

Origin of Primary and Diagenetic Carbonates in the
Lacustrine Green River Formation (Eocene),
Colorado and Utah

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By Janet K. Pitman

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ORIGIN OF PRIMARY AND DIAGENETIC CARBONATES IN THE LACUSTRINE GREEN RIVER FORMATION (EOCENE), COLORADO AND UTAH

By Janet K. Pitman

ABSTRACT

Stable isotope geochemistry was used to gain a better understanding of the origin of carbonate-rich, kerogen-bearing shales in the Eocene Green River Formation, which was deposited in an ancient lake complex. Isotopic, mineralogical, and oil-yield data are reported for two basin-center wells, one in the Piceance Creek Basin, Colorado, and the other in the Uinta Basin, Utah. The lakes in these basins evolved independently as separate water bodies, which led to unique depositional histories and lake-water chemistries. Results show that Ca-Mg-Fe carbonate minerals, the dominant constituents in oil shales in the formation, are primary or early diagenetic precipitates whose isotopic compositions were determined by environmental conditions and lake state at the time of deposition. Initially, primary carbonate precipitation took place in a hydrologically open lake regime that had abundant inorganic carbon dissolved from marine Paleozoic rock. Later, when the basin was hydrologically closed and organically productive, precipitation of primary carbonate was promoted by photosynthesis-respiration processes; CO₂ exchange between the atmosphere and lake water had a minor influence. Diagenetic carbonate precipitated in anoxic, lake-bottom sediments where bacterial methanogenesis was active due to high burial rates of organic carbon. Relative to seawater, carbonate-precipitating lake waters were brackish to slightly saline; during periods of saline-mineral precipitation, they were brines.

Evolutionary trends on carbon- and oxygen-isotope curves of carbonate provide an historic record of the effects of basin closure and hydrologic residence time on carbon and oxygen geochemical cycles. Major carbon trends record biologic processes that are related to levels of paleoproductivity and carbon burial. Major oxygen trends reflect changes in the ratio of lake inflow to evaporation. Cyclic excursions on the long-term carbon and oxygen trends record these changes over short time periods.

INTRODUCTION

The Eocene Green River Formation was deposited in a large lake complex, known as Lake Uinta, which occupied the Piceance Creek Basin, Colorado, and the Uinta Basin, Utah (fig. 1). During the early Eocene, the lakes were shallow, hydrologically connected water bodies open to freshwater input from areas to the south. Later, in the middle Eocene, the lakes were closed, each with its own depocenter, which led to distinct depositional histories and lake-water chemistries. Thick sequences of carbonate- and organic-rich marlstone, referred to as oil shale, were deposited in the lakes. In the Piceance Creek Basin, abundant nahcolite (sodium bicarbonate) accumulated along with organic-rich shales in the central part of the lake; nahcolite was deposited only locally in the Uinta Basin lake. Thinly bedded oil shale comprises rhythmically alternating, millimeter to submillimeter, light- and dark-colored laminations. The light laminations are composed predominantly of carbonate minerals, whereas the dark laminations contain primarily silicate minerals. Considerable controversy remains regarding the origin of the organic-rich shales and their fine-grained carbonate minerals, calcite and dolomite.

Two lake-basin models have been proposed for deposition of the Green River Formation and its carbonate-rich shales. The stratified lake model proposed by Bradley and Eugster (1969) defines a deep (greater than 30 m), permanently stratified, saline, alkaline lake that has high organic productivity in surface waters and organic-matter deposition in anoxic bottom waters. Bradley and Eugster (1969) infer that calcite in organic-rich shales was chemically precipitated in the water column, but they did not determine whether dolomite was primary, diagenetic, or a replacement mineral. The playa-lake model, originally advanced by Eugster and Surdam (1973), suggests that broad playa flats surrounding a large, ephemeral lake were sites of extreme evaporation. The model proposed that calcite precipitated in the capillary

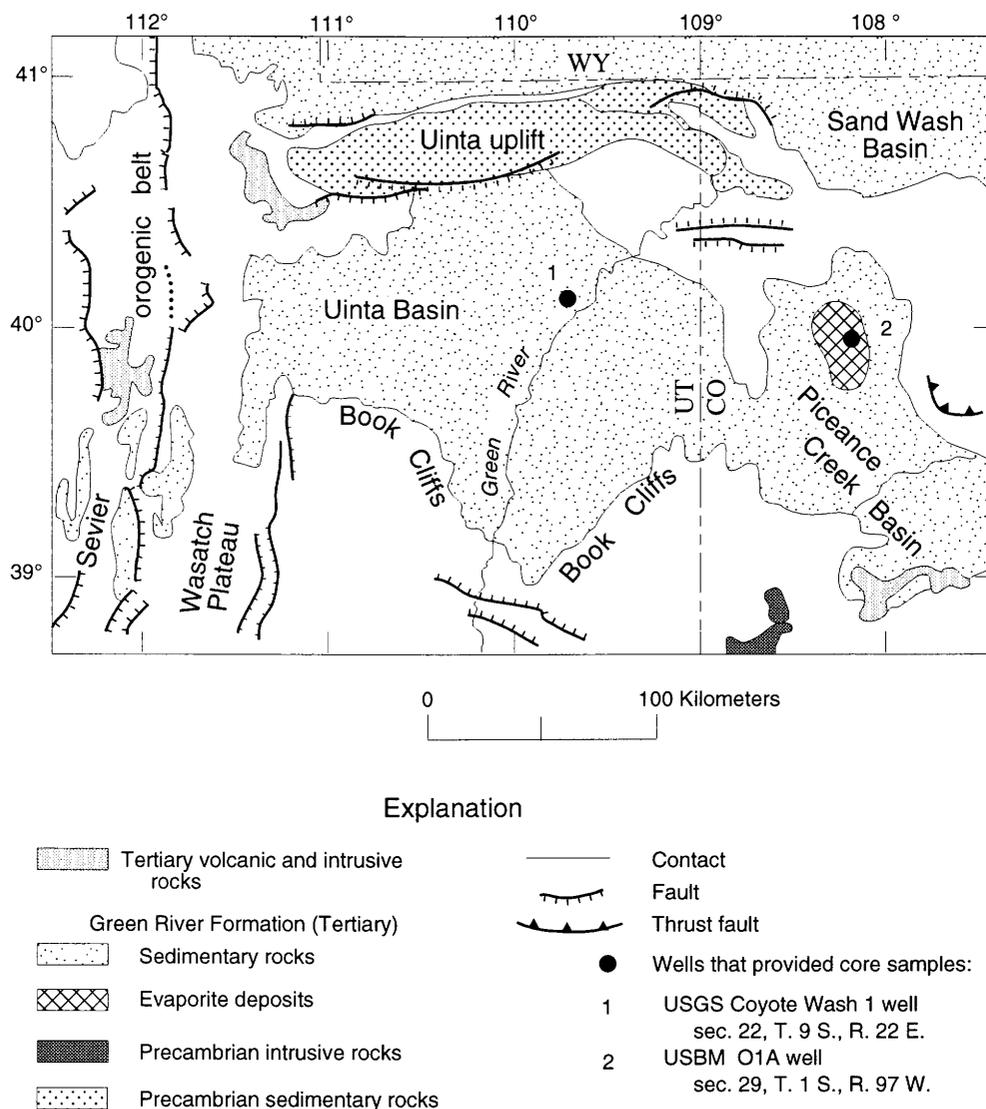


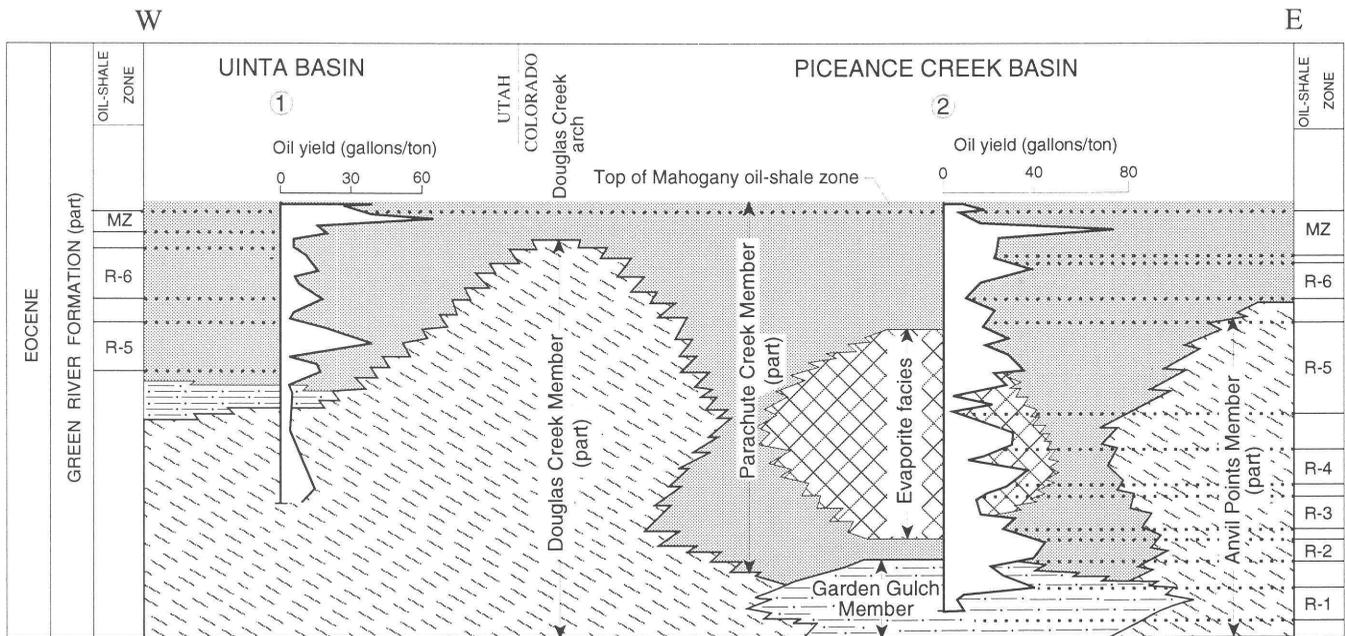
Figure 1. Generalized geologic map of east-central Utah and northwest Colorado showing the location of the Piceance Creek and Uinta Basins and the two study wells.

zone near the surface of the mudflats and later was incorporated into deeper water sediments where the calcite was altered to dolomite.

This study utilized isotopic, mineralogic, and oil-yield data to (1) delineate major hydrologic states within the Lake Uinta system, (2) establish the origin of carbonate mineral phases (primary versus diagenetic) within these regimes, and (3) determine the controls on the geochemical cycles of carbon and oxygen. Two basin-center wells that have continuous core (U.S. Bureau of Mines O1A well, Piceance Creek Basin, and U.S. Geological Survey Coyote Wash 1 well, Uinta Basin) were analyzed (fig. 2). As part of the study, successive members of the formation were subdivided into major lithofacies and assigned to interpreted lake states and depositional environments (as defined by Ryder and others, 1976) within the Lake Uinta system (table 1).

ANALYTICAL METHODS

Representative samples of carbonate-bearing shales in the Green River Formation were sampled for stable isotope analysis. Because the carbonate fractions on which isotopic analysis was performed represent mixtures, a timed-dissolution procedure based on different reaction rates for chemically distinct carbonate phases was used to obtain carbon and oxygen isotope ratios (Walters and others, 1972). To prevent contamination by CO_2 from organic matter during acid digestion, kerogen was removed from the samples by ashing prior to reaction. The inability to physically separate discrete carbonate phases in most samples led to attributing CO_2 gas evolved in the first hour to calcium carbonates (calcite) and CO_2 gas evolved after several hours to Mg-Fe carbonates (dolomite and ankerite). Carbon isotope analysis of



EXPLANATION

- | | | | | | |
|--|---|---|----------------------------------|---|---|
|  | Dolomitic oil shale |  | Intertonguing contact | ① | USGS Coyote Wash 1 well
sec. 22, T. 9 S., R. 22 E. |
|  | Argillaceous oil shale,
mudstone, marlstone |  | Member boundary (heavier line) | ② | USBM O1A well
sec. 29, T. 1 S., R. 97 W. |
|  | Limestone, siltstone,
argillaceous shale, sandstone |  | Sampled interval | | |
|  | Evaporite minerals—nahcolite, halite
(interbedded with dolomitic oil shales) | MZ | Mahogany oil-shale zone | | |
| | |  | Boundary of rich oil-shale zones | | |

Figure 2. Generalized stratigraphy of the Eocene Green River Formation, Colorado and Utah (W.C. Cashion, written commun., 1994). Diagram not to scale.

Table 1. Generalized lithofacies, depositional environments, and hydrologic states in the lower to middle Eocene Green River Formation, Colorado and Utah.

[“Open lacustrine” corresponds to lake-center deposition; “Marginal lacustrine” corresponds to lake-margin deposition]

Member	Lithofacies	Depositional environment ¹	Hydrologic state
Piceance Creek Basin, Colorado			
Parachute Creek	Oil shale, evaporite	Open lacustrine	Closed
Garden Gulch	Argillaceous shale	Open lacustrine	Semi-restricted to closed
Douglas Creek ²	Mixed carbonate-clastic	Marginal lacustrine	Open
Uinta Basin, Utah			
Parachute Creek	Oil shale	Open lacustrine	Closed
Douglas Creek	Mixed carbonate-clastic	Marginal lacustrine	Open to semi-restricted

¹ After Ryder and others (1976).

² Not cored in U.S. Bureau of Mines O1A well.

the Na-bicarbonate mineral nahcolite was performed using standard techniques (Global Geochemistry Corporation, written commun., 1989), and measurements of $\delta^{13}\text{C}$ in organic matter (see Dean and Anders, 1991) were made on splits of samples for which carbonate isotopes were

analyzed. All isotope results are reported as the per mil (‰) difference relative to the Peedee belemnite (PDB) standard using the delta (δ) notation and are accurate to ± 0.2 ‰.

Dolomite/calcite ratios were determined by X-ray diffraction for isotopically analyzed samples. The ratio of

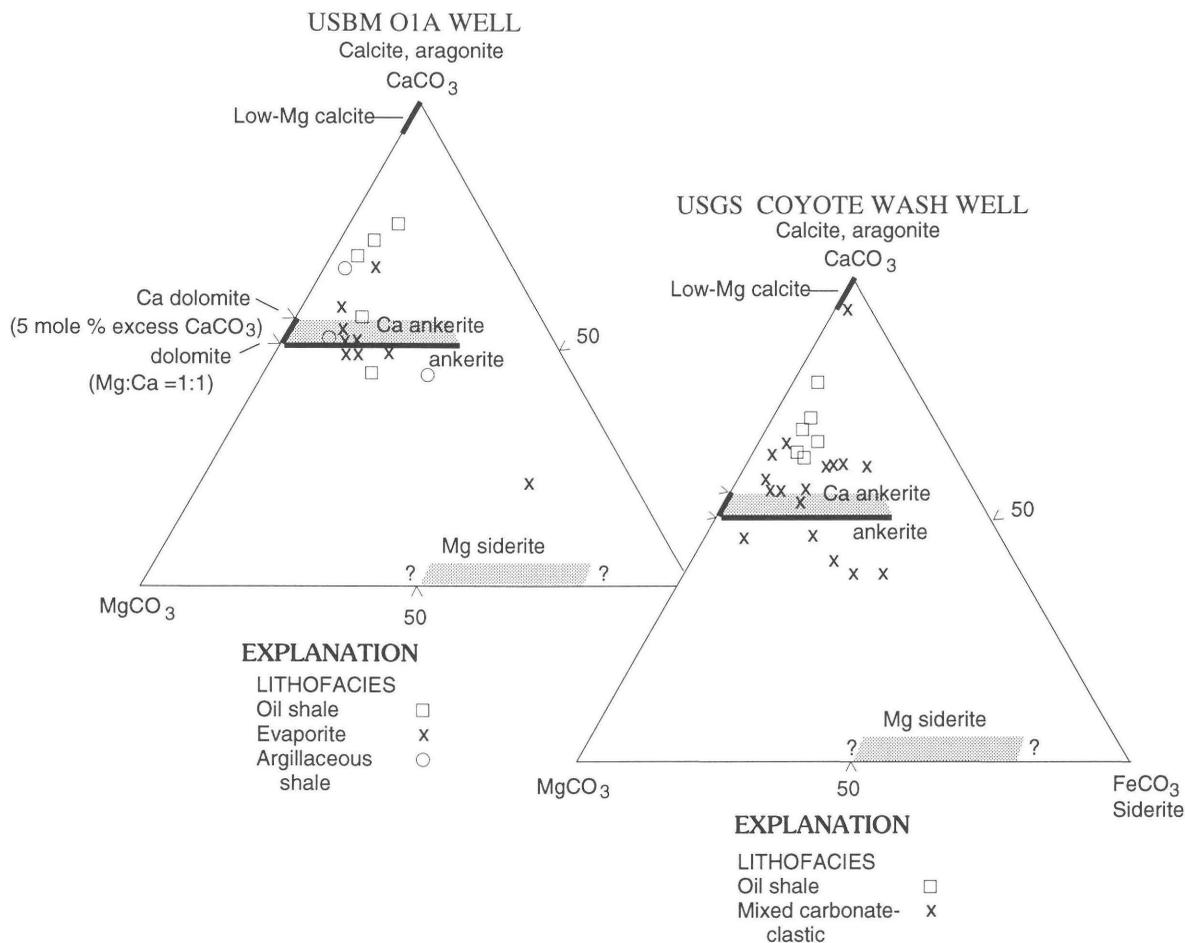


Figure 3. Ternary diagram showing the range of $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$ compositions of carbonate in the Piceance Creek and Uinta Basins.

dolomite to calcite is reported as peak height above background. The very fine grain size and complexly intergrown nature of the carbonate minerals prevented an accurate calculation of the weight percent calcite or dolomite. Oil-yield determinations (in gallons per ton—"ton" throughout this report refers to "short ton" or 2,000 pounds) were made using high-precision Fischer Assay pyrolysis (Stanfield and Frost, 1949) and are reported for samples containing carbonate. This technique is a measure of a rock's ability to generate oil; thus, it provides a means of estimating organic-matter content.

RESULTS

CARBONATE MINERALOGY

Finely disseminated Ca-Mg-Fe carbonate minerals are abundant constituents in the organic-rich and organic-lean shales examined in the Piceance Creek and Uinta Basins in

this study. X-ray diffraction analysis revealed considerable compositional variability between individual carbonate phases in the two wells (fig. 3). Varieties of dolomite ranging from ideal dolomite to Ca-dolomite to Fe-rich dolomite (ankerite) tend to predominate over calcite in intervals that have high oil yield. Calcite containing small amounts of Mg and Fe is most abundant in zones that have low oil yield. In the upper part of Parachute Creek Member, calcite is ubiquitous. Aragonite, siderite, and Mg-siderite are sparse throughout the formation.

STABLE ISOTOPES, CARBONATE-MINERAL ABUNDANCE, AND OIL YIELD

Carbonate isotope ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), organic-carbon isotope ratios ($\delta^{13}\text{C}$), carbonate mineralogy (dolomite-calcite peak-height ratios), and oil yield (gallons per ton) contents of whole-rock samples from the Piceance Creek and Uinta Basins are reported in tables 2 and 3 and are illustrated relative to depth and stratigraphic position in

Table 2. Stable isotopes, carbonate mineralogy, and oil yield in the Green River Formation, Piceance Creek Basin, Colorado.

[Data from U.S. Bureau of Mines O1A well. Leaders (--) indicate not determined; isotope values in per mil PDB]

Depth (meters)	Calcite		Dolomite		Nahcolite ($\delta^{13}\text{C}$)	Organic matter ($\delta^{13}\text{C}$)	Dolomite-calcite peak-height ratio	Oil yield (gallons per ton)
	($\delta^{13}\text{C}$)	($\delta^{18}\text{O}$)	($\delta^{13}\text{C}$)	($\delta^{18}\text{O}$)				
PARACHUTE CREEK MEMBER (closed hydrologic facies)								
Oil-shale facies								
268	7.51	-3.46	9.08	-2.03	--	-29.90 ¹	3.27	15.0
272	5.34	-5.23	6.01	-3.48	--	-28.29	1,513.00	4.0
285	7.34	-2.96	8.60	-1.19	--	-31.75	2,025.00	14.0
290	3.83	-5.00	6.31	-3.53	--	-30.90 ¹	0.84	70.0
304	7.29	-2.90	8.52	-1.84	--	-30.68	1.14	22.0
321	6.90	-3.30	7.48	-2.27	--	-29.80 ¹	0.78	21.0
328	5.72	-3.30	5.98	-2.36	--	-31.20	1.73	20.0
340	5.50	-2.29	5.33	-1.56	--	-30.59	2.15	36.0
358	9.75	-0.39	10.36	0.58	--	-29.20 ¹	10.23	15.0
378	2.63	-4.60	3.09	-3.62	--	-31.56	1,340.00	8.0
Leached zone								
395	-1.20	-4.08	-2.40	-3.18	--	-30.70	38.02	21.0
415	-0.18	-2.86	-0.40	-0.81	--	-30.10 ¹	11.08	16.0
429	--	--	--	--	--	-33.21	1,325.00	27.0
Evaporite facies								
437	0.90	-4.21	1.49	-3.75	8.46	-31.40 ¹	7.10	17.0
448	2.33	-3.48	3.25	-3.73	4.92	-32.54	36.54	27.0
468	3.74	-3.64	5.69	-2.19	--	-30.60 ¹	12.77	34.0
474	3.95	-3.36	5.83	-2.02	4.76	-31.13	14.76	21.0
486	5.55	-3.37	7.10	-2.17	--	-31.48	27.83	27.0
504	2.51	-2.98	4.05	-2.22	5.15	-30.90 ¹	7.53	4.0
510	1.20	-3.18	1.27	-2.85	2.68	-31.25	14.50	21.0
521	2.10	-3.61	2.90	-2.63	4.97	-30.10 ¹	462.00	4.0
541	3.68	-3.78	4.46	-3.17	--	-31.51	10.11	25.0
547	4.08	-3.24	6.75	-1.61	--	-29.68	1,632.00	30.0
559	4.52	-3.69	6.42	-2.43	--	-31.10 ¹	156.80	30.0
578	5.95	-3.78	6.94	-3.06	--	-33.65	16.05	18.0
583	5.19	-4.69	4.66	-4.42	12.41	-30.53	272.00	11.0
595	4.73	-4.17	7.17	-2.73	--	-31.00 ¹	33.60	37.0
614	1.86	-3.28	3.12	-4.75	13.99	-30.99	388.00	28.0
625	2.46	-4.55	3.31	-5.49	--	-30.73	3.54	20.0
632	4.47	-5.30	6.48	-2.64	11.53	-32.03	--	16.0
651	5.43	-4.70	6.11	-4.31	9.17	-32.30 ¹	1,714.00	17.0
657	7.05	-4.29	7.77	-3.00	11.08	-30.79	15.33	32.0
669	6.69	-4.64	7.62	-4.27	--	-32.60	29.35	27.0
677	--	--	--	--	7.99	-31.46	--	--
679.5	--	--	--	--	12.99	-32.90	--	--
679.6	4.67	-5.97	5.02	-5.29	11.68	-30.00	--	--
680	4.60	-5.71	4.34	-5.92	11.40	--	--	--
687	5.50	-6.43	4.68	-5.85	19.92	-31.12	534.00	46.0
GARDEN GULCH MEMBER (closed hydrologic facies)								
Argillaceous shale facies								
705	6.84	-2.70	7.60	-2.65	--	-30.90 ¹	3.60	41.0
717	3.36	-7.95	3.09	-8.74	--	-30.84 ¹	484.00	23.0
728	--	--	--	--	--	-29.90	276.00	28.0
743	7.16	-7.78	6.37	-9.87	--	--	185.00	42.0
755	6.04	-8.15	5.66	-8.56	--	--	930.00	12.0
760	3.10	-8.29	1.51	-7.53	--	--	0.34	9.0
773	10.50	-4.99	11.40	-4.04	--	--	2,704.00	12.0

¹ Value reported by Dean and Anders (1991).

Table 3. Stable isotopes, carbonate mineralogy, and oil yield in the Green River Formation, Uinta Basin, Utah.

[Data from U.S. Geological Survey Coyote Wash 1 well. Leaders (--) indicate not determined; isotope values in per mil PDB]

Depth (meters)	Calcite		Dolomite		Organic matter $\delta^{13}\text{C}$	Dolomite-calcite peak-height ratio	Oil yield (gallons per ton)
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$			
PARACHUTE CREEK MEMBER (closed hydrologic facies)							
Oil-shale facies							
670	9.31	-0.70	9.55	-0.10	-32.45	750.00	35.4
672	7.93	-2.86	9.75	-0.89	--	--	23.3
681	11.13	0.13	11.76	0.30	-28.50 ¹	4.52	35.4
685	12.90	0.89	13.38	0.96	--	--	61.4
697	8.80	-1.15	10.45	1.05	--	7.17	12.2
706	7.16	-1.73	7.52	-0.92	-31.15	2.31	16.0
716	4.95	-2.11	6.40	-1.67	-30.80 ¹	400.00	2.2
725	4.52	-2.62	4.28	-0.60	-27.17	427.50	2.0
734	4.87	-1.88	5.11	-1.37	-31.07	5.25	7.6
752	6.99	-0.44	7.61	0.22	-30.99	20.00	12.8
762	6.27	-1.55	6.49	-0.42	-31.53	2.65	3.5
771	5.44	-0.68	5.58	-0.43	-30.32	300.00	4.8
789	6.37	-0.21	6.54	0.00	-28.33 ¹	11.80	15.8
807	1.91	-2.02	2.41	-0.05	-28.33	2.35	3.0
815	1.41	-2.22	3.46	-0.43	-30.30 ¹	1.77	1.3
825	2.88	0.08	3.03	0.09	-30.84	570.00	17.6
843	4.94	-1.98	6.45	-1.45	-32.02	--	36.7
862	8.13	-0.67	10.09	0.87	-30.45	280.00	1.4
871	6.23	-0.05	6.64	0.07	-30.71	297.50	13.8
880	5.54	0.12	5.78	-0.04	-30.30 ¹	500.00	14.9
898	3.75	-2.68	5.31	-0.21	-29.97	10.46	1.9
907	1.82	-3.08	2.24	-2.18	-30.80 ¹	300.00	3.0
DOUGLAS CREEK MEMBER (open to semi-restricted hydrologic facies)							
Mixed carbonate-clastic facies							
917	1.08	-4.19	2.09	-1.97	-28.35	300.00	--
926	-2.35	-6.00	-0.48	-3.73	-26.45	--	--
935	-2.12	-6.86	0.13	-3.29	-26.33	600.00	--
953	-0.25	-4.86	2.10	-1.97	-30.16	0.93	3.2
971	--	--	--	--	-28.11	0.50	--
981	-1.30	-6.20	-0.69	-4.60	-27.70	0.27	--
990	-1.19	-8.15	-0.59	-5.25	-27.99	0.17	--
1,008	-2.74	-9.48	-1.05	-5.53	-26.13	0.32	--
1,026	4.07	-4.63	3.59	-6.02	-29.85	0.50	14.5
1,035	-2.04	-8.54	-0.21	-3.85	-26.04	0.33	--
1,043	5.44	-2.97	5.92	-3.21	-30.50 ¹	500.00	9.3

¹ Value reported by Dean and Anders (1991).

figures 4 and 5. Also shown on table 2 and figure 4 are carbon-isotope ratios ($\delta^{13}\text{C}$) for the sodium-bicarbonate mineral nahcolite.

Carbonate minerals in the Green River generally are enriched in ^{13}C and depleted in ^{18}O relative to the PDB standard. On the average, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite and dolomite in the same sample tend to show only small differences (figs. 6A and 6B). In the Piceance Creek Basin, the range of $\delta^{13}\text{C}$ values for calcite and dolomite is highly variable, -1 to +10 ‰ and -2 to +11 ‰, respectively; the majority of values fall between +4 and +8 ‰. Negative

$\delta^{13}\text{C}$ values (0 to -2 ‰) are from carbonate in brecciated shales at the top of the evaporite facies. $\delta^{13}\text{C}$ values of carbonate in the Uinta Basin also show large variations, -2 to +12 ‰ calcite and -1 to +13 ‰ dolomite. Most values are between +4 and +10 ‰.

Compared to $\delta^{13}\text{C}$, the $\delta^{18}\text{O}$ values of carbonate tend to show less variation. In the Piceance Creek Basin, $\delta^{18}\text{O}$ ranges from 0 to -10 ‰ (calcite and dolomite). In the Uinta Basin, $\delta^{18}\text{O}$ values of carbonate generally range from +2 to -3 ‰ (calcite) and +1 to -2 ‰ (dolomite) except in the open to semi-restricted hydrologic facies where the $\delta^{18}\text{O}$

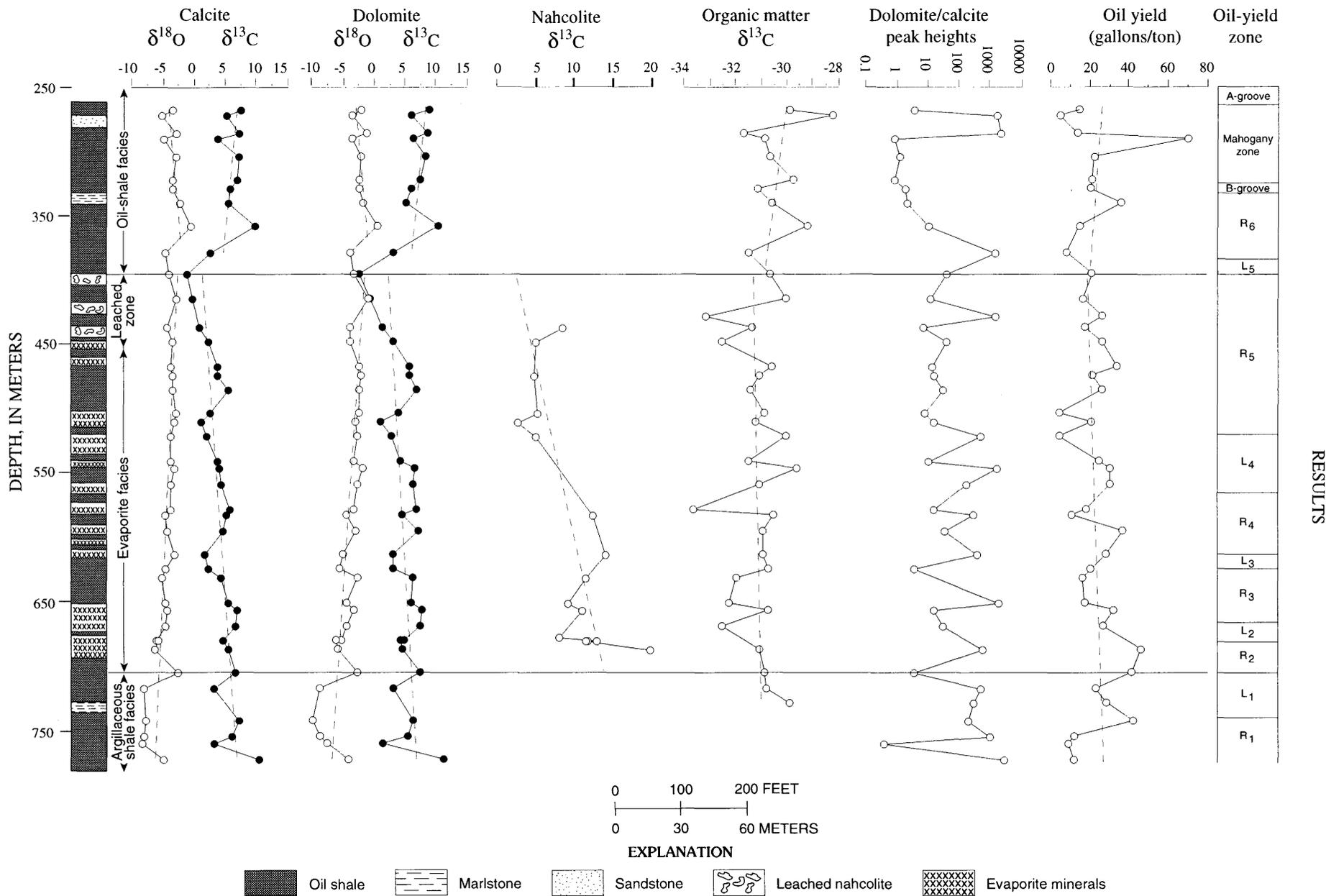


Figure 4. Chemostratigraphic profiles of stable-isotope ratios (calcite, dolomite, nahcolite, organic matter), carbonate mineralogy (dolomite-calcite peak heights), and organic-matter richness (oil yield, gallons per ton) in the USBM (U.S. Bureau of Mines) O1A well, Piceance Creek Basin. Isotope values reported in per mil PDB. Dashed regression lines represent temporal trends. R, organic-rich zone; L, organic-lean zone.

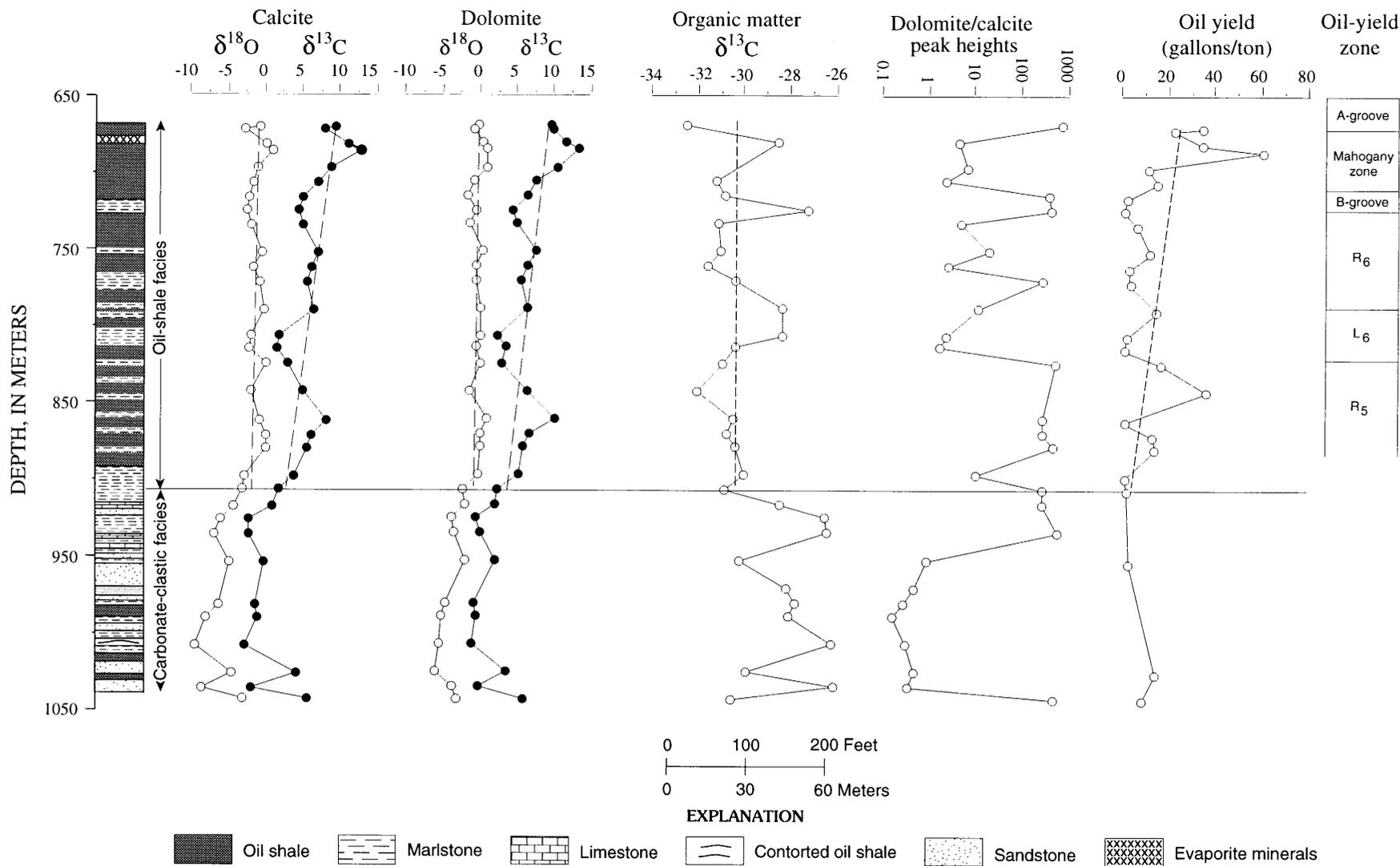


Figure 5. Chemostratigraphic profiles of stable-isotope ratios (calcite, dolomite, organic matter), carbonate mineralogy (dolomite-calcite peak heights), and organic-matter richness (oil yield, gallons per ton) in the USGS (U.S. Geological Survey) Coyote Wash 1 well, Uinta Basin. Isotope values reported in per mil PDB. Dashed regression lines represent temporal trends. Solid horizontal lines represent major lithostratigraphic boundaries. R, organic-rich zone; L, organic-lean zone.

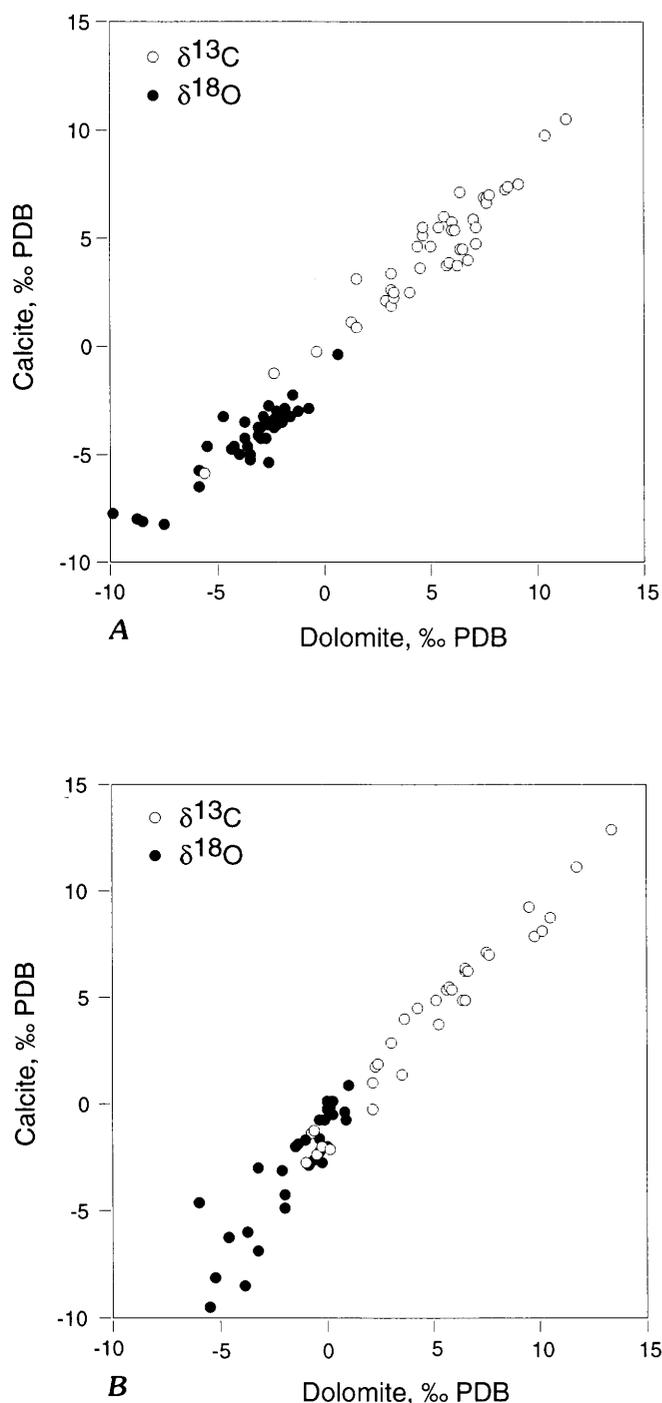


Figure 6. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ plots showing degree of correlation of $\delta^{13}\text{C}$ in calcite and dolomite and $\delta^{18}\text{O}$ in calcite and dolomite; A, USBM O1A well, B, USGS Coyote Wash 1 well. Each point on the graph represents an isotopic value of carbon versus oxygen for one sample.

values are more variable (-3 to -9 ‰ calcite; -2 to -6 ‰ dolomite).

$\delta^{13}\text{C}$ values of nahcolite in the Piceance Creek Basin display considerable variation and substantial enrichment ranging from $+2$ to $+20$ ‰. A comparison between values

of $\delta^{13}\text{C}$ in nahcolite and other carbonate minerals in the same sample show that nahcolite is enriched in ^{13}C by 2 to 10 ‰ relative to calcite and dolomite.

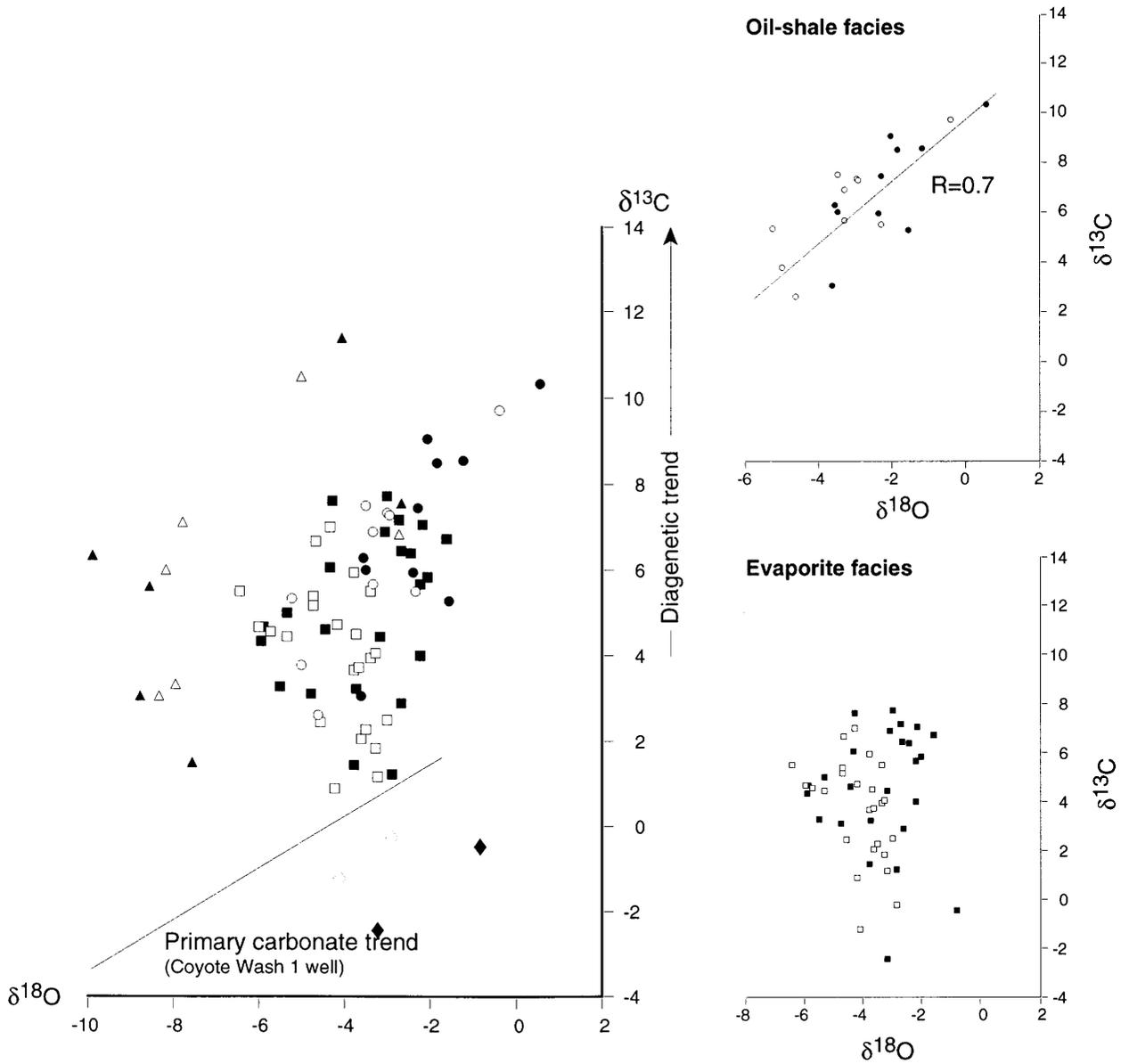
The $\delta^{13}\text{C}$ values of organic matter in the Piceance Creek and Uinta Basins remain relatively constant (-26 to -32 ‰) throughout the formation (Dean and Anders, 1991; this study). The highest values occur in the open to semi-restricted hydrologic facies in the Uinta Basin. The oil yield of shales generally varies significantly, ranging from about 4 to 70 gallons per ton. The highest oil yields are in the closed hydrologic facies; the lowest oil yields are in the open to semi-restricted hydrologic facies.

DISTRIBUTION OF CARBON AND OXYGEN ISOTOPES

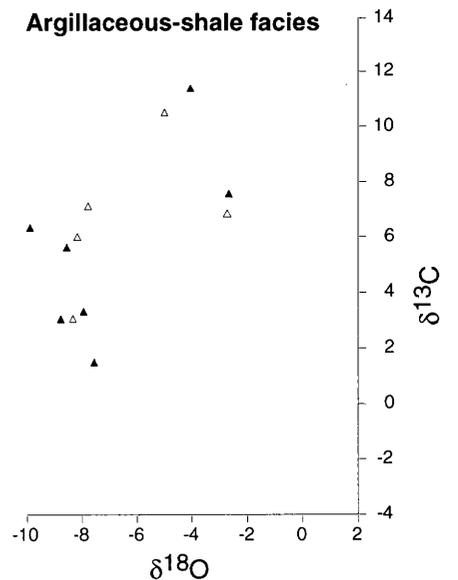
Three populations or types of carbonate are recognized in the Green River Formation on the basis of the range and distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions (figs. 7 and 8). One type characterizes the open to semi-restricted hydrologic facies in the Uinta Basin. This type has slight positive to negative $\delta^{13}\text{C}$ values ($\sim+4$ to ~-3 ‰) and generally negative $\delta^{18}\text{O}$ values (0 to ~-9 ‰) that define a linear trend and a high degree of correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($R = 0.8$; fig. 8). Stratigraphic equivalents were not cored in the study well in the Piceance Creek Basin; however, because comparable depositional and hydrologic environments existed in both basins, the Uinta Basin primary carbonate trend was superimposed on the O1A isotope plot (solid line in fig. 7) to facilitate interpretation of the data. The second type of carbonate is widespread in the closed hydrologic facies in both basins and displays extreme positive $\delta^{13}\text{C}$ values ($\sim+5$ to $\sim+13$ ‰) and generally negative $\delta^{18}\text{O}$ values (0 to ~-5 ‰) that are displaced well above the Uinta Basin linear carbonate trend; no correlation exists between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (figs. 7 and 8). The third type, which occurs only in the Piceance Creek Basin, has slight negative $\delta^{13}\text{C}$ values (0 to -2 ‰) and slight negative $\delta^{18}\text{O}$ values (0 to -4 ‰) that are displaced below the Uinta Basin linear trend (fig. 7). Some compositional overlap between the first two carbonate types may occur within individual lithofacies (see facies plots in figs. 7 and 8).

In the evaporite facies of the Piceance Creek Basin, two populations of nahcolite are distinguished on the basis of the range of $\delta^{13}\text{C}$ values (table 2). Nodular nahcolite has moderate to extreme positive $\delta^{13}\text{C}$ values ($+8$ to $+20$ ‰) and generally is restricted to the middle and lower part of the facies. Bedded nahcolite has slight to moderate positive $\delta^{13}\text{C}$ values ($+2$ to $+8$ ‰) and occurs in the upper part of the evaporite facies.

Figure 7 (following page). Relationship of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ in primary and diagenetic carbonate minerals in the USBM O1A well, Piceance Creek Basin. Primary carbonate trend in the Uinta Basin shown for reference. Isotope data for individual lithofacies are to right of plot. Note similarity between diagenetic trends in the Green River Formation and Lake Bosumtwi (see fig. 9).



Lithofacies	Hydrologic state	Calcite	Dolomite
Oil shale	Closed	○	●
Evaporite	Closed	□	■
Leached zone	Closed	◇	◆
Argillaceous shale	Closed	△	▲



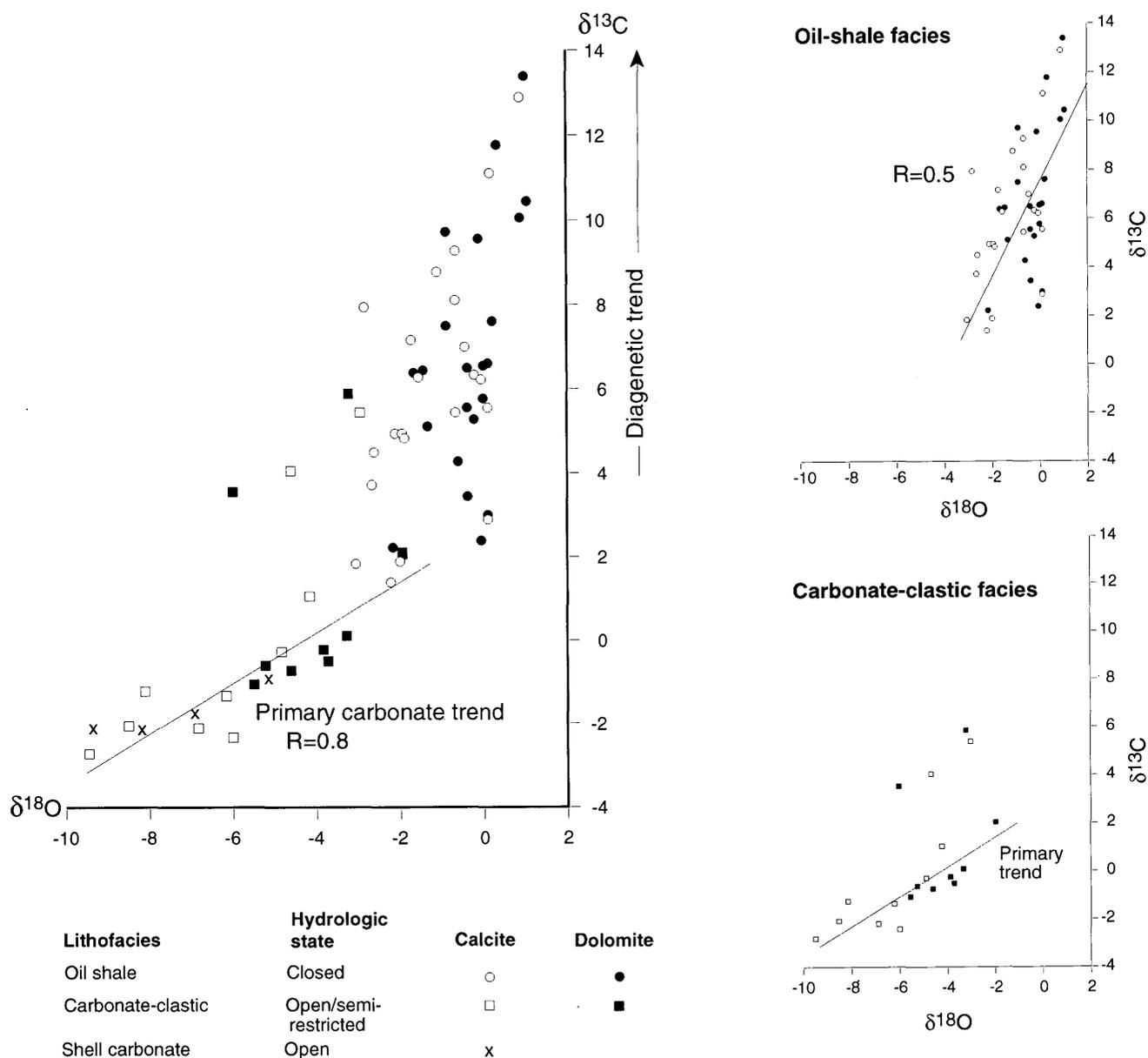


Figure 8. Relationship of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ in primary and diagenetic carbonate minerals in the USGS Coyote Wash 1 well, Uinta Basin. Primary carbonate trend shown as solid line drawn through the data points. Note compositional overlap between carbonate types in each facies; anomalous values were not included in regression calculations. Isotope data for individual lithofacies are to right of plot. Note similarity between diagenetic trends in the Green River Formation and Lake Bosumtwi (see fig. 9).

DISCUSSION

PRIMARY VERSUS DIAGENETIC CARBONATE

The degree of correlation between carbon- and oxygen-isotope compositions distinguishes primary versus diagenetic calcites and dolomites in modern closed, saline, alkaline lakes that have high organic productivity (Talbot and Kelts, 1986; data from Botz and others, 1988, replotted by Talbot, 1990). One such example is Lake Bosumtwi in

Ghana, Africa (Talbot and Kelts, 1986) (fig. 9). Carbonate minerals that form as primary precipitates in Lake Bosumtwi tend to show slight positive to negative $\delta^{13}\text{C}$ values (+6 to -2 ‰) that have a high degree of correlation with $\delta^{18}\text{O}$. Diagenetic carbonate precipitates display variable, moderate to extreme positive $\delta^{13}\text{C}$ values (+7 to +27 ‰) shifted above the primary carbonate trend. In the Green River Formation, carbonate minerals exhibit an isotopic distribution pattern comparable to Lake Bosumtwi carbonates (see figs. 7 and 8) despite a lower range in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. On the basis of the Lake Bosumtwi data,

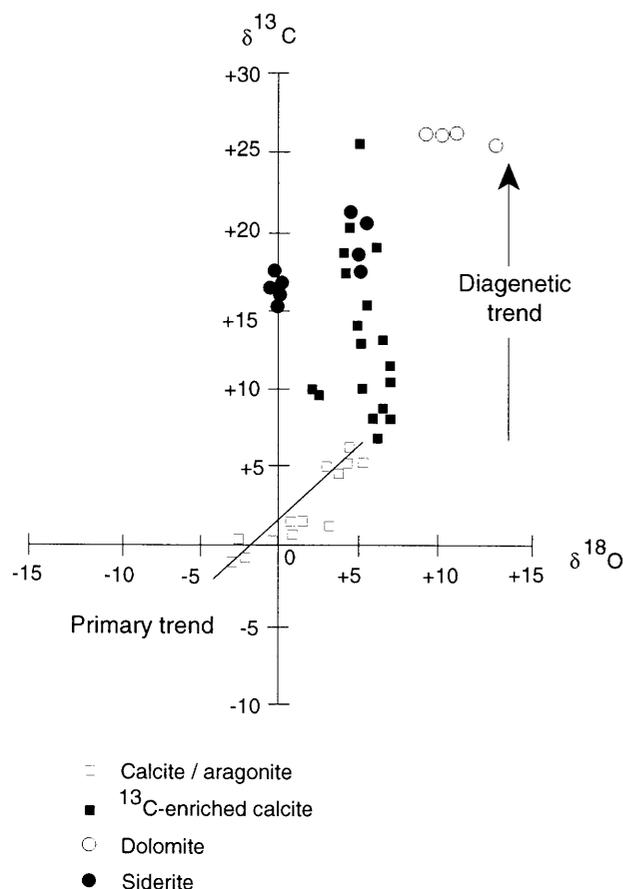


Figure 9. Isotopic compositions of primary and diagenetic carbonate minerals in Lake Bosumtwi, Ghana (from Talbot and Kelts, 1990). Solid lines depict primary and diagenetic (methanogenic) trends.

calcites and dolomites in the Green River that have slightly positive $\delta^{13}\text{C}$ values (0 to $\sim +4$ ‰) were formed mainly by primary precipitation in the water mass, whereas carbonate phases that have moderate to high positive $\delta^{13}\text{C}$ values (greater than $\sim +4$ ‰) were formed predominantly by diagenetic processes close to the sediment-water interface. Calcites and dolomites that have negative $\delta^{13}\text{C}$ values in the Piceance Creek Basin are interpreted to have formed by primary precipitation rather than by diagenesis.

CARBON ISOTOPES OF CARBONATE

The carbon isotopes of carbonates in the Green River Formation record the composition of the dissolved inorganic carbon (DIC) reservoir in the lake water and in the sediments at the time of carbonate precipitation. The carbon reservoir in the lake was modified by rates of organic productivity, atmospheric exchange of CO_2 , and bacterially mediated diagenetic reactions. The degree of basin closure and lake-water residence time also greatly influenced the DIC compositions.

PRIMARY CARBONATES

In the Uinta Basin, the carbon-isotope compositions of calcites and dolomites along the primary trend (see fig. 8) are interpreted to record the evolution of aqueous bicarbonate as the lake shifted from a hydrologically open, short water-residence-time regime to a hydrologically restricted, long water-residence-time regime. The most negative values on the trend (0 to ~ -3 ‰), correspond to the initial (starting) values for $\delta^{13}\text{C}$ of lake-water bicarbonate and are within the range reported for marine carbonate in near-shore and alluvial rocks (Keith and Weber, 1964; Weber, 1964)—this suggests that ground water containing dissolved CO_2 from eroded Paleozoic carbonate rock was the principal recharge source for the basin. The more positive values on the carbonate trend ($\sim +1$ to $\sim +4$ ‰) reflect the influence of increased basin closure and water residence time on the composition of the carbon reservoir. Values enriched in ^{13}C coupled with generally high organic-carbon richness of the host shales argues for a DIC reservoir regulated by the increased effects of photosynthesis paralleling progressive lake-water eutrophication. The effects of photosynthesis on the carbon-isotope composition were further enhanced by increased salinity stratification of the water. CO_2 exchange between the atmosphere and lake water appears to have played a less important role in the composition of the carbon reservoir during basin closure.

DIAGENETIC CARBONATES

In the Piceance Creek and Uinta Basins, there is substantial evidence suggesting that pore-water bicarbonate, rather than lake-water bicarbonate, governed the precipitation of ^{13}C -enriched (diagenetic) carbonates in organic-rich shales. First, the $\delta^{13}\text{C}$ values of the carbonates are moderately to highly positive ($\sim +4$ to $\sim +13$ ‰; figs. 7 and 8). The rapid reduction of sulfate accompanying a large carbon flux from organic matter undoubtedly caused pore-water alkalinities to increase greatly. This process led to the formation of organic-carbon compounds, methane, and associated CO_2 via acetate metabolism that, in turn, promoted the precipitation of diagenetic carbonate minerals enriched in ^{13}C . Second, the carbon-isotope compositions of ^{13}C -enriched carbonates are displaced to more positive values relative to a primary carbonate trend similar to diagenetic (methanic) calcites and dolomites in modern Lake Bosumtwi (compare figs. 7 and 8 with fig. 9). Diagenetic carbonates in Lake Bosumtwi form in sediment pore waters where the overlying lake waters have high rates of evaporation and methanogenesis (Talbot and Kelts, 1986). Third, changes in the carbon-isotope compositions of ^{13}C -enriched calcites and dolomites generally vary independently relative to changes in the carbon-isotope compositions of organic matter (figs. 7 and 8). This inverse relationship

suggests that either the isotopic record of organic matter is more complex, and thus distinct from that of carbonate, or the calcite and dolomite formed from a carbon reservoir not controlled exclusively by photosynthesis—the latter was more likely the case.

On the basis of the evidence presented above, ^{13}C -enriched calcites and dolomites ($\delta^{13}\text{C}$ greater than $\sim +4\text{‰}$) in the Green River Formation are early diagenetic products that formed in a bacterial regime where methanogenic processes were active and sedimentation of organic matter and burial rates of carbon were high. That bacterial methanogenesis had a strong affect on pore-water DIC and, in turn, the isotopic composition of diagenetic carbonates is supported by the occurrence of ^{34}S -enriched organically derived sulfur and disseminated disulfide minerals ($+16$ to $+52\text{‰}$, and $+12$ to $+49\text{‰}$, respectively) in organic-rich shales (Tuttle and Goldhaber, 1993). Tuttle and Goldhaber (1993) indicate that bacterial sulfate reduction was essentially completed in the lake water, which kept the sediments undersaturated with respect to sulfate minerals. After sulfate was depleted by sulfate-reducing bacteria, methanic bacteria became dominant. The high iron content in some carbonate species may have resulted from insufficient amounts of hydrogen sulfide to precipitate all the available ferrous iron as pyrite (Cole and Dyni, 1985).

^{13}C -DEPLETED (PRIMARY?) CARBONATES

Isotopically light $\delta^{13}\text{C}$ values of calcites and dolomites in brecciated shales of the evaporite facies (Piceance Creek Basin; fig. 7) can be interpreted in two ways. The values could reflect reequilibration (recrystallization) with meteoric water containing soil CO_2 late in the burial history; however, the oxygen-isotope compositions do not show lower values as would be expected if carbonate precipitation were related to recrystallization. Therefore, dissolution-zone carbonates are not an artifact of recrystallization. A more reasonable explanation for the light $\delta^{13}\text{C}$ values is that they reflect photosynthesis/respiration processes related to decreased organic-carbon burial rates. Respiration should have increased the ^{12}C content of CO_2 in the intermediate to deep waters of Lake Uinta. Upon reflux of this CO_2 into the overlying waters, the composition of surface-water bicarbonate and resulting carbonate precipitates would have shifted to lighter $\delta^{13}\text{C}$ values. Increased circulation of CO_2 through the water column indicates a water body that tended toward less stratification.

OXYGEN ISOTOPES OF CARBONATE

The oxygen isotope compositions of carbonate minerals in the Green River Formation are predominantly a

function of the $^{18}\text{O}/^{16}\text{O}$ ratio of the water that precipitated the carbonates. The distribution of oxygen-isotope compositions along the primary carbonate trend in the Uinta Basin (fig. 8) records the isotopic evolution of Lake Uinta as it shifted from an open, short water-residence-time regime to a closed, saline, long water-residence-time regime. The $\delta^{18}\text{O}$ values of carbonate near the negative end of the trend, including data for shell carbonate from lake-margin environments (La Rocque, 1960), reflect the composition of inflow water, the freshest waters in the lake. $\delta^{18}\text{O}$ values near the more positive end of the trend record compositions of the most evolved waters in the lake. These waters occurred in areas where evaporation was high. Progressive isotopic evolution of the water body paralleled increased lake-basin closure and residence time of the water, which resulted in primary carbonate minerals enriched in ^{18}O relative to the inflow water. The continuity of the primary trend through time suggests that major changes in the source of fresh water to the lake did not occur.

Like the primary carbonate minerals, diagenetic phases in the Green River also preserve a record of Lake Uinta's isotopic evolution. In both basins, $\delta^{18}\text{O}$ values of diagenetic carbonates partially to completely overlap the compositional range of oxygen in primary carbonate minerals (see figs. 7 and 8), which suggests that isotopically modified pore waters had essentially the same $\delta^{18}\text{O}$ composition as overlying evaporated lake waters. The $\delta^{18}\text{O}$ values of diagenetic carbonates in the Piceance Creek Basin (fig. 7) show wide scatter compared to a more limited range of values for diagenetic carbonates in the Uinta Basin. The more negative values reflect less saline pore waters and indicate shallow, fresher water conditions in the lake during the initial stages of lake-basin closure. The more positive values reflect more saline pore waters and imply highly evaporated waters in the overlying closed-basin lake. The linear $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ trend in the oil-shale facies (see facies plots, figs. 7 and 8) is consistent with pore waters that became progressively evolved as evaporation and residence time of the water in the lake increased.

The extent of lake-water evaporation and, in turn, isotopic evolution of the Green River lakes during the time they were closed and precipitating carbonate was evaluated using the carbonate-water fractionation equation of Friedman and O'Neil (1977) for calcite. Calculated water compositions (in SMOW, standard mean ocean water) are based on an estimated carbonate precipitation temperature of 10°C and average carbonate $\delta^{18}\text{O}$ values specific to various lithofacies. The freshest water existed when the lakes were open, short water-residence-time regimes and is estimated to have had an ^{18}O composition of about -12‰ . Later, upon closure of the basins, the lake waters evolved to heavier compositions. During periods of oil-shale formation, which alternated with episodes of evaporite-mineral deposition in the Piceance Creek Basin, carbonate-precipitating waters were brackish to slightly saline and had ^{18}O

compositions of approximately -6‰ . Relative to lake inflow, these waters had evolved isotopically as much as 6‰ . Presumably, the water mass became isotopically even heavier during periods of extreme evaporation that ended in saline-mineral deposition. At the same time evaporite minerals were forming in the Piceance Basin, lake waters with estimated ^{18}O compositions of approximately -4‰ were depositing oil shale in the Uinta Basin. These waters also were isotopically modified by about 8‰ relative to the inflow waters. Following the formation of the evaporite-mineral facies in the Piceance Creek Basin, the lakes in both basins increased in size and productivity. During this period, precipitating waters in the Piceance Creek Basin are estimated to have had ^{18}O compositions of about -7‰ , whereas, in the Uinta Basin, the water mass was slightly heavier, about -5‰ . The 2‰ ^{18}O enrichment in the Uinta Basin lake is consistent with lake waters farther from the source of inflow; these waters were thus affected by greater evaporation. A similar conclusion was reached by Tuttle and Goldhaber (1993) on the basis of sulfur isotope geochemistry of the formation.

ISOTOPIC TRENDS ON CARBONATE CURVES

Temporal trends on the isotope curves of carbonate (dashed lines in figs. 4 and 5) document the evolution of the carbon and oxygen cycles in the Green River lakes. Perturbations superimposed on the trends record alterations in these geochemical cycles over much shorter time periods. Variations in the carbon and oxygen budget of Lake Uinta probably were controlled by changes in climate and tectonic conditions during the Eocene.

In the Piceance Creek Basin, decreasing $\delta^{13}\text{C}$ values of carbonate (and nahcolite) from the bottom of the argillaceous-shale facies to the top of the evaporite facies parallel a slight increase in $\delta^{18}\text{O}$ of carbonate (fig. 4). In contrast, increasing $\delta^{13}\text{C}$ of carbonate corresponds to slight decreasing $\delta^{18}\text{O}$ values of carbonate in the oil-shale facies. In the Uinta Basin, increasing $\delta^{13}\text{C}$ of carbonate extends upward through the oil-shale facies and is accompanied by no associated long-term changes in $\delta^{18}\text{O}$ values (fig. 5).

Superimposed on the $\delta^{13}\text{C}$ trends in carbonate is a rhythmic succession of small- to large-scale (30 to 100 m), positive and negative excursions (figs. 4 and 5). The $\delta^{18}\text{O}$ trends, in contrast, display only minor fluctuations. The $\delta^{13}\text{C}$ excursions generally correlate with zones of organic-matter richness (oil yield) and with carbonate mineralogy (see Grabowski and Pavear, 1985). On the basis of their data, positive excursions correspond to zones that have increased oil yield and higher dolomite-to-calcite ratios, and negative excursions correspond to zones that have decreased oil yield and lower dolomite-to-calcite ratios. A positive correlation between these three parameters in the wells on which the present study is based is indistinct because of the large sample spacing.

CARBON TRENDS

A combination of biologic processes in the lake waters and in the sediments produced the evolutionary trends on the carbon curves of carbonate. The observed ^{13}C -enrichment trends in the Uinta Basin are what would be expected in an organic-productive lake closed to freshwater inflow. The increase in $\delta^{13}\text{C}$ to heavier values initially was related to intense photosynthetic activity through removal of ^{13}C -depleted organic carbon; however, as productivity increased with time, rates of organic-matter burial became very high, which promoted bacterial methanogenesis in the sediments and the formation of carbonate precipitates with heavier $\delta^{13}\text{C}$ values. This same set of processes can explain the carbonate trends in the oil-shale facies in the Piceance Creek Basin.

As shown in figure 4, the trends in $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ in the evaporite facies (Piceance Creek Basin) diverge through time. Thus, during the long period of evaporite-mineral deposition, the carbon-isotope compositions of the carbon reservoir progressively decreased as the oxygen-isotope compositions of the oxygen reservoir systematically increased, which suggests that carbonate precipitation was related to increased lake-water salinity caused by evaporation. Lazar and Erez (1992) have shown that atmospheric invasion of ^{12}C -enriched CO_2 into saline, alkaline water causes a large negative carbon-isotope fractionation (about -9‰) between brine and atmospheric CO_2 because of intense photosynthetic activity. The same photosynthetic effect has been reported for a freshwater lake (Herczeg and Fairbanks, 1987). The possibility of ^{13}C -depletion due to this kinetic isotope fractionation in the Piceance Creek Basin is compatible with the measured $\delta^{13}\text{C}$ values and with the ^{18}O enrichment in carbonate; however, it is inconsistent with the small changes ($-29 \pm 3\text{‰}$) in the carbon-isotope compositions of organic matter. In Eocene Lake Uinta, the partial pressure of dissolved CO_2 was much greater than that of atmospheric CO_2 because of the large bicarbonate reservoir in the water. Consequently, the organic carbon fixed would have only been depleted by a few per mil (Calder and Parker, 1973; Herczeg and Fairbanks, 1987). On the basis of these geochemical conditions, it is concluded that brine-to-atmospheric CO_2 exchange was not the dominant process controlling carbonate precipitation in the Piceance Creek Basin during deposition of the evaporite facies.

A more reasonable explanation of the carbonate ^{13}C -depletion trends in the evaporite facies is that they reflect the effects of increased respiration. Oxidation of organic matter is a source of ^{12}C -enriched CO_2 . A high input of isotopically light CO_2 originating from organic matter to the water mass by means of diffusion would have shifted the composition of the carbon reservoir in the water and the resulting carbonate precipitates to lighter values. The increased effects of respiration can also account for the 8‰ decrease in nahcolite from the bottom to the top of the

evaporite facies. Positive $\delta^{13}\text{C}$ values (as high as +20 ‰) in diagenetic nodules near the base of the facies clearly indicate generation of methane and associated ^{13}C -enriched CO_2 in organic-rich sediments. It has been demonstrated that nahcolite precipitates when CO_2 pressure in water is at least 10 times that of atmosphere (see fig. 19 in Bradley and Eugster, 1969). Lower values (as low as -4 ‰) in bedded nahcolite at the top of the facies can be attributed to precipitation in overlying lake waters where photosynthesis/respiration processes were active.

The ratio of biogenic CO_2 to organic matter in the Green River lakes varied substantially over short time intervals as recorded by the succession of broad positive and negative $\delta^{13}\text{C}$ excursions on the carbon trends in carbonate, particularly in the Piceance Creek Basin. Positive excursions reflect increases in organic-carbon burial and indicate the influence of bacterial methanogenesis; thus, they generally do not preserve the original (primary) carbon trend. In contrast, negative excursions reflect decreases in organic-carbon burial and represent the effects of photosynthesis-respiration; hence, they record a predominantly primary carbon trend. Rhythmically alternating carbon excursions ultimately may provide an historic record of paleoclimate change modified by local sedimentation effects.

OXYGEN TRENDS

Temporal trends on the $\delta^{18}\text{O}$ curves of carbonate record the inflow-evaporation history of the Green River lakes and the effects of long water residence time on the composition of the oxygen reservoir in the water. In the Piceance Creek Basin, slight increases in $\delta^{18}\text{O}$ parallel increased concentrations of nahcolite, implying progressive evaporation and shallowing of the Piceance Creek Basin lake through time. The buildup of the heavy isotope of oxygen was small in comparison to modern saline lakes, which suggests the lake received minor inflow that mitigated the effects of extreme evaporation. Long-term decreases in $\delta^{18}\text{O}$ of carbonate in the oil-shale facies are consistent with expansion and deepening of the lake. Near-vertical $\delta^{18}\text{O}$ trends in the Uinta Basin indicate a water body that tended toward long-term hydrologic stability. A stable water body implies only minor alterations in the ratio of freshwater inflow to evaporative loss and, hence, also implies isotopic continuity of the water.

Positive and negative $\delta^{18}\text{O}$ excursions on the oxygen-isotope curves record alterations in hydrologic balance; positive excursions correspond to increased lake-water evaporation and negative excursions correspond to increased lake inflow. In the Piceance Creek Basin, there is a pronounced positive $\delta^{18}\text{O}$ excursion at the base of the oil-shale facies that is not observed in the same stratigraphic position in the Uinta Basin. This excursion immediately overlies an interval where nahcolite formerly was widespread. If, in the Piceance Creek Basin, nahcolite precipitated in carbonate

mudflats during the period of maximum lake regression and, later, upon lake expansion, was reworked to the center of the lake, it may have added a component of heavy ^{18}O to the oxygen reservoir in the water that caused the composition of the precipitated carbonates to shift to heavier values. The return to light values above this interval suggests that the effect of this ^{18}O was short lived because of the large reservoir of ^{18}O in the water. The fact that a positive $\delta^{18}\text{O}$ excursion is not observed in the Uinta Basin may reflect the absence of nahcolite, assuming it was the source of the heavy oxygen.

CONCLUSIONS

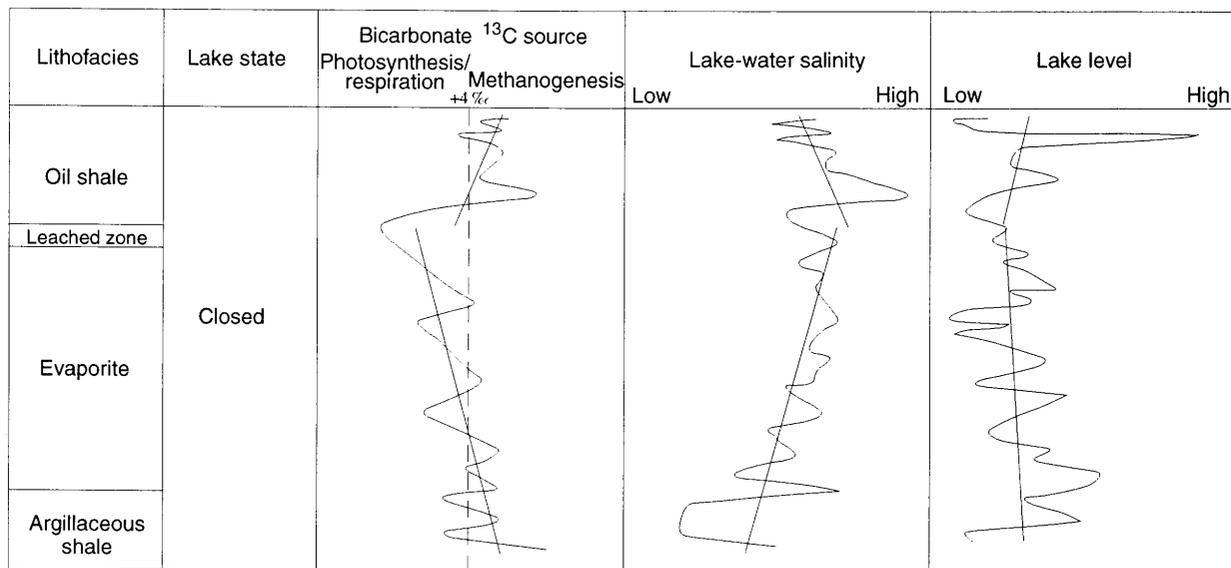
Geochemical evidence presented in this study indicates that lake processes in the Piceance Creek and Uinta Basins promoted ^{13}C enrichment relative to inorganic carbon (initially about 0 ‰) in the Green River systems. More enriched values (greater than ~+4 ‰) were caused by bacterial methanogenesis in sediment pore waters during early diagenesis. Less enriched values (less than ~+4 ‰) were produced by photosynthesis/respiration in lake waters, which resulted in organic matter being deposited beneath anoxic bottom waters (fig. 10).

The degree of lake-water stratification strongly influenced the processes (primary versus diagenetic) governing carbonate precipitation. When lake waters were well stratified, high levels of organic productivity and carbon burial promoted bacterial methanogenesis and the formation of diagenetic carbonates in anoxic sediments. Conversely, when lake waters were poorly stratified, photosynthesis/respiration processes resulted in primary carbonate precipitation in the water. Decomposition (respiration) of organic matter when the lake in the Piceance Creek Basin was poorly stratified reversed the bicarbonate ^{13}C enrichment caused by photosynthesis.

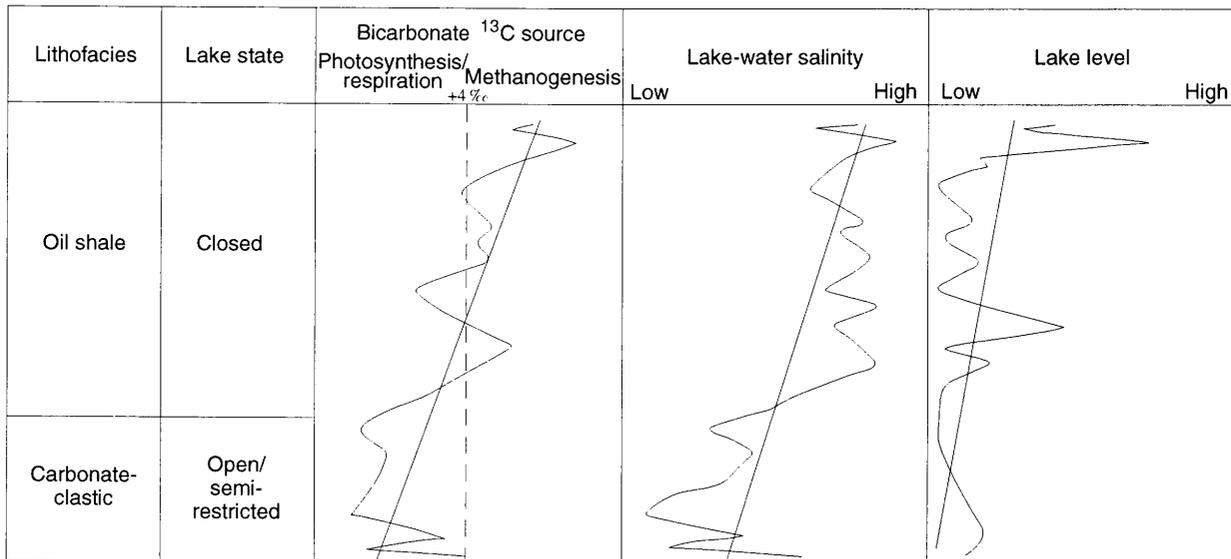
$\delta^{18}\text{O}$ values of carbonate indicate that carbonate-precipitating waters in the Green River lakes were predominantly brackish to slightly saline (relative to seawater) except during periods of evaporite-mineral deposition when the waters presumably were brines. Periods of lake-level rise and fall are recorded as variations in carbonate ^{18}O . During much of Eocene time, the Green River lakes were hydrologically closed, which resulted in significant increases in salinity due to evaporation and in the isotopic evolution of the ^{18}O in the water.

ACKNOWLEDGMENTS

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A



B

Figure 10. Schematic hydrologic model summarizing temporal changes in bicarbonate ¹³C source, lake level, and salinity in the Lake Uinta system; A, Piceance Creek Basin; B, Uinta Basin.

Denver, Colo.); analyses were also performed under contract to Global Geochemistry Corporation (La Habra, Calif.). The Laramie Energy Research Center kindly provided core material and Fischer Assay oil-yield analyses for the study.

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