Fossil meteoric groundwaters in the Delaware Basin of southeastern New Mexico

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Abstract—$^{18}O/^{16}O$ and D/H ratio measurements have been made on groundwaters sampled from the Rustler Formation (Ochoan, Permian) and related rocks in the northern Delaware Basin of southeastern New Mexico. Most confined Rustler Formation waters at the WIPP site and to the west in Nash Draw and confined waters from the Capitan Limestone constitute one population in $\delta D/\delta^{18}O$ space, while unconfined groundwaters inferred to originate as modern surface recharge waters constitute a distinctly different and non-overlapping population. A likely explanation for this distinction is that meteoric recharge to most of the Rustler and Capitan units took place in the geologic past under climatic conditions significantly different from those of the present. Available tritium and radiocarbon data are consistent with this hypothesis, and the apparent age of confined groundwaters is in excess of 12,000 radiocarbon years, suggesting that recharge took place under wetter conditions in the late Pleistocene. Water at the Rustler/Salado contact at the WIPP site is of meteoric origin but has experienced isotopic alteration that increases with decreasing permeability. Rustler dolomites have not recrystallized in isotopic equilibrium with Rustler Formation water. The absence of modern meteoric recharge to the Rustler Formation at and near the WIPP site indicates that the hydrologic system there is not at steady state. Instead, the system is responding to the cessation of local recharge, this cessation occurring more than 10,000 years ago.

INTRODUCTION

Rationale and objectives

UNDERSTANDING THE GEOLOGIC history of the Rustler Formation in the northern Delaware Basin of southeastern New Mexico is relevant to the evaluation of the ability of the bedded evaporite environment at the Waste Isolation Pilot Plant (WIPP) to contain waste radionuclides for long periods of time. The Rustler is important because it (1) is the uppermost evaporite-bearing unit in the Ochoan (Permian) sequence, (2) is experiencing active dissolution where it crops out west of the WIPP site, (3) immediately overlies the Salado Formation where the WIPP is being excavated, and (4) contains interbeds of brittle fractured rock that carry the most abundant and regionally persistent occurrences of groundwater associated with Delaware Basin bedded evaporites. The rates and directions of flow in a groundwater system such as the Rustler Formation are inferred from determinations of permeability and potentiometric head in individual boreholes. Groundwater geochemistry, however, provides information on the nature of processes governing recharge, groundwater residence time, the degree of connection among individual groundwater occurrences, and identification of discharge areas. Stable isotope studies of the Rustler groundwaters contribute to this supplemental information.

To facilitate the interpretation of groundwater flow in the Rustler Formation, isotopic compositions of other geologically and economically important Delaware Basin groundwaters were also de-termined, including those from the overlying Dewey Lake Red Beds, the Capitan Limestone bordering the Delaware Basin evaporites (both the vadose zone represented in Carlsbad Caverns and the phreatic zone to the east), the Ogallala Sandstone underlying much of the southern Great Plains, near-surface alluvium, and a spring discharging from local shallow-seated gypsum karst. The part of the Delaware Basin in southeastern New Mexico and west Texas relevant to this study is shown in Fig. 1, which illustrates large-scale geographic relationships among various water occurrences. Figure 2 shows the locations of boreholes and other features near the WIPP site, including Nash Draw, a solution-subsidence valley formed by the partial dissolution of outcropping Rustler evaporites.

Previous work

LAMBERT (1978) first documented the stable isotope compositions of confined groundwaters in the Capitan Limestone and the Rustler Formation and concluded that they are of meteoric origin. However, stable isotope ratios of most Capitan groundwaters under confined hydrologic conditions were distinctly different from those of other local meteoric groundwaters whose origins could be traced by observation and inference to infiltration of modern precipitation. In particular, groundwaters from Carlsbad Caverns, where active meteoric recharge is observed, were isotopically distinct from tightly clustered δD and $\delta^{18}O$ values of groundwaters from buried portions of the Capitan, extending from the
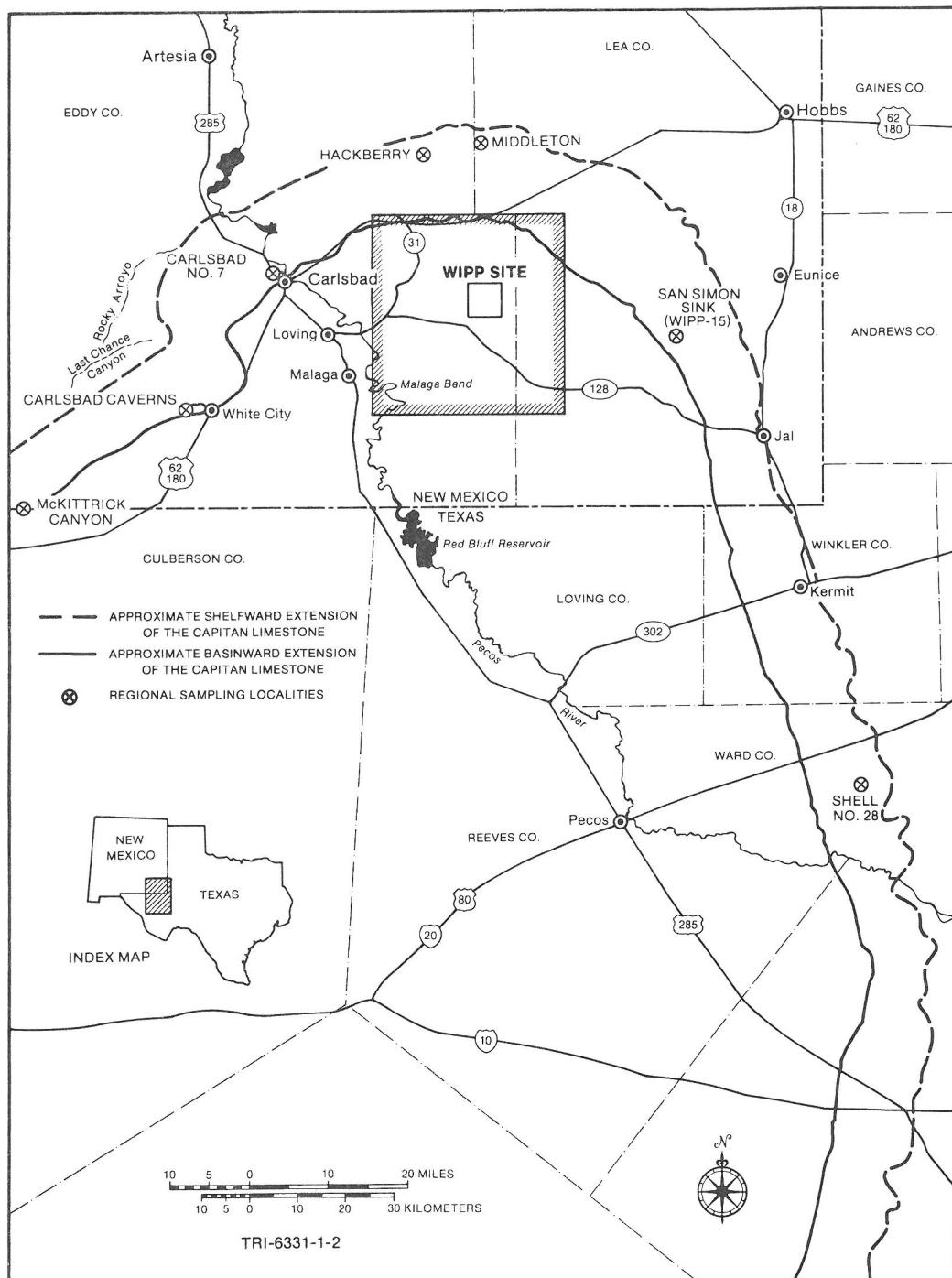
FIG. 1. Regional map of the Delaware Basin, southeastern New Mexico and West Texas. Approximate positions of basinward and shelfward extensions of the Capitan Limestone are taken from HISS (1975). Hachured rectangle is the area covered by Fig. 2.

city of Carlsbad eastward and southward into west Texas (Fig. 1). LAMBERT (1978) concluded that (except for Carlsbad Caverns) a $\delta^{18}O$ value of -7 and a δD value of -50 are good approximations to local meteoric water in the Delaware Basin, and the Caverns are part of a hydrologic system independent of the rest of the Capitan, with their enrichment in D and ^{18}O reflecting the water's origin from air-
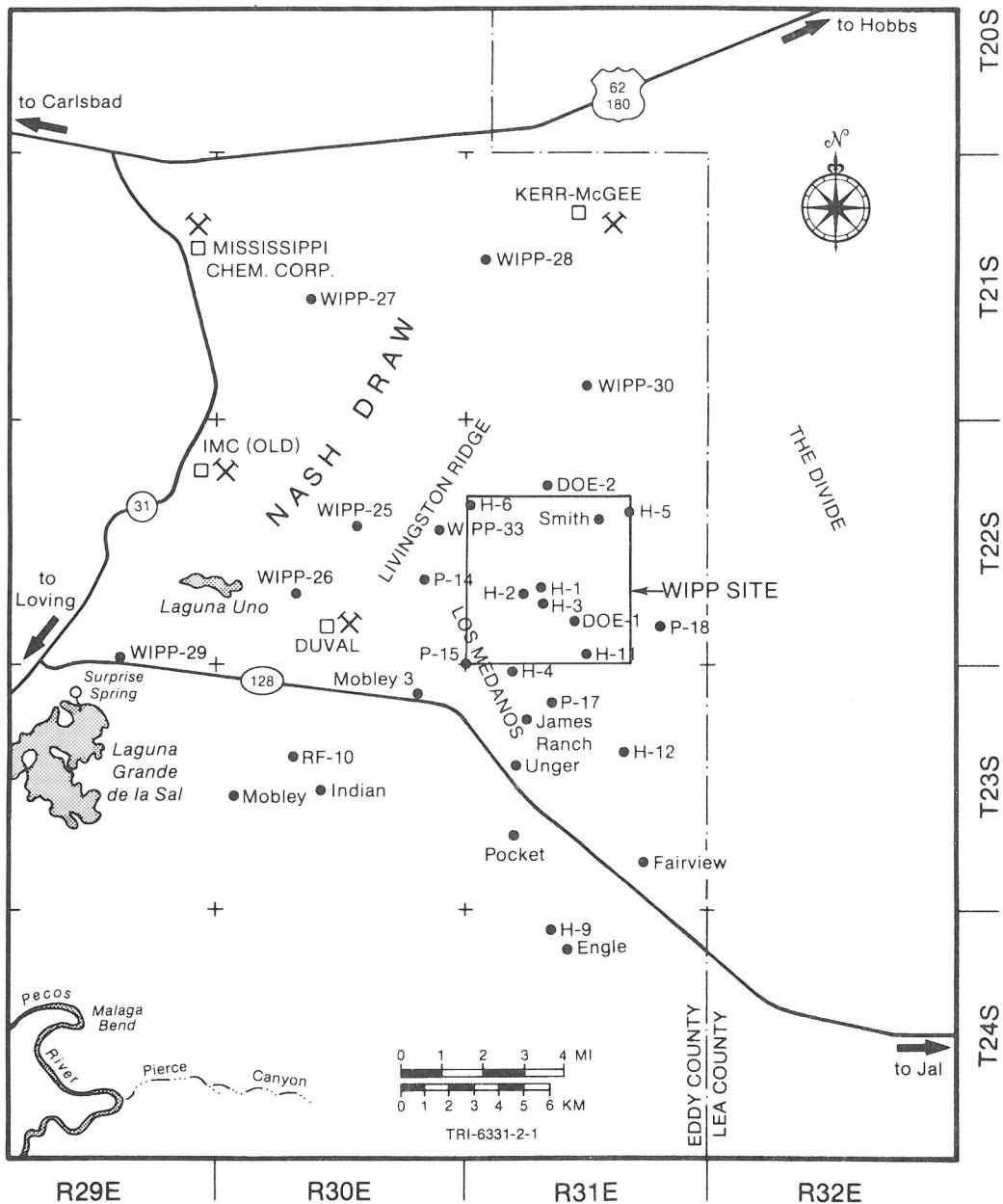
FIG. 2. Map of northern Delaware Basin, southeastern New Mexico. Detailed map of the area enclosed by hachures in Fig. 1 showing sampling localities, mostly boreholes. Modified from MERCER (1983).

mass conditions different from those which produce other Delaware Basin rains. This implied that most of the eastern (deeper) Capitan groundwaters were probably recharged under climatic conditions different from those prevalent in the Guadalupe Mountains (Fig. 1). At the time, no estimates were available of ages of recharge for Delaware Basin groundwaters. Similarly, it was not known to what

degree climatic and recharge conditions in the northern Guadalupe Mountains represented those in other parts of the northern Chihuahuan Desert throughout the northern Delaware Basin. Until recently (LAMBERT, 1987) the time of groundwater recharge to the Rustler Formation and the overlying Dewey Lake Red Beds was unknown, but independent paleoclimatic evidence indicated wetter con-

ditions, more conducive to recharge, at various times in the Pleistocene, ranging from 10,000 to 600,000 years ago (VAN DEVENDER, 1980; BACHMAN, 1984).

MERCER (1983) summarized the stratigraphy and hydraulic properties of the five members of the Rustler Formation, two of which are 8-m thick locally fractured dolomite units carrying groundwater under confined conditions. The distribution of halite removal by dissolution and the conversion of anhydrite to gypsum in the Rustler Formation across Nash Draw and the WIPP site was described in more detail by SNYDER (1985). In addition, the regional aspects of dissolution of Ochoan evaporites have been discussed by LAMBERT (1983).

METHODS

Sample collection

Several boreholes (Fig. 2) penetrate the three principal water-bearing units above the main evaporite sequence at the WIPP site: the Magenta and Culebra dolomite members of the Rustler Formation, and the zone near the contact between the Rustler and the underlying Salado Formation. In addition, some boreholes allowed sampling of local water-bearing horizons in the Dewey Lake Red Beds immediately overlying the Rustler Formation. The Culebra dolomite member of the Rustler Formation appears to be the most regionally pervasive and consistent water-producing horizon (MERCER, 1983). The Rustler/Salado contact was studied because it represents the uppermost horizon of Salado halite dissolution.

Readily accessible accumulations of water (springs, streams, and pools) were grab-sampled; subsurface sampling from wells required special equipment and procedures, primarily because of the low productivity. From the beginning of the WIPP project in late 1975 to 1980, all samples from wells were bailed or swabbed during hydrologic testing. Well-water samples resulting from pump tests in 1980 and 1981 were collected using the criteria and procedures described by LAMBERT and ROBINSON (1984). From 1981 to the present well-water samples were collected by subcontractor organizations whose sampling criteria were based on those of LAMBERT and ROBINSON (1984), although procedures differ in detail.

In several boreholes core samples of the water-bearing carbonate rock were available along with water samples. Oxygen isotope ratios of host rocks in most recent contact with the water were used to evaluate the degree of isotope exchange between carbonate and water, as an indicator of secondary precipitation. Because most waters were sampled from cased wells perforated in production zones isolated by packers, contact of water samples with rocks other than the producing horizons was avoided.

Analytical procedures

Water was first distilled in vacuum so that no salinity correction was necessary. Because the principal solutes in most water samples were sodium chloride and calcium sulfate, the effect of fractionation between vapor and low-volatility hydrous residue was small. The quantitatively distilled water was analyzed for oxygen isotope composi-

tion by the CO_2-equilibration technique at 25.4°C (EPSTEIN and MAYEDA, 1953).

Hydrogen gas was quantitatively produced from water samples by reaction with uranium metal at 800°C (BIGELEISEN et al., 1952). The hydrogen was collected by means of a Toepler pump and the HD/HH ratio was determined by mass spectrometry.

Ratios of the stable oxygen and carbon isotopes in carbonates were measured on the carbon dioxide liberated using a modification of the method described by EPSTEIN et al. (1964), in which CO_2 collected after one hour is attributed to calcite, and CO_2 collected after three hours is attributed to dolomite, allowing the determination of δ-values for both of these carbonates in a mixture. For all the carbonate samples a three-day reaction time yielded at least 60% of the gas and acceptably reproducible δ-values.

All stable isotope data are reported in per mil in the usual delta (δ) notation, expressed relative to internationally accepted references. Mean values of replicate analyses were used in the interpretations. The $\delta^{18}O$ and $\delta^{13}C$ values of pure calcite samples were precise to ±0.1 per mil or less, but the variation in measurements of dolomites was typically ≤ ±0.4 per mil.

Typical confidence limits (at the 95% level) for replicate analyses of water $\delta^{18}O$ values were about 0.25 per mil, whereas confidence limits for replicate δD analyses were typically ±2.5 per mil.

DISCUSSION

Hydrologic context for groundwaters

Distinctions made on more than one basis (isotopic as well as hydraulic) allow the identification of fossil as well as actively recharged groundwater systems. The occurrences of waters in the Delaware Basin are here categorized according to four types.

Vadose-zone waters. The most readily accessible sampling points in the unsaturated (vadose) zone were standing pools receiving dripwater in Carlsbad Caverns, in the northern Guadalupe Mountains (Fig. 1). The dominant mechanism of recharge to Carlsbad Caverns pools is vertical infiltration into near-surface outcrops of overlying dolomite of the Tansill and Yates Formations. Residence times of several weeks to months have been reported, "with no apparent relationship to depth below the surface" (WILLIAMS, 1983).

Near-surface waters. Samples of near-surface waters came from a geographically widespread area in the Delaware Basin (Fig. 1). Stormwaters were collected at the surface in the city of Carlsbad and at the WIPP-29 borehole site. A major through-flowing stream that drains the region, the Pecos River, was sampled at Lake Carlsbad. The surface elevations at these sampling sites (Table 1) are representative of the surface elevation over much of southeastern New Mexico and Texas. Surprise Spring, an intermittent spring issuing from the Tamarisk member of the Rustler Formation near the north end of Laguna Grande de la Sal (Fig. 2)

Table 1. Waters from the Vadose Zone and the surface

Location	Sampling date	Elev.[1] (ft asl)	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	Analyst[2]
Carlsbad Caverns Pools					
Green Lake Green Lake Room	29 Aug 76	3575	−24	−3.6	(a)
Mirror Lake Big Room	29 Aug 76	3660	−28	−4.3	(a)
Longfellow's Bathtub Big Room	29 Aug 76	3660	−29	−4.2	(a)
Celery Stalk Pool Big Room	29 Aug 76	3660	−20	−3.0	(a)
Devil's Spring Main Corridor	09 Jun 77	4100	−30	−4.4	(a)
Horsehead Lake New Mexico Room	09 Jun 77	3672	−39	−4.8	(a)
Lake of the Clouds	09 Jun 77	3311	−33	−5.1	(a)
Junction/Rope Pool Left-Hand Tunnel	09 Jun 77	3641	−32	−6.3	(a)
Lower Cave Pool	09 Jun 77	3625	−17	−1.7	(a)
Music Room Main Corridor	21 Dec 77	4100	−32 −31	−4.0 −4.0	(b), (c) (b), (c)
Naturalist's Room Lower Cave	21 Dec 77	3575	−24 −23	−3.5	(b), (c) (b)
Grass Skirt Pool New Mexico Room	21 Dec 77	3670	−37 −37	−4.2 −3.7	(b), (c) (b), (c)
Stream, Storm, and Spring Waters					
Pecos River Lake Carlsbad	08 Jun 77	3111	−36	−3.6	(a)
McKittrick Canyon stream	13 Jun 84	6000	−49 −50	−8.1 −8.1	(d) (d)
Carlsbad storm Rodeway Inn	05 May 77	3150	−80	−10.3	(a)
Carlsbad storm Rodeway Inn	11 Aug 77	3150	−18 −19		(b) (b)
Storm, WIPP-29 1750–1815 h	26 Aug 80	2975	−18 −20	−2.3	(b), (c) (b)
Surprise Spring SW Nash Draw	20 Dec 77	2950	−31 −30	−1.8 −1.2 −1.0	(b), (c) (b), (c) (c)

[1] Cavern elevations were provided by Dr. G. AHLSTRAND, National Park Service. Other elevations were taken from U.S.G.S. topographic maps.

[2] Analysts as follows:
  (a) δD and $\delta^{18}O$, J. R. O'NEIL, U.S. Geological Survey.
  (b) δD, C. J. YAPP, Univ. of New Mexico.
  (c) $\delta^{18}O$, LAMBERT and HARVEY, (1987).

was also sampled. Because of its location in southwestern Nash Draw, it is a likely discharge for some of the groundwater in the Rustler Formation. A local stream that drains a portion of the southern Guadalupe Mountains was sampled in McKittrick Canyon, together with the travertine it has deposited in historic times.

Shallow groundwaters. Shallow groundwaters, commonly under perched or water-table conditions, include groundwaters from alluvium, the late Permian Dewey Lake Red Beds, Triassic rocks, and the late Cenozoic Ogallala Formation. Groundwaters nearest the surface and under water-table conditions have a greater probability of receiving recharge by direct infiltration from the surface than do groundwaters under confined conditions.

Confined groundwaters of the Capitan Limestone and Rustler Formation. The Capitan Limestone east of the Pecos River contains groundwater under confined conditions (*i.e.,* water levels in wells rise above an upper confining horizon) in its cavernous porosity. Direct vertical infiltration into this portion

Table 2. Waters from shallow wells (post-Rustler units)

Location	Sampling date	Depth[1] (ft)	δD ‰ SMOW	$\delta^{18}O$ ‰ SMOW	Analyst[2]
James Ranch prob. Dewey Lake[3]	11 Dec 75	166.4	−40	−5.0	(a)
Smith Livingston Ridge prob. Triassic[4]	09 Jun 76	167.3	−52	−7.2	(a)
Fairview prob. Dewey Lake[5]	11 Dec 76	361.3	−53	−7.1	(a)
WIPP-15 (alluvium) San Simon Sink	12 Mar 77	445–540	−37 −40	−4.5	(b), (c)
Pocket Dewey Lake[6]	11 Nov 83	223.9	−45	−6.0	(d)

[1] Depth of slotted interval in casing, or total depth of well.

[2] Analysts as follows:

(a) δD and $\delta^{18}O$, J. R. O'NEIL, U.S. Geological Survey.

(b) δD, C. J. YAPP, Univ. of New Mexico.

(c) $\delta^{18}O$, LAMBERT and HARVEY (1987).

(d) δD, $\delta^{18}O$, Hydro Geo Chem, Tucson, AZ.

[3] "Ranch Headquarters Well," 23.31.6.444 as listed by COOPER and GLANZMAN (1971). Previously considered a Rustler well by LAMBERT (1978).

[4] 22.31.15.130a as listed by COOPER and GLANZMAN (1971).

[5] 23.31.26.340 as listed by COOPER and GLANZMAN (1971).

[6] "Walker Well," 23.31.29.113 as listed by COOPER and GLANZMAN (1971).

groundwaters from the Ogallala Sandstone in the High Plains province of Texas (NATIV and SMITH, 1987) were used for comparison, because the High Plains province, due east of the Delaware Basin, has latitudes, elevations, topography, vegetative cover, and climatic conditions similar to those of the Delaware Basin.

Groundwater in alluvium. The San Simon Sink (WIPP-15) water was sampled through slotted well-casing open to alluvium. The water-table conditions at WIPP-15 probably represent a greater degree of interconnection with surficial recharge than do confined conditions.

Groundwater in the Dewey Lake Red Beds. Groundwater occurrences in the Dewey Lake Red Beds near the WIPP site were described as localized, laterally discontinuous, perched or semiperched, developed in lenticular "sands," and probably depend largely on locally favorable conditions for recharge (MERCER, 1983). The isotopic compositions of Dewey Lake groundwaters vary significantly.

The isotopic composition of the James Ranch well is near the meteoric field and the WIPP-15 point. The well's proximity to a large area of sand dunes (MERCER, 1983) implies that infiltration can readily proceed there, and thus its δD and $\delta^{18}O$ values probably represent modern recharge. The δD and $\delta^{18}O$ values of the water from Pocket well (Table 2; Fig. 3) are significantly more negative than those from the James Ranch well and from alluvium in San Simon Sink. LAMBERT (1987) found that the

apparent radiocarbon age of Pocket water is 14,000 radiocarbon years, using the interpretive numerical model of EVANS *et al.* (1979). Its age suggests that its δD and $\delta^{18}O$ values, which are lower than those of James Ranch and WIPP-15 waters, are less affected by modern recharge. The δD and $\delta^{18}O$ values of Fairview water (Table 2) are significantly more negative than those of most other shallow groundwaters, including those having probable hydraulic connections with the surface at elevations of 3000 to 4000 ft, such as at WIPP-15 and James Ranch.

Groundwater in Triassic rocks. The isotopic composition of water from the Smith well, which appears to tap a water-producing horizon in the Triassic (COOPER and GLANZMAN, 1971), is indistinguishable from that of Dewey Lake water from Fairview (Table 2; Fig. 3). Its δD and $\delta^{18}O$ values are significantly different from those of probably modern recharge to local groundwaters (WIPP-15 and James Ranch).

Groundwater in sandstone of the Ogallala Formation. The δD, $\delta^{18}O$, and tritium values of groundwaters from the Ogallala Formation and related units underlying the Southern High Plains of Texas were reported by NATIV and SMITH (1987). Only those High Plains groundwaters having δD values more positive than −42 have significant levels of tritium (>10 Tritium Units; 1 TU = 1 tritium atom in 10^{18} hydrogen atoms), indicating that demonstrably modern (post-1950) recharge on the High Plains is relatively enriched in deuterium (Fig.

4). Values less than about 10 TU are not considered conclusively indicative of a large degree of hydraulic connection with the surface since about 1950 (ISAACSON *et al.,* 1974). Since the elevations, climate, and vegetative cover are similar in the Southern High Plains and the northern Delaware Basin, it is here inferred that conditions governing recharge of groundwaters are probably also similar.

Figure 5 shows the isotopic relations for High Plains Ogallala waters reported by NATIV and SMITH (1987), not including those judged by them to be contaminated. These data points do not deviate significantly from the meteoric field, supporting the contention that these waters have not undergone significant partial evaporation prior to recharge. Although the waters having >10 TU occur in the more positive half of the range of δD and $\delta^{18}O$ values, that half of the range also contains waters having <10 TU. This suggests that the prevalent climatic conditions governing modern Ogallala recharge on the High Plains, represented by more positive δ-values, began prior to 1950 when atmospheric tritium was less abundant. The low levels of tritium in waters with δD values more negative than −42, however, indicate that such waters contain only a minimal component recharged from the atmosphere since 1950. Thus, NATIV and SMITH's (1987) Ogallala waters having δD values more negative than about −42 may represent recharge prior to the time when present recharge and climatic conditions were established in the High Plains.

C. J. YAPP (unpubl. data) has measured several δD values for water from the Ogallala Formation from eastern New Mexico. These samples were from wells in Ogallala Sandstone and/or Quaternary alluvium. The Ogallala groundwater in this region is under water-table conditions (NICHOLSON and
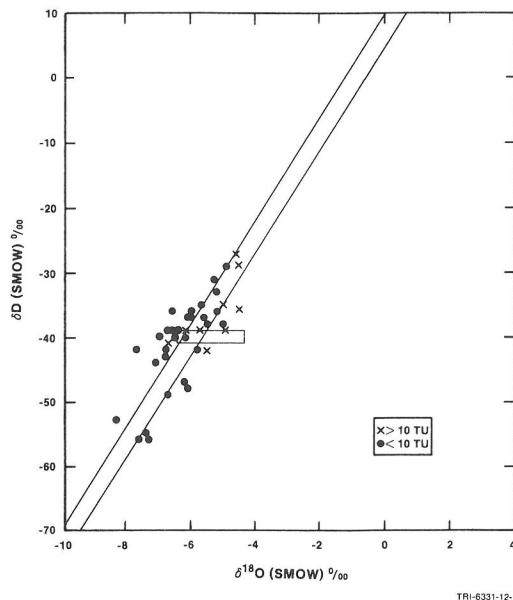
FIG. 5. Stable-isotope compositions of groundwaters from the Southern High Plains, Texas. Data are from NA-TIV and SMITH (1987). The δD range of Ogallala groundwaters (rectangle) from southeastern New Mexico analyzed by YAPP (unpublished) is shown for comparison.

CLEBSCH, 1961). The δD values are −39 to −41 (Fig. 3), well within the population of Ogallala δD values of the High Plains groundwaters having significant tritium levels (Fig. 5).

Isotopic signature of modern Delaware Basin recharge

Occurrences of groundwater in San Simon Sink, parts of the Ogallala Formation, and probably the Dewey Lake at James Ranch have demonstrable or inferred degrees of hydraulic connection with the surface, and their stable isotope compositions are typical of demonstrably modern meteorically derived recharge to groundwater in the northern Delaware Basin at elevations between 3000 and 4000 ft. Recharge to Carlsbad Caverns pools in the unsaturated zone of the Capitan Limestone is responsive to rainfall (WILLIAMS, 1983), but the seasonal variations in the isotopic compositions of vadose water are not known.

The seasonally averaged isotopic composition of modern recharge to groundwater systems in the north-central Delaware Basin is inferred to have a δD value more positive than −42 (Fig. 4). Modern Delaware Basin groundwaters having δD values more negative than about −42 generally originate as precipitation at higher elevations (*e.g.,* Mc-Kittrick Canyon). Summer precipitation in the
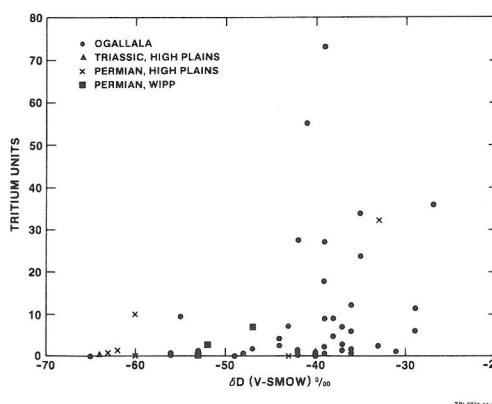

FIG. 4. Tritium and deuterium concentrations in groundwaters from the Southern High Plains, Texas, and the Delaware Basin, southeastern New Mexico. High Plains data are from NATIV and SMITH (1987).

Delaware Basin and surrounding areas is believed to be more abundant than that in winter over periods of several years (HUNTER, 1985) and thus may be volumetrically more important in recharging local shallow groundwater systems. Hence, groundwaters at lower elevations having δ-values more negative than those of modern recharge are likely to have been recharged under a different climatic regime, rather than during modern winters or at higher elevations.

Confined groundwaters in the Capitan Limestone

The stratigraphy and hydrology of the Capitan Limestone have been described in detail by HISS (1975). In the Guadalupe Mountains near Carlsbad Caverns, the elevation of the water table is approximately 3100 ft (BJORKLUND and MOTTS, 1959). This is at least 200 ft below the lowest surveyed level of the accessible vadose zone in Carlsbad Caverns (JAGNOW, 1979). East of the Pecos River, where the Capitan is buried (Fig. 1), water in the Capitan is under confined (artesian) conditions, making recharge by direct vertical infiltration unlikely.

The isotopic compositions of waters from four wells in the eastern (confined) part of the Capitan, whose locations are shown in Fig. 1, are given in Table 3. The small range of δ-values for waters from these wells, relative to the larger range in isotopic compositions of caverns waters, indicates that isotopic mixing and homogenization have been much more efficient in the confined zone than in the unsaturated zone. Such homogenization probably results from longer flow paths, longer residence times, or both.

Water from McKittrick Canyon (Table 1) is similar in δD and δ¹⁸O to eastern confined Capitan waters. This might imply that water from the southern Guadalupe Mountains recharges the confined zones in the eastern parts of the Capitan (*e.g.,* Middleton and Shell No. 28). However, HISS (1975) described the West Laguna Submarine Canyon, a local thinning of the Capitan between the Hackberry and Middleton wells (Fig. 1), as an efficient hydraulic constriction near the northern apex of the Capitan limestone.

Confined hydraulic conditions in the Capitan preclude a direct connection to the surface through the overlying evaporite section. The stable isotope compositions of Capitan groundwaters east of Carlsbad are significantly different from those of modern recharge at lower elevations in the Delaware Basin (Fig. 6) and were probably recharged under different climatic conditions than those that now govern recharge.

Groundwaters in the Rustler Formation

Rustler groundwaters confined within dolomite layers. MERCER (1983) has summarized the general hydrology of the water-bearing gypsiferous dolomite units in the Rustler Formation. Groundwater flow in the Magenta, based on density-corrected potentiometric contours, is westward from the WIPP site toward Nash Draw; Culebra flow is dominantly southward over the WIPP site, then westward. Culebra transmissivity values vary from about 10^{-1} ft²/day east of the WIPP site to 10^3 ft²/day in Nash Draw. Transmissivity values in the Magenta where saturated are about an order of magnitude smaller (MERCER, 1983). Static water-levels are about 100 ft higher in the Magenta than in the Culebra at H-1, H-2, and H-3 (MERCER, 1983) where halite, gypsum, or anhydrite has not been removed from the intervening Tamarisk member by dissolution (SNYDER, 1985); hence, this potentiometric differential indicates a poorly developed vertical connection.

Isotopic compositions of waters from the Rustler Formation are given in Table 3, and plotted in Fig. 6. The plot includes data for waters from the Magenta, Culebra, and Tamarisk members (*i.e.,* Surprise Spring), and shows that with the exception of WIPP-29 Culebra and Surprise Spring, all Rustler well waters are tightly clustered in δD/δ¹⁸O space on or near the meteoric field, spanning no more than 12 per mil in δD and no more than 2.2 per mil in δ¹⁸O. Despite their mutual hydraulic isolation, Magenta and Culebra waters have isotopic compositions that are indistinguishable from one another. These isotopic compositions do not overlap the range of modern meteoric recharge, represented by the modern Ogallala groundwaters.

The two discrete populations of isotopic compositions are divisible according to the hydrologic conditions they represent. The Rustler groundwaters under confined conditions which have meteoric isotopic signatures are more depleted in D and ¹⁸O than other Delaware Basin groundwaters from the vadose zone, perched bodies, or the water table. Thus, the dichotomy in stable isotope compositions of the Rustler waters and modern Delaware Basin recharge at comparable elevations is consistent with the hypothesis that the confined Rustler groundwaters are not currently receiving significant recharge.

The isotopic compositions of groundwaters under confined conditions from the Rustler occupy the same general position in δD/δ¹⁸O space as do the data points for confined groundwaters from the eastern portion of the Capitan Limestone. The tight clustering of δ-values of waters from a widespread

Table 3. Waters from confined units

Location[1]	Sampling date	Depth[2] (ft)	δD‰ SMOW	δ^{18}O‰ SMOW	Analyst[3]
Magenta Dolomite member, Rustler formation					
Collected by USGS					
H-1	04 Jun 76	563–589	−48	−6.8	(a)
H-2A	22 Feb 77	513	−46	−6.3	(a)
H-3	10 May 77	557–608	−53	−7.3	(a)
Collected by Lambert and Robinson					
WIPP-25	17 Sep 80	302–328	−44	−6.2	(b), (c)
			−43		(b)
WIPP-27	25 Sep 80	176–194	−46	−6.3	(b), (c)
			−47		(b)
H-3B1 (= H-3)	01 Jul 85	557–608		−6.7	(c)
				−6.7	(c)
Culebra Dolomite member, Rustler formation					
Collected by USGS					
H-1	02 Jun 76	676–699	−50	−7.0	(a)
H-2B	22 Feb 77	623–645	−53	−7.2	(a)
H-2C	16 Mar 77	623–645	−53	−6.9	(a)
H-3	17 Mar 77	672–694	−53	−7.0	(a)
H-6B	19 Dec 78	604–627	−49		(b)
			−47		(b)
H-9A	05 Feb 80	647–677	−48		(b)
			−49		(b)
H-9B	05 Feb 80	647–677	−51		(b)
			−51		(b)
P-14	14 Mar 77	573–595	−48	−6.3	(a)
P-15	10 May 77	413–435	−52	−7.3	(a)
Indian[4] prob. Culebra	08 Jun 76	203.6	−46	−6.3	(a)
Mobley[5] prob. Culebra	08 Jun 76	89.0	−44	−6.9	(a)
Mobley #3[6] prob. Culebra	08 Jun 76	318.4	−44	−5.9	(a)
Collected by Lambert and Robinson					
WIPP-25	20 Aug 80	447–472	−43	−6.4	(b), (c)
			−44		(b)
WIPP-26	24 Aug 80	186–209	−43	−6.5	(b), (c)
			−44		(b)
WIPP-27	05 Sep 80	292–318	−44	−6.1	(b), (c)
			−47		(b)
WIPP-28	11 Sep 80	420–446	−46	−6.6	(b), (c)
			−46		(b)
WIPP-29	28 Aug 80	012–042	−27	−0.5	(b), (c)
			−27	−0.4	(b), (c)
WIPP-30	06 Sep 80	631–654	−50	−7.1	(b), (c)
			−50		(b)
Collected by HGC					
H-3 [*sic*]	11 Jun 84	672–694	−54		(d)
			−56		(d)
			−53		(d)
			−54		(d)
H-3B3	04 Feb 85	672–694	−53		(d)
			−53		(d)
H-4C	10 Aug 84	490–516	−51		(d)
			−53		(d)
H-9 [*sic*]	06 Oct 83	647–677	−54	−8.0	(e)
DOE-1	20 Apr 83	821–843	−48	−6.1	(e)
Engle	11 Oct 83	423.6	−52	−7.2	(e)
RF-10 (H-13)	06 Oct 83	172–207	−45	−7.3	(e)
Collected by WQSP					
H-4B	25 Jul 85	498–522		−6.7	(d)
				−6.5	(d)

Table 3. (Continued)

Location[1]	Sampling date	Depth[2] (ft)	δD ‰ SMOW	δ18O ‰ SMOW	Analyst[3]
H-5B	27 Aug 85	897–920		−6.8	(d)
				−6.8	(d)
H-6B	15 Sep 85	604–627		−7.1	(d)
H-11B3	04 Jun 85	710		−6.8	(d)
H-12	09 Aug 85	825–852[7]		−6.8	(d)
				−6.9	(d)
				−7.2	(d)
				−6.8	(d)
DOE-1	24 Apr 85	821–843	−58	−6.8	(d)
			−55	−6.9	(d)
			−54	−7.0	(d)
DOE-2	11 Mar 85	822–848	−51	−6.9	(d)
			−51	−6.8	(d)
			−53	−7.1	(d)
			−53		(d)
Engle	04 Mar 85	WL = 423.6	−54	−7.0	(d)
			−57	−7.0	(d)
			−53		(d)
Rustler/Salado contact zone					
Collected by USGS					
Duval Nash Draw mine shaft collector ring	09 Dec 75	≈350	−48	−6.4	(a)
H-1	23 Feb 77	824	−29	1.6	(a)
H-2C	23 Feb 77	764	−41	−2.9	(a)
H-3	23 Feb 77	821	−38	0.2	(a)
H-4C	16 Mar 79	626	−57	−4.0	(a)
H-5C	16 May 79	1041	−44	−1.9	(a)
H-6C	09 Apr 79	721	−53	−4.9	(a)
P-14	24 Feb 77	687	−64	−9.0	(a)
P-17	11 May 79	715	−50	−1.4	(a)
Collected by Lambert and Robinson					
WIPP-25	17 Jul 80	565	−52	−7.1	(b), (c)
			−52		(b)
WIPP-26	23 Jul 80	309	−46	−6.7	(b), (c)
			−47		(b), (c)
WIPP-28	31 Jul 80	531	−58	−7.0	(b), (c)
			−57		(b)
WIPP-29	24 Jul 80	143	−47	−7.0	(b), (c)
			−48		(b)
WIPP-30	17 Jul 80	749	−53	−7.1	(b), (c)
			−51		(b)
Capitan Limestone					
Carlsbad #7	12 Dec 75	143[8]	−54	−7.9	(a)
Shell #28	13 Dec 75	5100	−56	−7.7	(a)
Middleton	10 Dec 75	1700	−55	−7.5	(a)
Hackberry	12 Dec 75	3900	−46	−6.5	(a)

[1] For collection methodologies used by the various indicated agencies, see the following:
USGS: Mercer and Orr (1979); MERCER (1983)
Lambert and Robinson: LAMBERT and ROBINSON (1984)
HGC: HYDRO GEO CHEM (1984)
WQSP: COLTON and MORSE (1985).

[2] Sampling depth or depth interval, from local datum (typically ground level), isolated by packers, casing, perforations, or combinations thereof. WL = depth to water level.

[3] Analysts as follows:
(a) δD and δ18O, J. R. O'NEIL, U.S. Geological Survey.
(b) δD, C. J. YAPP, Univ. of New Mexico.
(c) δ18O, LAMBERT and HARVEY (1987).
(d) δD and δ18O, LAMBERT and HARVEY (1987).
(e) δD and δ18O, Hydro Geo Chem, Tucson, AZ.

[4] 23.30.21.122 as listed by COOPER and GLANZMAN (1971).
[5] "South Well," 23.30.19.123 as listed by COOPER and GLANZMAN (1971).
[6] "Little Windmill Well," 23.30.2.444a as listed by COOPER and GLANZMAN (1971).
[7] Open-hole; no packers or perforations.
[8] Cased to 118 ft depth (HENDRICKSON and JONES, 1952).
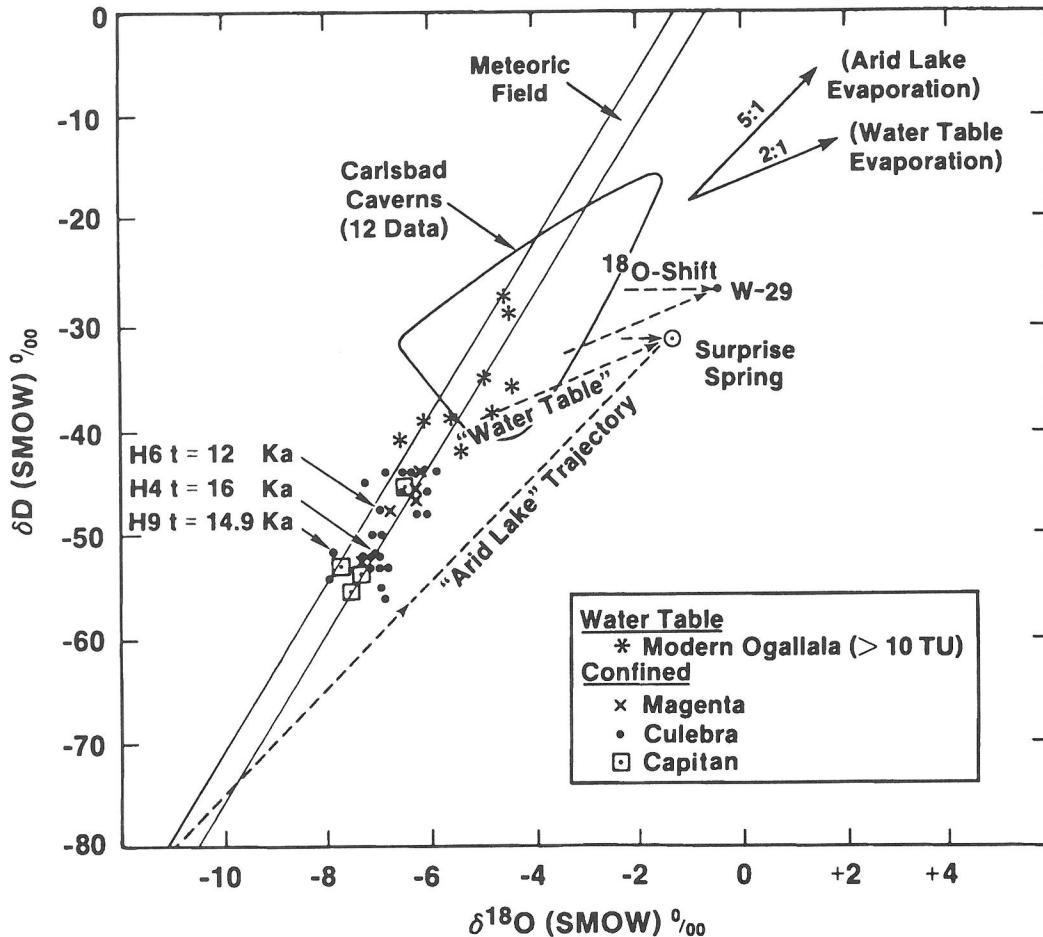
FIG. 6. Stable-isotope compositions of confined groundwaters from the Rustler Formation and Capitan Limestone. The isotopic compositions of demonstrably modern Ogallala groundwaters containing significant (>10 TU) tritium are shown for comparison.

geographic area indicates homogeneous conditions of recharge, long flow paths, long residence times, or a combination thereof, in the confined Capitan and in both the Culebra and Magenta; the last two units are not well connected, except at WIPP-25 and WIPP-27 in Nash Draw (Fig. 2).

WIPP-29 Culebra and Surprise Spring (in the southwestern part of Nash Draw) neither lie near the meteoric field nor bear any similarity to any of the other waters in Nash Draw. At this time it is not possible to determine a unique cause for the isolation of WIPP-29 Culebra and Surprise Spring in $\delta D/\delta^{18}O$ space. Their isotopic compositions, however, show that they are not derived by direct flowage from other Rustler waters, either in Nash Draw or the WIPP site. Discharge from Surprise Spring and its relation with WIPP-29 are discussed below.

Rustler/Salado contact zone. Groundwater flow in the Rustler/Salado contact zone (the "brine aquifer" of ROBINSON and LANG, 1938) as described by MERCER (1983) is southwest across the WIPP site toward Nash Draw. Stable isotope data for waters from the zone near the Rustler/Salado contact are given in Table 3 and are plotted in Fig. 7. There is no overlap between any of the data for Rustler/Salado contact waters and the field of modern recharge. Also, δ-values of waters from the Rustler/Salado contact in and near Nash Draw are clustered near the meteoric field. δ-values of waters from farther east near the WIPP site deviate significantly from the meteoric field. The cause of this deviation is probably related to the eastward decrease in transmissivity (*i.e.,* effective water/rock ratio), from 10^1 to 10^{-4} ft^2/day. Partial evaporation is not a plausible cause for the deviation from the meteoric field, because water from the zone near the Rustler/Salado contact is under confined conditions in Nash Draw and at the WIPP site (MERCER, 1983).
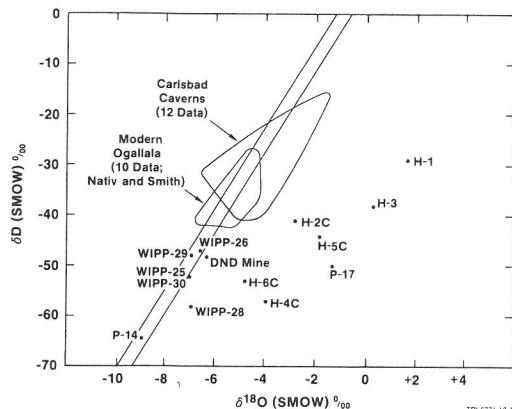
FIG. 7. Stable-isotope compositions of groundwaters from the Rustler/Salado contact.

The geographic distribution of isotopic variations of Rustler/Salado contact waters is shown in Fig. 8. The contours depict arithmetic deviations of the $\delta^{18}O$ values from the mean regional meteoric value of -7, represented by the isotopic compositions of meteoric Rustler/Salado contact waters in the high-permeability region of Nash Draw. These contours generally parallel the dissolution/subsidence scarp that defines the eastern boundary of Nash Draw. The zero contour is offset about 1.5 to 3 km east of the scarp, and roughly corresponds to the division between higher values of transmissivity to the west ($>10^{-2}$ ft^2/day) and lower values ($<10^{-2}$ ft^2/day) to the east.

Superimposed on the contours of oxygen isotope shift in Fig. 8 are the boundaries of zones delineated by SNYDER (1985) according to the uppermost occurrence of halite in the Rustler Formation. The zones are, from southeast to northwest: (1) top of halite in the Forty-niner member, above the Magenta Dolomite, (2) top of halite in the Tamarisk member, between the Magenta and Culebra Dolomites, (3) top of halite in the lower (unnamed) member, below the Culebra Dolomite, and (4) top of halite in the Salado Formation, with no halite in the Rustler Formation. The contours roughly parallel the boundaries of Rustler halite zones, and the +3 per mil contour partly coincides with the western-most occurrence of Rustler halite. The west-to-east increase in isotopic deviation indicates that circulation of meteoric fluids is more restricted toward the east, reflecting a smaller water/rock ratio. This is consistent with Mercer's conclusion that the extreme variability (i.e., east-to-west increase) of transmissivities in the various parts of the Rustler Formation results from the size and number of fractures, which in turn are related to the degree of evaporite dissolution within the Rustler Formation.

The $\delta D/\delta^{18}O$ trend for waters from zones of lower permeability, represented by H-1, H-2C, H-3, H-4C, H-5C, H-6C, and P-17 in Fig. 7, intersects with the meteoric field at isotopic compositions representative of much of the Rustler, reflecting a meteoric origin. Greater displacements from the meteoric field along this trend are generally correlative with smaller water/rock ratios. This trend is reminiscent of that resulting from water/rock interactions with small water/rock ratios, but whether such interactions consist of isotopic exchange between small amounts of meteoric water and mineral sources such as gypsum and polyhalite, or mixing with evaporite brines as proposed by KNAUTH and BEEUNAS (1986) and O'NEIL et al. (1986), is not known.

The age of Rustler groundwaters

LAMBERT (1987) found that application of the model of EVANS et al. (1979) to 12 of 16 selected Rustler groundwaters gave significantly large negative radiocarbon ages, reflecting the addition of excess modern (anthropogenic) carbon, introduced during drilling operations and contaminating the native fluid. The remaining four groundwaters have the following apparent ages (in radiocarbon years): H-4, 16,100; H-9, 14,900; H-6, 12,100 (all Culebra); Pocket (Dewey Lake), 14,000. These apparent ages are statistically indistinguishable from one another.

The stable isotope compositions of these dated groundwaters are marked in Fig. 6 and are distinct from those of the tritium-bearing Ogallala groundwaters inferred to have been recharged under present regional climatic conditions. Given that these groundwaters could contain traces of contaminant ^{14}C, their apparent radiocarbon ages are regarded as minimum times of isolation from the atmosphere. These residence times probably represent the time of cessation of recharge at the close of an interval of wetter climate in the Pleistocene. Independent evidence of wetter Pleistocene climate in southeastern New Mexico has been presented by VAN DEVENDER (1980), who determined from packrat middens in Rocky Arroyo east of Carlsbad (Fig. 1) that a juniper-oak plant community existed there 10,500 to 10,000 years ago, at an elevation of about 3600 ft, where desert scrub communities have been stable for the last 4,000 years.

A limited number of high-precision tritium measurements are also available for Culebra and Dewey Lake groundwaters near the WIPP site. Figure 9 shows the geographic distribution of wells whose waters were analyzed for tritium. Tritium values from the WIPP site and the area immediately south range from -0.08 to $+2.8$ TU. Such low but mea-
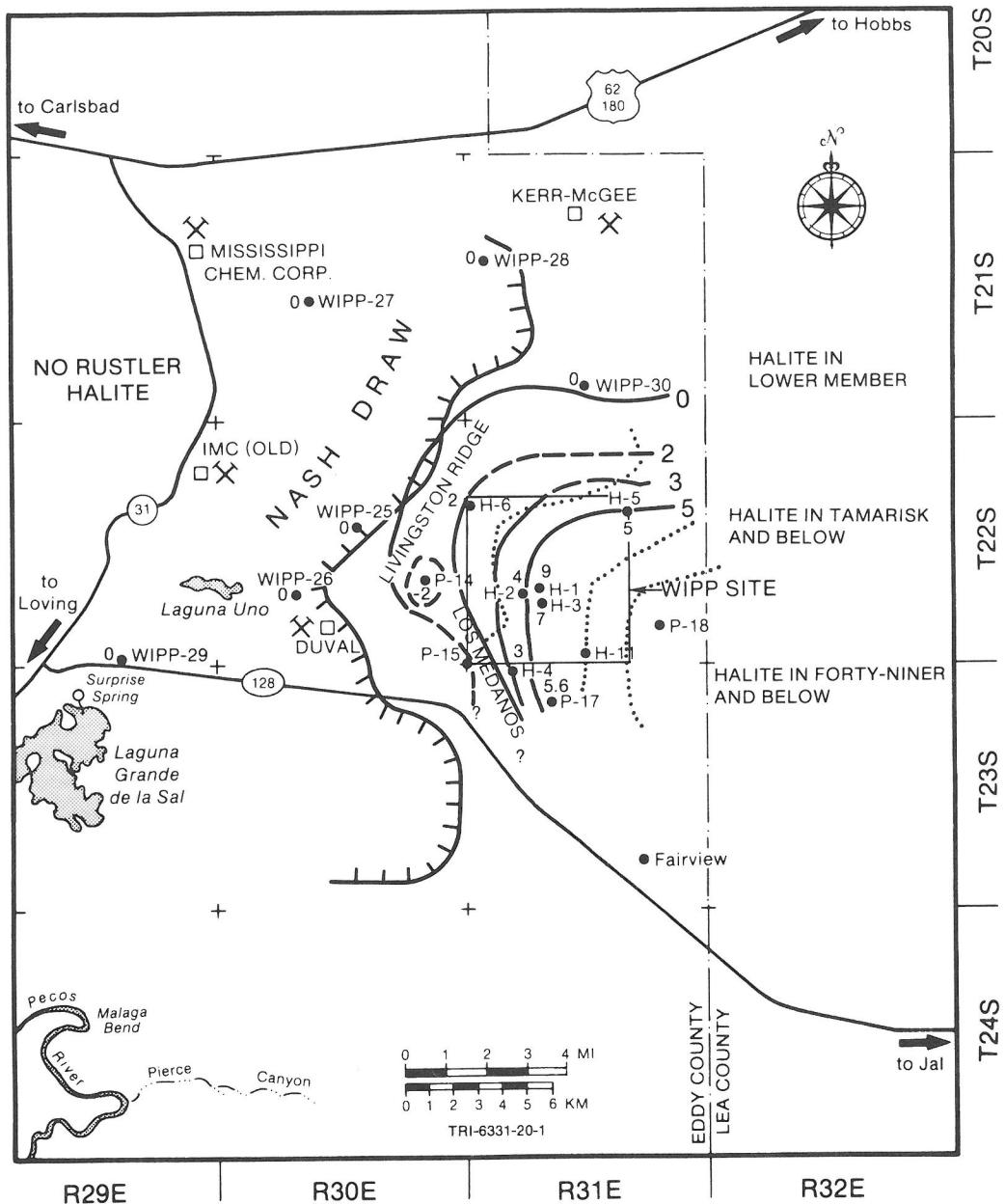
FIG. 8. Contour map of oxygen-isotope deviation in confined groundwaters at the Rustler/Salado contact, relative to $\delta^{18}O = -7$. Dotted lines are boundaries of SNYDER (1985) delineating the occurrences of halite in various members of the Rustler.

surable tritium counts are generally considered indistinguishable from zero, according to EVANS *et al.* (1979). Thus, the tritium data from seven localities show conclusively that the travel time between the surface and the Culebra or parts of the Dewey Lake has been greater than 40 years, since these waters do not contain the tritium spike that was introduced into the atmosphere by post-1950 nuclear detonations.

The radiocarbon dates show that the time of isolation from the atmosphere for groundwaters at four widely separated locations (Fig. 9) has been at least 12,000 years; in the absence of a statistically significant difference among the four radiocarbon dates, a significant north-to-south age gradient cannot be inferred. The age range 12,000 to 16,000 radiocarbon years is tentatively considered the minimum residence time of the Rustler, Dewey
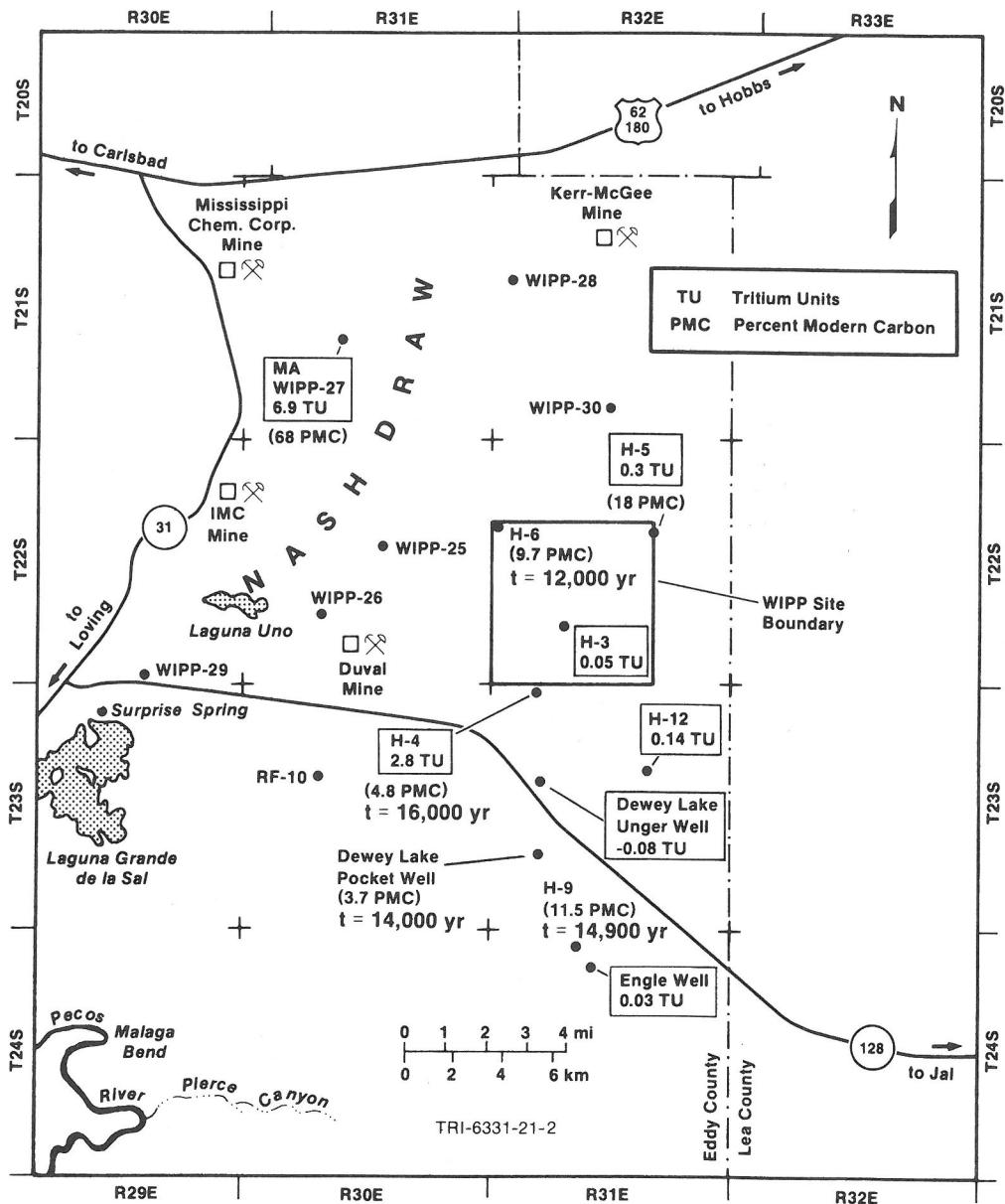
FIG. 9. Tritium and radiocarbon in Rustler and Dewey Lake groundwaters. Unless otherwise specified as Dewey Lake or Magenta (MA), measurements apply to water from the Culebra member of the Rustler Formation. Tritium Units (TU, 1 part tritium in 10^{18} total hydrogen) enclosed in rectangles. The PMC values at H-5 and WIPP-27 are probably contaminated.

Lake, Triassic, and Capitan groundwaters having similar stable isotope compositions throughout the northern Delaware Basin. Water at least this old is therefore a significant component of the confined Culebra waters having more negative meteoric δ-values. Despite differences in depth (Dewey Lake vs. Culebra), geographic position along a north-south line (H-4, H-6, and H-9 in the Culebra), and two and one-half orders of magnitude variation in

Culebra transmissivity (0.65, 33, and 110 ft²/day for H-4, H-6, and H-9, respectively; BEAUHEIM, 1987, 1989), carbon isotope systematics indicate uniform late Pleistocene ages for these four borehole samples. Holocene recharge and mixing have not been rapid enough to result in post-Pleistocene radiocarbon ages.

The isotopic data indicate that the Rustler groundwaters at the WIPP site and probably over

much of Nash Draw are not now receiving significant amounts of modern meteoric recharge. The four late Pleistocene apparent ages derived from radiocarbon measurements of waters more depleted in ^{18}O and D relative to modern recharge suggest that the isotopically lighter population represents southeastern New Mexico paleowater, distinct from recharge under modern climatic conditions, analogous to the findings of GAT and ISSAR (1974) for groundwater in the Sinai Desert. Even if the δD, $\delta^{18}O$, and percent modern carbon (PMC) values of radiocarbon-dated groundwater resulted from mixing of more than one reservoir, the hydrogen, oxygen, and carbon isotope data constitute compelling evidence that at least some of the confined groundwaters in the Delaware Basin having δD values more negative than -42 and $\delta^{18}O$ values more negative than -5.5 at elevations of about 3000–4000 ft are not 100% modern.

Discharge from Surprise Spring and WIPP-29 Culebra

Waters from Surprise Spring and WIPP-29 Culebra, the southwestern-most groundwater sampling point in Nash Draw (Fig. 2) both exhibit a profound difference in isotopic composition from other Rustler waters. Both have a significant deviation from a meteoric $\delta D/\delta^{18}O$ signature (see Fig. 6). MERCER (1983) argued, on hydraulic evidence, that Surprise Spring has no connection with the underlying Culebra member. Taken together, the solute and the stable isotope evidence confirm the independent behavior of Surprise Spring.

The WIPP-29 area is strategically located between Surprise Spring and points upgradient at the WIPP site and in Nash Draw. Hence, the WIPP-29 area (Fig. 2), where the top of the Culebra member is 12 feet beneath the surface, would intercept hypothetical flow paths from the Culebra to Surprise Spring, assuming the hydraulic conductivity is continuous along each path. The degree to which Surprise Spring discharges water from the Culebra and Rustler/Salado contact zone can be evaluated using the chloride/$\delta^{18}O$ systematics for the Culebra and Rustler/Salado zones at the WIPP site and Nash Draw, in relation to Surprise Spring, as depicted in Fig. 10. Evaporation will increase the solute concentrations and will also make the $\delta^{18}O$ and δD values more positive (CRAIG et al., 1963). Figure 10 shows that it is not possible to derive Surprise Spring water directly by evaporation of Culebra or basal brine-aquifer water having more chloride than Surprise Spring (30,000 mg/l). Such evaporation would indeed enrich the residual solution in ^{18}O, but would not dilute the chloride. Furthermore,
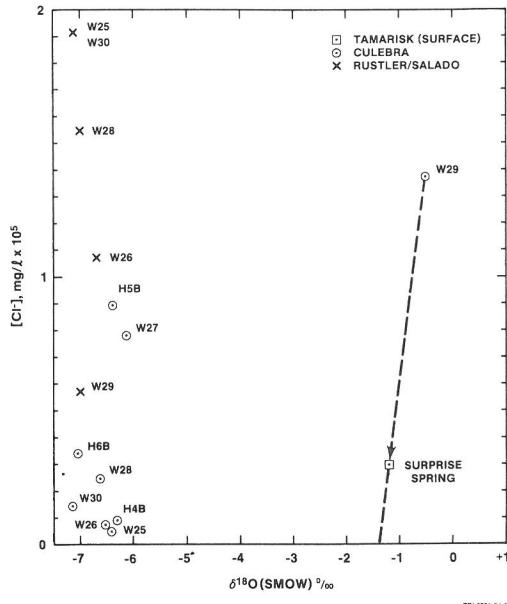

FIG. 10. Dissolved chloride versus $\delta^{18}O$ for Rustler groundwaters in Nash Draw and at the WIPP site.

derivation of WIPP-29-like Culebra water from any of the waters would require (1) a greater increase in total dissolved solids than could be achieved by evaporation alone, for the observed degree of evaporation-induced isotope shift (see CRAIG et al., 1963), and (2) a mechanism for evaporating water from a zone confined at its upper surface, since the Culebra at WIPP-29 is at least partially confined. Whereas the first requirement can be easily met by evaporite dissolution along the flow path, the second requirement is more demanding, since the condition of even partial confinement, by definition, precludes an unconfined surface from which water can evaporate.

Derivation of Surprise Spring directly from the nearby Culebra, represented by WIPP-29, would entail a reduction in chloride from 138,000 to 30,000 mg/l. This could be accomplished by dilution, but would require water with a $\delta^{18}O$ value of -1.4 (as indicated by the $[Cl^-] = 0$ intercept of the dashed line in Fig. 10). Water of this isotopic composition is in principle obtainable in the summer months (Table 1), but the required dilution factor of 4.6 in chloride alone would then make local surficial recharge a much more abundant component than water derived directly from WIPP-29.

The anomalous isotopic compositions of WIPP-29 Culebra and Surprise Spring waters are probably related to locally derived recharge from the surface, with enrichment in ^{18}O due to partial evaporation or rock-water interaction. HUNTER (1985) argued

for locally derived surface runoff recharging the Rustler in the vicinity of WIPP-29, originating as spillage of water imported from the Ogallala for potash refining. Less than 300 ft from WIPP-29, for example, is a small, relatively permanent pond that came into being since the beginning of local potash-refining activity. Laguna Uno (Fig. 2), upgradient from WIPP-29, is of similar origin (HUNTER, 1985).

Water having an isotopic composition similar to that of Surprise Spring or WIPP-29 Culebra might be derived by oxygen isotope shift (see CRAIG, 1966) from the inferred modern meteoric water represented by the James Ranch, San Simon, and many Ogallala data, along a nearly horizontal trajectory labelled "^{18}O-shift" in Fig. 6. Given the high local water/rock ratio (transmissivity = 10^3 ft^2/day as reported by MERCER, 1983), this is unlikely.

The origin of the WIPP-29 Culebra water and the Surprise Spring discharge water as spillage from nearby refineries would make them susceptible to kinetic fractionation by partial evaporation. One hypothetical $\delta D/\delta^{18}O$ trajectory is drawn through the WIPP-29 Culebra and Surprise Spring points in Fig. 6 with a slope of five, based on results of HOY and GROSS (1982) for two analyses of standing water from Bitter Lakes near Roswell, New Mexico. This trend is labelled "Arid-Lake Trajectory" and intersects the meteoric field in the δD range -70 to -80, not the -50 characteristic of the rest of the Rustler. As suggested above, such a mechanism of evaporation does not appear warranted by local conditions.

HUNTER (1985) proposed that Ogallala-derived imported water spilled on the surface in southwestern Nash Draw recharges a local water table. Evaporation taking place in the unsaturated zone above a water table would move the isotopic composition of the residual liquid along a $\delta D/\delta^{18}O$ trajectory having a slope of approximately two (ALLISON, 1982), rather than about five for evaporation from a free water surface. By such evaporation, it is possible to derive waters having isotopic compositions similar to those of WIPP-29 Culebra and Surprise Spring from waters having δD and $\delta^{18}O$ values similar to those of modern Ogallala groundwaters, as illustrated by the trajectory labelled "Water-Table" in Fig. 6. Therefore, local processes can account for the origin of Surprise Spring and WIPP-29 Culebra waters. However, imported Ogallala water cannot be distinguished from local modern recharge solely on the basis of isotopic compositions, due to their probable similarities.

Isotopic compositions of carbonates

Several samples of carbonate rock coexisting with water, including Magenta and Culebra reservoir rock from the Rustler Formation and surficial travertine deposits in McKittrick Canyon, were collected in order to evaluate the degree of rock/water interaction taking place in carbonate/water systems in the Delaware Basin, and to determine reasonable origins for the carbonates. The $\delta^{13}C$ and $\delta^{18}O$ values of carbonates, together with cumulative CO_2 yields, are given in Table 4.

McKittrick Canyon travertine. Calcite was sampled from the outermost layers of the travertine deposit coexisting with the water sampled from McKittrick Canyon (Fig. 1, Table 1), and its $\delta^{18}O$ and $\delta^{13}C$ values determined. The outermost (youngest) layers of an active travertine deposit are assumed to represent calcite deposition in isotopic equilibrium with its coexisting water. The travertine system sampled in this study consists of a small pond, approximately 10 ft wide and 20 ft long, recharged by an upstream spillway (a natural sluice) and discharging into another spillway downstream. The presumed-active travertine and its coexisting water were sampled from the upper sluice. $\delta^{18}O$ and $\delta^{13}C$ values for other nearby surficial calcites were determined as well.

Rustler Formation carbonates. Magenta and Culebra dolomite reservoir rock was sampled from several cored holes that produced water. The radioiodide tracejector tests of MERCER and ORR (1979) indicated that only a fraction of the total unit thickness produces most of the water. This zone is inferred to have a higher fracture density; such rock does not provide competent core, but falls out of the core barrel as poorly sorted angular to subrounded rubble. The most fractured zones were sampled in hopes that they would be most likely to have experienced rock/water interaction due to local maxima in rock surface-areas.

$\delta^{18}O$ values of all dolomites, both Magenta and Culebra, fall into a very narrow range, with a mean of $+33.4$; the mean $\delta^{13}C$ value is $+6.1$. Dolomite δ-values are independent of depth and geographic location, indicating either uniformity of geochemical conditions governing Permian deposition or a widespread episode of uniform postdepositional alteration.

The $\delta^{13}C$ values of Rustler dolomites are higher than those of most of the lacustrine Pleistocene dolomites from the west Texas high plains, reported by PARRY *et al.* (1970). Although one of their values was as high as $+5.8$, none of their dolomites with $\delta^{18}O$ values comparable to those in the Rustler had $\delta^{13}C$ values as high as in the Rustler. PARRY *et al.* (1970) suggested that their dolomites formed under conditions in which evaporation is extreme, with or without a calcite precursor.

S. J. Lambert

Table 4. Stable-isotope composition of carbonates

Sample name[1]	Extraction	Yield, %[2]	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$ ‰ SMOW
Culebra Dolomites				
H-4B 509/517	3-day	45 (D)	5.8	34.3
	6-day	19 (D)	5.8	35.1
		64 (Σ)		
	3-day	41 (D)	5.3	33.4
H-5B 912	3-day	32 (D)	5.8	32.3
	6-day	23 (D)	5.8	32.5
		55 (Σ)		
	3-day	41 (D)	5.9	32.6
H-6B 616	3-day	41 (D)	5.9	33.4
	6-day	24 (D)	6.1	33.9
		65 (Σ)		
	3-day	45 (D)	5.9	33.4
WIPP-25 461	3-day	44 (D)	6.2	33.7
	6-day	21 (D)	6.3	34.2
		65 (Σ)		
	3-day	48 (D)	6.1	33.7
WIPP-26 198/208	3-day	49 (D)	5.7	34.3
	6-day	24 (D)	5.7	34.8
		73 (Σ)		
	3-day	49 (D)	5.4	33.9
WIPP-27 307/308	3-day	40 (D)	6.1	33.7
	6-day	25 (D)	6.2	34.0
		65 (Σ)		
	3-day	42 (D)	5.9	33.6
WIPP-28 431	3-day	44 (D)	5.9	33.4
	6-day	27 (D)	6.0	33.7
		71 (Σ)		
	3-day	42 (D)	5.8	33.2
WIPP-29 35	3-day	52 (D)	5.5	33.4
	6-day	22 (D)	5.6	33.8
		74 (Σ)		
	3-day	53 (D)	5.4	33.4
	3-day	52 (D)	5.4	33.3
WIPP-30 640.2–640.3	3-day	44 (D)	6.0	33.4
	6-day	21 (D)	6.0	34.2
		65 (Σ)		
	3-day	44 (D)	5.8	33.0
WIPP-33 549.8–550.3	1-hour	7 (C)	−2.8	24.7
	2-hour	8 (C)	−2.9	24.5
	2-hour	7 (C)	−2.9	24.5
Magenta Dolomites				
WIPP-25 328.8–328.9	3-day	24 (D)	6.5	33.1
	6-day	12 (D)	5.9	32.0
		36 (Σ)		
	3-day	28 (D)	6.5	33.1
WIPP-28 293.7–294.1	3-day	44 (D)	6.6	33.1
	6-day	9 (D)	6.6	33.4
		53 (Σ)		
	3-day	45 (D)	6.6	33.0
	6-day	6 (D)	6.6	33.5
		51 (Σ)		
	3-day	53 (D)	6.6	32.5
WIPP-30 536.5–536.7	3-day	42 (D)	7.2	33.1
	6-day	22 (D)	7.4	33.3
		64 (Σ)		
	3-day	45 (D)	7.2	33.1
	6-day	13 (D)	7.4	33.5
		58 (Σ)		

Table 4. (Continued)

Sample name[1]	Extraction	Yield, %[2]	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$ ‰ SMOW
Travertine (McKittrick Canyon)				
Sluice crust	overnight	90 (C)	−7.9	+22.9
Dry crust # 1	overnight	90 (C)	−8.5	+23.4
Dry crust # 2	overnight	85 (C)	−7.1	+24.3
Dry crust # 3	overnight	88 (C)	−6.7	+24.5
Dry crust # 4	overnight	93 (C)	−7.3	+23.7

[1] Hole name and core depth, in feet. Hyphenated intervals are precisely known. Intervals delineated by "/" indicate that the sample originated from somewhere in the rubble between the tabulated depths. Single footages are given for rubble whose depth is known only to the nearest foot.

[2] (D) = weight % dolomite

(C) = weight % calcite

(Σ) = cumulative yield after 6-day reaction.

Isotope exchange between carbonates and water

Apparent oxygen isotope fractionation factors (α-values) for the coexisting carbonate/water pairs were calculated, using mean $\delta^{18}O$ values if replicate determinations were available, according to the relationship

$$\alpha = \frac{\dfrac{\delta^{18}O(calcite)}{1000} + 1}{\dfrac{\delta^{18}O(water)}{1000} + 1}. \qquad (1)$$

The calculated values of α are given in Table 5. No representative water sample was collected from WIPP-33, so the water $\delta^{18}O$ value is the mean of $\delta^{18}O$ values of confined Rustler waters from the other boreholes described in Table 5.

Dolomite/water. Except for WIPP-29 Culebra, whose isotopic composition deviates from the meteoric field (Fig. 6), the calculated dolomite/water fractionation factors are between 1.0395 and 1.0409. The equilibrium fractionation factor for $^{18}O/^{16}O$ partitioning between dolomite and water at ambient temperatures is not precisely known, because of extremely low exchange rates in experiments at low temperatures (*e.g.,* NORTHROP and CLAYTON, 1966). WEBER (1964) estimated that it is about 1.037. If this is the case, these dolomite-water pairs clearly cannot be in oxygen isotope equilibrium.

Regardless of the origin of the dolomites, they appear not to have participated in significant isotopic exchange with the water they contain at present. This does not preclude dissolution of dolomite, which leaves no material to preserve the isotopic record and which has probably occurred during the development of secondary porosity in the Rustler.

Calcite/water. The calculated $^{18}O/^{16}O$ fractionation factors for coexisting calcite and water allowed oxygen isotope equilibrium temperatures of calcite formation to be calculated, according to the equation of O'NEIL *et al.* (1969), and modified by FRIEDMAN and O'NEIL (1977):

Table 5. Carbonate/water isotopic fractionation factors

Locality	$\delta^{18}O$ (carbonate) ‰	$\delta^{18}O$ (water) ‰	α (carbonate/water) calculated
Calcites			
McKittrick Canyon Travertine			
Sluice crust	22.9	−8.1[1]	1.0313
Culebra Mbr., Rustler Fm.			
WIPP-33	24.6	−6.6[2]	1.0314
Dolomites			
Magenta Mbr., Rustler Fm.			
WIPP-25	33.1	−6.2	1.0395
Culebra Mbr., Rustler Fm.			
H-4B	34.0	−6.6	1.0408
H-5B	32.6	−6.8	1.0396
H-6B	33.5	−7.1	1.0408
WIPP-25	33.6	−6.4	1.0404
WIPP-26	34.1	−6.5	1.0409
WIPP-27	33.8	−6.1	1.0400
WIPP-28	33.3	−6.6	1.0402
WIPP-29	33.4	−0.5[3]	1.0339
WIPP-30	33.3	−7.1	1.0406

[1] Measured on water sample from upper sluice.

[2] Mean value from Culebra, other boreholes in this table.

[3] Deviates from meteoric signature.

$$1000 \ln \alpha = 2.78(10^6 T^{-2}) - 2.89. \quad (2)$$

A temperature of 14.1°C was calculated for the formation of McKittrick Canyon travertine in the sluice crust from the apparent $^{18}O/^{16}O$ fractionation factor for calcite in the sluice crust and the water running down the sluice (Table 5). This is a reasonable value for ambient conditions, indicating that the coexisting carbonate and water are very nearly at isotopic equilibrium. From the $\delta^{18}O$ values of the other travertines (Table 4) and the assumed temperature (14°C), $\delta^{18}O$ values were calculated for waters from which the older travertines were formed. These values range from -6.6 to -7.7. The total range -6.6 to -8.1 may be quite reasonable for the oxygen isotope composition of modern meteoric water at the elevation of McKittrick Canyon (6000 ft), and may reflect some seasonal variations.

Rustler calcite has been found only in the Culebra core from borehole WIPP-33, drilled in a surficial depression about 10 ft deep. The borehole stratigraphy, described by BACHMAN (1985), includes dissolution cavities in the subsurface Rustler gypsum; partial collapse of some of these cavities led to subsidence at the surface.

This cavity collapse resulted in conditions favorable to the local dissolution of the original dolomite and precipitation of secondary calcite in the Culebra. Calcite $\delta^{13}C$ and $\delta^{18}O$ values of -2.9 and $+24.6$, respectively, are much lower than those of the dolomites. The observed calcite-water $^{18}O/^{16}O$ fractionation factor, 1.0314, yields a temperature of crystallization of 13.8°C according to Eqn. (2). This reasonable temperature is consistent with the formation of calcite in oxygen isotope equilibrium with water having a $\delta^{18}O$ value of about -7, in a system where the water/rock ratio was large. The profound difference between the calcite $\delta^{13}C$ value (-2.9) and those of surrounding dolomites (about $+6$) implies that the calcite carbon was not derived from dissolved dolomites, but may have been influenced by introduced aqueous carbon species. The age of formation of the calcite is unknown.

CONCLUSIONS

Fossil groundwater in the Rustler Formation

Seasonally integrated modern precipitation that recharges groundwater in the northern Delaware Basin is represented by groundwaters in water-table and perched systems, which are inferred to have an existing hydraulic connection with the surface. The isotopic compositions of waters from wells in alluvium, the Ogallala Sandstone, and parts of the Dewey Lake Red Beds indicate that modern recharge water in the northern Delaware Basin has a

δD value more positive than about -42, and a $\delta^{18}O$ value generally more positive than -5.5. Groundwaters under hydraulically confined conditions in the Rustler Formation have more negative δ-values that do not overlap with those of demonstrably modern recharge. The differences in isotopic composition between the two populations indicate that modern recharge in the northern Delaware Basin is minimally contributing to the confined groundwaters.

Evidence of isotopic exchange between Ochoan rock and typical meteoric Rustler-type water has been found only in a local collapse structure. Interactions between Rustler groundwater and its host rock result mainly in the dissolution rather than recrystallization of dolomite, but calcite has locally precipitated in isotopic equilibrium with Rustler groundwater.

Among the confined Rustler Formation groundwaters, tritium concentrations show a residence time greater than about 40 years, and radiocarbon dating shows isolation from the atmosphere for at least 12,000 to 16,000 years. The climatic conditions that formerly governed Rustler recharge, inferred from contemporaneous packrat middens, were probably different from those at present. The difference in isotopic compositions between Rustler waters and waters receiving demonstrably modern active recharge from precipitation at surface elevations < 4000 ft is consistent with the hypothesis that the last major recharge event for Rustler waters was in the late Pleistocene. This hypothesis also applies to other confined groundwaters in the northern Delaware Basin that have stable isotope compositions similar to those of the three radiocarbon-dated Rustler waters and the one dated Dewey Lake water, and which have no hydraulic connection with mountainous recharge areas at elevations >4000 ft. Thus, confined groundwaters in the Capitan and Rustler formations may have been recharged under similar climatic conditions.

The stable isotope compositions of groundwater systems in the Delaware Basin appear to reflect at least two generations of meteoric recharge: localized recharge under modern climatic conditions and more widespread paleorecharge to groundwaters now under confined conditions. The cessation of recharge to the Rustler Formation in the late Pleistocene left a fossil groundwater system. Continued groundwater movement, suggested by potentiometric contours and inferred southward flowlines, implies that discharge may now exceed recharge.

Discharge from the Rustler Formation

Stable isotope, solute, and hydraulic evidence indicate that Surprise Spring and the near-surface

water in the Culebra at WIPP-29 are part of a shallow groundwater system, probably largely under water-table conditions, derived from surface water largely imported by potash refiners and recharging the Rustler through local gypsum karst developed above the Culebra. Any possible contribution from confined waters in east-central Nash Draw and the WIPP site is overwhelmed by the surficial contribution. This local system may increase in importance with an increase in rainfall recharging the local gypsum karst. At the present time, Rustler water from the WIPP site does not appear to be discharging at the surface in southwestern Nash Draw.

Paleoclimatic and hydraulic implications

An important implication of fossil water in the Rustler Formation is that hydraulic measurements of the present system are indicative of only modern transient conditions. These measurements, then, may not be relevant to the past steady-state conditions of the Rustler Formation (>10,000 years ago), nor will they necessarily be relevant over the next 10,000 years if the climate changes. The packrat-midden evidence shows that in the immediate vicinity of the Delaware Basin, a wetter climate prevailed more than 10,000 years ago. The correspondence between the climatic transition from wetter to drier and the residence time of some Rustler and Dewey Lake groundwaters (12,000 to 16,000 years) is probably significant.

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