Anomalous Carbon-Isotope Ratios in Nonvolatile Organic Material

Abstract. *Organic mats are associated with sulfur deposits in Upper Pleistocene sand ridges of the coastal plain of southern Israel; black, brittle, and nonvolatile, they show parallel layering but no other apparent cellular structure. Two independent carbon-14 determinations yielded ages of 27,750 ± 500 and 31,370 ± 1400 years. Four carbon-13:carbon-12 determinations fell within the range* $\delta C^{13} = -82.5$ *to* -89.3 *per mille relative to the PDB standard; these appear to be the lowest values yet reported for naturally occurring high-molecular-weight organic material. The origin of the carbon is probably complex; it must have passed through at least one biologic cycle before final deposition.*

The origin of an elemental sulfur deposit in Upper Pleistocene sand dunes near Beeri, Israel (7 km east of the Mediterranean, near the Gaza strip), has been discussed (*1*). The sediments in the area are permeated by elemental sulfur, some of which has oxidized to sulfuric acid and produced a *p*H of 1.0 or lower in some instances. This acidity has probably caused the leaching of carbonate, which is the normal cementing agent in similar Pleistocene sand ridges elsewhere along the Mediterranean coast. Quartz grains in this deposit are coated by organic matter, which often acts as a cementing agent.

Certain sediment horizons contain a brittle organic mat, distributed three-dimensionally in the sediment section in which it is found (Fig. 1); this material was studied during determination of the origin of the sulfur deposit, and we now report the surprising $C^{13}:C^{12}$ ratios obtained.

The mats appear as black, brittle layers, generally 1 to 5 mm thick. It is difficult to estimate their lateral continuity in the sediment beds, but they appear as irregular patches in an area of 2 km^2 and a sediment bed 4 to 5 m thick. Three gross features are striking: interbedding with the silt-sand matrix (Fig. 1*a*), close association with elemental sulfur (Fig. 1*d*), and a double-edged appearance (Fig. 1*b*) that seems to derive from layers of organic matter curling at the edges. In a horizontal plane, the mats show a preferred orientation in a polygonal pattern, similar to mud cracks, strongly resembling descriptions of dried algal mats from the Persian Gulf (*2*). A thin section of a mat, cut at right angles to the large surface, is shown in Fig. 1*c*; evidently there is some layering. So far we have failed to detect cell structure or obtain interpretable electron-microscope photographs.

Table 1 reports elemental analysis of the mats; neither benzene nor sodium hydroxide appeared to extract any significant quantity of soluble component. The originally deposited organic matter was probably subsequently altered by leaching by the sulfuric acid present in the sediment.

Four independent analyses for carbon-isotope ratios (*3*) returned δC^{13} values of −82.5, −84.5, −89.3, and −84.7 per mille relative to the PDB standard. Organic matter extractable from the sandstone with benzene and methanol and with sodium hydroxide gave δC^{13} values ranging from −75 to −85 per mille. One deuterium:hydrogen determination (*4*) yielded D = −15 percent relative to the SMOW standard; this value appears to correspond with fractionations performed by plants and algae living in coastal lagoons (*5*). In contrast, the δC^{13} values appear to be the most negative yet reported for a solid, nonvolatile organic material.

One acceptable explanation of the organic mats, as well as of the organic material coating the sand grains, would be seepage of petroleum; seepage could involve vertical migration into the very porous rocks, as liquid or light gases, with subsequent polymerization. The gases could originate from thermal cracking of hydrocarbons at depth, which would also markedly enrich the liberated gases in C^{12} (*6*). Two measurements of carbon-14 age were therefore made on the mats. One (*7*) gave 27,750 ± 500 years; the other (*8*), 31,370 ± 1400 years. In both samples the amount of relatively young carbon present was strong evidence against a direct origin from oil seepage.

Values for $C^{13}:C^{12}$ in nature (*9*) indicate that biologic fractionation can result in enrichment of the light isotope in the metabolic products as well as the cellular components. Detailed study (*10*) has shown, however, that algae enrich C^{12} by 10 to 12 per mille

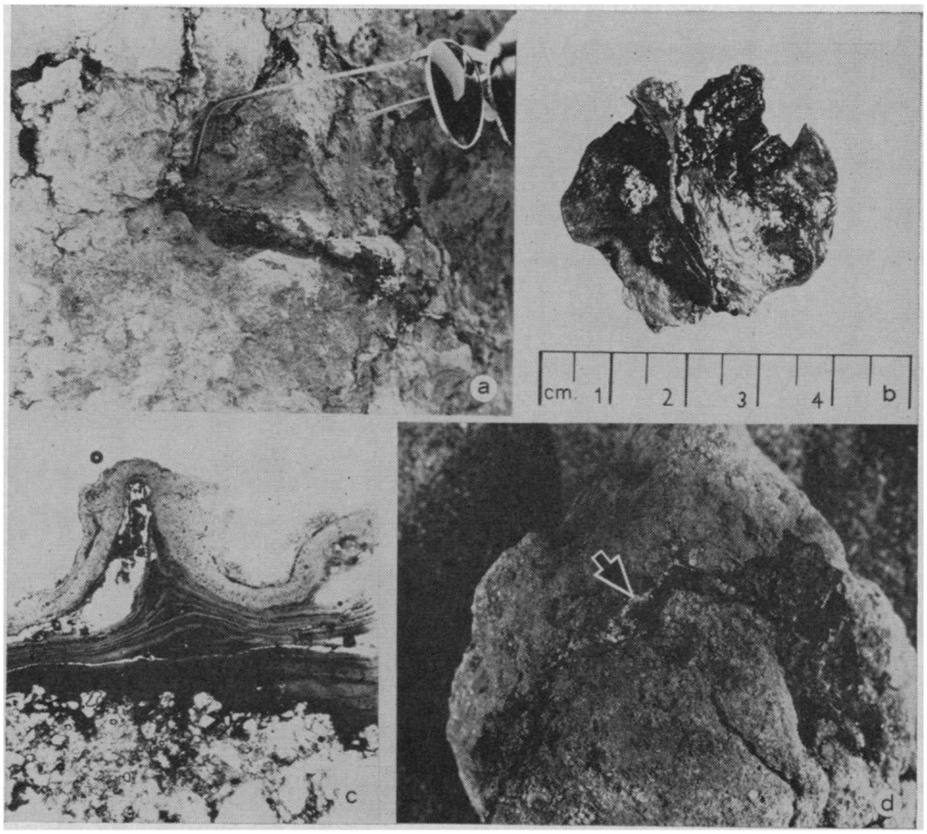

Fig. 1. Organic mats, showing (*a*) pseudopolygonal distribution of organic mats in sandstone (vertical view), (*b*) double-edged nature, (*c*) thin section (transmitted light, × 40), and (*d*) sulfur (arrow) association.

Table 1. Two elemental analyses of organic mat. Oxygen determined by difference; no halogens were detected.

Element (%)				
C	H	N	S	O
58.65	7.45	0.73	8.67	24.50
59.77	7.85	.70	8.60	23.08

and vascular plants do so by 20 to 30 per mille relative to the starting CO_2. Thus, no single-step photosynthetic process could have produced the measured enrichments. Methane bacteria can effect fractionations of $\delta C^{13} = -67.5$ per mille during the degradation of methanol to methane under laboratory conditions (*11*); the carbon dioxide produced during this process was depleted in C^{12} relative to the starting methanol.

Thus it appears that a mat is the end member of a series of transformations in which several fractionation steps have occurred. We consider two possibilities:

1) The release along fissures of methane, from either petroleum or gas reservoirs, or related to thermal activity; oxidation of this methane to carbon dioxide, and its subsequent fixation either photosynthetically by lagoonal algae and bacteria or chemosynthetically by sulfur-oxidizing bacteria.

2) Release of carbon dioxide at the bottom of a lagoon during anaerobic decomposition of algal and terrestrial plant remains; photosynthetic fixation of this CO_2 at the surface, and recycling.

In either case, dilution by dissolved and atmospheric carbon dioxide would occur. The C^{14} ages determined demand that such dilution occurred if step 1 was operating.

Our results point strongly to derivation of both the fractionation and organic material from vital processes *in situ*. It is further suggested (*1*) that these processes are also responsible for the high concentration of elemental sulfur localized in this area. It is obvious, however, that a complex set of conditions may have prevailed. The ability to test such relatively young material points to the dangers of offering interpretations of isotope ratios of old organic matter where single-step fractionations are invoked.

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Radio Sources: Angular Size from Scintillation Studies

Abstract. *The frequency spectrum of fluctuations caused by interplanetary scintillations may give a sensitive estimate of the diameter of a radio source. Observations of 3C 138, 3C 245, 3C 267, and 3C 273 give diameters of 0.1, ≤ 0.04, ≤ 0.2, and ≤ 0.02 second of arc, respectively. Resolution is at least a factor of 5 higher than that obtained to date by means of either radio interferometers or lunar occulations.*

A radio source may scintillate when observed close to Sun because the rays are diffracted by irregularities in the solar wind. These interplanetary scintillations (*1*) occur only for very narrow sources because a wide source produces overlapping fluctuation patterns on the ground and the net fluctuations are smoothed out (*2*).

Suppose the scintillations are produced in a layer of thickness $L << z$, where z is the distance from Earth (Fig. 1). A source consisting of two points separated by θ produces patterns separated laterally by θz. A source spread continuously through the angle θ produces a smearing over distances θz. If the scale S of the diffraction pattern caused by the irregularities themselves (the point-source pattern) is much greater than θz ($S/\theta z >> 1$), the source behaves as a point source. If $S/\theta z << 1$, there are no scintillations.

In intermediate cases, the pattern is the convolution of the point-source pattern with the brightness distribution of the source. If S is known, limits can be placed on the diameter of a source according to whether or not it scintillates (*1, 2*). A much more sensitive estimate, however, can be obtained by measuring the scintillation spectrum.

Figure 1 shows that all Fourier components with wavelength shorter than about $2\theta z$ are smoothed out. If the screen is moving parallel with itself with velocity u, the diffraction pattern also moves with velocity u. An observer at a fixed station sees the pattern as a function of time, and the frequency spectrum is cut off at $f_c \approx u/(2\theta z)$. If the cutoff frequency can be measured,

Table 1. Details of four radio sources (see text). Int, interferometer; occ, occulation; ct, component(s).

Source	Diameter (sec)	Relative strength	Posn. angle (deg)	$\Delta\lambda/\lambda_0$	Linear diameter (parsec)	Remarks
3C 138	~0.1	0.8 (195)	015			Int: ~ 0″.5 (*11*)
3C 138		.7 (430)				
3C 245	< .04	> .3 (430)	145	1.029 (*5*)	<145	Int: > 12″ (*6*); occ: ct < 0″.5 (12)
3C 267	< .2	> .3 (430)	037			Int: ~ 47″ (*13*); < 0′.7 (*14*)
3C 273	< .02	.2 (195)	160	0.158 (*10*)	< 34	Int: ct < 0″.1 (*6*); occ: ct < 1″ (*15*); ct < 0″.15 (*7*)
3C 273		.3 (430)				
3C 273		> .3 (611)				