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THE ORIGIN OF SALINE FORMATION WATERS, III: CALCIUM CHLORIDE WATERS

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THE ORIGIN OF SALINE FORMATION WATERS, III: CALCIUM CHLORIDE WATERS

D. L. Graf, W. F. Meents, I. Friedman, and N. F. Shimp

ABSTRACT

The latitude dependence of deuterium content in formation waters from the Alberta Basin, the Michigan Basin, the Illinois Basin, and the Gulf Coast establishes the fresh-water origin of the water molecules now present but does not explain the origin of the dissolved solids.

Two simple models are defined for deriving typical saline water compositions of the Illinois and Michigan Basins by shale ultrafiltration of the dissolved solids contained in different quantities and proportions of fresh water and sea water. For the limiting case of minimum volumes, it is assumed that in both these input liquids (1) SO_4 is reduced bacterially and simultaneously replaced in solution by an equivalent amount of HCO_3 derived from breakdown of organic matter; (2) HCO_3 passes through the ultrafilter, accompanied by an equivalent amount of Na; and either (3a) the Mg deficiency observed in the analyses results from Mg having reacted with limestone to form dolomite, thereby returning an equivalent amount of Ca to solution, or (3b) the lost Mg has gone into the regrading and diagenetic formation of chlorite and other silicates, returning no Ca to solution.

The simplest explanation for the dissolved solids of the Illinois Basin brines is that they are derived from original sea water, with a contribution from fresh water that is too small to alter ionic balance recognizably. A volume of sea water about five times that of the present pore volume is adequate, if Mg loss is divided equally between the processes described in (3a) and (3b).

A volume of sea water about 10 times the present pore volume plus as many as 2000 pore volumes of fresh water would be required to derive the more Ca-rich Michigan Basin brines. More rapid circulation of fresh water in the Michigan Basin than in the Illinois Basin is consistent with the much steeper hydraulic gradients in the former that may have existed through much of post-Silurian time. Because of the possibility of Ca supply through processes involving

bedded anhydrite and gypsum, however, the dissolved solids contribution from fresh water in the Michigan Basin has to be regarded as indeterminate in terms of the models used in this paper.

Two kinds of regularity in chemical composition among the brines of the Illinois Basin support these arguments. The decrease, near the structural low in Mississippian formations, in rate of increase of salinity with depth is consistent with moderate amounts of water from lower formations moving across shales and emerging with lowered salinity. In the same geographical area the increase in relative concentration of Ca with depth in these brines is reversed, consistent with the assumption that shale ultrafilters pass more Na than Ca.

The Cl/Br ratios of most of the brines from the Michigan Basin are those expectable if the anion content of these brines is that which was left in concentrated sea water after precipitation of some halite. Two Michigan Basin brines from near the solution edge of the Salina Group salt have Cl/Br ratios suggesting they have dissolved bedded salt.

A table of some 400 new total dissolved solids determinations on Illinois Basin brines is included.

INTRODUCTION

This is the third of a series of three papers on the origin of saline formation waters. In the first paper, Clayton et al. (in press) discussed the stable hydrogen and oxygen isotopic compositions of 95 such waters from the Illinois Basin, the Michigan Basin, the Gulf Coast, and the Alberta Basin. The sedimentary section of the Illinois Basin differs from those of the other three areas in containing no bedded salt and only a small amount of anhydrite. Most of the variations in O¹⁸ content of the samples of Clayton et al. can be explained as resulting from temperature-dependent equilibration with limestone wall rock, and most of the variation in deuterium content as original differences in the isotopic content of precipitation. The work of Clayton et al. establishes the fresh-water origin of the water molecules now found in the brines, but it does not explain the origin of the dissolved solids. In the second paper, Graf et al. (1965) sought to show from the data of Clayton et al. that an isotopic fractionation occurs during the passage of water through micropores in shale.

The detailed geographic and geologic locations of these 95 sampling points are given in table 1, and the chemical analyses of the samples are given in table 2. The reliability of the chemical analytical values is discussed in an appendix. Uncertainties in sampling, in situ temperature estimates, and isotopic analyses are discussed in Clayton et al., (in press). We believe that publication in this detail is desirable because (1) brine disposal and secondary and tertiary recovery practices may soon contaminate formation waters so extensively in these oil fields that further sampling programs will be difficult or impossible; and (2) there is not yet very much known (especially in Illinois and Michigan) about directions and rates of water movement in the deeper formations, so that comparison of our measurements with such information can be made only in a later paper.

In this paper, we consider in detail the relation between total dissolved solids content and position in the Illinois Basin rocks, using not only the analyses

of table 2 but also the approximately 500 analyses and 250 total dissolved solids values in Meents et al. (1952) and 400 new total dissolved solids determinations reported here as table 3. Because the latter two compilations include all analyses believed to be valid, some geographical areas and some geological units are over-represented. We also define models that can be applied to individual cation and anion values in the analyses of table 2 to yield the number of volumes of fresh water and sea water needed to derive these compositions by shale ultrafiltration. The discussions by Chave (1960) and White (1965) are particularly relevant to the paper.

The stratigraphic subdivisions used in table 3 are essentially those of Meents et al. (1952). Several additional named intervals are shown, and samples from Devonian and Silurian rocks are listed separately. Total dissolved solids values for all "Devonian-Silurian" samples of Meents et al. that with reasonable certainty can be assigned to either Silurian or Devonian are repeated here.

Our depth versus composition plots use depth below the surface rather than corrected to a datum such as sea level. This is partly a matter of convenience. We estimate that 90 percent of wellhead elevations in Illinois are between 350 and 550 feet, although extremes of 333 and about 800 feet are known. This 200-foot variation is small compared with the range of depths from about 300 to 5500 feet. Even considering that most wells have depths in the narrower range from 1000 to 3500 feet, the uncertainty in wellhead elevation does not introduce an error that is intolerable for our purposes. A second reason for using depth below the surface is our interest in the operation of shales as ultrafilters, a property that should be dependent upon hydrostatic (or lithostatic) pressure and thus upon the depth of overburden.

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THE ORIGIN OF CALCIUM CHLORIDE BRINES

Analyses of Michigan Basin brines, such as those given in table 2, are striking in at least two respects. The anion fractions of HCO_3 and SO_4 are at most only a few percent of those in sea water (e.g., the analysis in Sverdrup et al., 1942, p. 166) and in fresh water (e.g., that leaving Lake Michigan at St. Ignace, Clarke, 1924, p. 74). The Ca content of the brines is very high, greater than that of Na in some samples, and increases proportionately with increase in total dissolved solids.

In figure 1, Na/Ca ratios are plotted against total dissolved solids values for those samples of table 2 for which analyses of these two cations were made. The plot thus includes some samples from the Gulf Coast and the Alberta Basin. Decrease of the Na/Ca ratio with increase in total dissolved solids is evident for both Michigan Basin and Illinois Basin samples. The dilute waters of figure 1 with 0.5 g equiv/liter or less of dissolved solids show a wide range of Na/Ca values, and some of them, therefore, would appear to invalidate the generalization about this ratio that we have just made. But it is implicit in that generalization that the dissolved

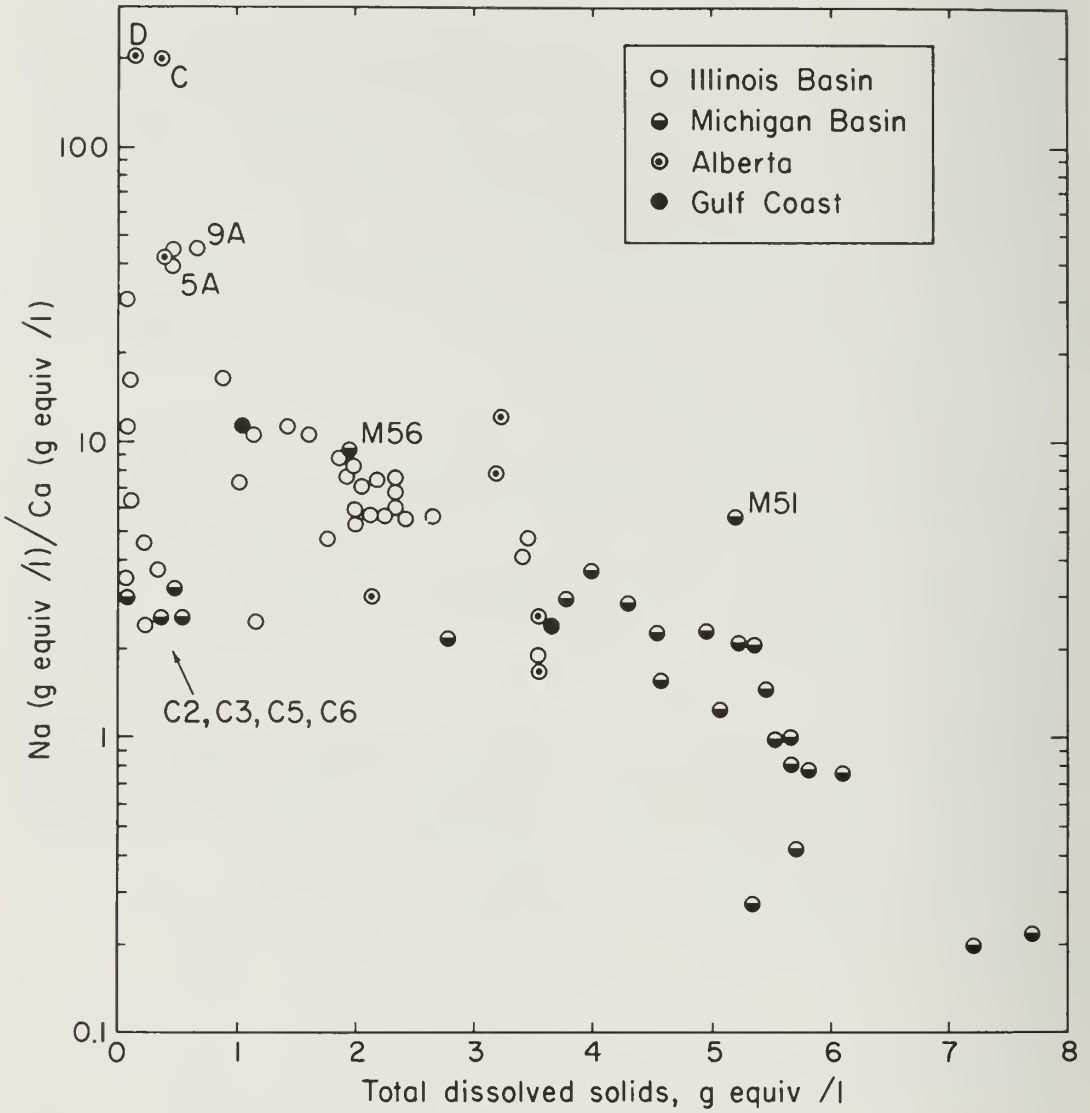


Figure 1. Total dissolved solids content plotted against Na/Ca ratio for the samples of table 2. The samples specifically identified are discussed in the text.

solids consist entirely of NaCl and CaCl₂, and a third of the dilute samples depart markedly in composition from the series of mixtures between these two end member solutions. The quantity (HCO₃ + CO₃) becomes a significant fraction of anions in two Alberta waters (C, D) and Mg exceeds Ca in several Ontario and Illinois samples (C2, C3, C6, 5A, 9A). Samples M51 and M56, which may have dissolved bedded salt, are discussed at greater length later in the paper.

The more obvious geologic processes are inadequate as explanations of the origin of these concentrated CaCl₂ brines, which occur in sedimentary basins in areas free of major orogeny. Igneous activity cannot be called upon to furnish acid water to dissolve limestones, and calcium is largely precipitated as carbonate and sulfate early in the normal evaporation of sea water. The surface water closest in composition to these subsurface brines is that of the Dead Sea, which has a considerable Ca content balanced by Cl, together with even greater amounts of MgCl₂ and NaCl. However, two thirds of the dissolved solids of the Dead Sea are estimated by Bentor (1961) to have been contributed by springs that discharge CaCl₂-rich subsurface waters of the type we are discussing. Borchert and Muir (1964) review the evidence for formation of CaCl₂ solutions by sulfate-reducing bacteria in environments where organic matter and anhydrite occur together. Whatever its significance in other areas, this process certainly cannot be important in the nearly anhydrite-free Illinois Basin.

Of particular interest, therefore, is the experimental demonstration by McKelvey and Milne (1962) and Hanshaw (1962) that a compacted clay aggregate subjected to directed fluid pressure acts as a charged ultrafilter that rejects electrolytes. Although these workers used only NaCl in their experiments, it should be possible in principle to ultrafilter all substances that form ions in solution and perhaps to exert an effect upon molecules of high dipole moment. Formation-water salinity might be built up by retention of ions dissolved in fresh or sea water moving through sedimentary rocks under a hydraulic gradient or being expelled under compaction. The efficiency of ion rejection decreases with increased solution concentration (Kemper, 1961; Hanshaw, 1962). White (1965, p. 350) has further suggested that efficiency in a mixed solution will not be the same among the several anions and cations nor among the various nonionized constituents. The compositions of the natural waters discussed in the next section of the paper have led us to adopt White's viewpoint as a central premise of our argument, even though the concept of selective ultrafiltration seems as yet not to have been verified experimentally.

From the crudely parallel example of van der Waals adsorption in micropores, ultrafiltration through a clay should be closely related to the ion exchange population on the clay at the particular pressure, temperature, and solution composition. Ash et al. (1963) found, for a mixture of H₂ and SO₂ being forced under pressure through porous silica or carbon at temperatures up to 0°C., that the adsorbed phase was transported to the virtual exclusion of the other. If a strict analogy is appropriate, a compacted clay in contact with a solution of mixed ionic composition should preferentially allow to pass that ion species occupying exchange positions.

But there is essentially no information available on the adsorbed cation population of clays in concentrated multi-cation brines, nor of the response of this population to progressive changes in solution composition. The specificity of clays for cation exchange varies with compaction; Hanshaw (1962), defining specificity by a comparison of activities of the several cationic species at the same potential, found experimentally that illite compacted to 5000 psi prefers Na and K to Ca and Mg. This specificity is the reverse of that generally reported for dispersed clay systems. A further complication is introduced by the studies of McAtee (1958) and by Mungan

and Jessen (1963), which showed different size fractions of the same sample, and perhaps even different regions within the same particle, to have different adsorbed cation populations.

Appeals to ion exchange to explain changes in water composition, such as that of Foster (1950), have not included measurements of the cation population of the clays in different hydrologic zones. For the problem of Michigan Basin brine origin, in particular, this explanation has the further disadvantage that a single loading of ion exchange positions is quantitatively inadequate to explain changes in solution composition. If our earlier assumption about preferential transport is correct, loading of exchange positions with a given cation can be considered the first phase of the ultrafiltration which follows, for both processes differentially remove the specified cation from the liquid remaining behind the barrier.

There are recognizable patterns of chemical and isotopic composition among the Illinois Basin and Michigan Basin analyses that lend support to our emphasis upon shale ultrafiltration. We consider these patterns in the next two sections of the paper.

PATTERNS IN CHEMICAL COMPOSITION

The Cypress, Bethel (Paint Creek), and Yankeetown (Benoist) Formations in the Chesterian (Upper Mississippian) section of the Illinois Basin are principally sandstone, and the intervening formations consist of limestone and shale. (These are the stratigraphic intervals used in table 3. The "'Benoist'-Bethel-Paint Creek" category of Meents et al (1952) combined the latter two.) Plots based upon the total group of analyses from these three units show several kinds of regularity. On the dissolved solids versus depth plot of figure 2, the samples fall into three groups (labeled A, B, and C) that correlate with geographical areas of the Illinois Basin (A, B, and C of figure 3). The rate of increase of salinity with depth from the west

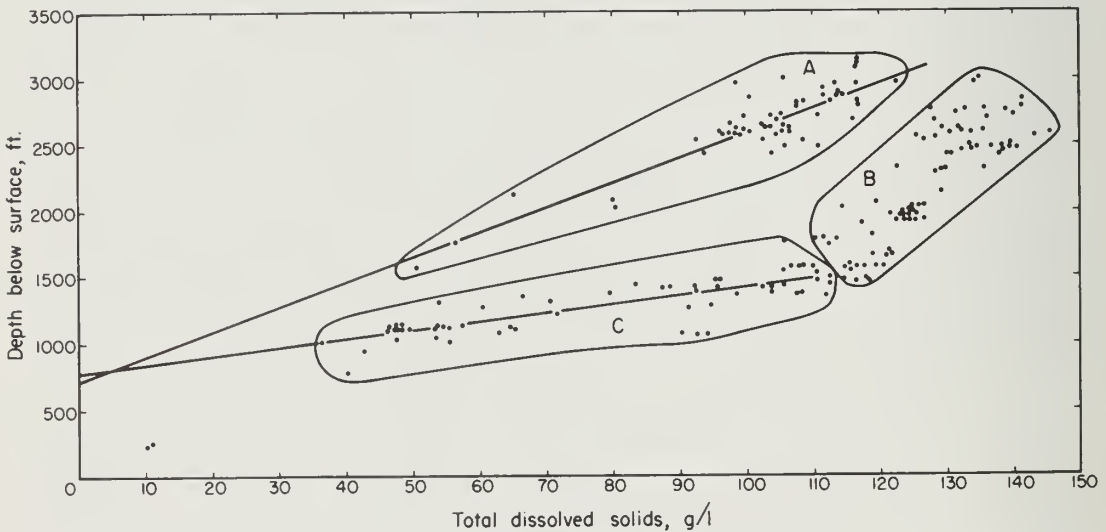


Figure 2. Total dissolved solids content plotted against depth for the Illinois Basin samples of table 1 from the Cypress, Bethel, and Yankeetown Sandstones and for the stratigraphically equivalent samples that Meents et al. (1952) listed under the headings "Cypress" and "'Benoist'-Bethel-Paint Creek." Sample groups A, B, and C correspond to areas A, B, and C of figure 3.

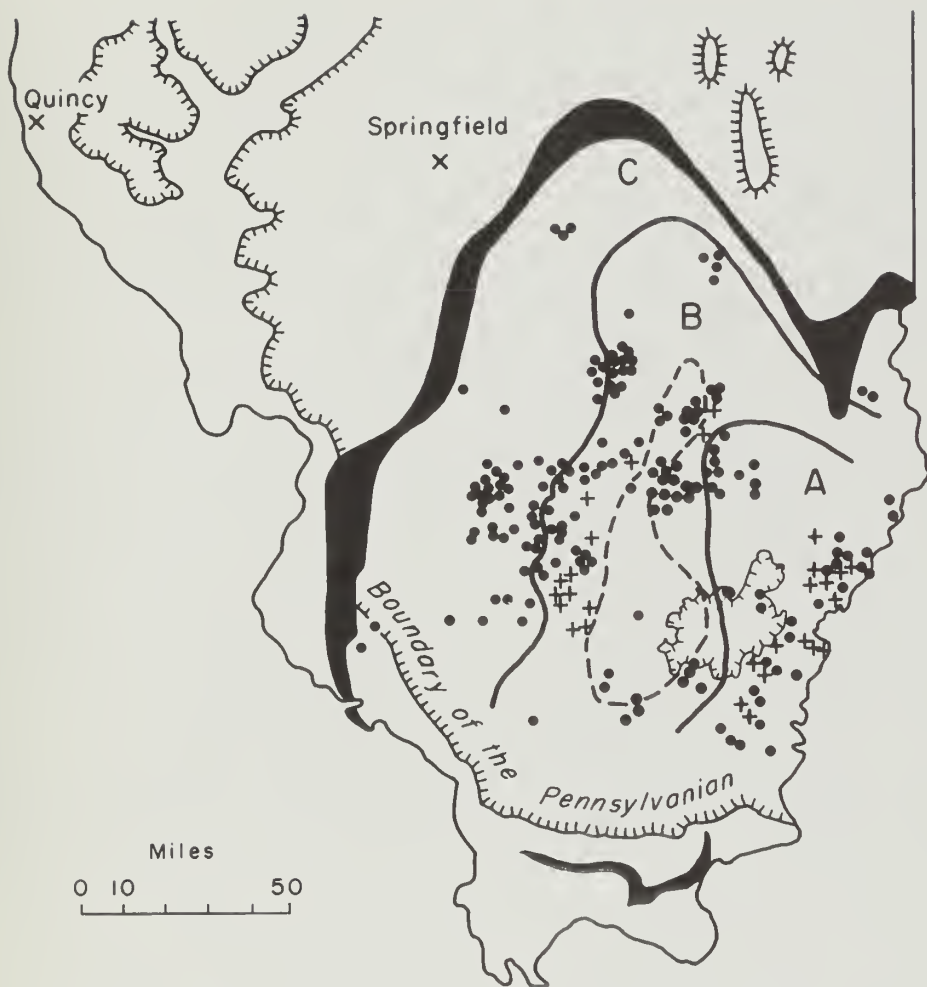


Figure 3. Location of the samples of figure 2. The outcrop belt of the Cypress-Yankeetown interval (subcrop where under the Pennsylvanian) is sketched in black, disregarding faults (see Swann and Bell, 1958). The closed dashed line is the isoconcentration contour for 130,000 mg/liter total dissolved solids (Meents et al., 1952, figs. 6 and 7). Samples with Ca equivalent fractions greater than 0.11 are shown as pluses. Dots represent both the samples for which this fraction is less than 0.11 and those for which only dissolved solids determinations are available. The depression contour shows the deepest part of the Illinois Basin north of the Shawneetown Fault Zone.

and northwest (sample group C) is greater than that from the southeast (sample group A). This difference in hydrologic behavior presumably is related to differences in lithology and attitude of the associated sections. Salinity increases the least of all with depth near the structural low of these beds (sample group B), a relation consistent with a moderate amount of water from lower formations moving across shales, emerging relatively free of dissolved solids, and diluting the brine with which it mixes. The change in Ca cation fraction with position in the basin, which is discussed subsequently, supports this explanation and makes it unlikely that the geometry of figure 2 can, for example, be related simply to the thickness of the underlying section from which dissolved solids could be concentrated during compaction. Bredehoeft et al. (1963, 1964) presented additional arguments in favor of upward moving water at the Illinois Basin center.

Lines fitted by least-squares analysis to sample groups A and C intersect the zero ordinate of figure 2 at essentially the same point, 750 feet depth. Two isolated samples from very shallow wells that may contain admixed fresh water were ignored in the fitting. Figure 4 shows for comparison a plot of brine samples from the Woodbine Sand of Late Cretaceous age in northeast Texas (Plummer and Sargent, 1931; those analyses of their table 7 for which both total solids and depth are given). The ordinate intercept of figure 4 is about 2900 feet, and a high-slope, low-salinity line of points extending down to the origin is evident. We interpret such ordinate intercepts as depths below which two conditions are fulfilled: (1) shale ultrafiltration is effective; and (2) the interstitial water originally present was sea water (or evaporite-sea water). The depth of 750 feet is in reasonable agreement with a minimum differential pressure for effective ultrafiltration estimated by B. B. Hanshaw (personal communication) to lie between 200 and 500 psi. Shallow samples with smaller dissolved solids contents than predicted by the ordinate intercept line might be explained by (1) failure of ultrafilters to operate, so that the dissolved solids originally contained in interstitial sea water were flushed out, or (2) nonmarine origin of the near-surface part of the formation, so that ultrafilters have been able to concentrate ions only from fresh water. If a salinity distribution were relict from an earlier geologic period (e.g., a consequence of compaction) and there had been significant erosion or deposition in the intervening time, an appropriate correction would have to be applied to the depth parameter for it to be descriptive of depths during the brine-generating process.

Those samples of figure 2 for which complete analyses are available have been replotted on figure 5 and this figure then divided into arbitrary regions according to the ratio of Ca equivalents to total cation equivalents. Points with ratio values outside the range of the region in which they plot are indicated by x's.

The zonation of Ca equivalent ratios in figure 5 is an approximate one, which could not be demonstrated as well if the numerical limits for the regions were shifted, but it suffices to show that the ratio increases with depth and salinity and then reverses. Points with ratios $>.11$ (excluding x points) are shown on the map of figure 3 as pluses. These samples lie immediately on either side of a central region of lower ratios, consistent with upward moving water emerging enriched in Na relative to Ca. The ratio distribution pattern is shifted southeastward relative to the distribution of total salinity, and the structural low of the formation is in turn southeastward from the center of the ratio distribution pattern.

It would be of great interest to compare sets of diagrams like figures 2, 3, and 5 for stratigraphic intervals throughout the entire section in the Illinois Basin. Unfortunately, there are only a few other intervals for which samples are available

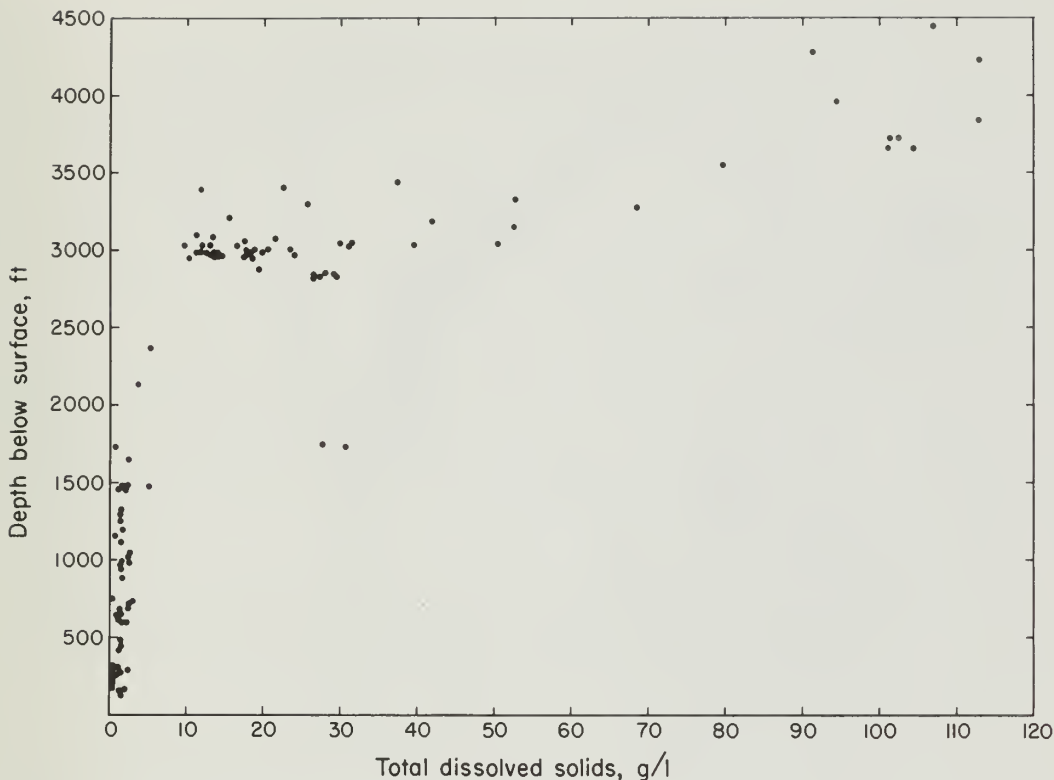


Figure 4. Total dissolved solids content plotted against depth for brines from the Woodbine Sand of northeast Texas (data of Plummer and Sargent, 1931).

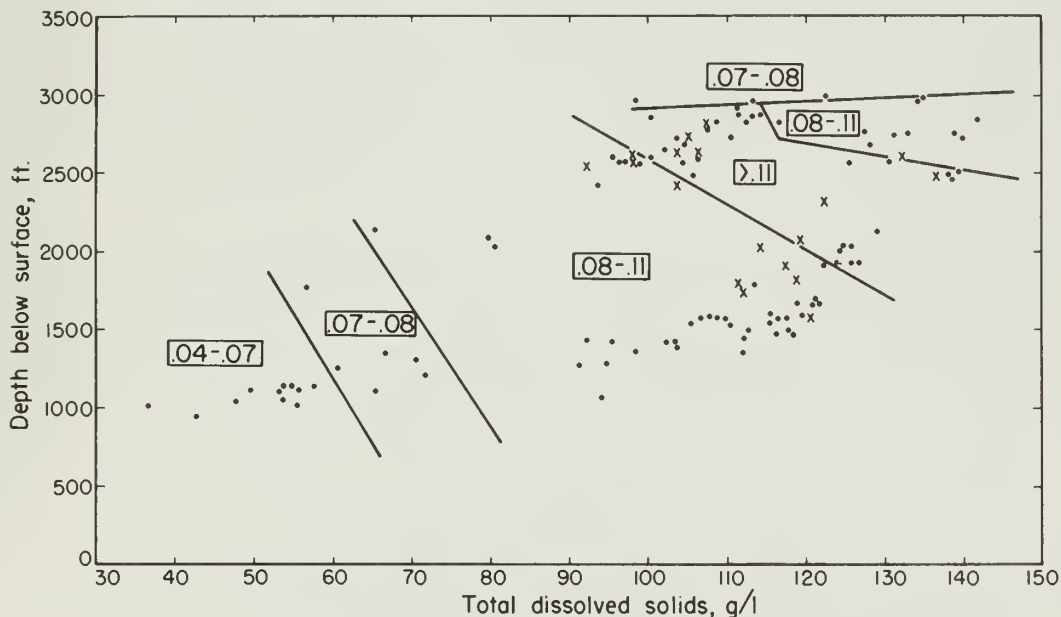


Figure 5. The plot of figure 2, omitting those samples for which chemical analyses are not available, zoned on the ratio of Ca equivalents to total cation equivalents. Points with ratio values outside the range of the region in which they plot are indicated by x's.

both near the basin center and on the basin flanks, and diagrams for these intervals (figs. 6-10) repeat only one or another of the regularities of figures 2, 3, and 5. Figures 6-10 are valuable, nevertheless, in showing that the relationships we have been discussing are not a peculiarity of the Cypress-Bethel-Yankeetown interval.

Samples from the Ste. Genevieve Limestone, a unit of Valmeyeran (Middle Mississippian) age that includes the Spar Mountain Sandstone Member, show a reversal in Ca equivalent ratios near the basin center (figs. 6 and 7). No great significance can be attached to the slopes of the zone boundaries in figures 5 and 6. At most, they suggest that the ratio is significantly dependent upon the variables expressed on both axes, rather than either one alone.

Samples from the Aux Vases Sandstone, which is also of Valmeyeran (Middle Mississippian) age and immediately overlies the Ste. Genevieve Limestone, repeat the three-fold regional division of figure 2 (figs. 8 and 9). There are in addition four samples much more saline for their depth than any of the others (region D). They could be brines from a lower formation that have risen unchanged along a fault, or they could be Aux Vases brines from an area bypassed by the cross-formational water flow we have assumed.

Samples from the dominantly carbonate Silurian section of the Illinois Basin show considerable scatter on a depth versus salinity plot. The average of the ordinate intercepts for the two limiting guide lines of figure 10 is about 800 feet. The guide lines are arbitrary; if enough analyses were available, the points presumably could be fitted to a bundle of subparallel lines corresponding to different local hydrologic environments.

A depth versus total dissolved solids plot of *all* the Illinois Basin analyses listed in Meents et al. (1952) and in our table 1 repeats some of the patterns just described. Figure 11 is a schematic representation of this plot; the main mass of points, which lies above the line OAC drawn tangent to it, is omitted. The eight

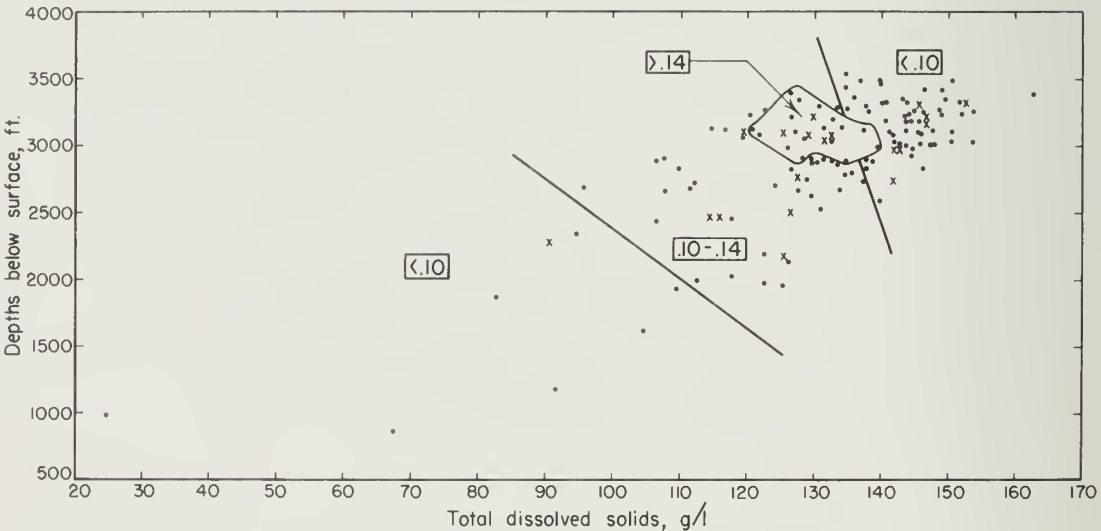


Figure 6. A plot of total dissolved solids content against depth for those Ste. Genevieve brines for which there are chemical analyses, zoned on the ratio of Ca equivalents to total cation equivalents. Points with ratio values outside the range of the region in which they plot are indicated by x's.

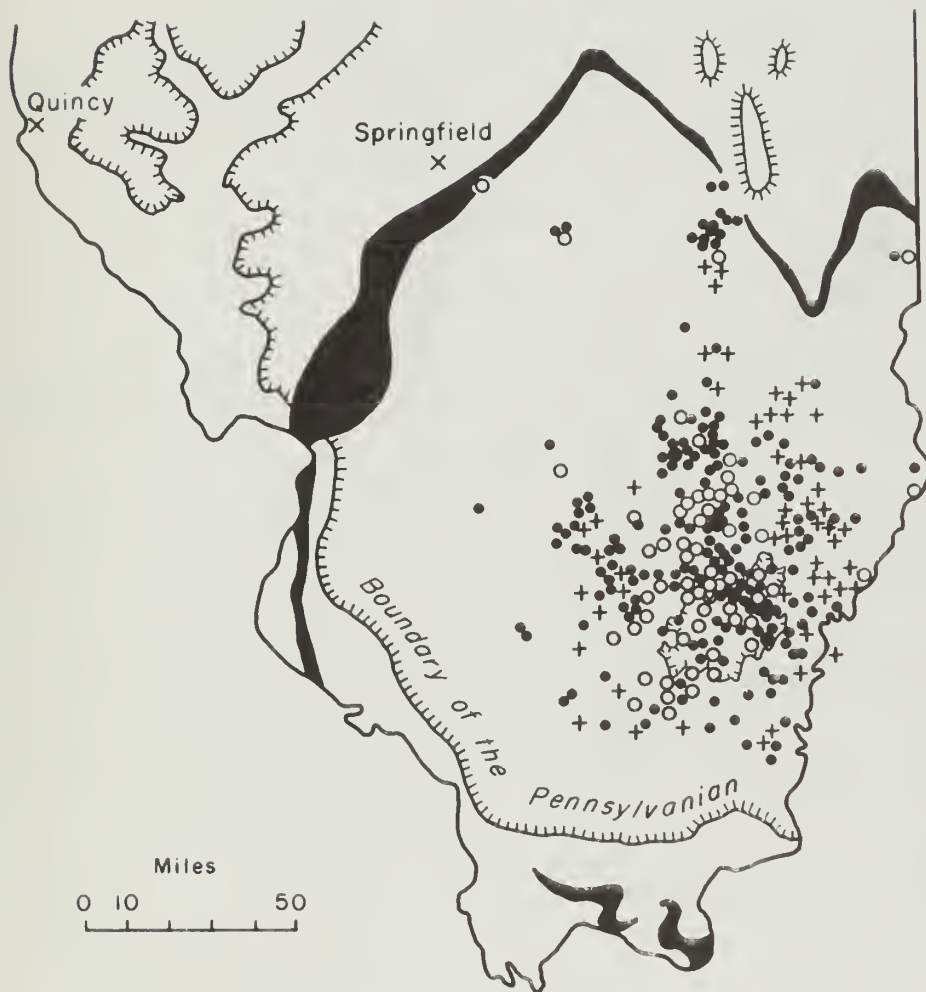


Figure 7. Location of brine samples from the Ste. Genevieve Limestone (Meents et al., 1952; table 1 of this paper). The outcrop of this formation (subcrop where under the Pennsylvanian) is sketched in black, disregarding faults (see Swann and Bell, 1958). Samples with Ca equivalent fractions greater than 0.10 are shown as pluses, and those with values less than 0.10 as open circles; dots indicate samples for which only dissolved solids determinations are available. The depression contour shows the deepest part of the Illinois Basin north of the Shawneetown Fault Zone.

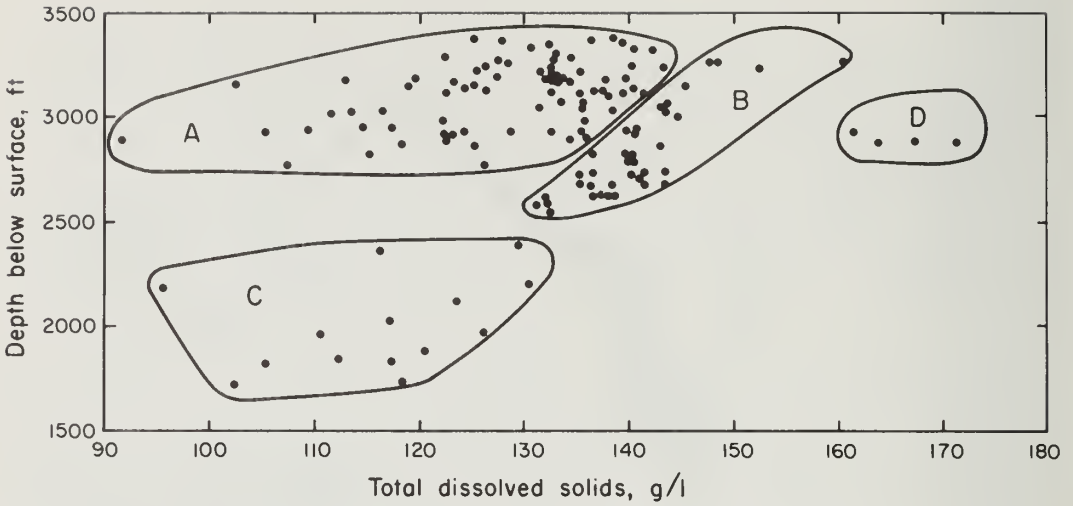


Figure 8. Total dissolved solids content plotted against depth for Illinois Basin samples from the Aux Vases Sandstone. Sample groups A, B, C, and D correspond to areas A, B, C, and D of figure 9.

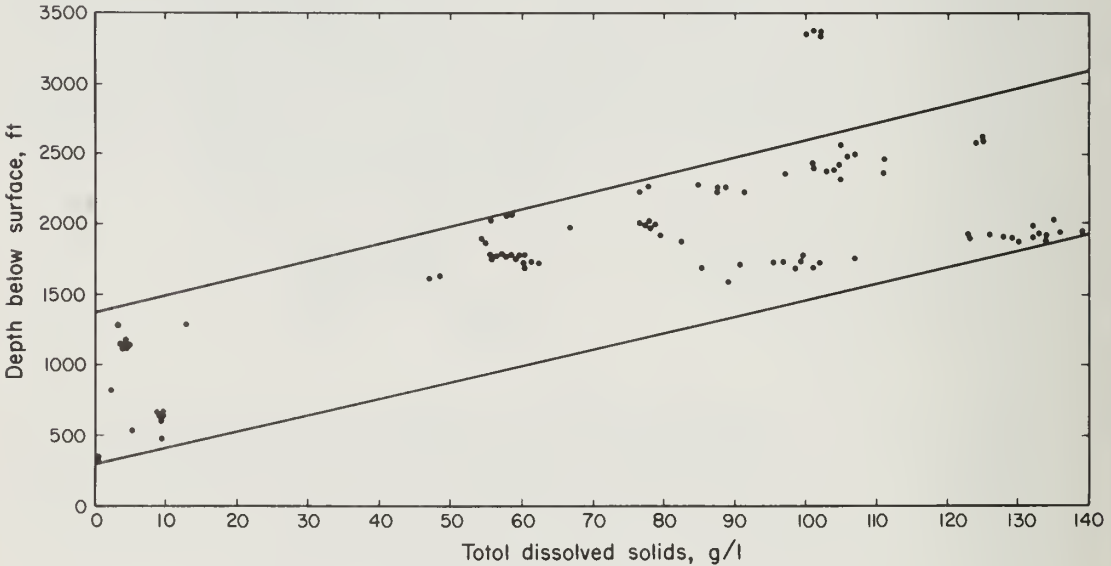


Figure 10. Total dissolved solids content plotted against depth for Illinois Basin samples from the Silurian System.

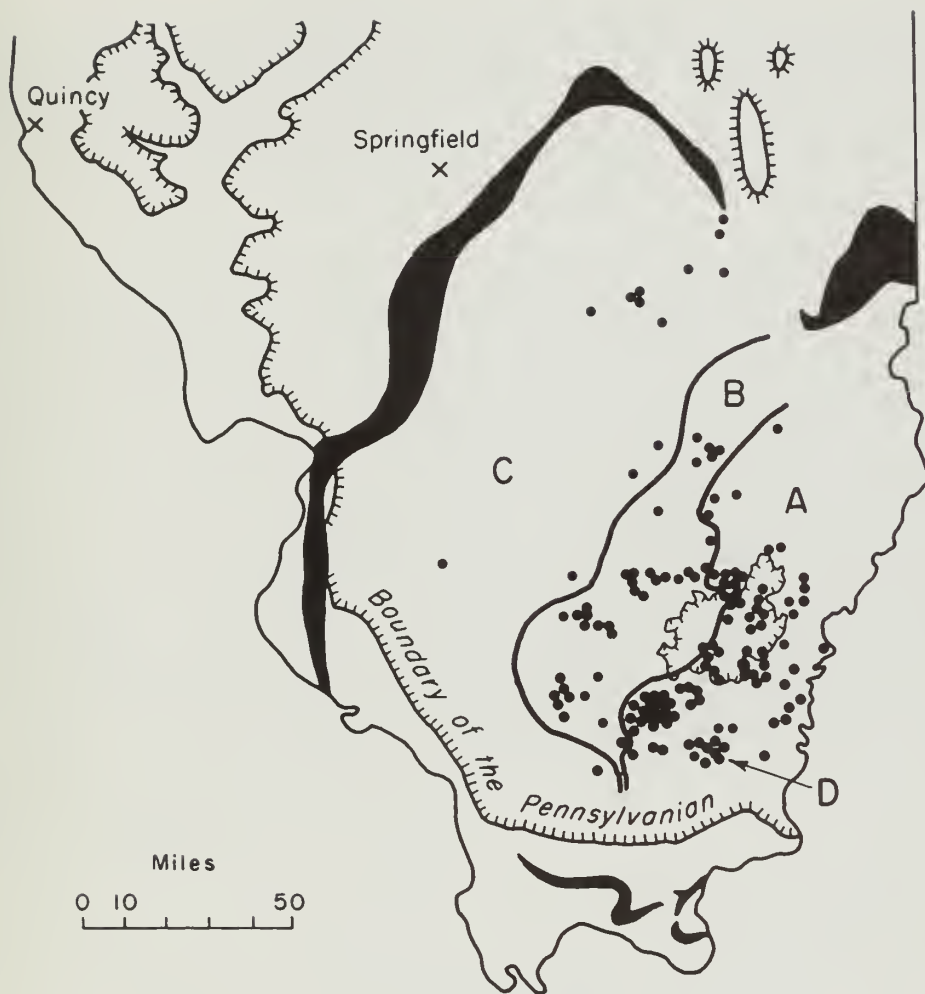


Figure 9. Location of the samples of figure 8. The outcrop belt of the Aux Vases Sandstone (subcrop where under the Pennsylvanian) lies within the somewhat greater stratigraphic interval sketched in black (see Swann and Bell, 1958). The depression contour shows the deepest part of the Illinois Basin north of the Shawneetown Fault Zone.

points below OA represent brines from Pennsylvanian age rocks, which show a great range in salinity/depth relations. The analyses in the area CAB, which postdate Meents et al. (1952), are mostly from the northern flank of the basin (Silurian-Devonian of Christian and Macon Counties, Ste. Genevieve Limestone of Coles and Douglas Counties), but the four anomalous Aux Vases Sandstone brines (region D, fig. 8) also are included. The slope AC, which was noted in figures 2 and 8, is further confirmed by a small group of highly saline brines from Devonian rocks in Wayne County.

The distribution patterns of those samples with the greatest relative amounts of SO_4 and HCO_3 do not show regularities comparable in significance with those of the total dissolved solids and Ca equivalent ratio plots. For convenience, we use concentrations expressed as g/liter and in figure 11 plot as x's those samples in which SO_4 is more than 3 percent of total anions. Of these samples, the ones with less than 40 g/liter total dissolved solids are scattered over a wide range of depth/salinity values. Although the more saline ones come from throughout the stratigraphic section, all but one of them are from a strip within 20 miles of the Wabash River in southeastern Illinois. Meents et al. (1952, figs. 9 and 10) observed that brines from the Ste. Genevieve Limestone with the highest SO_4 content occur southeastward from those of highest salinity. Extreme southeastern Illinois is extensively faulted, and it is possible that the SO_4 was introduced in fresh water relatively recently and has not yet been reduced, precipitated, or lost through ultra-filters (see following sections of this paper).

Brines in which HCO_3 is more than 3 percent of anions typically come from relatively shallow wells into Pennsylvanian rocks and into pre-Mississippian formations on the northern and western flanks of the basin.

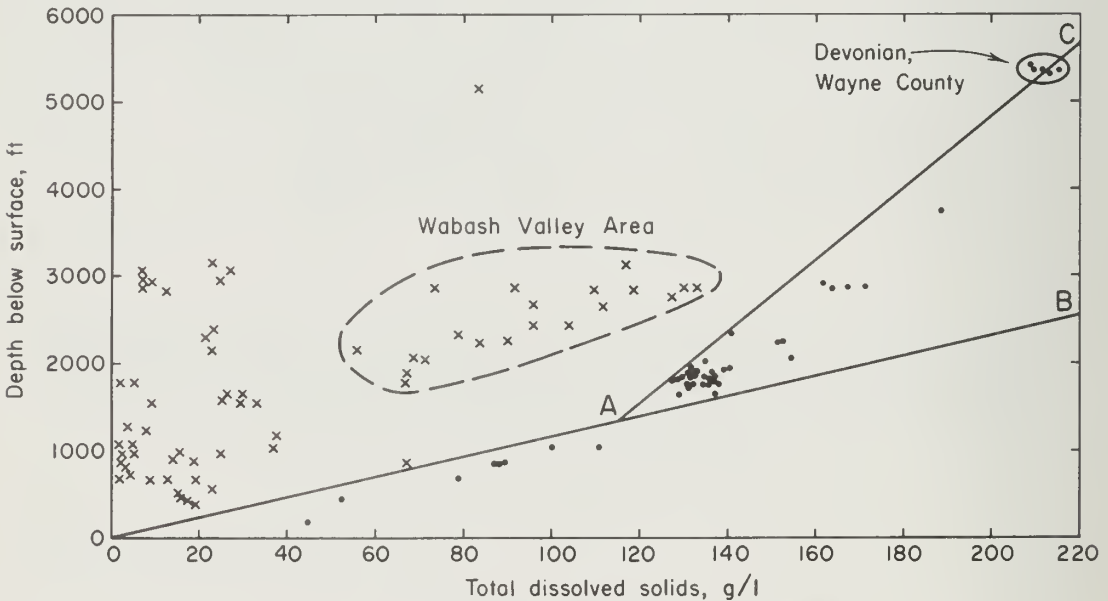


Figure 11. A schematic plot of the relation between depth and total dissolved solids content for the samples of table 1 and of Meents et al. (1952). All samples that plot below the line OAC are shown as dots. Above that line only those points are shown (x's) for which the concentration of SO_4 in g/liter is more than 3 percent of total anion concentration. The two named groups of samples are discussed in the text.

PATTERNS IN ISOTOPIC COMPOSITION

Figures 12-14 are plots of normalized deuterium concentration against total dissolved solids, against Ca, and against Na, respectively, for the samples of table 2. The symbol δD is defined as

$$\delta D (\%) = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{SMOW}}}{(D/H)_{\text{SMOW}}} \times 100.$$

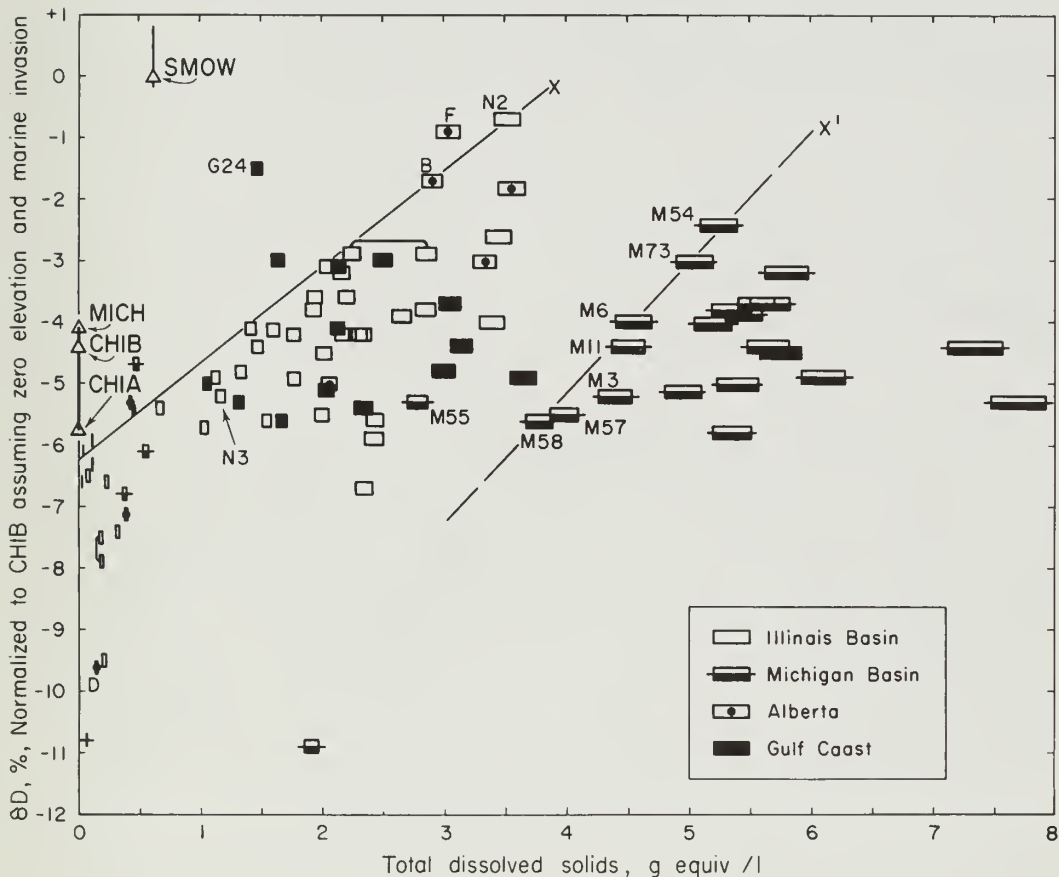


Figure 12. Normalized δD values plotted against total dissolved solids content for the samples of table 2 (see text). The slope of the X and X' lines is interpreted as measuring the operation of shale ultrafilters with good diffusional mixing in the liquid reservoir. There are no Gulf Coast samples containing less than 1 g equiv/liter dissolved solids. Figure 12 is the same as figure 4 of Graf et al. (1965), except that the features identified for discussion in the text are different.

SMOW is standard mean ocean water, as defined by Craig (1961), and MICH refers to a sample of Lake Michigan surface water from about 42° N latitude (Epstein and Mayeda, 1953). CHIA and CHIB are two estimates of the deuterium content of precipitation at Chicago (see Graf et al., 1965). The vertical bar through SMOW in figure 12 includes the isotopic compositions of those marine waters from which most marine sedimentary rocks are deposited. The dimensions of the rectangles in figures 12-14 give probable analytical errors, $\pm 0.1\%$ for δD and $\pm 3\%$ of the amount present for chemical quantities. The normalization of δD values to CHIB removes that variation in isotopic composition correlated with differences in the latitude and elevation at which precipitation occurred (see Graf et al., 1965).

Normalized δD values increase with Ca concentration for those Michigan Basin samples containing less than 2 g equiv/liter of Ca (fig. 13). The normalized δD values of Illinois Basin samples plotted in figure 13 either show the same relationship, or are independent of Ca concentration, depending upon the importance

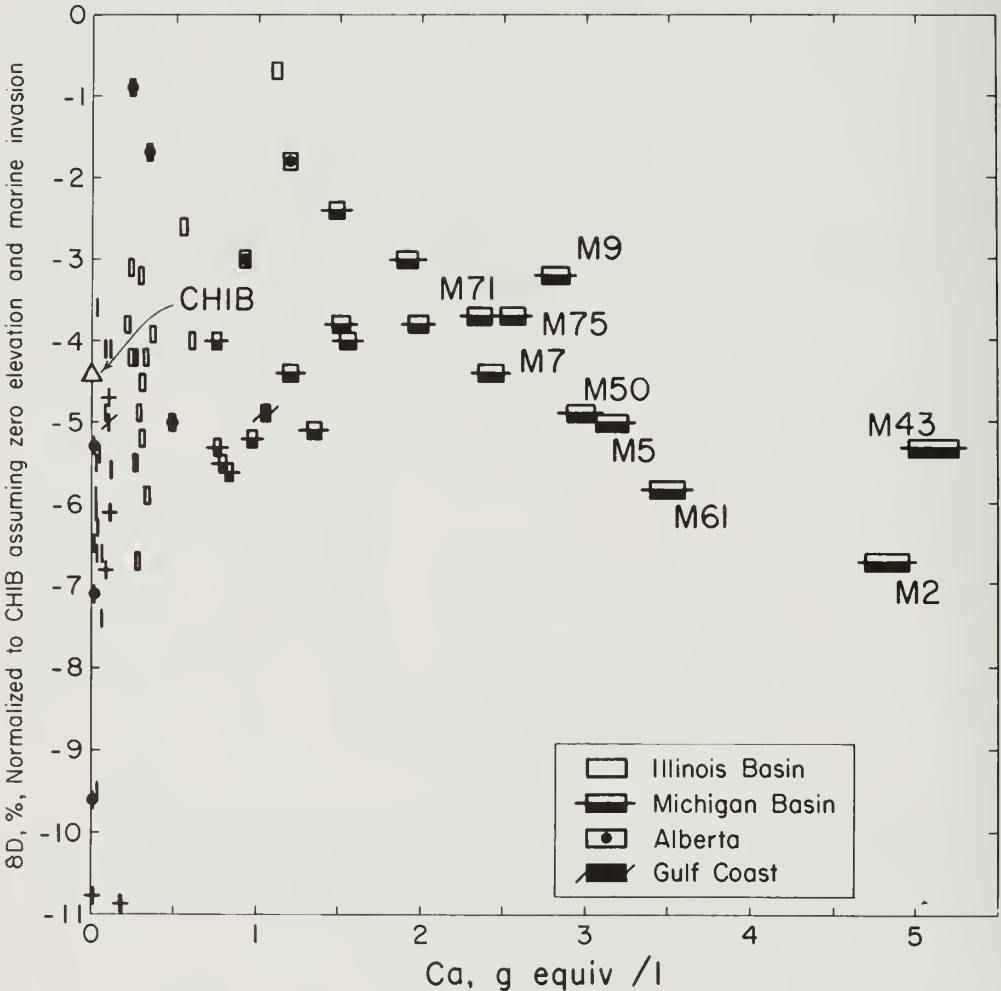


Figure 13. Normalized δD values plotted against Ca content for the samples of table 2 (see text). The samples specifically identified are discussed in the text.

that one attaches to the three samples that are most Ca-rich. A positive correlation between normalized δD values and Ca concentration is consistent with the assumptions that (1) water emerging from a shale micropore system will be isotopically lighter than that left behind (see Graf et al., 1965), and (2) more Na than Ca is passing through the particular shale ultrafilters. The geographic reversals in direction of change of the Ca equivalent ratio in the Illinois Basin (figs. 3 and 7) were interpreted within the scope of these assumptions as resulting from reversals in the direction of hydraulic flow.

But the relation between δD and Ca concentration reverses for 6 or 8 of the Michigan brines richest in Ca. This reversal clearly requires a change in process, whether in ultrafilter properties or in the nature of the input liquid. A hypothetical example of the latter would be the arrival of isotopically light, CaSO_4 -saturated water released by the dehydration of gypsum. It is not, in fact, clear how light such water would be. We shall not attempt to explain the geometry of figure 13 further or to incorporate it into a model of brine origin.

Plots of normalized δD against K and against Mg, which are not shown, can be constructed easily enough from the information contained in table 2 of this paper and table 1 of Graf et al. (1965). The first of these graphs has a limb of reversed slope defined by the 5 most K-rich Michigan brines, and thus duplicates the geometry of figure 13. That pattern is much less evident in the Mg plot, because samples M7, M5, M50, and M61 shift to the left against the other limb of the Michigan Basin sample distribution, leaving only samples M43 and M2 to suggest a reversal of slope.

The analogous plot against Na content (fig. 14) shows only a single linear trend, but this plot is different in kind from that of figure 13. Because the amount of Na in the samples richest in Ca decreases not only relative to Ca but also in absolute amount, samples arranged in order of increasing Na content are not in order of total dissolved solids content.

We next discuss the geometry of figure 12 at some length, realizing that we may be overinterpreting. We ignore the samples with less than 0.5 g equiv/liter dissolved solids, at least some of which may contain isotopically atypical water from Pleistocene glacial climates (Clayton et al., in press). There is a rather well-defined floor to the main field of plotted points at about $\delta D = -6\%$. The other side of the Illinois Basin point distribution is delimited by the diagonal line extending up to X with a slope of $(0.78\% \text{ in } \delta D)/(1.0 \text{ g equiv/liter})$. We interpret this slope as a maximum observed natural value for the ratio of two ultrafilter properties, (isotopic fractionation of hydrogen isotopes)/(ultrafiltration of ions). Considering the normalization shifts involved, samples from the Alberta Basin and the Gulf Coast conform remarkably well to the X line. Only Gulf Coast sample G24 lies more than one ordinate unit above it. There is among the Michigan Basin samples the limiting relationship indicated by the X' line, which is shifted to the right in figure 12 from the X line but has about the same slope. It is important to note that the samples which define the X' line all plot on the lefthand limb of figure 13, like the samples from the Illinois Basin, and therefore are not involved in the phenomenon responsible for the reversed slope of the righthand limb of that figure.

The most saline sample analyzed from the Illinois Basin, N2, lies near the outer end of the X line of figure 12, together with Alberta samples B and F. The anomalous position of these three samples on the plot of normalized $\delta^{18}\text{O}$ versus normalized δD (fig. 7) of Graf et al. (1965) led these authors to suppose that water movement through them had been slow enough to permit much better diffusional

mixing than for other samples. The fact that N2, F, and B lie at one end of the total Illinois Basin-Gulf Coast-Alberta Basin sample group in figure 12, rather than being separated from it, is encouraging, as is the position of sample N3 (from the Upper Cambrian Mt. Simon Sandstone, like N2) reasonably close to the X-line. According to the idea set forth by Graf et al. (1965), the Illinois Basin samples lying well to the right of the line are from regions of more rapid circulation, in which the realizable micropore effect is decreased because of the ineffectiveness of back diffusion, but dissolved solids in the aquifers accumulate steadily behind shale barriers. In other words, these points fall vertically below the X-line because of poor mixing in reservoirs behind barriers.

There will, of course, be no isotopic micropore effect corresponding to the dissolved solids concentration present in the original interstitial sediment water. Supposing the initial salinity of the Illinois Basin samples to have been that of present-day sea water, we can correct for this salinity component by moving the X line the proper amount to the left but allowing it to keep its present slope. It then cuts the ordinate in the CHIA-CHIB interval. An initial salinity double that of present-day sea water gives an intersection at CHIB. Either assumption improves the position of the intersection relative to the isotopic composition of fresh water. Cloud (1962) reported that salinities of the waters overlying the calcareous sediments accumulating west of Andros Island, Bahamas, average 10 percent higher than mean sea water and locally are 30 percent higher.

The same reasoning applied to the Michigan Basin samples yields an estimate of initial concentration six or seven times that of sea water. The alternative is accumulation of the total dissolved solids content by ultrafiltration, but downward

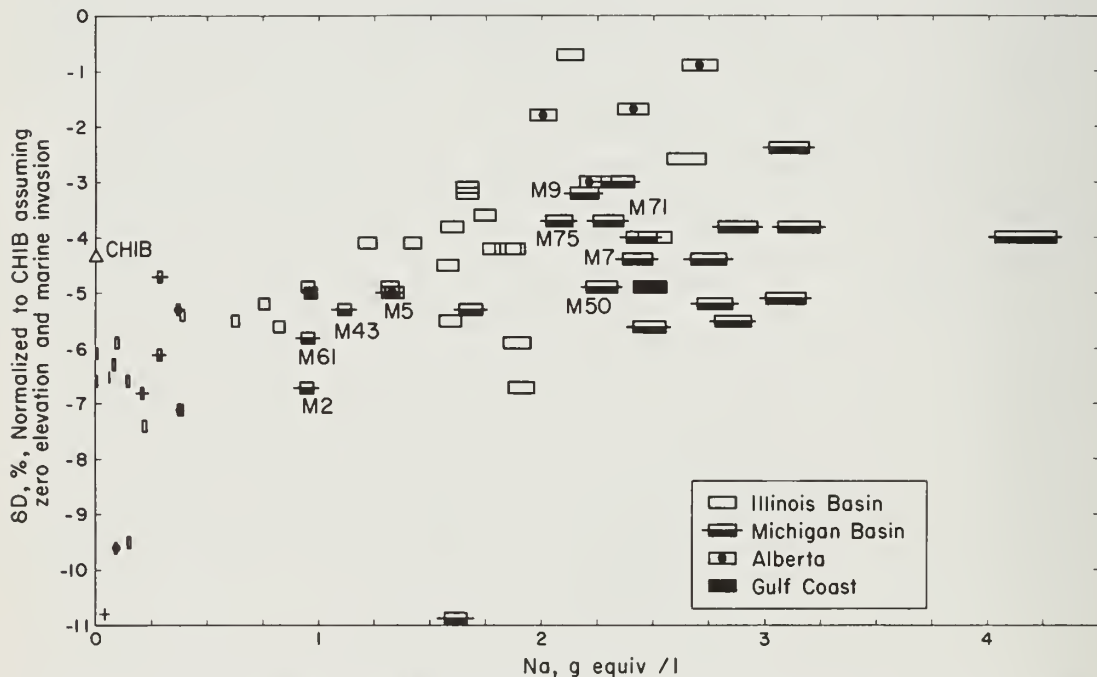


Figure 14. Normalized δD values plotted against Na content for the samples of table 2 (see text). Individual cation concentrations are known for only two Gulf Coast samples. The samples specifically identified are discussed in the text.

prolongation of the X' line to intersect the zero ordinate gives an improbably light isotopic value for the water participating in such a process.

The seven samples that define the X' line are well spread geographically, but their distribution in depth could be improved, and the X' line may be a fortuitous result of sample choice. For it to have validity, the transition zone (e.g., M55) between entering fresh waters and highly saline brines in Michigan must be quite narrow, so that the chance of encountering total dissolved solids values between 0.5 and 3.5 g equiv/liter is slight. It also follows that either (1) the dissolved solids concentrations of interstitial sediment solutions from successive depositional environments must have been averaged out by post-depositional mixing (there are beds of halite in the Michigan Basin, and halite begins precipitating from sea water at about ten-fold concentration), or (2) displacement of Michigan Basin points from the X' line results not only from imperfect isotopic mixing in brine reservoirs behind barriers (vertical shift downward in fig. 12), but also from original salinity differences (horizontal shift to the right).

The interpretation that we have suggested for the geometry of figure 12 has two further implications:

- (1) Because the base value upon which the variations within the Illinois Basin point cluster are superimposed is that of fresh water rather than that of sea water, replacement of sea water by fresh water in each formation must have taken place early enough in geologic history to allow the isotopic micropore effect of the X-line to build up later. If this fresh-water replacement occurred before most of the dissolved solids redistribution during compaction, the X-line slope may be a useful minimum estimate of the ratio (isotopic fractionation of hydrogen isotopes)/(ultrafiltration of ions) to be expected in laboratory experiments in which well-stirred solutions of known salinity are forced through compacted clay. The slope will not be meaningful for these experiments if it records a two-stage process in which the isotopic effect was generated by fresh water circulation that took place in later, hydrologically favorable periods after the distribution of chemical composition was well established;
- (2) Depending upon the exact isotopic value chosen as fresh-water reference point and upon the dissolved solids content that is believed to have been present when ultrafiltration commenced, either all or nearly all of the isotopic range of the figure is assigned to solutions that are somewhat enriched in O^{18} . These solutions have to be interpreted as occurring in environments where the increase in content of lighter isotope from water entering across an ultrafilter is less than the increase of heavier isotope because of water leaving across the ultrafilter on the hydraulically opposite side. These two isotopic changes must have been of comparable size for those samples that retain fresh-water isotopic composition and plot near the lower edge of the point distribution ($\delta D = -5$ or -6%). Finally, waters made isotopically lighter by ultrafiltration should not often be recovered from sedimentary sections because they are the mobile fraction and typically will

have returned to the earth's surface. In predicting chlorinity distributions in modern sediment cores, Siever et al. (1965, p. 64) presented an argument analogous to that which we have used here.

Plots of raw δO^{18} values against the several chemical parameters we have been using show good linear trends. However, after normalization of these values for temperature dependent equilibration with wall rock, there are no secondary regularities remaining like those for δD in figures 12-14. This result is hardly surprising, for the δO^{18} micropore effect, too, must decay by equilibration with wall rock, blurring the isotopic consequences of differences in reservoir mixing rates.

The ratio of divalent to univalent cations in the samples along both the X and X' lines is low enough so that plotting g moles/liter instead of g equiv/liter does not destroy the parallelism of the lines, and no clue is given as to whether ionic density or charge density is the more meaningful parameter.

Because neither $CaCO_3$ nor SiO_2 is a principal constituent of the dissolved solids in these brines, it is not surprising that brines from limestones and from sandstones do not fall in different parts of the Illinois Basin point cluster of figure 12. The lithology at a sample collecting point could, of course, be only one of several through which a brine water has passed, particularly if some of it has come across bedding.

CHANGES IN THE COMPOSITION OF PORE WATER

Before we can make calculations about ultrafiltration, we must select compositions typical of fresh water and sea water, the most probable input liquids for the ultrafilters. We need also to specify the principal pore water reactions by which we believe solids are dissolved or precipitated, if we are to distinguish their effects from pore water compositional changes that require the operation of ultrafilters.

We take the analysis in Sverdrup et al. (1942, p. 166) to be typical of sea water (table 4). The ionic balance of fresh water is assumed to be that of Clarke's (1924, p. 74) analysis of Lake Michigan water at St. Ignace. A reasonably well mixed sample of Lake Michigan water should adequately represent runoff from the terrain serving as recharge area for the Illinois and Michigan Basins—predominantly sedimentary but with a significant igneous-metamorphic component. Hough (1958, p. 59) concluded from thermal profiles, water analyses, and circulation patterns in Lake Michigan that "the waters are mixed sufficiently to have essentially the same content of dissolved solids at all depths." However, Lake Michigan takes up a third of its total drainage basin (Hough, 1958, p. 5), and water falling on the lake itself will have no opportunity to leach soil and rock except for the limited contact it may make with the lake bottom. We therefore have increased entries in the St. Ignace analysis by half (table 4). The (Na+K) value is resolved according to the relative amounts of these elements in three Great Lakes area analyses in Livingstone (1963, tables 6I, 7F, 7L).

The triangular plot of figure 15 shows the relative amounts of the principal cations in our selected fresh water (F) and sea water (S) and in the brines of table 2 that are from the Illinois and Michigan Basins. Virtually all brine points lie within the quadrilateral formed by FS and the extensions of Mg-S and Mg-F. In other words, the cation compositions of the brines could be formed by mixing the dissolved solids of fresh water and of sea water in suitable proportion and then removing about half the Mg.

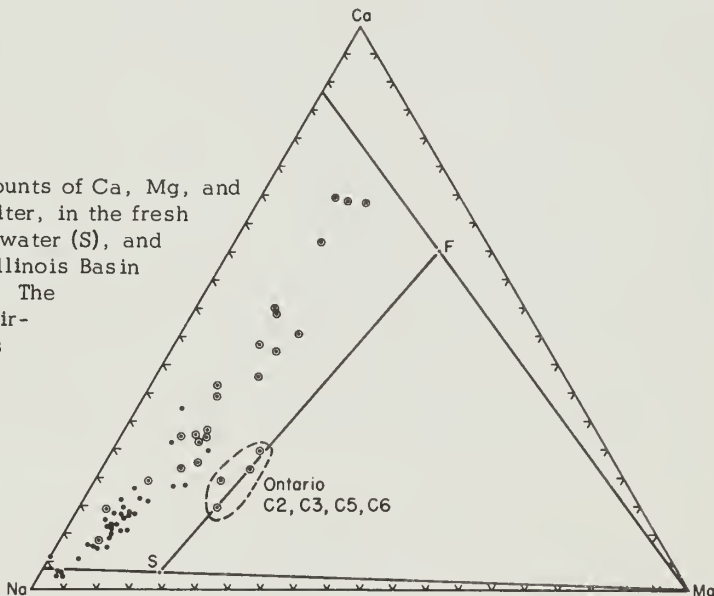
Anion facies metamorphism is not explained so easily. Loss schemes for HCO_3 and SO_4 , as well as for Mg, and their effect upon the Ca content of the brine, are involved in setting up models to estimate the amounts of fresh water and sea water required. There are several ways in which each of these ions is lost from natural solutions, and the process that we adopt for use in calculation ought to be quantitatively important in nature as well as satisfying any general considerations assumed in setting up the model. We next discuss some of these processes.

If SO_4 is precipitated in the sediments as anhydrite or gypsum, there will be a 1:1 loss of Ca and SO_4 from solution. If SO_4 is bacterially reduced to H_2S with an accompanying generation of HCO_3 from decomposition of organic matter, we can assume that the solution that results will differ only in containing additional HCO_3 equivalent to the SO_4 that was reduced.

It is, of course, possible to write inorganic SO_4 reactions that will yield H_2S and HCO_3 , but the widespread operation of bacterial SO_4 reduction is indicated by the conclusion of Thode and Monster (1965) that it is the major cause of sulfur-isotope fractionation in nature. As an example, Emery and Rittenberg (1952) found in marine beds off the southern California coast that the SO_4 content of interstitial water decreased rapidly with depth in the sediments, reaching zero at seven feet in one case. Much of the H_2S formed is believed to diffuse to the sediment surface. Bacterial SO_4 reduction is, however, limited by the amount of organic matter present. D. J. J. Kinsman (personal communication) found very little H_2S in the Recent sediments of the Trucial Coast, Persian Gulf, where there are high evaporation rates and little organic matter and where SO_4 loss is by precipitation of calcium sulfate minerals.

The classic study in the San Joaquin Valley by Rogers (1917) documented bacterial reduction of SO_4 below the water table in indurated rocks, with petroleum the organic participant. This mechanism also is supported by the compilation of Chebotarev (1955), which shows that SO_4 -rich subsurface waters occur at shallower depths than HCO_3 -rich ones and that the dominantly chloride waters are considerably deeper than either of the other two. The HCO_3 -rich zone referred to in this

Figure 15. The relative amounts of Ca, Mg, and Na, expressed as g equiv/liter, in the fresh water (F) of table 3, in sea water (S), and in the Michigan Basin and Illinois Basin formation waters of table 2. The Michigan Basin points are circled. The four dilute brines from shallow wells in Ontario contain the greatest relative amounts of Mg.



comparison is, of course, distinct from and deeper than the zone that occurs near the surface of limestone terrain.

Mg lost from solution in dolomitization by the reaction



returns Ca to solution. D. J. J. Kinsman (personal communication) has observed an increase of Ca content of interstitial waters as dolomitization proceeds, after SO_4 is exhausted by calcium sulfate precipitation, in carbonate sediments of the Trucial Coast, Persian Gulf. On the other hand, if all the ions of the dolomite were supplied from solution, there would be a Ca loss equivalent to the Mg loss. Some Mg must be consumed also in the regrading of partially weathered chlorite and in the diagenetic formation of chlorite from degraded illite (Powers, 1954). Fùchtbauer and Goldschmidt (1963) have described the increase of chlorite with depth at several European localities and its particular abundance in saline clays. The diagenetic formation of attapulgite and sepiolite might take up considerable Mg in some basins. These several clay mineral processes should return a minor but uncertain amount of K and Na to solution.

The buildup of Ca-rich chloride solutions from the dissolved solids contained in fresh water implies a mechanism involving HCO_3 loss. One possibility is that clay ultrafilters pass HCO_3 in preference to Cl, i.e., for the environments from which most of our Illinois Basin and Michigan Basin samples come, they pass Na^+ electrically balanced by HCO_3^- and retain Ca^{++} and Cl^- . No experimental ultrafiltration tests of this mechanism have been made. Nor have anion exchange properties of clays been studied in much detail (Grim, 1962). White (1965) also considers HCO_3 a mobile constituent, but he suggests that undissociated NaHCO_3 would pass more readily through ultrafilters. It is possible that information about the HCO_3 loss mechanism could be obtained from the distribution of water compositions in post-Paleozoic sections where chloride is not yet the dominant anion throughout. We consider two such examples next.

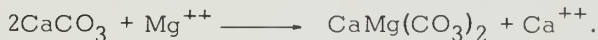
A lateral change within the same formation from CaMg bicarbonate water near the outcrop to Na bicarbonate water at moderate depth has been described for the nonmarine Lance and Fort Union Formations of Tertiary age in Rosebud County, Montana (Renick, 1929) and for the Cretaceous and Tertiary of the Atlantic Coastal Plain (Cederstrom, 1946; Foster, 1950), in greatest detail for the nonmarine Potomac Group in Virginia. The sampling patterns used by these authors are not elaborate enough really to decide whether the critical requirement of our argument, that Cl increase relative to HCO_3 in lower beds separated by shaly units, has been met. In a great majority of places where comparative data are available in the Na bicarbonate zone of the Potomac Group, Na bicarbonate content is greater at shallower depths, but chloride content is essentially the same throughout the limited depth range studied. In North Dakota to the east of the area described by Renick, the Cl anion fraction in formation water of the underlying Cretaceous Dakota Sandstone is markedly greater than in the Tertiary formations (Simpson, 1929). The value of the latter comparison is sharply reduced, however, because the Dakota is of marine origin, and its brine may have a large Cl anion fraction merely because the dissolved solids of sea water have been retained.

MODELS FOR BRINE ORIGIN

We now define the first of two simple models for estimating the amounts of fresh water and sea water from which ions would have to be concentrated to obtain

the observed brine compositions. We assume that

- (1) shale ultrafilters have perfect efficiency, except for the specific losses provided by the model;
- (2) all SO_4 is reduced bacterially, and replaced in solution by an equivalent amount of HCO_3 ;
- (3) all HCO_3 is lost through shale barriers, accompanied by an equivalent amount of Na;
- (4) Mg is lost by the reaction



The model treats a limiting and not necessarily realistic case that requires the least water possible. If cation discrimination by ultrafilters were less than absolute, or if part of the water bypassed the ultrafilters through fractures or around the ends of laterally discontinuous shaly units, more water would be required. Changes of permeability resulting from cementation associated with changes in water chemistry have not been considered. Although there must be a net loss of solid CaCO_3 equal to that given by the equation in (4), the model assumes that localized solution and deposition of CaCO_3 have no net effect upon brine composition and can be ignored. The possibility of Na^+ passing through ultrafilters balanced by SO_4^- , without the latter first having to be converted to HCO_3^- , is included in the total process defined by (2) and (3) above.

Consider a liter of brine as the unit volume and let

- x = volumes of fresh water from which ions are extracted,
- y = volumes of sea water from which ions are extracted,
- a = g equiv/liter of Mg lost from the unit volume,
- b = g equiv/liter of HCO_3 lost from the unit volume,
- Na, Ca, Mg = g equiv/liter of Na, Ca, and Mg, respectively,
- in the resulting brine.

Referring to table 3, we can write

$$\begin{aligned} \text{Na} &= .000266 x + .473 y - b \\ \text{Ca} &= .00196 x + .0210 y + a \\ \text{Mg} &= .00102 x + .108 y - a \\ b &= .00314 x + .0592 y \end{aligned}$$

Combining, we obtain

$$\begin{aligned} x &= 258 (\text{Ca} + \text{Mg}) - 80.4 \text{Na} \\ y &= 1.79 (\text{Ca} + \text{Mg}) + 1.86 \text{Na} \end{aligned}$$

The values yielded by this model for the samples of table 2 appear in the columns of table 5 entitled "First Calculation." The Ca return from dolomitization that we have postulated furnishes too much Ca for most of the Illinois Basin samples, leading to negative fresh water volume estimates. Before discussing these values further, we make a second calculation based upon a model in which all Mg lost from solution is used in the reconstitution and diagenetic growth of clay minerals, with no Ca return, so that

$$\begin{aligned} x &= 475 \text{Ca} - 24.1 \text{Na} \\ y &= 3.30 \text{Ca} + 2.25 \text{Na} \end{aligned}$$

The results of this calculation are given in the columns of table 5 entitled "Second Calculation."

The numbers in table 5 are, of course, multiples of that portion of the sedimentary rock volume now filled with liquid. Recognizing that such liquid has been redistributed among different lithologies during compaction and diagenesis, we make a rough basin-wide estimate that the liquid-filled volume is 10 percent of the

total volume. Thus the maximum amount of sea water involved in column 3 of table 5 is 1.35 times that of the present-day sedimentary rock volume, but as much as 150 times this volume of fresh water is called for in column 2. Lower pore-volume estimates would decrease these numbers proportionately.

The average quantity of sea water computed for the Michigan Basin samples (column 3, table 5) is about double that for the Illinois Basin samples. The difference is in the right direction. Some of the original interstitial liquids in Michigan Basin sediments must have been concentrated sea waters associated with salt and anhydrite deposition. Also, it follows from the existence of a solution margin for the Upper Silurian Salina salt that some of the brine salinity in wells near the edges of lower Michigan must result from solution of halite. Present-day hydraulic gradients are, of course, in the wrong direction to permit this dissolved salt to move deeper into the Michigan Basin. In our model, both of these salinity increments will appear as an increased volume estimate for normal sea water.

Sediments compacted sufficiently for ultrafiltration to be effective should still contain the amounts of interstitial liquid required by table 5. Emery and Rittenberg (1952) published a graph of depth versus porosity, based upon information from sea-floor cores and oil well samples, on which the porosity at 750-foot depth is 40 percent. There is, however, a question of timing involved if the dissolved solids contained in interstitial water of shales are not to be prevented by ultrafiltration from moving into more porous beds during compaction.

The amount of fresh water passing through the rocks of Illinois Basin can be held to a small number of pore volumes, for most of the samples, by taking Ca return to be intermediate between those of the two calculations of table 5. Clayton et al. (in press) argued from isotopic evidence that the water molecules now found in Illinois Basin and Michigan Basin brines originated as fresh water. Our model calculations indicate that the chemical composition of the Illinois Basin brines can be explained as concentration from interstitial sea water by compaction, and that too few volumes of fresh water passed through to alter chemical composition significantly.

The more rapid circulation of fresh water demanded for the Michigan Basin by the results of table 5 is qualitatively consistent with the hydrologic situation there, at least above the thick plate of Salina salt. Lakes Michigan and Huron are areally extensive piezometric lows, their surfaces lying some 550 feet below topographic highs at the southern edge and in the north central part of lower Michigan. This elevation difference in a lateral distance of only 75 to 90 miles far exceeds any gradient found in the Illinois Basin. Furthermore, K. E. Vanleir has suggested to us that the topographic and piezometric low along the outcrop of the Salina salt, now occupied by the lakes, may have existed during much of post-Salina time.

Fresh-water requirements would be increased if allowance were made for

- (1) possible leakage of CO_2 from some aquifers before it has had a chance to dissolve limestone. Foster (1950) cites an example in Virginia of free CO_2 found many miles from its presumed source area;
- (2) possible deposition of calcium carbonate and calcium sulfate minerals in pores, because SO_4 reduction and HCO_3 loss through ultrafilters has been too slow to prevent the solubility products of these compounds from being exceeded at some points in the sedimentary pile.

Fresh-water requirements would be decreased if

- (1) the HCO_3 content of incoming fresh water, balanced principally

by Ca, were assumed to reach the typical 250 mg/liter value reported by Foster (1950) for the Atlantic Coastal Plain, or the 450 mg/liter concentration said by this author to occur in a few places. Even after correction for the area occupied by Lake Michigan, and the assumption that HCO_3 substitutes for bacterially reduced SO_4 , our hypothetical fresh water contains only 190 mg/liter HCO_3 . One explanation may be that in some areas the SO_4 contribution from sulfide oxidation in the zone of aerated ground water is greater than that in the Lake Michigan drainage basin;

- (2) Ca were to be supplied to the Michigan Basin brines, without additional input of water from the surface, by solution of bedded calcium sulfate. As noted by Landes (1963a), solution by formation waters is limited by the impermeability of anhydrite and gypsum beds and by their tendency to be encased in shales or shaly solution residues. However, the water released during the conversion of gypsum to anhydrite is not subject to this limitation and would yield a solution essentially saturated in CaSO_4 , or in $\text{CaSO}_4 + \text{NaCl}$ if halite were associated closely with the gypsum. Because of the well-known metastable persistence of gypsum into the anhydrite field, water release from conversion to anhydrite might not occur until a gypsum bed was buried rather deeply. The greatest calcium chloride enrichment of the brine by this process would result if the newly dissolved $\text{SO}_4^{=}$ passed through ultrafilters balanced by Na^+ . If bacteria utilizing petroleum and other organic matter reduced this SO_4 , some CaCO_3 precipitation might take place before the HCO_3^- could pass through ultrafilters.

Bacterial reduction of SO_4 derived from anhydrite has been shown by isotopic measurements (Thode et al., 1954; Feely and Kulp, 1957) to take place around Gulf Coast salt domes, and at least part of the HCO_3 isotopically light in C^{13} that results is indeed precipitated as CaCO_3 . The general importance of the process is shown by the observation of Galley (1958) and Jones and Smith (1965) that oils in the Permian Basin of Texas and New Mexico that are rich in H_2S and S are found most often in anhydrite-bearing reservoir rocks;

- (3) there was a significant increase in dissolved Ca because of Na-Ca exchange during silicate diagenesis, but at a rate such that the precipitation discussed in (2) of the last paragraph does not take place. This process may have been important in forming the CaCl_2 brine described by White (1965, table I, anal. 2) from Precambrian Keweenaw lava, Houghton County, Michigan.

Graf et al. (1965) suggested, as an alternative to their preferred explanation, that the water in the relatively deuterium-rich brine samples N2, B, and F might simply be unflushed sea-water molecules. According to the calculations reported here in table 5, the chemical compositions of samples B and F could be derived by a six- or seven-fold concentration of sea water, without the intervention of fresh water. However, the Ca content of N2 (and of N3 from the same formation) is high enough so that an additional source of Ca is needed. Although the sea water concentration factor for samples B and F is not impossibly large, achieving it without

an isotopic micropore effect runs counter to the principal argument of the second and third papers of this series.

Cl/Br RATIOS

The chemical quantities involved in the discussion thus far have been the concentrations of ions that are quantitatively important in solution and that precipitate in large volume as rock-forming minerals. An additional means of studying brine histories is afforded by comparisons of major ion concentrations with those of minor elements that do not precipitate as separate compounds. We consider the Cl/Br ratio because there are Br analyses available for some of our brine samples and because there is a sufficient literature on Br in sedimentary materials so that we can hope to be able to interpret our values.

Table 6 gives Cl/Br atomic ratios for some of the saline formation waters of table 2, for sea water and Great Salt Lake water, for additional samples from the United States cited by White et al. (1963), and for samples from the Dead Sea system. Br analysis at the low concentrations found in fresh water is at present in the experimental stage, and the values from a mixed sedimentary-igneous terrain in California, cited by permission of B. F. Jones of the U. S. Geological Survey, should be considered tentative.

Ratios for the fresh waters of table 6 are less than that of sea water, but it does not follow that brine samples with similarly low ratios have a fresh-water genesis. In our model calculations, even for those brines through which the greatest volume of fresh water is assumed to have passed, less than 5 percent of the chloride is supplied from fresh water. The distribution factor

$$b = \frac{\text{Wt \% Br in NaCl crystals}}{\text{Wt \% Br in associated solution}}$$

varies at 25°C from .073 to .14 depending upon the concentration of Mg in solution (Braitsch and Herrmann, 1963). Sedimentary solutions with Cl/Br values less than that of sea water therefore may be residual after the precipitation of NaCl and other salts (assuming that volcanic and organic processes can be ignored), as supposed by Bentor (1961) for the Dead Sea. Conversely, solution of halite would shift the Cl/Br ratio to higher values.

The Cl/Br values of the Michigan brines of table 6 suggest that the first two samples (M51 and M56) have dissolved bedded salt, but that the salinity of the others is derived from the water of an evaporite sea. This interpretation is consistent with the positions of the sampling points relative to the edge of the basin, if we assume that the several analyses of the Dow Chemical Company from unspecified locations are from points relatively close to the Dow plant and the basin center at Midland. Landes (1963a) pointed out that bedded salt is protected effectively against leaching except in the near-surface zone where erosion breaches the enclosing shale and anhydrite. Samples M51 and M56 were taken geographically close to the solution-defined margin of the Salina salt (Landes, 1963b). Also consistent with our interpretation is the fact that the Na/Ca ratios of samples M51 and M56 are, in each case, at the high end of the range for Michigan samples with that total dissolved solids content (fig. 1, table 2). Finally, the high SO₄/Ca ratio of M56, four times greater than that of any other Michigan sample, can be interpreted as resulting from solution of calcium sulfate (often associated with halite) recently enough so that SO₄ loss by precipitation, bacterial reduction, or passage through ultrafilters has not yet taken place.

Some of the Illinois brines have Cl/Br ratios close to that of sea water, but even more have values well above that reference point. It is difficult to interpret the latter group without a better idea of the range of Br contents of fresh waters. There are no known salt beds from which large scale solution could have taken place, although there may have been minor amounts of salt deposited with the anhydrite in the Illinois Basin and also precipitated within sealed-off pores during compaction. Behne's (1953) mean Cl and Br concentrations for eruptive and sedimentary rocks correspond to atomic Cl/Br ratios of 109 and 89, respectively. However, he points out that Br is concentrated much more strongly in solid weathering products than is Cl, a process that would lead to increased Cl/Br ratios in the associated fresh waters.

We note in passing that the Cl/Br ratio of Alberta sample F is clearly different from those of the other Alberta samples.

DISCUSSION

In this paper, we have proposed a simplistic conceptual framework within which it appears possible to derive the brine compositions of the Illinois and Michigan Basins from reasonable volumes of sea water and fresh water. More detailed models probably are pointless without better knowledge of a number of physical quantities. Of these, present-day flow rates in sedimentary basins and the ultrafilter properties of clays are most obviously susceptible to direct measurement.

The discussion in the second paper of this series on the physical requirements for the removal of successive layers of adsorbed water from clays was based upon van Olphen's (1963) values, which assumed parallel orientation of clay flakes. Many shales, however, show random or partly random clay mineral orientation (Mitchell, 1956; Penner, 1963; Odom, 1963; Gipson, 1965; W. E. Parham, personal communication). The effect of these nonparallel orientations should be studied experimentally to see whether our conclusions need to be modified.

More detailed brine sampling programs are needed in individual basins where there is information available on the three-dimensional distribution of those entities that repeatedly have come under discussion earlier in the paper—organic matter, shales, unconformities, halite, dolomite, and the calcium sulfate minerals. Particularly valuable would be basins with thick sections of geologically young (i. e., Tertiary-age) sedimentary rocks in which liquid pressure measurements were made before extensive drilling had altered the original pressure distribution. The magnitudes of local deviations from hydrostatic pressure (suitably corrected for the variable density of the overlying brine column) are important in deciding whether ultrafiltration by shales is really as important geologically as we have postulated (see Berry, 1958; Berry and Hanshaw, 1960; Hanshaw, 1962). A deviation greater than the differential pressure calculated for a postulated micropore system indicates either that liquid does not pass through the enclosing rocks, even by ultrafiltration, or at least that pressure equalization by ultrafiltration proceeds at a slower rate than the processes generating the large differential pressures. On the other hand, local pressure abnormalities conforming to those calculated, if found in conjunction with expectable anomalies in isotopic and chemical composition, would greatly strengthen the case for shale ultrafiltration.

TABLE 1. THE GEOLOGIC AND GEOGRAPHIC LOCATIONS OF BRINE SAMPLING POINTS.

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|----------------|---|---|-----------------------------|--|-----------------------------------|
| ILLINOIS BASIN | | | | | |
| 4 | Anderson, #1 and 2, Arthur, Mattoon N. Pool, 2-12N-7E, Coles Co., Illinois | -1237 | 690 | Spar Mt. Sandstone Member, Ste. Genevieve Fm. | Valmeyeran (Middle Mississippian) |
| 4A | Anal. #589, Meents et al. (1952), Nat. Consumers, #1, Arthur, 2-12N-7E | | | | |
| 5 | Eager, #1, Wagner, Murdock Pool, 26-16N-10E, Douglas Co., Illinois | +268 | 640 | Spoon Formation (upper part) | (Middle Pennsylvanian) |
| 5A | Anal. #340, Meents et al. (1952), Taft, #1, Kinzel Heirs, 20-14N-10E, Coles Co., Illinois | | | | |
| 6 | Gulf Oil, #1 and 2, Heflin Unit, Harco Pool, 10-8S-5E, Saline Co., Illinois | -2494 and -2579 | 391 | Aux Vases Sandstone; Rosiclare Ss. Member, Ste. Genevieve Formation. | Valmeyeran (Middle Mississippian) |
| 6A | Resampling of same well | | | | |
| 7 | Zuhone, Tracy, Mattoon N. Pool, 22-13N-7E, Coles Co., Illinois | -1234 | 676 | Spar Mt. Sandstone Member, Ste. Genevieve Fm. | Valmeyeran (Middle Mississippian) |
| 7A | Resampling (output from 3 wells) | | | | |
| 8 | Nat. Assoc. Petrol., Krogman, Lillyville Pool, 31-9N-7E, Cumberland Co., Illinois | -1843 | 607 | Fredonia Limestone Member, Ste. Genevieve Formation. | Valmeyeran (Middle Mississippian) |
| 8A | Anal. #723, Meents et al. (1952), same well | | | | |
| 9 | Zink, Goble, Ashmore S. Pool, 19-12N-11E, Coles Co., Illinois (output of 4 wells) | +251 to +290 | 717 | Spoon Formation | (Middle Pennsylvanian) |
| 9A | Resampling of same output | | | | |
| 9B | Anal. #137, Meents et al. (1952), Miller, #1, Griffin, 22-11N-10E | | | | |
| 10 | Hennigman, "A", L. Brinkerhoff, Dudley Pool, 10-13N-13W, Edgar Co., Illinois | +292 | 702 | Spoon Formation (upper part) | (Middle Pennsylvanian) |
| 10A | Anal. #725, Meents et al. (1952), Faulkner, #1, Stoneburner, 3-13N-13W | | | | |
| 11 | Fear and Duncan, Earl Myers, Assumption C. Pool, 20-13N-1E, Christian Co., Illinois | -1693 | 620 | Cedar Valley Limestone | Middle Devonian |
| 11A | Resampling of same output (2 wells) | | | | |
| 11B | Anal. #735, Meents et al. (1952), Nat. Assoc. Petrol., #1, C. G. Sincx tr., 29-13N-1E | | | | |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|--------|--|---|-----------------------------|---|-----------------------------------|
| 12 | Sun Oil, #1, Aydt, Dahlgren W. Pool, 1-4S-4E, Jefferson Co., Illinois | -3635 to -3641 | 467 | Warsaw Limestone | Valmeyeran (Middle Mississippian) |
| 12A | Resampling of same well | | | | |
| 13 | Peake, #1, Ralston, Covington S. Pool, 14-2S-6E, Wayne Co., Illinois | -4000 estd. | 397 | Harrodsburg Limestone | Valmeyeran (Middle Mississippian) |
| 13A | Unpublished anal. of earlier sample from same depth, same well | | | | |
| 14 | Pierce, #1, Crouse, Sailor Springs C. Pool, 1-4N-7E, Clay Co., Illinois | -2488 to -2892 | 466 | Fredonia Limestone Member, Ste. Genevieve Formation | Valmeyeran (Middle Mississippian) |
| 14A | Anal. #796, Meents et al. (1952), Gulf, #3, W. Phillips, 12-4N-8E | | | | |
| 15 | Shore Line Petrol., Myer, Marine Pool, 15-4N-6W, Madison Co., Illinois | -1185 | 535 | Reef | Niagaran (Middle Silurian) |
| 15A | Resampling of same well | | | | |
| 15B | Anal. #439, Meents et al. (1952), Rockhill Oil (Eason), #1, Mayor, 1S-4N-6W | | | | |
| 16 | Mike Callahan, #1, Nofzt, Kellerville Pool, 2-2S-5W, Adams Co., Illinois | +87 to +88 | 712 | Kankakee-Edgewood Dolomites | Alexandrian (Early Silurian) |
| 16A | Sampling of nearby well in 2-2S-5W | | | | |
| 17 | Stortzum, #1, Swagler, Shattuc N. Pool, 10-2N-1W, Clinton Co., Illinois | -989 to -996 | 456 | Yankeetown Sandstone | Chesterian (Late Mississippian) |
| 17A | Resampling of same well | | | | |
| 18 | Eastern Petr. #1, Jones, Cordes Pool, 26-3S-3W, Washington Co., Illinois | -759 | 504 | Yankeetown Sandstone | Chesterian (Late Mississippian) |
| 18A | Corkwin Corp., Zelma-Jones, output of 2 nearby wells in 3S-3S-3W | -776 | 504 | | |
| 18B | Anal. #143, Meents et al. (1952), Shell Oil, Holston Lease | | | | |
| 19 | Nat. Assoc. Petr., #1, Miller-Nash, Sumpter E. Pool, 12-5S-9E, White Co., Illinois | -2732 to -2747 | 371 | Aux Vases Sandstone | Valmeyeran (Middle Mississippian) |
| 19A | Resampling of same well | | | | |
| 19B | Anal. #310, Meents et al. (1952), Seaboard, H. Gates, Carmi N. Pool, 3-5S-9E | | | | |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|--------|--|---|-----------------------------|---|-----------------------------------|
| 41 | Jenkins, #5, Fee, Goldengate C. Pool, 29-2S-9E, Wayne Co., Illinois | -4964 to -4976 | 384 | Dutch Creek Sandstone | Middle Devonian |
| 50 | Mosebath, #2, Peabody, Deering City Pool, 9-7S-3E, Franklin Co., Illinois | -2393 | 430 | Aux Vases Sandstone | Valmeyeran (Middle Mississippian) |
| 51 | Texas Co., #1, Mayberry-Land Comm., Mayberry Pool, 8-3S-6E, Wayne Co., Illinois | -2913 to -2923 | 423 | Fredonia ls. Member, Ste. Genevieve fm. | Valmeyeran (Middle Mississippian) |
| 51A | Anal. #223, Meents et al. (1952), M. I. O. U., #1, French, 4-3S-8E | | | | |
| 52 | Frederking, #1, Vonburg, Sorrento Pool, 32-6N-4W, Bond County, Illinois | -1361 to -1365 | 497 | Lingle Formation | Middle Devonian |
| 53 | Kykendale, #1, Cople, Wamac E. Pool, 29-1N-1E, Marion Co., Illinois | -316 | 555 | Palzo Sandstone Member, Spoon Formation | (Middle Pennsylvanian) |
| 54 | Shell Oil, 4-A, Headley, Patoka E. Pool, 34-4N-1E, Marion Co., Illinois | -823 to -836 | 512 | Cypress Sandstone | Chesterian (Late Mississippian) |
| 54A | Anal. #252, Meents et al. (1952), Eason Oil, #1, Keist, 27-4N-1E | | | | |
| 55 | Reasor, #1, Shaver, Eldorado E. Pool, 23-8S-7E, Saline Co., Illinois | -2576 to -2580 | 399 | Spar Mt. Sandstone Member, Ste. Genevieve Formation | Valmeyeran (Middle Mississippian) |
| 56 | Shell Oil, #1, Dye, Benton Pool, 25-6S-2E, Franklin Co., Illinois | -1660 | 455 | Tar Springs Sandstone | Chesterian (Late Mississippian) |
| 56A | Anal. #247, Meents et al. (1952), Adkins #1-7, Orient Coal, 24-6S-2E | | | | |
| 57 | McKelvy, #1, Heinzman, Patoka Pool, 32-4N-1E, Marion Co., Illinois | -3449 to -3495 | 500 | Kimmswick Limestone | Champlainian (Middle Ordovician) |
| 58 | Zinder Oil, #1 and 2, Rogier, Patoka S. Pool, 4-3N-1E, Marion Co., Illinois | -850 | 510 | Cypress Sandstone | Chesterian (Late Mississippian) |
| 59 | Obering, #1, Langhauser, Germantown E. Pool, 1-1N-4W, Clinton Co., Illinois | -1877 | 423 | Reef | Niagaran (Middle Silurian) |
| 60 | Lester, #1-D, Davidson, Patoka E. Pool, 34-4N-1E, Marion Co., Illinois | -2461 | 513 | Geneva Dolomite Member Grand Tower fm. | Middle Devonian |
| 61 | Texaco, #3, Silverman, Aden C. Pool, 16-3S-7E, Wayne Co., Illinois | -4938 to -4949 | 382 | Dutch Creek Sandstone | Middle Devonian |
| 62 | Obering Oil, "A" Schoeck, St. Jacobs Pool, 27-3N-6W, Madison Co., Ill. (output from 4 wells) | -1842 | 518 | Kimmswick Limestone | Champlainian (Middle Ordovician) |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|----------------|--|---|-----------------------------|--|-----------------------------------|
| 71 | Bufay Oil, #1, Stricklin, Raleigh S. Pool, 22-8S-6E, Saline Co., Illinois | -2473 to -2482 | 378 | Aux Vases Sandstone | Valmeyeran (Middle Mississippian) |
| 72 | Schoonmaker, #1, Sapp, Xenia Pool, 5-2N-5E, Clay Co., Illinois | -3688 to -3700 | 542 | Borden Siltstone | Valmeyeran (Middle Mississippian) |
| 73 | Brand, #1, Young, Mattoon S. Pool, 27-11N-7E, Cumberland Co., Illinois | -2361 to -2373 | 672 | Borden Siltstone | Valmeyeran (Middle Mississippian) |
| 74 | L. Harris, #1, J. Ryan, Wapella E. Pool, 21-21N-3E, DeWitt Co., Illinois | -332 to -345 | 805 | Reef | Niagaran (Middle Silurian) |
| 75 | L. Harris, #4, C. Ryan, Wapella E. Pool, 21-21N-3E, DeWitt Co., Illinois | -1373 to -1411 | 808 | St. Peter Sandstone | Champlainian (Middle Ordovician) |
| 78 | Union Hill Gas Storage Company, #1, Lange, 5-21N-7E, Champaign Co., Illinois | -849 to -859 | 747 | St. Peter Sandstone | Champlainian (Middle Ordovician) |
| 81 | Collins Bros., #1, Wilson-Carnes, Tilden Pool, 9-4S-5W, Randolph Co., Illinois | -1740 to -1760 | 508 | Reef | Silurian |
| 82 | W. Duncan, #S-1, Oliver, Mattoon Pool, 2-12N-7E, Coles Co., Illinois | +345 to +396 | 685 | Mattoon Formation | McLeansboro (Late Pennsylvanian) |
| 83 | Illinois Power Co., #1, B. Bristow, Hayes Pool, 4-16N-8E, Douglas Co., Illinois | -824 to -834 | 682 | St. Peter Sandstone | Champlainian (Middle Ordovician) |
| 84 | Ashland Oil, #2A, Sawyer, Mattoon Pool, 34-12N-7E, Coles Co., Illinois | -655 to -775 | 740 | McCormick Group | (Early Pennsylvanian) |
| 85 | Ashland Oil, #3, Hovious, Mattoon Pool, 34-12N-7E, Coles Co., Illinois | +355 to +404 | 740 | Mattoon Formation | McLeansboro (Late Pennsylvanian) |
| N1 | N. Ind. Publ. Serv., Well S-6, Gas Storage Proj., 6-28N-1E, Cass County, Indiana | -605 | 750 | St. Peter Sandstone | Champlainian (Middle Ordovician) |
| N2 | FMC Corp., #1, Newport, 9-16N-9W, Vermillion County, Indiana | -4808 to -5518 | 642 | Mt. Simon Sandstone | Late Cambrian |
| N3 | Bethlehem Steel Co., 28-37N-6W, Porter Co., Indiana | depth 2210-4292 | | Eau Claire Formation and Mt. Simon Sandstone | Late Cambrian |
| MICHIGAN BASIN | | | | | |
| M2 | H. and M. Welkes #1, 21-10N-10E, Lapeer County, Michigan | -2504 to -2514 | 801 | Sylvania Sandstone | Middle Devonian |
| M3 | McClure Oil, 21, Derimaker, 12-9N-8E, Genesee County, Michigan | -632 | 862 | Berea Sandstone | Late Devonian |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|--------|---|---|-----------------------------|--|-----------------------------|
| M4 | W. Sutherland, #1, Redman, 36-11N-3W, Gratiot County, Michigan | -121 | 732 | Stray sandstone, Michigan Formation | Late Mississippian |
| M5 | Perry Fulk, #1, Barry Unit, 18-2S-4W, Calhoun County, Michigan | -3266 to -3276 | 927 | Trenton Group | Middle Ordovician |
| M6 | Sohio Petrol., #1, Cummings, 33-16N-6W, Isabella County, Michigan | -2721 to -2728 | 974 | Dundee Limestone | Middle Devonian |
| M7 | M000, #1, McCulley, 25-11N-6W, Montcalm County, Michigan | -2002 to -2020 | 898 | Traverse Group | Middle to Late Devonian |
| M9 | M000, #2, Clark, 12-11N-4W, Gratiot Co., Michigan | -2065 | 767 | Traverse Group | Middle to Late Devonian |
| M11 | Vernon Oil Corp., #1, LaGrande and Reed, 7-6N-4E, Shiawassee County, Michigan | -724 | 766 | Berea Sandstone | Late Devonian |
| M43 | Dow Chemical Co., 24-14N-2W, Midland County, Michigan | -4112 to -4348 | 671 | Sylvania Sandstone | Middle Devonian |
| M50 | Consumers Power Co., #1, Wissman, 36-4N-15E, St. Clair County, Michigan | -1870 to -1878 | 622 | Niagara Group | Middle Silurian |
| M51 | C. J. Meyers, #1, Allison, 26-15N-16W, Oceana County, Michigan | -1834 to -1836 | 918 | Upper Detroit River Group | Middle Devonian |
| M52 | Central Oil #2, Taulker, 7-14N-1W, Midland County, Michigan | -2887 | 667 | Dundee Limestone | Middle Devonian |
| M53 | Daily Crude #1, F. Schuett, 28-20N-6W, Clare County, Michigan | -2659 to -2666 | 1113 | Dundee Limestone | Middle Devonian |
| M54 | Michigan Gas Storage Co., Well #330, 30-20N-6W, Clare Co., Michigan | -201 to -206 | 1145 | Stray sandstone, Michigan Formation | Late Mississippian |
| M55 | R. Ruland, Soderstrum #1, 5-11N-13W, Newaygo County, Michigan | +91 to -29 | 741 | Marshall Sandstone | Early Mississippian |
| M56 | Miller Bros., #1, Felt, 14-18N-17W, Mason County, Michigan | -960 to -962 | 682 | Traverse Group | Middle to Late Devonian |
| M57 | T and W Oil Co., R. Gray #1, 29-15N-17W, Oceana County, Michigan | -1099 to -1101 | 943 | Traverse Group | Middle to Late Devonian |
| M58 | Lilac Lane Farms, R. E. Mohney #2, 20-4S-13W, Van Buren County, Michigan | -246 to -247 | 941 | Traverse Group | Middle to Late Devonian |
| M61 | State Foster #1, 28-24N-2E, Ogemaw County, Michigan | -9707 to -9762 | 1457 | Oneota Dolomite | Early Ordovician |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock- Stratigraphic Unit) | Geologic Age of Source Unit |
|------------|--|---|--------------------------------|--|--------------------------------|
| M71 | Michigan Consol. Gas Co., Coldwater Storage Field, Gas Unit #8, 29-16N-6W, Isabella Co., Michigan | -399 to -418 | 1006 | Stray sandstone, Michigan Formation | Late Mississippian |
| M73 | Michigan Consol. Gas Co., Goodwell Storage Field, Billingsley #3, 8-14N-11W, Newaygo Co., Michigan | -61 | 1026 | Stray sandstone, Michigan Formation | Late Mississippian |
| M75 | Michigan Consol. Gas Co., Broomfield Storage Field, Hine #1, 18-14N-5W, Isabella Co., Michigan | -425 to -426 | 938 | Stray sandstone, Michigan Formation | Late Mississippian |
| C2 | Lot 7, Concession VIII, Zone Twp., Kent County, Ontario | +260 | 660 | Dundee Limestone | Middle Devonian |
| C3 | Lot 1, Concession B, Charlotteville Twp., Norfolk County, Ontario | +98 | 578 | Salina Group (Lower part) | Late Silurian |
| C5 | Lot 18, Concession IV, Plympton Twp., Lambton County, Ontario | +117 | 717 | Detroit River Group (Upper part) | Middle Devonian |
| C6 | Lot 14, Concession III, Bayham Twp., Elgin County, Ontario | +325 | 585 | Salina Group | Late Silurian |
| GULF COAST | | | | | |
| G3 | Washington County, Alabama, prob. 5N, 4W | -4900 to -4942 | 285 | Eutaw Formation | Late Cretaceous |
| G6 | Escambia County, Alabama, prob. 2N, 27W | -3833 to -3853 | 267 | Eutaw Formation | Late Cretaceous |
| G7A | Cherokee County, Texas, about 32.10°N, 95.38°W | -5281 to -5301 | 479 | Lower Woodbine Sand | Late Cretaceous |
| G10 | Marion County, Mississippi, prob. 2N, 14E | -7998 to -8033 | 130 | Eutaw Formation | Late Cretaceous |
| G13 | Lawrence County, Mississippi, prob. 6N, 20W | -6403 to -6433 | 210 | Eutaw Formation | Late Cretaceous |
| G14 | East Texas Field, Upshur County, Texas, about 32.60°N, 94.90°W | -3373 to -3485 | 339 | Woodbine Sand | Late Cretaceous |
| G14A | Anal. #72 (Hawkins et al., 1964), East Texas Field, Upshur County, Texas | depth 3600 to 3800 | | Woodbine Sand | Late Cretaceous |
| G15 | Titus Co., Texas, about 33.16°N, 94.98°W | -11,410 to -11,429 | 398 | Smackover Formation | Late Jurassic |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock-Stratigraphic Unit) | Geologic Age of Source Unit |
|---------|---|---|-----------------------------|--|-----------------------------|
| G24 | Cherokee Co., Texas, about 32.10°N, 95.38°W. | about -4650 to -4675 | about 480 | Upper Woodbine Sand | Late Cretaceous |
| G25 | Greene Co., Mississippi, prob. 2N, 7W | -7179 to -7207 | 261 | Eutaw Formation | Late Cretaceous |
| G30 | Marion Co., Mississippi, prob. 2N, 14E | -9195 to -9213 | 134 | Tuscaloosa Formation | Late Cretaceous |
| G30A | Anal. #276 (Hawkins et al., 1963), Hub Field, Marion County, Mississippi | depth 9125 to 9150 | | Tuscaloosa Formation (Lower part) | Late Cretaceous |
| G38 | Smith Co., Texas, about 32.50°N, 95.25°W | -4679 to -4720 | 443 | Woodbine Sand | Late Cretaceous |
| G39 | Jefferson Co., Mississippi, prob. 9N, 1W | -9731 to -9752 | 213 | Tuscaloosa Formation | Late Cretaceous |
| G79 | Houston Co., Texas, about 31.35°N, 95.32°W | -6939 to -6967 | 385 | Upper Woodbine Sand | Late Cretaceous |
| G79A | Same well as G79 | -7133 to -7151 | 385 | Lower Woodbine Sand | Late Cretaceous |
| G81 | Franklin Co., Texas, about 33.21°N, 95.13°W | -3726 to -3777 | 433 | Woodbine Sand | Late Cretaceous |
| ALBERTA | | | | | |
| A | Banff Can. Seaboard #7-3 Wimborne, Wimborne D-3 A Pool, 7-3-34-26, W 4 M, Alberta | -4310 to -4313 | 3243 | Leduc Formation | Late Devonian |
| B | Calstan Joffre Burbank Battery (3 wells), Joffre D-2 Pool, 3-14-39-27, W 4 M, Alberta | -4147 to -4284 | 2744, 2779, 2850 | Nisku Formation | Late Devonian |
| C | Empire State Calstan Bantry, Bantry Mannville Pool, 2-14-18-13, W 4 M, Alberta | -791 to -793 | 2471 | Sunburst Sandstone | Early Cretaceous |
| D | Canadian Montana Gas Well #11A, Pendant d'Oreille Bow Island Pool, 11-21-3-8, W 4 M, Alberta | +878 to +883, +825 to +830 | 2967 | Bow Island Formation | Early Cretaceous |
| E | Delhi Sun Southesk #1, Countess Bow Island A Pool, 11-32-20-16, W 4 M, Alberta | -398 to -430, -567 to -570 | 2490 | Bow Island Formation | Early Cretaceous |
| F | Imperial Judy West A12-28-63-H, Judy Creek West Beaverhill Lake Pool, 12-28-63-11, W 5 M, Alberta | -5470 to -5476 | 3638 | Swan Hills Formation | Late Devonian |

TABLE 1. CONTINUED

| Sample | Location | Brine Source Relative to Sea Level, ft. | Elevation at Well Head, ft. | Brine Source (Rock- Stratigraphic Unit) | Geologic Age of Source Unit |
|--------|--|---|--------------------------------|--|--------------------------------|
| G | Mobil Flint No. 1 Duhamel 13-17MU-45-21, Duhamel D-2 Pool, 13-17-45-21, W 4 M, Alberta | -2046 to -2056 | 2462 | Nisku Formation | Late Devonian |
| H | Mobil Oil Flint 17-12-45-21, Duhamel North D-3 Pool, 12-17-45-21, W 4 M, Alberta | -2314 to -2349 | 2481 | Leduc Formation | Late Devonian |

TABLE 2. CONTINUED

| Sample | As analyzed, mg./liter | | | | | | Computed, g. equiv./liter | | | | | | | | | |
|----------------|------------------------|--------|--------|--------|-----------------|---------|---------------------------|------------------------|--------|--------|-------|--------|-----------------|---------|------------------|------------------------|
| | Na | K | Mg | Ca | SO ₄ | Cl | HCO ₃ | Total Dissolved Solids | Na | K | Mg | Ca | SO ₄ | Cl | HCO ₃ | Total Dissolved Solids |
| 54 | | | | | | | 112,000 | | | | | | | | | 1.94 |
| 54A** | (36,700) | | 1,510 | 4,210 | 791 | 67,800 | 10 | 111,000 | (1.59) | | .124 | .210 | .0165 | 1.91 | .00016 | 1.93 |
| 55 | | | | | | | 130,000 or 165,000 | | | | | | | | | 2.25 or 2.86 |
| 56 | | | | | | | 118,000 | | | | | | | | | 2.04 |
| 56A** | (36,500) | | 1,730 | 5,380 | 29 | 70,800 | 21 | 114,000 | (1.59) | | .142 | .268 | .00060 | 2.00 | .00034 | 2.00 |
| 57 | | | | | | | 77,000 | | | | | | | | | 1.34 |
| 58 | | | | | | | 112,000 | | | | | | | | | 1.94 |
| 59 | | | | | | | 102,000 | | | | | | | | | 1.76 |
| 60 | | | | | | | 85,000 | | | | | | | | | 1.48 |
| 61 | 61,000 | 2,160 | 2,300 | 11,100 | 531 | 122,000 | 102 | 199,000 | 2.65 | .0552 | .189 | .554 | .0111 | (3.44) | .00167 | 3.45 |
| 62 | 5,080 | 138 | 480 | 1,190 | 1,620 | 10,200 | 232 | 18,900 | .221 | .00353 | .0395 | .0594 | .0337 | (.286) | .00380 | .324 |
| 71 | 36,400 | 334 | 1,580 | 5,930 | 1,930 | 70,300 | 50 | 117,000 | 1.58 | .00854 | .130 | .296 | .0402 | (1.97) | .00082 | 2.01 |
| 72 | 41,100 | 524 | 1,640 | 4,800 | 2,300 | 77,900 | 169 | 128,000 | 1.79 | .0134 | .135 | .240 | .0479 | (2.13) | .00277 | 2.18 |
| 73 | 41,800 | 626 | 1,540 | 6,270 | 139 | 86,500 | 17 | 137,000 | 1.82 | .0160 | .127 | .313 | .00289 | (2.27) | .00028 | 2.28 |
| 74 | 1,470 | 28 | 25 | 41 | 139 | 2,090 | 688 | 4,480 | .0639 | .00072 | .0021 | .0020 | .00289 | (.0545) | .0113 | .069 |
| 75 | 475 | 21 | 17 | 37 | 84 | 557 | 383 | 1,570 | .0207 | .00054 | .0014 | .0018 | .0017 | (.0165) | .00628 | .024 |
| 78 | 612 | n.a. | 68 | 149 | 111 | 1,170 | 285 | 2,400 | .0266 | n.a. | .0056 | .00744 | .00231 | (.0327) | .00467 | .040 |
| 81 | 30,300 | 286 | 2,070 | 5,660 | 775 | 65,500 | 24 | 105,000 | 1.32 | .00731 | .170 | .282 | .0161 | (1.76) | .00039 | 1.78 |
| 82 | 2,230 | 12 | n.d. | 120 | n.d. | 3,260 | 515 | 6,230 | .0970 | .00031 | n.d. | .00599 | n.d. | (.0919) | .00844 | .103 |
| 83 | 1,980 | 75 | 63 | 260 | 473 | 2,600 | 152 | 5,620 | .0861 | .0019 | .0052 | .0130 | .00985 | (.0934) | .00249 | .106 |
| 84 | 32,700 | 91 | 960 | 2,600 | 18 | 62,000 | 73 | 98,400 | 1.42 | .0023 | .0789 | .130 | .00037 | (1.63) | .0012 | 1.63 |
| 85 | 9,130 | 22 | 173 | 180 | n.d. | 15,800 | 161 | 25,500 | .397 | .00056 | .0142 | .00898 | n.d. | (.417) | .00264 | .421 |
| N1 | 3,290 | n.a. | 406 | 1,170 | 2,310 | 6,460 | 252 | 13,900 | .143 | n.a. | .0334 | .0584 | .0481 | (.183) | .00413 | .235 |
| N2 | 49,000 | 1,380 | 2,840 | 22,400 | 508 | 125,000 | 116 | 201,000 | 2.13 | .0353 | .234 | 1.12 | .0106 | (3.51) | .00190 | 3.52 |
| N3 | 17,400 | 610 | 1,110 | 6,100 | 1,060 | 41,700 | 98 | 68,100 | .757 | .0156 | .0913 | .304 | .0221 | (1.14) | .00161 | 1.17 |
| MICHIGAN BASIN | | | | | | | | | | | | | | | | |
| M2 | 21,300 | 12,100 | 14,700 | 94,900 | 44 | 256,000 | 261 | 399,000 | .945 | .315 | 1.23 | 4.83 | .00094 | (7.31) | .00437 | 7.32 |

TABLE 2. CONTINUED

| Sample | As analyzed, mg./liter | | | | | | | Computed, g. equiv./liter | | | | | | | | |
|------------|------------------------|--------|--------|--------|-----------------|---------|------------------|---------------------------|-------|--------|-------|--------|-----------------|---------|------------------|------------------------|
| | Na | K | Mg | Ca | SO ₄ | Cl | HCO ₃ | Total Dissolved Solids | Na | K | Mg | Ca | SO ₄ | Cl | HCO ₃ | Total Dissolved Solids |
| M3 | 64,000 | 396 | 7,560 | 19,600 | 14 | 163,000 | n.d. | 255,000 | 2.78 | .0101 | .622 | .978 | .00029 | (4.39) | n.d. | 4.39 |
| M4 | 72,500 | 840 | 8,240 | 30,300 | 231 | 202,000 | n.d. | 314,000 | 3.15 | .0215 | .678 | 1.51 | .00481 | (5.35) | n.d. | 5.36 |
| M5 | 30,300 | 4,450 | 8,440 | 65,400 | 192 | 194,000 | n.d. | 303,000 | 1.32 | .114 | .694 | 3.26 | .00400 | (5.38) | n.d. | 5.39 |
| M6 | 56,300 | 2,410 | 5,960 | 31,100 | 391 | 170,000 | 25 | 266,000 | 2.45 | .0616 | .490 | 1.55 | .00814 | (4.54) | .00041 | 4.55 |
| M7 | 55,900 | 2,510 | 8,630 | 48,600 | 115 | 202,000 | n.d. | 318,000 | 2.43 | .0642 | .710 | 2.43 | .00239 | (5.63) | n.d. | 5.63 |
| M9 | 50,400 | 3,070 | 8,870 | 56,400 | 86 | 207,000 | n.d. | 326,000 | 2.19 | .0785 | .729 | 2.81 | .00179 | (5.81) | n.d. | 5.81 |
| M11 | 63,300 | 530 | 6,570 | 24,100 | 65 | 162,000 | n.d. | 257,000 | 2.75 | .0136 | .540 | 1.20 | .00135 | (4.50) | n.d. | 4.50 |
| M43 | 24,400 | 7,660 | 14,300 | 97,300 | 50 | 251,000 | 209 | 395,000 | 1.12 | .206 | 1.24 | 5.12 | .00109 | (7.68) | .00361 | 7.69 |
| M50 | 52,300 | 3,920 | 9,060 | 59,300 | 173 | 215,000 | 272 | 340,000 | 2.27 | .100 | .745 | 2.96 | .00360 | (6.07) | .00446 | 6.08 |
| M51 | 96,200 | 1,510 | 2,610 | 15,100 | 484 | 179,000 | 49 | 295,000 | 4.18 | .0386 | .215 | .753 | .0101 | (5.18) | .00080 | 5.19 |
| M52 | 66,200 | 3,550 | 6,370 | 39,500 | 161 | 201,000 | 55 | 317,000 | 2.88 | .0908 | .524 | 1.97 | .00335 | (5.46) | .00090 | 5.46 |
| M53 | 71,000 | 2,320 | 5,400 | 27,000 | 262 | 185,000 | 60 | 291,000 | 3.09 | .0593 | .444 | 1.35 | .00545 | (4.94) | .00098 | 4.94 |
| M54 | 71,600 | 672 | 7,590 | 29,700 | 232 | 196,000 | n.d. | 306,000 | 3.11 | .0172 | .624 | 1.48 | .00483 | (5.23) | n.d. | 5.23 |
| M55 | 38,600 | 598 | 3,880 | 14,900 | 1,010 | 103,000 | 15 | 162,000 | 1.68 | .0153 | .319 | .744 | .0210 | (2.74) | .00025 | 2.76 |
| M56 | 37,300 | 282 | 1,320 | 3,350 | 2,490 | 70,000 | 120 | 115,000 | 1.62 | .00721 | .109 | .167 | .0518 | (1.85) | .00197 | 1.90 |
| M57 | 65,700 | 910 | 3,800 | 15,200 | 420 | 149,000 | 24 | 235,000 | 2.86 | .0233 | .313 | .758 | .00874 | (3.95) | .00039 | 3.95 |
| M58 | 57,100 | 614 | 5,350 | 16,200 | 157 | 141,000 | 5 | 220,000 | 2.48 | .0157 | .440 | .808 | .00327 | (3.74) | .00008 | 3.74 |
| M61 | 21,900 | 13,200 | 6,970 | 70,100 | 12 | 188,000 | n.d. | 300,000 | .953 | .338 | .573 | 3.50 | .00025 | (5.36) | n.d. | 5.36 |
| M71 | 52,900 | 602 | 10,800 | 46,900 | 105 | 203,000 | n.d. | 314,000 | 2.30 | .0154 | .888 | 2.34 | .00219 | (5.54) | n.d. | 5.54 |
| M73 | 53,800 | 768 | 9,410 | 38,300 | 259 | 188,000 | 25 | 291,000 | 2.34 | .0196 | .774 | 1.91 | .00539 | (5.04) | .00041 | 5.04 |
| M75 | 47,800 | 722 | 12,300 | 51,200 | 135 | 209,000 | n.d. | 321,000 | 2.08 | .0185 | 1.01 | 2.55 | .00281 | (5.66) | n.d. | 5.66 |
| C2 | 6,590 | 216 | 1,800 | 2,160 | 2,140 | 16,900 | 78 | 29,900 | .287 | .00552 | .148 | .108 | .0446 | (.502) | .0013 | .548 |
| C3 | 4,840 | 133 | 1,050 | 1,590 | 2,410 | 10,600 | 83 | 20,700 | .211 | .00340 | .0863 | .0793 | .0502 | (.328) | .0014 | .380 |
| C5 | 6,710 | 123 | 1,080 | 1,830 | 2,560 | 14,400 | 85 | 26,800 | .292 | .00315 | .0888 | .0913 | .0533 | (.419) | .0014 | .475 |
| C6 | 905 | 93 | 161 | 174 | 331 | 1,620 | 127 | 3,430 | .0394 | .0024 | .0132 | .00868 | .00689 | (.0541) | .00208 | .064 |
| GULF COAST | | | | | | | | | | | | | | | | |
| G3 | | | | | | | | | | | | | | | | 2.50 |
| G6 | | | | | | | | | | | | | | | | 1.64 |

88,400*

58,200*

TABLE 2. CONTINUED

| Sample | As analyzed, mg./liter | | | | | | Computed, g. equiv./liter | | | | | | Total Dissolved Solids | | |
|------------|------------------------|--------|--------|---------|-----------------|----------|---------------------------|------------------------|--------|--------|--------|--------|------------------------|-----------------|--------|
| | Na | K | Mg | Ca | SO ₄ | Cl | HCO ₃ | Total Dissolved Solids | Na | K | Mg | Ca | | SO ₄ | Cl |
| GULF COAST | | | | | | | | | | | | | | | |
| G7A | | | | | 75,200* | | | | | | | | | | 2.13 |
| G10 | | | | | 106,000* | | | | | | | | | | 3.00 |
| G13 | | | | | 111,000* | | | | | | | | | | 3.14 |
| G14 | | | | | 38,900* | | | | | | | | | | |
| G14A | (22,100) | | 85 | 1,720 | n.d. | 37,200 | 495 | 61,600 | (.965) | | .0070 | .0858 | n.d. | 1.05 | .00811 |
| G15 | | | | | 204,000* | | | | | | | | | | 5.75 |
| G24 | | | | | 51,600* | | | | | | | | | | 1.46 |
| G25 | | | | | 108,000* | | | | | | | | | | 3.05 |
| G30 | | | | | 129,000* | | | | | | | | | | |
| G30A | (57,200) | | 1,300 | 21,000 | 275 | 129,000 | 52 | 209,000 | (2.49) | | .107 | 1.05 | .00573 | 3.64 | .00085 |
| G38 | | | | | 58,800* | | | | | | | | | | 1.66 |
| G39 | | | | | 82,500* | | | | | | | | | | 2.33 |
| G79 | | | | | 71,600* | | | | | | | | | | 2.03 |
| G79A | | | | | 74,800* | | | | | | | | | | 2.12 |
| G81 | | | | | 46,200* | | | | | | | | | | 1.32 |
| ALBERTA | | | | | | | | | | | | | | | |
| A | 46,200 | 5,810 | *3,200 | *24,000 | *343 | 129,000 | *960 | 210,000 | 2.01 | .149 | .263 | 1.20 | .00714 | (3.60) | .0157 |
| B | 55,300 | *2,280 | *1,010 | *6,910 | *937 | 106,000 | *593 | 173,000 | 2.41 | .0583 | .0831 | .345 | .0195 | (2.87) | .00972 |
| C | (8,740) | *169 | *52 | *39 | *7 | *7,540 | *7,750 | 25,800 | (.380) | .00432 | .0043 | .0019 | .00015 | .213 | .127 |
| D | 2,090 | *15 | *10 | *14 | *3 | *1,530 | *2,330 | 6,290 | .0909 | .00038 | .00082 | .00070 | .00006 | (.0484) | .0382 |
| E | 8,610 | *37 | *69 | *197 | *218 | *14,600 | *357 | 24,100 | .375 | .00095 | .0057 | .00983 | .00454 | (.381) | .00585 |
| F | 62,200 | *1,490 | *607 | *4,690 | *914 | *113,000 | *218 | 183,000 | 2.71 | .0381 | .0499 | .234 | .0190 | (3.01) | .00357 |
| G | 30,900 | *2,450 | *1,980 | *9,740* | 1,120 | *74,200 | *550 | 121,000 | 1.34 | .0627 | .163 | .486 | .0233 | (2.02) | .00901 |
| H | 51,500 | *2,850 | *2,880 | *18,600 | *537 | *122,000 | *161 | 199,000 | 2.24 | .0729 | .237 | .928 | .0112 | (3.46) | .00264 |

The notation "n.d." indicates an ion analyzed for but not detected. Where "n.a." appears, no analysis was made. Carbonate is reported in the analyses of samples 72, 81, 82, 83, 85, M56, C2, C3, C5, C6, C, and D in amounts of 44, 24, 90, 14, 34, 17, 29, 24, 34, 19, *1510, and 302 mg/l, respectively. This carbonate content has been considered in computing the next to last and third to last columns of the table. Quantities in parentheses were obtained by difference. (†) Analyst, G. B. Wengert, Dow Chemical Co. (*) Analyst, Donald Shaw, Oil and Gas Conservation Board of Alberta. (**) Analysis from Meents et al. (1952). (#) Analysis by Humble Oil Company. Analysis 13A is by L. D. McVicker, G14A is from Hawkins et al. (1964), G30A is from Hawkins et al. (1963), and N2 and N3 are by the Indiana State Geological Survey. Other analyses are by D. B. Heck.

TABLE 3. TOTAL DISSOLVED SOLIDS CONTENT OF ILLINOIS BASIN BRINES
ANALYZED SINCE THE LISTING IN MEENTS ET AL. (1952).

Brines from Devonian and Silurian horizons are shown separately, including all "Devonian-Silurian" analyses from the earlier paper that can be assigned to either Devonian or Silurian with reasonable certainty.

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter |
|--|-------------|---------------|---------------------------|
| Pennsylvanian | | | |
| Champaign | 9-7N-10E | B-1415 | 8,920 |
| Coles | 10-11N-10E | 1947 | 28,300 |
| | 2-12N-7E | 1875 | 6,110 |
| | 34-12N-7E | 1880 | 104,000 |
| | 34-12N-7E | 1881 | 27,000 |
| | 12-12N-10E | 1640 | 42,100 |
| Douglas | 26-16N-10E | 1727 | 24,800 |
| Edwards | 7-2S-11E | 1788 | 36,900 |
| | 27-2S-14W | 1932 | 896 |
| | 18-3S-11E | 1941 | 33,100 |
| Gallatin | 19-7S-8E | 1924 | 75,300 |
| Grundy | 12-31N-7E | 1616 | 5,170 |
| Hamilton | 30-3S-7E | 1942 | 55,400 |
| | 35-4S-7E | 1925 | 3,260 |
| | 27-6S-6E | 1867 | 76,700 |
| | 35-6S-6E | 1866 | 75,200 |
| | 6-7S-5E | 1584 | 83,000 |
| | 19-1S-1E | 1518 | 111,000 |
| | 10-3S-2E | 1946 | 94,900 |
| Marion | 16-1N-1E | 1339 | 88,000 |
| | 29-1N-1E | 1321 | 89,600 |
| | 29-1N-1E | 1322 | 87,200 |
| Saline | 21-8S-6E | 1892 | 19,400 |
| | 7-8S-7E | 1926 | 33,300 |
| | 10-8S-7E | 1863 | 47,100 |
| | 15-8S-7E | 1859 | 41,200 |
| | 20-8S-7E | 1864 | 53,300 |
| Wayne | 23-1N-5E | 1944 | 111,000 |
| | 35-1N-5E | 1945 | 108,000 |
| | 24-1N-8E | 1758 | 79,100 |
| | 12-1S-7E | 1949 | 54,400 |
| | 29-1S-8E | 1757 | 29,900 |
| White | 31-5S-10E | 1243 | 48,700 |
| | 33-5S-10E | 1237 | 48,800 |
| Mississippian | | | |
| Degonia Fm. | | | |
| Saline | 3-10S-6E | 1544 | 44,100 |
| Waltersburg Fm. | | | |
| Gallatin | 28-9S-10E | 1609 | 46,700 |
| Richland | 29-3N-14W | 1285 | 87,000 |
| Saline | 25-8S-6E | 1537 | 87,800 |
| | 15-8S-7E | 1489 | 81,600 |
| | 15-8S-7E | 1490 | 82,200 |
| | 15-10S-6E | 1545 | 68,100 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter |
|--|-------------|---------------|---------------------------|
| Waltersburg Fm., continued | | | |
| White 33-6S-9E | B-1396 | 2431-2465 | 79,500 |
| Tar Springs Fm. | | | |
| Clay 36-4N-7E | 1354 | 2337-2341 | 126,000 |
| Saline 17-8S-7E | 1514 | 2229-2237 | 98,400 |
| Williamson 4-9S-3E | 1849 | 1910-1922 | 97,300 |
| Hardinsburg Fm. | | | |
| Saline 8-8S-7E | 1416 | 2334-2340 | 89,400 |
| | 1421 | 2348-2354 | 92,200 |
| Cypress Fm. | | | |
| Clinton 6-1N-2W | 1411 | 1092-1098 | 63,000 |
| | 1910 | 1130-1140 | 64,300 |
| Crawford 20-7N-12W | 1254 | 1198-1286 | 54,000 |
| | 1255 | 1198-1286 | 53,700 |
| | 1432 | 1365-1400 | 79,800 |
| Effingham 1-6N-6E | 1521 | 2459-2466 | 132,000 |
| | 1522 | 2459-2490 | 141,000 |
| | 1523 | 2463-2471 | 139,000 |
| | 1644 | 2424-2438 | 142,000 |
| | 1645 | 2420-2436 | 138,000 |
| | 1364 | 2432-2442 | 130,000 |
| | 1365 | 2432-2442 | 130,000 |
| | 1519 | 2486-2491 | 133,000 |
| Franklin 3-7S-4E | 1398 | 2773-2781 | 141,000 |
| Gallatin 27-7S-9E | 1360 | 2596-2610 | 106,000 |
| | 1353 | 2540-2550 | 103,000 |
| Jefferson 10-3S-4E | 1585 | 2762-2780 | 136,000 |
| Marion 4-3N-1E | 1455 | 1358-1365 | 108,000 |
| | 1457 | 1356-1375 | 108,000 |
| Richland 17-3N-9E | 1619 | 2601-2608 | 98,100 |
| | 1524 | 2612-2617 | 98,300 |
| | 1325 | 2694-2708 | 99,600 |
| St. Clair 33-3S-7W | 1743 | 228-253 | 10,400 |
| Washington 28-1S-1W | 1857 | 1456-1476 | 114,000 |
| White 24-5S-9E | 1334 | 2800-2808 | 117,000 |
| Bethel (Paint Creek) Fm. | | | |
| Edwards 15-3S-10E | 1392 | 3003-3008 | 106,000 |
| Gallatin 22-8S-8E | 1536 | 2660-2720 | 116,000 |
| Lawrence 13-2N-13W | 1362 | 2233-2312 | 80,000 |
| Saline 23-8S-5E | 1491 | 2670-2680 | 138,000 |
| Wayne 26-2S-9E | 1332 | 3085-3094 | 117,000 |
| | 1331 | 3098-3105 | 117,000 |
| Yankeetown (Benoist) Fm. | | | |
| Clinton 10-2N-1W | 1742 | 1445-1452 | 83,700 |
| Effingham 28-6N-5E | 1692 | 2302-2316 | 136,000 |
| Marion 33-1N-2E | 1369 | 1967-1974 | 124,000 |
| | 1905 | 2280-2285 | 128,000 |
| | 1388 | 2038-2044 | 127,000 |
| Washington 27-1N-1W | 1487 | 1479-1483 | 95,500 |
| | 1381 | 1482-1485 | 95,900 |
| | 1414 | 1429-1441 | 106,000 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | | |
|--|--------------------|---------------|---------------------------|-----------|---------|
| Aux Vases Fm. | | | | | |
| Clay | 1-4N-6E | 1426 | 2786-2808 | 140,000 | |
| | 1-5N-6E | 1463 | 2709-2718 | 135,000 | |
| | 22-3N-7E | 1431 | 2900-2947 | 135,000 | |
| Coles | 15-3N-8E | 1556 | 2913-2955 | 133,000 | |
| | 25-14N-7E | 1510 | 1739-1746 | 118,000 | |
| | 28-2S-10E | 1606 | 3167-3180 | 113,000 | |
| Edwards | 19-2S-11E | 1435 | 3002-3038 | 114,000 | |
| | 35-5S-1E | 1236 | 2623-2675 | 137,000 | |
| Franklin | 11-6S-1E | 1465 | 2626-2642 | 137,000 | |
| | 13-6S-1E | 1467 | 2598-2618 | 139,000 | |
| | 14-6S-1E | 1437 | 2693-2699 | 140,000 | |
| | 1-7S-1E | 1870 | 2620-2634 | 138,000 | |
| Hamilton | 9-7S-3E | 1630 | 2823-2837 | 140,000 | |
| | 29-4S-7E | 1535 | 3325-3331 | 142,000 | |
| | 9-5S-7E | 1533 | 3346-3370 | 140,000 | |
| Jasper | 9-5S-7E | 1534 | 3366-3377 | 138,000 | |
| | 28-6S-5E | 1401 | 3242-3282 | 129,000 | |
| | 29-6S-5E | 1400 | 3254-3278 | 133,000 | |
| Jefferson | 4-7S-5E | 1399 | 3206-3222 | 132,000 | |
| | 31-6N-10E | 1384 | 2765-2784 | 108,000 | |
| Madison | 30-1S-4E | 1371 | 2671-2677 | 135,000 | |
| | 11-2S-4E | 1590 | 2854-2870 | 143,000 | |
| | 10-3S-2E | 1335 | 2548-2555 | 133,000 | |
| Moultrie | 16-3N-6W | 1931 | 750-829 | 25,100 | |
| | 22-12N-6E | 1488 | 1962-1990 | 126,000 | |
| Saline | 15-8S-5E | 1551 | 2888-2900 | 136,000 | |
| | 16-8S-5E | 1550 | 2888-2900 | 134,000 | |
| | 16-8S-5E | 1552 | 2883-2895 | 138,000 | |
| | 14-8S-6E | 1546 | 2955-2961 | 117,000 | |
| | 25-8S-6E | 1774 | 2812-2830 | 115,000 | |
| | 8-8S-7E | 1419 | 2952-2965 | 115,000 | |
| | 9-8S-7E | 1628 | 2927-2938 | 105,000 | |
| | 23-8S-7E | 1479 | 2873-2901 | 167,000 | |
| | 23-8S-7E | 1480 | 2854-2904 | 171,000 | |
| | 23-8S-7E | 1482 | 2874-2881 | 164,000 | |
| | 23-8S-7E | 1483 | 2908-2912 | 162,000 | |
| | Shelby | 15-11N-4E | 1711 | 1889-1906 | 121,000 |
| | | 27-11N-4E | 1330 | 1814-1822 | 115,000 |
| Washington | 6-1S-4W | 1631 | 2178-2190 | 95,800 | |
| Wayne | 9-1N-7E | 1452 | 3042-3062 | 143,000 | |
| | 24-1N-9E | 1386 | 3146-3175 | 133,000 | |
| | 15-1S-7E | 1376 | 3136-3145 | 140,000 | |
| | 22-1S-8E | 1409 | 3042-3058 | 131,000 | |
| | 32-1S-8E | 1442 | 3170-3174 | 138,000 | |
| | 27-2S-8E | 1377 | 3257-3278 | 140,000 | |
| | 6-3S-9E | 1373 | 3352-3385 | 125,000 | |
| | 24-4S-8E | 1732 | 3325-3376 | 132,000 | |
| | 21-4S-9E | 1326 | 3182-3183 | 120,000 | |
| | 24-5S-8E | 1433 | 3122-3140 | 123,000 | |
| White | 32-5S-8E | 1390 | 3250-3265 | 128,000 | |
| | 22-5S-9E | 1267 | 3144-3154 | 126,000 | |
| | 6-8S-4E | 1613 | 2933-2949 | 140,000 | |
| Williamson | 28-8S-4E | 1629 | 2886-2898 | 123,000 | |
| | Ste. Genevieve Fm. | | | | |
| Clay | 7-3N-8E | 1511 | 2998-3000 | 148,000 | |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | |
|--|-------------|---------------|---------------------------|---------|
| Ste. Genevieve Fm., continued | | | | |
| Clay | 18-5N-7E | B-1387 | 2812-2869 | 140,000 |
| Coles | 2-13N-7E | 1509 | 1824-1831 | 111,000 |
| | 8-13N-7E | 1561 | 1952-1960 | 140,000 |
| | 9-13N-7E | 1562 | 1834-1849 | 137,000 |
| | 9-13N-7E | 1563 | 1861-1872 | 137,000 |
| | 10-13N-7E | 1586 | 1846-1850 | 136,000 |
| | 22-13N-7E | 1734 | 1910-1930 | 126,000 |
| | 34-14N-7E | 1575 | 1798-1814 | 133,000 |
| | 34-14N-7E | 1576 | 1810-1815 | 132,000 |
| | 35-14N-7E | 1572 | 1797-1825 | 135,000 |
| | 19-14N-8E | 1567 | 1791-1796 | 138,000 |
| | 19-14N-8E | 1568 | 1793-1830 | 129,000 |
| | 19-14N-8E | 1571 | 1778-1805 | 136,000 |
| | 19-14N-8E | 1574 | 1801-1822 | 127,000 |
| | 19-14N-8E | 1577 | 1796-1804 | 135,000 |
| Douglas | 13-14N-7E | 1579 | 1808-1818 | 133,000 |
| | 11-15N-7E | 1569 | 1648-1667 | 137,000 |
| | 12-15N-7E | 1573 | 1616-1624 | 129,000 |
| Edwards | 1-1N-10E | 1417 | 3249-3259 | 127,000 |
| | 28-1N-10E | 1338 | 3288-3289 | 126,000 |
| Effingham | 11-6N-6E | 1446 | 2717-2726 | 128,000 |
| | 24-7N-5E | 1633 | 2414-2431 | 121,000 |
| Franklin | 16-7S-3E | 1906 | 2924-2928 | 139,000 |
| Gallatin | 35-8S-9E | 1610 | 2865-2893 | 139,000 |
| Hamilton | 10-4S-7E | 1423 | 3336-3348 | 150,000 |
| | 29-4S-7E | 1314 | 3501-3506 | 145,000 |
| | 32-5S-6E | 1327 | 3335-3340 | 144,000 |
| Jasper | 5-5N-9E | 1427 | 3107-3113 | 137,000 |
| | 18-5N-10E | 1324 | 2926-2931 | 128,000 |
| | 21-5N-10E | 1269 | 2884-2910 | 129,000 |
| | 22-6N-9E | 1268 | 3088-3106 | 137,000 |
| | 4-7N-14W | 1251 | 1844-1850 | 88,900 |
| | 33-8N-9E | 1656 | 2840-2854 | 136,000 |
| | 33-8N-9E | 1657 | 2832-2852 | 134,000 |
| Jefferson | 16-1S-3E | 1328 | 2744-2750 | 137,000 |
| | 27-1S-3E | 1753 | 2785-2791 | 132,000 |
| | 2-2S-3E | 1589 | 2846-2852 | 134,000 |
| | 18-2S-3E | 1588 | 2674-2686 | 134,000 |
| | 34-2S-4E | 1272 | 3085-3092 | 148,000 |
| | 35-2S-4E | 1270 | 3060-3070 | 148,000 |
| | 36-2S-4E | 1903 | 3047-3069 | 145,000 |
| Lawrence | 12-2N-13W | 1361 | 2420-2424 | 88,600 |
| | 18-4N-10W | 1508 | 1563-1572 | 56,100 |
| Marion | 10-1N-2E | 1448 | 2144-2151 | 125,000 |
| | 17-1N-2E | 1449 | 2055-2065 | 124,000 |
| | 22-1N-2E | 1450 | 2124-2142 | 122,000 |
| | 5-2N-2E | 1763 | 2155-2161 | 128,000 |
| | 10-2N-4E | 1512 | 2714-2763 | 138,000 |
| Richland | 16-3N-10E | 1393 | 3128-3132 | 134,000 |
| Shelby | 32-10N-6E | 1884 | 2146-2158 | 107,000 |
| Washington | 33-3S-1W | 1469 | 1525-1534 | 103,000 |
| | 33-3S-1W | 1565 | 1530-1543 | 106,000 |
| Wayne | 21-2N-6E | 1288 | 3095-3105 | 150,000 |
| | 21-2N-6E | 1289 | 3097-3102 | 144,000 |
| | 21-2N-6E | 1290 | 3085-3088 | 150,000 |
| | 29-2N-7E | 1312 | 3140-3143 | 150,000 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | |
|--|-------------|---------------|---------------------------|---------|
| Ste. Genevieve Fm., continued | | | | |
| Wayne | 29-2N-7E | B-1313 | 3142-3148 | 148,000 |
| | 10-1S-8E | 1382 | 3222-3234 | 144,000 |
| | 29-1S-8E | 1453 | 3298-3308 | 144,000 |
| | 2-3S-9E | 1372 | 3294-3296 | 124,000 |
| White | 26-4S-10E | 1252 | 3021-3030 | 129,000 |
| | 18-4S-14W | 1356 | 3032-3038 | 132,000 |
| | 29-5S-8E | 1391 | 3260-3292 | 128,000 |
| | 16-5S-9E | 1333 | 3314-3374 | 134,000 |
| | 29-5S-10E | 1245 | 3112-3113 | 135,000 |
| | 1-6S-9E | 1344 | 3111-3154 | 132,000 |
| | 9-7S-10E | 1397 | 2951-2958 | 129,000 |
| St. Louis Fm. | | | | |
| Johnson | 25-13S-4E | 1319 | 1010-1020 | 14,800 |
| Salem Fm. | | | | |
| Franklin | 1-6S-2E | 1547 | 3566-3572 | 128,000 |
| Jefferson | 26-1S-3E | 1754 | 3224-3226 | 136,000 |
| Richland | 3-3N-9E | 1907 | 3625-3629 | 112,000 |
| Wayne | 17-2S-8E | 1762 | 3780-3790 | 163,000 |
| | 8-3S-9E | 1767 | 4115-4120 | 126,000 |
| White | 19-3S-8E | 1883 | 3784-3810 | 164,000 |
| | 27-4S-14W | 1352 | 3751-3794 | 189,000 |
| Harrodsburg (Warsaw) Fm. | | | | |
| Edwards | 5-3S-10E | 1915 | 4300-4310 | 128,000 |
| Hamilton | 1-4S-5E | 1665 | 4316-4329 | 182,000 |
| | 1-4S-5E | 1666 | 4316-4329 | 183,000 |
| | 14-2S-4E | 1739 | 4085-4095 | 170,000 |
| Jefferson | 1-4S-4E | 1707 | 4102-4108 | 166,000 |
| | 1-4S-4E | 1740 | 4102-4108 | 166,000 |
| | 14-2S-6E | 1744 | 4155-4194 | 172,000 |
| Wayne | 14-2S-6E | 1745 | 4196-4200 | 170,000 |
| | Sonora Fm. | | | |
| DeWitt | 1-20N-4E | 1852 | 640-670 | 35,300 |
| | 34-21N-4E | 1851 | 670-700 | 32,400 |
| Carper pay | | | | |
| Clark | 29-9N-14W | 1297 | 2222-2350 | 121,000 |
| | 7-11N-14W | 1443 | 875-925 | 59,700 |
| Clay | 5-2N-5E | 1784 | 4230-4242 | 138,000 |
| | 5-2N-5E | 1787 | 4230-4242 | 134,000 |
| Cumberland | 27-11N-7E | 1768 | 3035-3045 | 147,000 |
| Fayette | 6-5N-3E | 1781 | 3213-3217 | 147,000 |
| | 17-5N-3E | 1783 | 3280-3292 | 149,000 |
| Marion | 13-4N-2E | 1772 | 3387-3410 | 143,000 |
| Moultrie | 21-12N-6E | 1854 | 2963-3056 | 126,000 |
| Devonian | | | | |
| Bond | 6-4N-2W | 1466 | 2347-2380 | 53,100 |
| | 31-4N-2W | 124 | 2504-2515 | 57,000* |
| | 3-6N-2W | 1462 | 2294-2301 | 60,400 |
| | 10-6N-2W | 230 | 2300-2307 | 59,800 |
| | 16-6N-2W | 897 | 2278-2283 | 48,400* |
| | 33-6N-2W | 1663 | 2284-2296 | 45,700 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | |
|--|-------------|---------------|---------------------------|----------|
| Devonian, continued | | | | |
| Bond | 33-6N-2W | B-1664 | 2273-2288 | 44,200 |
| | 7-6N-4W | 1557 | 1910-1918 | 11,300 |
| | 16-6N-4W | 1558 | 1795-1799 | 10,800 |
| | 16-6N-4W | 1559 | 1834-1841 | 10,600 |
| | 16-6N-4W | 1560 | 1837-1839 | 10,700 |
| | 20-6N-4W | 1596 | 1937-1942 | 11,400 |
| | 29-6N-4W | 1594 | 1936-1939 | 11,700 |
| | 33-6N-4W | 1597 | 1921-1923 | 14,700 |
| | 33-6N-4W | 1598 | 1924-1936 | 14,900 |
| Champaign | 3-17N-8E | 1691 | 476-512 | 3,740 |
| | 17-20N-10E | 1729 | 252-353 | 1,290 |
| Christian | 15-13N-1E | 898 | 2312-2332 | 136,000* |
| | 15-13N-1E | 900 | 2316-2325 | 134,000 |
| | 15-13N-1E | 908 | 2316-2337 | 134,000 |
| | 17-13N-1E | 1407 | 2304-2350 | 140,000 |
| | 29-13N-1E | 735 | 2325-2356 | 136,000* |
| | 29-13N-1E | 736 | 2325-2356 | 138,000 |
| | 9-13N-3W | 1623 | 1809-1822 | 108,000 |
| Clark | 20-11N-10W | 911 | 2064-2100 | 12,000* |
| | 30-11N-14W | 670 | 1320-1350 | 18,000* |
| | 30-11N-14W | 683 | 1400-1550 | 14,300* |
| Clay | 4-2N-8E | 272 | 4702-4840 | 131,000* |
| Clinton | 13-1N-1W | 178 | 2906-2915 | 76,700* |
| | 15-1N-2W | 1424 | 2738-2746 | 132,000 |
| | 16-1N-2W | 1425 | 2734-2737 | 133,000 |
| | 12-1N-3W | 1441 | 2586-2600 | 116,000 |
| | 35-2N-1W | 1513 | 2884-2901 | 81,400 |
| | 31-2N-2W | 1580 | 2599-2627 | 118,000 |
| | 27-3N-1W | 1564 | 2850-2855 | 66,400 |
| Coles | 11-12N-7E | 594 | 3153-3165 | 40,200* |
| | 11-12N-7E | 709 | 3160-3172 | 40,500* |
| | 11-12N-7E | 710 | 3160-3172 | 45,700 |
| | 23-14N-7E | 1856 | 2874-2882 | 42,800 |
| | 35-14N-7E | 433 | 2940-2964 | 28,500* |
| | 26-14N-9E | 331 | 1052-1055 | 5,570* |
| Crawford | 9-6N-13W | 275 | 2795-2965 | 73,000* |
| Edgar | 22-13N-12W | 94 | 2209-2235 | 45,500 |
| | 3-13N-13W | 966 | 1340-1410 | 46,100* |
| Fayette | 13-5N-2E | 1671 | 3466-3470 | 112,000 |
| | 7-8N-1E | 481 | 2788-2814 | 72,000 |
| | 21-8N-3E | 319 | 3054-3060 | 93,100* |
| | 29-8N-3E | 318 | 3095-3097 | 90,200* |
| Ford | 27-25N-7E | 1618 | 603-605 | 1,080 |
| | 33-25N-7E | 1620 | 619-625 | 1,780 |
| Jefferson | 35-2S-1E | 763 | 3663-3746 | 84,500* |
| | 35-2S-1E | 1318 | 3710-3716 | 94,900 |
| | 2-3S-1E | 1349 | 3675-3677 | 96,800 |
| | 2-3S-1E | 1350 | 3670-3678 | 97,700 |
| | 2-3S-1E | 1351 | 3671-3679 | 98,600 |
| Lawrence | 27-5N-11W | 1773 | 3018-3026 | 142,000 |
| Macon | 1-16N-3E | 1495 | 2262-2283 | 151,000 |
| | 1-16N-3E | 1615 | 2263-2283 | 152,000 |
| Madison | 12-3N-6W | 1517 | 1842-1853 | 34,000 |
| | 29-4N-5W | 1687 | 1941-1948 | 31,300 |
| Marion | 3-1N-1E | 1213 | 3260-3344 | 103,000 |
| | 3-1N-1E | 1310 | 3346-3355 | 102,000 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | | |
|--|-----------------------------------|---------------|---------------------------|-----------|---------|
| Devonian, continued | | | | | |
| Marion | 30-1N-1E | B-1670 | 3014-3027 | 73,400 | |
| | 8-2N-1E | 155 | 2992-2994 | 86,700* | |
| | 34-2N-1E | 1309 | 3388-3398 | 102,000 | |
| | 34-3N-2E | 692 | 3510-3546 | 125,000* | |
| | 29-4N-1E | 358 | 2879-2908 | 75,900* | |
| | 34-4N-1E | 1298 | 2954-2956 | 84,500 | |
| Mason | 19-21N-5W | 584 | 1100-1336 | 7,770* | |
| McDonough | 15-4N-4W | 123 | 495 | 4,360* | |
| | 15-4N-4W | 186 | 480 | 4,640* | |
| | 19-4N-4W | 120 | 496 | 4,700* | |
| Montgomery | 31-9N-3W | 1846 | 1968-2016 | 44,400 | |
| Morgan | 22-13N-8W | 711 | 1020-1039 | 30,600* | |
| Piatt | 1-16N-5E | 1749 | 2396-2425 | 82,700 | |
| Sangamon | 12-14N-4W | 1541 | 1739-1744 | 99,300 | |
| | 29-15N-4W | 1696 | 1621-1629 | 83,700 | |
| | 23-1S-1W | 605 | 3116-3150 | 79,600* | |
| Washington | 16-1S-2W | 1581 | 2894-2906 | 138,000 | |
| | 10-2S-2W | 1174 | 3047-3080 | 103,000 | |
| | 10-2S-2W | 1278 | 3047-3080 | 102,000 | |
| | 10-2S-2W | 1302 | 3074-3080 | 101,000 | |
| | 10-2S-2W | 1346 | 3053-3090 | 112,000 | |
| | 10-2S-2W | 1379 | 3053-3090 | 111,000 | |
| | 8-2S-4W | 1604 | 2362-2368 | 91,100 | |
| | 33-2N-8E | 1728 | 4878-4898 | 166,000 | |
| | 24-2S-9E | 1751 | 5426-5447 | 209,000 | |
| | 29-2S-9E | 1766 | 5348-5360 | 210,000 | |
| Wayne | 29-2S-9E | 1790 | 5348-5360 | 210,000 | |
| | 33-2S-9E | 1779 | 5358-5373 | 216,000 | |
| | 33-2S-9E | 1904 | 5358-5373 | 211,000 | |
| | 16-3S-7E | 1911 | 5320-5331 | 213,000 | |
| | 23-1N-10W | 118 | 3308-3415 | 142,000* | |
| | Knox (Ind.) Sullivan (Ind.) | 30-9N-8W | 746 | 2021-2025 | 11,700* |
| | | 19-9N-9W | 759 | 2089-2156 | 18,300* |
| | | 5-9N-10W | 786 | 2158-2187 | 29,100* |
| Vigo (Ind.) | 15-10N-10W | 82 | 2115-2168 | 14,000* | |
| | 15-10N-10W | 86 | 2089 | 18,100 | |
| | 15-10N-10W | 87 | 2115 | 18,700 | |
| | 15-10N-10W | 159 | 2022-2171 | 14,000* | |
| | 16-10N-10W | 68 | 2103-2190 | 13,500 | |
| | 16-10N-10W | 84 | 2094 | 15,900 | |
| | 24-11N-8W | 765 | 1621-1641 | 3,840* | |
| | 11-11N-9W | 760 | 1782-1810 | 4,940* | |
| | 11-11N-9W | 761 | 1681-1704 | 6,180* | |
| Henderson (Ky.) | 22-Q-2S | 126 | 4290 | 170,000* | |
| Silurian | | | | | |
| Adams | 36-1S-5W | 1673 | 650-670 | 9,430 | |
| | 36-1S-5W | 1750 | 655-656 | 9,320 | |
| | 2-2S-5W | 1677 | 624-625 | 9,550 | |
| | 25-3S-5W | 1771 | 506-525 | 5,330 | |
| Brown | 8-2S-4W | 1676 | 615-630 | 9,110 | |
| | 8-2S-4W | 1678 | 568-651 | 9,180 | |
| Christian | 13-13N-4W | 1621 | 1854-1870 | 82,300 | |
| | 4-14N-2W | 1646 | 1919-1931 | 123,000 | |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | | |
|--|-------------|---------------|---------------------------|-----------|----------|
| Silurian, continued | | | | | |
| Christian | 4-14N-2W | B-1647 | 1914-1920 | 123,000 | |
| | 7-14N-2W | 1674 | 1893-1906 | 129,000 | |
| | 17-14N-3W | 1497 | 1688-1693 | 98,500 | |
| | 17-14N-3W | 1502 | 1682-1703 | 101,000 | |
| | 2-15N-1W | 1494 | 1898-1910 | 128,000 | |
| | 10-15N-1W | 1492 | 1865-1892 | 130,000 | |
| | 11-15N-1W | 1493 | 1880-1899 | 134,000 | |
| | 16-15N-1W | 1445 | 1894-1909 | 134,000 | |
| | 19-15N-1W | 1478 | 1900-1915 | 132,000 | |
| | 24-15N-2W | 1477 | 1921-1928 | 133,000 | |
| | 27-15N-2W | 369 | 1884-1905 | 126,000* | |
| | 34-15N-2W | 1460 | 1895-1935 | 126,000 | |
| | Clinton | 4-1N-3W | 203 | 2406-2432 | 105,000* |
| | | 9-1N-3W | 1865 | 2400-2504 | 111,000 |
| 20-1N-3W | | 619 | 2473-2516 | 107,000* | |
| 20-1N-3W | | 676 | 2470-2478 | 106,000* | |
| 23-1N-3W | | 1141 | 2499-2607 | 105,000 | |
| 24-1N-3W | | 1286 | 2550-2670 | 125,000 | |
| 24-1N-3W | | 1486 | 2547-2584 | 124,000 | |
| 25-1N-3W | | 1287 | 2545-2636 | 125,000 | |
| 1-1N-4W | | 1591 | 2423-2442 | 101,000 | |
| 2-1N-4W | | 1600 | 2342-2470 | 101,000 | |
| 9-1N-5W | | 1654 | 1926-2028 | 66,700 | |
| 33-1N-5W | | 1507 | 1883-1984 | 79,400 | |
| 1-2N-4W | | 1060 | 2238-2278 | 77,600 | |
| 36-2N-4W | | 1602 | 2342-2418 | 104,000 | |
| 31-3N-3W | | 1057 | 2227-2251 | 76,400 | |
| 3-1S-5W | | 1306 | 1932-2060 | 77,500 | |
| 3-1S-5W | | 1504 | 1942-2047 | 78,600 | |
| 4-1S-5W | | 1503 | 1944-2070 | 77,900 | |
| 4-1S-5W | | 1505 | 1904-2063 | 78,100 | |
| 4-1S-5W | | 1506 | 1940-2063 | 76,600 | |
| 17-1S-5W | | 1239 | 2000-2030 | 55,500 | |
| DeWitt | | 21-21N-3E | 1795 | 1137-1150 | 4,200 |
| | | 21-21N-3E | 1796 | 1121-1138 | 4,540 |
| | 21-21N-3E | 1841 | 1117-1137 | 4,540 | |
| | 21-21N-3E | 1842 | 1133-1135 | 4,270 | |
| | 21-21N-3E | 1843 | 1142-1164 | 4,200 | |
| | 21-21N-3E | 1848 | 1137-1150 | 4,210 | |
| | 1-24N-7E | 1624 | 354-385 | 648 | |
| Ford | 11-24N-7E | 1624 | 354-385 | 648 | |
| Logan | 7-19N-3W | 896 | 1207-1370 | 12,900* | |
| Macon | 6-15N-1E | 1461 | 1946-1952 | 136,000 | |
| | 6-15N-1E | 1475 | 1947-1954 | 139,000 | |
| | 5-16N-2E | 1405 | 2010-2047 | 135,000 | |
| | 32-17N-2E | 1496 | 1985-1987 | 132,000 | |
| Madison | 3-4N-6W | 618 | 1736-1781 | 56,200* | |
| | 4-4N-6W | 604 | 1739-1762 | 56,000* | |
| | 4-4N-6W | 608 | 1762-1775 | 59,500 | |
| | 4-4N-6W | 614 | 1741-1800 | 60,200 | |
| | 9-4N-6W | 613 | 1677-1690 | 60,700 | |
| | 9-4N-6W | 615 | 1747-1791 | 58,200* | |
| | 10-4N-6W | 611 | 1754-1789 | 58,000 | |
| | 11-4N-6W | 609 | 1738-1762 | 59,000 | |
| | 14-4N-6W | 617 | 1754-1793 | 57,300* | |
| | 15-4N-6W | 439 | 1736-1802 | 55,800* | |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter | |
|--|-------------|---------------|---------------------------|---------|
| Silurian, continued | | | | |
| Madison | 16-4N-6W | B-610 | 1720-1750 | 61,200 |
| | 16-4N-6W | 612 | 1712-1717 | 62,100 |
| | 17-4N-6W | 616 | 1706-1710 | 60,200* |
| Marion | 2-1N-1E | 1304 | 3358-3366 | 101,000 |
| | 3-1N-1E | 1305 | 3336-3343 | 102,000 |
| | 3-1N-1E | 1307 | 3338-3356 | 102,000 |
| | 3-1N-1E | 1308 | 3342-3353 | 100,000 |
| Peoria | 4-11N-8E | 750 | 548-1085 | 2,150 |
| Pike | 12-3S-2W | 967 | 425-510 | 9,760* |
| Randolph | 9-4S-5W | 1300 | 2169-2252 | 132,000 |
| | 16-4S-5W | 1240 | 2175-2219 | 132,000 |
| | 16-4S-5W | 1301 | 2160-2225 | 131,000 |
| | 16-4S-5W | 1869 | 2161-2223 | 133,000 |
| | 21-4S-5W | 1337 | 2180-2253 | 128,000 |
| | 7-4S-6W | 1412 | 1570-1670 | 48,100 |
| | 7-4S-6W | 1474 | 1569-1634 | 47,000 |
| | 9-14N-4W | 1927 | 1680-1700 | 85,300 |
| Sangamon | 10-14N-4W | 1498 | 1732-1743 | 96,800 |
| | 10-14N-4W | 1499 | 1728-1736 | 95,500 |
| | 12-14N-4W | 1539 | 1733-1741 | 99,000 |
| | 12-14N-4W | 1540 | 1710-1721 | 102,000 |
| | 20-14N-4W | 1770 | 1699-1710 | 90,800 |
| | 10-15N-3W | 953 | 1761-1777 | 99,600 |
| | 32-15N-3W | 1764 | 1735-1774 | 107,000 |
| | 21-15N-4W | 1695 | 1592-1605 | 89,000 |
| St. Clair | 25-1S-6W | 1850 | 1834-1947 | 54,700 |
| | 25-1S-6W | 1858 | 1834-1947 | 55,000 |
| Tazewell | 18-25N-3W | 136 | 1200-1390 | 3,210* |
| Washington | 3-1S-4W | 1538 | 2244-2262 | 87,900 |
| | 3-1S-4W | 1582 | 2244-2262 | 88,800 |
| | 3-1S-4W | 1693 | 2208-2229 | 91,100 |
| | 4-1S-4W | 1587 | 2221-2288 | 87,800 |
| | 15-1S-4W | 1138 | 2348-2386 | 103,000 |
| | 15-1S-4W | 1139 | 2308-2335 | 105,000 |
| | 16-1S-5W | 1530 | 1994-2134 | 57,800 |
| | 16-1S-5W | 1599 | 1994-2134 | 58,100 |
| | 32-2S-4W | 1531 | 2337-2367 | 97,000 |
| | 20-3S-4W | 737 | 2267-2284 | 84,900* |
| | 36-3S-5W | 1639 | 2290-2412 | 111,000 |
| Ordovician | | | | |
| Galena (Trenton of Meents et al., 1952) Gp. | | | | |
| Clark | 8-11N-14W | 1794 | 2320-2428 | 15,900 |
| Douglas | 4-16N-8E | 1913 | 950-1050 | 7,270 |
| Fayette | 21-8N-3E | 1548 | 3908-3920 | 53,500 |
| Marion | 18-3N-1E | 1627 | 3946-3978 | 78,700 |
| | 32-4N-1E | 1566 | 3949-3995 | 77,200 |
| Perry | 23-4S-1W | 1909 | 4135-4275 | 92,700 |
| | 10-4S-2W | 1608 | 3956-3968 | 71,800 |
| St. Louis (Mo.) | 6-47N-7E | 1428 | 1018-1060 | 12,800 |
| | 6-47N-7E | 1429 | 1018-1060 | 6,580 |
| Washington | 23-1S-1W | 1593 | 4283-4373 | 139,000 |
| | 21-3S-2W | 1343 | 3919-3954 | 72,800 |
| | 21-3S-2W | 1404 | 3902-3951 | 67,800 |
| | 22-3S-2W | 1342 | 3903-3928 | 70,500 |

TABLE 3. CONTINUED

| Geologic Period Stratigraphic Unit County and Location | Lab. no. | Depth, ft. | Total solids, mg/liter |
|--|-------------|---------------|---------------------------|
| St. Peter Fm. | | | |
| Champaign 21-17N-8E | B-1756 | 1640-1795 | 19,600 |
| DeWitt 1-20N-4E | 1912 | 2275-2295 | 3,350 |
| 29-21N-4E | 1930 | 2404-2427 | 3,240 |
| Douglas 4-16N-8E | 1882 | 1477-1624 | 21,800 |
| 26-16N-8E | 1765 | 1594-1734 | 22,700 |
| Macon 5-15N-1E | 1358 | 2895-2908 | 3,240 |
| White 27-4S-14W | 1242 | 7335-7407 | 199,000 |
| Shakopee Fm. | | | |
| Macon 5-15N-1E | 1359 | 3591-3606 | 5,640 |
| Oneota Fm. | | | |
| Macon 5-15N-1E | 1370 | 3685-3780 | 7,130 |
| Monroe 35-1S-10W | 1250 | 1655 | 21,400 |
| Cambrian | | | |
| Eau Claire Fm. | | | |
| Monroe 35-1S-10W | 1253 | 2760 | 20,000 |
| Mt. Simon Fm. | | | |
| Madison 27-3N-6W | 1669 | 4955-5018 | 98,500 |
| LaSalle 1-36N-5E | 1607 | 3500-3720 | 67,100 |
| 1-36N-5E | 1612 | 3500-3720 | 67,700 |

* Chemical analysis in Meents et al. (1952).

TABLE 4. SEA WATER AND FRESH WATER COMPOSITIONS
USED IN CALCULATIONS IN THIS PAPER.

| | Sea water* g/kg | Sea water g equiv/liter | Lake Michigan [†] mg/liter | Lake Michigan mg/liter, corrected | Lake Michigan corrected, g equiv/liter |
|-------------------------------------|--------------------|----------------------------|---|--|---|
| Na | 10.56 | .4730 | 4.08 | 6.12 | .000266 |
| K | .38 | .0100 | .66 | .99 | .000025 |
| Mg | 1.27 | .1077 | 8.27 | 12.40 | .001020 |
| Ca | .40 | .0210 | 26.21 | 39.32 | .001962 |
| Cl | 18.98 | .5514 | 2.73 | 4.10 | .000115 |
| SO ₄ | 2.65 | .0568 | 7.26 | 10.89 | .000227 |
| HCO ₃ | .14 | .0024 | | | .002917 |
| HCO ₃ as CO ₃ | | | 58.35 | 87.52 | |

* Sverdrup et al. (1942), p. 166.

† Computed from Clarke (1924), p. 74.

TABLE 5. NUMBER OF PORE VOLUMES OF FRESH WATER (x)
AND OF SEA WATER (y) NEEDED TO DERIVE THE BRINE COMPOSITIONS REPORTED IN TABLE 2.

| Sample Number | First Calculation | | Second Calculation | | Sample Number | First Calculation | | Second Calculation | |
|------------------|----------------------|------|-----------------------|------|------------------|----------------------|------|-----------------------|------|
| | x | y | x | y | | x | y | x | y |
| ILLINOIS BASIN | | | | | | | | | |
| 4A | -48 | 3.5 | 46 | 4.1 | 54A | -42 | 3.6 | 61 | 4.3 |
| 5A | -29 | .84 | -5.3 | 1.0 | 56A | -22 | 3.7 | 89 | 4.5 |
| 6A | -38 | 4.3 | 72 | 5.0 | 61 | -21 | 6.3 | 200 | 7.8 |
| 7A | -37 | 3.8 | 72 | 4.5 | 62 | 7.7 | .59 | 23 | .69 |
| 8A | -43 | 3.6 | 53 | 4.3 | 71 | -17 | 3.7 | 100 | 4.5 |
| 9A | -40 | 1.2 | -8.5 | 1.5 | 72 | -47 | 4.0 | 71 | 4.8 |
| 10A | -41 | 1.6 | 3.6 | 1.9 | 73 | -33 | 4.2 | 100 | 5.1 |
| 11A | -12 | 4.0 | 98 | 4.7 | 74 | -4.1 | .13 | -.59 | .15 |
| 12A | -18 | 4.9 | 120 | 5.8 | 75 | -.84 | .04 | .36 | .05 |
| 14A | -44 | 4.3 | 85 | 5.2 | 78 | 1.2 | .07 | 2.9 | .08 |
| 15A | -14 | 1.9 | 33 | 2.2 | 81 | 10 | 3.3 | 100 | 3.9 |
| 16A | .78 | .38 | 12 | .45 | 82 | -6.2 | .19 | .51 | .24 |
| 17A | -47 | 2.6 | 20 | 3.1 | 83 | -2.2 | .19 | 4.1 | .24 |
| 18A | -32 | 2.1 | 19 | 2.4 | 84 | -60 | 3.0 | 28 | 3.6 |
| 19A | -26 | 4.1 | 100 | 4.9 | 85 | -25 | .78 | -5.3 | .92 |
| 41 | 12 | 6.1 | 230 | 7.7 | N1 | 12 | .43 | 24 | .51 |
| 51A | -16 | 4.5 | 110 | 5.4 | N2 | 180 | 6.4 | 480 | 8.5 |
| | | | | | N3 | 41 | 2.1 | 130 | 2.7 |
| MICHIGAN BASIN | | | | | | | | | |
| M2 | 1500 | 12.6 | 2300 | 18.0 | M54 | 290 | 9.6 | 630 | 11.9 |
| M3 | 190 | 8.0 | 400 | 9.5 | M55 | 140 | 5.0 | 310 | 6.2 |
| M4 | 310 | 9.8 | 640 | 12.1 | M56 | -59 | 3.5 | 40 | 4.2 |
| M5 | 910 | 9.5 | 1500 | 13.7 | M57 | 46 | 7.2 | 290 | 8.9 |
| M6 | 330 | 8.2 | 680 | 10.6 | M58 | 120 | 6.8 | 320 | 8.2 |
| M7 | 610 | 10.1 | 1100 | 13.5 | M61 | 970 | 9.1 | 1600 | 13.7 |
| M9 | 740 | 10.4 | 1300 | 14.2 | M71 | 650 | 10.1 | 1200 | 12.9 |
| M11 | 230 | 8.2 | 500 | 10.1 | M73 | 500 | 9.2 | 850 | 11.6 |
| M43 | 1500 | 13.5 | 2400 | 19.4 | M75 | 750 | 10.2 | 1200 | 13.1 |
| M50 | 770 | 10.9 | 1400 | 14.9 | C2 | 43 | .99 | 44 | 1.0 |
| M51 | -86 | 9.5 | 260 | 11.9 | C3 | 16 | .62 | 33 | .74 |
| M52 | 410 | 9.8 | 870 | 13.0 | C5 | 23 | .87 | 36 | .96 |
| M53 | 210 | 9.0 | 570 | 11.4 | C6 | 2.5 | .11 | 3.2 | .12 |
| GULF COAST | | | | | | | | | |
| G14A | -54 | 2.0 | 17 | 2.5 | G30A | 98 | 6.7 | 440 | 9.1 |
| ALBERTA | | | | | | | | | |
| A | 220 | 6.4 | 520 | 8.5 | E | -26 | .73 | -4.4 | .88 |
| B | -83 | 5.2 | 110 | 6.6 | F | -145 | 5.5 | 46 | 6.9 |
| C | -29 | .72 | -8.3 | .86 | G | 60 | 3.7 | 200 | 4.6 |
| D | -6.9 | .17 | -1.8 | .21 | H | 120 | 6.3 | 390 | 8.1 |

TABLE 6. CONTENTS OF BR, Cl, AND Ca IN SELECTED SURFACE AND FORMATION WATERS.

Not all of this information is discussed in the text, because Table 6 also serves as data depository for a short paper to be written on the relation between Ca and Br concentrations in brines.

| Sample Number | Br Analysis by | Source of sample | Br, $\text{g}/10^6 \text{ g}$ | Cl, mg/liter | Cl, $\text{g}/10^6 \text{ g}$ | Cl/Br, atomic ratio | Ca, mg/liter | Ca, $\text{g}/10^6 \text{ g}$ | Reference for further sample description | Computed Specific Gravity, $20^\circ\text{C}/4^\circ\text{C}$ |
|---------------|----------------|---|-------------------------------|------------------------------|-------------------------------|---------------------|------------------------------|-------------------------------|--|---|
| M51 | 1 | Michigan formation water | 484 | 179,000 | 150,000* | 700 | 15,100 | 12,600* | Tables 1 and 2 | 1.1957 |
| M56 | 1 | Michigan formation water | 134 | 70,000 | 65,200* | 1,100 | 3,350 | 3,120* | Tables 1 and 2 | 1.0740 |
| M61 | 1 | Michigan formation water | 2,310 | 188,000 | 155,000* | 151 | 70,100 | 57,700* | Tables 1 and 2 | 1.2141 |
| | 1 | Michigan formation water | 1,310 | | 160,000 | 275 | | 32,800 | White et al. (1963, Table 13-7) | |
| | 1 | Michigan formation water | 2,910 | | 208,000 | 161 | | 74,800 | White et al. (1963, Table 13-8) | |
| | 1 | Dresbach Ss. Member, Munising Fm., Michigan | 1,100 | | 169,000 | 346 | | 30,300 | (R. J. Anderson, pers. comm.) | |
| A | 1 | Alberta formation water | 870 | 129,000 | 113,000* | 293 | 24,000 | 21,000* | Tables 1 and 2 | 1.1422 |
| B | 1 | Alberta formation water | 530 | 106,000 | 95,300* | 405 | 6,910 | 6,210* | Tables 1 and 2 | 1.1120 |
| C | 1 | Alberta formation water | 40 | 7,540 | 7,420* | 418 | 39 | 38* | Tables 1 and 2 | 1.0164 |
| D | 1 | Alberta formation water | 10 | 1,530 | 1,520* | 343 | 14 | 14* | Tables 1 and 2 | 1.0040 |
| E | 1 | Alberta formation water | 100 | 14,600 | 14,400* | 325 | 197 | 194* | Tables 1 and 2 | 1.0160 |
| F | 1 | Alberta formation water | 260 | 113,000 | 101,000* | 876 | 4,690 | 4,200* | Tables 1 and 2 | 1.1164 |
| G | 1 | Alberta formation water | 380 | 74,200 | 68,600* | 407 | 9,740 | 9,010* | Tables 1 and 2 | 1.0809 |
| H | 1 | Alberta formation water | 690 | 122,000 | 107,000* | 350 | 18,600 | 16,400* | Tables 1 and 2 | 1.1357 |
| 7A | 1 | Illinois formation water | 164 | 75,900 | 70,400* | 968 | 4,750 | 4,410* | Tables 1 and 2 | 1.0783 |
| 9A | 1 | Illinois formation water | 42 | 23,400 | 22,800* | 1,220 | 277 | 270* | Tables 1 and 2 | 1.0258 |
| 11A | 1 | Illinois formation water | 245 | 79,800 | 73,600* | 677 | 5,850 | 5,400* | Tables 1 and 2 | 1.0842 |
| 12A | 1 | Illinois formation water | 278 | 98,100 | 88,900* | 721 | 7,260 | 6,580* | Tables 1 and 2 | 1.1035 |

TABLE 6. CONTINUED

| Sample Number | Br Analysis by | Source of sample | Br, g/10 ⁶ g | Cl, mg/liter | Cl, g/10 ⁶ g | Cl/Br, atomic ratio | Ca, mg/liter | Ca, g/10 ⁶ g | Reference for further sample description | Computed Specific Gravity, 20°C/4°C |
|---------------|----------------|---|-------------------------|--------------|-------------------------|---------------------|--------------|-------------------------|--|-------------------------------------|
| | 2 | Resampling of 12A | 280 | | 89,900 | 724 | | | | |
| 15A | 1 | Illinois formation water | 130 | 35,700 | 34,300* | 595 | 2,220 | 2,130* | Tables 1 and 2 | 1.0404 |
| 16A | 1 | Illinois formation water | 16 | 7,270 | 7,220* | 1,020 | 670 | 666* | Tables 1 and 2 | 1.0067 |
| 17A | 1 | Illinois formation water | 142 | 49,200 | 46,600* | 740 | 2,100 | 1,990* | Tables 1 and 2 | 1.0550 |
| 18A | 1 | Illinois formation water | 134 | 44,500 | 42,600* | 717 | 1,780 | 1,710* | Tables 1 and 2 | 1.0437 |
| 19A | 1 | Illinois formation water | 204 | 80,400 | 74,000* | 818 | 6,140 | 5,650* | Tables 1 and 2 | 1.0861 |
| 61 | 1 | Illinois formation water | 404 | 122,000 | 108,000* | 603 | 11,100 | 9,800* | Tables 1 and 2 | 1.1332 |
| 62 | 1 | Illinois formation water | 49 | 10,200 | 10,100* | 465 | 1,190 | 1,180* | Tables 1 and 2 | 1.0126 |
| 71 | 1 | Illinois formation water | 198 | 70,300 | 65,100* | 741 | 5,930 | 5,490* | Tables 1 and 2 | 1.0799 |
| 72 | 1 | Illinois formation water | 206 | 77,900 | 71,700* | 785 | 4,800 | 4,420* | Tables 1 and 2 | 1.0858 |
| 73 | 1 | Illinois formation water | 237 | 86,500 | 79,500* | 756 | 6,270 | 5,760* | Tables 1 and 2 | 1.0887 |
| 75 | 1 | Illinois formation water | 2 | 557 | 556* | 627 | 37 | 37* | Tables 1 and 2 | 1.0010 |
| | 2 | Marathon, #1, Lingle, Markham City Pool, 36-2S-4E, Jefferson Co., Illinois, Ste. Genevieve Limestone, Valmeyeran (Middle Mississippian), 3049-3069r depth | 260 | | 79,000 | 686 | | | | |
| | 2 | Cities Service, #10, Vaught, Goldengate Pool, 33-2S-9E, Wayne Co., Illinois, Dutch Creek Sandstone (Middle Devonian), 5358-5373r depth | 440 | | 110,000 | 566 | | | | |

TABLE 6. CONTINUED

| Sample Number | Br Analysis by | Source of sample | Br, mg/liter | Br, g/10 ⁶ g | Cl, mg/liter | Cl, g/10 ⁶ g | Cl/Br, atomic ratio | Ca, mg/liter | Ca, g/10 ⁶ g | Reference for further sample description | Computed Specific Gravity, 20°C/4°C |
|---------------|----------------|--|--------------|-------------------------|--------------|-------------------------|---------------------|--------------|-------------------------|--|-------------------------------------|
| N2 | 2 | T. G. Jenkins, #5, Poorman, Mills Shoals Pool, 19-38-8E, White Co., Illinois, Salem Limestone, Valmeyeran (Middle Mississippian), 3784-3810' depth | 521 | 230 | 125,000 | 90,200 | 883 | 22,400 | 19,700* | Tables 1 and 2 | 1.1388 |
| N3 | 3 | Indiana formation water | 197 | 457* | 41,700 | | 478 | 6,100 | 5,820* | Tables 1 and 2 | 1.0474 |
| | | Sea water | | | | | 663 | | | Livingstone (1963); White et al. (1963) | |
| | 4 | Great Salt Lake, 150 yds NE Gunnison Island | | 136 | 152,000 | 2,520 | | 407 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | 4 | Wyman Creek, Deep Spring Valley, Calif. | | .06 | 2.8 | 105 | | 69 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | 4 | Stock well in alluvium, Deep Spring Valley, Calif. | | .07 | 9.5 | 306 | | 49 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | 4 | Antelope Spring #1, Deep Spring Valley, Calif. | | .04 | 8.5 | 479 | | 56 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | 4 | Spring in rocks of Early Cambrian age, Deep Spring Valley, Calif. | | .12 | 10 | 188 | | 39 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | 4 | Highway Station Well, Deep Spring Valley, Calif. | | .09 | 6.5 | 162 | | 67 | | U. S. Geol. Survey analysis (B. F. Jones, pers. comm.) | |
| | | California formation water | 58 | | 11,600 | 448 | | 543 | | White et al. (1963, Table 12-1) | |
| | | California formation water | 30 | | 9,840 | 730 | | 373 | | White et al. (1963, Table 12-2) | |
| | | California formation water | 32 | | 9,230 | 651 | | 211 | | White et al. (1963, Table 12-3) | |
| | | Louisiana formation water | 86 | | 89,700 | 2,340 | | 2,600 | | White et al. (1963, Table 12-4) | |
| | | California formation water | 108 | | 29,000 | 606 | | 2,190 | | White et al. (1963, Table 13-1) | |

TABLE 6. CONTINUED

| Sample Number | Br Analysis by | Source of sample | Br, mg/liter | Br, g/10 ⁶ g | Cl, mg/liter | Cl, g/10 ⁶ g | Cl/Br, atomic ratio | Ca, mg/liter | Ca, g/10 ⁶ g | Reference for further sample description | Computed Specific Gravity, 20°C/4°C |
|---------------|----------------|-------------------------------|--------------|-------------------------|--------------|-------------------------|---------------------|--------------|-------------------------|--|-------------------------------------|
| | | California formation water | | 91 | | 17,000 | 420 | | 5,890 | White et al. (1963, Table 13-2) | |
| | | Louisiana formation water | | 393 | | 124,000 | 713 | | 9,210 | White et al. (1963, Table 13-3) | |
| | | Kentucky formation water | | 92 | | 15,500 | 380 | | 1,340 | White et al. (1963, Table 13-5) | |
| | | West Virginia formation water | | 373 | | 68,400 | 413 | | 8,450 | White et al. (1963, Table 13-6) | |
| | | Dead Sea surface water | 4,100 | 3,450* | 181,000 | | 100 | 13,000 | 11,000* | Bentor (1961, Table 1-1) | 1.1868 |
| | | Dead Sea average | 5,920 | 4,870* | 208,000 | | 80 | 15,800 | 13,000* | Bentor (1961, Table 1-1a) | 1.2153 |
| | | Jordan River | 4.34 | 4.34* | 474 | | 246 | 80.0 | 79.9* | Bentor (1961, Table 1-2) | 1.0008 |
| | | Lake Tiberias | 2.35 | 2.35* | 283 | | 271 | 49.0 | 49.0* | Bentor (1961, Table 1-4) | 1.0002 |
| | | Beisan Springs | 3.65 | 3.65* | 599 | | 370 | 63.0 | 62.9* | Bentor (1961, Table 1-5) | 1.0008 |
| | | Fuliya Springs | 7.1 | 7.1* | 1,040 | | 330 | 151 | 151* | Bentor (1961, Table 1-6) | 1.0012 |
| | | Tabha Springs | 11.8 | 11.8* | 1,210 | | 231 | 223 | 223* | Bentor (1961, Table 1-7) | 1.0014 |
| | | Tannur Springs | 20.5 | 20.4* | 2,230 | | 245 | 364 | 363* | Bentor (1961, Table 1-8) | 1.0026 |
| | | Tiberias Hot Springs | 246 | 241* | 18,000 | | 165 | 3,500 | 3,430* | Bentor (1961, Table 1-10) | 1.0210 |
| | | Sdom I deep drilling | 3,100 | 2,390* | 275,000 | | 200 | 85,200 | 65,600* | Bentor (1961, Table 1-13) | 1.2984 |
| | | Zohar Sulphur Springs | 810 | 779* | 36,700 | | 102 | 2,990 | 2,870* | Bentor (1961, Table 1-15) | 1.0403 |

* Values in weight/weight units obtained by dividing weight/volume values by specific gravity. Specific gravities were calculated by combining dissolved ions into hypothetical compounds and then using the International Critical Tables to prepare plots of weight percent dissolved solid versus specific gravity for these compounds. Five or fewer cycles of a successive approximation calculation yield a specific gravity value that is the weighted mean of the several specific gravities the solution would have if the total dissolved solids consisted, in turn, of only one of the hypothetical compounds.

Brine analyses by: (1) The Dow Chemical Company; oxidation to bromate, iodometric titration (modified Doering-van der Meulen method); (2) Ethyl Corporation; (3) Indiana State Geological Survey; (4) S. L. Rettig, U. S. Geological Survey; catalytic method (Shiota et al., 1959).

APPENDIX I

Where chemical quantities are graphed, we show ± 3 percent of the amount present as a probable error. The actual discrepancies may be larger for those brines that are so concentrated that extreme dilution is needed for analysis.

It proved to be particularly difficult to dry residues from the Michigan brines without going to temperatures where volatilization of chlorides was a danger. We have used, therefore, as a total dissolved solids value for all samples the sum of Cl, HCO_3 , CO_3 , SO_4 , K, Na, Ca, and Mg. Where earlier brine analyses of the Illinois State Geological Survey are cited in this paper for comparison, the analytical chemical procedures are those described in Meents et al. (1952). It should be noted that Na values given in these earlier analyses were obtained by difference and include K, expressed as Na. The analyses by D. B. Heck of samples collected for the present study differs in that Ca and Mg were determined by EDTA titration and K and Na by flame photometry, using a Beckman DU instrument with flame attachment. The Ca values in Meents et al. (1952), based upon oxalate-method analyses, thus include Sr but probably not Ba, which is removed by that procedure if present in only small amounts (Hillebrand et al., p. 620, 1953). A parallel statement applies to the inclusion in total solids values of Sr expressed as CaCl_2 . Sr and Ba are included in the EDTA analysis for Ca (Amer. Public Health Assn., p. 67, p. 133, 1960).

The brine analysts of the Illinois Geological Survey measure concentrations as milligrams per liter but report them as "parts per million" without making a density correction. We have chosen to plot concentrations as gram equivalents per liter because the volume density of ionic charge is a parameter that one might expect to be useful in discussing ionic hydration and the effect on brine concentration of clays acting as charged membranes. Except in those analyses in which Na or (Na+K) is known only by difference, the chloride value (g equiv/liter) has been adjusted to bring anions into balance with cations.

For some groups of samples for which chemical analyses are incomplete or nonexistent, approximations of several kinds have been made. Some of the Illinois samples (4-19 inclusive) were collected in inadequate volume; the wells from which they came were resampled if still accessible, and, if not, specific analyses were sought in Meents et al. that might be applicable. If there was both a resampling and a pertinent literature analysis available, the chemical information from the former has been used in plotting. No analyses were made of a set of Illinois samples collected in 1957 (numbers 50-60 inclusive), but for samples 51, 54, and 56, analyses in Meents et al. (1952) are applicable. Estimates of total dissolved solids, in mg/liter, for the other samples of the 1957 Illinois set were obtained from the isocon maps of Meents et al. and converted to units of g equiv/liter by using an empirical plot constructed from analyses of Meents et al. Use of such a plot is made possible by the chemical similarity of the brines, in which Cl is the dominant anion and the Ca/Na ratio increases moderately with concentration. Sample 55 (see table 2) is from a region of rapid lateral compositional change; the nearest sample analyzed previously was from the other side of a fault, and all previously analyzed samples on the same side of the fault came from locations miles away, so that the uncertainty in composition of sample 55 is large.

Only Cl values were supplied with the Gulf Coast samples, but published brine analyses (Hawkins et al., 1963; Hawkins et al., 1964) are available close to brine sampling points G14 and G30 from the same stratigraphic units. The tabulated analyses in these two publications were used to estimate SO_4 and HCO_3

contents for the other samples of the 1947 set, and from these values, the total concentration of dissolved solids (g equiv/liter) was calculated. In these brines, the sum of SO_4 and HCO_3 is only from 0.1 to 1.5 percent of the Cl concentration; lower percentages are present at higher concentrations.

APPENDIX II

Analyses of two deep Illinois Basin samples were received after the manuscript was completed. Number B-1996 is from Texaco's R. S. Johnson No. 1 well, sec. 6, T. 1 N., R. 2 E., Salem Pool, Marion County, Illinois, which has a surface elevation of 525 feet. The depth interval sampled, 8450-8461 feet, lies in the Mt. Simon Sandstone of Late Cambrian age, and the brine contains (in mg/liter): Na, 66,800; K, 1250; Ca, 27,000; Mg, 2030; SO_4 , 328; Cl, 161,000; HCO_3 , 20. The sample was collected 250 feet above the tool during a drill stem test that yielded 940 feet of water. The calculated specific gravity ($20^\circ\text{C}/4^\circ\text{C}$) is 1.1714, and the estimated in-situ sample temperature is 92.9°C . The measured δO^{18} and δD values, both relative to standard mean ocean water (SMOW), are -3.25‰ and -1.5 percent, respectively, the sample contains 739 g/(10^6 g solution) of Br, and the Cl/Br atomic ratio is 419.

The analogous description for sample B-1979 follows: Texaco, Cuppy No. 1, sec. 6, T. 6S, R.7E., Dale-Hoodville Pool, Hamilton County, Illinois; surface elevation, 378 feet; 7614-7633 feet; St. Peter Sandstone, Champlainian (Middle Ordovician); Na, 59,400; K, 1330; Ca, 11,500; Mg, 1650; Cl, 118,000; 1900 feet above the tool during a drill stem test that yielded 4125 feet of water; calculated specific gravity ($20^\circ\text{C}/4^\circ\text{C}$), 1.1284; 74.6°C ; δO^{18} , $+1.50\text{‰}$; δD , -1.6 percent; Br, 397 g/(10^6 g solution); Cl/Br atomic ratio, 594.

The normalized isotopic values (using the "second normalization" of Graf et al., 1965, for δD) are: B-1996 δD , -3.5 percent; B-1996 δO^{18} , -13.6‰ ; B-1979 δD , -4.1 percent; B-1979 δO^{18} , -6.7‰ . The g equiv/l concentrations of total dissolved solids are 4.45 (B-1996) and 3.32 (B-1979), of Na, 2.90 and 2.58, of Ca, 1.35 and .572.

The plotted positions of these two samples on most of our graphs are not unusual. However, total dissolved solids and normalized δD values for both B-1996 and B-1979 fall close to the X-line of figure 12, and B-1996 occupies a highly anomalous position on figure 7 of Graf et al. (1965), which compares normalized δD and normalized δO^{18} values.

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