DOLOMITES FORMED UNDER CONDITIONS OF DEEP BURIAL: HUNTON GROUP CARBONATE ROCKS (UPPER ORDOVICIAN TO LOWER DEVONIAN) IN THE DEEP ANADARKO BASIN OF OKLAHOMA AND TEXAS

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ABSTRACT: Progressive burial diagenesis of Hunton Group (Upper Ordovician to Lower Devonian) rocks of the deep Anadarko Basin of Oklahoma and the Texas Panhandle is evident from petrographic and geochemical study of cores and cuttings from more than 25 boreholes up to 30,000 ft deep. Limestone of the Hunton Group, which originated as shallow shelf carbonates, has been replaced, chiefly below present depths of about 10,000 ft, by dolomite that is commonly ferroan and is associated with shale. This diagenetic dolomite is inferred to have formed under deep-burial conditions.

The dolomite occurs as finely disseminated, 10μm and larger rhombic crystals, and is most abundant near the base of the Hunton Group, particularly where an oolite unit (the Keel Formation) overlies the thick marine Sylvan Shale that is inferred to be the chief source of Fe^{2+} and Mg^{2+} ions. Ferroan dolomite also occurs where clay minerals are abundant in the Middle Hunton Group. In shallow wells, dolomite crystals are euhedral. Below 10,000 ft (3.0 km), where dolomitization of the oolite has been more complete, hypidiotopic and xenotopic textures result. Hydrocarbon-associated fluids are inferred to have dissolved the calcite that was not replaced, and to have created intercrystalline and moldic porosity.

X-ray diffraction verifies a trend of higher dolomite concentrations with increasing depth in the same oolite horizon. For example, oolite samples from outcrop lack dolomite and are 100% $CaCO_3$; cores from 9,200 ft (2.8 km) are about 25% dolomite; and cores from 15,000 ft (4.6 km) and below are more than 85% dolomite. Radioisotope-induced x-ray fluorescence shows that dolomites below 10,000 ft (3.0 km) are iron-enriched relative to both non-dolomitized oolite and dolomites of surface origin. Where the Hunton Group and the Sylvan Shale are buried below 10,000 ft (3.0 km), well logs show high densities in the lowermost Hunton (above the Sylvan Shale) which can be interpreted as the occurrence of Fe^{2+}-rich dolomite. Stable isotope ratios suggest a higher temperature of origin for burial dolomites than for dolomites of surface origin. Formation waters recovered from within the shale and carbonate are greatly depleted in Mg^{2+} ions compared to normal marine waters.

General restriction of this shale-associated ferroan dolomite to strata that are currently buried below 10,000 ft (3.0 km) in the Anadarko basin supports other lines of evidence for the belief that previously deeply buried strata can be recognized even if the strata have been subsequently uplifted. The transformation of smectite to illite in the Sylvan Shale (conformably underlying the oolite) is suggested as a possible source of Mg^{2+} and Fe^{2+}. Smectite/illite ratio decreases with increasing depth in the Sylvan Shale. Furthermore, Sylvan Shale below 10,000 ft (3.0 km) is depleted in iron by 70% relative to Sylvan Shale less than 10,000 ft (3.0 km) deep, suggesting that under deep conditions shales have given up their iron (and magnesium), presumably to the overlying carbonates.

INTRODUCTION

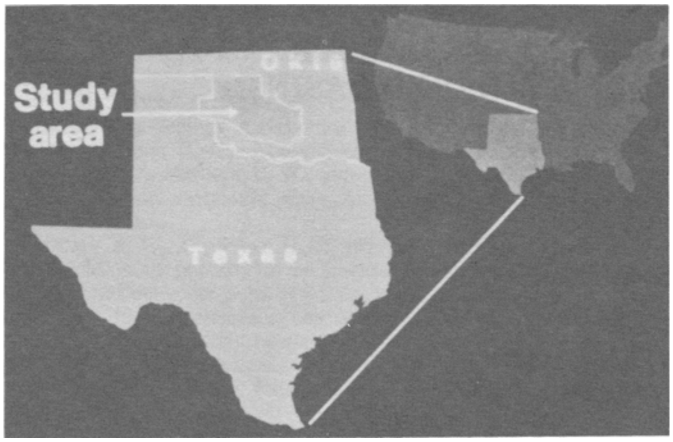
During the past ten years, deeply buried rocks have become the focus of extensive hydrocarbon exploration. Accelerated exploration in deep basins of the midcontinental United States has emphasized the need to understand the effects of deep burial on the generation and preservation of porosity, on cement-porosity relationships, on textural characteristics, and on the mineral compositions of carbonate rocks.

The influence of pressure and temperature on carbonate sediments and rocks is known mainly in the range consistent with surface to shallow-burial conditions and in the realm of regional metamorphism. As the search for oil and gas is extended to greater depths, study of deep-burial diagenesis is becoming increasingly important.

In the late 1950s and early 1960s, limestones became the chief carbonate reservoirs to be exploited for hydrocarbons. More recently, however, production has shifted away from primary depositional porosity in limestones, and towards dolomite (dolostones), which have become the major source of domestic hydrocarbon production from carbonates.

Numerous studies have addressed the diverse origins and compositional variations of dolostones (e.g., Friedman and Sanders, 1967; Zenger, Dunham, and Ethington, 1980). More recently, other studies have specifically addressed the origin and occurrence of ferroan dolomite and of burial dolomite, which is dolomite formed from a precursor limestone under burial conditions (Al-Shaieb and Shelton, 1978; Boles, 1978; Mattes

CARBONATES AND EVAPORITES, Vol. 1, No. 1, 1986, pp. 69-73



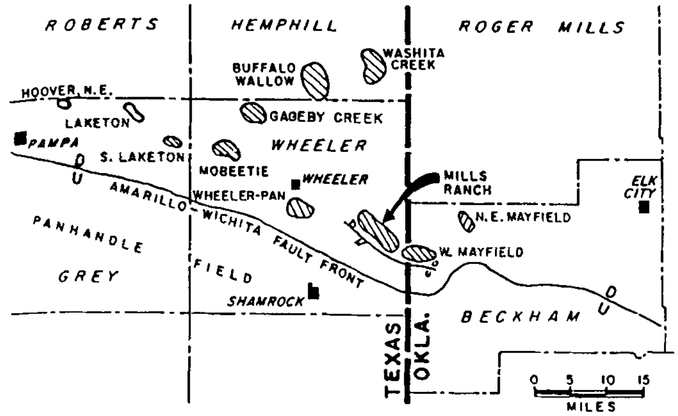
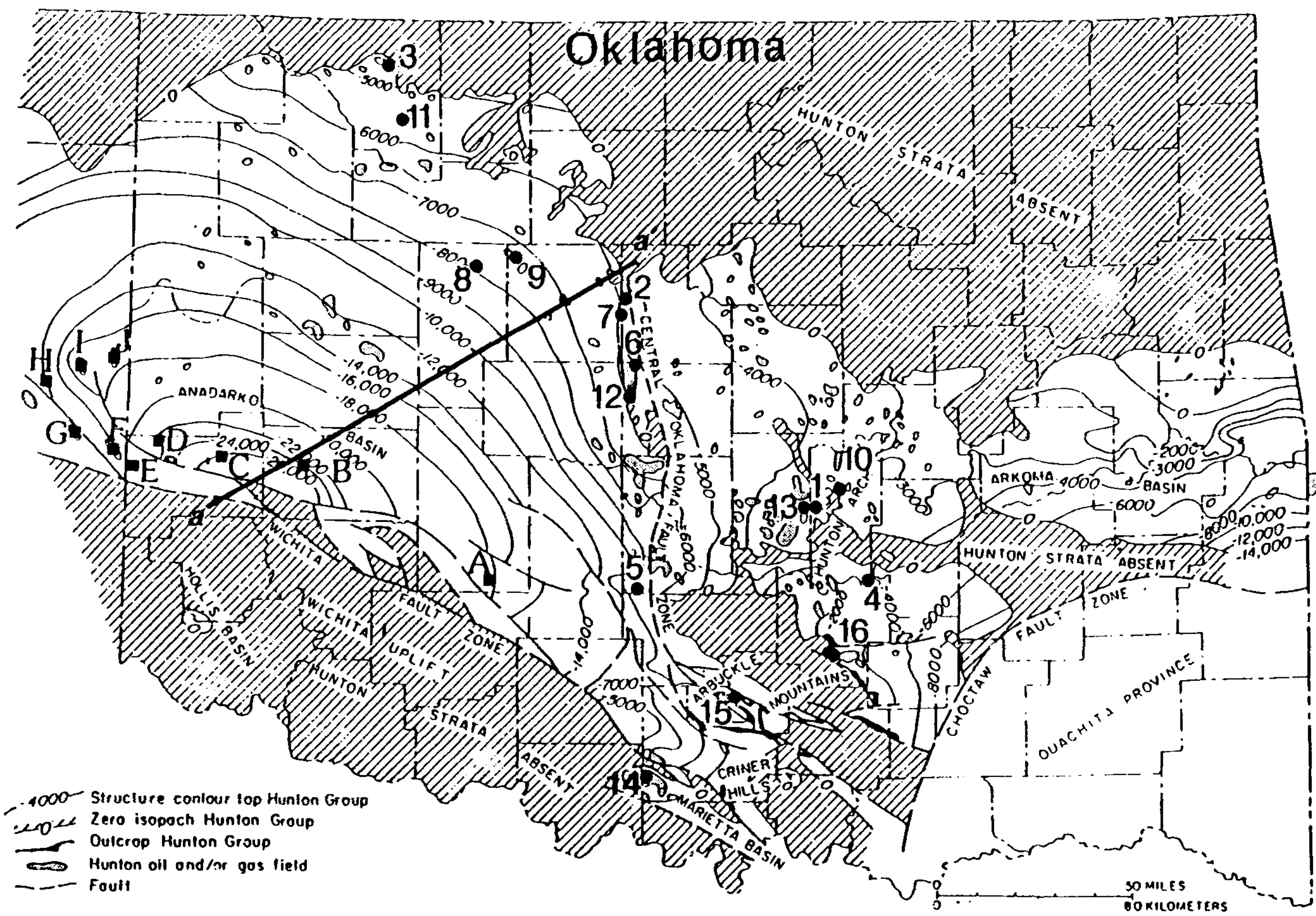


FIG. 1.—Maps of the Anadarko Basin of Oklahoma and the Texas Panhandle, U.S.A. A) Index Map. (Upper left corner.) B) Location map of wells studied in the Anadarko Basin of Oklahoma and the Texas Panhandle drawn on top of structural map of the Hunton Group. Contour values shown in feet (after Amsden, 1980: his text Figure 24). Stippled areas show Hunton oil and gas fields. (Upper right corner.) C) Location map of deep fields; shaded fields are part of this study (after Jemison, 1979: his Figure 1). (Lower bottom.)



and Mountjoy, 1980; McHargue and Price, 1982; Gregg, 1982; Taylor, 1982; Gregg and Sibley, 1984; Zenger, 1983; Sternbach and Friedman, 1983, 1984).

In the Anadarko basin, where wells have penetrated Paleozoic rocks to a depth of 30,000 ft (10.0 km), dolostones alone retain porosity. From one such producing well at a depth of 26,500 ft (8.1 km), a log porosity of as high as 26% was calculated. As much as 10% porosity was calculated in dolostones at 30,000 ft (10.0 km). The ability of dolostones to retain porosity at great depths and the tendency of limestones to lose porosity under the deep-burial pressures emphasizes the crucial economic importance of a better understanding of dolostones (Friedman, Cataffe, and Borak, 1983; Friedman, Sternbach, and Cataffe, 1982; Friedman, Reeckmann, and Borak, 1981; Borak and Friedman, 1981, 1982). Furthermore, zones of ferroan dolomite, common at depth, offer a special bonus. Ferroan dolomites contain higher porosities than indicated from log calculations that incorrectly assume them to be non-ferroan dolomite (Sternbach and Friedman, 1984).

GEOLOGIC BACKGROUND

We studied the Hunton Group carbonate rocks, which are of Late Ordovician to Early Devonian age, in the Anadarko basin of western Oklahoma and the adjacent Texas Panhandle (Figs. 1A and 1B). A detailed map of the western Anadarko basin indicates many of the deepest hydrocarbon-producing fields in the world, most of which supplied samples used in this study (Fig. 1C). A cross section (Fig. 2) shows that the Anadarko basin is an asymmetrical synclinal trough, with sedimentary rocks below 35,000 ft (10.7 km) in the deepest part of the basin (southwest). We investigated a single horizon, the oolite-shale contact, which nearly represents the Ordovician-Silurian boundary, from shallow to great depths to isolate textural and mineralogical differences caused by burial diagenesis (Fig. 2).

In addition to cores, cuttings, and well logs from more than 25 boreholes, well logs from 50 additional wells were studied. In those deep fields studied, we found evidence of iron-rich burial dolostones associated with shale.

The stratigraphic column (Fig. 3) shows the Keel Formation, an oolite grainstone, overlying the Sylvan Shale. The Sylvan Shale is a marine shale that approaches its greatest thickness of 150-200 ft (46-61 m) in the deep basin. The oolitic Keel Formation represents the rapid progradation of high-energy intertidal oolite shoals over a low energy (subtidal) marine shale. The Keel Formation was deposited in a widespread, shallow sea (Amsden, 1983). The thickness of the Keel Formation varies between several tens of feet (3-10 meters) and zero feet (where it is absent as a result of local erosion). The contact between the shale and the oolite appears to be conformable (Amsden, 1960, 1975, 1980). Core slabs of non-dolomitized Keel Formation oolite grainstone and the underlying Sylvan Shale show the contact (Fig. 4), as it appears in a shallow well.

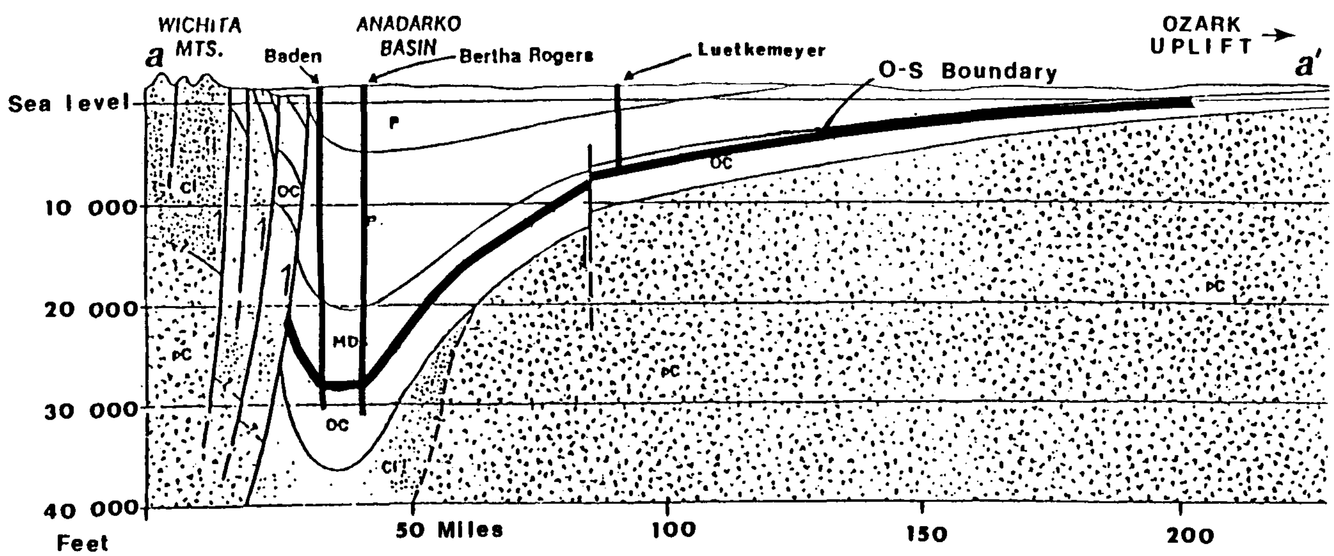


FIG. 2.—Cross section of Anadarko Basin (see line of section on Figure 1B, modified after Johnson, 1979). Heavy line denoted "O-S Boundary" represents the Ordovician-Silurian boundary, which closely approximates the contact of the Keel Formation oolite with the overlying Sylvan Shale.

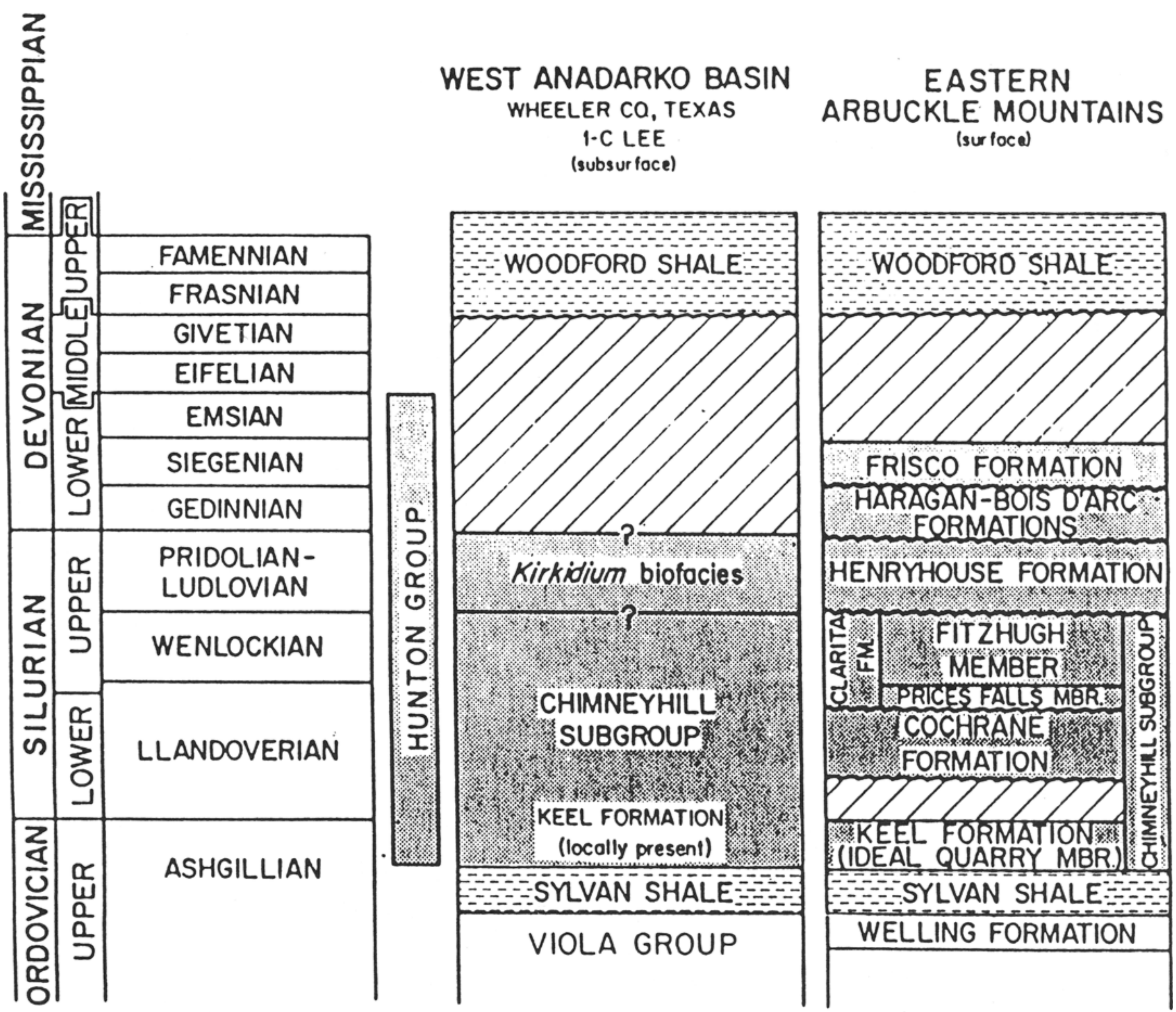


FIG. 3—Stratigraphic chart showing relationship of Middle Ordovician to Lower Mississippian strata (after Amsden 1960, 1975, 1980; Amsden and Sweet, 1983). Stratigraphic units included in Hunton Group are stippled. Chart not to scale in terms of stratigraphic thickness or time.

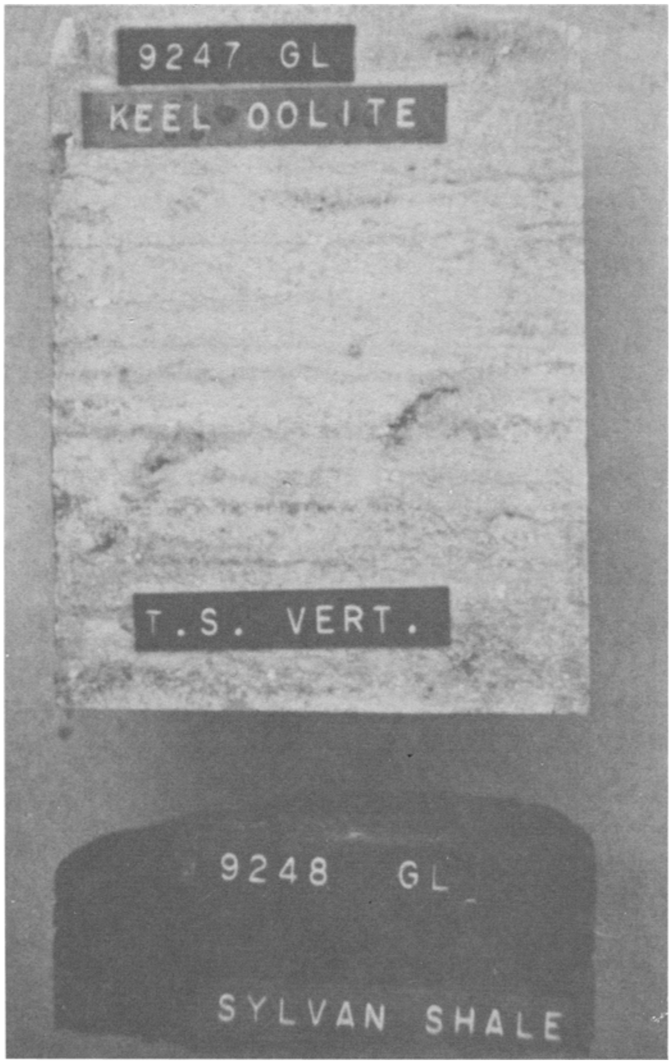


FIG. 4.—Core slabs of relatively non-dolomitized oolite (Keel Formation) overlying shale (Sylvan Shale). The slabs, which are about 4 inches wide (10 cm), are from depths of 9,247 and 9,248 ft (2.82 km), respectively.

METHODS AND RESULTS

Overview

The most conclusive method for establishing that dolomite formed under conditions of deep burial is to trace a single carbonate horizon from shallow to great depth. We can see under the microscope the increasing abundance of dolomite in samples from increasingly greater depths. X-ray diffraction verifies an abrupt increase in dolomite abundance in carbonates directly overlying the Sylvan Shale, but only in rocks that were very deeply buried, below 10,000 to 15,000 ft (3.0 to 4.5 km). Radioisotope-induced x-ray fluorescence shows that there is also an abrupt increase in the concentration of iron in dolomite close to the Sylvan Shale, but, again, only in the deep wells. Geophysical logs of deep wells show that matrix density increases abruptly next to the Sylvan Shale, thus paralleling the increased percentages of dolomite in the rock and of iron in the dolomite.

Additional lines of evidence support the contention that the dolomite formed under conditions of deep burial. Atomic absorption analyses of formation waters from deep wells show surprisingly low concentrations of Mg^{2+} ions. This suggests that Mg^{2+} has been precipitated out of the pore water. Oxygen isotopes of the dolostones that we believe formed under conditions of deep burial have average $\delta^{18}O$ values (PDB) of -5.4, compared to average $\delta^{18}O$ values of -1.2 in dolostones that we and other investigators (Amsden, 1960, 1975 and 1980) have inferred by independent criteria to have formed under near-surface conditions. The $\delta^{18}O$ values, as expected, suggest a higher temperature of formation for the burial dolomites. Shale analyses indicate that the iron concentration of the deep shales is depleted beneath the ferroan dolomites, whereas the shallow shales are iron-enriched below the shallow, non-dolomitized carbonate strata. The mineral composition of the shale at increasing depths shows a predictable trend: the abundance of smectite (montmorillonite) decreases as the abundance of illite increases, suggesting that the smectite to illite transition is currently taking place.

Although none of these lines of evidence is conclusive by itself, all of them taken together make a compelling case for the formation of dolomite under conditions of very deep burial (10,000 to 15,000 ft, 3.0 to 4.5 km). Each of these techniques is more closely examined in the following sections.

Petrography

Samples from outcrops of the Keel Formation, a nearly 100% $CaCO_3$ oolite grainstone, show fine detail (Fig. 5). Concentric laminae and a radial fabric are easily recognized within the ooids. Epoxy resin was vacuum-injected into the samples to highlight intra-ooid pores.

At 9,200 ft (2.8 km) this same oolite layer shows the beginning of ferroan dolomite crystal growth (Fig. 6). Euhedral dolomite crystals seem to have replaced the calcite ooid particles. Pore fluids in the former intra-ooid pores are inferred to have supplied Mg^{2+} and Fe^{2+} to the growing dolomite crystals. Many of the intra-ooid pores have thus been filled, leaving this rock very low in porosity ("tight"), and consequently a poor reservoir. Calcite spar surrounds the ooids, and microcrystalline calcite makes up the brown, non-dolomitized areas of the ooids. The ferroan dolomite crystals are unzoned. Meniscus and pendant cements, which would suggest dolomitization by a mixing-water model, are lacking.

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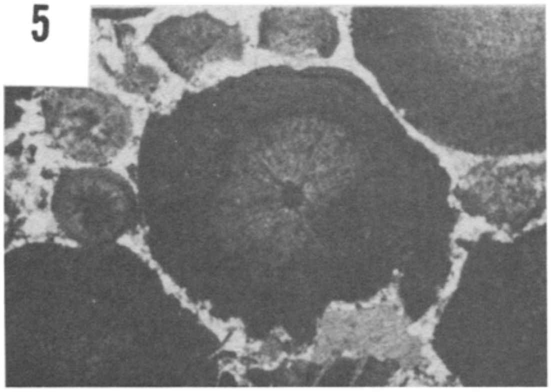

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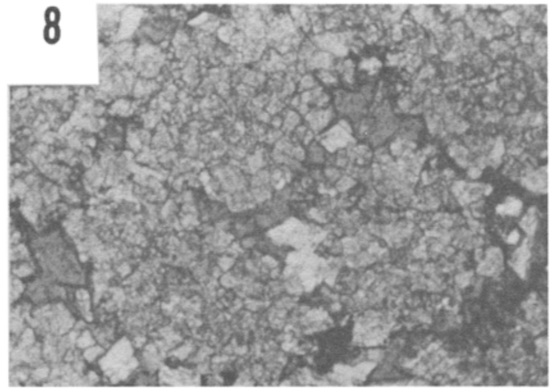

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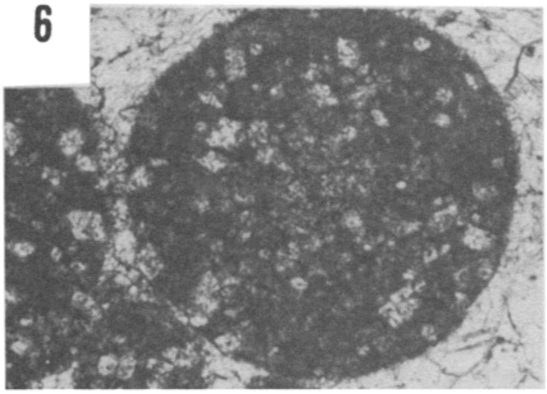

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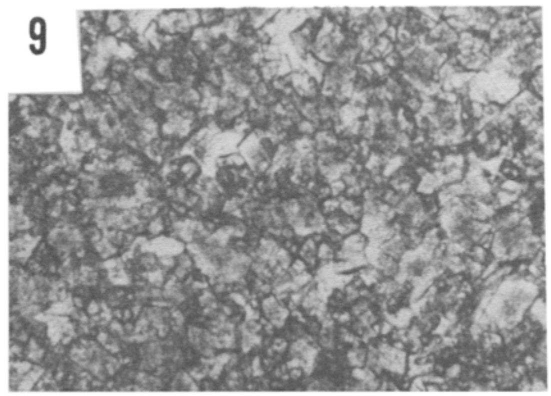

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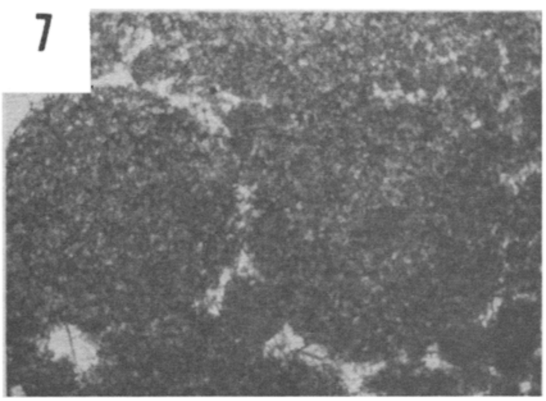

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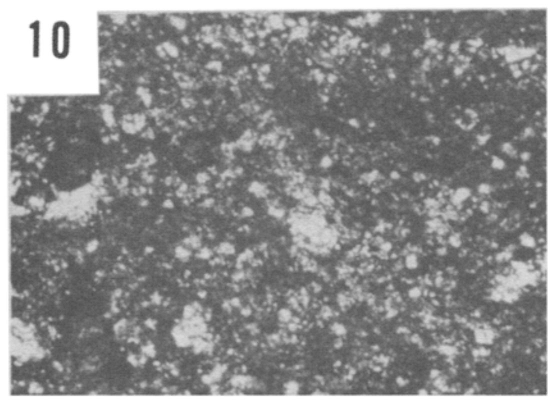

FIG. 5.—Photomicrograph of Keel Formation oolite grainstone from outcrop, Lawrence Quarry, Pontotoc Co., Oklahoma, (Location 16, Fig. 1). More than 99% $CaCO_3$. Dark-gray areas are former inter-ooid pores impregnated with epoxy resin under a vacuum. Sample courtesy of Dr. T. W. Amsden, Oklahoma Geological Survey. Scale bar represents 500 μm.

FIG. 6—Photomicrograph of Keel Formation oolite grainstone from 9,247 ft (2.8 km), GETTY Luetkemeyer well (location 8 on Fig. 1B). Notice that euhedral dolomite rhombs (20-50 μm.) have replaced some of the calcite matrix of the ooids and that inter-ooid pores are now lacking. Sample consists of 24% ferroan dolomite. Scale bar represents 100μm.

FIG. 7.—Photomicrograph of Keel Formation oolite grainstone from 15,000 ft (4.6 km), MOBIL Walker #1 well (Location G on Fig. 1B, Wheller-Pan Field on Fig. 1C), showing intra-ooid intercrystalline porosity in ferroan dolostone. Scale bar represents 100μm.

FIG. 8.—Photomicrograph of Keel Formation oolite grainstone from 15,330 ft (4.7 km), PHILLIPS Lee #1-C well (Location H on Fig. 1B, Gageby Creek Field on Fig. 1C). The Keel Formation oolite has been strongly dolomitized; dolomite is iron rich. However, unlike the sample of Fig. 7, the intercrystalline porosity is inter-oolitic rather than intra-oolitic. Scale bar represents 400μm.

FIG. 9.—Photomicrograph of ?Keel Formation oolite grainstone from 21,259 ft (6.5 km) APEXCO Green #1 well (Location E on Fig. 1B, West Mayfield Field on Fig. 1C). Even though it is in the stratigraphic location appropriate to the Keel Formation, dolomitization of the precursor carbonate is so pervasive, it is uncertain whether or not this sample represents the Keel Formation. Scale bar represents 100μm.

FIG. 10.—Photomicrograph of Keel Formation oolite grainstone from 25,760-70 ft (7.9 km), MESA Crook #1 well (Location D on Fig. 1B, Northeast Mayfield Field on Fig. 1C). Thin-section view shows approximately 85% dolomite; dolomite is iron-rich. Scale bar represents 100μm.

At 15,000 ft (4.6 km), dolomite constitutes more than 90% of the Keel Formation. Despite the dolomite replacement (Fig. 7), the original ooid outlines are still apparent. Leaching of the non-dolomitized calcite by hydrocarbon-associated fluids has formed intercrystalline dolostone porosity, which occurs in these and deeper oolite samples. The intercrystalline dolostone porosity can be either intra-ooid (Fig. 7) or inter-ooid (Fig. 8).

At 22,000 ft (6.7 km), in the deepest Hunton Group cores yet recovered, dolomite is so pervasive that the former ooid outlines are only faintly recognizable (Fig. 9). Cuttings reveal that the Keel Formation has been extensively dolomitized at 25,000 ft (7.6 km) and below (Fig. 10). Staining (Friedman and Sternbach, 1982) shows that these dolomites commonly contain high concentrations of Fe^{2+} substituting for Mg^{2+}.

X-Ray Diffraction

We determined the relative concentration of calcite, dolomite, and quartz in the samples by using x-ray diffraction to compare peak intensities of unknown samples to peak intensities of standards of known mineral concentrations (Table 1 shows sample calculations from 3 deep wells). Data obtained in this way verified the petrographic analysis and enabled us to quantify the relative abundances of calcite and dolomite with increasing depth. Relative proportions of the carbonate minerals were determined by comparing the X-ray diffraction peak heights (Gavish and Friedman, 1973) to calibrated curves of calcite, dolomite, and quartz (after Tenant and Berger, 1957). Volumes of shale in the Hunton Group were determined, using a microcomputer, from gamma-ray log curves (after Pirsson, 1977; Asquith and Gibson, 1982). For the basal Hunton, including the Keel Formation, clay content is generally less than 3 to 5% of the whole rock.

Table 1.—*Mineralogical compositions of carbonate rock samples as determined by x-ray diffraction. Wells A, B, and C are the Mesa Crook, Mesa Tipton, and Mesa Cox wells, respectively (Location D on Fig. 1B; Northeast Mayfield Field on Fig. 1C). Depth is in feet, mineral content is in weight percent, density is in g/cm^3.*

Well A. Note the increase, with greater depth (approaching the Sylvan Shale at 25,782 ft), of the dolomite-calcite ratio, the iron concentration of the dolomite, and the matrix density of the rock.

Well B. These samples are marlstones from the Haragan-Henryhouse Formation, in the middle of the Hunton Group (Fig. 3). Note that, in general, the dolomite and iron concentrations are greatest between 24,940 and 24,970 ft. Because the volume of shale in the carbonate of this interval may be as high as 20% (based on gamma ray well-log curves), the values shown have been corrected for shale. Sternbach and Friedman (1984, their Fig. 4) show that porosity of this reservoir rock is greatest between 24,940 and 24,970 ft, reaching as high as 14% at about 24,960 ft.

Well C. Spot samples from potential reservoirs. Note the higher concentration of dolomite in the lower two samples.

WELL	DEPTH	CALCITE	DENSITY	DOLOMITE	DENSITY	QUARTZ	DENSITY	MATRIX DENSITY
A	25,720-25	38	2.71	57	2.86	5	2.65	2.79
A	25,725-30	45	2.71	50	2.88	5	2.65	2.79
A	25,730-40	40	2.71	56	2.88	4	2.65	2.80
A	25,740-50	45	2.71	51	2.91	4	2.65	2.81
A	25,750-60	45	2.71	50	2.91	5	2.65	2.81
A	25,760-70	31	2.71	52	2.96	17	2.65	2.83
A	25,770-77	30	2.71	50	3.01	20	2.65	2.85
A	25,777-80	13	2.71	62	3.03	25	2.65	2.89
B	24,920-30	43	2.71	43	2.87	14	2.65	2.77
B	24,930-40	46	2.71	32	2.95	22	2.65	2.77
B	24,940-50	49	2.71	38	2.99	13	2.65	2.81
B	24,950-60	50	2.71	34	3.02	16	2.65	2.81
B	24,960-70	48	2.71	43	2.99	9	2.65	2.83
B	24,970-80	60	2.71	27	2.95	13	2.65	2.77
C	24,260-70	77	2.71	16	3.03	7	2.65	2.76
C	24,350-60	64	2.71	31	2.95	5	2.65	2.78
C	24,470-80	48	2.71	48	2.95	4	2.65	2.82
C	24,540-50	45	2.71	49	2.95	6	2.65	2.82

Radioisotope-Induced X-Ray Fluorescence

We determined the iron concentrations in the samples by radioisotope-induced x-ray fluorescence. In each deep well sampled, the concentrations of dolomite (Well A, Table 1; Fig. 11) and iron (Fig. 12) increase abruptly with depth in the basal 10 to 20 ft (3 to 6 m) of carbonate rock toward contact with the Sylvan Shale. In the correlative basal 10 to 20 ft (3 to 6 m), samples from outcrop and from 15 wells shallower than 10,000 ft (3 km) showed no similar increase in dolomite or ferroan dolomite.

In dolostones inferred to have formed under conditions of deep burial, iron is usually abundant; whereas the shales that underlie these dolostones are relatively depleted in iron (Figs. 13 and 14). In contrast, dolostones inferred to have formed under near-surface conditions are not ferroan, and the iron concentrations in the shales that underlie these dolostones are normal (Figs. 13 and 14). We infer that, in the deep wells, Mg^{2+} and Fe^{2+} have moved upward from the shales into the overlying carbonates.

Geophysical Well Logs

In the deepest of the 75 wells studied, well logs show high densities in the lowermost Hunton Group (above the Sylvan Shale) which can only be interpreted as due to the presence of Fe^{2+}-rich dolomite (Fig. 15). Negative porosity values are calculated when the high bulk densities in the strata above the deep shales are plotted for a matrix density of limestone (2.71g/cm^3). Because negative porosity does not exist, the rock must not be a limestone. When the high bulk densities of the carbonates above the shales in the deep wells are plotted for a matrix density of stoichiometric dolomite (2.87g/cm^3), a better fit results. However, even though the resulting bulk density of the rock may resemble that of dolomite, the rock may contain substantial quantities of lighter minerals, e.g., 20% quartz and 10 to 20% calcite (Table 1). Because the matrix densities of these poly-mineralic rocks are almost identical to the matrix density of 100% stoichiometric dolomite, the dolomite of these poly-mineralic rocks must be denser than average

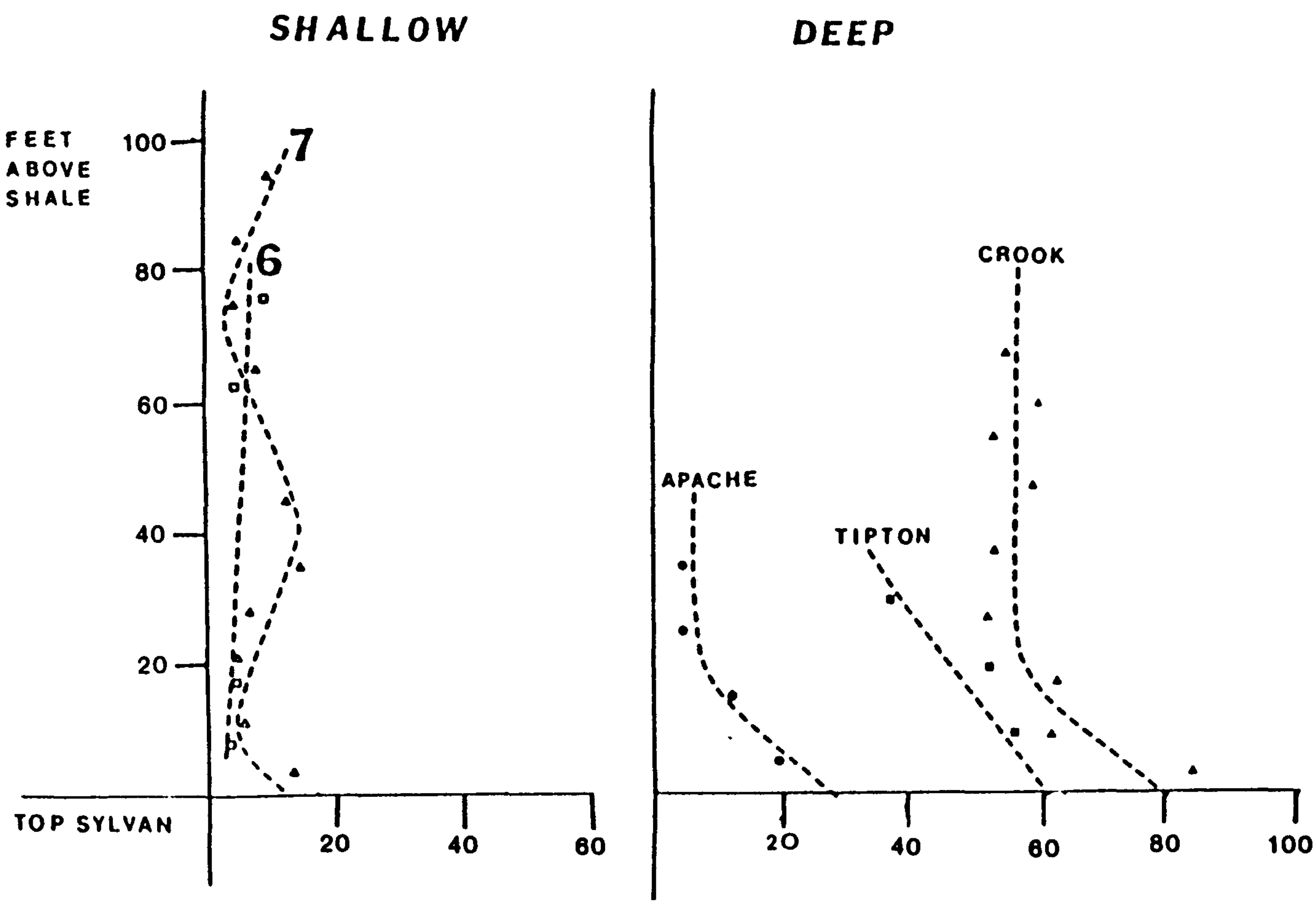

FIG. 11.—Percentage of dolomite, by x-ray diffraction, in the Chimneyhill Subgroup nearing the Sylvan Shale contact in shallow and deep wells. Note the increase in dolomite concentration toward the Sylvan Shale in the deep wells, but not in the shallow wells. The shallow wells are at locations 6 and 7 on Fig. 1B, where the depth of the Sylvan Shale is 6,661 and 7,099 ft (2.0 and 2.2 km), respectively. The locations of the deep wells are also shown on Fig. 1B, where the "Apache" well is at Location A (Apache Field on Fig. 1C), and the "Tipton" and "Crook" wells are at Location D (Northeast Mayfield Field on Fig. 1C). The depth of the Sylvan Shale in these wells is 20,040, 25,482, and 25,782 ft (6.1, 7.7, and 7.9 km), respectively.

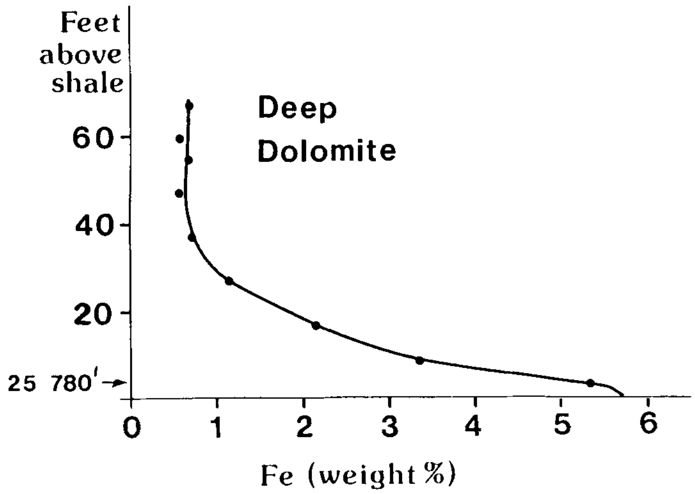

FIG. 12.—Iron concentration (in weight percent) near in the base of the Hunton Group carbonate rocks increases towards the Sylvan Shale in the deep wells. The example shown here is the Mesa Crook well, at Location D on Fig. 1B (Northeast Mayfield Field on Fig. 1C). Iron concentration of the carbonate samples was determined by radioisotope-induced x-ray fluorescence.

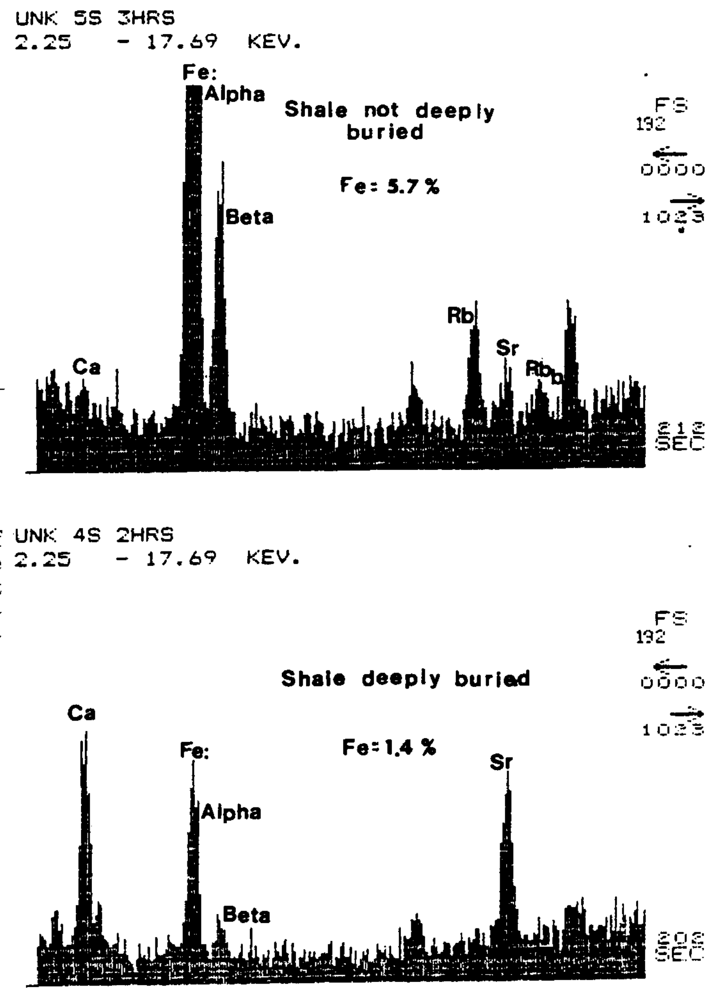

FIG. 14.—Elemental analysis by radioisotope-induced x-ray fluorescence shows that deeply-buried shale lying below iron-rich dolomite is depleted in iron. Shallowly-buried shale lying below iron-poor, supratidal dolomite is not depleted in iron, and its iron concentration is average for the Sylvan Shale. This is interpreted to mean that iron has migrated from the shale to the overlying carbonates only under conditions of deep burial. (above)

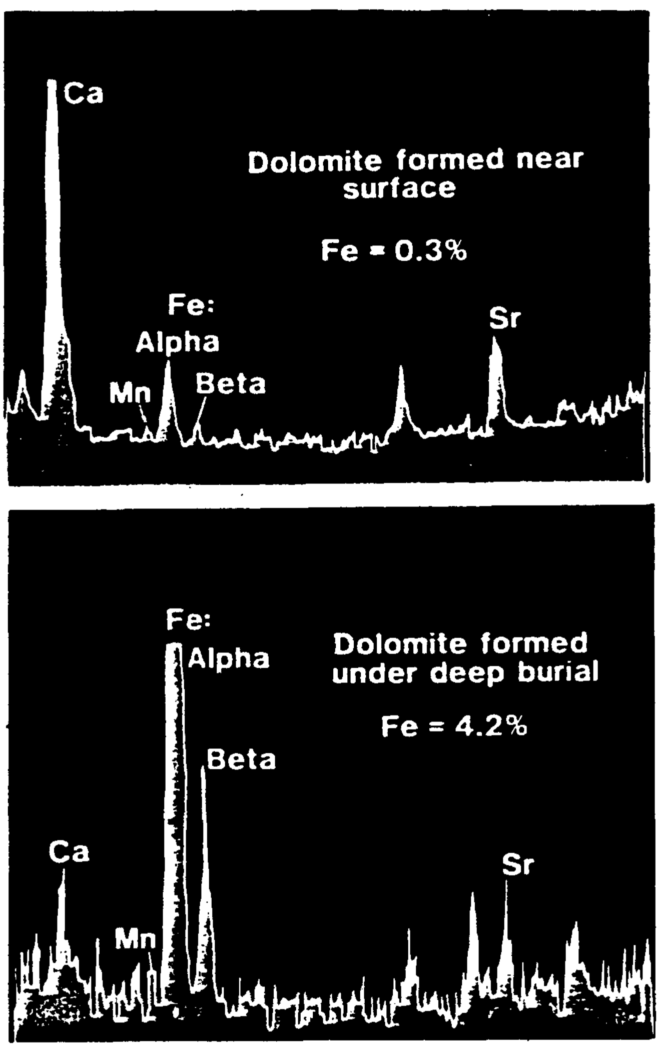

FIG. 13.—Elemental analysis by radioisotope-induced x-ray fluorescence shows that dolomite formed under conditions of deep burial may be iron-enriched relative to dolomite formed under near-surface conditions (e.g., supratidal). Note, also, the Sr^{2+}-enrichment of the inferred supratidal dolomite. Both samples were run for 3 hours. Vertical scale represents electron energies (2.25 to 17.69 kev, from left to right). (left)

stoichiometric iron-free dolomite to compensate for the lighter minerals. The substitution of Fe^{2+} for Mg^{2+} in the lattice of the mineral dolomite produces a mineral that is denser than dolomite in proportion to the extent of the substitution. The increasing matrix density of the carbonate overlying the shale parallels the increase in iron and dolomite concentrations indicated by x-ray analysis.

Oxygen Isotope Analyses

Oxygen isotope compositions determined by stable isotope ratio analysis for interpreted supratidal dolostones in the northern edge of the basin are 4-5 °/oo $\delta^{18}O$ (PDB) more positive than for dolostones inferred to have formed under conditions of deep burial. Specifically, oxygen isotopes of the dolostones inferred to have formed under conditions of deep burial have $\delta^{18}O$ values (PDB) that average −5.4, compared to average $\delta^{18}O$ values of −1.2 in dolostones formed under near-surface conditions. The evidence suggests a significantly lower temperature of formation for the dolomites in the northern supratidal facies than for ferroan dolomites in the deep part of the basin to the southwest, which we believe were formed during deep burial (Fig. 16). The supratidal dolomites in the northern part of the basin are non-ferroan, and overlie the Sylvan Shale at present depths of only 6,000 ft (1.8 km).

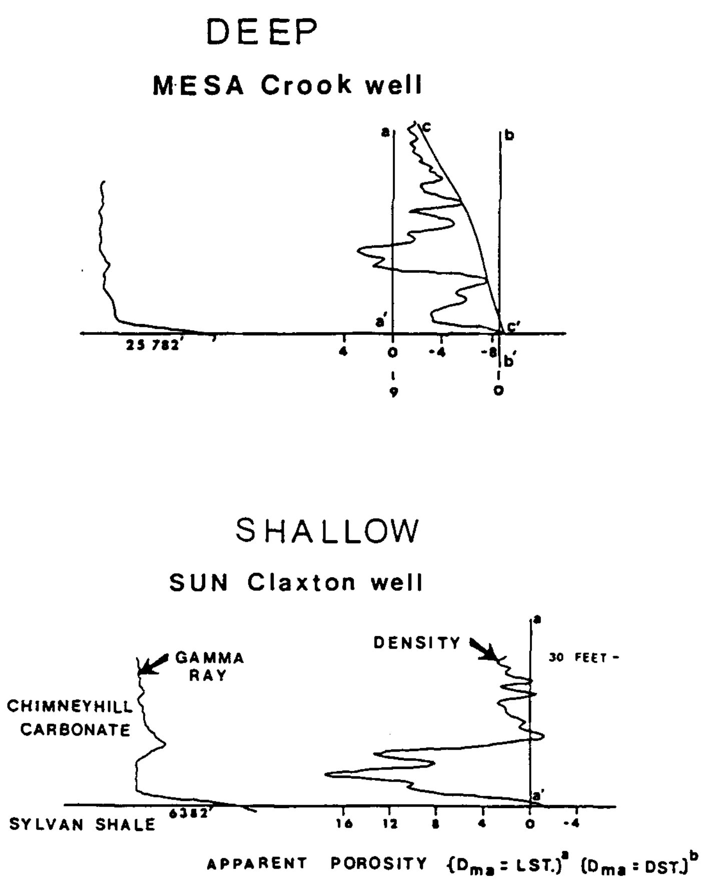

FIG. 15.—Deep vs. shallow well logs. The Claxton well shows an 18% porosity zone in limestone directly above the Sylvan Shale at 6,382 ft (1.9 km), (Location 14 on Fig. 1B).

$D_{\mu\alpha}$ (matrix density) of limestone (LST.) = 2.71 g/cm^3 (calcite matrix)

$D_{\mu\alpha}$ of dolostone (DST.) = 2.87 g/cm^3 (dolomite matrix)

Because the Crook well shows strongly "negative" porosities when plotted for a matrix density of limestone (2.71 g/cm^3), the carbonate in the Crook well must be dolomite above the Sylvan Shale at 25,782 ft (7.9 km) (Location D on Fig. 1B, Northeast Mayfield Field on Fig. 1C). Also, the Crook well shows the highest densities in the section above the shale, which is indicative of the increased iron concentration there. Line a-a′ represents zero porosity for a rock with the same matrix density as limestone (2.71 g/cm^3). Because a-a′ is a good fit for the zero porosity baseline of the shallow well, that rock must be a limestone. Line b-b′ represents zero porosity for a rock with the same matrix density as dolostone (2.87 g/cm^3). Because line c-c′ approaches line b-b′ towards the shale in the deep wells, the rock directly above the shale must be a dolostone. (See Fig. 11 for dolomite concentrations, and Fig. 12 for iron concentrations, in the Crook well.)

Trace-Element Geochemistry

Both the inferred supratidal dolomites and the burial dolomites contain very low concentrations of Sr^{2+}. Because the burial dolomites contain no celestite, it is unlikely that they were formerly enriched in Sr^{2+}. A low Sr^{2+} concentration in the precursor oolite is also inferred. In contrast, the supratidal dolostones contain minor amounts of celestite, as well as qualitatively greater Sr^{2+} concentrations, suggesting primary Sr^{2+}-enrichment. Modern marine and hypersaline Holocene dolomites are enriched in Sr^{2+} (600 ppm) (Land, 1982), and so the presence of minor celestite in the shallow dolostones supports their supratidal, syndepositional origin. The lack of minor celestite in the deep dolostones supports their origin in an environment other than a supratidal setting.

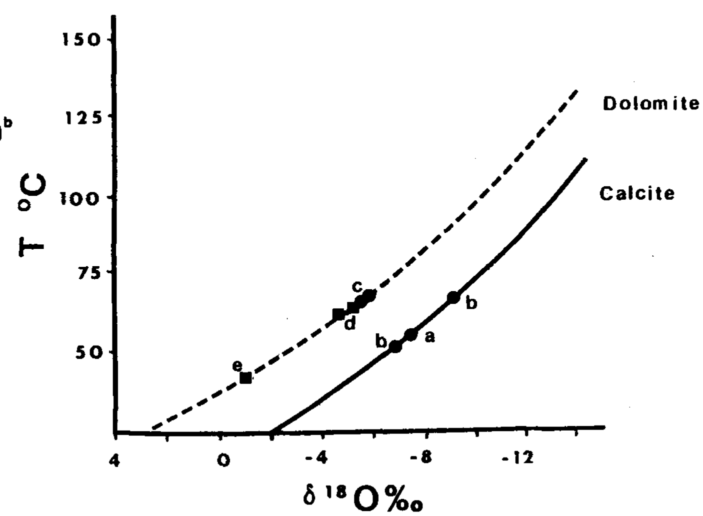

FIG. 16.—$\delta^{18}O$ values vs. inferred temperatures (after Arthur, et al., 1983; Sheppard and Schwarcz, 1970). Samples a and b are late calcite cements related to pressure solution (stylolitization). Samples c and d are saddle dolomites and burial dolomites, respectively. Sample e is an inferred supratidal dolomite of near-surface origin.

POSSIBLE MECHANISM OF DOLOMITIZATION

We believe that the conversion of smectite to illite in the deeply-buried Sylvan Shale served as a source of Mg^{2+} and Fe^{2+} for the ferroan dolomites of the overlying Keel Formation (Fig. 17). The smectite to illite conversion explains how dolostones, suggested by the oxygen isotope ratios to have formed at high temperatures, occur above the shales in the deep wells only and how many of these dolostones became iron rich.

$$\text{Smectite (montmorillonite)} + \text{Moderate temp.} \longrightarrow \text{Illite} + Si^{+4} + Ca^{+2} + Na^{+}$$

$$\text{Smectite (montmorillonite)} + \text{high temp.} \longrightarrow \text{Illite} + Fe^{+2} + Mg^{+2}$$

$$Fe^{+2} + Mg^{+2} + \text{Calcite } (CaCO_3) \longrightarrow \text{Ferroan dolomite } [CaMg_{1\text{-}X}Fe_X(CO_3)_2]$$

FIG. 17.—Reactants and products in the conversion of smectite to illite. Equations are after the discussion by McHargue and Price (1982).

Other workers have reported zones of ferroan dolomite at the contact between carbonates and marine shales (McHargue and Price, 1982). These carbonate and shale units are tens of feet (several meters) thick. The marine Sylvan Shale varies in thickness, but is up to 200 ft (60 m) thick in the deep Anadarko basin. If the smectite to illite transition at elevated temperatures is a reasonable source of Mg^{2+} and Fe^{2+} (Kahle, 1965; Dunoyer De Segonzac, 1970; Aronson and Hower, 1976; Hower et al., 1976; Foscolos and Powell, 1979; McHargue and Price, 1982; Hower et al., 1982), then the thick marine Sylvan Shale may have produced the Mg^{2+} and Fe^{2+} necessary for the ferroan dolomitization. The increasing loss of Mg^{2+} and Fe^{2+} ions from the shales as the contact with the overlying Keel Formation is approached supports the notion that the shales served as a source of these ions for dolomitization.

Directly beneath the Sylvan Shale (Late Ordovician) lies the Viola Limestone (Middle to Late Ordovician, Fig. 3). Petrography, x-ray analysis, and geophysical well logs suggest that little ferroan dolomite has formed in the Viola Limestone. Therefore, we believe that the Fe^{2+}– and Mg^{2+}– rich waters from the Sylvan Shale have chiefly migrated upward in response to the reduced pressure in the overlying Hunton carbonates. Fractures, particularly in the Sylvan Shale, serve as fluid conduits and are inferred to have been dominant factors in permitting the migration of the Mg^{2+} and Fe^{2+} necessary for the ferroan dolomitization.

At the high temperatures encountered below about 10,000 ft (3.0 km), smectite slowly yields Fe^{2+} and Mg^{2+}, and releases chemically bound water. At shallower depths, compaction of the clays releases seawater and adsorbed Mg^{2+} ions. Additional Mg^{2+} may have been supplied by the seawater retained in pore spaces of the carbonates during burial, an amount sufficient to account for the formation of a small volume of dolomite (Land, 1982).

The transformation of smectite to illite is a slow diagenetic process that is both time- and temperature-dependent (Fig. 18). The yield curves for the smectite to illite transition in the Anadarko basin appear to be slower than published generalized curves (Siever, 1983) by about a factor of two. This means that smectite in the Sylvan Shale was still being transformed into illite during Late Ordovician time. The slow yields of illite in the Anadarko basin may be explained by the low geothermal gradient known to exist in the area, by variations in original smectite composition, and by the effects of high pressures. Also, the deep Anadarko basin has only been deeply buried since about 300 million years B.P. (Fig. 19). The temperature-dependency of the smectite to illite transition in the Anadarko basin, which, in turn, depends upon the depth of burial, is observed by keeping time constant by following a single rapid progradational carbonate unit of well-documented age. In the samples of Sylvan Shale that we provided to Dr. M. S. Rutstein for analysis, the smectite/illite ratio was found to decrease with increasing depth of burial, as expected.

In four wells less than 10,000 ft (3.0 km) deep in the Sylvan Shale, the average iron concentration is 5.48 wt %, which is close to the 6.47% iron concentration in average shales (Potter et al., 1980). In contrast, the average iron concentration in wells deeper than 10,000 ft in four fields in the Sylvan Shale is only 2.19%, which indicates depletion in iron relative to average shales.

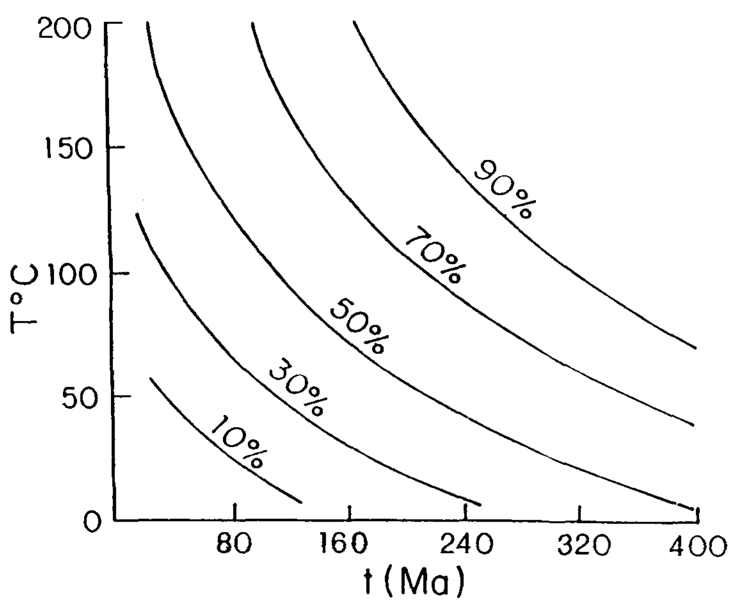

FIG. 18.—Generalized yield curves for the smectite to illite-transition (from Siever, 1983). Yield is dependent upon time (millions of years) and temperature. The yield curves in the Anadarko basin have the same shape as the generalized curves, but are somewhat slower.

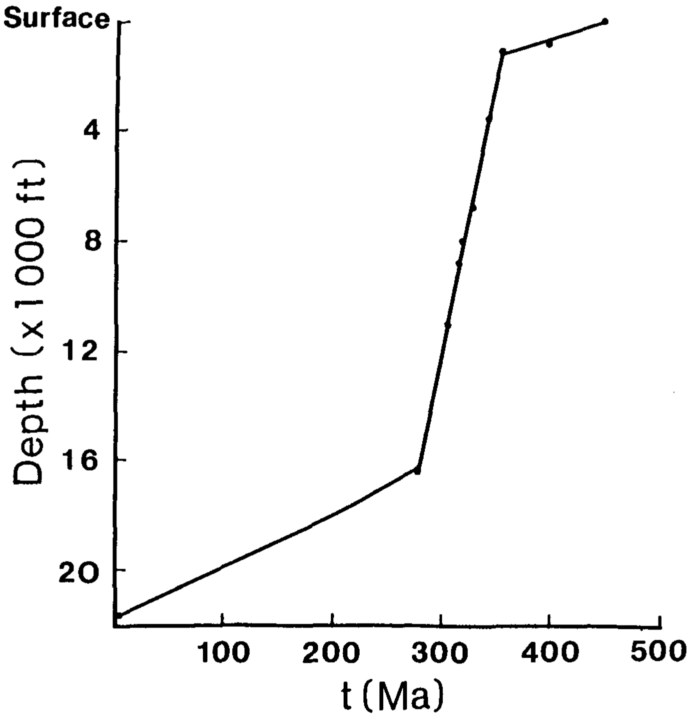

FIG. 19.—Minimum depth of burial vs. time (in millions of years) for a typical well of the Mills Ranch Field, deep Anadarko basin. Present depth of burial has been plotted for the age of the respective strata for the Chevron Bryant #1 (Location F on Fig. 1B; Mills Ranch Field on Fig. 1C).

The iron depletion in the deep shales is accompanied by iron enrichment in the overlying, deeply-buried carbonates. We believe that upward migration of Fe^{2+} ions from the deep shales into the overlying carbonates explains the difference in the iron concentrations of the deeply- and shallowly-buried shales.

CONCLUSIONS

(1) Dolomite can form at depth. This is shown, in the Hunton Group carbonate rocks of the Anadarko basin, by petrography, x-ray diffraction, radioisotope-induced x-ray fluorescence, geophysical well logs, and geochemistry.
(2) The association of ferroan dolomite with shale supports other evidence that suggests former deep burial for cores or outcrop samples that are now only shallowly buried. In any attempted reconstruction of paleo-burial depths, one must consider original clay mineralogy, geothermal gradients, time, and all available information regarding thermal history.
(3) The transformation of smectite to illite in shales, which increases with time and with increasing temperature, is probably an important mechanism in the formation of burial dolomite. It explains why the high concentrations of dolomite that occur directly above the shales are found only in the deep wells, where the smectite to illite transformation has taken place, and provides a source for the high concentrations of iron found in some of the dolostones. Because the time since deposition of the oolite and shale in different parts of the basin is relatively constant, the major factor controlling the occurrence of dolomitization must be the increased temperature that accompanies greater depth of burial.

ACKNOWLEDGMENTS

We thank the U. S. Department of Energy for grant No. DE-AC02-81ER10921 which funded this study. Fluid and rock samples, geophysical well logs, and information were supplied by the Oklahoma Geological Survey, the Texas Bureau of Economic Geology, Sun Gas, Mesa Petroleum, Chevron U. S. A., American Petrofina, Amarillo Sample Cut, and Ardmore Sample Cut. Further thanks go to Drs. I. L. Preiss and F. S. Tham, Rensselaer Polytechnic Institute Department of Chemistry, for radioisotope-induced x-ray fluorescence data; Dr. M. S. Rutstein, Department of Geology of the State University of New York at New Paltz, for analysis of clay mineralogy (smectite/illite ratios, illite crystallinity); and Drs. J. E. Sanders, Barnard College, Columbia University, and M. Raymond Buyce, Northeastern Science Foundation, for reviewing this manuscript.

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