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

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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 O^{18} 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

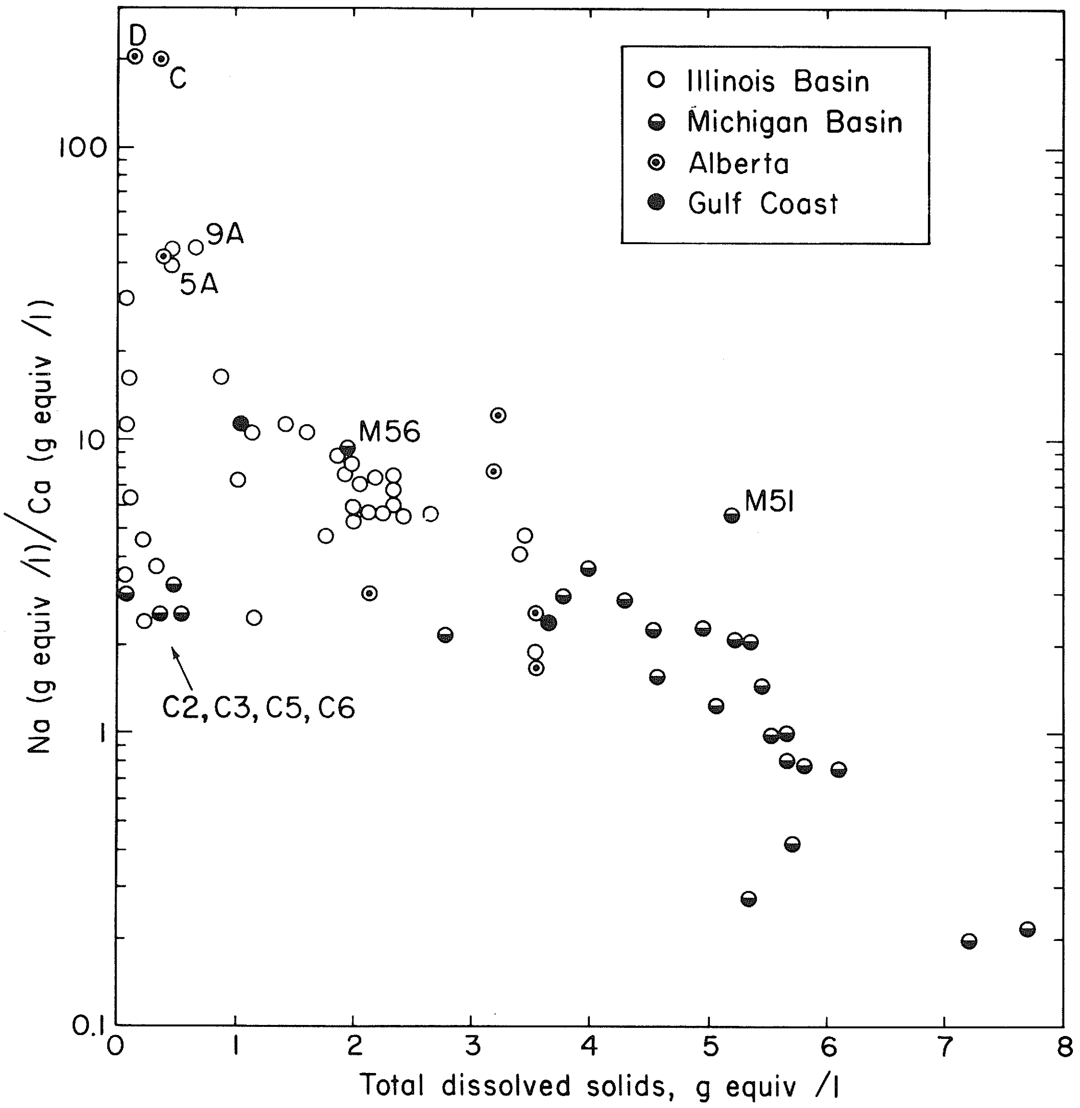

Figure 1. Total dissolved solids content plotted against Na/Ca ratio for the samples of table 2. The samples specifically identified are discussed in the text.

solids consist entirely of NaCl and $CaCl_2$, and a third of the dilute samples depart markedly in composition from the series of mixtures between these two end member solutions. The quantity (HCO_3 + CO_3) 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 $CaCl_2$ 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 $MgCl_2$ 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 $CaCl_2$-rich subsurface waters of the type we are discussing. Borchert and Muir (1964) review the evidence for formation of $CaCl_2$ 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 H_2 and SO_2 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

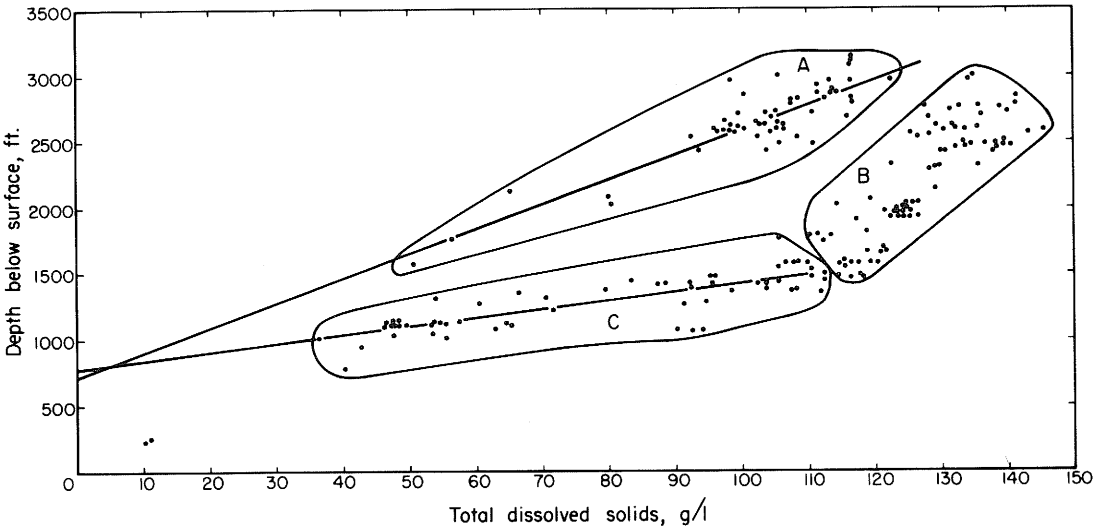

Figure 2. Total dissolved solids content plotted against depth for the Illinois Basin samples of table 1 from the Cypress, Bethel, and Yankeetown Sandstones and for the stratigraphically equivalent samples that Meents et al. (1952) listed under the headings "Cypress" and "'Benoist'–Bethel-Paint Creek."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

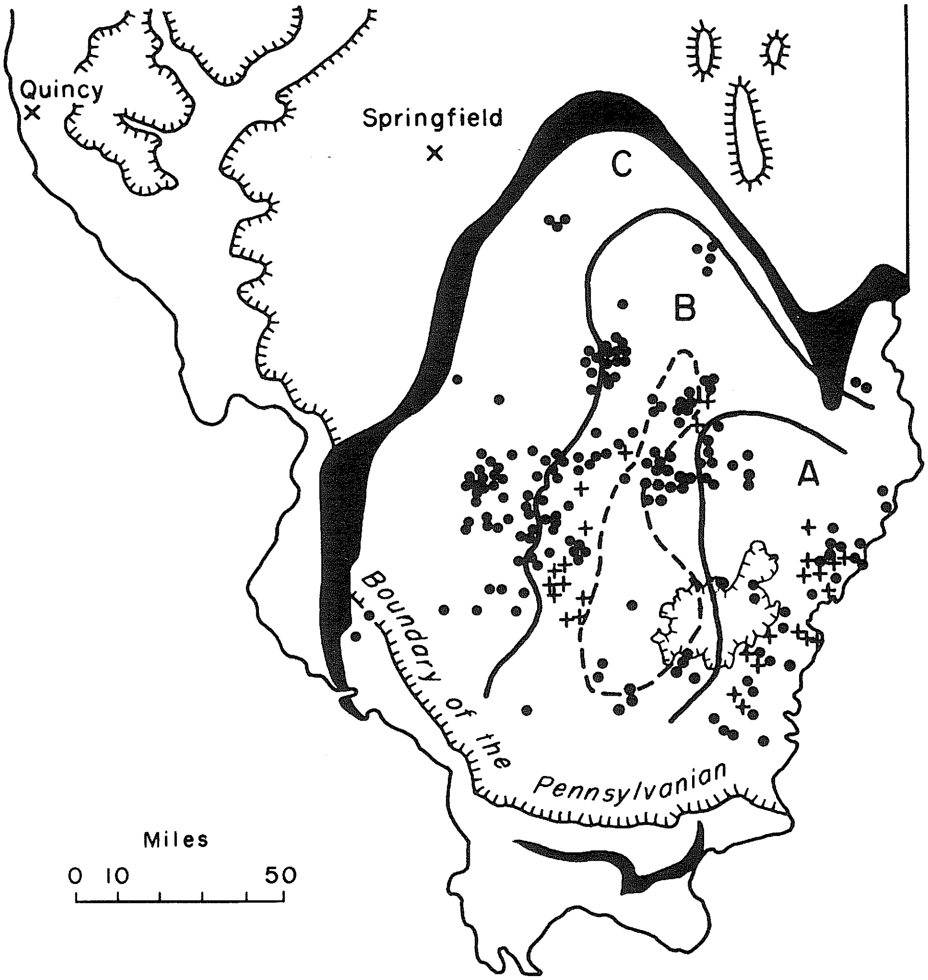

Figure 3. Location of the samples of figure 2. The outcrop belt of the Cypress-Yankeetown interval (subcrop where under the Pennsylvanian) is sketched in black, disregarding faults (see Swann and Bell, 1958). The closed dashed line is the isoconcentration contour for 130,000 mg/liter total dissolved 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

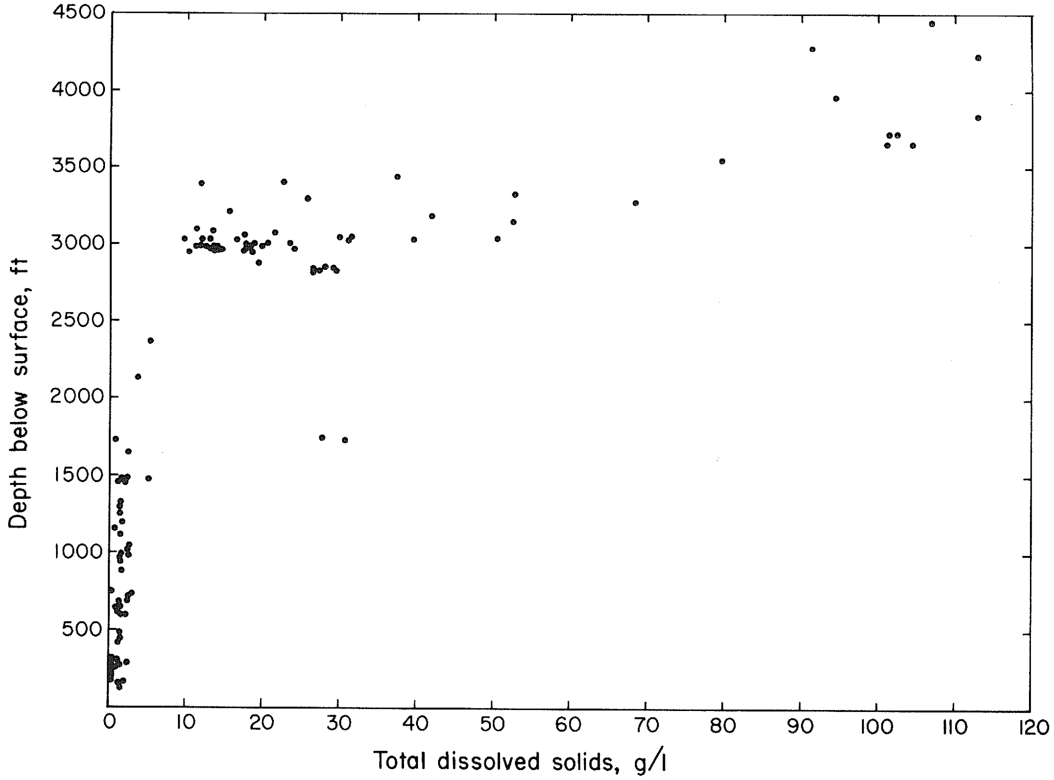

Figure 4. Total dissolved solids content plotted against depth for brines from the Woodbine Sand of northeast Texas (data of Plummer and Sargent, 1931).

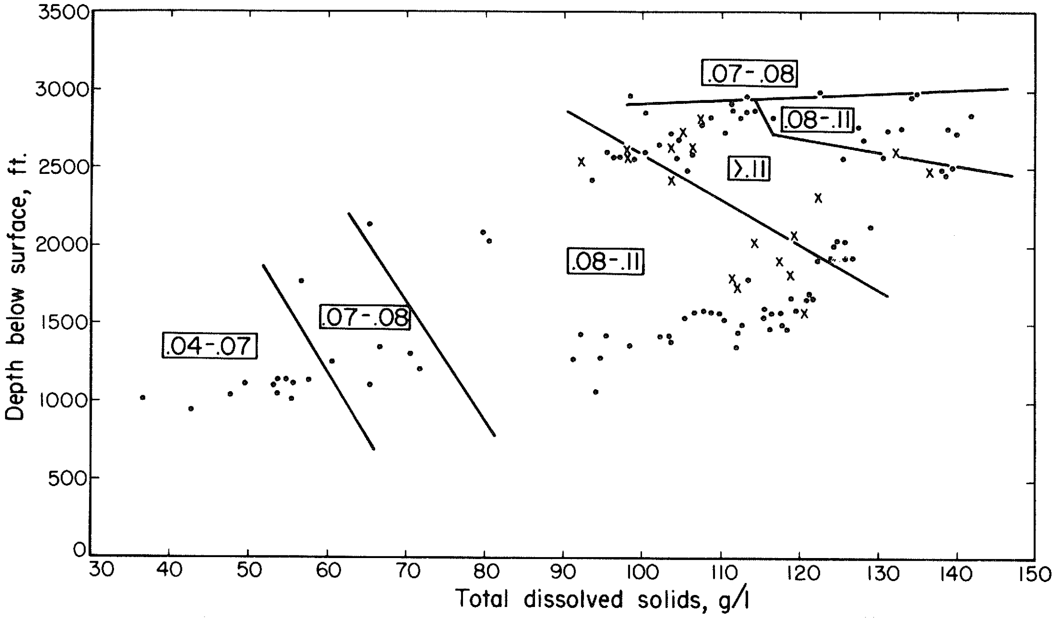

Figure 5. The plot of figure 2, omitting those samples for which chemical analyses are not available, zoned on the ratio of Ca equivalents to total cation equivalents. Points with ratio values outside the range of the region in which they plot are indicated by x's.

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

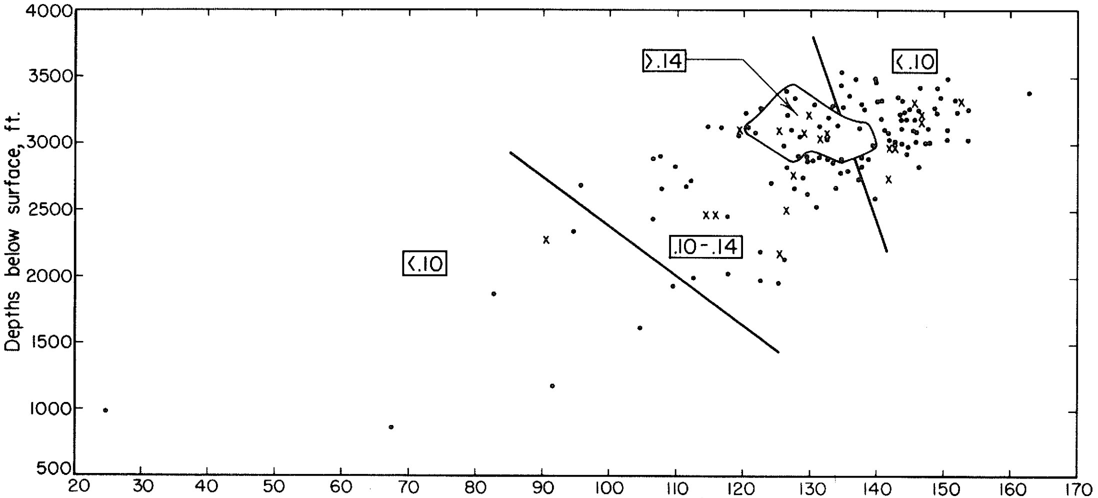

Figure 6. A plot of total dissolved solids content against depth for those Ste. Genevieve brines for which there are chemical analyses, zoned on the ratio of Ca equivalents to total cation equivalents. Points with ratio values outside the range of the region in which they plot are indicated by x's.

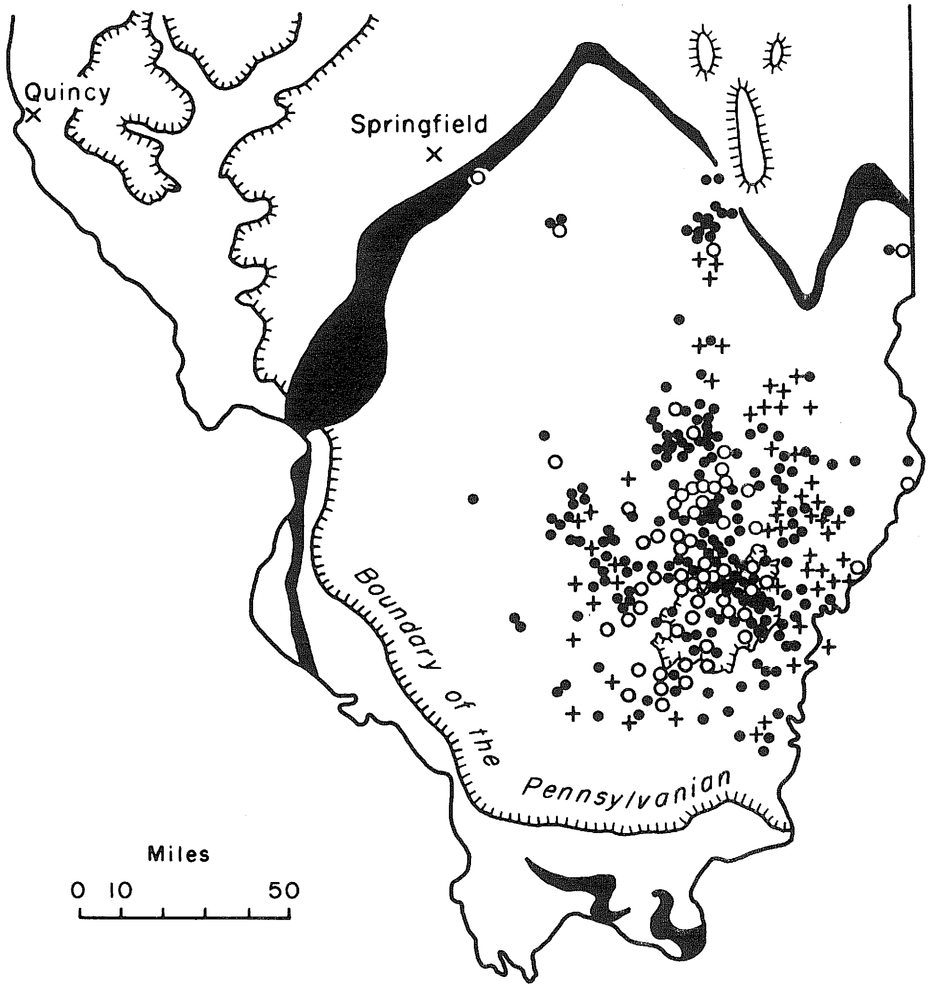

Figure 7. Location of brine samples from the Ste. Genevieve Limestone (Meents et al., 1952; table 1 of this paper). The outcrop of this formation (subcrop where under the Pennsylvanian) is sketched in black, disregarding faults (see Swann and Bell, 1958). Samples with Ca equivalent fractions greater 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.

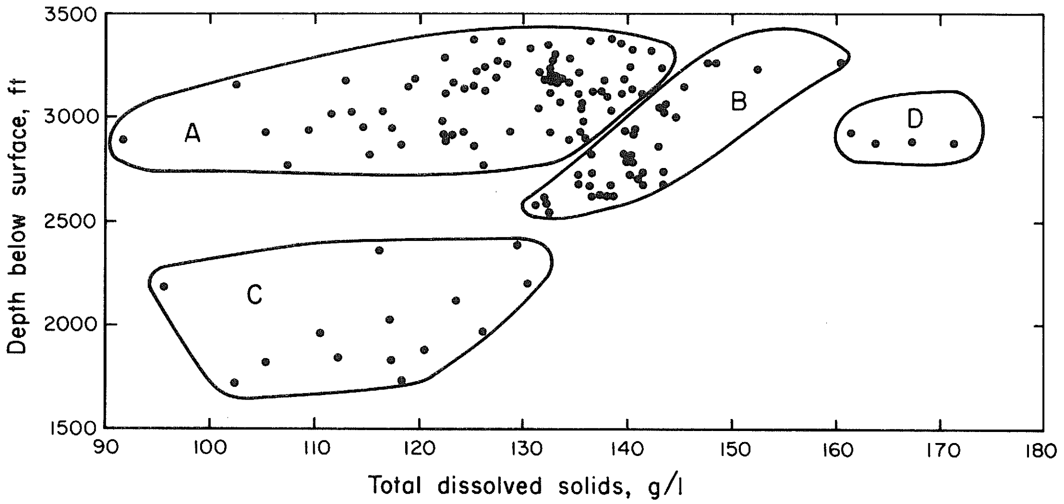

Figure 8. Total dissolved solids content plotted against depth for Illinois Basin samples from the Aux Vases Sandstone. Sample groups A, B, C, and D correspond to areas A, B, C, and D of figure 9.

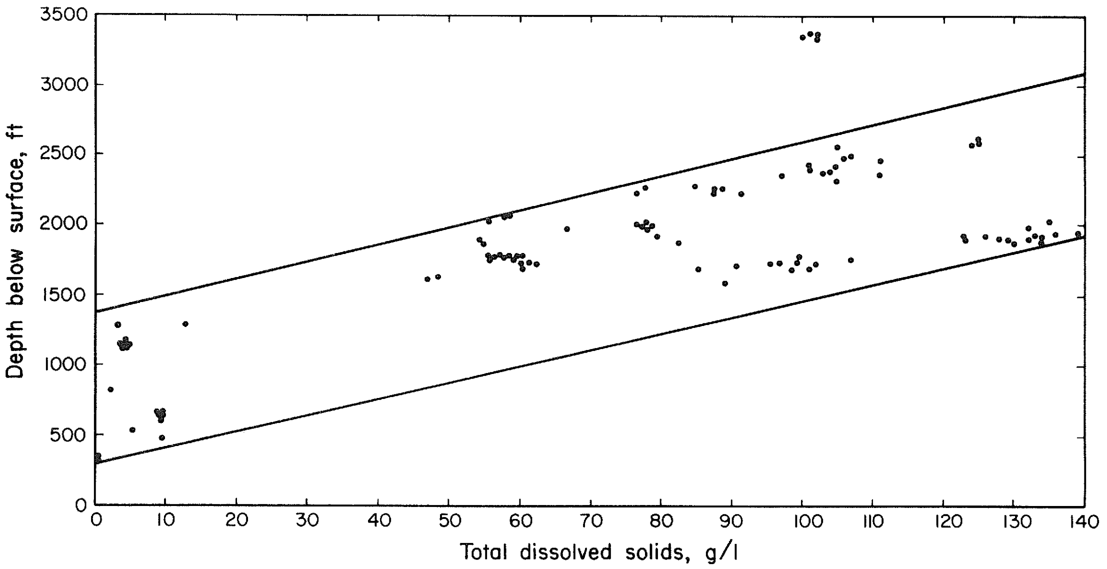

Figure 10. Total dissolved solids content plotted against depth for Illinois Basin samples from the Silurian System.

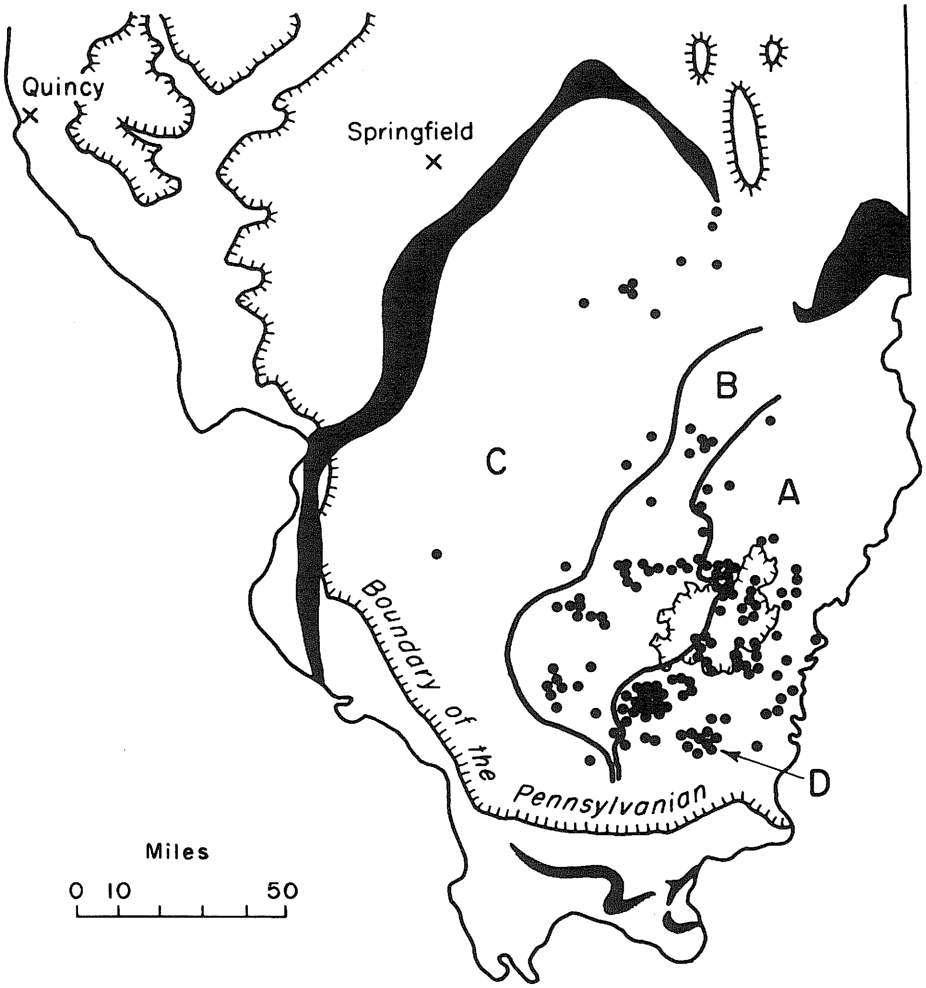

Figure 9. Location of the samples of figure 8. The outcrop belt of the Aux Vases Sandstone (subcrop where under the Pennsylvanian) lies within the somewhat greater stratigraphic interval sketched in black (see Swann and Bell, 1958). The depression contour shows the deepest part of the Illinois Basin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

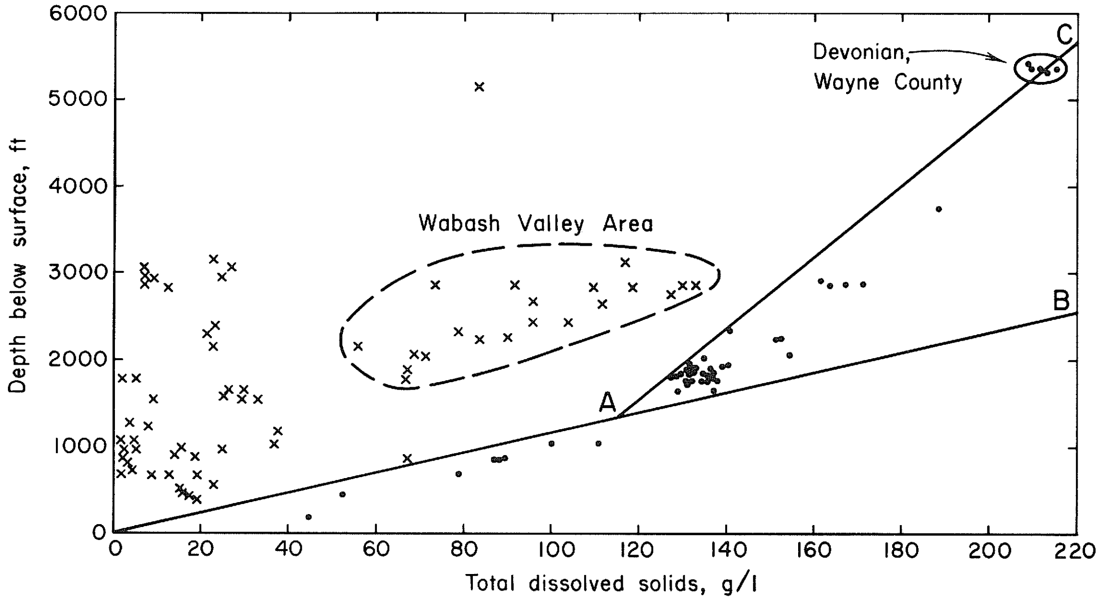

Figure 11. A schematic plot of the relation between depth and total dissolved solids content for the samples of table 1 and of Meents et al. (1952). All samples that plot below the line OAC are shown as dots. Above that line only those points are shown (x's) for which the concentration of SO_4 in g/liter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

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

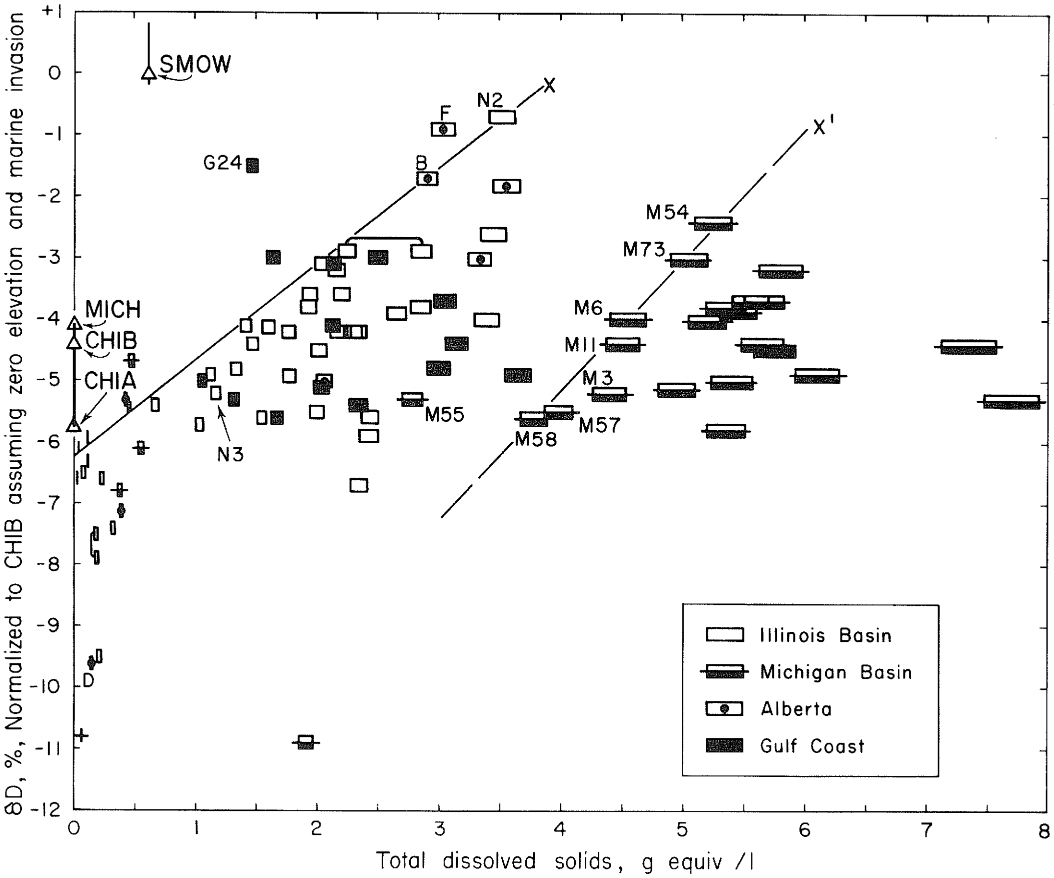

Figure 12. Normalized δD values plotted against total dissolved solids content for the samples of table 2 (see text). The slope of the X and X' lines is interpreted as measuring the operation of shale ultrafilters with good diffusional mixing in the liquid reservoir. There are no Gulf Coast samples containing 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, ±0.1 % for δD and ±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

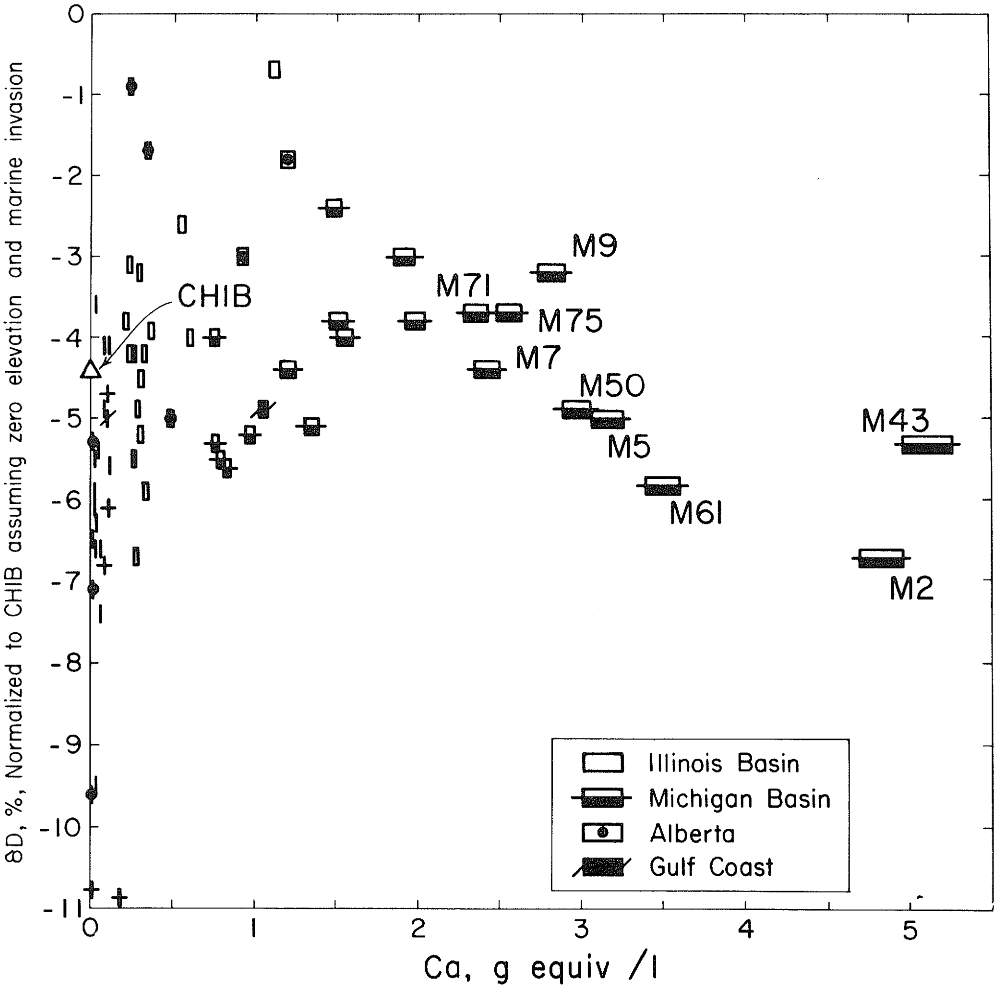

Figure 13. Normalized δD values plotted against Ca content for the samples of table 2 (see text). The samples specifically identified are discussed in the text.

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 δD = −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% in δD)/(1.0 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 δO^{18} 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

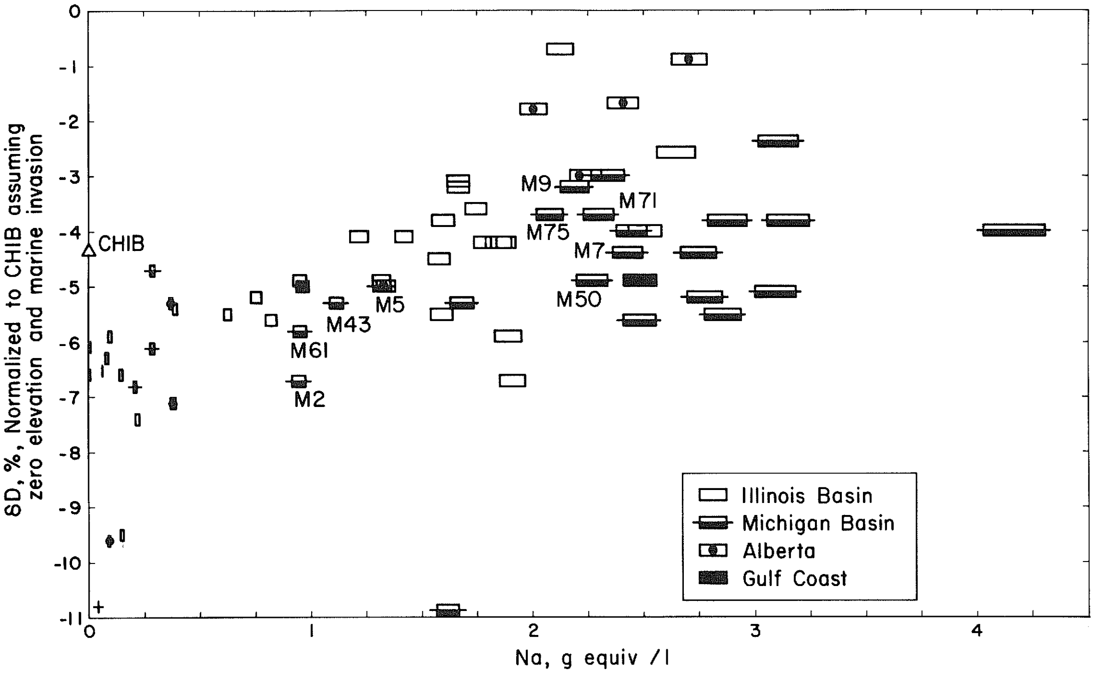

Figure 14. Normalized δD values plotted against Na content for the samples of table 2 (see text). Individual cation concentrations are known for only two Gulf Coast samples. The samples specifically identified are discussed in the text.

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

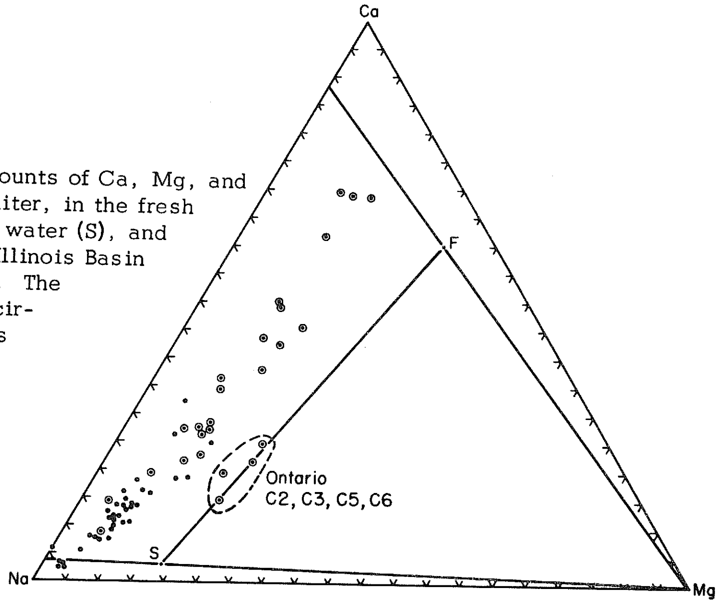

Figure 15. The relative amounts of Ca, Mg, and Na, expressed as g equiv/liter, in the fresh water (F) of table 3, in sea water (S), and in the Michigan Basin and Illinois Basin formation waters of table 2. The Michigan Basin points are circled. The four dilute brines from shallow wells in Ontario contain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

$$2CaCO_3 + Mg^{++} \longrightarrow CaMg(CO_3)_2 + Ca^{++}$$

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). Füchtbauer 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

$$2CaCO_3 + Mg^{++} \longrightarrow CaMg(CO_3)_2 + Ca^{++}.$$

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

$$Na = .000266\,x + .473\,y - b$$
$$Ca = .00196\,x + .0210\,y + a$$
$$Mg = .00102\,x + .108\,y - a$$
$$b = .00314\,x + .0592\,y\ .$$

Combining, we obtain

$$x = 258\,(Ca + Mg) - 80.4\,Na$$
$$y = 1.79\,(Ca + Mg) + 1.86\,Na\ .$$

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

$$x = 475\,Ca - 24.1\,Na$$
$$y = 3.30\,Ca + 2.25\,Na\ .$$

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 $CaSO_4$ + 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 $SO_4^{=}$ 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 Keweenanwan 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 SO_4/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 SO_4 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. Sincox 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, 15-4N-6W				
16	Mike Callahan, #1, Noftz, 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 35-3S-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	Mosebach, #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, Sorento Pool, 32-6N-4W, Bond County, Illinois	-1361 to -1365	497	Lingle Formation	Middle Devonian
53	Kykendale, #1, Copple, 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 Misssissippian)
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	MOCO, #1, McCulley, 25-11N-6W, Montcalm County, Michigan	-2002 to -2020	898	Traverse Group	Middle to Late Devonian
M9	MOCO, #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. CHEMICAL ANALYSES OF BRINE SAMPLES

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
ILLINOIS BASIN																
4A**	(36,300)		1,570	3,530	56	66,700	146	108,000	(1.58)		.129	.176	.00117	1.88	.00239	1.88
5A**	(9,940)		145	214	n.d.	15,600	881	26,800	(.432)		.0119	.0107	n.d.	.440	.0144	.454
6A	43,100	419	2,320	4,920	194	83,000	116	134,000	1.87	.0107	.191	.246	.00404	(2.31)	.00190	2.32
7A	38,300	124	1,700	4,750	476	75,900	90	121,000	1.67	.00317	.140	.237	.00991	(2.04)	.0015	2.05
8A**	(37,500)		1,740	3,900	338	69,500	136	113,000	(1.63)		.143	.195	.00704	1.96	.00223	1.97
9A	14,400	88	300	277	20	23,400	978	39,500	.626	.0022	.0247	.0138	.00042	(.650)	.0160	.667
9B**	(12,500)		178	340	n.d.	20,200	459	33,700	(.546)		.0146	.0170	n.d.	.570	.00752	.578
10A**	(18,100)		454	951	581	30,300	344	50,700	(.787)		.0373	.0475	.0121	.854	.00564	.872
11A	38,400	580	2,220	5,850	255	79,800	27	127,000	1.67	.0148	.183	.292	.00531	(2.15)	.00044	2.16
11B**	(40,800)		2,260	6,960	278	81,700	127	132,000	(1.77)		.186	.347	.00579	2.30	.00208	2.31
12A	47,300	838	2,580	7,260	1,460	98,100	87	158,000	2.06	.0214	.212	.362	.0304	(2.62)	.00143	2.66
13A						101,000										2.84
14A**	(44,000)		1,790	5,540	2,120	81,200	115	135,000	(1.91)		.147	.276	.0441	2.29	.00188	2.34
15A	18,900	166	1,110	2,220	574	35,700	317	59,000	.822	.00425	.0913	.111	.0120	(1.01)	.00520	1.03
15B**	(17,600)		976	2,260	528	33,400	378	55,100	(.766)		.0803	.113	.0110	.942	.00620	.959
16A	3,520	30	210	670	8	7,270	306	12,000	.153	.00077	.0173	.0334	.00017	(.199)	.00502	.204
17A	28,000	100	1,120	2,100	1	49,200	104	80,600	1.22	.00256	.0921	.105	.00002	(1.42)	.00170	1.42
18A	21,900	108	1,010	1,780	19	44,500	237	69,600	.953	.00276	.0831	.0888	.00040	(1.12)	.00388	1.13
18B**	(20,800)		783	1,550	395	36,800	119	60,400	(.908)		.0644	.0774	.00822	1.04	.00195	1.05
19A	40,300	184	1,700	6,140	1,260	80,400	46	130,000	1.75	.00471	.140	.306	.0261	(2.17)	.00075	2.20
19B**	(39,600)		1,310	6,240	1,320	74,900	57	123,000	(1.72)		.108	.311	.0275	2.11	.00093	2.14
41	57,600	2,410	2,650	12,200	521	(120,000)		195,000	2.51	.0616	.218	.609	.0108	(3.39)		3.40
50								140,000								2.43
51								146,000								2.54
51A**	(43,400)		2,340	6,720	1,800	84,400	122	139,000	(1.89)		.192	.335	.0375	2.38	.00200	2.42
52								11,000								.185
53								89,000								1.54

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						88,400‡										2.50
G6						58,200‡										1.64

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
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	1.06
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	3.65
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	3.62
B	55,300	†2,280	*1,010	*6,910	*937	106,000	*593	173,000	2.41	.0583	.0831	.345	.0195	(2.87)	.00972	2.90
C	(8,740)	†169	*52	*39	*7	*7,540	*7,750	25,800	(.380)	.00432	.0043	.0019	.00015	.213	.127	.391
D	2,090	†15	*10	*14	*3	*1,530	*2,330	6,290	.0909	.00038	.00082	.00070	.00006	(.0484)	.0382	.093
E	8,610	†37	*69	*197	*218	*14,600	*357	24,100	.375	.00095	.0057	.00983	.00454	(.381)	.00585	.391
F	62,200	†1,490	*607	*4,690	*914	*113,000	*218	183,000	2.71	.0381	.0499	.234	.0190	(3.01)	.00357	3.03
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	2.05
H	51,500	†2,850	*2,880	*18,600	*537	*122,000	*161	199,000	2.24	.0729	.237	.928	.0112	(3.46)	.00264	3.48

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	400-405	8,920
Coles	10-11N-10E	1947	630-637	28,300
	2-12N-7E	1875	289-340	6,110
	34-12N-7E	1880	1395-1515	104,000
	34-12N-7E	1881	336-385	27,000
	12-12N-10E	1640	476-530	42,100
Douglas	26-16N-10E	1727	374-396	24,800
Edwards	7-2S-11E	1788	1457-1472	36,900
	27-2S-14W	1932	280-286	896
	18-3S-11E	1941	316-445	33,100
Gallatin	19-7S-8E	1924	585-1640	75,300
Grundy	12-31N-7E	1616	130-132	5,170
Hamilton	30-3S-7E	1942	1606-1692	55,400
	35-4S-7E	1925	400	3,260
	27-6S-6E	1867	1605-1698	76,700
	35-6S-6E	1866	1557-1695	75,200
	6-7S-5E	1584	1654-1755	83,000
Jefferson	19-1S-1E	1518	1057-1067	111,000
	10-3S-2E	1946	1214-1360	94,900
Marion	16-1N-1E	1339	843-850	88,000
	29-1N-1E	1321	871-890	89,600
	29-1N-1E	1322	848-864	87,200
Saline	21-8S-6E	1892	977-1052	19,400
	7-8S-7E	1926	905-975	33,300
	10-8S-7E	1863	910-1057	47,100
	15-8S-7E	1859	1470-1530	41,200
	20-8S-7E	1864	1230-1290	53,300
Wayne	23-1N-5E	1944	1700-1860	111,000
	35-1N-5E	1945	1600-1710	108,000
	24-1N-8E	1758	653-722	79,100
	12-1S-7E	1949	635-804	54,400
	29-1S-8E	1757	751-890	29,900
White	31-5S-10E	1243	1839-1842	48,700
	33-5S-10E	1237	1828-1838	48,800
Mississippian				
Degonia Fm.				
Saline	3-10S-6E	1544	1328-1336	44,100
Waltersburg Fm.				
Gallatin	28-9S-10E	1609	1856-1890	46,700
Richland	29-3N-14W	1285	2362-2375	87,000
Saline	25-8S-6E	1537	2086-2093	87,800
	15-8S-7E	1489	2116-2256	81,600
	15-8S-7E	1490	2105-2179	82,200
	15-10S-6E	1545	1503-1509	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
	8-8S-7E	1421	2348-2354	92,200
Cypress Fm.				
Clinton	6-1N-2W	1411	1092-1098	63,000
	8-1N-2W	1910	1130-1140	64,300
Crawford	20-7N-12W	1254	1198-1286	54,000
	20-7N-12W	1255	1198-1286	53,700
	20-7N-12W	1432	1365-1400	79,800
Effingham	1-6N-6E	1521	2459-2466	132,000
	12-6N-6E	1522	2459-2490	141,000
	13-6N-6E	1523	2463-2471	139,000
	34-6N-6E	1644	2424-2438	142,000
	34-6N-6E	1645	2420-2436	138,000
	20-7N-7E	1364	2432-2442	130,000
	29-7N-7E	1365	2432-2442	130,000
	34-7N-7E	1519	2486-2491	133,000
Franklin	3-7S-4E	1398	2773-2781	141,000
Gallatin	27-7S-9E	1360	2596-2610	106,000
	8-1S-8E	1353	2540-2550	103,000
Jefferson	10-3S-4E	1585	2762-2780	136,000
Marion	4-3N-1E	1455	1358-1365	108,000
	4-3N-1E	1457	1356-1375	108,000
Richland	17-3N-9E	1619	2601-2608	98,100
	18-3N-9E	1524	2612-2617	98,300
	18-4N-9E	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
	35-2S-9E	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
	9-3N-4E	1905	2280-2285	128,000
	10-4N-3E	1388	2038-2044	127,000
Washington	27-1N-1W	1487	1479-1483	95,500
	34-1N-1W	1381	1482-1485	95,900
	33-2S-1W	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
	15-3N-8E	1556	2913-2955	133,000
Coles	25-14N-7E	1510	1739-1746	118,000
Edwards	28-2S-10E	1606	3167-3180	113,000
	19-2S-11E	1435	3002-3038	114,000
Franklin	35-5S-1E	1236	2623-2675	137,000
	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
	9-7S-3E	1630	2823-2837	140,000
Hamilton	29-4S-7E	1535	3325-3331	142,000
	9-5S-7E	1533	3346-3370	140,000
	9-5S-7E	1534	3366-3377	138,000
	28-6S-5E	1401	3242-3282	129,000
	29-6S-5E	1400	3254-3278	133,000
	4-7S-5E	1399	3206-3222	132,000
Jasper	31-6N-10E	1384	2765-2784	108,000
Jefferson	30-1S-4E	1371	2671-2677	135,000
	11-2S-4E	1590	2854-2870	143,000
	10-3S-2E	1335	2548-2555	133,000
Madison	16-3N-6W	1931	750-829	25,100
Moultrie	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
White	24-4S-8E	1732	3325-3376	132,000
	21-4S-9E	1326	3182-3183	120,000
	24-5S-8E	1433	3122-3140	123,000
	32-5S-8E	1390	3250-3265	128,000
	22-5S-9E	1267	3144-3154	126,000
Williamson	6-8S-4E	1613	2933-2949	140,000
	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
Jefferson	14-2S-4E	1739	4085-4095	170,000
	1-4S-4E	1707	4102-4108	166,000
	1-4S-4E	1740	4102-4108	166,000
Wayne	14-2S-6E	1744	4155-4194	172,000
	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
Washington	23-1S-1W	605	3116-3150	79,600*
	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
Wayne	33-2N-8E	1728	4878-4898	166,000
	24-2S-9E	1751	5426-5447	209,000
	29-2S-9E	1766	5348-5360	210,000
	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
Knox (Ind.)	23-1N-10W	118	3308-3415	142,000*
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
Ford	1-24N-7E	1626	313-319	452
	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
Sangamon	9-14N-4W	1927	1680-1700	85,300
	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, 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
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), 3049-3069' depth	260		79,000	686				
	2	Cities Service, #10, Vaught, Goldengate Pool, 33-2S-9E, Wayne Co., Illinois, Dutch Creek Sandstone (Middle Devonian), 5358-5373' 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
	2	T. G. Jenkins, #5, Poorman, Mills Shoals Pool, 19-3S-8E, White Co., Illinois, Salem Limestone, Valmeyeran (Middle Mississippian), 3784-3810' depth		230		90,200	883				
N2	3	Indiana formation water	521	457*	125,000		541	22,400	19,700*	Tables 1 and 2	1.1388
N3	3	Indiana formation water	197	188*	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° C/4° 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 $^{o}/oo$ 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° C/4° C), 1.1284; 74.6° C; δO^{18}, +1.50 $^{o}/oo$; 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 $^{o}/oo$; B-1979 δD, −4.1 percent; B-1979 δO^{18}, −6.7 $^{o}/oo$. 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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