Waste Isolation Pilot Plant

Compliance Certification Application

Reference 378

Lambert, S.J. and D.M. Harvey, 1987.
Stable-Isotope Geochemistry of Groundwaters In the Delaware Basin of Southeastern New Mexico, SAND87-0138, Albuquerque, NM, Sandia National Laboratories.

Submitted in accordance with 40 CFR §194.13, Submission of Reference Materials.

6335

SANDIA REPORT
SAND87—0138 • UC—70
Unlimited Release
Printed December 1987

Stable-Isotope Geochemistry of Groundwaters in the Delaware Basin of Southeastern New Mexico

Steven J. Lambert, Dixie M. Harvey

LONG-TERM REGULATORY COMPLIANCE

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789

LONG-TERM REGULATORY COMPLIANCE

SAND87-0138
Unlimited Release
Printed December 1987

Distribution
Category UC-70

STABLE-ISOTOPE GEOCHEMISTRY OF GROUNDWATERS IN THE DELAWARE BASIN OF SOUTHEASTERN NEW MEXICO

Steven J. Lambert and Dixie M. Harvey
Earth Sciences Division 6331
Sandia National Laboratories
Albuquerque, New Mexico 87185

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 waters at the Waste Isolation Pilot Plant (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 to alluvium, sandstones in the Ogallala Formation, the near-surface Rustler in southwestern Nash Draw, and the Capitan vadose zone in the Guadalupe Mountains (Carlsbad Caverns) constitute a distinctly different population; the two do not overlap. A likely explanation for this distinction is that meteoric recharge to most of the Rustler and Capitan took place in the geologic past under climatic conditions significantly different from 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. Processes governing recharge in the Delaware Basin are significantly different from those in the nearby Roswell Artesian Basin, but may be similar to those previously described for the Albuquerque (New Mexico) and Murray (South Australia) Basins. Rustler water from the WIPP site and east-central Nash Draw is not discharging from springs in southwestern Nash Draw; the discharge there is part of a local shallow groundwater system associated with surficial gypsum karst and discharge from nearby potash refining. Water at the Rustler/Salado contact at the WIPP site is of meteoric origin, but has experienced isotope shift that increases with decreasing permeability, and is part of the same isotopic trend as the ERDA 6 brine occurrence and fluid inclusions from Salado Formation halite core. Radiometric ages of secondary Salado minerals are not consistent with vertical mixing between deep brines and meteoric waters to form the fluid inclusions. Mine seeps and WIPP fluid inclusions have similar isotopic compositions, perhaps related to syndepositional mixing of evaporite brines and rainwaters. Rustler dolomites have not recrystallized in isotopic equilibrium with Rustler water, but much of the gypsum in the Ochoan section has done so.

The absence of modern meteoric recharge to the Rustler 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 some 10,000 to 30,000 years ago.

EXECUTIVE SUMMARY

A total of 118 samples from the northern Delaware Basin in southeastern New Mexico, from 106 discrete locations, has been analyzed for their stable-isotope compositions. The total number of replicate analyses was 181. These include 97 ground- and surface-water samples which were analyzed for their D/H and $^{18}O/^{16}O$ ratios. Nineteen carbonates, 14 of which were groundwater host-rocks and 5 of which were travertines, were analyzed for their $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios. D/H ratios were determined for the water of crystallization of two gypsums.

Most groundwaters were taken from pump- or bail-tests of wells in the Rustler Formation near the Waste Isolation Pilot Plant (WIPP) site. Three fluid-producing horizons in the Rustler Formation have been extensively hydraulically tested, sampled, and analyzed for various solution parameters; because these horizons occur near the WIPP site and nearby Nash Draw (a solution valley developed in the Rustler outcrops to the west), they have been identified as likely transport media for radionuclide-contaminated groundwaters. These three units are, in descending stratigraphic sequence, the Magenta dolomite member, the Culebra dolomite member, and the basal Rustler zone near its contact with the underlying Salado Formation. The Salado Formation contains the evaporite sequence in which the WIPP subsurface facility is being constructed. The hydrologic subunit that appears to have the most regionally persistent productivity is the Culebra, and it has supplied the most water (n=37) and aquifer-rock (n=9) samples in this study. Three Culebra waters have been successfully radiocarbon-dated, and tritium measurements have been performed on five Culebra waters and one Magenta water (Lambert, 1987). Rustler groundwaters are under confined conditions at the WIPP site and in many parts of east-central Nash Draw. In addition to the Rustler Formation, the overlying Dewey Lake Red Beds have been sampled in three localities near the WIPP site, one sample of which has been radiocarbon-dated. Water in the Dewey Lake is

believed to be perched in many localities, but is not regionally persistent in its occurrence.

For comparison, several other groundwaters in the region were analyzed. These include four samples from the Capitan limestone where it is under confined conditions, 12 from a long-suspected major vadose Capitan recharge zone (Carlsbad Caverns in the northern Guadalupe Mountains), one from the Triassic rocks, and one from alluvium. Three stormwaters, two streamwaters, and water from Surprise Spring (discharging from the Tamarisk member of the Rustler Formation in southwestern Nash Draw) complete the suite of major water-sampling. A few deep-basin groundwaters associated with Salado evaporites and deeper rocks were also analyzed, and include four samples from seeps in salt mines (two from the WIPP itself), one from Castile brine reservoir (the ERDA 6 occurrence), one from the underlying Bell Canyon sandstone, and two from the Morrowan (Pennsylvanian) limestone.

According to geological, hydrological, and geochemical criteria several samples from pump- or bail-tests were judged to be not representative of the fluid reservoir at depth, due to probable mixing and contamination. These include, but might not be restricted to: the Magenta water from WIPP-30, the Culebra water from P17, P15, and P18, and Rustler/Salado contact water from P15, P18, and WIPP-27. Even though some of these water samples were analyzed in the absence of additional criteria for evaluating their validity, their δ-values, if available, were not used in the interpretations here.

Capitan, Dewey Lake, Triassic, alluvial, most Rustler, and surface waters analyzed all have $\delta D/\delta^{18}O$ relationships that indicate a direct meteoric origin, with little alteration by partial evaporation or rock/water interaction. In this context the term "meteoric" implies only an origin from precipitation, <u>not</u> that the time of such origin is necessarily "modern." The meteoric groundwaters fall into one of two distinct populations of δD and

$\delta^{18}O$ values. The dichotomy is related to local hydrologic conditions. All confined Rustler and confined Capitan groundwaters fall into the range of more negative δD and $\delta^{18}O$ values; all have δD values more negative than -43 ‰. Meteoric waters from the vadose Capitan and water-table conditions in alluvium define the more positive range of isotopic compositions, and have δD values more positive than -41 ‰ and $\delta^{18}O$ values generally more positive than -5.5 ‰. Both populations came from areas in the northern Delaware Basin that have a relatively uniform climate typical of the northern Chihuahuan desert, at surface elevations of 3000 to 4500 ft. The three waters from the Dewey Lake are split: one from the isotopically heavier population and two from the lighter. One of the lighter Dewey Lake waters has been radiocarbon dated; it has been out of contact with the atmosphere for at least 14,000 radiocarbon years. Three of the confined Rustler waters from the Culebra near the WIPP site, falling in the lighter $\delta D/\delta^{18}O$ population, have radiocarbon dates between 12,000 and 16,000 radiocarbon years. The mean δD value of the lighter population (46 data), which contains the four late Pleistocene groundwater dates, is -50 ‰. The isotopically heavier population, most groundwaters of which can be inferred at present to have hydraulic connections with the surface (28 data), includes nine water samples from the Ogallala sandstone tapped by southeastern New Mexico municipal wells and analyzed by C. J. Yapp at the University of New Mexico. This population has a mean δD value of -33 ‰, taken to represent the isotopic composition of meteoric water that has recharged shallow groundwater systems under present climatic conditions at elevations of 3000 to 4500 ft in southeastern New Mexico. This elevation range includes the elevation of the WIPP site, 3300-3550 ft. The isotopic compositions of the two populations do not overlap, suggesting that climatic conditions governing recharge have not been identical for both populations in the Delaware Basin. Both populations of groundwaters are expected to have received recharge over at least several years; hence, their isotopic compositions would be expected to represent recharge over several cycles of year-to-year variations, and would reflect the dominance of recharge during certain seasons rather than necessarily coinciding with the isotopic composition of total weighted mean precipitation. Little systematic seasonal variation has been observed in the shallow (isotopically heavier) groundwaters, so the shallow (unconfined) groundwaters are taken to represent the seasonally integrated average isotopic composition of modern meteoric recharge.

A separation in mean δD values as small as 10 ‰ was used by Yapp (1985) to infer that Albuquerque Basin groundwaters more depleted in deuterium are relics of a previous recharge event typifying past (possibly wetter and/or cooler) climatic conditions. The difference in mean δD between the two populations defined here (-50 versus -33 ‰) is 17 ‰. The late Pleistocene radiocarbon age obtained for Rustler and Dewey Lake groundwaters in the isotopically lighter Delaware Basin population is consistent with the hypothesis that groundwaters now under confined conditions in the Rustler and Capitan were recharged during, and perhaps in response to, a past climatic event; the groundwater ages correspond to ages of late-Pleistocene-age local packrat middens, which preserve evidence of floral assemblages consistent with a cooler and/or moister environment than is reflected in the modern plant community. The extremely low tritium levels in Rustler groundwaters near the WIPP site suggest that the groundwaters are now receiving little if any active local recharge.

Confined groundwaters from the Rustler/Salado contact in Nash Draw have meteoric isotopic compositions typical of other Rustler waters. Toward the east, over the WIPP site, however, the isotopic composition of water from the Rustler/Salado contact shows progressively more positive deviation in δ-value ("isotope shift") from typical Rustler meteoric values. The amount of shift is correlative with (a) measured decreases in transmissivity, (b) increasing distance from the eastern dissolution scarp of Nash Draw, and (c) an increasing amount of halite surviving in the Rustler Formation. The isotope shift is attributable to an increasing amount of rock/water interaction accompanying a diminishing water/rock ratio. The precise mechanism of isotope exchange and the reactant solid phase have not been identified, but the potential effect of anhydrite hydration to gypsum, or the contribution of a relatively large reservoir of exchangeable water of crystallization in existing gypsum relative to a small amount of groundwater, should not be overlooked.

It has often been proposed that the more permeable units in the Rustler drain the WIPP site and Nash Draw and discharge into the alluvium and ultimately into the Pecos River near Malaga. It has, however, been proposed by some that the Rustler draining this area discharges to the surface a significant distance upgradient from Malaga, through a series of springs in southwestern Nash Draw, the best known of which is Surprise Spring on the northern shore of Laguna Grande de la Sal, the only perennial lake that existed prior to potash-refining activities. Various hypothetical flow paths in the Culebra from other parts of Nash Draw and the WIPP site to Surprise Spring pass through or near the near-surface occurrence of the Culebra at WIPP-29. A combination of isotopic and solute analyses has shown that (a) the isotopic compositions of WIPP-29 Culebra and Surprise Spring waters are similar, indicating that similar mechanisms governed the isotopic compositions of their water molecules, assuming that they were derived from a common source, (b) WIPP-29 Culebra water is not derived directly from water in other parts of the Rustler, but is largely a partially evaporated product of potash-refinery spillage of imported water from the Ogallala, and (c) derivation of Surprise Spring water from WIPP-29 Culebra water requires an immense dilution factor, using water that is isotopically heavier than most of the known Rustler waters upgradient. Thus, waters at Surprise Spring and WIPP-29 Culebra are of local near-surface derivation; neither their isotopic and solute compositions nor their geological occurrences are consistent with the proposal that they have been derived from other Rustler waters by simple evaporation, and they are not discharge points from either the WIPP site or east-central Nash Draw. They appear to be, instead, discharge points for a local, shallow (probably water-table) groundwater system manifest partly in the numerous ponds that have formed from a rising water table; the recharge for this local system appears to be potash-refinery spillage and/or local natural recharge entering the near-surface gypsum karst developed in the Tamarisk member of the Rustler Formation. In any case, the fluid volumes involved in the local system in southwestern Nash Draw overwhelm any possible contributions from Rustler water flowing from further east.

Rock/water interactions sufficient to result in isotopic shifts in waters of the Rustler Formation are largely restricted to the Rustler/Salado contact zone. Secondary calcite, however, has precipitated in isotopic equilibrium with typical meteoric Rustler water in the Magenta member at WIPP-33, a borehole drilled in a circular collapse feature located between the WIPP site and Nash Draw. None of the other analyzed aquifer rocks has isotopic compositions that reflect similar recrystallization of dolomite, but dissolution of some dolomite has probably occurred. The isotopic composition of the dolomites appears to be extremely uniform and is suggestive of an evaporitic rather than a biogenic origin, distinct from compositions expected from recrystallization in the presence of modern meteoric water. In addition, Rustler gypsum and Dewey Lake selenite vein material at AEC 8 have last been recrystallized in the presence of a water that isotopically resembles typical Rustler meteoric water; this precludes both total preservation of the gypsum as a primary seawater precipitate and recrystallization in response to infiltration typified by local modern meteoric isotopic compositions.

Waters from below the Rustler/Salado contact all show a significant isotope shift from the typical array of worldwide meteoric δD and $\delta^{18}O$ values. At greater depth, where the largely intact Salado evaporite section is unperturbed by postdepositional dissolution, no waters have been found that are derived directly, without isotopic modification, from meteoric sources.

O'Neil et al. (1986) have suggested that fluid inclusions in halite from the ERDA 9 corehole near the center of the WIPP site have isotopic compositions resulting from binary mixing of meteoric (Rustler-type) waters and water from the ERDA 6 brine occurrence in the Castile Formation. The existence of vertical fluid movement through the Salado necessary to facilitate such mixing would, however, be reflected in a notable degree of Salado recrystallization. A large number of radiometric dates for Salado minerals at various depths and geographic locations in the northern Delaware Basin show concordantly that no recrystallization of Salado evaporites has taken place since about 200 million years ago. Consequently, the proposed mechanism for mixing of Castile brines and meteoric water to yield the fluid inclusions in Salado halite is not consistent with the geochronological data.

The ERDA 9 Salado fluid inclusions lie on the same trend in $\delta D/\delta^{18}O$ space as do isotopically shifted Rustler/Salado contact brines. This suggests that Rustler/Salado brines, Castile brine, and ERDA 9 fluid inclusions have all evolved from an originally meteoric fluid by similar processes of variably extensive rock/water interaction. Fluid inclusions in halite from the WIPP subsurface facility itself (Knauth and Beeunas, 1986) isotopically resemble seeps from the nearby Duval Nash Draw potash mine and from Marker Bed 139 beneath the floor of the WIPP mine. Although the solutes (Stein and Krumhansl, 1986) are dissimilar, the water molecules in the two types of occurrences probably evolved along similar paths, perhaps as suggested by Knauth and Beeunas, by some ancient episode of mixing involving a primary evaporite brine and local rainfall when the evaporites were being deposited near the surface.

Two brines analyzed here (one Morrowan and one Bell Canyon) are typical "oilfield brines" and have isotopic compositions similar to the mine seeps and WIPP fluid inclusions; the other Morrowan sample has a unique isotopic composition. Material balance calculations have shown that the $\delta^{18}O$ value of the Bell Canyon brine can be obtained by oxygen-isotope exchange with coexisting calcite cement within the sandstone (which are at mutual isotopic equilibrium), at rock/water ratios of about 200; no appeal to evaporation or mixing is necessary. Neither the Bell Canyon nor the Morrowan limestone is associated with evaporites, and it is unlikely that the origin of either the high-calcium-chloride Bell Canyon brine or the Morrowan brine (which has a total dissolved solids content one-tenth that of saturated NaCl) has involved partially evaporated seawater. Their geological environments rather suggest that their observed isotopic compositions have arisen, as suggested originally by Lambert (1978), by profound rock/water interaction, whatever the ultimate origin of the water molecules.

Chapman (1986) compared the isotopic compositions of confined meteoric groundwaters in the Delaware Basin with groundwaters in the Roswell Artesian Basin, predominantly from the San Andres Limestone. Chapman proposed that (a) groundwaters in the Roswell Artesian Basin have δD values that are similar to the confined Rustler and Capitan waters in the Delaware Basin and (b) the presence of measurable tritium in Roswell Artesian Basin groundwaters makes them "verifiably young"; therefore, (c) "there is a good possibility that the Rustler is currently receiving recharge." We conclude here that direct comparison of the isotope systematics of the northern Delaware Basin and the Roswell Artesian Basin is not appropriate, because (a) natural recharge to the San Andres Limestone is <u>predominantly</u> at elevations greater than 5000 ft, thus imparting an artesian pressure to water pumped for irrigation in the Pecos River Valley and introducing more water with more negative δ-values typical of higher elevations, δ-values of precipitation at higher elevations being coincidentally similar to those produced during cooler, wetter paleoclimates at lower elevations, and (b) extensive pumpage since 1890 has allowed surface (tritium-rich) water to move downward into the San Andres aquifer and mix with older waters from higher elevations, giving a mixture that appears both spuriously young relative to travel time in the San Andres and spuriously depleted in deuterium relative to precipitation at the elevation of Roswell. Instead, present recharge conditions, if any, to be expected for the Rustler at and near the WIPP site would probably be more similar to those of the nearby Ogallala Formation than the San Andres aquifer of the Roswell Artesian Basin.

Both the Ogallala and the Rustler underlie portions of southeastern New Mexico and west Texas whose land surface is at elevations of <4300 ft above mean sea level, experiencing rainfall patterns significantly different from those of the mountainous recharge area for the Principal Aquifer (San Andres) in the Roswell Artesian Basin. Ogallala groundwaters from west Texas whose tritium contents are >10 TU, indicating historically modern derivation from the atmosphere, have δD and $\delta^{18}O$ values corresponding with the local groundwater population more enriched in heavier isotopes, as at Carlsbad Caverns and San Simon Sink; these modern Ogallala groundwaters are isotopically distinct in $\delta D/\delta^{18}O$ space from the confined Rustler and Capitan groundwaters. In addition, recent radiocarbon studies suggest that Culebra (Rustler) and Dewey Lake groundwaters near the WIPP site with the more negative δ-values and containing no significant tritium have been isolated from the atmosphere since the late Pleistocene, which is considered the age of recharge. The more negative δ-values are in some cases similar to those of groundwaters recharged to the San Andres in mountainous terrain at higher elevations in a cooler climate. Despite the isotopic similarities, the respective probable recharge areas for the Delaware and Roswell Artesian basins differ profoundly in present-day elevation, topography, degree of drainage development, climate, and vegetative cover. Whereas some isotopically lighter members of the Roswell population have a component of modern tritium probably due to pumpage-induced mixing, radiocarbon ages of some Delaware Basin groundwaters of the same stable-isotope composition are late Pleistocene, consistent with recharge under probably cooler and wetter conditions than now prevail in the Delaware Basin.

There is no significant monotonic gradient in groundwater radiocarbon age over a distance of 11 miles from north to south across the WIPP site. This suggests not an area of steady-state Culebra recharge in the north, as indicated by the modern potentiometric gradient, but that groundwater reached several points along a north-south line through the WIPP site at about the same time (e.g., a "slug"-type transient recharge event probably originating west of the WIPP site in the higher-permeability zone of Rustler outcrops in Nash Draw, during the late Pleistocene).

The late Pleistocene epoch was a time of significantly different climate in southeastern New Mexico, as indicated by the juniper-oak plant community preserved in the packrat middens of Last Chance Canyon and Rocky Arroyo at elevations of 3700 ft (Van Devender, 1980). At the same elevation, desert-scrub grassland now predominates. A climate that supported a juniper-oak community 10,000 to 10,500 radiocarbon years ago (the age of the packrat middens) would presumably be more conducive to groundwater recharge, if the juniper-oak community developed in response to higher rainfall.

Implications of there being little or no modern recharge to the Rustler groundwater near the WIPP site are that (a) the Rustler groundwater system is not at steady state; instead, discharge currently exceeds recharge, (b) present-day hydrologic measurements characterize a system in a transient stage that has persisted for 10,000 years, and which will continue to change its characteristics (e.g., potentiometric surface, permeability, etc.) in the future, and (c) groundwater flow (and evaporite dissolution) in the Rustler may presently be at temporally low volumes and rates, relative to the past, and may increase should a wetter climate again prevail in the next 10,000 years.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, contract number DE-AC04-76DP00789. Tyler Coplen (USGS) and Crayton Yapp (UNM) provided detailed reviews of the manuscript, and their incisive questions, criticisms, and suggestions helped us to make many of our discussions and arguments more precise. We have incorporated their recommendations where we felt that changes were most critical. In addition, the manuscript was read by Rick Beauheim and Al Lappin, who helped us clarify some of our arguments.

CONTENTS

FIGURES

PLATES

1. INTRODUCTION

1.1 Objectives, Scope, and Limitations

Groundwater occurrences in the Delaware Basin of southeastern New Mexico have been of considerable interest for many years, beginning with the time modern humans sought to build individual and collective lives in the arid southwest. In fact, the factor limiting development of land in the southwestern United States historically has been the availability and quality of water. As the sporadic occurrences of surface water became heavily overcommitted, the search continued underground with boreholes. In some areas, the search for groundwater has turned up other underground resources not preserved at the surface, in particular evaporites. Abundant potable groundwater associated with highly soluble evaporites is somewhat paradoxical, since (a) the evaporites do not long survive exposure to freely circulating groundwaters, and (b) such groundwaters, even if abundant, are seldom potable. Nevertheless, the mere presence of groundwater in or adjacent to evaporites has sparked considerable interest, especially if the evaporites are to be considered hosts for various long-term endeavors such as storage or permanent disposal of radioactive or hazardous wastes.

Particularly prominent occurrences of groundwater in southeastern New Mexico include the Capitan limestone, which borders the evaporites in the Delaware Basin, and the Rustler Formation, which overlies the main evaporite sequence of the Salado Formation. An understanding of the geologic history of the Rustler Formation in the northern Delaware Basin is considered to be fundamentally 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 deemed 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, and perhaps elsewhere, (3) immediately overlies the Salado Formation where the WIPP facility is being mined, and (4) contains interbeds of brittle fractured rock that carry the most abundant and regionally persistent occurrences of groundwater associated with Delaware Basin evaporites.

Ever since the beginning of scientific investigations relevant to the selection of the WIPP site in the middle-1970s, it has been apparent that the understanding of any aspect of the geology of the Delaware Basin and application of the geology to the WIPP site itself would require an understanding of that aspect throughout the basin. Thus, an understanding of the history of groundwater movement in the Rustler Formation would probably not be achieved without a consideration of the regional geological context, and of other waters in the Delaware Basin. Thus far, it has not been possible to derive the necessary data for understanding any aspect of Delaware Basin geology only from the immediate vicinity of WIPP; in almost every case the story had to be pieced together from many widespread parts of the basin (see, for example, Bachman, 1980). Consequently, although one major focus of this report is groundwater in the Rustler Formation, we present the stable-isotope geochemistry of several groundwater systems and sub-systems in the Delaware Basin, discussing their various similarities and differences in an attempt to set limits to the various interpretations that have been and can be made about them.

Geochemical determination of a groundwater system's origin and evolution through geologic time depends on (among other things) one's ability to unravel the effects of mixing of different reservoirs in the subsurface. In fact the effects of mixing, an event whose age is generally indeterminate, are typically sufficient to make the atmospheric-based "absolute" dating methods, for example, of limited value (Lambert, 1987). No single geochemical method, whether it be major or minor solutes or stable- or radoactive-isotopes, can be expected to provide a complete unique description or characterization of a groundwater system. Similarly, no interpretive model, regardless of how rigorous, can expect to provide unique, unambiguous, inescapable interpretations based solely on one kind of measurement. The consistency of a given interpretation must be compared to interpretations of all available geological data. These axioms have been recognized by various workers in quite different groundwater systems:

> Geochemical, isotopic, inert gas contents and radioelement measurements require a sound hydrogeological framework to aid interpretation. Individually these techniques can only provide limited information, but the combination of methods used have [sic] provided corroborative evidence concerning the direction of fluid circulation in the Harwell region. [Alexander and Andrews, 1984]
>
> The effect of mixing can be significantly greater than effects of different geochemical models and care should be taken that the use of highly sophisticated mathematical procedures does not in itself imply accuracy of interpretation. [Evans et al., 1979]
>
> Many types of rock/fluid interactions are evident in the geochemistry of ground waters found in Delaware Basin rocks. It is not possible to completely characterize these interactions from solutes or stable isotopes alone, nor through a study of water samples alone, without a similar study of rock. [Lambert, 1978]

Whereas discussions in this work are largely limited to the conclusions that can be made from stable isotopes in Delaware Basin waters, some stable-isotope systematics are considered for rocks also. Additionally, the discussion attempts to reconcile the inferences based on stable isotopes with the appropriate geological context. Hence, sources of data other than stable isotopes will be considered in formulating an overall interpretation.

Many of the data reported here are relevant to the origin and movement of groundwaters in the Rustler Formation near the WIPP site. In order to provide a regional context for interpretation of results, isotopic compositions of other Delaware Basin waters are reported and discussed here as well, including the overlying Dewey Lake Red Beds, seeps from potash mines and Marker Bed 139 in the WIPP mine, Castile brine reservoirs, Surprise Spring, San Simon Sink, and Capitan waters from the southern Guadalupe Mountains, Carlsbad Caverns, and the eastern Delaware Basin. The relevant part of the Delaware Basin in southeastern New Mexico and west Texas is shown in Figure 1, in which the large-scale geographic relationships among various water occurrences are illustrated. The locations of boreholes and other features near the WIPP site are shown at a more detailed scale in Figure 2.

1.2 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 (i.e., ultimately derived from precipitation). 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, developed in a zone of the Capitan where demonstrably active modern meteoric recharge by direct vertical infiltration 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 city of Carlsbad eastward and southward into west Texas. Lambert (1978) concluded that "except for Carlsbad Caverns, a $\delta^{18}O$ value of -7‰ and a δD value of -50 ‰ appears [sic] to be a good approximation to local meteoric water in the Delaware Basin" and that "the Caverns are part of a hydrologic system independent of the rest of the Capitan ... their enrichment in D and ^{18}O [reflecting] the water's origin from air-mass conditions different from those which produce other Delaware Basin rains."

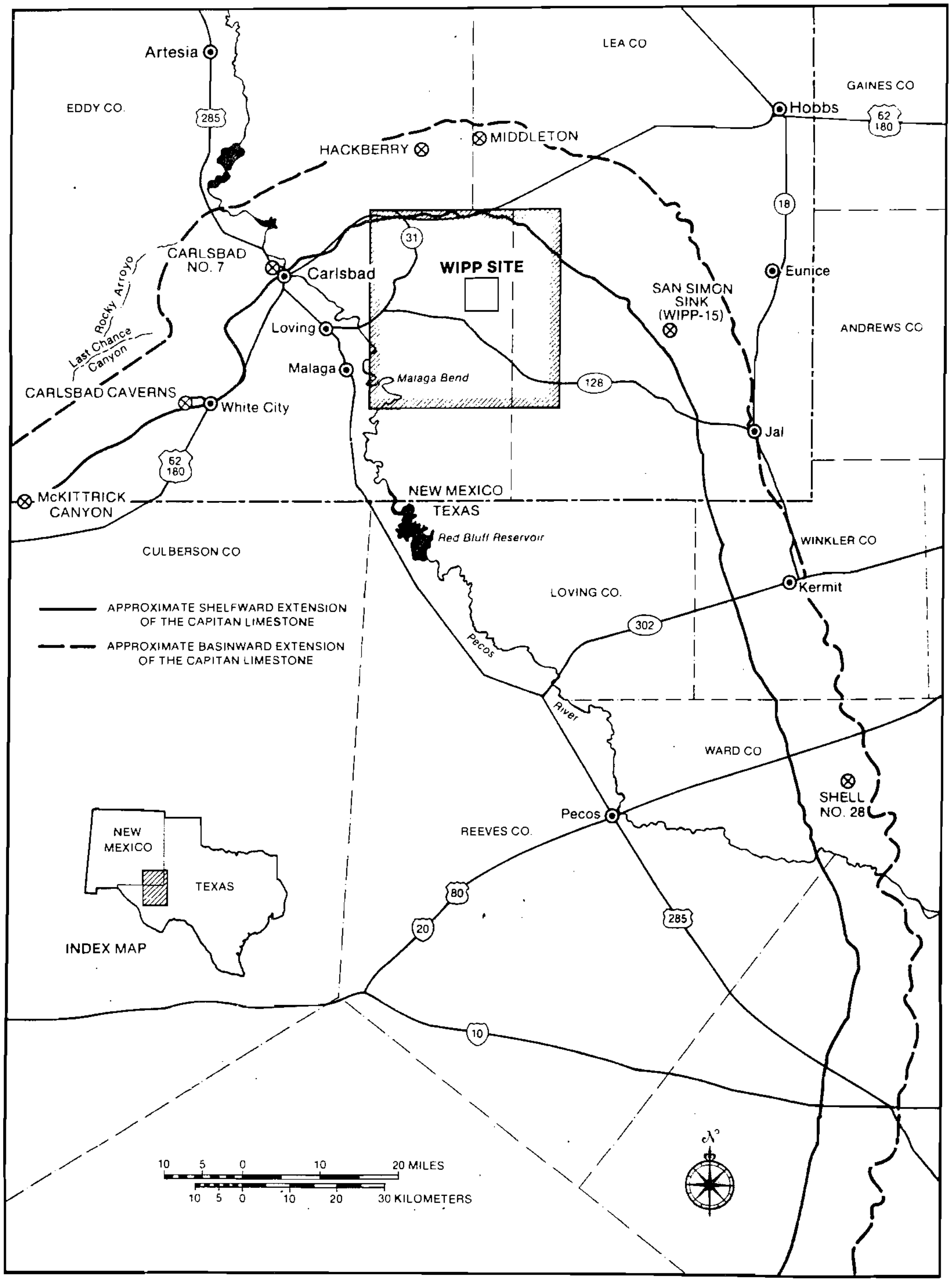


Figure 1. Regional map of the Delaware Basin, southeastern New Mexico and West Texas. Approximate positions of basinward and shelfward extensions of the Capitan Limestone are taken from Hiss (1975). Hachured rectangle is the area covered by Figure 2, which shows sampling localities cited in the text in greater detail. Sampling localities not covered by Figure 2 are shown here by X's.

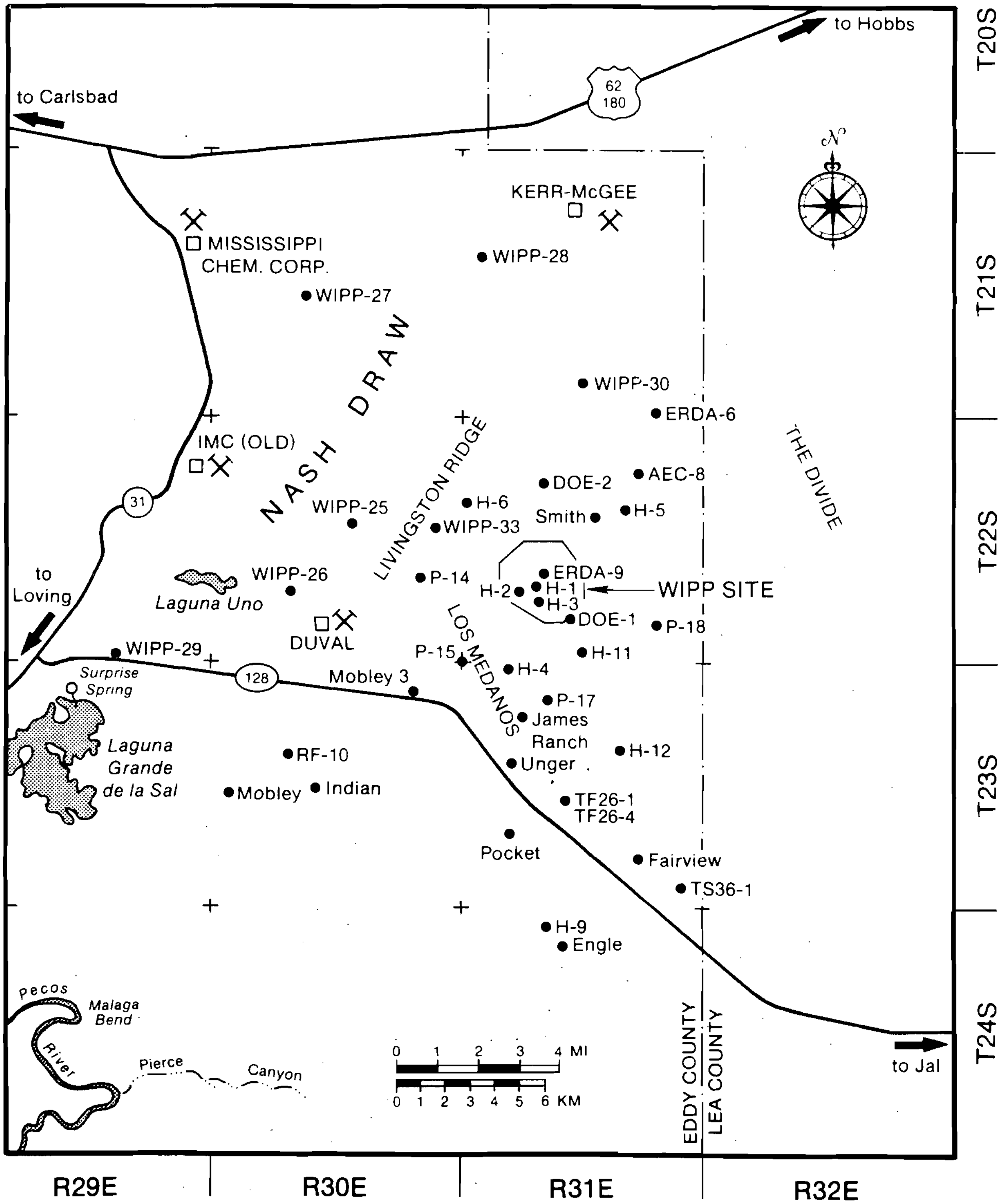


Figure 2. Map of northern Delaware Basin, southeastern New Mexico. This detailed map of the area enclosed by hachures in Figure 1 shows sampling localities cited in the text, mostly boreholes near the WIPP site and Nash Draw. Modified from Mercer (1983).

This implied that most of the eastern (deeper) Capitan groundwaters were probably recharged under climatic conditions different from those prevalent in the Guadalupe Mountains (Figure 1). Further, the isotopic similarity (i.e., statistically insignificant difference) between many Rustler groundwaters and many Capitan groundwaters suggested that these confined waters may have originated under the same climatic conditions. 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 the rest of the Delaware Basin. Until recently (Lambert, 1987) the time of groundwater recharge to the Rustler Formation and the overlying Dewey Lake Red Beds was indeterminate, but independent paleoclimatic evidence indicated much wetter conditions, more conducive to recharge, at various times in the Pleistocene, ranging from 10,000 to 600,000 years ago (Van Devender, 1980; Bachman, 1986).

1.3 Approach

The isotopic characteristics of Delaware Basin waters in various geohydrological environments are described herein. First, the environments will be considered that have origins that are reasonably understood. These include:

> Vadose (Caverns) Capitan waters. Caverns waters recharging the Capitan are (a) definitely meteoric in origin, and not derived from other waters by evaporation or other fractionation mechanism, and (b) demonstrably recent, as indicated by the correlation between drip rate and seasonal storm activity.
>
> Surface waters. Direct collection, analysis, and interpretation of modern meteoric precipitation is of limited relevance to local groundwaters systems, unless planned

> very carefully, since the groundwater systems may preferentially receive recharge at certain times of the year under certain transient conditions. Thus, isotopic compositions of individual stormwaters in general (or even a weighted average of several storms) will not necessarily provide a representative estimate of isotopic compositions of waters recharging groundwater systems. These sorts of averages <u>may</u> be used to bracket expected isotopic characteristics of recharge.

The next class of geohydrological environments entails groundwaters whose origins may be understood with less confidence, but which are at opposite extremes of a spectrum. In one case the waters appear to be associated with water-table conditions, or at most only a small degree of confinement. At the other extreme are waters completely confined:

> Shallow groundwaters. Due to their individual recharge characteristics, groundwater systems integrate out seasonal isotopic variations through mixing, and like springs "contain accumulations of water collected over varying periods of time" (Friedman et al., 1964).

> Confined Capitan (basin margin) groundwaters. The Capitan Limestone (or "Capitan Aquifer" of Hiss, 1975) east of the Pecos River contains in its cavernous porosity groundwater under artesian conditions (i.e., water levels in wells rise above the upper local confining horizon of the aquifer). Direct vertical infiltration into this portion of the Capitan is inhibited by the overlying soluble evaporites of low permeability (Snyder and Gard, 1982; Bachman, 1985).

The next class of environments is problematical, because although their waters are indicated to be meteoric in origin, their recharge and discharge phenomena are not directly observable, and therefore are somewhat poorly defined:

> Confined Rustler (central basin) groundwaters. In the water-bearing Magenta and Culebra members (both gypsiferous dolomite) of the Rustler Formation near the WIPP site, potentiometric levels increase and permeabilities are lower toward the east or northeast (Mercer, 1983). Thus, the amount of recharge by vertical infiltration required to pass through a low-permeability overburden (the Dewey Lake Red Beds) into a low permeability part of the Rustler may not be sufficient to produce the observed relatively high potentiometric levels. The physics alone of this relationship has always been problematical, and has led to various hypotheses regarding the mechanisms and locations of present recharge (or lack thereof) to the Rustler Formation. This last issue is of great interest in the long-term performance of the WIPP. If for example, recharge were now at a minimum, implying a system that is largely draining, hydraulic measurements obtained now may not be extrapolable over the next 10,000 years, should the area experience a wetter climate and resulting increase in effective recharge. Some parts of the Dewey Lake Red Beds are also in this condition, since increasing natural recharge might resaturate large portions of this formation, now believed to contain only local occurrences of perched water.

The final class of groundwaters will be discussed only after consideration of (a) isotopic systematics and relationships among groundwaters of demonstrably meteoric origin, and (b) geochemical processes that move isotopic compositions of waters away from meteoric trends in $\delta D/\delta^{18}O$ space. These groundwaters may be indeed problematical, in that there is probably not a unique and conclusive indication of their origin in their isotopic or other geochemical/geological records:

> Deep Basin Waters. By their very existence, waters entrapped in and surrounded by highly soluble Delaware Basin evaporites that show no evidence of active dissolution are not part of a freely circulating system directly connected to a meteorically derived source (Lambert, 1983a; 1983b).

2. METHODS

2.1 Sample Collection

The detailed stratigraphy of the Rustler Formation and the relevant stratigraphy of the Ochoan and Guadalupian (Permian) and related rocks in the northern Delaware Basin of southeastern New Mexico have been described by Lambert (1983a; 1983b) and Snyder (1985), and will not be reviewed here. Figure 3 diagrammatically illustrates the stratigraphic relationships of the relevant rocks. Figure 4 is a structure section showing how, due to the gentle eastward regional dip, progressively younger units (higher in the stratigraphic section) occur near the surface toward the east. Locations of boreholes relevant to this work are given in Figure 2. Three water-bearing units above the main evaporite sequence have been of primary relevance to the WIPP site, because of their occurrence there: the Magenta and Culebra dolomite members of the Rustler Formation, and the zone near the contact between the Rustler and 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).

Water samples came from either readily accessible accumulations (springs, streams, pools) or wells drilled into the subsurface, requiring special configuring/sampling equipment and procedures. All surface, spring, and caverns waters reported herein were grab-sampled by the senior author. From the beginning of the WIPP project (late 1975/early 1976) to 1980, all samples from wells were bailed or swabbed during hydrologic testing by the United States Geological Survey (USGS), which had primary responsibility for all well operations (Mercer, 1983). Well-water samples resulting from pump tests in 1980 and 1981 (WIPP-25 through -30, H-4 through -6) were collected by personnel of

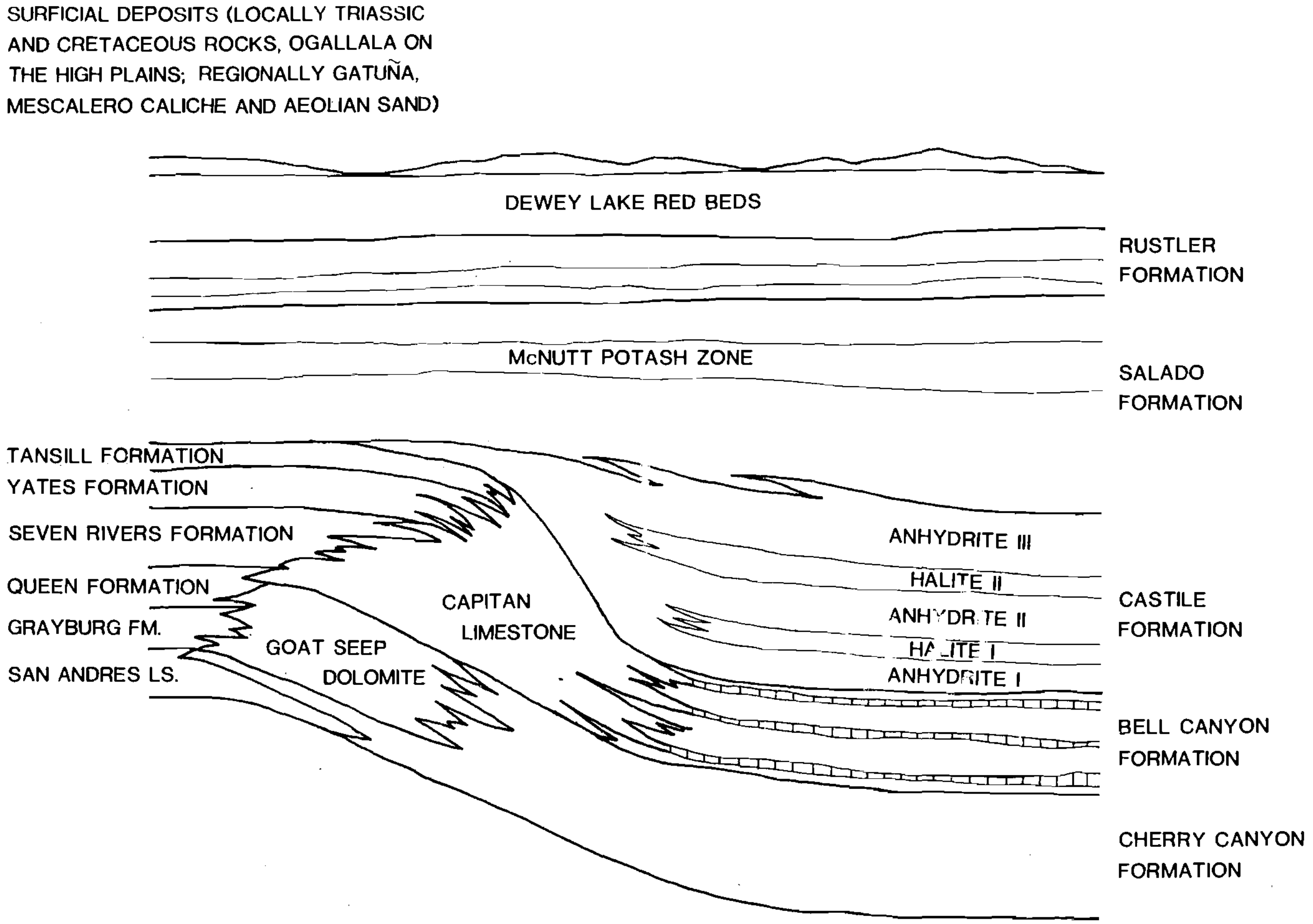


Figure 3. Generalized stratigraphy of Guadalupian (Permian) and younger rocks in the Delaware Basin. Note especially the intertonguing relationships between the Capitan Limestone and Guadalupian basin- and self-facies, and the lapping of the Ochoan evaporite section over the Capitan at the basin margin. This represents an idealized north-south section, looking east, at the northern apex of the Capitan Limestone, near the Eddy-Lea county line in Figure 1. From Lambert (1983a).

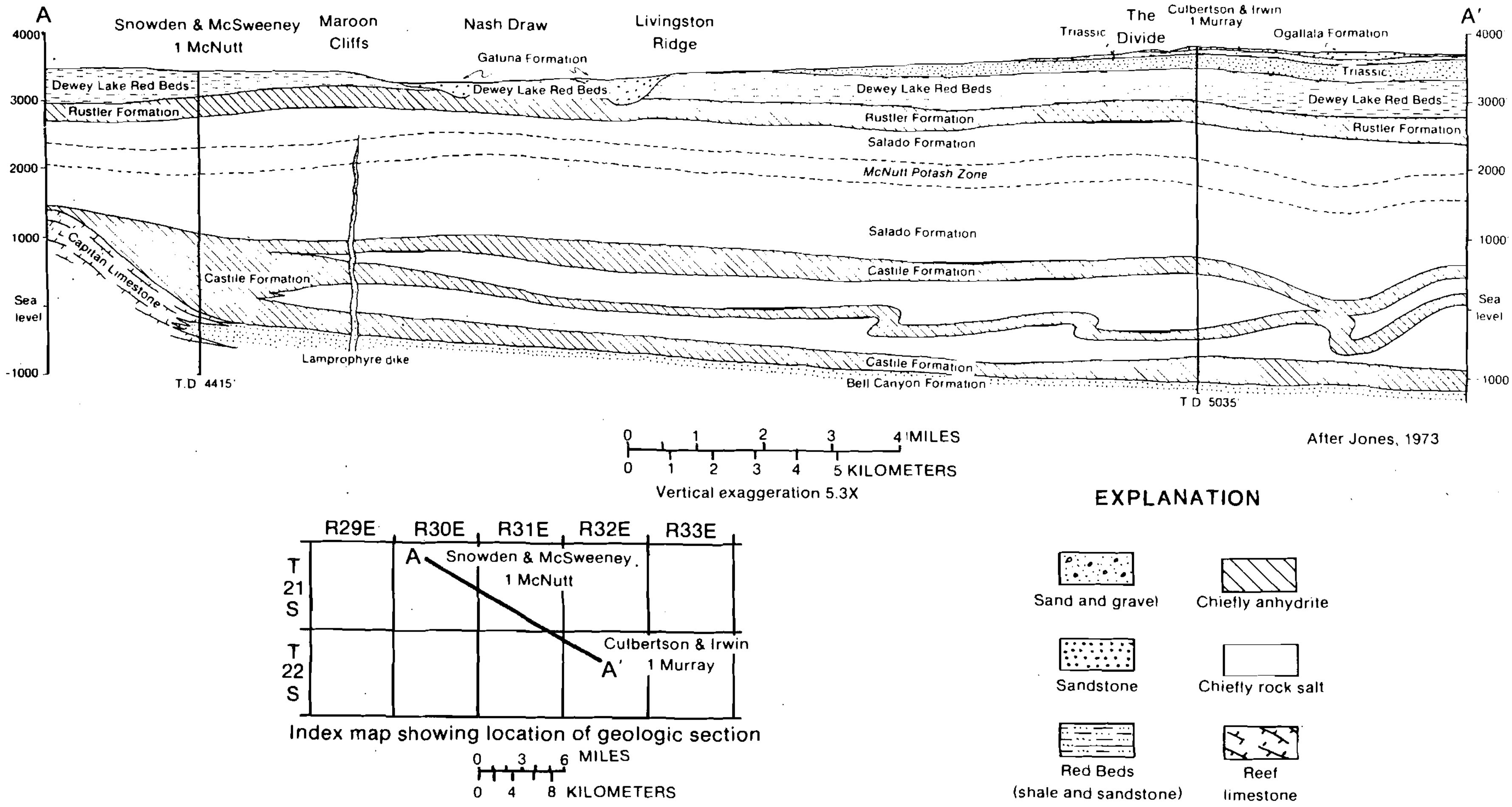


Figure 4. Generalized east-west geologic section in the northern Delaware Basin. Exaggerated vertical scale is in feet above sea level. Note that due to the gentle eastward tilt and subsequent erosional truncation, stratigraphically lower units are progressively nearer the surface toward the west, higher (younger) units toward the east. Adapted from Mercer and Orr (1977), who obtained it from Jones (1973).

Sandia National Laboratories, using the criteria and procedures described by Lambert and Robinson (1984). From 1981 to 1984 well-water samples were collected by Hydro Geo Chem, Inc., of Tucson, Arizona, a Sandia sub-contractor. The criteria and procedures used then were described by Hydro Geo Chem (1984), and bear little resemblance to those of Lambert and Robinson (1984). Since 1985 all well-water samples have been provided to Sandia as part of the Water Quality Sampling Program carried out by Westinghouse, DOE's WIPP operating contractor (Colton and Morse, 1985). The criteria were largely the same as those given by Lambert and Robinson (1984), although procedures differ in detail.

In several boreholes core samples of the water-bearing horizons were available along with water samples. Oxygen-isotope analyses of the rock in most recent contact with the water allow oxygen-isotope systematics of rock-water interactions to be considered in various interpretive models. This is especially useful in groundwaters from carbonate aquifers, in which isotope exchange in the carbonate/water system can be evaluated as indicative of dissolution or reprecipitation.

Boreholes WIPP-25, -26, -27, -28, -29, and -30 were drilled in 1978 with as complete recovery of core as possible. Boreholes H-4, H-5, and H-6 were rotary drilled but were cored only through the Magenta and Culebra members. Where the Culebra member contains significant (i.e., recoverable) amounts of water it is typically highly fractured, and is rubbled due to a combination of high fracture density and partial dissolution of its significant calcium sulfate component. Thus, complete recovery of intact core is not typical of the permeable horizons of the Culebra. It is more typical for loose fragments to fall out of the core barrel after it is brought to the surface, and hence the precise depths of many fragments of Culebra from permeable zones are unknown; however, the depth of origin for most fragments can be determined within an interval of a few feet.

The methods of collection and field preservation of water samples collected by Sandia in 1980 and 1981 were reported in detail (using boreholes WIPP-25 through -30 as case examples) by Lambert and Robinson (1984), and are briefly reviewed here, since these form the basis of all sampling done since 1984. In 1980 these boreholes (cored, cased, and cemented in 1978) were perforated in the zones of interest. Water samples were obtained during extended pump tests, lasting from 17 to 184 hours, in which each zone was isolated from the others by packers. At intervals of several hours during each pump test, various solution parameters were measured on the well effluent, notably chloride, total divalent cations, and alkalinity. Final samples were collected for solute and other isotope analyses after the chloride and divalent cations values had reached steady state, but in many cases it was judged that the concentrations of carbonaceous species would require too long to reach steady state. Hence, Lambert and Robinson judged that not all effluents from pump tests were considered suitable for radiocarbon sampling.

2.2 Preparation and Extraction

2.2.1 Water Hydrogen

Waters were converted to hydrogen gas 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 (see Section 2.3).

2.2.2 Water Oxygen

Water was first distilled in vacuum to the point of observable dryness and decrepitation of residue salts. This was to obviate the necessity of correcting for salinity in later treatments. 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 estimated to be small. Quantitatively distilled water was analyzed for oxygen by the equilibration of carbon dioxide with water at 25.4°C (Epstein and Mayeda, 1953). After a full week of equilibration an aliquot of gas was extracted and dried, and then its $^{18}O/^{16}O$ ratio was determined by mass spectrometry (see Section 2.3). After corrections to raw mass spectrometric data, a numerical conversion was made, accounting for carbon dioxide exchange in the equilibration between gas and water.

2.2.3 Carbonate Oxygen and Carbon

Ratios of the stable oxygen and carbon isotopes in carbonates were measured (at Sandia National Laboratories) on the carbon dioxide liberated according to the method described by Epstein et al. (1964). This procedure differs from the phosphoric acid extraction method of McCrea (1950), in that 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. The multiple collection steps described by Clayton et al. (1968) were unnecessary, since the fractions of gas liberated during the first hour and after the sixth day were negligible. For all the carbonate samples a 3-day reaction time was sufficient.

2.2.4 Mineral Hydrogen

Water was extracted from gypsum using a procedure modified from that described by Epstein and Taylor (1970). The gypsum was not preheated, due to the low temperature of dehydration of gypsum. Adsorbed water was driven off simply by pumping under high vacuum for one hour before devolatilization in the platinum crucible heated by induction. Hydrogen in the recovered water was then extracted and analyzed for its δD value as described elsewhere. This extraction and analysis was done at the California Institute of Technology (Caltech) by the senior author.

2.3 Mass Spectrometry

All stable-isotope measurements were made using single-focusing, double-collecting, dual, gas-fed mass spectrometers of the type described by Nier (1947) with modifications by McKinney et al. (1950). The instrument used at Sandia for hydrogen-, oxygen-, and carbon-isotope analyses was a Micromass Model 602E manufactured by VG Isogas, Ltd., Middlewich, Cheshire, United Kingdom. This instrument can be configured for analyzing hydrogen, carbon dioxide, nitrogen, or sulfur dioxide, with a separate analyzer system provided for hydrogen. The same electronics are used on the hydrogen analyzer as on the analyzer for the other gases, but not at the same time. Corrections for background, mass tail, and valve leakage are negligible on this instrument, but corrections were made for ^{17}O and ^{13}C. Correction for the m/e = 3 signal contributed by the triatomic hydrogen ion (H_3^+ produced by chemical ionization in the hydrogen source) was made by circuitry internal to the mass spectrometer.

The hydrogen instrument at the University of New Mexico was a model 3-60-RMS manufactured by the Nuclide Corporation. Corrections for background, mass tail, port leakage, and H_3^+, and conversions from working reference to V-SMOW were made externally.

Procedures and mass spectrometers used at Caltech, the USGS, and the University of Arizona are similar, but not necessarily identical to those described above.

All stable-isotope data are reported in the usual delta (δ) notation, expressed as the deviation of the isotopic ratio in parts per thousand (‰ or "per mil") from that of an internationally accepted reference

$$\delta = \frac{R_x - R_{std}}{R_{std}} \cdot 1000 \qquad (1)$$

where R = $^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, etc., and x and std represent sample and standard reference, respectively. For oxygen- and hydrogen-isotope ratio measurements the reference is Vienna Standard Mean Ocean Water, "V-SMOW" (Gonfiantini, 1978), which is very close to SMOW defined by Craig (1961a), and for the carbon-isotope ratio the reference is the Chicago Peedee Belemnite, "PDB" (Craig, 1957).

The δ value of the machine working-reference for oxygen and carbon (Harding Iceland Spar) was determined by comparison with NBS-18 (Fen Carbonatite) and NBS-19 (Taum Sauk Marble), whose $\delta^{18}O$ and $\delta^{13}C$ values (relative to V-SMOW and PDB, respectively) are reported by Coplen et al. (1983). Details of the determination of the $\delta^{18}O$ and $\delta^{13}C$ values of Harding Iceland Spar are given in Table 1 (part A).

Hydrogen gas extracted from V-SMOW was used directly as a machine working-reference, and hence no other conversions to machine δD values are necessary. Table 1 (part B) contains details of verification of machine operation in determining δD values. In particular, several replicates of SLAP and GISP (isotopic reference materials distributed by the National Bureau of Standards) were analyzed to (a) evaluate the reproducibility of the extraction and instrumental analysis, and (b) compare the typical Sandia results with the international mean values, particularly that of Standard Light Antarctic Precipitation, SLAP. SLAP is a particularly good test of reproducibility and accuracy, because it is the international reference material most depleted in deuterium. Hence, it serves as an extreme δD value bracketing the range of most meteoric δD values.

TABLE 1. STABLE-ISOTOPE STANDARDS
[δ-values expressed in parts per mil (‰)]

A. Individual values versus Harding Iceland Spar (HIS) obtained by analyses on indicated dates.

	$\delta^{18}O$	$\delta^{13}C$
NBS-18 (Fen Carbonatite)		
8 Dec 83	-4.84	-0.35
13 Dec 83	-4.84	-0.34
16 Dec 83	-4.84	-0.35
16 Aug 84	-4.83	-0.37
Mean (3 degrees of freedom)	-4.84	-0.35
Standard Deviation	0.01	0.01
NBS-19 (Taum Sauk Marble)		
8 Dec 83	16.29	6.89
13 Dec 83	16.45	6.89
16 Dec 83	16.35	6.87
22 Jun 84	16.46	6.87
Mean (3 degrees of freedom)	16.39	6.88
Standard Deviation	0.08	0.01

Mean values ($\delta^{18}O$ versus Standard Mean Ocean Water (SMOW), $\delta^{13}C$ versus Chicago Peedee Belemnite (PDB)) reported by Coplen et al. (1983)

	$\delta^{18}O$	$\delta^{13}C$
NBS-18 (with degrees of freedom)	7.20 (2)	-5.00 (5)
NBS-19 (with degrees of freedom)	28.65 (1)	1.92 (6)
HIS total carbonate (this laboratory, calculated[2])	12.02	-4.58

B. Individual values versus Vienna Standard Mean Ocean Water (V-SMOW) obtained by analyses on indicated dates.[3]

	δD
SLAP (Standard Light Antarctic Precipitation)	
1 May 84	-430.5
3 May 84	-431.5
1 Jul 85	-430.1
15 Jul 85	-432.5
Mean (3 degrees of freedom)	-431.2
Standard Deviation	1.1

TABLE 1. (Continued)

	δD
SGISP (Greenland Ice Sheet Precipitation)	
30 Apr 84	-192.6
1 May 84	-193.0
3 May 84	-195.0
16 Jul 85	-189.4
Mean (3 degrees of freedom)	-192.5
Standard Deviation	2.3
Accepted values, versus V-SMOW	
SLAP (NBS, official)	-428
GISP (unofficial concensus)	≈-190

---

1. Corrections were applied to raw measurements to obtain these numbers according to the procedures of Craig (1957) based on the working standard (HIS) of this laboratory. The correction was made for the contributions of ^{13}C and ^{17}O to the mass 45 and 46 beams.

2. Conversion algorithms have been applied according to the relevant fractionation factors and standard values given by Coplen et al. (1983) to obtain these numbers from the corrected data.

3. These δ-values have been corrected for the contribution of the triatomic hydrogen ion (H_3^+) by circuitry internal to the mass spectrometer. No other conversions or corrections have been applied; background and mass tail corrections in this instrument are negligible, and the reported δ-values result from direct instrumental comparisons with the hydrogen extracted from the primary reference, V-SMOW.

3. DATA

3.1 Precision

More than one replicate analysis was done on several samples, and especially for those whose results were different in some way from the bulk of the results. Replicates represent entirely independent distillations, equilibrations, extractions, purifications, and mass spectrometric measurements. All replicate analyses are reported, even for samples of questionable value (see Section 3.2.3). When interpretations are applied to the data, mean values of replicates are used. The $\delta^{18}O$ and $\delta^{13}C$ values of the reference carbonates (Table 1, part A) have typical s-values of 0.1 ‰ or less. Such a reproducibility will be typical of pure calcite samples, but dolomites may show a slightly larger variation, say ±0.4 ‰, due to the inherent nature of the extraction procedure.

Typical confidence limits (at the 95% level) for replicate analyses of water $\delta^{18}O$ values may be about 0.25 ‰, also due to the preparation and extraction procedure. Reproducibility can also be typically worse for very salty solutions that must be distilled before the CO_2-equilibration step. Some differences among replicates may reflect difficulties in exactly reproducing the conditions of distillation; hydrous minerals that form in the residue might not completely give up their water at the temperature of distillation.

Table 1, part B, shows that typical s-values for δD values of pure waters are of the order of 1 to 2 ‰. Again, variations among replicates may be greater, up to 3 or 4 ‰ for very salty solutions. Confidence limits for one replicate δD analysis (at the 95% level) are typically ±2.5 ‰.

Confidence limits, linear regressions, and variances of linear regressions were calculated according to the methods of Natrella (1963).

Stable-isotope ratio analysis is very precise. By the nature of the measurement (Nier, 1947; McKinney et al., 1950) the absolute standard deviation is not a function of the magnitude of the δ-value (Equation 1). Thus, the degree of reproducibility is expected to remain constant over the entire range of natural δ-values. A δ-difference of 0.1 ‰ (in $\delta^{18}O$) to 1 ‰ (in δD) corresponds to a difference of about 1 part in 5,000,000 **in the absolute ratio of the respective isotopes**. Thus, for example, if the δD value is known to within 1 ‰, the absolute abundance of deuterium in the sample is known to within 2 parts in 10^7. A large difference in δ-value can actually represent a very small difference in the abundance of the minor isotope.

3.2 Validity and Representation

3.2.1 Downhole and Subsurface Perturbations

The validity of the data from boreholes and resulting interpretations are subject to the limitations of the sampling conditions as described and discussed by Lambert and Robinson (1984). It is generally not possible to derive a quantitative field-estimate of the degree of contamination remaining in any of the samples discussed. Several sources of contamination of water samples taken from a pumped (or swabbed or bailed) well have been discussed previously, including, but not limited to (1) introduction of alien water (e.g., drilling brines or vertical leaks through packers or cement annuli), (2) introduction of alien solids (e.g., materials admixed to drilling fluid to control loss of circulation) that may slowly react with or infuse the water by degrading, partially leaching, or completely dissolving, (3) products of reaction between water and temporary equipment in the hole, and (4) scaling of coatings on permanent pipe or casing in the hole. In any man-made hole, it is virtually impossible to obtain an unperturbed sample; the act of drilling the hole irreversibly alters the local hydrologic system. A well-known example of such long-term unmitigable perturbations is given by McNitt (1963) for The Geysers geothermal field. In Nash Draw pump times varied from 17 to 184 hours, during which several solution parameters were measured in the field, including Eh, pH, specific conductance, specific gravity, bicarbonate and/or carbonate, chloride, divalent cations, calcium, hydrogen sulfide, sulfate and total iron. Based on the long-term observations in the pumped wells, the most reliable indicators of achievement of steady state in solution parameters were divalent cations and chloride (i.e., by the time Cl^- and X^{++} concentrations had reached steady-state, other field-measurable parameters, with the exception of carbonaceous species, had for the most part stabilized also). The length of time required for these solutes to achieve steady state values was typically greater than 24 to 48 hours, even at pump rates of several gallons per minute. During some of the pump tests, there was no indication of an asymptotic approach of some parameters to a steady-state value. This was particularly true of bicarbonate. In one case, the flow rate was consistently less than 100 mL/min (WIPP-30 Magenta), and Lambert and Robinson (1984) determined that after 184 hours chloride, divalent cations, and calcium were still monotonically decreasing with no indication of approach to steady-state. Thus, displacement of seven well-bore volumes, as prescribed by the rule-of-thumb (Hydro Geo Chem, 1984), may not be sufficient to ensure a representative sample. Even during long pump times at low pump rates, however, there is little likelihood of stable-isotope fractionation of the water due to partial evaporation (because of the relatively small amount of water exposed to dry air in the hole), rock-water interaction, or reaction with pipe (as will be illustrated below). The close juxtaposition of isotopic data from units of low productivity with data from units of high productivity (some of which were several miles apart, as discussed below) shows that, except in extreme cases of packer leakage, contamination of the low-productivity units did not affect the stable-isotope results as much as it may have affected some other ultratrace solution parameters such as radiocarbon (cf. Lambert, 1987) and uranium-isotope ratios (cf. Lambert and Carter, 1984).

3.2.2 The Effects of Mixing and Contamination

An extreme example of mixing and contamination is analytical results for multiple samplings of the borehole H1 (Table 2). The complete detailed history of H1 is given by Mercer and Orr (1979), and is briefly summarized here. H1 was the first hydrologic test hole at the WIPP site, and was begun May 20, 1976. Due to the low anticipated productivity of the zones to be tested, air was used as a circulating medium during rotary drilling. When moist zones or fluid influx was observed, mist or "foam" was added to the air; at no time was a continuous liquid medium such as mud or brine used in drilling. This eliminates the possibility of (a) obscuring small amounts of fluid influx by large amounts of liquid drilling fluid, and (b) introducing significant amounts of liquid drilling fluid into the zones to be tested and contaminating them. The first Culebra water sample was taken at the end of a drill-stem test on June 2, 1976. After the low fluid yields resulting from drill-stem testing showed that long-term testing and monitoring were more appropriate, the hole was reamed, cased, and perforated in zones of interest. The first zone to be perforated was at the Rustler/Salado contact. After much bailing, a sample was collected on February 23, 1977 from the contact zone. After isolating the Rustler/Salado contact zone with an inflatable packer, the Culebra zone was perforated. After bailing, a Culebra sample was collected on March 17 , 1977. On March 21 , 1977 a tracejector test (using ^{131}I) was performed to investigate the integrity of the cement bond behind the casing. This test indicated no fluid communication

TABLE 2. ISOTOPIC EFFECTS OF MIXING

If mixture Y is made of X and Z, % mix = % of X in Y

Analyte	X H1 Rus/Sal 02/23/77	% mix	Y H1 Culebra 03/17/77	Z H1 Culebra 06/02/76
Stable isotopes (δ-values in ‰)				
δD	-29	38	-42	-50
$\delta^{18}O$	+1.6	29	-4.5	-7.0
Solutes (values in mg/L)				
Cl^-	210000	19	49000	12000
$SO_4^=$	520		11000	7400
Ca^{++}	13000		820	780
Mg^{++}	30000	5	1800	280
Na^+	56000	42	29000	9400
K^+	17000	32	5600	190
TDS	325000	23	97000	30000
SiO_2	.0	22	0.6	2.7

between the Culebra and underlying zones via the cemented annulus. Hence, that was not a pathway for potential mixing and contamination.

The analytical results for the three samples described above are given in Table 2. For all the tabulated parameters except sulfate, the later Culebra sample of March 17, 1977 had values intermediate between those of the first Culebra sample and the Rustler/Salado sample. This suggested that linear mixing may have occurred, perhaps through the inflatable packer intended to isolate the previously perforated Rustler/Salado zone from the newly perforated Culebra zone. If δD is plotted versus $\delta^{18}O$ for these three samples (Figure 5A), a linear trend results, with a least-squares correlation coefficient (r-value) of 0.99, suggesting an excellent fit. $\delta^{18}O$ is probably more suitable than δD for showing this mixing, since the differences between $\delta^{18}O$ values are greater (relative to the magnitude of the confidence limits) than the δD values. Figure 5B shows the variation between $\delta^{18}O$ and total dissolved solids (TDS), and again the linear fit is excellent (r = 1.00). If the H1 Culebra sample of March 17, 1977 (Y in Table 2) is tentatively taken to be a result of mixing of H1 Rustler Salado-February 23, 1977 and H1 Culebra-June 2, 1977, then it is possible to calculate the apparent mixing proportions based on various analytes. The "% mix" column in Table 2 gives the results of such calculations, based on the assumption that X and Z are inert endmembers participating in the simple binary mixing. Except for calcium, magnesium, and sulfate, the results are consistent with the hypothesis that Y consists of 20 to 40% X, and that the remainder is Z. The anomalous behavior of calcium, magnesium, and sulfate is nonconservative, perhaps due to interaction between the water of March 3, 1977 and other solids and/or solutions of unknown origin, resulting in dissolution and/or precipitation of sulfates upon mixing of several components. Lambert and Robinson (1984) used total divalent cations as an indicator of steady state; stabilization of this parameter during a pump- or flow-test suggests that the rate of precipitation reactions involving these cations, as well as sulfate, has reached a constant value, with no further changes in the rate of admixture and contamination from other sources. By inference this observation has been used to various degrees to judge that after a long test the source of contamination of major solutes from other sources has been minimized.

Given the estimated analytical precision of both stable-isotope and solute measurements, it is possible to state with confidence that the H1 Culebra sample of March 17, 1977 is an admixture between H1 Culebra of June 2, 1976 and H1 Rustler/Salado of February 23, 1977. In this case, if X is taken to be reasonably

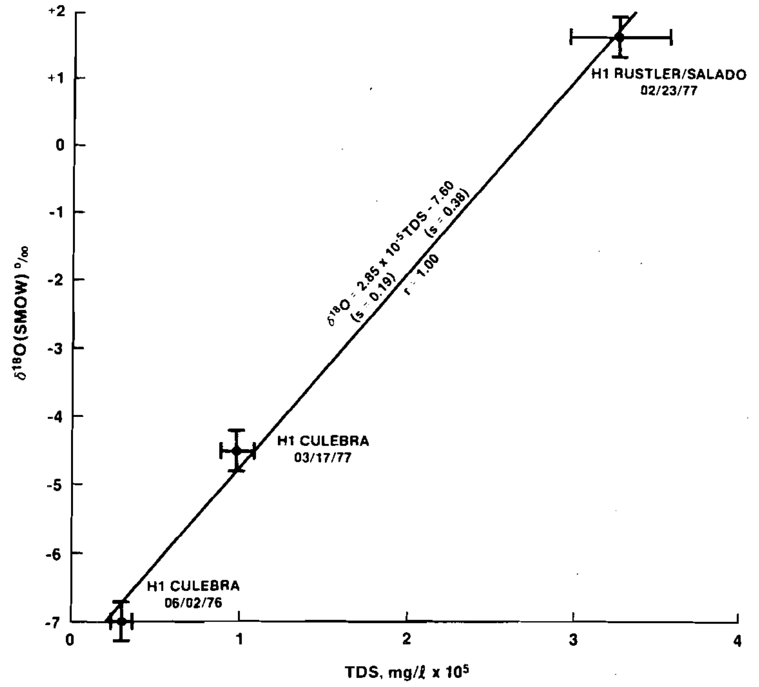
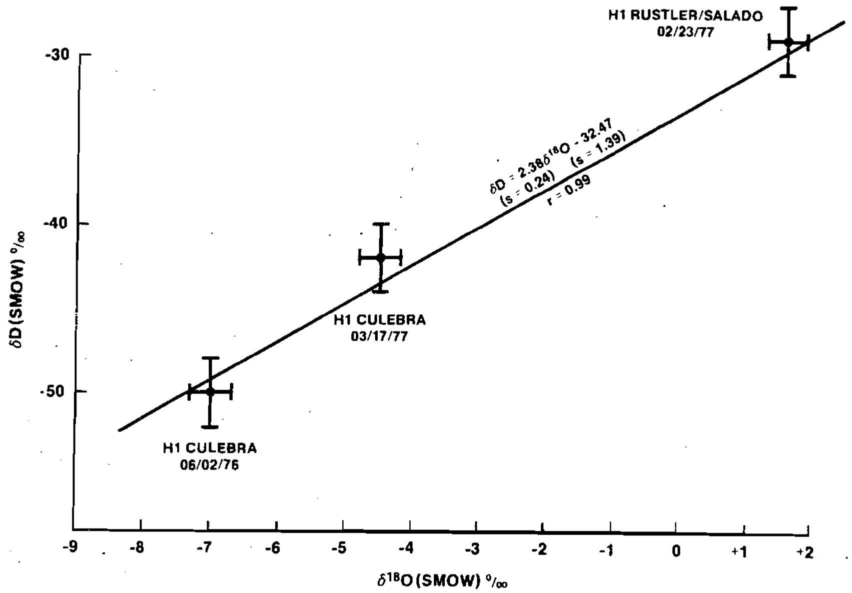


Figure 5. Mixing relationships in borehole H1. The later (17 Mar 77) H1 Culebra sample appears to be a binary mixture, whose endmembers consist of (a) water characteristic of the earlier Culebra sampling episode (2 Jun 76) and (b) water representative of the Rustler/Salado contact (23 Feb 77). S-values for least-squares slope and intercept were calculated by the method of Natrella (1960). A: Mixing inferred from δD and $\delta^{18}O$ values.



B: Mixing inferred from $\delta^{18}O$ and total dissolved solids (TDS) values.

representative of Rustler/Salado water in H1, then Z and not Y (showing good circumstantial evidence of mixing and contamination) would be more representative of Culebra water in H1, in terms of both solutes and stable isotopes. From this example it is evident that mixing and contamination affect the values of δD and $\delta^{18}O$ in the same way as they do major solutes (sodium, chloride, potassium, etc.). Thus, if it can be shown that major solute values have reached some sort of steady state characteristic of the local well system, the isotopic composition of the water molecules will probably also have reached steady state. If key major solutes (cf. Cl^-, total divalent cations, etc.) are judged to be minimally contaminated on the basis of transient measurements during a pump or flow test, then the δD and $\delta^{18}O$ values will be no more contaminated than the major solutes.

If the effects of contamination can be eliminated by such means as serial or multiple samplings as illustrated above, isotopic data for even low-flow-rate waters are expected to be accurately representative of their actual compositions at their sampling locations to within approximately 0.5 ‰ for $\delta^{18}O$ and approximately 5 ‰ for δD, based on twice the values of the typical confidence limits for individual measurements. Applied to the example from H1 above, these confidence limits allow one, using $\delta^{18}O$ values, to recognize and resolve degrees of mixing no smaller than about 7% (0.6 ‰ out of a span of 8.6 ‰ for the H1 example). For high-flow-rate waters, the "accuracy" is no better than the limits of reproducibility for the analytical methods (i.e., 0.2 to 0.3 ‰ for $\delta^{18}O$ and 2 to 3 ‰ for δD). As pointed out by Lambert and Robinson (1984), however, certain solution parameters (particularly trace constituents) are more susceptible to contamination than others, and the mitigation of contamination for some constituents is more difficult than for others. Thus, while the effects of volumetrically small amounts of contaminant water may be small for the stable-isotope measurements, the same is not necessarily true for certain ultratrace radioisotope measurements.

3.2.3 Samples and Data of Questionable Validity

During the course of WIPP investigations, several methods of well configuration and sampling were used. In some cases, such as H1 described above, circumstantial evidence indicates that mixing and contamination have occurred during fluid withdrawal from a wellbore, in the absence of certain precautions, or regardless of the precautions taken. An example of a packer leak and its effect on major solution parameters (involving testing of the Culebra in WIPP-30) is related from field evidence by Lambert and Robinson (1984). Other indications of irregularities have been described by Mercer (1983). All stable-isotope data for all water samples analyzed are reported here, but not all the data are used in interpretations. Samples whose integrity is suspect (i.e., whose precise origin may be in doubt, and whose stable-isotope compositions may not be representative of the sampling localities) are listed below, together with the rationales for their deletion from further consideration:

WIPP-30 Magenta. After 184 hours of pumping, there was no evidence of stability of field measurements (Lambert and Robinson, 1984).

H1 Culebra (March 17, 1977). This sample was discussed above.

P17 Culebra. A packer leak was suspected, since fluid levels from Culebra and Rustler/Salado contact were similar throughout the test that produced this sample (Mercer and Orr, 1979).

P15 Culebra (April 11, 1979). As in the second round of sampling in H1, the 1979 episode produced saltier water than the 1977 episode, and it is believed that old fluid left in the wellbore from the previous activities contaminated the 1979 sample (J. W. Mercer, pers. comm.), just as in the case of H1 described above.

H2C Rustler/Salado contact (February 24, 1979). Solute analyses were reported by Mercer (1983) only for water collected from this locality on February 23, 1977, although USGS multiple station listings show solute analyses (less sulfate) for a sample collected February 24, 1979 also. The latter was not tabulated by Mercer (1983) for reasons outlined in the discussions of the three samples above (J. W. Mercer, pers. comm.). In addition, the solute analysis of this sample departs markedly from those from nearby occurrences of Rustler/Salado water collected in 1977 (Table 3). Note particularly the depressed value of Na and the elevated values of Mg and Cl relative to the 1977 samples from H1, H2C, and H3.

H3 Rustler/Salado contact (May 10, 79). This sample was not reported by Mercer (1983) and did not appear in USGS multiple station listings. No solute analyses are available for it. Because of the resemblance in solute assemblage of the February 23, 1977 sample to the 1977 samples from nearby H1 and H2C (Table 3), and the likelihood that similar kinds of contamination result from process brine left over from the 1979 workover of several holes and incomplete purging, the 1977 sample is preferred to the 1979 sample.

P15 Rustler/Salado contact. Water from this test had lower solute concentrations than expected for the immediate vicinity. Similarities to the Culebra sample of April 11, 1979 indicate cross-contamination, according to USGS multiple station listings.

TABLE 3. RUSTLER/SALADO CONTACT BRINES, HOLES H1, H2C, AND H3

Borehole	H2C		H3		H1[1]
Date	23 Feb 77[2]	24 Feb 79[3]	23 Feb 77[4]	10 May 79[5]	
$\delta^{18}O$, ‰	-2.9	1.3	0.2	-4.9	1.6
δD	-41	-41	-38	-43	-29
Cl^-, mg/L	200000	280000	210000	?[6]	210000
SO_4^{-2}	1300	?	370	?	520
Ca^{+2}	9200	31000	18000	?	13000
Mg^{+2}	25000	66000	25000	?	30000
Na^+	66000	12000	59000	?	56000
K^+	9100	6400	14000	?	17000

---

1. USGS solute analyses, sample of 23 Feb 77; Mercer (1983).
2. USGS solute analyses; Mercer (1983).
3. USGS solute analyses; multiple station listings.
4. USGS solute analyses; Mercer (1983).
5. No solute analyses or other documentation available.
6. "?" = solute value not available.

P18 Culebra and Rustler/Salado contact. Neither unit was very productive, thus magnifying the possible effects of contamination by fluids left in the wellbore after perforating (Mercer and Orr, 1979). It is likely that perforations did not establish a sufficient connectivity between wellbore and water-bearing rock, or that the rock is not sufficiently productive to yield a desirable degree of purging of introduced fluid, as appears to be the case with WIPP-30 Magenta.

> WIPP-27 Rustler/Salado contact. "After 24 hr [of pumping], the field measurements showed evidence of stability. However, the continually dropping water level, dropping pump rate, and high Fe content (18 mg/L) indicated that the water had been in prolonged contact with the pipe and was no longer representative of the reservoir." (Lambert and Robinson, 1984)

Although no other accounts are available to indicate the integrity (or lack thereof) of certain other wellbore samples, the remaining data could contain some spurious values. For this reason, interpretations involving a single isolated data point, in the absence of a cluster or a trend, should be made with caution, and only in view of other information that provides confidence that the sample is reasonably representative.

4. DISCUSSION

4.1 The Meteoric Water Field

The data from this work are plotted in $\delta D/\delta^{18}O$ space. Each plot also includes the worldwide meteoric trends, defined by the equations

$$\delta D = 8 \times \delta^{18}O + 5 \quad \text{(Epstein, et al., 1965;1970)} \qquad (2)$$

and

$$\delta D = 8 \times \delta^{18}O + 10 \quad \text{(Craig, 1961b).} \qquad (3)$$

These equations describe least-squares lines fit to many thousands of data points, including meteoric waters from tropical, temperate, and polar regions. Equation (2) gives a better fit to isotopically lighter (more negative) values, as it includes many data points from the Antarctic. The intervening area bounded by these lines is called the meteoric field.

Observed $\delta^{18}O$ and δD values even for meteoric waters may not fall precisely on either line. Both Equations 2 and 3 are statistical as opposed to functional relationships. This fundamental difference has been described in detail by Natrella (1963). Predictions of δD calculated from a $\delta^{18}O$ and either linear relationship will have finite confidence limits arising from the scatter in both $\delta^{18}O$ and δD values used for the least-squares fits. $\delta^{18}O$ and δD values used for a fit have their own analytical confidence limits, and may also show natural yet significant scatter around the general trend of the fit, with variations greater than analytical confidence limits for single data points.

4.2 Local Recharge: Vadose Zone, Capitan Limestone

Water samples from Carlsbad Caverns were collected for isotopic analysis beginning in 1976, to aid in interpreting the groundwater systematics in the northern Delaware Basin, particularly near the WIPP site. It is fairly well known that Caverns water comes from vertical infiltration into near-surface outcrops of overlying dolomite of the Tansill and Yates Formations (Ronal Kerbo, pers. comm.), making its way downward along paths of varying tortuosity formed by fracturing and partial dissolution of the near-surface dolomites and underlying Capitan limestone. This recharge appears not as catastrophic flooding into sinkholes as would be more common in limestone karstlands of Kentucky or Jugoslavia, but appears as drips from the ceiling. This gradual sort of infiltration implies some finite residence time for the downward-percolating water in the zone between surface and cavern levels. Residence times of several months have been found for cavern waters infiltrating limestone karst in humid Jugoslavia. A residence time this long allowed a large degree of mixing and isotopic homogenization. Only when large storms swelled streamflow into sinkholes did isotopic signatures of short-term meteorological events show up in the cavern environment (Pezdic et al., 1985).

Table 4 contains information about the water samples from Carlsbad Caverns, including the elevations of sampling stations, dates of collection, and isotopic compositions. The isotopic compositions were plotted in $\delta D/\delta^{18}O$ space, shown in Figure 6.

The plot shows the Carlsbad Caverns waters identified by their two-letter locality codes as given in Table 4. All of them have δD values more positive than -40 ‰. Note that the Carlsbad Caverns points generally lie along the meteoric field. The deviation of some of the points from the meteoric field is small yet significant (i.e., outside the analytical confidence limits). Samples that fall to the right (toward more positive $\delta^{18}O$ values)

TABLE 4. CARLSBAD CAVERNS WATERS

Location[1]	Date[2]	Elev.[3]	δD[4]	$\delta^{18}O$[5]	Analyst[6]
Green Lake (GL) Green Lake Room	29 Aug 76	≈3575	-24	-3.6	[a]
Mirror Lake (ML) Big Room	29 Aug 76	≈3660	-28	-4.3	[a]
Longfellow's Bathtub (LB) Big Room	29 Aug 76	≈3660	-29	-4.2	[a]
Celery Stalk Pool (CS) Big Room	29 Aug 76	≈3660	-20	-3.0	[a]
Devil's Spring (DS) Main Corridor	09 Jun 77	4100	-30	-4.4	[a]
Horsehead Lake (HH) New Mexico Room	09 Jun 77	3672	-39	-4.8	[a]
Lake of the Clouds (LC)[7]	09 Jun 77	3311	-33	-5.1	[a]
Junction/Rope Pool (JR) Left-Hand Tunnel	09 Jun 77	3641	-32	-6.3	[a]
Lower Cave Pool (LO)	09 Jun 77	3625	-17	-1.7	[a]
Music Room (MU) Main Corridor	21 Dec 77	≈4100	-32 -31	-4.0 -4.0	[b],[c] [b],[c]
Naturalist's Room (NR) Lower Cave	21 Dec 77	≈3575	-24 -23	-3.5	[b],[c] [b]
Grass Skirt Pool (GS) NM Room	21 Dec 77	≈3670	-37 -37	-4.2 -3.7	[b],[c] [b],[c]

---

1. Location name consists of formal or informal name, followed by parenthesized two-letter code, and nearest major named room or passageway.
2. Date of collection.
3. Elevation, feet above sea level.
   Elevation of Natural entrance, Carlsbad Caverns: 4311
   Elevation of Visitor's Center, Carlsbad Caverns: 4406

TABLE 4. (Continued)

Exact elevations provided by Dr. G. Ahlstrand. Approximate ("≈") elevations are estimated from nearest surveyed cavern level (Jagnow, 1979).

4. In per mil (‰), vs V-SMOW.
5. In per mil (‰), vs V-SMOW.
6. 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] $\delta\ ^{18}O$, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.
7. Lowest known point in Carlsbad Caverns.

---

phenomenon are LO, NA, MU, GS, and HH. One possibility is that some waters have undergone a kinetically induced (e.g., nonequilibrium) isotopic fractionation due to partial evaporation from the surface of free-standing water in the humid speleal environment, as in Caverns pools (cf. Craig et al., 1963). If this mechanism of isotope shift is dominant, we would infer that loss of water from these pools is dominated by evaporation rather than by seepage, as might be typical in vadose (unsaturated-zone) caves. Detailed discussion of partial evaporation and its possible role in overall interpretation of Delaware Basin groundwater systematics is deferred to Section 4.6.

A second possible explanation for "isotope shift" (of meteorically derived groundwaters away from the meteoric field) is that evaporation (and isotope shift) took place in a saturated surface layer before the water migrated to great depth, analogous to water evaporating from a column of sand (cf. Allison, 1982).

A third alternative need not involve post-precipitation evaporation at all. Evans et al. (1979) found that groundwaters in parts of the United Kingdom had δD and $\delta^{18}O$ values that were better described by least-squares lines with slopes (6.6) and intercepts (1.4) significantly different from Equations 2 and 3. In addition, rainfall from "maritime Europe," taken as the "best

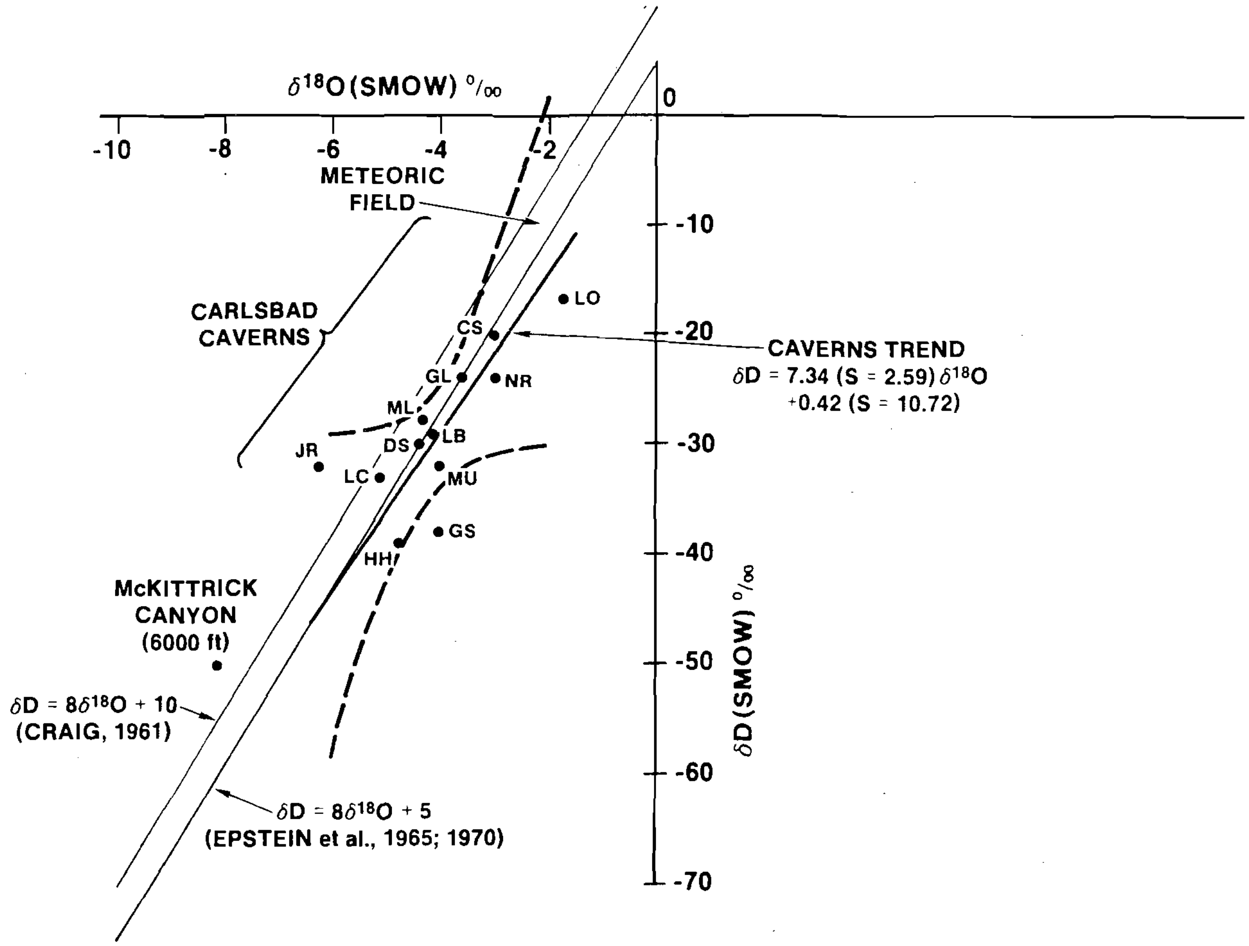


Figure 6. Stable-isotope compositions of near-surface waters from the Capitan Limestone. Individual data points for Carlsbad Caverns waters are identified by their two-letter codes in Table 4. The least-squares fit to the Caverns points (excluding LO and JR) is $\delta D = 7.34(s=2.59)\delta^{18}O + 0.42(s=10.72)$, depicted by the solid line; 95% confidence limits for the entire line are given by the dashed curves. The "meteoric field" in this and following $\delta D/\delta^{18}O$ plots is taken to be the area between the lines defined by Equations 2 and 3 in the text. Note that the Caverns trend corresponds closely to Equation 2. Note also the isotopic distinction between Capitan vadose water recharged at 4300 ft elevation (the Caverns points) and surface water at 6000 ft (McKittrick Canyon), indicating a profound elevation effect on well-mixed meteoric recharge to stream- and shallow groundwater.

representation for recent rainfall over Britain," was isotopically very similar to their groundwater samples. Specifically, the slope of the $\delta D/\delta^{18}O$ relationship for rainfall in maritime Europe was 6.9 and the intercept was -0.3. From this similarity Evans et al. concluded that "at no time was rainfall significantly affected by evaporation before recharge". Allison et al. (1985) observed nonevaporative isotopic deviations in local groundwater from the worldwide meteoric field. The trend of soil water in $\delta D/\delta^{18}O$ space had a slope of 8, as do the meteoric lines, but was displaced 11 ‰ **downward** along the δD axis relative to the Craig meteoric line. In view of such natural documented deviations, it should come as no surprise if a demonstrably meteoric point exhibits a small but statistically significant deviation from the line described by Equation 2 or 3. In the absence of other kinds of information (e.g., geologic or hydraulic observations, solute content, isotopic composition of constituents other than oxygen and hydrogen), such a deviation should not a priori be interpreted uniquely as fractionation by partial evaporation.

If the Caverns samples in Figure 6 having the highest and lowest $\delta^{18}O$ values are for the moment disregarded (their $\delta^{18}O$ values deviate from their nearest neighbors by more than 1.2 ‰; the highest [JR] probably having arisen from partial evaporation, the lowest [LO] by some unquantifiable low-temperature mineral/water interaction), the regression line through the remaining 10 points is:

$$\delta D = 7.34(s=2.59)\delta^{18}O + 0.42(s=10.72). \qquad (4)$$

The 95% confidence limits for a δD value predicted from a $\delta^{18}O$ value are approximately ±11 ‰. The line through the relatively tight cluster of caverns points, together with the estimated confidence limits for this line, are also plotted in Figure 6. JR is the only point that falls to the left of the line of Equation 3, but it falls within the estimated confidence limits of the line of Equation 4, as does LO, even though these two points were not included in the least-squares calculation. Interestingly, Equation 4 contains within its confidence limits the lines of Equations 2. Thus, there is no reason, on a statistical basis, to suspect that the Carlsbad Caverns waters do not represent modern meteorically-derived recharge to the unsaturated zone, minimally affected by evaporation, with the possible exception of sample GS. Other than this point, deviations from the meteoric field exhibited by the set of Caverns points are not statistically significant, and should not be regarded as nonrepresentative. There is no evidence that the remaining ten points have been significantly affected by partial evaporation or mineral/rock interaction (i.e., to the degree that they should be regarded as anomalous departures from scattered but purely meteoric behavior).

Note the considerable nonsystematic variation between isotopic composition of Caverns waters and depth. The Caverns waters probably carry seasonal (climatically induced) variations that give rise to the relatively wide spreading of the isotopic compositions along the meteoric field, due to incomplete mixing that would otherwise integrate out the seasonal variations. Thus, a seasonal record of the modern recharge to the Caverns would have to be obtained in such a way as to (1) minimize the possible effects of evaporation from the standing pools, (2) quantify the season-dependent variations in rate of recharge and its isotopic composition in various parts of the Caverns system, and (3) obtain an integrated average isotopic composition for water recharging the Caverns environment. This might be facilitated by sampling drip water as it falls from the caverns ceilings, collected monthly over a period of at least two years.

The water sample from JR in Carlsbad Caverns as well as that from the North McKittrick Travertine Site (Section 4.3.2) exhibit a deviation to the left of the meteoric field. Although the possible role of biological alteration of the waters' isotopic compositions has not been evaluated, especially for the McKittrick Canyon site, the observed isotopic shift of samples from JR and McKittrick Canyon is more likely due to interaction with carbonates that were somewhat depleted in ^{18}O relative to marine carbonates, given that such epigentic interaction took place at temperatures similar to those of deposition. Thus, it is possible that the Capitan limestone was indeed locally exposed to meteoric influences, such as fresh water, perhaps even during deposition, or that the water has interacted with older freshwater speleothems or travertine at temperatures lower than those of original deposition of speleothem or travertine carbonate (see Section 4.3.2).

Note that the waters with the most negative δD values in the Caverns came from the same room (the New Mexico Room), have similar isotopic compositions (-37 to -39 ‰), were collected at different seasons (June and December), and are in a relatively isolated part of the Caverns system. One of them, GS, coincidentally has a δD value displaced downward from the line of Equation 2 by 11 ‰. At the other extreme, the isotopically heaviest Caverns water, from Lower Cave, is displaced 13 ‰ downward from the line of Equation 2. These displacements are entirely consistent with the observations of Allison et al. (1985), and are not in themselves uniquely indicative of fractionation by partial evaporation, even though the negative displacement in δD corresponds to a positive displacement in $\delta^{18}O$.

In spite of the fact that some of the Caverns points exhibit deviations from the meteoric field, the overall isotopic distribution of Caverns waters in Figure 6 straddles the meteoric field. In addition, all of them have δD values significantly more positive than -41 ‰; **none** were found that were more negative. More than half the points correspond very closely to the line described by Equation 2, clearly reflecting their meteoric origin. The maximum deviation of these points from the line is 0.6 ‰ in $\delta^{18}O$, which is approaching the limit of analytical resolution (see Section 3.2.2). Points that lie within the meteoric field (or within 0.6 ‰ of it along the $\delta^{18}O$ axis) include CS, GL, NR, ML, LB, DS, MU, and LC. It is not reasonable that these points have evolved by partial evaporation from more negative meteoric values, since evaporation does not take place with a trajectory of slope 8 in $\delta D/\delta^{18}O$ space, regardless of humidity. Thus, there is no reason to expect that the Caverns pools are <u>not</u> representative of modern meteoric recharge to the Capitan Limestone in the northern Guadalupe Mountains. Also, it is significant that no such waters from this locality had δD values more negative that -41 ‰. With the exception of JR, no such waters from this locality had $\delta^{18}O$ values more negative than -5.4 ‰. Thus, even the contributions of isotopically lighter winter precipitation do not appear to push the negative limit of seasonally integrated modern meteoric Caverns recharge below about -41 ‰. In some subsequent plots the Carlsbad Caverns field in $\delta D/\delta^{18}O$ space will be delineated by an envelope drawn around the points, rather than by the individual points.

4.3 Other Near-Surface Waters

4.3.1 Geographic Distribution

Samples of near-surface waters came from a geographically widespread area in the Delaware Basin (Figure 1). Groundwater under inferred water-table conditions was sampled from the alluvial fill of San Simon Sink (SNL and UNM, 1981). 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 were between 3000 and 4000 ft, representative of the surface elevation of the WIPP site.

An intermittent spring issuing from the Tamarisk member of the Rustler Formation near the north end of Laguna Grande de la Sal

(Figure 2) was also sampled. Named "Surprise Spring" by Robinson and Lang in 1938, it was, at that time, of interest with respect to refinery effluent from local potash operations. It has recently been proposed, largely by virtue of its existence and location in southwestern Nash Draw, as a likely discharge for much of the water in the Culebra member. This proposal will be evaluated in view of the available geochemical and hydraulic data for groundwaters in the vicinity of Surprise Spring. The sample reported in this study and by Lambert (1983a) was collected in December, 1977. In recent years outflow at Surprise Spring has steadily and observably diminished.

A local stream that drains a portion of the southern Guadalupe Mountains at elevations above 6000 ft (1830 m) was sampled in McKittrick Canyon, together with the travertine it has deposited in historic times, to determine the degree to which the isotopic record in the travertine preserves the integrated average isotopic composition of the stream water. It is expected that stream- and spring-waters will have relatively constant isotopic compositions, as discussed by Friedman et al. (1964).

4.3.2 McKittrick Canyon

We assume that travertine deposits, particularly in the Guadalupe Mountains, represent calcite deposition in isotopic equilibrium with its parent water; hence, the uppermost (and youngest) layers of an active travertine deposit will record the isotopic compositions of the water from which it precipitated. In order to test these assumptions, and obtain an isotopic record of recharge in the southern Guadalupe Mountains at a higher elevation than Carlsbad Caverns, a known, active, wet travertine deposit was analyzed. The outermost layers were analyzed for their $^{18}O/^{16}O$ ratio, and compared with the same ratio in the water. If the resulting observed fractionation factor is consistent with the theoretical value at some reasonable value for the ambient temperature, the possibility of anomalous isotopic behavior (such as biogenic and evaporative effects) can be neglected. Such a test system, recently sampled and analyzed, is available in the canyon called "Devil's Den" on King's 1948 map, and is adjacent to North McKittrick Canyon a short distance northward from Texas across the state line into New Mexico (Figure 1). Although the locality is just outside the boundary of Guadalupe Mountains National Park in Lincoln National Forest, the area is under the administrative protection of the National Park Service. Because of the ambiguities associated with changes in name usage on maps, the locality will herein be called the North McKittrick Travertine Site (NMTS).

The NMTS is at an elevation of approximately 6000 ft (1830 m), and is underlain by the Goat Seep limestone of King (1948). This outcrop of Goat Seep at NMTS is surrounded by the Capitan limestone, and the watershed upstream from NMTS is dominated by outcrops of the Capitan. Hence, we infer here that the Capitan, and not the Goat Seep, is actually the source of the carbonate in the travertine. The travertine system sampled in this study (Figure 7) consists of a small pond, approximately 3 m wide and 6 m long, recharged by an upstream spillway, a natural "sluice" (Plate 1), and discharging into another spillway downstream. At the time of the visit (June 13, 1984) the upper sluice was covered with green(?) algae, as was the terrace immediately below (Plate 1), and from this we infer that active travertine deposition is in part attributable to the removal of carbon dioxide by the algae for photosynthesis, which locally diminishes the solubility of calcium carbonate.

The presumably active travertine and its coexisting water were sampled from the upper sluice. $\delta^{18}O$ and δD values for the water flowing into the NMTS pool via the upper sluice are given in Table 5, part A.

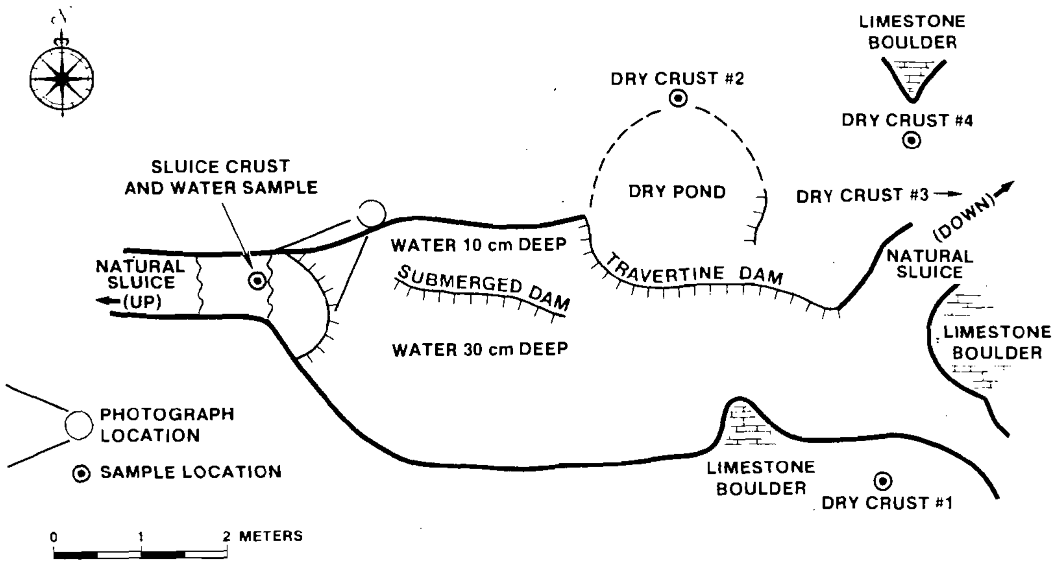


Figure 7. Sketch map of main pond at North McKittrick Travertine Site (SW 1/4 NW 1/4 S.34, T26S, R21E, New Mexico). Sampling locations are shown for travertine and water whose δ-values are given in Table 5, as well as location of view in Plate 1.

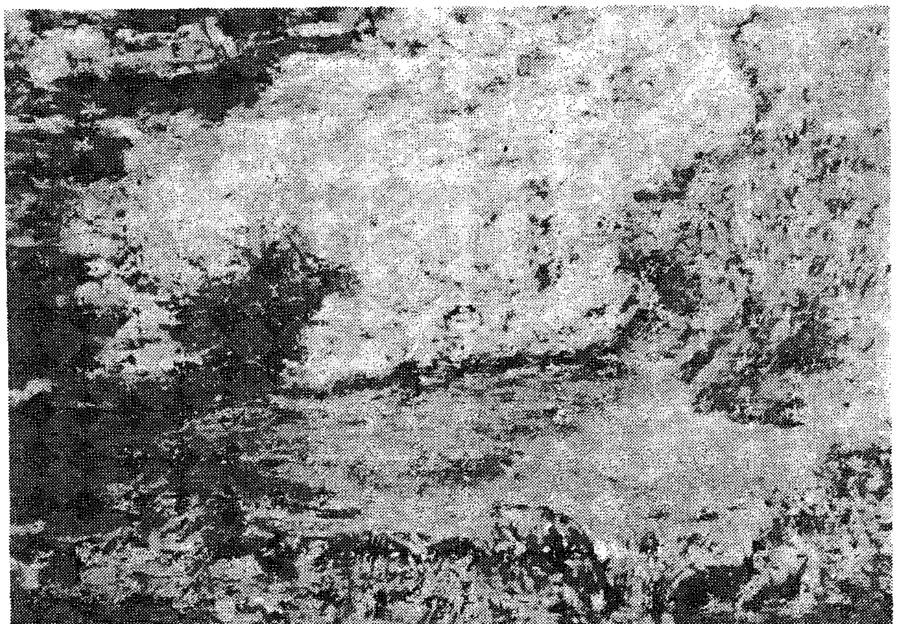


Plate 1. Active travertine deposition at upper sluice, North McKittrick Travertine Site. Water flows over flat surface covered with green algae. At the bottom of the sluice is an actively growing travertine terrace, not yet lithified, also associated with abundant organic material. Photo location shown in Figure 7.

TABLE 5. ISOTOPIC RECORDS IN TRAVERTINE

A. STABLE-ISOTOPE δ-VALUES, NORTH MCKITTRICK TRAVERTINE SITE

Travertine Sample Name	yield, wt % calcite	$\delta^{18}O$ ‰ (SMOW)	$\delta^{13}C$ ‰ (PDB)
Sluice crust	90	+22.9	-7.9
Dry crust #1	90	+23.4	-8.5
Dry crust #2	85	+24.3	-7.1
Dry crust #3	88	+24.5	-6.7
Dry crust #4	93	+23.7	-7.3

Water Sample Name	$\delta^{18}O$ ‰ (SMOW)	δD ‰ (SMOW)
Upper sluice	-8.1,-8.1	-49,-50

B. CALCULATED TEMPERATURES AT THE NORTH MCKITTRICK TRAVERTINE SITE

$\delta^{18}O$ of water = -8.1 ‰ (measured at Upper Sluice)

Travertine	$\delta^{18}O$(calcite) ‰ (SMOW)	Calculated T (°C)
Sluice crust	+22.9	12.1
Dry crust #1	+23.4	10.2
Dry crust #2	+24.3	6.7
Dry crust #3	+24.5	5.9
Dry crust #4	+23.7	9.0

TABLE 5. (Continued)

C. CALCULATED $\delta^{18}O$ VALUES OF WATERS AT THE NORTH MCKITTRICK TRAVERTINE SITE

T = 12.1°C (calculated at Upper Sluice)

Travertine	$\delta^{18}O$(calcite) ‰ (SMOW) Measured	$\delta^{18}O$(water) ‰ (SMOW) Calculated
Sluice crust	+22.9	-8.1
Dry crust #1	+23.4	-7.7
Dry crust #2	+24.3	-6.8
Dry crust #3	+24.5	-6.6
Dry crust #4	+23.7	-7.4

NOTE: Calculations in Parts B and C above were performed using the equation of O'Neil et al. (1969):

$$1000 \ln \alpha = 2.78\ (10^{6} T^{-2}) - 3.39$$

$$\text{where } \alpha = \frac{1 + \frac{\delta^{18}O(\text{calcite})}{1000}}{1 + \frac{\delta^{18}O(\text{water})}{1000}}$$

For 35 years it has been well known that the fractionation of trace isotopes among coexisting phases at equilibrium is temperature dependent. One of the first applications of this stable-isotope geochemistry was in fact calculation of paleotemperatures from the $\delta^{18}O$ values of carbonate in a Cretaceous belemnite (Urey et al., 1951). This calculation required the following assumptions: (1) a specific $\delta^{18}O$ value of the water in which the belemnite grew, (2) that the oxygen isotope composition of the carbonate in the belemnite was governed only by the equilibrium physicochemical partitioning of ^{18}O and ^{16}O between calcite and water, (3) that the amount of water with an assumed oxygen isotope composition was in great abundance relative to the amount of calcite, (4) that no postdepositional alteration had taken place, and (5) that laboratory determinations of the variation in oxygen isotope fractionation with temperature were applicable to the natural system. Since that pioneering work, the calcite-water oxygen isotope fractionation has been experimentally determined at various temperatures ranging from ambient to several hundred degrees (O'Neil et al., 1969). Thus, from the oxygen isotope compositions of coexisting calcite and water, and under the above assumptions, it is possible to calculate the deposition temperature of travertine. Similarly, from an assumed temperature and the oxygen isotope composition of either travertine or water, it is possible to calculate the oxygen isotope composition of the other phase. Variations in the oxygen isotope composition of natural water, for example, are indicative of climatic variations.

Calculations here were performed using the equation of O'Neil et al. (1969):

$$1000 \ln \alpha = 2.78\,(10^6 T^{-2}) - 3.39 \qquad (5)$$

$$\text{where } \alpha = \frac{\dfrac{\delta^{18}O(\text{calcite})}{1000} + 1}{\dfrac{\delta^{18}O(\text{water})}{1000} + 1}\,. \qquad (6)$$

First, the oxygen isotope composition of water from the upper sluice at NMTS was used with the oxygen isotope composition of travertine from the sluice crust to calculate the value of α, the apparent $^{18}O/^{16}O$ fractionation factor between the coexisting travertine and water. Next, it was assumed that the outermost crust of travertine had precipitated in isotopic equilibrium with the water, so that the apparent fractionation factor was taken to be the equilibrium fractionation factor. Then, from the above equation the temperature was calculated.

The temperature was calculated (12.1°C) for the formation of travertine in the sluice crust (Table 5, part A) from the $\delta^{18}O$ values of the sluice crust and the water running down the sluice. It is significant that the isotopic equilibrium temperature calculated by Equation 5 is (a) calculable (i.e., the calculated temperature is within the temperature limits for liquid water at one atmosphere pressure) and (b) a reasonable value for ambient conditions. These two observations suggest that the coexisting carbonate and water are very nearly at isotopic equilibrium. This temperature is quite reasonable as an average temperature of travertine formation in late spring at 1800 m elevation. The rate of travertine deposition at NMTS is not precisely known, but a few cm of crust thickness probably represents several weeks or months of growth, but not years (Roger Reisch, National Park Service, personal communication). Thus, a travertine sample a few centimeters thick could integrate as much as a single year's worth of deposition, and hence at least several months' worth of water from which it grew. No attempt was made in this preliminary study of McKittrick Canyon travertine to identify growth surfaces representing different episodes of travertine deposition.

In calculating temperatures of formation of older inactive travertines, it is necessary to assume that the $\delta^{18}O$ value of the water is some discrete value. In part B of Table 5 the $\delta^{18}O$ value of the water from which all travertines grew is assumed to be -8.1 ‰. This results in calculated temperatures lower than observed for the actual coexisting calcite/water pair in the upper sluice, because the $\delta^{18}O$ values of the dry crusts are all higher than that of the active travertine. If the water from which these older travertines were deposited actually had the same isotopic composition as assumed, then these travertines formed at average temperatures of 6.7 to 10.2°C. This implies that some of these travertines may actually have formed at lower temperatures. Alternatively, some of these isotopically heavier travertines may have formed at 12°C in the presence of isotopically heavier water.

In part C of Table 5, it is assumed that a constant temperature (or at least a very narrow temperature range) prevailed during the formation of all the travertines at NMTS. From the $\delta^{18}O$ values of the travertines and the assumed temperature (12°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 apparent variation, including the observed value of -8.1 ‰, is -6.6 to -8.1 ‰. This range may be quite reasonable for local seasonal variations, if the various samples of inactive travertine resulted from deposition governed by waters having somewhat variable isotopic compositions according to changing seasons, or year-to-year variations in average isotopic composition of runoff in the southern Guadalupe Mountains. In fact, it is more reasonable that the variation in $\delta^{18}O$ values among the travertines is due to variations in oxygen-isotope composition of water rather than to variations in temperature. Since the solubility of carbon dioxide actually increases with decreasing temperature, thus favoring the dissolution (not the deposition) of travertine, about 12°C might be considered a reasonable minimum for the temperature of travertine deposition at NMTS, neglecting any presumed active biological role of the algae in determining the dissolved carbon concentration or the isotopic composition of the travertine. Our tentatively preferred interpretation is that variations in $\delta^{18}O$ values among different generations of travertine probably reflect variations in $\delta^{18}O$ values of waters from which they deposited. Regardless of whether the variations are due to changes in temperature or isotopic composition of water, this implies that $\delta^{18}O$ values in travertines do indeed preserve some part of the climatic history of a local area. This climatic history may be only the small differences in air-mass characteristics (season, previous path, temperature or altitude of nucleation in clouds, etc.). In any case, it appears that meteorically derived modern water at an elevation of 1800 m (6000 ft) in southeastern New Mexico has a $\delta^{18}O$ value of between -6.6 to -8.1 ‰, but in no case is as positive as that found at lower elevations in Carlsbad Caverns further north, which has values more positive than -5.5 ‰.

Note that the measured δD value of water at the NMTS, taken with the measured $\delta^{18}O$ value, does not exactly obey either Equation 2 or Equation 3 (i.e., this sample does not fall within the statistically defined "meteoric field"). However, its source is meteoric water (i.e., rapid runoff) whose isotopic composition has been little altered by processes such as evaporation, which would tend to shift the isotopic composition **to the right** of the meteoric field (Figure 6), if the unaltered water originated near the field. Instead, the McKittrick Canyon point falls **to the left** of the meteoric field; thus, evaporation does not appear to have significantly contributed to the observed magnitude or even direction of isotopic shift of McKittrick Canyon water away from the meteoric field. Note that the same argument applies to sample JR from Carlsbad Caverns. This illustrates that these equations must not be used rigorously to calculate either δD or $\delta^{18}O$ when only one or the other is known for an individual sample. The equations are statistical relationships only, and do not necessarily precisely describe the relationships between δD and $\delta^{18}O$ values for local meteoric waters. The pitfalls of misusing statistical relationships as rigorous mathematical relationships were described by Williams (1983). Isotopic compositions of waters in local groundwater systems may exhibit significant deviations from the worldwide averages (cf. Allison, 1982), even when there is little evidence to indicate that they have been isotopically modified by such processes as evaporation. In subsequent discussions, we shall use the term "meteoric" to refer to those isotopic compositions that lie sufficiently close to the meteoric field (or within it) in $\delta D/\delta^{18}O$ space such that it is difficult to argue for isotopic modification (e.g., partial evaporation, etc.) solely on the basis of a small isotopic shift with respect to the meteoric field. This will presumably clarify the distinction between water originating as precipitation whose occurrence contains no evidence of significant isotopic modification relative to the original composition of the precipitation (to which the term "meteoric" is here applied), and water whose primary origin was meteoric, but whose isotopic composition was subsequently modified.

The isotopic composition of the water from NMTS is plotted in Figure 6, together with the Caverns points. It lies to the left of the line described by Equation 3, as does JR. If the isotopic shifts to the left of the meteoric field are consequences of processes other than precipitation, such shifts may have arisen by processes involving oxygen-isotope exchange between rock and water at low temperatures, and relatively low water/rock ratios, but probably not by partial evaporation. Alternatively, sample JR, like NMTS water, may reflect simple local variability in isotopically unmodified precipitation.

Water from McKittrick Canyon is significantly different in isotopic composition from waters at lower elevations in the Capitan, and hence it serves as a demonstration that waters with a δD value more negative than about -40 ‰ in the Delaware Basin can originate under different climatic conditions (in this case, significantly higher elevation) than those that prevail now at elevations no higher than about 4500 ft. The occurrence of more negative δD values in precipitation at higher elevations is a concept originally developed and demonstrated by Friedman et al. (1964). Data and arguments are presented below to show that other shallow groundwaters with probable local connection with the surface (i.e., actively recharged) have δD values consistent with those of the Caverns.

4.3.3 Seasonal, Climatic, and Orographic Variations

Direct collection, analysis, and interpretation of modern meteoric precipitation is generally of limited relevance to ground water systems. Due to their individual recharge characteristics, groundwater systems integrate out seasonal isotopic variations through mixing, and may preferentially receive recharge at certain times of the year under transient conditions that allow infiltration to various degrees. Thus, a weighted average of isotopic compositions of several stormwaters in general may, but need not necessarily, provide a representative estimate of isotopic compositions of waters actually recharging groundwater systems. Isotopic compositions of individual precipitation events are given here only to illustrate the range of such compositions in the Delaware Basin. A more reliable estimate of local meteoric water isotopic compositions is probably obtained from perennial streams and springs, as suggested by Friedman et al. (1964).

Isotopic compositions for additional surface waters in the northern Delaware Basin are given in Table 6, including δD and $\delta^{18}O$ values for storms in May and August, the Pecos River at Lake Carlsbad in June, the McKittrick Canyon stream (see Section 4.3.2), and Surprise Spring, which issues from the Tamarisk member of the Rustler Formation near the northern end of Laguna Grande de la Sal. Figure 8 shows the positions of these data in $\delta D/\delta^{18}O$ space, together with the meteoric field and the Carlsbad Caverns field. Table 6 also lists a δD value for a stormwater (August 11, 1977) for which a $\delta^{18}O$ value was not available; its δD value is marked along the δD axis in Figure 8.

At the upper (heavier) extreme of deuterium in Figure 8 is summer rain collected during a storm at WIPP-29 on August 26, 1980. This point falls into the Caverns ("modern") field, but must be viewed as a single climatic incident. The position of another stormwater collected in Carlsbad on August 11, 1977 is indicated on the δD axis, as there was insufficient quantity of sample to analyze for $\delta^{18}O$. The δD values of these two stormwaters are

TABLE 6. SURFACE WATERS

Location	Date[1]	Elev.[2]	δD[3]	$\delta^{18}O$[4]	Analyst[5]
Pecos River Lake Carlsbad	08 Jun 77	3111	-36	-3.6	[a]
Carlsbad storm Rodeway Inn	05 May 77	≈3150	-80	-10.3	[a]
Storm, WIPP-29 1750-1815 h	26 Aug 80	2975	-18	-2.3	[b],[c]
			-20		[b]
Surprise Spring	20 Dec 77	2950	-31	-1.8	[b],[c]
			-30	-1.2	[b],[c]
				-1.0	[c]
Carlsbad storm Rodeway Inn	11 Aug 77	≈3150	-18		[b]
			-19		[b]
McKittrick Canyon stream	13 Jun 84	6000	-49	-8.1	[d]
			-50	-8.1	[d]

---

1. Date of collection.
2. Elevation, feet above sea level.
3. In per mil (‰), vs V-SMOW.
4. In per mil (‰), vs V-SMOW.
5. 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] $\delta^{18}O$, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.

[d] δD, S. J. Lambert, Sandia Nat'l Labs.

statistically indistinguishable (Table 6). They are probably, however, more representative of modern rainfall (especially in the summer when most of the precipitation falls in the Delaware Basin) than, say, the springtime stormwater from Carlsbad on May 5, 1977, in the lower left part of Figure 8. Individual climatic events, even when combined into a weighted average over a year, should not be used to infer a unique value for the isotopic composition of modern recharge, because (1) the recharge water may be most dominant in a particular season, and (2) a

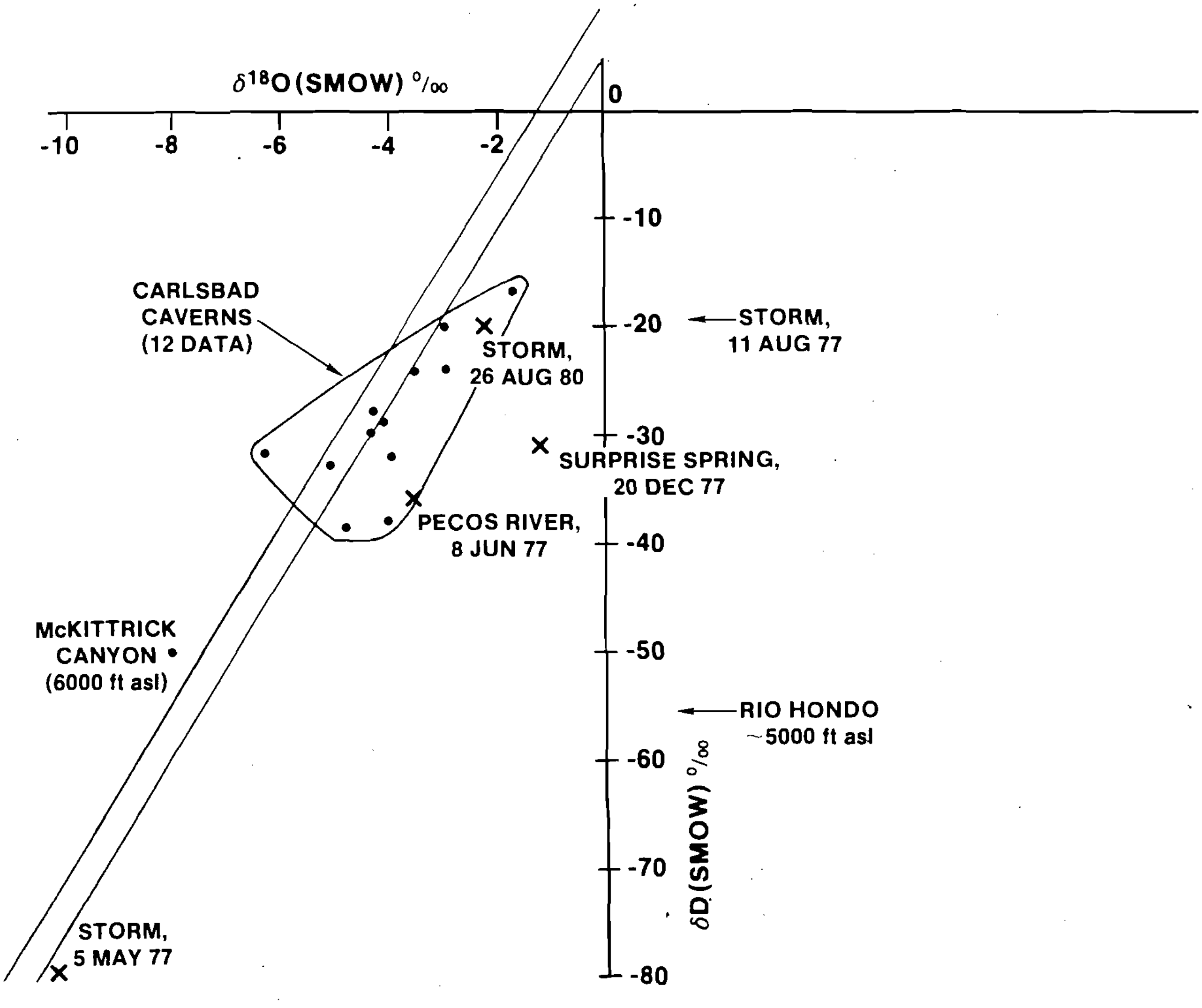


Figure 8. Stable-isotope compositions of near-surface waters in southeastern New Mexico. In addition to the data points from Figure 6, data are shown for stormwaters, the Pecos River, and Surprise Spring in southwestern Nash Draw (Figure 2). δD values are indicated for a summer storm in Carlsbad (3111 ft elev) and stream water from the Rio Hondo (5000 ft elev) on the dip-slope of the Sacramento Mountains west of Roswell. The Carlsbad Caverns data field is taken from Figure 6 and includes all 12 analyzed samples.

single year may not be representative of precipitation that has occurred over tens to hundreds of years (Hunter, 1985).

The isotopic composition of the Pecos River, sampled at Lake Carlsbad in June, probably represents the period of highest runoff feeding the river's tributaries upstream. This isotopic composition falls near the field of the other surface-derived waters. The Pecos River generally has been regarded as a feature along which discharge has taken place (Hale et al., 1954), especially for waters escaping the Rustler Formation in alluvium near Malaga (Figure 1). According to the convention of Friedman et al. (1964), it is probably a reasonably good representation, as a perennial stream, of average isotopic compositions of local meteoric waters. A major role for the Pecos River of recharge directly to the Rustler Formation in the detailed study area (Figure 2) east of the river would be inhibited due to a general lack of contiguous hydraulic connections between the river and the Rustler Formation north of Malaga (cf. Bachman, 1980, Figure 12).

Another water for which only δD was available is marked on the δD axis of Figure 8: Rio Hondo. The Rio Hondo drains the dip slope of the Sacramento Mountains in the area between Capitan and Picacho (underlain by the San Andres and Yeso Formations), and becomes intermittent between Picacho and the Pecos River at Roswell. The role of the Rio Hondo, dip slope, San Andres, and Yeso will be discussed in greater detail with respect to their roles in recharging groundwater in the Roswell Artesian Basin in Section 4.8. The Rio Hondo water sample came from an elevation of about 5000 ft (Yapp, written communication), and as a perennial stream at that locality should be reasonably representative of δD values in mountainous portions of southeastern New Mexico, including some higher-elevation component in the headwaters. Its drainage collects water from higher elevations upstream, is a losing stream, and serves as a significant source of "rapid" recharge for the Glorieta, Yeso, and San Andres units that underlie it and into which its water infiltrates (Gross et al., 1976, pp. 55-57). Therefore, the Rio Hondo sample probably represents precipitation in its upstream collection area, rather than only the elevation at the sampling point. Its δD value (-56 ‰) corresponds more closely to the δD value of the McKittrick Canyon stream (-50 ‰ at an elevation of 6000 ft, Table 6) than it does to either the Pecos River at Carlsbad (-36 ‰) or the lightest of the Carlsbad Caverns waters (-39 ‰). From these elevation/δD relationships we tentatively conclude that **modern** waters demonstrably derived from the surface (according to direct observation) in southeastern New Mexico with δD values more negative than about -50 ‰ are characteristic of elevations higher than about 5000 ft. Surface-derived waters from lower elevations have δD (and, of course, $\delta^{18}O$) values significantly more positive than those at higher elevations (Friedman et al., 1964).

Data for Surprise Spring, observably yet intermittently issuing from the Tamarisk member of the Rustler Formation, are plotted with the other data in Figure 8 because Surprise Spring water is considered surface water, regardless of its origin. Consideration of the somewhat anomalous position of Surprise Spring's isotopic composition in Figure 8 is deferred until discussions about the isotopic and solute compositions have been developed for the Rustler Formation (Section 4.5.5).

4.3.4 Shallow Groundwaters

An additional data source, one step removed from direct observable recharge in the unsaturated zone, is shallow groundwater inferred to have various degrees of hydraulic connection with the surface. Obviously, this class of waters includes those under water-table conditions. In this section shallow groundwaters from alluvium, the Dewey Lake Red Beds, Triassic rocks, and the Ogallala Formation will be considered. All these units overlie the Rustler Formation (Figure 4). Groundwaters nearest the surface at water-table conditions, such as the vadose caverns waters, have a greater probability of receiving recharge by direct infiltration from the surface than do groundwaters under confined conditions. Groundwaters from caverns, from alluvium, and from sandstone of the Ogallala Formation, where under water-table or vadose conditions, are here taken as waters representative of modern recharge conditions, because of their observable or inferred hydraulic characteristics. We propose that given these local hydraulic characteristics it is <u>possible</u> in principle to demonstrate recent or ongoing recharge to these occurrences; consequently, we refer to these occurrences as having "demonstrable," but not necessarily "demonstrated" recharge. Waters from the Dewey Lake Red Beds and Triassic rocks may be either under confined or water-table conditions, and may or may not receive a modern recharge component. The near-surface groundwaters, together with their isotopic compositions, are described in Table 7, and the data are plotted in Figure 9.

<u>Groundwater in Alluvium</u>. The San Simon Sink (WIPP-15) water was sampled through slotted casing open to alluvium, apparently under water-table conditions (SNL and UNM, 1981). Its isotopic composition could have arisen by partial evaporation, accounting for its slight deviation from Equation 2 of deeper Capitan-like waters. Based on potentiometric levels (R. L. Hunter, pers. comm.), however, a leakage path from the underlying Capitan is unlikely. Indeed, water in WIPP-15 may be a product of mixing of two or more reservoirs. San Simon's position slightly off the meteoric field suggests it may have undergone either partial evaporation or oxygen-isotope shift by exchange with local minerals, but this interpretation is not uniquely required by either the data or the geological context (cf. Allison et al., 1985).

Water from a well developed in alluvium near Carrizozo (5426-ft elevation) has a δD value of -64 ‰ (Yapp, written communication), and this value is indicated along the δD axis of Figure 9. While not a groundwater from the Delaware Basin, this sample relatively

TABLE 7. WATERS FROM MISCELLANEOUS SHALLOW WELLS

Location	Date[1]	Depth[2]	δD[3]	$\delta^{18}O$[4]	Analyst[5]
James Ranch prob. Dewey Lake[6]	11 Dec 75	166.4	-40	-5.0	[a]
Smith Livingston Ridge prob. Triassic[7]	09 Jun 76	167.3	-52	-7.2	[a]
Fairview prob. Dewey Lake[8]	11 Dec 76	361.3	-53	-7.1	[a]
WIPP-15 (alluvium) San Simon Sink	12 Mar 77	445-540 WL≈100 ft	-37 -40	-4.5	[b],[c]
Pocket Dewey Lake[9]	11 Nov 83	223.9	-45	-6.0	[d]

---

1. Date of collection.
2. Depth of slotted interval in casing, or total depth of well, in feet.
   Additional depth data (Cooper and Glazman, 1971):
   James Ranch--depth to water 105.6
   Smith Livingston Ridge--depth to water 150.9
   Pocket--depth to water 138.4
3. In per mil (‰), vs V-SMOW.
4. In per mil (‰), vs V-SMOW.
5. 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] $\delta^{18}O$, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.
   [d] δD, $\delta^{18}O$, Hydro Geo Chem, Tucson, AZ.
6. "Ranch Headquarters Well", 23.31.6.44 (Cooper and Glanzman, 1971). Well probably developed in Dewey Lake, as no Triassic rocks occur here.
7. 22.31.15.130a as tabulated by Cooper and Glanzman (1971).
8. 23.31.26.340 (Cooper and Glanzman, 1971), but probably developed in the Dewey Lake, as no Triassic rocks occur here.
9. "Walker Well", 23.31.29.113 as listed by Cooper and Glanzman (1971). Probably developed in the Dewey Lake, since no Triassic rocks occur here.

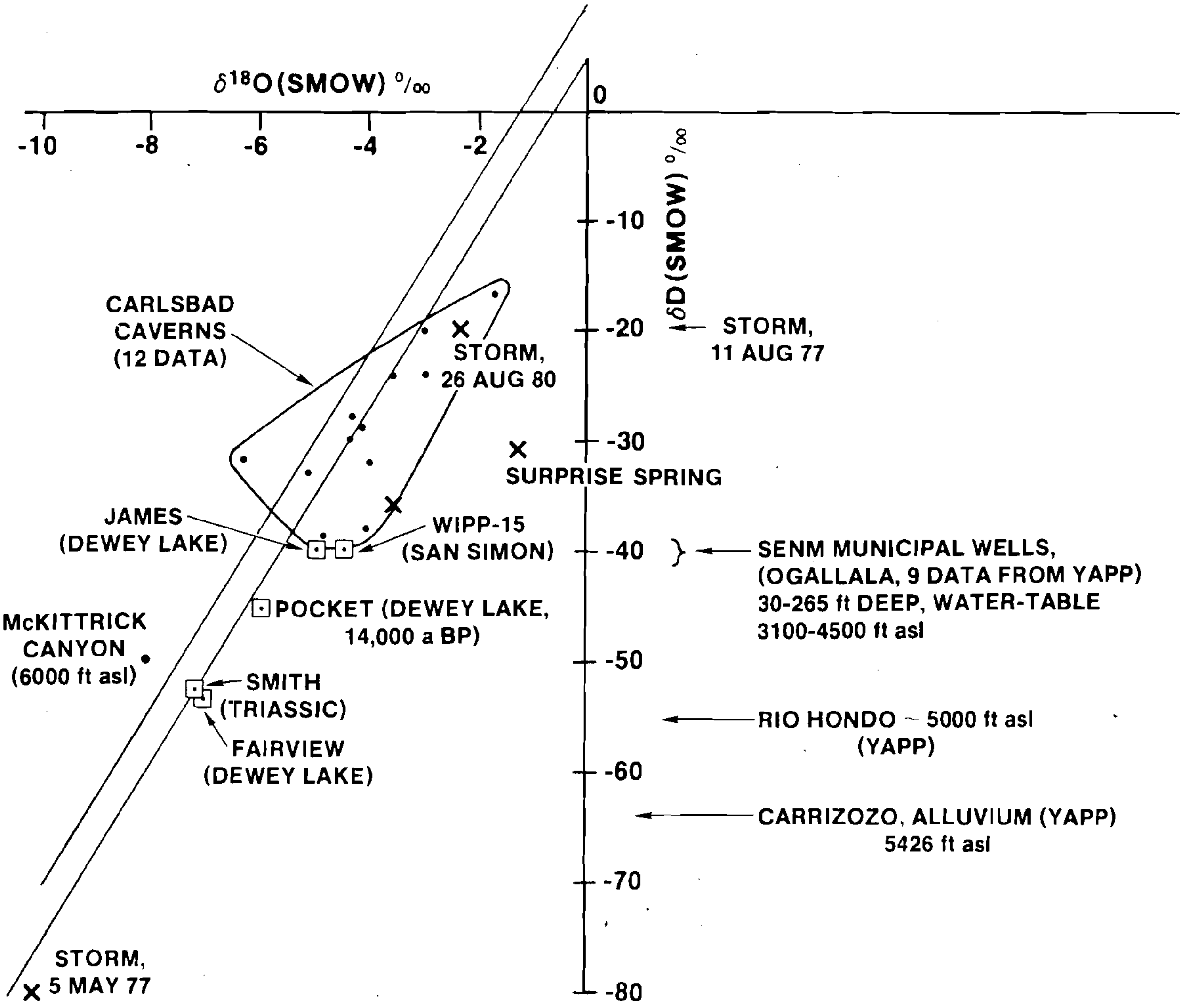


Figure 9. Stable-isotope compositions of shallow groundwaters in southeastern New Mexico. In addition to the data points from Figure 8, data are shown for groundwaters from alluvium in San Simon Sink (Figure 1), Triassic rocks, and the Dewey Lake Red Beds. δD values are indicated for groundwaters from alluvium at Carrizozo (5426 ft elev) and from nine municipal wells in the Ogallala sandstone, spread throughout southeastern New Mexico. Note the profound relationship between higher elevations and more negative δD value. Note also that one water from the Dewey Lake (Pocket: δD = -45 ‰; $\delta^{18}O$ = -6 ‰) has been out of contact with the atmosphere for 14,000 radiocarbon yr.

depleted in deuterium serves to illustrate that more negative modern δD values in southeastern New Mexico are associated with significantly higher (>5000 ft) elevations than those of the Pecos River Valley, the WIPP site, or the plains to the east.

Groundwater in the Dewey Lake Red Beds. Groundwater occurrences in the Dewey Lake Red Beds near the WIPP site have been described by Mercer (1983, p. 70):

> Drilling during areal geohydrologic evaluation did not identify a continuous zone of saturation within the Dewey Lake Red Beds; however, localized zones of permeability were detected. In the geologic test holes, the presence of these zones was indicated by minor losses of circulation during drilling. Detailed data collected during air-drilling of the hydrologic test holes (Mercer and Orr, 1979) did identify minor zones of saturation, particularly in several of the thin lenticular sands in the upper part of the Dewey Lake at test holes H-1, H-2, and H-3.
>
> In most instances, the only indication of ground water was the presence of moist cuttings. In test hole H-2C, an attempt was made to test the moist sands present at a depth of 185 ft. After monitoring the zone for 5 hours, very little water had entered the hole and the test was stopped (Mercer and Orr, 1979, p. 58). Geologic data from the wells at the WIPP site indicate the sands to be lenticular, pinching out laterally. Where water is present, it probably is perched or semiperched, and its occurrence is very localized, probably depending to a great extent on locally favorable conditions for recharge.
>
> The Dewey Lake has not normally been found to yield water to wells; however, several wells used for domestic and stock purposes at the James Ranch could possibly be completed in one of these lenticular sands. These wells in T. 23 S., R. 31 E., sections 6 and 7, range in depth from 94 to 212 ft (Cooper and Glanzman, 1971, p. A16). These wells have either saline water or small yields; geologic data indicate they are completed in the upper part of the Dewey Lake. Just east of this area there is an extensive, thick, active area of sand dunes, which could be a recharge area for these water-bearing sand units. No other wells in the area are known to produce water from the Dewey Lake.

> Recharge of sand units in the Dewey Lake could result from localized conditions, as in the James Ranch area, or could occur by downward percolation of water through fractures or along bedding planes in the mudstone and siltstone. Discharge towards deeper zones through existing fractures or through dissolution of the gypsum veinlets [in the Dewey Lake Red Beds] is minor ... If the ground water penetrated to the top of the Rustler Formation in the WIPP site, then the upper anhydrite should be altered to gypsum. Cores and geophysical logs do not indicate that this alteration is present except where the Dewey Lake is thin or absent. Ground-water movement within the Dewey Lake is restricted because of the perched character of the water in these lenticular sands.

Water from the James Ranch well in Table 7 was previously attributed to the Rustler by Lambert (1978). This water originated from a relatively shallow well on the James Ranch property due south of the WIPP site (Figure 2). A detailed examination of well location and sampling records revealed, however, that total depth of the well is less than 170 ft (3144 ft above sea level, "asl"). The top of the Rustler at this locality has been reported at an elevation of 3030 ft (Powers et al., 1978), and surface elevation at this locality is about 3310. Thus, this well is most likely completed in the Dewey Lake, and not the Rustler. The water level reported by Cooper and Glanzman (1971) was 3244 ft asl. Consequently, the water definitely is being produced from the Dewey Lake, although on the basis of the local stratigraphy and water level the depth of the producing horizon within the Dewey Lake cannot be precisely identified, nor can it be said with any confidence whether the producing zone is confined from above. The well is not completed in the Triassic, as previously reported by Cooper and Glanzman (1971), since no Triassic occurs at this locality at all, much less at 170 ft depth (Bachman, 1985). Its isotopic composition is very near the meteoric field (particularly near the WIPP-15 point), and very near the field of Carlsbad Caverns. The well's proximity to a large area of sand dunes implies that infiltration can readily proceed there, and thus it probably represents conditions conducive to active modern recharge, as do Carlsbad Caverns, the Ogallala, and the alluvium of San Simon Sink.

In the context of the groundwater conditions in the Dewey Lake described above by Mercer (1983), the water sample from Pocket (Table 7; Figure 9) is particularly noteworthy. According to the same sources of stratigraphic and hydraulic information as for James Ranch well, Pocket (called "Walker" by Cooper and Glanzman, 1971) produces water from the Dewey Lake and not the Triassic. There is also no indication of whether artesian or water-table conditions prevail in the producing horizon. Its δD and $\delta^{18}O$ values are significantly more negative than the James Ranch well, water in alluvium in San Simon Sink, and all but one (JR) of the Carlsbad Caverns waters. The water was also one of the four that Lambert (1987) found could be successfully radiocarbon-dated using the interpretive numerical model of Evans et al. (1979). The apparent age is 14,000 radiocarbon years. According to the arguments of Lambert (1987), which will not be reviewed in detail here, this is a reasonable age of isolation from the atmosphere for several groundwaters in the Rustler also. In the absence of a modern, well-defined, connected flow system in the Dewey Lake (Mercer, 1983), this is a reasonable age of recharge. Even if both the percent modern carbon (PMC) and the δD and $\delta^{18}O$ values resulted from mixing of more than one reservoir, the hydrogen-, oxygen-, and carbon-isotopic data constitute compelling evidence that at least some groundwater in the Delaware Basin with $\delta D \approx -45$ ‰ and $\delta^{18}O \approx -6.0$ ‰ at the elevation characteristic of the WIPP site ($\approx$3400 ft) is <u>not</u> 100% modern.

Similar stratigraphic and hydraulic conditions prevail for Fairview (Figure 2) and Pocket. The well is developed in the Dewey Lake (and not the Triassic as reported by Cooper and Glanzman, 1971, or Rustler as reported by Lambert, 1978), and the water level does not apparently rise above the top of the Dewey Lake.

The δD and $\delta^{18}O$ values of Fairview water (Table 7) are significantly more negative than those of any other groundwater discussed so far. Although its position in $\delta D/\delta^{18}O$ space is plotted in Figure 9, discussion of waters with more negative δ-values is deferred until Section 4.5. It is sufficient to note here that its isotopic composition is significantly different from groundwaters that have probable hydraulic connections with the surface at elevations of 3000 to 4500 ft.

The isotopic distinctions noted here between Pocket and James wells, both in the Dewey Lake, imply that a portion of the Dewey Lake may be undergoing modern meteoric recharge. By the logic and hypotheses used here, the Dewey Lake at and near the James Ranch and surrounding active dune fields may be experiencing recharge. Dewey Lake groundwater in Pocket, however, has an "old" radiocarbon age, and shows minimal effects of modern recharge.

<u>Groundwater in Triassic Rocks</u>. The single well from the Triassic, Smith Livingston Ridge (Figure 2) appears actually to tap a water-producing horizon in the Triassic, as reported by Cooper and Glanzman (1971). In spite of its name, it is not near Livingston Ridge, and will hereafter be abbreviated as "Smith". The top of the Dewey Lake is not precisely known at the locality of Smith, but is at an elevation of 3300 to 3320 ft. The bottom of the well is at an elevation of 3293 ft, and the measured water level was about 3309 ft (Cooper and Glanzman, 1971). Thus, rather than being developed at the top of the Dewey Lake, we tentatively consider the producing horizon to be more likely near the bottom of the Triassic, since the regionally persistent zone of lost circulation in the Dewey Lake is near the bottom of that unit, not the top (Mercer, 1983). The isotopic composition of water from Smith is indistinguishable from that of Fairview (Table 7; Figure 9), and hence is significantly different from

that of demonstrably modern recharge to local shallow groundwaters. Further discussion of such tightly-clustered, more negative meteoric δ-values will be deferred to Section 4.5.4.

Groundwater in Sandstone of the Ogallala Formation. C. J. Yapp (written communication) has reported several δD values for water from the Ogallala Formation from eastern New Mexico. These samples were from wells completed in Ogallala sandstone and/or Quaternary alluvium to serve the municipalities of Eunice, Hobbs, Lovington, Tatum, Dora, Portales, Clovis, Texico, and Melrose. According to Nicholson and Clebsch (1961) the Ogallala groundwater in the region covered by the nine samples is under water-table conditions. The data fall within the δD range -39 to -41 ‰. This range is indicated on the δD axis of Figure 9. The water-table conditions in the Ogallala imply, but do not alone require (as in the case of San Simon Sink), that the Ogallala could receive modern recharge in the region more readily than it could were it confined from above. Also, Ogallala δD values are at the lower (lighter) limit of the Carlsbad Caverns field.

These Ogallala waters have δD values similar to those reported by Nativ and Smith (1987) for the Southern High Plains of Texas. There, only waters (regardless of whether they are from the Ogallala, Triassic, or Permian) having δD values more positive than -42 ‰ have significant levels of tritium (>10 TU), indicating that demonstrably modern recharge (post-1950) there is relatively enriched in deuterium (Figure 10). Nativ and Smith (1987), Osterkamp and Wood (1987), and Wood and Osterkamp (1987) have concluded that the Ogallala groundwater of the Southern High Plains (a) is recharged rapidly through playas representing localities of dissolved caliche caprock, (b) does not experience significant partial evaporation prior to recharge, and (c) contains a preferential concentration of heavier isotopes relative to the entire range of isotopic compositions of High Plains rainfall. Since the elevations, climate, and vegetative cover are similar in the Southern High Plains and the northern Delaware

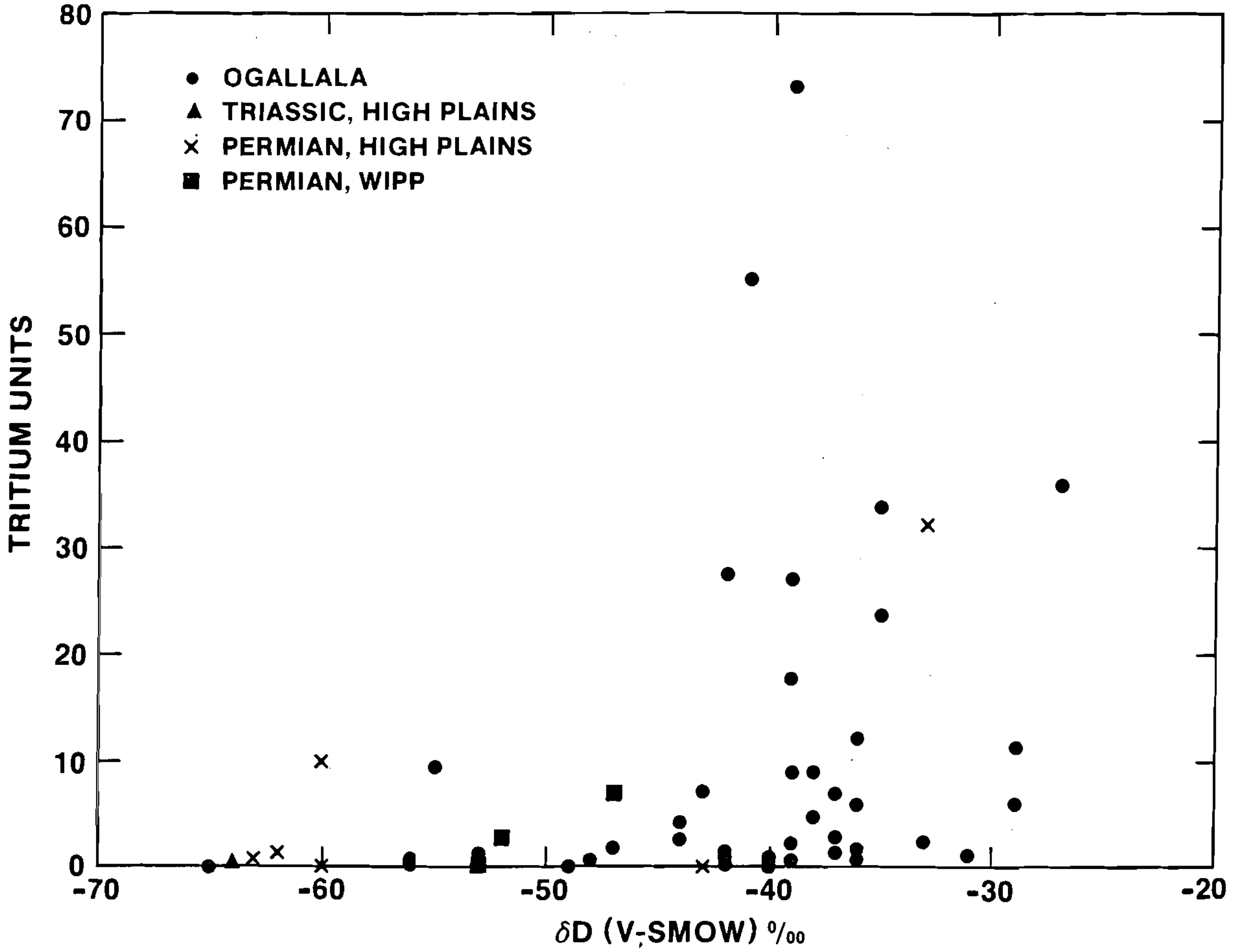


Figure 10. Tritium and deuterium concentrations in groundwaters from the Southern High Plains, Texas, and the Delaware Basin, southeastern New Mexico. High Plains data are from Nativ and Smith (1987); WIPP data are from Lambert and Harvey (1987) and Lambert (1987). Significantly high tritium concentrations (>10 TU), indicating derivation from a meteoric source since 1950, are restricted largely to groundwaters having δD values more positive than about -42 ‰. Ogallala waters from nearby southeastern New Mexico (not shown) have δD values between -39 and -41 ‰, corresponding with δD values of modern groundwater recharge in the Texas High Plains. Hydrogen-isotope characteristics of groundwaters from the nearby climatically similar Delaware Basin (WIPP data), having more negative δD values and little tritium, are not consistent with significant post-1950 recharge, but rather modern groundwater recharge in the Delaware Basin is better represented by δD values more positive than -42 ‰ and not by the confined Rustler waters having more negative δD values (see Figure 16).

Basin, it is here concluded that regional groundwaters more enriched in deuterium (δD >≈ -42 ‰) represent modern recharge at the latitude and elevation of the Delaware Basin of southeastern New Mexico. We have used values >10 TU as indicative of modern, post-1950 recharge to avoid the ambiguity resulting from the subsurface mixing of high-D, high-T waters with low-D, low-T waters to yield intermediate hydrogen isotope compositions having 4 to 10 TU, a range which is not conclusively significant of modern recharge (see Section 4.8.3). A significant modern component in the groundwater would yield values of 20 TU or more; values less than ≈10 TU are not considered conclusively indicative of a large degree of hydraulic connection with the surface (Isaacson et al., 1974).

Low tritium concentrations alone, however, do not preclude the possibility of surface-derived recharge in the recent past prior to 1950. Figure 11 shows the δD vs $\delta^{18}O$ relationships for High Plains Ogallala waters reported by Nativ and Smith (1987), not including those judged by Nativ and Smith to be "contaminated." Note that 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 half of the range of δD and $\delta^{18}O$ values having more deuterium (representing modern conditions), that half of the range also contains waters having <10 TU, suggesting that the prevalent climatic conditions, represented by more positive δ-values and governing Ogallala recharge on the High Plains, began some indeterminate time prior to 1950 when atmospheric tritium was less abundant. The low levels of tritium in waters with δD values less than -42 ‰, however, strongly suggest that such waters contain only a minimal component recharged from the atmosphere in recent historic times. Yapp's δD values for Ogallala waters from southeastern New Mexico fall well within the population of Ogallala waters from the High Plains having significant tritium levels. Thus, we conclude that the Ogallala waters having δD values more negative than about

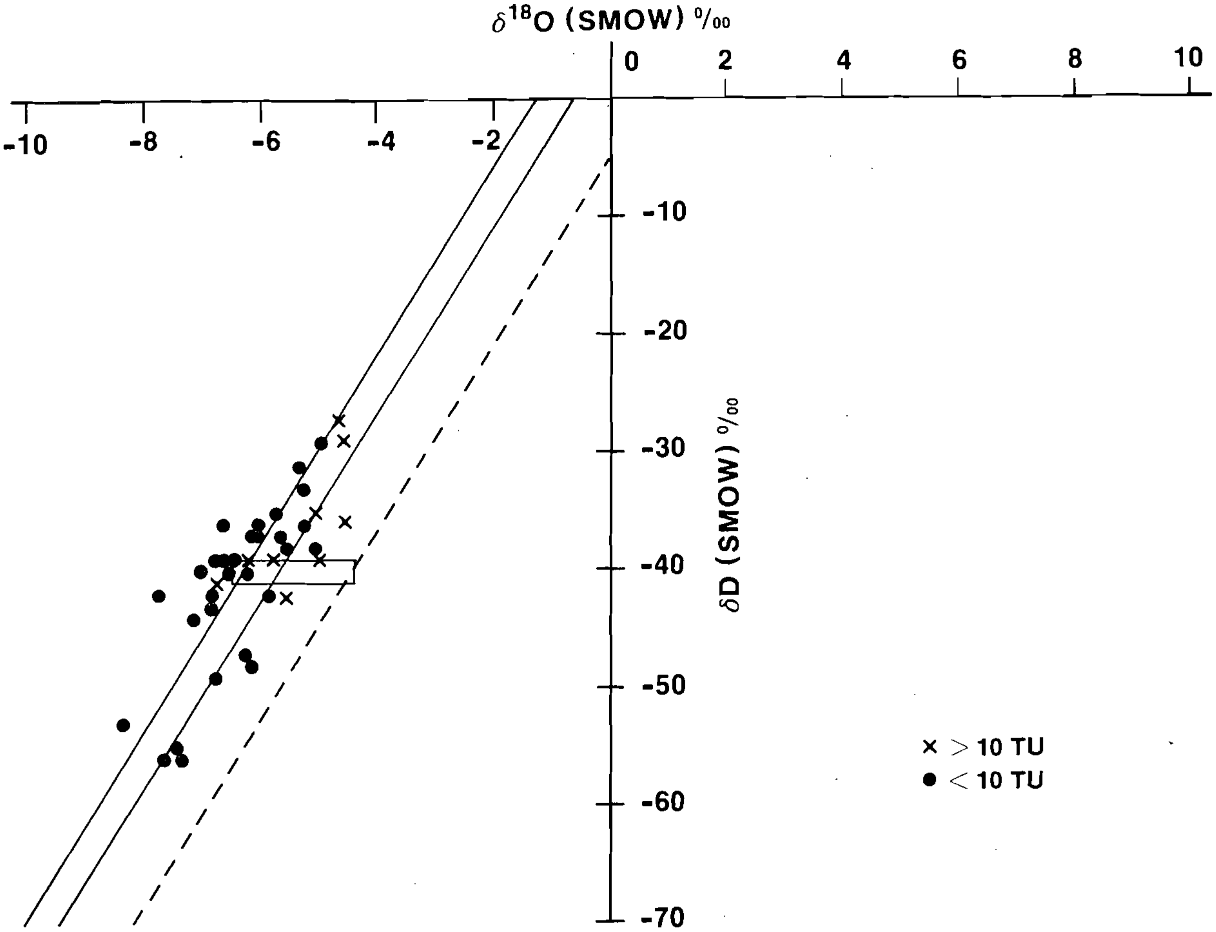


Figure 11. Stable-isotope compositions of groundwaters from the Southern High Plains, Texas. Data are from Nativ and Smith (1987). Note that the δD-$\delta^{18}O$ data points show no significant deviation from the meteoric field (solid lines), indicating minimal evaporation effects, nor do they fall outside the -10 ‰ deviation in δD (dashed line) described for some groundwaters by Allison et al. (1985). Stable-isotope data plotted as "x's" have more than 10 Tritium Units, indicating a significant modern meteoric recharge component since 1950. Note no such modern component in waters having δD values more negative than -42 ‰. The δD range of Ogallala groundwaters (rectangle) from southeastern New Mexico analyzed by Yapp is shown for comparison.

-42 ‰ represent recharge prior to the time when present climatic conditions were established in the High Plains.

Regardless of the values of meteoric precipitation collected at the surface in the northern Delaware Basin, the δD values of groundwaters that have apparently modern meteoric origins (as is here inferred for the Ogallala) might be considered representative of meteoric waters that actually recharge groundwater bodies. Hence, in the absence of reliable age determinations to the contrary, stable-isotope compositions of groundwaters from Carlsbad Caverns, alluvium, and the Ogallala sandstone should be considered typical of demonstrably-modern, meteorically-derived recharge (at elevations between 3000 and 4500 ft) to groundwater in the northern Delaware Basin.

4.3.5 Summary: Isotopic Signature of Modern Recharge

Occurrences of groundwater in San Simon Sink, Carlsbad Caverns, the Ogallala, and probably the Dewey Lake at James Ranch have demonstrable or inferred degrees of hydraulic connection with the surface. Hydraulic observations in these localized geological environments are consistent with the proposal that these groundwaters could be dominated by modern surface recharge. δD values of these waters are no more negative than -41 ‰.

A likely explanation for the variation in isotopic compositions of modern Capitan waters (from NMTS and Carlsbad Caverns) is climatic variations in the isotopic composition of precipitation. Different sampling localities at different elevations might receive their dominant precipitation in different seasons. Carlsbad Caverns, developed in the unsaturated zone, is not an extremely well-mixed system. Water infiltrating near-surface carbonate rocks on the Guadalupe escarpment (4300 ft above sea level) and recharging Caverns pools probably is mostly summer rain, when δD and $\delta^{18}O$ values would be less negative. This could be tested by sampling the drip water from the Caverns ceilings about once a month over the course of two years to determine if the Caverns recharge is seasonably variable in rate, D/H, and $^{18}O/^{16}O$. The δD values of Caverns pools are no more negative than -39 ‰. The close correspondence of most of the Caverns points to the worldwide meteoric field and suggests that Caverns waters have not evolved by evaporation in a humid environment from waters having much more negative δD values, as was proposed by Chapman (1986). The Caverns points that apparently deviate in isotopic composition from the worldwide meteoric trends do so by no more than has been previously reported for meteorically derived shallow groundwaters (Allison et al., 1985; Leaney and Allison, 1986), and evidence for derivation of Caverns waters by evaporation of waters significantly more depleted in D and ^{18}O is difficult to infer from the isotopic data. Water supplying the NMTS (1800 m above sea level) in mid-June, when the sample was collected, is probably drainage from higher elevations, where even in the summer runoff would have more negative δD and $\delta^{18}O$ values.

Summer precipitation in the Delaware Basin is believed to be more abundant than that in winter, over periods of several years (Hunter, 1985), and to be more important in recharging local shallow groundwater systems in the unsaturated zone of the Capitan (e.g., Carlsbad Caverns). Whereas snowmelt may be important as a source of groundwater at higher elevations in the mountains of southeastern New Mexico, such runoff drains into neither Carlsbad Caverns nor the central Delaware Basin, both of which are isolated from areas of snow accumulation by intervening local surface-drainage systems.

Groundwater in the alluvium of San Simon Sink is probably derived by runoff in the surrounding San Simon Swale (Nicholson and Clebsch, 1961) and has a δD value of about -41 ‰. Groundwater in the Ogallala sandstone from nine localities in southeastern New Mexico at elevations similar to that of the WIPP site has δD values tightly clustered between -39 and -41 ‰; these Ogallala waters in turn have δD values indistinguishable from those of Ogallala groundwaters from the Texas High Plains that have higher tritium concentrations indicative of modern recharge. The fact that the Ogallala is under water table conditions does not itself require modern recharge; municipalities pumping the Ogallala water may actually be "mining" older waters. This uncertainty does not significantly alter the argument herein. No Delaware Basin waters demonstrable or inferable as modern, recharged at elevations ≤ 4500 ft, have δD values less than -41 ‰. Some older groundwaters might have more negative δD values, but young ones originating at lower elevations do not.

In summary, the isotopic composition of modern recharge to groundwater systems in the north-central Delaware Basin, encompassing the WIPP site, has been indicated to be more positive than -41 ‰ in δD, and (with the exception of one point in Carlsbad Caverns which is probably affected by rock/water interactions at low temperatures) more positive than -5.5 ‰ in δ^{18}O (Figure 9). This range of compositions includes the James Ranch well in the Dewey Lake Red Beds, but not the Pocket (Walker) well in the Dewey Lake, which has a δD value of -45 ‰, a δ^{18}O value of -6.0 ‰, and an apparent radiocarbon age of 14,000 a (Lambert, 1987), and also not the Fairview ($\delta^{18}O = -7.1$ ‰). The significance of this range of isotopic compositions of modern recharge, together with that of radiocarbon dates for other groundwater and tritium contents, will be discussed in more detail in Sections 4.5. and 4.8.

4.4 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 water-table conditions prevail in the Capitan Limestone, but at great depth. In the vicinity of 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 Carlsbad Caverns (Jagnow, 1979). In the eastern part of the Capitan, where it is buried (Figure 12) water levels are at elevations of 2400 to 3100 ft, whereas the top of the unit is at elevations of +1000 to -1000 ft (Figure 12). This indicates that from the vicinity of Carlsbad eastward, water in the Capitan is under confined (artesian), not water-table conditions. This makes recharge by direct vertical infiltration unlikely.

Stable-isotope compositions have already been reported and discussed for waters from Carlsbad Caverns (Section 4.2). In addition, Lambert (1978) and Barr et al. (1979) reported stable-isotope compositions for waters from the eastern (artesian) part of the Capitan. Also, Barr et al. (1979) reported and discussed $^{234}U/^{238}U$ activity ratios (ARs) for these same waters. Lambert and Carter (1984) included a discussion of uranium-isotope systematics in an occurrence of standing water in association with uraninite-bearing silt from the New Mexico Room. The water was the same as "Grass Skirt Pool" in Table 4.

Table 8 contains the previously reported data for four wells in the eastern part of the Capitan: Carlsbad #7, Middleton, Hackberry, and Shell #28. Their locations, δD, $\delta^{18}O$, and AR values are given in Figure 12. All available stable-isotope data for Capitan waters are plotted in Figure 13, together with the by-now-familiar meteoric field.

The fields of Caverns and eastern Capitan waters do not overlap, and the two fields are separated by a statistically significant difference, even though the two fields are entirely consistent with a purely meteoric origin for all the waters, with little deviation from the field. These differences in isotopic compositions in various parts of the Capitan suggest that if the presumably summer-dominated Caverns waters do represent the isotopic composition of modern waters that would be available to recharge the Capitan, active-recharge meteoric waters in the unsaturated

TABLE 8. CAPITAN WELL WATERS

Location	Date[1]	Depth[2]	δD[3]	$\delta^{18}O$[4]	Analyst
Carlsbad #7	12 Dec 75	14[5]3	-54	-7.9	O'Neil
Shell #28	13 Dec 75	5100	-56	-7.7	O'Neil
Middleton	10 Dec 75	1700	-55	-7.5	O'Neil
Hackberry	12 Dec 75	3900	-46	-6.5	O'Neil

---

1. Date of collection.
2. Depth of sample, feet below land surface.
3. In per mil (‰), vs V-SMOW.
4. In per mil (‰), vs V-SMOW.
5. Cased to 118-ft depth (Hendrickson and Jones, 1952).

zone of the Guadalupe Mountains do not govern the isotopic composition of Capitan waters farther east. This inference is part of the basis for a proposal that the deeply buried Capitan groundwaters along the northern and eastern margins of the Delaware Basin are not receiving significant amounts of modern recharge. The isotopic compositions of northern and eastern Capitan groundwaters are represented by waters from the wells Carlsbad #7, Shell #28, Middleton, and Hackberry in Table 8. The small range of δ values indicates that isotopic mixing and homogenization have been much more efficient than in the unsaturated zone. Such homogenization is probably indicative of long flow paths, long residence times, or both.

Water from McKittrick Canyon (Section 4.3.2) is similar in δD and $\delta^{18}O$ to eastern confined Capitan waters (Figure 13). This might imply that water from the southern Guadalupe Mountains quickly seeks the local water table at elevations of 6000 ft or more and flows northward in the saturated zone beneath the unsaturated zone represented by caverns in the northern Guadalupe Mountains. Although it is conceivable that underflow occurs from a recharge

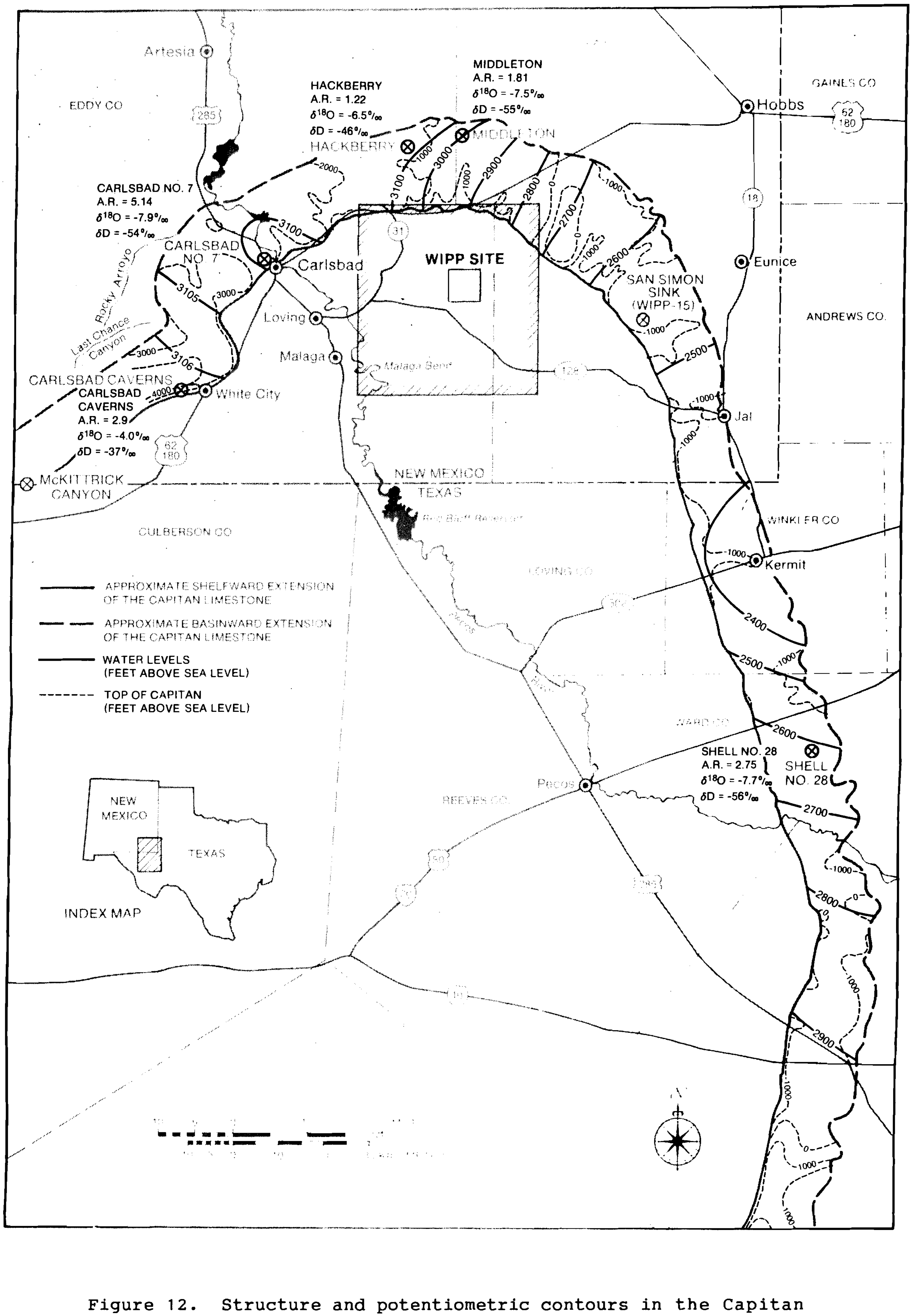


Figure 12. Structure and potentiometric contours in the Capitan Limestone. West of Carlsbad Caverns the potentiometric (water) levels are far below the top of the Capitan, suggesting water-table conditions there. East of Carlsbad the situation is reversed, indicating confined conditions not conducive to recharge by direct infiltration from the surface. For key localities (Carlsbad Caverns, Carlsbad #7, Hackberry, Middleton, Shell #28) uranium- and stable-isotope data are given. Note the drawdown in the vicinity of Kermit, TX, reflecting pumpage of water from the Capitan for use in flooding operations for secondary oil-recovery. Contours are compiled from Hiss (1975), Bjorklund and Motts (1959), and Motts (1957).

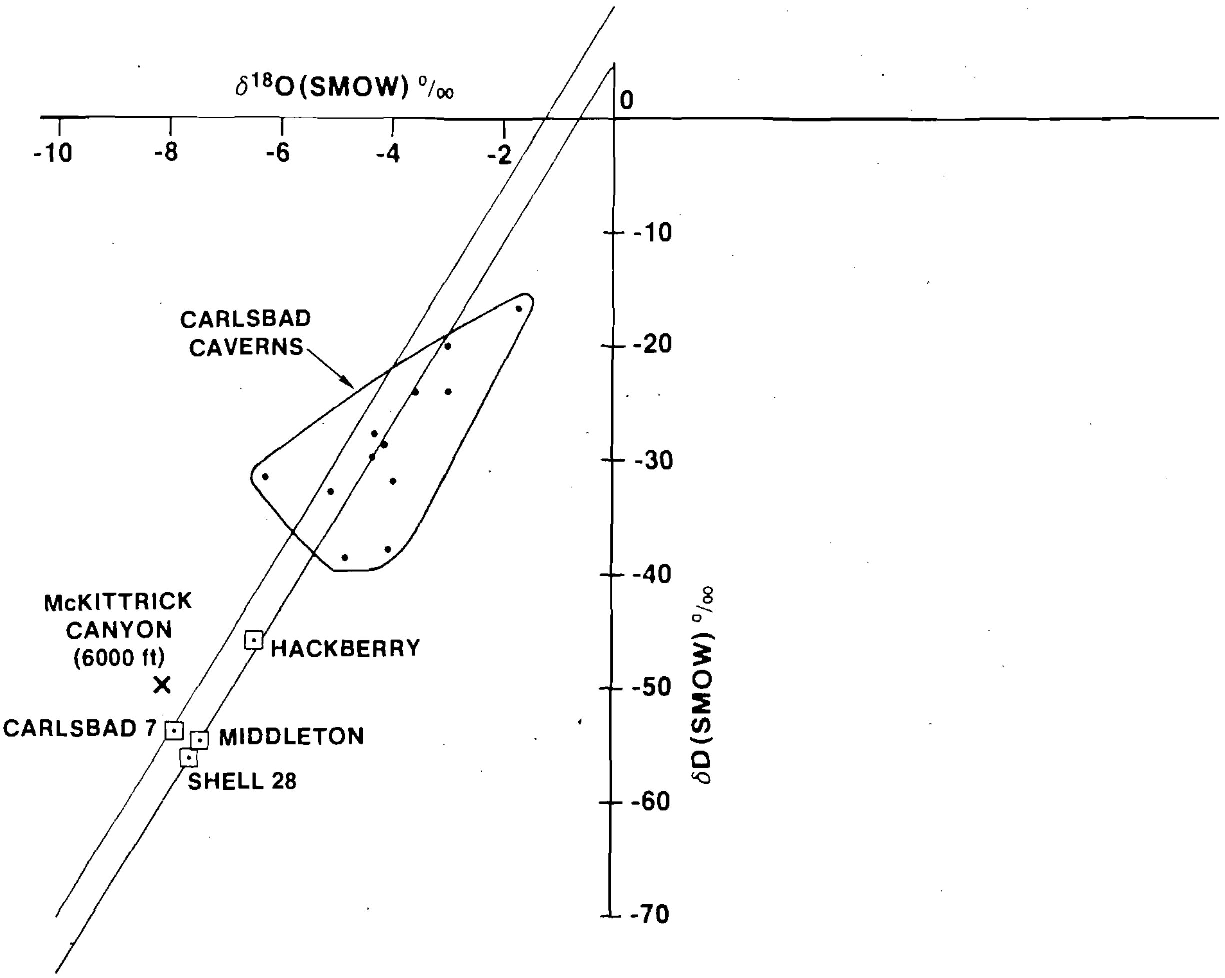


Figure 13. Stable-isotope compositions of groundwaters from the Capitan Limestone. Groundwaters under confined conditions (squares) have isotopic compositions distinctly different from the vadose waters (dots) close to a known active modern recharge in the Capitan. All Capitan waters have a meteoric origin, indicated by their proximity to the meteoric field, but the confined waters more resemble the isotopic composition of McKittrick Canyon, which is at a significantly higher elevation than either the Caverns or occurrences of confined groundwaters.

area in the southern Guadalupe Mountains, bypassing Carlsbad Caverns and replenishing water pumped from the Capitan east of Carlsbad, we consider this unlikely. Hiss (1975) described the effect of the West Laguna Submarine Canyon, a local thinning of the Capitan between Hackberry and Middleton (Figure 12). He said that drawdown from pumpage in the vicinity of Kermit (near Shell #28) did not extend west of the West Laguna Submarine Canyon, attesting to the efficiency of the barrier resulting from this hydraulic constriction near the northern apex of the Capitan limestone. Although the similarity in stable-isotope compositions between McKittrick Canyon and the eastern (confined) Capitan is consistent with modern recharge of the eastern Capitan coming rapidly from the Guadalupe Mountains, the hydraulics and uranium-isotope data are not.

Barr et al. (1979) estimated the isolation times for confined waters in the Capitan based on uranium-isotope systematics and a set of inferences about groundwater flow in the Capitan. Under the inference that the uranium-isotope systematics in the Capitan behave conventionally, as described by Osmond and Cowart (1976), and that groundwater flow is generally clockwise as described by Hiss (1975), isolation times between Carlsbad and various other points are as follows: Hackberry, 1,100,000 a; Middleton, 580,000 a; Shell #28, 310,000 a. Built into these calculations are the assumptions that

- $^{234}U/^{238}U$ activity ratios as high as 5 (near Carlsbad) have occurred as a post-recharge aging effect, as described by Kronfeld et al. (1975)

- No further uptake of ^{238}U has occurred as a result of rock/water interaction, after the establishment of the initial AR

- The only decreases in the uranium-isotope activity ratio after the end of uranium-isotope exchange (that resulted in the high initial AR) were due to radioactive decay.

Lambert and Carter (1983) showed that if the second assumption is true, the closed-system calculation of Barr et al. (1979) results in a **minimum** isolation time. Regardless of the absolute isolation time, estimated by Barr et al. to be at least 300,000 a, if water in the Carlsbad area is assumed to be representative of major recharge for the rest of the confined Capitan waters, these results indicate that these waters have been confined since some time in the Pleistocene, even if the δD value of modern recharge were -46 to -56 ‰. As has been discussed in Section 4.3.5, and as will be discussed in Section 4.8, such a range in δD values for modern recharge at the elevation of Carlsbad is unlikely. As discussed above, the hydraulic relationships of the Capitan where it is under confined conditions preclude a direct connection to the surface through the overlying evaporite section. Thus, the stable-isotope compositions of Capitan groundwaters east of Carlsbad are not representative of modern recharge at most elevations in the Delaware Basin, and the waters are indicated to be very old.

4.5 Groundwaters in the Rustler Formation

4.5.1 Geohydrology of the Rustler Formation

The most succinct description of the Rustler Formation, from a geohydrologic view, is given by Mercer (1983):

> The Rustler Formation, named by Richardson (1904) is the youngest unit in the Ochoan evaporite sequence. The Rustler is a key marker bed of the upper Permian in Texas and New Mexico. Hydrologically this unit is one of the most extensively investigated units at the WIPP site because it contains the most productive water-bearing units in the study area.

> In the vicinity of the WIPP site, Vine (1963, p. B-14) has described a five-fold division of the Rustler ... The division includes: (1) at the base, an unnamed unit of clayey siltstone and very fine grained sandstone with thin interbeds of anhydrite and halite in its upper part; (2) the Culebra Dolomite Member, a unit of thin-bedded, solution-pitted finely crystalline dolomite; (3) the Tamarisk Member, anhydrite with a single thin interbed of unconsolidated clayey silt (residuum from a thick seam of halite and associated polyhalite and halitic siltstone); (4) the Magenta Dolomite Member, a unit of thinly cross-laminated, fine-grained dolomite; and (5) the Forty-niner Member, anhydrite with a single thin interbed of unconsolidated clayey silt (residuum from a much thicker seam of clayey and silty halite). The anhydrite beds may be partially altered to gypsum in places where dissolution has occurred. The dolomite units are not only hydrologically important but are distinctive marker beds throughout the Delaware Basin (Adams, 1944, p. 1614) [pp. 16-17].
>
> The Tamarisk and Forty-niner Members also contain halite in areas where dissolution has not been active. The Culebra and Magenta Dolomite Members at the WIPP site are the most significant units from a hydrologic standpoint and consequently were the most extensively studied [p. 43].

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 has been described in more detail by Snyder (1985). In addition, the regional aspects of dissolution of Ochoan evaporites have been discussed by Lambert (1983a; 1983b).

4.5.2 Rustler Groundwaters from the WIPP Site and Nash Draw

Magenta Dolomite Member. Mercer (1983) has summarized the general hydrology of the Magenta as follows:

> The Magenta Dolomite Member is the uppermost hydrologic unit in the Rustler Formation. Water is present in the area of the WIPP site, usually in thin siltstone beds or silty dolomite and less commonly in fractures. In Nash Draw [Figure 2], the occurrence of water in the Magenta Dolomite member is variable because of localized drainage from the unit that results from the chaotic structure created by extensive evaporite dissolution. In the

> southern end of Nash Draw, the Magenta has been completely removed by erosion. Transmissivities calculated for the Magenta Dolomite in the northern end of Nash Draw range from 53 ft^2/day at test hole W-27 to 375 ft^2/day at test hole W-25; these relatively large values result from the increased permeability in the fractured rock. The transmissivity in the vicinity of the WIPP site ranges from 4×10^{-3} ft^2/day at test hole W-30 to 3×10^{-1} ft^2/day at test hole H-6A. The movement of ground water in the site area, as estimated from density-corrected potentiometric-surface maps, is west toward Nash Draw at a gradient of as much as 32 ft/mile and then southwest in Nash Draw at a gradient of 13 ft/mile [p. 78].

Isotopic compositions of waters from the Magenta dolomite member of the Rustler Formation are given in Table 9, and plotted in Figure 14. The five data points (excluding W-30, as discussed in Section 3.2.3) are tightly clustered in $\delta D/\delta^{18}O$ space, spanning no more than 10 ‰ in δD and no more than 1.1 ‰ in $\delta^{18}O$. These isotopic compositions do not overlap the range of modern meteoric recharge (δD more positive than -41 ‰, $\delta^{18}O$ more positive than -5.5 ‰; Section 4.3.5). The field of modern recharge in the Delaware Basin, based on the vadose (unsaturated) Capitan, alluvium, and Ogallala sandstone, developed in Section 4.3.5, is also depicted in Figure 14.

Culebra Dolomite Member. Mercer (1983) has summarized the general hydrology of the Culebra as follows:

> The Culebra Dolomite Member of the Rustler Formation is the most persistent and productive hydrologic unit in the WIPP vicinity. Its hydraulic properties vary considerably from place to place, primarily as a result of the size and number of fractures and openings. These fractures are related to the degree of evaporite dissolution within the Rustler, which causes subsidence and collapse of the overlying dolomite. The most extensive evaporite dissolution and fracturing are present in Nash Draw [Figure 2]. Transmissivities calculated for the Culebra in Nash Draw range from 18 ft^2/day at test hole W-28 to 1,250 ft^2/day at test hole W-26. At the WIPP site, east of Nash Draw, transmissivities range from 1.0×10^{-3} ft^2/day at test hole P-18 to 140 ft^2/day at test hole P-14. Density-corrected potentiometric-surface maps indicate that flow at the WIPP site is to the south

TABLE 9. MAGENTA (RUSTLER) WELL WATERS

Location	Date[1]	Depth[2]	δD[3]	$\delta^{18}O$[4]	Analyst[5]
H1	04 Jun 76	563-589	-48	-6.8	[a]
H2A	22 Feb 77	513	-46	-6.3	[a]
H3	10 May 77	557-608	-53	-7.3	[a]
WIPP-25	17 Sep 80	302-328	-44 -43	-6.2	[b],[c] [b]
WIPP-27	25 Sep 80	176-194	-46 -47	-6.3	[b],[c] [b]
WIPP-30	09 Dec 80	513-537	-43 -41	-6.5	[b],[c] [b]
H3B1 (original H3)	01 Jul 85	557-608		-6.7 -6.7	[c] [c]

---

1. Date of collection.
2. Sampling depth or depth interval, in feet from local datum (usually ground level), isolated by packers, perforated casing, or both.
3. In per mil (‰), vs V-SMOW.
4. In per mil (‰), vs V-SMOW.
5. 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] $\delta^{18}O$, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.

at a hydraulic gradient that ranges from 7 to 20 ft/mile; the flow is then to the southwest to Nash Draw, where gradients range from 16 ft/mile in the north end to less than 5 ft/mile near Malaga Bend. Flow directions may be affected significantly by directional differences in permeability in the dolomite. In Nash Draw, the Culebra Dolomite is extensively fractured and flow is south to a discharge area at the Pecos River near Malaga Bend [p. 78].

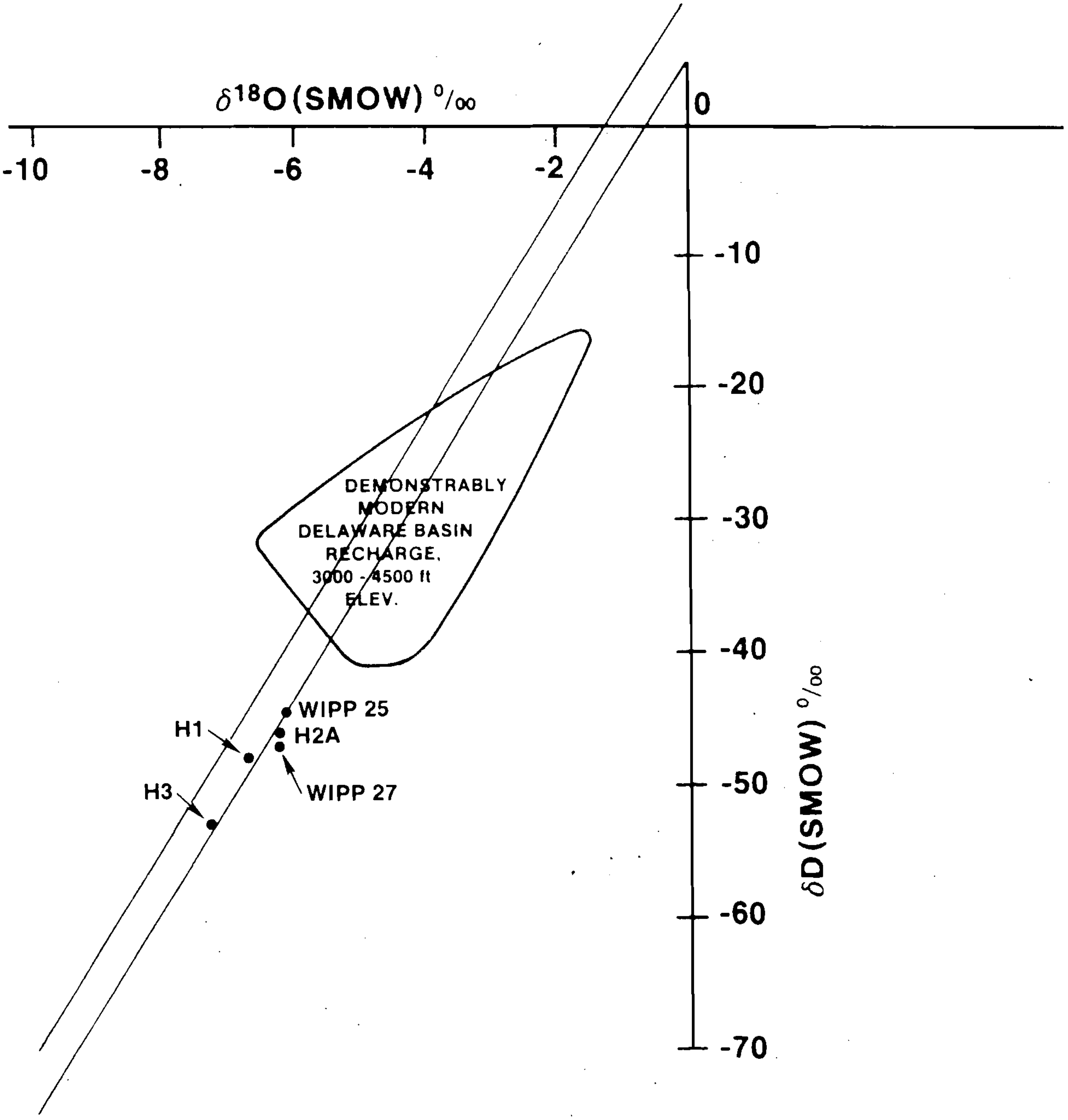


Figure 14. Stable-isotope compositions of groundwaters from the Magenta gypsiferous dolomite member of the Rustler Formation. None of the Magenta groundwaters have isotopic compositions corresponding to those of demonstrably modern Delaware Basin recharge at elevations of 3000 to 4500 ft, based on Carlsbad Caverns, the alluvium in San Simon Sink, and a shallow Dewey Lake well. In addition, Magenta waters have δD values significantly more negative than those of the near-surface Ogallala sandstone occurring at similar elevations throughout southeastern New Mexico.

Isotopic compositions of waters from the Culebra dolomite member are given in Table 10, and are plotted in Figure 15, in addition to Magenta data shown in Figure 14. The scale in Figure 15 has been expanded relative to other similar plots of waters in $\delta D/\delta^{18}O$ space, so that individual data points can be identified. Where the Rustler Formation is represented by a complete stratigraphic section, from which calcium sulfate (gypsum or anhydrite) has not been removed from the Tamarisk member by dissolution (Snyder, 1985), the Magenta dolomite is about 100 ft nearer the surface at the WIPP site than the Culebra. Water levels for the Magenta and Culebra are also about 100 ft apart at H1, H2, and H3; hence, the hydraulic evidence indicates that there is poorly developed vertical connection between the two units where this potentiometric differential occurs. Also plotted on Figure 15 are the five Magenta points, together with their identifications. Note that in all cases the Magenta and Culebra samples from the same well overlap within the 95% confidence limits. This shows that isotopic similarity alone should not be used to infer a connection between two occurrences of water, especially if other kinds of data (e.g., hydraulic and in some cases solutes) reflect only limited interconnection. Conversely, a significant difference between isotopic compositions for two moving reservoirs of groundwater is compelling evidence that the two waters have not homogenized by mixing induced by flow, density gradients, etc., and that they are therefore probably not hydraulically connected. The **only** exception to this occurs if the flow path between two isotopically distinct waters entails a significant amount of rock/water interaction (see Lambert, 1978; Barr et al., 1979). The exception is likely to be more important for oxygen isotopes than for hydrogen, if the abundance of exchangeable rock-hydrogen is significantly smaller than that of oxygen. This is the normal case, although minerals rich in hydrogen (e.g., gypsum) may amplify the contribution of exchangeable rock-hydrogen in certain evaporite environments, relative to water-bearing rocks dominated by carbonates or silicates.

TABLE 10. CULEBRA (RUSTLER) WELL WATERS

Location[1]	Date[2]	Depth[3]	δD[4]	$\delta^{18}O$[5]	Analyst[6]
Collected by USGS					
H1	02 Jun 76	676-699	-50	-7.0	[a]
	17 Mar 77		-42	-4.5	[a]
H2B	22 Feb 77	623-645	-53	-7.2	[a]
H2C	16 Mar 77	623-645	-53	-6.9	[a]
H3	17 Mar 77	672-694	-53	-7.0	[a]
H6B	19 Dec 78	604-627	-49		[b]
			-47		[b]
H9A	05 Feb 80	647-677	-48		[b]
			-49		[b]
H9B	05 Feb 80	647-677	-51		[b]
			-51		[b]
P14	14 Mar 77	573-595	-48	-6.3	[a]
P15	10 May 77	413-435	-52	-7.3	[a]
	11 Apr 79	413-435	-43	-5.0	[a]
P17	10 May 77	558-583	-51	-5.8	[a]
P18	10 May 77	909-938	-45	-4.8	[a]
Indian[7] prob. Culebra	08 Jun 76	203.6	-46	-6.3	[a]
Mobley[8] prob. Culebra	08 Jun 76	89.0	-44	-6.9	[a]
Mobley #3[9] 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]

TABLE 10. (Continued)

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]
<u>Collected by HGC</u>					
H3 [sic]	11 Jun 84	672-694	-54		[d]
			-56		[d]
			-53		[d]
			-54		[d]
H3B3	04 Feb 85	672-694	-53		[d]
			-53		[d]
H4C	10 Aug 84	490-516	-51		[d]
			-53		[d]
H9 [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	WL=423.6[10]	-52	-7.2	[e]
RF-10 (H13)	06 Oct 83	172-207	-45	-7.3	[e]
<u>Collected by WQSP</u>					
H4B	25 Jul 85	498-522		-6.7	[d]
				-6.5	[d]
H5B	27 Aug 85	897-920		-6.8	[d]
				-6.8	[d]
H6B	15 Sep 85	604-627		-7.1	[d]
H11B3	04 Jun 85	710		-6.8	[d]
				-6.8	[d]
H12	09 Aug 85	825-852[11]		-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]

TABLE 10. (Continued)

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]

---

1. Multiple sampling episodes are listed for some wells. For collection methodologies used by the various indicated agencies, see the following references:
   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. Date of collection.
3. Sampling depth or depth interval, in feet from local datum (usually ground level), isolated by packers, casing perforations, or combinations thereof.
4. In per mil (‰), vs V-SMOW.
5. In per mil (‰), vs V-SMOW.
6. 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] $\delta^{18}O$, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.
   [d] δD and $\delta^{18}O$, S. J. Lambert and D. M. Harvey, SNL.
   [e] δD and $\delta^{18}O$, Hydro Geo Chem, Tucson, AZ.
7. 23.30.21.122 as listed by Cooper and Glanzman (1971). Total depth is given. Depth to water 179.2.
8. "South Well", 23.30.19.123 as listed by Cooper and Glanzman (1971). Total depth is given. Depth to water 70.4.
9. "Little Windmill well", 23.30.2.444a as listed by Cooper and Glanzman (1971). Total depth is given. Case to 314; depth to water 260.5.
10. Water level measured 13 Mar 59; TD-626.5 (Cooper and Glanzman, 1971).
11. Open-hole; no packers or perforations.

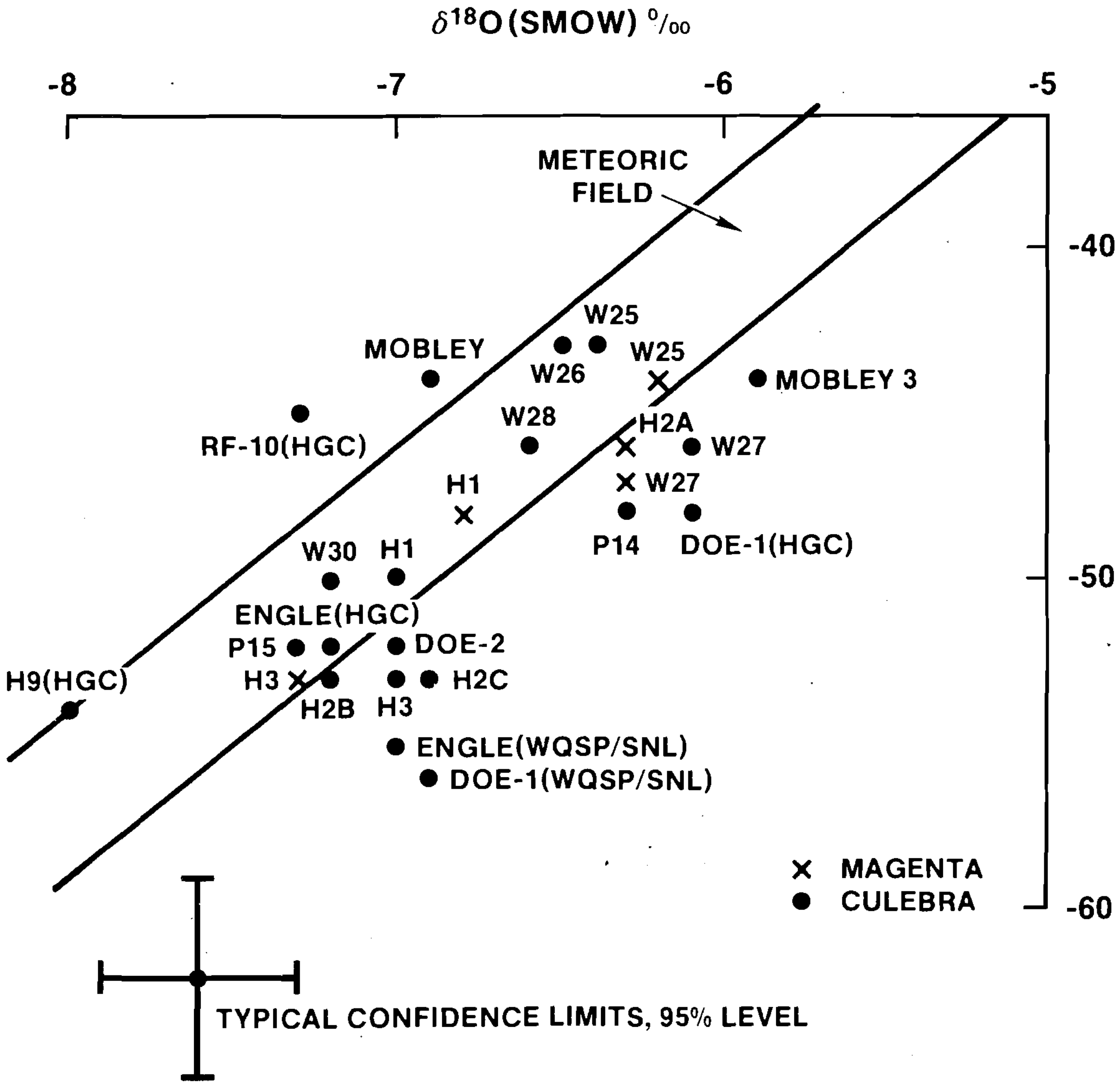


Figure 15. Stable-isotope compositions of groundwaters from the Magenta and Culebra dolomite members of the Rustler Formation. The scale is expanded to allow identification of individual data points. Typical confidence limits at the 95% level are shown for a single analysis. The Magenta and Culebra data points are tightly clustered in $\delta D/\delta^{18}O$ space.

Stable-isotope data for Rustler Formation waters above the Rustler/Salado contact are plotted in Figure 16, to the same scale as most of the other plots. The plot includes data for waters from the Magenta, Culebra, and Tamarisk members (e.g., Surprise Spring). Figure 16 shows that with the exception of WIPP-29 Culebra and Surprise Spring, all Rustler well waters are tightly clustered together on or near the meteoric field. There is no overlap with the field labeled "demonstrably modern Delaware Basin recharge, 3000-4500 ft elev;" a continuum of values would be expected to fill the gap between the fields if mixing between modern recharge and confined Rustler groundwaters were taking place. This nonoverlap between stable-isotope data for the Rustler and that for modern Delaware Basin recharge at comparable elevations is not consistent with the proposal of Chapman (1986) that "there is a good possibility that the Rustler is currently receiving recharge" (p. 64).

For several of the wells listed in Table 10 either δD or $\delta^{18}O$ values are available, but not both. Given the uniformity of both δD and $\delta^{18}O$ values of Culebra waters for which both parameters are available, it is not likely that a water for which only δD is known will have a $\delta^{18}O$ value significantly outside the range represented by the known $\delta^{18}O$ values, and vice versa. However, no attempt is here made to calculate one from the other using a statistical linear regression, as was done by Chapman (1986). An example of the misinterpretations that may arise from this practice has been discussed in Section 4.3.2, and will be further discussed in Section 4.8.

The Rustler data occupy the same general position in $\delta D/\delta^{18}O$ space as do waters from the eastern Capitan Limestone (Section 4.4). The lack of significant deviation from the meteoric field shows that the influence of rock-water interaction on the isotopic compositions of these waters has been minimal since time of recharge as precipitation. In Section 4.6,

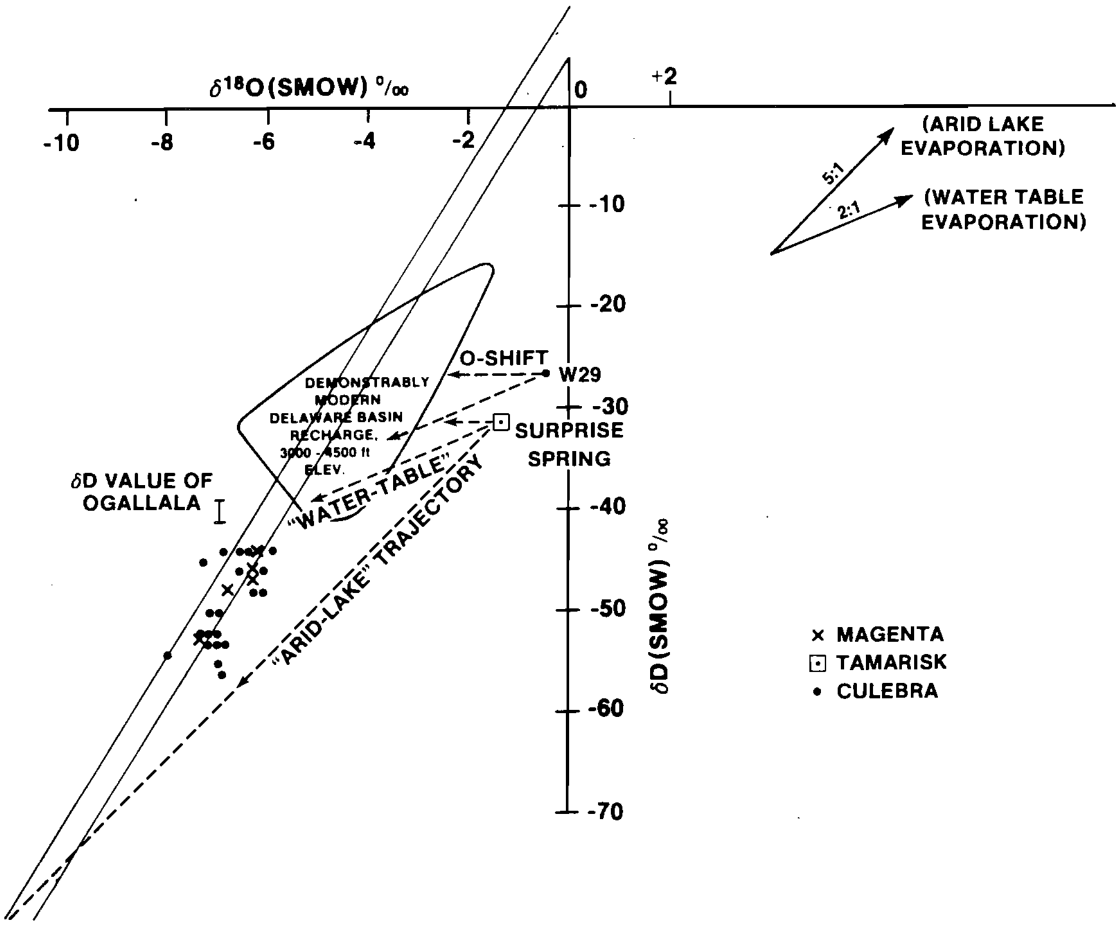


Figure 16. Stable-isotope compositions of groundwaters from the Rustler Formation. None of the Rustler data, even from Surprise Spring (issuing from the Tamarisk member) and the near-surface WIPP-29 occurrence of Culebra, have isotopic compositions that coincide with the field of "demonstrably modern Delaware Basin recharge 3000-4500 ft elev." Based on inferences from stable-isotope and solute data taken together, WIPP-29 Culebra and Surprise Spring are not derived directly from any other part of the Rustler in Nash Draw or near the WIPP site. Rather, their solute and stable-isotope compositions are consistent with their having evolved by evaporation with a $\delta D/\delta^{18}O$ slope of 2 (under conditions typical of a shallow local water-table) from water imported (from the Ogallala, which has a δD value of about -40 ‰) for use in nearby potash-refining operations. Whereas their isotopic compositions are consistent with derivation from such imported water by oxygen-isotope shift (horizontal dashed lines), they are not consistent with evaporation under arid-lake conditions (slope = 5), nor is Rustler water exposed in a natural lake from which such evaporation could occur upgradient from either Surprise Spring or WIPP-29.

however, we posit that the Rustler rocks do contain isotopic records of interaction with meteoric water. The tight clustering indicates homogeneous conditions of recharge, long flow paths, or long residence times in both the Culebra and Magenta (which, except in two locations, are not well connected), or a combination thereof.

WIPP-29 Culebra and Surprise Spring 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 uniquely and inescapably a cause for the isotopic isolation of WIPP-29 Culebra and Surprise Spring. Their isotopic isolation, however, shows that they are not derived by direct flowage from other Rustler waters, either in Nash Draw or the WIPP site. Limitations on interpreting their origin will be discussed in Section 4.5.5.

Rustler/Salado Contact. Mercer (1983) has summarized the general hydrology of the Rustler/Salado contact as follows:

> Brine at the Rustler-Salado contact "brine aquifer" of Robinson and Lang (1938) is present either in a clay residuum bed or along the bedding planes between these units. The residuum is common along Nash Draw and is most extensive between Laguna Grande de la Sal and Malaga Bend [Figure 2], where transmissivities are as large as 8,000 ft^2/day. In the northern end of Nash Draw, transmissivities range from 2 x 10^{-4} ft^2/day in test hole W-27 to 8 ft^2/day in test hole W-29; in the WIPP site proper, transmissivities range from 3 x 10^{-5} ft^2/day at test holes H-5C and P-18 to 5 x 10^{-2} ft^2/day at test hole P-14. The ground-water flow in the eastern part of the site primarily is along bedding planes. Density-corrected potentiometric-surface maps indicate flow is southwest across the WIPP site towards Nash Draw at a gradient of 39 ft/mile and then south-southwest down Nash Draw to Malaga Bend on the Pecos River at a gradient of about 10 ft/mile [p. 77].

Stable-isotope data for waters from the zone near the Rustler/Salado contact are given in Table 11, and are plotted in Figure 17. Again, there is no overlap between any of the data

TABLE 11. RUSTLER/SALADO WELL WATERS

Location[1]	Date[2]	Depth[3]	δD[4]	$\delta^{18}O$[5]	Source[6]
Collected by USGS					
Duval Nash Draw mine shaft collector ring	09 Dec 75	≈350	-48	-6.4	[a]
H1	23 Feb 77	824	-29	1.6	[a]
H2C	23 Feb 77	764	-41	-2.9	[a]
	24 Feb 79	764	-41	1.3	[a]
H3	23 Feb 77	821	-38	0.2	[a]
	10 May 79	821	-43	-4.9	[a]
H4C	16 Mar 79	626	-57	-4.0	[a]
H5C	16 May 79	1041	-44	-1.9	[a]
H6C	09 Apr 79	721	-53	-4.9	[a]
P14	24 Feb 77	687	-64	-9.0	[a]
P15	03 Apr 79	542	-52	-6.6	[a]
P17	11 May 79	715	-50	-1.4	[a]
P18	11 May 79	1088	-48	-1.6	[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-27	07 Aug 80	416	-48	-7.0	[b],[c]
			-49		[b]
WIPP-28	31 Jul 80	531	-58	-7.0	[b],[c]
			-57		[b]

TABLE 11. (Continued)

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]

---

1. A grab sample was taken from the mine shaft collector ring. For other sampling procedures consult the following:
   USGS: Mercer and Orr (1979); Mercer (1983)
   Lambert and Robinson: Lambert and Robinson (1984)
2. Date of collection.
3. Depth to top of sampling interval (typically open-hole), in feet from local datum (typically ground level), isolated from overlying zones by packers, perforated casing, or both.
4. In per mil (‰), vs V-SMOW.
5. In per mil (‰), vs V-SMOW.
6. Sources 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] $\delta^{18}O$, S. J. Lambert, Sandia Nat'l Labs.

for Rustler/Salado contact waters and the field of modern recharge. In addition, the entire group of data exhibits a phenomenon that for the Delaware Basin was discussed first by Lambert (1983a): deviation of basal Rustler waters from the meteoric field. In particular, waters from the Rustler/Salado contact in Nash Draw, where the "basal brine aquifer" of Robinson and Lang (1938) is well developed and represented by an abundance of water in this zone, are clustered near the meteoric field (DND, P14, W25, W26, W28, W29, and W30). Waters from farther east near the WIPP site have significant deviations from the meteoric field (H1, H2, H3, H4, H5, H6, and P17). A likely cause of this dichotomy may entail the relationships between permeability (i.e., effective water/rock ratio) and degree of water/rock interaction.

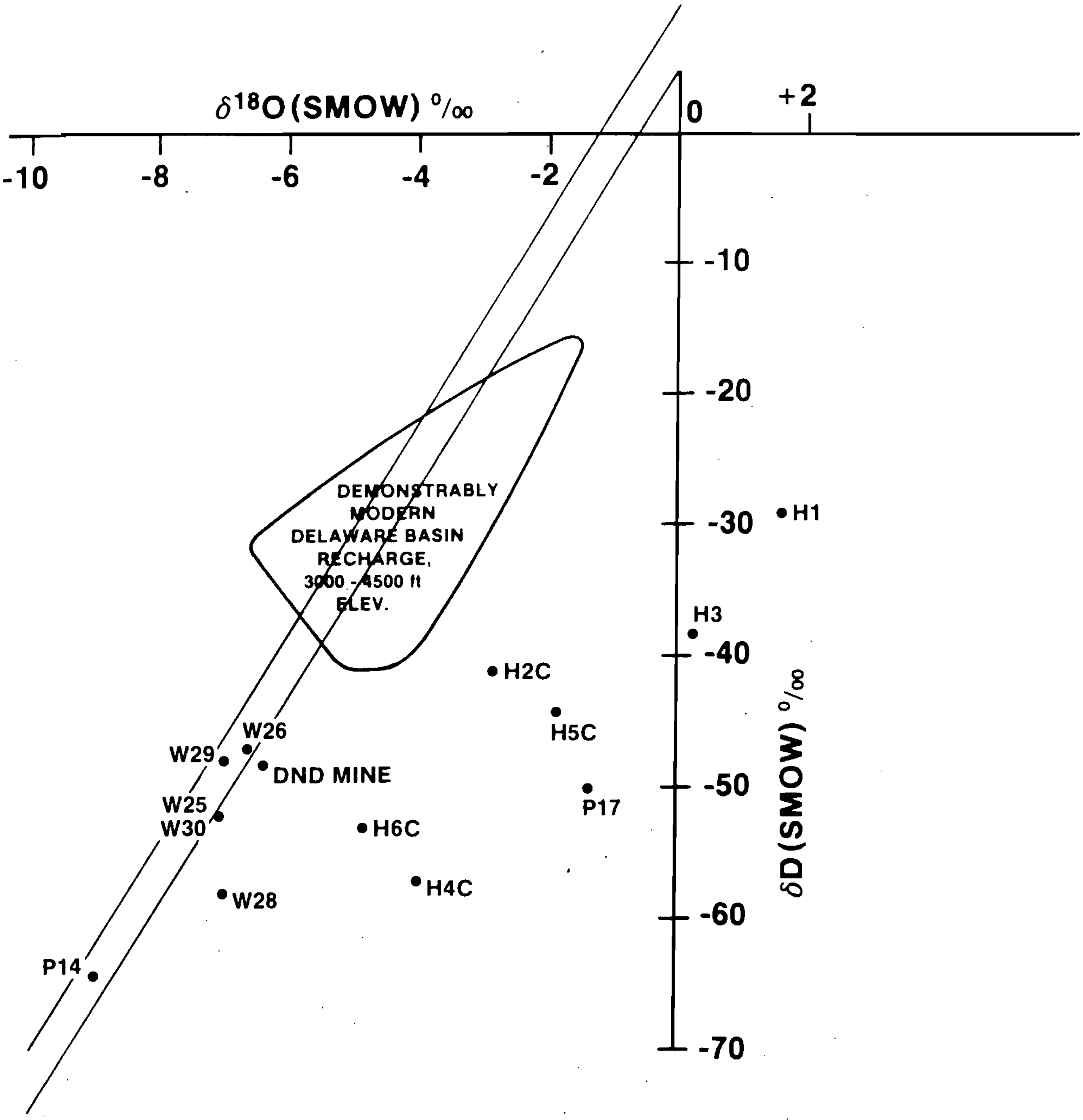


Figure 17. Stable-isotope compositions of groundwaters from the Rustler/Salado contact. Rustler/Salado contact waters near Nash Draw, where the permeability of this zone is high, have isotopic compositions that plot very near the meteoric field. Oxygen- and hydrogen-isotope shift is observed for waters from the same zone further east, near the WIPP site.

Figure 18 is a plot of $\delta^{18}O$ versus transmissivity. Values of transmissivity (Mercer, 1983) are taken from pump tests or slug tests just before or during the pumping or bailing episodes that furnished samples for stable-isotope analyses. The plot shows that the waters whose $\delta^{18}O$ values have the greatest deviation from the meteoric field (H1, H3, P17, H2C, H4C, and H6C) also came from zones of lower transmissivity ($T < 10^{-2}$ ft²/day). This corresponds to a greater "oxygen-isotope shift" (cf. Section 4.6) where the rock/water ratio is greater (i.e., the lower transmissivity allows a greater number of exchangeable oxygen atoms in the rock to observably contribute to the isotopic composition of the water). Only at transmissivity values of about 0.01 ft²/day or greater does the water show Rustler-typical meteoric $\delta^{18}O$ values of -6.7 ‰ or less. Since water from the zone near the Rustler/Salado contact is under confined conditions in Nash Draw and the WIPP site (Mercer, 1983), partial evaporation is not a plausible cause for the isotope shift (cf. Section 4.6), since there is no freely circulating air/water interface. Mercer (1983) described a bimodal distribution of Rustler/Salado transmissivity values, a distinction between those with less than 0.001 ft²/day and those with greater than 0.1 ft²/day. Figure 18 shows that this distinction is also reflected in the $\delta^{18}O$ values: waters showing significant oxygen-isotope shift, and waters showing virtually no oxygen-isotope shift with respect to meteoric values. We attribute the oxygen-isotope shift to interaction between rock and water, involving oxygen-isotope exchange and a lesser degree of hydrogen-isotope exchange. Note in Figure 17 that the hydrogen shift between WIPP-26 and H1 is a relatively modest 18 ‰, but the oxygen shift is a respectable 8.3 ‰. A greater degree of rock/water interaction is reflected in greater isotope shifts. This phenomenon will be discussed in more detail in Section 4.6.

In order to illustrate the progressive degree of isotope shift eastward across the WIPP site, a $\delta^{18}O$ value of -7 ‰, characteristic of 100% meteoric Rustler/Salado contact waters in the high-

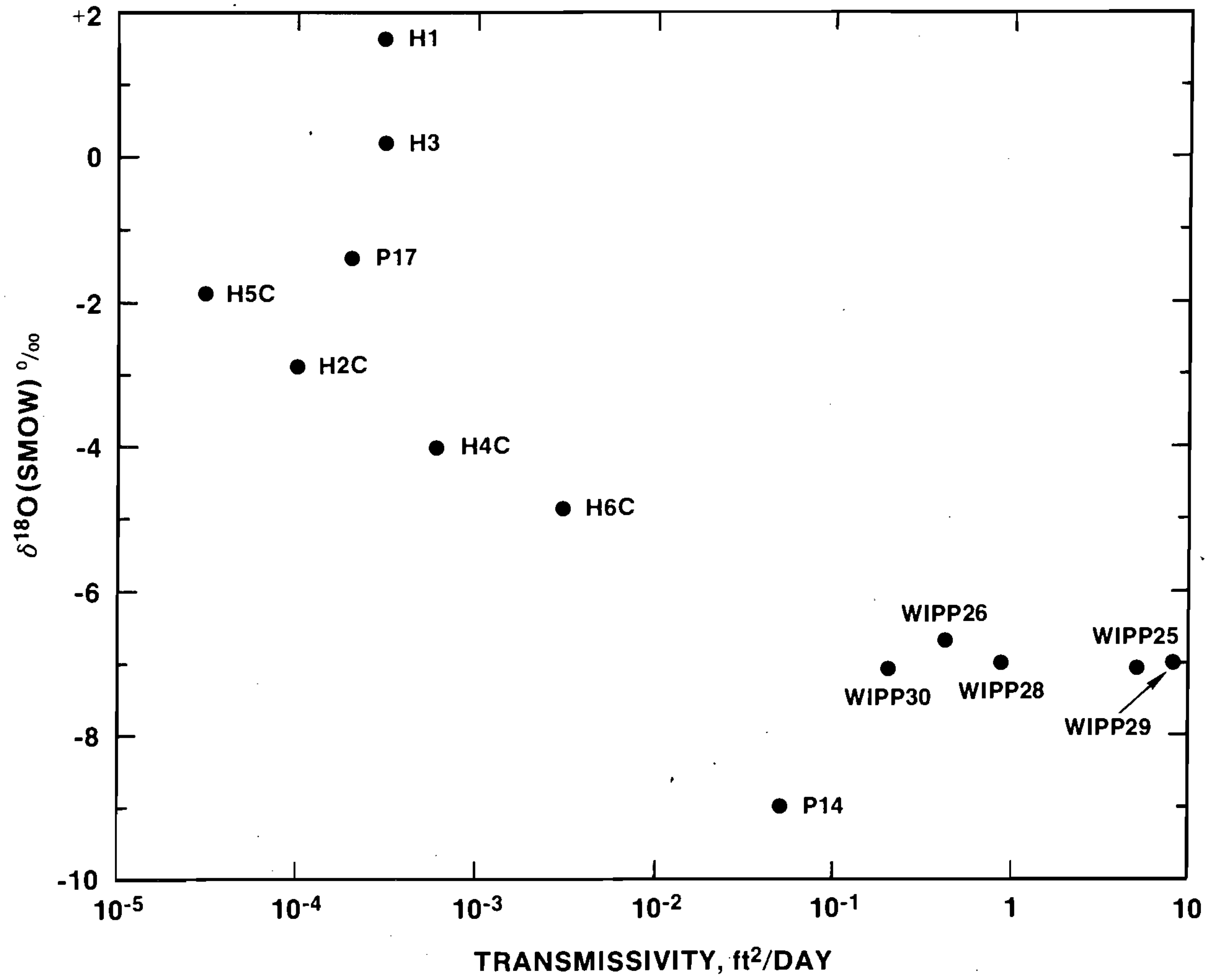


Figure 18. Semilogarithmic plot of $\delta^{18}O$ value of water versus transmissivity at the Rustler/Salado contact. At transmissivity values (from Mercer, 1983) greater than 0.01 ft²/day $\delta^{18}O$ values are similar to those of most of the Rustler groundwaters under confined conditions. Conversely, where this zone has a transmissivity of less than 0.01 ft²/day, the water/rock ratio is smaller and a significant oxygen-isotope shift is observed.

permeability region of Nash Draw, was assigned a shift of 0. Arithmetic deviations therefrom were plotted on the map and contoured; the result is Figure 19. Also included in Figure 19 is the position of the scarp that defines the eastern boundary of Nash Draw. The contours generally parallel the scarp. The zero-shift contour on the north and southwest is offset 1 to 2 miles east of the scarp. This is consistent with the persistently high values of permeability at the Rustler/Salado contact found as much as 1 to 2 miles east of the scarp.

Superimposed on the oxygen-isotope shift contours of Figure 19 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 none in the Rustler. The oxygen-isotope shift contours roughly parallel the boundaries of Rustler halite zones, and the 3 ‰ contour partly coincides with total removal of halite in the Rustler. Mercer (1983) drew a boundary between greater and lesser developed Rustler/Salado-contact flow systems, based on combined concentrations of potassium and magnesium, which he roughly correlated with transmissivity. We accept Mercer's conclusion that the extreme variability 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."

Even in areas where all Rustler halite has been removed, the permeability at the Rustler/Salado contact has not been sufficiently augmented by dissolution and collapse to allow free circulation of groundwater with a high water/rock ratio and no isotope shift. This is illustrated by the significant amounts of oxygen-isotope shift in the zone between the zero-shift contour

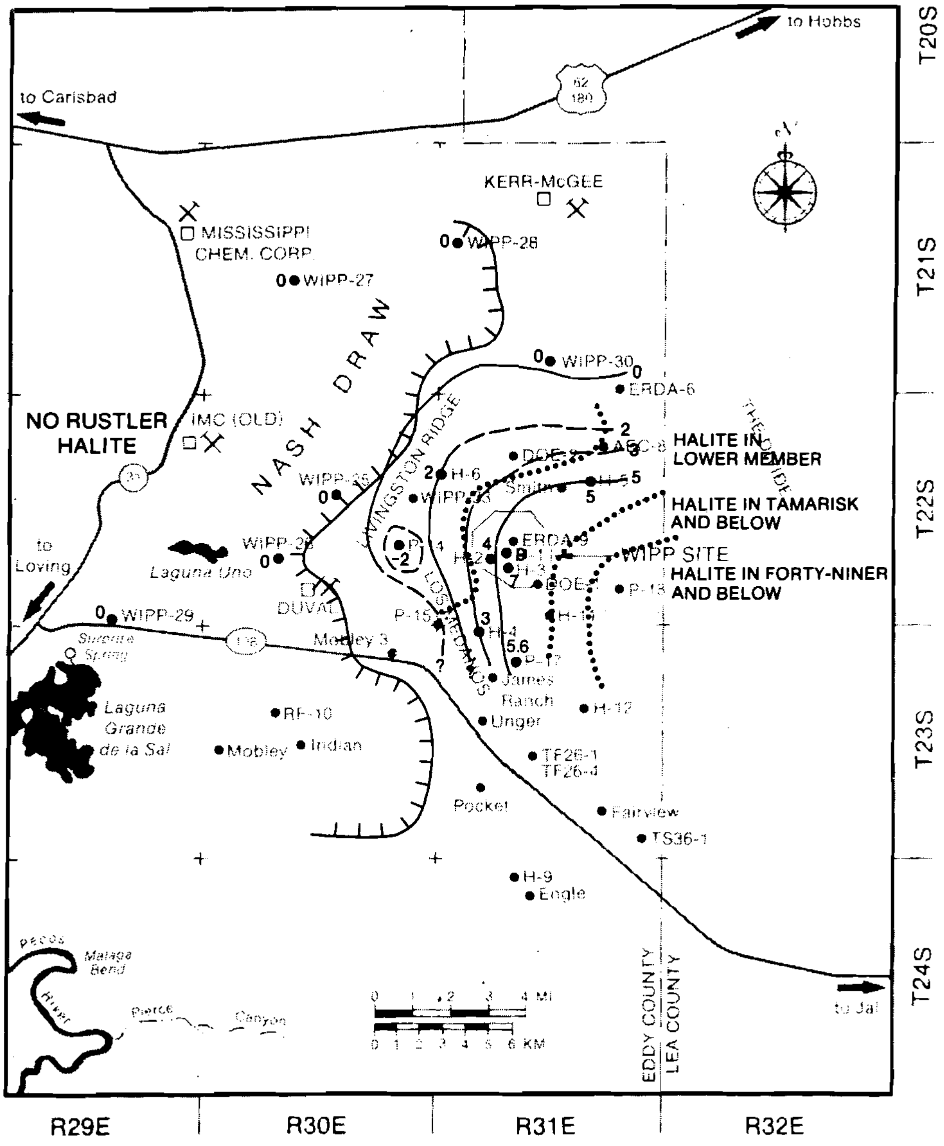


Figure 19. Contour map of oxygen-isotope shift in confined groundwaters at the Rustler/Salado contact, relative to -7 ‰. Dotted lines are boundaries of Snyder (1985) delineating the occurrences of halite in various members of the Rustler. Shift-contours parallel the halite boundaries, and the 0-shift contour parallels the scarp defining Nash Draw at Livingston Ridge. Magnitude of oxygen-isotope shift appears inversely related to transmissivity (Figure 18) and directly related to amount of halite remaining in the Rustler. Assuming an eastward-progressing halite-dissolution front, neither (1) eastward scarp retreat, nor (2) development of increased permeability due to subsidence-induced fracturing, nor (3) flushing of isotopically shifted water has kept pace with total removal of halite by dissolution in the Rustler.

and line marking the absence of halite in the Rustler (Figure 19). We do not propose that oxygen-isotope shift is a direct measurement of groundwater residence time, but we observe that water having undergone isotopic exchange with rock in the "basal brine aquifer" has not been entirely flushed from the system. This observation will tend to limit estimates of flow rates at the fringes of a zone of active evaporite dissolution.

The isotopic data in Tables 9 and 10 show that different parts of the Rustler Formation even within the same hole can be isotopically (and probably hydraulically) isolated from one another. For example, the Culebra and Rustler/Salado waters in WIPP-28 are isotopically different by 1.4 ‰ in oxygen and 11 ‰ in hydrogen, even though they both lie in the meteoric field. Thus, as will be discussed subsequently, the isotopic data show that waters of different isotopic compositions entered their respective horizons of the Rustler Formation under somewhat different recharge conditions, probably indicative of somewhat different climatic regimes.

There are other cases of both similarities and differences among waters in a single well in different parts of the Rustler. Connections cannot be argued solely on the basis of isotopic similarities; a case can be made for relatively uninhibited mixing through vertical connection if superposed occurrences of water in the Rustler have simultaneous isotopic, solute, and potentiometric similarities. Such appears to be the case in WIPP-25 and WIPP-27 for the Magenta and Culebra. At each of these localities, the δD and $\delta^{18}O$ values are indistinguishable, the static water levels are indistinguishable (Mercer, 1983), and the major solute concentrations are indistinguishable (Robinson, 1987).

Groundwaters near the Rustler/Salado contact having undergone rock-water interaction are probably represented at H1, H2, H3, H4, H5, H6, and P17. All of these are from zones of lower permeability, and have isotopic compositions that define a trajectory away from the meteoric field. These groundwaters still reflect an original meteoric origin, as indicated by the intersection of this trajectory with the meteoric field at isotopic compositions representative of much of the Rustler. For additional discussion of rock-water interaction in the Rustler Formation, see Lambert (1983a) and Section 4.6.4.

4.5.3 The Age of Rustler Groundwaters

Lambert (1987) studied the natural atmospherically generated nuclides in Rustler groundwaters, particularly radiocarbon and tritium. Those results will be briefly reviewed here, as relevant to the question of possible age of recharge.

Chapman (1986) raised the issue (and cited Fontes, 1981) that "groundwater ... could be depleted in heavy isotopes and misinterpreted as paleowater if no tritium or carbon-14 measurements are available," and suggested that "the use of hydrogeologic evidence and carbon-14 dates to support the hypothesis is a consistent feature of valid paleoclimate studies." This is not an adequate representation of the published literature. First, the literature is replete with paleoclimatic inferences based largely on stable-isotope evidence, in the absence of absolute "dating" (see, for example, Yapp, 1985 and Section 4.8.1 below). Second, Lambert (1987) showed that although radiocarbon and tritium measurements can be made to very low detection levels in Rustler groundwaters, interpretation of the data as dates is limited by (1) the particular numerical interpretive model used to calculate the date from the data, (2) the degree to which the interpretive model reasonably represents, describes, and accounts for the various geochemical processes, natural and anthropogenics, affecting the concentrations of various trace nuclides in solution, (3) mixing and contamination, which may or may not be evident, and (4) the dangers of overinterpreting a single date (whether very old or very young) based on a single data point, which may give rise to a spurious interpretation of the systematics of the entire groundwater system. Lambert (1987) suggested that "dates" in a groundwater system were likely to be reliable **only** given (1) more than one occurrence of a date, (2) a relatively tight cluster of dates, or (3) a monotonic trend of dates (say, as a function of distance along a potentiometric gradient). The second instance was observed for the Rustler.

The dates one obtains for groundwaters by the radiocarbon method are **entirely** dependent on the choice of a numerical interpretive model. The most critical parameter in any such model is the initial ^{14}C activity in the groundwater at the time of entry to the subsurface system. Several strategies for inferring the initial ^{14}C activity have been proposed, and the premises and assumptions of several strategies have been reviewed by Fontes and Garnier (1979). The model Lambert (1987) chose was developed specifically for carbonate aquifers by Evans et al. (1979). This model, like all the others, relates time of isolation from the atmosphere to the time-dependent radioactive decay of radiocarbon. In addition, this model adjusts for radiocarbon loss that has arisen from processes other than radioactive decay. The Evans et al. model (hereafter called the Evans model for brevity) accounts for radiocarbon loss by a two-stage process: (1) radiocarbon is diluted to half its initial activity when the water enters the carbonate aquifer, owing to stoichiometric dissolution of ^{14}C-free rock carbonate equal in amount to dissolved carbon dioxide in water recharging the unit; (2) radiocarbon is absorbed on the rock by isotope exchange reactions in an amount proportional to the degree of ^{13}C exchange between rock and water.

Application of the Evans model required the assumption of additional values: (1) the $\delta^{13}C$ value of dissolved carbon species having 100 PMC after infiltration of the original recharge water through the organic soil horizon, and (2) the equilibrium $^{13}C/^{12}C$

fractionation factor between dolomite and dissolved bicarbonate. The second, as discussed by Lambert (1987) and in Section 4.6 below, is not known precisely for ambient temperatures. The first can be measured directly only for soil water that has passed through the oxidized organic layer, and which can be shown to ultimately enter the aquifer whose water is being dated. Until the existence and location of the modern recharge area can be ascertained to a high degree of certainty, an assumed value must be used, following the discussions of Evans et al. (1979).

Given the nonoverlapping stable-isotope compositions of demonstrably modern recharge and Rustler water, an ascertainable modern recharge area for Rustler waters at the WIPP site probably does not exist. An additional difficulty is presented by very old groundwaters, for which paleorecharge areas representative of their recharge conditions (and initial carbon-isotopic composition) may no longer exist.

Lambert found that application of the Evans model to most Rustler groundwaters gave significantly large negative radiocarbon ages. The model, in adjusting the observed ^{14}C activity upward based on $\delta^{13}C$, yielded an excess ^{14}C activity. If the modern activity is greater than the inferred initial activity, negative ages result. Another way of obtaining this situation was if the measured ^{14}C activity was greater than the 50% modern carbon (PMC) assumed at the time of recharge to the carbonate unit. The resulting large negative ages are consistent with the premise that excess modern carbon has been introduced by contamination during well drilling and development. Other manifestations of this contamination were observed by Lambert and Robinson (1984) during the pump tests that provided the radiocarbon samples. Thus, Lambert concluded that any perturbation to the carbon-isotope systematics apart from those natural variations handled by the model would invalidate the assumptions on which radiocarbon dating of groundwaters is based.

Four groundwater (three Rustler and one Dewey Lake) gave significant positive ages, all of which were found to be statistically indistinguishable (in radiocarbon years): H4, 16,100 a; H9, 14,900 a; H6, 12,100 a (all Culebra); Pocket (Dewey Lake), 14,000 a. Given that these groundwaters could contain traces of contaminant ^{14}C, these were regarded as **minimum** times of isolation from the atmosphere. If the flow path to the vicinity of the WIPP site is long, these results represent travel times from the recharge area. If recharge was originally local, these results more likely represent a discrete recharge event or the end of a discrete recharge-time interval, probably indicative of wetter climate in the Pleistocene. Other evidence of a 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 (Figure 1) that a juniper-oak plant community existed there 10,500 to 10,000 years ago, at an elevation of about 3700 ft, where now desert scrub communities have been stable for the last 4,000 years. Thus, a limited number of the groundwaters interpreted here to be distinct from modern meteoric precipitation, in fact have radiocarbon ages indicative of late Pleistocene recharge.

A limited number of high-precision tritium measurements is also available for Culebra and Dewey Lake groundwaters near the WIPP site. All the tritium and some of the radiocarbon results are plotted on the map in Figure 20. The radiocarbon dates for the four datable waters are also depicted, together with some PMC values. Note the high (>50) PMC value for WIPP-27, which results in a large negative age, especially when adjusted on the basis of ^{13}C. WIPP-27 Culebra also had the highest tritium: 6.9 TU. The high PMC and TU values reflect the contamination that was independently documented by Lambert and Robinson (1984), and high (contaminated) PMC values are typical of confined Rustler groundwaters in Nash Draw. Tritium values from the WIPP site and the area immediately south range from -0.08 to +2.8 TU. Such low but

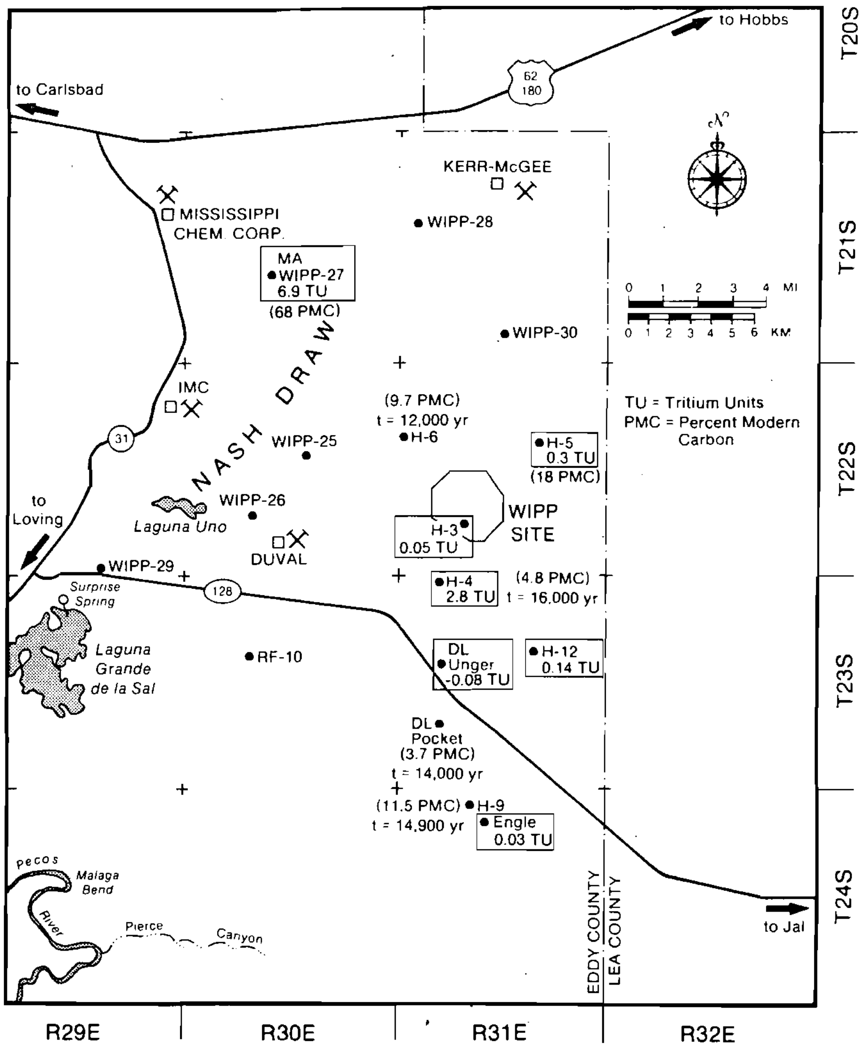


Figure 20. Tritium and radiocarbon in Rustler and Dewey Lake groundwaters. Unless otherwise specified as Dewey Lake (DL), measurements (all from Lambert, 1987) apply to water from the Culebra member of the Rustler Formation. Tritium units (TU, 1 part tritium in 10^{18} total hydrogen) are enclosed in rectangles. The uniformly low (<3 TU) tritium concentrations near the WIPP site indicate no contact with the atmosphere since 1950. Higher tritium concentration at WIPP-27 (6.9 TU) is associated with a percent modern carbon (PMC) value of 68, which is greater than 50 and therefore shows modern contamination. Three Culebra and one Dewey Lake water had combinations of PMC and $\delta^{13}C$ values amenable to dating by the carbonate-aquifer model of Evans et al. (1979), giving times of isolation from the atmosphere ranging from 12,000 to 16,000 radiocarbon years. The 18 PMC value at H5 appears to be contaminated. These data indicate long residence times or long travel times from recharge areas.

measurable tritium counts are generally considered indistinguishable from zero, according to the discussion of Evans et al. (1979). Thus, the tritium data from seven localities conclusively show that there is no direct hydraulic connection between the Culebra (or parts of the Dewey Lake) and the surface that has allowed recharge near those localities (including near the center of the WIPP site proper at H3) in the last 36 years, during which time atmospheric testing of hydrogen bombs has introduced a large tritium spike into the atmosphere and rapidly-recharged groundwater systems. Either the residence time is very long, or travel time from the recharge area at the surface is greater than 36 years. The radiocarbon dates show that the time of isolation from the atmosphere at four widely separated locations (three Culebra and one Dewey Lake) has been at least 12,000 years. By inference, we tentatively consider this age applicable to all Rustler, Dewey Lake, Triassic, and Capitan groundwaters with similar stable-isotope compositions, throughout the northern Delaware Basin. Either water at least this old is a significant component of all the Culebra waters discussed by Lambert (1987), or else the rates of recharge (if any) and mixing (due to subsurface flow) have not been rapid enough to influence the widely-separated wells H4, H6, and H9, whose carbon-isotope systematics still indicate late Pleistocene ages. No tritium values as high as those observed in parts of the Roswell Artesian Basin (Section 4.8) receiving recharge from mountain-runoff, or in the population of High Plains Ogallala groundwaters with δD values more positive than -42 ‰ (Section 4.3.4) have been found in the Rustler near the WIPP site. Unfortunately, no radiocarbon data are available for the Roswell Artesian Basin, so no further comparisons can be made, although comparisons based on stable-isotope compositions have been attempted by Chapman (1986). This will be discussed in Section 4.8.

4.5.4 Summary: Meteoric Recharge of Rustler Groundwaters

Several lines of mutually independent evidence are relevant to how much recharge the Rustler groundwaters are receiving from the area occupied by the Rustler in the northern Delaware Basin. The first to become available, and perhaps the most self-evident, was hydraulic (Mercer, 1983, p. 79):

> The relative static heads or formation pressures of the hydrologic units in the Rustler Formation decrease with depth; that is, hydraulic heads are highest in the Magenta and lowest at the Rustler-Salado contact. There appear to be two regional flow systems; one in the area around the proposed WIPP site and one in Nash Draw. In the WIPP site area, the presence of impermeable interbeds of halite and anhydrite and the differences in static head and water quality probably indicate restricted vertical hydraulic connection between units; however, in Nash Draw, where dissolution and subsidence are more common, hydraulic connection between units probably exists.

Compelling evidence of vertical connection has been observed in two boreholes in Nash Draw: WIPP-25 and WIPP-27, where the Culebra and Magenta appear to be hydraulically interconnected, and have similar potentiometric levels, solutes, and isotopic compositions.

The absence of significant (e.g., >5-10 TU) tritium in groundwaters of the Rustler Formation is another compelling bit of evidence that argues against direct (rapid) recharge to the Rustler. If recharge is taking place, its rate is very slow, in that no tritium has shown up in the 36 years of atmospheric testing of nuclear weapons, or the amount of recharge is miniscule, being diluted by mixing with older groundwater to concentrations indistinguishable from zero. Not even background levels of tritium have been found (10 TU is estimated as the local upper concentration limit for precipitation containing tritium generated by cosmic rays; Gross et al., 1976). If the Rustler receives its water by direct infiltration, either the expected tritium spike has not yet reached the Rustler, or the amount of tritium in this recharge is diluted by mixing with older groundwater to concentrations not significantly different from zero. If the dilution factor is indeed large, one should question whether this minute amount of recharge is to be considered significant.

Figure 21 is a histogram of δD values for waters from southeastern New Mexico whose $\delta D/\delta^{18}O$ relationships bear a meteoric signature. Included are the δD values for the Ogallala samples, whose $\delta^{18}O$ values are assumed not to have been modified by evaporation or rock/water interaction. Ranges are shown for various classes of waters. Only waters are shown whose collections sites have surface elevations of less than 4500 ft, be they in confined groundwater systems, water-table conditions, or areas of active recharge. First, Figure 21 shows that there is no overlap in δD values between the confined Rustler/Capitan collection of points and the modern collection; the Rustler/Capitan set of values includes the Pocket and Fairview (Dewey Lake) and Smith (Triassic) data, which are taken to represent conditions of hydraulic confinement. Second, there is a gap in the region -42 to -43 ‰; no meteoric waters with these δD values have been found. This distinction is not as clearcut as might be desired based solely on δD value; nevertheless the distinction is observed. We recognize that there is not a continuum in δD values for the modern waters, but the fact remains that no Delaware Basin groundwaters under confined conditions have been found with a δD value as positive as -41 ‰. The inferences of youthful recharge are made on the basis of local hydrologic conditions. Several of the Rustler (and some Dewey Lake) points have no significant levels of tritium, implying no direct rapid connection with the surface. We do not have tritium measurements for waters we infer to be modern according to hydrologic conditions. Hence we know that waters with δD values more negative than -43 ‰ are not extremely young (<35 years); we do not know that some of the waters with δD values more positive than -42 ‰ (even those inferred to be

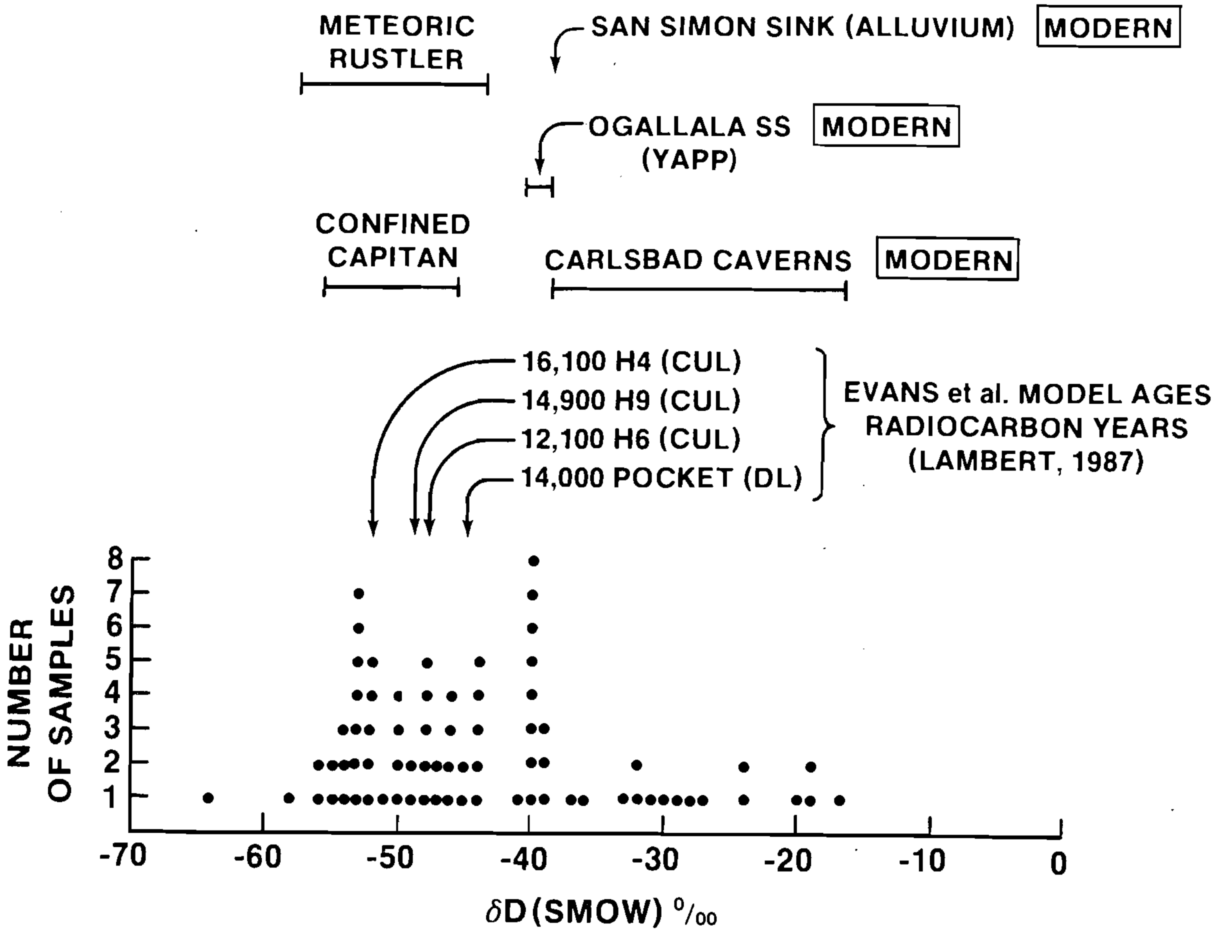


Figure 21. Histogram of δD values for meteoric groundwaters in the Delaware Basin. Forty-six confined Rustler and Capitan groundwaters showing no isotope shift from the meteoric field have a mean δD value of -50.3 ‰, with confidence limits (at the 95% level) of -42 to -59 ‰. These do not statistically overlap, in the most liberal sense, with δD values of groundwaters from water-table (San Simon Sink, Ogallala sandstone) or vadose (Carlsbad Caverns) conditions, all of which have δD values more positive than -42 ‰. Also, four confined groundwaters from the more negative δD range have radiocarbon ages of 12,000 to 16,000 yr.

"modern") are not "old". In addition, we know that four of the waters with δD values more negative than -43 ‰ (three Rustler and one Dewey Lake) have been isolated from the atmosphere at least 12,000 to 16,000 radiocarbon years.

Taken as a whole, the combined body of available evidence indicates 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. It is here inferred that the four late Pleistocene apparent ages derived from radiocarbon measurements of waters more depleted in ^{18}O and D relative to known or inferred 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. The absence of significant vertical hydraulic connection is not conducive to direct vertical infiltration from the surface, even in areas of high potentiometric level where one would conventionally infer recharge. The absence of tritium is consistent with this observation. Groundwaters whose stable-isotope compositions are typical for the Rustler have been dated at least 12,000 to 16,000 years old, and their stable-isotope compositions do not correspond to those characteristic of modern recharge. Possible implications and consequences of these findings in a geological context will be discussed in Section 4.6. In Section 4.8.2 we will briefly review a case study involving estimates of amount of groundwater recharge to a water table, in which recharge was too small to be directly observed by conventional hydraulic methods, but required the use of sophisticated isotopic studies.

4.5.5 Discharge from Surprise Spring and WIPP-29 Culebra

Because of their geographic proximity and isotopic similarity to one another, waters from Surprise Spring and WIPP-29 Culebra will be discussed together. They both exhibit a profound difference in isotopic composition from other Rustler waters, and both have a significant deviation from the meteoric field in $\delta D/\delta^{18}O$ space, greater than that attributable to isotopically unmodified precipitation (see Figure 16).

The geological and hydraulic systematics of the Rustler Formation in the Surprise Spring area of southwestern Nash Draw have been summarized by Mercer (1983, pp. 48-50):

In conjunction with the 'brine aquifer' study, Robinson and Lang (1938) also made a study of Laguna Grande de la Sal and the area between it and Malaga Bend to determine if brine in the lake was a source of recharge to the system. They determined, at the time of their study, that the sources of the water in the lake were precipitation and surface drainage, ground-water inflow from units above the "brine aquifer", and effluent from the U.S. Borax and Chemical Company operation. Since that time, the U. S. Borax and Chemical Company plant has been closed; however, there still may be some inflow from mining activities that take place farther north in Nash Draw [e.g., International Minerals and Chemicals Corporation refinery; Figure 2]. Robinson and Lang identified several factors that led to their conclusion that the lake and underlying "brine aquifer" were not connected. These factors were: (1) test holes drilled into the hydrologic units under the lake contained water with a different chemical composition and a much smaller chloride concentration; and (2) water levels in the fill indicated movement toward the lake and not away from it (in fact, the hydraulic heads were above the lake level in most test holes). Theis and Sayre (1942, p. 71) supported this conclusion because they found water levels in the lake to be high in winter and low in summer, whereas the hydraulic head in the "brine aquifer" is high in the irrigation season and low between seasons.

Discharge of ground water into Laguna Grande de la Sal and probably into the fill is by the flow of springs and seeps, particularly along the northern end of the lake. The largest of these springs was identified by Robinson and Lang (1938, p. 95) and called Surprise Spring (SW 1/4 NE 1/4 SW 1/4 sec. 4, T. 23 S., R. 29 E.), which was reported to discharge 115 to 125 gallons per minute. More recent WIPP studies indicate that the spring and accompanying seeps now discharge over such a broad area that accurate measurements of flow could not be made. This increase in the areal extent of the discharge area indicates an increase in discharge, probably resulting from the effects of effluent added by mining activities since Robinson and Lang's (1938) studies. The discharge of the spring probably comes from the cavernous gypsum of the Tamarisk Member of the Rustler Formation even though alternative sources, the Culebra Dolomite Member or the Rustler-Salado contact residuum, have been proposed. Data from more recent WIPP investigations indicate that the water chemistry and hydraulic-head information identify the source of the water to be something other than the Culebra or the residuum. Analyses of water samples from the Culebra Dolomite Member and Rustler-Salado contact residuum in test hole WIPP-29 ... near Surprise Spring indicate an increase in both sodium and chloride concentrations compared to Surprise Spring. However,

> there is 2.5 times more calcium in the water discharging from Surprise Spring. Additionally, hydraulic-head data from a potash test hole drilled for AMOCO in Laguna Grande de la Sal (T. 23 S., R. 29 E., sec. 4) show the Culebra to have a hydraulic head about 21 feet above the lake level, indicating a confined system although there may be some minor upward leakage. The Culebra was confined under about 40 feet of gypsum mud and flowed at a rate of approximately 20 gallons per minute when first penetrated during drilling activities. This evidence indicates that neither the water present in the Culebra Dolomite Member nor in the Rustler-Salado residuum are in good hydraulic connection with the brine from the spring that flows into Laguna Grande de la Sal. The most likely source of the brine is the Tamarisk Member.

There is compelling hydraulic evidence that Surprise Spring discharges dominantly from the Tamarisk, and has no connection with the underlying Culebra member. Taken together, the solute and stable-isotope evidence confirms the independent behavior of Surprise Spring.

The differences in isotopic composition between Surprise Spring and the rest of the Rustler are significant (Table 6; Figure 16). The differences in δD and $\delta^{18}O$ values between WIPP-29 Culebra and the rest of the Culebra are even greater (Table 10; Figure 16). Barrows (in Chaturvedi and Channell, 1985) and Chapman (1986) have proposed that Surprise Spring, and by implication, nearby Laguna Grande de la Sal (both of which are a significant distance upstream from Malaga Bend) are discharge points for the Rustler. Surprise Spring discharges from the surface outcrop of the gypsiferous Tamarisk Member of the Rustler Formation, between the Magenta and Culebra Members, and the profound difference in isotopic composition between Surprise Spring and all the rest of the Rustler groundwaters (excluding WIPP-29 Culebra) shows that Surprise Spring is not directly discharging water derived primarily from either the nearby Culebra or the "basal brine aquifer" near the Rustler/Salado contact. If there were a direct connection, rapid subsurface mixing would have homogenized the local groundwaters, and isotopic differences would not be preserved. Either an additional process has altered the isotopic composition of Surprise Spring and WIPP-29 Culebra, if they are derived directly from Rustler groundwaters having a tight cluster of δD and $\delta^{18}O$ values, or there is no such direct derivation. Lambert (1983a) concluded, on the basis of solute concentrations, that "the water of Surprise Spring is not derived from either the Culebra dolomite or the 'basal brine aquifer', both of which in that vicinity have chloride contents at least 60000 mg/L chloride" (Surprise Spring has 30000). The availability of stable-isotope data, together with solute concentrations, makes it possible to evaluate the origin of both the water molecules and the dissolved constituents.

Figure 22 shows hypothetical straight-line paths from various points in Nash Draw and the WIPP site to Surprise Spring, assuming the hydraulic conductivity is continuous along each path. Note the strategic location of WIPP-29. If the Culebra is a continuous hydraulic conductor, virtually all paths within the Culebra postulated here to discharge at Surprise Spring must pass through or near WIPP-29, where the Culebra is 12 ft beneath the surface. The chloride/$\delta^{18}O$ systematics for the Culebra and "basal brine aquifer" at the WIPP site and Nash Draw, in relation to Surprise Spring, are shown in Figure 23. Evaporation will increase the solute concentrations until saturation with one or more phases is reached. Evaporation will also make the $\delta^{18}O$ and δD values more positive, more details of which will be discussed in Section 4.6. Figure 23 shows that it is not possible to derive Surprise Spring water by evaporation of Culebra water characteristic of H5B, H6B (near the WIPP site) or WIPP-27; such an evolutionary path would indeed entail enrichment in ^{18}O, but a dilution of chloride. By similar reasoning, it is not possible to derive a water similar to Surprise Spring by evaporation of any water of the "basal brine aquifer" (Rustler/Salado contact). As shown in Figure 22, water in the Culebra flowing down the potential gradient in Nash Draw toward Surprise Spring passes near WIPP-29. Derivation of WIPP-29-like Culebra water from <u>any</u> of the waters would require (1) addition of more solutes than

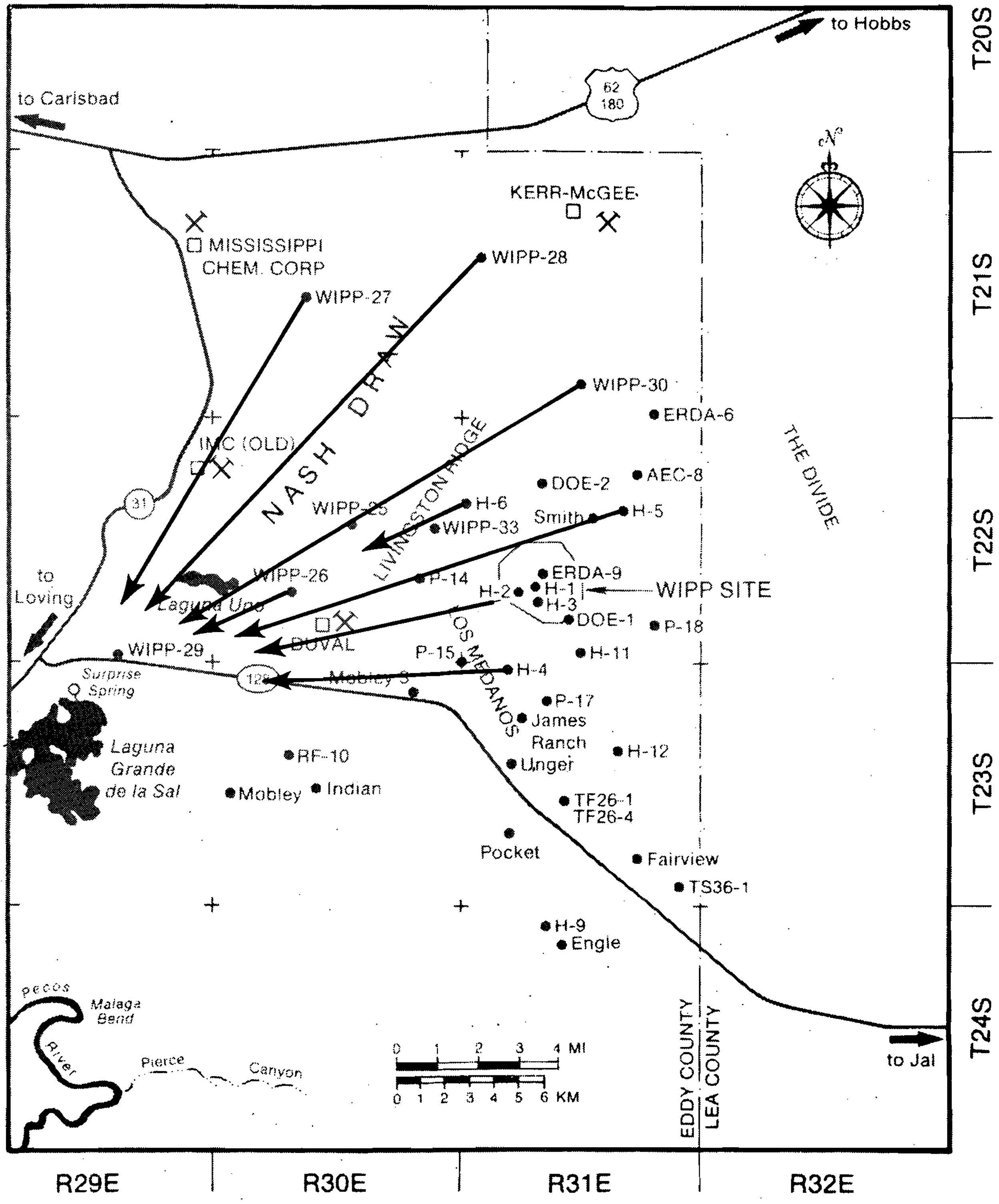


Figure 22. Hypothetical direct flow paths between Nash-Draw/WIPP-site Culebra (Rustler) points and Surprise Spring, discharging from the Tamarisk. Note that all such postulated paths in the Culebra must pass through or near WIPP-29.

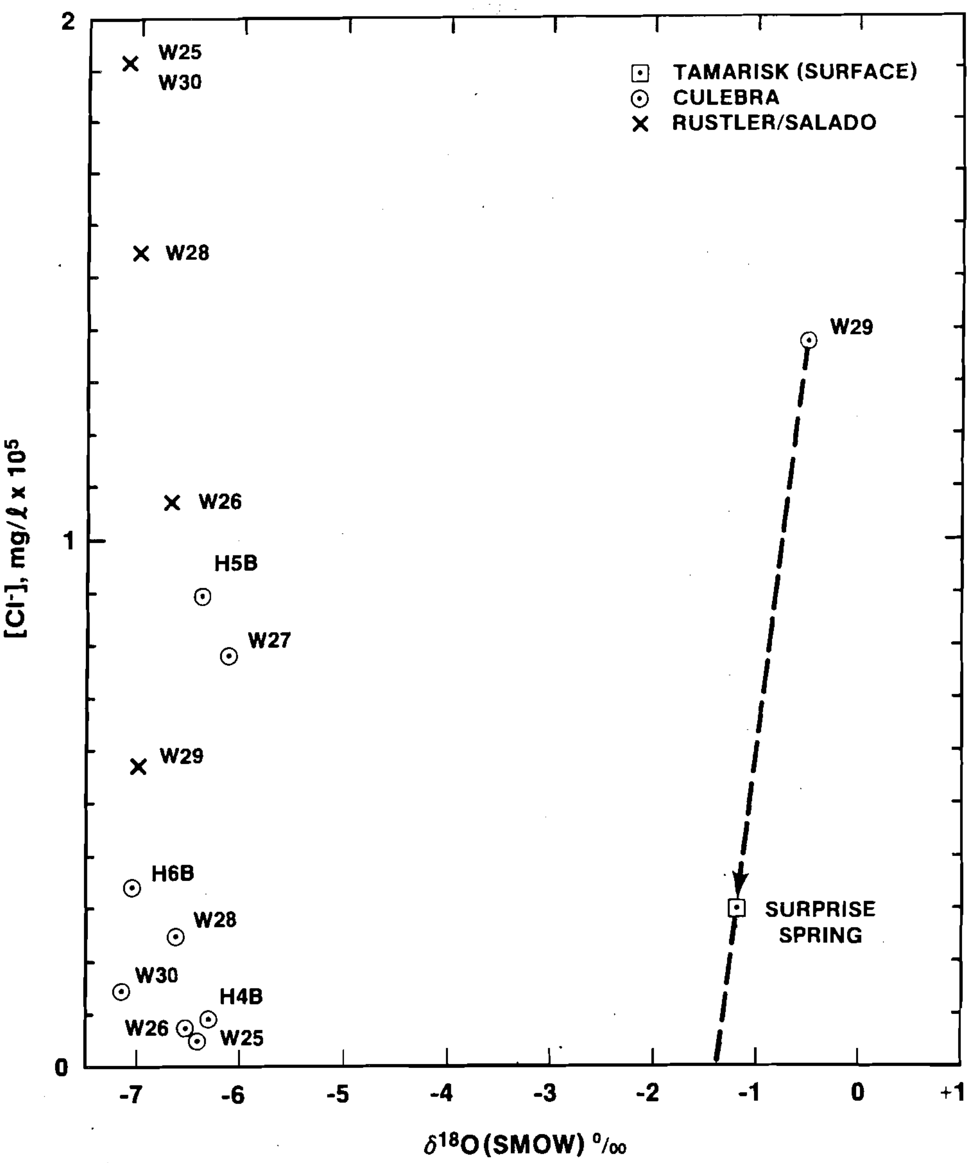


Figure 23. Total dissolved chloride versus $\delta^{18}O$ for Rustler groundwaters in Nash Draw and at the WIPP site. Evolution of a water similar to WIPP-29 Culebra by evaporation of many other Rustler waters (entailing an increase in both chloride and ^{18}O) is possible in principle. Given the path constraints of Figure 22, derivation of Surprise Spring from WIPP-29 Culebra requires a large dilution with water having a $\delta^{18}O$ value significantly different from other Rustler waters. Solute (including potassium) and stable-isotope relationships indicate that WIPP-29 Culebra water is derived from imported potash-refinery water by evaporation, not by evaporation directly from the Rustler. Both it and Surprise Spring are part of a locally dominated, near-surface groundwater system, not direct discharges of the Culebra waters originating further east in Nash Draw or at the WIPP site.

could be accounted for by evaporation alone, for the observed degree of evaporation-induced isotope shift (see Craig et al., 1963), and (2) a mechanism for evaporating water being conducted in 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 extremely demanding, since the condition of even partial confinement, by definition, precludes an unconfined surface from which water in the zone of confinement can evaporate.

Derivation of Surprise Spring from the nearby Culebra, represented by WIPP-29, is even more difficult. This hypothetical evolutionary path 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 ‰ (Figure 23). Water of this isotopic composition is in principle obtainable in the summer months (Table 6), but this requires a dilution factor of 4.6 in chloride alone.

An additional constraint on hypothetical evolutionary paths of groundwaters in the area is provided by potassium. Table 12 lists potassium and chloride concentrations for Culebra waters (from Robinson, 1987), together with the $\delta^{18}O$ values. The Cl/K ratios for the Culebra waters and Surprise Spring are in the range 38 to 73, with the notable exceptions of WIPP-27 (10) and WIPP-29 (9). WIPP-27 is located downslope from the tailings ponds of Mississippi Chemical Corporation's potash refinery, and WIPP-29 is downslope from the tailings ponds of International Minerals and Chemicals potash refinery. Plate 2 shows the location of WIPP-29, where the Culebra is only 12 ft below the surface, in relation to several large lakes that have formed since the potash activity began in the early 1930s. The anomalously high admixture of potassium in WIPP-27 and -29 waters, considering their geographic positions, appears directly related to

TABLE 12. GEOCHEMISTRY OF THE CULEBRA AND TAMARISK MEMBERS

Name	K^+ mg/L	Cl^- mg/L	Cl/K	$\delta^{18}O$ (SMOW) ‰
CULEBRA[1]				
H4B	210	7980	38	-6.6
H5B	1290	89500	69	-6.8
H6B	450	33000	73	-7.1
WIPP-25	73	5200	71	-6.4
WIPP-26	170	7200	42	-6.5
WIPP-27	8060	78500	10	-6.1
WIPP-28	480	24700	51	-6.6
WIPP-29	15500	138000	9	-0.5
WIPP-30	250	14600	58	-7.1
TAMARISK[2]				
Surprise Spring	580	30000	52	-1.3

---

1. Solute analyses from Robinson (1987).
2. Solute analyses from Lambert (1093a).

runoff from potash spoils piles. In any case, it would be relatively easy to add potassium to WIPP-29 Culebra water by upgradient potash spillage; such spillage is the most probable source of potassium, since in western Nash Draw virtually all the soluble potassium (largely polyhalite) in the Rustler and upper Salado Formations where groundwater now occurs has been removed by near-surface dissolution of evaporites during the formation of Nash Draw, which began about 600,000 years ago (Bachman, 1981). It is considerably more difficult to **reduce** potassium and chloride (by factors of 27 and 4.6, respectively) in the same water to generate the observed solute relationships in Surprise Spring downgradient from WIPP-29, even if there were a direct hydraulic

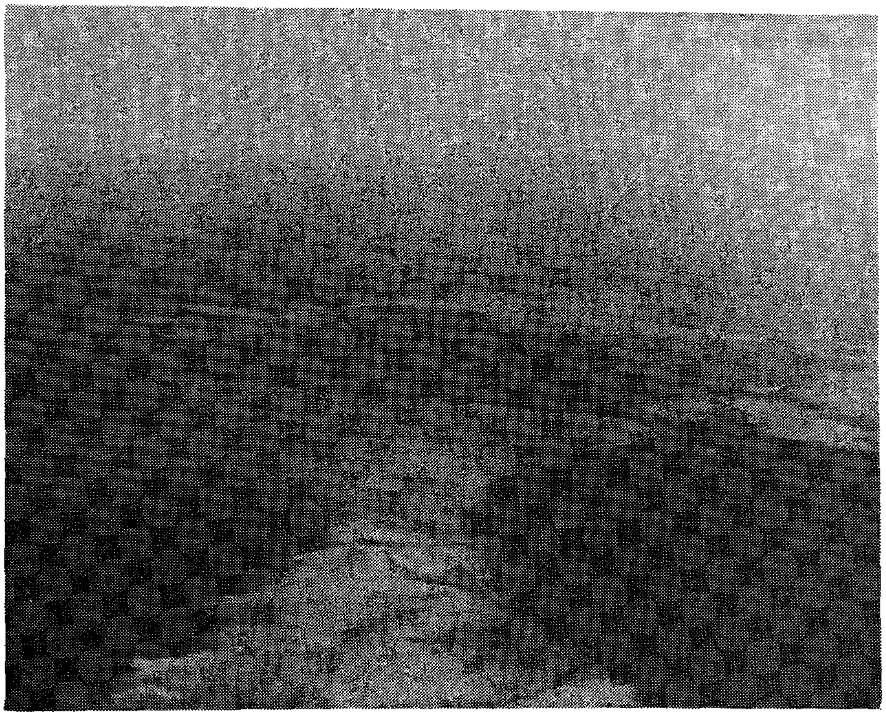


Plate 2. Aerial view of modern ponds in Nash Draw. Salt delta in foreground is overflow from spoil pile at International Minerals and Chemicals potash refinery. Pond at its toe is Laguna Uno (see Figure 2). At extreme right is Tamarisk Flat, near borehole WIPP-29, where the Culebra dolomite member of the Rustler Formation is 12 ft below the surface. Beyond is a northern embayment of Laguna Grande de la Sal, the only permanent lake in Nash Draw, near which is Surprise Spring, which discharges from the Tamarisk member of the Rustler Formation. To the left is an area pockmarked with sinkholes developed in outcrops of the Tamarisk, one of which is illustrated in Plate 3.

connection (which there is not, since the Culebra is confined and Surprise Spring issues from the Tamarisk member).

Thus, we conclude that (1) Surprise Spring water has not evolved by any set of simple processes from the nearest occurrence of Culebra water in Nash Draw (WIPP-29), and (2) WIPP-29 Culebra water cannot have evolved solely from any of the Culebra waters in other parts of Nash Draw or the WIPP site, without an overwhelming input (a factor of about 5) of water and solutes derived locally from the surface, as a result of potash refining. Even though water now in WIPP-29 Culebra and Surprise Spring has similar stable-isotope compositions (Figure 16), suggesting that their water molecules may have similar origins, the respective fluids themselves are not genetically related otherwise, nor is it likely that they lie on the same evolutionary path, considering the significant difference in their solute relationships. There remains the question of the transient nature of fluids at WIPP-29 Culebra and Surprise Spring; if they are indeed largely artifacts of potash refining, it appears that the present volumes of water generated by local industry have recently dominated the water in these occurrences, masking the contribution, if any, of the Rustler water flowing from the east and northeast in Nash Draw.

Waters of these isotopic compositions probably have a completely different origin from that of the rest of the Rustler. A likely origin is locally derived recharge from the surface, with or without some degree of evaporation or rock-water interaction tending to enrich the water in ^{18}O (see Section 4.6). Only a few tens of feet from WIPP-29, for example, is a relatively permanent pond that has come into being since the beginning of local potash-refining activity. Thus, there is a case for locally derived surface runoff recharging the Rustler in the vicinity of WIPP-29, whereas the Culebra at WIPP-29 itself is at least partially confined. Nevertheless, the isotopic isolation demonstrates the dominance of local effects over mixing of water like WIPP-29 with the rest of the Culebra (i.e., the composition of water at WIPP-29 is less influenced by the rest of the Rustler by at least an order of magnitude than by purely local effects, whether those effects be local recharge [see discussion below], isotope shift, or evaporation).

The isotopic composition of the water in Surprise Spring and WIPP-29 Culebra is probably more akin to that of modern meteoric recharge than is any of the rest of the Rustler. Oxygen-isotope shift could conceivably be a mechanism by which water with the isotopic composition of Surprise Spring might be derived from the inferred modern meteoric water represented by the Carlsbad Caverns, James Ranch, San Simon, and many Ogallala data. Such a path is depicted in the horizontal dashed lines in Figure 16. This mechanism alone does not, however, provide a means to derive Surprise Spring water from the other, obviously meteoric, Rustler groundwaters in Nash Draw and the WIPP site. This isotopic isolation may be related to the very shallow depth of the Culebra water in WIPP-29 (about 12 ft), in contrast to the equivalent depth of a few hundred feet in the other Nash Draw holes. If, for example, the shallowness of the water makes it susceptible to kinetic fractionation by partial evaporation, such a process could conceivably lead to the evolution of a water such as this from isotopic values characteristic of the rest of the Rustler. Evaporation-induced fractionation would tend to make residual liquids more enriched (i.e., "heavier") in both D and ^{18}O. One hypothetical $\delta D/\delta^{18}O$ trajectory is drawn through the WIPP-29 Culebra and Surprise Spring points in Figure 16 with a slope of 5, based on results of Hoy and Gross (1982) for two analyses of Bitter Lakes near Roswell. This trend is labeled "Arid-Lake Trajectory" in Figure 16. Depending on local conditions (cf. Section 4.6) the slope of an evaporation trajectory may be anywhere between 2 and about 5.5; slopes near 5 are the result of free-surface evaporation. We do not attempt here to choose with precision a slope for the evaporative evolution of the isotopic composition of these two waters. A slope as high as 5 (which extrapolates to a δD value of -70 to -80 ‰ at the meteoric field, and not the -50 ‰ characteristic of the rest of the Rustler) does not appear warranted by local conditions, because waters have been underground, and therefore have <u>not</u> been exposed to a free-standing surface such as Bitter Lakes. Thus, derivation of WIPP-29 and Surprise Spring from other Rustler waters ($\delta D \approx -50$ ‰, $\delta^{18}O \approx -7$ ‰) by free-surface evaporation is not a likely cause for the origin of the isotopic composition of water from WIPP-29 Culebra.

It is also conceivable that the isotopic composition of WIPP-29 Culebra could have arisen by oxygen-isotope shift (e.g., along a nearly horizontal trajectory labeled "O-shift" in Figure 16), a process whereby the oxygen isotope composition of a water changes by isotope exchange with local oxygen-bearing minerals, with little change in hydrogen (Craig, 1966); given the apparently high water/rock ratio (transmissivity = 1000 ft^2/day), this is unlikely.

A likely source of water observed in WIPP-29 Culebra and Surprise Spring has been described by Hunter (1985):

> Industrial water is pumped either from the Ogallala Fm. outside the study area or from Pre-Ochoan oil fields. It is disposed of either in water-flooding operations in the oil fields or in brine tailings ponds. Currently all or nearly all of the industrial water is ultimately evaporating, although past disposal has caused large increases in storage in Nash Draw [p. 51].
>
> Geohydrology Associates (1978, p. 59) calculated the total 1978 evaporation from the potash spoil piles and ponds (taking Laguna Uno as the IMC pond) to be 11,950 ac-ft. The remainder of the imported water, 7818 ac-ft seeped from the ponds [p. 21].
>
> The water, after use in refining operations, is dumped onto large spoil piles, where some of it evaporates. Below the spoil piles are large unlined spoil ponds, where more water evaporates. Water seeps from some of the ponds, recharging the water table locally. The relative amount of water that evaporates, versus the amount that seeps from the ponds and joins the water table, is highly sensitive to local geology and hydrology. The ponds investigated allow 43% to 87% of the plant discharge to seep into the water table [p. 20].
>
> Industrial brines, mostly from potash refineries but also from oil fields, have been discharged into surface ponds for more than 40 yr. Brine seeps from many of the ponds into the ground, eventually joining and creating a mound in the water-table aquifer. In some cases, the water table has risen above the land surface, creating new ponds that do not receive industrial brines directly [p. 49].

> Without industrial brines, the brine lakes in Nash Draw and Clayton Basin, except for Laguna Grande de la Sal, would disappear and the water level in the brine aquifer would drop locally [p. 47].

Plate 2 shows several of these ponds in southwestern Nash Draw, featuring Laguna Uno at the foot of the IMC overflow apron. To the upper right is a small portion of northern Laguna Grande de la Sal in the region of Surprise Spring, and where the Culebra in WIPP-29 occurs within 25 ft of the surface. We see that there is no lack for surface water imported from the Ogallala in the area. Plate 3 shows a sinkhole formed from dissolution-widened fractures in gypsum of the Tamarisk member of the Rustler Formation. These features are common in the area in the left (eastern) portion of Plate 2, and are believed to be a manifestation of "erosion by solution and fill", described by Lee (1925). Thus, there is no lack for evidence of connection between the surface and a groundwater flow system in the Tamarisk. We cannot evaluate the degree of connection between the Tamarisk and the underlying Culebra in such areas, but where the Culebra is confined in Nash Draw (as at WIPP-26, -28, -29, and -30) we have presented the evidence favoring only limited amounts of direct modern recharge to the Culebra.

The descriptions of Hunter (above) in brief entail an Ogallala-derived imported water spilled on the surface in southwestern Nash Draw, where it finds a local water table. Evaporation taking place in the unsaturated zones above a water table would yield a $\delta D/\delta^{18}O$ trajectory with a slope of approximately 2 (Allison, 1982), rather than ≈5 obtained during evaporation of free water. Extrapolating the isotopic compositions of WIPP-29 Culebra and Surprise Spring waters along a slope of 2 toward the meteoric field (the trajectory labeled "Water-Table" in Figure 16) yields an intersection with the field at δD values very similar to those of the Ogallala Formation, -39 to -41 ‰. Given the obvious derivation of the WIPP-29 Culebra water solutes from nearby potash refining activity, together with the inferred

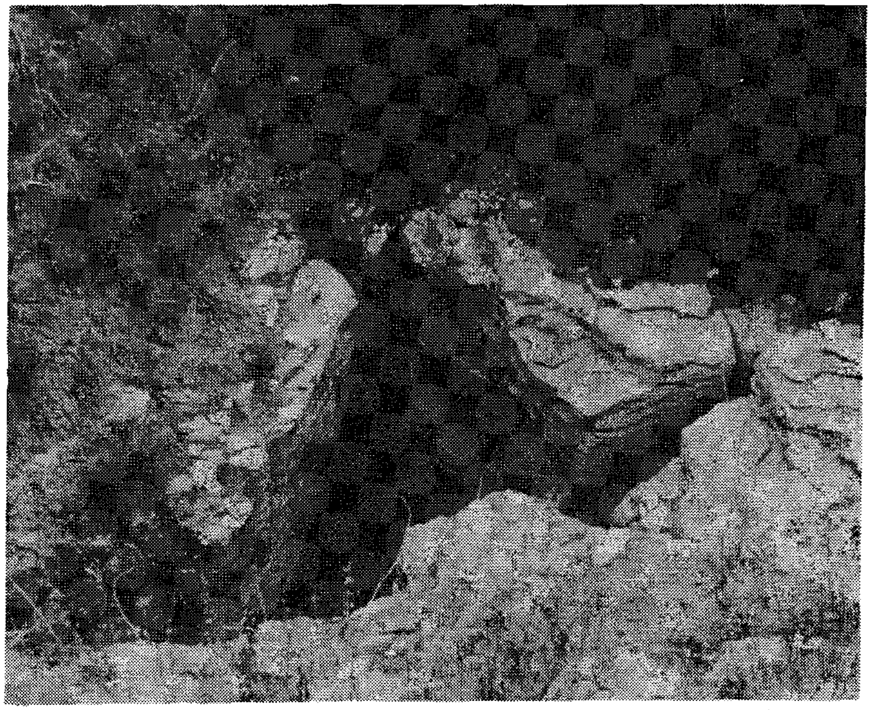


Plate 3. Sinkhole, Tamarisk member (Rustler Fm.) Nash Draw. Located in NE 1/4 S. 17, T. 22 S., R. 30 E. Gypsum sinkholes in Nash Draw originate as fractures subsequently widened by dissolution as part of "erosion by solution and fill" (Lee, 1925). The floor of this sinkhole is about 12 ft below the surface, where a side passage captures drainage from a nearby blind arroyo. Features such as this are common in the area shown in the lower left part of Plate 2. Grasses and sunflowers for scale.

derivation of these waters from imported Ogallala waters by sand-column-type (water-table) evaporation, we consider that purely local processes can best account for the origin of Surprise Spring and WIPP-29 Culebra. We are, however, not able to distinguish imported Ogallala water from natural local modern meteoric recharge uniquely on the basis of δD and $\delta^{18}O$ values, due to their similarities. There may still be a contribution of water from the Rustler units that are confined upgradient, but this contribution, if extant, is overwhelmed by industrial dumping. According to Hunter (1985), "the imported water changes the volumes, rates, and gradients of ground- and surface-water flow in the region. It also changes the chemistry of samples collected to assist in determining the values of the same flow variables." It probably also changes the amount and composition of water discharging from Surprise Spring, as originally observed by Robinson and Lang (1938). We believe we have identified manifestations of the imported water, together with its use, in the stable-isotope and solute compositions of WIPP-29 Culebra and, by inference, the stable-isotope composition of Surprise Spring. Surprise Spring may even be a natural discharge point for modern meteoric recharge, without having acquired a high-potassium signature of potash spoil brine. If this is the case, water-table type (as opposed to open-lake type) of evaporation has altered its isotopic composition from that inferred to be representative of modern meteoric recharge according to the self-consistent discussion herein.

The isotopic differences between the Culebra and the Rustler/Salado in WIPP-29 (6.5 ‰ for oxygen, 20 ‰ for hydrogen) do not support the plausibility of a direct vertical connection between these two horizons in this hole, considering the high permeabilities and flow rates found there. The geological, geochemical, and isotopic observations together indicate that the source of Culebra water at WIPP-29 is not dominated by the Culebra water in other parts of Nash Draw, but is more locally derived; this in turn implies that either the Culebra does not have as uniformly connected a porosity in Nash Draw as formerly believed, or local surface effects now dominate the groundwater in very shallow occurrences of the Culebra, which is 12 ft below the surface at WIPP-29. We propose that the latter is more likely.

4.6 Isotopic Records of Groundwater Evolution Paths

4.6.1 Introduction

In this section we offer examples of processes that appear to have influenced the isotopic composition of waters in the Delaware Basin. The first will deal with processes that yield

$\delta D/\delta^{18}O$ relationships characteristic of variations in precipitation. Then, processes that tend to alter the isotopic composition of water in its terrestrial habitat (post-precipitation) will be considered.

4.6.2 Climatic Influence

Principles. Under the assumption that all major meteoric precipitation originates as water evaporated from the oceans, there are several factors that can govern the oxygen- and hydrogen-isotopic composition of meteoric water. These include temperatures of evaporation and condensation, latitude, elevation, and the previous precipitation history of the air mass; the last, integrating the past effects of the other factors, is generally considered to be the most important.

As a moist air mass moves from its oceanic source area over the land and begins to precipitate, the isotopic equilibrium fractionation factors between water liquid and vapor for oxygen and hydrogen determine that the liquid (or solid) precipitation is slightly enriched in ^{18}O and D with respect to the water vapor remaining in the air mass. By the interacting processes of: (1) equilibrium isotopic exchange between vapor and precipitate, and (2) Rayleigh fractionation, the air mass becomes increasingly depleted in heavier isotopes as precipitation proceeds, leaving subsequent precipitation progressively more depleted. Under extreme conditions, such as at the South Pole, depletions can become as large as -56 ‰ in oxygen and -430 ‰ in hydrogen with respect to ocean water. This progressive rainout accounts for the distribution of isotopic compositions along the meteoric field. Combinations of factors such as elevation and distance inland from the ocean can contribute large geographic variations in isotopic composition (see Figure 24). The isotopic compositions of local groundwaters in Figure 24 were deduced by Craig (1963) to be representative of local meteoric precipitation; he

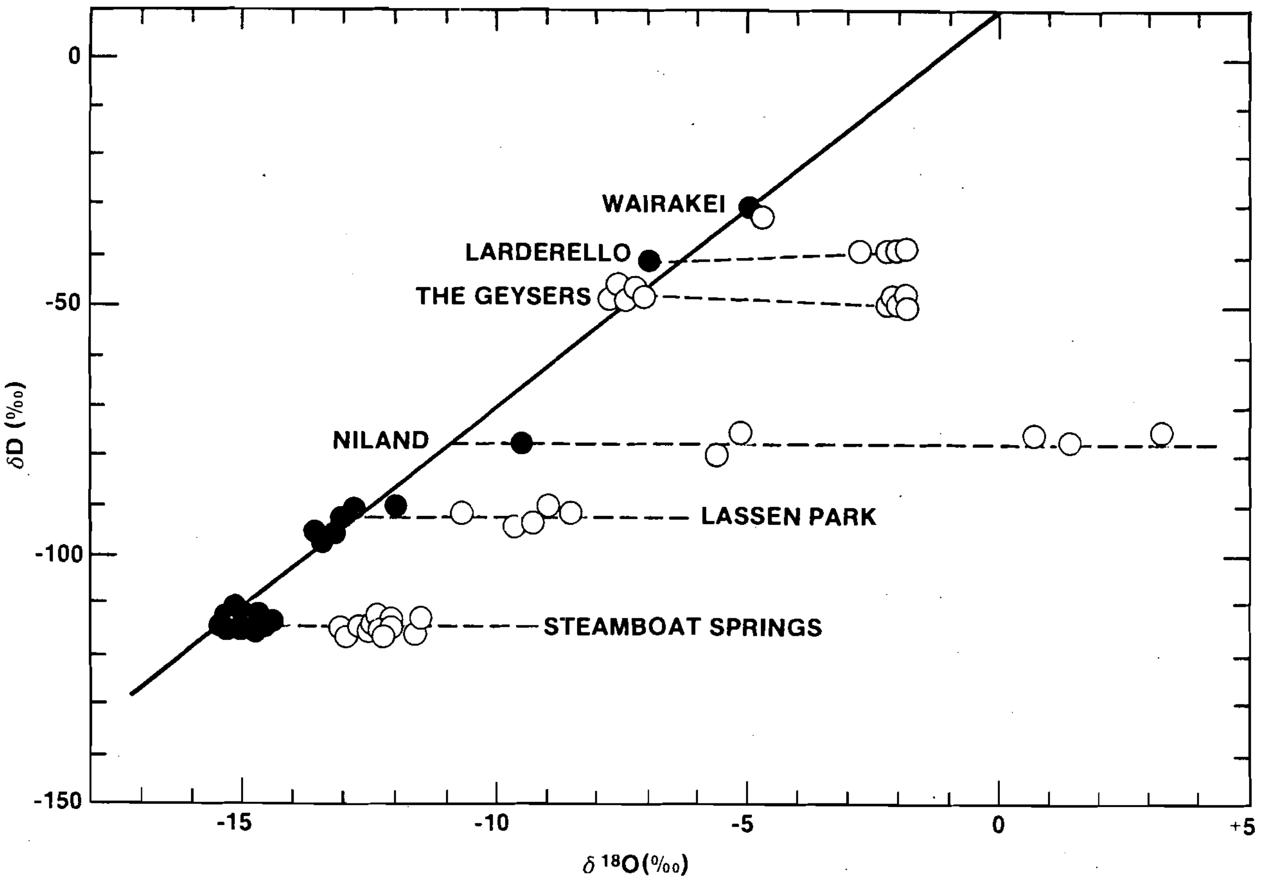


Figure 24. Variations in $\delta^{18}O$ and δD values of near-neutral chloride-type thermal waters and geothermal steam from geothermal areas (after Craig, 1963). Solid circles are local meteoric groundwaters, showing geographic (climatic dependent) variation. Note horizontal "oxygen-isotope shift" of thermal waters (open circles) from the worldwide meteoric line of Craig (1961a).

reasoned that mixing in the local groundwater reservoir homogenized the seasonal variations induced by annual climatic cycles. Thus, while summer precipitation would be different from winter precipitation, with a climate stable for hundreds of years the isotopic composition of local groundwater would remain within a fairly narrow range. Figure 24 shows that the different climatic regimes represented by the geographic variations (from desert Niland to temperate Italy to mountainous Lassen) do not overlap. This need not always be the case; some combinations of climatic conditions can give rise to the same isotopic composition for local meteoric precipitation. The inverse, however, is axiomatically true: different isotopic compositions of meteoric precipitation are always indicative of different climatic conditions.

Other than evaporation **coupled with** isotopic exchange processes in the air mass, and reprecipitation involving large (necessarily atmospheric) air masses, there is no known natural process of fractionation that will move isotopic compositions along the meteoric field. Evaporation alone does not, in general, cause isotopic translation along the meteoric field; the evaporation trajectory in $\delta D/\delta^{18}O$ space will in general not have a slope of 8. Figure 24 also illustrates the phenomenon of oxygen-isotope shift under temperatures typical of active hydrothermal systems. Note that the isotopically shifted waters clearly have their origins traceable to their meteoric parents, but no longer plot near the meteoric field. The principles and applications of this process will be discussed in Section 4.6.4.

Applications. In the groundwaters in southeastern New Mexico whose isotopic compositions fall on or near the meteoric field, those waters that have penetrated only to very shallow depths under water-table conditions (e.g., San Simon Sink, and possibly some of the Dewey Lake) and waters from caverns in the Guadalupe Mountains (whose demonstrable source is modern meteoric precipitation) have isotopic compositions that overlap one another, and they occupy a position in Figure 16 that tends toward higher $\delta^{18}O$ and δD values relative to the confined groundwaters of the Rustler and Capitan in the northern Delaware Basin. The nonoverlapping isotopic compositions of Guadalupe Mountains (caverns) recharge, and confined Capitan and Rustler groundwaters under the topographically flat parts of the Delaware Basin was first discovered by Lambert (1978), who at the time thought that a different air mass was supplying the Guadalupe Mountains with precipitation that was isotopically distinct from that supplying the rest of the Delaware Basin. The correspondence of the modern Guadalupe Mountains values with those of waters well within the flat part of the Delaware Basin both west and east of the WIPP site (e.g., Ogallala, San Simon Sink, and some Dewey Lake waters) shows that an air mass difference is probably not the explanation for the isotopic distinction; it would be highly fortuitous if one air mass selectively but perennially supplied the Guadalupe Mountains, the southwestern part of Nash Draw, the Dewey Lake due south of the WIPP site, and San Simon Sink, while another supplied the rest of Nash Draw and the WIPP site. Thus if the juxtaposition of two different air masses at the same time (separated by a somewhat convoluted boundary, but never more than 50 km apart) is not the explanation, the only alternative is to have different air mass patterns governing the climate of southeastern New Mexico at different times. Time-dependent variations in climate at a given location would result in different ranges of isotopic compositions of waters available to recharge various bodies of groundwaters at different times. This has led us to suggest that most of the Rustler contains "fossil" groundwater, no longer being actively recharged but not necessarily "stagnant."

The data in Figure 16 appear to represent at least two generations of meteoric recharge to the groundwater systems in the Delaware Basin. Considering only the waters whose isotopic compositions lie on or near the meteoric field (i.e., those which have not lost their meteoric character by isotope-shift due to advanced partial evaporation or rock-water interaction), there is a gap in values between those associated with demonstrably modern meteoric recharge now being derived from the surface (the "heavier" group with a δD value more positive than about -40 ‰) and the others (Figure 21). No data points have yet been found that occur in the gap. The 95% confidence interval (-42 to -59 ‰, 45 degrees of freedom) of δD values for confined Rustler and Capitan groundwaters does not include any δD values observed for groundwaters that are demonstrably receiving active modern meteoric recharge. Thus, the isotopic compositions of the meteorically-derived groundwaters that have demonstrable recent recharge from the surface also have an isotopic signature that is characteristically heavier. As noted above, the fact that New Mexico Ogallala fluids have not been demonstrated to be young does not affect the arguments here. If Ogallala fluids were "old" in the sense used here, it would only mean that some Ogallala, San Simon, and Dewey Lake waters thought modern were not; it would not imply that any of the Rustler and Capitan waters thought old might be "young."

4.6.3 Partial Evaporation

We have discussed (Section 4.5) and will discuss (Section 4.8) what we do and do not consider examples of waters with isotopic compositions resulting largely from alteration of their inferred source by kinetically induced (nonequilibrium) fractionation during partial evaporation. These are WIPP-29 Culebra and Surprise Spring. We do not believe that evaporation alone has significantly affected any other waters in this study. The isotopic compositions of other samples (Rustler/Salado contact) falling well outside the meteoric field are attributed to rock-water interaction, since increasing isotope shift in these samples correlates with decreasing transmissivity and increasing rock/water ratio.

4.6.4 Rock/Water Interaction

Principles. Perhaps the earliest fundamental treatment of stable-isotope systematics in rock/water interaction was that of Engel et al. (1958), who applied the principles of isotopic equilibrium to ancient hydrothermal alteration in the Leadville Limestone. A depletion in ^{18}O of host rock as large as 10 ‰ indicated that the water might have been meteoric, but the water had lost its meteoric character by exchange with rock. This illustrates the difficulty of documenting degrees of isotopic alteration among several coexisting and reacting phases: in many cases one or more of the reacting phases may no longer be present (e.g., fluids), or it may be possible to derive the initial isotopic composition of the reactants only by inference rather than by direct observation.

Figure 24 illustrates the phenomenon of oxygen-isotope shift under temperatures typical of active hydrothermal systems. Note that the isotopically shifted waters clearly have their origins traceable to their meteoric parents, but no longer plot near the meteoric field. Craig (1963; 1966) interpreted these data, for near-neutral chloride-type thermal waters and geothermal steam, as indicative of oxygen-isotope exchange between limited amounts of local meteoric groundwaters and a large reservoir of oxygen in minerals at elevated temperatures. Shifts are largely horizontal, because the mineral reservoir of hydrogen is either small or unreactive.

Another example, typical of somewhat lower temperature environments, appears to involve changes in δD and $\delta^{18}O$, but still with meteoric affinities associated with the process (Figure 25). Of the isotopic compositions of these oil-field brines from the Illinois, Michigan, and Gulf Coast basins, Clayton et al. (1966) said:

> There is a striking resemblance between the patterns of isotopic behavior seen here and those described by Craig et al. (1956) for normal chloride or for near-neutral hot springs from a large number of thermal areas: "Isotopically, these springs are either identical in composition with the associated surface river or lake waters, or they have about the same deuterium concentration as the local meteoric waters, but are enriched in O^{18} with respect to these waters by amounts ranging up to about 0.4%. This enrichment is generally observed in the higher temperature, deeper circulating springs." These authors suggested that the observed enrichment of O^{18} in the waters results from isotopic exchange between water and rock at elevated temperatures.
>
> Our data can be presented on a plot of δD versus $\delta^{18}O$ [Figure 25] similar to those used by Craig et al. to discuss hot spring systems. The least saline waters in each basin approach the line for meteoric waters, and the

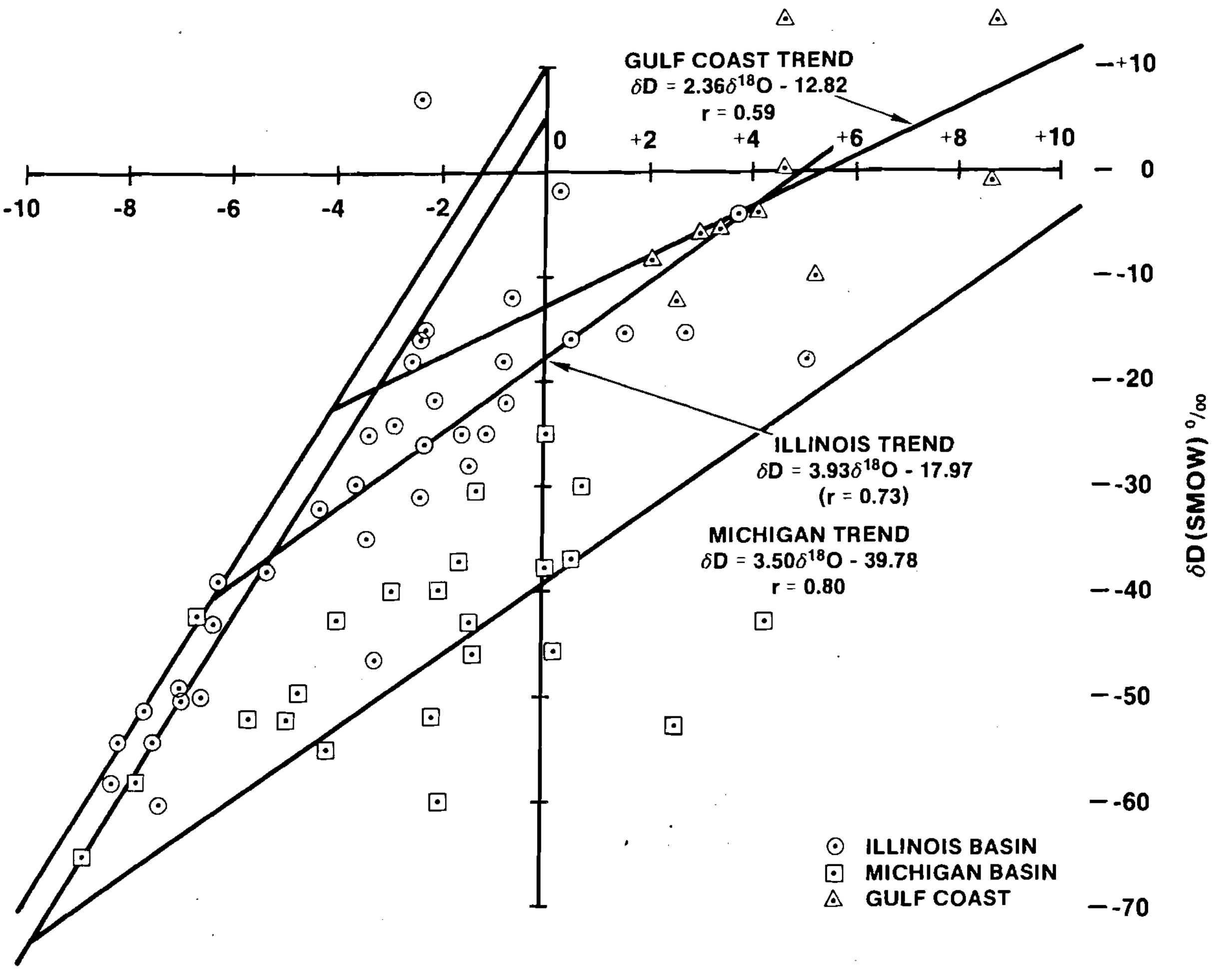


Figure 25. Variations in $\delta^{18}O$ and δD values of oilfield brines from the Illinois Basin, Michigan Basin and Gulf Coast. The data are from Clayton et al. (1966), who said of the relationship, "the picture for oil-field brines is qualitatively like that for hot springs: series of points for each area extend from the value of local meteoric water and show a large enrichment in ^{18}O but a relatively small enrichment in deuterium. However, the 'oxygen shift' is very large compared with that observed in most hot spring systems, probably because the ratio of water to rock is smaller for the brine exchange system."

> more saline ones depart from that line in the direction of O^{18} enrichment. No simple relationship between the isotopic compositions of brines and ocean water is evident. Rather, the picture for oil-field brines is qualitatively like that for hot springs: series of points for each area extend from the value of local meteoric water and show a large enrichment in O^{18} but a relatively small enrichment in deuterium. However, the "oxygen shift" is very large compared with that observed in most hot spring systems, probably because the ratio of water to rock is smaller for the brine exchange system.

Although the evolution of oil-field brines in the Illinois, Michigan, and Gulf Coast basins was concluded by Clayton et al. (1966) to have evolved from local meteoric water by extreme degrees of rock/water interaction involving both oxygen- and hydrogen-isotope exchange, more recent work (Knauth and Beeunas, 1986; O'Neil et al., 1986) has proposed other models involving evaporation and mixing; these models will be discussed below. Additional explanations proposed for the origins of brines of unusual solute and isotopic composition include shale-micropore ultrafiltration (Graf et al., 1965), and osmosis (Graf, 1982). Regardless of the specifics of the mechanism of isotopic evolution, Figure 25 shows a clear relationship between the oil-field brines and waters of meteoric origin, even despite the generally low values of the r-statistic (0.59-0.80).

At the other extreme in rock/water ratios is the case in which water is abundant (i.e., an essentially "open" system with respect to fluid circulation), and the isotopic composition of the oxygen and hydrogen in the fluid reservoir remains relatively constant. At higher temperatures, at which isotopic equilibrium fractionation factors are generally smaller, this results in a shift in the isotopic composition of the mineral phases to come to equilibrium with the large fluid reservoir. For a more detailed relevant discussion of rock/water interaction with a small rock/water ratio, the reader is referred to Lambert and Epstein (1980), who applied these principles to an active hydrothermal system of low to moderate temperature in Valles Caldera, Jemez Mountains, New Mexico.

Application: Oxygen-Isotope Exchange, Open System. Here we exhibit a special case of rock/water interaction involving one of the reactants in essentially unlimited supply. This instance, where the water/rock ratio is very high, results in significant changes in the isotopic composition of one of the reactants (the solid phase), and little change in the water. It is also more difficult to document reliably that one phase is very abundant over the other, unless there is a high degree of confidence in the initial isotopic compositions of the reactants, as is the case in this example.

Carbonate reservoir rock was collected from several holes that produced water. We tried to take samples of reservoir rock representative of the actual water-producing zone within either the Magenta or Culebra. 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 rubblized zones were sampled in hopes that they would have facilitated the greatest opportunity for rock/water interaction due to maximization of exposed rock surface.

Carbonate reservoir rock from the Rustler Formation was analyzed for its $\delta^{13}C$ and $\delta^{18}O$ values by a procedure modified from Epstein et al. (1964). Except in one case (WIPP-33 Magenta) the 1-hour fraction of CO_2 liberated by the phosphoric acid reaction (attributable to calcite) was negligible. The reaction had gone to completion in all cases by the end of the sixth day, except for WIPP-33 Magenta, which was complete in one hour. The 3-day extraction proved to be highly reproducible, yielded at least 60% of the gas, and is taken to be representative of dolomite. In most cases the 6-day extraction was enriched in ^{18}O by a few tenths ‰ over the 3-day fraction, but the $\delta^{13}C$ values of the respective fractions were indistinguishable. The data, including the cumulative yields, are presented in Table 13.

TABLE 13. STABLE-ISOTOPE COMPOSITION OF CARBONATES

Sample Name[1]	Extraction	Yield, %[2]	$\delta^{13}C$[3]	$\delta^{18}O$[4]
CULEBRA DOLOMITES				
H4B 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
H5B 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
H6B 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

TABLE 13. (Continued)

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
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 13. (Concluded)

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
BELL CANYON SANDSTONE				
AEC8 4823.4	overnight	5(C)	-0.4	25.1

---

1. Hole name and core depth, in feet. Hyphenated intervals are precisely known. Intervals delineated by "/" indicated 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) = cumulate yield after 6-day reaction
3. ‰, versus Chicago Peedee Belemnite.
4. ‰, total oxygen versus Standard Mean Ocean Water (SNOW).

To facilitate the presentation, mean $\delta^{13}C$ and $\delta^{18}O$ values for replicate (3-day) analyses of carbonates are plotted with the mean $\delta^{18}O$ values of coexisting waters in Figure 26. No representative water sample was collected from WIPP-33 Magenta, so the plotted water $\delta^{18}O$ value is the mean of all available Magenta waters, which is very typical of Culebra waters also.

$\delta^{18}O$ values for all dolomites, both Magenta and Culebra, fall into a very narrow range, with a mean of +33.4 ‰; the 95% confidence limits for one replicate of each are ± 0.97. Similarly, the mean $\delta^{13}C$ value is +6.1 ‰; the corresponding 95% confidence limits are ±1.09 ‰. This uniformity over the WIPP site and Nash Draw, independent of depth, is remarkable. Either there has been no post-depositional alteration of the carbonate isotopic composition, or such alteration has affected a large area to a remarkably uniform degree.

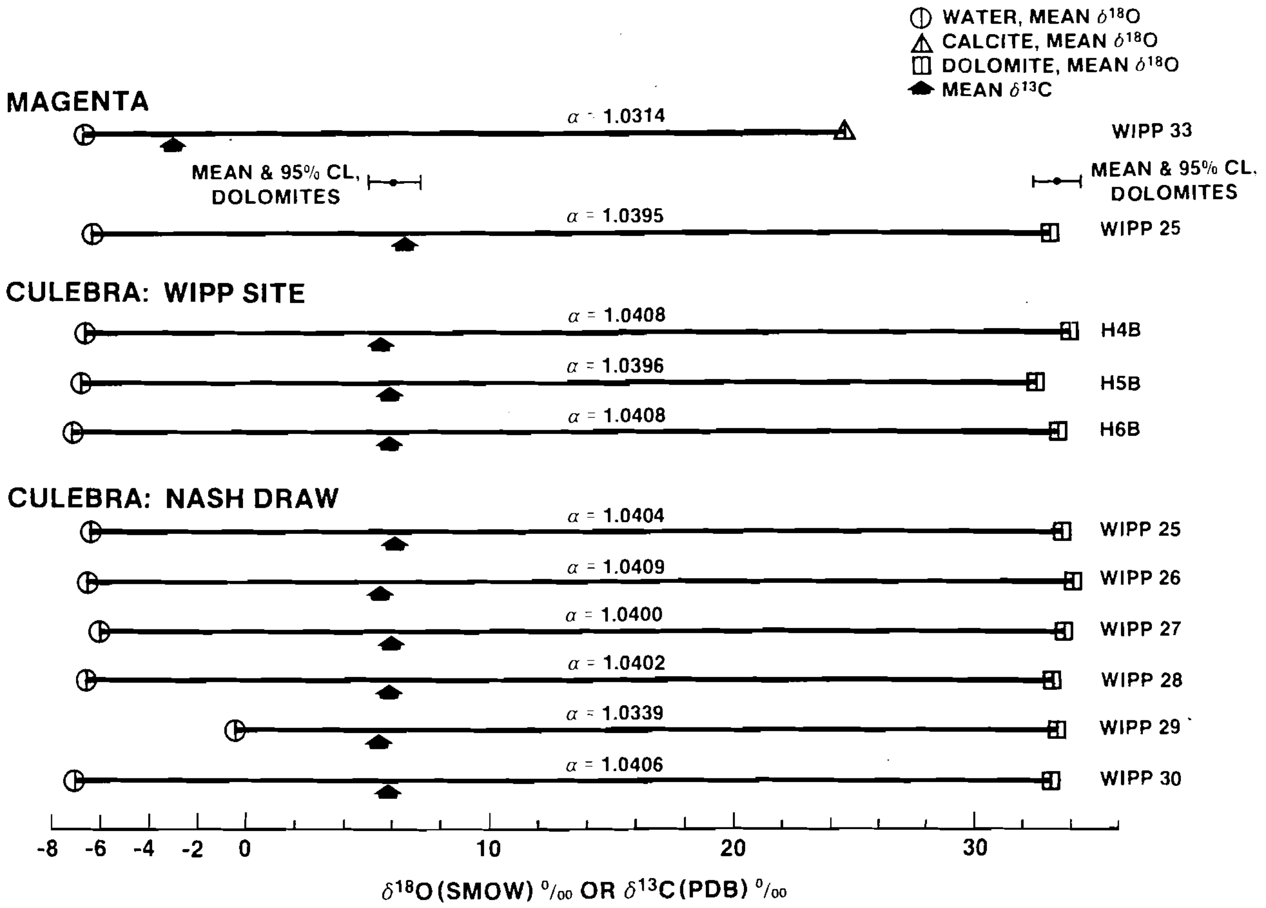


Figure 26. $\delta^{18}O$ values for coexisting carbonates and waters in the Rustler Formation. Dolomite $\delta^{18}O$ and $\delta^{13}C$ values for both Magenta and Culebra are all very uniform (33.4 ± 1.0 and 6.1 ± 1.1 ‰, respectively), and are indicative of evaporitic, rather than purely biogenic dolomite precipitated under extremely uniform conditions. Except for WIPP-29 Culebra, which shows both oxygen- and hydrogen-isotope shift, all the waters have a uniform $\delta^{18}O$ value of -6.6 ± 0.8 ‰. Calculated dolomite/water oxygen-isotope fractionation factors are between 1.0395 to 1.0409, and are too high to reflect isotopic equilibrium. The only carbonate mineral that appears to be at isotopic equilibrium with typical meteoric Rustler groundwater at ambient temperature is the calcite in the Magenta rubble from WIPP-33. There is no other indication of carbonate recrystallization in the Rustler in isotopic equilibrium with meteoric Rustler groundwater.

Oxygen-isotope fractionation factors for the dolomite-water coexisting pairs were calculated from Equation 6, and are given for the coexisting pairs in Figure 26. Except for WIPP-29 Culebra, whose water shows an isotope shift from the meteoric field (Section 4.5), the observed fractionation factors, between 1.0395 and 1.0409, are also quite uniform. We see immediately that if the isotope shift in WIPP-29 Culebra arose in part from isotope exchange with its host rock, the rock/water ratio was very large. The high transmissivity there (1000 ft^2/day; Mercer, 1983) indicates that this is not the case. In fact, the fractionation factor remains constant even with large variations in transmissivity (4 orders of magnitude between H5B and WIPP-29 in the Culebra). The small negative deviation in the rock at H5B might be interpreted as a small amount of isotopic alteration, but its $\delta^{18}O$ value falls within the confidence limits of the entire dolomite population, so it is statistically indistinguishable from the others.

Clayton et al. (1968) observed that their measured dolomite-water fractionation factors in Deep Springs Lake (California) were outside the possible range for calcite-water, precluding a calcite precursor to dolomite formation. Our dolomite-water fractionation factors are even larger; we conclude that these dolomites did not recrystallize from a calcite precursor in isotopic equilibrium with the water presently in the dolomites ($\delta^{18}O \approx -7$ ‰). We do not know precisely the equilibrium fractionation factor for $^{18}O/^{16}O$ partitioning between dolomite and water at ambient temperatures, because of extremely low exchange rates in experiments at low temperatures (Northrop and Clayton, 1966). It may be on the order of 1.037 (Weber, 1964). If this is the case, these dolomite-water pairs clearly cannot be at oxygen-isotope equilibrium.

The origin of these Permian dolomites is somewhat problematical, since they have relatively high $\delta^{18}O$ and $\delta^{13}C$ values. Clayton et al. (1968) pointed out that "it is known that bicarbonate solutions losing carbon dioxide and precipitating carbonates become relatively richer in C^{13}. Hence carbonates precipitated sequentially from a solution will show a trend of increasing δC^{13}." Due to the uniform significant enrichment of these dolomites in ^{13}C and ^{18}O we tentatively propose that their origin has been more evaporitic than biogenic. Aside from ripple-drift cross bedding prominent in the Magenta, neither appears to be dominated by conspicuous sedimentary structures, organic or otherwise. In addition, petrographic examination of relatively intact core shows individual crystallites of dolomite in a matrix consisting of much larger optically continuous crystals of gypsum. This texture, if primary, is more suggestive of evaporitic than biogenic origin.

The $\delta^{13}C$ value of Rustler dolomites is higher than most of the lacustrine Pleistocene dolomites from the west Texas high plains, reported by Parry et al. (1970). Although one of their samples was as high as 5.8 ‰, none of their dolomites with $\delta^{18}O$ values comparable to ours had $\delta^{13}C$ values as high as ours. Parry et al. (1970) suggested that their dolomites formed "from solutions of widely differing isotopic composition and temperatures, conditions which could be expected in isolated desiccating pluvial lake systems in which evaporation is extreme," with or without a calcite precursor.

In any case, the similarity in isotopic composition between the Magenta and Culebra dolomites is remarkable, especially since they are separated stratigraphically by a dominantly non-carbonate evaporite facies represented by the Tamarisk member. Either the environments of their formation were identical, or some pervasive process active throughout the Rustler has homogenized their isotopic composition.

Regardless of the origin of the dolomites, they appear not to have participated in significant isotopic exchange with the water they presently host. The possible exception is WIPP-33 in the Magenta. The WIPP-33 locality is unique in that it was drilled in a surficial feature of negative relief, with a topographic closure of about 10 ft. The stratigraphy here was described by Bachman (1985):

> In the subsurface at WIPP-33 the Dewey Lake Red Beds are 357 ft (110 m) thick. This is an incomplete stratigraphic section that was eroded before the Mescalero caliche was deposited. The Rustler Formation, which is 276 ft (84 m) thick, is a diminutive section as compared with more complete sections where the Rustler may be as much as 450 ft (137 m) thick. This thinning of the Rustler at WIPP-33 may be attributed to dissolution of salt and gypsum; anhydrite has been hydrated to gypsum at this locality. Returns from drilling and a later video examination of the borehole indicated extensive cavities within the formation, straddling the gypsiferous Magenta dolomite member.

The cavity collapse apparently seated in the gypsiferous layers adjacent to the Magenta, together with the depression on the surface and its geographic relationship to the WIPP site made Magenta carbonate in WIPP-33 particularly interesting, even though no representative water sample was available. Observed $\delta^{13}C$ and $\delta^{18}O$ values, -2.9 ‰ and +24.6 ‰, respectively, for the calcite are much depleted in heavy isotopes relative to the dolomites. The total carbonate assay (7 to 8% calcite), together with the fact that calcite was the only analyzeable carbonate from WIPP-33 Magenta, suggests that carbonate recrystallization has taken place. The isotopic criteria of Keith and Weber (1964) indicate that the WIPP-33 Magenta calcite is borderline between marine and fresh-water calcite, with a slight tendency toward fresh-water. The observed calcite-water $^{18}O/^{16}O$ fractionation factor, 1.0314, yields a temperature of crystallization of 11.7°C according to Equation 5. This is the only calculable temperature for any of the carbonate-water pairs. This, together with the fact that 12°C is a reasonable subsurface temperature at 550 ft depth, suggests that the calcite formed by secondary recrystallization after dolomite, involving oxygen-isotope exchange between water and carbonate, resulting in calcite in isotopic equilibrium with water having a $\delta^{18}O$ value of about -7 ‰. It is not possible to determine uniquely the time of this recrystallization event, without the complete history of carbon-isotope evolution of the mineral/water minisystem. Similarly, it is not possible to infer any particular residence time for the Magenta water that caused the recrystallization, presumably in response to the collapse; oxygen isotope exchange in the calcite-water system can be very rapid when dissolution/reprecipitation is involved, even on laboratory time scales, and the mere presence or absence of mineral/water interaction is not itself an indicator of even relative age. If our assumption that water with a $\delta^{18}O$ value of about -7 ‰ was responsible for the recrystallization is true, as seems to be found in much of the Magenta, then the water/rock ratio involved in the isotope exchange during recrystallization was very large. The small carbonate assay is consistent with this.

Further, we conclude that the calcite formed entirely from solution, rather than by dedolomitization in the solid state. The fact that the calcite $\delta^{13}C$ value (-2.9 ‰) is so different from those of surrounding dolomites (≈+6 ‰) implies that the calcite $\delta^{13}C$ value was influenced by introduced aqueous carbon species rather than derived from dissolved dolomites elsewhere in the Magenta. It is conceivable that this lower-^{13}C reservoir, perhaps derived from organic material, was introduced as a pulse when recharge at WIPP-33 and discharge at the gypsite springs in Nash Draw were active. Bachman (1985) has suggested that this was at least 20,000 years ago. In any case, no other record of carbonate reprecipitation as conclusive as the isotopic evidence has yet been found in the Rustler, even in apparently active dissolution zones in Nash Draw. Carbonate rock/water interaction in the Rustler Formation appears now to involve dominantly dissolution, which leaves no material in its wake to preserve the isotopic record, rather than precipitation, which appears to be rare, or isotopic exchange without complete dissolution and reprecipitation, which appears to be nonexistent.

<u>Application: Hydrogen-Isotope Exchange, Open (?) System</u>. As part of an early survey, δD values were determined for two samples of gypsum from borehole AEC 8: one from a selenite vein in the Dewey Lake Red Beds, and one from the Tamarisk member of the Rustler Formation, just above the Culebra dolomite member. The data are given in Table 14.

TABLE 14. HYDROGEN ISOTOPE COMPOSITION OF GYPSUMS

Borehole	Depth, ft	Unit	wt % H_2O[1]	δD (SMOW) ‰
AEC 8	215.7	Dewey Lake selenite vein	98	-68
AEC 8	725.0	Rustler Tamarisk	93	-73

---

1. Relative to 100% $CaSO_4 \cdot 2H_2O$

Using the hydrogen-isotope fractionation factor for the gypsum-water system of 0.980 (Fontes and Gonfiantini, 1967; Sofer, 1978), the calculated δD value of water in equilibrium with these two gypsums is -49 ‰ and -54 ‰ for the Dewey Lake and Rustler, respectively. These values are remarkably similar to the δD values typical of the Rustler (and some Dewey Lake) groundwaters previously discussed. Although these are but two measurements, and other similar measurements from several boreholes are contemplated, we tentatively propose that the gypsification of anhydrite took place by the agency of water whose isotopic composition is similar to that of the meteoric Rustler, with a δD value of about -50 ‰. Thus, the gypsums have last recrystallized in the presence of fresh water, and are not primary seawater evaporites, in which case their δD values would be much more positive.

The similarity in δD values for Rustler gypsum and Dewey Lake selenite, separated by 500 ft vertically, suggests that the hydrated calcium sulfates may have crystallized in the presence of a hydrogen reservoir whose D/H ratio was uniform over some part of the Dewey Lake/Rustler stratigraphic section.

Application: Oxygen-Isotope Exchange, Closed System. In this case, where both reactants are in limited supply, only bounding calculations can be made on the water/rock ratio, which is finite. In a reacting system involving little introduction of material from outside, assumptions must be made about the initial isotopic composition of both reacting phases, since samples of unaltered reactants are not likely to be found in the immediate environment. Nevertheless, it is in some cases useful to make such bounding calculations, to show that the water/rock ratio is finite, regardless of its absolute value.

A case example of rock/water interaction involving a limited supply of both reactants is given by water-bearing zones in the Bell Canyon Formation. The Bell Canyon water cannot be directly connected to a rapidly recharged source of meteoric water coming from the surface, because of its nonmeteoric stable isotope composition (Section 4.7.3). If we assume that water in the Bell Canyon Formation (Todd Federal 26-4) is relatively uniform in $\delta^{18}O$ value ($\approx$+2.2 ‰), and that the $\delta^{18}O$ value of calcite from AEC-8, 4823.4 ft depth, (+25.1 ‰, Table 13) is fairly representative of diagenetic calcite throughout the Bell Canyon sandstones, then the temperature calculated (by Equation 5) from the calcite-water pair of $\delta^{18}O$ values in the Bell Canyon is 54°C (129°F). The temperature measured in the Bell Canyon Formation in the AEC 8 and ERDA 10 boreholes is between 90° and 128°F, in reasonable agreement with the isotopically calculated temperature based on the temperature dependence of the $\delta^{18}O$ fractionation factor between calcite and water. Consequently, the evidence suggests that calcite and water in the Bell Canyon Formation are in oxygen-isotope equilibrium.

Material balance allows a calculation of the minimum rock/water ratio participating in the calcite-water interaction that led to this inferred oxygen-isotope equilibrium. The Bell Canyon sandstone in Table 13 consisted of 5 wt% calcite, which in this calculation is assumed to have had a marine origin with an original $\delta^{18}O$ value of ≈+30 ‰. This assumption is reasonable, since the $\delta^{13}C$ value (-0.4 ‰) is very close to the typical values for marine calcites. Generally fresh-water carbonates are somewhat more depleted in ^{13}C ($\delta^{13}C$ more negative than about -4 ‰; Keith and Weber, 1964). It is remarkable, however, that a carbonate recrystallized in the presence of meteorically-derived water would retain a marine $\delta^{13}C$ value. This suggests that the Bell Canyon water recrystallizing the calcite did not contain an appreciable amount of terrestrial organic material, which commonly contributes lower-^{13}C carbon to near-surface fresh-water carbonates during their deposition.

The post-depositional interaction between this calcite and water resulted in a decrease in calcite $\delta^{18}O$ value to the observed +25.1 ‰. Similarly, if the Bell Canyon water was of local meteoric origin, introduced under the same set of climatic conditions that appear to have recharged most of the confined Rustler and Capitan waters ($\delta^{18}O$≈-7 ‰), its $\delta^{18}O$ was raised to +2.2 ‰ by reaction with the calcite to achieve isotopic equilibrium. By closed-system material-balance calculation, the molar ratio of oxygen in calcite relative to that in water in the Bell Canyon water-bearing zones would be at least 1.88, if water now in the Bell Canyon was of meteoric and not marine or diagenetic origin. The equivalent weight ratio of calcite to water is ≈3.50. Thus, the amount of water in the water-bearing zones of the Bell Canyon Formation is indicated to be 1.4 wt%, for an effective rock/water ratio of about 70. This is an absolute minimum rock/water ratio, if the Bell Canyon calcite is inferred to be of marine origin, and all Bell Canyon water is inferred to be of meteoric (post-depositional) origin. It may be an upper limit if minerals other than calcite have participated in the isotope exchange reactions that have altered the $\delta^{18}O$ value of the water.

This sample calculation of a rock/water ratio illustrates the magnitude of such ratios **integrated over the entire flow path** necessary to produce an oxygen-isotope shift of about 5 ‰ relative to meteoric water. Smaller shifts will of course reflect a smaller rock/water ratio, or a lower temperature of interaction, lesser degrees of approach to equilibrium, smaller isotopic differences between reactants, or a combination of these factors. Except for the last, none of these factors would be expected to dominate deep basin groundwaters in evaporite environments. If the last prevailed (initial reactant δ-values closer together), perhaps arising from a more ^{18}O-rich initial water, it is more likely that the initially heavier water would be of secondary (diagenetic) rather than primary meteoric origin. Larger isotope shifts will be observed in the water if the mineral/water ratio for the reacting (i.e., isotope-exchanging) phases is greater. Hydrogen-isotope shifts will, of course, involve different reactants (notably, hydrous minerals), different exchange mechanisms and rates, and different equilibrium fractionation factors, and will result in different effective water/rock ratios for exchangeable hydrogen. Except on the basis of circumstantial evidence as in this example, it may not be possible to identify the cause or causes of an exchange reaction if one of the reaction products is not available for isotopic analysis. This can occur if the water underwent rock/water interaction in a host rock other than the present host, and migrate in after the interaction.

4.7 Waters Below the Rustler

4.7.1 Introduction

Several treatments of waters below the Rustler/Salado contact have appeared in the literature, particularly dealing with brines in evaporites of the Salado and Castile Formations. This work will not review all the interpretations of their origin in detail, but will summarize relevant information from sources that may have been unavailable to previous workers. Brines in evaporites have been of particular interest, especially with respect to a radioactive waste repository to be constructed within bedded evaporites. However, fluids in adjacent and underlying non-evaporitic clastics and carbonates (similar to "oilfield brines", according to the nomenclature of Collins, 1975) have also attracted attention as occurrences of potential interest to WIPP. The Bell Canyon Formation fluids, for example, were at one time proposed as agents and/or products of dissolution of the overlying evaporites (cf. Anderson, 1981; Davies, 1983).

4.7.2 Brines in Evaporites

Until recently, the origin of brines of unusual solute- and stable-isotope composition in the Delaware Basin evaporites has received little attention since their initial characterization by Lambert (1978). This section will address certain models for the origin as suggested by O'Neil et al. (1986), who dealt specifically with the Delaware Basin evaporites, featuring fluid inclusions from the ERDA 9 core, and by Knauth and Beeunas (1986), who dealt primarily with the Palo Duro Basin, but who also presented stable-isotope compositions of fluid inclusions from the WIPP mine drifts (2162 ft depth).

Table 15 shows the stable-isotope compositions of waters collected under the auspices of Sandia National Laboratories, which also funded or performed the analyses. Table 16 contains the

TABLE 15. DEEP BASIN WATERS

Location	Date[1]	Depth[2]	δD[3]	δ^{18}O[4]	Analyst[5]
Collected by USGS					
ERDA-6 Castile Fm.	14 Sep 75	≈2711	0	10.3	[a]
Duval Nash Draw Mine, BT26 seep Salado Fm.	10 Dec 75	1070	-10	3.0	[a]
Duval Nash Draw Mine, BT48 seep Salado Fm.	11 Dec 75	1070	-12	2.6	[a]
Todd State 36-1 Morrowan	10 Dec 75	14862-14898	-15	2.7	[a]
Todd Federal 26-1 Morrowan	10 Dec 75	14862-14898	-18 -18	9.2 9.2	[a] [a]
Todd Federal 26-4 Bell Canyon Fm.	10 Dec 75	6160	-13	2.2	[a]
Collected by F. Hensley from coreholes in WIPP facility					
MB 139-4 WIPP Salado Fm.	20 Aug 84	≈2160	-19 -19	-0.3 -0.5	[b] [b]
MB 139-850 WIPP Salado Fm.	24 Aug 83	≈2160	-14 -15 -11	1.5 0.8 1.5 1.1 1.1	[b] [b] [b] [b] [b]

---

1. Date of collection.
2. Sampling depth or depth interval, in ft. from local datum (usually ground level), isolated by packers, perforated casing, or both.
3. In per mil (‰), vs V-SMOW.
4. In per mil (‰), vs V-SMOW.
5. Analysts as follows:

   [a] δD and δ^{18}O, J. R. O'Neil, U.S. Geological Survey.

   [b] δ^{18}O, S. J. Lambert and D. M. Harvey, Sandia Nat'l Labs.

TABLE 16. ISOTOPIC COMPOSITION OF FLUID INCLUSIONS
(O'Neil et al.)

Core Depth[1]	Corrected Depth (KB)[2]	δD[3]	$\delta^{18}O$[4]
2058.8-2059.0	2081.8-2082.0	-21	3.4
2070.4-2070.6	2093.4-2093.6	-28	1.2
2606.5-2606.9	2631.6-2632.0	-14	8.4
2617.2-2617.7	2642.3-2642.8	-10	8.0
2626.7-2627.0	2651.8-2652.1	-14	5.8
2659.0-2659.2	2664.7-2664.9	-2	9.9
2665.0-2665.1	2670.7-2670.8	-8	7.5
2692.4-2692.6	2698.1-2698.3	-4	8.1
2699.8-2700.0	2705.5-2705.7	-5	9.5

---

1. Depth, in ft., as marked on core
2. Corrected depth, in ft., below Kelly Bushing (KB) in borehole ERDA 9 (SNL and USGS, 1983).
3. ‰, vs SMOW (O'Neil et al., 1986)
4. ‰, vs SMOW (O'Neil et al., 1986)

stable-isotope compositions of fluid inclusions extracted by E. Roedder (USGS) from Salado Formation core selected by us from borehole ERDA 9 (Figure 2). These were analyzed by O'Neil, and reported by O'Neil et al. (1986). As illustrated by O'Neil et al., the points representing the fluid inclusions form a trend, with the ERDA 6 (Castile) brine reservoir at one extreme, and the other extreme intersecting with the meteoric field. O'Neil et al. had a gap in the data between the fluid inclusion with the most negative δ-values and the meteoric field.

<u>Fluid Inclusions</u>. In Figure 27 we have plotted the O'Neil et al. fluid-inclusion data, the ERDA 6 (Castile) brine datum, and all the data for waters from the Rustler/Salado contact (Figure 17).

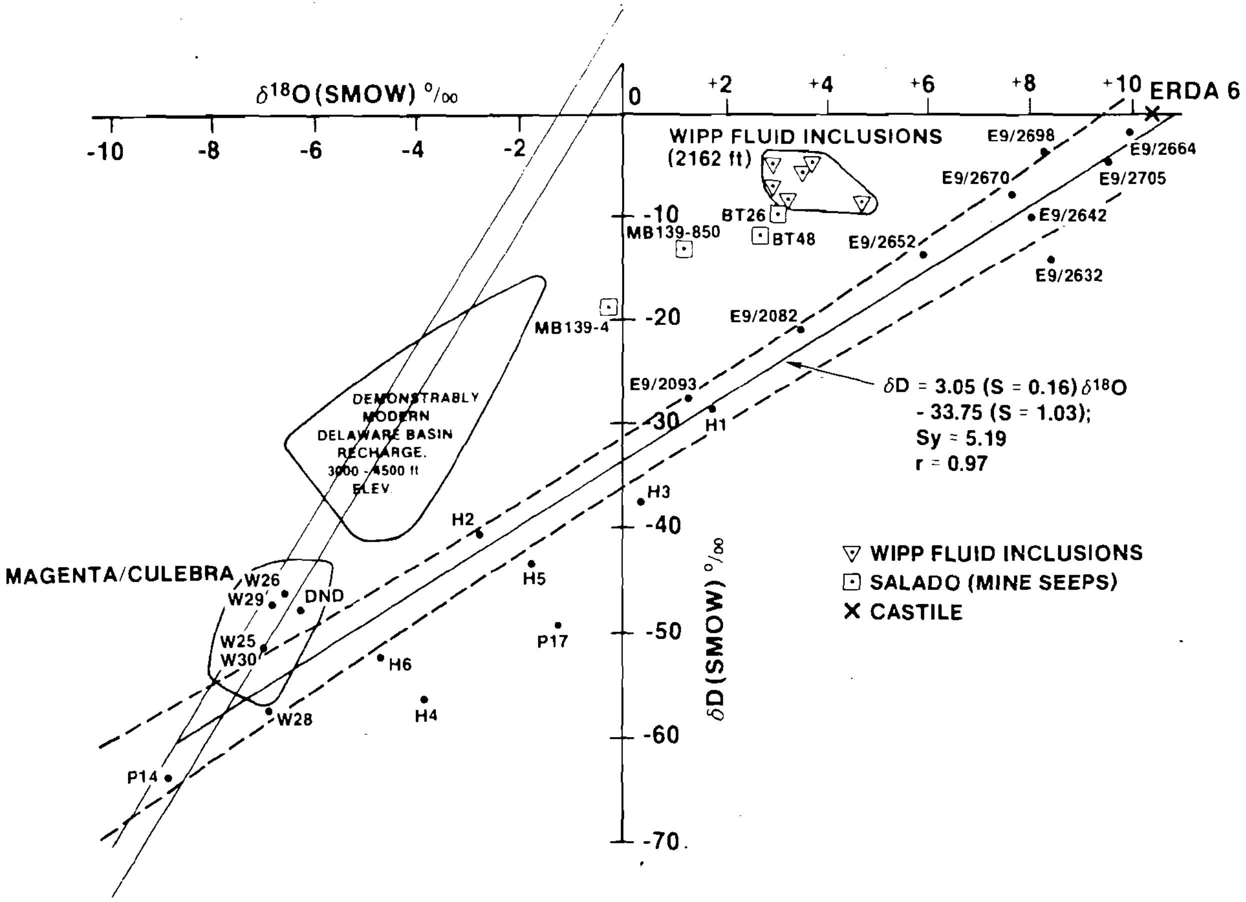


Figure 27. Stable-isotope compositions of brines associated with Ochoan evaporites in the Delaware Basin. Least-squares line is calculated from fluid inclusions in ERDA 9 halite core ("E9/XXXX") and ERDA 6 brine ("ERDA 6") from the Castile Formation (O'Neil et al., 1986) together with brines under confined conditions at the Rustler/Salado contact, indicated by simple dots bearing only a well designation (H-, P-, or W-series), or "DND" (Duval Nash Draw Mine). The Rustler/Salado contact data are from Figure 17. The ERDA 9 fluid inclusions have isotopic compositions significantly different from those from the WIPP mine (Knauth and Beeunas, 1986) and seeps in both the WIPP mine and the nearby Duval Nash Draw potash mine. The linear "fluid inclusion trend" (all simple dots) also seems to fit the Rustler/Salado contact; this implies that there may be some similarity in genesis for the ERDA 6 brine, the ERDA 9 fluid inclusions, and the Rustler/Salado contact, all of which may share meteoric Rustler-type water as a common participant.

The resulting trend, including the lower-δD and $\delta^{18}O$ Rustler/Salado data, is much better defined than a trend based solely on ERDA 6 brine and ERDA 9 fluid inclusions. The fluid-inclusion data points seem to form the more positive half of a trend whose more negative half is suggested by waters from the Rustler/Salado contact, both those with a purely meteoric isotopic signature and those at the equivalent stratigraphic position further east, but isotopically shifted in both $\delta^{18}O$ and δD. Thus, the ERDA 9 fluid-inclusion and ERDA 6 Castile brine reservoir data appear to be a continuation of the same trend suggested by changes in isotopic composition related to changes in transmissivity (e.g., water/rock ratio) at the Rustler/Salado contact. The least-squares line calculated for these data is

$$\delta D = 3.05(s=0.16)\delta^{18}O - 33.75(s=1.04) \qquad (7)$$

For this fit r = 0.97; overall s = 5.19. For comparison, the line calculated by O'Neil et al. (1986) for only the ERDA 9 fluid-inclusion data and ERDA 6 is

$$\delta D = 2.8\delta^{18}O - 31 \qquad (8)$$

with $r^2=0.95$. For the same data, we calculate

$$\delta D = 2.85(s=1.01)\delta^{18}O - 31.12(s=7.81) \qquad (9)$$

with $r^2=0.89$; $r=0.95$.

We consider the ERDA 9 fluid-inclusion and Rustler/Salado trends mutually consistent; in fact, the H1 Rustler/Salado point and one of the fluid-inclusion points are statistically indistinguishable. The trend that includes the Rustler/Salado contact data, according to our calculations, gives a better fit (a higher r-value) and lower values of s for slope and intercept. This probably is due to the fact that the combined trend has $\delta^{18}O$ values spread over 19 ‰, rather than the 9 ‰ of O'Neil et al.

Also shown in Figure 27 are stable-isotope compositions of fluid inclusions from the actual WIPP mine, at 2162 ft depth (from Knauth and Beeunas, 1986), seeps from the nearby Duval Nash Draw potash mine (Figure 2), and two new data points for brines found in fractures in Marker Bed 139, a polyhalitized anhydrite bed just under the floor of the WIPP mine. The tight cluster of fluid-inclusion data from the WIPP evaporites reported by Knauth and Beeunas (1986) does not correspond to any of the fluid inclusion data reported by O'Neil et al. (1986). Similarly, actual seeps of free water from both WIPP and the nearby Duval Nash Draw mine have isotopic compositions significantly different from the fluid inclusions of O'Neil et al., but are similar to those of Knauth and Beeunas. In particular, δD values for fluid inclusion samples from ERDA 9 at corrected (Kelly Bushing) depths 2082 and 2093 ft (-21 and -28 ‰, respectively) are significantly different from those of the WIPP (-5 to -9 ‰) even though the $\delta^{18}O$ value of 2082 (3.4 ‰) is similar to that of the WIPP fluid inclusions (2.9 to 4.7 ‰). The adjusted ERDA-9 sample depths below surface are about 2070 and 2081 ft, respectively (SNL and USGS, 1983), which are very close to the mine depth. We do not know the reason for this remarkable difference in δD value for samples of Salado Formation fluid-inclusions taken from similar depths separated laterally by only a few hundred meters. It may arise from the fact that Knauth and Beeunas (1986) drew fluid inclusions into capillaries whereas O'Neil et al. (1986) extracted fluid inclusions by vacuum crushing and mild (350°C) heating. We will not presume to comment on which method gives more reliable results. Alternatively, assuming isotopic homogeneity in fluid inclusions over several hundred meters within a single stratigraphic horizon in the evaporites, the isotopic difference may represent a distinction imposed by the geological environment, implying some fundamental geochemical difference between evaporite beds below and above, say, Marker Bed 138, which occurs at a depth of about

2108 ft below surface near ERDA 9 and the WIPP. For the rest of this discussion, we shall assume that the difference is geologically significant, and is not an analytical artifact.

O'Neil et al. (1986) argued that the fluid-inclusion trend in $\delta D/\delta^{18}O$ space (Figure 27, exclusive of "WIPP Fluid Inclusions" and "Salado (Mine Seeps)") was due to mixing between water liberated from gypsum dehydration (the ERDA 6 endmember) and local meteoric water (represented by that now found in the western part of the WIPP area and east- and north-central Nash Draw). While this is certainly a plausible model for the origin of the water molecules themselves, the great variety in solute compositions do not support such mixing as an origin of the various solutions as a whole. Although this was acknowledged by O'Neil et al. (1986), they suggested that:

> Recent K-Ar and K-Ca isotope measurements of evaporite minerals from the Salado Formation (Obradovich, pers. comm.) show that they have undergone extensive recrystallization as recently as a few million years ago and have not been stable for the last 215 M.Y., as suggested by the K-Ar study of Brookins et al. (1980).

Unless and until the data from "[J.] Obradovich [U.S Geological Survey], pers. comm." are published and become readily available, we cannot evaluate them. However, there is an undeniable body of geochronological evidence strongly suggesting the **absence** of evaporite recrystallization in the Salado Formation in the last 200 Ma.

Table 17 is a summary of available radiometric dates for minerals of the Salado Formation, summarized from several sources (Register and Brookins, 1980; Brookins, 1980; Brookins et al., 1980; Brookins, 1981; Register, 1981; Brookins and Lambert, 1987). The distribution of dates shows that:

TABLE 17. AGE DETERMINATIONS OF THE SALADO FORMATION

Description[1]	Age, Ma[2]	Method[3]	Source[4]
41 evaporite minerals	199 ± 20	Rb-Sr isochron	[1]
32 evaporite minerals	214 ± 15	Rb-Sr isochron	[2]
evaporite whole rocks	171 ± 36	Rb-Sr isochron	[1]
clay minerals in evaporites	390 ± 77	Rb-Sr isochron	[2]
WIPP site clay minerals	428 ± 7	Rb-Sr isochron	[3]
<u>PURE POLYHALITES</u>			
E9-15A	216 ± 7	K-Ar	[4]
E9-59	212 ± 7	K-Ar	[4]
E9-84	200 ± 7	K-Ar	[4]
MCC-Rc	212 ± 7	K-Ar	[4]
MCC-121a	198 ± 7	K-Ar	[4]
E9-15b	209 ± 7	K-Ar	[5]
E13-1	201 ± 7	K-Ar	[3]
E13-7 (plus clay)	205 ± 7	K-Ar	[3]
E13-11	205 ± 7	K-Ar	[3]
E13-12a	195 ± 7	K-Ar	[3]
<u>IMPURE POLYHALITES (polyhalite + halite ± sylvite ± anhydrite)</u>			
E9-99	174 ± 6	K-Ar	[4]
A8-18	154 ± 15	K-Ar	[4]
E9-84B	184 ± 6	K-Ar	[5]
E9-91	187 ± 7	K-Ar	[5]
MCC-121b	183 ± 6	K-Ar	[5]

TABLE 17. (Continued)

E13-2b	183 ± 6	K-Ar	[3]
E13-3	183 ± 6	K-Ar	[3]
E13-12b	181 ± 6	K-Ar	[3]
POLYHALITE IN LAMPROPHYRE DIKE CONTACT ZONE			
MB7622	21.4 ± 0.8	K-Ar	[4]
DATES FROM THE IMCC POTASH MINE			
IMC-1 (magnesite-talc-sylvite-halite	183 ± 15	Rb-Sr model	[6]
	304 ± 12	K-Ar	[6]
IMC-2A,2B (leonite)	78 ± 15	Rb-Sr model	[6]
	109 ± 15	Rb-Sr model	[6]
	12.6 ± 0.5	K-Ar	[6]
IMC-3A,3B (langbeinite)	173 ± 15	Rb-Sr model	[6]
	205 ± 12	Rb-Sr model	[6]
	202 ± 7	K-Ar	[6]
	188 ± 6	K-Ar	[6]
IMC-4 (kieserite)	260 ± 20	Rb-Sr model	[6]
	103 ± 5	K-Ar	[6]
IMC-5A,5B (sylvite)	180 ± 12	Rb-Sr model	[6]
	177 ± 12	Rb-Sr model	[6]

---

1. "MCC" denotes a sample from the Mississippi Chemical Corporation mine, taken near the faulted contact with the subsurface expression of the "breccia pipe" (Hill, Cnyder, and Gard, 1982)
2. Ma = million years, with ± estimated standard deviation
3. Rb=Sr model ages are calculated assuming initial $^{87}Sr/^{86}Sr = 0.71$
4. [1] Register, 1981
   [2] Register and Brookins, 1980
   [3] Brookins, 1981
   [4] Brookins et al., 1980
   [5] Brookins, 1980
   [6] Brookins and Lambert, 1987

1. Rubidium-strontium isochron determinations on evaporite minerals, largely sylvite, (179-229 Ma) are in good agreement with K-Ar determinations on pure polyhalites (195-216 Ma).

2. K-Ar dates on impure polyhalites, containing minor amounts of admixed halides, are slightly younger, due to the admixtures which extrapolate to the pure polyhalite dates at zero halide content.

3. Langbeinite gives concordance between Rb-Sr model ages and K-Ar ages, both in agreement with the sylvite and polyhalite ages.

4. Leonite does not seem to reflect accurately the concordantly older dates for coexisting minerals, since it gives significantly younger apparent ages which do not correspond to any other geochronological event preserved in the isotopic record.

5. The only recrystallization event found younger than early Jurassic (200 Ma) was known to be a contact phenomenon associated with emplacement of an Oligocene lamprophyre dike (21 Ma for polyhalite versus 32-34 Ma for the dike; Calzia and Hiss, 1978).

6. Clay minerals have both Rb-Sr isochron and K-Ar ages significantly older than the evaporites, reflecting their probable detrital origin rather than participation in the Triassic/Jurassic recrystallization event that appears to have affected the evaporite minerals.

It has long been known that sylvite yields significantly younger K-Ar ages than Rb-Sr ages. This has been explained as loss of radiogenic argon that is not tightly bound within its crystal lattice. Radiogenic strontium, as a solid, is not subject to the mechanism of loss by gaseous diffusion that argon is; hence, dating by the Rb-Sr isochron method is not considered as likely to give spurious results, especially if the isochron is well defined. It is probable that the very young K-Ar dates attributed by O'Neil et al. (1986) to "Obradovich, pers. comm." are K-Ar determinations on sylvites.

The data in Table 17 argue strongly for the absence of pervasive recrystallization of the Salado evaporite section in the last 200 Ma. The number of replicate determinations, the wide distribution of dated minerals throughout the stratigraphic section as well as throughout the Delaware Basin, and the concordance of dates obtained by various radiometric methods all indicate that this conclusion cannot be in great error.

If a vertical connection were to exist through the Salado Formation, allowing mixing between brine similar to that found in pressurized occurrences in the Castile (whatever its origin) and meteoric water, the geochronological systematics in the Salado Formation have not responded to this fluid movement by means of recrystallization of evaporite minerals. Due to its low potassium concentration relative to Salado brines (Lambert, 1978), it is not likely that the solute assemblage in ERDA 6-type brine has been significantly influenced by reactions involving polyhalite. Consequently, if such a fluid migrated upward through the Salado from depth, polyhalite with which it came in contact would at least recrystallize if not incongruently dissolve to form calcium sulfate. This would reset the geochronological systematics in the polyhalite to reflect the age of recrystallization. Studies by Borns (1985) indicate that at least for one marker bed in the Salado, polyhalite occurs as fracture fillings in anhydrite and overgrowths, implying polyhalite deposition after anhydrite rather than polyhalite dissolution leaving a residue of anhydrite. In short, we have no evidence of Salado recrystallization in response to vertical fluid movement from below. Thus, while the simple (vertical) mixing model of O'Neil et al. (1986) is consistent with the stable-isotopic composition alone of the fluid inclusion trend in Figure 27, it is not strictly consistent with other observations, particularly the published geochronological data involving ages of both the evaporite minerals in the Salado and the meteoric water in confined reservoirs such as the Rustler.

We tentatively propose, alternatively, a reiteration of the rock/water interaction model of Lambert (1978), with refinements. Whereas it is indeed unlikely that clay minerals alone (as originally suggested by Lambert, 1978) may be sufficient to provide the mineral sources of hydrogen for the interactions that causes deviations from the meteoric field, there is no lack for exchangeable mineral hydrogen in the Ochoan evaporite section. Both the Rustler and Salado Formations contain documented occurrences of hydrous evaporite minerals (Lambert, 1983; Snyder, 1985), dominantly gypsum where fresh waters have circulated through the evaporites and removed the halite and hydrated the anhydrite, dominantly polyhalite where the evaporites have not been so exposed. At isotopic equilibrium, gypsum has a δD value 20 ‰ more negative than the coexisting water. As shown in Section 4.6 above, several Delaware Basin evaporite occurrences illustrate the principle that different rock/water ratios in isotopic exchange reactions result in different magnitudes of change in δ-value from the original δ-values. Thus, if the initial water/anhydrite ratio is small during gypsification, a hydrogen-isotope shift can occur in the water, leaving the water enriched in deuterium relative to the water of hydration in the gypsum. If a small amount of water exchanges hydrogen and oxygen isotopes with a large amount of pre-existing gypsum, the gypsum will determine both δD and $\delta^{18}O$ of the water (according to the fractionation factors for oxygen- and hydrogen-isotope exchange), with little change in the isotopic composition of the gypsum. Thus, gypsification of anhydrite can result in a residual water enriched in deuterium relative to the initial isotopic composition of the water. Isotopic exchange between old gypsum and water can enrich or deplete the water in deuterium, depending on the initial isotopic compositions of both gypsum and water, and the gypsum/water ratio.

The stratabound dissolution model of Lambert (1983) allows water to move through evaporite interbeds made permeable by fracturing. Several of these interbeds in the Rustler Formation are anhydrite, and show evidence of gypsification, whereas anhydrite beds above and below are intact. This phenomenon was observed especially in Nash Draw. At the WIPP site, the water-bearing Magenta and Culebra members of the Rustler Formation are sandwiched between anhydrite beds, which are altered to gypsum very near the water-bearing layer. The same has happened at the Rustler/Salado contact; where the "basal brine aquifer" is well developed with a high permeability, dissolution and gypsification has proceeded apace. Where it is less developed to the east, the dissolution and gypsification is only incipient; with less permeability and the greater rock/water ratio progressively toward the east, the isotope shift toward increasingly positive δ-values in the water there becomes greater. Thus, mixing between meteoric water at the Rustler/Salado contact and a brine similar to that of ERDA 6 need not be invoked to explain the isotope shift in waters of the Rustler/Salado contact where the flow system is less developed. If the isotopic compositions of the ERDA 9 fluid inclusions and ERDA 6 brine have resulted from rock/water interaction similar to that at the Rustler/Salado contact (as is inferred to be the case from the trend in Figure 27), it is similarly unnecessary to ascribe the origin of ERDA 9 fluid inclusions to mixing between meteoric water and Castile-type brine.

It is conceivable that the coincidence between the Rustler/Salado contact trend in Figure 27 and the fluid inclusion trend (defined by the data of O'Neil et al., 1986) is accidental, i.e., that the two populations have originated by different processes, both of which have given similar patterns but different amounts of isotope shift. Small amounts of meteoric water may have migrated along bedding planes downdip from their outcrop areas to the west, or from the adjacent Capitan limestone to the north (Figure 4), to mix with some pervasive reservoir of brine with isotopic composition similar to that of ERDA 6. The crude correlation between isotope shift of fluid inclusions and depth, as observed by O'Neil et al. (1986) may then be related to longer flow paths required to reach greater depths, resulting in a greater dominance by the pervasive brine relative to meteoric water. Alternatively, isotopically-shifted waters of the Rustler/Salado contact, the ERDA 9 fluid inclusions, and the ERDA 6 brine reservoir may all have arisen from a similar series of mineral/water interactions, reflected in the relatively well defined linear relationship of isotope shift in $\delta D/\delta^{18}O$ space.

Given the choice of (1) the rock/water-interaction hypothesis, and (2) and binary mixing between ERDA 6-type brine and meteoric water, to explain the Rustler/Salado-fluid inclusion trend, and given the evidence for no vertical fluid migration through the Salado section, we favor the rock/water-interaction model proposed here. However, the quantitative details of this model remain to be developed. Whereas the D/H and $^{18}O/^{16}O$ fractionation factors are reasonably well known for gypsum, the same is not true for other hydrous evaporite minerals such as polyhalite (Halas and Osmolski, 1986). We are willing to entertain the possibility, however, of small amounts of meteorically derived water migrating along bedding planes from outcrop areas in the geologic past. Timing of such processes, however, ranges from greater than 12,000 a, assuming that all meteoric water in the Delaware Basin with isotopic compositions characteristic of the confined Rustler and Capitan were recharged prior to that time (Lambert, 1987), to less than 300,000 to 600,000 a, assuming that the ERDA 6 brine was originally derived from a meteoric source (Barr et al., 1979; Lambert and Carter, 1984).

Mine seeps. In Figure 28 the isotopic compositions of brines other than ERDA 9 fluid inclusions are examined. The WIPP fluid

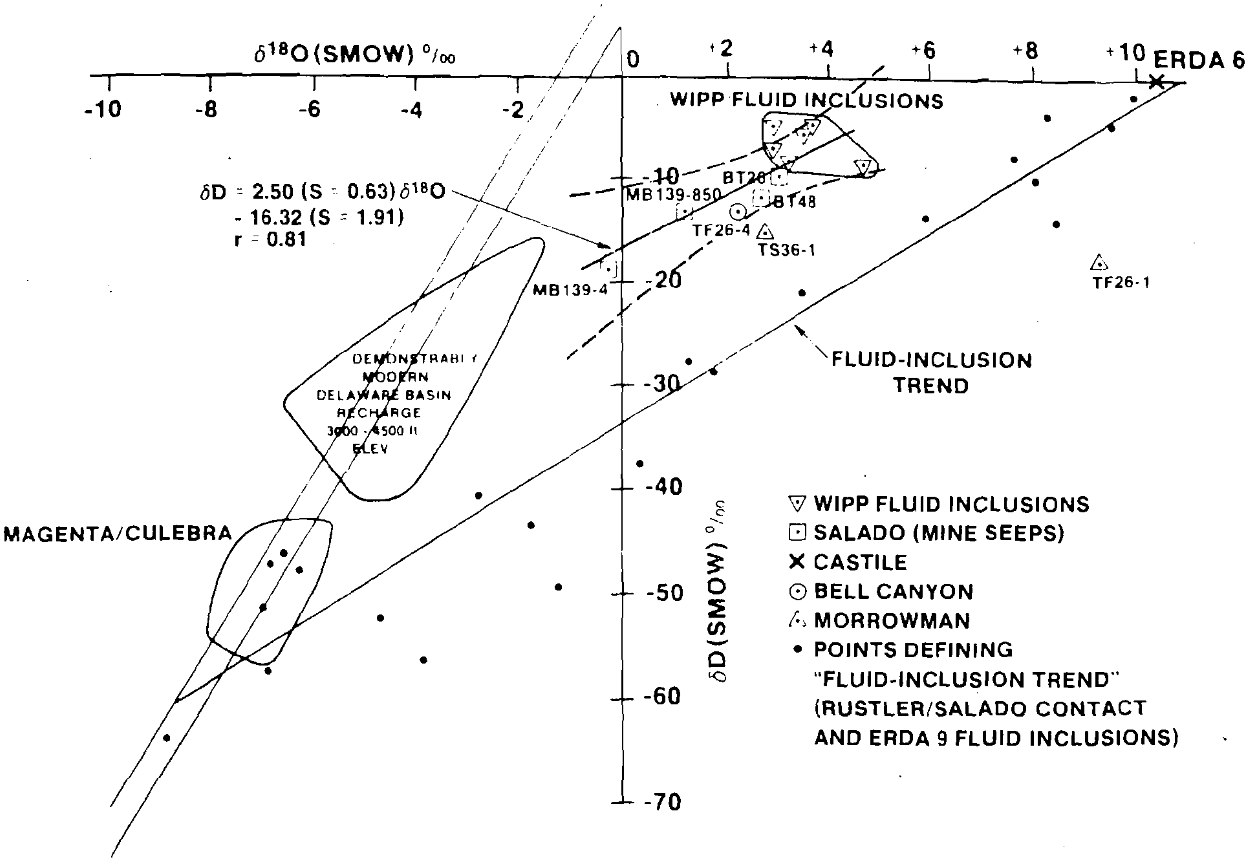


Figure 28. Stable-isotope compositions of brines associated with Ochoan evaporites and older rocks in the Delaware Basin. The WIPP fluid inclusions of Knauth and Beeunas (1986), together with seeps from Marker Bed 139 under the WIPP mine and from the nearby Duval Nash Draw potash mine appear to describe a trend in $\delta D/\delta^{18}O$ space that is distinct from yet parallel to the "fluid inclusions trend" defined in Figure 27. The "seep trend", $\delta D = 2.50(s=0.63)\delta^{18}O - 16.32(s=1.91)$, $r=0.81$, is shown with its confidence limits at the 95% confidence limits. Water from the Bell Canyon and one Morrowan occurrence have isotopic compositions similar to the "seep trend", while the other Morrowan locality is significantly different from either the seep trend or the fluid inclusion trend. There are ways of accounting for the isotope shift in Bell Canyon and Morrowan waters other than partial evaporation and mixing, since the hosts for these waters do not have a close evaporite association.

inclusions of Knauth and Beeunas (1986) are here considered together with the mine seeps (i.e., free water) from the Duval Nash Draw potash mine (Figure 2) and from Marker Bed 139 under the floor of the WIPP drifts. Together, they appear to form a trend of their own, distinct from the "fluid inclusion trend" discussed above. Due to the limited spread in δ-values, the trend is much less well defined than the fluid inclusion trend; the least-squares line is described by the equation

$$\delta D = 2.50(s=0.63)\delta^{18}O - 16.32(s=1.91) \qquad (10)$$

with r = 0.81. Note the wide 95% confidence limits on the line in Figure 28. Whether or not there is a genetic relationship between the water molecules in the seeps and fluid inclusions at the WIPP facility horizon cannot be determined conclusively, but these samples appear to be indistinguishable from those used by Knauth and Beeunas (1986) to define the trend for fluid inclusions in halite from the nearby Palo Duro Basin, east of the Delaware Basin in the Texas panhandle.

A clear genetic relationship cannot be inferred from this relatively isolated cluster of data, and no clear derivation from meteoric-like fluids can be drawn by extrapolating our "seep trend" to the meteoric field across an area devoid of data points. Nevertheless, we note the preferred interpretation of Knauth and Beeunas (1986), applied to both evaporite brines and oil field brines:

> We consider an interpretation in which meteoric waters mix with evaporated sea water during deposition or early diagenesis of the salt deposit to be the simplest explanation for the samples more depleted in ^{18}O and D. The fluids have isotopic compositions unlike the hydration water of gypsum and have probably not been derived from any gypsum-anhydrite transformation. Penetration of the salt by external formation waters cannot easily yield the observed isotopic data. Any penetration of the salt by younger ground waters of meteoric origin has been insufficient to imprint a meteoric water isotopic signature.

> Regardless of whether they are marine or mixed meteoric-marine evaporite waters, connate fluids associated with evaporite deposits have negative δD values and sometimes negative $\delta^{18}O$ values. They are isotopically similar to many formation waters and oil field brines. It is possible, if not probable, that the δD-$\delta^{18}O$ data arrays observed for many sedimentary basins represent, in part, mixing of meteoric fluids with ancient evaporite brines and are not purely meteoric waters which have evolved isotopically through water-rock interaction.

Despite the isotopic similarity between WIPP fluid inclusions and seeps from Marker Bed 139, Stein and Krumhansl (1986) have shown that the WIPP fluid inclusions and seeps are not part of a uniformly interconnected system, on the basis of a clear distinction in solute compositions between fluid inclusions and macroscipic fluid occurrences. Although we have no basis for attacking the conclusions of Knauth and Beeunas (1986), the known oilfield brines from the Bell Canyon Formation and the Morrowan limestone, both a significant depth below the evaporite section, may not have origins akin to brines in evaporites. Oilfield brines are discussed next.

4.7.3 Oilfield Brines

The isotopic compositions of two waters from the Morrowan limestone (Pennsylvanian) and one from sandstone of the Bell Canyon Formation (Guadalupian, Permian) are given in Table 15 and Figure 28. First we note that although the Bell Canyon and one of the Morrowan points are very near the "seep trend", the other Morrowan (TF26-1) is not; it lies even on the opposite side of the "fluid inclusion trend". We can immediately conclude that brine in the Morrowan is not part of a well-mixed flow system. The basal Pennsylvanian represented by the Morrowan rocks of New Mexico is typified not by evaporites, but by limestone, shaly limestone, and fine-grained clastics (Powers et al., 1978). Although rather briny, Morrowan waters do not approach saturation with NaCl (total dissolved solids = 35,600 and 92,400 for Todd State 36-1 and Todd Federal 26-1, respectively; Lambert, 1978).

Waters from the Morrowan were last in contact with organic-rich carbonates, not evaporites. If the Morrowan waters were ever in contact with halitic evaporites, this encounter was brief; otherwise the solutions would have become saturated with NaCl, given access to an adequate volume of halite. Despite similarities in isotopic composition, we propose that different processes gave rise to the isotopic compositions of the Morrowan waters than those discussed above for evaporite environments. An extreme degree of rock/water interaction does not seem to be precluded for the very deep (around 15,000 ft) Morrowan waters.

Hiss (1975) has in part addressed the origin of water in the Bell Canyon Formation. He suggested that since salinity decreases in Bell Canyon water to the west toward the outcrop areas, accompanied by an increase in potentiometric head, water in the Bell Canyon is of meteoric origin, and flows beneath the floor of the evaporite basin to the east. Lambert (1983b) has shown that solutes in the Bell Canyon water cannot have originated from simple dissolution of common evaporite minerals, but contain a sizeable component of normative calcium chloride. Possible origins of calcium-chloride oilfield brines have been discussed by Graf et al. (1966), and the reader is referred to that work for pertinent details. We have shown above, however, that it is possible to account for the oxygen-shift in Bell Canyon water, assuming a meteoric origin, entirely by calcite/water isotope exchange; no appeal to mixing or partial evaporation is necessary. Whereas we cannot uniquely identify a mineral reservoir of exchangeable hydrogen in the Bell Canyon, we note that several hydrous minerals are known to occur in the Bell Canyon, including a matrix of (apparently) diagenetic chlorite and kaolinite (Powers et al., 1978) whose possible role as a source of exchangeable hydrogen should not be overlooked.

4.8 Regional Comparisons

4.8.1 The Albuquerque Basin

Yapp (1985) surveyed the δD values of groundwaters in the Albuquerque (New Mexico) Basin. The basin is drained by the Rio Grande, a major perennial stream extending from the San Juan Mountains of southwestern Colorado to the Gulf of Mexico. The basin is bounded on the east by the Sandia and Manzano Mountains, whose crest rises as much as 1500 m above the valley floor as a manifestation of faulting along the east side of the Rio Grande Rift. Valley fill consists of the Miocene/Pliocene Santa Fe Group, which is poorly consolidated gravel, sand, silt, clay, and interbedded volcanic rocks, overlain by younger surficial deposits. Arroyos running down the west face of the granitic/ metamorphic mountain block are considered to serve as significant recharge areas to the groundwater system developed in the valley fill.

Yapp found three distinct populations of groundwaters, divided according to δD values:

1. Water attributable to recharge from the Rio Grande. The stream had a 2-year average δD value of -92 ‰, which included negative swings to -102 ‰ during spring runoff and positive swings during summer. Groundwaters from the western part of the basin where the Rio Grande flows had δD values between -89 and -96 ‰, suggesting a close affinity between groundwaters there and direct recharge from the River.

2. Water running off the mountains in the eastern part of the basin. The groundwaters here had δD values between -75 and -87 ‰, corresponding to mountain stream, well, and spring water between -70 and -83 ‰.

3. Deep groundwater underlying the zone of recharge from the Rio Grande. These groundwaters had δD values of -102 to -104 ‰.

Yapp noted that some wells were isotopically stratified, producing waters of types 2 and 3 at different depths. Yapp considered type 3 especially noteworthy:

> Of particular interest is the deeper groundwater component in the western domain with a δD value of ≈-102 ‰ (a probable upper limit). It is concluded that this comparatively deuterium-depleted water probably did not originate from modern Rio Grande recharge. Instead it may have its origins at a time when average Rio Grande δD-values were ≈10 ‰ more negative than at present. Regional evidence of temporal variations in precipitation D/H ratios suggests the "Little Ice Age" as one interval when river waters might have been at least 10 ‰ more negative than at present. However, it has not yet been established that the deuterium-depleted groundwaters actually date from this time.
>
> If the deuterium-depleted deep groundwater actually did originate under different climatic conditions, it suggests that at least a portion of the groundwater in the study area is being "mined" [pp. 82-83].

The similarities between the situation described by Yapp (1985) for the Albuquerque Basin and confined groundwaters of the Capitan and Rustler Formations in the Delaware Basin are significant. The difference between the average δD of confined groundwaters from the Capitan and Rustler (-50 ‰; Figure 21) and the most negative δD value from water-table conditions (represented by the Ogallala, -40 to -41 ‰) is also ≈10 ‰. This difference, together with the fact that confined Delaware Basin groundwaters (a) have no detectable tritium, and (b) have apparent radiocarbon ages of 12,000 to 16,000 a, suggest that they did not originate from modern recharge, analogous to the reasoning of Yapp. The principal difference is that the Rustler groundwaters having δD values of around -50 ‰ are **significantly older** than the "Little Ice Age". Epstein and Yapp (1976) proposed that the "Little Ice Age" may have covered the interval from ≈1450 to ≈1620 A.D. in parts of North America, when precipitation δD values were ≈15 ‰ more negative than at present, as recorded by a bristlecone pine in the White Mountains of California.

4.8.2 The Murray Basin of South Australia

The River Murray is the largest river system in Australia, draining about 14% of the total continental area; recharge to the underlying water table (25-50 m depth) has been the subject of detailed isotopic studies by Allison et al. (1985) and Leaney and Allison (1986). The region is semi-arid with a mean annual precipitation of ≈300 mm and an evaporation of ≈1800 mm (Allison et al., 1985). Compare 277 mm and 1859 mm for equivalent parameters, respectively, reported by Hunter (1985) for the WIPP region. The principal difference seems to be that in Australia most of the precipitation occurs in winter, whereas summer precipitation dominates the plains of southeastern New Mexico. Calcrete is developed near the surface over much of the Murray Basin, and is commonly covered by dune sand, similar to the near-surface geology of Los Medaños at the WIPP site. Sinkholes a few meters deep resulting from the dissolution of gypsum near the surface pock-mark the Murray Basin area, and secondary sinkholes appear to have formed from dissolution of the regional limestone aquifers at several tens of meters depth (Allison et al., 1985). This may be analogous to the solution dolines developed on the caprock of the Llano Estacado northeast of the WIPP site.

Rates of recharge in the dune areas to the water table of the Murray Basin were estimated by Allison et al. (1985), on the basis of tritium and chloride in the unsaturated zone, to be less than 0.1 mm/yr, prior to the clearing of large stands of eucalyptus trees that covered much of the area. The results of Leaney and Allison (1986) for recharge as determined on water samples from the water table were based on radiocarbon, and were 0.1 to 0.2 mm/yr, in good agreement with the previous determinations.

One other observation of Leaney and Allison (1986, p. 137) is noteworthy: "...in arid conditions, low recharge and preferential winter precipitation, as experienced in the study area, may cause large displacements from the meteoric line regardless of the climatic conditions under which the precipitation fell." This serves as a warning that deviations of groundwater isotopic compositions from a least-squares fit ascribed to a meteoric trend should not in every case be interpreted as significant indicators of isotopic modification of precipitation and/or recharge.

Whereas we do not propose that the results for the Murray Basin be applied directly to the Delaware Basin (any more than should the results from the Roswell Artesian Basin; see Section 4.8), these findings illustrate a vital concept. "The very low rates of recharge found for the aquifer studied here [in the Murray Basin] make evaluation of the water balance difficult using standard hydraulic techniques" (Leaney and Allison, 1986). This is at variance with the statement of Chapman (1986, p. 65) that "actual physical measurements of the flow system of the Rustler are probably the only way the amount and location of recharge to the Rustler can be defined." If recharge through dune sand to a water table in the Murray Basin was so slow as to be undetectable by standard hydraulic techniques, we have little hope of determining definitive values for recharge to the confined Rustler at the WIPP site. We maintain that isotopic methods are the best way of quantifying recharge in semi-arid environments.

4.8.3 The Roswell Artesian Basin

Setting. The Roswell Artesian Basin offers itself for comparison with the Delaware Basin principally because the southern portion of the Roswell (at Artesia, Figure 1) adjoins the northern portion of the Delaware. The hydrogeology of the Roswell Artesian Basin has been thoroughly described by Welder (1983), who also considered the human impact on the aquifers of the basin as a result of extended withdrawal of water for agricultural and domestic use since 1891. In addition, several parallel studies, relying heavily on tritium concentrations in groundwater, surface water, and precipitation, have probed the details of the Roswell Artesian Basin, including Gross et al., 1976, Duffy et al., 1978, Gross et al., 1979, Davis et al., 1980, Gross and Hoy, 1980, and Hoy and Gross, 1982.

For a description of the general hydrology of the Roswell Artesian Basin, we turn to Welder (1983):

> The Roswell ground-water basin...consists of an eastward-dipping carbonate aquifer that is overlain in the east by a leaky confining bed, which in turn is overlain by an alluvial water-table aquifer. The carbonate aquifer is under artesian conditions in the east part of the basin, but in the western outcrop area the carbonate aquifer is unconfined and water-table conditions prevail. Along much of the eastern boundary of the basin the alluvial aquifer is hydraulically connected with the Pecos River [p. 4].
>
> In the Roswell basin, water recharges the artesian-aquifer system principally by infiltration from precipitation, by runoff along intermittent losing streams that flow eastward across the outcrop of the aquifer to the Pecos River, and by subsurface underflow. Some recharge by downward leakage to the artesian aquifer from the shallow aquifer might occur in summer if artesian water levels are lowered by pumping below shallow water levels. Most of the water entering the artesian-aquifer system generally moves downdip from the outcrop, then upward through the leaky confining bed into the shallow aquifer, and thence to the river. Additional recharge to the shallow aquifer is from precipitation and return flow from irrigation.
>
> The principal means of discharge from both aquifers is through wells. In 1978, there were about 1,500 active and relatively high-yielding irrigation, commercial, industrial, and public-supply wells in the basin (domestic and stock wells excluded). Additional discharge from the shallow aquifer is by seepage to the Pecos River and by evapotranspiration in places where the water table is relatively shallow. Discharge from the artesian aquifer to the Pecos River might also occur directly through fractures and solution channels in the confining bed without passing through the alluvial

> aquifer. In many places, the river flows directly on the Permian rocks of the confining bed and no alluvium is present [p. 6].

Figure 29 is a schematic cross section of the Roswell Artesian Basin, taken from Hoy and Gross (1982), illustrating the relationships between the Sacramento Mountains, where the principal artesian aquifer rock crops out in its recharge area, and the region along the Pecos River, where the aquifer is under confined conditions and is extensively pumped.

The Roswell Artesian Basin differs from the Delaware Basin in several significant ways. First, the well established presence of its principal recharge area, at relatively high elevations (>5000 ft) on a mountainous slope, implies that the isotopic composition of recharge will be characteristic of higher elevations, rather than <4500 ft as in most of the Delaware. Second, Delaware Basin aquifers (Rustler, Ogallala, alluvium, etc.) appear to be effectively separated from mountainous regions (>4500 ft) in the Delaware Basin by the Pecos River, which is generally taken to be a discharge point for shallow aquifers in both the Delaware and the Roswell basins. Perhaps most importantly, the Roswell Artesian Basin has been extensively pumped since the late nineteenth century, perturbing the natural potentiometric relationships among the Roswell aquifers. These perturbations have caused complex mixing relationships within the aquifer systems that have also perturbed various isotopic systematics, particularly the distribution of tritium, deuterium, and ^{18}O. For these reasons we do not consider the Roswell Artesian Basin a credible analog to the Delaware Basin for interpreting the stable-isotope geochemistry of the latter.

Discussion. Chapman (1986) has used selected aspects of the Roswell Artesian Basin to draw conclusions about the hydrogeology of the Rustler Formation in the Delaware Basin, and that comparison of the two basins is discussed here. In this section we show that (a) the hydrologic and physiographic characteristics of

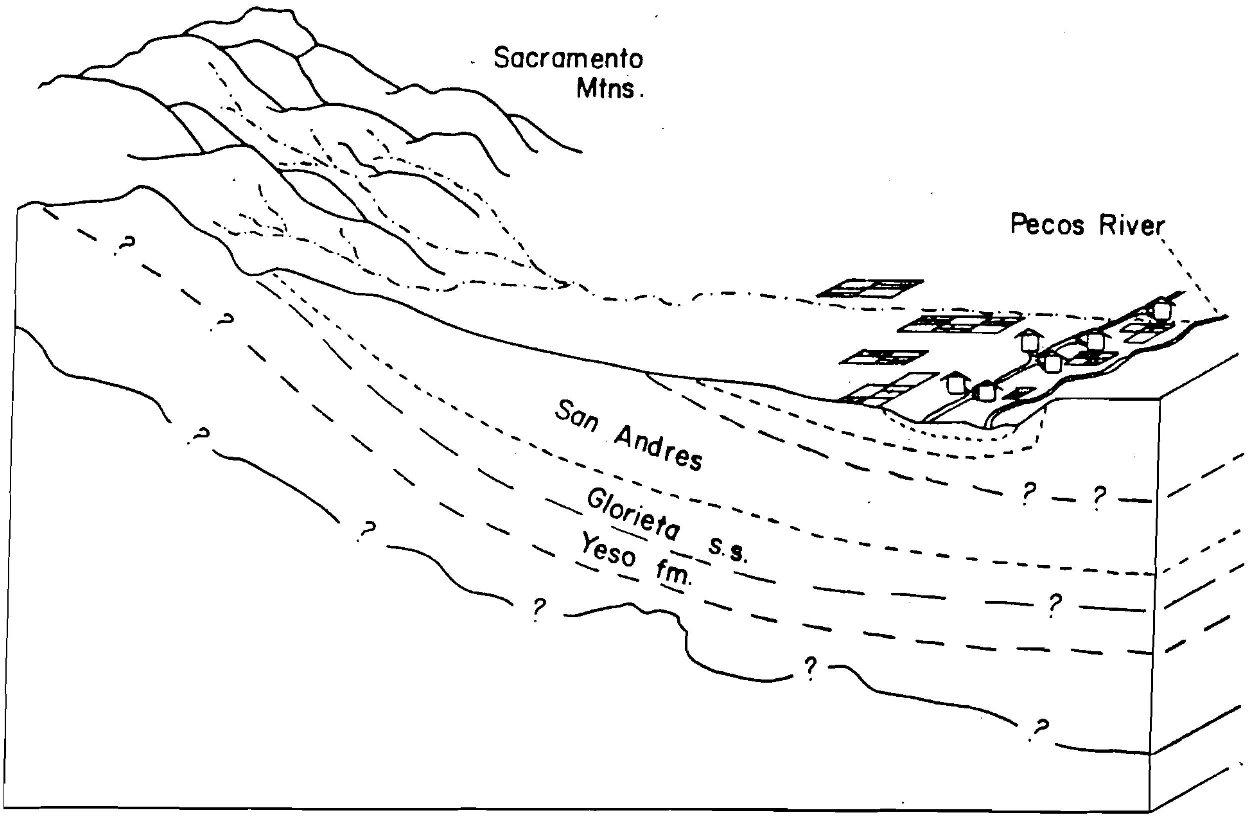


Figure 29. Schematic block diagram of aquifers in the Roswell Artesian Basin. Taken from Hoy and Gross (1982). Note streams having sources high in the Sacramento Mountains running down over the outcrop area of the artesian aquifer, principally the San Andres Limestone. Immediately overlying the San Andres is a leaky confining layer, which allows the development of artesian head in the San Andres at seasons when pumpage is not extreme. The leaky confining layer (Grayburg, Queen, and Seven Rivers Formations; Figure 3) allows water to leak upward and discharge into the alluvial aquifer under natural conditions, and downward from the alluvial aquifer when extreme pumpage drops the potentiometric levels in the San Andres.

the Roswell and Delaware Basins (particularly with respect to the Rustler Formation) are sufficiently dissimilar to make a comparison based solely on isotopic parameters invalid, and (b) certain simplifications in Chapman's representation of previous work have led to misinterpretation of the nature of recharge to aquifers in the Roswell Artesian Basin.

The major issues, in sequence, of Chapman's (1986) arguments for comparing recharge characteristics of the Roswell Artesian and Delaware Basins are as follows:

1. δD values were calculated from $\delta^{18}O$ values reported by Hoy and Gross (1982), to facilitate comparison with the $\delta D/\delta^{18}O$ distribution of Rustler and other groundwaters in the Delaware Basin [p. 21].

2. Examples of groundwaters were chosen from Hoy and Gross (1982), such that they had more than 4 TU, and were from wells at an elevation of less than 5000 ft [p. 26].

3. "The coincidence between the isotopic composition of the verifiably young [sic] Roswell Basin groundwater and the composition of the Rustler water" was noted to be "striking" [pp. 53-55].

4. The "lighter isotopic composition of groundwater relative to the composition of weighted mean precipitation" [in the Delaware Basin] was noted, and attributed to "either a seasonal or an amount effect" [p. 55].

5. It was argued that "Roswell Basin groundwater has an isotopic content consistent with that of precipitation at low-to-intermediate elevations in the basin. In addition, some of the data, particularly from the Alluvial Aquifer in the Artesia area, are from aquifers that receive major portions of their recharge by direct infiltration of precipitation at low elevations and these groundwaters are also substantially lighter isotopically than the [Carlsbad] Caverns' water" [p. 56].

6. The arguments culminated in the statement that "the isotopic similarity between the Rustler water and verifiably young groundwater in the area, and the lack of isotopic exchange between Culebra and Magenta water and the carbonate matrix, imply that there is a good possibility that the Rustler is currently receiving recharge" [p. 64].

We explore and evaluate each of these major points, in view of both the data presented in this work and the conclusions reached by previous investigations of the Roswell Artesian Basin. Relevant descriptions of various aspects of the Roswell Artesian Basin are cited and briefly reviewed in turn.

1. Calculation of δD Values from $\delta^{18}O$ Values. The first step in Chapman's comparison of Delaware Basin with Roswell Artesian Basin groundwaters was to calculate expected δD values from measured $\delta^{18}O$ values according to a statistical relationship:

> On some samples, Hoy and Gross (1982) have reported only the oxygen-18 analysis and the Ogallala data in Lambert (1986) consist only of deuterium analyses. To facilitate presentation, the other isotope for these data is calculated by using the local meteoric water line determined by Hoy and Gross (1982) for the Roswell Basin. The local line is based on data from aquifers, springs, snow, and surface water, and three years of precipitation and is expressed by the following equation:
>
> $$\delta D = 7.27\ (\pm 0.38)\ \delta^{18}O + 5.36\ (\pm 1.25) \qquad [11]$$
>
> [We have assigned the equation number for convenience.] The potential error introduced by calculating a $\delta^{18}O$ or δD value is small because the samples involved are generally accepted as recent, unaltered meteoric water by virtue of either their tritium contents or their location in shallow aquifers [Chapman, 1986, p. 21].

First, the mere presence of tritium, even at levels (4-10 TU), is not conclusive proof of "recent, unaltered meteoric water." Much of the tritium-bearing water, even in the principal aquifer at depths of several tens to hundreds of feet under Roswell, is believed to be artificial recharge of irrigation return or inter-aquifer leakage arising from the drawdown-induced reversal of head differential between shallow and deep aquifers (this is the interpretation preferred by Gross et al., 1976, pp. 60-61). This will be discussed in greater detail under points 2 and 5 below. Second, and perhaps more importantly, we shall show that calculation of a δD value from a measured $\delta^{18}O$ value and a statistical relationship is subject to very large error.

Hoy and Gross (1982, pp. 35) omitted six data points "because they exhibit obvious evaporation effects and would have unduly flattened the slope and reduced the intercept." Even with these selective omissions the $\delta D/\delta^{18}O$ pairs used to calculate the least squares line show considerable scatter. Figure 30 shows the replotted data of Hoy and Gross. Five of the six omitted points are identified. The least squares line was recalculated to provide intermediate results for additional statistical parameters.

The dashed curves flanking the solid least-squares line are the confidence limits for the entire line, at the 95% level, determined by the method of Natrella (1963). This means that the "true" best least-squares fit has a 0.95 probability of lying somewhere between the dashed curves. Note that: (1) the scatter in the data is so great that most of the points fall outside the 95% confidence interval, despite the decision by Hoy and Gross to omit certain obvious deviations from unaltered meteoric derivation, and (2) several of the points retained by Hoy and Gross, although identified as "recent, unaltered meteoric water," exhibit larger deviations from the line than those omitted from the calculation. The largest of these deviations is the point for a sample from Gates well (WP14, Hoy and Gross, 1982, pp. 88). This point deviates from the line of Equation 11 by 33 ‰ in the δD direction, and 3.6 ‰ in the $\delta^{18}O$ direction. We do not presume to

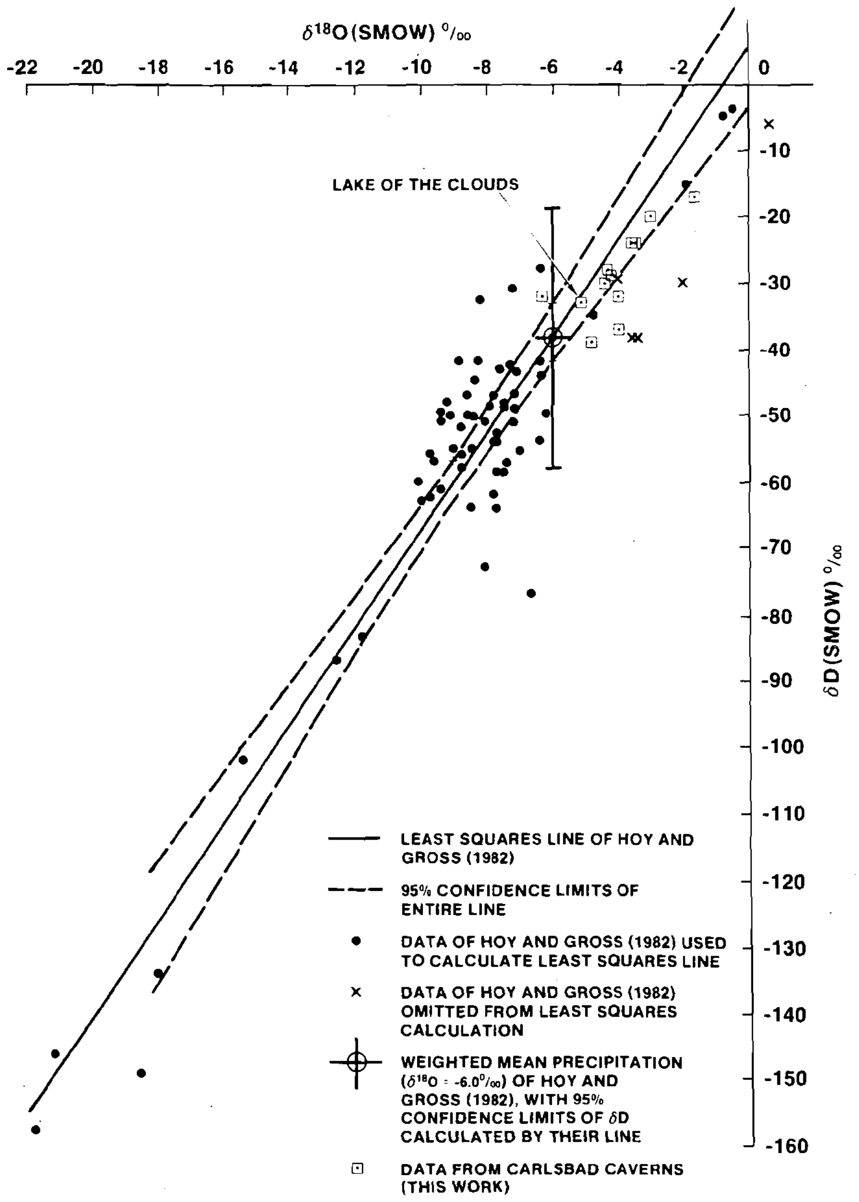


Figure 30. Stable-isotope compositions of waters from the Roswell Artesian Basin. Replotted from Hoy and Gross (1982). Least-squares line (solid), together with its confidence limits at the 95% level (dashed curves) are shown for the dots. Large "error" bar, ± 19 ‰ on the δD axis, is the 95% confidence limits for a δD value calculated from the $\delta^{18}O$ and the equation for the line. This shows that the δD value calculated for the $\delta^{18}O$ value of mean weighted annual precipitation (-6.0 ‰; Hoy and Gross, 1982) is not very precise. Isotopic compositions of Carlsbad Caverns waters, which Chapman (1986) attributes to evaporation, lie mostly within the 95% confidence limits for the line, and much closer to the line than do several of the widely scattered points used by Hoy and Gross to calculate the line.

reinterpret the data of Hoy and Gross here, and we are willing to acknowledge the possibility that this point represents "unaltered" meteoric water. We suggest that deviations from a least-squares line not be uniquely or circumstantially interpreted as evaporation (see discussion of point #5 below), when much larger deviations of points are actually used to calculate the line. Hoy and Gross admitted the likelihood that "this minor [sic] departure of the Roswell data from the meteoric line reflects a slight evaporation effect in a predominantly semiarid environment."

In least-squares fits to $\delta D/\delta^{18}O$ data pairs for natural waters, it is always assumed that the meteoric trend (described by Craig, 1961) is a statistical relationship. That is, we plot $\delta^{18}O$ on the horizontal axis by convention, not because it is an independent variable that fixes the δD value according to a rigorous mathematical function. Thus, both δD and $\delta^{18}O$ values will have a statistical variance. In actual fact, both may be related to another parameter upon which they do have a functional dependence. The essential differences in the two cases (statistical versus functional relationships) have been discussed in detail by Natrella (1963).

The degree of scatter in the data used to calculate the least-squares line becomes especially apparent when the confidence limits of a calculated δD value are estimated. Again, using the method of Natrella (1963), we derived ± 19.5 ‰ as the estimated confidence interval (at the 95% level) for any δD value calculated from Equation 11. This says that the statistics inherent in Equation 11 allow one only to say that the δD value calculated by Chapman (1986) from the weighted mean $\delta^{18}O$ value for Roswell precipitation (-6.0 ‰) can actually be anywhere between -19 ‰ and -58 ‰. This uncertainty limits the significance of comparing any calculated δD values from the Roswell Artesian Basin with any measured values from the Delaware Basin (which have a confidence interval of about ±3 ‰). Similar-sized confidence intervals will be applicable to any calculation of δD value from $\delta^{18}O$ value and Equation 11. Thus, the potential uncertainty in calculating either δD or $\delta^{18}O$ from the other is very large in the case of the Roswell Artesian Basin.

Several δD values calculated by Chapman (1986) from $\delta^{18}O$ values using Equation 11 are given in Table 18. Two of the calculations apparently used Equation 3. The reason for this is not known. These two (O8 and WR5) were not identified by Chapman (1986, pp. 23) as calculated δD values; no δD measurements were reported for these samples by Hoy and Gross (1982, pp. 86). As noted by Hoy and Gross (pp. 59), "there is a danger to overinterpret these statistically insufficient data."

One of the $\delta^{18}O$ values used by Chapman (Table 18) to calculate a δD value drew specific attention from Hoy and Gross:

> Only two samples are available for the Pecos River. The extremely light (-12.6 ‰) sample at Roswell is considered in error. A more reasonable value is the -5.5 ‰ value at Artesia (and perhaps the even heavier values of Boiling Spring), due to evaporation and the heavier oxygen 18 content of precipitation along the Pecos River than in the western mountainous belt [p. 51].

Thus, the Pecos River value at Roswell probably does not represent the relevant part of the Roswell Artesian Basin, nor should this $\delta^{18}O$ value be used to calculate a δD value for comparison with data from the Delaware Basin. As discussed above, any calculated δD value based on the $\delta^{18}O$ data of Hoy and Gross has large uncertainty.

2. <u>The Significance of Detectable Tritium</u>. Table 18 contains the tritium data used by Chapman (1986, pp. 23). This very limited subset of available tritium data does not accurately represent the distribution of the tritium measurements. According to Chapman:

TABLE 18. TRITIUM AND OTHER DATA USED BY CHAPMAN (1986)

Source[1]	Station[2]	Date[3]	$\delta^{18}O$[4]	δD[5]	TU[6]
Pecos River, Artesia	S-13	4-1-78	-5.5	C -35	36.0
Pecos River, Roswell	S-10	4-1-78	-12.6	C -86	40.7
Glorieta/Yeso	07	77-78	-7.4	C -48	12
Glorieta/Yeso	08	77-78	-8.2	C -56	33
San Andres	WR5	78	-9.2	C -64	16
San Andres	WP14	"mean"	-6.5	C -42	7
San Andres	WP14	4-78	-7.3	-42.6	
San Andres	WP14	4-79	-7.9	-48.6	
San Andres	WP16	7-77	-7.5	-48.4	16.4
Alluvium/Gatuña	WA10	75-78	-7.1	C -46	6.3
Alluvium/Gatuña	WA11	77	-7.2	-51.1	6.8
San Andres	WP4	76-78	-7.1	C -46	7.3
San Andres	WP2	4-79	-7.7	-55.4	10.4
San Andres	WR14	5-77	-7.2	-47.3	9.1
[Boiling] Spring	F5	77-78	-2.7	-34.3	36.9

---

1. "Formation" as used by Chapman (1986). "San Andres" is what Hoy and Gross (1982) called "Principal Aquifer" and is not restricted entirely to the San Andres.
2. Map number of Hoy and Gross (1982). WP14 as reported here entails more than one well.
3. Sampling date. Absence of a specific date indicates that tabulated measurements are mean values, averaged from two or more samples taken on different dates.
4. ‰, vs SMOW.
5. ‰, vs SMOW. Entries marked "C" are calculated by Chapman (1986), using to the relation $\delta D = 7.3\ \delta^{18}O + 10$ (Footnote, Table 3), which was attributed to Hoy and Gross (1982). The actual relation reported by Hoy and Gross was $\delta D = 7.27\ \delta^{18}O + 5.36$ (p. 35). δD values for 08 and WR5 were not tabulated by Hoy and Gross, but were also calculated by Chapman (1986), although not so indicated in her Table 3. The relation used to calculate these two $\delta D = 8\ \delta^{18}O + 10$, Equation 3 in the text.
6. tritium units

> Only selected data from Hoy and Gross (1982) are presented here. The selection is based on tritium values higher than 4 Tritium Units (TU) to include only water which has been recharged in the last thirty years, and based on locations as geographically and topographically similar to the Carlsbad area as possible. Only lower altitude wells in the Roswell Basin are used in this study (<5000 ft msl).

Two issues here require critical comment: first, the implication that any water containing more than 4 TU has been naturally recharged in the last thirty years; second, the tacit implication that deep artesian wells whose surface elevation is <5000 ft in the Roswell Artesian Basin produce water recharged under the same conditions that prevail at Roswell, and by extension, at Carlsbad. The second matter will be addressed in more detail under point #5 below. We focus on the first here.

Figure 31 is a histogram of most tritium measurements reported by Hoy and Gross (1982). Omitted from the diagram (but not the calculation of the mean) are the extremely high TU values (up to 149) observed only in precipitation. Note the pronounced bimodal distribution. Most of the well measurements (55 out of the 67) have 10 TU or less. 10 TU represents the upper limit of background tritium concentration produced by cosmic rays before the high levels generated by atmospheric nuclear tests (Gross et al., 1976). Hence, before the early 1950s 10 TU would have been the expected tritium concentration of 100% modern groundwater rapidly recharged by precipitation. A tritium content lower than 10 TU does not require <u>any</u> modern recharge (R. Otlet, personal communication). Further, values less than ≈10 TU are not considered conclusively indicative of a large degree of hydraulic connection with the surface (Isaacson et al., 1974). Thus, the inference that all waters having > 4 TU includes "water which has been recharged in the last thirty years" is equivocal.

From Figure 31 one can determine that the median tritium concentration for precipitation in the Roswell Artesian Basin at all

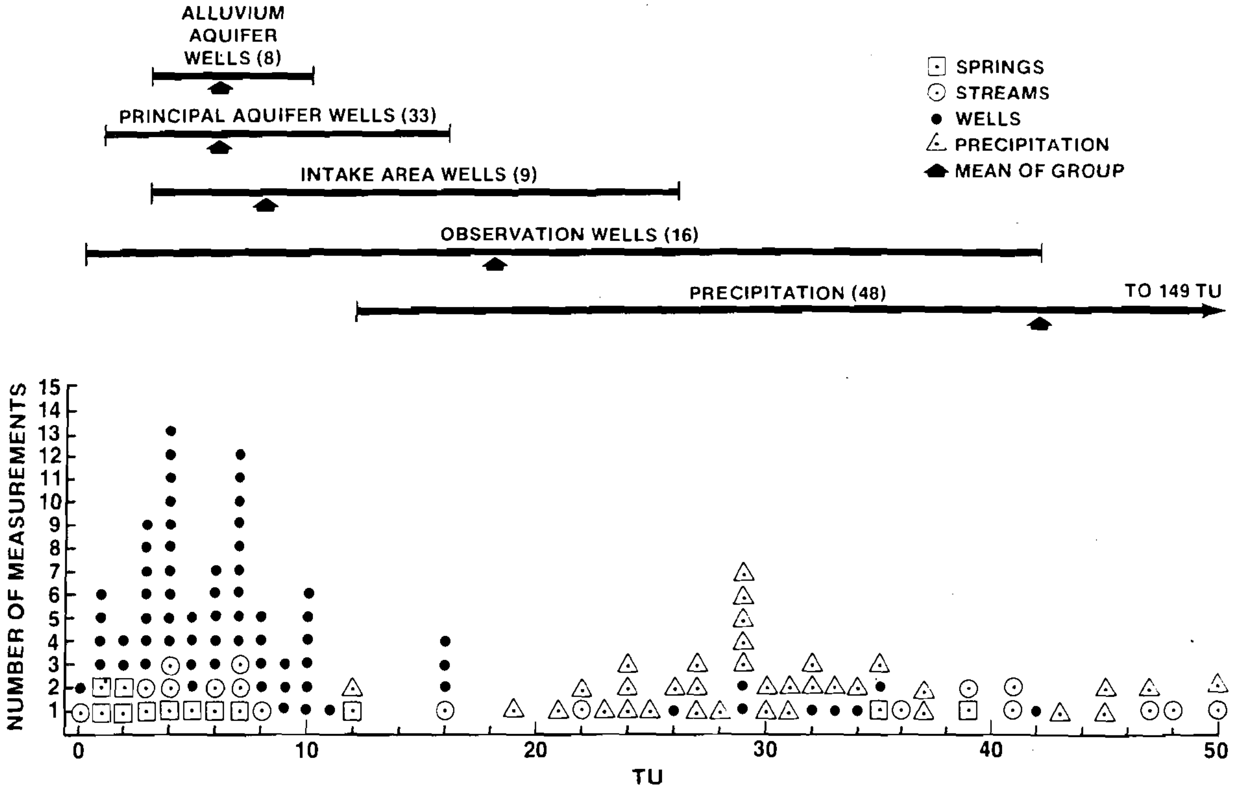


Figure 31. Histogram of tritium values for waters in the Roswell Artesian Basin. Plotted from Hoy and Gross (1982), in Tritium Units. Note the pronounced bimodal distribution. The higher-TU peak has a mean of 42 TU, but a median of 32 and a mode of 29; it is dominated by modern precipitation. The lower-TU peak is characteristic of wells in the recharge area (Sacramento Mountains) and discharge area (pumpage in the Pecos River Valley). The bimodal distribution shows that the waters in the principal (artesian) aquifer, streams running off the Sacramento Mountains, and most spring waters are not 100% modern, as their tritium concentrations are in general significantly lower than modern precipitation. Hoy and Gross, as well as previous workers, suggested that there was a large component of older groundwater contributing to these groundwater and surface water occurrences, thus diluting the tritium with water of more negative δ-values derived from higher elevations in the Sacramento Mountains.

elevations is 32 TU, close to the modal (most abundant) value of 29. Note that only a few wells, all of them in the Principal Intake Area located upslope from Roswell at higher elevations in the western mountains, have tritium concentrations in the range 26 to 42 TU. Thus, this range of concentrations (26 to 42 TU) is indicative of 100% modern meteoric recharge to the Principal Aquifer, the San Andres limestone. The San Andres, as noted above, is under artesian conditions at the major discharge area where the aquifer is extensively pumped at Roswell.

As noted by Evans et al. (1979), the effects of mixing and contamination must always be considered a likely source of high concentrations of atmospheric nuclides like radiocarbon and tritium. This advice seems to have been followed by several workers in the Roswell Artesian Basin when they were interpreting the tritium data. For example:

> Interaquifer leakage between the Principal Aquifer and the Alluvium Aquifer plays an important role in the basin's hydrologic cycle. In addition, there may be leakage of unknown extent between the Principal aquifer and deeper aquifers.
>
> Prior to the intense development of the basin during the last 25 or 50 years, groundwater discharge took place as leakage from the Principal into the Alluvium Aquifer, as springs along the Pecos river, and as base flow in the latter. Irrigation now drains a water volume in excess of natural discharge; most of the springs have ceased to flow, and base flow to the Pecos river is greatly reduced.
>
> Direction and amount of leakage between two aquifers depend on the sign and the amplitude of the head difference between the two and their hydraulic connection. In the Roswell basin the leakage is therefore a function of both precipitation and pumpage.
>
> In the early stages of basin development, the piezometric head of the Principal Aquifer was always higher than the water table of the Alluvium Aquifer. Consequently, leakage was, in general, from the Principal into the Alluvium Aquifer ... As the basin was developed and pumpage from the Principal aquifer increased, seasonal reversals began to be observed,

> although net annual leakage still remained, in general, from the Principal into the Alluvium Aquifer... . It is, however, possible that in a sequence of dry years and consequently increased pumpage the net annual leakage may also become reversed. This point may be of considerable importance for the understanding of tritium measurements... .
>
> In principle, leakage from the Alluvium to the Principal Aquifer will increase tritium concentration of water pumped from the Principal Aquifer, while leakage from deeper aquifers would dilute it [Gross et al., 1976, pp. 13-14].
>
> The synchronicity of tritium peaks throughout the basin, their failure to broaden appreciably downgradient, and their apparent absence in the Artesia area all point to interaquifer leakage as an important factor in explaining the distribution of environmental tritium in both space and time [Gross et al., 1976, p. 63].
>
> The alluvial plain on the west bank of the Pecos River has major agricultural developments. Large-scale irrigation takes most of the water from the Principal Aquifer, which is confined in this zone; the resultant depression of the piezometric head causes leakage from the alluvial aquifer into the San Andres Limestone. This leakage consists of groundwater from the alluvial aquifer as well as of irrigation return flow [Gross et al., 1979, p. 18].

Other recharge investigations cited by Gross et al. (1979) also refer to the importance of leakage and mixing:

> The first of these [tritium] studies [Rabinowitz et al., 1977] was based entirely on tritium measurements of precipitation and of wells located in the confined part of the Principal Aquifer and in the covering alluvium ... . One of the recommendations of this work was that groundwater from the Principal Recharge Area should be investigated systematically... [p. 22].

The tritium measurements of Gross et al. (1976) were interpreted by Gross et al. (1979) to indicate that:

> "...a substantial fraction of the groundwater in the ... unconfined part of the Principal Aquifer was not derived from local precipitation and infiltration. Therefore it must come from deeper aquifers which receive their recharge in outcrop areas further west [at higher elevations]" [p. 22].

The degree to which mixing has profoundly influenced the tritium concentrations in the "confined" portion of the San Andres limestone in Roswell is illustrated below. These non-zero (as low as 4 TU) tritium concentrations have been used by Chapman (1986) to conclude that significant natural recharge has occurred to the San Andres at Roswell, and by inference, at Carlsbad.

Welder (1983) has thoroughly documented the history of human development's effect on the hydrology of the Roswell Artesian Basin. For this exercise four of Welder's maps were used to construct profiles of the potentiometric contours along the west-east section line between T. 15 S. and T. 16 S.:

> Potentiometric surface of the artesian aquifer in January, 1926 (Welder's Figure 9).
>
> Potentiometric surface of the artesian aquifer in January, 1975 (Welder's Figure 12).
>
> Configuration of the water levels in the shallow aquifer, January, 1938 (Welder's Figure 16).
>
> Configuration of the water levels in the shallow aquifer, January, 1975 (Welder's Figure 20).

Figure 32A shows the comparison between profiles of potentiometric surfaces on the water table, January 1938 versus January 1975. Since the two profiles are very similar (although there is some indication of about 10 to 30 ft of drawdown by 1975) we shall assume that the error involved in representing the 1926 profile by the 1938 profile is insignificant. Figure 32B is the comparison between the Artesian (confined San Andres) aquifer potentiometric surface for January 1926 versus January 1975. In this case the drawdown is significant. In Figure 32C we see the comparison between the Artesian in January 1926 and the shallow (alluvial) aquifer in January 1938 (which we use here to approximate that of January 1926). Note that the head differential tends to drive water from the Artesian into the shallow aquifer; this has been described by Welder (1983) as the natural configuration before the extensive pumpage that began in 1891:

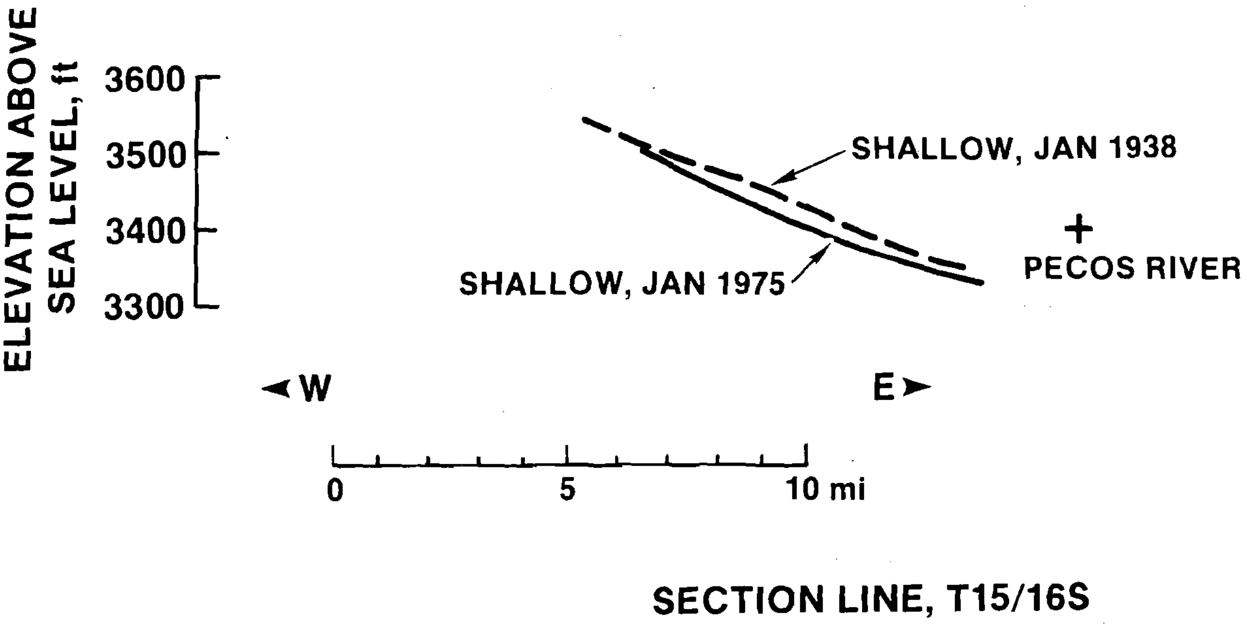
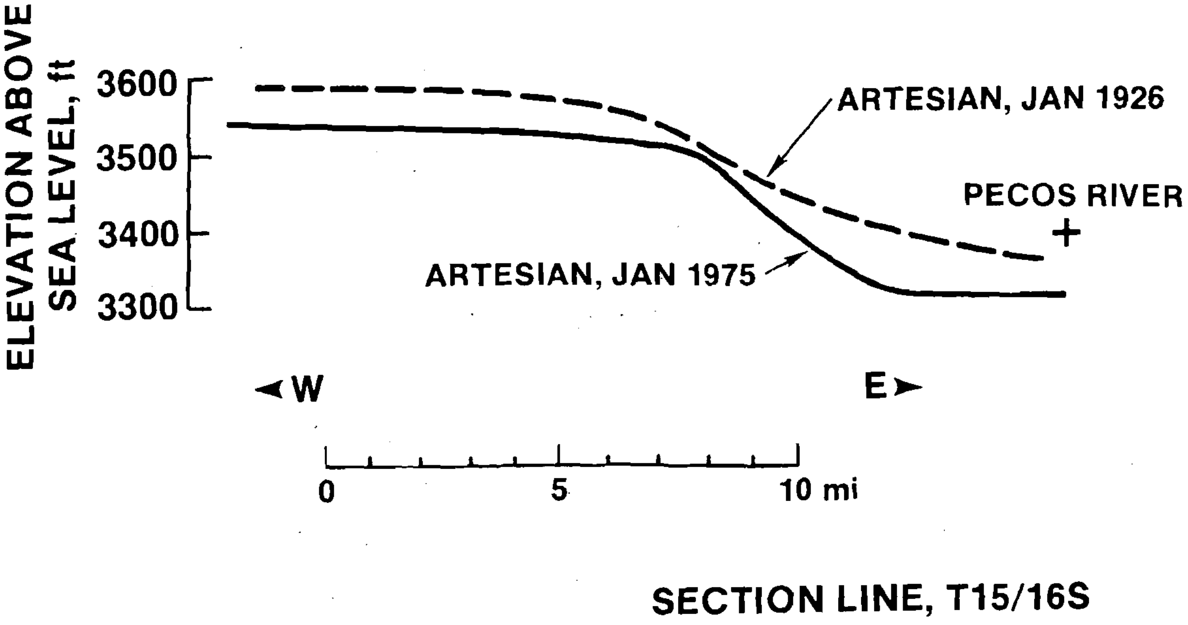
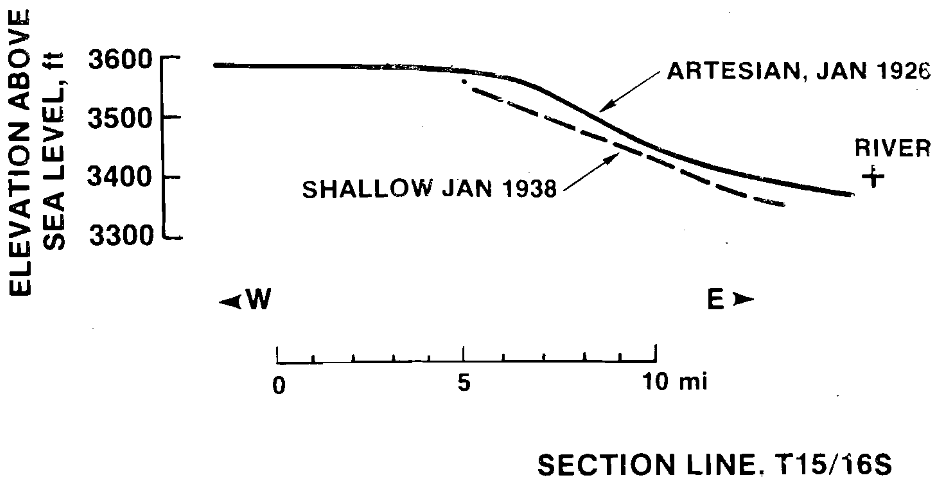


Figure 32. Potentiometric level profiles along the section line between T. 15 S. and T. 16 S., Roswell Artesian Basin. From Welder (1983). A: Shallow aquifer, January 1938 versus January 1975. Note little change due to pumpage-induced drawdown.



B: Artesian aquifer, January 1926 versus January 1975. Note significant changes due to pumpage-induced drawdown.

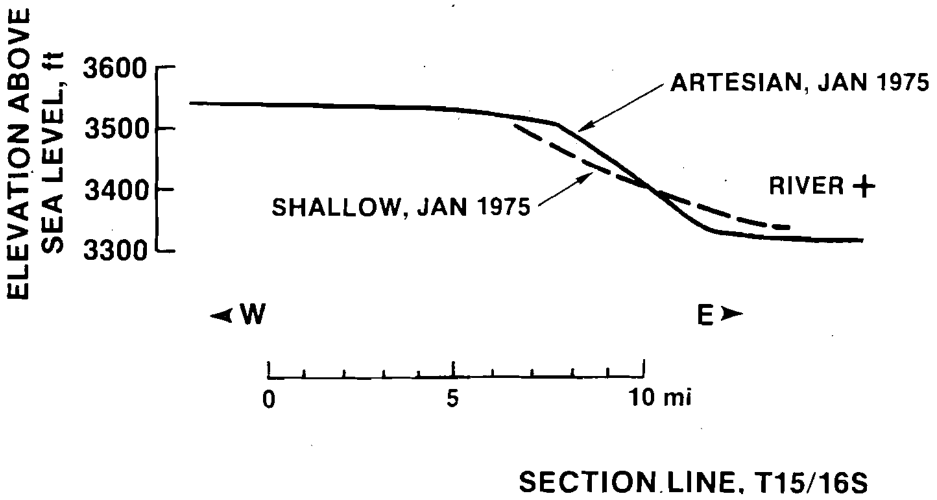


C: Artesian aquifer, January 1926 versus shallow aquifer, January 1938. This is the relatively unperturbed relationship, implying upward leakage from the artesian aquifer through the confining layer into the alluvial aquifer. This is a likely pathway for water of more negative δ-value derived from higher elevations mixing with high-tritium surface water, producing a mixture that appears spuriously light relative to the elevation at which it occurs.

> The lower boundary of the shallow aquifers normally acts as a "recharge boundary" because water generally leaks upward from the artesian aquifer through the confining bed. In recent years, however, the potentiometric surface of the artesian aquifer sometimes is lowered by pumping during the summer to a position below the shallower water table. At these times ground water from the shallow aquifer moves downward through the confining bed, and the lower boundary becomes a "discharge boundary" [p. 14].

Figure 32D shows evidence of this reversal in potentiometric head differential. The confining bed is known to be leaky:

> The quantity of water produced from the confining-bed interval is estimated to be about 10 percent of the total amount of ground water pumped in the Roswell basin...
>
> Hantush (1957, p. 69) estimated the net upward rate of leakage for the Roswell basin to be about 12,400 acre-ft. per month for January 1954 [Welder, 1983, p. 12].



D: Artesian aquifer, January 1975 versus shallow aquifer, January 1975. This is typical of the present relationship, showing local reversal of potentiometric differential, allowing downward leakage from the alluvial aquifer through the confining layer into the artesian aquifer, due to an extreme amount of pumpage-induced drawdown. This is a likely pathway for higher-tritium surface water appearing in the deeper aquifer, mixing with water of more negative δ-value derived from higher elevations, producing a mixture that appears spuriously young relative to the time of travel between its upslope recharge area and its appearance in the Pecos River Valley.

Hoy and Gross (1982, p. 63) also acknowledged leakage from the Alluvial Aquifer to the Principal Aquifer during pumping season.

Figure 33 is a mixing diagram showing various hypothetical components that appear to be combining in the Principal Aquifer to yield the δD and TU values observed by Hoy and Gross (1982). All data for the Principal Aquifer are from Hoy and Gross (1982). TU values from the Pecos River are those of Hoy and Gross, but the δD value is from this work (Table 6), since Hoy and Gross report no δD measurements for the river. The δD value for Roswell precipitation is that calculated (having inescapably wide con-

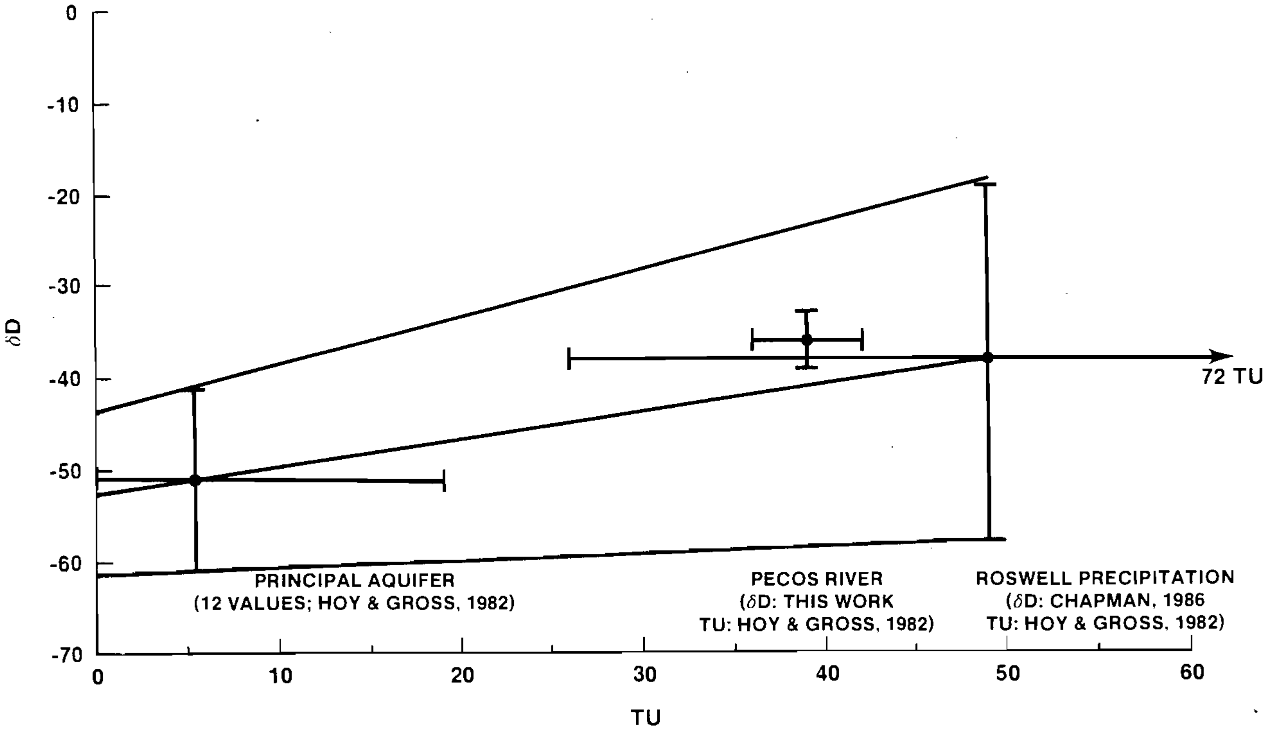


Figure 33. Mixing diagram involving δD- and TU-values of groundwaters in the Roswell Artesian Basin. Water of more negative δD- and a low TU-value combines with water having a more positive δD- and a higher TU-value to produce a mixture whose δD-value is not statistically distinguishable from the more negative endmember. The TU value of the mixture, however, is appreciable, since the TU values of the endmembers are much further apart.

fidence limits) by Chapman (1986), and the TU value is the mean of TU values for samples reported by Hoy and Gross for which they also reported δD values. The "error bars" represent one standard deviation for the river data, and the 95% confidence limits for the Principal Aquifer and Roswell precipitation. Confidence limits will always be larger than standard deviations, due to the multiplicative effect of the t-statistic (Natrella, 1963).

We see from Figure 33 that by mixing essentially "dead" (tritium-free) water from the Principal Aquifer with downward leakage of surface water (represented by Roswell precipitation that recharges the river and the Alluvial Aquifer to some degree) the nonzero TU values observed in the Principal Aquifer near Roswell are easy to obtain, with little change in δD value. The isotopic data are consistent with mixing induced by aquifer exploitation, and do not require natural recharge of the Principal Aquifer at the elevation of Roswell.

If indeed the "older" groundwater in the limestone aquifer is believed to have an age of one hundred to several hundred years, as attributed by Chapman to Gross, personal communication, its natural tritium concentration (uncontaminated by mixing) should be 0. This estimated time interval would indeed include the "Little Ice Age" climatic perturbations (cf. Epstein and Yapp, 1976), and is not, as suggested by Chapman (p. 28) "a time period too short to encompass the large scale climatic changes necessary to dramatically alter the isotopic composition of the precipitation." It was acknowledged by Chapman that "water from [Hoy and Gross'] alluvial aquifer wells ("WA" wells) and the observation wells ("O" wells) may be affected by mixing with irrigation returns from Pecos River water and from well water from the limestone aquifer."

In summary, we disagree with Chapman's assertion that all groundwaters in the Roswell Artesian Basin containing measurable tritium are "verifiably young." The only statement that can be made about tritium-bearing waters is that they may contain a component of water that has been admixed within the last 36 years, but this is equivocal for waters having between 4 and 10 TU. The time or circumstances of this mixing is unknown, without (a) a knowledge of the tritium concentration of the tritium-poor endmember, and (b) the relative amount of tritium-bearing water admitted to the mixture. Thus, groundwaters in the Principal Aquifer pumped from wells in the Roswell Artesian Basin, regardless of surface elevation, **cannot** be 100% modern (recharged <<40 years ago) if their tritium concentrations are $\leq$ 10 TU.

3. *Similarities in Stable-Isotope Compositions*. We acknowledge certain similarities between stable-isotope compositions of some groundwaters in the Delaware Basin and some of those in the Roswell Artesian Basin. We believe these similarities to be largely coincidental, and that direct comparisons and implications inferred by Chapman (1986) are misleading, in view of the *dis*similarities of the elevations and conditions of active recharge, as discussed in point #5 below. In addition, direct comparison of isotopic systematics is complicated by the mixing phenomena that have occurred in the Roswell artesian Basin during historic times.

4. *Recharge Isotopically Lighter than Precipitation*. Following the observation by Chapman (1986) that the "coincidence between the isotopic composition of the verifiably young [sic] Roswell Basin groundwater and the composition of the Rustler water is striking" (p. 55), the argument continued:

> The isotopic composition of the weighted mean precipitation in the Roswell Basin [$\delta^{18}O = -6.0 \pm 0.3$ ‰)] is somewhat enriched in heavy isotopes compared to groundwater from both the Roswell and Delaware Basins. The lighter composition of the groundwater relative to the weighted mean precipitation could be either, or both, of the following processes. First, though the majority of rainfall may occur in the summer, this is also the time of the highest evapotranspiration rate. Because of cooler temperatures, lower evaporation, and reduced plant activity, recharge from isotopically lighter winter precipitation may be favored over recharge from summer rain. A second possibility is that recharge in this arid area may occur primarily from intense, infrequent storms. Rainfall events with high total precipitation volumes are characterized by lighter isotopic compositions (Gat and Gonfiantini, 1981; Vogel [et al.], 1963). Therefore, the lighter isotopic composition of groundwater relative to the composition of weighted mean precipitation could be due to either a seasonal or an amount effect [p. 55].

Vegetation (and presumably the relationships between precipitation and evapotranspiration) where San Simon Sink and the Ogallala occur is similar to that over the WIPP site and similar elevations in southeastern New Mexico. The characteristic association of mesquite (*Prosopis juliflora*) and creosotebush (*Larrea divaricata*) is used by some botanists to define the limits of the Chihuahuan Desert (Mabry et al., 1977), and occurs near the nine communities whose wells in the Ogallala were sampled for the reported δD analyses. Thus, assuming that the Ogallala is experiencing recharge at the localities sampled, evapotranspiration and other effects on recharge, such as "intense, infrequent storms" should be manifest in Ogallala (both in the Delaware Basin and on the Texas High Plains) and alluvial aquifers in the area to the same degree as in postulated local, downward-percolating recharge to aquifers in either the Roswell Artesian Basin or the Delaware Basin. Water recharged to alluvium in San Simon Sink and to sandstone in the shallow water table of the Ogallala would incorporate effects of evapotranspiration, seasonal variations, and "amount" effects, and is here considered representative of the isotopic composition of modern groundwater (cf. Nativ and Smith, 1987; Osterkamp and Wood, 1987; Wood and Osterkamp, 1987). These waters have δD values **no more negative than -41 ‰**. These groundwater occurrences are assumed to embody mixing over several seasons of groundwater recharge to water tables. Thus, -41 ‰ is concluded to be about the most negative δD value to be expected for water presently recharging groundwater systems to the Delaware Basin at low (<4500 ft) elevations under the present climatic regime; in no case has it been observed as negative as -50 ‰ at these elevations.

It is not reasonable to argue that the isotopic composition of water recharging alluvium, the Ogallala sandstone, and Carlsbad Caverns is significantly different from that recharging any other hydrostratigraphic unit in southeastern New Mexico, given similarities in elevation, topography, and degree and type of vegetative cover. The "extreme karst conditions at the Caverns" proposed by Chapman (1986) to allow "rapid infiltration of all precipitation" is actually no different from recharge conditions anywhere else, since most aquifers in southeastern New Mexico underlie a surficial layer of sandy or gravelly soil. The karst conditions associated with caverns in the Guadalupe Mountains are generally not conducive to flooding, as there is no profound capture of drainage systems by sinkholes, as might be found in more humid karstic regions such as Kentucky, the Dinaric Alps, etc. The open fractures exposed at the surface that lead downward into Guadalupe caverns are relatively few in number, and have formed by upward stoping into the less soluble, brittle silty dolomites of the overlying Yates and Tansill Formations (Jagnow, 1979). This makes the recharge area for each local fracture system extremely diffuse, especially where such systems are commonly overlain by (a) vegetative cover no sparser than exists elsewhere in the basin, and (b) porous soils of finite storage capacity. Further, "rapid infiltration of all precipitation" is not consistent with the description of the more sporadic, infrequent infiltration described for Carlsbad Caverns by McLean (1971). Chapman (1986) has argued that "Caverns' water is more enriched [heavier] than both the mean precipitation and verifiably young [sic] groundwater in the Roswell Basin, and therefore is not representative of all young groundwater in the area." Further, Chapman relates that the "weighted mean precipitation" of Hoy and Gross (1982) has a calculated δD value of about -38 ‰. This coincides closely with the most negative limit for shallow groundwaters throughout the Delaware Basin, **including** the Caverns (-40 to -41 ‰). Thus, we see that the most negative limit of Caverns δD values is very close to Chapman's "weighted mean precipitation" (calculated) δD value, even though we have shown above that the precision of this calculation is poor. Chapman's (1986) calculated δD value, however, is not significantly different from the measured δD values observed in alluvium, the Ogallala, and the unsaturated caverns zone, where modern recharge is inferred here to be active. It is significantly different, however, from that of confined Rustler and Capitan waters. If indeed the climate (and therefore the recharge characteristics) are uniform over much of southeastern New

Mexico, there is little reason to argue that "seasonal or amount effect" would selectively deplete the deuterium and ^{18}O in any ongoing recharge to confined Rustler and Capitan waters, but not in recharge to alluvium, Ogallala, and caverns waters, the climate and recharge conditions being fairly uniform throughout the Delaware Basin.

The isotopic data used by Chapman to argue that the groundwater in the Roswell Basin is "verifiably young" on the basis of a measurable content of tritium do not compel the acceptance of the conclusion that all groundwater with a δD value of about -50 ‰ in the area is modern. This is especially true if elevation and other orographic differences are considered correlative to isotopic composition, as pointed out by Hoy and Gross (1982). In fact, the only waters reported for the elevations comparable to Roswell (and the WIPP site) by Hoy and Gross (1982) that had tritium contents identical to modern values (around 40 TU) had δD values more positive than -40 ‰, which is close to the estimated δD value for inferred modern recharge to groundwater in the northern Delaware Basin (Section 4.3.5). A component of the water from some parts of the Rustler and Dewey Lake (with δD values of -45 ‰ or less) is demonstrably Pleistocene in age or older (Section 4.5.3). In addition, groundwaters from the Rustler Formation (with δD values of -45 ‰ or more negative) around the WIPP site contain no significant tritium (see Lambert, 1987). Thus, the <u>available</u> Rustler data are consistent with the hypothesis that Rustler groundwater near the WIPP site is not receiving significant modern recharge; the availablility of such site-specific data makes inferences based on comparison with the Roswell Artesian Basin less relevant.

The "seasonal or amount effect," hypothesized by Chapman (1986) to have resulted in an isotopic composition lighter for groundwater than weighted-average rainfall, is absent in groundwaters of the Ogallala aquifer, Carlsbad Caverns, and alluvium in the northern Delaware Basin, as discussed above, if these occurrences of groundwater are receiving modern recharge. In fact, if there were such a lightening effect, the meteoric precipitation from which these groundwaters were derived would be even <u>heavier</u> than the groundwaters. However, on p. 56, Chapman stated that "some of the [Hoy and Gross] data, particularly from the Alluvial Aquifer in the Artesia area, are from aquifers that receive major portions of their recharge by direct infiltration of precipitation at low elevations, and these groundwaters are also substantially lighter isotopically than the Caverns' water." This interpretation is at variance with the findings of other workers, who have indicated that, when the groundwater systems in the Roswell Artesian Basin were not perturbed by pumpage (i.e., under "natural" conditions), the isotopically lighter water leaked upward from the artesian aquifer, which is recharged at higher elevations. That "the Roswell Basin, Carlsbad Caverns, and the WIPP area are all located in the Southeastern Plains of New Mexico and experience fairly uniform climatic conditions," (Chapman, 1986, p. 26) appears to form the backbone of comparisons between the Roswell Artesian and the Delaware Basins. If the statement were true, however, there should be no substantial "seasonal or amount effect" that is manifest in one basin but not the other.

5. <u>Elevations and Conditions of Active Recharge</u>. This issue is based on the interpretation that "Hoy and Gross (1982, p. 70) have concluded that 'Groundwaters in the Roswell Basin, therefore, represent present climatic conditions.'" This quotation needs to be put into context; Hoy and Gross immediately preceded their cited statement (p. 70) with the observation that "nothing like the highly atypical saltbrines reported by Lambert (1978) from the Carlsbad area, indicative of intense isotopic exchange between water and evaporite bedrock, seems to exist in the Roswell Basin." Thus, indeed the isotopic composition of Roswell Artesian Basin groundwaters are more indicative of largely isotopically unmodified meteoric recharge than of rock/water interaction (cf. Section 4.6), but the precise conditions of recharge

to the Principal Aquifer in the Roswell Artesian Basin seem to be a point worthy of discussion. Hoy and Gross (1982, p. 71) said that "with the two major history effects (evaporation and wallrock interaction) evaluated, it is assumed that, in general, the isotopic composition of the recharge is not significantly altered during infiltration through the groundwater system, except by mixing and dispersion, as indicated in tritium studies (Gross et al., 1976), and verified by the stable isotope values." As discussed above, the "direct infiltration through the groundwater system" into the Principal Aquifer, to which this statement refers, occurs dominantly at elevations >5000 ft. Several works have concluded that direct infiltration to the Principal Aquifer **from the ground surface** at Roswell, except through pumping-induced interaquifer leakage, is minimal.

Chapman correctly represented the conclusions of Hoy and Gross by saying that "water levels in the observation wells responded rapidly to runoff events in nearby stream courses, indicating that recharge from surface water is important in the system (Hoy and Gross, 1982)." Unfortunately, this is not sufficiently relevant to the lower elevations to allow a comparison with the Delaware Basin, since both the observation wells and the runoff in the nearby stream courses were both doubtless receiving significant amounts of water derived from precipitation at elevations >5000 ft in the recharge area for the Roswell Artesian Basin. A significant difference in δ^{18}O value was observed by Hoy and Gross (1982) for "weighted mean" precipitation at Roswell (-6.0 ‰, 3700 ft elev.) versus that at Elk (-7.1 ‰, 5700 ft elev.). No elevations >≈4000 ft are known for areas proposed to provide recharge to the Rustler, especially since a major drainage (the Pecos River), long considered a discharge boundary for local shallow aquifers, separates higher elevations to the west from lower elevations to the west.

The stream courses mentioned are the three principal drainages coursing down the east slope (dipslope) of the Sacramento Mountains west of Roswell; from north to south they are the Rio Hondo, Rio Felix, and Rio Peñasco. The importance of these streams to recharging the Principal Aquifer, which eventually gets pumped down at Roswell, has been described, for example, by Duffy et al., 1978:

> The major streams in the basin can generally be described as perennial in the headwaters and ephemeral (flow in response to rainfall) in the central and eastern parts of the basin. There are also sections of the Peñasco, Felix and Hondo rivers which can be classified as intermittent; they flow in response to seasonal sources such as snowmelt or springs [p. 14].
>
> It has been found by several investigators that channel leakage to the groundwater reservoir in the basin is considerable. Fiedler and Nye (1933) observed that stream losses from the Rio Hondo and Rio Peñasco were greater where these streams cross the Principal Intake Area. They also noted that above the Diamond 'A' Ranch headquarters [5056 ft elev.] the Rio Hondo normally flows, while between the Diamond 'A' headquarters and Hondo Reservoir [3900 ft elev.] the entire flow sinks into the limestone. The Rio Peñasco will normally flow at Elk [5700 ft elev.] while the steam gauge at Dayton [3300 ft elev.] has flow only after large precipitation events [p. 25].

The effects of these losing streams were succinctly summarized by Hoy and Gross (1982):

> The isotope composition of wells in the Roswell area may reflect the high-altitude runoff which disappears into the San Andres and lower formations along the course of the Rio Hondo. Generally speaking, recharge to the northern wells (Arroyo del Macho and Rio Hondo drainage system) seems to include more contributions from higher altitudes than recharge to wells near the Peñasco. The Rio Hondo drainage includes Sierra Blanca (11,977 ft a.m.s.l.), highest peak in the Sacramento Mountains, in its source area. Arroyo del Macho drains the northeast side of the Capitan Mountains (10,179 ft a.m.s.l.). The Peñasco drainage basin includes vast highlands of somewhat lower elevation. As investigated elsewhere (Rehfeldt and Gross, 1982), deep leakage (from underlying

> aquifers, notably the Yeso Formation) supplies a significant fraction of the groundwater, and the isotopic composition of this source is presumably determined by the elevation of its outcrops along the Sacramento-Sierra Blanca-Capitan mountain front [pp. 59-60].

Stream systems that disappear to become recharge in the Principal Intake Area (where the San Andres outcrops near the surface on the dipslope of the Sacramento Mountains) would derive virtually all their water from upstream at higher elevations. Thus, the isotopic composition of water pumped out of the Principal Aquifer at Roswell would be characteristic of meteoric recharge at higher elevations, and not the isotopic composition of 100% directly-infiltrated precipitation at Roswell. This is illustrated in Figure 34. The diagram has mean $\delta^{18}O$ values and standard deviations and/or 95% confidence limits for several classes of waters discussed by Hoy and Gross (1982): springs, production wells in the Principal Intake Area, observation wells in the Principal Intake Area, pumped wells in the Principal Aquifer in the Pecos River Valley, pumped wells in the Alluvial Aquifer in the Pecos River Valley, precipitation at Elk (5700 ft elev.), and precipitation at Roswell (3670 ft elev.). Note the difference in mean $\delta^{18}O$ values for Roswell and Elk, which are at significantly different elevations. Although this difference is not as large as expected for such a difference in elevation (Hoy and Gross, 1982, p. 45) it is nevertheless apparent. Note that the 95% confidence limits of the weighted mean $\delta^{18}O$ value for precipitation at Roswell **DO NOT** overlap those of the "intake wells" or "observation wells" in the Principal Intake Area for the Principal (confined) Aquifer. Thus, the isotopic composition of wells pumped from the artesian Principal Aquifer at Roswell cannot be taken as representative of recharge at the elevation or climatic conditions at Roswell. The reason for overlap between precipitation and water in the Alluvial Aquifer is obviously mixing, since direct precipitation is taken as a recharge source for the Alluvial Aquifer, together with a substantial amount of tritium-poor leakage from the Principal Aquifer below, under "natural" (non-pumped) conditions. Partial recharge of the Principal Aquifer

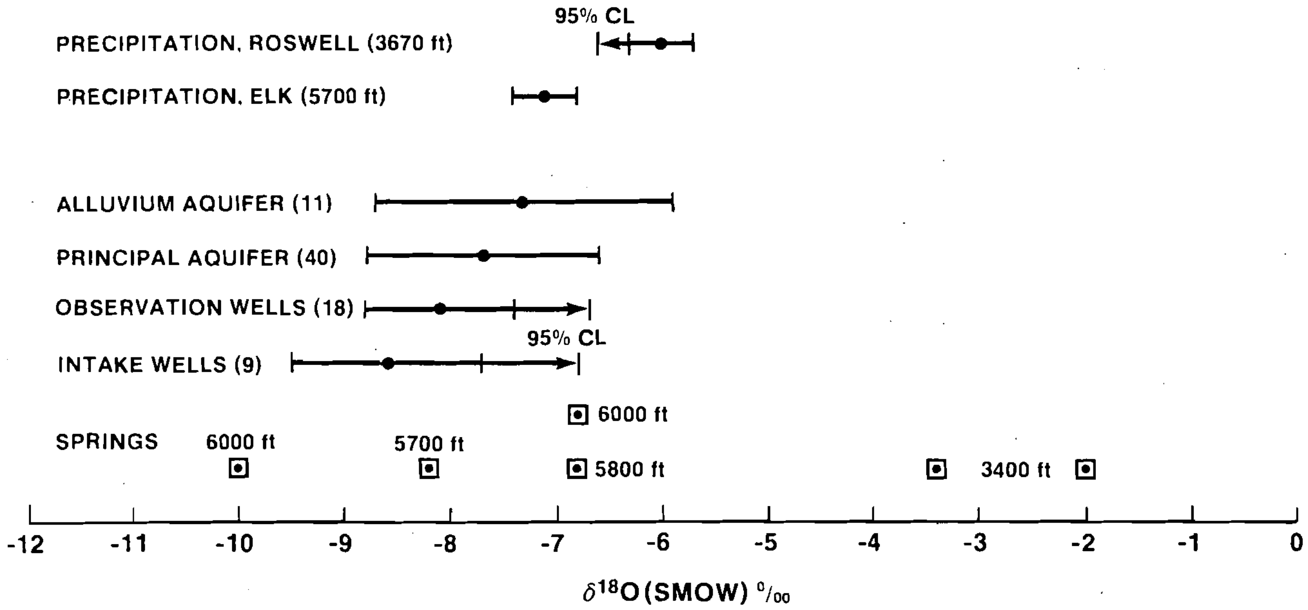


Figure 34. Mean $\delta^{18}O$ values for waters in the Roswell Artesian Basin. Calculated from Hoy and Gross (1982). Means, standard deviations, and confidence limits at the 95% level are shown. Note that the 95% confidence limits for the three-year record of mean weighted precipitation (-6.6 to -5.4 ‰) at Roswell, at an elevation of 3670 ft, do not overlap with the 95% confidence limits for either observation wells or intake wells. This shows that recharge of the principal (artesian) aquifer in the principal intake area on the dipslope of the Sacramento Mountains is statistically distinct from precipitation at Roswell. Thus, recharge to the principal aquifer is dominated by precipitation falling at higher elevations, not at Roswell. The principal aquifer receives water not only from recharge at higher elevations but also from leakage through the confining layer when extreme pumpage-induced drawdown reverses the potentiometric differential (cf. Figure 32).

due to leakage from above at Roswell, during times of extreme pumpage, is a probable cause of the isotopic overlap between precipitation and the Principal Aquifer, as discussed above in point #2.

For these reasons we disagree with the statement (Chapman, 1986, p. 56) that "Roswell Basin groundwater has an isotopic content consistent with that of precipitation at low-to-intermediate elevations in the basin. In addition, some of the data, particularly from the Alluvial Aquifer in the Artesia area, are from aquifers that receive major portions of their recharge by direct infiltration of precipitation at low elevations and these groundwaters are also substantially lighter isotopically than the Caverns' water." Not only has it been show by several workers that the Roswell Artesian Basin is recharged naturally by water from dominantly higher elevations in the Sacramento Mountains, but groundwaters from the Roswell Artesian Basin bear a heavy isotopic imprint characteristic of mixing from several sources. It is this complex, partially anthropogenic mixing, in addition to its recharge occurring dominantly at significantly higher elevations, that make the Roswell Artesian Basin a poor choice for a natural analog to groundwater recharge in the Delaware Basin.

Note Chapman's argument that "the enrichment in heavy isotopes in water in Carlsbad Caverns could also be explained by evaporation from pools in the humid environment of the cave...Indeed, an evaporation 'window' leading from the value for weighted mean precipitation and outlined by evaporation-line slopes between 2.5 and 6, encompasses almost all of the Caverns' data ([Chapman's] Figure 14)." While one could argue that an evaporation trajectory of slope 6 in $\delta D/\delta^{18}O$ space is typical of high humidity, the high relative humidity of the Caverns does not lend itself to other evaporation trajectories (as low as 2.5). Note also that Lake of the Clouds, a pool specifically cited by Chapman (pp. 7-8) was used as an example of evaporation from a pool where "the evaporation surface is large and changes in barometric pressure result in active air circulation." First, one who has been to Lake of the Clouds can attest to the relatively stagnant air in the deepest surveyed point in Carlsbad Caverns. Second, water from Lake of the Clouds was included in our early analytical program (Table 4; Figure 6; Figure 30). It shows little deviation from the meteoric relationships of Craig (1961), Epstein et al. (1965;1970), or Hoy and Gross (1982). Thus, one cannot rationally argue evaporation for a point that does not significantly deviate from a line calculated from points that show <u>much more</u> deviation, but which were themselves not considered artifacts of partial evaporation.

Finally, Chapman's statement (p. 62) that "no groundwater in southeastern New Mexico has been found that has an isotopic composition within the range defined by water from Carlsbad Caverns," is not strictly true. As shown in Section 4.3.5 (Figure 9), water from both San Simon Sink (alluvium, water table) and James Ranch Well (Dewey Lake) have meteoric δD values statistically indistinguishable from δD values of Ogallala waters (both those of Yapp for New Mexico and those of Nativ and Smith (1987) for the Texas Panhandle; Section 4.3.4) and from the most negative δD values of Carlsbad Caverns waters. We therefore consider that the Carlsbad Caverns waters are more representative of recharge conditions in the northern Delaware Basin than are groundwaters from the Principal (artesian) Aquifer in the Roswell Artesian Basin, considering the high degree of mixing of multiple sources of water together with significantly higher elevations of recharge in the latter.

6. <u>Isotopic Exchange Between Water and Carbonate</u>. "Lack of isotopic exchange between Culebra and Magenta water and the carbonate matrix" was used by Chapman (1986, p. 64) to argue in part that "there is a good possibility that the Rustler is currently receiving recharge." First, as discussed in Section 4.6, there has been isotopic exchange between some Magenta carbonate

and water with an isotopic composition similar to other Magenta/ Culebra waters from the WIPP site and Nash Draw, in borehole WIPP-33. Second, as also discussed in Section 4.6, no implication of great age should be drawn from the mere presence of rock/water interaction reflected in isotopic exchange. The exchange can take place rapidly (e.g., even in the laboratory at ambient temperatures, under conditions of dissolution coupled with reprecipitation) or slowly. Many of the confined Capitan and Rustler waters occur in isotopically unaltered carbonates; independent geochronologic evidence indicates some of them are very old (Section 4.5.3).

Summary. We do not consider comparisons between the Roswell Artesian Basin and the Delaware Basin appropriate, nor do we consider the former a suitable natural analog for the latter. Direct comparison of individual values of δD, $\delta^{18}O$, and tritium concentrations cannot be used to argue that recharge to the Rustler Formation is recent, especially in view of the significant difference between demonstrably recent recharge in the Delaware Basin and the Rustler, and of the absence of tritium in the Rustler at the WIPP site. The comparison is complicated by complex mixing phenomena in the Roswell Artesian Basin, due in part to human development, which affects the isotope systematics. It is also complicated by several sources of recharge at various elevations, due to a large orographic effect imposed by a mountain range that forms a major source of recharge in the Roswell Artesian Basin. Neither factor is present in the Rustler Formation in the northern Delaware Basin.

Several factors can and do complicate comparison of different isotopic studies and hydrologic basins. For example, high degrees of precision should not be assigned to statistical relationships, or to calculations resulting therefrom, or to comparisons between such calculations and actual measurements elsewhere. Rigorous functional significance should not be ascribed to Equation 3, the "meteoric water line," implying that all meteoric precipitation or meteorically derived groundwaters lie precisely on the line by definition, and that all deviations therefrom are significant nonmeteoric perturbations. Equation 3 is a **statistical** relationship, although the slope of 8 probably has physical significance relevant to **worldwide** meteorological conditions. We have argued for most of southeastern New Mexico that significant deviations from the "line" shown by meteoric waters can arise without the agency of either evaporation or rock/water interaction. A rigorous construction of the "meteoric water line" unduly restricts the identification of isotopically unmodified precipitation and groundwater recharge derived therefrom, especially if other available data indicate that even waters isotopically deviated from the "meteoric water line" are reasonable representations of unmodified precipitation. We have shown the large confidence limits associated with the predictions of δD values, calculated from measured $\delta^{18}O$ values and a statistical relationship for meteoric waters in the Roswell Artesian Basin. Predictions of δD in the Roswell Artesian Basin are not sufficiently precise to allow a meaningful comparison between δ-values of complex mixtures of groundwaters in the Roswell Artesian Basin and those of isotopically homogeneous waters from the Rustler Formation near the WIPP site.

Given the variations in temperature, elevation, and orographic effects, similarities in stable-isotope compositions for groundwaters of different provenance should not be considered indicative of identical climatic conditions, unless recharge at various provenances can be shown to be contemporaneous. Conversely, stable-isotope differences coupled with age differences are powerful evidence against climatic similarities in recharge conditions.

Measurable tritium in groundwaters of the Roswell Artesian Basin that has arisen from mixing and/or contamination should not be interpreted as verifiably modern natural recharge. Similarly, waters with a stable-isotope composition similar to high-tritium waters elsewhere should not be even tentatively interpreted as "young", especially when age determinations of Delaware Basin groundwaters contradict such an interpretation.

Nonzero tritium measurements in the Roswell artesian (San Andres) aquifer cannot be used to argue for "verifiably young groundwater" recharged under the climatic conditions prevalent at the elevation of Roswell, given the high probability of pumping-induced downward leakage of surface water through the confining layer in certain seasons. Similarly, more negative δ-values from the Alluvial Aquifer near the surface at Roswell cannot be used as natural characteristics of modern recharge, given the natural upward leakage of water from the artesian aquifer (in the absence of pumping), which is actually recharged at higher elevations, and therefore brings water of more negative δ-values down to lower elevations. It is unfortunate that two historical perturbations (high post-1950 levels of atmospheric tritium and artificial post-1890 reversal of potentiometric levels between aquifers) have led to an extremely complex pattern of mixing, and even recycling of irrigation return, which was originally pumped from two distinct aquifers. Tritium levels of the hydraulically unperturbed system are unavailable. As it is, the Roswell Artesian Basin itself is **not** at steady state; withdrawal in excess of recharge has led to steadily declining water levels since 1890. Consequently, the complicated isotopic systematics of a system **not** at steady state should not be compared with another system, such as the Rustler Formation, and used to argue that it is at steady state. All factors considered, the basis for drawing analogies between the Roswell Artesian Basin and the Rustler is tenuous.

5. CONCLUSIONS AND IMPLICATIONS

5.1 Isotopic Composition of Modern Local Recharge

We have characterized the stable-isotope compositions of groundwaters in the northern Delaware Basin that appear, according to hydraulic observations, to be actively recharged with a short travel time between surface and groundwater occurrence. The most isotopically diverse collection of such waters in the Basin is from the unsaturated zone of the Capitan Limestone, in Carlsbad Caverns. Allowing for partial evaporation and precipitation derived from isotopically heavier storms (say, air masses from the Gulf of Mexico bringing summer thunderstorms), the lower limit of δD value in the Caverns is around -40 ‰. Other groundwaters from near-surface water-table occurrences in alluvium and sandstones, including the Ogallala Formation, have isotopic compositions that correspond with this lower limit. We conclude that the δD value of effective modern meteoric recharge in the northern Delaware Basin at elevations less than 4500 ft is no more negative than about -40 ‰.

5.2 Recharge to the Rustler Formation

Robinson and Lang (1938) postulated that "water percolating into the ground in the vicinity of Bear Grass Draw may pass into the truncated edges of the lower Rustler formation and may migrate south and east as porosity and structure determine." Hunter (1985) summarized current thinking regarding recharge at Bear Grass Draw reaching the WIPP site and Nash Draw:

> The current configuration of the water table in Bear Grass Draw and Clayton Basin does not support Lang's suggestion. Bear Grass Draw does not seem to have an important impact on water levels one way or the other, although there are so few water wells in the area that no firm conclusion can be drawn. Recharge to the Rustler Fm. seems to be occurring at the ground-water ridge between Lakes McMillan and Avalon [in] Northern Eddy County and also to the east of Clayton Basin. Local

> ground-water discharge from the Rustler Fm., Triassic rocks, and alluvium takes place in Clayton Basin [p. 34].
>
> If the discharge area and ground-water mound are natural, and therefore permanent under existing climatic and geologic conditions, then much of the current study area is hydraulically separate from the portions of the aquifers in and near the WIPP site. If, on the other hand, the ground-water mound is an artifact of brine disposal by the potash industry, then after cessation of refining, evaporative discharge in Clayton Basin will decrease and the hypothesized flow from Bear Grass Draw to Malaga Bend might become a reality [p. 52].

If we consider the isotopic composition of the modern precipitation that actually infiltrates to be somewhere in the field of demostrably modern meteoric recharge that we have established on the basis of waters from the vadose (unsaturated) Capitan, alluvium, and water-table occurrences, and we assume that this composition prevails near Bear Grass Draw as well as in other parts of the northern Delaware Basin, then modern recharge at Bear Grass Draw, or anywhere else in the northern Delaware Basin, if any, is minimally contributing to the groundwater in the Rustler Formation at the WIPP site or in Nash Draw under existing climatic and geologic conditions. Recharge to the Rustler Formation could have taken place near Bear Grass Draw, however, during an erosional cycle that stripped the overburden from the Rustler in that area (J. W. Mercer, personal communication). The climatic conditions that governed that hypothetical episode of recharge would probably have been significantly different from those prevailing in the present cycle of intermittent fluvial and eolian alluvial and colluvial deposition; we would expect that recharge episode's isotopic signature as well to be different from that of the present. A few prominent erosional/depositional cycles are preserved in the geologic record, such as that around Gatuña time, 600,000 years ago (Bachman, 1985); others may have existed before and after that time, but if so, evidence of them has since been obliterated. Age determinations of Rustler waters indicate (a) no significant concentrations of measurable tritium at the WIPP site, and (b) isolation of Rustler water from the atmosphere for the last 12,000 to 16,000 years. Thus, the difference in isotopic compositions between Rustler waters and waters receiving demonstrably modern active recharge, from precipitation at surface elevations <4500 ft, is consistent with the hypothesis that the last major recharge event for Rustler waters was in the late Pleistocene. We extend this hypothesis to apply to all confined groundwaters in the northern Delaware Basin that have stable-isotope compositions similar to the three dated Rustler waters and the one dated Dewey Lake water, and which have no hydraulic connection with mountainous recharge areas at elevations >4500 ft. We conclude that the isotopic differences between confined Rustler and inferred modern recharge waters reflect the natural relationship, established before the onset of potash refining, whether or not such human activities have generated a groundwater divide between Bear Grass Draw and the principal study area in Figure 2. If this is the case, we expect that the cessation of potash refining will have little effect on the already-small contribution, if any, of active recharge originating at Bear Grass Draw or in any other postulated area, with respect to east-central Nash Draw and the WIPP site. This is irrespective of the nature of the apparent groundwater divide, unless the climate changes to favor increased amounts of recharge to confined groundwater systems. As suggested by Hunter (1985) a simple moderate increase in rainfall may not be sufficient to significantly increase the amount of such recharge, if surface drainage and runoff become better developed.

It is probably not possible to infer a modern recharge area in the Rustler simply by following the presently observed potentiometric contours upgradient, especially since the permeability significantly decreases in that direction; the water now being recovered may be a relic of past climatic conditions no longer prevalent, and the present potentiometric distribution in the Rustler may be a transient response to continued or enhanced discharge. Furthermore, potentiometric contour lines are interpolated generalizations of the pressure distribution in a given hydrostratigraphic unit, and at any specific point it may not be valid to draw flow lines perpendicular to the local inferred hydraulic gradient.

Just as it is difficult to infer the area upgradient to the east of the WIPP site to be an active recharge area, it is difficult to infer a significant amount of direct infiltration at or near the WIPP site. The Mescalero caliche is virtually unbreached, except at borehole WIPP-33 west of the WIPP site, where an obvious surface depression is underlain by a zone of cavities and inferred collapse in the Rustler gypsum. The only evidence of carbonate precipitation in isotopic equilibrium with the "average" Rustler water was found in the subsurface carbonate aquifer rock at WIPP-33. Although we do not know the age of this secondary carbonate, we surmise that it formed at a time when spring-sapping at WIPP-33 and spring discharge nearby in Nash Draw were active, about 20,000 years ago, based on horse and camel fossils found in the spring deposits (Bachman, 1985). To the north and east, where the potentiometric levels in the Rustler Formation are generally higher, the caliche is regionally continuous, except in the northeastern lobe of Nash Draw due north of the WIPP site (see Figure 19). The existence of caliche over much of the WIPP site area attests to climatic conditions favoring formation and/or preservation, rather than dissolution of caliche; the latter condition would be a necessary consequence of significant amounts of downward-infiltrating recharge.

Another possible reason for the lack of apparent recharge to the deeper Rustler groundwaters may be underflow, implying multiple channels of flow within a single layer such as the Culebra. This would imply that a different system of channels is carrying groundwater derived from modern meteoric precipitation, while the main channel system sampled thus far carries fossil water. This possibility is not likely, given the isotopic homogeneity of the Rustler groundwaters over a wide area (i. e., in the many holes sampled, only near-surface Rustler waters bear an isotopic resemblance to modern recharge). Also, the many geophysical and hydrologic tests performed in holes drilled with air have sought to identify all possible detectable fluid-bearing zones (cf. Mercer and Orr, 1979); in each case the 8-m-thick dolomitic Culebra member appears to have one principal saturated horizon within it that could be tested and sampled. Results of radioiodine tracer surveys, however, have suggested that the thickness of the saturated fluid-producing zone within the Culebra, for example, may be less than half its total thickness.

One could also argue that groundwater in the Rustler Formation is flowing from a modern recharge area outside the immediate vicinity of the WIPP site and Nash Draw; there are, however, observations that limit the credibility of such an argument. Due to the virtually identical isotopic compositions of Rustler groundwaters and Capitan groundwaters east of the Pecos River (i.e., older Capitan waters discussed by Barr et al., 1979, as opposed to actively recharged Capitan water in Carlsbad Caverns first characterized isotopically by Lambert, 1978), these two regionally pervasive bodies of groundwater must have been recharged under similar climatic conditions. One could argue that recharge to much of the Rustler and Capitan occurred at significantly different times, between which a much different climate prevailed. In view of the identical isotopic compositions, it would be extremely fortuitous to reproduce climatic conditions and isotopic compositions at different geologic times to such a precise degree, given the high sensitivity of isotopic compositions to local conditions. Although this hypothesis remains to be tested through an examination of the paleoclimatic record throughout the Pleistocene in southeastern New Mexico, we tentatively consider recharge to the Capitan east of the Pecos and of the deeper Rustler horizons to be contemporaneous. Lambert (1978) argued that rain presently falling on conspicuous outcrops of Capitan limestone in the Guadalupe Mountains has not influenced the isotopic composition of groundwater in the rest of the Capitan.

If modern recharge is thus somehow inhibited within such a permeable unit as the Capitan, it is difficult to infer a significant amount of modern recharge entering the Capitan from adjacent hydrostratigraphic units (the lagoonal-facies section including the Tansill to the San Andres, for example), since permeability contrasts would be greater across stratigraphic boundaries than within a unit such as the Capitan (cf. Hiss, 1975). Thus, even though areas such as the Sacramento Mountains to the north would be expected to receive isotopically lighter recharge, areas far removed from the northern Delaware Basin are not considered likely active recharge points for the Rustler Formation (or the Capitan) within the northern Delaware Basin.

5.3 Discharge from the Rustler Formation

We find no evidence to support the inference that Surprise Spring and similar discharges from the Tamarisk member of the Rustler Formation in southwestern Nash Draw are currently discharging directly from the principal water-bearing units that carry water from the WIPP site through the Rustler Formation, particularly the Culebra member. In fact, stable-isotope, solute, and hydraulic evidence indicate that Surprise Spring and even the near-surface water in the Culebra at WIPP-29 are part of a shallow groundwater system, probably under largely water-table conditions, that derives its recharge from surface water largely imported by potash refiners that finds its way into the 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, which probably mixes with the other waters before ultimately discharging into the Pecos River from the alluvium near Malaga. This shallow local groundwater system has generated ponds in Nash Draw in addition to the only permanent lake, Laguna Grande de la Sal. As suggested by Hunter (1985), this local system may diminish in importance with the cessation of potash refining. It may also increase in importance with an increase in rainfall that finds its way into the gypsum karst. In any case, Rustler water from the WIPP site does not appear to be discharging at the surface in southwestern Nash Draw at the present time, under the present climatic and geological conditions.

5.4 Paleoclimatic and Hydraulic Implications

The isotopic data suggest that modern meteorically derived water that can be inferred to recharge local groundwater bodies at the present time is distinct from that in most of the Rustler near the WIPP site. The corollary of this conclusion also appears to be true: the Rustler groundwaters tapped by WIPP holes (with the possible exception of WIPP-29 Culebra) are not receiving significant amounts of modern meteoric recharge. The water that actually infiltrates, ultimately to recharge local groundwater bodies is not necessarily identical in isotopic composition to any inferred weighted-average value of the modern precipitation accumulating at the surface.

One implication of a trivial amount of modern recharge at and near the WIPP site is that groundwater may be draining from the Rustler Formation with a large change in storage, i.e., with no recharge and an inferred discharge at Malaga Bend on the Pecos River, the change in storage would be the dominant nontrivial variable in the water-balance equation. This in turn implies that the Rustler groundwater system over the WIPP site and in much of Nash Draw is not at steady state with respect to any regional "water balance" or "water budget".

Another implication that cannot be entirely dismissed is permeability changing with time. Although the permeability that is measurable in holes today is relatively low by commercial water-well standards, the permeability may have been higher in the past, decreasing as dissolved material precipitated in pore space when the recharge rate fell. Conversely, the paleopermeability may have also been lower at various times in the past, rising with the influx of fresh recharge that could have dissolved additional rock and enlarged the pore space. Although such time dependence in properties has not yet been conclusively demonstrated, portions of the Rustler Formation may contain stagnant fossil water entrapped during an episode of permeability reduction. Through a meticulous examination of secondary mineralization (such as gypsum veining), it may be possible to deduce a paragenetic sequence of multiple generations of permeability changes; it may even be possible to characterize the waters that participated in these changes, and determine their age from the isotopic systematics of the secondary mineralization. Multiple generations of water migrating through the Rustler Formation may account for the dissolution patterns of the halite and gypsum, and may also account for the complex distribution of solutes in the groundwaters observed today.

An important implication of fossil water in the Rustler 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 (>10,000 years ago), nor will they necessarily be relevant over the next 10,000 years. The packrat-midden evidence of Van Devender (1980) shows that in the immediate vicinity of the Delaware Basin, a wetter climate prevailed more than 10,000 years ago; the present desert scrub plant communities have been stable in the last 4000 years. 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.

The concept of "fossil" (i. e., relic of former recharge conditions) water being "mined" (removed without replacement) is not unique to the northern Delaware Basin. Yapp (1985) reported a body of groundwater in the Albuquerque Basin whose isotopic composition was distinct (δ values 10 ‰ more negative) from inferred recharge from either the Rio Grande or the Sandia Mountains. None of the three Albuquerque Basin groundwater bodies had isotopic compositions that corresponded exactly with the weighted-average value of modern surface precipitation. Yapp tentatively concluded that the isotopically lighter water at greater depth was a relic of a past, perhaps wetter and/or cooler, climatic regime. This conclusion was made in the absence of dating studies of the water. Hypotheses involving paleowater inferred from only stable-isotope data are neither new nor revolutionary; the fact that isotopically lighter waters from the Delaware Basin are apparently old according to radiocarbon determinations, however, is a compelling argument for a dominant amount of paleorecharge in the northern Delaware Basin.

There is a fairly wide distribution of isotopic compositions in waters in Carlsbad Caverns, and a profound separation between inferred isotopic values of modern meteoric recharge (including waters from San Simon Sink, Surprise Spring, WIPP-29 Culebra, and the shallow Dewey Lake as well as from Carlsbad Caverns) and values of most Rustler groundwaters. These observations emphasize the need to obtain an accurate representation of the isotopic composition of modern infiltrating precipitation for the Delaware Basin, in order to provide additional testing of the hypothesis that groundwaters in the Rustler Formation over the WIPP site and in most of Nash Draw are not receiving significant modern recharge.

5.5 Evaporites, Oilfield Brines, and Rock/Water Interactions

We have concluded here that fluid inclusions from the Salado halite core of ERDA 9 have not arisen from simple binary mixing of meteoric Rustler-type waters and water released from the dehydration of gypsum. The concordant K-Ar and Rb-Sr radiometric dates on a wide variety of widespread Salado minerals gives no indication of post-Jurassic recrystallization resulting from upward migration of deeper fluids through the Salado to participate in such mixing. We conclude that the ERDA 9 fluid inclusions have arisen from the same types of rock/water interaction that generated the ERDA 6 brine occurrence and the eastern extension of the "basal brine aquifer" (Rustler/Salado contact) near the WIPP site. Deeper oilfield brines from sandstone in the Bell Canyon Formation and Morrowan limestone have isotopic compositions that can be generated by relatively simple rock/water interactions involving carbonates; neither units contain evaporites, and the solute compositions of their contained waters are not consistent with mixing between evaporite brines and meteoric waters.

Evidence of isotope exchange between Ochoan rock and typical meteoric Rustler-type water has been found only in the Magenta member at WIPP-33, and in gypsums from the Rustler and Dewey Lake at AEC 8. This shows that: (a) dolomite/water interactions are largely dissolutional, involving removal of material rather than exchange in the solid state or dolomite recrystallization, (b) the carbonate phase likely to be reprecipitated from Rustler-type waters is calcite rather than dolomite, and (c) massive and bedded gypsum in the Rustler and selenite veins in the Dewey Lake were last recrystallized in the presence of Rustler-type water, and are neither relics of original precipitation from sea water nor products of recrystallization in the presence of modern meteoric groundwater characteristic of the northern Delaware Basin.

REFERENCES

Adams, J. E., 1944, "Upper Permian Ochoa Series of Delaware Basin, West Texas and Southeastern New Mexico," Am. Assoc. Petrol. Geol. Bull., V. 28, pp. 1596-1625.

Alexander, J. and J. N. Andrews, 1984, "Hydrogeological Investigations in the Harwell Region: The Use of Environmental Isotopes, Inert Gas Contents, and the Uranium Decay Series," Fluid Processes Research Group, British Geological Survey Report FLPU 84-7.

Allison, G. B., 1982, "The Relationship Between ^{18}O and Deuterium in Water in Sand Columns Undergoing Evaporation," Jour. Hydrology, V. 55, pp. 163-169.

Allison, G. B., W. J. Stone and M. W. Hughes, 1985, "Recharge in Karst and Dune Elements of a Semi-arid Landscape as Indicated by Natural Isotopes and Chloride," Jour. Hydrology, V. 76, pp. 1-25.

Anderson, R. Y., 1981, "Deep-seated Salt Dissolution in the Delaware Basin, Texas and New Mexico," New Mexico Geol. Soc. Special Publication No. 10, pp. 133-145.

Bachman, G. O., 1980, "Regional Geology and Cenozoic History of Pecos Region, Southeastern New Mexico," U. S. Geol Surv. Open-file Report 80-1099, pp. 1-116.

Bachman, G. O., 1985, Assessment of Near-Surface Dissolution At and Near the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico, Sandia National Laboratories, SAND84-7178, pp. 1-33.

Bachman, G. O., 1986, Karst in Evaporites in Southeastern New Mexico, Sandia National Laboratories, SAND86-7078 (in printing).

Barr, G. E., S. J. Lambert and J. A. Carter, 1979, "Uranium Isotope Disequilibrium in Groundwaters of Southeastern New Mexico and Implications Regarding Age-dating of Waters," in Proceedings of the International Symposium on Isotope Hydrology, STI/PUB/493, V. 2 (Int. Atomic Energy Agency, Vienna).

Bigeleisen, J, M., L. Perlman and H. C. Prosser, 1952, "Conversion of Hydrogenic Materials to Hydrogen for Isotopic Analysis," Anal. Chem. V. 24, pp. 1356-1357.

Bjorklund, L. J. and W. S. Motts, 1959, Geology and Ground-water Resources of the Carlsbad Area, New Mexico, U. S. Geol. Survey Open-file Report, pp. 1-322.

Borns, D. J., 1985, "Marker Bed 139: A Study of Drillcore From a Systematic Array," Sandia National Laboratories, SAND85-0023, pp. 1-32.

Brookins, D. G., 1980, "Polyhalite K-Ar Radiometric Ages From Southeastern New Mexico," Isochron/West, V. 29, pp. 29-31.

Brookins, D. G., 1981, "Geochronologic Studies Near the WIPP Site, Southeastern New Mexico," in Environmental Geology and Hydrology in New Mexico, New Mexico Geological Society Special Publication No. 10, pp. 147-152.

Brookins, D. G. and S. J. Lambert, 1987, "K-Ar and Rb-Sr Age Determinations From Clay Minerals and Related Minerals From the WIPP (Waste Isolation Pilot Plant), Southeastern New Mexico," (submitted for publication to Isochron/West).

Brookins, D. G., J. K. Register and H. Krueger, 1980, "Potassium-Argon Dating of Polyhalite in Southeast New Mexico," Geochim. et Cosmochim. Acta, V. 44, pp. 635-637.

Calzia, J. P. and W. L. Hiss, 1978, "Igneous Rocks in Northern Delaware Basin, New Mexico and Texas, in Geology and Mineral Deposits of Ochoan Rocks in Delaware Basin and Adjacent Areas," New Mexico Bur. of Mines and Min. Resources, Circular 159, pp. 39-45.

Chapman, J. B., 1986, "Stable Isotopes in Southeastern New Mexico Groundwater: Implications for Dating Recharge in the WIPP Area," New Mexico Environmental Evaluation Group, EEG-35, pp. 1-76.

Chaturvedi, L. and J. K. Channell, 1985, "The Rustler Formation as a transport medium for contaminated groundwater," New Mexico Environmental Evaluation Group, EEG-32, pp. 1-85 with appendices.

Clayton, R. N., I. Friedman, D. L. Graf, T. K. Mayeda, W. F. Meents and N. F. Shimp, 1966, "The Origin of Saline Formation Waters, I. Isotopic Composition," Jour. Geophys. Res., V. 71, pp. 3869-3882.

Clayton, R. N., B. F. Jones and R. A. Berner, 1968, "Isotope Studies of Dolomite Formation Under Sedimentary Conditions," Geochim. et Cosmochim. Acta, V. 32, pp. 415-432.

Collins, A. G., 1975, "Geochemistry of Oilfield Waters," Elsevier Scientific Publishing Company, Amsterdam, pp. 1-496.

Colton, I. D. and J. G. Morse, 1985, Water Quality Sampling Plan Technical Support Contractor Report WIPP-DOE-215 (prepared for the U. S. Department of Energy).

Cooper, J. B. and V. M. Glanzman, 1971, "Geohydrology of Project Gnome Site, Eddy County, New Mexico," U. S. Geol. Surv. Prof. Paper 712-A, pp. A1-A24.

Coplen, T. B., C. Kendall and J. Hopple, 1983, "Comparison of Stable Isotope Reference Samples," Nature, V. 302, pp. 236-238.

Craig, H., 1957, "Isotopic Standards for Carbon and Oxygen and Correction Factors for Mass-Spectrometric Analysis of Carbon Dioxide," Geochim. Cosmochim. Acta, V. 12, pp. 133-149.

Craig, H., 1961a, "Isotopic Variations in Meteoric Waters," Science, V. 133, pp. 1702-1703.

Craig, H., 1961b, "Standard for Reporting Concentrations of Deuterium and Oxygen-18 in Natural Waters," Science, V. 133, pp. 1833-1834.

Craig, H., 1963, "The Isotope Geochemistry of Water and Carbon in Geothermal Areas," in Nuclear Geology on Geothermal Areas, (Spoleto, Italy), ed. E. Tongiorgi, Pisa, pp. 17-53.

Craig, H., 1966, "Isotopic Composition and Origin of the Red Sea and Salton Geothermal Brines," Science, V. 154, pp. 1544-1548.

Craig, H., G. Boato and D. E. White, 1956, Isotopic Chemistry of Thermal Waters Natl. Acad. Sci., Nucl. Sci. Ser., Rept. 19, pp. 29-36.

Craig, H., L. I. Gordon and Y. Horibe, 1963, "Isotopic Exchange Effects in the Evaporation of Water, I. Low-temperature Experimental Results," Jour. Geophys. Res., V. 68, pp. 5079-5087.

Davies, P. B., 1983, "Assessing the Potential for Deep-Seated Salt Dissolution and Subsidence at the Waste Isolation Pilot Plant (WIPP)," prepared for the State of New Mexico Environmental Evaluation Group Conference WIPP Site Suitability for Radioactive Waste Disposal, May 12-13, 1983, Carlsbad, New Mexico.

Davis, P., R. Wilcox and G. W. Gross, 1980, Spring Characteristics of the Western Roswell Artesian Basin, New Mexico Water Resources Research Institute Report No. 116, Las Cruces, pp. 1-93.

Duffy, C. J., L. W. Gelhar and G. W. Gross, 1978, Recharge and Groundwater Conditions in the Western Region of the Roswell Basin, New Mexico Water Resources Research Institute Report No. 100, Las Cruces, pp. 1-111.

Engel, A. E. J., R. N. Clayton and S. Epstein, 1958, "Variations in Isotopic Composition of Oxygen and Carbon in Leadville Limestone (Mississippian, Colorado) and in its Hydrothermal and Metamorphic Phases," Journal of Geology, V. 66, pp. 374-390.

Epstein, S., D. L. Graf and E. T. Degens, 1964, "Oxygen Isotope Studies on the Origin of Dolomites," in Isotopic and Cosmic Chemistry, ed. by H. Craig, S. L. Miller, and G. J. Wasserburg, North Holland Publishing Company, Amsterdam, pp. 169-180.

Epstein, S. and T. Mayeda, 1953, "Variation of O-18 Content of Waters from Natural Sources," Geochim. Cosmochim. Acta, V. 4, pp. 213-224.

Epstein, S., R. P. Sharp and A. J. Gow, 1965, "Six-Year Record of Oxygen and Hydrogen Isotope Variations in South Pole Firn," *Jour. Geophys. Res.*, V. 70, pp. 1809-1814.

Epstein, S., R. P. Sharp and A. J. Gow, 1970, "Antarctic Ice Sheet: Stable Isotope Analyses of Byrd Station Cores and Interhemispheric Climatic Implications," *Science*, V. 168, pp. 1570-1572.

Epstein, S. and H. P. Taylor, Jr., 1970, "The Concentration and Isotopic Composition of Hydrogen, Carbon and Silicon in Apollo 11 Lunar Rocks and Minerals," Proceedings of *Apollo 11 Lunar Sci. Conf.*, V. 2, pp. 1085-1096.

Epstein, S. and C. J. Yapp, 1976, "Climatic Implications of the D/H Ratio of Hydrogen in C-H Groups in Tree Cellulose," *Earth and Plan. Sci. Letters*, V. 30, pp. 252-261.

Evans, G. V., R. L. Otlet, R. A. Downing, R. A. Monkhouse and G. Rae, 1979, "Some Problems in the Interpretation of Isotope Measurements in United Kingdom Aquifers," in *Proceedings of the International Symposium of Isotope Hydrology*, STI/PUB/493, V. 2 (Int. Atomic Energy Agency, Vienna).

Fiedler, A. G. and S. S. Nye, 1933, *Geology and Ground-water Resources of the Roswell Artesian Basin, New Mexico*, U. G. Geol. Surv. Water Supply Paper 639, pp. 1-372.

Fontes, J. C., 1981, "Paleowaters," in J. R. Gat and R. Gonfiantini, eds., *Stable Isotope Hydrology*: International Atomic Energy Agency Technical Report Series No. 210, pp. 273-302.

Fontes, J. C. and J. M. Garnier, 1979, "Determination of the Initial ^{14}C Activity of the Total Dissolved Carbon: A Review of the Existing Models and a New Approach," *Water Resources Research*, V. 15, p. 399-413.

Fontes, J. C. and R. Gonfiantini, 1967, "Fractionement Isotopique de l'Hydrogène dans l'Eau de Cristallisation du Gypse," *C. R. Acad. So. Paris, Ser. D.*, V. 265, pp. 4-6.

Friedman, I., A. C. Redfield, B. Schoen and J. Harris, 1964, "The Variation of the Deuterium Content of Natural Waters in the Hydrologic Cycle," *Reviews of Geophysics*, V. 2, No. 1, pp. 177-224.

Gat, J. R. and R. Gonfiantini, 1981, *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*, International Atomic Energy Agency Technical Report Series No. 210, Vienna, pp. 1-337.

Gat, J. R. and A. Issar, 1974, "Desert Isotope Hydrology: Water Sources of the Sinai Desert," *Geochimica et Cosmochimica*, V. 38, pp. 1117-1131.

Geohydrology Associates, 1978, Ground-water Study Related to Proposed Expansion of Potash Mining Near Carlsbad, New Mexico, Albuquerque, NM, Geohydrology Associates, Inc.

Gonfiantini, R., 1978, "Standards for Stable Isotope Measurements in Natural Compounds," Nature, V. 271, pp. 534-536.

Graf, D. L., 1982, "Chemical Osmosis, Reverse Chemical Osmosis, and the Origin of Subsurface Brines," Geochim. et Cosmochim. Acta, V. 46, pp. 1431-1448.

Graf, D. L., I. Friedman and W. F. Meents, 1965, The Origin of Saline Formation Waters, II: Isotopic Fractionation by Shale Micropore Systems, Illinois State Geol. Surv. Circ. 393, pp. 1-32.

Graf, D. L., W. F. Meents, I. Friedman and N. F. Shimp, 1966, The Origin of Saline Formation Waters, III: Calcium Chloride Waters, Illinois State Geol. Surv. Circ. 397, pp. 1-60.

Gross, G. W., P. Davis and K. R. Rehfeldt, 1979, Paul Spring: An Investigation of Recharge in the Roswell (N.M.) Artesian Basin, New Mexico Water Resources Research Institute Report No. 113, Las Cruces, pp. 1-135.

Gross, G. W. and R. N. Hoy, 1980, A Geochemical and Hydrological Investigation of Groundwater Recharge in the Roswell Basin of New Mexico: Summary of results and updated listing of tritium determinations, New Mexico Water Resources Research Institute Report No. 122, Las Cruces, pp. 1-141.

Gross, G. W., R. N. Hoy and C. J. Duffy, 1976, Application of Environmental Tritium in the Measurement of Recharge and Aquifer Parameters in a Semi-arid Limestone Terrain, New Mexico Water Resources Research Institute Report No. 080, Las Cruces, pp. 1-212.

Halas, S. and T. Osmolski, 1986, "Stable Isotopes Study of Permian Polyhalites [abstr.]," Terra Cognita, V. 6, No. 2, p. 218. (Sixth International Conference on Geochronology, Cosmochronology and Isotope Geology, Cambridge, June 30-July 4, 1986.)

Hale, W. E., L. S. Hughes and E. R. Cox, 1954, Possible Improvement of Quality of Water of the Pecos River by Diversion of Brine at Malaga Bend, Eddy County, New Mexico, Pecos River Commission, New Mexico and Texas, in cooperation with USGS Water Resources Division, Carlsbad, NM.

Hantush, M. S., 1957, Preliminary Quantitative Study of the Roswell Ground-water Reservoir, New Mexico, New Mexico Institute of Mining and Technology Research and Development Division, Socorro, pp. 1-118.

Hendrickson, G. E. and R. S. Jones, 1952, Geology and Groundwater Resources of Eddy County, New Mexico, New Mexico Bureau of Mines and Mineral Resources Ground-water Report 3, pp. 1-169.

Hiss, W. L., 1975, Stratigraphy and Ground-Water Hydrology of the Capitan Aquifer, Southeastern New Mexico and Western Texas, Ph.D. diss., Univ. of Colorado, Boulder, pp. 1-396.

Hoy, R. N. and G. W. Gross, 1982, A Baseline Study of Oxygen 18 and Deuterium in the Roswell, New Mexico, Groundwater Basin, New Mexico Water Resources Research Institute Report No. 144, Las Cruces, pp. 1-95.

Hunter, R. L., 1985, "A Regional Water Balance for the Waste Isolation Pilot Plant (WIPP) Site and Surrounding Area," Sandia National Laboratories, SAND84-2233, pp. 1-83.

Hydro Geo Chem, 1984, Water Quality Sampling Criteria for Pumped Wells: Hydro Geo Chem, Inc. Tucson, Arizona, (prepared for Sandia National Laboratories), pp. 1-38.

Isaacson, R. E., L. E. Brownell, R. W. Nelson, and E. L. Roetman, 1974, "Soil-Moisture Transport in Arid Site Vadose Zones," in Proceedings of the International Symposium on Isotope Hydrology, 1973, (Int. Atomic Energy Agency, Vienna), pp. 97-114.

Jagnow, D. H., 1979, Cavern Development in the Guadalupe Mountains, Cave Research Foundation," Columbus, Ohio, pp. 1-55.

Jones, C. L., 1973, Salt Deposits of Los Medaños Area, Eddy and Lea Counties, New Mexico, with sections on Ground-water Hydrology," by M. E. Cooley, and Surficial Geology, by G. O. Bachman: U. S. Geol. Surv. Open-file Report 4339-7, pp. 1-67.

Keith, M. L., and J. N. Weber, 1964, "Carbon and Oxygen Isotopic composition of selected limestones and fossils," Geochim. et Cosmochim. Acta, V. 28, pp. 1787-1816.

King, P. B., 1948, Geology of the Southern Guadalupe Mountains, Texas, U. S. Geol Surv. Prof. Paper 215, pp. 1-183.

Knauth, L. P., and M. A. Beeunas, 1986, "Isotope Geochemistry of Fluid Inclusions in Permian Halite with Implications for the Isotopic History of Ocean Water and the Origin of Saline Formation Waters," Geochim. et Cosmochim. Acta, V. 50, pp. 419-434.

Lambert, S. J., 1978, "Geochemistry of Delaware Basin Groundwaters," in Geology and Mineral Deposits of Ochoan Rocks in Delaware Basin and Adjacent Areas, New Mexico Bur. of Mines and Min. Resources Circular 159, pp. 33-38.

Lambert, S. J., 1983a, Dissolution of Evaporites in and Around the Delaware Basin, Southeastern New Mexico and West Texas, Sandia National Laboratories, SAND82-0461, pp. 1-96.

Lambert, S. J., 1983b, "Evaporite Dissolution Relevant to the WIPP site, Northern Delaware Basin, Southeastern New Mexico," Mat. Res. Soc. Symp. Proc. V. 15, pp. 291-298.

Lambert, S. J., 1986, "Stable-Isotope Studies of Groundwaters in Southeastern New Mexico," in L. Chaturvedi (ed.), The Rustler Formation at the WIPP Site, New Mexico Environmental Evaluation Group Report EEG-34 (to be published).

Lambert, S. J., 1987, Feasibility Study: Applicability of Geochronologic Methods Involving Radiocarbon and Other Nuclides to the Groundwater Hydrology of the Rustler Formation, Sandia National Laboratories, SAND86-1054 (in preparation).

Lambert, S. J., and J. A. Carter, 1984, Uranium-Isotope Disequilibrium in Brine Reservoirs of the Castile Formation, Northern Delaware Basin, Southeastern New Mexico, I. Principles and Methods, Sandia National Laboratories, SAND83-0144, pp. 1-18.

Lambert, S. J., and S. Epstein, 1980, "Stable Isotope Investigations of an Active Geothermal System in Valles Caldera, Jemez Mountains, New Mexico," Jour. Volcanology and Geothermal Res., V. 8, pp. 111-129.

Lambert, S. J., and K. L. Robinson, 1984, Field Geochemical Studies of Groundwaters in Nash Draw, Southeastern New Mexico, Sandia National Laboratories, SAND83-1122, pp. 1-38.

Leaney, F. W., and G. B. Allison, 1986, "Carbon-14 and Stable Isotope Data for an Area in the Murray Basin: Its Use in Estimating Recharge," Jour. Hydrology, V. 88, pp. 129-145.

Lee, W. T., 1925, "Erosion by Solution and Fill, in Contributions to Geography in the United States, 1923-24," U. S. Geol. Surv. Bull. 760-C, pp. 107-121.

Mabry, T. J., J. H. Hunziker, and D. R. D. Feo, Jr., 1977, "Creosote Bush: Biology and Chemistry of 'Larrea' in New World Deserts: Dryden, Hutchinson, and Ross," US Int. Biol. Prog. Synthesis Series No. 6.

McCrea, J. M., 1950, "On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale, "Jour. Chem. Phys., V. 18, pp. 849-857.

McKinney, C. R., J. M. McCrea, S. Epstein, H. Allen, and H. C. Urey, 1950, "Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios," Rev. Sci. Instr., V. 21, pp. 724-730.

McLean, J. S., 1971, "The Microclimate in Carlsbad Caverns, New Mexico," U. S. Geol. Surv. Open-file Report 71-198, pp. 1-67.

McNitt, J. R., 1963, "Exploration and Development of Geothermal Power in California," Calif. Div. of Mines and Geology 75, pp. 1-44.

Mercer, J. W., 1983, Geohydrology of the Proposed Waste Isolation Pilot Plant site, Los Medaños area, Southeastern New Mexico, U. S. Geol. Surv. Water-Resources Investigation 83-4016, pp. 1-113.

Mercer, J. W., and B. R. Orr, 1979, Interim Data Report on the Geohydrology of the Proposed Waste Isolation Pilot Plant Site, Southeast New Mexico, U. S. Geol. Surv. Water-resources Investigations 79-98, pp. 1-178.

Motts, W. S., 1957, Geology and Ground Water Resources of the Carlsbad Area, New Mexico, Ph. D. diss., Univ. of Illinois, Urbana, pp. 1-120.

Nativ, R., and D. A. Smith, 1987, "Hydrogeology and Geochemistry of the Ogallala Aquifer, Southern High Plains," Journal of Hydrology, V. 91, pp. 217-253.

Natrella, M. G., 1963, Experimental Statistics: National Bureau of Standards Handbook 91, (reprinted October 1966 with corrections).

Nicholson, A., Jr., and A. Clebsch, Jr., 1961, Geology and Ground-Water Conditions in Southern Lea County, New Mexico, New Mexico Bureau of Mines and Mineral Resources Ground-water Report 6, Socorro, New Mexico, pp. 1-123.

Nier, A. O., 1947, "A Mass Spectrometer for Isotope and Gas Analysis," Rev. Sci. Instr., V. 18, pp. 398-411.

Northrup, D. A., and R. N. Clayton, 1966, "Oxygen-Isotope Fractionations in Systems Containing Dolomite," Jour. Geology, V. 74, pp. 174-196.

O'Neil, J. R., R. N. Clayton, and T. K. Mayeda, 1969, "Oxygen Isotope Fractionation in Divalent Metal Carbonates," Jour. Chem. Phys., V. 51, pp. 5547-5558.

O'Neil, J. R., C. M. Johnson, L. D. White, and E. Roedder, 1986, "The Origin of Fluids in the Salt Beds of the Delaware Basin, New Mexico and Texas," Jour. Applied Geochemistry, V. 1, pp. 265-272.

Osmond, J. K., and J. B. Cowart, 1976, "The Theory and Uses of Natural Uranium Isotopic Variations in Hydrology," Atomic Energy Review, V. 14, pp. 621-679.

Osterkamp, W. R., and W. W. Wood, 1987, "Playa-Lake Basins on the Southern High Plains of Texas and New Mexico: Part I. Hydrologic, Geomorphic, and Geologic Evidence for Their Development," Geol. Soc. America Bull., V. 99, pp. 215-223.

Parry, W. T., C. C. Reeves, Jr., and J. W. Leach, 1970, "Oxygen and Carbon Isotope Composition of West Texas lake carbonates," Geochim. et Cosmochim. Acta, V. 34, pp. 825-830.

Pezdic, J., H. Leskovsek-Sefman, T. Dolenec, and J. Urbanc, 1985, Isotopic Study of Karst Water, final report on research contract 2845/RB, Institut "Josef Stefan", Univerza e. Kardelj, Ljubljana, Jugoslavia; Report No. IAEA-R-2845-F, International Atomic Energy Agency, Vienna.

Powers, D. W., S. J. Lambert, S. E. Shaffer, L. R. Hill, and W. D. Weart, eds., 1978, Geological Characterization Report, Waste Isolation Pilot Plant (WIPP) site, Southeastern New Mexico, Sandia Laboratories, SAND78-1596.

Rabinowitz, D. D., G. W. Gross, and C. R. Holmes, 1977, Environmental Tritium as a Hydrometeorologic Tool in the Roswell Basin, NM, I. Tritium Input Function and Precipitation/Recharge Relation; II. Tritium Patterns in Ground Water; III. Hydrologic Parameters," Jour. Hydrology, V. 32, pp. 3-46.

Register, J. K., 1981, Rubidium-Strontium and Related Studies of the Salado Formation, Southeastern New Mexico, Sandia National Laboratories, SAND81-7072, pp. 1-119.

Register, J. K., and D. G. Brookins, 1980, Rb-Sr Isochron Age of Evaporite Minerals From the Salado Formation (Late Permian), Southeastern New Mexico, Isochron/West, No. 29, pp. 29-31.

Rehfeldt, K. R., and G. W. Gross, 1982, The Carbonate Aquifer of the Central Roswell Basin: Recharge Estimation by Numerical Modeling, New Mexico Water Resources Research Institute Report No. 142, pp. 1-136.

Richardson, G. B., 1904, Report of a Reconnaissance in Trans-Pecos Texas, North of Texas and Pacific Railway, Texas University Mineralogical Survey Bulletin 9, and Texas University Bulletin 23, pp. 1-119.

Robinson, K. L., 1987, Analysis of Solutes in Groundwaters From the Rustler Formation at and Near the WIPP site, Sandia National Laboratories, SAND86-0917 (in preparation).

Robinson, T. W., and W. B. Lang, 1938, "Geology and Ground-water Conditions of the Pecos River Valley in the Vicinity of Laguna Grande de la Sal, New Mexico, with Special Reference to the Salt Content of the River Water: in 12th and 13th Biennial Reports, New Mexico State Engineer, pp. 77-100.

Sandia National Laboratories and U. S. Geological Survey, 1983, Basic Data Report for Drillhole ERDA 9 (Waste Isolation Pilot Plant--WIPP), Sandia National Laboratories, SAND79-0270, pp. 1-54 (with appendices).

Sandia National Laboratories and University of New Mexico, 1981, Basic Data Report for Drillhole WIPP-15 (Waste Isolation Pilot Plant--WIPP), Sandia National Laboratories, SAND79-0274, pp. 1-31 (with appendices).

Sofer, Z., 1978, "Isotopic Composition of Hydration Water in Gypsum," Geochim. et Cosmochim. Acta, V. 42, pp. 1141-1149.

Snyder, R. pp., 1985, Dissolution of Halite and Gypsum, and Hydration of Anhydrite to Gypsum, Rustler Formation, in the Vicinity of the Waste Isolation Pilot Plant, Southeastern New Mexico, U. S. Geol. Surv. Open-file Report 85-229, pp. 1-11.

Snyder, R. P., and L. M. Gard, Jr., 1982, Evaluation of Breccia Pipes in Southeastern New Mexico and Their Relation to the Waste Isolation Pilot Plant (WIPP) Site, with a Section on Drill-stem Tests by J. W. Mercer, U. G. Geol. Surv. Open-file Report 82-968, pp. 1-73.

Stein, C. L., and J. L. Krumhansl, 1986, Chemistry of Brines in Salt from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico: A preliminary investigation, Sandia National Laboratories, SAND85-0897, pp. 1-37.

Theis, C. V., and A. N. Sayre, 1942, Geology and Ground Water, in U. S. National Resources Planning Board, 1942, Pecos River Joint Investigation--Reports of the participating agencies, Washington, U. S. Government Printing Office, pp. 27-75.

Urey, H. C., H. A. Lowenstam, S. Epstein, and C. R. McKinney, 1951, Measurement of Paleotemperatures and Temperatures of the Upper Cretaceous of England, Denmark, and the Southeastern United States: Geol. Soc. America Bull., V. 62, pp. 399-416.

Van Devender, T. R., 1980, "Holocene Plant Remains from Rocky Arroyo and Last Chance Canyon, Eddy County, New Mexico," The Southwestern Naturalist V. 25, pp. 361-372.

Vine, J. D., 1963, Surface Geology of the Nash Draw Quadrangle, Eddy County, New Mexico, U. S. Geol. Surv. Bull. 1141-B, pp. 1-46.

Vogel, J. C., D. Ehhalt, and W. Roether, 1963, A Survey of the natural isotopes of water in South Africa, in Radioisotopes in hydrology, International Atomic Energy Agency, Vienna, pp. 407-415.

Weber, J. N., 1964, "Oxygen Isotope Fractionation Between Coexisting Calcite and Dolomite, Science, V. 145, pp. 1303-1305.

Welder, G. E., 1983, Geohydrologic Framework of the Roswell Ground-Water Basin, Chaves and Eddy Counties, New Mexico, New Mexico State Engineer Technical Report 42, (prepared by the U. S. Geological Survey), pp. 1-28 (with 28 illustrations).

Williams, G. pp., 1983, "Improper Use of Regression Equations in Earth Sciences," Geology, V. 11, pp. 195-197.

Wood, W. W., and W. R. Osterkamp, 1987, "Playa-Lake Basins on the Southern High Plains of Texas and New Mexico: Part II. A Hydrologic Model and Mass-Balance Arguments for Their Development," Geol. Soc. America Bull., V. 99, pp. 224-230.

Yapp, C. J., 1985, D/H Variations of Meteoric Waters in Albuquerque, New Mexico, USA, Jour. Hydrology V. 76, pp. 63-84.

FEDERAL AGENCIES

U.S. Department of Energy, (5)
Office of Civilian Radioactive
Waste Management
Attn: Stephen H. Kale - RW-20
Associate Director
T.H. Isaacs - RW-20
Deputy Associate Director
James C. Bresee - RW-22
Director, Repository
Coordination Div.
Ralph Stein - RW-23
Director, Engineering &
Geotechnology
James P. Knight - RW-24
Director, Siting,
Licensing and Quality
Assurance
Office of Geologic Repositories
Forrestal Building
Washington, DC 20585

U.S. Department of Energy (3)
Albuquerque Operations Office
Attn: Bruce G. Twining
J. E. Bickel
R. Marquez, Director
Public Affairs Division
P.O. Box 5400
Albuquerque, NM 87185

U.S. Department of Energy
Attn: National Atomic Museum
Library
Albuquerque Operations Office
P.O. Box 5400
Albuquerque, NM 87185

U.S. Department of Energy
Ecological Research Division, ER-75
Office of Health and Environmental
Research
Office of Energy Research
Attn: F. J. Wobber
Washington, DC 20545

U.S. Department of Energy (9)
WIPP Project Office (Carlsbad)
Attn: J. Tillman (4)
A. Hunt
T. Lukow (2)
V. Daub
B. Young
P.O. Box 3090
Carlsbad, NM 88221

U.S. Department of Energy
Research & Technical Support
 Division
Attn: D. E. Large
P.O. Box E
Oak Ridge, TN 37830

U.S. Department of Energy
Richland Operations Office
Nuclear Fuel Cycle & Production
 Division
Attn: R. E. Gerton
P.O. Box 500
Richland, WA 99352

U.S. Department of Energy (5)
Office of Defense Waste and
 Transportation Management
Attn: T. B. Hindman----- DP-12
 G. Daly ---------- DP-124
 M. Duff ---------- DP-123
 A. Follett ------- DP-122
Washington, DC 20545

U.S. Department of Energy (2)
Idaho Operations Office
Fuel Processing and Waste
 Management Division
785 DOE Place
Idaho Falls, ID 83402

U.S. Department of Energy (3)
Savannah River Operations Office
Defense Waste Processing
 Facility Project Office
Attn: S. Cowan
 W. J. Brumley
P.O. Box A
Aiken, SC 29802

U.S. Department of the Interior (4)
Attn: E. Roedder
 T. Coplen
 B. F. Jones
 I. J. Winograd
Geological Survey
959 National Center
Reston, Virginia 22092

U.S. Department of the Interior
Attn: J. S. McLean
Geological Survey
Box 25046, MS406
Denver, CO 80225

U.S. Department of the Interior
Attn: Librarian
Carlsbad Caverns National Park
3225 National Parks Highway
Carlsbad, NM 88220

U.S. Geological Survey
Branch of Regional Geology
Attn: R. Snyder
MS913, Box 25046
Denver Federal Center
Denver, CO 80225

U.S. Geological Survey
Conservation Division
Attn: W. Melton
P.O. Box 1857
Roswell, NM 88201

U.S. Geological Survey (2)
Water Resources Division
Attn: Cathy Peters
Suite 200
4501 Indian School, NE
Albuquerque, NM 87110

U.S. Nuclear Regulatory
  Commission (4)
Division of Waste Management
Attn: Michael Bell
  Hubart Miller
  Jacob Philip
  NRC Library
Mail Stop 623SS
Washington, DC 20555

STATE AGENCIES

Environmental Evaluation Group (3)
Attn: Robert H. Neill, Director
Suite F-2
7007 Wyoming Blvd., N.E.
Albuquerque, NM 87109

Environmental Evaluation Group (3)
505 North Main Street
P.O. Box 3149
Carlsbad, NM 88221-3149

New Mexico Bureau of Mines
  and Mineral Resources (2)
Attn: F. E. Kottolowski, Director
  J. Hawley
Socorro, NM 87801

NM Department of Energy & Minerals
Attn: Kasey LaPlante, Librarian
P.O. Box 2770
Santa Fe, NM 87501

LABORATORIES/CORPORATIONS

Battelle Memorial Institute (17)
Project Management Division
Attn: ONWI Library
W. Carbiener, General Manager (3)
V. Adams
S. Basham
P. Hoffman
H. R. Hume
H. N. Kalia
J. Kirchner
S. Matthews
D. Moak
J. Moody
G. Raines
J. Schornhorst
O. Swanson
J. Treadwell
P.O. Box 2360
Hereford, TX 79045

Battelle Pacific Northwest Laboratories (6)
Attn: D. J. Braadley
J. Relyea
R. E. Westerman
S. Bates
H. C. Burkholder
L. Pederson
Battelle Boulevard
Richland, WA 99352

Bechtel Inc. (2)
Attn: E. Weber
H. Taylor
P.O. Box 3965
45-11-B34
San Francisco, CA 94119

Ben Donegan
Leonard Minerals Co.
3202 Candelaria, N.E.
Albuquerque, NM 87107

Brookhaven National Laboratory (1)
Associated Universities, Inc.
Attn: Paul W. Levy, Senior
Scientist
Upton, NY 11973

C. S. Fore
Ecological Sciences Information
Center
Oak Ridge National Laboratory
Bldg. 2001
P.O. Box X
Oak Ridge, TN 37830

E. I. Dupont de Nemours Company (6)
Attn: N. Bibler
E. L. Albenisius
M. J. Plodinec
G. G. Wicks
C. Jantzen
J. A. Stone
Savannah River Laboratory
Aiken, SC 29801

Dr. Shosei Serata
Serata Geomechanics
4124 Lakeside Drive
Richmond, CA 94806-1941

Dupont Company
Attn: Richard G. Baxter
Building 704-S
Savannah River Plant
Aiken, SC 29808

G. O. Bachman
4008 Hannett Avenue, N.E.
Albuquerque, NM 87110

Geohydrology Associates
Attn: T. E. Kelly
4015 Carlisle Blvd., N.E.
Albuquerque, NM 87110

George Dymmel
SAIC
101 Convention Center Dr.
Las Vegas, NV 89109

Harry Legrand
331 Yadkin Drive
Raleigh, NC 27609

INTERA Technologies, Inc. (4)
Attn: G. E. Grisak
J. F. Pickens
A. Haug
A. M. LeVenue
#300
6850 Austin Center Blvd.
Austin, TX 78731

INTERA Technologies, Inc.
Attn: Wayne Stensrud
P.O. Box 2123
Carlsbad, NM 88221

IT Corporation (2)
Attn: Roy McKinney
J. Myers
Suite 306
2340 Alamo, S.E.
Albuquerque, NM 87106

IT Corporation (2)
Attn: D. Deal
P.O. Box 2078
Carlsbad, NM 88221

Los Alamos Scientific Laboratory
Attn: B. Erdal, CNC-11
Los Alamos, NM 87545

Martin Marietta Energy Systems,
Inc.
Oak Ridge National Laboratory
Attn: J. A. Carter
Box Y
Oak Ridge, TN 37830

Oak Ridge National Laboratory (4)
Attn: R. E. Blanko
E. Bondietti
C. Claiborne
G. H. Jenks
Box Y
Oak Ridge, TN 37830

RE/SPEC, Inc.
Attn: P. F. Gnirk
P.O. Box 14984
Albuquerque, NM 87191

RE/SPEC, Inc. (7)
Attn: W. Coons
L. L. Van Sambeek
D. B. Blankenship
G. Callahan
T. Pfeifle
J. L. Ratigan
P.O. Box 725
Rapid City, SD 57709

Rockwell International (1)
Attn: C. E. Wickland
Rocky Flats Plant
Golden, CO 80401

Rockwell International (3)
Atomics International Division
Rockwell Hanford Operations
Attn: J. Nelson (HWVP)
P. Salter
W. W. Schultz
P.O. Box 800
Richland, WA 99352

Rockwell International
Atomics International Division
Rockwell Hanford Operations
Attn: M. J. Smith
P.O. Box 800
Richland, WA 99352

Systems, Science, and Software (2)
Attn: E. Peterson
P. Lagus
Box 1620
La Jolla, CA 92038

Westinghouse Electric
Corporation (7)
Attn: Library
W. Moffitt
V. DeJong
W. Chiquelin
T. Dillon
V. Likar
R. Kehrman
P.O. Box 2078
Carlsbad, NM 88221

UNIVERSITIES

University of Arizona
Attn: J. G. McCray
Department of Nuclear Engineering
Tucson, AZ 85721

University of Arizona
Department of Nuclear Engineering
Attn: J. G. McCray
J. J. K. Daemen
Tucson, AZ 85721

Dr. R. O. Pohl
Department of Physics
Clark Hall
Cornell University
Ithaca, NY 14853

Florida State University (2)
Attn: J. K. Osmond
J. B. Cowart
Department of Geology
Tallahassee, FL 32308

New Mexico Institute
of Mining and Technology (3)
Attn: L. Brandvold
G. W. Gross
F. Phillips
Socorro, NM 87801

University of New Mexico
Department of Geology
Attn: C. J. Yapp
Albuquerque, NM 87131

University of New Mexico (2)
Geology Department
Attn: D. G. Brookins
Library
Albuquerque, NM 87131

University of Minnesota
Department of Energy and Materials
Science
Attn: R. Oriani
151 Amundson Hall
421 Washington Ave., S.E.
Minneapolis, MN 55455

Pennsylvania State University (1)
Materials Research Laboratory
Attn: Della Roy
University Park, PA 16802

George Pinder
Department of Civil Engineering
Princeton University
Princeton, NJ 08540

John Handin
Center of Tectonophysics
Texas A&M University
College Station, TX 77840

Texas A&M University
Center of Tectonophysics
College Station, TX 77840

Edward C. Bingler
Deputy Director
Texas Bureau
of Economic Geology
University of Texas at Austin
Austin, TX 78712

D. W. Powers
Department of Geological Sciences
University of Texas at El Paso
El Paso, TX 79968

G. Ross Heath
College of Ocean
and Fishery Sciences
University of Washington
Seattle, WA 98195

LIBRARIES

Thomas Brannigan Library
Attn: Don Dresp, Head Librarian
106 W. Hadley St.
Las Cruces, NM 88001

Hobbs Public Library
Attn: Ms. Marcia Lewis, Librarian
509 N. Ship Street
Hobbs, NM 88248

New Mexico State Library
Attn: Ms. Ingrid Vollenhofer
P.O. Box 1629
Santa Fe, NM 87503

New Mexico Tech
Martin Speere Memorial Library
Campus Street
Socorro, NM 87810

Pannell Library
Attn: Ms. Ruth Hill
New Mexico Junior College
Lovington Highway
Hobbs, NM 88240

Roswell Public Library
Attn: Ms. Nancy Langston
301 N. Pennsylvania Avenue
Roswell, NM 88201

WIPP Public Reading Room
Attn: Lee Hubbard, Head Librarian
Carlsbad Municipal Library
101 S. Halagueno St.
Carlsbad, NM 88220

Zimmerman Library
Attn: Zanier Vivian
University of New Mexico
Albuquerque, NM 87131

NATIONAL ACADEMY OF SCIENCES, WIPP PANEL

Dr. Konrad B. Krauskopf, Chairman
Department of Geology
Panama Street
Stanford University
Stanford, CA 94305

Dr. John O. Blomeke
Route 3
Sandy Shore Road
Lenoir City, TN 37771

Dr. John D. Bredehoeft
Western Region Hydrologist
Water Resources Division
U.S. Geological Survey (M/S 439)
345 Middlefield Road
Menlo Park, CA 94025

Dr. Karl P. Cohen
928 N. California Avenue
Palo Alto, CA 94303

Dr. Fred M. Ernsberger
250 Old Mill Road
Pittsburgh, PA 15238

Dr. Rodney C. Ewing
Department of Geology
University of New Mexico
200 Yale N.E.
Albuquerque, NM 87131

Dr. Charles Fairhurst
Department of Civil and
Mineral Engineering
University of Minnesota
500 Pillsbury Dr. S.E.
Minneapolis, NM 55455

Dr. William R. Muehlberger
Department of Geological Sciences
University of Texas at Austin
P.O. Box 7909
Austin, TX 78712

Dr. Frank L. Parker
Department of Environmental
Engineering
Vanderbilt University
Nashville, TN 37235

Dr. D'Arcy A. Shock
233 Virginia
Ponca City, OK 74601

Dr. Peter B. Myers, Staff
Director
National Academy of Sciences
Committee on Radioactive
Waste Management
2101 Constitution Avenue
Washington, DC 20418

Ms. Remi Langum
Staff Officer
Board on Radioactive Waste
Management
GF462
2101 Constitution Avenue
Washington, DC 20418

FOREIGN ADDRESSES

Studiecentrum Voor Kernenergie (1)
Centre D'Energie Nucleaire
Attn: Mr. A. Bonne
SCK/CEN
Boeretang 200
B-2400 Mol
BELGIUM

Atomic Energy of Canada, Ltd. (2)
Whiteshell Research Estab.
Attn: Peter Haywood
John Tait
Pinewa, Manitoba, CANADA
ROE 1L0

Dr. D. K. Mukerjee
Ontario Hydro Research Lab
800 Kipling Avenue
Toronto, Ontario, CANADA
M8Z 5S4

Mr. Jean-Pierre Olivier
OECD Nuclear Energy Agency
Division of Radiation Protection
and Waste Management
38, Boulevard Suchet
75016 Paris, FRANCE

Claude Sombret
Centre D'Etudes Nucleaires
De La Vallee Rhone
CEN/VALRHO
S.D.H.A. BP 171
30205 Bagnols-Sur-Ceze
FRANCE

Bundesministerium fur Forschung und
Technologie
Attn: Rolf-Peter Randl
Postfach 200 706
5300 Bonn 2
FEDERAL REPUBLIC OF GERMANY

Bundesanstalt fur Geowissenschaften
und Rohstoffe
Attn: Michael Langer
Postfach 510 153
3000 Hannover 51
FEDERAL REPUBLUC OF GERMANY

Hahn-Mietner-Institut fur
Kernforschung (1)
Attn: Werner Lutze
Glienicker Strasse 100
100 Berlin 39
FEDERAL REPUBLIC OF GERMANY

Hermann Gies
Institute fur Tieflagerung,
Gruppe Geochemie
Gesellschaft fur Strahlen und
Umweltforschung mbH
Theodor-Heuss-Strasse 4
D-3300 Braunschweig
FEDERAL REPUBLIC OF GERMANY

Institut fur Tieflagerung (4)
Attn: K. Kuhn
Theodor-Heuss-Strasse 4
D-3300 Braunschweig
FEDERAL REPUBLIC OF GERMANY

Kernforschug Karlsruhe (1)
Attn: K. D. Closs
Postfach 3640
7500 Karlsruhe
FEDERAL REPUBLIC OF GERMANY

Physikalisch-Technische
Bundesanstalt
Attn: Peter Brenneke
Postfach 33 45
D-3300 Braunschweig
FEDERAL REPUBLIC OF GERMANY

British Geological Survey (2)
Hydrogeology Group
Attn: G. Darling
R. L. F. Kay
Maclean Building
Crowmarsh Gifford
Wallingford
Oxfordshire 0X10 8BB
GREAT BRITAIN

D. R. Knowles
British Nuclear Fuels, plc
Risley, Warrington, Cheshire WA3
6AS
1002607 GREAT BRITAIN

U.K. Atomic Energy Authority (3)
Attn: M. Ivanovich
R. Otlet
A. J. Walker
Centre for Nuclear Applications
Isotope Measurement Laboratory
Harwell
Oxfordshire OX11 ORA
GREAT BRITAIN

Shingo Tashiro
Japan Atomic Energy Research Institute
Tokai-Mura, Ibaraki-Ken
319-11 JAPAN

Netherlands Energy Research Foundation ECN (2)
Attn: Tuen Deboer, Mgr.
L. H. Vons
3 Westerduinweg
P.O. Box 1
1755 ZG Petten, THE NETHERLANDS

Svensk Karnbransleforsorjning AB
Attn: Fred Karlsson
Project KBS
Karnbranslesakerhet
Box 5864
10248 Stockholm, SWEDEN

WIPP Peer Panel

G. Ross Heath, Chairman
College of Ocean & Fishery Sciences
University of Washington
Seattle, Washington 98185

Robert J. Budnitz
President, Future Resources Associates, Inc.
Suite 418
2000 Center Street
Berkeley, CA 94704

Thomas A. Cotton
4429 Butterworth Place, NW
Washington, DC 20016

Patrick A. Domenico
Geology Department
Texas A&M
College Station, TX 77843-3115

Charles D. Hollister
Dean for Studies
Woods Hole Oceanographic Institute
Woods Hole, MA 02543

Thomas H. Pigford
Department of Nuclear Engineering
4153 Etcheverry Hall
University of California
Berkeley, CA 94270

Benjamin Ross
Disposal Safety Incorporated
Suite 600
1629 K Street NW
Washington, DC 20006

John Mann
Department of Geology
245 Natural History Building
1301 West Green Street
University of Illinois
Urbana, Illinois 61801

SANDIA INTERNAL:

1510	J. W. Nunziato
1520	C. W. Peterson
1521	R. D. Krieg
1521	J. G. Arguello
1521	H. S. Morgan
3141	S. A. Landenberger (5)
3151	W. L. Garner, (3)
3154-1	C. H. Dalin (8) for DOE/OSTI
6000	D. L. Hartley
6230	W. C. Luth
6232	W. R. Wawersik
6233	T. M. Gerlach
6233	W. H. Casey
6233	J. L. Krumhansl
6233	C. L. Stein
6300	R. W. Lynch
6310	T. O. Hunter
6313	T. Blejwas
6330	W. D. Weart
6330	S. Pickering, Acting QA Chief
6331	A. R. Lappin
6331	R. L. Beauheim
6331	D. J. Borns
6331	P. B. Davies
6331	S. J. Lambert (10)

6331	R. Z. Lawson
6331	K. L. Robinson
6331	M. D. Siegel
6332	L. D. Tyler
6332	R. Beraun
6332	B. M. Butcher
6332	B. L. Ehgartner
6332	R. V. Matalucci
6332	M. A. Molecke
6332	D. E. Munson
6332	E. J. Nowak
6332	R. J. Roginski
6332	J. C. Stormont
6332	T. M. Torres
6332	Sandia WIPP Central Files (10) (Geochemistry)
6333	T. M. Schultheis
6334	D. R. Anderson
6334	S. Bertram-Howery
6334	K. Brinster
6334	L. Brush
6334	M. S. Y. Chu
6334	L. S. Gomez
6334	R. Guzowski
6334	R. L. Hunter
6334	M. G. Marietta
6334	R. R. Rechard
6334	A. Rutledge
7100	C. D. Broyles
7110	J. D. Plimpton
7120	M. J. Navratil
7125	R. L. Rutter
7125	J. T. McIlmoyle
7130	J. O. Kennedy
7133	O. Burchett
7133	J. W. Mercer
7135	P. D. Seward
8524	P. W. Dean (SNLL Library)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1989—673-049/81014