compounds are sedimented indicating the relative distribution now.
- B. Environmental reconstruction of the Cambrian Period based on interpretations of carbon and sulfur isotope data.
- C. Environmental reconstruction of the Permian Period based on interpretations of carbon and sulfur isotope data.

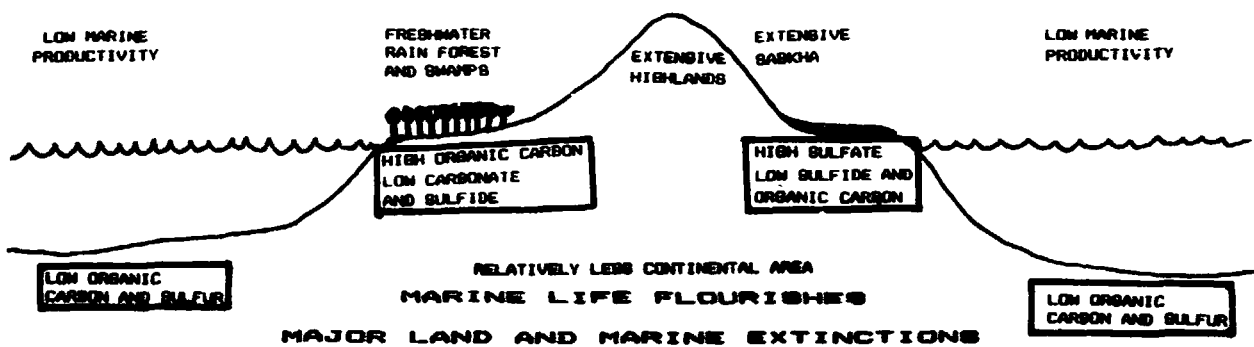
**CAMBRIAN TIME 540 MILLION YEARS AGO**  
 Sulfates with high  $\delta^{34}\text{S}$   
 Carbonates with low  $\delta^{13}\text{C}$

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B

**PERMIAN TIME 190 MILLION YEARS AGO**  
 Sulfates with low  $\delta^{34}\text{S}$   
 Carbonates with high  $\delta^{13}\text{C}$



C

*Des Narais based on hypothesis of Berner and Raiswell, 1983*