

# Chemical Constraints and Origins of Four Groups of Gulf Coast Reservoir Fluids<sup>1</sup>

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## ABSTRACT

Pitzer's method for computing activity coefficients has been applied to reported fluid compositions in four groups of Gulf Coast reservoirs: the Mississippi and Arkansas Smackover Formation, the Texas Edwards Group, The Texas Frio Formation, and the Louisiana Miocene sequence. The activity quotients in fluids from carbonate reservoirs imply a reaction relation between calcite and disordered dolomite, in which ordering increases at higher temperatures. This relationship indicates that an increasing Mg:Ca molality ratio with decreasing temperature does not necessarily imply dolomite dissolution by an updip-moving fluid. Instead, it may reflect an approach to equilibrium between calcite and metastable dolomite. Activity quotients in fluids from clastic reservoirs imply a reaction relation between chlorite, illite, potassium feldspar, and quartz at temperatures above 100°C (212°F).

Present fluid compositions in the Smackover and the Edwards appear to be related to the updip movement of Louann brines from the Gulf Coast basin, accompanied by dolomitization. In particular, bromide plots for the Edwards fluids indicate simple dilution of Louann brines with interstitial fluids. Similar plots for fluids from the Smackover show the complicating effects of illite formation, sylvite dissolution, and halite recrystallization. Albitization may have occurred during fluid movement through clastics prior to entering the Smackover and Edwards.

Present fluid compositions in the Frio and Miocene are apparently not related to Louann brines. The compositional data reflect the effects of halite dissolution, the subsequent albitization of plagioclase and potassium feldspar, and the dissolution of carbonates during secondary porosity formation.

## INTRODUCTION

Reservoir fluids refer to the aqueous solutions within nonshale sedimentary units. These units may sometimes

be open to fluid flow during their geologic history. The effects of fluid movement and mixing, mineral dissolution and precipitation, diffusion from adjacent shales, and organic maturation reactions are reflected in the present-day chemical compositions of reservoir fluids.

In this paper we attempt to explain the origin of fluid compositions within selected Gulf Coast reservoirs, based on chemical relationships between mineral diagenesis and fluid compositions. This study is part of a continuing research effort to delineate geochemical constraints on diagenesis within reservoirs.

## PROCEDURES

The conclusions reached in this study are based on a reexamination of the data and ideas of other researchers (e.g., Carpenter et al, 1974; Merino, 1975; Hower et al, 1976; Kharaka et al, 1977; Carpenter, 1978, 1980; Boles and Frank, 1979; Moore and Druckman, 1981; Land and Prezbindowski, 1981). Present fluid chemistries and late diagenetic events are discussed in terms of fluid mixing and water-rock interactions. We have not attempted to integrate stable isotope data into our arguments.

Unless otherwise noted, conditions governing mineral equilibria were calculated from the thermodynamic data base and standard state computational procedures developed by Helgeson and coworkers (Helgeson, 1969; Helgeson and Kirkham, 1974a, 1974b, 1976; Walther and Helgeson, 1977; Helgeson et al, 1978; Helgeson et al, 1981). Phase relations referenced to Robie were computed using the 25°C (77°F) standard-state properties from Robie et al (1979), and the heat-capacity power function coefficients from Helgeson et al (1978). The 25°C standard-state properties of NaBr<sub>s</sub> were taken from Wagman et al (1981) and the heat-capacity power coefficients were fitted with the data of Gardner and Taylor (1964). The stabilities of illites were estimated from solid solution models developed by Stoessel (1979, 1981). Chlorite solubility data (Kittrick, 1982) and an estimated clinoclhorite stability (Helgeson et al, 1978) were used in a six end-member regular solution site-mixing model (Stoessel, 1983) to predict chlorite stabilities. Equilibrium computations were done with *Maddog*, a computer program written by Stoessel (1977).

Pitzer's method (Pitzer, 1975, 1979; Harvie and Weare, 1980) was utilized to compute mean salt single-ion activity coefficients in computations of activities in brines. The temperature dependencies at 25°C (77°F) for the single-salt parameters in Pitzer's equation for salt mixtures were used to correct these parameters to reservoir temperatures. We realize this may produce significant error in calculated activity coefficients; however, use of activity ratios will

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presumably cancel much of this error. The possibly significant amounts of chloride complexing in these brines (Kester and Pytkowicz, 1975; Johnson and Pytkowicz, 1978) make it difficult to compute free-ion activities, necessitating a mean-salt approach.

Molality units are used in this study. Densities, required to compute molalities, were not always reported for reservoir fluids. For these cases, densities were estimated from a plot of total dissolved solids versus measured densities of Gulf Coast fluids. Data plotted on the figures representing the 25°C evaporation of seawater are from Carpenter (1978, Table 4) for water from the Black Sea.

Lines representing equilibrium between mineral phases as a function of temperature are plotted on several figures. These lines were interpolated from the following PT points: 20°C (68°F), 1 bar; 60°C (140°F), 150 bars; 100°C (212°F), 300 bars; 150°C (302°F) 500 bars; and 200°C (392°F) 700 bars. These points correspond to a PT gradient of about 0.26°C/bar (0.032°F/psi) or a hydrostatic gradient of approximately 0.8°C/30 m (1.4°F/100 ft).

## RESERVOIR FLUIDS

### Edwards Group

Prezbindowski (1981) described the diagenetic sequence within the Lower Cretaceous carbonates of the Edwards Group in south-central Texas. Documented late diagenetic events, following hydrocarbon migration, include dedolomitization, precipitation of strontium-rich equant spar calcite, and minor limestone replacement by fluorite and galena. The present chemical compositions of aqueous solutions within the Edwards Group were reported by Land and Prezbindowski (1981). Their hypothesis for the origin of these fluids depends on halite dissolution and albitization occurring deep within the Gulf of Mexico basin at temperatures between 200 and 250°C (392 and 482°F). These temperatures are considerably greater than those existing in the reservoirs from which fluid samples were taken. Albitization was not actually observed; however, it was justified on the basis of being a known diagenetic process in Gulf Coast reservoirs. Halite dissolution and albitization were used to explain high dissolved-salt contents in the deeper reservoirs and the low Na:Cl ratio in all solutions. The brines were assumed to undergo dilution and to be "grossly undersaturated with respect to dolomite." Dedolomitization by an updip-moving fluid was used to explain the increase in the concentration ratio of aqueous magnesium to calcium in the updip direction.

We have used the data from Land and Prezbindowski (1981, Table 1) in Figures 1 to 5. There is an excellent fit to the 25°C (77°F) seawater evaporation line for the molality of chloride plotted versus molality of bromide in the waters of the Edwards Group. Similarly excellent fits are shown in Figures 2 and 3 for the molality of potassium and equivalents of calcium + magnesium per kilogram of water, respectively, plotted versus chloride molality. These correlations imply that the aqueous fluids in the Edwards Group are the result of mixing of seawater evaporated to halite saturation with waters of present-day seawater composition. In Figure 4, sodium molality is plotted versus

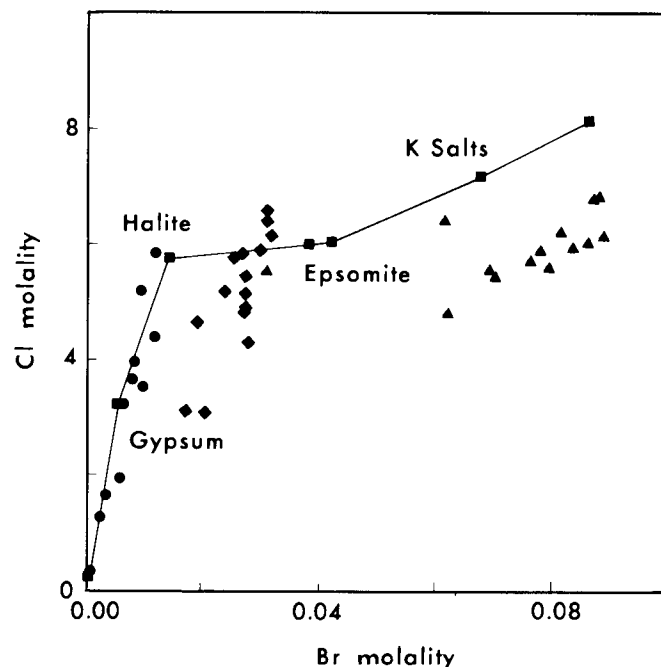
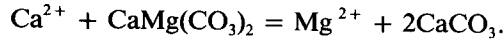


FIG. 1—Plot of chloride molality versus bromide molality in reservoir fluids from Texas Edwards (black dots), Arkansas Smackover (black triangles), and Mississippi Smackover (black diamonds). Solid line on this and subsequent molality plots represents 25°C (77°F) seawater evaporation. Where appropriate, points marking saturation with respect to evaporite minerals are labeled.

chloride molality for waters from the Edwards Group. These data define an almost straight mixing line between a solution similar to present-day seawater and a fluid having a lower Na:Cl molality ratio than present-day seawater concentrated to initial halite saturation.

The relationships shown on Figures 1 to 3 could not be obtained by dissolving halite. Clearly, an aqueous solution, related to the precipitation of an evaporite deposit, has moved updip through the Edwards Group, mixing with interstitial waters of marine origin. This solution was probably a Louann brine. The decrease in sodium relative to chloride could be due to albitization, as suggested by Land and Prezbindowski (1981), or it could be due to seawater having a lower Na:Cl ratio at the beginning of the Mesozoic. We believe albitization within clastics at higher temperatures to be the most probable cause. The Louann brine could have passed through clastics prior to entering the Edwards. However, massive albitization in the clastic Frio Formation of Texas (Land and Milliken, 1981) has failed to lower the Na:Cl ratios in solutions of lower salinity than those in the deep Edwards. The average Na:Cl molality ratio is 1.00 in the Frio (Kharaka et al, 1977) compared to 0.71 in the Edwards. Similarly high ratios are shown in subsurface waters within other Gulf Coast clastic reservoirs. For example, Dickey et al (1972) and Kharaka et al (1978) reported average values of 0.98 and 0.88, respectively, from Tertiary reservoirs in southwest Louisiana. Presumably, the lower temperatures in the Tertiary units account for the ineffectiveness of albitization in lowering the Na:Cl ratio, by lowering the reaction rate.

Computed activity ratios of magnesium to calcium are plotted on Figure 5 versus temperature. We can test for equilibrium between calcite and dolomite in the reaction:



Ratios denoting equilibrium are plotted on the figure, using mineral data from Helgeson et al (1978) and Robie et al (1979). The effect of disorder on dolomite stability is shown by the separation of the two lines computed with Helgeson's data. Not shown is the destabilizing effect of the high density of lattice growth defects which are common in Holocene calcium-rich dolomites (Reeder, 1981). Solution data from the Edwards show a consistent trend, going from an apparent reaction relationship at low temperatures with a disordered dolomite to one with an ordered dolomite at higher temperatures. This is precisely what we would expect. We realize that a consistent trend is no proof of metastable equilibrium between calcite and dolomite; however, it does suggest the possibility.

A similar trend is shown in molality ratios of magnesium to calcium. Pitzer's method for computing activity coeffi-

cients predicts somewhat higher values for magnesium than calcium, making the molality ratios slightly lower than the activity ratios shown on Figure 5. We want to emphasize that an increasing ratio of magnesium to calcium molalities with decreasing temperature does not necessarily indicate that a fluid moving updip is dissolving dolomite. The same trend would be expected if calcite and metastable dolomite were to maintain aqueous equilibrium over the temperature range.

#### Smackover Formation

Carpenter and coworkers (Carpenter et al, 1974; Trout, 1974; Carpenter and Trout, 1978) have reported chemical compositions of subsurface waters in the carbonate Smackover Formation (Jurassic) in Mississippi and Arkansas. They concluded that these waters probably originated as interstitial fluids in the underlying Louann Salt. They supported this conclusion with plots of compositional data similar to Figures 1 to 4, but in log units. Their hypothesis has a Mg-SO<sub>4</sub>-K brine moving up through the Jurassic section, resulting in dolomitization of calcite, precipitation of anhydrite as well as sulfate reduction, and illitization of smectites and kandites. The result-

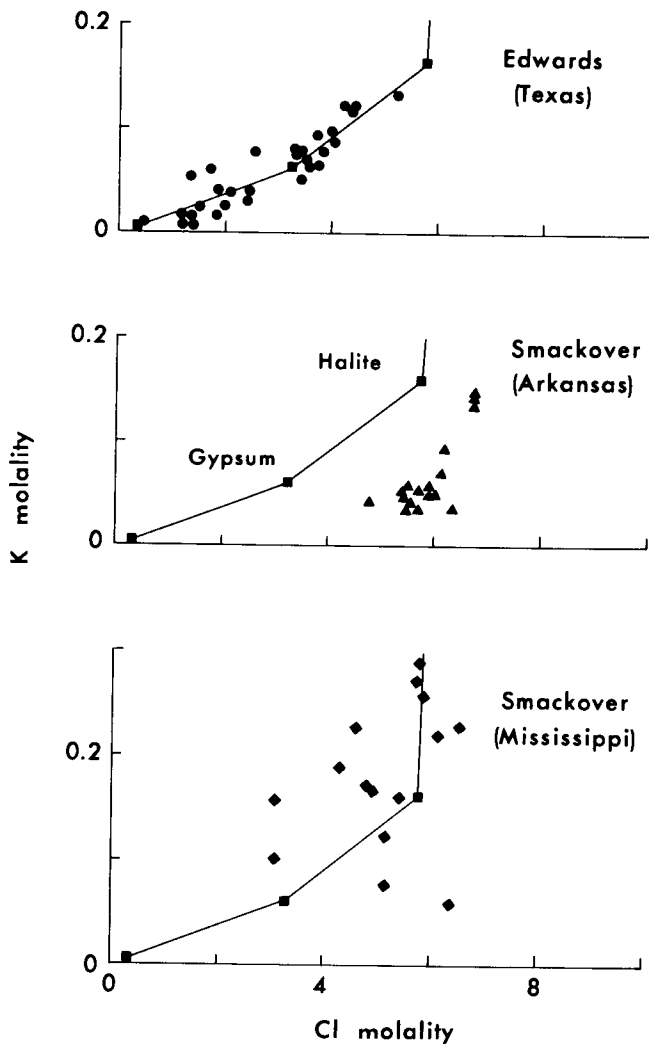


FIG. 2—Plot of potassium molality versus chloride molality in reservoir fluids from Edwards and Smackover.

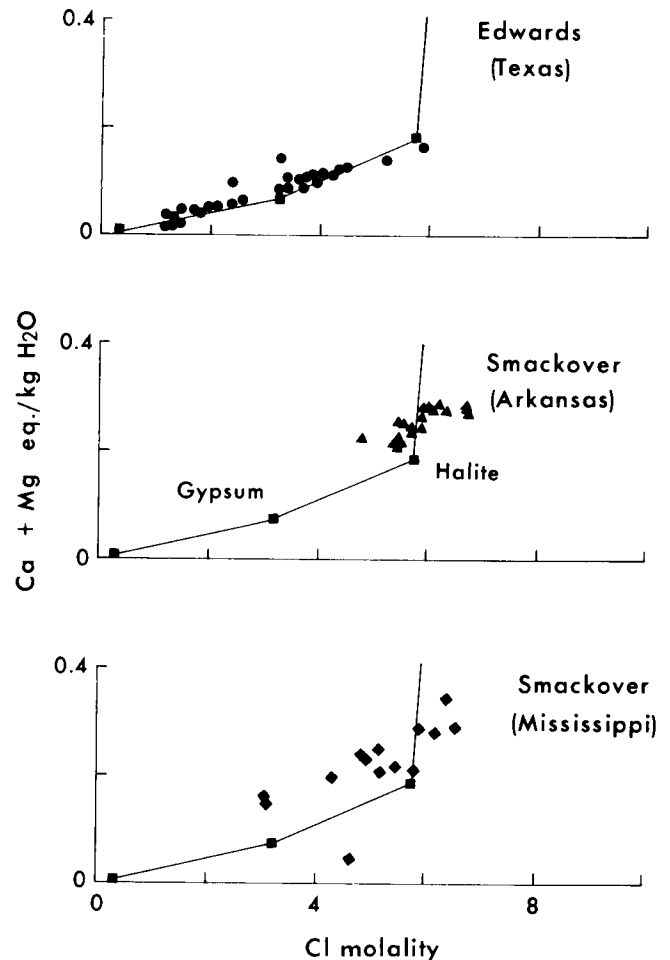


FIG. 3—Plot of calcium plus magnesium per kilogram of water versus chloride molality in reservoir fluids from Edwards and Smackover.

ing reactions will transform a brine having a similar composition to that produced by seawater evaporation into one resembling the Na-Ca-Cl brines characteristic of the Smackover. They could not explain the large excess of bromide in Smackover fluids in Arkansas.

Moore and coworkers (Moore and Druckman, 1981; Druckman and Moore, in press; Vinet, 1983) have described the diagenetic sequence within the upper Smackover of Arkansas, Louisiana, Mississippi, and Alabama. Documented late diagenetic events include anhydrite replacing calcite, precipitation of calcite and dolomite cements, and carbonate leaching. These reactions are consistent with Mg-SO<sub>4</sub> brines moving through the Smackover as a post-compaction fluid event.

We have used the Smackover data from Carpenter et al (1974) and Carpenter and Trout (1978) in Figures 1 to 5. The fit to the 25°C (77°F) seawater evaporation line on Figures 1 to 3 for Smackover fluids is not nearly as good as it was for waters from the Edwards. Relative to chloride molality, the Arkansas Smackover waters are depleted in potassium and enriched in bromide molalities, whereas compositions in Mississippi Smackover waters show large scatter. The equivalents of calcium plus magnesium per kilogram of water in the Smackover can be explained by mixing normal marine waters with one or more end-member fluids concentrated to halite saturation under in-situ temperatures. Halite solubility increases with rising temperature, so that halite dissolution will increase chloride molality past the 25°C (77°F) evaporation line. More

evidence for Smackover fluids dissolving halite under reservoir conditions is shown on Figure 4 for sodium molality plotted versus chloride molality. In this plot, the data can be most simply explained by mixing of end-member fluids with generally low Na:Cl ratios. Local halite dissolution has, in some cases, increased this ratio. A low Na:Cl ratio in the concentrated end-member was due to evaporation past initial halite saturation. This end-member was probably a Louann brine which precipitated anhydrite and dolomite while mixing with the more dilute interstitial waters in the Smackover. The origin of the low Na:Cl ratio in the dilute waters could be due to albitization, assuming these waters were previously flushed through clastic units.

Carpenter and Trout (1978) concluded the excess bromide in the Arkansas Smackover fluids was not supplied by degradation of organic matter or by recrystallization of halite. The former conclusion was based on the presence of low iodide aqueous concentrations, and the latter, on the abnormally high bromide contents of Louann Salt in Arkansas (Collins, 1974). Bromide concentrations reported by Collins (1974) average nearly 250 ppm and were obtained on a sample of Louann Salt from the Kerlin field in southern Arkansas. Halite normally contains about 100 ppm bromide at initial Na:Cl saturation in evaporated seawater (Herrmann, 1980). The bromide content in halite decreases with increasing evaporation of seawater and with recrystallization (Braitsch and Herrmann, 1963; Herrmann, 1980). Recently, Stirling et al (in press) and Dix and Jackson (in press) reported average bromide contents of 33 and 45 ppm, respectively, for the Louann Salt in the Vacherie dome in north Louisiana and the Oakwood dome in east Texas. Bromide contents aver-

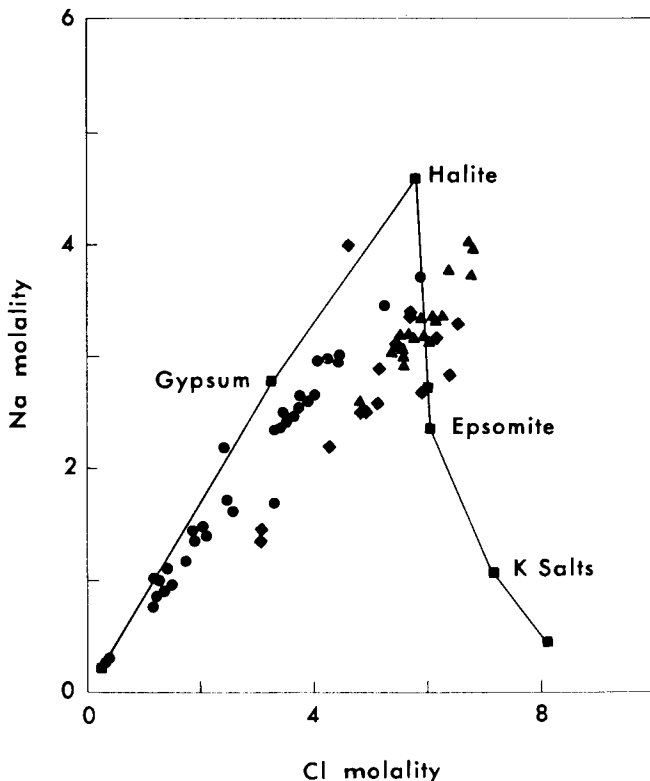


FIG. 4—Plot of sodium molality versus chloride molality in reservoir fluids from Texas Edwards (black dots), Arkansas Smackover (black triangles), and Mississippi Smackover (black diamonds).

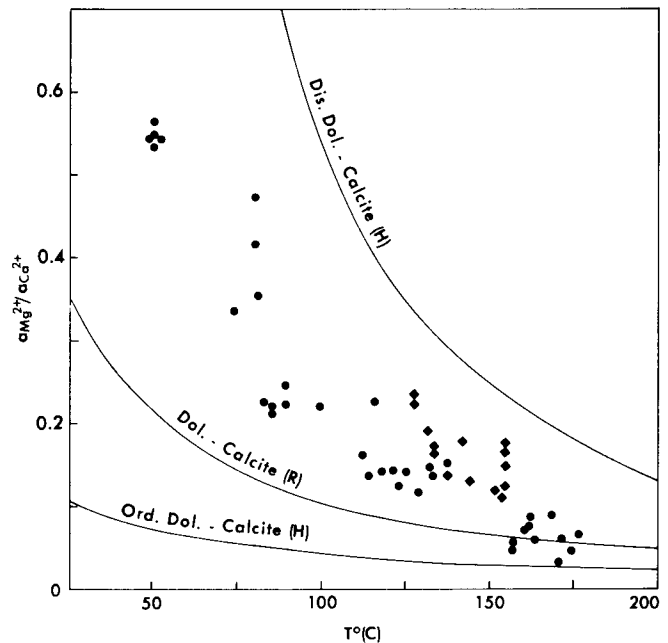
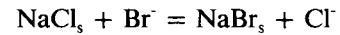


FIG. 5—Plot of  $a_{Mg^{2+}}/a_{Ca^{2+}}$  versus temperature in reservoir fluids from Texas Edwards (black dots) and Mississippi Smackover (black diamonds). Calcite-dolomite equilibrium lines, (H) and (R), depend, respectively, on data from Helgeson et al (1978) and Robie et al (1979). These lines are also shown on Figures 10 and 15. Dol., dolomite; Dis., disordered; Ord., ordered.

age only 23 ppm in halite in the cap rock in the Oakwood dome (Dix and Jackson, in press). Holser (1966) has reported average bromide contents of 43 and 48 ppm, respectively, for Louann Salt from the domes at Grand Saline, Texas, and Weeks Island, Louisiana. These low values contrast with the high values reported by Collins (1974). We think the low values represent bromide contents of recrystallized halite. Brines moving updip from the basin will encounter piercement salt structures.

Recrystallization of this halite can account for the excess bromide in Smackover fluids.

This hypothesis assumes that excess bromide is partitioned into halite from evaporating seawater. This assumption is supported by the decrease in measured bromide partition coefficients in experiments involving very slow growth of halite (Puchelt et al 1972; Lutz, 1975). Under these conditions, the bromide content in halite should be below 50 ppm, in agreement with the low values mentioned above. In addition, Herrmann (1980) has shown that recrystallization of hopper crystals in artificial salt pans lowers the bromide content in halite. Herrmann (1980) has also suggested that aqueous magnesium decreases the bromide content in halite by complexing aqueous bromide. A thermodynamic analysis of data from Braitsch and Herrmann (1963) does not support this conclusion. Computed Henry's law constants for NaBr in halite are not constant, indicating a kinetic control. The effect of temperature is not significant on bromide partitioning into halite. Computed equilibrium constants for the reaction



predict a small increase in bromide content in halite at constant solution composition going from surface to reservoir temperatures and pressures. In summary, observational, experimental, and thermodynamic data analyses support nonequilibrium excess amounts of bromide in halite at the time of initial precipitation and the subsequent loss of this bromide to solution with recrystallization.

The Smackover fluids have a more complex origin than the Edwards fluids. We agree with Carpenter (1978) that there is a mixing relationship with magnesium-rich Louann brines moving up through the section. These brines were more concentrated than those moving through the Edwards, as shown by the lower Na:Cl ratios. Modern examples of subsurface magnesium-rich brines associated with evaporite deposits are those reported by Mayhew and Heylman (1966). The excess bromide is due to extensive recrystallization of halite by the Louann brines moving updip from the basin. Low potassium molalities in the Arkansas Smackover fluids are due to illitization removing potassium from the brines while downdip in the basin. The scatter in potassium concentrations in the Mississippi Smackover fluids reflects dissolution of sylvite associated with salt domes in that area. The more dilute fluid existing within the Smackover which mixed with the Louann brines had a low Na:Cl ratio that may have been due to albitization. If so, this occurred prior to the fluid entering the Smackover.

Computed activity ratios of magnesium to calcium are plotted on Figure 5 versus temperature for Mississippi Smackover fluids. Ratios could not be computed for Arkansas Smackover fluids because temperature data were not reported by Trout (1974). The plotted ratios are consistent with equilibrium between calcite and metastable dolomite and fit with the trend from the Edwards. The regional late dolomitization events reported by Moore and Druckman (1981) correspond to the movement of the Louann brines into the Smackover as a late event. This

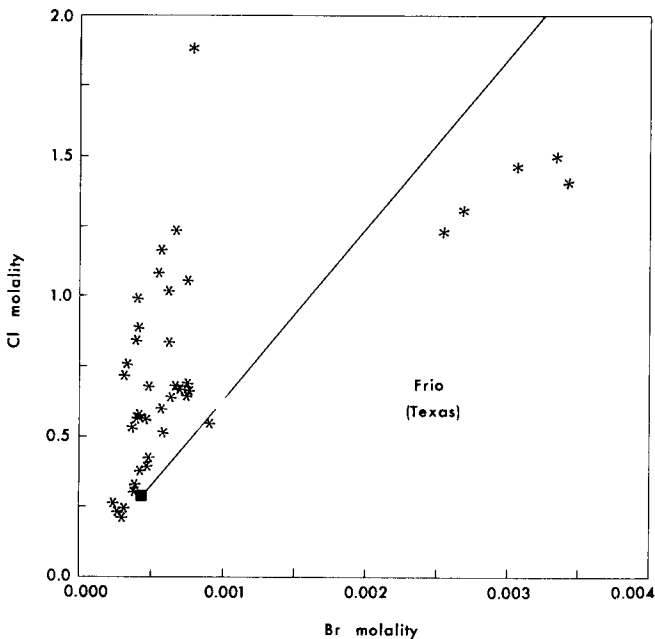


FIG. 6—Plot of bromide molality versus chloride molality in reservoir fluids from Texas Frio.

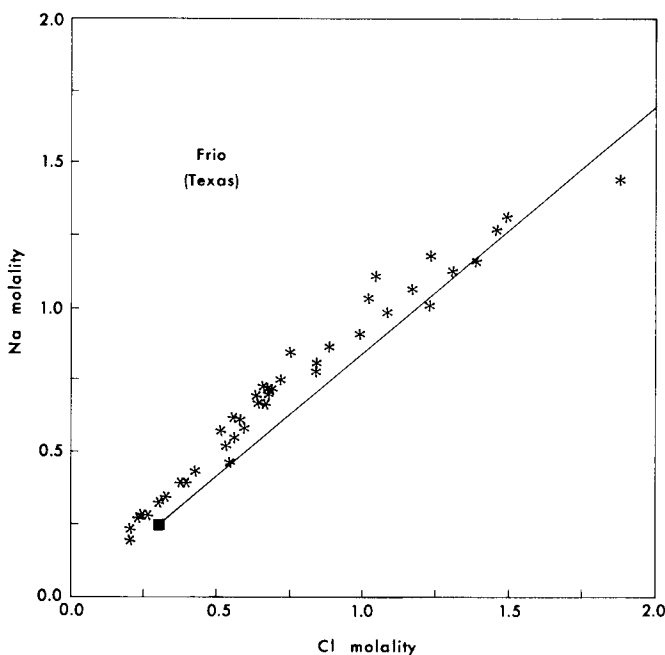


FIG. 7—Plot of sodium molality versus chloride molality in reservoir fluids from Texas Frio.

flow could have been controlled by the opening and closing of faults (Moore and Druckman, 1981; Vinet, 1983) and probably does not represent a continuous movement with time.

Carpenter (1980) used Smackover fluid compositions in an attempt to determine a trend in log activity ratios of Mg:Ca versus  $1,000/T^{\circ}K$ . He used fluids from clastic reservoirs at Kettleman North Dome (reported by Merino, 1975) as well as from carbonate units. Mean salt activity coefficients were estimated from  $25^{\circ}C$  ( $77^{\circ}F$ ) single-salt data at similar ionic strengths. Carpenter's conclusions that a trend was absent is apparently due to comparing data from both clastic and carbonate reservoirs, the inclusion of low temperature groundwater data, and the neglect of mixed-salt interactions and temperature effects in computing activity coefficients.

**Frio Formation**

Kharaka et al (1977, 1978) have reported water chemistries from the clastic Frio Formation (Oligocene) of east and southeast Texas. They used modifications of marine waters by halite dissolution and water-rock interactions plus membrane filtration through shales to account for the formation fluid chemistries.

Late diagenetic events in the Texas Frio Formation include post-compaction leaching of feldspar, volcanic and carbonate fragments, and calcite, followed by precipitation of kaolinite (dickite polymorph?) and ferroan cal-

cite and dolomite cements (Lindquist, 1977; Loucks et al, 1977). Albitization of potassium feldspar and plagioclase has occurred concurrently with the leaching stage (Land and Milliken, 1981). Boles (1982) estimated temperatures of albitization in the Frio to be between  $110$  and  $120^{\circ}C$  ( $230$  and  $250^{\circ}F$ ) in the Rio Grande embayment.

Data from Kharaka and his coworkers have been plotted on Figures 6 to 10. Samples showing evidence of significant dilution by condensed water vapor, produced with

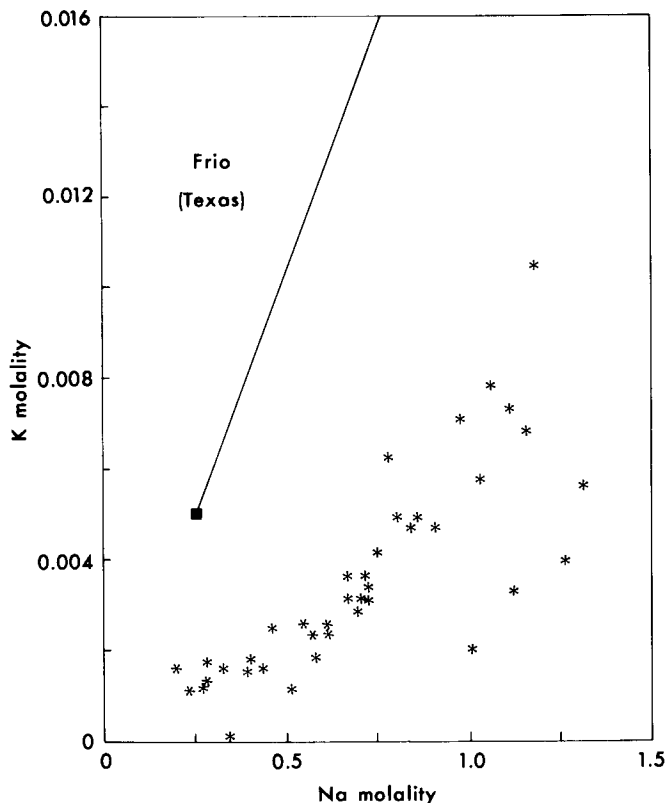


FIG. 8—Plot of potassium molality versus sodium molality in reservoir fluids from Texas Frio.

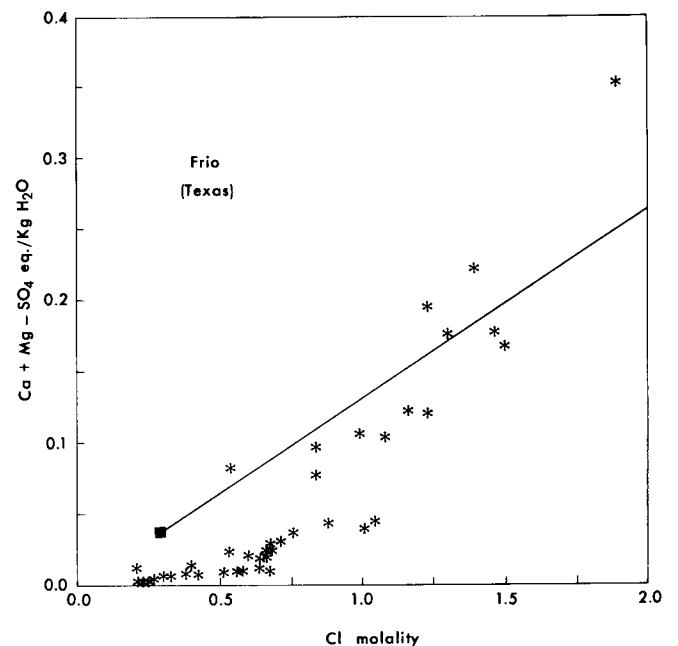


FIG. 9—Plot of  $Ca + Mg - SO_4$  equivalents per kilogram of water versus chloride molality in reservoir fluids from Texas Frio.

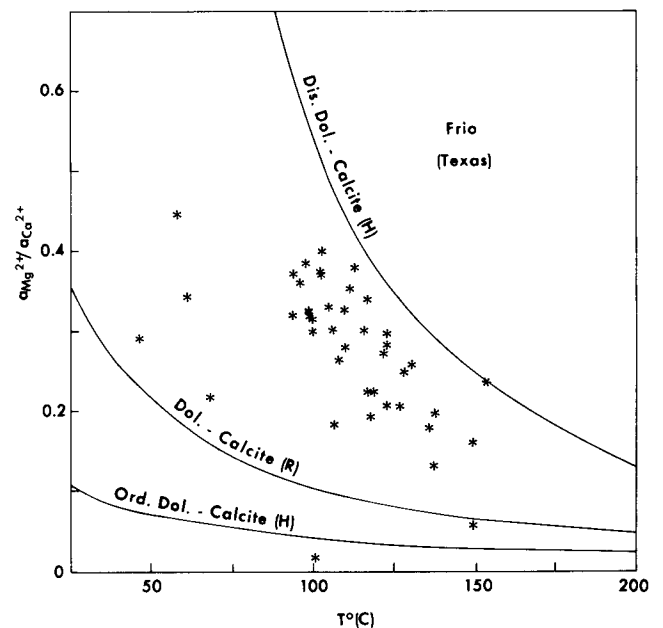
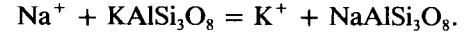


FIG. 10—Plot of  $a_{Mg^{2+}} / a_{Ca^{2+}}$  versus temperature in reservoir fluids from Texas Frio (see Fig. 5).

natural gas, are not plotted. Low silica concentrations, below quartz saturations for the measured subsurface temperatures, were the dilution criteria. Relative to the 25°C (77°F) seawater evaporation line, there is a deficiency in bromide relative to chloride concentrations on Figure 6, except for five samples from the Rio Grande embayment. The deficiency can be explained by halite dissolution without recrystallization. Remember, the excess bromide in the Smackover fluids was due to recrystallization of the halite. Clear evidence of halite dissolution is shown by the sodium versus chloride molalities on Figure 7. Halite dissolution by a single fluid composition would result in the approximate 1:1 ratio in Na:Cl up to molalities of about 1.0 for both components. This trend is followed by a gradual decrease in Na:Cl ratios with increasing chloride concentrations, representing the modifying influence of albitization on halite dissolution. This is somewhat different from the Edwards fluids, which have a more constant Na:Cl ratio.

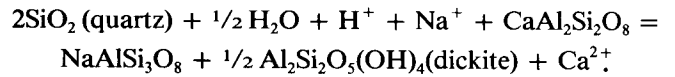
Potassium molalities are plotted versus sodium molalities on Figure 8. The two components show a rough positive correlation. There is a large deficiency in potassium relative to sodium concentrations for the 25°C (77°F) seawater evaporation line, indicating the lack of a dilution relationship with a Louann-type brine. Potassium concentrations are modified by the post-compaction leaching of potassium feldspars and concurrent formation of albite. Although most of this albite is due to albitization of the

anorthite component in plagioclase, some of it could have resulted from the following reaction:



The positive correlation between potassium and sodium may be due to halite dissolution promoting albitization by the release of sodium.

On Figure 9, equivalents of Ca + Mg - SO<sub>4</sub> per kilogram of water are plotted versus chloride molality. Post-compaction leaching of plagioclase, carbonates, and volcanic fragments will increase calcium and magnesium concentrations. The reason for the positive correlation with chloride molalities above 0.5 is probably due to halite dissolution promoting albitization of the anorthite component in plagioclase by the following reaction (Boles, 1982):



The computed Mg:Ca activity ratios versus temperatures are plotted on Figure 10. These data show more spread than those from the Edwards and the Smackover, particularly at lower temperatures. However, above 100°C (212°F) there is a consistent trend of decreasing Mg:Ca activity ratios with increasing temperature. The trend suggests a reaction relationship of metastable equilibria between calcite and a disordered dolomite, having increasing order at higher temperatures.

In summary, fluids in the Frio Formation appear to be unrelated to Louann-type brines. The major component aqueous chemistries result from the promotion of albitization by halite dissolution and by leaching of potassium

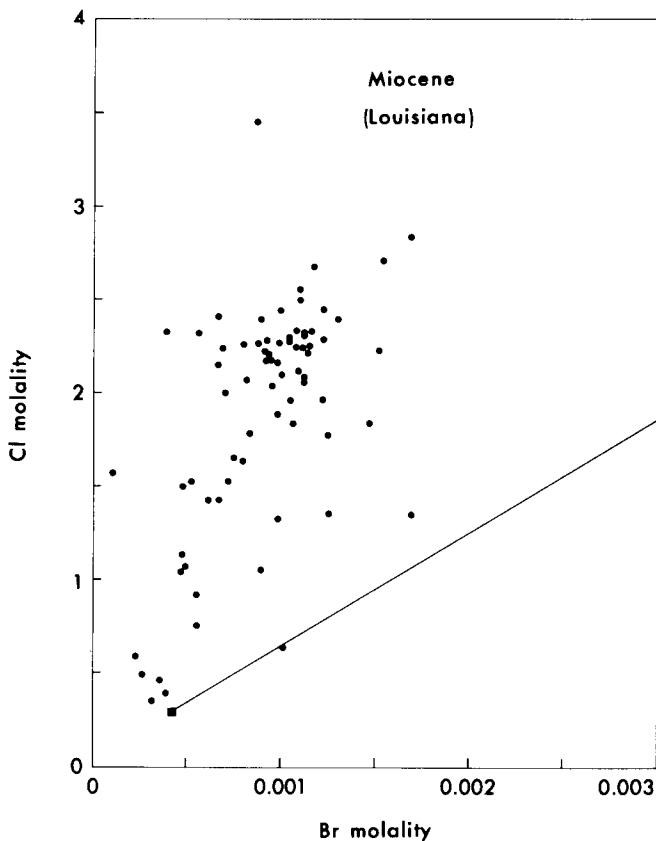


FIG. 11—Plot of chloride molality versus bromide molality in reservoir fluids from Louisiana Miocene formations.

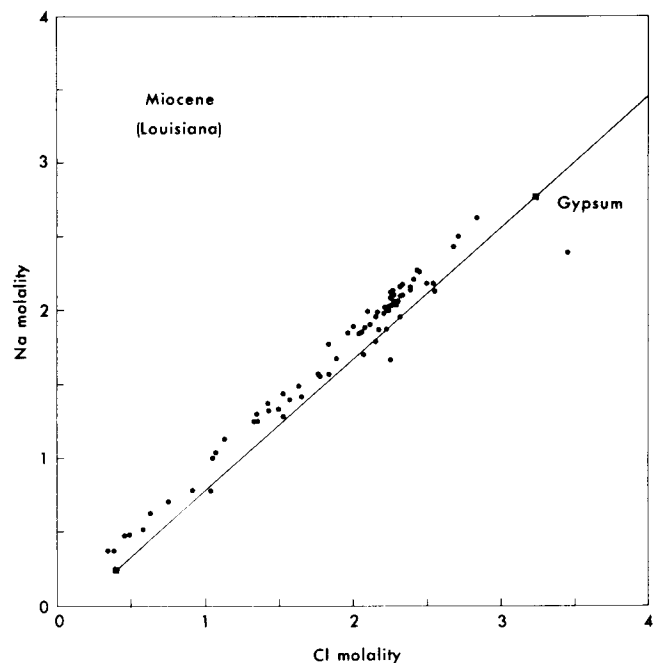


FIG. 12—Plot of sodium molality versus chloride molality in reservoir fluids from Louisiana Miocene formations.

feldspar, plagioclase, carbonates, and volcanics. Reactions between calcite and disordered dolomite may help control the Mg:Ca activity ratios at temperatures above 100°C (212°F).

**Miocene Formations**

Collins (1970) and Kharaka et al (1978) have reported water chemistries from clastic Miocene formations of the coastal parishes of Louisiana. Regional diagenetic studies of these formations are lacking in the literature. Flournoy and Ferrell (1980) reported significant secondary porosity from carbonate dissolution in the Lirette field area and late-stage precipitation of kaolinite. They believed these events were related to the release and migration of dilute geopressed waters up fault zones.

Collins (1970) did not report reservoir temperatures. We have estimated those temperatures using a 20°C (68°F) near-surface temperature and the 1.6°F/100 ft gradient reported by Kharaka et al (1978). Water compositional data are plotted on Figures 11 to 15. As was the case for the Frio Formation in Texas, when compared to the 25°C (77°F) seawater evaporation line on Figure 11, there is a deficiency in bromide relative to chloride concentrations. Again, this deficiency can be explained by halite dissolution without recrystallization. Halite dissolution is supported by the linear correlation between sodium and chloride molalities, which is shown on Figure 12. There is a rough positive correlation between potassium and

sodium molalities on Figure 13. As was the case for the Frio Formation, this can be explained by halite dissolution promoting albitization of potassium feldspar. The amount of albitization was not significant enough to lower the Na:Cl ratio on Figure 12. The explanation for the rough positive correlation between Ca + Mg - SO<sub>4</sub> equivalents and chloride molalities shown on Figure 14 is probably related to albitization of the anorthite component in plagioclase, as previously discussed for the Frio Formation. On Figure 15 the decrease in computed activity ratios of Mg:Ca with increasing temperature falls within the general trend predicted by reaction relationships between calcite and metastable dolomites.

There are significant decreases in  $a_{Mg}^2 + / (a_K + )^2$  at temperatures above 100°C (212°F; Fig. 16). Similar low activity ratios occur in fluids from the Texas Frio. These trends can be explained assuming chlorite formation. Chlorite forms as a relatively early diagenetic mineral in Louisiana Miocene formations (Flournoy and Ferrell, 1980), probably below 100°C (212°F). Increasing temperatures would accelerate the reactive kinetics, allowing the fluid chemistry to approach equilibrium with the chlorite and the associated minerals. The overall reaction can be approximated as follows:

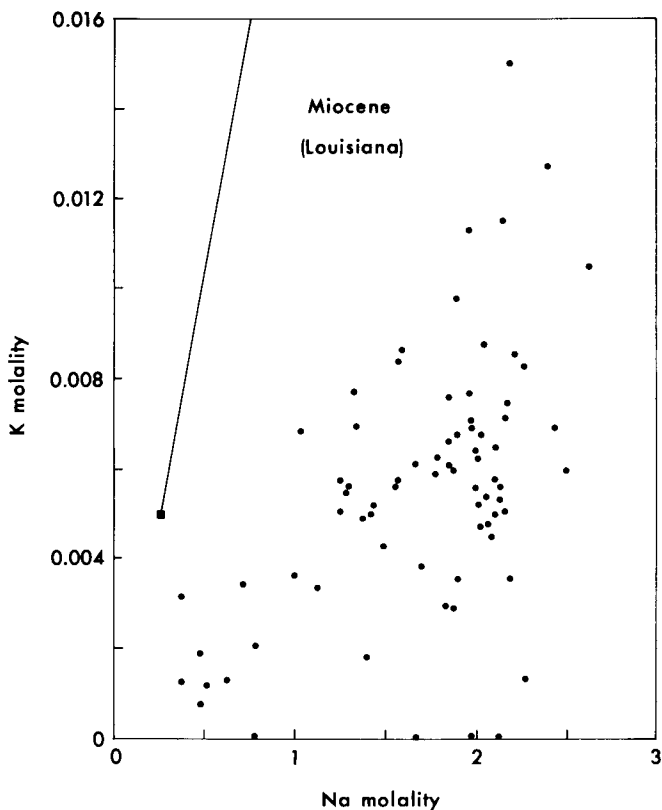
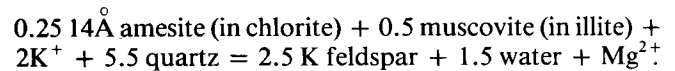


FIG. 13—Plot of potassium molality versus sodium molality in reservoir fluids from Louisiana Miocene formations.

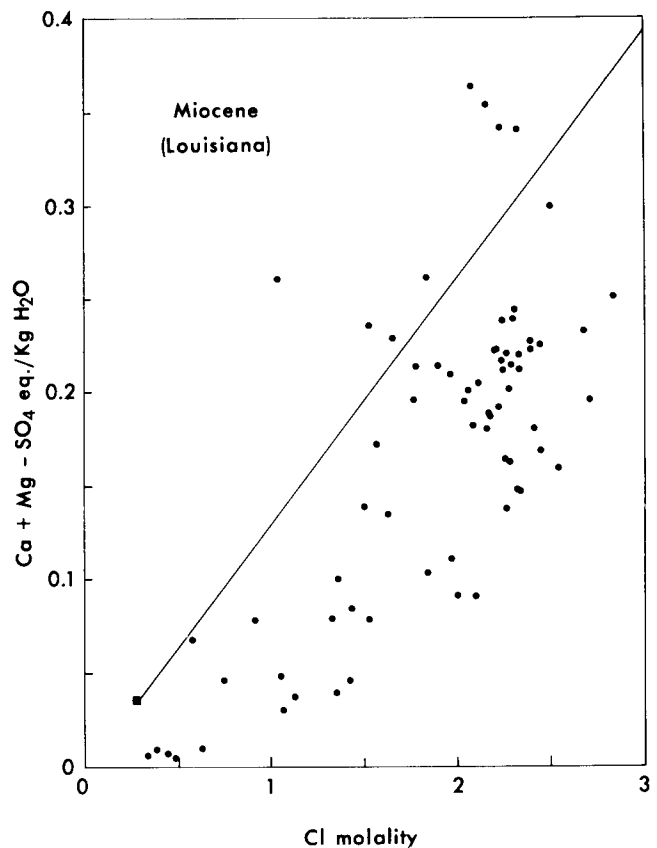


FIG. 14—Plot of Ca + Mg - SO<sub>4</sub> equivalents per kilogram of water versus chloride molality in reservoir fluids from Louisiana Miocene formations.



Several equilibrium lines are plotted on Figure 16; each assumes a constant chlorite and illite composition during diagenesis. This is an unreasonable assumption for minerals of variable compositions; however, the curves show the general solution trends resulting from reaction within the assemblage. These trends agree with the observed decrease in  $a_{Mg}^{2+}/(a_K + )^2$  at temperatures above 100°C (212°F). Note that in moving from curves a through c, the chlorite goes from a magnesium-rich to an  $Fe^{2+}$ -rich composition, whereas the illite moves from a potassium-rich to potassium-depleted composition.

In summary, fluids within the Miocene formations of southern Louisiana are similar to those in the Texas Frio Formation. Their major component chemistries are unrelated to Louann-type brines and are the result of halite dissolution, albitization of plagioclase and potassium feldspar, and the leaching of carbonates. Their calcium and magnesium activities appear to be related through reactions between calcite and metastable dolomites, and their magnesium and potassium activities may be related through equilibration with chlorite at temperatures above 100°C (212°F).

#### SUMMARY DISCUSSION

The present fluid compositions of the four reservoirs fall into two groups: (1) waters in the Mesozoic formations, which were derived partially by dilution with Louann brines, and (2) the less saline waters in the Cenozoic formations, which show the effects of halite dissolution. The former occurs within the carbonate units, which were shelf deposits, and the latter, within the clastic units, which were deposited off the shelf as part of thick wedges of alternating sand and shale sequences.

Most of the late diagenetic events within these reservoirs likely represent major changes in fluid chemistries. This supports the idea that these reservoirs acted as relatively open systems during parts of their burial histories. Hydraulic gradients within the Gulf of Mexico basin force fluids by various pathways up through the shallower reservoirs. The actual flow rates are very small, but significant over geologic time. Differences between water compositions in the Mesozoic and Cenozoic reservoirs are primarily due to the difference in fluids available to slowly flush the reservoirs. Burial and compaction of the downdip shelf carbonate units cannot generate the volumes of fluids resulting from similar processes in the downdip shale units of a thick clastic wedge. With time, brines generated during the formation of the Jurassic Louann Salt sequence have moved into the overlying Jurassic-Cretaceous carbonate units in the basin and then updip to the basin edge. This movement is in response to the updip movement of the initial fluids within the carbonate units. In the Cenozoic units, shale compaction has generated sufficient water volumes to replace fluids within the clastic reservoirs.

The rough positive correlation between potassium and sodium molalities in the two Cenozoic clastic units can be explained by albitization of potassium feldspar resulting from the release of sodium during halite dissolution. In the same units there is also an approximate positive correla-

tion between equivalents of  $Ca + Mg - SO_4$  and chloride molality. This results from a positive correlation between calcium and chloride molalities due to halite dissolution promoting albitization of plagioclase. It may also be related to the leaching of carbonates during the formation of secondary porosity.

The application of Pitzer's method to computing activity coefficients for reservoir fluids has revealed reaction relationships which exert some control over fluid compositions. In carbonates, there is a relationship between calcite and disordered dolomite in which the dolomite becomes more ordered at higher temperatures. In clastics, a relationship may exist between chlorite, illite, potassium feldspar, and quartz. Pitzer's method lacks reliable temperature coefficients for some of the parameters, making the results qualitative. However, these results clearly indicate that trends in concentration ratios with depth should not be arbitrarily interpreted as dissolution or precipitation by fluids grossly out of equilibrium with the associated mineral assemblages.

Fluids within the carbonates of the Edwards appear to result primarily by dilution with Louann brines. The highly saline fluids within the Smackover carbonates show the effect of dilution with Louann brines combined with illite formation, sylvite dissolution, and halite recrystallization. Albitization may have occurred during fluid movement through clastics prior to entering these reservoirs. The more dilute fluids within the Frio and Miocene clastic units show the effects of halite dissolution and subsequent albitization of plagioclase and potassium feldspar and carbonate dissolution. Albitization in these clastic units had a significant effect on potassium concentrations, but only a minor effect on sodium concentrations.

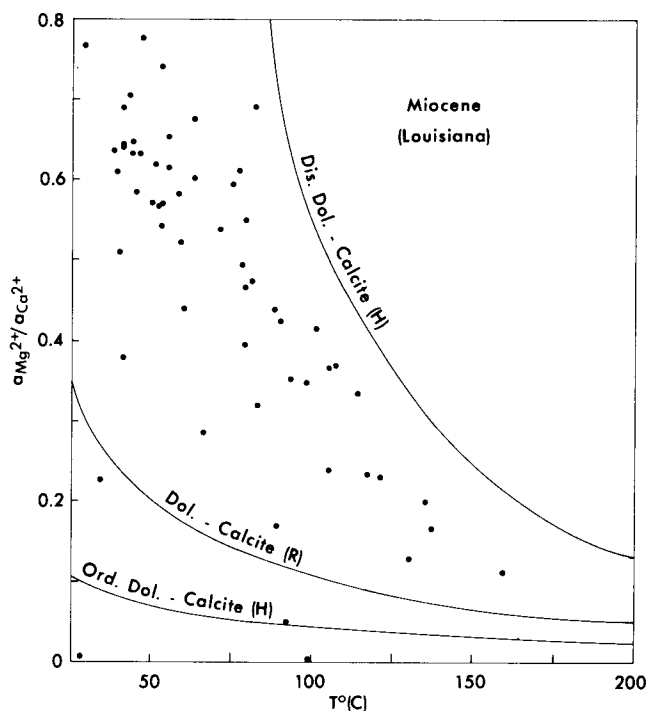


FIG. 15—Plot of  $a_{Mg}^{2+}/a_{Ca}^{2+}$  versus temperature in reservoir fluids from Louisiana Miocene formations (see Fig. 5).

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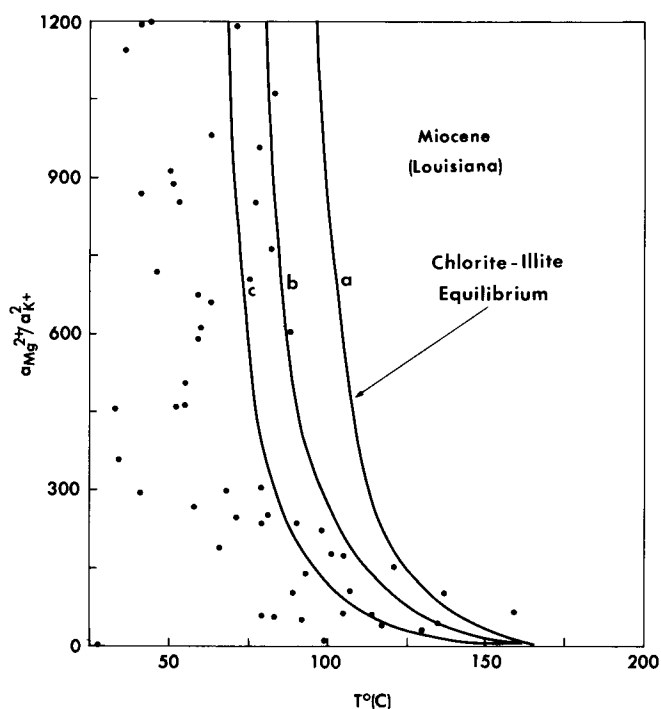


Fig. 16—Plot of  $a_{Mg^{2+}} / (a_k +)^2$  versus temperature in reservoir fluids from Louisiana Miocene formations. Solid lines represent equilibrium between chlorite, quartz, potassium feldspar, and illite. Chlorite compositions are  $(Fe^{2+} Mg_{3.3} Al_{1.6}) (Al_{1.4} Si_{2.6}) O_{10} (OH)_8$  for curve a and  $(Fe^{2+} Mg_{3.3} Al_{1.6}) (Al_{1.4} Si_{2.6}) O_{10} (OH)_8$  for curves b and c. Illite compositions are  $K_{0.75} (Al_2) (Al_{0.75} Si_{3.25}) O_{10} (OH)_2$  for curves a and b and  $K_{0.45} (Al_2) (Al_{0.45} Si_{3.55}) O_{10} (OH)_2$  for curve c.

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