Stable Isotope Geochemistry: A Tribute to Samuel Epstein
© The Geochemical Society, Special Publication No. 3, 1991
Editors: H. P. Taylor, Jr., J. R. O'Neil and I. R. Kaplan

The hydrogen and oxygen isotope history of the Silurian-Permian hydrosphere as determined by direct measurement of fossil water

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Abstract—Hydrogen and oxygen isotope analyses of fluid inclusions in 236 halite samples from undeformed Permian, Silurian, and Devonian bedded salt deposits are most readily interpreted in terms of connate evaporite brines trapped during initial halite precipitation or during early diagenesis. The synsedimentary fluids may represent evaporated sea water, evaporated meteoric water, or any mixture between the two depending upon the interplay between marine flooding and continental runoff in the original depositional environment.

$\delta^{18}O$ values for Devonian, Silurian, and Permian fluid inclusions have the same range and approach the same maximum values. Silurian values are not 4 to 5.5 per mil depleted in ^{18}O relative to Permian values as expected if the oceans were 4 to 5.5 per mil lower in the Silurian as widely claimed. The data indicate that $\delta^{18}O$ of sea water did not vary by more than 1–2 per mil during the interval Silurian-Permian, strongly contradicting interpretations of sea water history based on $\delta^{18}O$ analyses of carbonates.

As a group, δD for Silurian samples is about 20 per mil lower than values for Permian samples, and the Devonian samples have intermediate values. The possibility arises that the inclusions are recording a progressive deuterium enrichment of the hydrosphere between the Silurian and the Permian.

INTRODUCTION

THE OXYGEN ISOTOPE history of ocean water is important to many areas of geochemistry. The present ocean is 5.5 per mil depleted in ^{18}O relative to the total reservoir of oxygen in the crust and mantle, and the process or processes that produced this large depletion may have varied with time. Continental weathering and rock/water interactions at sea floor spreading centers affect $\delta^{18}O$ of the oceans, so evidence of past changes in $\delta^{18}O$ of sea water might carry major implications for tectonism, or even for questions of ocean origin and growth through time. In addition, estimates of paleotemperatures and diagenetic environments based upon isotopic analyses of ancient carbonates, cherts, phosphates, and clays depend critically upon the isotopic history of the hydrosphere.

MUEHLENBACHS and CLAYTON (1976) argued that the current 5.5 per mil ^{18}O depletion of ocean water relative to the whole earth value is basically fixed at mid-ocean spreading centers where sea water is cycled through hot basalts. GREGORY and TAYLOR (1981) presented further evidence for this rock/water buffering and argued that it would be operative as long as worldwide spreading rates are greater than one km^2/yr. Assuming that these processes have worked throughout geologic time, $\delta^{18}O$ of sea water should be invariant within about ± 1 per mil.

At present, it is not clear whether the sedimentary rock record is in accord with this model for constancy in the isotopic history of ocean water. In a general way, $\delta^{18}O$ of cherts, carbonates, and phosphates decreases for progressively older samples (*e.g.* PERRY, 1967; KNAUTH and LOWE, 1978; VEIZER and HOEFS, 1976; KARHU and EPSTEIN, 1986). Archean examples are up to 12 per mil lower in ^{18}O than their Phanerozoic counterparts, and changes on the order of 5 per mil occur within the Paleozoic alone. Of particular interest is the remarkable 4 to 5 per mil "jump" in $\delta^{18}O$ for carbonates between the Devonian and Mississippian shown in Fig. 1 (FRITZ, 1971; VEIZER *et al.*, 1986; POPP *et al.*, 1986a,b; CARPENTER and LOHMANN, 1989). All of these authors have attributed the lower values of the early Paleozoic to a change in $\delta^{18}O$ of the oceans.

Isotopic variations in the sedimentary rock record are difficult to interpret because there are at least three major variables that can strongly influence $\delta^{18}O$ of a phase that precipitates from an aqueous fluid: (1) $\delta^{18}O$ of the fluid, including the problems of whether the fluid was sea water or had a component of low-^{18}O meteoric water; (2) temperature, which is important because sedimentary temperatures are low and isotopic fractionation is quite sensitive to temperature in the low-temperature range; and (3) diagenetic and metamorphic recrystallization, which can lead to obliteration of the original isotopic record. Various authors have dealt in various ways with these problems. There appears to be a consensus that petrographic examination can screen out altered and recrystallized samples,

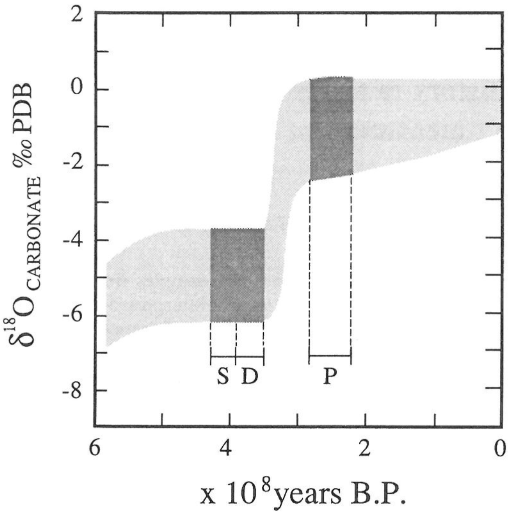

FIG. 1. Oxygen isotope history of Phanerozoic carbonates according to VEIZER *et al.* (1986). Changes in $\delta^{18}O$ of carbonates putatively correspond to changes in $\delta^{18}O$ of sea water. Salt samples for this investigation bracket the time interval proposed for the dramatic change in $\delta^{18}O$ of sea water.

but there is much controversy over the importance of temperature versus possible changes in the past $\delta^{18}O$ of sea water. KARHU and EPSTEIN (1986) attempted to resolve the problem by analyzing coexisting phosphate-chert pairs, but this has also not settled the controversy (*cf.* PERRY, 1990).

Instead of analyzing the precipitated phases in ancient sedimentary rocks, we have attempted to evaluate the isotopic history of sea water by direct analysis of samples of the ancient hydrosphere preserved as fluid inclusions in undeformed bedded salt deposits. The background, analytical methods, and approach for using such samples to evaluate past changes in both $\delta^{18}O$ and δD of the hydrosphere were given in KNAUTH and BEEUNAS (1986). In short, fluid inclusions in halite crystals in some bedded salt deposits (excluding deformed, totally recrystallized, and diapiric salt) are most readily interpreted as connate evaporite brines trapped during initial halite precipitation or during early diagenesis. The fluids may represent evaporated sea water, evaporated meteoric water, or any mixture between the two depending upon the interplay between marine flooding and continental runoff in the original depositional environment. In spite of this range of source waters and the fact that the inclusions represent fluids isotopically altered by evaporation, it is nevertheless possible to evaluate isotopic changes in sea water, especially changes as large as those proposed by several of the authors above.

We have analyzed fluid inclusions from three giant bedded salt deposits that span the age range during which $\delta^{18}O$ of the oceans may have changed by 4 to 5.5 per mil (Fig. 1). As discussed in KNAUTH and BEEUNAS (1986), changes this large should be readily detectable from isotopic analyses of fluid inclusions in halite. An underlying assumption of our approach is that the general range of isotopic compositions expected for a giant evaporite deposit is represented by data for the Permian salt deposits of the Palo Duro Basin, Texas. Since publication of KNAUTH and BEEUNAS (1986), the data base for fluid inclusions in this evaporite deposit has been greatly expanded. We first review general results for the Palo Duro Basin in order to defend our assumptions and to understand better the meaning of isotopic measurements of fluid inclusions in halite.

ANALYTICAL PROCEDURE

Backlighted core samples of bedded salt were scanned for fluid inclusions with a hand-lens. The smallest possible piece of halite containing fluid inclusions was quarried out along cleavage planes using a small chisel and a razorblade. For the larger inclusions it was often possible to cleave away surrounding salt to within one millimeter of the inclusion.

All samples were examined under a polarizing binocular microscope to insure that no cracks had penetrated to the inclusions and to verify the purity of the salt with respect to organic matter, oil, anhydrite, hydrous minerals, or the presence of rarely observed gas bubbles in the inclusions which might indicate leakage.

For inclusions larger than about 2–3 mm, a pyrex capillary tube was forced into the inclusion. The capillary tube was flame-sealed at both ends after the inclusion fluid was drawn in. Total water was extracted from the capillary brine using the technique given in KNAUTH and BEEUNAS (1986). Large inclusions were sampled only in the Permian salt and are so indicated by a "C" suffix on the depth listings in Table 1.

For the smaller inclusions, total water was extracted from the screened solid salt samples using the vacuum volatilization method of KNAUTH and BEEUNAS (1986). Isotopic analyses of extracted water were done using a variant of the method of KISHIMA and SAKAI (1980) (see KNAUTH and BEEUNAS, 1986, for details). Results are reported in the standard δ-notation. Routine accuracy using this method is probably better than ±0.5 per mil for $\delta^{18}O$ and ±5.0 per mil for δD.

PALO DURO BASIN

Isotopic analyses of 182 samples from ten wells in the Palo Duro evaporites are given in Table 1 and are shown in Fig. 2. The envelope drawn around the data excludes five points which are clearly atypical. These atypical data are reproducible and may have significance for the evaporite sedimentology but will not be discussed further here. The other data overlap completely the initial data of KNAUTH and BEEUNAS (1986).

The salt beds sampled in the Palo Duro Basin range in age from Mid- to Upper Permian and were therefore deposited over a time interval on the order of 30 million years. Halite interbedded with anhydrite, minor clastic layers, and carbonate occurs over a depth interval of 600 meters. Halite-anhydrite interbeds often occur in cycles, and it is clear that the evaporites represent numerous, repeated incursions of sea water into a shallow, coastal basin. An individual cycle may involve simple flooding by sea water followed by evaporation to total desiccation. In another case, flooding may occur before complete desiccation of the previous cycle is achieved. Upon renewed evaporation, halite might precipitate and trap remnants of the parent fluid (in this case, initially a mixture of sea water and partially evaporated sea water). In other cases, runoff from the surrounding area and/or local precipitation could flood the evaporite flat with meteoric waters. Virtually any mixture of sea water with meteoric water at any stage of partial evaporation is possible for depositional fluids in this type of setting. HOVORKA (1990) has documented petrographic and sedimentologic evidence of this interplay for the Palo Duro evaporites.

KNAUTH and BEEUNAS (1986) give the isotopic systematics expected for the mixed marine-meteoric system of this sort. Briefly, data which lie toward the positive, upper-right end of the δD-$\delta^{18}O$ data array in Fig. 2 approach the isotopic composition of halite-facies, evaporated sea water. During the initial evaporation of sea water, the lighter isotopes are removed and the residual fluid becomes enriched in ^{18}O and D. However, upon further evaporation, the residual fluid apparently evolves isotopically along a curved trajectory toward progressively lower δD and $\delta^{18}O$ (GONFIANTINI, 1965; HOLSER, 1979; PIERRE *et al.,* 1984). The cause of this reversal is not fully understood, but its validity is not an issue for this discussion. Evaporated sea water will clearly be enriched in ^{18}O, and possibly in D relative to normal sea water. For halite that forms in a mixed marine-meteoric system, fluid inclusions with the most positive δ-values are the ones with the greatest component of sea water evaporite brine, whether the trajectory reversal is valid or not.

δ-values near the negative end of the array are very close to the meteoric water line. These samples are interpreted as having formed on a desiccated flat that was flooded by meteoric waters. The influx of fresh water dissolved the previously deposited salt to the point of halite saturation. Upon subsequent evaporation, halite precipitated immediately in water which had undergone only a small amount of evaporation and therefore had become only slightly enriched in ^{18}O and D relative to the meteoric water line. δ values intermediate between the positive and negative ends of the array in Fig. 2 are interpreted as various mixtures of evaporated marine-meteoric fluids.

In order to test the concept that the isotopic composition of fluid inclusions is preserved in ancient halite and is related to the depositional environment, analyses were made of a suite of samples that records the transition from a marine dominated system to a meteoric-water dominated system. Sedimentologic and petrographic arguments for this transition are given by HOVORKA (1990). The isotopic results are given in Fig. 3.

The interval shown is overlain by clastic redbeds and represents progradation of surrounding continental clastic deposits over the evaporite section. On the basis of sedimentologic interpretations, the top of the salt cycle was repeatedly reworked by the influx of meteoric waters as the environment gradually shifted from predominantly marine to continental HOVORKA (1990). The transition is clearly recorded in the isotopic data in Fig. 3; $\delta^{18}O$ decreases from just under +5 to below −6, a change in $\delta^{18}O$ of over 10 per mil. δD shifts concurrently from values around 0.0 to below −45. As shown in Fig. 4, values for this one interval span the entire range of δ values encountered in the whole Palo Duro sample suite. The strong correspondence between isotopic composition and depositional environment is a compelling argument that the inclusions are accurately recording major changes in the nature of the parent evaporite fluids and that they have not been altered since the Permian.

PALO DURO DATA AS A REFERENCE

There are no modern evaporite deposits on the scale of those in the Silurian, Devonian, and Permian examined here. It is therefore not possible to examine in a modern setting the range of isotopic compositions associated with all the possible flooding and evaporation scenarios that surely occurred during deposition of a 0.6 km-thick evaporite deposit like that sampled in the Palo Duro Basin. Considering the large number of data, it is likely that the data domain in Fig. 2 is representative of that of the most typical evaporite waters that oc-

Table 1. Isotopic analyses of fluid inclusions in halite.

Permian Palo Duro Basin

County	Well	Depth (m)	$\delta^{18}O$†	δD†
DO	S	255.8C	0.8	−20
DS	D	409.0	−5.2	−55
		409.3C	−5.3	−51
		409.3C	−2.9	−44
		409.3C	3.5	−10
		410.2C	3.9	−16
		421.8	1.7	−23
		422.7C	0.9	−30
		423.1	2.5	−17
		423.4	1.4	−43
		423.5	0.5	−32
		423.6	−1.6	−51
		729.3	3.3	−21
		733.3C	3.6	−3
		734.9C	−0.7	−19
		742.9	0.6	−18
		752.0C	0.5	−27
		752.0	1.3	−33
		753.0C	0.6	−25
		754.7C	1.4	−29
		786.1	0.0	−26
		786.1C	0.6	−33
		786.2C	−1.0	−30
		803.0	0.8	−16
		864.4C	2.7	−21
		864.4C	2.6	−37
		864.4C	2.0	−36
	GF	389.4	−0.3	−53
		389.4	−1.1	−50
		389.4	4.1	−25
		389.7	0.4	−1
		394.8C	1.8	−29
		707.2C	1.9	−24
		705.0C	−0.3	−29
		705.0	1.7	−13
		710.4C	1.1	−41
		710.5	−0.5	−26
		712.1C	1.9	−14
		712.1C	2.8	−28
		742.2C	0.9	−28
		742.2C	1.6	−18
		757.3	2.0	−19
		758.9	3.0	−27
		768.7	2.3	−33
		773.6C	−1.3	−33
	JF	417.1	−5.8	−53
		418.0	−5.9	−54
		418.2	−6.3	−56
		418.2	−3.5	−41
		418.4	−5.7	−54
		418.4	−0.9	−27
		419.2	−6.2	−54
		419.7C	0.1	−27
		421.0	1.7	−8
		422.7	−1.0	−35
		423.6	3.4	−11
		424.3	0.8	−24
		442.4	4.4	7
		442.2	3.0	−1
		443.1	4.1	−2
		443.1	2.5	−12
		443.2	3.9	−2
		443.3	4.2	−1
		707.2C	1.3	−28
		722.2	1.2	−18
		722.4	2.2	−14
		722.4C	1.8	−20
DS	JF	722.4C	1.9	−24
		742.1C	1.6	−31
		746.6	3.1	−17
		751.8C	1.6	−37
		773.6C	−0.7	−34
		784.9	0.8	−26
		786.2	0.3	−27
		800.2	1.3	−12
		800.3	0.7	−19
		800.4	1.7	−14
		800.4	1.6	−30
		860.7	−5.4	−45
		861.1	3.3	−23
O	M	351.7	3.8	−26
		470.6	2.8	−13
		470.6C	2.8	−12
		470.6C	−0.2	−20
		471.8	1.5	−26
		483.7	1.7	−21
		483.8	1.5	−27
		484.5	0.9	−30
		484.6	1.9	−18
		492.3	1.3	−18
		494.6	2.0	−15
		494.7	−0.2	−37
		494.7	0.5	−58
		494.8	1.7	−6
		494.9	1.1	−18
		494.9	1.6	−23
		499.6	1.6	−26
		499.8	2.3	−26
		499.8	1.6	−21
		515.4	−0.5	−29
		513.5C	0.2	−29
		525.7C	1.0	−35
		525.8C	0.7	−30
		525.8C	−1.9	−32
		915.5	4.3	−11
		915.5	3.9	−27
		915.5	2.8	−33
		921.0	3.9	−10
		921.0	2.8	−17
R	HO	415.9	3.9	−5
		425.0	2.8	−7
		425.0	4.4	−11
	RW	206.0	−5.4	−45
		206.1	−4.6	−54
		206.1	−5.0	−81
		206.7	−6.2	−53
		210.5	−2.9	−36
		217.8C	1.6	−22
		217.8	0.0	−34
		217.8	−0.7	−33
		217.8	0.3	−17
		221.2	0.9	−22
		403.9	2.7	−20
		403.9	2.2	−10
		403.9	1.2	−36
		408.0	2.4	−30
		512.2	2.2	−21
		512.2C	3.1	−31
		565.7	0.9	−36
		565.7	0.2	−48
		574.2	0.8	−27
		574.2	3.4	−25
		869.1C	1.9	−11
		869.1C	2.3	−12

Table 1. (Continued)

Permian Palo Duro Basin

County	Well	Depth (m)	$\delta^{18}O$†	δD†	County	Well	Depth (m)	$\delta^{18}O$†	δD†
SW	G	318.7	−6.2	−45	SW	G	812.1	1.2	−80
		323.0	−6.8	−55			812.1	−1.5	−75
		321.6C	−4.1	−56			812.9	2.2	−20
		321.6C	−4.0	−44			853.0C	2.4	−29
		323.0	−3.6	−41		H	388.8C	1.2	−22
		356.4	3.8	−27			395.8C	5.4	−2
		370.8C	5.6	−8			396.5	4.1	−8
		373.0	6.1	−4			780.1	−1.2	−30
		374.6	3.8	−12			819.4	1.3	−27
		375.0	5.7	−7			819.9	1.7	−17
		377.6	4.6	−1			831.3	1.7	−15
		378.0	4.1	0			831.3	−0.8	−44
		388.8	4.1	0		Z	348.3C	2.0	−19
		390.7	3.4	−6			786.4	0.9	−22
		398.7	2.3	−27			786.4	1.3	−12
		399.0	3.3	−15			805.8	3.1	−10
		399.1	3.6	−27			833.7C	1.9	−28
		739.9	0.9	−33			833.7C	2.1	−34
		764.8C	0.0	−36			834.2	1.5	−27
		765.0	1.5	−25			846.2	2.3	−16
		765.0C	−1.6	−26			847.0	1.0	−26
		765.0C	1.9	−12			847.0	−0.1	−28
		765.0C	−1.4	−27			854.7	0.4	−18
		765.0C	1.9	−6			856.5	1.5	−14

Silurian Michigan Basin

County	Well	Depth (m)	$\delta^{18}O$†	δD†	County	Well	Depth (m)	$\delta^{18}O$†	δD†
GT	NC	2283.3	6.9	−59	MD	DC	2483.8	2.5	−73
		2283.3	5.3	−58			2486.9	0.2	−66
K	NX	2025.7	3.3	−48			2559.1	−2.0	−43
		2036.4	4.9	−46			2559.1	−1.8	−43
		2036.4	5.5	−45			2612.1	5.7	−31
	NP	1868.4	4.4	−52			2612.1	5.5	−26
		1868.9	4.4	−52			2613.1	5.9	−26
	PA	2046.1	5.2	−30			2618.8	5.8	−44
		2120.2	2.8	−45			2618.8	5.6	−53
		2123.3	5.0	−54	N	SB	1566.7	4.9	−32
		2125.4	4.7	−51					
		2127.8	5.8	−49					

Devonian Alberta Basin

Formation	Depth (m)	$\delta^{18}O$	δD	Formation	Depth (m)	$\delta^{18}O$	δD
MU	679.2-A	1.3	−30	MU	677.3-G	1.6	−30
	679.2-B	1.6	−20		677.3-H	1.8	−18
	679.2-C	1.7	−26		681.8	1.7	−19
	679.2-D	1.6	−25		Slide 3A	2.2	−16
	679.2-F	4.0	−24	PE	998.5-A	1.3	−16
	679.2-G	4.7	−22		998.5-B	1.6	−16
	679.2-H	1.2	−27		998.5-C	1.6	−15
	690.7-A	2.4	−31		998.5-B1	1.5	−15
	690.7-B	0.7	−43		222.1-E	2.4	−7
	690.7-C	3.0	−31		222.1-F	3.2	−7
	677.3-A	1.1	−24		222.1-G	2.1	−25
	677.3-B	1.3	−26		466.6-C	−1.3	−77
	677.3-C	1.4	−29		466.6-D	0.0	−65
	677.3-D	1.4	−29		466.6-E	−1.2	−57
	677.3-E	0.9	−32		466.6-F	−1.1	−62
	677.3-F	2.6	−27				

† $\delta^{18}O$ and δD relative to SMOW.

Permian Palo Duro Basin County: DO = Donley, DS = Deaf Smith, O = Oldham, R = Randall, SW = Swisher; Well: S = Sawyer, D = Detten, GF = G. Friemel, JF = J. Friemel, M = Mansfield, HO = Holtzclaw, RW = Rex White, G = Grabbe, H = Harmon, Z = Zeeck; Depth: C = capillary sample.

Silurian Michigan Basin County: GT = Grand Traverse, K = Kalkaska, MD = Midland, N = Nawago; Well: NC = NMEC-ST-FIFE 1-20, NX = NMEX-ST KALK 2, NP = NMEP-ST 1-18, PA = PanAm Simpson 2, DC = Dow Chemical Salt #8, SB = Sun Bradley #4.

Devonian Alberta Basin Formation: MU = Muskeg, PE = Prairie Evaporite.

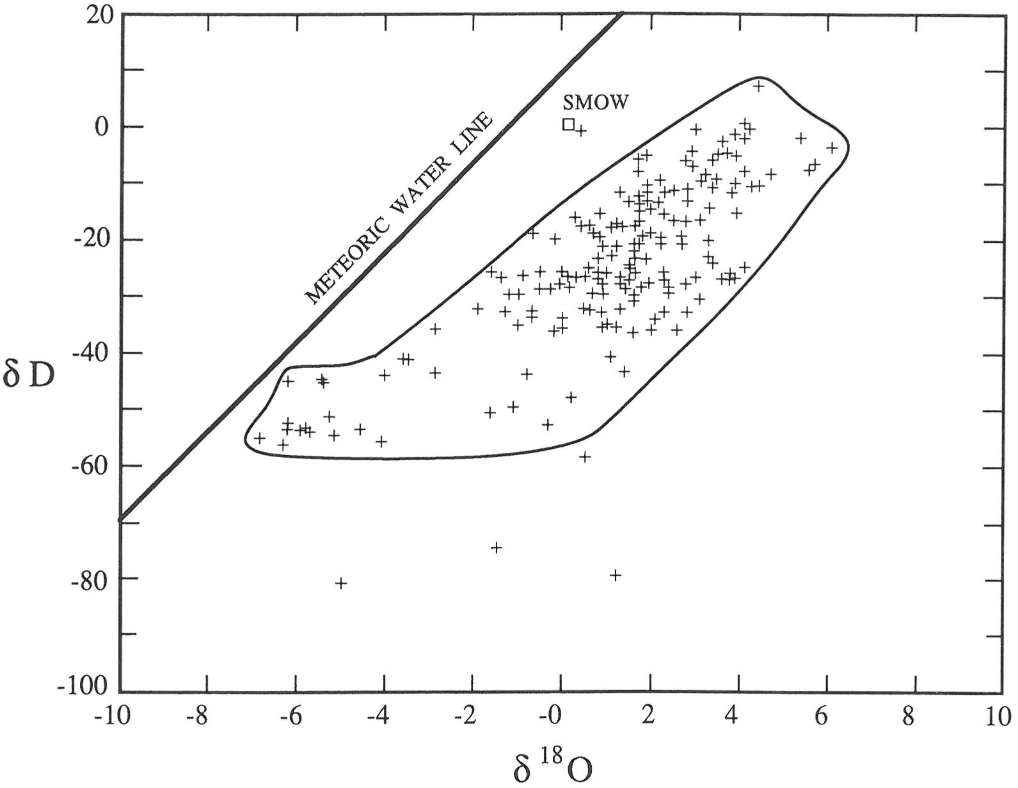

FIG. 2. Isotopic analyses of Permian fluid inclusions from the Palo Duro Basin, Texas. This data array is considered representative of the range of isotopic compositions of a giant, shallow-water, bedded salt deposit. The salt accumulated during repeated floodings of an evaporite basin over tens of millions of years. The isotopic variations are a result of the evaporation trajectory of sea water and mixing of various stages of evaporated sea water with renewed influxes of sea water and influxes of meteoric water, all followed by renewed evaporation to halite facies.

curred in the Palo Duro Basin. If the Palo Duro evaporites are representative of typical saline giants, then a similar domain with respect to the position of the meteoric water line is probable for any saline giant throughout geologic time. However, the isotopic composition of the meteoric waters that enter an evaporating basin is likely to depend on the specific geographic setting and various climatic variables. In the case of the Palo Duro evaporites, $\delta^{18}O$ and δD values have a typical minimum value of about -7 and -55, respectively. In other basins of other geologic ages these minimum values may have been different, depending on the average isotopic composition of the local meteoric water. Because of this, the $\delta^{18}O$-δD domain for these other evaporites may have been more or less elongated. The shape of this domain could also be affected by the amount of meteoric water present in the evaporating brine. Nevertheless, the concept that data for evaporite brines will define some domain to the right of the meteoric water line similar to the Palo Duro domain provides a basis for exploring the possibility that the meteoric water line was strongly displaced in the Silurian and/or Devonian. If ocean water was 4–5.5 per mil lower in the Silurian than in the Permian and the same type of evaporation processes that created the Palo Duro Basin were active, then the domain of fluid inclusion data would plot as shown by the shaded domain in Fig. 4. Many of the data would lie above the modern meteoric water line and maximum $\delta^{18}O$ values would be only about $+1$ per mil enriched relative to SMOW. The data could be kept below the modern meteoric water line if δD were also dramatically different, but this would also produce a major offset of the domain relative to the Palo Duro data.

COMPARISON OF SILURIAN, DEVONIAN, AND PERMIAN DATA

Data for the Devonian and Silurian fluid inclusions are given in Table 1 and are shown together

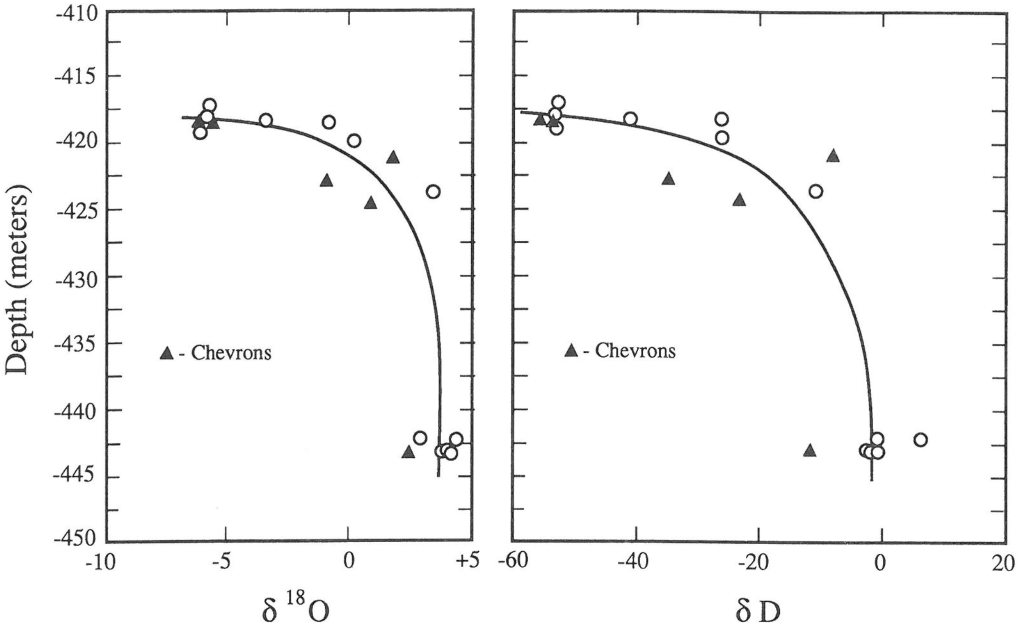

FIG. 3. Isotopic composition versus stratigraphic position for the transition from marine-dominated to meteoric water runoff-dominated salt in the Upper Seven Rivers unit of the Permian salt in the Palo Duro Basin (J. Friemel well). Much of the salt toward the top of this section was reworked (dissolved-reprecipitated) by meteoric waters. The overlying horizon is made up of clastic deposits that flooded the evaporite flats.

with the data envelope for the Palo Duro evaporites in Fig. 5. Although there are fewer data for the Devonian and Silurian, it is clear that the data domains for the older deposits are not strongly shifted to lower $\delta^{18}O$ values. Both Permian and Silurian $\delta^{18}O$ values approach a maximum value of about +6, and the Devonian data approach +5. None of the Silurian or Devonian data plot above, or even near, the meteoric water line. δD values for the Devonian samples strongly overlap the Permian data, but may be slightly lower as a group than the Permian counterparts. The Silurian data are lower as a group in δD relative to either of the other two groups, and this will be considered as a separate issue below.

Oxygen isotope variations

If the same types of processes operated to produce the fluid inclusions in these evaporite deposits, then these data are fatal to the idea that $\delta^{18}O$ of ocean water changed by 4–5 per mil between the Silurian and Permian. Evaporation processes in the Silurian would have to have enriched residual brines in ^{18}O by an additional 4–5 per mil in order for the maximum values to coincide with the Permian maximum values. Additionally, all three age groups appear to approach a +6 per mil enrichment relative to ocean water, the maximum value proposed by LLOYD (1966) that evaporating sea water can reach. For $\delta^{18}O$ of ocean water to have been 4–5.5 per mil lower in the Devonian and Silurian, Lloyd's maximum value would need to be specially extended to 10–11.5 per mil for the Silurian and Devonian in order for the data fields to coincide as shown. There is no inherent reason why the maximum evaporative enrichment in ^{18}O should be tied to the numerical value for $\delta^{18}O$ of sea water, so this is unlikely.

Because of the variable number of samples in the three age groups, there is not a complete overlap of $\delta^{18}O$. A number of Permian samples are significantly lower in $\delta^{18}O$ than any of the Devonian or Silurian samples. This is probably because selected horizons were targeted within the Permian salts where sedimentologic evidence had suggested synsedimentary reworking of the salts by meteoric waters. While prominent on the diagram, these horizons are minor in abundance and probably would not have been sampled if only a limited number of samples were available. Because of the sampling limitations for the older data, it cannot be stated that $\delta^{18}O$ is exactly coincident for the three age groups. Also, because of the multitude of evaporation processes that can

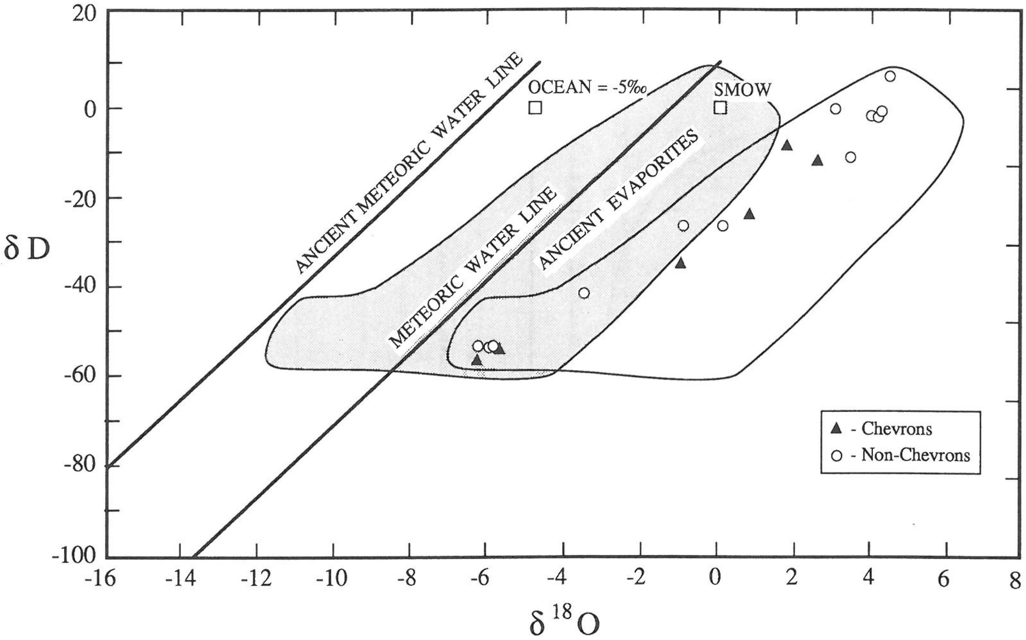

FIG. 4. δD-δ^{18}O array for the data shown in Fig. 3. The transition from marine-dominated salt to meteoric water runoff-dominated salt spans the data domain for the Permian reference domain. Some of the most ^{18}O- and D-depleted salts are chevron-zoned crystals, indicating that these light values represent connate fluids and not later meteoric waters that somehow penetrated the salt.

The shaded domain is the hypothetical position of isotopic compositions that would result if a giant salt deposit formed under similar conditions in a hydrosphere where sea water was depleted in ^{18}O by 5.5 per mil relative to SMOW. Many fluid inclusion data would plot above the position of the modern meteoric water line and maximum δ^{18}O would be less than +2.

go on in evaporite environments it is unlikely that the data for any two saline giants would be identical. These uncertainties mean that δ^{18}O of the parent sea water for the data domains in Fig. 5 could easily have varied by ±1 per mil, but not by 4–5.5 per mil. Although this approach cannot yet yield the exact isotopic composition of past ocean water, it is sensitive to the large variations that have been previously proposed, and appears to be sufficient to rule out the large changes that have been advocated for the interval Silurian-Permian on the basis of isotopic analyses of carbonates. Secular variations in δ^{18}O of Paleozoic shelf carbonates are probably better interpreted in terms of climatic temperature variations, diagenetic alteration, and possible meteoric water contributions to the coastal or epieric sea environments in which these carbonates formed.

Preservation of fluid inclusions in halite

O'NEIL *et al.* (1986) analyzed the isotopic composition of fluid inclusions in Permian bedded salt from the Delaware Basin, New Mexico, and concluded that the inclusions were a mixture of meteoric water and connate brine. They suggested that relatively recent meteoric ground waters had partially penetrated the salt deposit. As argued in the previous sections, all giant, shallow-water marine evaporite deposits are likely to contain mixed meteoric-marine fluids at the time of deposition and early burial, so it is not clear that isotopic data alone can be used to decide if bedded salt has been penetrated by later waters. The issue is of utmost importance to the present investigation; if later fluids have penetrated the salt, then the fluids are not synsedimentary fluids and cannot be used to obtain information about the ancient hydrosphere.

The problem is typified by the data in Fig. 3. An alternative explanation is that the clastic sequence over the salt interval might be interpreted as a subsurface conduit which allowed later meteoric waters to enter the basin. Water descending below this conduit might somehow have entered the salt and been preserved as fluid inclusions. We offer four arguments that the inclusions analyzed throughout this investigation are synsedimentary evaporite fluids, and not later groundwaters that have penetrated the salt.

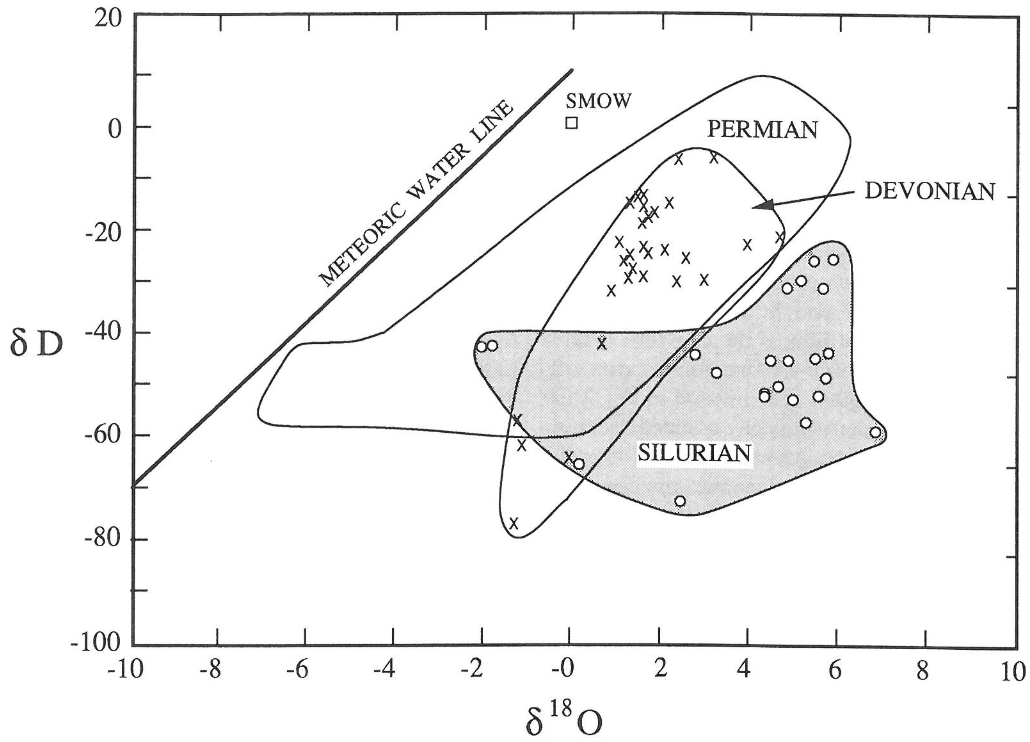

FIG. 5. Isotopic data for Devonian and Silurian fluid inclusions compared with the Permian reference domain. The range of $\delta^{18}O$ values is similar for all three age groups, but δD is lower for the Silurian inclusions. The possible trend of increasing D with time can be explained if δD of sea water has increased with time.

(1) Fluid inclusions in salt are completely isolated within individual halite crystals, and are not interconnected even if they are lodged near grain boundaries. Brine therefore cannot move in a salt deposit in response to gravity or to pressure differences that normally drive subsurface movement of basinal fluids.

Water *can* move in a salt deposit in response to recrystallization, deformation of the salt, or fracturing. Examples of each of these have been documented in diapiric salt by TESORIERO and KNAUTH (1988), KNAUTH *et al.* (1980), and KNAUTH and KUMAR (1983). Many of the samples analyzed here contained locally recrystallized salt. This was most evident where chevron-zoned crystals were partially obliterated by coarser crystals of halite. However, the coarse crystals of the recrystallized halite are often truncated by deposition of the overlying halite layers (HOVORKA, 1990). This indicates that the recrystallization was early; fluid inclusions trapped in this second generation halite represent synsedimentary evaporite fluids, not basinal fluids that entered the salt during deep burial.

The salt beds from which these samples were taken are undeformed, unfractured, and have not undergone wholesale recrystallization. In any case, recrystallization at depth is very likely an expulsion mechanism for water in salt, not a mechanism for water entry. Salt recrystallized at depth has the lowest water content of any known terrestrial rock (KNAUTH and KUMAR, 1981). All of the salts sampled here were water-rich (average water content of Palo Duro halite is 0.5 wt%; FISHER, 1985).

A mechanism involving inclusion migration within single KCl crystals in response to a strong thermal gradient was documented in laboratory experiments by ANTHONY and CLINE (1974), and a widespread misconception has apparently developed that fluid inclusions can migrate through natural salt beds in response to the natural geothermal gradient. OLANDER (1982) clarified the mechanism whereby inclusions might migrate within single NaCl crystals in response to a strong thermal gradient around nuclear waste cannisters but indicated that such inclusions become immobilized at grain boundaries. Migration across grain boundaries has never been demonstrated in laboratory experiments or under natural conditions. In any case, the natural geothermal gradient is far below the thermal gradients used to induce fluid inclusion migration in laboratory experiments. The speculation that the geothermal gradient can move water into or through salt under natural conditions remains to be demonstrated.

(2) Many of the inclusions are arrayed in chevron zonations which point stratigraphically upward. This is a well-documented synsedimentary texture indicating preservation of the originally precipitated crystals (WARDLAW and SCHWERDTNER, 1966). The isotopic composition of the chevrons is typically similar to that of co-existing non-chevron salt. For example, throughout the interval in Fig. 3 the salt contains abundant vertically oriented chevron-zoned fluid inclusions. Many of the salt crystals, including the chevron-zoned crystals, are displacive halite crystals with respect to mudstone lamellae. In other words, halite displaced delicate layers of clay during crystal growth. Many of these displacive crystals are chevron-zoned crystals pointing stratigraphically upward. These textures and fabrics are diagnostic of synsedimentary halite crystal growth, not recrystallization during deep burial. Unless the standard criteria used to interpret these evaporite fabrics are seriously in error, the inclusions were trapped before deposition of the overlying clastic sequence. The data in Fig. 3 are therefore best interpreted in terms of connate fluids and not in terms of water percolating downward from the overlying clastic sequence.

(3) DAS *et al.* (1990) have analyzed the fluid inclusion chemistry and argued that the inclusions in the same Silurian deposits represent syndepositional or early diagenetic brines. Several of the Silurian samples analyzed by DAS *et al.* (1990) were splits from the same core samples analyzed here. ROEDDER *et al.* (1987) analyzed the fluid inclusion chemistry of the Palo Duro salts but did not reach conclusions regarding the origin of the fluids. Their data show that the fluids are never simple NaCl brines as might be expected if meteoric ground waters penetrated the salt, but instead are strongly concentrated brines. BEIN *et al.* (1991) refined and reanalyzed the same data set and concluded that the inclusions are syndepositional evaporite fluids. Many of the isotopic data reported here are for sample splits of the actual fluids analyzed by BEIN *et al.* (1991). Large fluid inclusions that can be multiply sampled in this manner for both isotopic and chemical analysis are most prevalent in the locally recrystallized salt, the salt type most suspect of not preserving syndepositional fluids. The fact that even these inclusions are best interpreted chemically as syndepositional evaporite brines is strong evidence that the salt beds as a whole have not been penetrated by later fluids.

(4) Formation water in deep sedimentary basins often has chemical and isotopic compositions that can be reasonably interpreted as having a component of evapo-concentrated sea water (CARPENTER, 1978; KNAUTH, 1988). Penetration of subsurface salt beds by this water via some unknown mechanism might possibly yield fluid inclusions with the observed chemistry and isotopic composition. However, if this occurred in the case of the Paleozoic samples analyzed here, the Devonian data should be isotopically lighter as a group than the Silurian data because Alberta Basin formation waters are strongly depleted in both D and ^{18}O relative to Michigan Basin formation waters. The reverse is observed, so this possibility is unlikely. Also, KNAUTH and BEEUNAS (1986) have shown that the Palo Duro fluid inclusions are isotopically dissimilar from formation waters in the Palo Duro Basin; the inclusions cannot represent intrusions of water presently in the Palo Duro deep aquifers.

Gypsum dehydration waters

Gypsum is normally considered to be a primary precipitate in marine evaporite deposits. During burial, gypsum converts to anhydrite with release of water. All sulfate in the samples analyzed here is in the form of anhydrite. O'NEIL *et al.* (1986) and KNAUTH and BEEUNAS (1986) explored the isotope systematics associated with the potential water release from gypsum. The latter authors concluded that this had not had a major effect on the isotopic composition of the Permian fluid inclusions at Palo Duro. HOVORKA (1990) has subsequently argued on the basis of petrographic studies that the gypsum-anhydrite conversion in the Palo Duro evaporites occurred at or near the sediment water interface. The likely mechanism involved back reaction of more evapo-concentrated brine with gypsum precipitated during earlier stages of evaporation. The water is released back into the evaporite brine and does not appear as a halo of fluid inclusions in salt around the gypsum pseudomorphs.

In the salt cores of the Michigan Basin, dense arrays of brine inclusions are often found immediately above or beneath anhydrite bands. These were specifically sampled on the chance that these inclusions might represent water released in the subsurface from the sulfate layer when it was originally gypsum. However, data for these inclusions do not define any specific part of the Silurian data array. It is possible that all of the Silurian inclusions nevertheless represent water released from gypsum, and that this is the reason the Silurian data array is different from the Devonian data array. Since gypsum hydration water is enriched in ^{18}O by about +5.5 per mil relative to its parent brine (SOFER, 1978), it is possible under this scenario that the parent evaporite fluids are all displaced about 5.5 per mil to the left of the array shown in Fig. 5. In this case, the position of the Silurian data array relative to that of the Permian arises via a sampling bias, and Silurian sea water could indeed have been depleted in ^{18}O relative to Permian sea water. A similar argument might be made for the Devonian data. However, neither Devonian nor Silurian fluid inclusions are simple NaCl brines (DAS *et al.*, 1990; BRODYLO and SPENCER, 1987) as would be expected if water from gypsum were simply released into halite. All are concentrated brines requiring evaporative processes. Also, this putative mechanism would not lead to chevron zonations with halite crystals. While it is possible that release of water from gypsum has somewhat altered the isotopic composition of the inclusions, it is very unlikely that this is the major control, and it is equally unlikely that all Silurian samples just happened to be sampled from inclusions that originated purely through gypsum dehydration while none were encountered in almost 200 samples of Permian halite.

Hydrogen isotope variations

The most striking difference in the three data sets in Fig. 5 is the overall depletion in D of the Silurian data relative to the Permian and Devonian data. A shift upward of about 20 per mil in δD would bring the Silurian domain coincident with the Permian reference domain. One interpretation of the data is therefore that the Silurian parent waters were depleted in D about 20 per mil relative to the Permian waters. The Devonian δ-values may also be somewhat lower relative to the Permian, and it is possible to read into Fig. 5 a progression in which δD increases going from Silurian to Devonian and Permian.

Although the oxygen isotope history of the oceans has been extensively debated, the hydrogen isotope history has generally been considered an intractable problem. Many sedimentary minerals do contain structural water and fluid inclusions, but these have never been considered as indicators of sea water isotopic composition. The rock record therefore offers no indication of hydrogen isotope evolution with which the fluid inclusion data can be compared.

In principle, it is likely that the hydrosphere has undergone some enrichment in D over geologic time. Photodissociation of water in the upper atmosphere yields free hydrogen which can escape from the Earth. Protium should escape preferentially to deuterium, and recombination of the residual, D-enriched hydrogen gas with oxygen causes the hydrosphere to become enriched in D. The fractionation of hydrogen isotopes during the complicated dissociation-escape-recombination processes is unknown. The effect today on δD of the hydrosphere is surely small because such a small amount of water is involved at any given time relative to the mass of the entire hydrosphere. It is difficult to imagine that this process could account for the large shifts shown in Fig. 5, but the possibility cannot be dismissed because so little is known about the current process or how it may have varied in the past.

Another possibility relates to the process whereby basalts become hydrated at mid-ocean ridges and release water at subduction zones. Part of the water that hydrates mid-ocean ridge basalts is returned via dehydration reactions at subduction zones and part may be recycled through the mantle and outgassed again at spreading centers. It is not clear, however, that a steady state has been achieved; a clear demonstration has never been made that water subducted equals water emitted at spreading centers. It is conceivable that the hydrosphere was outgassed early in Earth history and that it is being slowly returned to the crust and mantle by hydration of ocean crust and incomplete dehydration at subduction zones. The hydrogen isotope fractionation between hydroxyl in hydrous minerals and water is normally such that the lighter isotopes are preferentially taken into the mineral, so this process works in the right direction to account for the shift shown in Fig. 5. Unlike the photodissociation process, this one has the potential of working on a scale large enough to cause changes in δD as large as those suggested by the fluid inclusion data.

Unlike the Permian and Devonian salt samples, many of the Silurian samples contain enough dissolved gas to yield microscopic bubbles when small chips are dissolved in water. The possibility arises that the Silurian samples are depleted in D because they have been contaminated by water that has exchanged with, or been derived from, D-depleted organic matter. Every sample was microscopically screened for freedom from any visible impurity, but the sample aliquots actually analyzed could not be tested for dissolved gases by the water dissolution method. Additional confirmation of the D-deple-

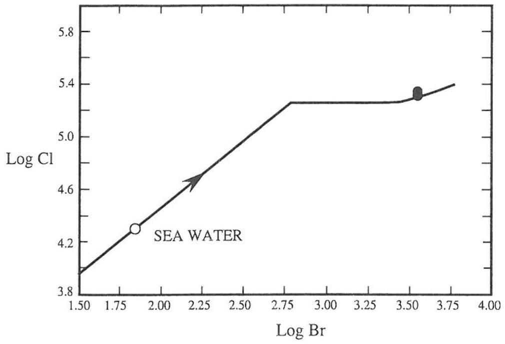

FIG. 6. Two Cl-Br analyses of brine encountered in the Silurian salt of the Retsof Mine, New York. The correspondence of these data with the trajectory shown for the evaporation of sea water makes this brine a good candidate for connate evaporate brine.

tion in Silurian salt is desirable and has been provided by a fortuitous occurrence of brine in the Retsof salt mine of the International Salt Company (now Akzo Salt Inc.) in western New York.

The Retsof Mine is a large mine in bedded Silurian salt that is generally recrystallized (T. LOWENSTEIN, pers. comm.). For the first time in 20 years, a brine "pocket" was encountered in late 1987 (A. G. GEARY, International Salt Co., written comm., 1987). The seep area was quickly grouted to stop further entry of brine into the mine, but multiliter quantities were sampled by the mine engineers. Seeps in salt mines can represent a variety of water sources, including external aquifers which could potentially enter a mine along fractures. The chemical analysis supplied by International Salt Company gives the following concentrations (mg/l): Na = 26,815; Cl = 217,775; Ca = 73,705; Mg = 8,365; K = 12,650; Br = 3,600; S.G. = 1.254. Figure 6 shows the Br-Cl data together with the trajectory for the evaporation of sea water (CARPENTER, 1978). Although the use of chemical analyses to determine the source of brines is a controversial subject, the agreement of the Br-Cl data with the sea water evaporation trend makes this brine a good candidate for evaporite brine trapped in the Retsof salt since the Silurian. The other chemical data are consistent with a marine evaporite brine that has been involved in dolomitization reactions, precipitation of anhydrite, and possible K exchange with clays (using the treatment of CARPENTER, 1978). The most likely explanation for the Retsof brine is that it is "connate water," a remnant of the parent Silurian evaporite brine trapped within the salt. Dewatering of the salt during recrystallization may have contributed to the brine, but this released fluid would also have been parent Silurian evaporite brine. Isotopic data for the Retsof leak are shown in Fig. 7. The isotopic composition of this Silurian sample is just like those of the Silurian samples from Michigan and plots below the data fields for the Devonian and Permian. This result supports the interpretation that the fluid inclusions are recording a Silurian signal that is really depleted in D relative to the younger samples.

CONCLUSIONS

1. New isotopic analyses of fluid inclusions in Permian halite confirm the earlier results of KNAUTH and BEEUNAS (1986), and support the interpretation that the inclusions are connate brines trapped at the time of halite precipitation or during early diagenesis. The fluids represent evaporated sea water, meteoric water, or any mixture between the two depending upon the interplay between marine flooding and continental runoff in the original depositional environment.

2. $\delta^{18}O$ of fluid inclusions from Devonian and Silurian bedded salts falls within the range of the Permian data. Maximum $\delta^{18}O$ of all three groups approaches a "limiting" value of about +6; Silurian values are not 4 to 5.5 per mil depleted in ^{18}O relative to Permian values as expected if the oceans were 4 to 5.5 per mil lower in the Silurian. The data indicate that sea water did not vary by more than

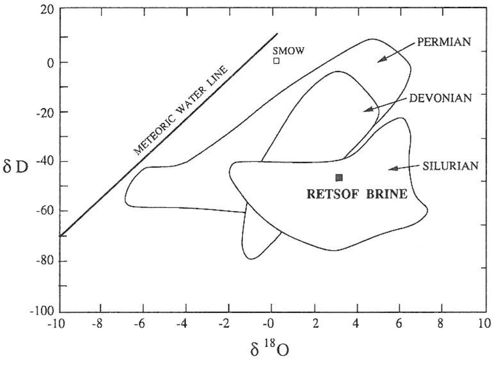

FIG. 7. Isotopic datum for the Retsof brine in relation to the fluid inclusion data. The isotopic composition of this large brine sample is similar to that of fluid inclusions in the Michigan Basin Silurian salt. The Retsof sample is large enough to analyze by conventional methods. This lends support to the interpretation that Silurian evaporite brines are depleted in D relative to younger evaporite brines and that the observed depletion is not some quirk associated with the analysis of small water samples in halite or special conditions in the Michigan Basin that might alter the isotopic composition of fluid inclusions.

1–2 per mil during the interval Silurian-Permian, strongly contradicting interpretations of sea water history based on oxygen isotopic analyses of carbonates. Secular variations in $\delta^{18}O$ of Paleozoic carbonates are therefore probably best interpreted in terms of climatic temperature variations, diagenetic alteration, and/or possible contributions of meteoric water to the original coastal or epieric sea depositional environment, and not in terms of lower ^{18}O content of past sea water.

3. δD for the Silurian samples is about 20 per mil lower than for the Permian samples, and the Devonian samples have intermediate values. A viable interpretation of these differences is that the Earth's hydrosphere became progressively enriched in deuterium between the Silurian and the Permian.

Acknowledgements—Devonian samples were generously provided by Ron Spencer, University of Calgary. Many of the Permian samples were selected and transmitted by Sue Hovorka, Texas Bureau of Economic Geology. We thank both for sharing sedimentologic information about the samples. Sarah Larimer carefully prepared every sample. Her painstaking efforts are gratefully acknowledged. We thank A. G. Geary and Akzo Salt Inc. for the Retsof Mine brine sample, chemical data, and permission to publish the Retsof results. We also thank personnel at the University of Michigan core lab for their cooperation and generosity. Editorial comments by Jim O'Neil improved the manuscript. Funding was by NSF EAR-8618369 and Battelle Memorial Institute Contract #E 512-08100.

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