
Chemical Constraints and Origins of Four Groups of Gulf Coast Reservoir Fluids: Reply¹

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We welcome the opportunity to correct the misrepresentations of Land and Prezbindowski (1985) concerning the ideas and conclusions presented by Stoessell and Moore (1983). In addition, we will modify those conclusions to exclude albitization as the major explanation for the low Na:Cl ratio in fluids from the Edwards. Finally, we apologize for the drafting error on Figure 3. The y axis scale should be 0 to 4, not 0 to 0.4.

We (Stoessell and Moore, 1983) reviewed some of the data and ideas on the origin of formation fluids in four groups of Mesozoic and Cenozoic Gulf Coast reservoirs, of which one was the Edwards Group. The data were analyzed using (1) concentration plots and (2) equilibrium thermodynamics. We divided the fluids into two types based on the presence or absence of an apparent mixing relation with a modified Louann brine. The proposed origin of the fluids in each reservoir group, within each type, involved a sequence of diagenetic events in addition to the mixing of end-member solutions. Land and Prezbindowski (1985) used a quote, referring to Figures 1, 2, and 3 of our paper, to misrepresent our conclusions by inferring that we neglected the effects of diagenetic processes in the Edwards.

Our ideas on the origins of the present formation fluids in the Edwards were based on the data of Land and Prezbindowski (1981, Table 1). The conclusions support the general brine evolution model put forth by Carpenter (1978) for the origin of fluids in the Gulf Coast Smackover Formation. We concluded the fluids were related to the movement of "modified" Louann brines toward the basin margin and subsequent mixing with interstitial fluids in the Edwards. Major constituents in the Louann brines had been modified by dolomitization of calcite and albitization of plagioclase. Aqueous sulfate was depleted by anhydrite precipitation (following dolomitization) and sulfate reduction.

Our conclusions are supported by the fluid composition plots (Figure 1) of molality and cation equivalents per kilogram of H₂O. These plots also contain the Black Sea evaporation data of Zherebtsova and Volkova (1966; listed in Table 4 of Carpenter, 1978) and two estimated compositions reported by Carpenter (1984, personal communication) for initial saturation of gypsum and halite during seawater evaporation. These data are connected by straight line segments to represent a "general" seawater evaporation trend, not a precise path of seawater evapora-

tion. The solution compositions for the initial saturation points for epsomite, Mg salts, and K salts have been taken from the Black Sea data and are only shown for qualitative reference. The dashed lines on the plots are examples of solution compositions formed by mixing two end-member brines.

Land and Prezbindowski (1985) object to the "kink" in the seawater evaporation trend between the initial Black Sea water and the point of halite saturation on several of the plots in our paper (Stoessell and Moore, 1983, Figures 1-4). The "kink" resulted from connecting straight line segments between the data points for Black Sea water evaporation. Contrary to the assertions of Land and Prezbindowski (1985) these data points are plotted correctly. We did not mean to imply that the precise path of seawater evaporation followed these straight line segments, and we apologize for any confusion to the reader. The kink is absent in the plots presented here, because we have used the composition estimated by Carpenter (1984, personal communication) for initial saturation of halite, which is more accurate than that reported by Zherebtsova and Volkova (1966).

The data from the Edwards on each of the plots define an apparent linear mixing relationship in which brines, saturated with halite, appear to have mixed with more dilute interstitial fluids. The plot showing the greatest scatter, Figure 1C, can be explained by precipitation of potassium aluminum silicates by some of the concentrated end-member brines prior to moving into the Edwards. The general displacement of the data from the seawater evaporation trend indicates the concentrated end-member brines had been evaporated past initial halite saturation. This important point was not apparent in Figures 1, 2, and 3 of Stoessell and Moore (1983) because of the imprecision of their seawater evaporation trend. The low Na:Cl ratios in the Edwards' fluids are primarily due to halite precipitation from evaporating seawater during formation of the Louann brines. This is an important point, because the Land and Prezbindowski model must use massive albitization to explain this ratio.

The occurrence of some important diagenetic events are not apparent from the plots in Figure 1. Sulfate was not reported by Land and Prezbindowski (1981); however, low concentrations are implied by neutrality balances. Anhydrite formation and sulfate reduction are needed to explain depleted sulfate concentrations. Dolomitization is needed to explain the high aqueous Ca:Mg ratios indicated by the data in Table 1 of Land and Prezbindowski (1981).

The additional points raised by Land and Prezbindowski (1985) are discussed below.

Their first two points are: 1. "Edwards brines are significantly enriched in bromide relative to chloride over sea-

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water evaporated to halite saturation," and 2. "Edwards brines have significantly higher K:Cl and Ca + Mg:Cl ratios than seawater evaporated to halite saturation." We agree that some significant excesses exist, and explain them by mixing brines concentrated past initial halite saturation with less concentrated interstitial fluids. Note the good linear agreement of most of the data on the plots in Figure 1 with the dashed "mixing" lines. This observation by Land and Prezbindowski is consistent with our model and we welcome their acknowledgment. Unfortunately, they have to use coincidence to explain the relationships on Figure 1 in terms of their alternative model.

Point 3 continues, "Edwards brines cannot achieve molar Ca:Mg ratios of 16 by dolomitization." Thermodynamic calculations refute this statement. The Ca:Mg activity ratio predicted from equilibrium between calcite and ordered dolomite, using data from Helgeson et al (1978), is 33 at 150°C (302°F) and 500 bars, as shown on Figure 2. (See Stoessell and Moore, 1983, for calculation procedures.) Land and Prezbindowski (1985, their Figure 1) use a straight line extrapolation (in reciprocal temperature and log space) of apparent equilibrium constants from the elevated temperature ($\geq 275^\circ\text{C}$ or 527°F) experimental data of Rosenberg and Holland (1964), Rosenberg et al (1967), and Land (1967) to the ground-water data of Langmuir (1971). The effects of pressure and lattice order in the dolomite are neglected, and the high temperature end of the extrapolation appears arbitrary in view of the apparent ionic strength effect on the experimental data trends. Land and Prezbindowski (1985) have mixed low-temperature field data, involving reactions presumably controlled by disordered dolomite, with laboratory data from higher temperature reactions controlled by ordered dolomite. The linear extrapolation assumes, from thermodynamics, a constant standard state change in reaction enthalpy over a temperature range of more than 250°C (450°F), an invalid assumption. The correct way to compute the temperature dependence of the equilibrium constant is to use standard thermodynamic procedures and thermodynamic parameters that are consistent with results of the multitude of reliable, high temperature, reversed experiments involving calcite and/or dolomite and other minerals (e.g., see Helgeson et al, 1978).

From thermodynamics, as shown on Figure 2, the activity ratio of Mg:Ca is expected to increase with decreasing temperature in a fluid in equilibrium with both calcite and dolomite. A family of curves can be drawn between the two curves computed from the data of Helgeson et al (1978) in which the dolomite lattice goes from total order to total disorder in the placement of Ca and Mg atoms. Therefore, an increase in the aqueous Mg:Ca ratio with decreasing temperature does not prove dedolomitization by updip moving fluids that are "grossly undersaturated with respect to dolomite" (Land and Prezbindowski, 1981, p. 61, for depths > 1 km). Assuming a fluid moving updip, the trend in activity ratios of the data from the Edwards on Figure 2 can be explained by minor dolomite dissolution to maintain equilibrium between calcite and a metastable, disordered dolomite in which the ordering on the dolomite lattice decreases with a drop in temperature. These activity ratios were computed using Pitzer's method for calculating mean ionic activity coefficients (Pitzer,

1979; for computational procedure, see Stoessell and Moore, 1983).

4. "Progressive stabilization of metastable dolomite (Land, 1980) by updip fluid flow cannot raise the magnesium content of Edwards water in the absence of dolomite dissolution." This is shown by the equilibrium lines on Figure 2. The disagreement is on how far the fluids are from equilibrium with calcite and metastable dolomite. The data on Figure 2 from the Edwards imply that the fluids could be close to equilibrium.

It is unlikely that brines of Jurassic age could be displaced from a Jurassic salt basin into the Edwards Formation above without encountering and interacting first with underlying Jurassic units such as the Smackover. If the brines evolved as Land and Prezbindowski indicate, with the major chemistry fixed by halite dissolution and albitization, the Upper Jurassic Smackover and its limestone equivalents should contain no late dolomite, a small amount of late replacement anhydrite, and all dolomite should exhibit extensive dedolomitization. In truth, however, Smackover and associated limestones contain significant amounts of dolomite and extensive post-compaction anhydrite across the entire Gulf rim. Dolomitization occurred early, related to overlying Buckner evaporites, in the moderate subsurface associated with pressure solution and compaction, and in the deeper subsurface as Louann and hydrocarbon-related brines moved through the Smackover. These latest Louann-related dolomites are primarily concentrated along the basin margin and are rarely calcitized (dedolomitized). This is in contrast to the earlier Buckner and pressure solution related dolomites that generally show some moderate dedolomitization (Moore and Druckman, 1981; Stamatedes, 1982; Loucks and Budd, 1981). The paragenetic sequences present in the Smackover across the Gulf rim favor a Carpenter-style brine evolution for the Jurassic-Edwards brines rather than the Land alternative.

5. "The volume of brine contained in the Cretaceous section at the present time exceeds any reasonable volume of hypothetical connate Mesozoic brine." Land and Prezbindowski argue that sufficient volumes of Louann-related brines could not be derived from the interstitial fluids of the salt. In this point we differ from Carpenter (1978), noting that the interstitial waters in the salt are not necessarily the major source of the brine. Enormous volumes of concentrated brine were generated during the actual salt precipitation. Some of this high-density brine may well have displaced interstitial fluids in coarse, porous clastic sequences interfingering with the Louann Salt (see Murray, 1961, p. 287-289). The brine would remain in these units until burial and compaction forced fluid movement up through units such as the Edwards and the Smackover.

Land and Prezbindowski might argue that we have not demonstrated the presence of a deeply buried, thick clastic wedge adjacent to the Louann Salt where the Louann-related brine could be stored prior to migration. The important point is that their model also calls for the existence of thick clastic units, because they are calling for brines ("water source unspecified") older than the Cretaceous (Land and Prezbindowski, 1981; 1985) to albitize plagioclase and move upward through the Edwards.

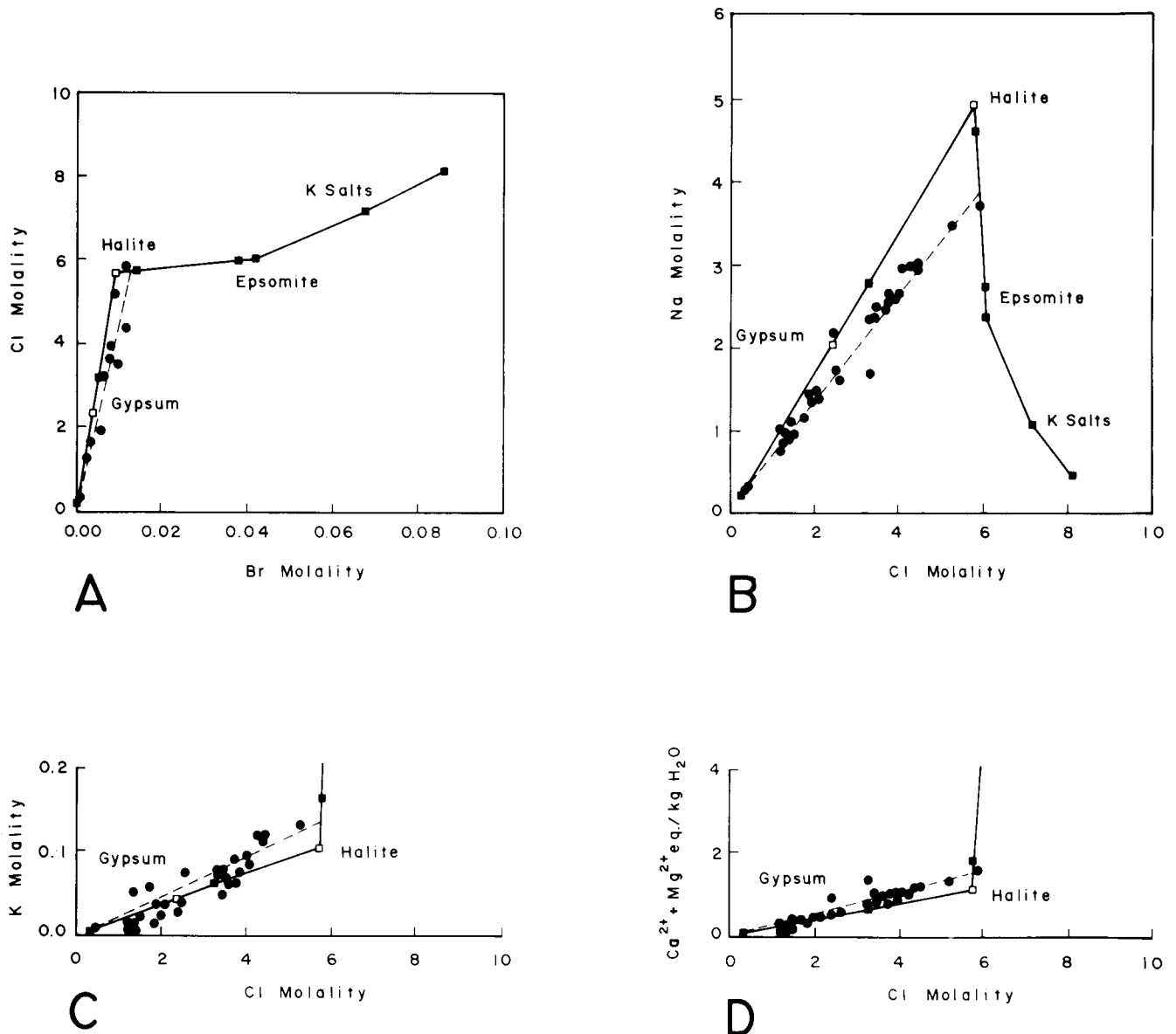


Figure 1—Plots of molality and cation equivalents per kilogram of H₂O vs. molality plots for reservoir fluids from Texas Edwards Group. Straight line segments connect evaporating seawater compositions (■) listed by Carpenter (1978) from Zherebtsova and Volkova (1966) for evaporating Black Sea water and two solution compositions (□) from Carpenter (1984, personal communication) for initial saturation with respect to gypsum and halite. Initial saturation points of epsomite, Mg salts, and K salts are from Black Sea data and are shown only for qualitative reference. Straight line segments can be used as a “general” trend line for evaporating seawater as discussed in text. Dashed lines represent examples of compositions resulting from mixing of two end-member fluids.

6. “Isotopic differences between Edwards brines and Jurassic seawater evaporated to halite saturation are extreme, and therefore preclude recognition of any primary Jurassic component in the present brines.” The deuterium depletion in the Edwards brines may not reflect, as Land and Prezbindowski would have us believe, an overwhelming meteoric source for the parent brine, but may instead reflect the progressive mixing of an evaporative brine with waters highly depleted in deuterium. For example, organic matter (CH₂O) from which hydrocarbons may mature, average -70 ‰ deuterium (Van Der Stranen, 1981). Land and Prezbindowski (1981) noted the

relationship of their brines with Jurassic hydrocarbons. Methane (CH₄), with which Gulf Coast brines are commonly saturated, contains deuterium compositions of -150 to -250 ‰ (Hoefs, 1980). As a brine evolves from a sulfate-rich to sulfate-depleted fluid, the reduction of sulfate by the oxidation of hydrogen in organic molecules (such as methane) will release deuterium-depleted water. Finally, clays have deuterium compositions ranging from 0 down to -120 ‰ (Hoefs, 1980). Deuterium exchanges between brines and clays, as well as any diagenetic changes of clays involving water release, should also effect deuterium depletion. In addition, Carpenter (1984, personal

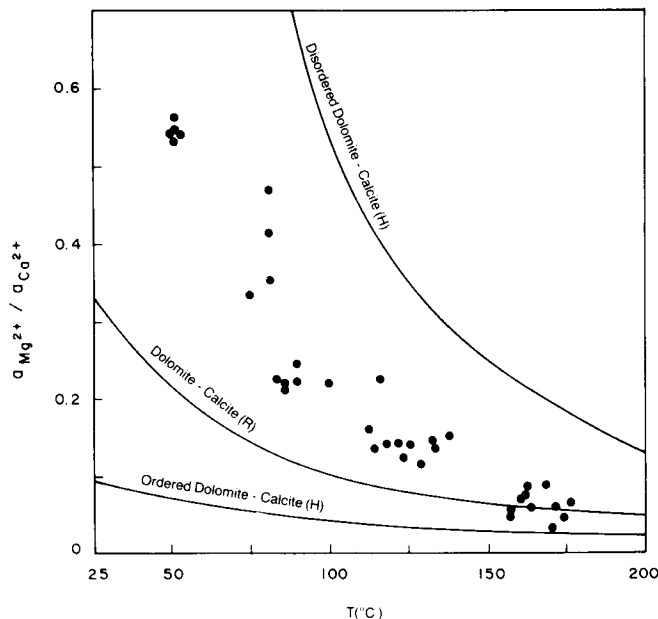


Figure 2—Plot of $a_{Mg^{2+}}/a_{Ca^{2+}}$ versus temperature in reservoir fluids from Texas Edwards Group. Equilibrium lines were constructed from the following PT points: 20°C, 1 bar; 60°C, 150 bars; 100°C, 300 bars; 150°C, 500 bars; and 200°C, 700 bars. Calcite-dolomite equilibrium lines (H) and (R) depend, respectively, on data from Helgeson et al (1978) and Robie et al (1979).

communication) noted that condensation of water vapor depleted in deuterium, as the brine moves up the well bore, will significantly lower the deuterium composition of the brine. The large variation of total dissolved solids in samples from within the same field in the data of Land and Prezbindowski (1981) suggests major contributions of condensed water vapor. While admittedly, we know little about the processes affecting deuterium evolution in the subsurface, it is obvious that Land and Prezbindowski's use of depleted deuterium in the Edwards brine, as a definitive constraint on its origin, is a gross oversimplification and must be reevaluated.

Land and Prezbindowski also used the $^{87}Sr:^{86}Sr$ ratios of Edwards brines to preclude a Louann origin for these brines and to support their albitization model. They state, "In addition, the $^{87}Sr:^{86}Sr$ ratio of Edwards brines is about 0.7091 (Woronick and Land, in press), containing a significant excess of ^{87}Sr over the composition of Jurassic or Cretaceous seawater (Burke et al, 1982), presumably as a result of extensive albitization." Our explanation begins with the Louann-derived brines having an initial ratio of 0.7070, the value for Jurassic seawater. The brines migrate updip along the margin of the basin through units such as the porous upper Smackover. As burial progresses and hydrocarbon maturation-migration processes commence, fluids driven from adjacent, thick organic-rich basinal shales and limestone, accompanying hydrocarbons, begin to mix with the Louann-derived brines, driving up the $^{87}Sr:^{86}Sr$ ratio and depleting deuterium.

This model is supported by the $^{87}Sr:^{86}Sr$ ratio of late calcite cements and saddle dolomites of the upper Smackover in southern Arkansas as reported by Moore (in press) and

Stueber et al (1984). Late post-compaction, pre-hydrocarbon calcite cements have $^{87}Sr:^{86}Sr$ ratios that are only slightly higher than Jurassic seawater, whereas demonstrably older (Moore, in press) and perhaps post-hydrocarbon saddle dolomites contain $^{87}Sr:^{86}Sr$ ratios that are close to present Smackover-Edwards brine compositions of about 0.7090. These relationships effectively demonstrate a clear chemical evolution of the Smackover-Edwards brine as a function of the introduction and mixing of hydrocarbon and hydrocarbon-related fluids to and with Louann-derived brines, raising serious doubts of the validity of the Land and Prezbindowski brine model.

An additional point that should be discussed is Land and Prezbindowski's use of albitization to explain the aqueous Na:Cl ratio. Their model requires massive albitization to lower the Na:Cl molal ratio from unity to 0.69, the ratio of the average sodium and chloride compositions reported by Land and Prezbindowski (1981, Table 1). The initial value of unity is set by using halite dissolution to explain the chloride content of the brine. Calculations based on their model require the formation of 0.80 moles of albite for each kilogram of H_2O in the Edwards. Assuming similar compositions and reasonable flow rates of one pore volume change per million years over a 100 m.y. period, the total amount of albite formed would be 80 moles or 8,000 cm^3 of albite for each kilogram of H_2O presently in the Edwards. Where is this albite? Albitization of anorthite, balanced on aluminum, involves massive quartz dissolution; otherwise, the increase in volume of the solids would rapidly plug the flow path of the fluid. Quartz dissolution is generally not a major diagenetic event, as contrasted with quartz precipitation. Land and Prezbindowski need to present mass balance calculations and justify their "obsession" with albitization. We do not argue that albitization did not occur, only that it is not the major explanation for the low Na:Cl ratios in fluids from the Edwards.

SUMMARY

In summary, we note that enormous volumes of brines were generated during the precipitation of the Louann salt. We propose some brines moved into adjacent porous units along the edge of the basin by displacing less dense pore fluids. Following burial and compaction, the brines were expelled up the basin margin, mixing with interstitial fluids. Magnesium concentrations decreased and calcium concentrations increased by calcite dolomitization. Sulfate concentrations were depleted by anhydrite precipitation and by sulfate reduction. Some potassium may have been depleted by precipitation of potassium aluminum silicates. Albitization occurred but was not the primary cause of the low Na:Cl ratios in the brines. These ratios reflect halite precipitation from evaporating seawater during formation of the Louann brines. Deuterium was depleted and $^{87}Sr:^{86}Sr$ ratios were elevated by both organic and inorganic processes affecting the evolution of the brines along their migration paths up the basin margin into the Texas Edwards. Within the Edwards, the fluids are moving updip, mixing with interstitial fluids, and dissolving enough dolomite to maintain near equilibrium

with calcite and metastable dolomite. The lattice disorder in this metastable dolomite increases with decreasing temperatures.

We appreciate the opportunity that Land and Prezbindowski and the editors of AAPG have provided us to clarify and refine the Carpenter model for Mesozoic brine evolution in the Gulf Coast.

REFERENCES CITED

- Burke, W. H., R. E. Denison, E. A. Hetherington, R. B. Keopnick, H. F. Nelson, and J. B. Otto, 1982, Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time: *Geology*, v. 10, p. 516-519.
- Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins, *in* K. S. Johnson and J. R. Russell, eds., 13th industrial minerals forum: Oklahoma Geological Survey Circular 79, p. 60-77.
- Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D. K. Bird, 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: *American Journal of Science*, v. 278-A, 229 p.
- Hoefs, J., 1980, *Stable isotope geochemistry*: Berlin, Springer Verlag, 208 p.
- Land, L. S., 1967, Diagenesis of skeletal carbonates: *Journal of Sedimentary Petrology*, v. 37, p. 914-930.
- 1980, The isotopic and trace element geochemistry of dolomite—the state of the art, *in* Concepts and models of dolomitization: SEPM Special Publication 28, p. 87-110.
- and D. R. Prezbindowski, 1981, The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A.: *Journal of Hydrology*, v. 54, p. 51-74.
- 1985, Chemical constraints and origins of four groups of Gulf Coast reservoir fluids: *Comments: AAPG Bulletin*, v. 69, this issue.
- Langmuir, D. L., 1971, The geochemistry of some carbonate ground waters in central Pennsylvania: *Geochimica et Cosmochimica Acta*, v. 35, p. 1023-1045.
- Loucks, R. G., and D. A. Budd, 1981, Diagenesis and reservoir potential of the Upper Jurassic Smackover Formation of South Texas: *Gulf Coast Association of Geological Societies Transactions*, v. 31, p. 339-346.
- Moore, C. H., in press, Upper Jurassic subsurface cements: a case history, *in* Carbonate cements revisited: SEPM Special Publication.
- and Y. Druckman, 1981, Burial diagenesis and porosity evolution, Upper Jurassic Smackover, Arkansas and Louisiana: *AAPG Bulletin*, v. 65, p. 597-628.
- Murray, G. E., 1961, *Geology of the Atlantic and Gulf coastal province of North America*: New York, Harper and Brothers, 692 p.
- Pitzer, K. S., 1979, Theory: ion interaction approach, *in* R. M. Pytkowicz, ed., *Activity coefficients in electrolyte solutions*: Boca Raton, Florida, CRC Press, p. 157-208.
- Robie, R. A., B. S. Hemingway, and J. R. Fisher, 1979, Thermodynamic properties of minerals and related substances at 298.15°K and 1 bar (10^5 pascals) pressure and at higher temperatures: U.S. Geological Survey Bulletin 1452, 456 p.
- Rosenberg, P. E., and H. D. Holland, 1964, Calcite-dolomite-magnesite stability relations in solutions at elevated temperatures: *Science*, v. 145, p. 700-701.
- D. M. Burt, and H. D. Holland, 1967, Calcite-dolomite-magnesite stability relations in solutions—the effect of ionic strength: *Geochimica et Cosmochimica Acta*, v. 31, p. 391-396.
- Stamatedes, M. R., 1982, Dolomitization of the upper Smackover in Miller County Arkansas and adjacent areas: M.S. thesis, Louisiana State University, Baton Rouge, Louisiana.
- Stoessel, R. K., and C. H. Moore, 1983, Chemical constraints and origins of four groups of Gulf Coast reservoir fluids: *AAPG Bulletin*, v. 67, p. 896-906.
- Stueber, A. M., P. Pushkar, and E. A. Hetherington, 1984, A strontium isotopic study of Smackover brines and associated solids, southern Arkansas: *Geochimica et Cosmochimica Acta*, v. 48, p. 1637-1649.
- Van Der Strannen, C. M., 1981, Deuterium in organic matter: PhD dissertation, University of Groningen, Groningen, Netherlands.
- Woronick, R. A., and L. S. Land, in press, Late burial diagenesis, Lower Cretaceous Pearsall and lower Glen Rose Formations, south Texas, *in* Carbonate cements: SEPM Special Publication 37.
- Zherebtsova, I. K., and N. N. Volkova, 1966, Experimental study of behavior of trace elements in the process of natural solar evaporation of Black Sea water and Sasyk-sivash brine: *Geochemistry International*, v. 3, p. 656-670.