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Diagenesis and Water Chemistry of the Woodbine Group in the East Texas Basin

Helmuth Victor Wuerch

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DIAGENESIS AND WATER CHEMISTRY OF THE WOODBINE GROUP
IN THE EAST TEXAS BASIN

by

Helmuth Victor Wuerch III

A thesis submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Geology

Approved:

UTAH STATE UNIVERSITY
Logan, Utah
1986
To My Parents
ACKNOWLEDGEMENTS

I wish to thank my advisor Dr. Peter T. Kolesar for his help and guidance over the course of this study. I would also like to thank my committee members Dr. Robert Q. Oaks and Dr. James P. McCalpin for their critical review of the manuscript.

The Bureau of Economic Geology, University of Texas at Austin provided thin sections, core samples, results of chemical analyses and technical advice critical to the completion of this study. Special thanks to the following Bureau personnel: Dr. Charles W. Kreitler, Robert Conti, Steve Seni, Dr. Steve Fisher and Graham Fogg. Thanks also to K.L. Milliken for help on petrographic identification.

Exxon Production Research, Houston, Texas donated time and personnel for SEM indentification of clay minerals. I would like to express my gratitude to Exxon personnel Dr. Theresa Schwartzer and Robert Klimentides for their efforts.

Finally, I would like to thank my friends Lonn and Mike, without whom it would not have been the same.
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ABSTRACT


by

H. Victor Wuerch, Master of Science
Utah State University, 1986

Major Professor: Dr. Peter T. Kolesar
Department: Geology

Petrographic and SEM study of fluvial-deltaic sections of the Woodbine Group in the East Texas Basin indicates that authigenic mineral suites are controlled, in part, by the presence of organic-rich matrix.

During early, precompaction diagenesis, organic matter supplied the metabolic fuel required by sulfate-reducing bacteria to reduce sulfate in depositional waters ultimately to pyrite. With burial the sulfate supply was ultimately exhausted, and bicarbonate activity thereafter controlled the precipitation of siderite and Fe-calcite.

Matrix material supplied the components and reaction sites for the most important porosity-occluding reaction: kaolinite → Fe, Mg chlorite. Matrix physically inhibited the growth of quartz overgrowths, yet, through compaction and as a product of the above reaction, provided a supply of silica for quartz cementation. Dissolution of salt dome cap rock has played a minor role in the cementation of the Woodbine in
the East Texas Basin. Pore-filling calcite, barite, and pyrite were observed in the Woodbine where the Woodbine is in direct hydraulic communication with salt dome cap rock.

In the deep, central portion of the basin Na-Cl brine resulting from salt-dome dissolution is evolving toward a Na-Ca(Mg)-Cl brine. The evolution of the brine chemistry may be the result of cation exchange on clay minerals, albitization of plagioclase feldspars, or the dissolution of magnesium- and calcium-chloride-rich phases. The present study could not confirm any of these reactions.

WATEQF was used to calculate mineral-saturation states in Woodbine waters. Program output appears to represent accurately in situ individual mineral-saturation states at measured pH, as confirmed by petrographic and SEM identification of authigenic minerals. Relative stability between mineral pairs can be tested with thermodynamically-derived activity diagrams for the mineral pairs.

(129 pages)
INTRODUCTION

General Statement

Under a Department of Energy contract the Texas Bureau of Economic Geology undertook a study of salt domes in the East Texas Basin as potential nuclear-waste repositories (Kreitler et al., 1981). Included in that study was an attempt to determine the hydrologic stability of salt domes through geologic time (Kreitler et al., in press). Detailed investigation of water-rock interactions in the Woodbine Group in the basin was abandoned when federal funds were shifted to bedded evaporites in West Texas.

This report summarizes a study of water-rock interactions in the Woodbine in the East Texas Basin. Water-chemistry data and thin sections supplied by the Bureau of Economic Geology were supplemented with additional thin sections and whole rock samples from outcrop and drill cores within the basin to complete the present study.

The Woodbine Group is a major oil producer in the East Texas Basin. Knowledge of its diagenetic history would aid in understanding hydrocarbon occurrence and migration.

Purpose of Investigation

This study was conducted to: 1) describe the diagenesis of the Woodbine Group in the East Texas Basin; 2) determine the impact of salt-dome dissolution on Woodbine diagenesis and pore-water evolution; and 3)
assess the validity of mineral-saturation states calculated by the computer program WATEQF (Plummer et al., 1976) from water-chemistry data.

**Location of Study Area**

The study area is located in the East Texas Basin in northeastern Texas (Fig. 1). The area of study was delineated by the accessibility of oil wells for sampling for water-chemistry analyses, and the availability of drill cores for thin sections and whole rock samples. The study area is comprised of 13 counties or portions of counties within the basin. It is bounded on the west and north by the Mexia-Talco Fault System, on the east by the eastern boundaries of Wood, Smith, and Cherokee Counties, and on the south by approximate latitude 31° 30'N in Houston, Leon, and Limestone Counties (Fig. 2).

**Study Methods**

**Field Procedures** - Water-chemistry samples were collected by the author as close to the well head as possible. The oil/water ratio was sufficiently low to allow collection at the well head for all but two samples. These were collected from an oil/water separator away from the well head.

Samples were initially filtered through a funnel filled with pyrex glass wool to remove oil and large particulate matter. The water was then filtered through a 0.45 micron filter under nitrogen pressure to minimize atmospheric contamination. At each sampling site the following
FIG. 1- Map showing location of East Texas Basin, basin boundaries, and major structural elements of eastern Texas and Gulf Coast area (from Jackson, 1982).

EXPLANATION:  

/\ Normal Faults

\ Thrust Faults
FIG. 2 - Map of the East Texas Basin showing basin boundaries, local normal-fault systems, and well locations from which water and whole-rock samples were collected (after Kreitler et al., 1981).

EXPLANATION:

★ Wells from which water samples were collected as part of this study.

■ Wells for which water chemistry data were used from previously published analyses.

□ Wells from which whole rock samples were collected.

△ Locations of salt domes in probable hydraulic contact with the Woodbine.
samples were collected in sequence from one gallon of filtered water: 1) 125 ml preserved with 5 ml CdAc for H_2S analysis; 2) one liter, unacidified, for individually analyzed ions; 3) one liter, unacidified, for storage at the Mineral Studies Lab, Bureau of Economic Geology, Austin Texas; 4) 250 ml, acidified with 10 ml 6N HCl, for I.C.P. analysis of cations; and 5) 24 ml, diluted with 100 ml distilled water, for SiO_2 analysis.

All chemical analyses were performed by Bureau of Economic Geology personnel at the Mineral Studies Lab, Austin, Texas.

Woodbine outcrops are located on Figure 4. Rock samples from Woodbine outcrops located approximately five miles southwest of Dallas in Tarrant County, Texas (Fig. 1) were collected for x-ray-diffraction analysis and thin sectioning. Samples were selectively chosen from channel sands and overbank deposits to represent the two facies. Whole-rock samples from wells in the East Texas Basin were sampled on the basis of availability and depth. Locations of wells sampled for water-chemistry analyses, and whole-rock samples for thin sectioning, for x-ray diffraction, and for scanning-electron-microscope observation are presented in Table 1 and shown on Figure 2.

Laboratory Procedures- Thin sections and drill cores for thin sectioning were selected strictly on the basis of availability. An attempt was made to describe diagenesis in as much of the basin as possible. However, most attempts to acquire drill cores were frustrated by lack of information on depth and/or location which resulted from poor curating procedures through time.
Table 1 - Detailed description of well locations and depths from which samples on Figure 2 were collected. Symbols are the same as on Figure 2.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Field</th>
<th>Lease</th>
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<th>Sample Depth (Ft.)</th>
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<tbody>
<tr>
<td>★ 1</td>
<td>Mexia</td>
<td>Gamble Louise</td>
<td>#11</td>
<td>3,100</td>
</tr>
<tr>
<td>★ 2</td>
<td>Richland</td>
<td>Jewell Weaver</td>
<td>_</td>
<td>3,300</td>
</tr>
<tr>
<td>★ 3</td>
<td>Powell</td>
<td>Mackie</td>
<td>_</td>
<td>3,000</td>
</tr>
<tr>
<td>★ 4</td>
<td>Nesbett</td>
<td>_</td>
<td>_</td>
<td>3,390</td>
</tr>
<tr>
<td>★ 5</td>
<td>Cayuga</td>
<td>Wortham</td>
<td>_</td>
<td>4,030</td>
</tr>
<tr>
<td>★ 6</td>
<td>Long Lake</td>
<td>Little Reeves Tract</td>
<td>#2</td>
<td>5,272</td>
</tr>
<tr>
<td>★ 7</td>
<td>Concord Dome</td>
<td>_</td>
<td>_</td>
<td>4,404</td>
</tr>
<tr>
<td>★ 8</td>
<td>Van</td>
<td>J.A. Bracken</td>
<td>#35-9</td>
<td>2,900</td>
</tr>
<tr>
<td>★ 9</td>
<td>Slocum-Northwest</td>
<td>George Springman</td>
<td>_</td>
<td>5,400</td>
</tr>
<tr>
<td>★ 10</td>
<td>Neches</td>
<td>Broyles-State</td>
<td>#2</td>
<td>4,704</td>
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<tr>
<td>★ 11</td>
<td>Boggy Creek</td>
<td>H.L. Carter</td>
<td>C</td>
<td>3,600</td>
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<tr>
<td>★ 12</td>
<td>Barkley</td>
<td>D.D. Martin</td>
<td>#1</td>
<td>4,259</td>
</tr>
<tr>
<td>★ 13</td>
<td>Hawkins</td>
<td>Atkins</td>
<td>_</td>
<td>4,531</td>
</tr>
<tr>
<td>□ 1</td>
<td>Stewards Mill</td>
<td>_</td>
<td>_</td>
<td>4,001-4,006</td>
</tr>
<tr>
<td>□ 2</td>
<td>Ham Gossett S.E.</td>
<td>_</td>
<td>_</td>
<td>3,256-3,265</td>
</tr>
<tr>
<td>□ 3</td>
<td>Buffalo</td>
<td>_</td>
<td>_</td>
<td>5,642-5,645</td>
</tr>
<tr>
<td>□ 4</td>
<td>Navarro Crossing</td>
<td>_</td>
<td>_</td>
<td>5,870-5,875</td>
</tr>
<tr>
<td>□ 5</td>
<td>Newton Branch</td>
<td>_</td>
<td>_</td>
<td>5,148-5,151</td>
</tr>
<tr>
<td>□ 6</td>
<td>Good Omen</td>
<td>_</td>
<td>_</td>
<td>3,950-3,954</td>
</tr>
<tr>
<td>□ 7</td>
<td>Merigale-Paul</td>
<td>_</td>
<td>_</td>
<td>5,237-5,488</td>
</tr>
<tr>
<td>□ 1</td>
<td>Oakwood Dome</td>
<td>_</td>
<td>_</td>
<td>6,000</td>
</tr>
<tr>
<td>□ 2</td>
<td>Neches</td>
<td>Boyle</td>
<td>#1</td>
<td>4,650</td>
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<tr>
<td>□ 3</td>
<td>Larissa</td>
<td>Stockton</td>
<td>#1</td>
<td>4,380-4,504</td>
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<tr>
<td>□ 4</td>
<td>Chandler</td>
<td>S. Chandler</td>
<td>#1</td>
<td>4,845-4,880</td>
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<tr>
<td>□ 5</td>
<td>Tyler South</td>
<td>Humble</td>
<td>#1</td>
<td>5,038-5,068</td>
</tr>
<tr>
<td>□ 6</td>
<td>Van</td>
<td>Clark</td>
<td>#1</td>
<td>3,255-3,304</td>
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</table>
Nineteen thin sections from three wells, acquired from The Bureau of Economic Geology, were prepared as part of the original Bureau of Economic Geology study. Five thin sections were made from core pieces from two wells acquired through the Bureau of Economic Geology core library. Two thin sections were made from samples collected by the author from Woodbine outcrops. All thin sections were cut perpendicular to bedding, and a blue-stained epoxy was used to impregnate samples to aid in porosity recognition. One half of each thin section was stained with sodium cobaltinitrite for potassium-feldspar identification (Hutchison, 1974). After initial examination, 14 thin sections of Woodbine sandstones were selected for detailed examination. Thin sections were point-counted at regular intervals on a grid system until 200 grains were counted. A Zeiss polarizing microscope with a mechanical stage and calibrated eyepiece was used to describe: 1) grain composition, size, shape, and roundness; 2) quartz type; 3) matrix mineralogy and abundance; 4) cement mineralogy and abundance; 5) paragenetic sequence; and 6) primary and secondary porosity. The remaining 12 thin sections, too fine-grained to yield significant results on grain populations, were described without being point counted.

After thin section grain-size frequencies were compiled, they were converted to sieve-size equivalents using the conversion chart developed by Friedman (1958). All of the thin sections met Friedman's criterion of being finer than -1 phi; however, none of the thin sections were well sorted. Cumulative-frequency-percent and frequency-percent-distribution curves were plotted using the corrected data, and mean grain size ($M_z$),
standard deviation ($O_z$), skewness ($Sk_z$), and kurtosis ($K_G$) were calculated (Folk and Ward, 1957; Folk, 1974).

Twenty-four whole-rock samples were analyzed for mineral content with an x-ray diffractometer. All samples were powdered and passed through a 115-mesh sieve. Random mounts were prepared and scanned from $2^\circ$ 2 theta to $45^\circ$ 2 theta at $2^\circ$ 2 theta per minute, using Ni-filtered CuK radiation at 35kv and 16mA on a Siemens Krystalloflex IV diffractometer. Clay minerals were identified by glycolation and heating to $550^\circ$ C, following the procedure outlined in Carroll (1970). The kaolinite peak was distinguished from the Fe-chlorite peak by heating the sample to $90^\circ$ C in 1N HCl for an hour. This treatment removes the Fe-chlorite peak but not the kaolinite peak (Carroll, 1970). The results are reported in Appendix A.

Three samples were examined using scanning electron microscopy: #1 Humble (5062 ft), #1 Clark (3263 ft), and #1 Stockton (4504 ft). Samples #1 Clark (3263 ft) and #1 Stockton (4504 ft) were examined with a Model 1000 AMR scanning electron microscope with an energy-dispersive analyzer at the Biology Department, Utah State University, Logan, Utah. Samples #1 Humble (5062 ft) and #1 Clark (3263 ft) were examined with a Model 1200 B Amray scanning electron microscope with a Link Systems series 2 energy dispersive-analyzer at Exxon Production Research Company, Houston, Texas.

The computer program WATEQF (Plummer et al., 1976) was used to calculate saturation states of minerals in Woodbine waters. WATEQF is a FORTRAN IV version of an earlier program, WATEQ (Truesdell and Jones, 1973), used to model thermodynamic speciation of inorganic ions and
complexes in solution from water analyses (Plummer et al., 1976). Saturation states of minerals (log (Ion Activity Product/K_{sp})) are calculated from the distribution of aqueous species using mineral-dissociation reactions, solubility products (log K_{sp}) taken from various thermodynamic data compilations (e.g. Garrels and Christ, 1965; Robie and Waldbaum, 1968; and Helgeson, 1969), and calculated-ion activity products. Experimentally determined ionic concentrations are converted to activities by multiplying concentrations by calculated activity coefficients. Activity coefficients are calculated using the Davies equation, which is accurate in more saline waters than the Debye-Huckle equation. Experimentally determined water-chemistry data and calculated mineral- saturation states are presented in Appendix B. WATEQF uses an almost identical thermodynamic data base and calculating procedure as WATEQ.
Geologic Setting

Basin Evolution and Infilling- The general structural and stratigraphic evolution of the East Texas Basin is summarized by Jackson and Seni (1983). The basin originated as a failed continental rift marginal to the major rift zone which formed the Gulf of Mexico. Prior to rifting the Paleozoic Ouachita fold belt was uplifted, and it provided a sediment source for the subsiding basin through Woodbine time (Fig. 1).

Stratigraphic nomenclature is summarized in Figure 3. Sedimentation began with the Triassic Eagle Mills continental red beds. The Jurassic Louann Salt was deposited in a restricted, evaporitic marine environment over an angular unconformity across the Eagle Mills and eroded Paleozoic basement.

Carbonate platform deposition dominated through Smackover time, during the first major transgressive episode.

During the Late Jurassic and Early Cretaceous, Shuler and Travis Peak deposition document major regression. Influx of clastic terrigenous sediment was predominantly from the north-northwest from the exposed Ouachita fold belt. The overlying Glen Rose represents a general transgressive sequence with minor terrigenous influxes.

Prior to Woodbine deposition, fluvial-deltaic sedimentation dominated during Paluxy time. Sediment influx was again from the north-northwest, and deltaic sandstones graded into shales toward the center of the basin. Subsequent Washita deposition documents another
FIG 3- Stratigraphic column of the East Texas Basin (from Wood and Guevara, 1981).
transgressive phase just prior to Woodbine time.

The beginning of the Late Cretaceous marks the onset of a major regressive sequence, that started with the Woodbine and ended in the Oligocene when basin subsidence ended.

**Woodbine Deposition**—Deposition of the Woodbine in the East Texas Basin is presented in detail by Oliver (1971). Figure 4 (from Oliver, 1971) shows the relation between present-day Woodbine outcrop and depositional systems in the basin. Thin sections from wells 1, 2, and 3 in Table 1 are located in the Freestone Delta System, and thin sections 4, 5, and 6 in Table 1 are located in the Dexter Fluvial System.

Oliver (1971) identified two members in the Woodbine Formation: the lower, Dexter, and the upper, Lewisville. These members have been subsequently termed formations, and the Woodbine a group. The Dexter Formation is comprised of the fluvial system, and the Lewisville is comprised of the deltaic and prodelta-shelf systems.

Oliver (1971) divided the fluvial system into two facies: 1) the updip tributary facies; and 2) the down dip meander belt facies. The distinction between the two is based on the ratio of channel sand to over-bank mud deposits. The tributary facies is dominated by over-bank mud deposits with well defined, discrete channel sand deposits. The meander belt facies is dominated by channel sand deposits which have coalesced into a semi-continuous sheet sand body. Over-bank mud deposits are less well developed than in the tributary facies.

The fluvial system dominates the northern one-third of the basin. Channel axes are oriented predominantly toward the south-southwest. In
FIG. 4 - Map showing generalized depositional systems of the Woodbine in northeastern Texas and the relationship between depositional systems and present-day Woodbine outcrops (from Oliver, 1971).
In extreme northeast Texas counties the fluvial system is dominated by tributary facies. Deposition occurred as channel sands and overbank muds. To the southwest these facies grade into meander-belt facies where overbank deposits are poorly developed and sands predominate. The meander belt facies interfingers with the coastal barrier facies of the delta system. The delta system represents the greatest volume of Woodbine sediments. This system is predominantly sand in updip sections, and becomes increasingly fine-grained to the south where prodelta muds dominate.

**Structural Modification of the Woodbine** - During deposition of the Woodbine, growth faulting occurred along the western and north-western margins of the basin, represented by the Mexia-Talco fault zone (Fig. 1). Normal faulting also occurred in the Elkhart Graben-Mt. Enterprise fault zone (Fig. 1). Salt movement began in the Late Jurassic and salt domes continued to grow during and after Woodbine deposition (Jackson and Seni, 1983), which caused faulting and folding of the Woodbine. Salt-dome growth locally modified the general southeast dip of the Woodbine toward the central portion of the basin (Fig. 5). The Sabine Uplift borders the eastern margin of the basin (Fig. 1). It is believed to have been emergent near the end of Woodbine deposition (Oliver, 1971; Siemers et al., 1981), and thus partially controlled deposition in the basin, and allowed late-stage reworking of Woodbine sediments southwestward into the prodelta-shelf system of the Woodbine/EagleFord (Siemers et al., 1981).
FIG. 5 - Dip cross section, East Texas Basin. Section line A-A' is located on Figure 2 (from Kreitler et al., in press).
Hydrologic Setting

General Statement- Present Woodbine waters in the East Texas Basin range from approximately 13,000 to over 100,000 ppm total dissolved solids. Salinities are lowest near the up-dip margin of the basin near the Mexia-Talco fault zone, and increase toward the central portion of the basin where the Woodbine is in contact with salt domes (Fig. 6). Salinities in the Woodbine increase from approximately 2,000 ppm total dissolved solids outside the basin, northwest of the Mexia-Talco fault zone, to 13,000 ppm immediately basinward of the fault zone. Waters north-west of the fault zone are Na-HCO₃-SO₄-Cl type whereas those in the basin are Na-Cl type. Woodbine waters in the basin have been hydraulically closed to waters outside the basin northwest of the fault zone probably since barrier conditions were imposed by faulting along the Mexia-Talco Fault Zone (Kreitler et al., in press).

Origin of Water- The origin of the waters in the saline aquifers in the East Texas Basin is discussed by Kreitler et al.,(in press) and is summarized below. Based on hydrogen- and oxygen-isotopic data from formation waters it was concluded that present waters have a continental meteoric origin. Formation waters probably have long residence times, and recharge likely began during the Cretaceous. The Woodbine apparently had two hydrogeologic regimes (Kreitler et al., in press). Initially, shortly after deposition, the Woodbine was probably a through-flowing meteoric system that flushed original marine water out
FIG. 6 - Isochloride map of Woodbine waters in the East Texas Basin. Contour values are mg/l X 1000. Symbols are the same as in Figure 2. Note that high chloride concentrations do not necessarily coincide with locations of salt domes. Data from Appendix B.
at discharge points at topographic lows around salt domes, which formed salt dome cap rock. Later, with burial, the system probably became stagnant as water flow was restricted by Woodbine pinchout against the Sabine Uplift to the east, and the down-dip facies change into prodelta muds to the south. Timing of the change in flow systems has not been resolved, but it appears that Woodbine waters in the basin have been isolated from waters outside the basin for a considerable length of time.

Pressure conditions in the Woodbine are presently hydrostatic to subhydrostatic (Kreitler et al., in press). A decline in hydraulic head has been caused by hydrocarbon production over approximately the past fifty years. Because of this pressure decline there is a potential for water from deeper, over pressured aquifers to move up along faults and salt-domes into the Woodbine, and water from shallow, fresh-water aquifers to move down into the Woodbine. The potential also exists for dewatering of overlying and underlying shale aquitards/aquicludes into the Woodbine.

Source of Dissolved NaCl- Kreitler et al. (in press), consider the source of dissolved NaCl in all the saline aquifers in the East Texas Basin to be dissolution of salt-dome halite. This conclusion was reached by two mass- balance approaches: 1) amount of dissolved NaCl compared to the amount of Louann halite which has been lost; and 2) amount of dissolved NaCl compared to the amount of halite required to produce the volume of salt-dome cap rock in the basin. Both approaches yield volumes of halite lost through dissolution greater than that required to produce
the total amount of dissolved NaCl. The excess NaCl apparently was lost through expulsion during burial compaction. Formation pore-water volumes, and thus total amount of dissolved NaCl, were estimated using average porosities for each formation.

Kreitler et al. (in press) also concluded that salt-dome dissolution occurred early in the history of the basin, and is not presently occurring. Salinity distributions around salt domes in the Woodbine were examined. No consistent increase in salinity was found near domes. Considerations based on Cl^{36} age dating of dissolved chloride (Kreitler et al., in press), and timing of the formation salt-dome rim syncline (Jackson and Seni, 1983) and cap rocks (Kreitler and Dutton, 1983) indicate that dissolution occurred early.

Geochemical Trends- Kreitler et al. (in press) divided the saline aquifers in the East Texas Basin into two groups based on water chemistry and depth. Post-halite-dissolution water chemistry in the deeper, more saline aquifers of the Glen Rose and Travis Peak formations has been modified by feldspar dissolution and by albitization and dedolomitization. Dissolution of potassium feldspars results in increased aqueous potassium concentrations in formation waters. The albitization and dedolomitization reactions result in increased aqueous calcium and magnesium concentrations. These reactions would cause a Na-Cl brine to evolve toward a Na-Ca-Cl brine with increased K and Mg concentrations. This is the case in the deep aquifers.

It was concluded that minimal water/rock interaction has occurred in the shallower, less saline aquifers of the Nacotoch, Woodbine and Paluxy...
formations, where it was determined that brines have not significantly evolved from a Na-Cl brine (Kreitler et al., in press). Potassium and magnesium are less concentrated in shallow formation waters than in deep waters, in support of the above argument.
RESULTS

Petrography

General Statement- Woodbine sandstones in the East Texas Basin plot in the quartzarenite and subarkose fields of the Q-F-L sandstone-classification ternary diagram of Folk (1974) (Fig. 7). Sandstones are poorly- to moderately well-sorted, very fine- to medium-grained, immature to submature, and poorly to well cemented. Cements range from 5 to 28 percent of the rock by volume. Sandstone porosities in the basin range from a trace to 21.8 percent of the rock by volume, and average 7.4 percent of the rock by volume (Appendix D). Secondary porosity is significant in only one sample, #1 Humble (5057-5068 ft).

Detailed mineralogy of thirteen point-counted thin sections and summaries of quartz type, grain roundness and equantness, statistical parameters, and sandstone-classification parameters are presented in Appendix D. Statistical parameters were derived from cumulative-frequency plots (after Friedman, 1958). These plots, as well as detailed rock name, annotated statistical parameters, and paragenetic sequence of each point counted thin section are presented in Appendix D. Mineralogy and grain size data are also presented in Appendix D.

Mineralogy- Quartz is the dominant mineral in all samples; it ranges from 78.1 to 96.4 percent of grains, and averages 91.6 percent of grains. Quartz populations were divided into three categories by the criteria presented by Basu et al. (1975): 1) nonundulant - grains with extinction angle less than or equal to 5 degrees; 2) undulose - grains
FIG. 7 - Mineralogic classification of Woodbine sandstones. Only grains >0.03 mm diameter are considered.

- outcrop samples
- basin samples
with extinction angle greater than 5 degrees; and 3) polycrystalline -
grains which contain 2 or more crystal units. Undulant grains are the
most abundant; they range from 60.5 to 84.5 percent of quartz grains and
average 70.7 percent of quartz grains. Nonundulant grains are the next
most abundant; they range from 11 to 35.2 percent of quartz grains and
average 23 percent. Polycrystalline quartz ranges from 3.9 to 10.8
percent of quartz grains, and averages 6.3 percent.

Feldspars are the next most abundant mineral present in Woodbine
sandstones. Orthoclase is the most abundant feldspar, ranging in
abundance from a trace to 11.5 percent of grains, and averaging 5.1
percent. Plagioclase and microcline are present in trace amounts in
about half of the thin sections point-counted.

Schist and quartzite metamorphic rock fragments are present in all of
the point-counted thin sections, and comprise from a trace to 3 percent
of grains. Siltstone and mudstone sedimentary rock fragments are
generally less abundant, and are present in all but three of the point-
counted thin sections. They comprise from a trace to 4.2 percent of
grains. Chert, less abundant still, is present in all point-counted
thin sections, and comprises from a trace to 3.6 percent of grains.

All other detrital grains observed in thin section - tourmaline,
iron oxides, muscovite, biotite, and zircon - are present mostly in
trace amounts.

Detrital grains comprise from 59.6 to 75.8 percent of rock by volume
in point-counted thin sections, and average 69.1 percent of rock by
volume.

Matrix, detrital material less than 0.03 mm in diameter, comprises
from a trace to 22 percent of rock by volume in point-counted thin sections, and averages 8 percent rock by volume. It is comprised of admixtures of clay minerals, quartz, iron oxides, and organic matter, of which clay minerals are most abundant. Percentages of matrix components are subject to error due to their fine-grained and admixed nature. Also, examination of three samples by scanning-electron microscope indicates that clay minerals are being recrystallized. Distinguishing detrital from recrystallized or replaced clay minerals through a petrographic microscope is tenuous at best. Although Folk (1974) considers recrystallized matrix clays as being part of the matrix, they are considered to be cements in this study because they partially occlude porosity.

Cement minerals observed in the Woodbine include: chlorite, kaolinite, siderite, calcite, overgrowths of quartz and feldspar, iron oxide, pyrite, fluorapatite, and barite. The most abundant cements are, typically, chlorite and kaolinite. Cement abundances are presented in Appendix D as percent of rock by volume.

Grain Size, Sorting, and Skewness—The inclusive graphic mean was calculated from the formula of Folk and Ward (1957): $M_Z = \bar{Q}_{16} + (\bar{Q}_{50} + \bar{Q}_{84})/3$. Mean grain size of point-counted thin sections ranges from 3.52 $\bar{Q}$ (0.09 mm) to 1.86 $\bar{Q}$ (0.28 mm), and averages 2.72 $\bar{Q}$ (0.15 mm).

Sorting (standard deviation) and skewness were also calculated from the formulae of Folk and Ward (1957). Sorting ($\sigma_1$) = $(\bar{Q}_{84} - \bar{Q}_{16})/4 + (\bar{Q}_{95} - \bar{Q}_{5})/6.6$; and skewness ($SK_1$) = $(\bar{Q}_{16} + \bar{Q}_{84} - 2\bar{Q}_{50})/2(\bar{Q}_{84} - \bar{Q}_{16}) + (\bar{Q}_{5} + \bar{Q}_{95} - 2\bar{Q}_{50})/2(\bar{Q}_{95} - \bar{Q}_{5})$. Verbal descriptions of sorting and
skewness follow Folk (1974).

Sorting in Woodbine sandstones ranges from 1.97 $\phi$ to 0.53 $\phi$ (poorly to moderately well sorted), and averages 1.00 $\phi$ (moderately-sorted). Skewness of Woodbine sandstones ranges from -0.38 to +0.25 (strongly coarse skewed to fine skewed), and averages -0.01 (near symmetrical).

**Diagenesis**

**General Statement**—Diagenesis of the Woodbine Group in the East Texas Basin was controlled largely by the presence of organic-rich matrix. Matrix material both inhibited and enhanced diagenesis by: 1) restricting the movement of pore water through the sediment column; and 2) providing a site and a supply of ions for reaction.

Diagenesis has been divided into two major categories based on depth of burial. Organic-rich matrix was a major factor in each. In the early stage of diagenesis, near the sediment-water interface shortly after deposition, matrix material controlled diagenesis by restricting the amount of hydraulic communication between sediment and the overlying water column, and by providing the conditions and materials necessary for bacterial sulfate reduction. In the later stage, sometime after the system was closed to water in the depositional environment, matrix material again controlled reaction kinetics by restricting water movement. However, it also provided a supply of ions for diagenesis of cleaner sands, and reaction sites for replacement and recrystallization reactions.
**Early Diagenesis** - In the early stage of diagenesis organic matter in the matrix is metabolized by bacteria to produce CO₂ and to reduce aqueous sulfate to sulfide by the general reaction (Irwin, et al., 1977):

\[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{S}^{2-} \]  
(1)

The resulting aqueous sulfide reacts with iron in the matrix to produce pyrite (Berner, 1970). The factors which control the precipitation of pyrite in this situation are: 1) the occurrence of organic matter; 2) the presence of sulfate-reducing bacteria; 3) a supply of aqueous sulfate, generally from sea water; and 4) the availability of reactive iron species (Berner, 1970).

Early diagenesis in the Woodbine will be discussed under two major conditions: 1) in bioturbated, organic-rich siltstones; and 2) in sandstones with various amounts of organic-rich matrix present.

In organic-rich siltstones burrows are almost totally free of pyrite. It is only in the unburrowed areas where pyrite, and iron oxides, are abundant. The burrowing organisms may have consumed most or all of the organic matter, or the burrowed areas may have remained open to oxygenated marine waters. Both of these situations would greatly decrease the ability of bacteria to reduce sulfate, the former by restricting the required metabolic fuel, and the latter by establishing conditions too oxidizing for pyrite stability.

In unburrowed areas conditions were favorable for pyrite formation. Pyrite occurs in irregular, patchy masses up to approximately one centimeter in diameter, which have been partially altered to iron oxide. The fine-grained nature of the sediment caused anaerobic conditions to result shortly after deposition. This allowed bacteria that metabolize
organic matter to reduce aqueous sulfate ultimately to pyrite. The occurrence of these pyrite masses seems not to have been controlled totally by the presence of organic matter, since areas free of pyrite contain some organic matter.

Deformation from vertical pressure of platy clay particles around many of the iron-cemented masses indicates that pyrite formed as an early cement, prior to compaction.

In Woodbine sandstones early diagenesis is characterized by: 1) formation of pyrite and iron-carbonate nodules (Fig. 8); 2) precipitation of disseminated pyrite, siderite, and iron-rich calcite; and 3) replacement and infilling of foraminiferal tests with pyrite, iron oxide, siderite, and iron-rich calcite.

Nodules in rather clean sands range in size from 0.40mm to 1.50mm in diameter. They generally nucleated around partially oxidized pyrite, and grew outward, and replaced matrix material between detrital grains. The carbonate becomes more iron-stained away from the center of the nodules. The same general reaction (1) is considered to control pyrite precipitation in iron-carbonate nodules (Gautier, 1982), under conditions similar to those conducive to pyrite precipitation alone. In this case all aqueous sulfate is reduced to sulfide and forms pyrite before the available reactive iron is consumed. The bicarbonate activity increases to a point beyond siderite or iron-rich calcite saturation, and precipitation occurs. It has been suggested by Curtis et al. (1972) that a fermentation reaction is responsible for siderite formation after all aqueous sulfide has been precipitated as pyrite:

\[
4\text{CH}_3\text{OH} = 3\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O}
\] (2)
FIG. 8 - Photomicrograph of #1 Clark (3255 ft) showing a nodule composed of: 1) authigenic pyrite; 2) authigenic pyrite being oxidised to iron oxide around edges; and 3) siderite/Fe-calcite. Note differences in grain densities within and outside of nodule. Crossed polarizers, medium power.
Because sandstone permeabilities are greater than those in siltstones, high sedimentation rates were probably necessary for closing the sediment to influx of marine water, thus cutting off the sulfate supply.

Disseminated pyrite, siderite, and iron-rich calcite are also present in matrix-rich sandstones. The fact that the minerals are disseminated rather than in nodular form seems to be related to the distribution of matrix material. Nodules are well-developed in cleaner sands with patches of matrix, whereas disseminated minerals occur where matrix is more uniform in distribution. Siderite is a major constituent compared to pyrite in some areas, which suggests higher sedimentation rates than in areas where carbonate phases are absent. Higher sedimentation rates would cause the sediment column to pass rapidly through the region dominated by the sulfate-reducing bacteria reaction to sediment depths that may be dominated by a fermentation reaction where CO₂ is produced without aqueous sulfate input.

Grain densities are lower within nodules than in surrounding areas, which suggests that compaction occurred after cementation of the nodules.

Some foraminiferal tests have been totally replaced by iron oxide, siderite, and iron-rich calcite. Tests have been progressively filled from the center with pyrite, iron oxide and, in some cases, alternating stages of siderite and iron-rich calcite. The pyrite was probably associated with organic remains and, therefore, would have formed first. Since the infilling does appear to have occurred from the center outward, it is likely that it occurred as a replacement of some initial
material. The presence of early carbonate associated with pyrite, and the larger grain size of the detrital grains, very fine to medium sand, suggests rather rapid burial. However, it is difficult to explain the fluctuations in iron activity required to produce the alternating phases of siderite and iron-rich calcite if the system were quickly closed to influx of sea water.

Isolated traces of apatite cement are present in the thin sections from the #1 South Chandler well. It is present in matrix-rich sandstones, and results from early, precompaction precipitation within the depositional environment (Berner, 1980).

On some grains in most thin sections an early, pre-consolidation, pre-quartz-overgrowth, isopachous chlorite rim cement is present. It is unclear whether the rims formed as grain coatings prior to deposition, or as true cements after deposition, prior to compaction.

Figure 9 is a schematic representation of the sites and processes of early diagenesis.

Late Diagenesis—Organic-rich matrix partially controls post-consolidation diagenesis of the Woodbine. However, following deep burial (>3000 ft), the problem of distinguishing detrital matrix from recrystallized matrix and authigenic clay cements becomes enigmatic. Dickinson (1970) discussed the problem of distinguishing detrital clay minerals from those which have been recrystallized or have formed after deposition. He introduced four terms which describe clay minerals in immature arenites and arkoses which are commonly confused with authigenic clay cements when observed through a petrographic microscope.
FIG. 9 - Schematic diagram of relative time of formation of early Woodbine cements, with possible sources of ions and compounds and reaction paths.
As defined by Dickinson (1970): 1) protomatrix refers to unrecrystallized detrital clay minerals; 2) orthomatrix refers to recrystallized or replaced clay minerals of detrital origin; 3) epimatrix refers to the clay minerals formed by diagenetic recrystallization or replacement of detrital sand grains (micas and feldspars); and 4) pseudomatrix refers to deformed, clay-rich sedimentary rock fragments.

Through petrographic examination of Woodbine sandstones interstitial clay minerals were suspected by the author to be, in part, a product of replacement and recrystallization (orthomatrix) (Fig. 17). Examination of the sandstones with a scanning electron microscope confirmed the presence of orthomatrix. Figure 10 shows compacted, detrital kaolinite (protomatrix), whereas Figure 11 shows progressive recrystallization of chlorite of possible replacement origin to a euhedral chlorite orthomatrix. Figure 12 shows protomatrix and/or orthomatrix acting as nucleation sites for an authigenic, pore-filling clay mineral cement.

Wilson and Pittman (1977) defined allogenic clay minerals as being formed prior to deposition and mixed with the sand fraction during deposition. Authigenic clay minerals are defined as those formed after deposition, and include new, recrystallized and replaced clay minerals. The difficulty in distinguishing between the two types is well recognised (Dickinson, 1970). Accordingly, the amount of matrix (allogenic clay minerals) present in the Woodbine, presented in Appendix D, is probably overestimated. As defined by Wilson and Pittman (1977), the types of allogenic clays present in the Woodbine include: dispersed matrix, intercalated laminae, detrital mica, mudstone rock fragments,
FIG. 10 - SEM photograph of compacted, detrital clay mineral (protomatrix), with EDX spectrum similar to that of a typical kaolinite. Horizontal scale measures energy in eV, the vertical cursor is on 5080 eV. Vertical scale is linear in counts, and measures relative peak height.
FIG. 11 - SEM photograph showing progressive recrystallization of poorly crystallized, possible orthomatrix (4) to a euhedral clay mineral of similar composition (6). EDX spectra of (4), (5) and (6) are representative of an Fe-Mg chlorite. Horizontal scale measures energy in eV, vertical cursor is on 5080 eV. Vertical scale is linear in counts and measures relative peak height.
Fig. 12 - SEM photograph showing a poorly crystallized clay mineral in the background, with euhedral chlorite (Ch) growing from it into pore space. Chlorite appears to postdate quartz overgrowth (Qog).
and infiltration residues. Authigenic clay minerals present in the Woodbine include: pseudomorphous replacement of feldspar, pore-linings, pore-fillings, and recrystallization of matrix.

Wilson and Pittman (1977) found that the most reliable criteria in distinguishing authigenic clay minerals from allogetic clay minerals are: 1) absence of impurities; 2) greater degree of crystallinity; 3) tendency of authigenic clay mineral flakes to align radially; and 4) where present as pore-linings, authigenic clay minerals will not be present at grain contacts. Clay minerals in the Woodbine which fit some or all of these criteria for clay minerals are: 1) isopachous, iron-rich chlorite rims on detrital grains; 2) pore-filling kaolinite cement; 3) recrystallization of matrix to an iron-rich chlorite; and 4) pore-filling, iron-rich chlorite.

The general paragenetic sequence in the Woodbine in the East Texas Basin subsequent to compaction is: 1) feldspar dissolution; 2) development of quartz and feldspar overgrowths; 3) development of chlorite rim cement; 4) formation of pore-filling kaolinite cement, from feldspar alteration; 5) replacement and recrystallization of matrix clay minerals to iron-rich chlorite; 6) precipitation of pore-filling calcite; and 7) precipitation of pore-filling barite.

No thin section contains all of the authigenic phases. Therefore, the timing of the above sequence is not absolute because the relative times of formation of all the phases cannot be determined, and appear to overlap in many cases. Many of the reactions which control the stability of the authigenic minerals are probably the result of localized physical and chemical processes. This would make the
occurrence of authigenic minerals a function of the local chemical and physical environment and not strictly depth and time.

**Feldspar dissolution**- Dissolution of detrital feldspar is extensive in only one thin section (#1 Humble 5057-5068 ft) (Fig. 13). Original feldspar abundance was higher in this sample than in any other sample, and kaolinite cement comprises a greater percent by volume of the rock than in any other thin section. Mudstone and siltstone sedimentary rock fragments, and what appears to have been organic matter, have also been leached in this sample. Anerobic decomposition of organic matter produces CO₂ which reduces the pH. Low-pH environments favor kaolinite over feldspar, this a reasonable explanation for the observed feldspar instability. Thin section #1 Humble (5057-5068 ft) is also the coarsest sample examined. This coarseness could have increased feldspar vulnerability to leaching through increased permeability. Feldspar leaching is minor or absent in all other samples.

**Chlorite rims**- There are two stages, and possibly types, of chlorite rims. One of the stages occurred early, prior to compaction. The rims formed as an isopachous cement on detrital grains prior to overgrowth cement (Fig. 14). It is unclear whether the rims formed prior to deposition, i.e. are allogenic, or are true authigenic cements. Pre-overgrowth chlorite rims were observed on some grains in most samples.

The second stage of chlorite, rim cement was observed only in sample #1 Humble (5057-5068 ft) (Figs. 13 and 14). Here, the rims formed as isopachous rinds on most detrital grains after quartz overgrowths had
FIG. 13 - Photomicrograph of #1 Humble (5057-5068 ft) showing in sequence: 1) quartz overgrowth; 2) isopachous chlorite rim cement; 3) formation of secondary porosity from feldspar dissolution; 4) pore filling kaolinite cement; and 5) residual feldspar (orthoclase). High power, plane light.
FIG. 14 - Photomicrograph of #1 Stockton (4504 ft) showing: 1) chlorite rims; 2) quartz overgrowth; 3) secondary porosity from feldspar dissolution; and 4) residual feldspar (orthoclase). Note quartz overgrowth in upper right of photo growing into secondary porosity. High power, plane light.
Fig. 15 - SEM photograph with EDX spectra showing chlorite rim cement (1, 2, 4 and 6) and pore-filling kaolinite (3); (5) is a detrital quartz grain. The chlorite spectrum (2) is on the left, kaolinite (3), on the right. Quartz overgrowths are not present in this field of view and cannot be timed relative to the chlorite rims in this photograph.
formed. They are not present where grains are in contact.

Quartz and feldspar overgrowths—Feldspar overgrowths are present in trace amounts in three thin sections (Sun #1 Boyling, 4650 ft; #1 South Chandler, 4845-4850 ft; and #1 Stockton, 4465-4484 ft) (Fig. 16). Syntaxial quartz overgrowths are present in all point-counted thin sections except #1 South Chandler (4880 ft) which contains 57.4% matrix. Quartz overgrowths comprise up to 7% by volume of the rock in the point-counted thin sections. The volumetric significance of silica-overgrowth cementation has been stressed by many workers since the use of cathodoluminescence has identified its occurrence (e.g., Sibley and Blatt, 1976; Land and Dutton, 1978; Odom et al., 1979; and Milliken et al., 1981).

Overgrowth volume decreases as the amount of matrix and/or pseudomatrix increases. Overgrowths are well developed only in clean sands where pores were initially open. Because overgrowths only develop in rather clean sands, and because overgrowths are in contact with chloritic matrix, this suggests that the chloritic matrix is authigenic in origin and formed after quartz overgrowths (Fig. 17).

Generally, quartz overgrowths are absent at grain contacts, so that silica cementation occurred after compaction. In thin section, lath-shaped pores with minor amounts of residual feldspar were observed to contain silica cement (Fig. 13). Silica cementation postdates the onset of feldspar dissolution, but it is unclear whether the two processes occurred synchronously or if silica cementation began after feldspar dissolution ended.
FIG. 16 - Photomicrograph of #1 Stockton (4465-4484 ft) showing a syntaxial overgrowth (1) on an orthoclase grain. High power, crossed polarizers.
FIG. 17 - Photomicrograph of #1 Clark (3263 ft) showing poorly crystallized matrix (1) being recrystallized to a euhedral chlorite (3). Quartz overgrowths (2) initially developed in matrix free areas but now terminate against authigenic chlorite. P = porosity. Medium power, plane light. See Figures 11 and 12 for SEM photographs of authigenic chlorite and quartz overgrowths in the same sample.
**Kaolinite cement**- Kaolinite cement is most abundant in thin section #1 Humble (5057-5068 ft) where it comprises 17% of the rock. It is present as a pore filling around residual feldspar grains (Fig. 13), and formed when waters were in equilibrium with kaolinite (Fig. 20). In all other point-counted thin sections, kaolinite is less abundant, and occurs as an alteration product of feldspar or, more commonly, as a possible orthomatrix. EDX spectra indicate that the poorly crystallized protomatrix and/or orthomatrix is closer to a kaolinite composition than to a chlorite composition (Fig. 10). No attempt was made to determine the proportion of protomatrix versus orthomatrix, but it is possible that recrystallized kaolinite is present.

Kaolinite as a product of feldspar alteration formed after quartz overgrowths. Where kaolinite is present as a possible replacement of protomatrix, quartz overgrowths are poorly developed, and timing of the replacement cannot be determined relative to quartz overgrowths.

**Chlorite as a pore-filling, replacement and recrystallization product**- The most volumetrically significant porosity-occluding cement in the studied thin sections is an iron-rich chlorite. Intergranular clay minerals in the Woodbine are a mixture of kaolinite and iron chlorite. Terminology describing the diagenesis of these minerals becomes confusing because the origin of the clay minerals themselves is unclear. Whenever compacted clay minerals of obvious detrital nature
were observed through the SEM they had a composition similar to that of kaolinite (Fig. 10). Clay minerals in the Woodbine which are uncompacted but lack an observable crystalline structure have a composition closer to that of an iron chlorite (Fig. 11). Clay minerals with an obvious crystalline structure were observed to have a similar chlorite composition.

Whether or not some of the uncompacted, uncrystallized chlorite is detrital is unclear, but a large portion might have resulted from replacement of kaolinite. This replacement chlorite appears to be recrystallizing to a euhedral chlorite of very similar composition (Fe$_{3.6}$Mg$_{1.4}$Al$_{1.4}$Si$_{2.6}$O$_{10}$(OH)$_8$). Because kaolinite and chlorite presently co-exist in the Woodbine, replacement and recrystallization are probably still occurring. Morad (1984) documented a similar reaction in immature arenites where iron and magnesium from biotite alteration are fixed by matrix clays during recrystallization to form an iron-rich chlorite. A source of iron from alteration of biotite not required in the Woodbine because early diagenetic reactions indicate that sediments were initially iron-rich.

To supplement scanning-electron-microscope observations and EDX data, thermodynamic calculations were used to determine whether kaolinite or chlorite should be the stable phase in present waters (Fig. 18). See Appendix E for discussion on calculation of thermodynamic data used to plot Figure 18. Plotted on Figure 18 are the stability fields for kaolinite and chlorite at 25°C and 60°C, the approximate minimum and maximum temperatures measured in the Woodbine in the basin. The graph can then be used to test whether a particular water is in
FIG. 18 - Activity diagram for the reaction kaolinite = chlorite at 25°C and 60°C, the minimum and maximum temperatures measured in the Woodbine in the East Texas Basin, and 1 bar pressure. Activities calculated by WATEQF from data in Appendix B using measured pH values of Woodbine waters. Data points 1-5 are from updip waters near the western basin margin, data points 6-13 are from waters from the deep, central portion of the basin.
equilibrium with one or the other of the minerals. Water chemistry analyses which plot above the equilibrium line are waters in which chlorite is the stable phase, while those which plot below the line represent waters in which kaolinite is the stable phase. Data points (1-5) of updip waters near the western basin margin plot in the kaolinite stability field at 25°C, whereas most data points (6-13) of waters in the deep, central portion of the basin plot in the iron-rich chlorite stability field at 60°C.

From scanning-electron-microscope observations (Figs. 11 and 12) it appears that chlorite is presently precipitating, or is at least stable, in Woodbine waters in the deep, central portion of the basin. These observations plus the data presented on Figure 18 support the theory that detrital clays were originally kaolinite-rich and are still being replaced by and recrystallized to an iron-rich chlorite in the central portion of the basin. Evidence of replacement by and recrystallization to chlorite is shown in Figure 11, and chlorite as a pore-filling in Figure 12.

From Figure 19 it appears that chlorite formation initiated prior to or contemporaneously with quartz-overgrowth formation. The reaction:

\[ 1.4 \text{ kaolinite} + 3.6\text{Fe}^{+2} + \text{Mg}^{+2} + 6.2\text{H}_2\text{O} = \text{chlorite} + 0.2\text{H}_4\text{SiO}_4 + 9.2\text{H}^+ \]  

shows that silica activity in solution increases as chlorite is formed. This provides a possible source of silica for quartz-overgrowth formation. From Figure 20 it is apparent that chlorite formation continued after the cessation of quartz-overgrowth formation.
Fig. 19 - SEM photograph of #1 Stockton (4504 ft) showing a quartz overgrowth (Qog) enveloping euhedral, vermicular chlorite (arrow). X 5000.

Fig. 20 - SEM photograph of #1 Stockton (4504 ft) showing euhedral chlorite flakes growing on a quartz overgrowth (Qog). X 10,000.
Pore-filling calcite cement- Pore-filling calcite cement formed after quartz-overgrowth cementation in clean sands without significant matrix (Figs. 21 and 22). This suggests that organic matter in the matrix has been anarobically fermented to produce carbon dioxide, which lowers local pH conditions. As pH values decrease calcite becomes less stable, and thus is less likely to precipitate. Because calcite and matrix are mutually exclusive in the Woodbine samples studied, textural relationships and relative time of formation of calcite and chlorite cannot be determined.

The thin section from the Woodbine on the flank of the Oakwood Salt Dome (Oakwood, 5500 ft) contains more pore-filling calcite than any other thin section (10.6% of the rock by volume). The Woodbine is truncated by the Oakwood Dome (Giles, 1981), and is therefore in hydraulic contact with the dome. The dome has a well-developed cap rock of anhydrite, calcite, pyrite, and sulfur (Dutton and Kreitler, 1981) which extends down the dome flanks (Giles and Wood, 1981). The presence of calcite in the Woodbine near the dome may indicate that calcite in the cap rock has been dissolved and reprecipitated in the Woodbine, or that the Woodbine was cemented by calcite during cap-rock formation through diagenesis of salt-dome-anhydrite by sulfate-reducing bacteria and oxidation of organic matter (Kreitler and Dutton, 1983).

Pyrite is also present in the Oakwood thin section. Because little or no matrix is present, the pyrite does not appear to be a product of early diagenetic reactions. Pyrite in this thin section also appears to be a product of interaction between the Woodbine and the cap rock.
FIG. 21 - Photomicrograph of #1 Stockton (4504 ft) showing pore-filling calcite (2) after quartz-overgrowth formation (1). High power, crossed polarizers.

Fig. 22 - Same field of view with plane-polarized light.
FIG 23 - Photomicrograph of #1 South Chandler (4855-4860 ft) showing pore-filling barite (2) after quartz overgrowth (1) formation. High power, crossed polarizers.
Pore-filling barite cement- Barite cement also formed after quartz overgrowths in clean sands (Fig. 23). Barite was not observed in contact with pore-filling calcite, and the relative time of formation of the two phases cannot be determined. Timing of the barite cement also cannot be determined relative to chlorite formation.

Barite is present in the Oakwood thin section. This suggests that sulfate activity in Woodbine waters near the Oakwood Salt Dome has been increased due to dissolution of cap rock sulfate minerals, or that barite precipitation was contemporaneous with cap-rock formation. The source of barium required for barite precipitation is unclear. Barite is also present in thin sections #1 South Chandler (4855-4860 ft) and #1 Stockton (4504 ft). Because the Woodbine is not in direct contact with a salt dome near the points represented by the thin sections, cap rock minerals are ruled out as a source of sulfate.

A schematic diagram representing the various late-stage diagenetic events is shown in Figure 24.

Water Chemistry

Water/Rock Interaction- Waters in the Woodbine Group in the East Texas Basin are predominantly Na-C1 type waters (Fig. 25). An isochloride map shows the distribution of salinities in the Woodbine in the basin (Fig. 6). If the area of the cation trilinear diagram in which Woodbine waters plot is expanded (Fig. 26) a trend becomes apparent. As waters become more saline toward the central portion of the basin, calcium concentrations increase relative to sodium.
FIG. 24 - Schematic diagram of relative time of formation of late Woodbine cements, with possible sources of ions and compounds and reaction paths.
FIG. 25 - Piper diagram of common ions in Woodbine water samples in the East Texas Basin. Chemical constituents are plotted as percentages of total milliequivalents. Data points are schematic and represent more than one analysis. Data were derived from Appendix B. See Fig 26 for details of Ca-Na-Mg diagram.
FIG. 26 - Expanded portion of trilinear cation field of previous figure. Numbers are sample numbers from Fig. 2. Salinity increases from points 2,3 to points 7,10.
FIG. 27 - Plot of Na⁺ (moles/1) versus Cl⁻ (moles/1). The dashed line represents a 1:1 molar ratio between Na⁺ and Cl⁻. Note that the data trend below the line, indicating a relative increase of Cl⁻ over Na⁺. Data from Appendix B.

The linear regression line through the data points is:

\[ y = 0.8803x + 0.0390 \ ; \ r = 0.998 \]
In the present study several other trends were observed in Woodbine water chemistry as salinity increases toward the basin center. The dashed line plotted on Figure 27 represents the 1:1 molar ratio of Na⁺ and Cl⁻ which would be expected if dissolution of halite were the only reaction controlling Na⁺ and Cl⁻ concentrations in Woodbine waters. Note that the data deviate from the 1:1 line in the direction of relative enrichment of Cl⁻ over Na⁺. Such enrichment may occur either because excess Cl⁻ is being added to the water, or because Na⁺ is being preferentially removed.

Ca⁺² concentration is plotted against Cl⁻ concentration on Figure 28. There is a marked increase in the Ca⁺² concentration relative to Cl⁻ at approximately 1.3 moles/l Cl⁻.

Both the relative enrichment of Cl⁻ over Na⁺ and the increase in Ca⁺² relative to Cl⁻ may be explained by a 1:1 equivalent exchange of Ca⁺² for Na⁺ on clay minerals. Figure 29 examines the exchange process in more detail. Plotted on Figure 29 are equivalents of Ca⁺² and (Cl⁻ - Na⁺), which represents the excess Cl⁻ over Na⁺. If a 1:1 equivalent exchange of Ca⁺² for Na⁺ is occurring, the data points should plot along the dashed 1:1 line. Note that all but three of the points fall below the line, suggesting that an additional factor is involved.

Plotted on Figure 30 are equivalents of (Ca⁺² + Mg⁺²) and (Cl⁻ - Na⁺). Note that the addition of equivalents of Mg⁺² to equivalents of Ca⁺² causes the data from Woodbine waters to plot very near the dashed 1:1 line. This suggests that Mg⁺² is also involved in the exchange for Na⁺.

Kreitler et al. (in press) suggest two processes as possible
FIG. 28 - Plot of Ca$^{+2}$ (moles/l) versus Cl$^{-}$ (moles/l). Note the marked increase in slope at approximately 1.3 moles/l Cl$^{-}$. Data from Appendix B. Line A ($y = 0.0446x - 0.0121; r = 0.929$); Line B ($y = 0.0895x - 0.0893; r = 0.995$)
FIG. 29 - Plot of Ca\(^{2+}\) equivalents/l (2Ca\(^{2+}\) moles/l) versus excess Cl\(^{-}\) equivalents/l ((Cl\(^{-}\) - Na\(^{+}\)) moles/l). The dashed line represents a 1:1 equivalent ratio between Ca\(^{2+}\) and excess Cl\(^{-}\). Note that the data trend below the line, indicating that a 1:1 equivalent exchange of Ca\(^{2+}\) for Na\(^{+}\) does not entirely account for the excess Cl\(^{-}\) over Na\(^{+}\). Data from Appendix B.

The linear regression through the data points is:
\[ y = 0.8684x + 0.0119; \quad r = 0.928 \]
FIG. 30 - Plot of (Ca\(^{2+}\) + Mg\(^{2+}\)) equivalents/l (2(Ca\(^{2+}\) + Mg\(^{2+}\)) moles/l) versus excess Cl\(^{-}\) equivalent/l ((Cl\(^{-}\) - Na\(^{+}\)) moles/l). The dashed line represents a 1:1 equivalent ratio between (Ca\(^{2+}\) + Mg\(^{2+}\)) and excess Cl\(^{-}\). Note that the data trend close to the 1:1 line, indicating that a 1:1 equivalent exchange of (Ca\(^{2+}\) + Mg\(^{2+}\)) for Na\(^{+}\) may account for the excess Cl\(^{-}\) over Na\(^{+}\). Data from Appendix B. The linear regression line through the data points is:

\[
y = 0.8684x + 0.0119; \ r = 0.928
\]
explanations for the apparent 1:1 equivalent exchange of Ca$^{+2}$ for Na$^{+}$. 

Albitization, as defined by Land and Prezbindowski (1981):

$$\text{plagioclase + halite + water} = \text{Na-Ca-Cl brine + albite},$$

is considered to be the primary reaction responsible for the exchange in the East Texas Basin in waters from formations deeper than the Woodbine. The second process, considered to be less important, is by 2Na$^{+}$ for Ca$^{+2}$ exchange (i.e. a 1:1 equivalent exchange) on clay minerals. The paucity of either plagioclase feldspars or smectites in the Woodbine argues against these reactions as causing the observed changes in water chemistry. However, the presence of Na$^{+}$ on EDX spectra of authigenic chlorite suggests that the exchange might have taken place if the precursor clay was rich in Ca$^{+2}$.

The increase in Ca$^{+2}$ concentration relative to Cl$^{-}$ may also be explained by dissolution of CaSO$_4^{-2}$ in salt dome cap rock, but this would not explain the decrease in Na$^{+}$ concentration relative to Cl$^{-}$, nor do high Ca$^{+2}$ concentrations necessarily correlate with high SO$_4^{-2}$ concentrations (Appendix B). If the SO$_4$ has been reduced to H$_2$S, then high H$_2$S concentrations would be expected to correlate with high Ca$^{+2}$ concentrations. Such a correlation was not observed in Woodbine waters (Appendix B).

Kreitler and Muehlberger (1981) reported the presence of high concentrations of Mg$^{+2}$ in halite and sylvite from the Grand Saline salt dome in the East Texas Basin. The dissolution of these minerals, plus the dissolution of cap-rock anhydrite and subsequent reduction of aqueous sulfate to sulfide, could explain the increase of Ca$^{+2}$, Mg$^{+2}$ and Cl$^{-}$ concentrations relative to Na$^{+}$. 
Authigenic-Mineral-Stability Prediction by WATEQF- Based on petrographic and scanning-electron-microscope examination of Woodbine sandstones, stable authigenic minerals in the deep, central portion of the East Texas Basin appear to be: silica, Fe-Mg chlorite, siderite, calcite, hematite, pyrite, and barite. Appendix C shows the saturation states of authigenic minerals as calculated by WATEQF under three pH conditions: 1) measured pH, 2) measured pH minus 1 unit, and 3) measured pH minus 2 units. Values of pH were reduced in an attempt to compensate for pH increases caused by CO$_2$ out-gassing during sampling. Samples 6 to 13 (Appendix C) are waters in contact with Woodbine sediments represented in part by thin sections point-counted as part of this study.

If measured pH values are used by WATEQF to calculate mineral saturation indices (S.I. = log(IAP/K$_{sp}$)), values greater than zero (supersaturated) are obtained for all authigenic minerals in samples 6-13 except for siderite in sample 8. Sample 8 was taken from a well near the #1 Clark well at approximately the same depth as the thin sections from the #1 Clark well. Authigenic siderite is present in all point-counted thin sections from the #1 Clark well. A yellow-orange precipitate was observed in some water samples as they were transported from the field to the Mineral Studies Lab for analysis. If iron compounds precipitated from sample waters, the possible decrease in measured iron concentration could cause the apparent undersaturation with respect to siderite. However, hematite supersaturation remains high in sample 8. Measured pH could be in error in this sample.

If pH is reduced by 1 unit before it is entered into WATEQF,
calculated saturation states of carbonate minerals and Mg-chlorite drop below saturation in some samples. If pH is reduced by 2 units, Woodbine waters approach or reach undersaturation with respect to all authigenic phases except barite, silica, hematite and pyrite.

As previously discussed, thermodynamic considerations and petrographic and scanning-electron-microscope observations indicate that chlorite is the stable phase relative to kaolinite in Woodbine waters in the deep basin. In the expression for the equilibrium constant for the reaction between chlorite and kaolinite, pH values are raised to the 9.2 power (see Appendix E). This makes stability between the two minerals very sensitive to changes in pH. Reducing pH values by less than one unit causes all data points on Figure 18 to shift into the kaolinite stability field.

Based on the above data and petrographic observations, measured pH values seem to more accurately represent in situ pH in Woodbine waters, and WATEQF gives a fairly accurate representation of individual mineral stability using measured pH values.

WATEQF uses dissociation reactions to calculate saturation states of minerals. As indicated in Appendix C, WATEQF calculates Woodbine waters in the deep basin to be supersaturated with respect to both chlorite and kaolinite, although calculated saturation indices of chlorite are at least four orders of magnitude greater than those calculated for kaolinite at measured pH values. If WATEQF calculates that a solution is supersaturated with respect to two minerals, and those two minerals might potentially interact in the fluid, then thermodynamic calculations based on reactions between the minerals must be utilized to determine
which is the stable phase. Such an approach was described for the reaction between kaolinite and Fe-Mg chlorite in the derivation of Figure 18.
All phases of diagenesis of the Woodbine in the East Texas Basin were controlled largely by the occurrence of organic-rich matrix. Diagenesis was both inhibited and enhanced by matrix material, which restricted pore-water movement but also provided a supply of ions for reaction. Figure 31 is a schematic summary of diagenetic events.

Early diagenesis was largely a product of the interaction between sulfate in waters in the depositional environment, organic-matter-consuming bacteria and iron within Woodbine sediments. Sulfate-reducing bacteria produced sulfide which reacted with iron in the matrix to produce pyrite. After the sulfate influx was shut off with burial the bicarbonate activity controlled the reaction path, and siderite and Fe-calcite precipitated.

The nature of occurrence of matrix material controlled the distribution of early diagenetic minerals. Patches of matrix caused pyrite-siderite-Fe-calcite nodules to form, while disseminated matrix caused disseminated early cements to form.

Late diagenetic reactions were partially controlled by the occurrence of matrix material. Matrix supplied the components and reaction sites for the most important porosity-occluding diagenetic reaction:

\[
\text{matrix kaolinite } \xrightarrow{\text{Fe-Mg chlorite}} \]

Through compaction, and as a product of the above reaction, matrix material provided a supply of silica for quartz-overgrowth cementation of clean sands. However, the presence of matrix physically inhibited the
Fig. 31 - Schematic diagram of relative time of formation of Woodbine cements. Note that "feldspar leaching" is not a cement.
development of quartz overgrowths.

Based on petrographic examination of one thin section from the Woodbine in direct hydraulic communication with a salt dome (Oakwood, 5500 ft), it appears that salt-dome cap rock has been dissolved and locally reprecipitated. The resulting cements (calcite, barite, and pyrite) appear to be volumetrically insignificant.

The low primary porosity values and lack of significant secondary-porosity development in Woodbine sandstones examined in this study suggest that permeability is controlled by structurally induced fracturing. The fact that most oil production in the East Texas Basin occurs near salt structures and faults (Kreitler et al., in press) supports this conclusion.

Woodbine waters in the East Texas Basin have been shut off from Woodbine waters outside the basin northwest of the Mexia-Talco fault system. Woodbine waters in the basin have evolved separately from those outside the basin in response to salt-dome dissolution within the basin. Water/rock interaction has been minimal, but an evolutionary trend from a Na-Cl brine toward a Na-Ca(Mg)-Cl brine has begun in Woodbine waters in the deep, central portion of the basin.

Exchange of Na\(^+\) for Ca\(^{2+}\) on clay minerals and albitization of plagioclase feldspars could explain the concurrent decrease in dissolved-sodium concentrations and increase in calcium concentrations in Woodbine waters. However, neither reaction has been confirmed in this study. The increase in calcium, magnesium, and chloride concentrations relative to sodium concentrations could be the result of the dissolution of anhydrite and magnesium-rich chlorides in salt domes.
WATEQF output appears to accurately represent in situ individual mineral-saturation states in Woodbine waters at the pH values measured. However, to get an accurate picture of relative mineral stability between mineral pairs, individual mineral pairs must be tested thermodynamically.
REFERENCES


———, and Ward, W. C., 1957, Brazos River bar, a


APPENDICES
Appendix A. Mineral Identification by X-Ray Diffraction.

Non-clay minerals are listed in order of decreasing abundance based on relative peak heights. The major clay mineral, based on relative peak height, is underlined.
<table>
<thead>
<tr>
<th>WELL NAME AND DEPTH (Ft.)</th>
<th>MINERALOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC-3 (outcrop)</td>
<td>Quartz, Chlorite, Illite</td>
</tr>
<tr>
<td>OC-4 (outcrop)</td>
<td>Quartz, Chlorite</td>
</tr>
<tr>
<td>OC-40B (outcrop)</td>
<td>Quartz, Kaolinite, Chlorite, Illite</td>
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<td>Oakwood Dome (5500)</td>
<td>Quartz, K-Feldspar, Calcite, Chlorite, Kaolinite</td>
</tr>
<tr>
<td>Sun #1 Boyling (4650)</td>
<td>Quartz, Calcite, Kaolinite, Illite, Chlorite</td>
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<td>#1 South Chandler (4845-4850)</td>
<td>Quartz, Siderite, Pyrite, Kaolinite, Chlorite, Illite</td>
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<td>#1 South Chandler (4855-4860)</td>
<td>Quartz, Calcite, Kaolinite, Chlorite, Illite</td>
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<tr>
<td>#1 South Chandler (4865)</td>
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Appendix B. Water Chemistry Data.

Water chemistry data are from wells listed in Table 1 and located on Figure 2. All concentrations are listed as mg/L as reported by the Mineral Studies Lab, Bureau of Economic Geology, Univ. of Texas at Austin.
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<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>SO₄</th>
<th>HCO₃</th>
<th>Br</th>
<th>I</th>
<th>Al</th>
<th>Fe</th>
<th>SiO₂ (C°)</th>
<th>Temp.</th>
<th>pH</th>
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<td>19</td>
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Appendix C. Saturation Indices Calculated by WATEQF.

WATEQF output of mineral saturation indices of Woodbine waters. Saturation indices were calculated at the measured pH (pH), measured pH - 1 pH value (pH - 1), and measured pH - 2 pH values (pH - 2). Samples are listed in Table 1 and located on Figure 2. Input water chemistry data are listed in Appendix B.
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## AUTHIGENIC MINERALS

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Appendix D. Petrographic Data.

Summaries of detailed mineralogies, and textural and statistical parameters of point-counted and visually estimated thin sections precede individual data sheets.

Percentages of matrix and authigenic clays are approximate, based on observations through a petrographic microscope.

Cumulative-frequency plots have been corrected to account for estimated weight percent matrix (lower curve).

Where matrix comprises greater than 5% of the rock by volume only the graphic mean and median grain size can be calculated.
## Composition and Proxosity of Point-Counted Thin Sections

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All Data From Point-counted Thin Sections.  TR = Trace
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<th>Grain Shape (% of grains)</th>
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All Data From Point-Counted Thin Sections  TR = Trace
### Composition, Porosity and Grain Size of Visually Estimated Thin Sections

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All data from Visually Estimated Thin Sections. TR = Trace
THIN SECTION: OC-3 (outcrop)

Rock Name

Very fine-grained, poorly sorted, submature, chlorite- and iron oxide- cemented, metamorphic- and sedimentary-rock-fragment-bearing quartzarenite.

Porosity

21.3%, all of which is primary.

Statistics

Graphic mean ($M_2$): 3.03 $\phi$, 0.12 mm - very fine-grained.
Median grain size: 3.00 $\phi$, 0.13 mm - very fine-grained.
Inclusive graphic standard deviation ($\phi_1$): 1.11 $\phi$, very poorly sorted.
Inclusive graphic skewness ($SK_1$): +0.07, near-symmetrical.
Graphic kurtosis ($K_C$): +0.82, platykurtic.

Paragenetic Sequence

1. formation of chlorite rims
2. compaction
3. feldspar leaching (minor)
4. syntaxial quartz overgrowths (minor)
5. pore-filling iron oxide/chlorite cement
THIN SECTION: OC-3
(Outcrop)
THIN SECTION: OC-4 (outcrop)

Rock Name


Porosity

21.5%, all of which is primary.

Statistics

Graphic mean ($M_z$): 2.65 $\phi$, 0.16 mm - fine-grained.
Median grain size: 2.61 $\phi$, 0.17 mm - fine-grained.
Inclusive graphic standard deviation ($\sigma_1$): 1.02 $\phi$, poorly-sorted.
Inclusive graphic skewness ($SK_1$): +0.25, strongly fine-skewed.
Graphic kurtosis ($K_G$): +0.65, platykurtic

Paragenetic Sequence

1. formation of chlorite rims (minor)
2. compaction
3. feldspar leaching (minor)
4. syntaxial quartz overgrowths
5. pore-filling iron oxide with minor admixed chlorite
THIN SECTION: OC-4
(Outcrop)
THIN SECTION: OAKWOOD DOME (5500 ft) (1)

Rock Name

Very fine-grained, poorly sorted, submature, calcite-, quartz-overgrowth-, chlorite-, and pyrite-cemented, chert-bearing quartzarenite.

Porosity

8%, all but a trace of which is primary.

Statistics

Graphic mean ($M_z$): 3.52 $\phi$, 0.09 mm - very fine-grained.
Median grain size: 3.50 $\phi$, 0.09 mm - very fine-grained.
Inclusive graphic standard deviation ($\phi_I$): 1.22 $\phi$, poorly-sorted.
Inclusive graphic skewness ($SK_1$): +0.03, near-symmetrical
Graphic kurtosis ($K_G$): +1.21, leptokurtic.

Paragenetic Sequence

1. formation of chlorite rims (minor)
2. compaction
3. feldspar leaching (minor)
4. syntaxial quartz overgrowths
5. kaolinite cement (minor)
6. chlorite cement
7. pore-filling pyrite cement
8. pore-filling calcite cement
9. pore-filling barite cement (minor)
THIN SECTION: Oakwood Dome (5500 ft)
Rock Name


Porosity

0.5%, all of which is primary.

Statistics

Median grain size: 2.66 Ø, 0.24 mm - fine-grained.

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide
3. formation of Fe-calcite (minor)
4. compaction
5. feldspar leaching (minor)
6. syntaxial quartz overgrowths
7. syntaxial feldspar overgrowths (minor)
8. kaolinite cement
9. chlorite cement
THIN SECTION: Sun #1 Boyling (4650 ft)
THIN SECTION: #1 STOCKTON (4465-4484 ft) (03)

Rock Name

Fine-grained, immature, chlorite-, quartz-overgrowth-, and iron oxide-cemented, iron oxide-, chert-, and tourmaline-bearing subarkose.

Porosity

7.4%, all but a trace of which is primary.

Statistics

Graphic mean ($M_2$): 2.85 $\Phi$, 0.14 mm - fine-grained.
Median grain size: 2.80 $\Phi$, 0.15 mm - fine-grained.

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide
3. formation of Fe-calcite (minor)
4. compaction
5. syntaxial quartz overgrowths
6. syntaxial feldspar overgrowths (minor)
7. kaolinite cement (minor)
8. chlorite cement
THIN SECTION: #1 Stockton
(4465-4484 ft)
THIN SECTION: #1 STOCKTON (4504 ft) (03)

Rock Name


Porosity

18.5%, all but a trace of which is primary.

Statistics

Graphic mean ($M_z$): 2.56 $\bar{D}$, 0.17 mm - fine-grained.
Median grain size: 2.50 $\bar{D}$, 0.18 mm - fine-grained.
Inclusive graphic standard deviation ($\varphi_1$): 1.04 $\bar{D}$, poorly-sorted.
Inclusive graphic skewness ($SK_1$): +0.14, fine-skewed.
Graphic kurtosis ($K_G$): +0.94, mesokurtic.

Paragenetic Sequence

1. nodular pyrite (minor)
2. oxidation of pyrite to iron oxide (minor)
3. formation of Fe-calcite/siderite
4. formation of chlorite rims (minor)
5. compaction
6. feldspar leaching (minor)
7. syntaxial quartz overgrowths
8. kaolinite cement (minor)
9. chlorite cement
10. pore-filling calcite cement
11. pore-filling barite cement (minor)
THIN SECTION: #1 Stockton
(4504 ft)
Rock Name

Very fine-grained, immature, siderite-, chlorite-, kaolinite-, quartz-overgrowth-, iron oxide-, and pyrite-cemented, metamorphic-, and sedimentary-rock-fragment-, and chert-bearing subarkose.

Porosity

A trace, all of which is primary.

Statistics

Graphic mean ($\bar{M}_2$): 3.21 $\phi$, 0.19 mm - very fine-grained.  
Median grain size: 3.22 $\phi$, 0.18 mm - very fine-grained.

Paragenetic Sequence

1. nodular pyrite  
2. oxidation of pyrite to iron oxide  
3. formation of Fe-calcite/siderite  
4. formation of chlorite rims (minor)  
5. compaction  
6. feldspar leaching (minor)  
7. syntaxial quartz overgrowths  
8. syntaxial feldspar overgrowths (minor)  
9. kaolinite cement  
10. chlorite cement
THIN SECTION: #1 South Chandler
(4845-4850 ft)

PHI SCALE

CUMULATIVE WEIGHT PERCENT

WEIGHT PERCENT

Gravel  v.cse  cse  med  fine  v.f.  cse  med  fine  v.f.
Sand    Silt

MODIFIED WENTWORTH SCALE
THIN SECTION: #1 SOUTH CHANDLER (4855-4860 ft) (14)

Rock Name

Very fine-grained, immature, chlorite-, calcite-, quartz-overgrowth-, and pyrite-cemented, metamorphic-rock-fragment-bearing quartzarenite.

Porosity

4.2%, all but a trace of which is primary.

Statistics

Graphic mean ($M_2$): 3.07 $\bar{\phi}$, 0.12 mm—very fine-grained.
Median grain size: 3.15 $\bar{\phi}$, 0.11 mm—very fine-grained.

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide (minor)
3. formation of Fe-calcite/siderite
4. formation of phosphatic cement
5. formation of chlorite rims (minor)
6. compaction
7. feldspar leaching (minor)
8. syntaxial quartz overgrowths
9. kaolinite cement (minor)
10. chlorite cement
11. pore-filling calcite and barite cements (minor)
THIN SECTION: #1 South Chandler
(4855-4860 ft)
THIN SECTION: #1 SOUTH CHANDLER (4885 ft) (□4)

Rock Name


Porosity

A trace, all of which is primary.

Statistics

Graphic mean ($M_2$): 2.60 $\phi$, 0.16 mm - fine-grained.
Median grain size: 2.42 $\phi$, 0.19 mm - fine-grained.

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide (minor)
3. formation of Fe-calcite/siderite
4. formation of chlorite rims (minor)
5. compaction
6. syntaxial quartz overgrowths (minor)
7. kaolinite cement
8. chlorite cement
9. pore-filling calcite cement
THIN SECTION: #1 South Chandler
(4885 ft)

MODIFIED WENTWORTH SCALE
THIN SECTION: #1 HUMBLE (5057-5068 ft) (D5)

Rock Name

Medium-grained, moderately well-sorted, submature, kaolinite-, chlorite-, and quartz-overgrowth-cemented, sedimentary-, and metamorphic-rock-fragment-, and chert-bearing subarkose.

Porosity

12.4%, 60% of which is secondary.

Statistics

Graphic mean ($M_2$): 1.86 $\phi$, 0.28 mm - medium-grained.
Median grain size: 1.85 $\phi$, 0.28 mm - medium-grained
Inclusive graphic standard deviation ($\phi_1$): 0.53 $\phi$, moderately well-sorted.
Inclusive graphic skewness ($SK_1$): +0.05, near-symmetric.
Graphic kurtosis ($K_G$): +0.93, mesokurtic.

Paragenetic Sequence

1. nodular pyrite (minor)
2. oxidation of pyrite to iron oxide (minor)
3. compaction
4. feldspar leaching
5. syntaxial quartz overgrowths
6. formation of chlorite rims
7. pore-filling kaolinite cement
THIN SECTION: 1 Humble
(5057-5068 ft)
Rock Name

Very fine-grained, immature, siderite-, calcite-, and chlorite-cemented, metamorphic-rock-fragment-, iron oxide-, and chert-bearing subarkose.

Porosity

4.6%, all but a trace of which is primary.

Statistics

Median grain size: 3.37 Ø, 0.10 mm - very fine-grained.

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide
3. formation of Fe-calcite/siderite
4. compaction
5. syntaxial quartz overgrowths (minor)
6. kaininite cement (minor)
7. chlorite cement
THIN SECTION: #1 Clark
(3255 ft)
THIN SECTION: #1 CLARK (3263 ft) (16)

Rock Name


Porosity

8.7%, all but a trace of which is primary.

Statistics

Graphic mean ($M_z$): 2.49 $\phi$, 0.18 mm - fine-grained.
Median grain size: 2.42 $\phi$, 0.19 mm - fine-grained.
Inclusive graphic standard deviation ($\phi_i$): 0.66 $\phi$, moderately well-sorted.
Inclusive graphic skewness ($SK_1$): +0.01, near-symmetrical
Graphic kurtosis ($KG_1$): +1.20, leptokurtic

Paragenetic Sequence

1. nodular pyrite
2. oxidation of pyrite to iron oxide (minor)
3. formation of Fe-calcite/siderite
4. compaction
5. feldspar leaching (minor)
6. syntaxial quartz overgrowths (minor)
7. kaolinite cement
8. chlorite cement
THIN SECTION: #1 Clark (3263 ft)
Rock Name

Bimodal, very fine- and fine-grained, immature, chlorite-, calcite-, and siderite-cemented, metamorphic- and sedimentary-rock-fragment-, and chert-bearing subarkose.

Porosity

4.3%, all but a trace of which is primary.

Statistics

Median grain size: 3.30 φ, 0.10 mm - very fine-grained

Paragenetic Sequence

1. nodular pyrite (minor)
2. oxidation of pyrite to iron oxide (minor)
3. formation of Fe-calcite/siderite
4. formation of chlorite rims (minor)
5. compaction
6. feldspar leaching (minor)
7. syntaxial quartz overgrowths (minor)
8. kaolinite cement (minor)
9. chlorite cement
10. pore-filling calcite cement
THIN SECTION: #1 Clark
(3304 ft)
Appendix E. Thermodynamic-Data Calculations for Chlorite-Kaolinite Stability Predictions.
Thermodynamic Data Calculations for Chlorite-Kaolinite

Stability Predictions

Thermodynamic Theory - For any reaction, equilibrium is approached as the energy of reaction ($\Delta G_T$) approaches zero. The energy conditions for any reaction can be defined by the expression

$$\Delta G_T = \Delta G_T^0 + RT \ln Q$$

where $G_T^0$ is the free energy of the system in its standard state at temperature $T$, $R$ is the gas constant, and $Q$ is the quotient of the product and reactant activities. At equilibrium $\Delta G_T = 0$, and

$$\Delta G_T^0 = -RT \ln Q$$

where $Q$ has a constant value, the equilibrium constant $K$

$$\Delta G_T^0 = -RT \ln K$$

$\Delta G_T^0$ of a reaction can be calculated by the difference between summed $\Delta G_T^0$ values of products and reactants involved in the reaction at the desired temperature. $\Delta G_T^0$ values of the contributing components in the reaction at temperature $T$ are calculated by the expression

$$\Delta G_T^0 = \Delta H_{f,T}^0 - T \Delta S^0$$

where $\Delta H_{f,T}^0$ and $\Delta S^0$ are the enthalpy of formation and the entropy respectively. Values for these functions at 25°C are listed in Robie et al. (1978). To calculate $\Delta H_{f,T}^0$ and $\Delta S^0$ at higher temperatures, the values at 25°C must be adjusted by using heat-capacity power functions or, for aqueous species, average heat capacities (Helgeson, 1969)

$$\Delta H_{f,T}^0 = \Delta H_{f,298}^0 + 298 \int_{298}^{T} Cp \, dT \quad (1)$$

$$\Delta S_T = \Delta S_{298}^0 + 298 \int_{298}^{T} \frac{Cp}{T} \, dT \quad (2)$$
where $C_p$ is the heat-capacity expression.

At temperature $T$, $\log K$ can be calculated by the expression

$$\log K = -\frac{\Delta G_{fT}}{2.303RT}$$

For any reaction $K = \frac{a_{\text{PRODUCTS}}}{a_{\text{REACTANTS}}}$, where $a$ is the activity. Taking the log of both sides of the equation, an equation for a straight line results in:

$$\log(a_{\text{PRODUCTS}}) - \log(a_{\text{REACTANTS}}) = \log K$$

which represents equilibrium between the phases and species in the reaction. The equation can be plotted using $a_{\text{REACTANTS}}$ and $a_{\text{PRODUCTS}}$ as the axes. Water chemistry data from wells can then be plotted on the diagram, and, depending on which side of the line representing the above equation the data plot, will indicate whether products or reactants will be stable in a given water.

**Thermodynamic-Data Calculations for Woodbine Chlorite**—During an attempt to predict the thermodynamic stability of a member of the chlorite solid-solution series, a problem arises because there are no measured values of $\Delta G_{f}^{\circ}, \Delta S_{f}^{\circ}$, or $C_p$ other than those for the iron and magnesium end-members. In order to predict the stability of a given chlorite, enthalpy and entropy must be estimated from measured values of components which could theoretically react to produce the chlorite (Tardy and Garrels, 1974; Eugster and Chou, 1973; Nriagu, 1975; and Ballantyne, 1981). Once these data have been estimated at $25^\circ C$ they can be calculated at higher temperatures by combining them with heat-capacity power functions as in equations (3) and (4) (Helgeson, 1969)

$$\Delta H_{fT}^{\circ} = \Delta H_{f}^{\circ, 298} + a(T-298) + b/2(T^2-298^2) - c(1/T-1/298) \quad (3)$$
\[ \Delta S^0_T = \Delta S^0_{298} + a \ln T/298 + b(T-298) - c/2(1/T^2 - 1/298^2) \quad (4) \]
in which the last three terms in each expression represent the integrated heat-capacity power function for the mineral. The heat-capacity power function can be approximated from known power functions of mineral end-members, or by summation of the power functions of components used to produce the mineral hypothetically (Helgeson et al., 1978; Ballantyne, 1981). The calculated values of \( H^0_{f,T} \) and \( S^0_T \) for chlorite can then be used in calculating the equilibrium constant for a reaction involving another mineral, as in equation (5) (Helgeson, 1969):

\[ \log K(T) = T(\Delta S^0_{T,PRODS.} - \Delta S^0_{T,REACTS.}) - (\Delta H^0_{f,T,PRODS.} + \Delta H^0_{f,T,REACTS.})/2.303RT \quad (5) \]

**Chlorite-Kaolinite Stability in the Woodbine**—Based on qualitative EDX spectra from the scanning-electron-microscope, the composition of authigenic chlorite identified in the Woodbine was estimated to be

\[ Fe_{3.6}MgAl_{1.4}(Al_{1.4}Si_{2.6}O_{10})(OH)_8 \]

Based on scanning-electron-microscope observations, EDX spectra, x-ray diffraction, and petrographic techniques, kaolinite was also identified in the Woodbine. Thermodynamic data are well established for kaolinite. In order to predict chlorite-kaolinite stability, thermodynamic data must be estimated for the chlorite. Thermodynamic data were estimated by two methods.

The first method follows the preceding outline. The hypothetical reaction used to produce the observed chlorite was:
Talc rather than brucite was used to produce the chlorite because
talc's structural state is similar to that of chlorite. This minimizes
the error induced by differences in structural bond energies between
silicates of different structural complexity.

\[ \Delta H_f^{25} (-1795 \text{ kcal/mole}) \text{ and } \Delta S_f^{25} (0.162 \text{ kcal/mole K}) \]
were obtained by summing the values for the reactants (Robie et al., 1978) in the
above reaction. Enthalpy and entropy for the chlorite at 60°C were
calculated using equations (3) and (4) respectively. The heat-capacity
power function for an iron-magnesium chlorite (Kaiser, 1984) was used
for the chlorite in this study. \( \Delta H_f^{0,T} \text{ and } \Delta S_f^{0,T} \) were calculated to be
-1790 kcal/mole and 0.174 kcal/mole K respectively.

The reaction used to calculate equilibrium between kaolinite and
chlorite is:

\[
1/3\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3.6\text{H}_2\text{O} + 1.4\text{Al}_2\text{O}_3 + 3.6\text{FeO} + 1.3\text{SiO}_2 = \]

\[
\text{Fe}_{3.6}\text{MgAl}_{1.4}(\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_{10})(\text{OH})_8
\]

from which the equilibrium constant

\[
K = (a_{H^+})^{9.2}(a_{\text{H}_4\text{SiO}_4})^{0.2}/(a_{\text{H}_2\text{O}})^{6.2}(a_{\text{Mg}^2})(a_{\text{Fe}^2})^{3.6}
\]  

In order to calculate log \( K \) for the kaolinite-chlorite reaction
\( \Delta H_f^{0,T} \text{ and } \Delta S_f^{0,T} \) must be calculated for all phases and species in the
reaction using equations (1) and (2) respectively. The heat-capacity
power function for kaolinite was taken from Helgeson et al. (1978).

Average heat capacities of \( \text{Fe}^{+2} \) and \( \text{Mg}^{+2} \) were calculated by the
relationship:
\[ C = 35 - 0.41S^0_{25} \] (Criss and Cobble, 1964),
where \( S^0_{25} \) = absolute entropy.

Average heat capacity, entropy, and enthalpy of \( H_4SiO_4 \) at 25°C were calculated from the reaction:

\[ SiO_2 + 2H_2O = H_4SiO_4 \]

Enthalpy and entropy for water were assumed to remain constant over the 35°C temperature range. Values were taken from Robie et al. (1978).

The equilibrium constant for the reaction between chlorite and kaolinite at 60°C was calculated from equation (5):

\[ \log K_{60°C} = -60.2 \text{ kcal/mole} \]

The second method used to calculate an equilibrium constant for the chlorite-kaolinite reaction assumed that entropy and enthalpy remain constant for all phases and species involved in the reaction over the 35°C temperature range. The same hypothetical reaction was used to produce the chlorite, and the same reaction between kaolinite and chlorite was used to predict mineral stability.

Enthalpy and entropy of chlorite at 25°C were again calculated by summation of contributing components in the reaction.

\[ \Delta H_f = -1795 \text{ kcal/mole} \]
\[ \Delta S^0 = 0.162 \text{ kcal/mole} \]

However, \( \Delta C^O_r \) at 60°C was then calculated from the relationship:

\[ \Delta G_{f,T} = H_f - T\Delta S^0 \]
\[ = -1848.9 \text{ kcal/mole} \]

This value was then used to calculate \( \Delta G^O_r \) for the kaolinite-chlorite reaction by the expression:
reaction by the expression:

$$\Delta G^0_T = \Delta G^0_{f,Y PRODS} - \Delta G^0_{f,Y REACTS}.$$  

Thermodynamic data for all other phases and species involved in the reaction were taken from Robie et al. (1978); and

$$\log K_{60^\circ C} = -\frac{\Delta G^0_T}{2.303RT} = -49.5 \text{ kcal/mole}$$

Expression (6) can be written in the form of an equation for a straight line and plotted on a graph:

$$\log (a_{H^+})^9.2(a_{H_4SiO_4})^{0.2}/(a_{H_2O})^{6.2} - \log (a_{Mg^{+2}})(a_{Fe^{+2}})^{3.6} = \log K$$

where $$\log (a_{H^+})^9.2(a_{H_4SiO_4})^{0.2}/(a_{H_2O})^{6.2}$$ and $$\log (a_{Mg^{+2}})(a_{Fe^{+2}})^{3.6}$$ are represented by the x and y axes respectively (Fig.17). The resulting straight line represents kaolinite-chlorite equilibrium, and marks the boundary between stability fields of the two minerals. The graph can then be used to test whether a particular water is in equilibrium with one or the other of the minerals. Water-chemistry analyses which plot above the line represent waters in which chlorite is the stable phase, while those which plot below the line represent waters in which kaolinite is the stable phase.

From scanning-electron-microscope observations (Figs.10 and 11) it appears that chlorite is presently precipitating, or is at least stable, in Woodbine waters in the deep, central portion of the basin. If the first approach outlined above is used to estimate chlorite thermodynamic data, the resulting line representing chlorite-kaolinite equilibrium plots well above water chemistry data points 6 through 13. These data points are from waters from the central portion of the basin...
which are apparently at least saturated with respect to chlorite at 60° C. For this reason the second approach is considered to more accurately represent stability relationships between kaolinite and chlorite in the Woodbine, and is used to construct the stability fields in Figure 17.

The source of error between log K values calculated by the two methods probably lies in the calculated $\Delta H^\circ_{f,T}$ values of iron and, to a lesser extent, magnesium. The discrepancy may result from the use of average heat capacities in calculating the enthalpy of iron and magnesium at 60° C.