Isotopic Composition of Diagenetic Carbonates in Marine Miocene Formations of California and Oregon

GEOLOGICAL SURVEY PROFESSIONAL PAPER 614-B

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Isotopic Composition of Diagenetic Carbonates in Marine Miocene Formations of California and Oregon

By K. J. MURATA, IRVING FRIEDMAN, *and* BETH M. MADSEN

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

GEOLOGICAL SURVEY PROFESSIONAL PAPER 614-B

A discussion of the isotopic composition
of diagenetic carbonates in terms of
chemical processes that operate in
deeply buried marine sediments

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1969

UNITED STATES DEPARTMENT OF THE INTERIOR

WALTER J. HICKEL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, ***Director***

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 45 cents (paper cover)

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ISOTOPIC COMPOSITION OF DIAGENETIC CARBONATES IN MARINE MIOCENE FORMATIONS OF CALIFORNIA AND OREGON

By K. J. MURATA, IRVING FRIEDMAN, and BETH M. MADSEN

ABSTRACT

Diagenetic carbonates, mostly protodolomite, occur as thin beds or concretionary zones in marine Miocene shales of California and Oregon. They manifest an unusually wide range of carbon isotopic composition (δC^{13} of -25 to $+21$ per mil relative to Peedee belemnite standard) and are divisible into a light-carbon group (δC^{13} of -2 to -25 per mil) and a heavy-carbon group (δC^{13} of $+5$ to $+21$ per mil). The range of their oxygen isotopic composition coincides generally with that of normal marine carbonate (δO^{18} of 26 to 34 per mil relative to standard mean ocean water).

Calcite of Foraminifera and other fossils (δC^{13} of 0 ± 4 per mil) in consolidated sediments was dissolved and redeposited along certain favorable zones to form diagenetic calcite. The formation water involved must have contained at least as much O^{18} as sea water for the δO^{18} of diagenetic calcite to lie in the range of normal marine carbonate. Dissolved in the water were carbonate methane, naphthenates, and other substances formed through diagenetic alteration of organic matter in the sediments. The δC^{13} of the deposited calcite differed substantially from that of the original fossils, the carbon being heavier or lighter depending on whether or not isotopic equilibrium was attained between the carbonate ion and methane.

Isotopic exchange equilibration between carbonate ion and methane concentrates C^{13} in the carbonate and is the most likely mechanism for producing heavy-carbon carbonates. Without this equilibration, the carbonate ion will be rich in C^{12}, in keeping with its derivation from organic matter, and will yield diagenetic carbonates of the light-carbon group. The exchange could take place between finely porous carbonate and methane gas without necessarily involving water; this could lead to variation in the carbon isotopic composition among some heavy-carbon carbonates without a concomitant variation in oxygen composition or in crystalline texture.

At most places, the first-stage diagenetic calcite was soon dolomitized by brines that tended to make the oxygen somewhat heavier (maximum δO^{18} of 35.4 per mil) and the carbon, as well, if the carbonate-methane equilibration was operating. Protodolomite with a calcium content as high as 58 mol percent formed first, but in time exsolved the excess calcium to become ideal dolomite. Among some heavy-carbon dolomites, these several adjustments led to an inverse relation between the content of calcium and either the carbon or oxygen isotopic composition.

The temperature implications of the carbon isotopic composition can be explored in a preliminary way if it is assumed that the methane involved in the equilibration had the same isotopic composition as the methane of natural gas from oil fields (most prevalent δC^{13} values of -52 to -38 per mil). Under this assumption, the heaviest and the lightest carbonates (δC^{13} of $+21$ and $+5$ per mil) within the heavy-carbon group limit equilibrium temperatures to 34° to 140°C. Existing data on genesis of petroleum indicate that transformation of organic matter into petroleum proceeds at an appreciable rate only at temperatures higher than about 115° C. Most of the diagenetic carbonates seem to have formed at somewhat lower temperatures, but their isotopic and mineralogical natures clearly suggest them to be byproducts of petroleum-generating reactions.

An interesting variant of diagenetic carbonate is the calcite cement of the Miocene oil-bearing sands that occur as coastal plain deposits lapping onto the granite of the Sierra Nevada. The formation water in these marine sands is virtually fresh. The presence of fresh water accounts for the fact that the carbon and oxygen isotopic composition of the calcite cement is similar to that of fresh-water limestone and explains why the cement escaped the almost universal dolomitization that occurred elsewhere.

INTRODUCTION

Diagenetic carbonate in the form of indurated beds of concretionary zones is a minor but conspicuous rock in the Miocene Nye Mudstone of Oregon and the Monterey Shale of California (Snavely and others, 1964; Bramlette, 1946). Recently, interest in this carbonate has grown because of the realization that it is mostly dolostone rather than limestone and that, in many places, it is extraordinarily rich in carbon isotope C^{13} (Murata and others, 1967).

In the present paper, we discuss the mineralogy and the carbon and oxygen isotopic composition of 79 samples of this and related carbonates from widely scattered localities (fig. 1). The main impetus for the study springs from the possibility of gaining new insight into the diagenesis of organic-rich sedimentary rocks such as the Monterey Shale.

For our purpose, we adopt the broad definition of diagenesis given in the "Dictionary of Geological Terms" of the American Geological Institute (1962): "Process involving physical and chemical changes in sediment after deposition that converts it to consolidated rock; includes compaction, cementation, recrystallization, and perhaps replacement as in the development of dolomite." Existing data on the formation and diagenesis of limestone and dolostone have been well summarized in two recent reviews (Pray and Murray, 1965; Chilingar and others, 1967).

Diagenesis of the Monterey Shale has attracted the attention of many investigators because the shale is unusually rich in opaline silica (diatoms) and because it is considered to have been the source bed of much petroleum in California. Besides the carbonates that constitute the subject of our inquiry, diagenesis has produced chert from the opaline silica of diatoms (Bramlette, 1946), zeolites and montmorillonite from volcanic tuffs (Bramlette and Posnjak, 1933), and oil from sedimentary organic matter (Trask, 1932; Philippi, 1965). The middle Miocene part of the Monterey Shale is highly phosphatic (Gower and Madsen, 1964; Dickert, 1966). Although no diagenetic effects have been noted so far in the phosphorite, future studies will probably disclose such effects even in this relatively stable material.

FIGURE 1.—Localities of the carbonates that were studied. Numbers in parentheses are the sample numbers listed in table 1.

ACKNOWLEDGMENTS

We are indebted to Prof. D. L. Inman of Scripps Institution of Oceanography for sample 78 from La Jolla Canyon. Advice regarding stratigraphy, paleontology, and isotope geology of west coast Tertiary rocks was generously given by Prof. M. N. Bramlette and Dr. Arthur Jokela of Scripps Institution of Oceanography, by Prof. R. H. Jahns of Stanford University, by Dr. S. R. Silverman of Chevron Research Co., and by our colleagues, W. O. Addicott, Ivan Barnes, R. H. Campbell, T. W. Dibblee, Jr., D. L. Durham, G. W. Moore, J. R. O'Neil, R. O. Rye, J. E. Schoellhamer, Patsy J. Smith, P. D. Snavely, Jr., H. F. Tourtelot, and R. E. Zartman. Laboratory investigations were carried through with the able assistance of R. R. Bruegger, Chere N. Barnett, Joy Church, and James Gleason.

MODE OF OCCURRENCE OF DIAGENETIC CARBONATE

Figure 2*A* shows the typical mode of occurrence of diagenetic carbonate. It is found in conformable beds or concretionary zones, generally less than 3 feet thick, spaced 5 to 50 feet apart in the shale or mudstone of the west coast Miocene. The associated shale or mudstone may be devoid of any carbonate or may be moderately rich in calcareous Foraminifera. Figure 2*B* illustrates an occurrence of diagenetic carbonate in a sequence of alternating layers of shale and sandstone; the thin sandstone layers are hardened by a calcite cement. A closer view of the lowest of the three carbonate beds of figure 2*B* is shown in figure 2*C*. Although very ordinary in appearance, this bed has an exceptionally heterogeneous composition. Its top is dolomitic; its bottom, calcitic; and the middle part, a variable mixture of the two carbonates. It apparently represents an incompletely dolomitized bed of diagenetic limestone; all the dolostone beds may originally have been limestone. Thin sections of the dolomitic and calcitic parts of the bed are shown in figures 5*C* and 5*F*.

In demonstrating the secondary (diagenetic) origin of carbonate concretions and lenticular beds in the Monterey Shale, Bramlette (1946) called attention to the relation of carbonate concretions to the bedding in the enclosing strata. Beds continue through the concretions and are thicker inside of them than outside, as if the concretions had preserved an earlier thickness of

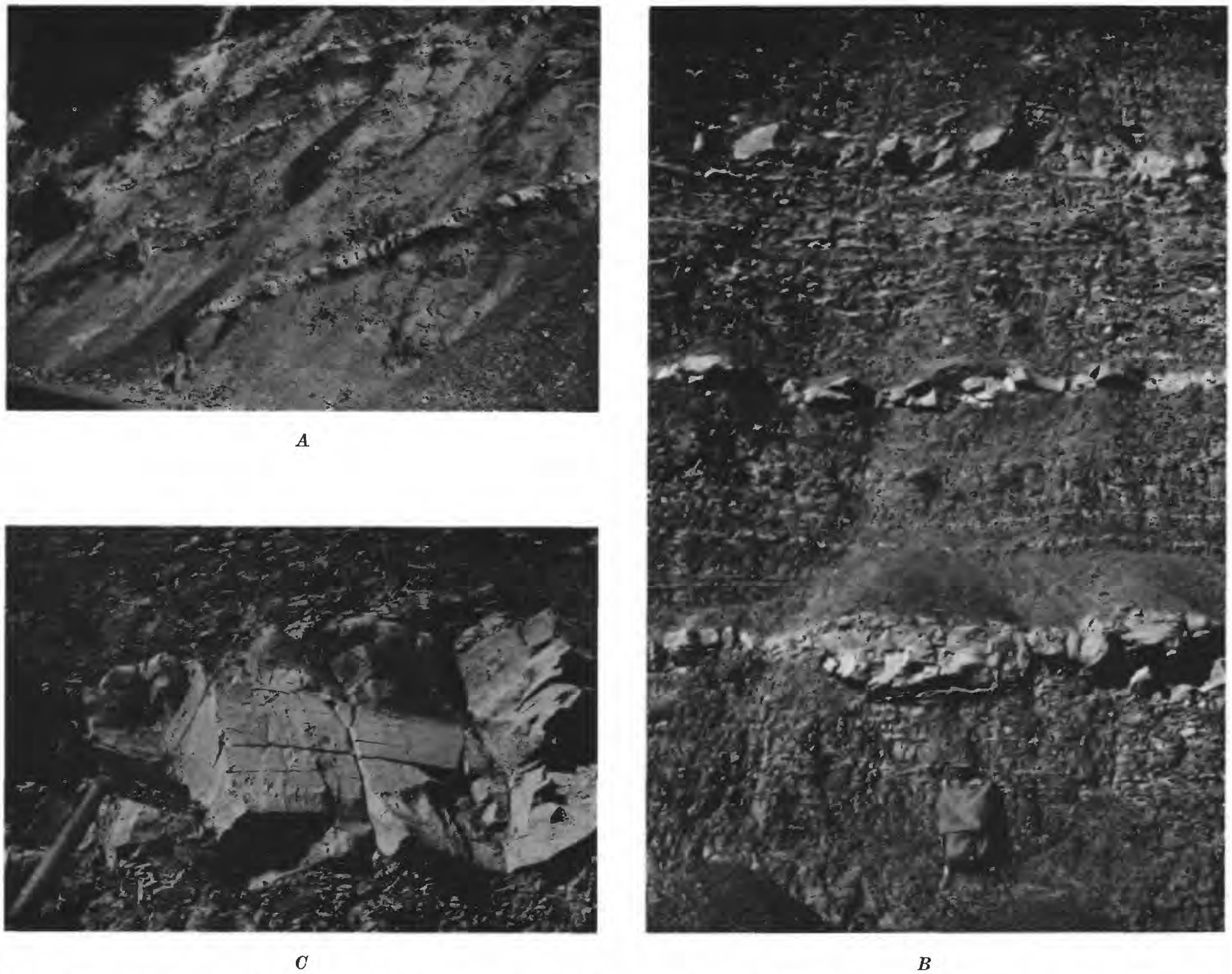

FIGURE 2.—Typical outcrops of Miocene diagenetic carbonates. *A*, Dolomitic beds and lenses in the Nye Mudstone, north side of Yaquina Bay, Lincoln County, Oreg. Sample 2 of table 1 was obtained from the bed near the man. Photograph by P. D. Snavely, Jr. *B*, Carbonate zones (the three thicker beds) in the Monterey Shale of Pine Mountain, Ventura County, Calif. At this locality, the shale contains numerous thin layers of calcite-cemented sandstone. The rucksack is 30 inches long. *C*, Detail of the lowest carbonate bed in view *B*. The upper part of this bed is dolomitic; the lower part, calcitic; the two parts are represented by samples 56 and 57, respectively, in table 1. The hammer is 11 inches long.

the beds against the compressive load of the overlying sediment. He emphasized the general impurity of the carbonate: "All the concretions include more or less sedimentary material similar to that forming the adjacent beds, and most of them are little more than carbonate-cemented nodular masses of the sedimentary material forming these adjacent beds." In some places, impregnation by carbonate protected opaline diatoms from being dissolved and glassy pumice from altering to montmorillonite.

The dolomite content of the dolostone generally depends on the porosity of the host sediment and varies among our samples from about 40 weight percent in dolomite-cemented sandstone to about 85 percent in dolomitized diatomite. The massive, apparently laminated, dolostone shown in figure 3 contains 84 percent dolomite without any calcite; its insoluble residue consists almost entirely of tests of diatoms with very few detrital minerals. Pure diatomite may have a porosity as high as 75 percent and upon impregnation with dolomite could yield a rock containing about 80 percent dolomite. Thus, this sample of dolostone probably formed mainly through impregnation rather than replacement of laminated diatomite, a type of sediment common in the Monterey Shale. A few dolomitized tests of Foraminifera in the dolostone further indicate that any and all calcite originally present in the diatomite would have been converted to dolomite. A thin section of this sample is shown in figure 5*B*.

Two aspects of the diagenetic carbonate are especially significant with regard to its origin and nature. First, the widely spaced thin beds of the carbonate constitute a minor constituent, making up perhaps a percent or so of the total thickness of a typical section. Second, with a few exceptions, the diagenetic carbonate is dolomite rather than calcite. The frequent presence of dolomite along sharply delimited horizons in moderately calcareous shale sections indicates that dolomitization was effected only along certain favorable zones by solutions introduced from outside.

Later in the report, we shall postulate certain isotopic reactions between methane (generated by burial metamorphism of organic matter) and the carbonate, in order to account for abnormally heavy carbon in the carbonate of Monterey Shale. The effect of such reactions would be greatest in a formation like the Monterey Shale in which the ratio of organic shale to carbonate is large and in which the reacting fluids moved only along certain zones rather than by diffusing throughout the section.

FIGURE 3.—Dolomite (sample 8 of table 1) from the Miocene of the Berkeley Hills, Calif. This hard massive rock originated through impregnation of laminated diatomite with dolomite (84 weight percent). Insoluble matter consists largely of opaline tests of diatoms with very few detrital minerals. Vertical cracks contain very late calcite.

FACTORS THAT CONTROL CARBON AND OXYGEN ISOTOPIC COMPOSITION

Because comprehensive reviews of the general geochemistry of carbon and oxygen isotopes have been published recently (Craig, 1963; Rankama, 1963; Silverman, 1964; and Degens, 1965), only data and concepts that are pertinent to the origin of diagenetic carbonates need to be considered here. Carbon isotopes of sedimentary rock can be discussed in terms of two major categories of materials with distinctly different isotopic composition: (1) Marine limestone ($\delta C^{13}=0\pm4$ per mil relative to the PDB, or Peedee belemnite, standard of University of Chicago), and (2) organic substances (such as coal, oil, and dispersed organic matter of soils or shales), containing much lighter carbon ($\delta C^{13}=-35$ to -8 per mil) and carbon dioxide derived through oxidation of these organic substances. The relatively constant isotopic composition of marine limestone results from precipitation of the limestone under conditions of isotopic equilibrium with the bicarbonate of sea water, which is virtually constant isotopically ($\delta C^{13}=-2.5$ to -1.3 per mil according to Craig, 1954).

The light carbon that characterizes all organic substances originates in the marked preference shown by plants for isotope C^{12} during photosynthesis. Carbon of plant tissues can be deficient in C^{13} by as much as 30 per mil relative to atmospheric carbon dioxide (Park and Epstein, 1961). The following table gives the isotopic composition of atmospheric carbon dioxide, plant tissue, derivative sedimentary organic matter, and other related substances. The isotopic composition of organic matter of animals is similar to that of the plants on which they feed.

Material	δC^{13} *(per mil, PDB)*	*Reference*
Atmospheric CO_2	-7.4 to -6.7	Keeling (1958).
Marine bicarbonate	-2.5 to -1.3	Craig (1954).
Marine limestone	-4 to $+4$	Baertschi (1957).
Marine plants	-30 to -12	Deuser and Degens (1967).
Terrestrial plants	-29 to -23	Craig (1953).
Organic matter of marine sediments.	-31 to -14	Craig (1953) and Sackett (1964).
Coal	-27 to -22	Craig (1953).
Petroleum	-34 to -22	Silverman (1964).
Bicarbonate in fresh water.	-23 to -4	Oana and Deevey (1960).
Fresh-water limestone	-18 to -3	Clayton and Degens (1959) and Münnich and Vogel (1959).

In comparison to sea water and marine limestone, terrestrial waters and limestone contain carbonate whose carbon is generally lighter and more variable isotopically, as indicated in the table. Fresh water contains, besides the normal bicarbonate based on carbon dioxide of the atmosphere, substantial and variable amounts of much lighter bicarbonate (δC^{13} of −30 to −20 per mil), based on the carbon dioxide derived from the decaying organic matter of soils. The variation of isotopic composition of fresh-water bicarbonate and limestone from such light values to those of marine limestone depends on the extent to which circulating fresh water encounters and dissolves marine limestone (Oana and Deevey, 1960).

Oxygen isotopic composition of sea water is fairly constant at δO^{18} of 0 ± 1 per mil relative to standard mean ocean water (SMOW), according to Epstein and Mayeda (1953) and Craig and Gordon (1965). In the hydrologic cycle, water is evaporated from the ocean under nonequilibrium conditions to yield vapor of light H_2O with δO^{18} of −14 to −10 per mil (Craig and Gordon, 1965). Water-laden air from lower latitudes moves poleward and precipitates rain or snow on land and sea, as it encounters progressively lower temperatures. H_2O^{18} tends to condense preferentially from the migrating vapor, giving rise to changes in the isotopic composition of the precipitation depending upon the latitude. As a result, polar ice can be as light as δO^{18} of −50 to −40 per mil (Epstein, 1959). The contrast between sea water and fresh water in the middle latitudes would be δO^{18} of zero for the former and of −15 to −5 per mil for the latter.

This contrast in oxygen isotopic composition of marine and terrestrial waters also appears in marine and fresh-water limestones. Besides the original isotopic composition of the water, temperature of the water also determines the amount of O^{18} in carbonates. Because oxygen of sea water is nearly constant isotopically, the range of δO^{18} in marine limestones (mostly 26 to 34 per mil, SMOW) is largely attributable to variations in temperature of the water, and indeed such variations form the basis for determining the paleotemperatures of ancient seas (Urey and others, 1951; Bowen, 1966). Fresh-water carbonates (δO^{18} mostly in the range of 9 to 23 per mil) are more complex because they form from solutions that vary widely in both isotopic composition and temperature (Weber, 1964).

With both carbon and oxygen tending to be lighter in terrestrial than in marine limestone, isotopic composition would seem to be a useful indicator of the depositional environment. The criterion has proved to be ambiguous for some samples because of moderate overlap of isotopic compositions, but is accurate in some 80 percent of the samples (Clayton and Degens, 1959; Keith and Weber, 1964; Keith and others, 1964). The isotopic composition of most of our diagenetic carbonates indicates derivation from neither fresh water nor sea water, but rather from a different category of natural water, probably that which is commonly called formation water or oil-field brine.

TIME AND CIRCUMSTANCE OF DIAGENESIS

Diagenetic carbonate of the Monterey Shale evidently formed before the final compaction of the host sediment (Bramlette, 1946), but neither the circumstance of its formation nor the kind of chemical solution involved is known. Lithification of modern calcareous sediments lying exposed on the sea floor has been reported by Fischer and Garrison (1967). However, the hard carbonate layers in the Monterey Shale could not have formed in this way, because their carbon isotopic composition indicates equilibration with solutions very different from sea water and because they commonly involve carbonate-poor materials, such as diatomite and volcanic tuff.

Studies of modern marine sediments and their interstitial waters (Emery and Rittenberg, 1952; Siever and others, 1965; Berner, 1966; among others) have generally disclosed little diagenetic change in these sediments to a depth below the sea floor of 10 meters or so, representing a timespan of 10^5 to 10^6 years. The interstitial water of some modern marine sediments, however, is enriched in phosphate and silica and depleted in sulfate as the result of diagenetic reactions (Emery, 1960; Brooks and others, 1968).

Even older sediments, such as the Miocene ooze recovered during experimental mohole drilling of the Pacific sea floor (Riedel and others, 1961; Murata and Erd, 1964), are soft and porous and have no indurated zones of carbonate or chert. The interstitial water in this ooze differs very little from normal sea water (Rittenberg and others, 1963; Siever and others, 1965); it is, however, somewhat deficient in deuterium (Friedman, 1965). The calcite and dolomite of the ooze have carbon and oxygen isotopic compositions in the range of normal marine carbonate (Degens and Epstein, 1964).

Compared to such relatively unaltered sediments, the Monterey Shale and overlying sediments accumulated to much greater thickness in nearshore basins, underwent moderate burial metamorphism, and at many places were uplifted into the zone of weathering during Pliocene and later orogenies. The Los Angeles basin contains over 25,000 feet of Miocene and Pliocene sedimentary rocks (Barbat, 1958; Yerkes and others, 1965), and other basins, such as Chico Martinez Creek (Bramlette, 1946) and Reliz Canyon (Durham, 1963), have more than 7,000 feet of middle and upper Miocene sedimentary rocks which, before much of the cover of younger deposits was eroded away, must have lain at depths of 10,000 to 12,000 feet. At such depths, sediments would have been subjected to temperatures higher than 100° C, which would be sufficient to convert sedimentary organic matter into petroleum (Philippi, 1965), accelerate the reconstitution of biogenic opaline silica into chert, and induce many other chemical changes in a geologically short time.

Unlike the sea-water-like interstitial solutions found in undisturbed deep-sea oozes of even Tertiary age, formation waters (oil-field brines) that occur in the Monterey Shale and related formations vary greatly in salinity and composition. They range in salinity from fresh water to brines several times more saline than sea water (Jensen, 1934; White, 1965). Deeply circulating meteoric water becomes converted into saline formation water by passage through semipermeable shales and by undergoing numerous other chemical reactions that alter and reconstitute sedimentary materials (Clayton and others, 1966; Anderson and others, 1966; Rittenhouse, 1967). As will be shown later, the isotopic composition of the diagenetic carbonates indicates that formation waters from which most of the carbonates separated resemble neither fresh water nor sea water, but rather constitute a different category of natural water.

METHODS OF PREPARATION AND ANALYSIS OF THE SAMPLES

To prepare the samples, one or two pieces of each carbonate were first sawed perpendicularly to the bedding plane and stained with alizarin red sulfonate (Friedman, 1959). Samples shown by the staining test to be finely intergrown mixtures of dolomite and calcite were discarded. Many of these consisted of calcareous Foramnifera imbedded in a fine-grained dolomitic groundmass and probably represented a stage of alteration of calcareous shale transitional to dolostone in which both the Foraminifera and the groundmass are dolomitic. Some of the rejected samples were fractured dolostones extensively veined by late calcite.

X-ray diffractometer patterns of all samples that passed the staining test were made with nickel-filtered copper radiation at a scanning speed of 1° of 2Θ per minute, in order to verify the purity of the carbonate and to determine the nature of the associated noncarbonate minerals. Special X-ray patterns were prepared, by using a scanning speed of ¼° of 2Θ per minute and elemental silicon as the internal standard, to determine accurately the unit-cell dimensions of 14 dolomite samples by means of the computer method of Evans, Appleman, and Handwerker (1963). The relationship between cell dimension and composition of dolomite (Goldsmith and Graf, 1958) indicated that the calcium content of the 14 samples varied substantially, ranging from 50 to 58 atomic percent.

A crude but useful index of the cell dimension and composition was also obtained for all other dolomites from the patterns taken at 1° per minute, by determining the d-spacing of the {222} reflection, using the main quartz peak at 3.343A (angstroms) as the internal standard. The principal {211} peak of dolomite is so broad in these patterns that its spacing could not be measured as precisely as that of the {222} peak. The working curve that relates atomic percent of calcium (determined on the ¼° per min patterns) and the d_{222} spacing (determined on the 1° per min patterns) is given in figure 4, and compositions derived from this curve are listed in table 1. Even a crude estimate of the composition is of much interest from the viewpoint of the thermal history of the samples, because dolomites containing more than 50 atomic percent of calcium (protodolomites) are unstable above about 200°C (Goldsmith, 1959).

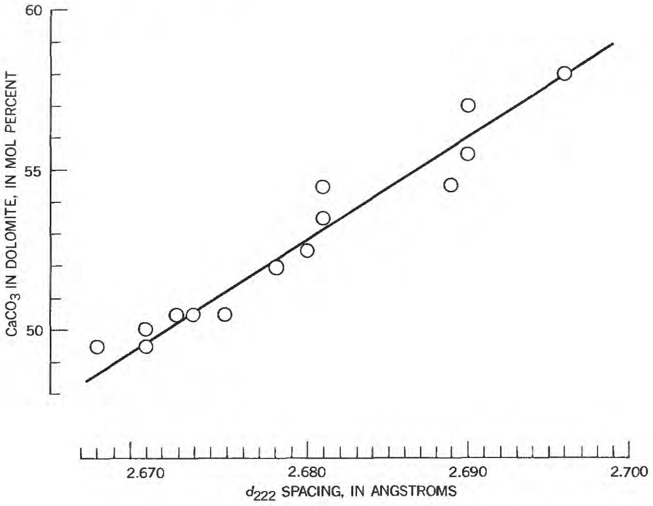

FIGURE 4.—Covariance of $CaCO_3$ content of dolomite and the d-spacing of {222}, Equation for the line is as follows:
$CaCO_3$ (mol percent) $=322.6(d_{222}-2.668)+49.0$.

Carbon and oxygen isotopic compositions were determined on carbon dioxide, which was obtained by decomposing the samples with 100 percent phosphoric acid (McCrea, 1950) and was analyzed in an isotope ratio mass spectrometer (McKinney and others, 1950). Prior to decomposition by acid, many of the samples were held at 300°C for an hour in a stream of helium in order to remove the more labile organic matter. Carbon isotopic composition is expressed relative to University of Chicago PDB standard (Craig, 1957), and oxygen isotopic composition, relative to SMOW (Epstein and Mayeda, 1953; Craig, 1961). The reproducibility of the determinations is ±0.1 per mil.

The analytical results are given in table 1. Where two or more samples are listed from a given locality, they are in stratigraphic order, the youngest sample being given first. The sampled beds represent from a quarter to a half of the total available and are usually spaced 30 to 100 feet apart with one or more unsampled beds in between; a few pairs of samples (such as Nos. 10 and 11, and 59 and 60) are from beds over 500 feet apart. Of the 79 samples listed in table 1, 60 represent dolomite beds or concretions; 1, vein dolomite; 1, dolomitic cement of sandstone; 8, calcareous fossils or Foraminifera-rich shales; 4, limestone lenses; 4, calcareous cement of sandstones; and 1, vein calcite.

PETROGRAPHY OF SAMPLES

Photomicrographs of thin sections of a dozen samples of different textural type and isotopic compositions are presented in figure 5 in order to show the microscopic character of the carbonate, whose megascopic appearance was illustrated in figures 2 and 3. The individual samples are described in detail in the legends to the figures. The photomicrographs were made at a magnification of ×100, because at this high magnification inherited textures can be largely ignored and attention focused on the crystalline character of the diagenetic carbonate itself.

Figure 5 shows clearly that diagenetic calcite and dolomite, though differing greatly in isotopic composition, are commonly very fine grained with crystal diameters of the order of 5 microns (compare figs. 5*A* and 5*L*). The lack of correlation between isotopic composition and grain size of dolostone has already been emphasized by Weber (1964). The texture of dolomite sample 8, the hand specimen of which was illustrated in figure 3, is shown in figure 5*B*; its variability is simply inherited from the original varved diatomite. Thin sections of the dolomitic and calcitic parts of a single bed are shown in figures 5*C* and 5*F*, respectively. The coarser texture of the dolomitic part suggests that a considerable enlargement of crystal size sometimes occurs when fine-grained calcite is dolomitized.

Figure 5*I* illustrates a type of dolostone that is made up of euhedral crystals of dolomite each with a nucleus of oily material or a gas, probably carbon dioxide. The carbonate-carbon of this dolomite is so light ($\delta C^{13} = -11.7$ per mil) that it suggests a genetic relationship to the light carbon of the nuclear material (Spotts and Silverman, 1966). Simple impregnation of a carbonate rock with tar or other organic matter, however, does not automatically introduce light carbon into the carbonate mineral. Sample 21 of table 1 (+0.03, 28.4) is a tar-soaked coquina of Foraminifera which well illustrates a lack of isotopic exchange between organic matter and carbonate. Although organic matter clearly has a role in determining the carbon isotopic composition of many samples, no general correlation between concentration of organic matter and isotopic composition could be established; this agrees with the results of Jeffrey, Compston, Greenhalgh, and De Laeter (1955).

The state of oxidation of many samples can be judged roughly from the relative abundance of small blebs of authigenic pyrite and blebs of hematitic pseudomorphs of the pyrite. However, no consistent relationship between the state of oxidation and the isotopic composition is apparent.

Primary calcite still retaining to a large degree the isotopic composition of normal marine carbonate is exemplified by the barnacle shell in figure 5*E* and by foraminiferal debris in the shale in figure 5*G*. A type of secondary calcite, with isotopic characteristics indicating equilibration with fresh water, cements the grains of the marine sandstone shown in figure 5*J*. The calcite consists of crystals as coarse as the sand grains and very irregular in shape (almost amoebiform).

We have been able to attach genetic significance to only a few of the different petrographic features illustrated in figure 5. The figure is presented mainly to show typical samples and to indicate concisely the apparent lack of correlation between petrographic character and isotopic composition.

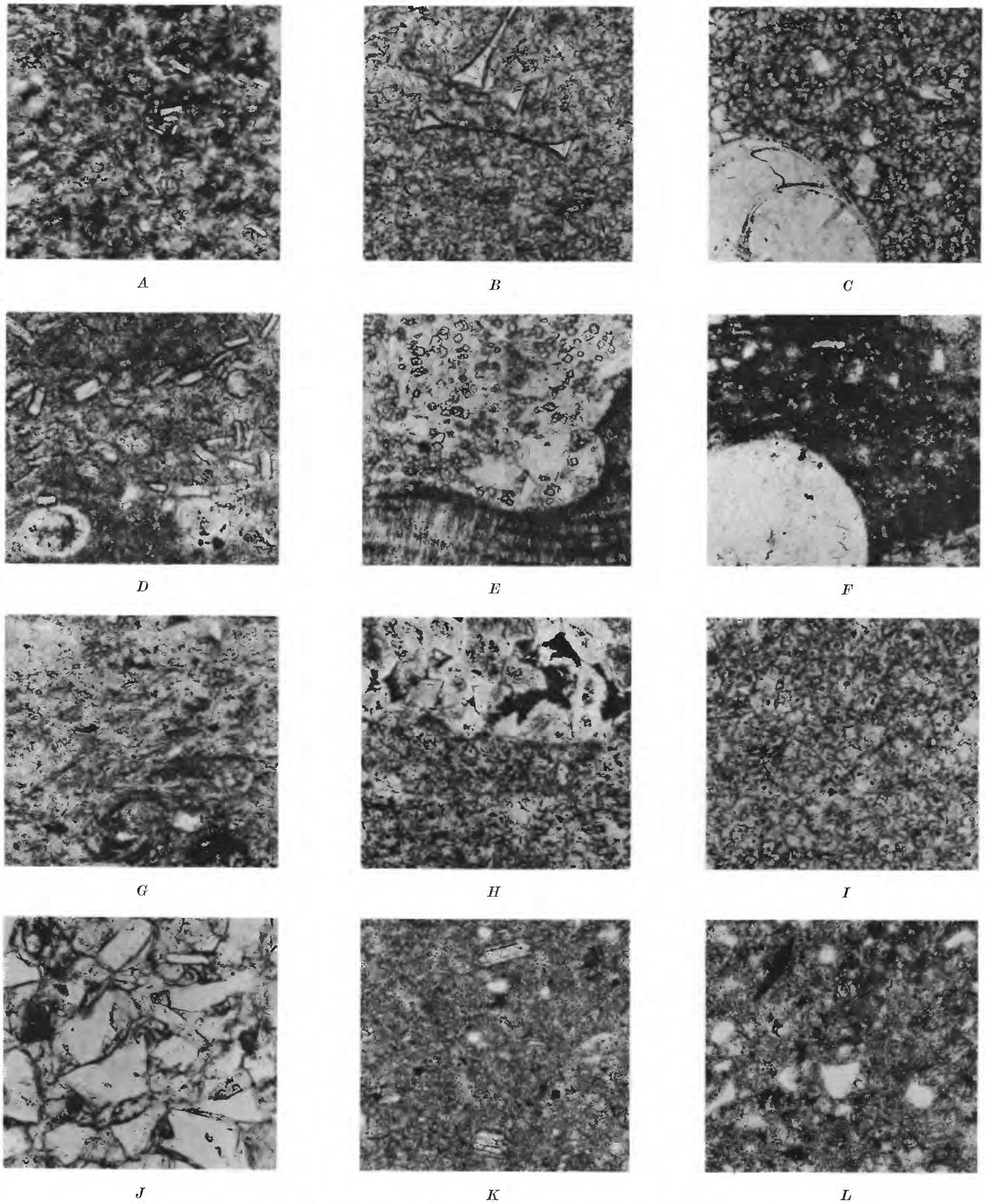

FIGURE 5.—Photographs of thin sections. (Explanation on facing page.)

FIGURE 5.—Photomicrographs of thin sections of carbonate rocks, all taken with plain light at magnification of × 100. All sections were cut perpendicularly to the bedding. In the legend for each sample, the first of two numbers enclosed in parentheses is the carbon isotopic composition relative to the PDB standard, and the second is the oxygen isotopic composition relative to SMOW. Sample numbers are the same as those used in table 1.

A. Dolomite sample 33 (+20.8, 33.8). Fine-grained impregnation of a diatom-rich sediment; contains the heaviest carbon.

B. Dolomite sample 8 (+19.4, 33.1). Vertical variation in grain size in part of a varve layer was inherited from the original varved diatomite; rich in diatoms (elongate objects in figure) and formless opal that fills the porous parts of each varve. A hand specimen of this sample is illustrated in figure 3.

C. Dolomite sample 56 (+12.5, 31.4). From same bed as calcite sample 57 of *F* below. Upper part of bed shown in figure 2*C*. Moderately coarse texture. Foraminifera in lower left corner is partly dolomitized and is filled with sparry crystals of both dolomite and calcite.

D. Calcite sample 51 (+15.2, 28.8). Fine-grained groundmass. Interior of diatoms and Foraminifera are filled with sparry calcite, chalcedony, or hematite probably after pyrite. Dolomite of *A* above may have had calcite like this as a precursor.

E. Calcitic shell sample 14 (−1.4, 27.7) of a barnacle is seen in cross section along the bottom of the figure. Tiny euhedral dolomite crystals (+7.0, 30.2) and opal make up the light-colored matrix; the matrix also contains a moderate amount of detrital minerals, such as those lying in the concavity of the shell.

F. Calcite sample 57 (+10.2, 27.3) from the same bed as dolomite sample 56 of *C* above. Fine-grained calcite with much brown organic matter. Foraminifera is filled with sparry calcite. This rock probably was precursor to the dolomite of *C*.

G. Calcareous shale sample 29 rich in foraminiferal debris (−0.69, 27.6) and disseminated opal.

H. Dolomite sample 28 (+11.1, 30.8) from a bed in the calcareous shale of *G*. Unusually large dolomite crystals in vuggy parts.

I. Dolomite sample 66 (−11.7, 31.6). Moderately coarse grained; each dolomite crystal has a nucleus of an oily material or of carbon dioxide. This type of dolomite was described in detail by Spotts and Silverman (1966).

J. Calcite sample 44 (−14.4, 20.8), cement of marine sandstone. Calcite crystals (gray) are as coarse as the sand grains (white) and very irregular (almost amoebiform).

K. Dolomite sample 62 (−15.4, 34.3). Uniformly fine grained rock moderately rich in remains of diatoms. Other parts have many dolomitized tests of Foraminifera.

L. Dolomite sample 78 (−25.3, 34.6). Fine-grained dolomite enclosing many detrital minerals along with blebs of pyrite and organic material; contains the lightest carbon.

TABLE 1.—*Carbon and oxygen isotopic composition of diagenetic carbonates and calcium carbonate content of diagenetic dolomites in Miocene rocks of Oregon and California and of comparison materials*

[Samples 1, 2, and 3 are from Oregon; samples 4 through 79, from California. Carbon isotopic results are relative to University of Chicago PDB standard; oxygen isotopic results are relative to SMOW; $CaCO_3$ results are in mol percent]

Sample	Lab. No.	Locality	Latitude and longitude	Formation	Rock	δC^{13} per mil	δO^{18} per mil	$CaCO^3$ in dolomite	Reference
1	3277-4	Yaquina Bay, Lincoln County.	44°38′ N., 124°01′ W	Nye Mudstone	Dolomite bed 1	+5.8	32.7	55	Snavely and others 1964.
2	3277-5	do	do	do	2	+7.8	33.2	53	Do.
3	3277-6	do	do	do	3	+11.0	34.0	51	Do.
4	3277-3	Point Arena, Mendocino County.	38°52′ N., 123°39′ W	Skooner Gulch Formation.	Dolomite cement of sandstone.	−9.5	29.3	57	W. O. Addicott, 1967.
5	3279-1	Drakes Bay, Marin County.	38°02′ N., 122°58′ W	Unnamed upper Miocene.	Dolomite bed	+11.3	31.9	51	Galloway, 1962, pl. 26.
6	3279-7	Bolinas Point, Marin County.	37°54′ N., 122°43′ W	Monterey Shale	Dolomitized porcelanite	+10.2	35.4	50	Jennings and Burnett, 1961; Clark Blake, oral commun., June 1967.
7	3277-1	Berkeley Hills, Contra Costa County.	37°52′ N., 122°14′ W	Claremont Shale	Dolomite bed 1	+17.7	32.9	49	Lawson, 1914, pl. 7.
8	3279-30	do	do	do	2	+19.4	33.1	51	Do.
9	3277-2	do	do	do	3	+11.3	33.1	52	Do.
10	3279-2	Santa Cruz Mountains, Santa Cruz County.	37°15′ N., 122°08′ W	Mindego Basalt	Dolomite bed 1	−2.8	23.6	58	Cummings and others, 1962.
11	3279-3	do	do	do	2	+9.6	30.4	52	Do.
12	3277-31	Ano Nuevo Point, San Mateo County.	37°07′ N., 122°20′ W	Monterey Shale	Dolomite bed	+6.4	30.4	52	Jennings and Burnett, 1961.
13	3277-23	Reliz Canyon, Monterey County.	36°13′ N., 121°17′ W	Pancho Rico Formation (Pliocene).	Dolomite cement of coquina.	+7.0	30.2	57	Durham, 1963; Durham and Addicott, 1965.
14	3279-28	do	do	do	Calcitic shell of *Balanus* in coquina.	−1.4	27.7		Do.
15	3277-22	do	do	Monterey Shale	Dolomite bed 1	+16.5	30.3	51	Do.
16	3277-21	do	do	do	2	+17.6	31.3	52	Do.
17	3277-20	do	do	do	3	+14.9	30.0	52	Do.
18	3277-19	do	do	do	4	+16.2	30.9	52	Do.
19	3277-18	do	do	do	5	+17.0	31.2	53	Do.
20	3277-17	do	do	do	6	+17.2	32.3	52	Do.
21	3277-16	do	do	Sandholdt Member of Monterey Shale.	Foraminiferal coquina	+0.03	28.4		Do.
22	3277-15	do	do	do	Foraminiferal shale	−1.9	28.0		Do.
23	3277-14	do	do	do	Dolomite bed 7	+13.5	31.9	52	Do.
24	3277-13	do	do	do	8	+11.6	31.3	52	Do.
25	3277-11	do	do	do	9	+5.7	27.1	55	Do.
26	3277-12	do	do	do	Vein calcite in bed 9	−4.1	19.5		Do.

TABLE 1.—*Carbon and oxygen isotopic composition of diagenetic carbonates and calcium carbonate content of diagenetic dolomites in Miocene rocks of Oregon and California and of comparison materials*—Continued

Sample	Lab. No.	Locality	Latitude and longitude	Formation	Rock	δC^{13} per mil	δO^{18} per mil	$CaCO_3$ in dolomite	Reference
27	3277-25	Nacimiento Dam, San Luis Obispo County.	35°45′ N., 120°52′ W	Sandholdt Member of Monterey Shale.	Dolomite bed 1	+7.1	28.9	56	Jennings 1959.
28	3277-26	do	do	do	2	+11.1	30.8	54	Do.
29	3277-27	do	do	do	Foraminiferal shale	−0.69	27.6		Do.
30	3277-28	do	do	do	Dolomite bed 3	+9.5	29.3	55	Do.
31	3277-29	do	do	do	4	+11.3	31.5	53	Do.
32	3277-30	do	do	do	Foraminiferal shale	−1.4	27.4		Do.
33	3279-12	Chico Martinez Creek, Kern County.	35°26′ N., 119°47′ W	Chico Martinez Chert of McMasters (1947).	Dolomite bed 1	+20.8	33.8	49	Woodring and others, 1940; McMasters, 1947, fig. 36.
34	3279-13	do	do	do	2	+11.1	32.0	49	Do.
35	3279-14	do	do	do	3	+11.2	34.0	50	Do.
36	3279-15	do	do	do	4	+11.2	32.4	52	Do.
37	3279-16	do	do	do	5	+14.7	34.6	51	Do.
38	3279-17	do	do	do	6	+8.2	33.1	50	Do.
39	3279-18	do	do	do	7	+12.1	32.5	51	Do.
40	3279-19	do	do	do	8	+11.4	32.9	49	Do.
41	3279-20	Round Mountain oil field, Kern County.	35°28′ N., 118°55′ W	Round Mountain Silt of Diepenbrock (1933).	Calcite cemented sandstone.	−13.0	23.7		Godde, 1928; Addicott, 1965.
42	3279-21	do	do	do	Limestone bed	−14.7	30.3		Do.
43	3279-22	do	35°29′ N., 118°50′ W	Jewett Sand of Godde (1928).	Calcite cemented sandstone 1.	−15.8	21.1		Do.
44	3279-23	do	do	do	Calcite cemented sandstone 2.	−14.4	20.8		Do.
45	3279-29	do	do	do	Calcitic shell of pecten in sandstone 2.	+2.9	30.5		Do.
46	3276-18	Temblor Range, San Luis Obispo County.	35°05′ N., 119°35′ W	Monterey Shale	Dolomite bed	+19.3	31.6	50	J. G. Vedder, oral commun., September 1967.
47	3279-26	Pismo syncline area, San Luis Obispo County.	35°13′ N., 120°42′ W	Obispo Tuff Member of Monterey Formation.	Dolomite-impregnated tuff.	−17.3	26.5	49	Hall and Surdam, 1967.
48	3279-24	do	35°10′ N., 120°42′ W	Monterey Shale, immediately underlying Pismo Formation.	Dolomite concretion	−2.7	27.0	49	Do.
49	3279-25	do	35°09′ N., 120°41′ W	Monterey Shale	Dolomite bed in tidal zone.	−10.2	27.4	53	Do.
50	3279-27	Cuyama Valley, Santa Barbara County.		Santa Margarita, Sandstone.	Limestone lens	−10.1	24.0		J. G. Vedder, oral commun., September 1967.
51	3276-15	San Rafael Mountains, Santa Barbara County.	34°47′ N., 119°36′ W	Monterey Shale	Limestone lens 1	+15.2	28.8		Do.
52	3276-16	do	34°47′ N., 119°36′ W	do	2	+5.3	24.6		Do.
53	3276-17	do	34°47′ N., 119°41′ W	do	Dolomite bed	−12.5	32.6	56	Do.
54	3279-9	Santa Ynez River area, Santa Barbara County.	34°35′ N., 120°23′ W	do	Dolomite bed (100 ft thick).	−13.1	30.6	55	Dibblee, 1950.
55	3279-10	do	34°35′ N., 120°09′ W	do	Dolomitized reef rock (40 ft thick).	−14.6	28.0	56	Do.
56	3279-32	Pine Mountain, Ventura County.	34°38′ N., 119°23′ W	Monterey Shale, muddy phase.	Dolomitic upper part of bed.	+12.5	31.4	55	Dickinson and Lowe, 1966.
57	3279-33	do	do	do	Calcitic lower part	+10.2	27.3		Do.
58	3279-6	Point Dume, Los Angeles County.	34°01′ N., 118°47′ W	Monterey Shale	Dolomite bed 1	+10.1	34.9	55	Durrell, 1954; R. H. Campbell, oral commun., September 1967.
59	3279-5	do	do	do	2	+10.2	34.2	53	Do.
60	3279-4	do	do	do	3	−5.6	30.2	55	Do.
61	3276-3	Palos Verdes Hills, Los Angeles County.	33°48′ N., 118°24′ W	Repetto Siltstone (lower Pliocene).	Foraminiferal sand	−0.52	30.8		Woodring and others, 1946.
62	3276-5	do	do	Malaga Mudstone Member of Monterey Shale.	Dolomite bed	−15.4	34.3	56	Do.
63	3276-10	do	33°48′ N., 118°21′ W	Valmonte Diatomite Member of Monterey Shale.	Dolomitized diatomite (soft).	−8.5	33.3	54	Do.
64	3276-2	do	33°47′ N., 118°20′ W	Lomita Marl Member of San Pedro Formation (lower Pleistocene).	Foraminiferal sand	−3.3	27.5		Do.
65	3276-11	do	33°45′ N., 118°22′ W	Valmonte Diatomite Member of Monterey Shale.	Dolomite bed 1	−8.3	34.1	55	Do.
66	3276-6	do	do	do	2 (8 ft thick).	−11.7	31.6	52	Do.
67	3277-7	do	do	do	Dolomite bed 3	−6.5	33.4	52	Do.
68	3276-12	do	do	Upper part of Altamira Shale Member of Monterey Shale.	4	−5.2	32.6	55	Do.
69	3276-7	do	do	do	5	−8.8	32.4	57	Do.
70	3276-13	do	do	Middle part of Altamira Shale Member of Monterey Shale.	6	−11.3	30.9	56	Do.
71	3276-14D	do	do	do	7 (dark core).	−10.5	28.1	50	Do.
72	3276-14L	do	do	do	Dolomite bed 7 (bleached exterior).	−10.2	28.5	50	Do.
73	3276-8	do	do	do	Dolomite bed 8	−6.8	28.9	50	Do.
74	3276-9	do	33°45′ N., 118°23′ W	do	Dolomite cement of glassy tuff.	−14.9	28.4	50	Do.

TABLE 1.—*Carbon and oxygen isotopic composition of diagenetic carbonates and calcium carbonate content of diagenetic dolomites in Miocene rocks of Oregon and California and of comparison materials*—Continued

Sample	Lab. No.	Locality	Latitude and longitude	Formation	Rock	δC^{13} per mil	δO^{18} per mil	$CaCO^3$ in dolomite	Reference
75	3276-1	do	33°44′ N., 118°21′ W	Intrusive basalt	Drusy dolomite in fractures.	−18.1	25.1	54	Do.
76	3276-4	San Juan Capistrano, Orange County.	33°35′ N., 117°40′ W	Niguel Formation (upper Pliocene).	Dolomite cement of sandstone.	−15.3	33.5	53	Vedder and others, 1957.
77	3279-8	San Clemente Island	33°00′ N., 118°33′ W	Monterey Shale	Dolomite bed	−1.8	33.0	57	Olmstead, 1958.
78	3279-11	La Jolla submarine canyon.	32°55′ N., 117°34′ W	Cored sediment EM3-5(8-17) (cm).	do	−25.3	34.6	51	Inman and Goldberg, 1963.
79	3276-19	Coronado submarine canyon.	32°31′ N., 117°19′ W	Rock broken off canyon wall at 200 fathoms.	do	+12.1	33.4	52	J. G. Vedder, oral commun., September 1968.

GENERAL ASPECTS OF THE ISOTOPIC COMPOSITION

The extreme values reported in table 1 are tabulated as follows:

	δC^{13} or δO^{18} *per mil*	*Sample*	*Material*
Heaviest carbon	+20.8 PDB	33	Dolomite.
Lightest carbon	−25.3 PDB	78	Dolomite.
Heaviest oxygen	35.4 SMOW	6	Dolomite.
Lightest oxygen	19.5 SMOW	26	Vein calcite.

As previously noted (Murata and others, 1967), the most remarkable aspect of these values is the heaviness of the carbon in many of the samples. Carbon +10 per mil and heavier has rarely been found in carbonate rocks. Yet table 1 contains 30 samples with such heavy carbon from the Monterey Shale and related formations. Twenty-eight of these samples are dolomite but sample 51 (δC^{13} of +15.2 per mil) is limestone and so is sample 57 (δC^{13} of +10.2 per mil). These two samples indicate that heavy carbon is not restricted to dolomites and can be generated independently of the dolomitization process.

The total range of carbon isotopic composition (47.1 per mil) is so large as to be inexplicable in terms of any single reaction involving geologically reasonable conditions and materials. Of the several theoretically possible ways of producing such large differences in isotopic composition (Kemp and Thode, 1968), we prefer to invoke two different reactions, namely, nonequilibrium oxidation of organic matter over a wide range of temperature to obtain light-carbon carbonate, and equilibration of carbonate with methane at moderate to low temperatures to obtain heavy-carbon carbonates.

Oxygen isotopic composition of most samples falls in the range of δO^{18} from 26 to 34 per mil. This range would be considered normal for marine carbonate (Lowenstam and Epstein, 1954) and would represent sea-water temperatures of 30° to 0°C. However, for diagenetic carbonates these values do not relate in a simple way to the temperature of formation waters, as will be discussed later. The oxygen and carbon isotopic compositions of many, but not all, of the samples listed in table 1 are plotted in figures 6*A* and 6*B*, in order to illustrate several modes of compositional variations that characterize different materials or the same material from different localities.

NORMAL MARINE CARBONATE

Calcareous tests and shells of Miocene, Pliocene, and Pleistocene Foraminifera (samples 21, 22, 29, 32, 61, and 64) of a Pliocene barnacle (sample 14) and of a Miocene pecten (sample 45) were analyzed incidental to the study of diagenetic carbonates of several localities. Their compositions are plotted as open circles in figure 6*A*; all samples lie within the rectangle at *a*, which defines the composition of normal marine limestone. The close grouping of compositions in the range of normal marine limestone suggests that the shells were secreted in virtual isotopic equilibrium with sea water and that the original composition is largely retained.

That the original composition may not have been retained perfectly is suggested by the rough alinement of points along the dashed diagonal line in figure 6*A*. This line marks a trend of secondary alteration of marine limestone by circulating fresh water, as found in the Bermudas by Gross (1964). The identical trend is also noted for shells deposited in the Gulf of Mexico at various distances from land (Keith and Parker, 1965). Thus terrestrial waters and organic matter may have an appreciable influence on the primary secretion of marine carbonate even many miles offshore. Such complications discourage the use of oxygen isotopic composition to derive precise paleotemperatures. They do not obscure the fundamental fact, however, that these calcareous fossils represent primary marine carbonate and serve as a reference against which secondary carbonates can be compared.

In contrast to the shells, only a few (three out of 71) diagenetic carbonates have a composition in the range of normal marine limestone. This striking compositional distribution divides the diagenetic carbonates naturally into a light-carbon group and a heavy-carbon group and has led us to treat the two groups in terms of different isotopic reactions.

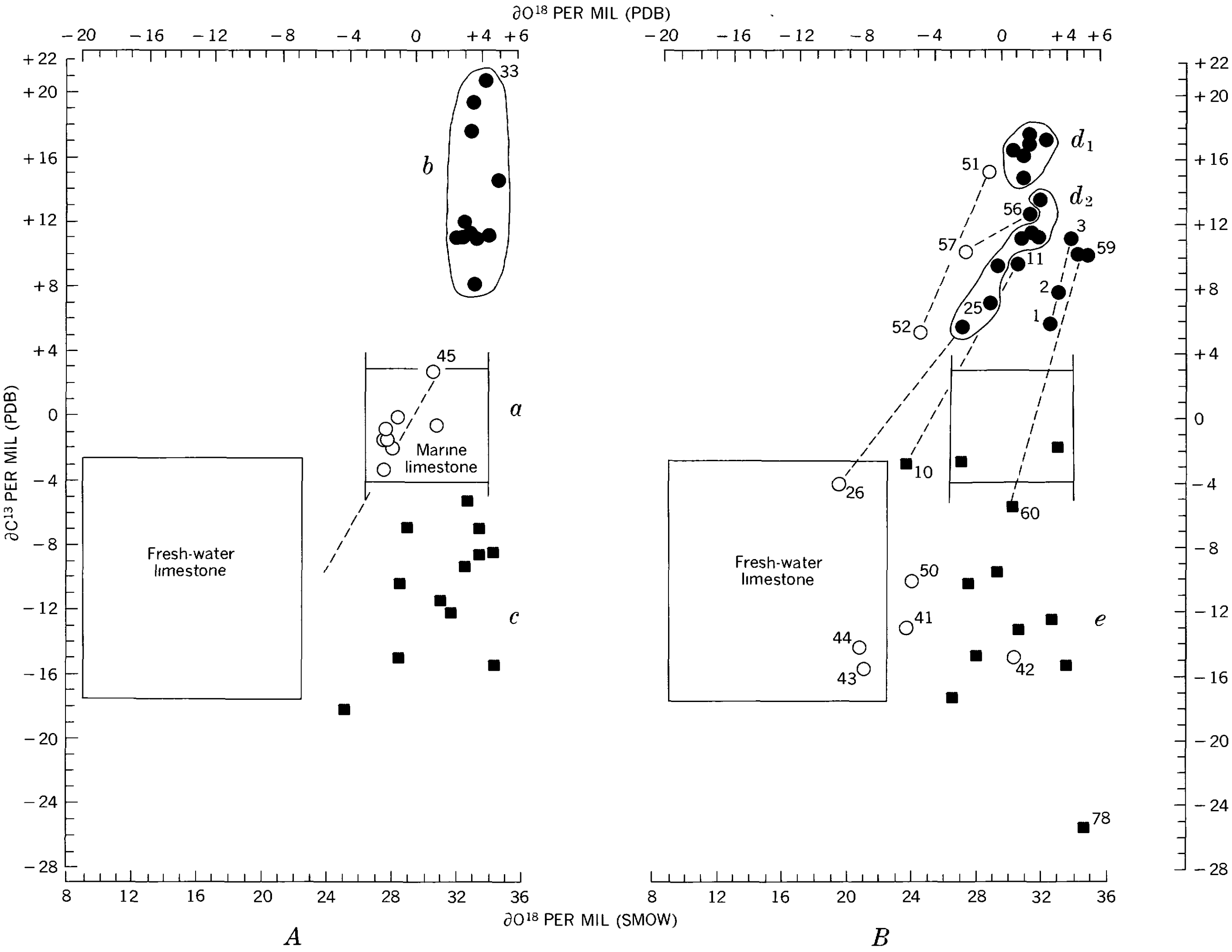

FIGURE 6.—Relationship between isotopic compositions of carbon and oxygen in carbonates. Black circles denote dolomite with positive values of δC^{13}; black squares, dolomite with negative values of δC^{13}; open circles, calcite. Compositional limits of marine and fresh-water limestones are from Graf (1960), and Keith and Weber (1964). The grouping of samples in parts *A* and *B*, including *a*, *b*, *c*, d_1, d_2, and *e*, is discussed in the text. The meaning of dashed lines is discussed in text and in the caption to figure 11.

DIAGENETIC LIMESTONE

Beds and concretionary horizons of diagenetic limestone are considered by Bramlette (1946) and others to have formed from normal marine carbonate that was dispersed throughout a formation dissolved, and then redeposited in certain favorable zones. The fact that the resultant diagenetic limestone does not have the carbon isotopic composition of normal marine carbonate throws light on the nature of the formation waters that dissolved and transported the carbonate. Diagenetic limestone is rare among our samples, but its isotopic composition is of great interest because the limestone was probably a precursor of the more abundant dolostone.

The nine diagenetic limestones shown as open circles in figure 6*B* differ widely in isotopic composition, which is to be expected for a precursor to dolostones that have equally variable composition. Samples 41, 43, and 44 from Round Mountain oil field show the clearest relationship between isotopic composition and geological environment. They represent calcite-cemented horizons in nearshore marine sandstones that were deposited on a shelf marginal to the landmass of the Sierra Nevada (Brooks, 1952). A thin section of sample 44 is illustrated as figure 5*J*. The isotopic composition of the calcite cement is like that of fresh-water limestone and indicates equilibration with, if not deposition from, fresh water probably of artesian circulation. At some places, the cemented zones contain abundant macrofossils (Addicott, 1965), including pectens (sample 45 of fig. 6*A*) with the isotopic composition of normal marine carbonate. Fresh-water solutions deposited light-carbon light-oxygen calcite all around the fossils shells but did not alter the isotopic composition of the shells.

The involvement of fresh water is strongly supported by the prevalence of waters of unusually low salinity ($<4,000$ parts per million) in Round Mountain and other nearby oil fields (Jensen, 1934). The low salinity is attributed to extensive circulation of runoff from the Sierra Nevada through the sedimentary formations of these fields. Such a circulation could have begun early in the sedimentary history of the region, flushed out any connate water from the sediments, and prevented the development of highly saline brines like those found in most other California oil fields. A present-day example of this kind of artesian circulation is provided by the fresh water that was found during recent drilling on the continental shelf, 45 kilometers off the Florida coast (JOIDES, 1965).

Besides accounting for the isotopic composition of the calcite cement of sandstone samples 41, 43, and 44, the presence of fresh water would also explain why this calcite escaped the almost universal conversion of diagenetic limestone into dolostone. According to present views (Friedman and Sanders, 1967), dolomitization takes place most commonly in the presence of concentrated brines of appropriate composition.

Sample 42 (fig. 6*B*) (also from Round Mountain oil field) is from a bed of rather pure limestone associated with diatomite instead of sandstone. Although it has carbon as light as that of the three calcite cements, its oxygen is too heavy (δO^{18} of 30.5 per mil) to have been derived from fresh water. The origin of this limestone will be included in a later discussion of the many dolostones that have similar composition.

Another limestone with a fresh-water compositional aspect (sample 50) is from the late Miocene Santa Margarita Sandstone of Cuyama Valley. Little information is available on the paleogeography of this rock. But the Santa Margarita Sandstone is certainly a nearshore marine deposit that, in the region of Cuyama Valley, grades into the continental Quatal Formation of Hill, Carlson, and Dibblee (1958). These stratigraphic relations suggest that fresh water could have easily entered the sandstone to form diagenetic limestone.

Sample 26 is coarse sparry calcite that fills cracks in a bed of diagenetic dolomite. It appears to be a very late secondary product deposited from percolating ground water—an origin that would account for the fresh-water aspect of the isotopic composition.

Unlike the limestones described above, the three remaining samples (Nos. 51, 52, and 57) from muddy facies of the Monterey Shale contain heavy carbon with δC^{13} of $+5.3$ to $+15.2$ per mil and thus must be related to fluids very different from simple fresh water. The origin of such heavy-carbonate will be discussed in a later section dealing with heavy-carbon dolostones.

The isotopic composition of the calcitic materials can be summarized at this point. Tests and shells of fossils show a narrow range of carbon and oxygen isotopic composition that corresponds to that previously established for normal marine carbonate. Shell calcite is a primary precipitate whose isotopic composition is narrowly controlled by equilibria between solid calcite and sea water, relative to carbon and oxygen.

Dissolution of the primary calcite and redeposition in favorable zones during diagenesis form beds of secondary limestone, whose carbon isotopic composition is highly variable and generally lies outside the range for normal marine carbonate. Fresh water was involved in the formation of diagenetic calcite with light carbon and oxygen, especially that occurring in sandstone of nearshore facies. Other fluids, to be discussed in the following sections, produced diagenetic limestone with normal oxygen and either heavy or light carbon. The few samples of diagenetic limestone vary almost as much in their isotopic composition as the more abundant samples of dolostones. This similar variability suggests that limestones could be a precursor to dolomite and that dolomite could inherit the isotopic composition of the precursor (Degens and Epstein, 1964). Associated primary calcite and dolomite could likewise have similar oxygen composition if their isotopic fractionation factors relative to water were virtually the same (Friedman and Hall, 1963).

OXYGEN ISOTOPIC COMPOSITION OF DOLOMITE

Figure 6 (*A* and *B*) well illustrates the striking fact that although the carbon isotopic composition of the dolomite (and also of diagenetic calcite samples 42, 51, and 57) is decidedly not that of normal marine carbonate, the oxygen composition lies mostly in the range of normal marine carbonate ($\delta O^{18}=26$ to 34 per mil). One possible explanation for these isotopic relationships might be that the diagenetic carbonate inherited the oxygen composition of primary marine calcite, but assumed a widely different carbon isotopic composition. Many examples of coexisting low-temperature calcite and dolomite show the same oxygen (and carbon) isotopic composition in both minerals (Degens and Epstein, 1964), and calcite has been converted to dolomite in laboratory experiments without developing a difference in oxygen composition (Epstein, Graf, and Degens, 1964).

On the other hand, results of other studies (Clayton and Epstein, 1958; Weber, 1964; Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Clayton, Jones and

Berner, 1968) suggest that for dolomite and calcite in equilibrium at 25°C the oxygen of dolomite is 4 to 7 per mil heavier, and the amount of the difference varies inversely with temperature. Figure 6 (*A* and *B*) indicates that dolomite on the whole tends to be richer in O^{18} than calcite. To consider this point more closely, we tabulated the oxygen isotopic composition of some of the most closely associated calcite and dolomite, as follows:

Locality	Samples in table 1	Material	δC^{13} per mil	δO^{18} per mil	Δ* per mil
Reliz canyon	21 and 22	Foraminiferal calcite.	−1.9 to +0.03, avg −0.9	28.0 to 28.4, avg 28.2	3.4
	23 and 24	Dolomite	+11.6 to +13.5, avg +12.6	31.3 to 31.9, avg 31.6	
Nacimiento Dam	29 and 32	Foraminiferal calcite.	−0.7 to −1.4, avg −1.0	27.4 to 27.6, avg 27.5	3.7
	27 and 30	Dolomite	+11.1 to +11.3, avg 11.2	30.8 to 31.5, avg 31.2	
Pine Mountain	57	Limy part of bed.	+10.2	27.3	4.1
	56	Dolomitic part of bed.	+12.5	31.4	

*Extent to which δO^{18} of dolomite is greater than that of associated calcite, computed from the averages given in table.

For the Reliz Canyon and Nacimiento Dam localities, pairs of dolostones richest in O^{18} were averaged to compute the maximum difference in O^{18} content between dolomite and associated foraminiferal calcite. At these two localities, beds of diagenetic dolostone formed through the dolomitization of certain zones of a thick section of foraminiferal shale, and it seems reasonable to postulate that calcite of Foraminifera was a major precursor of the dolomite. The two samples from Pine Mountain are from different parts of a single carbonate bed (fig. 2*C*) and thus constitute the most closely associated calcite-dolomite pair.

Samples from all three localities show that the oxygen of the dolomite can be about 4 per mil heavier than that of the associated calcite. This may be an expression of the isotopic equilibrium between the two minerals, or it may be that dolomite has accurately preserved the oxygen composition of primary marine calcite while the associated foraminiferal calcite had its composition altered by the action of isotopically light meteoric water. The superior resistance of dolomite to such alteration effects has been emphasized by Epstein, Graf, and Degens (1964).

Although the oxygen composition of both calcite and dolomite is within the range possible for normal marine carbonate, the 4-per-mil difference indicates very different temperatures (Epstein and others, 1953)—22° to 26°C for calcite and 7° to 10°C for dolomite. With such Foraminifera-bearing sediments, an independent estimate of the original temperature can be derived from existing knowledge of depth of habitat of Foraminifera (Kleinpell, 1938; Bandy, 1953; Natland, 1957; Smith, 1964). According to Patsy J. Smith (written commun., July 1967 and February 1968), Foraminifera from all three localities indicate a bathyal environment with a probable temperature of 7°C or less, clearly closer to dolomite temperatures than to those of calcite.

The oxygen of dolomite from Palos Verdes Hills (samples 62, 63, 65 to 74 of table 1) tends to be heavier the higher the position of the bed in the section (fig. 7). Sample 75 (drusy dolomite) is excluded from the figure because its oxygen is abnormally light. All carbonates collected from the Miocene of this locality proved to be dolomite, so that a comparison with calcite is not possible. Translated into paleotemperatures, the oxygen composition of dolomite indicates a general lowering of water temperature during middle through late Miocene time (from the middle part of the Altamira Shale Member to the Malaga Mudstone Member of the Monterey Shale); this trend is in agreement with the regional trend previously recognized by others (Woodring and others, 1946; Natland, 1957) through studies of Foraminifera and other fossils in these sedimentary rocks.

The temporal trend of water temperature (8° to 3°C) deduced from the nature of fossils (Natland, 1957) is shown by the dashed line in figure 7; the oxygen isotopic results agree reasonably well with the trend, except those of samples 72 to 74 from the lowest part of the sampled section. It is possible that the isotopic composition of the lower dolomite layers was affected by nearby underlying igneous intrusions (Macdonald, 1939; Woodring and others, 1946; Schleicher, 1965)—a possibility that merits further study. Thus, dolomites from Palos Verdes Hills, like those previously discussed from other localities, seem to yield roughly correct isotopic temperatures in situations where associated foraminiferal calcites give too high a temperature. However, as will be shown in following sections, dolomite temperatures are not always correct; they appear to be most accurate for low temperatures (<10°).

Some dolomite cannot be interpreted in terms of inheritance of oxygen composition from a primary marine carbonate; therefore this process may not be generally valid. For example, the upper Pliocene sandstone of sample 76 (table 1) was deposited in shallow water (probably less than 400 feet deep according to J. G. Vedder oral commun., February 1968), yet the isotopic temperature derived from the dolomite cement of the sandstone is 1.5°C—obviously too low to be explained in terms of temperature of depositional or postdepositional environment. Presumably, the original calcite cement had a value of δO^{18} appropriate for shallow waters, and the value increased during dolomitization.

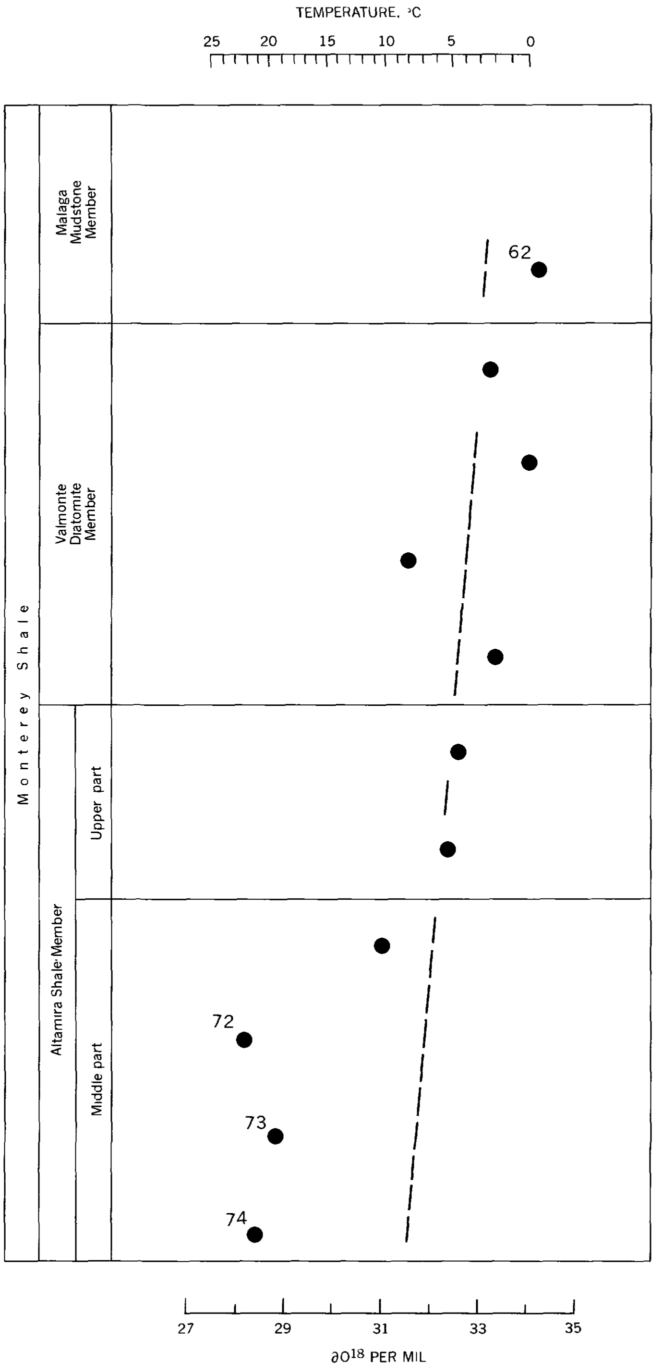

FIGURE 7.—Temperatures indicated by the oxygen isotopes of dolomites from the Monterey Shale of Palos Verdes Hills. Trend of temperature (Natland, 1957), inferred from nature of fossils in the Monterey Shale of the region, is shown by the dashed line.

Our dolomite samples 6, 37, 58, and 78 have δO^{18} values of 34.6 to 35.4 per mil, signifying apparent temperatures of −1° to −3°C. Russell, Deffeyes, Fowler, and Lloyd (1967) described a dolomite with δO^{18} of 35.5 per mil from an offshore environment similar to that of our sample 78. The indicated temperatures are so low as to be questionable. Here again is a suggestion that dolomite attains a somewhat higher content of O^{18} than calcite—a result that could be achieved in more than one way. We shall next discuss the possibility that the dolomitizing solutions are generally richer in O^{18} than normal sea water. The previously mentioned equilibrium relationship (O'Neil and Epstein, 1966) that would automatically make the oxygen of dolomite substantially heavier than that of accompanying calcite seems to be too inflexible a mechanism for our purpose.

NATURE OF FORMATION WATER AND ITS INFLUENCE ON OXYGEN ISOTOPIC COMPOSITION OF DOLOMITE

The control exerted by the oxygen isotopic composition of water on the composition of a carbonate precipitated from it is indicated by the well-known isotopic difference between marine and fresh-water limestone. The diagenetic carbonates are genetically related to some kind of formation water—a most variable class of natural water, ranging in chemical composition from fresh water to brine several times more concentrated than sea water (Jensen, 1934; Gullikson and others, 1961; White and others, 1963). Salinity of formation waters generally increases with depth of occurrence; the deep warm brines are thought to be derived from fresh water by a process of micropore filtration that occurs during passage of water through shales. It is the more saline waters (oil-field brines) that are of interest here for two reasons: (1) Such brines are involved in the genesis of dolomite (Anderson and others, 1966; Rittenhouse, 1967), and (2) the water of many such brines is greatly enriched in O^{18} (up to +8.8 per mil compared to 0.0 of SMOW), according to Clayton and others (1966). Brines of the Cymric oil field in California show a δO^{18} range of +2.9 to +5.9 per mil at depths of 3,000 to 5,000 feet (Harmon Craig in White, 1965).

The enrichment in O^{18} in formation waters has been ascribed to very different processes: (1) To partial evaporation of the water while still at the surface (Degens, 1965, p. 193; Lloyd, 1966), and (2) to isotopic equilibration of the migrating water with the carbonate and silicate minerals of sediments (Clayton and others, 1966). The variability in the D/O^{18} ratio among oil-field brines suggests that both processes may be involved (Craig, 1963). Because carbonates are rather scarce in the Monterey Shale, formation water more likely equilibrates with silicate minerals such as clays or opaline silica, its δO^{18} varying directly with the temperature that prevails at different depths.

According to Clayton and others (1966), the rate of equilibration between water and calcite is much faster than between water and silicate minerals. This difference raises the interesting possibility that a deep-lying water which had attained equilibrium with silicate minerals, might move upward into cooler strata without an appropriate reduction of its O^{18} content and form a carbonate that was richer in O^{18} than would be expected from its temperature of formation. Presumably, such an effect based on differing kinetics of equilibration would be largest at the lower temperatures, say, less than 100°C.

The δO^{18} of calcite at equilibrium with water of different O^{18} content (δO^{18} of -6 to $+9$ per mil) at different temperatures has been computed from the equation of Epstein and Mayeda (1953) and plotted in figure 8. The compositional range (δO^{18} of 26.5 to 34 per mil) of normal marine carbonate, which includes the composition of most of the diagenetic carbonates, is delimited by the two dashed lines. Mean ocean water (δO^{18} of 0.0 per mil) yields calcite in this range between 0° and 30°C. Heavier water, with δO^{18} of $+6$ per mil, yields the same calcite O^{18} composition between 23° and 67°C, corresponding, for example, to temperatures prevailing at depths of 100 to 4,000 feet in the sedimentary section of the Los Angeles basin (Philippi, 1965). Heavier water, therefore, shifts the equilibrium temperatures into a higher range, which could be more appropriate for the formation and preservation of a diagenetic mineral.

If δO^{18} of water were as high as $+9$ per mil (the maximum known value), calcite with normal marine isotopic composition would have equilibrium temperatures between 40° and 88°C, which corresponds roughly to depths of 2,000 to 6,000 feet in the sedimentary section. Such a water could yield calcite with δO^{18} of 35.5 per mil (the largest value on record for any carbonate) at 32°C, corresponding to a depth of about 1,000 feet. A restriction on considering heavier and heavier water is imposed by the fact that such waters increase the likelihood of producing, at lower temperatures, a carbonate with δO^{18} greater than 36 per mil, which does not seem to exist.

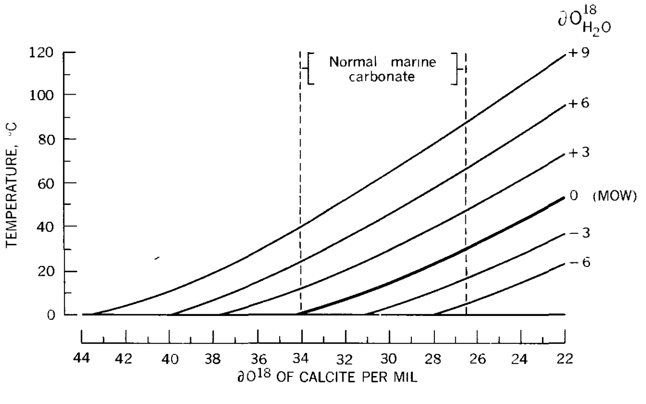

FIGURE 8.—Temperature dependence of O^{18} content of calcite that is in isotopic equilibrium with water of different O^{18} content. The curves were computed from the equation of Epstein and Mayeda (1953), and MOW refers to their mean ocean water.

Figure 8 also shows that postulating a high temperature of equilibration (say, greater than 100°C) increases the chance of putting light oxygen ($\delta O^{18} < 20$ per mil) into diagenetic carbonates and of making them similar isotopically to carbonates of hydrothermal origin (Engel and others, 1958; Lovering and others, 1963; Rye, 1966). However, the virtual absence of such light oxygen among our samples and the general mineralogy and organic chemistry of Monterey Shale make clear that the diagenetic carbonates were subjected to temperatures well below the hydrothermal range.

The observed enrichment of O^{18} in oil-field brines thus is of interest for at least two reasons: (1) It allows carbonate oxygen to become heavier than 34.5 per mil, which is not likely with water of normal O^{18} content, and (2) it counteracts the tendency of higher temperature to lower δO^{18} values in carbonates and yields values in the range of normal marine carbonate at temperatures higher than 30°C.

DOLOMITE WITH VARIABLE LIGHT CARBON AND INDEPENDENTLY VARIABLE OXYGEN

Dolomite of Palos Verdes Hills (samples 62, 63, and 65 to 75 of table 1) is characterized by variable light carbon (δC^{13} of -18.1 to -5.2 per mil) and variable oxygen (δO^{18} of 25.1 to 34.3 per mil). The individual values are plotted as black squares in figure 6*A* at *c*. The δC^{13} of a dolomite from this locality was previously determined to be -16.4 per mil by Spotts and Silverman (1966), who attributed the lightness of the carbon to the presence of much carbonate derived through the oxidation of petroleum and other organic matter. Thin sections of samples 62 and 66 are illustrated in figures 5*K* and 5*I*, respectively.

No regular covariation of carbon and oxygen isotopic composition, such as the previously discussed freshwater alteration trend of the dashed line in figure 6*A*, is evident. Single dolomite samples containing light carbon from other localities are plotted as black squares in figure 6*B* at *e*. They collectively show the same irregular variations as the samples from Palos Verdes Hills, except that sample 78 extends the range of δC^{13} down to -25.3 per mil.

Carbon lighter than about -5 per mil in diagenetic carbonate is derived most simply by forming light carbon dioxide through the nonequilibrium oxidation of some form of organic matter such as humus or petroleum (Thode and others, 1954; Vogel, 1959; Spotts and Silverman, 1966). Virtually all the diagenetic carbonates of marine formations studied by Hodgson (1966) contained such light carbon; he also ascribed this light carbon to organic matter. The oxygen of his samples was mostly lighter than 26 per mil, suggesting extensive equilibration with fresh water. Only one out of 12 dolomites from Palos Verdes Hills contains such light oxygen (fig. 6*A* at *c*).

We follow previous investigators in believing that the light carbon of the dolomites under discussion was derived from sedimentary organic matter. Carbon dioxide, probably so derived and with δC^{13} as light as −38 per mil, occurs in marine formations as a component of natural gas (Wasserburg and others, 1963) and could equilibrate with preexisting marine carbonate or become incorporated into carbonate precipitated diagenetically. Low-temperature equilibration with meteoric water could not have played an important part in the formation of these dolomites because that reaction changes the oxygen isotopic composition without greatly affecting the carbon composition (Degens and Epstein, 1962; Keith and Weber, 1964; Weber and others, 1965) or that reaction induces covariation of oxygen and carbon (Gross, 1964; Gross and Tracey, 1966).

In the next section, we shall discuss how isotopic equilibrium between carbon dioxide and methane in natural gas leads to very heavy carbon in carbonates. Thus both light and heavy carbon carbonates are genetically linked to natural gas and the accompanying formation waters. The key point of difference is whether or not isotopic equilibrium prevails between carbon dioxide and methane; when it does not, the carbon in carbonate will be light.

When equilibrium prevails, the heaviness of the carbonate-carbon will depend on the temperature and on the relative amounts of methane and carbon dioxide. Methane is by far the most abundant component of most natural gas, and only rarely would variations in the ratio of methane to carbon dioxide be expected to affect the isotopic composition of the carbonate.

DOLOMITE WITH VARIABLE HEAVY CARBON AND RELATIVELY CONSTANT HEAVY OXYGEN

Dolomites from Berkeley Hills (samples 7 to 9) and Chico Martinez Creek (samples 33 to 40) exemplify a class of diagenetic carbonate in which carbon is heavy and variable ($\delta C^{13}=+5.4$ to $+20.8$ per mil) and oxygen is heavy and relatively constant ($\delta O^{18}=32.0$ to 34.6 per mil). These samples, plotted in figure 6*A* at *b*, are strikingly different from those of Palos Verdes Hills and raise the question of the genesis of heavy carbon.

A few examples of carbon dioxide gas with δC^{13} as heavy as +16 per mil had been found previously in natural gas by Wasserburg, Mazor, and Zartman (1963). The heaviest carbon dioxide found so far in gas of California oil fields was from the Huntington Beach field of the Los Angeles basin and had δC^{13} of +6 per mil (S. R. Silverman, written commun., November 1967). Because methane is the dominant constituent of natural gas, Zartman, Wasserburg, and Reynolds (1961) and Wasserburg, Mazor, and Zartman (1963) employed isotopic equilibrium between methane and carbon dioxide as a mechanism for obtaining such heavy carbon dioxide and hence heavy carbonate ion. Theoretical equilibrium constants computed by Bottinga (1968) show that C^{13} will concentrate strongly in carbonate. At 25°C, carbon in calcite would be 78 per mil heavier than that in methane; at 100°C, it would be 53 per mil heavier. Unfortunately, the CH_4-CO_3^{-2} exchange reaction has not been investigated experimentally and nothing is known about the kinetics of exchange. However, some samples of coexisting methane and carbon dioxide, to be discussed below, suggest that these compounds do equilibrate isotopically in nature.

Histograms of carbon isotopic compositions of coexisting methane and carbon dioxide from three different geological environments are presented in figure 9. Rows *A*, *B*, and *C* represent methane-rich gases generated through bacterial decay of organic matter at low temperature. Rows *F* and *G*, on the other hand, represent gases that are relatively rich in carbon dioxide and are emitted from hot springs. Between these two groups, methane-rich oil-field gases are plotted in row *D*, and carbon from the diagenetic carbonates of this study, in row *E*.

Figure 9 shows that average δC^{13} of methane is about −72 per mil if derived from low-temperature sources; about −44 per mil, from oil-field gases; and about −27 per mil, from gases of thermal waters. These values suggest that the isotopic composition of methane alone can serve as a crude index of temperature. The plotted points indicate that the contrast in isotopic composition between coexisting methane and carbon dioxide generally becomes less with rising temperature, a condition agreeing with the theoretical requirement for isotopic equilibrium (Craig, 1953; Bottinga, 1968). Hot spring temperatures, computed on the basis of the equilibrium between methane and carbon dioxide, average around 300°C, which falls well within the range observed or inferred at these springs. Isotopic temperatures of the cool sources of rows *A*, *B*, and *C* in figure 9 are of the order of 30°C. These results substantiate the view that methane and carbon dioxide do equilibrate isotopically in nature and probably play a fundamental role in generating the heavy carbon found in so many of our carbonates.

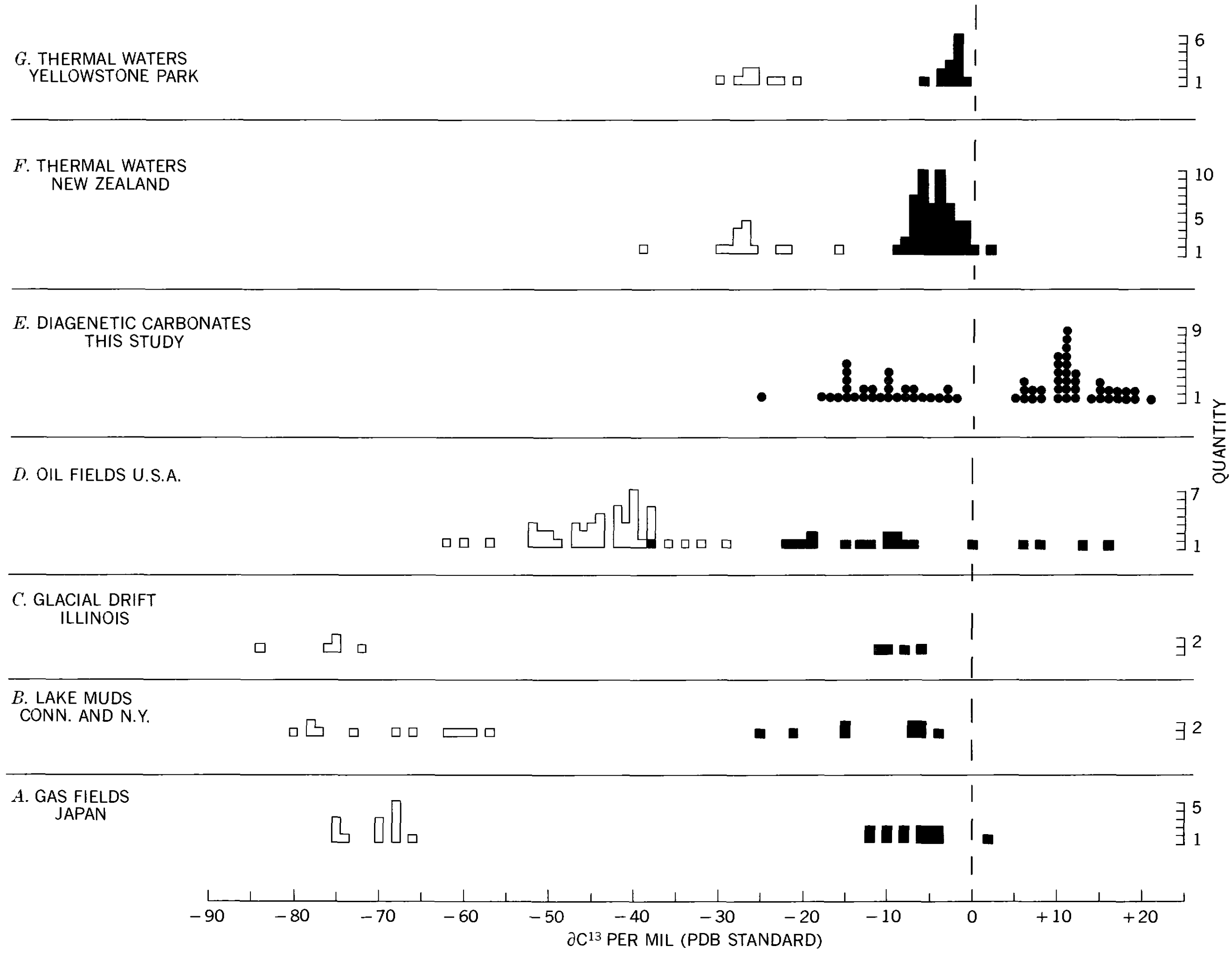

Figure 9.—Histograms of carbon isotopic composition of coexisting methane (open figures) and carbon dioxide (black figures) from sources (rows *A*, *B*, *C*, *D*, *F*, and *G*) of different temperature. Isotopic composition of carbon in carbonates of the present study are given in row *E* as black circles. References for the data in the several rows are as follows:

A. Nakai (1960).
B. Oana and Deevey (1960). Similar data on methane from Russian swamps are given by Ovsyannikov and Lebedev (1967).
C. Wasserburg, Mazor, and Zartman (1963).
D. Zartman, Wasserburg, and Reynolds (1961); Wasserburg, Mazor, and Zartman (1963); S. R. Silverman (unpub. data, November 1967).
F. Hulston and McCabe (1962).
G. Craig (1953 and 1963).

The isotopic composition of any methane that equilibrated with the diagenetic carbonate is indeterminate, but all criteria suggest that it must have been like that of oil-field methane. In order to gain some insight into the temperature implications of the heavy carbon in the carbonate, we tabulate below the isotopic composition of four of the five heaviest carbon dioxides from oil fields (row *D* of fig. 9) along with the composition of associated methane. One other sample has been added at the bottom of the table for consideration with the four samples.

Depth of gas source, in feet	δC^{13} of CH_4 per mil	δC^{13} of CO_2 per mil	Calc temp, in ° C	Reference and sample
360	−50.9	+16.4	25	Wasserburg, Mazor, and Zartman (1963), sample 22.
2,605	−41.5	+12.8	72	Zartman, Wasserburg, and Reynolds (1961), sample 38.
4,885	−39.7	+8.1	101	Zartman, Wasserburg, and Reynolds (1961), sample 9.
8,400	−38.3	−0.5	162	Zartman, Wasserburg, and Reynolds (1961), sample 41.
12,768	−38.5	−8.8	233	Zartman, Wasserburg, and Reynolds (1961), sample 39.

Zartman, Wasserburg, and Reynolds (1961) tested for isotopic equilibrium between methane and carbon dioxide in their samples of natural gas by using the reasonableness of the computed temperature as a criterion. They noted that reasonable temperatures were generally obtained for samples containing carbon dioxide that was rich in C^{13}, such as those tabulated above; and unreasonably high temperatures, for samples containing carbon dioxide poor in C^{13}. These relations are made clear when the computed temperatures are plotted against the depth of origin of the gas samples, as in figure 10.

In figure 10, the reasonable temperatures obtained from the five tabulated samples are seen to be the minimum value for each depth. Collectively, the five samples define a geothermal gradient of 54°C per kilometer, which is above average and its matched or exceeded by gradients of only a few American oil-fields (Birch and others, 1942). Higher gradients involving the other samples are thus unlikely; the line in the figure probably signifies virtual attainment of the equilibrium between methane and carbon dioxide, and samples that plot away from the line are out of equilibrium. Samples out of equilibrium far outnumber those in equilibrium.

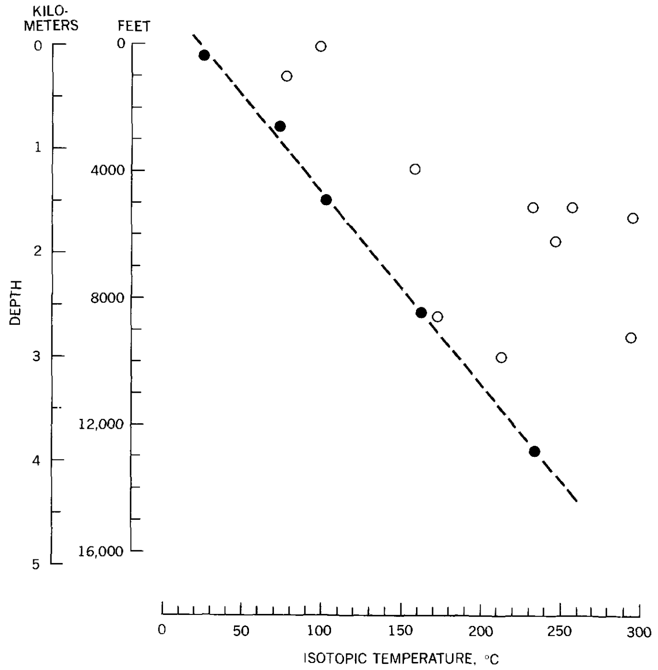

FIGURE 10.—Isotopic temperature and depth of origin of natural gas. Temperature was calculated from the carbon isotopic composition of methane and carbon dioxide in natural gas, assuming that these compounds were in isotopic equilibrium. Black circles represent the five samples tabulated on page B18. The dashed line through the five circles defines a geothermal gradient of 54°C per kilometer. Four samples with calculated temperatures greater than 350°C are omitted. All data from Zartman, Wasserburg, and Reynolds (1961) and Wasserburg, Mazor, and Zartman (1963).

These relationships suggest that heavy-carbon carbonates, such as the ones under consideration, probably reached equilibrium with methane; therefore their temperature of equilibration could be determined if the isotopic composition of the methane were known. In figure 9, the great majority of oil-field methanes (row *D*) are seen to have δC^{13} values between −52 and −38 per mil, a range that includes the five critical samples tabulated above. Therefore, using the lowest and highest of the values cited above for both methane and carbonate, we computed equilibration temperature for methane-carbonate couplets by means of the Bottinga equation (Bottinga, 1968); the results are tabulated below (values in brackets were computed for the specific temperature of 45°C).

δC^{13} of CH_4 per mil	δC^{13} of CO_3^{-2} per mil	Computed temp, in °C
−52	+21	34
[−48]	[+21]	[45]
[−52]	[+17]	[45]
−38	+21	76
−52	+5	80
−38	+5	140

The range of 34° to 140°C in the tabulation represents the best estimate that can now be made of the temperature of equilibration between methane and the heavy-carbon carbonates ($\delta C^{13} > +5$ per mil). Using the average geothermal gradient of the Los Angeles basin (39.1°C per kilometer according to Philippi, 1965) for illustration, these temperatures would correspond to depths of 1,100 to 10,000 feet. As the δC^{13} of the carbonate becomes more negative, the indicated temperature becomes higher; carbonate with δC^{13} of −4.0 per mil and methane with δC^{13} of −38 per mil would be at equilibrium at 192°C, corresponding to a depth of about 14,500 feet.

Judging from the temperature data on couplets of methane and carbon dioxide from oil field gas (fig. 10), very few, if any, of our carbonates would have been subjected to temperatures higher than about 190°C. The conclusion seems inescapable that carbonates with δC^{13} more negative than about −5 per mil could not have equilibrated with much methane. They, therefore, constitute the separate class of light-carbon carbonate previously discussed, whose carbon was largely derived through nonequilibrium oxidation of organic matter and whose carbon isotopic composition has no relevance to the temperature of formation. An upper limit of about 190°C would also be in harmony with the fact that a great many of the dolomites hold excess calcium, which would exsolve at around 200°C (Goldsmith, 1959).

The computed temperatures of 34° to 140°C in the tabulation given above and the correlative depths of about 1,100 to 10,000 feet are only crude indications of the conditions under which these dolomites could have formed. In detail, no systematic variation of δC^{13} with stratigraphic position is observed at the two localities concerned. At the Berkeley Hills (samples 7 to 9), the sampled interval was only about 100 feet, corresponding to a temperature difference of only 1°C along a normal geothermal gradient, whereas the spread of temperature indicated isotopically (assuming methane of constant composition) is as high as 26°C. At Chico Martinez Creek (samples 33 to 40) the sampled section was 2,200 feet thick, which would allow a temperature contrast of around 25°C; the difference between minimum and maximum carbon-isotopic temperature is 41°C.

These apparent temperature discrepancies among heavy-carbon dolomites are resolved if it is assumed that equilibration between methane and a normal marine carbonate either proceeded at variable rates or involved natural gas with variable content of methane. Such conditions could yield carbonates manifesting all compositions between some maximum value of δC^{13} for the locality and the value of around zero for the original marine carbonate. Thus, the spread of isotopic values at each place would be a measure of the kinetic or concentration limitations on isotopic exchange rather than an indication that the exchange process had occurred at widely different temperatures.

The heavy carbonates under consideration in this section (points in envelope *b* in fig. 6*A*) contain heavy oxygen, with δO^{18} of 32.0 to 34.6 per mil and an average of 33.2 per mil—values which would limit the maximum temperature to about 45°C (according to fig. 8) if oxygen isotopic equilibrium were also to be considered. In this case, δC^{13} of methane must lie between -52 and -48 per mil; δO^{18} of formation water, between $+7$ and $+9$ per mil; and the temperature, between 34° and 45°C, as indicated in the tabulation given above. Only δC^{13} values between $+17$ and $+21$ per mil in carbonates would then represent equilibrium compositions. These conditions are so restrictive that we rejected attainment of oxygen isotopic equilibrium as a necessary condition in the final equilibria involving these carbonates.

CARBONATE WITH VARIABLE HEAVY CARBON AND COVARIABLE OXYGEN

Examples of this isotopic category are grouped together in the upper right side of figure 6*B*. Group d_1 consist of samples of a slightly variable dolomite from the Monterey Shale of Reliz Canyon (samples 15 to 20 of table 1). Its average δO^{18} value of 31.0 per mil is too light for the group to have been included in the heavy-carbon heavy-oxygen group of figure 6*A* at *b*. Group d_2 consists of samples from a lower member of the Monterey Shale in Reliz Canyon and in a section near Nacimiento Dam (samples 23 to 25, 27, 28, 30, and 31 of table 1); these samples are isotopically more variable than those of group d_1, carbon varying directly with oxygen. Paleotemperatures of the four samples with the heaviest oxygens in group d_2 were discussed on page B11. Other representatives of this isotopic category are three from Oregon (samples 1 to 3) and pairs of samples (Nos. 10 and 11, 51 and 52, 56 and 57, and 59 and 60) from several localities.

A simple explanation for the covariation of carbon and oxygen isotopic composition would be to have these carbonates undergo exchange reactions with meteoric water. The presence of late fresh-water calcite (sample 26) in cracks in dolomite sample 25 would corroborate the view that this dolomite was more affected by meteoric water than any others of group d_2, and that the isotopic trends within the group were due to the variable degree of equilibration of an originally heavy-carbon heavy-oxygen carbonate with meteoric water. The same action of meteoric water was already used on page B11 to explain the discordant paleotemperatures within the dolomite-calcite pair of samples 56 and 57. However, the calcium content of the dolomites under consideration in this section cannot be reconciled with the postulated reaction with meteoric water, as will be shown next.

CALCIUM CONTENT OF DOLOMITE AS RELATED TO ISOTOPIC COMPOSITION

The calcium content of the dolomites is plotted against the carbon isotopic composition in figure 11, and several significant relationships are apparent. Calcium appreciably in excess of the 50 mol percent of ideal dolomite is common among both heavy-carbon and light-carbon dolomites. Graf and Goldsmith (1956) and Goldsmith (1959), who gave the name protodolomite to dolomites of such nonideal composition, have shown that protodolomite is a widespread and persistent metastable phase in sedimentary rocks. It can be made to invert to stable ideal dolomite by heating to temperatures greater than about 200° C.

Among the samples from Palos Verdes Hills (black circles in fig. 11) only samples 72 to 74 are ideal dolomites. Previously, in figure 7, these very samples were seen to have deviant oxygen compositions—deviations which were explained in terms of possible heating effects of nearby igneous sills; the same effects could have accelerated the inversion to normal dolomite. Otherwise, no relationship between isotopic and calcium

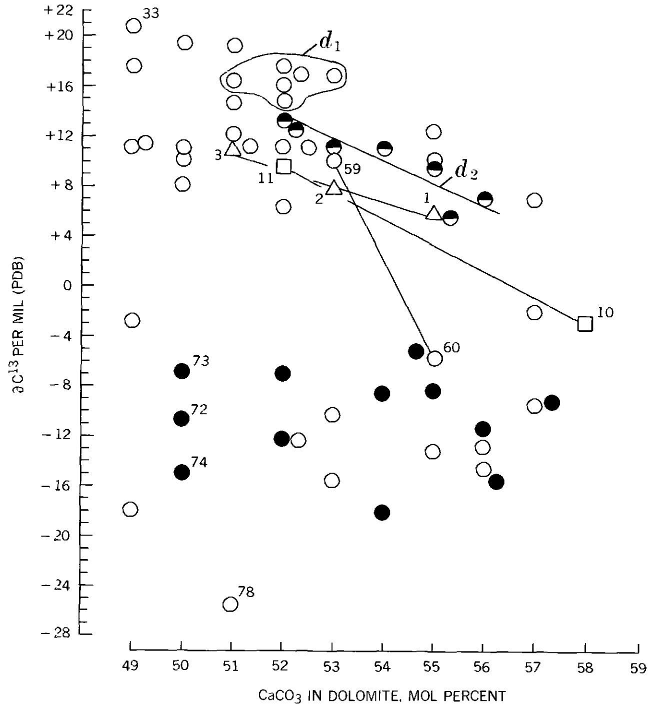

FIGURE 11.—Carbon isotopic composition as related to the CaCO$_3$ content of a diagenetic dolomite. Groups d_1 and d_2 are the same as those so labeled in figure 6*B*. Numbered triangles, squares, and open circles that are linked by tie lines denote the same dolomite samples as those linked by the dashed lines in figure 6*B*. Black circles represent samples from Palos Verdes Hills; open circles without tie lines, samples from all other localities.

compositions is apparent among light-carbon dolomites in figure 11.

Among the heavy-carbon dolomites in the upper half of figure 11, group d_2 outlines an inverse trend between δC^{13} and the calcium content. Other heavy-carbon dolomites (samples 1 to 3, 10 and 11, and 59 and 60) also show the same trend. The increase in calcium content with decrease in δC^{13} might be interpreted to mean that ideal dolomite alters into protodolomite in the zone of weathering—a direct contradiction of earlier work (Graf and Goldsmith, 1956), which indicated that ideal dolomite, not protodolomite, is the stable phase under near-surface conditions.

The contradiction is removed if the trends in question are illustrating the reverse process, namely the transformation of protodolomites into ideal dolomites at moderate depths, the carbonate equilibrating with the carbon of methane and the oxygen of oil-field brines. The lack of comparable trends among light-carbon dolomites would be due to the general failure of these isotopic equilibria, which causes the protodolomite-dolomite transformation to proceed without any reference to isotopic compositions.

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U. S. GOVERNMENT PRINTING OFFICE : 1969 O - 334-795