Groundwater Flow, Late Cementation, and Petroleum Accumulation in the Permian Lyons Sandstone, Denver Basin

Ming-Kuo Lee and Craig M. Bethke

ABSTRACT

The gray diagenetic facies of the Permian Lyons Sandstone, which is associated with all known petroleum accumulations in the formation, formed late in the history of the Denver basin as an alteration product of the formation's red facies. The red facies that makes up most of the sandstone contains iron oxide coatings, quartz overgrowths and calcite cements. The gray facies, which occurs locally in the deep basin, is distinguished by pore-filling dolomite and anhydrite cements and by a lack of iron oxide and calcite. The dolomite and anhydrite cements overlie bitumen that was deposited by migrating oil, and hence formed after oil was first generated in the basin, late in the Cretaceous or early in the Tertiary. The isotopic composition of oxygen in the dolomite ranges to such light values that the cement must have formed deep in the basin in the presence of meteoric water.

The gray facies likely formed in a regime of groundwater flow resulting from Laramide uplift of the Front Range during the Tertiary. In our model, saline groundwater flowed eastward through the Pennsylvanian Fountain Formation and then upwelled along the basin axis, where it discharged into the Lyons Sandstone. The saline water mixed with more dilute groundwater in the Lyons, driving a reaction that dissolved calcite and, by a common-ion effect, precipitated dolomite and anhydrite. The facies' gray color resulted from reduction of ferric oxide in the presence of migrating oil or the Fountain brine. Underlying source beds by this time had begun to generate petroleum, which migrated by buoyancy into the Lyons. The association of the gray facies with petroleum accumulations can be explained if the Fountain brines discharged across aquitards along the same fractures that transmitted oil. As petroleum accumulated in the Lyons, the newly formed cements prevented continued migration, as is observed in shallower strata, by sealing oil into the reservoirs from which it is produced today.

INTRODUCTION

Geologists have long puzzled over the nature of diagenetic alteration in the Permian Lyons Sandstone of the Denver basin because the occurrence of diagenetic cements in the formation mirrors the distribution of petroleum reservoirs. Most of the Lyons consists of a red diagenetic facies. The red Lyons is familiar to many geologists because it crops out at the basin's western margin on the Flatirons, a series of hogbacks along the Front Range of the Rocky Mountains, and because of its use as a distinctive building stone in the area. The facies is barren of petroleum, is characterized by hematite stain, clay minerals, quartz overgrowths, and calcite cements. A gray diagenetic facies occurs locally deep in the basin. The gray Lyons, distinguished by anhydrite and dolomite cements that overlie bitumen stains and by a lack of calcite and hematite, hosts all known oil fields in the formation.

There has been no convincing explanation of the
origin of the gray facies nor the reason for its association with petroleum accumulations. The anhydrite and dolomite cements of the gray facies might have formed soon after the Lyons was deposited, as suggested by the high intergranular volume preserved in the sandstone. Anhydrite occupies up to 25% and dolomite cements occupy up to 15% of the rock’s pre-cement pore volume. For this reason, Dimelow (1972) suggested that these cements might have precipitated from formation water deposited with the sediment.

Dolomite and anhydrite might also have precipitated in an environment open to flow of saline groundwater. For example, they could have formed where evaporated seawater infiltrated carbonate platforms in sabkha environments (Butler, 1969; Patterson and Kinsman, 1977; Achauer, 1982); some geologists working in the Denver basin have suggested such an origin to us. Levandowski et al. (1973), on the basis of the cement distribution in the sandstone, argued that the cements precipitated when underlying strata compacted during burial, driving saline groundwater upwards through the Lyons.

Anhydrite and dolomite cements of the gray Lyons Sandstone might also have formed in an environment open to regional groundwater flow, long after the formation was buried. Such an origin is not unusual: dolomite cements can form where fresh and saline groundwaters mix (Badiozamani, 1973; Land, 1973; Harrison, 1991), where migrating groundwater reacts with host sediments (Banner et al., 1988; Gregg and Shelton, 1989; Bethke and Marshak, 1990), and where carbon dioxide escapes from migrating brine (Leach et al., 1991).

In this study, we use hydrologic and geochemical models to develop an explanation of the origin of gray Lyons facies that is consistent with petrographic observations as well as the stable isotopic compositions of the Lyons cements. The results of our modeling suggest a strong relationship between diagenetic alteration of the sandstone, the basin’s paleohydrology, and the accumulation of petroleum in the Lyons.

GEOLOGIC SETTING

The present-day Denver basin is an elongate, asymmetric structure whose axis runs north-south in Colorado and Wyoming, just to the east of the Front Range uplift. The Laramide and Front Range uplifts bound the basin to the west. Basin strata extend eastward across parts of eastern Colorado, southeastern Wyoming, southwestern Nebraska, and northwestern Kansas. The deepest part of the basin lies near Denver, Colorado, where more than 4 km of sediments are preserved. Because of the basin’s hydrocarbon potential, its structure, stratigraphy, and tectonic history have attracted considerable study (e.g., Hoyt, 1962; Martin, 1965; Izett, 1975; Trimble, 1980; Sonnenberg and Weimer, 1981).

The Denver basin was a marine shelf that subsided slowly through most of the Paleozoic and Mesozoic. Figure 1 shows the stratigraphic column near the Front Range. Pennsylvanian sediments consist mainly of carbonate and shale, although sandstones predominate in the west along the uplift of the ancestral Rocky Mountains. During the Permian, a broad sea intermittently covered a surface of low relief where sediments, including the Lyons Sandstone, were deposited in environments ranging from fluvial to normal marine to hypersaline. During the Mesozoic, Triassic and Jurassic sediments consisting mainly of sandy shale buried the Paleozoic section. The basin downwarped rapidly in the Cretaceous, when an interior seaway covered much of western North America. During this period, more than 3 km of shale and shaly sandstone were deposited at the

<table>
<thead>
<tr>
<th>System</th>
<th>Formations</th>
<th>Thickness (m)</th>
</tr>
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<tbody>
<tr>
<td>Tertiary</td>
<td>Green Mountain Conglomerate</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>Denver-Dawson Fm.</td>
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<tr>
<td></td>
<td>Arapahoe Fm.</td>
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<td>Laramie Fm.</td>
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<td></td>
<td>Fox Hills Fm.</td>
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<td>Upper Cretaceous</td>
<td>Pierre Fm.</td>
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<td></td>
<td>Niobrara Fm.</td>
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<td></td>
<td>Benton Fm.</td>
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</tr>
<tr>
<td>Lower Cretaceous</td>
<td>South Platte Fm.</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Lylte Fm.</td>
<td></td>
</tr>
<tr>
<td>Jurassic</td>
<td>Morrison Fm.</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>Ralston Creek Fm.</td>
<td></td>
</tr>
<tr>
<td>Triassic</td>
<td>Lykins Fm.</td>
<td>120</td>
</tr>
<tr>
<td>Permian</td>
<td>Lyons Sandstone</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>U. Satanka</td>
<td></td>
</tr>
<tr>
<td></td>
<td>L. Satanka</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ingelside</td>
<td></td>
</tr>
<tr>
<td>Pennsylvania</td>
<td>Fountain Fm.</td>
<td>305</td>
</tr>
</tbody>
</table>

Figure 1—Stratigraphic column for the Denver basin near the Front Range (after Weimer, 1973).
basin's depocenter.

With the onset of the Laramide orogeny near the end of the Cretaceous, the area west of the present-day basin began to be uplifted. Orogeny continued into the Tertiary and reached its peak during the Eocene. The basin tilted eastward as the Front Range began to emerge. Uplift resumed during the middle Oligocene (Trimble, 1980; Morse, 1981). The most recent uplift, about 5–6 million years ago, caused about 450–600 m of Tertiary sediments to be eroded from the basin (Trimble, 1980). With this final adjustment, the basin assumed its present configuration.

For purposes of hydrologic analysis, strata in our study area can be divided into five hydrostratigraphic units (Belitz and Bredehoeft, 1988): (1) Pennsylvanian-Permian, (2) Permian-Triassic, (3) Triassic-Jurassic, (4) basal Cretaceous sandstones, and (5) Cretaceous shales. Mississippian carbonates form a sixth unit that, because of extensive secondary porosity, constitutes an important aquifer system in the northern Great Plains (Downey, 1982; Back et al., 1983). This lowermost unit, however, is absent in our study area.

The Pennsylvanian-Permian unit consists primarily of interbedded carbonates and shales, but sandstones predominate toward the basin's western margin. In the western basin, sandstones of the Fountain Formation lie at the base of the unit. These sandstones grade eastward to dolomite and shale. Secondary porosity and permeability are less well developed in carbonates of this unit than they are in Mississippian limestones, which constitute aquifers in the southern basin.

Interbedded red beds and evaporites dominate the strata of the Permian-Triassic unit. In eastern Colorado, the Permian Lyons Sandstone lies between anhydritic siltstones. The Lyons, a regional aquifer, serves as a supply of potable water where it is shallowly buried and as a petroleum resource in the deep basin. The overlying Triassic-Jurassic unit contains shale interbedded with local sandstone layers. The unit acts as a regional aquitard.

The basal Cretaceous sandstones, which include the Dakota Sandstone, make up the most important aquifer system within the basin, providing the main water supply for consumption and irrigation in the central Great Plains area. The Cretaceous shale unit confines the aquifer system. This unit, the thickest in the basin, is predominantly shale, but contains minor amounts of limestone, sandstone, and chalk.

DEPOSITION AND DIAGENESIS OF THE LYONS SANDSTONE

The Denver basin in the Permian contained two major subbasins where evaporites accumulated: the Alliance basin to the north and the Sterling basin to the south (Figure 2). The Lyons Sandstone formed as a nearshore deposit along a band between the slightly emergent ancestral Rocky Mountains to the west and the evaporite basins to the east. Fluvial, marine, and eolian processes transported sand to the coast (e.g., Blood, 1970; Walker and Harms, 1976; Adams and Patton, 1979), where the Lyons was deposited eastward about 150–200 km from the present-day position of the Front Range. Figure 3 shows the relationship of the Lyons Sandstone to aquitards and other aquifers within the basin. Anhydrite-rich siltstones bounded the Lyons above and below. The Pennsylvanian Fountain Sandstone underlies the Lyons to the west, but pinches out into carbonate and shale facies as it grades eastward.

Lyons sediments have been extensively altered since deposition in a pattern suggesting that the process of diagenesis was closely related to oil accumulation (Levandowski et al., 1973). Figure 4 shows that the zone of greatest cementation lies close to all known Lyons oil fields, including Pierce, Black Hollow, and New Windsor fields. Two diagenetic facies of the Lyons (one red and the other creamy gray) can
be distinguished by mineralogy and color. The red Lyons is nonpetroliferous. Hematite and clay rim the grains of quartz sand and much of the pore space is filled by quartz overgrowths and calcite cement (Figure 5A). Textural relations in the facies suggest a general paragenetic sequence of hematite and clay overlain by secondary quartz and then calcite. Detailed petrographic study of samples from outcrops along the Front Range (Hubert, 1960), however, shows that the Lyons contains at least two generations of calcite cements that precipitated at different times. Some calcite formed even earlier than the hematite, which is commonly cited as the first phase to form in the diagenetic history of the sandstone.

The gray Lyons facies, which is associated with oil fields, is distinguished (Levandowski et al., 1973) by anhydrite and dolomite cements that overlie organic matter (Figure 5B). The organic matter, which is bitumen deposited by migrating petroleum, covers quartz grains and their overgrowths. For this reason, the anhydrite and dolomite cements must have formed after oil first migrated into the Lyons. Together, the anhydrite and dolomite occupy as much as...
40% of precement porosity, or about 8% of the formation's total volume.

Calcite cements are ubiquitous in the red Lyons facies, but have yet to be observed in the gray facies. Calcite cementation almost certainly preceded deposition of anhydrite and dolomite because some calcite in the red facies underlies the early hematite cement (i.e., Hubert, 1960), which in turn underlies the quartz overgrowths, whereas the anhydrite and dolomite overlie the quartz overgrowths and later bitumen. If the gray facies is an alteration product of the red facies, the alteration process must have consumed the calcite. Alteration, in contrast, seems to have consumed little quartz. The photomicrograph of the detrital quartz grains (Figure 5C), made by scanning electron microscope after carbonate and sulfate in the samples had been chemically digested, shows shallow solution pits indicating that quartz surfaces beneath the late cements were only slightly etched.

**ISOTOPIC COMPOSITIONS OF LATE CEMENTS**

**Oxygen in Carbonate Cements**

Levandowski et al. (1973) analyzed the δ^{18}O and δ^{13}C compositions of carbonate cements; their results are shown in Table 1. The analyses did not distinguish among carbonate minerals, but the dominant carbonate mineral from gray facies samples is dolomite. The cements range in δ^{18}O from +8.8 to +21.2‰ relative to SMOW. These values are significantly lower than would be expected in marine carbonates, which normally fall in the range +30 to +32‰ (Figure 6).

The low oxygen ratios implicate meteoric water in the emplacement of the late dolomites, especially those samples strongly depleted in ^{18}O, and suggest that the cements formed at depth in the basin. Using the equation of Northrop and Clayton (1966), we can estimate at any temperature the fluid composition that would be required to explain dolomite of a given composition. At 25°C, groundwaters with δ^{18}O values in the range −26 to −13‰ would be required. Such fluids are much lighter than any seawater, especially seawater concentrated by evaporation, and are difficult to reconcile with the likely compositions of meteoric water in the latitude of about 40°N.
High-altitude runoff of the Rocky Mountains in the Tertiary and present-day have \( \delta^{18}O \) values as low as \(-14\%\) (Taylor, 1974; Lander and Anderson, 1989). Since this part of the North America craton was not in far northern latitudes during the past 300 m.y. (Irving, 1979), it is unlikely that \( \delta^{18}O \) values of meteoric waters in this area could range as low as \(-26\%\). The \( ^{18}O \) contents of the cements appear incompatible with an early diagenetic origin, and therefore, preclude (barring the possibility of later isotopic reequilibration) the possibility that the cements formed in a sabkha environment.

Formation temperatures of about 100°C would be expected in the Lyons Sandstone at present burial depths of about 3 km (Table 1), assuming a normal geothermal gradient of about 30°C/km. Groundwater having \( \delta^{18}O \) values between \(-13\%\) and about \(0\%\) would be required to precipitate dolomite at this temperature. Because Tertiary rainfall in this area could have \( \delta^{18}O \) values down to \(-14\%\), infiltration of meteoric water deep into the basin could explain even the lightest \( ^{18}O \) compositions determined. The scatter in the \( \delta^{18}O \) data (Figure 6) could arise from mixing in varying proportions of meteoric water with a basin brine. If a brine had a \( \delta^{18}O \) value of about \(0\%\), for example, mixing it with meteoric water having a \( \delta^{18}O \) value of about \(-13\%\) would produce fluids spanning the required range in isotopic composition.

### Carbon in Carbonate Cements

The small \( CO_2 \) contents of many groundwaters lead many investigators to assume that the \( \delta^{13}C \) composition of a carbonate cement simply reflects the \( \delta^{13}C \) of its precursor mineral (Mates and Mountjoy, 1980; Meyers and Lohmann, 1985). This assumption may not be true, however, if the sediment is open to flow of a groundwater charged with \( CO_2 \). Especially in sandstone, where carbonate minerals occupy a small fraction of the rock volume, carbonate dissolved in the fluid can represent a second important reservoir of carbon.

In the red facies, the \( \delta^{13}C \) of calcite cements ranges widely from \(-26\%\) to \(-2\%\) (Figure 6). These samples likely represent calcite from different origins and generations, as already discussed. The depleted \( \delta^{13}C \) values (< \(-20\%\)) might result from oxidation of organic matter, whereas the heavier \( ^{13}C \) compositions suggest that these calcite samples could have formed from seawater or from isotopically heavy fluids in the deep basin.

On the other hand, dolomite cements of the gray facies span a smaller range and are enriched in \( ^{13}C \) compared to many of the calcite samples. It is difficult to argue from these data that the dolomite reflects the carbon isotopic compositions of a calcite precursor. The composition is also inconsistent with oxidation of organic matter. The dolomite can be

### Table 1. Isotopic Composition (‰) of Carbonate and Anhydrite Cements in the Lyons Sandstone

<table>
<thead>
<tr>
<th>Sample Number*</th>
<th>Well</th>
<th>Depth (ft)**</th>
<th>( \delta^{18}OSMOW**</th>
<th>( \delta^{13}CPDB**</th>
<th>( \delta^{34}SCDT)†</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gray Facies</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11326-11</td>
<td>Calco 1 Winder</td>
<td>8903</td>
<td>—</td>
<td>—</td>
<td>+11.4</td>
</tr>
<tr>
<td>13390-6</td>
<td>Calco 3 UPRR</td>
<td>9073</td>
<td>+9.5</td>
<td>-1.3</td>
<td>+12.4</td>
</tr>
<tr>
<td>14385-200</td>
<td>Calco 1 Ferch</td>
<td>9136</td>
<td>+19.6</td>
<td>-0.5</td>
<td>+11.5</td>
</tr>
<tr>
<td>14385-236</td>
<td>Calco 1 Ferch</td>
<td>9206</td>
<td>+9.2</td>
<td>-2.1</td>
<td>+9.6</td>
</tr>
<tr>
<td>14431-14</td>
<td>Calco 1 Brunner</td>
<td>8997</td>
<td>+21.2</td>
<td>-5.5</td>
<td>+11.8</td>
</tr>
<tr>
<td>14433-25</td>
<td>Pridly 4</td>
<td>9219</td>
<td>+18.9</td>
<td>-3.3</td>
<td>+9.6</td>
</tr>
<tr>
<td>14435-21</td>
<td>Troy 1 Jones</td>
<td>9279</td>
<td>+11.5</td>
<td>-4.6</td>
<td>+12.5</td>
</tr>
<tr>
<td>14435-23</td>
<td>Troy 1 Jones</td>
<td>9235</td>
<td>+12.5</td>
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<tr>
<td>14441-13</td>
<td>Venable Fee-1</td>
<td>8997</td>
<td>+8.8</td>
<td>-1.9</td>
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<td><strong>Red Facies</strong></td>
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<td></td>
</tr>
<tr>
<td>13398</td>
<td>Horsetooth Reservoir†</td>
<td>+16.4</td>
<td>-15.5</td>
<td>—</td>
<td>□□</td>
</tr>
<tr>
<td>14674-6</td>
<td>Owl Canyon Outcrop‡</td>
<td>+15.6</td>
<td>-4.0</td>
<td>—</td>
<td>□□</td>
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<tr>
<td>14452-2</td>
<td>Hummel 1 Allison</td>
<td>7829–7834</td>
<td>+15.4</td>
<td>-11.0</td>
<td>□□</td>
</tr>
<tr>
<td>14883-23</td>
<td>Calco 1 Hayes</td>
<td>9148–9149</td>
<td>+6.7</td>
<td>-26.2</td>
<td>□□</td>
</tr>
<tr>
<td>14883-5</td>
<td>Calco Hayes</td>
<td>9089–9090</td>
<td>+15.7</td>
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<tr>
<td>14875-1</td>
<td>Nebraska Drillers Ball</td>
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<td>+3.4</td>
<td>-16.6</td>
<td>□□</td>
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</table>

*Numbered by Chevron Oil Field Research.
**Levandowski et al. (1973).
†This study.
‡Outcrop samples.
††Sample contains insufficient anhydrite for analysis.
interpreted to reflect the composition of a deep CO₂-
charged groundwater that has δ₁³C values similar to
that of seawater, which ranges from –4 to +4‰. The
"normal" carbon-isotopic composition of the
dolomite cements likely reflects in large part the
composition of marine carbonate that dissolved into
a brine deep within the basin, rather than carbon
derived from early calcite cements or from oxidation
of hydrocarbons in the Lyons Sandstone. The carbon
composition of dolomite is compatible with a fluid-
mixing origin suggested by the oxygen composition;
in a fluid mixture, the dissolved carbon derived from
a CO₂-charged brine overwhelms that from meteoric
waters; hence, the carbon isotopic composition of
dolomite that forms from such a mixture will largely
reflect the δ₁³C values of species in the brine.

Sulfur in Anhydrite Cement

We analyzed the sulfur isotopic composition of
anhydrite cements from nine Lyons core samples
from various wells, using the method of Westgate
and Anderson (1982) for extraction and analysis. The
cements have sulfur isotopic compositions (Table 1)
ranging from +9.6 to +12.5‰ relative to the CDT
standard. These values span almost exactly the range
in isotopic composition of sulfate derived from Per-
mian evaporites worldwide, which is +9.6 to +13.0‰
(Claypool et al., 1980). For reference, the composi-
tion of sulfate from modern seawater is about +20‰.
The sulfur isotopic composition of the anhydrite
cements suggests that the anhydrite could have
formed from seawater during the Permian or from
sulfate that was derived from evaporite rocks in the
basin and imported into the Lyons Sandstone. The
anhydrite is unlikely to have formed from sulfur
derived from H₂S, organics, or from sulfide minerals
that oxidized to form sulfate. Sulfur isotopes are
strongly fractionated between sulfide and sulfate,
mostly as a result of the bacterial reduction of sulfate
in the near surface; consequently basin sulfide reser-
voirs are typically depleted in ³⁴S (Thode et al., 1951).
The ³⁴S values of reduced sulfate dissolved in natural
waters normally range from −32 to 0‰ on the CDT
scale (Hartmann and Nielsen, 1969). Sulfide that
reoxidizes does not fractionate significantly, so any
sulfate derived from the oxidation of sulfide would
be depleted in ³⁴S. The anhydrite cements are too
enriched in ³⁴S to be consistent with such an origin.

The anhydrite is more likely a late diagenetic
phase, because the cement precipitated after oil first
migrated into the Lyons. Oil usually forms late in a
basin’s history because source beds must be deeply
buried long enough to become thermally mature.
We show in the next section that most Paleozoic oil
in the Denver basin did not form until the Late Cre-
taceous or early Tertiary, long after the sandstone
was deposited. In addition, even seawater evaporat-
ed to the point of anhydrite saturation would contain
only about 14 g/kg of dissolved sulfate to account
for 0.7% of the sandstone’s compacted volume,
much less than is present in the formation. For these
reasons, anhydrite cements in the Lyons likely
formed long after burial in an environment open to
groundwater flow, rather than precipitated from sea-
water or as pore fluid deposited with the sediment.

PETROLEUM GENERATION AND MIGRATION

Reservoirs in Cretaceous strata provide most of
the oil and gas produced from the Denver basin. Of
this oil, most samples can be traced by geochemical
correlation to source beds, including the Carlisle,
Graneros, and Mowry shales and the Greenhorn
Limestone, which also lie in the Cretaceous section
(Clayton and Swetland, 1980). Some oil in the Creta-
ceous section has migrated as far as 150 km from the
deep basin toward the basin’s eastern flank. Oil pro-
duced from the Lyons, on the other hand, is a Paleo-
zoic variety that is chemically distinct from oils com-
mon in younger rocks (Clayton and Swetland, 1980).
Unlike overlying strata, the Lyons Sandstone is not
known to have served as a carrier bed for long-dis-
tance migration.

Several theories explaining the source of the
Lyons oils have been proposed: the oil formed from
(1) adjacent Permian and Pennsylvanian shales
(Levandowski et al., 1973), (2) the Permian Satanka
Formation (Berman, 1978), or (3) the Permian Phosphoria Formation near the Idaho-Wyoming border (Dimelow, 1972; Momper, 1978). The third theory seems unlikely because the oils differ in carbon isotope composition from that of Phosphoria oils in the Big Horn basin (Clayton et al., 1987). Middle Pennsylvania black shales, however, are rich in organic material and are considered to have excellent source potential over much of the northern Denver basin (Clayton and Ryder, 1984; Clayton, 1989); the Lyons oils could well have been derived from these beds. In a Cretaceous reservoir, Clayton (1989) found oil from a Middle Pennsylvanian source, demonstrating that oil has migrated vertically upward through the Paleozoic and into the Mesozoic section. There is no reason to believe that oil could not have migrated vertically from a Pennsylvanian source to Permian reservoirs.

Dolomite and anhydrite cements in the gray Lyons Sandstone, as already discussed, formed after oil first migrated into the formation. We can place a limit on the age of the cements by calculating when oil generation began in Pennsylvanian rocks. According to kinetic theory, time and temperature control the generation and preservation of oil in sedimentary basins. For our calculations, we use the simple model of Lopatin (Lopatin, 1971; Waples, 1980). In the model, source-bed maturity is described by a time-temperature index (TTI). The TTI of a sediment is given as the sum of maturities developed in each temperature interval

\[
TTI = \sum_{n} (\Delta t_n)(2^n).
\]  

(1)

Index \( n \) varies from the lowest to the highest temperature interval encountered by the sediment. The interval from 100–110°C was chosen as the base interval and given the index value \( n = 0 \). For each 10°C increase or decrease in temperature, the index value increases or decreases by 1. \( \Delta t_n \) is the length of time (in million years) that the sediment spends within each temperature interval. The factor \( 2^n \) assumes the doubling of the maturation rate with each 10°C rise in temperature. According to the method, source beds are immature until they attain TTI values of about 15. Oil forms when TTI falls between 15 and 160, which corresponds to vitrinite reflectance measurements (\( R_o \), in percent reflectance in oil) from 0.65 to 1.3. When the TTI exceeds 160, oil begins to break down to form natural gas.

For a given burial history, models of thermal maturation depend on the choice of thermal conductivity and basal heat flow into the basin. We assume that sediment thermal conductivity (\( K \), in cal/cm·s °C) increases during compaction according to the correlation with porosity \( \phi \):

\[
K = (5.35 - 4.4\phi) \times 10^{-3},
\]  

(2)

which is taken from the data of Sclater and Christie (1980) for North Sea shales. We calibrate heat flow, assuming that it remained constant through time, against the maturity in Cretaceous source beds determined by Clayton and Swetland (1980) by vitrinite reflectance measurement. Heat flow values, ranging from 1.2 to 1.8 HFU (1 HFU = 10^{-6} cal/cm²·s), reproduce individual measurements made near our study area. Much of this range, however, likely reflects the uncertainty in estimating the depth of past burial and the timing of uplift and exhumation for samples taken from outcrop in the western basin. We find that a heat flow of about 1.5 HFU, near the average for continental crust, gives the best fit to the pattern of maturity basinwide in Cretaceous strata.

Basin strata were rather shallowly buried during most of the Paleozoic and Mesozoic, until thick shale sequences were deposited in the Cretaceous. For this reason, even the deepest strata did not become thermally mature until late in the basin’s history. Figure 7 shows how the thermal maturity of Pennsylvanian source beds from the deepest basin evolved through geologic time, as calculated for differing heat flows. According to the calculation, the deepest sources began to generate oil between 78 and 50 Ma, during the Late Cretaceous or the early Tertiary.
Assuming our best-fit value for heat flow of 1.5 HFU, the first oil probably formed about 68 Ma, near the end of the Cretaceous. Most Paleozoic oil in the basin, according to these results, migrated from source to reservoir in the Tertiary, after infilling of the basin was complete. This timing provides a further argument that the cements of the gray Lyons Sandstone formed late in the basin’s history. The inferred timing also suggests that the cements did not precipitate from fluids remobilized by compacting sediments, as some have suggested, because sediment compaction was complete or nearly so by the time oil generation began.

### BASIN PALEOHYDROLOGY

We used BASIN2, a numerical model of groundwater flow in sedimentary basins, to simulate fluid migration through the Denver basin in the geologic past. The model calculates the groundwater flow that arises from sediment compaction and topographic relief, the transfer of heat by conduction and advecting groundwaters, the maturity of petroleum source beds through time, the evolution of porosity and permeability, and cementation by migrating groundwater. The mathematical basis of the calculation technique is described in detail elsewhere (Bethke, 1985; Bethke et al., 1988, 1993; Corbet and Bethke, 1992).

We show the results of two reconstructions of the basin’s paleohydrology. The first simulation depicts how the basin’s groundwater flow regime evolved as the basin subsided and infilled with sediments; the second portrays flow resulting from Eocene uplift of the Front Range along the basin’s western margin. Model results provide quantitative estimates of various parameters needed to evaluate diagenetic models, including past rates and directions of fluid migration as well as pressure and thermal gradients along flow paths.

Table 2 shows the hydrostratigraphy assumed in the simulations. The basin surface in our calculations is held at a constant temperature of 10°C and atmospheric pressure. The sides of the basin remain at hydrostatic pressure and are open to groundwater flow. The bottom of the cross section is the contact with crystalline Precambrian basement, which we take as a barrier to fluid flow and the source of a constant heat flux of 1.5 HFU.

Each stratigraphic unit in the calculations is composed of varying fractions of four rock types: sandstone, carbonate, shale, and evaporite-rich siltstones. We calculate the evolution of porosity and permeability as each rock type is buried, using correlations shown in Table 3; thermal conductivity is set accord-

---

### Table 2. Hydrostratigraphy Assumed in the Hydrologic Models

<table>
<thead>
<tr>
<th>System</th>
<th>Rock Stratigraphy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cretaceous Shales</td>
<td>Pierre Shale, Niobrara Formation, Carlile Shale, Greenhorn Limestone, Graneros Formation</td>
</tr>
<tr>
<td>Lower Cretaceous Sandstones</td>
<td>Dakota Group</td>
</tr>
<tr>
<td>Triassic-Jurassic</td>
<td>Morrison Formation, Sundance Formation, Ralston Creek Formation upper Lykins Formation, Jelm Formation</td>
</tr>
<tr>
<td>Permian-Triassic (1)</td>
<td>lower Lykins Formation</td>
</tr>
<tr>
<td>Permian-Triassic (2)</td>
<td>Lyons Sandstone</td>
</tr>
<tr>
<td>Permian-Triassic (3)</td>
<td>Owl Canyon Formation, Satanka Shale</td>
</tr>
<tr>
<td>Pennsylvanian-Permian</td>
<td>Ingleside Formation</td>
</tr>
<tr>
<td>Permian</td>
<td>Fountain Formation</td>
</tr>
</tbody>
</table>

### Table 3. Correlations used in the Hydrologic Models to Calculate Porosity and Permeability

<table>
<thead>
<tr>
<th></th>
<th>ϕ₀</th>
<th>b (km⁻¹)</th>
<th>ϕ₁</th>
<th>A</th>
<th>B</th>
<th>kₓ/kᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandstone</td>
<td>0.40</td>
<td>0.50</td>
<td>0.05</td>
<td>15</td>
<td>−3</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.40</td>
<td>0.55</td>
<td>0.05</td>
<td>6</td>
<td>−4</td>
<td>2.5</td>
</tr>
<tr>
<td>Shale</td>
<td>0.55</td>
<td>0.85</td>
<td>0.05</td>
<td>8</td>
<td>−7</td>
<td>10</td>
</tr>
<tr>
<td>Evaporite</td>
<td>0.55</td>
<td>0.85</td>
<td>0.05</td>
<td>8</td>
<td>−7</td>
<td>10</td>
</tr>
</tbody>
</table>

*ϕ = ϕ₀ exp(-bZ) + ϕ₁, expressed as a fraction; Z is burial depth (km).
**log kₓ (µm²) = A₀ + B; kₓ ≤ 1 µm²; 1 µm² = 1 darcy.
Figure 8—Cross section used in simulations of the compaction-driven groundwater flow shown at the end of Cretaceous. Section extends 400 km across the northern Denver basin (BB'). Hydrostratigraphic units are described in Table 2.
The correlations for porosity and permeability of all rock types, except the evaporitic siltstones, are taken from previous studies of basins from the cratonic interior (Bethke et al., 1991); because of a lack of data, correlations for the hydrologic properties of shales were assigned to the evaporitic siltstones.

**Flow Driven by Sediment Compaction**

The first paleohydrologic model simulates groundwater flow resulting from sediment compaction as the basin infilled through most of the Paleozoic and Mesozoic. The simulation follows cross section BB' (Figure 8), which traverses the northern Denver basin. Figure 9 shows the results of the calculation for the final time slice in the calculation, at the end of the Cretaceous. In the calculation, fluids migrate from compacting shale and carbonate strata upward and downward, primarily into the Cretaceous aquifer complex and, to a lesser extent, into the Lyons and Fountain sandstones. These aquifers act as drains that carry fluid laterally from deep strata to the basin margins. Because groundwater flow here is too slow to alter the thermal structure of the basin, temperatures in the calculation fall along a conductive gradient that corresponds to the assumed thermal conductivity correlation and heat flux from basement.

Contours in Figure 9 are equipotentials, which represent the drive for fluid migration; groundwater migrates toward areas of lower hydraulic potential. The equipotentials in this case (where there is no topographic relief and the reference elevation is sea level) also show the extent to which pressure exceeds hydrostatic. The calculation predicts that excess pressures developed in the Cretaceous shales were very small, about 1 atm (0.1 MPa), near the basin’s depocenter. Greater pressures result when permeability is set smaller, but it seems unlikely that sediments in this basin were impermeable enough to allow genuine overpressures, such as those observed in the Gulf of Mexico basin (e.g., Bethke, 1986) to have developed. Overpressure in the Gulf basin results from burial rates sometimes exceeding 10,000 m/m.y. (Harrison and Summa, 1991), about 100 times more rapid than rates of burial in the Denver basin.

The role that fluids displaced by sediment compaction could have played in precipitating cements is limited by the modest flow rates predicted by the calculation. The estimated flow velocities (true rather than Darcy) through the Lyons Sandstone are everywhere less than about 2 cm/yr or 20 km/m.y. The small flow rates reflect the slow rates of burial and compaction in the basin, which infilled over 30 m.y. at a rate less than 100 m/m.y. Such slow rates of subsidence, filling, and fluid expulsion from compacting sediments are common to basins of the cratonic interior (e.g., Bethke et al., 1991).
Figure 10—Cross section used in simulations of the past groundwater flow during the Eocene. Section extends 350 km across the northern Denver basin (CC). Hydrostratigraphic units are described in Table 2. s.l. = sea level.
Flow Driven by Topography

The second paleohydrologic model simulates groundwater flow driven by Eocene uplift of the Front Range in the western basin (Figure 10). On the basis of the thicknesses of the Laramie Formation and the Dawson sandstone, which represent materials eroded and deposited during the Eocene, Trimble (1980) estimated that the Front Range was uplifted during the Laramide orogeny to between 2500 and 6000 m above sea level. As the Front Range emerged during the Laramide orogeny, basin fluids migrated eastward in response to the hydraulic gradient created by the slope on the water table. Groundwater recharged at high elevation along the basin’s uplifted western margin and discharged toward the eastern margin. Groundwater flow continues in this regime today (Belitz and Bredehoeft, 1988), but modern flow rates are presumably somewhat smaller now than in the past because the Front Range has eroded over time.

In Figure 10, we assume that the Front Range in the Eocene was uplifted 2000 m above the elevation of the basin’s eastern margin. The topographic relief drives groundwater through the Cretaceous aquifers at velocities of tens of meters per year (Figure 11). The velocities predicted, however, reflect two poorly constrained assumptions: the past elevation of the western basin and the aquifer permeabilities. Present-day flow rates in these aquifers are not known, but a model calculated by Belitz and Bredehoeft (1988) predicted flow velocities of about 3 m/yr. By this standard, the predicted velocities shown here are perhaps optimistically high. The predicted flow velocities are somewhat slower (<20 m/yr) in the Lyons and Fountain sandstones because these aquifers are more deeply buried and hence more compacted and less permeable, and because neither aquifer is hydraulically continuous across the basin. The Lyons pinches out near the eastern margin of the cross section, and the Fountain sandstone grades into dolomite and shale near the basin axis.

The greatest hydraulic potentials in the deep basin develop within the Fountain aquifer (Figure 11). Hydraulic potential is greater deep in this aquifer than along the land surface directly overhead; therefore, a hypothetical well drilled into the aquifer in the Eocene would have been somewhat

Figure 11—Calculated Eocene groundwater flow and the hydraulic potential distribution (gray contours; in atm) in the Denver basin. Calculation shows relatively rapid groundwater migration in response to the uplift of the Front Range. Flow in this gravity-driven regime is much more rapid than in the compaction-driven system shown in Figure 9.
overpressured. Potentials in the Cretaceous aquifer complex are slightly overpressured to the west and underpressured to the east; the complex is underpressured over broad areas in the present day (Belitz and Bredehoeft, 1988). The present-day underpressuring in these shallow aquifers likely reflects erosion of the uplifted basin margin and poor hydraulic continuity across Front Range faults.

The Lyons Sandstone serves as an aquifer for eastward flow. Along the basin axis, the aquifer is also a zone of dispersive mixing. Fluids migrating along the underlying Fountain Formation discharge upward across stratigraphy where the sandstone grades into less permeable facies near the basin axis. As shown in Figure 11, the drive for cross-formational flow is provided by the hydraulic potentials in the Fountain which, along the basin axis, are greater than the potentials in overlying strata. In the calculated flow regime, Fountain fluids along the basin axis discharge upward across the lower Satanka Formation and into the Lyons, mix with Lyons groundwaters, and then continue to migrate eastward.

Simple Models of Cementation

Groundwater migrating through a sedimentary basin alters the sediments through which it flows because mineral solubility varies with temperature and pressure along the flow path. Quartz, for example, is increasingly soluble with rising temperature. Groundwater saturated with quartz precipitates quartz cement as it migrates along a path of decreasing temperature, whereas it dissolves quartz as it migrates toward higher temperatures. It is possible, therefore, to calculate the rates at which various minerals dissolve and cements precipitate throughout a basin from knowledge of mineral solubility and the groundwater flow pattern; Appendix 1 gives the mathematical basis for the calculation. We refer to this type of calculation as a simple model of cementation because it accounts only for the effects of changing temperature and pressure along flow paths.

We applied this type of calculation to predict the amounts of anhydrite and quartz that could form and be consumed as a result of (1) compaction-driven groundwater flow occurring as the basin subsided during the Paleozoic and Mesozoic, and (2) flow driven by uplift of the western basin during the Eocene. Appendix 2 gives the correlations we used to compute mineral solubility. We did not attempt to calculate the distribution of dolomite cementation, because the solubility of this mineral varies more strongly with pH than with temperature or pressure.

The calculation results for the compaction-flow regime (Figure 12) show the cumulative amounts of anhydrite and quartz formed or dissolved within the Lyons Sandstone in this hydrologic regime by the end of the Cretaceous. In the hydrologic models, groundwater flowed upward relative to the subsiding strata, but downward over much of the basin relative to fixed elevation. For this reason, groundwater in the deep basin warms with time and, because of the retrograde solubility of anhydrite, precipitates anhydrite cement. The cumulative amount of anhydrite precipitated in this regime, however, is less than about 0.1% of the formation's volume. Not only is this volume too small to account for the origin of the sandstone's gray facies, but the cement is distributed across the sandstone, not just in deep strata where the gray facies occurs.

Cementation rates near the Lyons oil fields calculated for groundwater flow in the Eocene (Figure 13) are small (<1%/m.y.). The model predicts that the most extensive cementation or dissolution occurs along the flanks of the basin, where the fluid is descending or ascending across temperature gradients. This predicted cementation pattern, again, is not consistent with the observation that the greatest enrichment of anhydrite cements occurs within the Lyons oil fields (Figure 4). Therefore, the simple
ideas of cementation by flow through temperature and pressure gradients cannot explain the origin of the gray facies. These simple models of cementation, however, do not account for other potential causes of cementation in the Eocene flow regime, such as the mixing of groundwaters of varying composition or common-ion effects in which species produced by dissolution of one mineral might drive the precipitation of another.

**REACTIONS ACCOMPANYING FLUID MIXING**

From the results of paleohydrology modeling, we interpret that, in the Eocene, the Lyons Sandstone at depth contained a zone of fluid mixing. The location of the mixing zone corresponds generally to the area in which rocks of the gray facies are found. In this section, we use quantitative modeling techniques to predict which chemical reactions occurred and how stable isotopes fractionated during the mixing process. The modeling results show that fluid mixing could have driven a reaction by which calcite dissolved and dolomite and anhydrite precipitated, creating the gray Lyons facies as an alteration product of the red facies.

**Reaction Modeling**

We used the computer program REACT (Bethke, 1992) to solve for the overall reaction that would accompany fluid mixing in the deep Lyons Sandstone. REACT is one of a class of reaction path models (Helgeson, 1968; Helgeson et al., 1970; Wolery, 1979; Reed, 1982; Plummer et al., 1983) that trace the chemical evolution of systems open to mass fluxes. Calculations here are based on version R46 of the thermodynamic database compiled at Lawrence Livermore National Laboratory (Delany and Lundeen, 1990; Johnson et al., 1991), and employ the extended Debye-Hückel method (Helgeson, 1969) for calculating activity coefficients.

The conceptual basis of our calculation is shown in Figure 14. A packet containing 1 kg of dilute fluid migrates along the Lyons sandstone, maintaining equilibrium with calcite and quartz in the formation. The packet, which originated as meteoric recharge along the Front Range, is initially dilute. A second fluid discharges upward into the Lyons and mixes into the fluid packet. The second fluid is more saline, having reacted with evaporite beds in the Pennsylvanian and Permian section. As the fluids mix over the course of the calculation, any minerals that become supersaturated precipitate.
tion by heating the analyzed fluid in the presence of calcite and quartz. We assumed that the composition of the Fountain groundwater reflects equilibrium with minerals in the evaporite strata that lie beneath the Lyons. The Fountain groundwater in our calculations is a 3-molal NaCl solution that has equilibrated with dolomite, anhydrite, magnesite, and quartz.

The choice of NaCl concentration represents the upper limit of validity of the activity coefficient correlations we used. We fixed pH by setting the CO₂ fugacity to reflect a partial pressure of 50 atm. The resulting Lyons groundwater is predominantly a sodium-bicarbonate solution, whereas the Fountain brine is mostly a sodium-chloride-bicarbonate solution (Table 4).

In the model, we set the Ca²⁺ concentration in the brine by assuming equilibrium with dolomite, and fixed the fluid’s Mg²⁺/Ca²⁺ activity ratio to an end-member value of about 20 by specifying saturation with magnesite. In fact, we do not know whether magnesite occurs in the evaporite strata, so the actual brine from these rocks could have been undersaturated with respect to this mineral and hence have a smaller activity ratio than predicted. Fortunately, the mineralogic results of the fluid mixing reaction vary little over a broad range of activity ratios. As long as the Mg²⁺/Ca²⁺ activity ratio is greater than about 0.06, calcite is undersaturated in the brine, as would be expected in a saline groundwater from evaporite beds, and we found that mixing the Fountain brine into the Lyons Sandstone causes dolomite and anhydrite to precipitate at the expense of calcite.

The choice of CO₂ fugacity for the Fountain brine reflects our interpretation of the isotope data, as previously explained. We might have chosen a different fugacity, but the degree to which calcite is undersaturated in the brine, the critical variable in the calculation, is independent of pH or CO₂ fugacity. The fluid has equilibrated with dolomite and magnesite, so the saturation state is fixed by the reaction,

$$\text{CaCO}_3 \rightleftharpoons \text{CaMg(CO}_3\text{)_2} - \text{MgCO}_3$$

calcite  dolomite  magnesite

As a result, calcite has a saturation index ($\log Q/K$, where $Q$ is the activity product for the dissolution reaction, and $K$ is the equilibrium constant) of about −1.3, regardless of pH or CO₂ fugacity. Hence, there is no petrographic basis for determining the pH of the Fountain brine.

The reaction model (Figure 15) traces the chemical consequences of progressively mixing the Fountain brine into the Lyons aquifer at 100°C. As calcite dissolves into the undersaturated brine, the Ca²⁺ and HCO₃⁻ added to solution drive precipitation of anhydrite and dolomite by a common-ion effect. The overall reaction predicted by the model is

$$5 \text{CaCO}_3 + 2 \text{SO}_4^{2-} + 5/2 \text{Mg}^{2+}$$
calcite
$$\rightarrow 2 \text{CaSO}_4 + 5/2 \text{CaMg(CO}_3\text{)_2} + 1/2 \text{Ca}^{2+}$$
anhydrite  dolomite

This reaction reduces porosity in the sandstone because the volume of anhydrite and dolomite produced is greater than the volume of calcite dissolved (Figure 15). The predicted reaction explains the origin of anhydrite and dolomite cements, as well as the lack of calcite in the gray facies. It does not explain, however, the slight predominance of anhydrite over dolomite cements observed in the facies; dolomite is a more voluminous reaction product than anhydrite in the calculation results (Figure 15). This apparent
discrepancy might be accounted for by slower precipitation rates of dolomite, or a brine with a higher SO\(_4^{2-}\)/Mg\(^{2+}\) ratio than assumed in the calculation.

Reaction models, such as the one we used, are quite useful because they trace the effects among all of the reactions that occur in a system in order to predict the overall reaction. Treating reactions individually without concern for their interactions can be misleading. For example, the solubility of anhydrite varies with temperature and fluid salinity. The solubility vs. salinity curves are convex upward (see Figure 6 of Blount and Dickson, 1969), indicating that mixing a dilute and a saline fluid should dissolve, not precipitate, anhydrite. The flaw in this reasoning, which would seem to negate the analysis presented above, is that the solubility curve or function represents the single reaction,

\[
\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-},
\]

in isolation, whereas the reaction model correctly accounts for the effects of other reactions occurring in the system. An analysis that considers only anhydrite solubility would incorrectly predict that fluid mixing could not account for the cementation observed.

Isotope Fractionation

To test whether the reaction model presented in the previous section can explain the isotopic compositions of cements in the gray facies of the Lyons Sandstone, we traced how the stable isotopes \(^{13}\text{C}\) and \(^{18}\text{O}\) fractionate during the predicted reaction. The calculation technique employs mass balance equations similar to those derived by Bowers and Taylor (1985) and Bowers (1989). The technique, as implemented in REACT, accounts for fractionation among the solvent, dissolved species, gases, and minerals. Table 5 shows the fractionation factors assumed in the calculation. Instead of assuming that minerals maintain isotopic equilibrium with the fluid, as is commonly done in this type of model, the calculation segregates minerals from isotopic exchange. Only the increments of minerals precipitated during a reaction step are in isotopic equilibrium with the fluid, and only the mass of minerals dissolved over a step affects the fluid's isotopic composition. In this way, the calculation procedure models the fractionation that results from the reaction process in the absence of isotope exchange.

We assumed that the initial system contained a meteoric water having an initial \(\delta^{18}\text{O}\) of –13‰ (SMOW), which matches estimates for Tertiary rainfall in the region, as already discussed. The \(\delta^{18}\text{O}\) of calcite was set to +11‰, the mean \(^{18}\text{O}\) composition of this cement. The \(^{18}\text{O}\) composition of calcite assumed in the model, however, has very little effect on the results since the amount of oxygen in the system provided by water overwhelms the small amount obtained by dissolving calcite. We further assumed that quartz was in equilibrium with the initial fluid, but so little of this mineral reacts that its isotopic effect can be neglected. The \(\delta^{13}\text{C}\) of the initial fluid was –12‰ (PDB), which was set to reflect the mean isotopic composition of calcite cements (–11‰) found in the red facies of the Lyons Sandstone. We further assumed that the Fountain brine, which migrates into the Lyons during the reaction process (Figure 14), is isotopically heavier. The brine has \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) values of 0‰, as might be expected in a sedimentary brine.

Figure 16 shows how the isotopic compositions of dolomite cements (assuming varying CO\(_2\) fugacities for the Fountain brine) evolved as the Fountain brine mixed into the Lyons Sandstone. Results show that the range in \(\delta^{18}\text{O}\) values observed for the dolomite cements can be explained by mixing in differing proportions of Lyons groundwater with Fountain brine, as we previously hypothesized. The \(\delta^{13}\text{C}\) values predicted by the model depend on the CO\(_2\) fugacity assumed for the Fountain brine. As previously noted, the value chosen for CO\(_2\) fugacity has little effect on the mineralogic results of the reaction path, and hence is not constrained by petrographic observations.

When we assumed small values for the CO\(_2\) fugacity of the Fountain brine, the calculation predicted dolomite compositions similar to the \(\delta^{13}\text{C}\) of the precursor calcite. Assuming CO\(_2\) fugacities in the range of about 25 to 100, however, gives dolomite compositions near the observed range. In this case, the dolomite \(\delta^{13}\text{C}\) more closely reflected the isotopic composition of carbon species in the brine than carbon from the precursor calcite. A reaction model

<table>
<thead>
<tr>
<th></th>
<th>(^{18}\text{O})</th>
<th>(^{13}\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite</td>
<td>18.3</td>
<td>—</td>
</tr>
<tr>
<td>Calcite</td>
<td>17.1</td>
<td>3.38</td>
</tr>
<tr>
<td>Dolomite</td>
<td>21.5</td>
<td>1.91</td>
</tr>
<tr>
<td>Quartz</td>
<td>21.1</td>
<td>—</td>
</tr>
<tr>
<td>CO(_2)(aq)</td>
<td>28.0</td>
<td>0</td>
</tr>
<tr>
<td>HCO(_3)</td>
<td>0**</td>
<td>3.5</td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>0**</td>
<td>3.5</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>17.1</td>
<td>—</td>
</tr>
</tbody>
</table>

*Fractionation factors calculated from regression curves compiled by J.K. Bohke from the following sources: Northrop & Clayton (1966), Malinin et al. (1967), Biotina (1968), O'Neil et al. (1969), Sheppard and Schwarcz (1970), Clayton et al. (1972), Richet et al. (1977), Chiba et al. (1981).

**Assumed.
that calls on migration of a CO₂-charged brine into
the Lyons, therefore, explains both the petrography
and isotopic compositions of cements in the Lyons
grey facies.

The fugacities suggested by the above analysis are
somewhat greater than those measured in the Gulf
Coast, where CO₂ pressures are less than 5 bars at
100°C (Smith and Ehrenberg, 1989). The fugacities
suggested for the Denver basin might better be com-
pared to CO₂ concentrations and temperatures mea-
sured in fluid inclusions in late dolomite cements
throughout the Ozark region (Leach et al., 1991). The
CO₂ contents in fluid inclusions there are greater than
0.35 molal, indicating that CO₂ pressures at about
120°C could range up to at least 40 bars.

DISCUSSION

In this study, we integrated quantitative models of
groundwater flow and chemical reaction with petro-
ographic and isotopic observations to explain the ori-
gin of the petroliferous grey facies of the Lyons
Sandstone. Our results show how past groundwater
flow in the Denver basin drove diagenetic reactions
in the Lyons that are intimately related to the accu-
mulation of petroleum into present-day reservoirs.

We argue that the grey facies of the Lyons formed
as an alteration product of the sandstone’s red facies
in zones where fluids, including groundwater and
petroleum, migrated into the formation from under-
lying strata. In our model, Laramide uplift of the
Front Range along the basin’s western margin, which
reached its peak in the Eocene, set up a regime of
eastward groundwater flow. Meteoric water
recharged into the Lyons and moved deep into the
basin. Flow in the underlying Fountain Formation
was much more restricted because sandstones in this
formation pinched out to carbonate and shale beds
along the basin axis. The slowly flowing Fountain
groundwater became saline by reaction with miner-
als in the evaporite beds.

Oil in the Lyons Sandstone probably derived from
source beds in underlying Pennsylvanian strata. Oil
generation began toward the Late Cretaceous or the
early Tertiary, before the peak of the Laramide oroge-
ny. The orogeny likely produced fractures along the
basin axis along which the oil could migrate upward
by buoyancy across aquitards and into the Lyons
Sandstone. The regime of groundwater flow set up
by the orogeny drove brines along the Fountain
sandstone. Where Fountain sandstone facies pinch
out, the brines migrated upward across confining
aquitards, likely along the same fractures that trans-
mited the oil, and discharged into the Lyons.

Calcite dissolved as the brine mixed into the
Lyons because the upwelling brine was undersatu-
rated with this mineral after having reacted with
dolomite and evaporite minerals. In a common-ion
effect, calcium from the dissolving calcite reacted
with magnesium, sulfate, and CO₂ carried in the
brine to form the dolomite and anhydrite cements of
the grey facies. This reaction accounts for the iso-
topic compositions of the cements. The broad range
of δ¹⁸O in dolomite requires mixing of an isotopically-
ally heavy fluid, such as the Fountain brine, with
meteoric water. ¹³C in the dolomite is consistent with
deriving the CO₂ by dissolving Paleozoic marine car-
bonate into the brine, and ³⁴S in the anhydrite
matches the composition of sulfate from Permian
evaporite beds.

Hematite stains of the red facies were also con-
sumed in the mixing zone by reduction in the pres-
ence of the migrating petroleum, and perhaps by the
brine itself. Kilgore and Elmore (1989) documented
a similar reaction in which hydrocarbons removed
hematite cements from red beds of the Triassic
Chugwater Formation in Montana. By this process of
fluid mixing, rocks of the red facies of the Lyons
Sandstone were transformed locally along the basin
axis into the grey facies.

The association in time and space of oil migration
and groundwater mixing explains the fact that all known petroleum reservoirs in the formation are found within the gray facies, and the observation that some dolomite and anhydrite cements overlie bitumen stains left behind by migrating oil. The model also explains why oil in the Lyons apparently did not continue to migrate eastward through the sandstone, as occurred higher in the section along the Cretaceous aquifers. Since the migration and cementation processes were so closely linked, the cements probably began to seal the oil into reservoirs as it accumulated, preventing farther migration.

APPENDIX 1: SIMPLE MODEL OF CEMENTATION BY GROUNDWATER FLOW

To test the relationship between regional groundwater flow and cementation in the basin, we calculated the amounts of anhydrite and quartz that would have precipitated from groundwaters migrating along temperature and pressure gradients. The solubility of quartz, for example, increases with temperature. Quartz cements form where groundwater flows in a direction of decreasing temperature and hence decreasing solubility. Quartz dissolves where groundwater migrates toward higher temperatures because the fluid must acquire silica to remain in equilibrium with quartz. Anhydrite has a retrograde solubility, on the other hand, and thus would precipitate and dissolve in an opposite pattern.

Anhydrite has a retrograde solubility, on the other hand, and thus would precipitate and dissolve in an opposite pattern. If a mineral's solubility depends on temperature and pressure alone, the fluid can be assumed to remain in local equilibrium, and hence the species has an activity coefficient of about 1. In this case, the correlation gives molal solubility as a function of temperature and pressure, and fluid salinity. To calculate the role that fluids migrating across temperature and pressure gradients play in anhydrite precipitation, we correlated solubility to values measured by Blount and Dickson (1969) for a 2-molal NaCl solution. Blount and Dickson's measurements span the range of about 100 to 250°C and 5 to 1350 bars, so the correlation serves to extrapolate the data to temperatures found in shallow strata. The resulting regression, which gives molal solubility as a function of temperature \( T \) (°C) and pressure \( P \) (bars), is

\[
\ln n_{\text{anhy}} = -2.35 - 1.59 \times 10^{-2} T + 6.1 \times 10^{-4} P + 1.82 \times 10^{-5} T^2 - 7.05 \times 10^{-8} P^2 + 3.14 \times 10^{-7} T P. \tag{4}
\]

By this correlation, anhydrite solubility decreases with increasing temperature but increases with increasing pressure, especially at lower temperatures. The net effect is that anhydrite is less soluble at depth in a basin than at surface conditions.

Quartz solubility increases rapidly with increasing temperature, but depends only weakly on pressure and fluid salinity over the temperature range considered in this study (Kitahara, 1960; Walther and Helgeson, 1977). To calculate quartz solubility, we assume that the mineral is soluble as SiO₂(aq), and as generally the case except under alkaline conditions, and that the species has an activity coefficient of about 1. In this case, the correlation of Rimstidt and Bames (1980) gives the molal solubility of quartz as a function of absolute temperature \( T_k \) (in kelvins). The dimensionless solubility \( V_i \) the volume of a mineral soluble per unit volume of groundwater, can be calculated from a mineral's molar solubility, \( n_i \), as

\[
V_i = \frac{M_i n_i \rho_f (1 - TDS/10^6)}{1000}, \tag{6}
\]

where \( M_i \) is the mineral's molar volume in cm³/mole, \( \rho_f \) is the fluid density in g/cm³, and \( TDS \) is the total dissolved solids (in mg/kg) in the fluid. Because the largest uncertainty in calculating cementation rates is the estimation of groundwater flow rates, it is sufficient for our calculations to carry \( \rho_f \) as 1 and TDS as 0 in equation 6.

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