Biological versus abiological mechanisms explaining isotopically heavy Isua organic matter

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The anomalously heavy organic carbon from Isua rocks of 3.8 billion years ago has been explained as an artifact of metamorphism (Schidlowski, 1988). The $\delta^{13}C$ value of -13.0 ± 4.9‰ does not fit within the $\delta^{13}C$ values 'characteristic' for biological debris (Hayes, 1996). The relatively small ^{13}C content of organic matter considered 'typical' for biological CO_2 fixation is based on the assumption that the Calvin cycle is the major CO_2 fixation pathway and that other carbon fixation pathways with different carbon isotope fractionation effects have played a minor role in the Earth's history. However, assuming that the Isua organic matter is of a Calvin cycle origin the effect of metamorphism on the ^{13}C content of the organic matter must have been large, an increase of more than 10‰. Recently the effect of metamorphism on the ^{13}C content of organic matter is being discussed and an increase in ^{13}C of 2–3‰ due to metamorphism has been suggested (Watanabe *et al.*, 1997; DesMarais, 1997). This implies that the $\delta^{13}C$ value of the original Isua organic matter of -15 to -16‰.

Based on analyses of organic matter produced by green non-sulphur bacteria preserved in modern laminated microbial mat systems resembling stromatolites, a biological alternative for the heavy organic matter in the Isua formation is suggested. The organic matter produced by these bacteria, representing an early divergence from the tree of life, is substantially enriched in ^{13}C relative to organic matter assimilated via the Calvin cycle. *Chloroflexus aurantiacus*, such a green non-sulphur bacterium, uses the 3-hydroxypropionate pathway for carbon fixation (Holo and Sirevag, 1986). This pathway

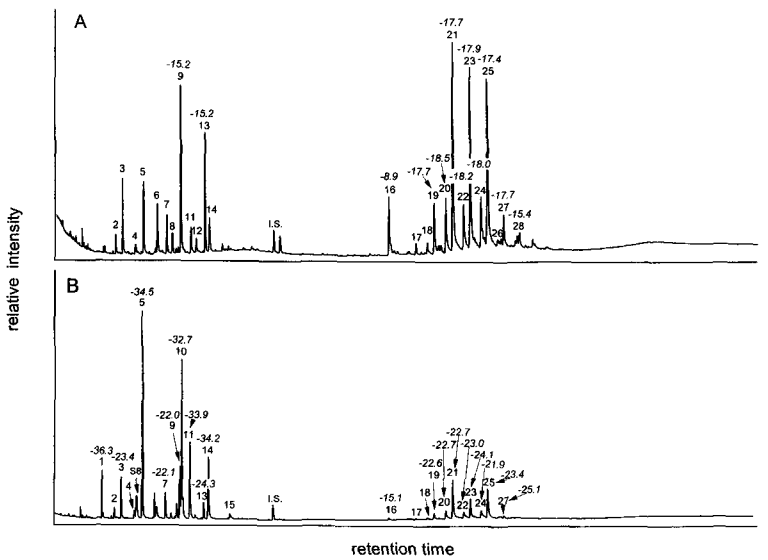

FIG. 1. Lipid distribution of the total extracts of the 'New Mound Annex' source (a) and downstream (b) mats. The numbers 1 to 28 relate to the lipids summarised in Table 1.

TABLE 1. Summary of different lipids found in the NMA source and downstream mat and their ^{13}C contents including standard deviations

Compound	Nr.	$\delta^{13}C$ (‰) Source (Fig. 1A)	$\delta^{13}C$ (‰) Downstream (Fig. 1B)
Bulk		−14.9 (0.0)	−23.5 (0.5)
n-C_{17} alkane	1		−36.3 (0.2)
i-$C_{15:0}$ fatty acid	2		
$C_{15:0}$ fatty acid	3		−23.4 (3.3)
i-$C_{16:0}$ fatty acid	4		
$C_{16:0}$ fatty acid	5		−34.5 (1.4)
n-$C_{16:0}$ alkanol	6		
$C_{17:0}$ fatty acid	7		−22.1 (0.6)
i-$C_{17:0}$ alkanol	8		
n-$C_{17:0}$ alkanol	9	−15.2 (0.3)	−22.0 (0.4)
$C_{18:1}$ fatty acid	10		−32.7 (1.8)
$C_{18:0}$ fatty acid	11		−33.9 (0.2)
i-$C_{18:0}$ alkanol	12		
n-$C_{18:0}$ alkanol	13	−15.2 (0.4)	−24.3 (0.8)
$C_{19:1}$ fatty acid	14		−34.2 (1.1)
$C_{20:1}$ fatty acid	15		
$C_{31:3}$ alkatriene	16	−8.9 (0.3)	−15.1 (0.1)
C_{30} wax ester	17		
i-C_{31} wax ester	18		
C_{31} wax ester	19	−17.7 (0.8)	−22.6 (2.0)
i-C_{32} wax ester	20	−18.5 (0.7)	−22.7 (0.4)
C_{32} wax ester	21	−17.7 (0.7)	−22.7 (1.0)
i-C_{33} wax ester	22	−18.2 (0.5)	−23.0 (1.5)
C_{33} wax ester	23	−17.9 (0.6)	−24.1 (0.3)
i-C_{34} wax ester	24	−18.0 (0.4)	−21.9 (0.3)
C_{34} wax ester	25	−17.4 (0.6)	−23.4 (0.0)
i-C_{35} wax ester	26		
C_{35} wax ester	27	−17.7 (1.0)	−25.1 (0.8)
C_{36} wax ester	28	−15.4 (0.5)	

discriminates less against ^{13}C.

The bulk ^{13}C content of the Yellowstone hot spring New Mound annex source mat consiting of *Chloroflexus* spp. is −14.9‰. Based on previous studies of the lipids of *Chloroflexus* (Shiea *et al.*, 1991), it was possible to determine the isotopic signatures of specific biomarkers produced by this type of organism using isotope-ratio-monitoring GC-MS (irm-GC-MS). For example, the $\delta^{13}C$ values for hentriacontriene ($C_{31:3}$ alkatriene) and $C_{31\ to\ 36}$ wax esters are −9 and −18‰, respectively (Table 1, Fig. 1a).

We presume that the differences in isotopic composition reflect differences in biosynthetic pathways by which these compounds are produced. In contrast, the bulk ^{13}C contents of the downstream mat consisting of *Chloroflexus* spp. and cyanobacteria is −23.5‰. The cyanobacterial biomarkers, *n*-C_{17} alkane and *n*-C_{16} and *n*-C_{18} fatty acids, have $\delta^{13}C$ values of −36, −34.5 and −33.9‰, respectively (Table 1, Fig. 1b). In this downstream mat the $C_{31:3}$ alkatriene and $C_{31\ to\ 36}$ wax esters have $\delta^{13}C$ values of −15 and −23‰, respectively. The lighter values for *Chloroflexus* biomarkers in the downstream mat compared to those of the source mat presumably result from cross-feeding of cyanobacterial fixed carbon. However, the ^{13}C values of the *Chloroflexus* biomarkers are much heavier than those of the cyanobacterial biomarkers. Apparently, a significant amount of *Chloroflexus* autotrophy via the 3-hydroxypropionate pathway also occurs in the presence of cyanobacteria. This might be due to the presence of residual sulphide.

Based on the early divergence of green non-sulphur bacteria from the tree of life it can be concluded that the 3-hydroxypropionate pathway evolved before the Calvin cycle. This provides not only a biological explanation for isotopically heavy organic matter from the Archaean but also shows that organic matter does not have to be isotopically light to be considered 'biological debris'.

Our results thus strongly indicate that Isua organic matter is of biological origin, thereby stretching the record of life on Earth to 3.8 billion years ago.

References

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