solubility [(cm^3 of gas (STP)/cm^3, cm-Hg)] of the solute in the solvent. The values of the solubility of carbon dioxide and oxygen in water were taken from the *Handbook of Chemistry and Physics*. The values of the diffusivity of carbon dioxide and oxygen in water were taken from L. E. Scriven and R. L. Pigford, *Amer. Inst. Chem. Eng. J.* **4**, 439 (1958), and J. F. Davidson and E. J. Cullen, *Trans. Inst. Chem. Eng. London* **35**, 51 (1957), respectively.
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Carbon-13–Rich Diagenetic Carbonates in Miocene Formations of California and Oregon

Abstract. *Carbon unusually rich in C^{13} ($\delta C^{13} = +5.4$ to $+19.0$ per mil relative to the Peedee belemnite carbonate standard of the University of Chicago) is characteristic of certain diagenetic limestones and dolomites in the Miocene Monterey Shale of California and the Nye Mudstone of Oregon. This heavy carbon may have originated through low-temperature equilibration between CO_3^{--} and CO_2 in migrating carbonated waters or between CH_4 and CO_2 in natural gas. Light carbon ($\delta C^{13} = -5.6$ to -18.2 per mil) derived through nonequilibrium oxidation of organic matter also occurs in the carbonate of Monterey Shale in some localities, but at most places it is much less common than heavy carbon.*

Carbon in primary marine limestone varies only slightly in its C^{13}/C^{12} isotopic composition, most of the samples falling within the range of $\delta C^{13} = 0 \pm 4$ per mil relative to the Peedee belemnite carbonate standard of the University of Chicago (PDB) (*1–3*). This relative constancy of composition results from precipitation of marine carbonate in isotopic equilibrium with oceanic bicarbonate that is virtually constant isotopically. A few marine organisms secrete carbonate with δC^{13} as light as −9.3 (*4*) or as heavy as +5.9 (*5*), but most, including the quantitatively important pelagic Foraminifera, produce carbonate that is isotopically near equilibrium (*6, 7*).

Carbon in carbonate rocks of other environments and in marine carbonates affected by certain postdepositional processes varies greatly in isotopic composition, generally in the direction of relative enrichment in C^{12}. Examples of such variable carbon are given in Table 2. The values for markedly light carbon are believed to reflect a large amount of carbon from organic matter of various kinds, all of which are invariably rich in C^{12} (*1, 8*). That bacterially decomposed petroleum was the source of the extremely light carbon in salt-dome limestones is well documented (*9, 10*). Diagenetic carbonates with light carbon commonly occur in sediments that are rich in organic matter. During some stage of diagenesis, light CO_2 derived from decomposing organic matter equilibrates with preexisting or newly forming carbonate (*11, 12*).

Our interest in diagenetic carbonates of marine formations arises from a current geochemical study of the Miocene

Table 1. Carbon isotopic composition of diagenetic dolomites and limestones in Miocene rocks of Oregon and California.

Sample No.	Locality	Geographic coordinates	Formation	Rock	δC^{13} per mil*
			Oregon samples		
1	Yaquina Bay, Lincoln County	44°38'N 124°01'W	Nye Mudstone	Dolomite bed 1	+5.4
2	Yaquina Bay, Lincoln County	44°38'N 124°01'W	Nye Mudstone	Dolomite bed 3	+10.6
			California samples		
3	Point Arena, Mendocino County	38°52'N 123°39'W	Monterey Shale	Dolomite cement of sandstone	−12.2
4	Berkeley Hills, Contra Costa County	37°52'N 122°14'W	Monterey Shale	Dolomite bed 1	+17.3
5	Berkeley Hills, Contra Costa County	37°52'N 122°14'W	Monterey Shale	Dolomite bed 5	+10.1
6	San Rafael Mts., Santa Barbara County	34°47'N 119°36'W	Monterey Shale	Limestone lens 1	+15.1
7	San Rafael Mts., Santa Barbara County	34°47'N 119°36'W	Monterey Shale	Limestone lens 2	+5.4
8	San Rafael Mts., Santa Barbara County	34°47'N 119°42'W	Monterey Shale	Dolomite bed	−12.8
9	Temblor Range, San Luis Obispo County	35°05'N 119°35'W	Monterey Shale	Dolomite bed	+19.0
10	Palos Verdes Hills, Los Angeles County	33°48'N 118°24'W	Malaga mudstone member of Monterey Shale	Dolomite bed	−16.0
11	Palos Verdes Hills, Los Angeles County	33°45'N 118°22'W	Valmonte diatomite member of Monterey Shale	Dolomite bed	−12.1
12	Palos Verdes Hills, Los Angeles County	33°45'N 118°22'W	Upper part of Altamira shale member of Monterey Shale	Dolomite bed	−5.6
13	Palos Verdes Hills, Los Angeles County	33°44'N 118°22'W	Middle part of Altamira shale member of Monterey Shale	Dolomite cement of tuff bed	−18.2

* Relative to University of Chicago Peedee belemnite carbonate standard.

Table 2. Carbonate rocks with highly variable carbon isotopic composition. Numerals in parentheses are references.

Material	C^{13} per mil
Freshwater carbonates (*21*)	−2.6 to −17.7
Limestones from salt-dome cap rocks (*9, 10*)	−23.9 to −51.1
Permian crinoids believed to have undergone post-depositional isotopic reequilibrium (*22*)	+4.7 to −17.0
Diagenetic carbonates in marine formations (*11, 12*)	+2.4 to −54.0

Monterey Shale of California. This widespread, highly diatomaceous and cherty formation is rich in organic matter in many places and is considered to be the source bed of much of California's petroleum. In certain zones, many carbonate beds, typically 0.3 to 0.9 m (1 to 3 feet) thick, occur 1.5 to 9 m (5 to 30 feet) apart among siliceous shales of the Monterey Shale. For the formation as a whole, however, they make up only a percent or so by volume. Our x-ray diffraction studies show that most of the beds consist of dolomite of the protodolomite variety (*13*).

Bramlette (*14*) has clearly demonstrated the diagenetic origin of these carbonate beds. At some period or periods in the postdepositional history of the Monterey Shale, dolomite-depositing solutions impregnated or replaced preexisting beds of foraminiferal marl, diatomaceous shale, sand, and pyroclastic tuff.

The C^{13}/C^{12} isotopic ratio of the Miocene carbonates are tabulated by regions in Table 1. The samples were first heated at 300°C for 1 hour in a stream of helium to eliminate the more labile organic matter, and then decomposed with phosphoric acid (*15*).

The first samples we analyzed were from Palos Verdes Hills, Los Angeles County (Nos. 10 to 13 in Table 1), and these showed the usually observed light carbon ($\delta C^{13} = -5.6$ to -18.2 per mil). Spotts and Silverman (*16*) recently reported a value of −16.4 per mil for a dolomite from Palos Verdes Hills. Most of our samples from other localities contain unexpectedly heavy carbon ($\delta C^{13} = +5.4$ to $+19.0$). Values more positive than 11 per mil have not been previously reported for terrestrial carbonate minerals. Because our study is incomplete at this time, we discuss here only three possible modes of origin of heavy carbon suggested by the existing data on its occurrence in (i) calcareous tufa, (ii) sedimentary organic matter residual to bacterial decomposition, and (iii) CO_2 in methane-rich natural gas.

The first possible mode of origin would relate the heavy-carbon carbonates to calcareous tufa (samples Nos. 4 and 5 in Table 3) formed by deposition from cold, highly carbonated spring and river waters. Baertschi (*2*) considers such tufa as a low-temperature precipitate that formed in equilibrium with free CO_2 whose δC^{13} was about −2 per mil, derived through complete decomposition of normal marine carbonate. If the solution in such a system were to migrate and fractionally precipitate carbonate over some distance through continued loss of light CO_2, the last precipitates might attain a δC^{13} value in excess of +9 per mil. This mechanism for producing heavy carbon, like all others that depend on equilibrium fractionation between different kinds of carbon-bearing molecules or ions, will be favored by low temperatures and by a starting material (CO_2 in this case) whose carbon is not excessively light. In a current study of hot springs deposits of Yellowstone National Park, the highest δC^{13} found so far among calcareous tufa being deposited today is +5 per mil and the highest among prehistoric tufa is +8.5 per mil.

Table 3. Carbon isotopic composition of CO_2 and of calcareous tufa previously found to be rich in C^{13}.

Sample No.	Locality	Formation	Reference	C^{13} per mil
	CO_2 in methane-rich natural gas of various localities			
1	Moffat County, Colorado	Fort Union (Paleocene)	(*18*)	+8.1
2	Sweetwater County, Wyoming	Frontier (Upper) Cretaceous)	(*18*)	+12.8
3	Coles County, Illinois	Sandstone (Pennsylvanian)	(*19*)	+16.4
	Tufa deposited from cold carbonated waters			
4	Engadine Springs, Switzerland	Calcareous tufa	(*2*)	+6.3 to +11
5	Tivola River, Italy	Calcareous tufa	(*1*)	+9.8

The second mode of origin invokes the formation of isotopically light methane through bacterial decomposition of organic matter. In laboratory cultures, Rosenfeld and Silverman (*17*) noted methane with δC^{13} of −119 per mil being produced initially during bacterial fermentation of methanol with δC^{13} of −45.7 per mil. Over a period of several weeks, the cultures yielded progressively heavier methane, the final portion of which had a δC^{13} of +20.5 per mil. The last remaining methanol was presumably even richer in C^{13}. These experimental results suggest the possibility that residual sedimentary organic matter remaining after extensive bacterial decomposition might be a source of heavy carbon in nature.

Carbon in natural methane ($\delta C^{13} = -29$ to -60 per mil) (*18, 19*) from marine formations is generally lighter than that in petroleum ($\delta C^{13} = -22$ to -29 per mil) (*20*) or in organic matter of marine formations ($\delta C^{13} = -14$ to -31 per mil) (*1*). However, none of these natural organic materials are known to attain positive values of δC^{13} like those of methane produced in the laboratory experiments. Thus, production of very heavy residual carbon through long-continued generation and removal of light methane from organic matter does not seem to take place in nature.

The third possible mode of origin of heavy carbon is suggested by the occasional occurrence of extremely heavy CO_2 ($\delta C^{13} = +8.1$ to $+16.4$ per mil) in natural gas (sample Nos. 1 to 3 in Table 3). Zartman and others (*18*) believe that such CO_2 attained its isotopic composition by equilibrating with methane ($\delta C^{13} = -40$ to -50 per mil) at geologically reasonable temperatures of 40° to 70°C. Inasmuch as the Monterey Shale is the source bed of much petroleum in California, a process that involves isotopic equilibrium between CO_2 and another carbon compound in natural gas could be very relevant to genesis of carbonates in this formation.

Further studies in progress on carbonates of known stratigraphic relations within the Monterey Shale may allow us eventually to determine the mode of origin of the extremely heavy carbon in many of these carbonates.

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Lunar Surface Strength Estimate from Orbiter II Photograph

Abstract. *Lunar Orbiter II photographed a 13-meter boulder which has rolled down the inner slope of a 3-kilometer crater leaving a track 6 meters wide. A static-bearing strength of* 4×10^6 *dynes per square centimeter at 75-centimeter depth is estimated from these data if certain assumptions are made.*

A portion of western Mare Tranquillitatis photographed in high resolution mode (Frame H-76, resolution ~ 1 meter) by Lunar Orbiter II (*1*) contains the small crater Sabine D (23°40′W; 1°20′N). The crater is about 3 km in diameter and has no ray pattern or ejecta field; it has only a low rim rising above the mare surface.

Around the rim crest and on the inner portions of the rim, clusters of rocks as large as 15 m in diameter are exposed (Fig. 1). Some appear half buried, while others appear to rest almost completely on top of the surface. A few rocks are seen scattered about the inner slope of the crater, and many of these appear also to rest on the surface.

During early screening of photographs at the Jet Propulsion Laboratory, it was noted that one of these rocks appeared to have a track leading to the rock (*A′*) from a point higher up the slope (*A*). It was suggested that the rock had become dislodged and had rolled down the inner slope. The boulder, approximately 13 m in diameter, apparently traveled about 650 m along a line roughly radial to the crater center.

The portion of crater wall down which the rock rolled has a slope of $\sim 25°$ at *A* (which decreases to *A′*) as estimated from considerations of Sun angle (27.4° from horizontal) and crater depth and diameter.

The track left by the boulder varies in width from 5 to 8 m (average 6 m) and passes through a 15-m crater (*B*). A 3-m rock lies in the track at *C*. Some portions of the track are missing, suggesting three possible conditions: (i) the boulder bounded down the slope and left the surface at certain spots, (ii) subsequent processes have erased portions of the track, or (iii) the surface at certain points is so strong that the boulder made no imprint. The boulder has come to rest on the downslope rim of a 10-m crater; the presence of the crater coupled with the decreasing slope apparently prevented the boulder from rolling further.

An estimate of the static-bearing strength of the inner slope of Sabine D along *A-A′* can be obtained if cer-

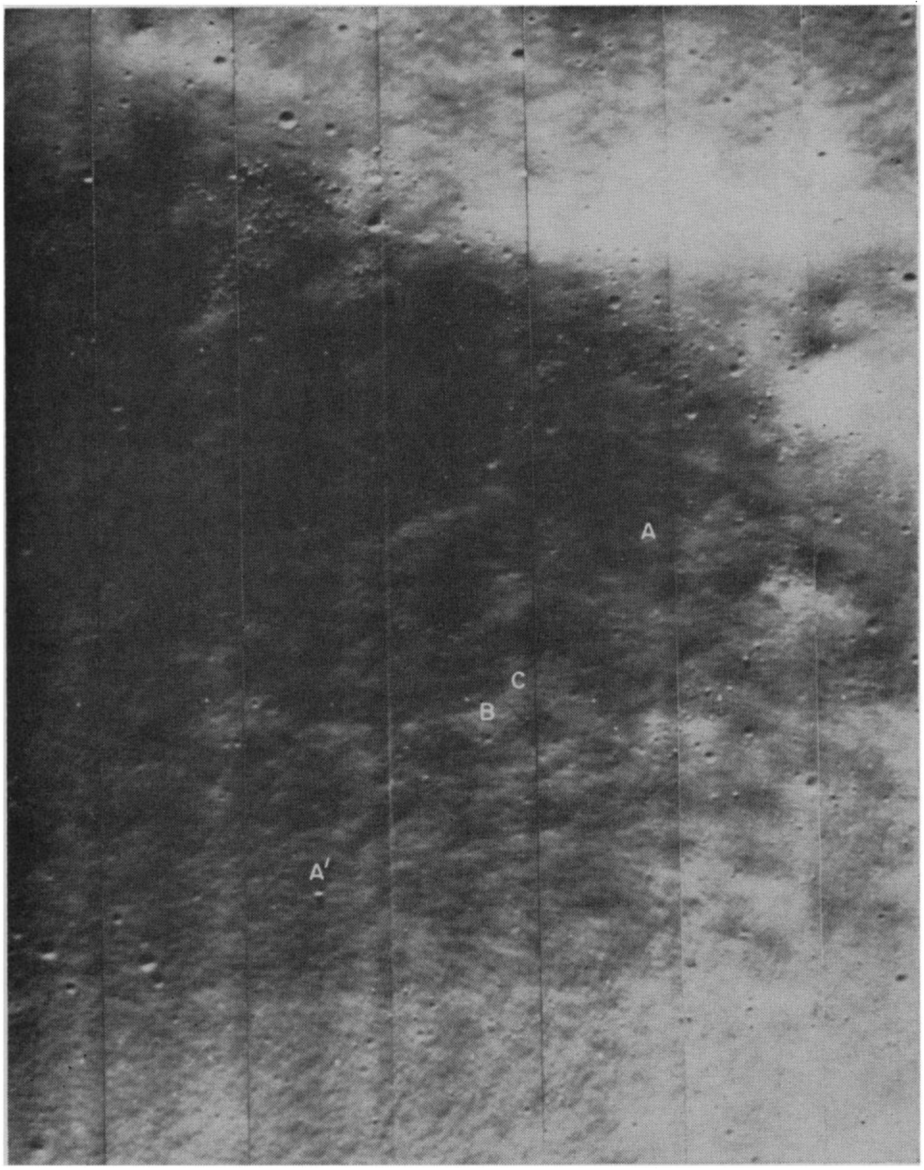

Fig. 1. Portion of Lunar Orbiter II frame H-76.