

ORGANIC DOLOMITE FROM POINT
FERMIN, CALIFORNIA

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ABSTRACT

Petrography and stable carbon isotope data indicate that small dolomite rhombohedra that occur with tar as cement in some California Miocene sands were partially derived from the alteration of the tar or other organic matter. The dolomite cement occurs in blue-schist turbidite sandstones that are exposed in sea cliffs at Point Fermin, Los Angeles County, California. The euhedral crystals are attached to sand grains and are also apparently embedded in the tar cement. The dolomite crystals have several types of nuclei: (1) rhombohedral to spherical tar globules similar to the tar surrounding the euhedra, (2) gaseous bubbles, and (3) combinations of these. Carbon isotope values of the rhombohedra indicate that the carbonate in the dolomite was partially derived from oxidation of organic matter. The dolomite probably crystallized around oil or tar droplets and carbon dioxide bubbles that were produced as discontinuous phases during the oxidation of the organic matter. The rhombohedra exhibit unusual growth habits related to the symmetry. Complex apical grooves rather than simple dihedral edges are developed along the six rhombohedral edges that intersect the *c*-axis. In addition to tar and dolomite, the cement complex in these sandstones contains sparry calcite and a zeolite mineral, clinoptilolite.

INTRODUCTION

Recent geochemical and mineralogical evidence indicates that organic and inorganic geological materials are not necessarily independent of each other and thus cannot be considered as separate and unrelated entities. Isotope geochemistry and clay mineralogy have shown in the past few years that organic and inorganic substances can be intimately and systematically intermixed. In an increasing number of occurrences, co-existing "so-called" organic and inorganic materials have proven to be genetically related and we might anticipate that detailed isotope studies will reveal many more such hybrid organic-inorganic substances. Organosilicate complexes and several types of carbonate derived directly from organic material are examples of different types of mergence of organic and inorganic substances. Dolomite rhombohedra formed partially from carbon dioxide derived from the oxidation of bitumen were revealed in a petrographic study of Miocene sandstones of the Los Angeles Basin. The rocks are well exposed in the sea cliffs at Pt. Fermin in San Pedro, California, near the Los Angeles-Long Beach Harbor area.

This occurrence of organic carbonate is described in detail here because microscopy of the dolomite in tar sands provides evidence on the physico-chemical mechanisms of the formation of carbonates from oil. Another unique characteristic of the Pt. Fermin dolomite is the unusual crystal habit. It is possible that there is a genetic relationship between

the modified rhombohedral habit and the organic influence in carbonate deposition but this is impossible to determine on the basis of one occurrence.

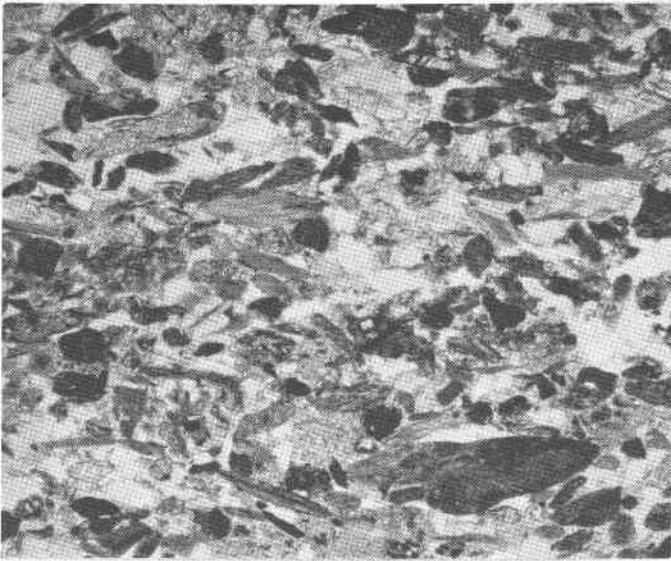
A similar occurrence of dolomite enclosing globular hydrocarbon nuclei is described by Osipova (1964) from Paleogene carbonate rocks in the northeastern part of the Fergana Depression in the Kara-Dar'i area of Central Asia. Osipova observed that dolomite grains that form the linings of cavities grew around petroleum microglobules and thus were formed later than the petroleum. Diagenesis in these carbonate rocks is enhanced by the presence of petroleum and the associated waters which are rich in carbon dioxide.

MINERALOGY AND PETROGRAPHY

The dolomite occurs as cement embedded in tar in the pores of an unusual sandstone or schist arenite in the Altamira sand member of the Monterey Formation. The sandstone (Fig. 1) consists predominantly of low grade metamorphic rock fragments derived from the Catalina schist facies of the Franciscan Series. These rock and mineral fragments include glaucophane, epidote, lawsonite, fibrous glaucophane schist, quartz-glaucophane schist, chlorite schist, quartzite, lawsonite schist, epidote-albite schist, and various combinations or gradations among these rock types. Quartz and feldspar are the other principal grain types in the sandstone and these minerals account for approximately 10–20 per cent of the rock (Fig. 1).

The dolomite crystals are rhombohedral and occur as disseminated individual rhombs and aggregates. The crystals range up to 0.10 mm on the rhombohedral edge with an average edge length of approximately 0.045 mm. In thin section, most of the dolomite rhombs are attached to the sand grains although there are many grains that appear to be unattached and "floating" in the tar that fills many of the pores. Textural evidence indicates that the dolomite has crystallized in fluid-filled pore space exclusively and has not replaced any of the preexisting mineral constituents of the sandstone. Some pores contain several rhombohedra that project inward from the pore walls and have been subsequently filled with a zeolite, clinoptilolite. Portions of the sandstone are also cemented by sparry calcite and veins transverse to bedding are also calcite-filled. Clinoptilolite occurs with both types of carbonate cement; however, dolomite has not been observed adjacent to calcite.

The dolomite is colorless to very light brown; the color is apparently due to hydrocarbon inclusions. The refractive indices are $\omega=1.678 \pm 0.002$ and $\epsilon=1.506 \pm 0.002$ ($\omega-\epsilon=0.172$). No zonation was observed, and there are no twin lamellae. The dolomite does not show wavy ex-



1.0 mm

1



0.1 mm

2

inction or curvilinear crystal faces that are characteristic of many types of dolomite.

The most unique petrographic property of the dolomite is the presence of hydrocarbon and gaseous nuclei that occur in most of the grains. The discovery of the abundant nuclei first led us to suspect a genetic relationship between the carbonate and the hydrocarbons. There are three types of nuclei; (1) small globular to rhombohedral masses of tar and (2) gaseous inclusions or nuclei and (3) combinations of these (Fig. 2). The tar nuclei are the larger of the two types and range up to 0.03 mm in diameter. The tar masses usually represent approximately one tenth of the volume of the crystal and the masses are commonly centrally located in the grains. The shape ranges from perfectly spherical to irregularly globular to rhombohedral. The rhombohedral tar masses could be described as negative crystals of dolomite filled with tar. The gaseous inclusions which are interpreted as carbon dioxide bubbles derived from the oxidation of organic material also range in shape from spherical to rhombohedral. These gaseous nuclei or inclusions are also located near the centers of the crystals but they tend to be smaller in size and more predominantly and perfectly spherical than the tar nuclei. A small per cent of the rhombohedra contain compound nuclei consisting of a tar globule and a gas bubble that is attached or enclosed in the tar (Fig. 2, Nos. 3 and 6). Dolomite rhombohedra with the presumed gaseous nuclei were dissolved under the microscope. The nuclei were observed to rise to the top of the acid and disappear just as the carbon dioxide produced by acidization, thus indicating that the nuclei are gaseous.

In thin section, approximately half the crystals contain nuclei; however, the actual percentage is considerably higher because a random thin section could not intersect nuclei in every case. Grain mounts of dolomite separated by disaggregation and heavy liquids indicate that approximately 75 per cent of the dolomite rhombohedra contain observable tar or gaseous nuclei. It seems likely that submicroscopic globules and bubbles may also have served as nucleation centers, thus possibly accounting for the small per cent of rhombohedra without observable nuclei.



FIG. 1. Photomicrographs of Altamira Sandstone, a schist sandstone cemented with tar, organically derived dolomite and locally with calcite and clinoptilolite. No. 1 Sand grains consist of several types of schist and minor quartz and feldspar. Matrix consists of tar and dolomite. Plane polarized light. No. 2 Tar-filled pores of schist sandstone with fine grained rhombohedral organic dolomite and clinoptilolite (C).

The crystal habit is modified rhombohedral $r\{100\}$. The modifications of the regular rhombohedron are such that the six normal dihedral edges leading to or intersecting the c -axis are actually grooves or trenches or a series of trenches bounded by $r\{100\}$ planes or crystal faces. This habit is illustrated in Fig. 3. There are therefore two types of unique views in thin section and grain mounts as a result of this crystal habit (Fig. 4). One consists of a lensoid section with the apparent rounding due to the grooves or trenches on the apical edges of the rhombs. The other unique cross-section is the view down the c -axis which is a hexagon modified by three to six notches related to the apical grooves or trenches.

X-ray diffraction spectrometry indicates that the organic dolomite is ideal dolomite as defined by Goldsmith and Graf (1958). Ideal dolomite approximates 1:1 molar $\text{CaCO}_3:\text{MgCO}_3$ in composition and Goldsmith and Graf have shown that non-ideal dolomite with an excess of a few mol per cent CaCO_3 has weakened order reflections relative to the ideal or stoichiometric dolomite. The x -ray diffraction pattern for Pt. Fermin dolomite is shown in Table 1. The spacings and relative intensities were determined with an x -ray diffractometer, using Ni-filtered Cu radiation and hand ground packed-pellet samples prepared from essentially pure dolomite separations obtained through heavy liquid and magnetic separator techniques.

Diffractometer traces for Pt. Fermin dolomite compare closely with those for ideal dolomite from Gabbs, Nevada and Binnental, Switzerland reported by Goldsmith and Graf (1958). The data in Table 2 indicate this comparison for selected diffraction lines. The $\{10\bar{1}\}$ and $\{11\bar{2}\}$ are sets of planes parallel to the c -axis; $\{222\}$ and $\{444\}$ are sets of planes perpendicular to c . The reflection labelled $\{01\cdot5\}$ is an order reflection. The two reflections from $\{444\}$ and $\{11\bar{2}\}$ are both sharp and of equal intensity which is also characteristic of ideal dolomites.

ISOTOPE GEOCHEMISTRY

The mode of occurrence of the dolomite rhombs, especially their close association with organic matter in the rock suggested that the dolomite



FIG. 2. Photomicrographs of dolomite rhombohedra and tar cement (brown) in schist sandstone, illustrating several types of nuclei and dolomite. No. 1. Several dolomite euhedra with spherical to irregular globular nuclei. No. 2. Subhedral rhombohedral nucleus of tar. Crystal is surrounded by tar. No. 3. Bubble nucleus which is interpreted as carbon dioxide bubble. Extremely thin "membrane" of tar surrounds bubble; nucleus is two-phase. No. 4. Two negative crystal nuclei (rhombohedral), one is tar (brown) and one is gaseous, possibly carbon dioxide (black, actually it is colorless but with extreme negative relief). No. 5. Cluster of rhombohedra with gaseous nuclei (dark bubbles) with extreme negative relief. No. 6. Two-phase nucleus consisting of relatively large tar mass and small bubble inclusion. Note glaucofane sand grain at bottom of photomicrograph.

may have been wholly or partly derived from oxidized organic matter. Evidence for this type of carbonate formation mechanism has been demonstrated by isotopic studies of carbonates from a wide range of localities (Silverman *et al.*; in press). C^{13}/C^{12} δ -values of organically derived carbonates range from -10 to -55 per mil. Primary carbonates deposited under typical marine conditions, as well as secondary carbonates formed by recrystallization of primary inorganic carbonate minerals, have a distinctly higher range of carbon isotope ratios ($+4$ to -4 per mil). This range of differences is illustrated and compared with carbon isotope ratios of organic materials in Fig. 5.

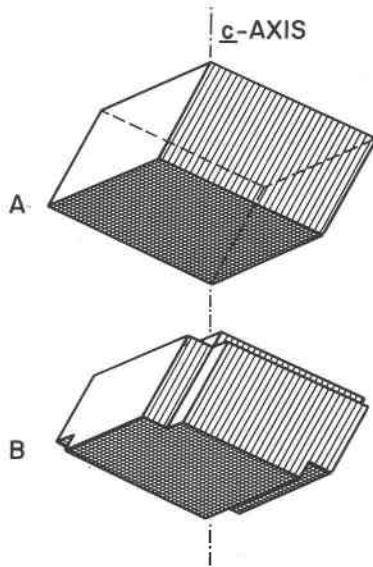


FIG. 3. Crystal habits of organic dolomite from Point Fermin, California. A. Common dolomite rhombohedral habit $r\{100\}$ which is rare at Point Fermin. B. Characteristic modified rhombohedral habit for Point Fermin dolomite with rhombohedral "grooves" along apical rhomb edges, i.e. rhombohedral edges that intersect the C -axis.

Two Pt. Fermin samples were selected for isotope analysis. One sample (Sample A) contained organic matter which was not associated with dolomite rhombs, although this specimen contained calcite cement. In a second sample (Sample B), the organic matter was associated with aggregates of rhombohedral dolomite crystals. The calcite cement and dolomite rhombs were isolated from Samples A and B, respectively. Both isolates were purified and treated in the manner described by Epstein *et al.* (1953). Carbon dioxide liberated from the purified carbonate by acid treatment was analyzed for C^{13}/C^{12} ratio by mass spectrometry. These measurements are reported as deviations (δ -values), in parts per

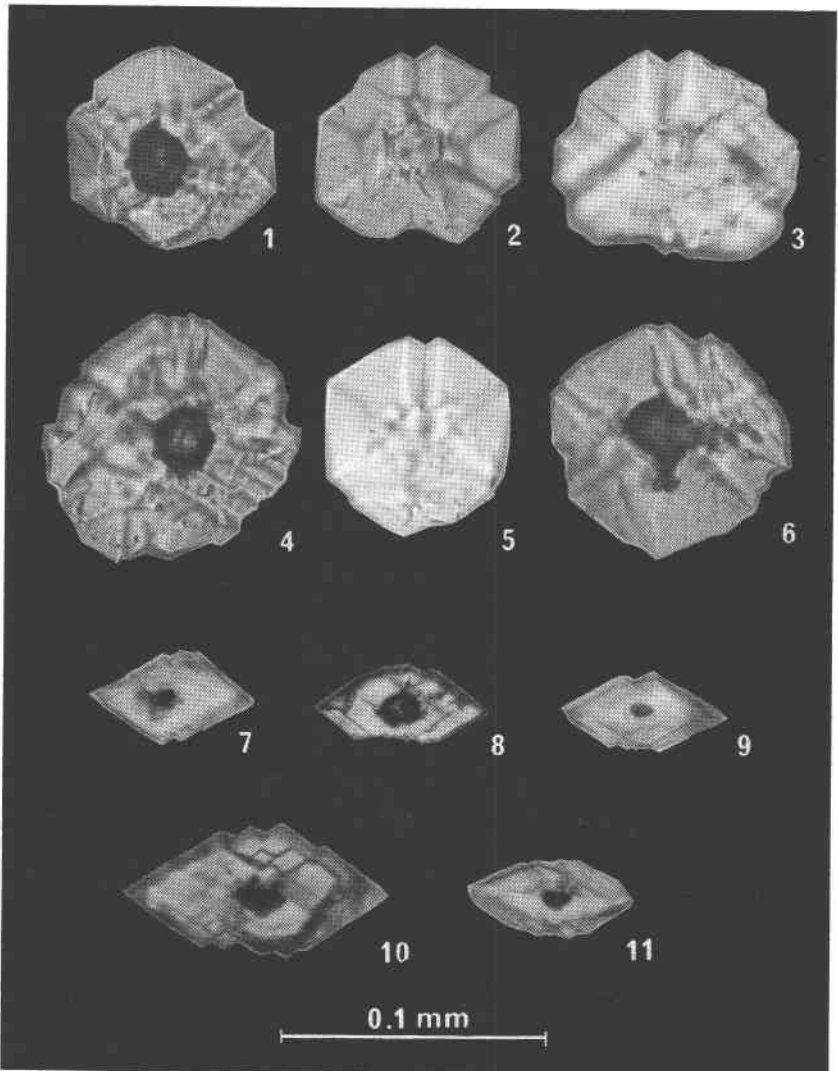


FIG. 4. Photomicrographs of organic dolomite grains illustrating unusual crystal habit. Grain mount photographs in Aroclor 4465, Nos. 1-6. Dolomite crystals oriented with *c*-axis normal to plane of photograph. Note pseudo-twin appearances and re-entrants at periphery of figures which are actually due to sets of apical edge grooves. See Fig. 3. Three crystals (Nos. 1, 4 and 6) have gaseous nuclei with extreme negative relief. Two rhombohedra (Nos. 2 and 3) have pale hydrocarbon nuclei. No. 5 shows no apparent nucleus. Nos. 7-11. Dolomite crystals oriented with *c*-axis approximately parallel to plane of photograph. "Abraded" lensoid outline is again due to prevalence of sets of apical edge grooves which have not affected non-apical edges and thus these appear with sharp points in sections with this orientation.



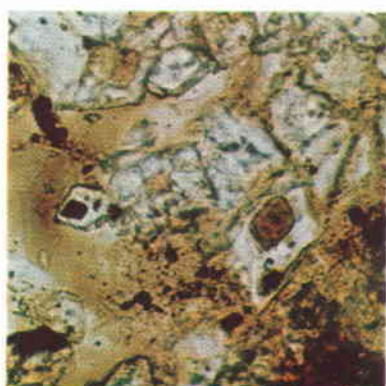
1



2



3



4



5



6

0.1 mm

TABLE 1. X-RAY DIFFRACTION DATA FOR ORGANIC DOLOMITE, PT. FERMIN, CALIFORNIA

2θ (CuK α Radiation)	d	I
10.9	4.46	VW
24.1	3.69	VW
31.1	2.87	VS
33.6	2.67	M
35.4	2.53	W
37.4	2.40	W
41.2	2.19	W
43.9	2.06	VW
45.0	2.01	W
49.3	1.85	VW
50.5	1.80	M
51.1	1.78	M
59.9	1.54	VW
63.3	1.46	VW
64.3	1.44	VW
65.0	1.43	W
67.7	1.38	W
70.3	1.33	W
72.7	1.29	VW
79.8	1.20	W

thousand (per mil), of the C^{13}/C^{12} ratio of sample from that of PDB-1 standard. Bitumen content of both samples was removed by extraction with carbon disulfide. Isotope ratios of the bitumen carbon were determined by analysis of the carbon dioxide prepared from the bitumen by

TABLE 2. COMPARISON OF SEVERAL DOLOMITE REFLECTIONS
(2θ , CuK α Radiation)

	Sets of Planes				
	{00·6}	{01·5}	{111·0}	{03·0}	{00·12}
Hexagonal Indices	{00·6}	{01·5}	{111·0}	{03·0}	{00·12}
Rhombohedral Indices	{222}	{221}	{10 $\bar{1}$ }	{112}	{444}
<i>Sample Locality</i>					
Gabbs, Nevada (Goldsmith and Graf, G-424)	33.45	35.25	37.30	67.35	70.50
Binnental, Switzerland (Goldsmith and Graf, G-1199)	33.40	35.25	37.25	67.35	70.45
Pt. Fermin, California	33.45	35.35	37.40	67.65	70.25
Levy County, Florida (Goldsmith and Graf G-371) 54.6 mol per cent CaCO $_3$	33.15	35.05	37.10	67.10	69.90

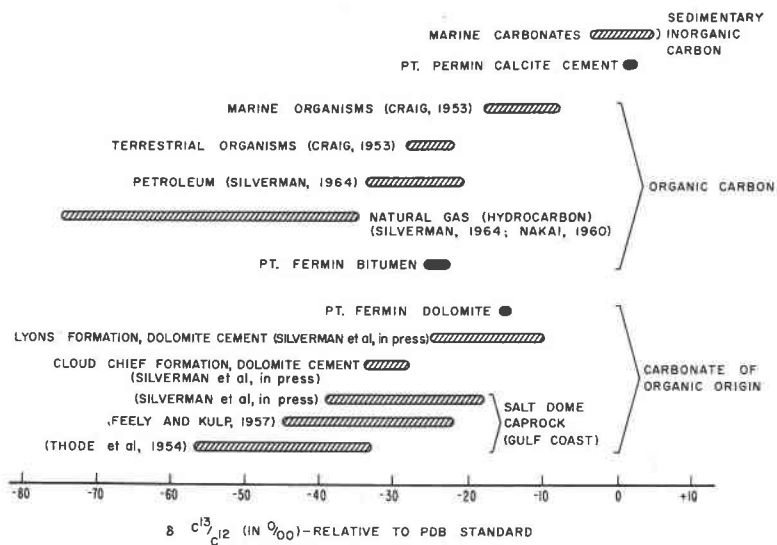


FIG. 5. Carbon isotope ratios of carbonates and organic materials.

the combustion technique described by Silverman and Epstein (1958). Results of these determinations, shown in Table 3, indicate that the δ -values of the bitumen fractions fall within the range of values noted for petroleum. The calcite fraction of Sample A is typical of inorganic marine carbonate, but the C^{13}/C^{12} ratio of the dolomite rhombs in Sample B is sufficiently lower than that of inorganic carbonate to imply that its carbon is derived, at least in part, from oxidized organic matter. Carbonate cements and vein materials from several other boulders from the same outcrop but essentially devoid of tarry material were analyzed and the isotopic compositions are typical of inorganic marine carbonate, similar to the calcite cement in Sample A.

The intimate association of organic dolomite, gaseous and tarry nuclei

TABLE 3. C^{13}/C^{12} δ -VALUES OF CARBONATE AND BITUMEN FRACTIONS OF PT. FERMIN SAMPLES A AND B

Sample	Fraction	C^{13}/C^{12} (in ‰) ¹
A	Dolomite-free Calcite Cement	+1.8
	Bitumen Fraction	-25.0
B	Dolomite Crystals	-16.4
	Bitumen Fraction	-22.9

¹ Relative to PDB-1 Standard.

in the dolomite, and the tar in which the rhombohedra are embedded suggests but does not necessarily prove *in situ* oxidation of the tar to produce carbon dioxide that became incorporated in the dolomite. Oxidation of the organic matter, regardless of the *in situ* possibility, can occur by several means:

(1) reaction with oxygenated formations waters in the subsurface or by aerial exposure in the outcrop, (2) oxidation-reduction reactions involving the organic matter and oxygen-bearing ions in the water such as sulfate, and (3) oxidation-reduction reactions involving other oxygen-bearing minerals.

Organic carbonates in the Lyons Formation (Permian, Colorado) were formed by this latter mechanism, in which iron oxide was reduced simultaneously with oxidation of bitumen and with subsequent precipitation of organic dolomite cement (Silverman, *et al*, in press). The abundance of gaseous and tarry nuclei centrally located in the rhombohedra suggests (1) that the carbonate formed in a multi-phase medium, possibly water-tar-CO₂ and (2) that the crystallization of the dolomite began selectively on the fluid phase boundaries or bubble (globule) surfaces.

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REFERENCES

- CRAIG, H. (1953) The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta*, **3**, 53-92.
- EPSTEIN, S., R. BUCHSBAUM, H. A. LOWENSTAM AND H. C. UREY (1953) Revised carbonate-water isotopic temperature scale. *Bull. Geol. Soc. Am.* **64**, 1315-1326.
- FEELY, H. W. AND J. L. KULP (1957) Origin of Gulf Coast salt-dome sulfur deposits. *Bull. Am. Assoc. Petroleum Geol.* **41**, 1802-1853.
- GOLDSMITH, J. R. AND D. L. GRAF (1958) Structural and compositional variations in some natural dolomites. *Jour. Geol.* **66**, 678-693.
- NAKAI, N. (1960) Carbon isotope fractionation of natural gas in Japan. *Jour. Earth Sci. Nagoya Univ.* **8**, 174-180.
- OSIPOVA, A. I. (1964) Catagenic changes in petroleum-bearing carbonate rocks. In, *Chemistry of the Earth's Crust* (Khimiya Zemnoi Kory) Vol II, ed. A. P. Vinogradov. Izdatel'stvo "Nauka," Moscow, 415-427.
- SILVERMAN, S. R. (1964) Investigations of petroleum origin and evolution mechanisms by carbon isotope studies. In, *Isotopic and Cosmic Chemistry*, ed. H. Craig, S. L. Miller and G. J. Wasserburg. North-Holland Publishing Co., Amsterdam, 92-102.
- SILVERMAN, S. R. AND S. EPSTEIN (1958) Carbon isotopic composition of petroleum and other sedimentary organic materials. *Bull. Am. Assoc. Petroleum Geol.* **42**, 998-1012.
- , D. W. LEVANDOWSKI, L. C. BONHAM AND W. G. TOLAND (in press) Carbonates from oil. *Bull. Am. Assoc. Petroleum Geol.*
- THODE, H. G., R. K. WANLESS AND R. WALLOUCH (1954) The origin of native sulfur deposits from isotope fractionation studies. *Geochim. Cosmochim. Acta* **5**, 286-298.