Geochemistry of Diagenetic Dolomites in Miocene Marine Formations of California and Oregon

Geochemistry of Diagenetic Dolomites

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of California and Oregon

By K. . MURATA, IRVING FRIEDMAN, and MARCELYN CREMER

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

*The alteration history of deeply buried marine
sediments as revealed by the chemical and
isotopic compositions of secondary dolomites*

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GEOCHEMISTRY OF DIAGENETIC DOLOMITES IN MIOCENE MARINE FORMATIONS OF CALIFORNIA AND OREGON

By K. J. Murata, Irving Friedman, and Marcelyn Cremer

ABSTRACT

The unusually high concentration of C^{13} ($\delta C^{13} > +5$ per mil relative to the Peedee belemnite standard) in many diagenetic dolomites of California and Oregon Miocene formations was brought about by isotopic exchange between methane and carbonate. Computations based on the temperature-dependent equilibrium constant for this exchange reaction yield $58°-110°C$ as the approximate temperature of formation of the dolomite.

Chemical composition of the dolomite lies within the following limits, expressed in mol percent: $FeCO_3$, 0.0–16.6; $MnCO_3$, 0.0–0.5; $MgCO_3$, 27.9–51.1; and $CaCO_3$, 47.8–58.0. The $d(10\cdot4)$ X-ray spacing is related to the composition according to the equation

$$d(10\cdot4)\,\text{angstroms} = 2.8855 + 0.00301[\,(CaCO_3 + 0.19\ FeCO_3 + 0.37\ MnCO_3) - 50.0].$$

Virtually all light-carbon dolomites ($\delta C^{13} < -5$ per mil relative to the Peedee belemnite standard) and some heavy-carbon dolomites are poor in iron, because of the generally low concentration of iron in interstitial water of pyrite-bearing reduced sediments. Other heavy-carbon dolomites contain as much as 17 mol percent $FeCO_3$, and $CaCO_3$ in these samples increases with $FeCO_3$, whereas δC^{13} and δO^{13} decrease. The chemical and isotopic interrelations among high-iron dolomites were probably brought about by postorogeny invasion of the reduced sediments by initially oxygenated meteoric water.

The overall chronological succession of dolomite types, throughout the history of a sediment rich in organic matter, seems to be (1) light-carbon dolomite, (2) heavy-carbon–low-iron dolomite, and (3) heavy-carbon–high-iron dolomite. Types 1 and 2 belong to the long anaerobic phase of sediment history, and type 3 marks the first stage of the postorogenic aerobic phase.

INTRODUCTION

Diagenetic carbonates in Miocene marine formations of California and Oregon have an unusually wide range of carbon-isotopic composition and are divisible into a light-carbon group (δC^{13} of -25 to -5 per mil relative to the Peedee belemnite (PDB) standard) and a heavy-carbon group (δC^{13} of $+5$ to $+21$ per mil) (Murata and others, 1969). The starting material for these carbonates is believed to be minor amounts of marine carbonate (δC^{13} of 0 ± 4 per mil) in the form of shells of Foraminifera and other calcareous organisms. A long series of diagenetic reactions involving decomposing organic matter and formation waters converted primary carbonate into lenticular and concretionary masses of diagenetic calcite and dolomite.

Dolomite is by far the most abundant mineral among diagenetic carbonates in the California Miocene, and it commonly occurs along restricted horizons in moderately calcareous shales that were deposited in deep marine basins. Dolomitization apparently was effected by solutions that migrated mostly along certain favorable zones in consolidated sediments. The mode of origin was very different from that of early diagenetic carbonates, which formed in tidal flats and other coastal environments through the agency of evaporated brines (Alderman and Skinner, 1957; Degens and Epstein, 1964; Deffeyes and others, 1965; Mueller and Tietz, 1966; among others). It may be noted that in the Cretaceous marine formations of California, dolomite is rare and ferroan calcite is the dominant diagenetic carbonate.

Both primary marine carbonate and organic matter are important reservoirs of carbon in California Miocene formations. Diagenetic carbonate in these formations rarely has the carbon-isotopic composition of marine carbonate, but is lighter or heavier, depending on whether or not isotopic exchange equilibrium became established between carbon dioxide and coexisting methane. Light-carbon carbonates are rich in carbon derived through oxidation of sedimentary organic matter (δC^{13} of -31 to -14 per mil). Such carbonates are common in marine formations throughout the world (Spotts and Silverman, 1966; Hodgson, 1966; Galimov and Girin, 1968, Hoefs, 1970; Fontes and others, 1970; among others). None of the California specimens have the extremely light carbon (δC^{13} of -60 to -35 per

mil) that is produced through oxidation of methane (Hathaway and Degens, 1969).

Heavy-carbon carbonates are rich in heavy carbon produced through isotopic exchange between carbon dioxide and methane:

$$C^{12}O_2 + C^{13}H_4 \rightleftarrows C^{13}O_2 + C^{12}H_4. \tag{1}$$
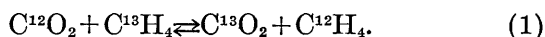
With sufficient methane, this exchange strongly concentrates C^{13} in the carbon dioxide, the extent of concentration being inversely related to the temperature (Bottinga, 1969). The origin of diagenetic carbonates is thus an aspect of diagenesis of sedimentary organic matter; the main features of this diagenesis have been clearly outlined by Silverman (1965), Philippi (1965), and Davis (1967, p. 23).

The factors that promote or hinder isotopic exchange between carbon dioxide and methane, and hence determine the carbon-isotopic composition, are not known, but a certain consistency in isotopic composition is evident among dolomites from several California localities. Dolomites from Palos Verdes Hills contain light carbon only, whereas those from Reliz Canyon and from Chico Martinez Creek have heavy carbon only. As will be discussed later, the prevalence of light carbon in dolomites of Palos Verdes Hills may be due to the unusually shallow burial (<1,000 ft) of the Miocene section at this locality (Woodring and others, 1946). At several localities of heavy-carbon dolomites, the spread of isotopic composition is large enough to suggest that the methane-carbon dioxide exchange equilibrium was approached but not attained by many samples.

ACKNOWLEDGMENTS

METHANE-CARBON DIOXIDE ISOTOPIC EXCHANGE IN NATURAL GAS

Because the isotopic composition of the methane that was associated with the diagenetic carbonates studied by us is unknown except within broad limits, a direct discussion of isotope geochemistry of the carbonates is not possible. But the required data are available for the closely related system of methane and carbon dioxide gas in natural gas from various oil fields of the United States, and these data are presented in figure 1. The left half of the figure shows the isotopic compositions of coexisting methane and carbon dioxide plotted against the depth of origin of the natural gas (Zartman and others, 1961; Wasserburg and others, 1963); the right half, apparent equilibrium temperatures, also plotted against depth of origin, computed under the assumption that the methane-carbon dioxide isotopic values represent equilibrium compositions (Bottinga, 1969). Methane is the dominant constituent in all samples and is 12–340 times more abundant than carbon dioxide.

The filled points in figure 1 denote samples that contain the heaviest carbon dioxide and that yield the most reasonable temperature for their respective depths of origin (Wasserburg and others, 1963). The temperature-depth curve defined by the five filled circles corresponds to a gradient of 54°C per kilometer (1°C/60 ft), the lowest gradient allowed by the data if the top of the curve is to be fixed to a surface temperature of about 20°C. Although rather high, the computed gradient is equalled or exceeded by gradients of a few American oil fields (Birch and others, 1942). Higher gradients involving the unfilled circles in figure 1 are therefore unlikely. These considerations of geothermal gradient suggest that (1) the five samples represented by filled points most completely satisfy the basic requirement for accurate isotopic temperatures, which is attainment of exchange equilibrium between carbon dioxide and methane, and (2) all other samples are out of equilibrium.

In keeping with the theoretical expectations, equilibrated samples show the greatest difference in δC^{13} values of methane and carbon dioxide at the lowest temperature, the difference decreasing progressively with rising temperature. In these samples from marine formations, the δC^{13} of methane is heavier than -60 per mil, and the isotopic difference appropriate to methane and carbon dioxide in equilibrium is usually attained by the δC^{13} of carbon dioxide rising above the generally prevaling value of about -10 per mil to as high as $+16$ per mil.

Isotopic exchange equilibrium between methane and dolomite cannot be expressed precisely at present, but the data for methane-calcite equilibrium (Bottinga, 1969) suggest that δC^{13} in a carbonate would be 10–0 per mil heavier than in carbon dioxide, within the temperature range of about 30° to 200°C. A finely dashed curve in the middle of figure 1 shows this higher content of C^{13} in calcite as compared with carbon dioxide when in equilibrium with the same methane. From all these considerations, we conclude that δC^{13} values in dolomite which are greater than about $+5$ mil signify
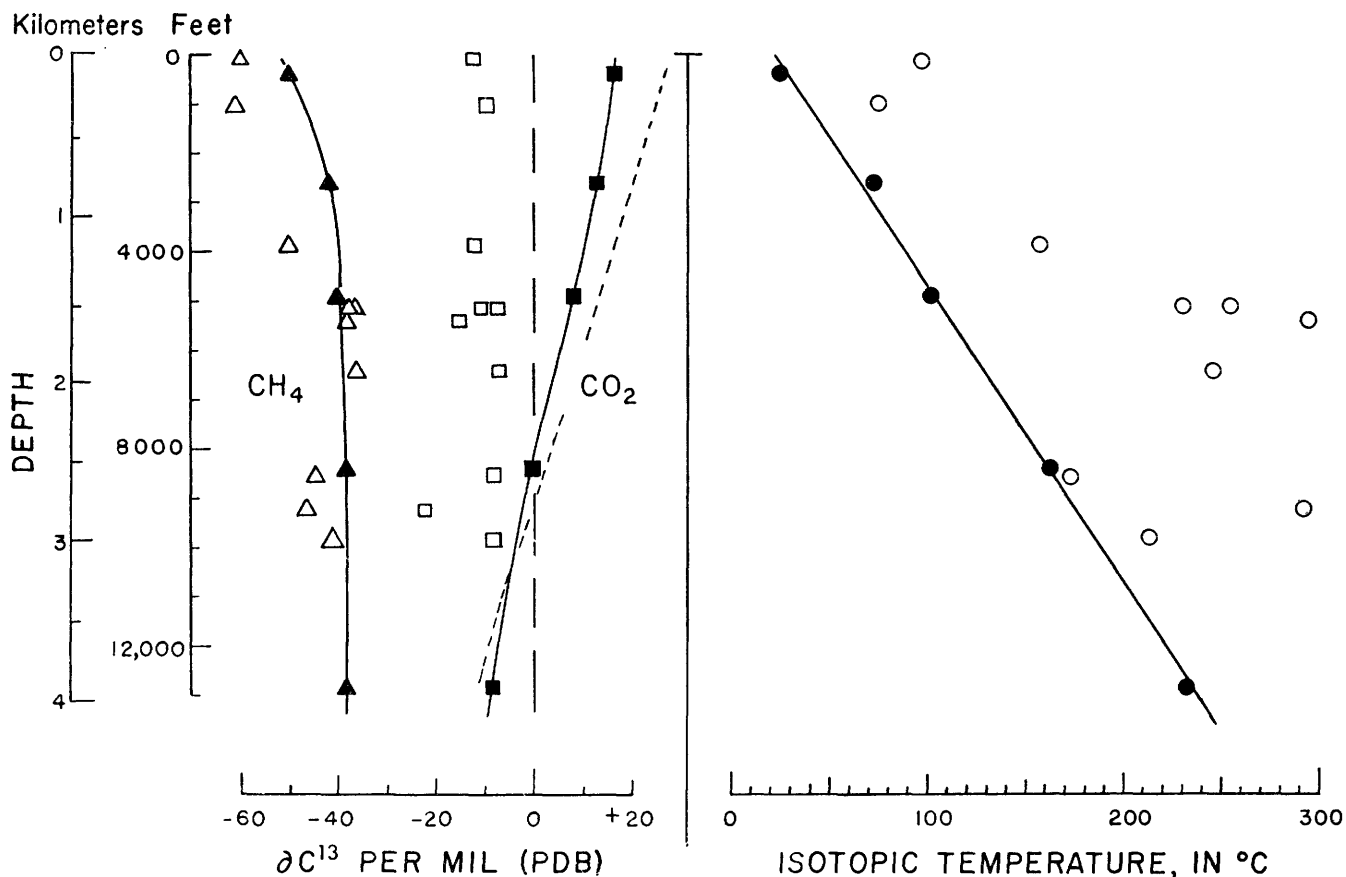
FIGURE 1.—Carbon-isotopic compositions of coexisting methane (triangles) and carbon dioxide (squares) in natural gas of widely scattered American oil fields (Zartman and others, 1961; Wasserburg and others, 1963) and temperatures (circles) computed by assuming isotopic exchange equilibrium between methane and carbon dioxide (Bottinga, 1969). All quantities are plotted against the depth of origin of the natural gas. Filled points represent isotopic compositions and computed temperatures for samples containing the heaviest carbon dioxide at various depths. The thin dashed curve in the middle is δC^{13} of calcite in exchange equilibrium with methane whose δC^{13} lies along the curve defined by filled triangles (Bottinga, 1969).

an appreciable influence of the methane-carbonate exchange and that values less than about −5 per mil indicate the lack of this influence.

We shall attempt to explain the varied isotopic and chemical composition of the dolomites in terms of chronological changes of physical-chemical conditions within the host sediments. Generally, preexisting carbonates are pictured as adjusting their composition to that appropriate to each new condition. As direct exchange of elements between solid carbonate and fluids is extremely slow (Anderson, 1969), the adjustments probably took place through solution-recrystallization of the preexisting carbonate. Because of the many variables involved, only broad trends of change can be identified and given tentative explanations.

FORMATION WATERS INVOLVED IN DOLOMITE GENESIS

The interstitial water of Holocene and Tertiary marine sedimentary deposits to a depth of 140 meters or

so below the sea floor is virtually the same as normal sea water, except for compositional changes induced by bacterial decomposition of organic matter (Siever and others, 1965). The changes of greatest interest in connection with genesis of diagenetic carbonates are the increase in bicarbonate and the generation of hydrogen sulfide through bacterial reduction of sulfate. The interstitial water of sediments in the San Pedro basin off the southern California coast (Emery and Rittenberg, 1952; Presley and Kaplan, 1968) contains about 20 times more bicarbonate than normal sea water, but only 1/200 of the sulfate, and the δC^{13} of the bicarbonate is as low as −21 per mil. Methane is present (Emery and Hoggan, 1958), but does not enter into isotopic exchange with the bicarbonate, judging from the lightness of the bicarbonate. The prevailing temperature is approximately a few degrees centigrade.

According to Presley and Kaplan (1968), the interstitial solution of San Pedro basin further contains 40–110 ppb (parts per billion) iron, 200–460 ppm (parts per

million) calcium, and around 1,300 ppm magnesium. (Normal seawater of the region contains 0.8 ppb iron, 400 ppm calcium, and 1,350 ppm magnesium, according to Brooks and others (1968).) Also, about 8 percent of primary sedimentary carbonate is present in the sediment. These proportions suggest that any light-carbon carbonate (initially calcite) formed through interaction of such a solution and primary carbonate would be poor (hundredths of a percent by weight) in iron.

Bacterial decomposition of organic matter declines with progressive burial of the sediment, although some bacteria, like those that reduce sulfate, seem to function at depths of several thousand feet and temperatures of approxmiately 50°C (Davis, 1967). The later degradation of organic matter at temperatures higher than about 70°C proceeds largely through inorganic reactions (Silverman, 1964; Philippi, 1965), some of which may involve isotopic exchange between carbon dioxide and methane. Reducing conditions would prevail at all depths, and concentration of iron would be held to low levels through precipitation of pyrite (Hem, 1960a) or possibly through reactions involving organic matter (Hem, 1960b).

Phase relations bearing on dolomitization of calcite in deeply buried sediments by formation waters have been reviewed recently by Rosenberg, Burt, and Holland (1967) and by Usdowski (1968). The process is generally favored by a rise in temperature and salinity, which tends to reduce the degree of hydration of magnesium ions in solution and thereby promotes the entry of magnesium into an anhydrous carbonate structure. At temperatures around 60°C, solutions with a magnesium/calcium atomic ratio of about 0.33 to 2.00 are at equilibrium with dolomite; those with lower and higher ratios are at equilibrium with calcite and magnesite, respectively.

Magnesium/calcium atomic ratios within the dolomite stability range are very common among oil field brines of California (Jensen, 1934; Gullikson and others, 1961; White and others, 1963; Weddle, 1968), and this fact may be the basic reason for dolomite being the predominant diagenetic carbonate in these fields. Miocene sedimentary rocks of the Round Mountain oil field on the east side of San Joaquin valley are exceptional in having diagenetic calcite rather than dolomite (Murata and others, 1969). Although the pore water in these formations has a magnesium/calcium atomic ratio of 0.54 (Jensen, 1934), its low salinity (<4,000 ppm) and relatively low temperature (about 45°C; Moses, 1962) apparently were not favorable for dolomitization.

Certain organic acids have been found to promote the entry of magnesium into the calcite structure (Kitano and Kanamori, 1966) and could conceivably have a role in the dolomitization process. Organic acids (especially naphthenic acid) are byproducts of petroleum-generating reactions and amount to 10–35 percent of the total anion equivalents in brines of some California oil fields (Gullikson and others, 1961). We have previously noted that dolomitization is favored by the reduction in the degree of hydration of magnesium ions induced by increases in salinity and temperature of solutions (Usdowski, 1968). According to M. N. A. Peterson (written comm., May 1971), the favorable effect of organic acids may be essentially the same, namely decreasing the degree of hydration of magnesium by means of magnesium-organic acid complex ions.

That natural dolomites have a variable content (48–57 mol percent) of $CaCO_3$ in solid solution was shown by Goldsmith, Graf, Witters, and Northrop (1962), and the samples studied by us manifest a comparable variation, as did those described recently by Watanabe (1970). In solutions producing dolomite under equilibrium conditions, the factors that lead to calcium carbonate in excess of 50 mol percent seem to be (1) magnesium/calcium ratios in the lower part of the allowed range, (2) temperature in the lower part of the allowed range (Glover and Sippel, 1967), (3) salinity in the lower part of the allowed range (Füchtbauer and Goldschmidt, 1965), and (4) concentrations of organic acids in the lower part of the allowed range (Kitano and Kanamori, 1966). As discussed later, under some circumstances all four factors could become lowered simultaneously to create conditions favorable for dolomite with excess calcium, as when meteoric water becomes mixed with oil field brines.

Bacterial reduction of sulfate to the sulfide and precipitation of pyrite are well known reactions that hold the iron content of formation waters to low levels (Davis, 1967). This control of iron concentration operates during most of the postdepositional history of sediments; consequently, most diagenetic calcites and dolomites are poor in iron.

When orogenic forces deform and raise sedimentary formations out of the sea, oxygenated meteoric water can circulate through the formations, decomposing pyrite and greatly increasing the concentration of dissolved iron to 7 ppm Fe^{2+} or more (Langmuir, 1969). Only an edge of the formations need be exposed, as illustrated by the seaward-dipping Coastal Plain formations of Florida, which contain fresh water under artesian pressure, even 27 miles offshore (JOIDES, 1965).

The increase in concentration of dissolved iron occurs only where the oxygenated water shifts Eh-pH conditions out of the stability field of pyrite into the field of ferrous carbonate, but stops short of the field

of ferric hydroxide (James, 1966, fig. 5; Hem, 1967). Diagenetic calcites and dolomites formed in this high-iron environment would be expected to contain substantial amounts of ferrous iron. Analyses of oil field brines show iron in the range of 1–100 ppm (Rittenhouse and others, 1969), but how much of this iron might be due to corrosion of steel pipes of the wells is uncertain.

For some reason, siderite is extremely rare among the samples studied by us. Scanty data suggest that it is formed in deep-lying brines charged with sufficient carbon dioxide to maintain a pH of less than 5 (Carlson, 1949), under which condition both calcite and dolomite may be unstable. Siderite is a common diagenetic mineral in some fresh-water deposits, in which it seems to form not far below the water-sediment interface (Fritz and others, 1971).

CHEMICAL ANALYSIS OF DIAGENETIC DOLOMITES

Our previous report on the California diagenetic carbonates included a general description of their mode of occurrence and isotopic analyses of oxygen and carbon in 79 samples (Murata and others, 1969). We have subsequently made chemical analyses of 24 of these samples and two new samples in order to characterize the carbonates in greater detail and to establish a correlation between chemical and isotopic composition. Sample numbers used in the present paper are the same as those in the earlier report, which contains details on the nature and locality of the samples. The two new samples, 80 and 81, are cored dolomites from Ohio Oil Company's deep test well KCL–A–72–4, drilled in an extremely thick Miocene section of Kern County (Emery, 1956). Sample 80 is from a depth of 12,060 feet, sample 81, from 15,300 feet.

Because diagenetic carbonates occur as fine-grained cement of sandstones and shales, separation of pure carbonate samples for chemical analysis is generally impractical. We deduced the approximate composition of diagenetic dolomite by analyzing dilute-acid ($0.2N$ HCl) extracts of whole-rock samples, shown by X-ray diffraction patterns to contain no other carbonate, gypsum, or laumontite. A source of error inherent in this approach is the possibility of the acid dissolving materials other than dolomite. However, the analytical results in table 1 show a general agreement in chemical equivalence between carbon dioxide and the sum of Ca, Mg, Fe, and Mn; thus errors are relatively small. A preliminary estimate of the iron content was obtained by staining sawed slabs of the specimens with a solution of potassium ferricyanide (Friedman, 1959).

In computing the equivalences, an amount of CaO equal to 1.45 times the weight percentage of P_2O_5 was first deducted from soluble CaO to allow for the small amount of apatite in the samples. Total dissolved iron is reported as FeO. The amount of acid-insoluble matter in the samples ranges between 3 and 49 percent.

The strontium content of some of the samples was determined through X-ray fluorescence analysis of calcium oxide separated during gravimetric chemical analysis of the acid extracts. Semiquantitative spectrographic analyses made by Chris Heropoulos of sample 10 and its insoluble residue showed that the bulk of the strontium is soluble in acid, whereas virtually all of the barium (700 ppm) is insoluble.

Dolomite compositions will be discussed in terms of mol percent of iron, manganese, magnesium, and calcium carbonates, as computed in table 1. The ranges of these components among the 26 samples are as follows:

$FeCO_3$	0. 0–16. 6
$MnCO_3$	. 0– . 5
$MgCO_3$	27. 9–51. 1
$CaCO_3$	47. 8–58. 0

When compositions are plotted on the triangular diagram of figure 2, two compositional groups become evident:

1. Solid solutions between $CaMg(CO_3)_2$ and $CaFe(CO_3)_2$ but with 1–5 mol percent excess $CaCO_3$.
2. Iron-poor dolomites that depart substantially in content of $CaCO_3$ from the end-member composition of $CaMg(CO_3)_2$, ranging between 48 and 58 mol percent $CaCO_3$.
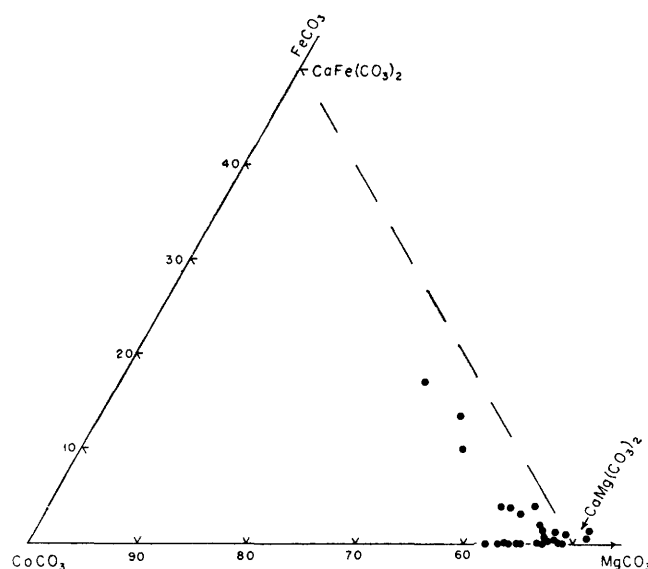

FIGURE 2.—Composition of diagenetic dolomites in mol percent $CaCO_3$, $MgCO_3$, and $FeCO_3$; the small amounts of $MnCO_3$ have been lumped with $FeCO_3$.

TABLE 1.—*Partial chemical analyses of diagenetic dolomites from Miocene marine formations of California and Oregon*

[Analysts: Marcelyn Cremer for samples with CO_2 determined; K. J. Murata for samples with CO_2 undetermined; B. P. Fabbi and Laureano Espos for strontium determinations. Localities of samples 1–78 described in detail in Murata, Friedman, and Madsen (1969). Samples 80 and 81 were obtained from Ohio Oil well KCL–A–72–4 in Paloma Oil Field, Kern County, Calif., at subsurface depths of 12,060 and 15,300 feet, respectively (Emery, 1956)]

	1	3	4	7	9	10	11	24	25	27	31	33	37
Whole sample (weight percent)													
FeO	2.2	1.1	1.5	0.56	2.2	8.8	2.5	0.22	8.0	0.09	0.02	0.31	0.21
MnO	.15	.18	.02	.02	.04	.28	.04	.02	.26	.05	.00	.02	.04
MgO	13.3	17.0	9.2	18.6	16.4	8.3	16.1	18.9	10.7	15.0	18.7	17.5	19.2
CaO	24.3	26.8	16.9	26.8	28.0	23.1	25.9	29.6	24.9	27.8	29.3	23.3	28.8
SrO			.014		.036	.025		.063	.026			.058	.054
CO₂	34.78	40.34		42.52	41.12	32.29	39.72			38.32	43.95	37.23	43.63
P₂O₅	.08	.04	.38	.14	.17	.22	.11	.13	.14	.13	.10	.15	.06
Insoluble, 105°C			47.5					6.0	16.0				
Insoluble, 1000°C	21.8	11.4		9.3	10.0	23.5	12.4			17.0	6.0	17.5	5.7
Acid-soluble dolomite fraction (mol percent)													
FeCO₃	3.8	1.7	3.9	0.8	3.3	16.6	3.9	0.3	13.6	0.1	0.0	0.5	0.3
MnCO₃	.3	.3	.1	.0	.1	.5	.1	.4	.4	.1	.0	.0	.1
MgCO₃	41.5	46.1	42.3	48.9	43.6	27.9	44.6	47.0	32.4	43.0	47.1	51.1	48.0
CaCO₃	54.4	51.9	53.7	50.3	53.0	55.0	51.4	52.7	53.6	56.8	52.9	48.4	51.6
$d(10\cdot4)$ angstroms	2.898	2.891	2.898	2.886	2.896	2.911	2.892	2.891	2.902	2.904	2.895	2.882	2.891
δC^{13} per mil (PDB)	+5.8	+11.0	−9.5	+17.7	+11.3	−2.8	+9.6	+11.6	+5.7	+7.1	+11.3	+20.8	+14.7

	46	47	48	53	55	62	66	69	74	77	78	80	81
Whole sample (weight percent)													
FeO	1.0	0.15	0.11	0.30	0.07	0.28	0.09	0.07	0.18	0.05	0.67	5.7	1.2
MnO	.05	.04	.02	.03	.03	.00	.01	.00	.01	.04	.01	.24	.06
MgO	19.8	10.4	20.4	15.2	17.6	17.0	17.2	17.6	10.8	16.1	14.3	11.7	16.4
CaO	26.2	15.7	30.0	27.4	31.3	29.3	28.6	30.9	16.7	31.0	21.6	25.8	26.3
SrO	.054		.025	.027	.015	.015					.023	.021	
CO₂	42.56						39.60	42.60	24.0	41.85			
P₂O₅	.13	.07	.06	.24	.18		1.2	.57	.06	.19		.10	.34
Insoluble, 105°C		49.3	3.0	19.1	7.1	10.3			46.1		29.3	18.4	16.0
Insoluble, 1000°C	8.1						11.0	6.5		8.6			
Acid-soluble dolomite fraction (mol percent)													
FeCO₃	1.4	0.4	0.1	0.5	0.1	0.4	0.1	0.1	0.4	0.1	1.2	9.4	1.9
MnCO₃	.1	.1	.0	.0	.0	.0	.0	.0	.0	.1	.0	.4	.1
MgCO₃	50.7	47.9	48.7	43.5	43.9	44.6	47.0	44.7	47.3	41.8	47.7	35.0	46.0
CaCO₃	47.8	51.6	51.2	56.0	56.0	55.0	52.9	55.2	52.3	58.0	51.1	55.2	52.0
$d(10\cdot4)$ angstroms	2.882	2.889	2.887	2.903	2.903	2.903	2.894	2.901	2.889	2.906	2.889	2.904	2.892
δC^{13} per mil (PDB)	+19.3	−17.3	−2.7	−12.5	−14.6	−15.4	−11.7	−8.8	−14.9	−1.8	−25.3	+9.6	+9.8

1, 3 Yaquina Bay, Lincoln County, Oreg., Nye Mudstone.
4 Point Arena, Mendocino County, Calif., Skooner Gulch Formation.
7, 9 Berkeley Hills, Contra Costa County, Claremont Shale.
10, 11 Santa Cruz Mountains, Santa Cruz County, Mindego Basalt (Oligocene and (or) Miocene).
24, 25 Reliz Canyon, Monterey County, Sandholdt Member of Monterey Shale.
27, 31 Nacimiento Dam, San Luis Obispo County, Sandholdt Member of Monterey Shale.
33, 37 Chico Martinez Creek, Kern County, Chico Martinez Chert.
46 Temblor Range, San Luis Obispo County, Monterey Shale.
47 Pismo syncline area, San Luis Obispo County, Obispo Formation.
48 Pismo syncline area, San Luis Obispo County, Monterey Shale, immediately underlying Pismo Formation.

53 San Rafael Mountains, Santa Barbara County, Monterey Shale.
55 Santa Ynez River area, Santa Barbara County, dolomitized reef rock (40 ft thick).
62 Palos Verdes Hills, Los Angeles County, Malaga Mudstone Member of Monterey Shale.
66 Palos Verdes Hills, Los Angeles County, Valmonte Diatomite Member of Monterey Shale.
69 Palos Verdes Hills, Los Angeles County, upper part of Altamira Shale Member of Monterey Shale.
74 Palos Verdes Hills, Los Angeles County, middle part of Altamira Shale Member of Monterey Shale.
77 San Clemente Island, Monterey Shale.
78 La Jolla Submarine canyon, cored sediment EM3–5(8–17 cm).

THE $d(10\cdot4)$ X-RAY SPACING AND COMPOSITION

The substitution of iron, manganese, and calcium in the place of magnesium expands the unit cell of dolomite; calcium by virtue of its large ionic radius has the greatest expansive power. In terms of the principal $d(10\cdot4)$ spacing, which in end member dolomite has a value of 2.8855 Å (angstroms), each mol percent of $CaCO_3$ in excess of 50 will enlarge the spacing

0.00301 Å (Goldsmith and Graf, 1958) ; thus

$$d(10\cdot4) \text{ dolomite} = 2.8855 + 0.00301(CaCO_3 - 50.0) \quad (2)$$

The $d(10\cdot4)$ spacing of dolomite can be precisely determined (standard deviation = ±0.0013) by means of an X-ray diffractometer and by the use of the principal reflection of quartz (3.3433 Å) as internal standard. A single parameter like the $d(10\cdot4)$ spacing cannot give a unique solution to the composition of a multicomponent phase. But it can serve as valuable check on the

overall accuracy of the chemical analysis, especially with respect to percentage of calcium. Advantage is taken of equation 2 by converting the determined percentages of $FeCO_3$ and $MnCO_3$ into equivalent $CaCO_3$ (in terms of expansive power), in the following way.

The $d(10\cdot4)$ spacing of $CaMg(CO_3)_2$, $CaFe(CO_3)_2$ $CaMn(CO_3)_2$, and $CaCa(CO_3)_2$ (calcite), as computed by Graf (1961), is shown diagrammatically in figure 3.
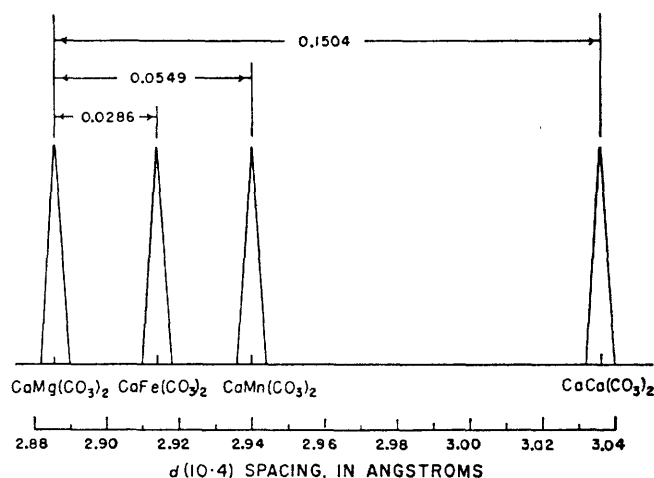

FIGURE 3.—The principal $d(10\cdot4)$ X-ray spacing of dolomite and related carbonates. Data from Graf (1961).

The separation in angstroms of the several peaks from that of $CaMg(CO_3)_2$ is a measure of the expansive power of an ion of Fe, Mn, or Ca when substituted for an ion of Mg. The expansive power of Fe and Mn relative to Ca is thus Ca : Fe : Mn : : 1.00 : 0.19 : 0.37, and the determined molar percentages of $FeCO_3$ and $MnCO_3$ are converted to equivalent of $CaCO_3$ by multiplying by 0.19 and 0.37, respectively. The sum of the actual percentage of $CaCO_3$ plus the converted percentages of of $FeCO_3$ and $MnCO_3$ may be called apparent $CaCO_3$, and

apparent $CaCO_3$ = actual $CaCO_3$

$$+0.19FeCO_3 + 0.37MnCO_3 \quad (3)$$

Because the amounts of $MnCO_3$ in the studied dolomites are negligible, only $FeCO_3$ contributes significantly to apparent $CaCO_3$, and about 5 mol percent $FeCO_3$ is needed to displace $d(10\cdot4)$ to the extent produced by 1 mol percent $CaCO_3$.

Equation 2, relating the $CaCO_3$ content of dolomite to its $d(10\cdot4)$ spacing, is indicated by the straight line in figure 4. The points in the figure represent the content of apparent $CaCO_3$ in the analyzed dolomites plotted against their $d(10\cdot4)$ spacing. For samples having less than 2 mol percent $FeCO_3$ (represented by single open circles), the $d(10\cdot4)$ spacing may be considered to be determined solely by $CaCO_3$. The apparent $CaCO_3$ of

samples containing more than 2 mol percent $FeCO_3$ (filled circles of connected samples) is computed according to equation 3.

Except for a single sample (No. 77), all samples conform to the relation of equation 3, within ±1 mol percent apparent $CaCO_3$. Thus, a plot of this kind serves as a safeguard against gross errors in chemical analysis, especially with regard to calcium, and assures that the
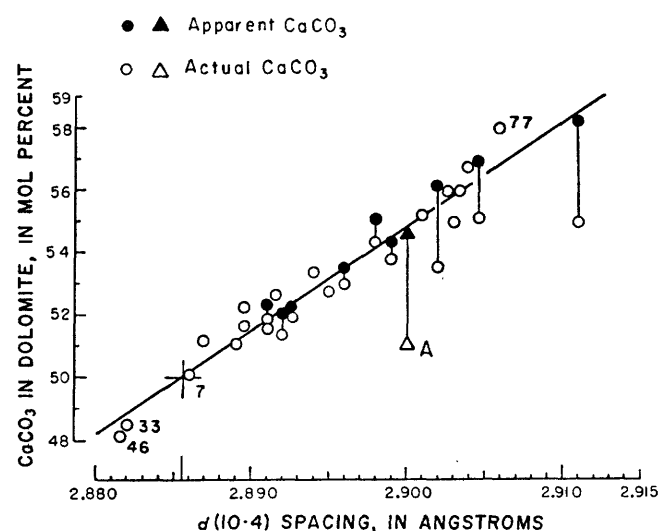

FIGURE 4.—Relation between the $d(10\cdot4)$ X-ray spacing and the apparent $CaCO_3$ content of dolomite, where apparent $CaCO_3$ in mol percent = actual $CaCO_3 + 0.19FeCO_3 + 0.37MnCO_3$. Single open circles represent actual $CaCO_3$ percentage in samples with less than 2 percent $FeCO_3$. Samples denoted by interconnected open and filled circles contain more than 2 percent $FeCO_3$, the open circles representing actual $CaCO_3$, the filled circles, apparent $CaCO_3$. Sample A (represented by triangles) is a ferroan dolomite from England, described by Howie and Broadhurst (1958).

determined components were in solid solution in dolomite and not present as separate phases. Figure 4 also emphasizes the rarity of ideal dolomite, approximated by sample 7, and how common samples with more than 50 mol percent $CaCO_3$ are among diagenetic dolomites. Samples 33 and 46 exemplify the rare type that contains less than 50 mol percent $CaCO_3$

INTERRELATION OF CHEMICAL AND CARBON-ISOTOPIC COMPOSITIONS

In our previous study of these dolomites (Murata and others, 1969), a curious inverse relation was noted between the contents of C^{13} and calcium among samples of the heavy-carbon group. The relations did not hold among members of the light-carbon group. No chemical analyses were made in that study, and the apparent calcium content was calculated from the magnitude of the $d(00\cdot6)$ spacing. In figure 5, the inverse relation
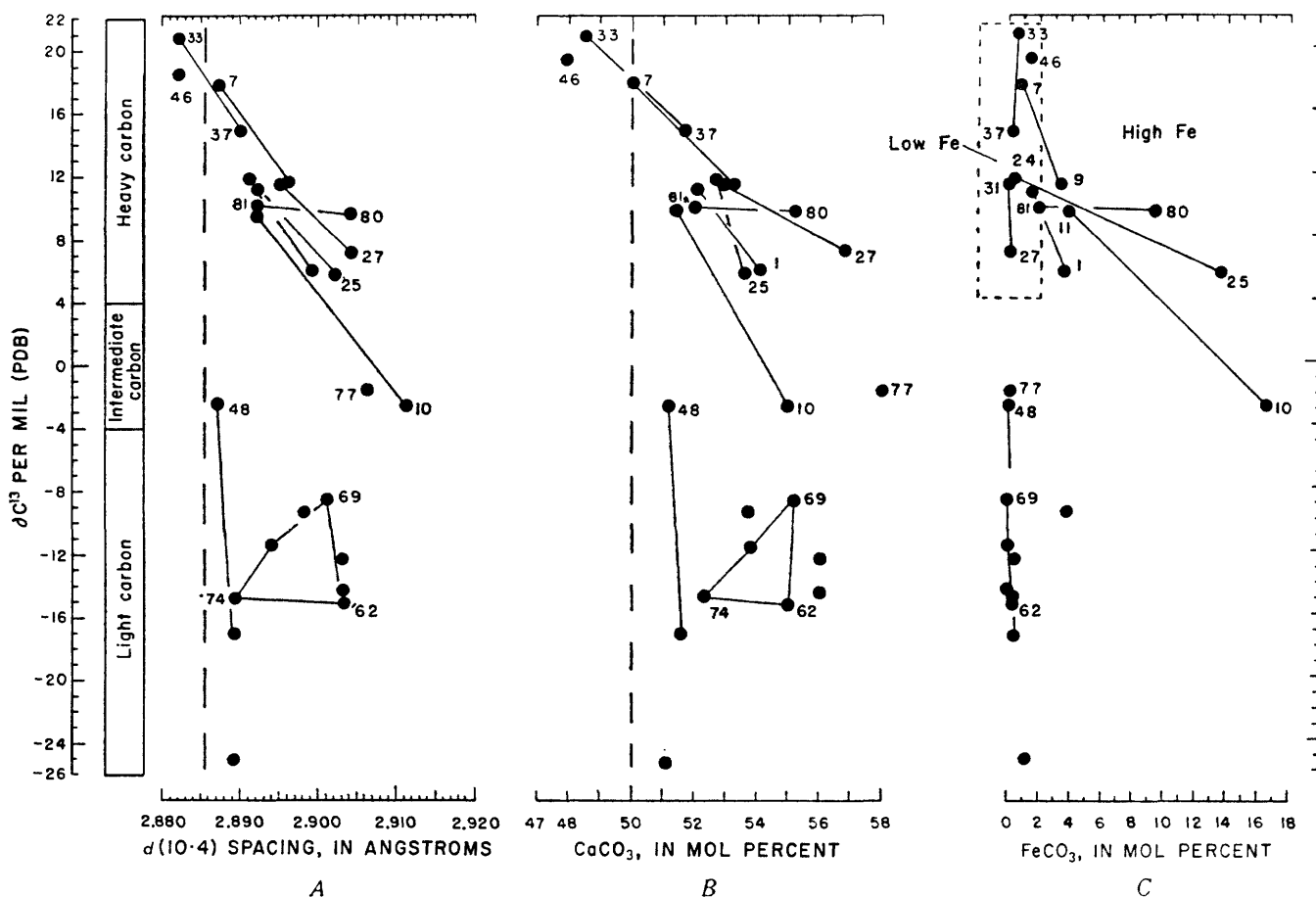
FIGURE 5.—Relation between carbon-isotopic composition of dolomite (ordinate) and A, the $d(10\cdot4)$ X-ray spacing; B, mol percent of $CaCO_3$; and C, mol percent of $FeCO_3$. C shows the basis for classifying these dolomites into a light-carbon group, an intermediate-carbon group, a heavy-carbon–low-iron ($FeCO_3 < 2.0$ percent) group, and a heavy-carbon–high-iron ($FeCO_3 > 2.0$ percent) group. Two or more samples from the same locality are linked by tielines. Numbered samples are discussed in the text.

between C^{13} content and the $d(10\cdot4)$ spacing is well shown, again among heavy-carbon dolomites only. The chemical analyses now allow us to examine the relation in greater detail.

The mol percents of $CaCO_3$ and $FeCO_3$ in the dolomites are plotted against the carbon-isotopic composition in figures $5B$ and $5C$ respectively. Light- and heavy-carbon dolomites have similar amounts of calcium, but light-carbon dolomites are poor in iron, generally less than 2 mol percent $FeCO_3$. The $d(10\cdot4)$ spacing of light-carbon dolomites is controlled solely by the content of calcium, according to equation 2.

Heavy-carbon dolomites (excepting samples 80–81) show a general inverse trend between the contents of calcium and heavy carbon C^{13}, which is not evident among light-carbon dolomites. With regard to the iron content (fig. $5C$), heavy-carbon dolomites are of two types:

1. Those exemplified by samples 7, 24, 27–31, and 33–37 that are poor in iron (<2.0 percent $FeCO_3$), resembling light-carbon dolomites in this respect but manifesting the inverse relation between calcium and C^{13}.

2. The remainder, which holds appreciable amounts of iron (>2.0 percent $FeCO_3$) varying directly with the content of calcium and, hence, inversely with the content of C^{13}.

Thus, in place of our previous classification into light- and heavy-carbon dolomites, the chemical data indicate a threefold division of (1) light-carbon dolomite, (2) heavy-carbon–low-iron dolomite, and (3) heavy-carbon–high-iron dolomite. We shall attempt to deduce the interrelation among the three types in subsequent sections of this report. As seen in figure $5C$, a region of overlap exists between heavy- and light-carbon dolomites in the δC^{13} range of 4 to -4 per mil. Samples 10

and 77 lie within this range; by using the content of iron carbonate as a criterion, sample 10 (16.6 mol percent) would be assigned to the heavy-carbon group, sample 77 (0.1 mol percent), to the light-carbon group.

LIGHT-CARBON DOLOMITES

In sediments rich in organic matter, the absence of any isotopic exchange between carbon dioxide and organic compounds is the basic condition for genesis of light-carbon dolomites. Without the control exerted by exchange equilibria, which inherently are dependent on temperature and composition, such dolomites show a generally random variation of isotopic composition with respect to physical-chemical parameters. Their light carbon originates from oxidation of sedimentary organic matter (Spotts and Silverman, 1966), and the isotopic composition varies between the limits set by organic matter ($\delta C^{13} \approx -30$ per mil) and by sedimentary marine carbonate ($\delta C^{13} = 0 \pm 4$ per mil).

The calcium content of light-carbon dolomites is independent of the content of C^{13}, but correlates weakly with the content of O^{18}, as shown in figure 6. We have not been able to attribute this correlation to any of the four calcium-controlling factors given under "Formation Waters Involved in Dolomite Genesis" (magnesium/calcium ratio, temperature, salinity, concentration of organic acids), for there are many more variables than interrelating equations.

Only a crude picture can be drawn of the conditions under which light-carbon dolomites form. In view of the demonstrated generation of light-carbon carbonate in Holocene marine sediments (Presley and Kaplan, 1968) and the samples from the shallow section of Palos Verdes Hills as examples, light-carbon dolomites (or their precursors) are thought to form at a depth of 1,000 feet or less in moderately compacted sediments rich in organic matter.

HEAVY-CARBON–LOW-IRON DOLOMITES

Heavy-carbon–low-iron dolomites are abundant at such classic California Miocene localities as Chico Martinez Creek, Nacimiento River, and Reliz Canyon. Compared with light-carbon dolomite, these dolomites probably formed at somewhat greater depth, where there was greater probability of carbon dioxide and methane undergoing isotopic exchange.

As previously discussed, exchange equilibrium imposes constraints on the isotopic composition of the involved compounds and allows the apparent temperature of equilibration to be calculated from the isotopic composition (Bottinga, 1969). Such calculations yield only rough estimates of temperature, but these are good enough to set highly useful limits on the physical-chemical conditions of diagenesis. Two assumptions necessary for the calculations are that (1) the isotopic composition of the methane involved in the equilibrium lies on the curve defined by the filled triangles in figure 1 or has some other parallel values permitted by existing data and (2) the equilibrium composition for dolomite is the same as that for calcite at all temperatures and will lie along the finely dashed curve in the middle of figure 1 when the methane composition is defined by the curve of filled triangles.

Samples 27, 31, and 33 will be used to illustrate the mode of calculation, and the pertinent data are tabulated below. The depth of origin of the dolomite is based on the calculated temperature and on the average geothermal gradient of the Los Angeles basin (Philippi, 1965).

	Nacimiento	River	Chico Martinez Creek
Sample No.	27	31	33
δC^{13} of dolomite, per mil	+7. 1	+11. 3	+20. 8
δC^{13} of methane from fig. 1, per mil	−39	−40	−44
Calculated temperature, °C	125	103	58
Calculated depth, feet	8, 800	7, 000	3, 200

The results for sample 27, namely 125°C and a depth of 8,800 feet, seem to be somewhat excessive, whereas those for sample 31, 103°C and 7,000 feet, are more reasonable in terms of the stratigraphy of the Nacimiento River region southwest of the Jolon fault (Durham, 1968).

This conclusion is in agreement with the general indication of figure 1 that in any given formation or locality, the carbon dioxide (or carbonate) with the heavist carbon most closely approached exchange equilibrium. The computed temperature and depth (58°C, 3,200 ft) for sample 33, with the heaviest carbon from Chico Martinez Creek, are also acceptable in terms of probable depth of burial of the formation sampled (Elliott and others, 1968).

The low-iron content of these dolomites suggests that they were derived directly from light-carbon–low-iron dolomites through the operation of isotopic exchange between carbon dioxide and methane. If the exchange reaction and recrystallization occurred with the involvement of a minimum of solution (smallest reservoir of dissolved calcium and magnesium), the resultant heavy-carbon dolomites could essentially inherit the widely ranging calcium content of the precursor light-carbon dolomite. The decrease in $CaCO_3$ that accompanies the rise in δC^{13}, as in samples 27–31 and 33–37 in figure 5B, is probably a gradual adjustment toward thermodynamic stability through elimination of excess calcium, a process paralleling the gradual attainment of isotopic exchange equilibrium.

HEAVY-CARBON–HIGH-IRON DOLOMITES

Examples of heavy-carbon–high-iron dolomites are samples 1, 10, 25, and 80, with 4–17 mol percent $FeCO_3$. In figure 5C, each of these samples is seen to be linked to another from the same locality (3, 11, 24, or 81) that is poorer in iron and richer in C^{13}. All four of the latter samples have δC^{13} of about +10 per mil, corresponding to a formation temperature of about 110°C, which may be near the maximum for diagenetic dolomites. The higher temperature corresponding to the lighter carbon of iron-rich members of each pair is probably fictitious, and the lightness of the carbon is more a measure of departure from exchange equilibrium. For example, if the δC^{13} of −2.8 per mil of sample 10 from the Santa Cruz Mountains is assumed to be an equilibrium value, an excessively high temperature of 180°C is obtained, which contrasts with the 110°C computed for sample 11 from the same locality.

The high concentration of iron in dolomites of this category requires a fundamentally different chemistry from that of the other categories. And the interpretation of seemingly identical relations, such as that between the contents of $CaCO_3$ and C^{13}, is radically different.

A high-iron dolomite like sample 10 could be derived from a lower iron dolomite like sample 11 by a dissolution-reprecipitation process that would increase the content of iron and calcium of dolomite as it lowered the content of C^{13}. The most direct way to effect this would be to introduce oxygenated meteoric water into the dolomite-bearing formation. This would most likely happen after orogenic movements raise a part of the sedimentary formation out of the sea, thereby exposing it to fresh water.

The great increase in soluble iron that occurs when oxygenated fresh water enters a reduced marine sediment has been well described by Langmuir (1969). Although the solubilization of iron was observed at depths of only a few hundred feet, in principle the reaction should be possible to far greater depths. Further effects of the intermixing of meteoric and deep-lying waters would generally include a reduction of salinity and a shift of the magnesium/calcium ratio to lower values; both of these effects would favor an increase of calcium in dolomite that was simultaneously being enriched in iron. Meteoric water would also raise the concentration of light-carbon bicarbonate, derived through oxidation of organic matter either in surface soils or in the dolomite-bearing formation itself. The net result of all of these reactions would be a trend of alteration of a given dolomite toward a composition richer in iron and calcium and poorer in C^{13} and O^{18}.

Strong support for a mode of forming iron-rich dolo-

mites through the influence of fresh water is provided by the oxygen-isotopic composition (Murata and others, 1969) of the dolomites (fig. 6). The δO^{18} of deep-lying
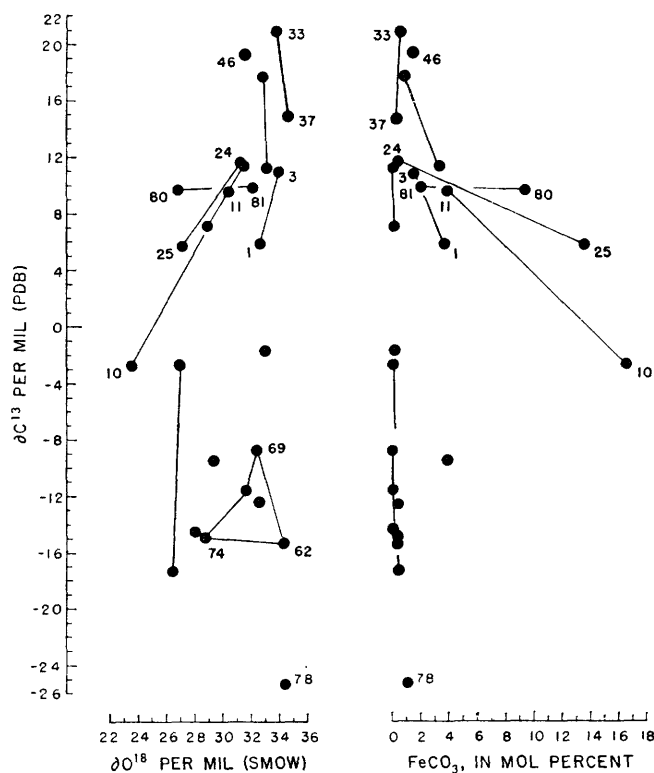

FIGURE 6.—Relation of oxygen-isotopic composition of dolomite and the content of $FeCO_3$ to the carbon-isotopic composition (ordinate). Note in the upper half of the figure the symmetrically divergent patterns among certain pairs of heavy-carbon–high-iron dolomites (samples 1–3, 10–11, 24–25, and 80–81).

formation waters can be as heavy as +9 per mil relative to standard mean ocean water (SMOW) (Clayton and others, 1966), whereas that of fresh water is always lighter than sea water, with δO^{18} of −15−−5 per mil SMOW in the middle latitudes (Epstein, 1959). As the oxygen-isotopic composition of a formation water becomes lighter through increasing admixture of fresh water, the oxygen of dolomite will tend to become lighter through isotopic exchange with the water.

The correlation of a higher content of iron with lighter oxygen in dolomite is well shown in the upper half of figure 6, in the symmetrically divergent pattern of several pairs of samples (1–3, 10–11, 24–25, and 80–81). The δO^{18} of these samples decreases at the rate of −0.3−−0.7 per mil for every mol increase of $FeCO_3$, a rate too great to be ascribed to any specific effect of iron on the equilibrium constant of oxygen exchange between dolomite and formation water (O'Neil and others, 1969). The pair 80–81 differs from the other three by not

showing a decrease in δC^{13} commensurate with the decrease in δO^{18}. Such a unilateral change could result if the introduced fresh water were low in bicarbonate, possibly through prior precipitation of a carbonate.

The generally interrelated variations of O^{18}, C^{13}, $CaCO_3$, and $FeCO_3$ in dolomites of the present category are consequences of meteoric water gaining access to once deeply buried marine formations. If this interpretation is essentially correct, iron in diagenetic dolomites of California has a very interesting connotation of time, pointing to a postorogeny period of formation for the iron-rich samples.

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Shorter Contributions

to General Geology,

1971

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