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**THE ORIGIN OF SALINE
FORMATION WATERS, II:
ISOTOPIC FRACTIONATION
BY SHALE MICROPORE
SYSTEMS**

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Irving Friedman
Wayne F. Meents**

**ILLINOIS STATE GEOLOGICAL SURVEY
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THE ORIGIN OF SALINE FORMATION WATERS, II: ISOTOPIC FRACTIONATION BY SHALE MICROPORE SYSTEMS

Donald L. Graf, Irving Friedman, and Wayne F. Meents

ABSTRACT

The concentrations of deuterium, normalized to the value for meteoric precipitation at Chicago, and O^{18} , normalized to the value at $25^{\circ}C$ for equilibrium with pre-Tertiary marine limestone, are given for 95 formation waters from the Illinois Basin, the Michigan Basin, the Alberta Basin, and the Gulf Coast. A small isotopic fractionation resulting from passage of water through micropores in shales is postulated as explanation for the regularity remaining between the two isotopic parameters after both have been normalized. This postulate generates predicted directions of fluid movement, between pairs of nearby samples, that are in reasonable agreement with the limited hydrologic information available. Several samples with unusually high deuterium content, from two areas of restricted ground-water recharge, may result from flow rates small enough to permit significant diffusional mixing behind shale barriers.

INTRODUCTION

This is the second 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. Most of the variation in O^{18} content of these samples could 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 composition of precipitation.

In this paper, we seek in the data of Clayton et al. residual regularities that may be attributed to isotopic fractionation during passage of water through micropores in shales. The evidence is suggestive but incomplete, and succeeding portions of the paper that discuss geological consequences of micropore fractionation should be viewed as speculative.

The third paper (Graf et al., in prep.) uses the chemical compositions of Illinois Basin and Michigan Basin brines and the findings of the first two papers to suggest mechanisms for the formation of waters rich in calcium chloride.

Deuterium concentrations in this paper are reported relative to standard mean ocean water (SMOW) in units of δD , defined as

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

Oxygen isotopic concentrations are also given relative to SMOW, but in parts per thousand:

$$\delta O^{18} (\text{‰}) = \frac{(O^{18}/O^{16})_{\text{sample}} - (O^{18}/O^{16})_{\text{SMOW}}}{(O^{18}/O^{16})_{\text{SMOW}}} \times 1000$$

Samples from Illinois and Indiana are indicated on the various plots of this paper by open symbols, those from Michigan and Ontario by half-filled symbols, those from the Gulf Coast by filled symbols, and those from Alberta by open symbols with central dots. Samples specifically identified in the illustrations are mentioned in the text. Where the symbols are rectangular, the dimensions give probable analytical errors, $\pm 0.1 \text{ ‰}$ for δO^{18} , $\pm 0.1\%$ for δD , and $\pm 3\%$ of the amount present for chemical quantities. These probable errors for isotopic composition are used in plotting even where subsequent normalizations may have introduced additional errors not easily estimated. The probable errors in chemical analysis are considered at greater length in Graf et al. (in prep.). Uncertainties in sampling, in situ temperature estimates, and isotopic analyses are discussed in Clayton et al. (in press).

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PROPERTIES OF MICROPORE SYSTEMS

Isotopic fractionation has been observed in experiments in several micro-pore systems. Huber et al. (1956) measured an enhanced flow rate of H_2O relative to D_2O through micropores in carbon rods, and attributed it principally to the differing viscosities of the two liquids. They pointed out that this mechanism will not be effective either in pores that are too large or in those too small to permit laminar flow (i.e., for small molecules, less than about 10 \AA diameter). An enhanced flow rate for H_2O relative to D_2O was measured across a sulfonated polystyrene membrane by Meleshko and Myagkoy (1963). The rate difference decreased with increasing temperature and with the change in membrane type from Ba to Na to Li. In experiments on the flow of adsorbed gaseous H_2O and DHO through porous alumina, Sapet (1962) and Eyraud et al. (1963) observed minimum permeability and maximum discrimination between the two molecules for a relative pressure corresponding to a monolayer. These authors also studied other gases and found the mass effect less important than molecular configuration. Klemm (1963)

found that a liquid mixture of Li^6 and Li^7 forced at 250°C through a tube filled with Fe spheres of 1.5 - 2.5 μ diameter emerged enriched 7% in Li^6 . Colombo et al. (1965) measured a fractionation of 3 ‰ in the carbon isotopic composition of methane flowing in a current of oxygen through a chromatographic column filled with hydrogen-bentonite. The isotopically lighter fraction emerged first in this experiment. Smaller but still detectable fractionations were observed for columns packed with limestone and dolomite.

An isotopic fractionation effect has not been reported for water passing through compacted clay aggregates. However, McKelvey and Milne (1962) and Hanshaw (1962) demonstrated that such aggregates do act as charged ultrafilters that reject dissolved electrolytes, a common property of micropore systems. Accordingly, we postulate an associated isotopic fractionation, the effluent on the low pressure side being isotopically lighter, and seek support for this postulate in the observed variation of isotopic composition in formation waters.

In each of the four geographical areas discussed by Clayton et al. (in press), these authors cited a single estimate of the isotopic composition of present-day precipitation. Because we wish to inspect the total body of measurements for a possible residual effect, we utilize a different means of comparison and attempt to normalize the raw values for the two major effects noted by Clayton et al. The marine- and fresh-water values referred to in these calculations require explanation.

THE ISOTOPIC COMPOSITION OF FRESH AND MARINE WATER

Standard mean ocean water (SMOW) was defined by Craig (1961b). Surface oceanic water has δD values relative to SMOW that range from about +1 to -3‰ (Friedman et al., 1964). We show for marine water on our plots a range of δD from +0.8 to -0.2‰, corresponding to those depositional environments in which the great majority of marine sedimentary rocks are deposited. Epstein and Mayeda (1953) reported a total variation in δO^{18} of some 6 ‰ for marine waters ranging in salinity from 29 to 40 ‰. We show on our plots the range from +1.5 to -1.0 ‰, which includes the bulk of Epstein and Mayeda's observations both for waters that receive meltwater contributions and for those that do not.

Precipitation from air masses moving from the equator toward the poles is a Rayleigh distillation process resulting in a primary dependence of isotopic composition upon mean air temperature, reflected in dependence upon latitude and altitude (see Kirschenbaum, 1951; Dansgaard, 1961, 1964; Craig, 1961a; Friedman et al., 1964). Fresh waters thus show a wide range of isotopic composition, including that of sea water, and discussion about them is facilitated by choosing some one place as reference. We use Chicago for this purpose, and we show a group of three closely related values on our plots: MICH, Lake Michigan surface water from 580 ft. elevation and about 42°N latitude; CHIA, a weighted average of the isotopic compositions of snow and rain falling on Chicago; and CHIB, the same kind of weighted average as CHIA but read from a smoothed plot (Friedman et al., 1964, fig. 17) for North America of δD versus latitude versus elevation.

MICH has a value relative to SMOW of $\delta\text{O}^{18} = -5.91$ ‰ (Epstein and Mayeda, 1953; see Craig, 1961b, for the factor used to shift from the PDB standard to SMOW). The comparable δD value was given by Kokubu et al. (1961) as -4.08%, and by Friedman et al. (1964) as -4.2%, an insignificant difference.

The δD value of CHIB is -4.4%. Using Craig's (1961a) relation for meteoric waters, and necessarily neglecting possible kinetic effects that could disrupt that relation, we get a corresponding δO^{18} value of -6.23 ‰.

The mean annual total precipitation at Chicago over a 21-year period has been 33.18 inches, and the mean annual snowfall, 37 inches (U. S. Weather Bureau, 1963). If we assume (after Friedman et al., 1964) that 10 inches of snow yield one inch of water and compare Epstein and Mayeda's (1953) value for the δO^{18} content of Lake Michigan water (MICH) with the weighted average of their δO^{18} values for snow and rain at Chicago (CHIA), MICH is 2.1 ‰ heavier in oxygen than CHIA. Using the 8:1 slope of Craig's (1961a) relation for meteoric waters, we get an analogous deuterium difference of 1.7%. These difference estimates are minimum values, because the MICH sampling point is at the south end of the lake and the south end of the lake drainage basin, and any non-local water brought in by lake currents must be from a more northerly source and isotopically lighter.

The MICH-CHIB and MICH-CHIA differences presumably measure the change in isotopic composition of Lake Michigan because of evaporation. The latter difference, in particular, may seem very large for a fresh water lake. And, indeed, the calculation must remain tentative until enough additional isotopic analyses of Chicago snow, Chicago rain, and Lake Michigan water have been made to assure statistical validity. However, several bits of evidence indicate that even the MICH-CHIA differences cannot be more than twice too large. They are closely similar in size to the scatter (which results at least in part from evaporation) about Craig's (1961a) curve. Friedman et al. (1964) estimated a water loss of 11% by evaporation from Lake Superior and a corresponding deuterium effect of 0.8%. For Lake Tahoe, which has an outlet and remains fresh in spite of an evaporation of 60%, Friedman et al. measured a deuterium evaporation effect of 4.2%. Evaporation effects for fresh waters could thus be a third or more of the difference between SMOW and MICH, and it is appropriate that our fresh water reference be shown as the range MICH-CHIB-CHIA.

THE DEUTERIUM NORMALIZATION

The measured δD concentrations for all brine samples are given in table 1 and plotted against total dissolved solids content in figure 1. Locations of sampling points in the Michigan and Illinois Basins are shown on the map of figure 2. The group of isotopically light, low salinity samples identified by Clayton et al. as originating during Pleistocene glaciation is evident in figure 1. A dependence of deuterium content on latitude is shown for the remaining samples; the four groups of samples from successively more northerly areas are progressively lighter. The sample sets from the Gulf Coast and Michigan, which include some of the deepest, hottest, most saline samples, alternate with the two other sets in the progression, indicating that the major isotopic dependence is on latitude rather than on these other variables.

The most obvious explanation of these results, as noted by Clayton et al., is that the original water from the depositional basin has been lost during compaction and subsequent flushing (whatever theories one may entertain about the behavior of dissolved solids during these events) and that the formation water now encountered originated as precipitation over land. Latitude dependence also

would be observed if original fluids were retained from a time of sediment deposition in shallow or evaporite seas that were cut off from the main oceanic reservoir and received a large part of their water input as drainage from a nearby land-mass. However, the existence of oil pools and the relatively simple pattern made by brine isoconcentration contours (Meents et al., 1952) require postdepositional fluid movement. The probable presence in some of our samples of Pleistocene glacial water, tens of miles downdip from outcrops, is further evidence for fresh-water flushing.

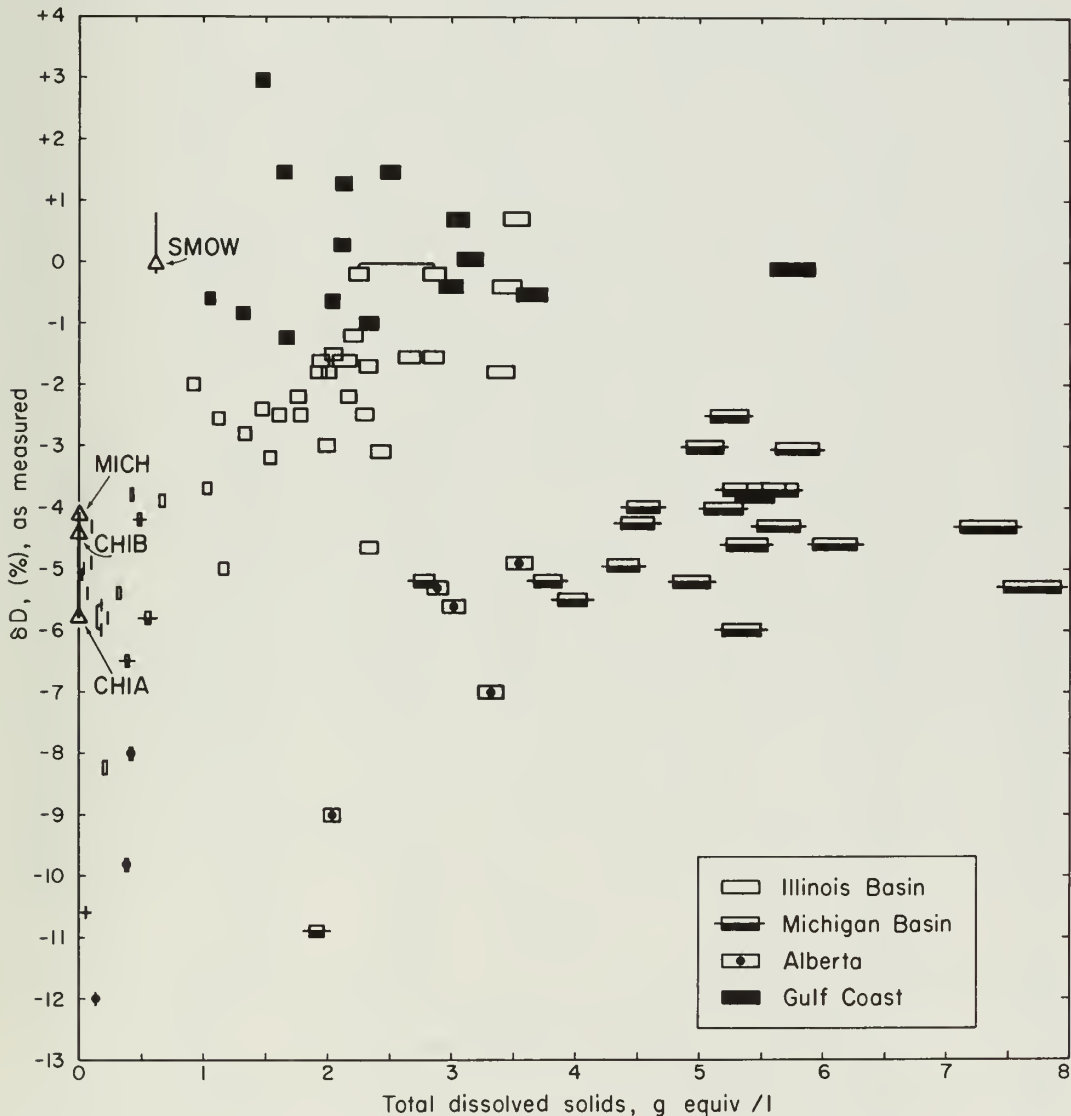


Figure 1. The relation between total dissolved solids and measured δD values. The ocean-water and fresh-water reference points, SMOW, MICH, CHIA, and CHIB, are indicated. The bars associated with these reference points are explained in the text. Equally probable values for the same sample are connected by a bar. There are no Gulf Coast samples with less than 1 g equiv/l total dissolved solids.

TABLE 1. THE ISOTOPIC COMPOSITIONS AND

Sample no.	δO^{18} , ‰		δD , ‰			Calculated temperature, °C
	As analyzed (Fig. 5)	Normalized to 25 °C. (Fig. 6)	As analyzed (Fig. 1)	First normalization (Fig. 3)	Second normalization (Fig. 4)	
ILLINOIS BASIN						
4	-1.82	-2.5				28.3
5	-6.65	-4.4				14.8
6	-0.94	-3.5				
6A			-1.7	-2.8	-4.2	38.0
7	-2.12					
7A	-2.32	-3.0	-1.5	-2.1	-3.1	28.1
8	-4.79	-6.2				32.6
9	-5.78					
9A	-6.21	-4.3	-3.9	-4.1	-5.5	16.0
10	-5.72	-3.7				15.6
11	+0.49	-0.8	-1.60	-2.3	-3.2	31.5
12	+1.51	-3.3	-1.55	-2.4	-3.9	50.7
13	+2.74	-1.7	-1.55	-2.4	-3.8	48.5
14	-3.20	-6.0	-4.66	-5.6	-6.7	39.1
15	-2.96	-3.5				
15A			-3.7	-4.4	-5.6	27.1
16	-10.15	-8.4	-8.23	-8.8	-9.5	16.6
16A	-10.21		8.53			
17	-2.17	-2.5				
17A			-2.0	-2.9	-4.1	26.5
18	-2.27	-2.1	-2.57	-3.6	-4.9	23.9
19	-0.65	-2.9	-1.20	-2.2	-3.6	37.0
41	+5.10	-0.5	-1.8	-2.7	-4.0	56.2
50	-2.41	-4.8	-3.1	-4.2	-5.6	37.1
51	-3.35	-6.3	-3.5	-4.4	-5.9	40.0
52	-7.30	-8.0	-6.0, -5.6	-6.8, -6.4	-7.5, -7.9	28.3
53	-4.34	-3.5	-3.2	-4.1	-5.6	20.8
54	-2.49	-2.6	-1.8	-2.6	-3.8	25.1
55	+0.26	-2.5	-0.2	-1.3	-2.9	39.0
56	-3.56	-4.8	-3.0	-4.0	-5.5	31.2
57	-1.47	-5.5	-2.8	-3.7	-4.8	45.8
58	-2.36	-2.5	-1.6	-2.4	-3.6	25.2
59	-2.07	-3.9	-2.2	-3.0	-4.2	34.5
60	-2.86	-5.8	-2.4	-3.2	-4.4	40.0
61	+3.76	-1.7	-0.4	-1.3	-2.6	55.2
62	-7.47	-9.0	-5.4	-6.2	-7.4	32.4
71	-0.80	-3.4	-1.8	-2.9	-4.5	38.0
72	-0.76	-5.2	-2.2	-3.0	-4.2	48.1
73	-1.58	-4.1	-2.5	-3.2	-4.2	37.5
74	-8.12	-6.9	-5.4	-5.7	-6.5	19.0
75	-7.62	-7.9	-5.1	-5.4	-6.6	26.1
78	-6.90	-6.3	-5.0	-5.0	-6.1	22.1
81	-1.13	-2.6	-2.5	-3.6	-4.9	32.2
82	-6.30	-3.7	-4.3	-4.9	-5.9	13.7
83	-6.98	-6.2	-4.9	-5.4	-6.3	21.3
84	-3.40	-2.5	-2.5	-3.1	-4.1	20.9
85	-5.34	-2.8	-3.8	-4.4	-5.4	13.9
ILLINOIS BASIN (INDIANA)						
N1	-8.22	-6.8	-5.8	-6.0	-6.6	18.2
N2	-2.42	-8.6	+0.7	+1.3	-0.7	60.0
N3	-6.50	-6.4	-5.0	-4.4	-5.2	24.5
MICHIGAN BASIN						
M2	+4.34	+2.2	-4.3	-3.8	-4.4	35.9
M3	-3.65, -4.64	-2.7, -3.7	-4.95	-4.6	-5.2	20.8
M4	-1.63	+0.4	-3.72	-3.2	-3.8	15.4

(at 3200')

IN SITU TEMPERATURES OF BRINE SAMPLES.

Sample no.	δO^{18} , ‰		δD , ‰			Calculated temperature, °C
	As analyzed (Fig. 5)	Normalized to 25°C. (Fig. 6)	As analyzed (Fig. 1)	First normalization (Fig. 3)	Second normalization (Fig. 4)	
MICHIGAN BASIN (continued)						
M5	-1.38	-5.1	-4.60	-4.4	-5.0	44.2
M6	-2.00	-4.6	-4.00	-3.3	-4.0	38.0
M7	-1.39	-2.7	-4.30	-3.8	-4.4	31.7
M9	-1.32	-2.6	-3.05	-2.6	-3.2	31.1
M11	-3.95	-3.1	-4.27	-4.0	-4.4	20.8
M43	+2.58	-2.4	-5.3	-4.7	-5.3	52.2
M50	+0.16	-1.2	-4.6	-4.2	-4.9	30.0
M51	-2.90	-4.0	-4.0	-3.4	-4.0	30.2
M52	+0.06	-2.3	-3.8	-3.2	-3.8	36.8
M53	-2.12	-4.7	-5.2	-4.5	-5.1	38.4
M54	+0.02	+1.4	-2.5	-1.8	-2.4	18.2
M55	-4.94	-2.4	-5.2	-4.6	-5.3	13.4
M56	-13.11	-12.2	-10.9	-10.2	-10.9	20.9
M57	-4.09	-4.0	-5.5	-4.8	-5.5	24.2
M58	-5.64	-4.4	-5.2	-5.2	-5.6	19.1
M61	-1.95	-11.8	-6.0	-4.6	-5.8	87.8
M71	+0.55	+1.9	-3.7	-3.1	-3.7	19.0
M73	+0.78	+2.7	-3.0	-2.4	-3.0	16.3
M75	+0.57	+2.0	-3.7	-3.1	-3.7	18.6
MICHIGAN BASIN (ONTARIO)						
C2	-7.79	-4.2	-5.8	-5.4	-6.1	9.1
C3	-8.79	-5.3	-6.5	-6.2	-6.8	9.2
C5	-6.58	-3.1	-4.2	-3.8	-4.7	9.5
C6	-13.31	-9.6	-10.6	-10.0	-10.8	8.7
GULF COAST						
G3	+8.76	+0.9	+1.44	-1.0	-3.0	72.5
G6	+4.56	-3.5	+1.45	-1.0	-3.0	59.9
G7A			+1.27	-1.0	-3.1	85.8
G10	+4.05	-6.4	-0.40	-2.8	-4.8	93.9
G13	+4.60	-4.6	+0.03	-2.4	-4.4	83.3
G14	+2.96	-3.7	-0.60	-2.6	-5.0	63.5
G15	+8.65	-6.3	-0.11	-2.1	-4.5	142.8
G24			+2.94	+0.6	-1.5	79.1
G25			+0.69	-1.7	-3.7	89.2
G30	+3.35	-8.1	-0.53	-2.8	-4.9	104.3
G38	+2.54	-6.1	-1.23	-3.4	-5.6	77.3
G39	+5.19	-8.6	-1.00	-3.1	-5.4	129.5
G79			-0.66	-3.0	-5.1	115.1
G79A			+0.28	-2.0	-4.1	117.4
G81	+2.05	-5.2	-0.86	-3.1	-5.3	67.3
ALBERTA						
A	+7.80	-1.3	-4.9	+3.6	-1.8	82.3
B	+3.61	-5.0	-5.3	+3.2	-1.7	77.8
C	-5.07	-6.5	-9.8	-2.2	-7.1	32.2
D	-12.81	-13.2	-12.0	-4.4	-9.6	26.7
E	-4.58	-6.5	-8.0	+0.1	-5.3	35.0
F	+4.03	-6.7	-5.6	+4.1	-0.9	96.7
G	-3.01	-8.6	-9.0	-0.3	-5.0	55.6
H	+2.31	-3.4	-7.0	+1.7	-3.0	56.7

If the water of the brines is indeed of fresh-water origin and if we can define the geographical distribution of deuterium in the precipitation that supplied that water, we can then normalize all measurements to a reference fresh water such as that at present-day Chicago. If latitude dependence is the dominant factor determining observed deuterium concentrations in the waters, the normalized points should lie in a horizontal band centered at the reference value.

We first normalized on the basis of the present-day latitude and altitude dependence of δD , to see whether it is adequate to explain the distribution of figure 1. This normalization, in other words, compares the isotopic composition of present day mean precipitation in an area with that of the formation waters in the area. An enlarged, more closely gridded copy of figure 17 of Friedman et al. (1964) was used to estimate differences of deuterium concentration between mean

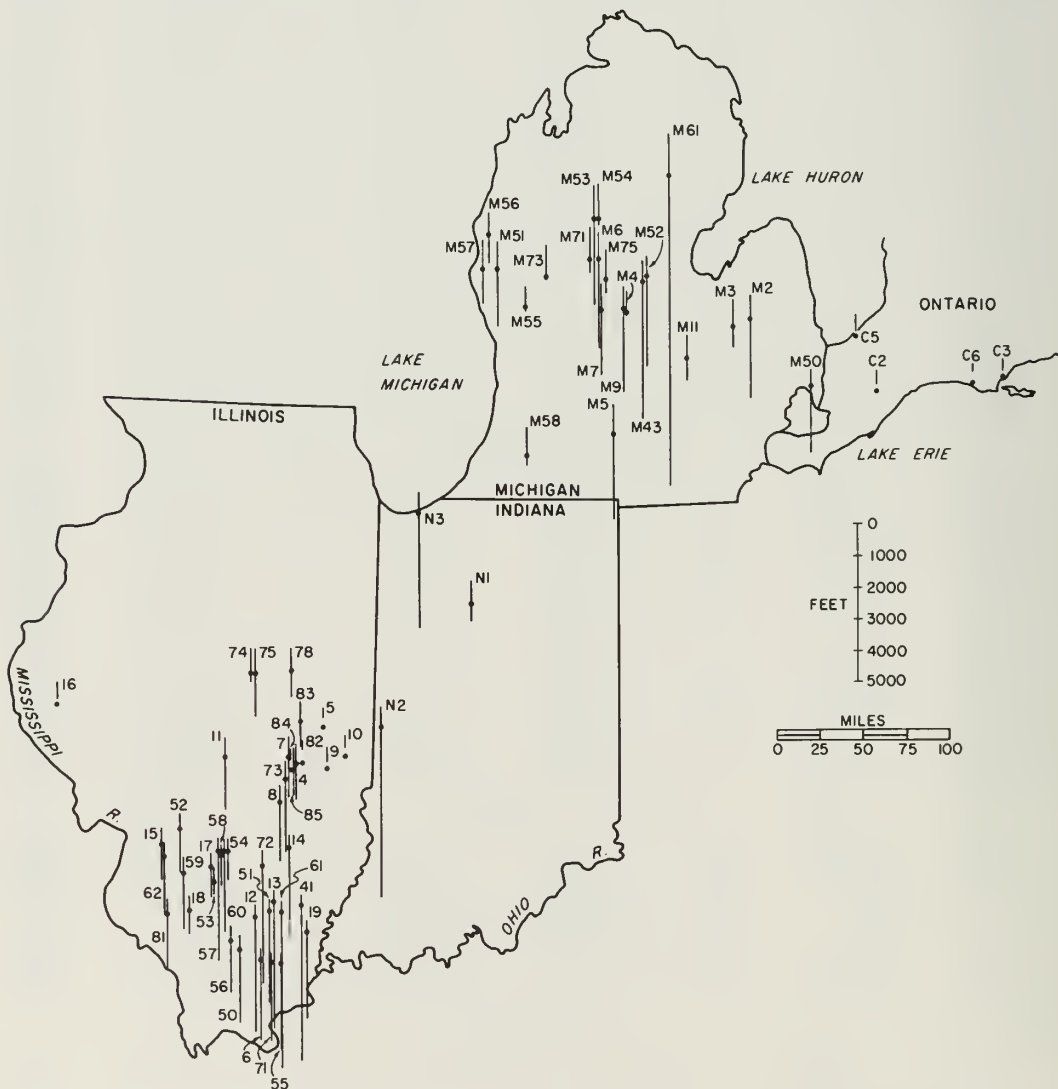


Figure 2. The geographic locations of samples from the Illinois and Michigan Basins, shown as dots projected onto the plane of sea level, with the lengths of well above and below sea level drawn to scale.

Chicago precipitation (CHIB) and present-day precipitation at outcrop areas updip from brine sampling points. Approximate directions of present-day fluid migration are known for the Alberta formations (Hitchon, 1963, 1964), and in that province we selected outcrop areas by proceeding up the hydraulic gradient. This procedure yielded some Alberta outcrop positions at elevations of about 6,000 feet, beyond a zone of major faults that are believed to be sealed against recharge because of the closeness with which highly saline formation waters approach them on the basinward side (Hitchon, 1964, p. 210). We were thus prepared in advance to be skeptical of the Alberta points normalized in this manner.

The deuterium values, normalized to CHIB, are given in table 1 and plotted in figure 3. The normalization shifts the several areal groups of points closer to a common deuterium value than in figure 1, but it does not greatly change the

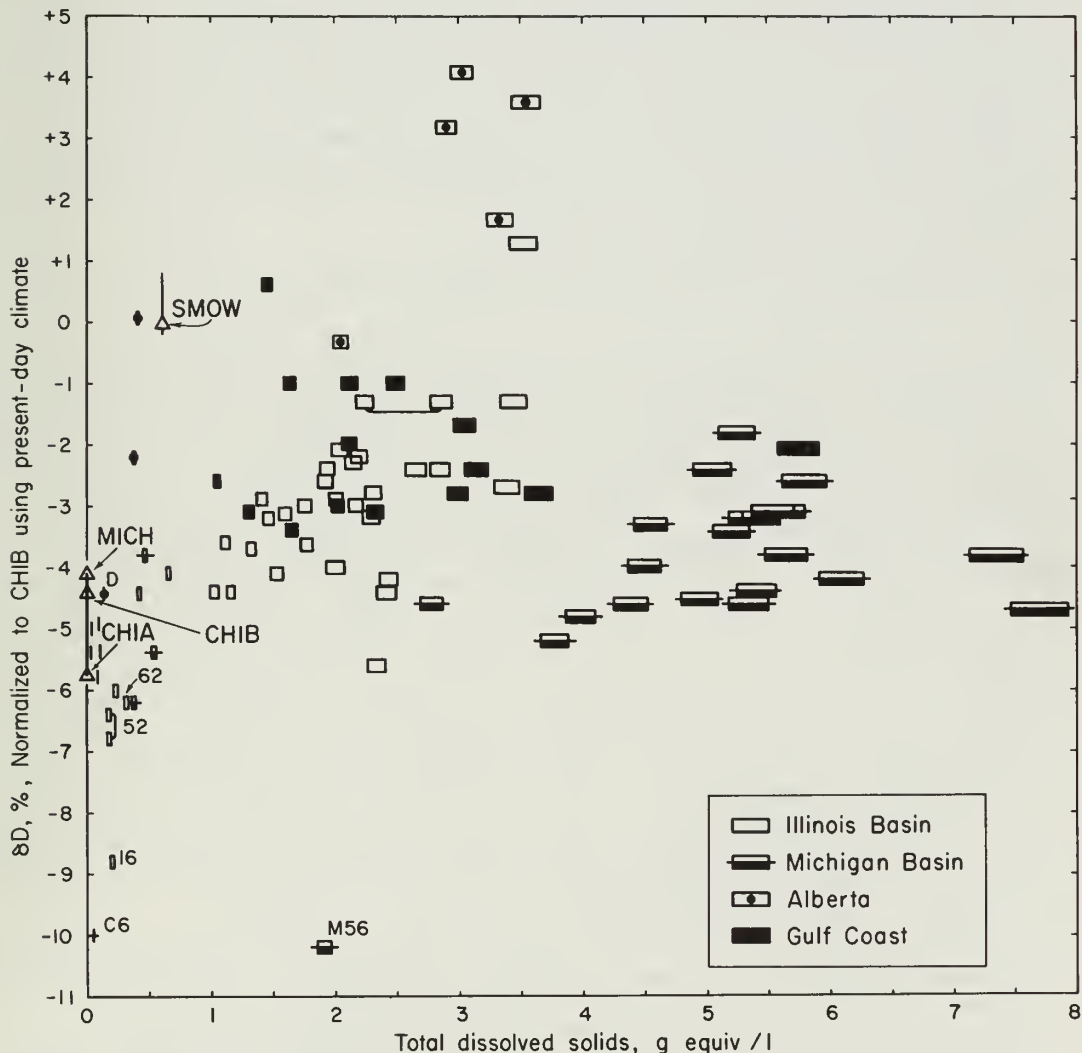


Figure 3. An initial attempt at normalizing the δD values of figure 1 by considering present-day latitude and altitude dependences. The ocean-water and fresh-water reference points, SMOW, MICH, CHIA, and CHIB, are indicated. The bars associated with these reference points are explained in the text.

relative positions of points within each areal group. Relative to CHIB, the Alberta points in figure 3 have been strongly overcorrected, those from the Gulf Coast moderately undercorrected, and those from Illinois slightly undercorrected.

The majority of our samples, more saline and from greater depths than those we believe to have originated during Pleistocene glaciation, must be pre-Pleistocene. The deuterium distribution in pre-Pleistocene precipitation may have differed from that at present because of differences in (1) climate, (2) elevation of the land surface, and (3) areal extent of isotopically mixed ocean extending into North America. The relevance of the last factor is shown by the fact that rainfall over the Gulf of Mexico today has the isotopic composition of sea water (Friedman et al., 1964, p. 218).

Retention of the SMOW and MICH-CHIB-CHIA reference intervals and present-day deuterium distribution is probably the best climatic assumption we can make, even though present-day climate may be atypical to the extent that it is still an interglacial climate. The effect that the Permo-Carboniferous Ice Age of the Southern Hemisphere had upon climate in the Northern Hemisphere is not well understood. The areally extensive cyclic sedimentation found in rocks of Mississippian to Permian age has been attributed to worldwide sea level fluctuations resulting from growth and waning of glaciers (Wanless and Shepard, 1936; Wanless, 1950; Weller, 1956, in rebuttal).

In a second attempt at normalizing the data of figure 1, we assume that the MICH-CHIB-CHIA reference interval retains the same absolute value, but that:

(1) The water of our Gulf Coast samples entered these Cretaceous aquifers during Paleocene time from outcrops that were essentially at the shore of a sea known to have reached north into southern Illinois (Dunbar, 1949). If the amelioration of climate by this added body of water is taken to extend as far north as the MICH fixed point, δD will have a gradient with latitude steepened across Illinois, and the normalization shifts for samples from Illinois as well as from the Gulf Coast will be increased. For normalizing Illinois samples, we take as a typical shoreline position the latitude of the southern edge of Tennessee, 35° N.

(2) The water of all our samples entered aquifers from outcrops lying within a few hundred feet of sea level (we use sea level for convenience in reading the chart of Friedman et al.). This is a statistically attractive assumption because of the extensive Paleozoic sedimentation in this Interior Lowland region of North America. In the absence of more specific information, we take the latitudes of water intake points in Illinois, Michigan, and Alberta to be those of the brine sampling points. The principal effect of assuming low-lying outcrops is to decrease the normalization shift for those of the Alberta samples that were assumed in figure 3 to have originated at intake areas having elevations of about 6,000 feet. Virtually all the Tertiary rocks of Western Canada are continental in origin, but most of the uplift and deformation of the Canadian Rocky Mountains did not take place until the Eocene (Taylor et al., 1964).

This normalization is necessarily an unsophisticated one. It incorporates no information about flow rates in aquifers, supposing that a paleogeography involving an invading Paleocene sea can be used to normalize samples from all depths in the Illinois Basin. It localizes recharge during one interval in geologic time, when in fact recharge would have taken place whenever there was a favorable difference in elevation between outcrop and aquifer, not cancelled out by excess (lithostatic) pressure from compaction. Many of the beds in Michigan from which brine samples were collected crop out under present-day Lake Michigan

and Lake Huron. Because the net flow is from Lake Michigan into Lake Huron (Hough, 1958, p. 3), the only effect of the entrance of Lake Michigan water into these beds would be a wiping out of local latitude dependence because of mixing within Lake Michigan. Because Lake Huron also receives the outflow from Lake Superior, its water is anomalously light for its latitude and would give rise to an apparent latitude shift if it entered the beds in lower Michigan. With the present topography, however, ground water flows from those beds into Lakes Michigan and Huron. There is, furthermore, no good evidence that the Great Lakes existed before Wisconsinan time (see Hough, 1958, p. 113).

The desired band of points centered at the fresh-water reference point has been achieved in considerable part in figure 4, for which δD values were normalized on the basis of the new assumptions. The figure does not, of course, prove the correctness of the specific assumptions; it shows only that variations in paleogeography have isotopic consequences of the proper magnitude to achieve the horizontal coincidence chosen a priori as reasonable. Initial recognition of a δD latitude dependence, from which the normalization developed, must be ascribed to a fortunate choice of sampling areas. All four lie in the Central Lowland of the

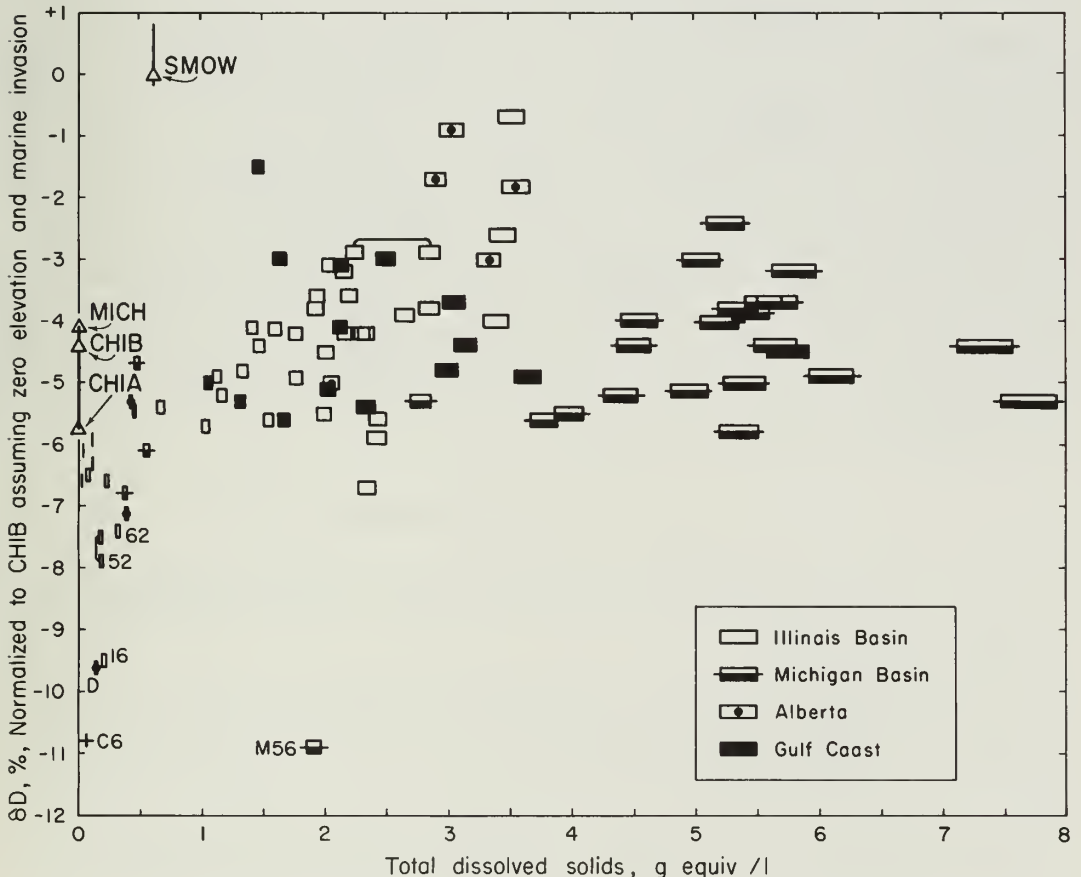


Figure 4. Measured δD values normalized assuming sea-level elevation and Paleocene paleogeography. The ocean-water and fresh-water reference points, SMOW, MICH, CHIA, and CHIB, are indicated. The bars associated with these reference points are explained in the text. See figures 1 and 3.

continent, for which the simplified relationships of Friedman et al. (1964) hold particularly well. The great bulk of the water that falls as precipitation over the Lowland is carried there by air masses from the Gulf of Mexico, even though the precipitation is triggered by interaction with the drier, colder air masses from the Arctic Ocean. Masses of Pacific maritime air sometimes are involved, too, but their importance has been distinctly secondary since the elevation of the Rocky Mountain barrier at the end of Cretaceous time.

Two further comments should be made about figure 4. The reference value CHIB = -4.4%, corresponding to an elevation of 600 feet, was inadvertently used in preparing the figure, instead of -4.0%, which would have been consistent with the sea level elevation assumed for the individual samples. This difference is surely within the gross climatic assumptions, and the conclusions drawn from figure 4 would not be changed by replotting for a normalization based upon CHIB = -4.0%. Second, the normalizations for both figures 3 and 4 are based upon complete replacement of marine water by meteoric water. Retention of a significant fraction of sea water of reasonably constant isotopic composition would have decreased the observed isotopic gradient.

There is another means of achieving an increased δD /latitude gradient between the Gulf Coast and Chicago. On the graph of figure 17 of Friedman et al., this gradient increases at a maximum rate in a zone extending north from Chicago, where there is a rapid increase in the snow/rain ratio. If both CHIB and the individual sample latitudes are shifted north by 10° , assuming a colder climate than at present, a horizontal coincidence like that of figure 4 can be achieved. CHIB would then lie at -8.5%, SMOW at perhaps +0.5%, having become slightly heavier because of the relatively light H_2O in an enlarged ice cap. The lightest of the low-salinity samples (number 16) would be explained then as normal meteoric precipitation in the colder climate, but a major problem would be created in trying to explain why most of the samples lie about halfway between "glacial fresh water" and "marine water." That part of the Pleistocene during which there was extensive glaciation could hardly have been long enough to move into the rocks of the Illinois Basin water equal to half their pore volume, particularly if part of the recharge area was blocked by glaciers and permafrost.

THE OXYGEN NORMALIZATION

The measured δO^{18} values are given in table 1 and plotted in figure 5. The samples from Illinois, from Michigan, and from Alberta lie along rather well defined straight lines.

The waters of these samples must initially have shown latitude-dependent variation in δO^{18} , just as in δD . Knowing the δD corrections used in preparing figure 4 and choosing from Craig's (1961a) diagram some slope between 5:1 and 8:1 for the relation between δD (‰) and δO^{18} (‰), we could normalize the δO^{18} values for latitude. Such a correction (not illustrated in this paper) leaves the plotted points still arranged along diagonal trends. Latitude dependence cannot, therefore, be the principal reason for the distribution; Clayton et al. (in press) demonstrate that temperature-dependent equilibration with carbonate wall rocks is largely responsible.

We proceed to normalize the measured δO^{18} values to an arbitrary reference temperature, $25^\circ C$, assuming that: (1) Calcite is the dominant solid phase in oxygen isotope exchange, because it is widely distributed and rather rapidly

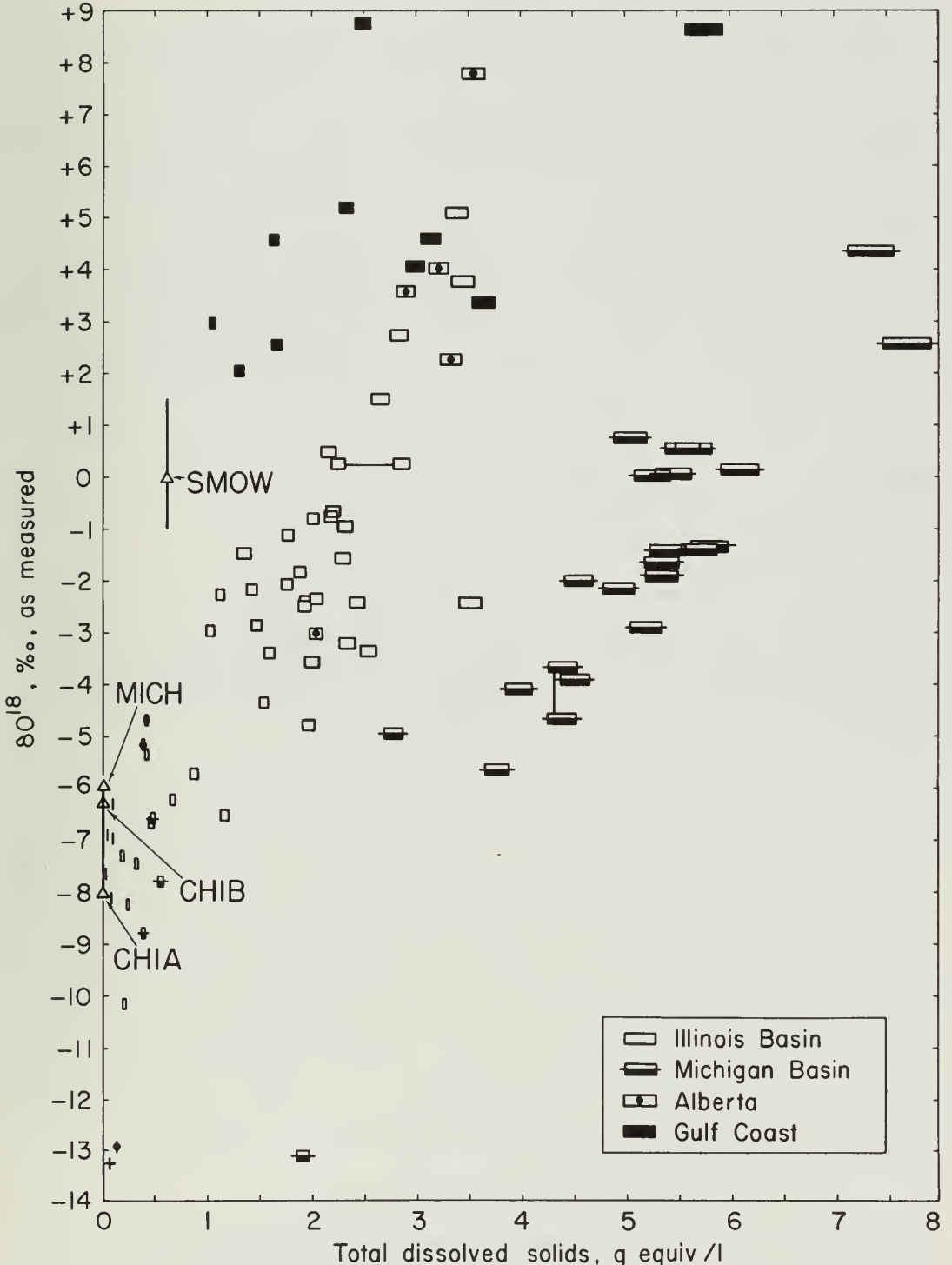


Figure 5. The relation between total dissolved solids and measured $\delta^{18}O$ values. The ocean-water and fresh-water reference points, SMOW, MICH, CHIA, and CHIB, are indicated. The bars associated with these reference points are explained in the text. Equally probable values for the same sample are connected by a bar. There are no Gulf Coast samples with less than 1 g equiv/l total dissolved solids.

soluble and because exchange between calcite and water is measurable at moderately elevated temperatures (Clayton et al., in press); (2) The temperature-dependent equilibrium between calcite and water observed by Epstein et al. (1951; 1953) in the temperature range from 5° to 30°C and by Clayton (1961) in the interval 190°–750°C is achieved in the brine-limestone systems we are considering. Specifically, from a plot of temperature against 1000 ln K constructed from Clayton's (1961) data, read values of 1000 ln K for 25°C and for each of the insitu brine temperatures. For each sample, the normalization shift $\delta_{\text{H}_2\text{O}, 25}^{\text{O}^{18}} - \delta_{\text{H}_2\text{O}, T}^{\text{O}^{18}}$ is taken to a good approximation to be equal to $1000 \ln K_{25} - 1000 \ln K_T$.

The justification for this approximation follows. The equilibrium constant K for oxygen isotopic exchange in the system $\text{CaCO}_3(\text{s})-\text{H}_2\text{O}(\ell)$ is simply the $\text{O}^{18}/\text{O}^{16}$ value for CaCO_3 over that for H_2O (see Clayton, 1961). We assume that the oxygen isotopic composition of limestone in sedimentary basins is a constant independent of present-day temperature. The right hand side of the assumed equality, $(1000 \ln K_{25} - 1000 \ln K_T)$, then simplifies to $1000 \ln (\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, 25} - 1000 \ln (\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, T}$. Next manipulating the left hand side, by definition

$$\delta_{\text{H}_2\text{O}, 25}^{\text{O}^{18}} - \delta_{\text{H}_2\text{O}, T}^{\text{O}^{18}} = 1000 \left[\left(\frac{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, 25}}{(\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}} - 1 \right) - \left(\frac{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, T}}{(\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}} - 1 \right) \right].$$

This simplifies to

$$1000 \left[\frac{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, 25}}{(\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}} - \frac{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, T}}{(\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}} \right].$$

For numbers between .98 and 1.02, $\ln N = N$ to 1% accuracy, and we can replace the two quotients in the last expression by their natural logarithms. Expanding each ln term into the difference of two terms and simplifying, we obtain finally $1000 (\ln (\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, 25} - \ln (\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}, T})$, which is identical with the expression we obtained starting with ln K terms.

The temperature-normalized $\delta_{\text{H}_2\text{O}}^{\text{O}^{18}}$ values are given in table 1 and plotted in figure 6, and fall into two groups. Most of them lie in a horizontal band about 6 ‰ in width, corresponding to the maximum vertical distance across the diagonal arrays of points from the Michigan and Illinois Basins in figure 5. This band in figure 6 assumes a fan-like appearance because of the positions of five shallow, isotopically heavy Michigan Basin samples (M4, M54, M71, M73, M75) and about eight other scattered samples. The average $\delta_{\text{H}_2\text{O}}^{\text{O}^{18}}$ value of the points in the fan is -3.9 ‰, which for isotopic equilibrium at 25°C corresponds to limestone having $\delta_{\text{H}_2\text{O}}^{\text{O}^{18}} = +24.3$ ‰. The calcite of marine sediments typically has an $\delta_{\text{H}_2\text{O}}^{\text{O}^{18}}$ value of +29 or +30 ‰, which falls to +22 to +24 ‰ in indurated limestones that have been exposed to fresh water. Isotopic equilibrium therefore appears to have been substantially achieved between limestone and most of these waters.

A number of samples containing less than 0.5 g equiv/liter of dissolved solids are anomalously light and lie below the fan, as does sample M56. These are the waters that Clayton et al. (in press) identify with precipitation during Pleistocene glaciation.

If the points in the fan are normalized a second time for latitude dependence, the Gulf Coast points become isotopically lighter and those from Alberta, isotopically heavier. The resulting plot, not shown, consists of samples grouped according to geographical source, similar to the plot of raw δD data (fig. 1) but with the groups reversed in order. Normalizing for latitude thus imposes an

unnecessary correction, and we conclude that the original δO^{18} latitude effect has been erased by equilibration of brine water with wall rock. Conversely, the absence of an δO^{18} latitude effect strengthens our assumption that wall rock equilibration is a process of major importance.

The oxygen isotopic equilibrium between carbonate and water that we have assumed will not in fact have been achieved in some natural environments, either because the elapsed time was too short, the temperature was too low, or the amount of carbonate surface exposed was too small. To shift fresh water to the heavier of the values of figure 5 by oxygen exchange with dissolved oxy-anions would require dissolving about ten times the amount of calcite in solution at equilibrium. Significant cycling of oxy-anions in and out of solution would thus be required, and the cycling rate may be temperature dependent. Siever et al. (1965) reported that many interstitial sediment waters are undersaturated with respect to $CaCO_3$ because $CaCO_3$ has not yet dissolved in sufficient amount to balance the

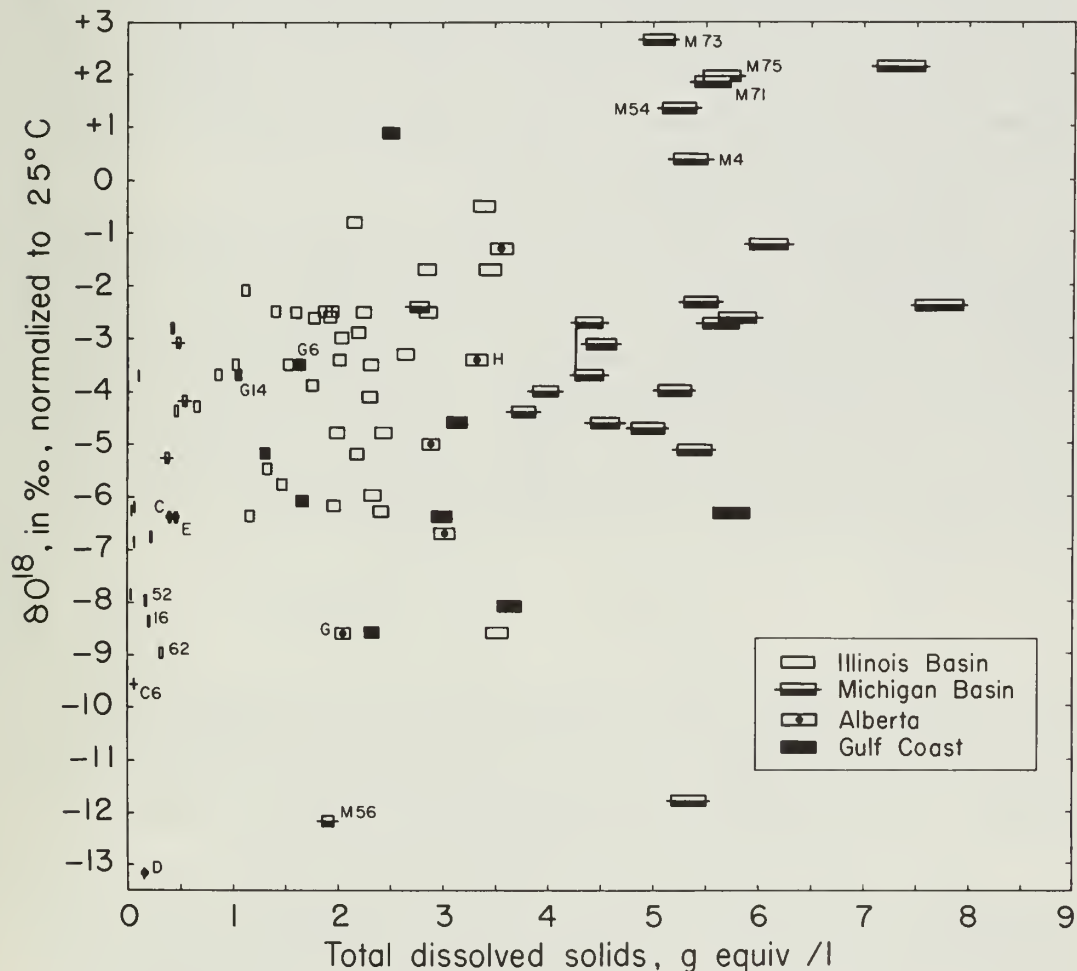


Figure 6. δO^{18} values normalized to an arbitrary temperature of 25°C. See figure 5.

increase of p_{CO_2} from bacterial oxidation of organic matter. The water samples closest to saturation in the Siever study came from sediments with the highest percentages of carbonate.

The persistence of Pleistocene anomalies in samples 16, M56, C6, and D gives one combination of time and temperature that is inadequate for equilibration ($8.7^\circ - 26.7^\circ\text{C}$, $10^4 - 10^6$ years). Unfortunately shallow Illinois samples, other than 16, cannot be used for monitoring because precipitation over central Illinois is only about 1.5 ‰ too heavy in O^{18} to be in equilibrium with limestone of +24 ‰ at the mean annual temperature there, and it is in equilibrium at the temperature existing at a depth of a thousand feet. Shallow samples from latitudes markedly different from Illinois, of which we have very few, would be ideal. Alberta samples C and E, with temperatures of 32° and 35°C , respectively, lie about 2.5 ‰ too low on figure 6, enough to make their significance questionable. Of the four samples G, H, G6, and G14 ($55.6^\circ - 63.5^\circ\text{C}$, wall rock ages $\sim 0.7 \times 10^8$ and $\sim 3.4 \times 10^8$ years, but water ages unknown), three have δO^{18} values on figure 6 close to -3.9 ‰, and they probably represent a time-temperature combination adequate for isotopic equilibrium to be reached. The temperature normalizations that we have applied are, of course, in error for samples not in oxygen isotopic equilibrium with wall rocks, but no useful purpose would be served by further attempts at manipulating these numbers.

The importance of thermal gradient errors as source of the scatter of figure 6 can be tested by reversing the normalization calculation by which figure 6 was constructed and, thus, obtaining a new thermal gradient ($^\circ\text{F}/100$ ft. depth) for each sample collecting point so that the corresponding sample has the normalized value, $\delta\text{O}^{18} = -3.9$ ‰. In this calculation, as in those yielding thermal gradients, we use degrees Fahrenheit in order not to lose accuracy in making comparisons with published values. The hypothetical gradients obtained range from 0.25 to 6, only about 60% of them lying between 1 and 2.25, the common range observed by Moses (1961) for the Gulf Coast. Furthermore, a geographical plot of these gradients shows juxtaposition of such radically different values as to make contouring impossible. The uncertainty of in situ temperature estimates is not by itself adequate to generate the scatter of figure 6.

A RESIDUAL ISOTOPIC EFFECT

Two kinds of evidence support the postulate of isotopic fractionation by shale micropore systems: (1) The residual scatters among the normalized δD (second normalization) and normalized δO^{18} values are related; (2) Predicted directions of brine movement between pairs of nearby samples, based upon this postulate, are in reasonably good agreement with what hydrologic information is available. In this section we discuss the first kind of evidence.

Most of the points in figure 7, a plot of normalized δD (second normalization) against normalized δO^{18} values, fall into a rectangular area. The points representing each geographical region are fairly well distributed throughout the rectangle and confirm the general slope of 3.1 determined by least squares analysis. The samples that are believed to contain either precipitation from Pleistocene glacial stages or water moved southward by the Mississippi River plot together in a group. Four points (M61, N2, B, and F) that lie well apart from the rectangle are discussed in a later section of the paper. A particularly encouraging

feature of figure 7 is the fact that the group of shallow Michigan Basin samples (M4, M54, M71, M73, and M75) that was anomalous in figure 6 falls into line at one end of the rectangular area.

The configuration of figure 7 is not of much help in defining further the mechanism of the postulated micropore fractionation by clays. The fractionation might, in general, be expected to affect δD and δO^{18} values unequally. Unfortunately, the slope of the main point distribution of figure 7 is not a measure of this micropore effect ratio because it presumably records the full deuterium effect but only part of the δO^{18} effect, which decays by equilibration with wall rocks. Indeed, to see any δO^{18} effect, the time constant for the micropore system must be less than that for equilibration with wall rocks. The 3:1 slope of figure 7 sets an upper limit for the real slope. The lower limit for that slope is presumably 0.5, the value for fractionation processes such as diffusion that depend only on the molecular weight of the diffusing species. Hydrogen bonding, which is one principal reason for the 5:1 to 8:1 slopes observed in evaporation of water (Craig, 1961a), should likewise increase the slope for a micropore process to some value greater than 0.5.

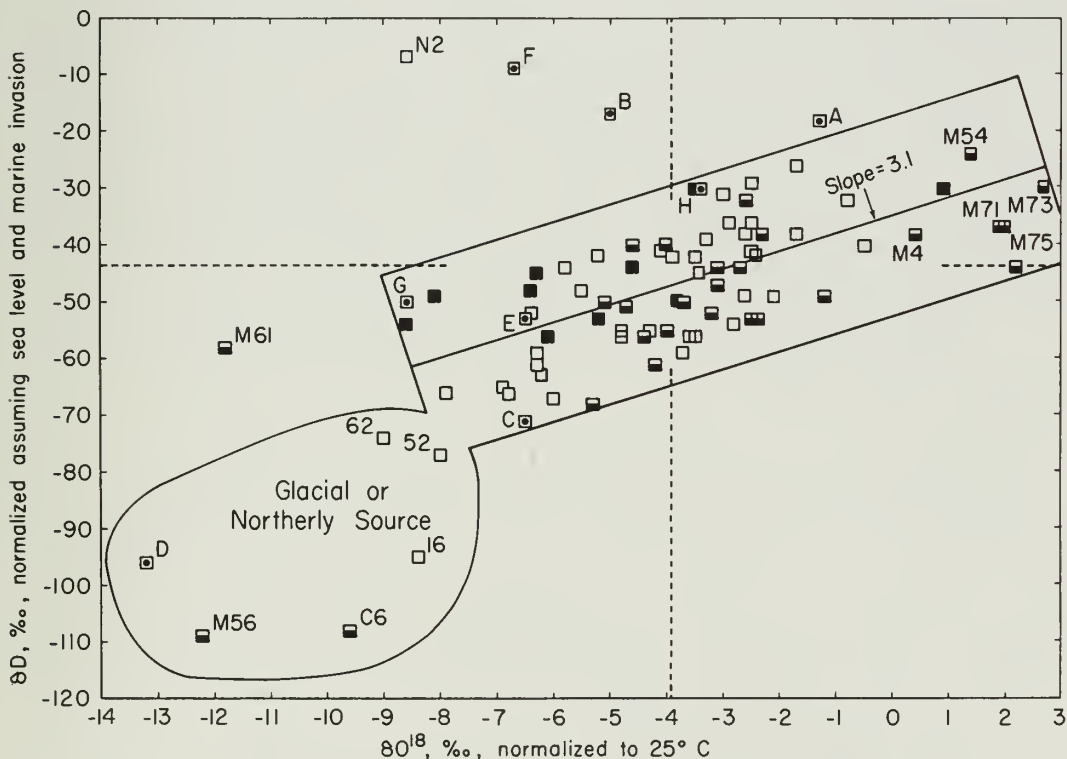


Figure 7. The residual regularity between normalized δD and normalized δO^{18} values. The former are given in ‰ so that slopes will be comparable with those in the plot of Craig (1961a). The line with a slope of 3.1 has been fitted by least squares analysis to the points within the rectangle. The dotted lines repeat key values from the ordinate scales of figures 4 and 6. Samples from the Illinois Basin are shown by open symbols, those from the Michigan Basin by half-filled symbols, those from the Gulf Coast by filled symbols, and those from Alberta by open symbols with central dots.

The smallness of the residual deuterium effect for the rectangular area of figure 7, $\pm 2.2\%$ in δD , leads to interest in the rate of mixing in the brine reservoir behind each shale barrier. If this rate is small relative to the rate of passage through the shale, the heavy fraction left behind from a given unit of brine will (essentially) be pushed through next, and not much more than a single stage fractionation will be observed for each shale barrier. It might be possible to calculate the magnitude of the single-stage deuterium effect if the physical processes involved in the flow of water through micropores were understood in detail. Rama and Hart (1965) concluded from the fractionation of Ne^{20} and Ne^{22} during transient permeation through vycor that a simple diffusion mechanism is involved. However, Frank et al. (1961) found that interpretation of results on diffusion of hydrogen and deuterium through fused quartz was complicated by the fact that these diffusing species are diatomic molecules. Water is an even more complex molecule, with a large dipole moment, for which a simple diffusion mechanism clearly cannot be assumed. We attempt, therefore, to make an estimate of the rate of brine reservoir mixing based upon other kinds of evidence.

An isotopic fractionation is observed between water molecules bound to cations and those in the bulk of a liquid, H_2O^{16} being enriched over H_2O^{18} in the latter (Hunt and Taube, 1951; Feder and Taube, 1952). However, the half-times for H_2O substitution in the inner coordination spheres of the principal cations are only about 10^{-9} second for Na^+ and K^+ , 10^{-8} second for Ca^{++} , 10^{-5} second for Mg^{++} (Eigen, 1963). All water molecules in the solution immediately behind a clay layer are thus available for isotopic mixing, including those coordinated to cations, and the relatively heavy water left behind from the action of the clay micropore system will be redistributed, releasing light water from the immediate reservoir of coordinated water. The increasing inefficiency of ultrafilters as solution concentration increases probably results from the gradual disappearance in the solution of a water fraction not coordinated to cations.

The degree of mixing within the larger reservoir contained in the aquifer behind the shale barrier is not so immediately evident. By analogy with a calculation by Bredehoeft et al. (1963, p. 266) for dissolved ions, the ratio of interest is that between the rate of diffusive transport of water molecules back from the high-pressure side of the barrier and the rate of fluid transport of water molecules toward the high-pressure side of the barrier. Two of the quantities used in the calculation are subject to experimental measurement as well as geologic estimate: the permeability of the shale barrier for water and the self-diffusion coefficient of water.

Recent measurements give for the self-diffusion coefficient, in pure H_2O at $25^\circ C$, between 2.25 and 2.27×10^{-5} cm^2/sec (Longworth, 1960; Devell, 1962). Andreev (1963) found a change with temperature from 1.32×10^{-5} at $5^\circ C$ to 3.51×10^{-5} at $45^\circ C$, an increase of 165% in $40^\circ C$, which is in good agreement with earlier determinations he reviewed.

Both Longworth and Devell observed that plots of inverse viscosity versus solute concentration have a course similar to those of self-diffusion coefficient versus solute concentration. We make the further assumption that self-diffusion coefficients vary in direct proportion to inverse viscosity. The viscosity of pure H_2O decreases by 60% in going from $5^\circ C$ to $45^\circ C$ (International Critical Tables, 1929), yielding an inverse of 165%, the same percentage found by Andreev (1963). More appropriately for our purposes, this viscosity decreases by 80% from $25^\circ C$ to $150^\circ C$, the highest temperature of interest to us. At $30^\circ C$ the viscosity of pure

H₂O increases only about 5% in going from 1 kg/cm² to 1000 kg/cm² (Bridgman, 1926), a range that includes the hydrostatic and lithostatic pressures possible for our samples. The maximum concentrations of the principal dissolved salts in our various samples are NaCl, 4.2 molar, KCl, 0.3 molar, MgCl₂, 0.6 molar, and CaCl₂, 2.4 molar. The corresponding increases in viscosity, measured for the different salts at temperatures in the interval from 25° to 40°C (International Critical Tables, 1929) are 55%, 1%, 25%, and 215%. The relative viscosity of a 4 molar NaCl solution, compared to that of pure H₂O at the same conditions, increases by only about 3% in going from 25°C to 100°C (International Critical Tables, 1929). The relative viscosity of a 0.16 molar MgCl₂ solution increases by 0.06% from 15°C to 42.5°C (Kaminsky, 1957). We therefore take the temperature, salinity, and pressure dependences of viscosity to be additive, and we estimate in situ brine viscosities and self-diffusion coefficients of water for those samples of table 2 for which individual chemical constituents are given. The range of estimates for the self-diffusion coefficient is from 0.7 to 3.4 x 10⁻⁵ cm²/sec.

Bredehoeft et al. (1963, 1964) took a value of 1 x 10⁻⁶ darcy for confining layer permeability, based upon flow rates across the Ordovician Maquoketa Shale observed in northeastern Illinois by Suter et al. (1959) and Walton (1962). Rittenhouse (1964) cited published laboratory measurements two and three orders of magnitude smaller. Young et al. (1964) measured permeabilities from 10⁻⁷ to 10⁻¹⁰ darcy for argillaceous sandstones and siltstones, suggested that shales high in clay may reach 10⁻¹³ darcy or less, and cautioned against errors resulting from ignoring in situ values of pressure, temperature, and interlayer water viscosity. That there should not be good mixing in reservoirs behind shale barriers requires merely that the critical ratio defined earlier be less than 1. Permeabilities as small as 2 x 10⁻⁸ darcy satisfy this requirement for our whole range of estimated self-diffusion coefficients. A value of 10⁻⁷ or 10⁻⁸ darcy is probably reasonable for a real formation in which there is some transport through macro-openings.

COMPARISON BY PAIRS

We turn next to the second kind of evidence suggesting isotopic fractionation by shale micropore systems. If such fractionation occurs, the sign of the difference in isotopic composition between the two samples of a pair taken from different depths but closely similar geographic position should indicate the direction of cross-formational flow in that local area. In general, there should also be a lateral micropore effect if the formation is shaly enough so that a significant fraction of the flow must pass through micropores. The analysis by pairs cancels latitude normalization errors and much of the error resulting from thermal-gradient assumptions. Differences between pairs of δO¹⁸ values should be somewhat less reliable than δD differences because the former are still affected by vertical variation of thermal gradient and by variation in the rate of equilibration with wall rocks.

There are obvious risks in making comparisons by pairs without knowing the local three-dimensional permeability distributions. One of the samples in a vertical pair could be a water that has moved from its recharge area much more rapidly and with less isotopic fractionation than the waters stratigraphically above or below it. Because the maximum micropore effect per unit volume of water will be in some direction in which the rate of flow is very low, the maximum observable effect will

TABLE 2. DIFFERENCES IN NORMALIZED ISOTOPIC COMPOSITION BETWEEN SELECTED PAIRS OF SAMPLES.

Sample Pair	ΔD	ΔO^{18}	Sample Pair	ΔD	ΔO^{18}
MICHIGAN BASIN (pairs involving Stray sandstone)					
M51 - M73	-1.0	-6.7	M43 - M75	-1.6	-4.4
M57 - M73	-2.5	-6.7	M9 - M4	+0.6	-3.0
M53 - M54	-2.7	-6.1	M9 - M75	+0.5	-4.6
M6 - M71	-0.3	-6.5	M7 - M75	-0.7	-4.7
M6 - M75	-0.3	-6.6	M43 - M4	-1.5	-2.8
			M7 - M4	-0.6	-3.1
MICHIGAN BASIN (other pairs)					
M51 - M55	+1.3	-1.6	M43 - M52	-1.5	-0.1
M2 - M3	+0.8	+4.9, +5.9	M2 - M11	0	+5.3
M57 - M55	-0.2	-1.6	M61 - M43	-0.5	-9.4
M50 - C5	-0.2	+1.9	M61 - M52	-2.0	-9.5
M50 - C2	+1.2	+3.0	M43 - M9	-2.1	+0.2
M61 - M53	-0.7	-7.1	M6 - M9	-0.8	-2.0
M51 - M57	+1.5	0	M6 - M7	+0.4	-1.9
GULF COAST					
G25 - G3	-0.7		G38 - G14	-0.6	-2.4
G30 - G13	-0.5	-3.5	G79 - G7A	-2.0	
G10 - G13	-0.4	-1.8	G79 - G24	-3.6	
			G15 - G81	+0.8	-1.1
ALBERTA					
A - H	+1.2	+2.1	B - G	+3.3	+3.6
ILLINOIS BASIN (deep central portion)					
41 - 19	-0.4	+2.4	13 - 71	+0.7	+0.1
12 - 56	+1.6	+1.5	61 - 55	+0.3	+0.8
13 - 51	+2.1	+4.6	72 - 14	+2.5	+0.8
61 - 51	+3.3	+4.6	41 - 14	+2.7	+5.5
12 - 50	+1.7	+1.5	61 - 19	+1.0	+1.2
			12 - 6	+0.3	+0.2
ILLINOIS BASIN (north flank, pairs involving samples from Pennsylvanian rocks)					
60 - 53	+1.2	-2.3	84 - 85	+1.3	+0.3
72 - 53	+1.4	-1.7	7 - 85	+2.3	-0.2
57 - 53	+0.8	-2.0	4 - 85		+0.3
59 - 53	+1.4	-0.4	7 - 82	+2.8	+0.7
7 - 9	+2.4	+1.3	4 - 82		+1.2
N2 - 10		-4.9	83 - 5		-1.8
N2 - 5		-4.2	73 - 84	-0.1	-1.6
			78 - 5		-1.9
ILLINOIS BASIN (north flank, other pairs)					
75 - 74	-0.1	-1.0	57 - 58	-1.2	-3.0
73 - 7	-1.1	-1.1	57 - 17	-0.7	-3.0
72 - 54	-0.4	-2.6	59 - 18	+0.7	-1.8
60 - 54	-0.6	-3.2	81 - 18	0.0	-0.5

not likely be in a direction either parallel or perpendicular to bedding. Interpretation based upon sampling in these two fixed directions must operate therefore reduced sensitivity. Because the stratigraphic units functioning as hydrologic units are not known in detail in the Michigan and Illinois Basins, we have imposed on pairs for vertical comparison the arbitrary requirement that the samples differ at least 1,000 feet in elevation to increase the chance of there being enough intervening shaly units to generate a micropore effect.

Table 2 lists such pairs, and gives the quantities ΔD and ΔO^{18} , where $\Delta D = \delta D_{\text{deeper sample}} - \delta D_{\text{shallower sample}}$, etc. We have eliminated from comparison only the four samples that we believe contain Pleistocene glacial water - 16, M56, C6, and D.

The signs of vertical pair differences in table 2 are consistent in indicating water moving downward on the Gulf Coast and on the north flank of the Illinois Basin (pairs not involving samples from Pennsylvanian rocks), but upward in the deeper part of the Illinois Basin. These findings for the Illinois Basin are consistent with the model that Bredehoeft et al. (1963) fitted to salinity distribution by assuming a piezometric low at the deep part of the basin. The structural low of the Illinois Basin, the major Shawneetown-Rough Creek Fault Zone, and the piezometric low of the Ohio and Wabash River valleys are geographically close in southeastern Illinois (Bell, 1943), and it is difficult to separate their hydrologic effects.

The two lateral pairs from Alberta, which were selected with this test in mind, indicate water moving upward out of that basin to the east in agreement with the local variation of salinity and original reservoir pressure (Hitchon, 1964). Lateral pairs chosen from the other geographical areas show no convincing evidence of a micropore effect. The samples from a given formation are too few in number and too widely separated to permit a reliable test of the concept, there is some difficulty in subsurface correlation, and indeed there probably is no measurable lateral effect in many cases. Degens (1961) and Knetsch et al. (1962) have reported δO^{18} values in an Egyptian aquifer that varied by only 1 per mil in a distance of 700 miles.

The ΔD values for pairs which include a sample from a shallow well in Pennsylvanian rocks have signs opposite to those for other pairs from the north flank of the Illinois Basin. The normalized δD values of the brines from Pennsylvanian rocks show 1.2 to 1.7% less deuterium than MICH-CHIB, rather than the 0.5 to 2.0% more than MICH-CHIB they require to be in the expected relation to deeper samples. A plausible explanation is that these samples are water emerging from separate, shallow hydrologic cells. There is a high incidence of shale in the Pennsylvanian, which would make possible the build-up of a detectable micropore effect in a rather short distance, and there are numerous opportunities for local differences in head. In east-central Illinois, where all the samples from Pennsylvanian rocks (except sample 53) were collected, there is the structural relief of the LaSalle Anticlinal Belt, and there are bedrock valleys (buried or only partly filled by alluvium) that cut as much as 300 feet (Horberg, 1950) into the approximately 900 feet of Pennsylvanian beds. Saline springs along the Salt Fork of the Vermilion River are only about 45 miles northeast of the collecting points for samples 9, 82, and 85. The Pennsylvanian rocks from which the springs emerge are 50 to 150 feet lower in elevation than the subcrop of the same beds under glacial drift on the anticline 30 miles to the west, the difference in the two figures encompassing bedrock relief in the subcrop area. This argument is also favored by the linearity of a plot of measured δD against depth for samples 9, 53, 82, 84, and 85.

The signs of two-thirds of the ΔO^{18} values for pairs like those just discussed are opposite to those of the ΔD values for the same pairs. This discrepancy would be explained if the δO^{18} micropore effect were preserved to a greater degree in the cool Pennsylvanian aquifer sample of each pair than in the deeper, warmer aquifer used for comparison.

Three-fourths of the Δ values for the Michigan Basin have negative signs, indicating downward moving water. This direction of movement is consistent with a hydrologic cell in which water falling on topographic highs at the southern edge and in the north-central part of lower Michigan moves downward into the rocks above the thick plate of salt and anhydrite of the Salina Group and then laterally outward and upward to the piezometric lows of Lake Huron and Lake Michigan. We are unable to find published measurements of the permeability of salt or anhydrite rock, but indirect evidence such as the characteristic dryness of salt mines indicates exceedingly low values.

But there are questions about some of the Michigan Basin Δ values. The large negative ΔO^{18} values for the three pairs involving sample M61 stem from the unusual normalized oxygen isotopic composition of M61 (fig. 7). This sample is unique among the Michigan Basin set because it comes from such a great depth and because a thick section of Salina salt lies between it and the surface. Its use in pair comparisons may be meaningless, but we have not eliminated from consideration other pairs separated by thinner salt and anhydrite beds. Sample M61 falls reasonably close to the extension of the least-squares line of figure 7, and without more samples the possibility cannot be excluded that it is a valid measure of a separate hydrologic environment. On the other hand, the point may be in error because of an erroneous temperature normalization. But, in order to shift it all the way to the edge of the rectangle, the true in situ temperature would have to be an improbable 62°C , 14°C cooler than actually measured, and, assuming a thermal gradient of $0.25^{\circ}\text{F}/100$ ft. in 2500 feet of salt, the remaining 8,600 feet of sediments would still have a thermal gradient of only $0.7^{\circ}\text{F}/100$ ft.

Pairs involving samples M4, M54, M71, M73, and M75, from five relatively shallow wells into the Pennsylvanian Stray Sandstone of the Michigan Basin, have Δ values with highly consistent negative signs. The negative signs are a consequence of these five brines having the heaviest normalized oxygen isotopic compositions of any in the study (fig. 7). For these isotopic compositions to be valid, (1) the five brine waters must be residual fractions of water that moved downward through the unusually thick Coldwater-Ellsworth-Antrim Shale barrier, and (2) oxygen isotopic equilibration with wall rocks must have been slowed appreciably at the rather low insitu temperatures of the samples. The samples were collected from observation wells around gas storage reservoirs, and some concern remains about possible evaporation during release of the gas-water mixtures under pressure.

TWO MODELS INVOLVING COMPACTION

Samples N2, F, and B after normalization are unusually heavy in deuterium but have δO^{18} values within the range of the main group of samples in figure 7. Shifting the assumed latitude of original meteoric precipitation of N2 all the way to the Gulf of Mexico would still leave this point above the rectangle of the figure by 1% in δD . Sample F would have to have originated 50 miles south of the Canadian border, an impossibility, for its normalized δD value to fall at the upper edge of the rectangle.

If water in beds not receiving recharge were expelled by compaction, slowly enough to permit significant diffusional mixing of the water remaining, a large δD micropore effect would build up in that reservoir, but the δO^{18} effect would decay

by equilibration with wall rocks. The increase in deuterium content would be greatest in the lowermost bed, lying upon some essentially impermeable floor (igneous, metamorphic, salt-anhydrite), because no isotopically light fraction would be contributed from below. The same effect could be achieved without compaction if the bed overlying an aquifer were thick enough and impermeable enough so that recharge into the aquifer and across the poorly permeable bed was slowed greatly.

The Mt. Simon Sandstone, from which sample N2 comes, lies directly on the Precambrian, reaching a maximum of 2,900 feet in thickness in northeastern Illinois on the north flank of the Illinois Basin. The nearest Cambrian outcrops are hundreds of miles away in Missouri, northwest Wisconsin, and the Appalachians, and the formation lenses out to the north and northeast (Cohee, 1945, 1948) and is overlapped at the west edge of the basin against some isolated Precambrian hills by shale of the Eau Claire Formation (Bell et al. 1964). Recharge from the southwest and southeast is sharply curtailed by thinning, increasing shale content, and major faults with initial movement dating from at least as early as the Pennsylvanian and possibly from the Devonian (Weller and Sutton, 1940; King, 1950; Rubey, 1952; Desborough, 1961). The Mt. Simon is only 235 feet thick at its type section near Eau Claire, Wisconsin; the overlying Eau Claire Formation contains more shale and becomes thicker southward into Illinois (Bell et al., 1964). Compaction of the thicker Eau Claire-Mt. Simon section to the south during the early Paleozoic could, therefore, have replaced at least part of the water lost on the northern flank by upward movement across bedding, and reduced the need for recharge. In later geologic time, the rate of movement of water across the thick Eau Claire section in the vicinity of the N2 collecting point should have been very small.

Foley and Smith (1954) concluded, from coincidence of piezometric highs and very low sulfate contents (compared with laterally adjacent values), that recharge of "the deep sandstone aquifers" through overlying bedrock and Pleistocene deposits is taking place in two areas of northwestern Illinois. This factor could require reconsideration of the model we have just presented. However, it appears from a careful reading of the paper by Foley and Smith that they are talking about sandstones above the Eau Claire Formation. Furthermore, present-day hydrologic relations in northern Illinois and southern Wisconsin are abnormal in two important respects: (1) the major cones of depression from pumpage at Milwaukee, Joliet, and Chicago create local piezometric gradients steeper than were present earlier in geologic time; and (2) it seems probable that reconstructed sections would show that the overlying cover was hundreds of feet thicker during much of pre-Cretaceous time than it is at present. Some recharge of the Mt. Simon Sandstone, by water moving downward from the St. Peter Sandstone through relatively thin and sandy Eau Claire Formation, may take place in Wisconsin south of the Mt. Simon outcrop belt.

We have already noted that recharge from the west into the Alberta Basin appears to be blocked by a zone of faults and that the water moving updip eastward from the center of the Alberta Basin is probably that expelled by compaction. Deuterium distribution is consistent with this premise, although the geologic environment is not so simple as that for the Mt. Simon Sandstone. The collecting point for deuterium-rich sample F, from the Upper Devonian Swan Hills Formation, is separated from the Precambrian basement by Middle Devonian and Cambrian strata. Samples A and B, both of which are also quite heavy in deuterium (fig. 7), come from formations of late Devonian age stratigraphically higher than the

Swan Hills and south of where sample F was taken. Samples G and H, somewhat lighter, come from the same stratigraphic level as A and B but to the northeast away from the mountain front. Samples C, D, and E contain the least deuterium of the Alberta set and are from even higher in the section and even farther to the south, where recharge from Montana becomes important (Hitchon, 1964).

There is an alternate explanation possible for the unusual deuterium content of these samples. We have thus far assumed that, even though recharge to collecting points N2, B, and F was restricted, it was adequate to replace the water of sea water. If excess (lithostatic) pressure from compaction prevented even this minimal flushing, the water of these samples could be residual from the ocean. The distance that N2 and F lie above the rectangle of figure 7, 3%, is comparable with the difference, 4.4%, between SMOW and the reference point for normalization. Graf et al. (in prep.) discuss mechanisms for deriving the chemical compositions of these particular samples.

DISCUSSION

Plots like that of figure 7 may be useful in distinguishing waters that are isotopically light because of micropore fractionation from those originating during Pleistocene glaciation. The former will lie in the main band of points of the figure, in the lower left of the four quadrants formed by the dotted lines at the reference values for deuterium and oxygen isotope normalizations. We do not know that the isotopically light end of the band as shown in figure 7 really represents a limit to the size of the micropore effect observable in nature, so the fact that samples 16, M56, C6, and D are isotopically lighter in oxygen than points in the band is not conclusive. Their δD values, however, clearly place them outside the main band of points even if it is extended. For a climatic change less severe than that of the Pleistocene glaciation, even this distinction would blur. Thus, we said earlier that samples 52 and 62 could be interpreted as having been transported by the Mississippi River from some hundreds of miles north of the latitude for which their δD normalization was calculated, a different kind of climatic shift. But 52 and 62 lie within the immediate extension of the main band of points of figure 7, and it is not possible to distinguish them from products of micropore fractionation.

A number of well-known properties of clay minerals are involved in discussing the geological importance of micropore phenomena. Experiments made by B. B. Hanshaw (personal communication) suggest that the minimum differential pressure under which clays will be effective as ultrafilters is between 200 and 500 psi. This conclusion is in good agreement with the suggestion of van Olphen (1963) that pressures of, at most, several tens of atmospheres should be adequate to prevent increase of clay particle separations as small as 10 \AA . The significance of these two observations is that ion filtration and isotopic fractionation should operate from rather early in compaction history, provided there are no macroscopic channels such as fissures and joints. Typically, such channels develop later in the rock history. Skempton (1964) observed them most commonly in over-consolidated clays, now under lower pressure than that reached at some earlier time when, for example, there was more overburden, and especially in clays subjected at some earlier time to weathering.

For still closer approach of clay particles van Olphen (1963) computed, from water vapor desorption isotherms and concomitant basal spacing changes, the compaction pressures needed at 25°C and 50°C to remove the next to the last and

the last adsorbed water layers. Lower pressures are required at the higher temperature. For a mean surface temperature of 50°F, a temperature gradient of 1.5°F/100 feet, and the hydrostatic pressure of a column of fresh water, assuming the temperature dependence of the calculation to continue linearly with increasing temperature, we find that all adsorbed water should have been removed at depths below 17,500 feet and all but the last layer at depths below 5,600 feet. If the entire brine column had the salinity of the deep Michigan Basin, these depths would be reduced by about 20%. Granting the uncertainty in the specific values, two implications are clear: (1) at depths reached in the deepest sedimentary basins, cross-formational water movement may be curtailed by adsorbed water expulsion from clays, and the observed chemical and isotopic distributions may be relict from an earlier time of shallower burial. The extrapolations of measured porosities made by von Engelhardt and Gaida (1963) for shales from Germany, the Po Valley, and Venezuela, which predict zero porosity at depths from 10,000 to 14,500 feet, are relevant here. These conclusions, of course, have physical meaning only if the pressure applied to the clays is hydrostatic (or at least less than lithostatic) so that volumes filled with free water can continue to exist; (2) at depths attainable in many basins, clays with but a single layer of adsorbed water may exist in NaCl-CaCl₂ brines.

Hydration-dehydration reactions for clay minerals usually have been measured for montmorillonite, because the effects are larger, but the results are also valid for other clay minerals with smaller base-exchange capacities. Partial dehydration occurs with increasing electrolyte concentration (Hendricks et al., 1940; Posner and Quirk, 1964). For Na saturation, there is a drop from three to two interlayers of water between 1 1/2 and 2 molal, and for Ca or Mg saturation the drop is at about 1 1/2 molal. For K saturation, the number of interlayers of water decreases from 2 to 1 at about 1 1/2 molal. At 1 atm pressure, a montmorillonite with monolayer water is an impossibility in a NaCl or CaCl₂ brine, whatever its strength. It can also be shown from the data of van Olphen (1963) that the pressure-temperature region for monolayer water, described under (2) above, lies beyond the regions studied in the room temperature ultrafiltration experiments of Hanshaw (1962) to 5,000 psi and McKelvey and Milne (1962) to 10,000 psi. The effect that the amount and structure of interlayer water have upon the ultrafiltration and isotopic fractionation properties of shales is thus largely unexplored.

We turn next to some considerations prompted by two published papers. Czike and Fodor (1957) measured the densities of waters distilled from 31 Hungarian oil field brines, attributing differences observed to variation in D₂O content without considering oxygen isotopic composition. Density increased linearly with depth, which ranged from about 1,000 to 8,000 feet.

Straight line fits of our raw δD values versus depth, obtained by least squares analysis, are shown in figure 8 for samples from the deeper part of the Illinois Basin, from the Gulf Coast, and from the Michigan Basin (omitting M56 and C6, and ignoring the single very deep Michigan sample, M61). The first of these sample groups qualitatively repeats the relation found by Czike and Fodor, although the distribution of points does not permit defining the slope with any accuracy. This relation also holds for five shallow samples from Pennsylvanian rocks in Illinois (9, 53, 82, 84, and 85, not shown in fig. 8) and for the Alberta samples. It is reversed for Gulf Coast samples, underlining the importance of considering the hydrologic system. Plotting all Illinois Basin samples in figure 8 would yield a broadened band of points with the same qualitative slope as that now shown, obscuring pair analyses for pre-Pennsylvanian rocks on the north flank of

the basin that indicate the opposite relation. The fact that the plot of Michigan points shows δD to be independent of depth is a reflection of our not having the sample distribution and understanding of the hydrologic system to break the samples into meaningful subgroups, as was done for the Illinois Basin. The difference in pattern among the plots for these four geographical areas is a strong argument against simple temperature-dependent (depth-dependent) deuterium exchange with hydrocarbons or hydrates.

The isotopic arguments we have advanced are of little help in estimating the fraction of total water movement in the various basins that occurred after compaction. Isotopic evidence for downward moving water at a basin center, such as we have described for the Michigan Basin, must be an overprint that has reversed the evidence left during compaction and, therefore, indicates the importance of post-compaction water movement. More typically, as in the Illinois Basin, the topography is such that the two effects are superimposed. Washburne and Lahee (1934) described circulation in a number of Wyoming oil fields that proceeds on curved paths around the peripheries of basins, from higher to lower outcrops, rather than across the basins. The extent to which post-compaction flow has modified the chemical and isotopic composition of formation waters, in basins

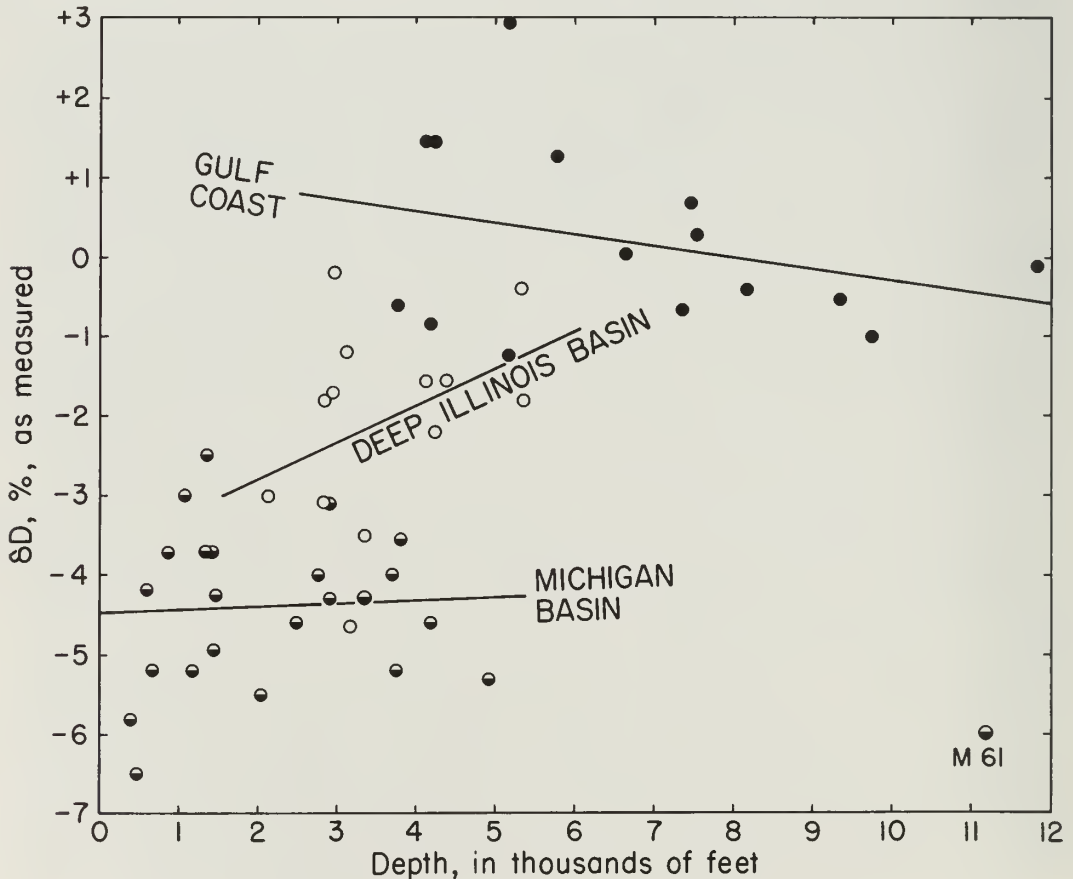


Figure 8. The relation between depth and measured δD value for three groups of samples. The trend lines have been fitted by least squares analysis.

such as these, must be strongly dependent upon the distribution of unconformities in the geological record.

Our results have led us to an interpretation differing in several respects from that of Degens et al. (1964), and these differences afford focal points toward which more detailed programs might be directed. We do not share the optimism of those authors about using δO^{18} compositions of brines to monitor the constancy of this quantity in ancient oceans. We believe that experimental programs testing isotopic fractionation in shale micropore systems are needed, and we find the statement of Degens et al. about this phenomenon unconvincing. They write, "Compaction and filtration by charged-net clay membranes, on the other hand, should not noticeably influence the oxygen isotope ratios of waters. These processes are relatively slow and, since only one phase is participating, yield no fractionation when equilibrium is reached." It follows that we do not regard waters enclosed in shales as superior samples for measuring original isotopic composition; the volume of water moving across bedding in this environment may not be large, but it could be sharply altered in isotopic composition because of micropore effects. The conclusion of Degens et al. that "the age difference between rock and petroleum brine in most instances is comparatively small" can only be true if there has been insignificant post-compaction water movement. It is obviously untrue for our Pleistocene glacial water samples 16, C6, M56, and D, which occur in rocks ranging in age from Silurian to Cretaceous.

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