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Feasibility Study: Applicability of Geochronologic Methods Involving Radiocarbon and Other Nuclides to the Groundwater Hydrology of the Rustler Formation, Southeastern New Mexico

Steven J. Lambert

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Albuquerque, New Mexico 87185 and Livermore, California 94550
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Feasibility Study: Applicability of Geochronologic Methods Involving Radiocarbon and Other Nuclides to the Groundwater Hydrology of the Rustler Formation, Southeastern New Mexico

Steven J. Lambert
Earth Sciences Division 6331
Sandia National Laboratories
Albuquerque, New Mexico 87185 USA

ABSTRACT

Radiocarbon, tritium, and ^{36}Cl were measured in groundwaters from the dolomite aquifers of the Rustler Formation in the northern Delaware Basin of southeastern New Mexico to determine the feasibility of using these nuclides in dating the groundwater at and near the Waste Isolation Pilot Plant, a facility for geological disposal of radioactive waste. No measurable ^{36}Cl was found in any of these groundwaters, which derive their dissolved chloride from Permian evaporites. Demonstrably uncontaminated groundwaters contained no significant amounts of tritium (<0.2 TU). Percent modern carbon (PMC) correlates linearly and directly with bicarbonate concentration, indicating mixing of a high-PMC/high-bicarbonate reservoir with a low-PMC/low-bicarbonate reservoir. This relationship, together with the history of development of the wells sampling the groundwaters, indicates contamination by anthropogenic modern carbon rather than simple dilution by dissolving rock carbonate. $\delta^{13}\text{C}$ does not linearly correlate with bicarbonate, indicating no single source of contaminant radiocarbon. Values of PMC and $\delta^{13}\text{C}$ for groundwaters were used to calculate apparent radiocarbon ages according to an interpretive model that accounts for water/rock interactions in carbonate aquifers. All but six pairs of values gave significant negative ages (-1,000 to -7,000 years). This suggests that in contaminated samples the model over-adjusts (based on $\delta^{13}\text{C}$) for radiocarbon loss due to dilution and isotopic exchange with the rock. Four groundwater samples (3 from the Rustler and 1 from the overlying Dewey Lake Red Beds) gave apparent radiocarbon ages $>10,000$ a, and their carbon-isotope systematics suggest that their apparent ages are all the result of a single evolutionary trend of rock/water interaction involving carbon isotope exchange, with a probable recharge age of 13,000 a b. p. This time of isolation from the atmosphere, which is unrelated to travel time within the Rustler, is consistent with paleoclimatic evidence of wetter conditions more conducive to recharge in the late Pleistocene than at present.

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The services of Karen Robinson in compiling and verifying data from voluminous contractor files have been indispensable. Dixie Harvey performed extractions of carbon dioxide from carbonate rock for stable-isotope analysis. Karen Robinson and Al Lappin were available for valuable feedback during the development of the manuscript. Meredith Edwards of Tech Reps, Inc., created the illustrations. Dan Garber served as final editor and arbiter of style and format, and arranged for final publication. Bob Otlet and Jill Walker of AERE Harwell kindly participated in helpful discussions and provided a tour of their laboratory facilities. George Darling and Lin Kay of the British Geological Survey gave helpful suggestions and much-needed moral support. Lin provided a critical review of this work. Also, Joe Pearson gave a thorough review of an early version of the manuscript, with many penetrating comments. The comments of Fred Phillips also helped to inspire many necessary clarifications.

EXECUTIVE SUMMARY

Several nuclide systems have been examined for possible application to the groundwater hydrology of the Rustler Formation (Permian, Ochoan) in the Delaware Basin of southeastern New Mexico. An understanding of the geologic history of the Rustler Formation is fundamental 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 outcrops west of the WIPP site, (3) immediately overlies the Salado Formation where the WIPP facility is being mined, and (4) contains interbeds of brittle fractured rock that contain the most abundant and regionally persistent occurrences of groundwater associated with the evaporites. One class of atmospherically generated nuclides of interest in groundwater studies, together with their approximate half-lives, includes ^3H (12 years), ^{85}Kr (10 years), ^{90}Sr (29 years), and ^{137}Cs (30 years). These fission or activation products are generated principally by atmospheric testing of nuclear weapons. Another class of atmospherically generated nuclides arises principally from neutron-activation or spallation reactions involving cosmic rays; these also can be generated by the atmospheric testing of nuclear devices and by some subsurficial neutron-activation, given a suitable neutron flux from spontaneous fission. This class includes ^{14}C (half-life 5730 years), ^{81}Kr (200,000 years), ^{36}Cl (300,000 years), ^{10}Be (1,600,000 years), and ^{129}I (15,900,000 years).

Sampling and analytical methods, and interpretive models have been developed extensively in the literature for ^3H , ^{14}C , and ^{36}Cl . Samples of wellbore fluids were collected from three regionally persistent water-producing units in the Rustler (Magenta and Culebra dolomite members and the basal Rustler zone near the contact with the underlying Salado Formation) to be analyzed for these nuclides, using procedures designed to minimize contamination of major and certain minor solutes arising from wellbore effects. Even with such precautions, the nature of the contamination associated with newly emplaced hydrologic test holes designed for maximum core recovery is not limited to simple mixing of fluids, but microbial metabolism of solid cellulosic material introduced to control lost circulation has apparently contributed a more or less steady infusion of modern anthropogenic carbon to the total dissolved carbon in the wellbore effluent. Nuclide systems generated in the atmosphere from neutron-activation by cosmic rays are particularly susceptible to contamination by even small amounts of modern sources, especially organic carbon in the case of radiocarbon. This is demonstrated by a linear mixing relationship between percent modern carbon (PMC) and dissolved carbon concentration (represented by the alkalinity, which is here assumed approximately equal to bicarbonate). The PMC varies directly with $[\text{HCO}_3^-]$, and shows that ^{14}C -rich carbon has been added to the baseline value of dissolved carbon in the Rustler Formation. If the low-PMC values in this relationship had arisen through dilution with dead carbon, the slope would be negative. In the absence of any solid/liquid interaction, the slope would be vertical.

Whereas the PMC/bicarbonate relationship indicates simple binary mixing between low- and high-PMC reservoirs, the actual number of carbon reservoirs is greater than two. This

is indicated by the nonsystematic variation of $\delta^{13}\text{C}$ values with bicarbonate. A linear relationship between $\delta^{13}\text{C}$ and dissolved carbon concentration would result if there were only two reservoirs of carbon, because $\delta^{13}\text{C}$ values are indicative of a carbon source (i.e., rock carbonate versus organic material). In the PMC/ $\delta^{13}\text{C}$ relationships, there is a conspicuous dichotomy in carbon isotope systematics between waters with less than 10 PMC and those with greater than 10 PMC (for which one could argue that contamination had taken place during well development). The mathematical relationships among the data from the contaminated wells suggest that the mechanism of contamination due to nonsystematic modern mixing has involved three carbon reservoirs as endmembers: ancient organic material dissolved in the water at the time of recharge, carbonaceous species dissolved from the host carbonate rock, and modern organic material introduced during water-well development. The last two dominate the more contaminated samples (PMC > 10), but such samples probably contain some component of original dissolved carbon dioxide. Consequently, it is assumed here that the contaminated waters were derived from the original widespread low-PMC waters. In view of the likely effects of contamination of the Rustler, the lower limit of resolution for PMC measurements may represent the baseline value of radiocarbon in the Rustler groundwater system. Thus, the possibility that the true minimum age of recharge of the Rustler groundwater system at the WIPP site and in eastern Nash Draw is greater than 30,000 years cannot be ruled out.

The tritium concentrations of groundwaters from the Rustler Formation (especially the Culebra member, which contains the most abundant water) and the overlying Dewey Lake Red Beds are all less than 7 tritium units (TU). This includes one value of about 7 TU and one value of about 3 TU; the remaining 5 are less than 0.3 TU. The extremely low values show that the confined groundwaters in the Rustler and at least one instance of possibly "perched" water in the Dewey Lake have not received significant amounts of recharge from meteoric precipitation in the last 30 years. TU values as high as 7 are attributable to contamination, in view of the demonstrated radiocarbon contamination in the well that produced this TU value. A significant modern component in the groundwater would yield values of 20 TU or more.

The ^{36}Cl concentrations in groundwaters of this study were below the limit of detectability, even with high-sensitivity accelerator mass spectrometry. Despite claims of very low detection limits allowed by such instruments as accelerator mass spectrometers, the overwhelming amount of ^{35}Cl and ^{37}Cl (as chloride) in Rustler waters makes inapplicable the assumption of a known initial concentration of chloride (including ^{36}Cl) that is entirely atmospheric in origin. Thus, with the breakdown of assumptions fundamental to dating models (such as mixing and contamination as have been demonstrated here for radiocarbon, tritium, and ^{36}Cl), analyses of the atmospherically-generated nuclides alone will but little aid in the determination of flow paths, groundwater velocity, and the recharge/discharge areas.

Groundwater-dating methods based on the atmospheric generation of nuclides by cosmic rays should not be used by themselves, without a due consideration of their geological context. This is especially true in slow-moving groundwater systems in carbonates and

evaporites where the "purging" effect (cf. Lambert and Robinson, 1984) during sampling is small and the contamination effect can be large due to the relatively small amount of natural water recoverable from the system. Confidence should not be placed in an age calculation made on the basis of a single nuclide measurement together with only its inferred initial value and half-life, without the support of regionally derived trends of groundwater behavior.

Several of the existing radiocarbon-dating models were applied to the PMC and $\delta^{13}\text{C}$ values obtained from groundwaters thought to be minimally contaminated on the basis of their carbon-isotope systematics. The various models were first evaluated for the applicability of their assumptions to the Rustler geology. The models considered include (1) the fundamental decay equation, (2) Vogel (1970), (3) Tamers (1975), (4) Pearson and Swarzenki (1974), (5) Mook (1976), (6) Fontes and Garnier (1979), (7) Wigley et al. (1978), and (8) Evans et al. (1979). Several of the models account for dilution of the PMC value with dead carbon by dissolution of mineral carbonate. Others account for the additional loss of radiocarbon by processes other than radioactive decay, such as precipitation from solution. Some of the models examined (decay equation, Fontes and Garnier, Wigley) were found inapplicable, either because their necessary assumptions were not consistent with observed systematics in the Rustler Formation, or their level of sophistication and rigor required too many unsupportable inferences to account for unobtainable input data. Of the remaining models, those of Tamers, Pearson and Swarzenki, Mook, and Evans et al. accounted for radiocarbon loss by dilution, but only that of Evans et al. handled loss by precipitation in a way that could conceivably be supported by observations of the Rustler. Application of some of the models resulted in indeterminate ages (due to taking the logarithm of a negative number), indicating either failure of fundamental assumptions, or some degree of contamination even in the low-PMC waters, or both. The model of Evans et al. gives the youngest calculable radiocarbon ages for groundwaters thought to be (1) minimally contaminated with drilling-introduced modern carbon, and (2) part of the same carbon-isotope systematics. However, the numerical model of Evans et al. for calculating the radiocarbon age of groundwaters in carbonate aquifers yields the "correct" radiocarbon age only when:

1. The PMC value is less than 50 (i.e., there is no contamination of the water by modern carbon introduced after the initial infiltration).
2. The steady, progressive equilibration of the $^{13}\text{C}/^{12}\text{C}$ ratio of dissolved carbon with the equivalent ratio in the rock has not been perturbed by an event that adds nonradioactive carbon dioxide to the water by instantaneous leaching (congruent dissolution) of the rock.
3. There has been no mixing of waters of significantly different ages to produce the water sampled.

If any of these conditions have been violated, the radiocarbon age is indeterminate. For the cases of severe contamination (PMC > 10) in these data, significant negative ages

commonly resulted. If independent information is not available to show that none of these conditions has been violated, a high degree of confidence should not be placed in the premise that even positive radiocarbon ages are maxima.

The radiocarbon dating method cannot be applied to groundwaters without a consideration of the geological/geochemical context. Despite the detailed development of the method in well-characterized sandstone aquifers (cf. Pearson et al., 1983), spurious results are very likely to ensue if the method is blindly applied to any other system, especially carbonate aquifers. Radiocarbon dating of groundwater should not be attempted without a reasonably complete understanding of the carbon-isotope systematics in the groundwater system.

The age of the uncontaminated carbon reservoir is estimated to be at least 13,000 and possibly in excess of 30,000 radiocarbon years. The confidence limits, based on replicate analyses, applied to the least contaminated waters having less than about 6 PMC imply that these values are statistically indistinguishable from 0 PMC. In other words, the "age" (time of isolation from the atmosphere) of the natural carbon in these waters may exceed the limit of resolution of the radiocarbon method. This result is consistent with the hypothesis proposing that regional meteoric recharge of Rustler groundwater in the WIPP area has been effectively inactive since the Pleistocene.

The minimum estimated age of surface-derived recharge for groundwaters in the Rustler and parts of the Dewey Lake "aquifers" near the WIPP site is 12 to 16 Ka, and this age range is supported by other paleoclimatic evidence (fossil packrat middens) in the region. The recharge may actually be part of an earlier Pleistocene event older than the age range of the radiocarbon method, about 30 Ka, given the possibility of even a small amount of contamination of these waters by modern carbon introduced during well development, which would make apparent radiocarbon ages spuriously young. These ages should **not** be used to calculate a travel time for Rustler groundwater across the WIPP site, since (a) residence times of the four least contaminated groundwaters show no coherent, statistically significant, monotonic trends becoming younger toward some recharge point, (b) residence times (or ages of isolation from the atmosphere) of least contaminated groundwaters are statistically indistinguishable from one another, and may represent pulse-type recharge in a discrete event rather than continuous flow away from a recharge area, and (c) the relatively uniform residence times of least contaminated groundwaters may have arisen through homogenization after recharge.

The wide geographic separation of wells in the >10,000 a age range suggests that water of this apparent age was originally widespread throughout the area near the WIPP site. In some cases, insufficient time had elapsed between well development and sampling to allow for dilution of modern contaminants to the expected 50 PMC value, which would be derived from the reaction of new carbon dioxide with host rock.

Calculations of **maximum** age should not be done on any individual value of PMC available for the Rustler Formation groundwaters, since it is impossible to eliminate the effects of

anthropogenic contamination or natural mixing for any individual value. This contamination has had the effect of raising the PMC values significantly above probable native values and lowering the apparent age; this is exactly the opposite effect that is usually obtained in groundwater systems involving exchange of carbon species between water and host rock. If this were the usual case (i.e., if contamination due to well development had not occurred), one would expect to find a decrease in PMC with increasing bicarbonate, owing to the dilution and "sorption" of radiocarbon as carbon dissolved from the host rock. In such usual cases, the lowering of the PMC value by rock-water interactions would give a spuriously old apparent age, unless the PMC value could be corrected for rock-water interactions.

Taken as a group, these radiocarbon data indicate mixing phenomena between a source of dead carbon, probably in the rock carbonate, and modern carbon, probably in the organic matter introduced during drilling and developing wells. There is no indication of a preponderance of original soil- or atmosphere-derived carbon dioxide in most of these wells. The most comprehensive applicable model for interpreting radiocarbon data as ages fails for most of the data because of the complex mixing phenomena. Given the highly variable climatological history of the Delaware Basin, and the fact that the area has not always been arid, the soil cannot be excluded as an important source of the original carbon dioxide introduced into the groundwater system.

Enhanced analytical capabilities designed to allow detection of smaller amounts of radiocarbon have no bearing on the interpretability of PMC values as ages, since the effects of contamination and mixing in groundwater systems of nonuniformly low productivity cannot be precisely quantified.

Because of better ways of identifying meteoric water (D/H and $^{18}\text{O}/^{16}\text{O}$ ratios), and due to surface contamination associated with the venting of the Gnome event in the area, the usefulness of the class of weapons-generated nuclides (e.g., tritium and krypton) is limited. Furthermore, the relatively small content of native radiocarbon shows that the Rustler groundwater has been out of contact with the atmosphere for so long (at least several half-lives) that no native tritium, ^{90}Sr , ^{137}Cs , or ^{85}Kr should be observable. If significantly nonzero concentrations of these nuclides were observed, they would surely be attributable to contamination.

Because of the questionable validity of the assumptions necessary in applying radiocarbon and radiochlorine dating methods in the evaporite environment of southeastern New Mexico, and because of the previously demonstrated susceptibility of these components to contamination in this groundwater system, these methods will not be pursued beyond this feasibility study with the expectation of obtaining additional or more definitive absolute dates. As a general recommendation to those who would apply the radiocarbon method in studies of other areas, auxiliary measurements (such as concentration of dissolved carbon) should be determined in the field at the time of collection of radiocarbon samples. Any variations observed in time or space, together with the history of past drilling in the area,

should be evaluated to test the validity of the assumption that the **PMC** measurements are representative of the carbon native to the groundwater.

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1. INTRODUCTION

1.1 Relevant Questions

An understanding of the geologic history of the Rustler Formation in the northern Delaware Basin of southeastern New Mexico is considered fundamental 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 outcrops west of the WIPP site, (3) immediately overlies the Salado Formation where the WIPP facility is being mined, and (4) contains interbeds of brittle fractured rock that contain the most abundant and regionally persistent occurrences of groundwater associated with the evaporites.

Lambert and Harvey (1987) documented the stable-isotope compositions of confined groundwaters in the Rustler Formation and concluded that they are of meteoric origin. However, stable-isotope ratios of most Rustler groundwaters are distinctly different from those of other local meteoric groundwaters whose origins could be traced by observation and inference to infiltration of modern precipitation. This implied that most of the Rustler groundwaters were probably recharged under climatic conditions different from those at present. Thus, Lambert and Harvey suggested that the Rustler Formation near the WIPP site contains mostly "fossil" groundwater, no longer being actively recharged by direct influx of surface-derived modern meteoric water.

Until now, the time of major recharge to the Rustler was indeterminate, but independent paleoclimatic evidence indicated much wetter conditions, more conducive to recharge, at various times in the Pleistocene, ranging from about 20,000 to 600,000 years ago (Bachman, 1987). If the inferences of Lambert and Harvey (1987) based on stable isotopes are correct, it is of interest to know how long the groundwater has been isolated from the atmosphere (i.e., how long since the water fell as rain). Closely related, and perhaps of more direct interest is how long the groundwater has been isolated from other groundwaters that are demonstrably modern. The extent to which either question can be addressed for a given groundwater system depends on one's ability to determine the effects of mixing of different reservoirs in the subsurface. In fact the effect of mixing, an event the age of which is generally indeterminate, is typically so nontrivial as to make "absolute" dating of limited value.

1.2 Residence Time versus Travel Time

Under the best of circumstances the radiocarbon and related methods for dating groundwater give a **residence time**, or age of isolation from a source of a natural nuclide that is assumed to be entirely of atmospheric origin at the time of recharge. Determination of minimum **travel time** between points along an inferred flow path in a groundwater system requires additional inferences and/or assumptions that: (1) the fastest possible flow

path between points has been identified, (2) time markers can be determined for points along the path, and (3) the travel time between points is the difference between the dates determined at the markers.

Travel times are of particular interest in characterizing groundwater systems that have the potential of carrying radionuclides away from a radioactive waste repository. Regulations proposed for such facilities by some governmental agencies (such as the United States Environmental Protection Agency) have specified minimum travel times for groundwater in such systems. One way of determining representative minimum groundwater travel time in a local area is to take the difference in apparent recharge times for two different points along the fastest flow path; this requires assumptions that: (1) a common recharge area has been identified for both points, (2) both points lie along a common flow path emanating from the recharge area, and (3) the flow path thus identified is the fastest possible in the local area.

One of the purposes of this report is to examine and evaluate the assumptions and inferences necessary to interpret radiocarbon data as recharge ages in carbonate aquifers. The assumptions necessary to calculate travel times from apparent recharge times are based on physical hydrology and well hydraulics, and their evaluation is beyond the scope of this report.

1.3 Origins of the Nuclides

One class of atmospherically generated nuclides of interest in groundwater studies, together with their approximate half-lives, includes ^3H (half-life = 12 a), ^{85}Kr (10 a), ^{90}Sr (29 a), and ^{137}Cs (30 a). These nuclides are fission or activation products generated principally by atmospheric testing of nuclear weapons. Waters that have been out of contact with the atmosphere for several tens of years theoretically contain none of these constituents, apart from some background level; these nuclides may be found in groundwater samples contaminated during sample collection and handling. Small amounts of these nuclides may also be generated during subsurface activation of stable nuclides by neutrons from spontaneous fission.

Another class of atmospherically generated nuclides arises principally from neutron-activation or spallation reactions involving cosmic rays. These also can be generated by nuclear bomb effects and by some subsurface neutron-activation, given a suitable neutron flux from spontaneous fission. This class includes ^{14}C (half-life = 5730 a), ^{81}Kr (200,000 a), ^{36}Cl (300,000 a), ^{10}Be (1,600,000 a), and ^{129}I (15,900,000 a).

Samples for analysis of ^{81}Kr must under no circumstances come in contact with the atmosphere; because of the small solubility of Kr, even a few ^{81}Kr atoms added to the water could produce such a high degree of contamination as to give a spuriously young age. Sampling techniques to ensure this minimal level of contamination are virtually nonexistent.

^{129}I has been measured in marine sediments, where it has accumulated from both anthropogenic and cosmogenic sources, in petroleum, where its possible origin is spontaneous fission of uranium (Elmore, 1986), and in the well characterized groundwater system in the Great Artesian Basin of Australia (Fabryka-Martin et al., 1985). Due to the chemical and biological reactivity of iodine along poorly defined flow paths (especially in bedded evaporites), and the possible contamination of sampled groundwater with drilling brine, the use of this nuclide will not be actively pursued. Application of ^{129}I in the groundwaters in evaporites of southeastern New Mexico would require extensive developmental work.

^{10}Be concentrations measured in groundwaters range from 1×10^3 to 2×10^5 atoms/g, "with the higher values being consistently associated with low pH and/or high salinity" (Valette-Silver et al., 1986). Furthermore, at pH higher than 5.6 (i.e., most groundwaters) the sorption and retention of ^{10}Be by fine-grained material is "very effective." Due to its exceedingly low solubility, making it highly susceptible to small amounts of contamination, and its high degree of sorption, involving a high degree of rock-water interaction, the use of ^{10}Be , would also require a large amount of developmental work before its applicability to groundwater "dating" in southeastern New Mexico could be determined.

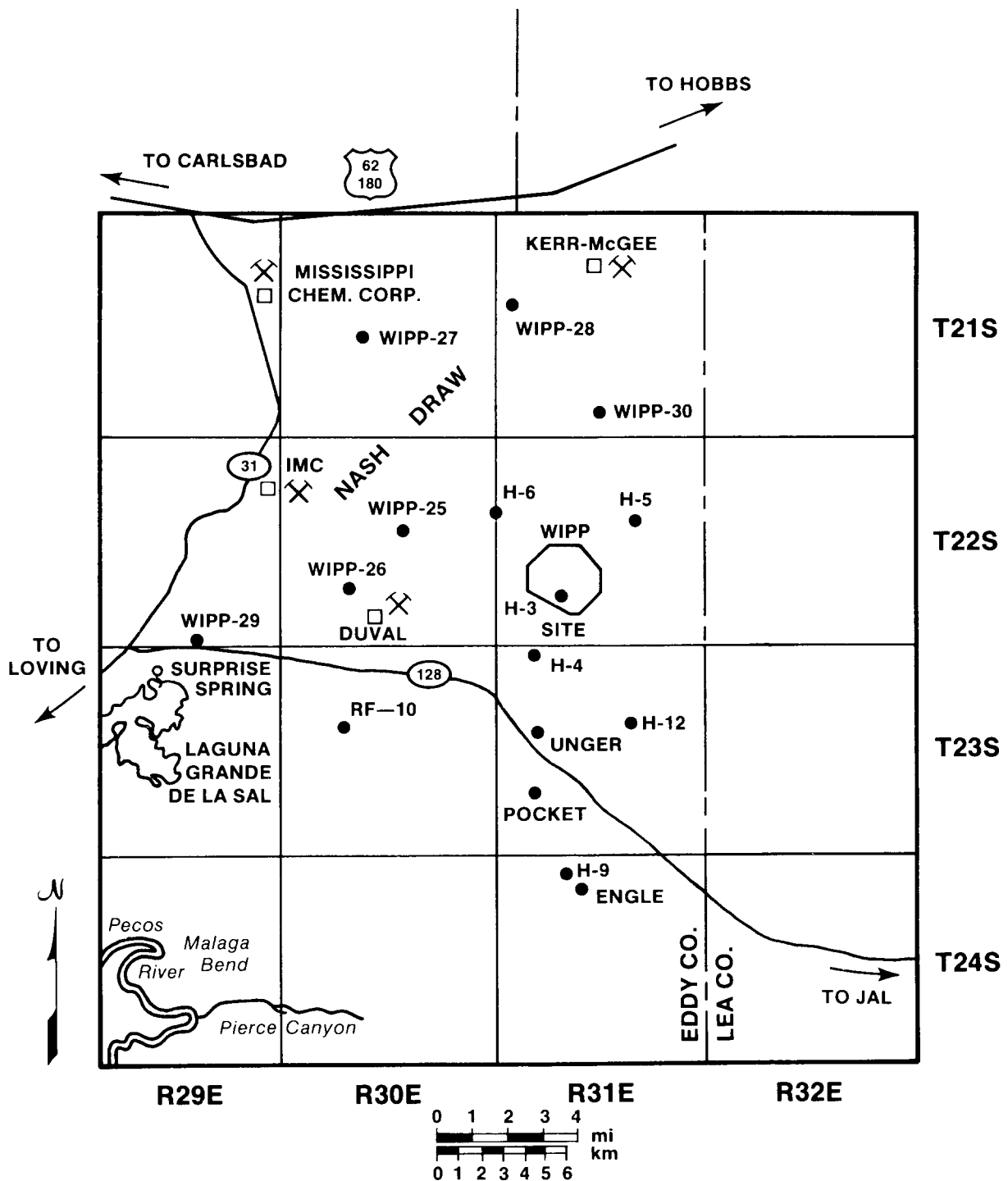
Methods for sampling, analyses, and systematic interpretation have been developed extensively in the literature for ^3H (tritium, abbreviated "T"), ^{14}C (radiocarbon), and ^{36}Cl (radiochlorine or radiochloride). The balance of this work is a detailed evaluation of the applicability of these nuclide systematics to the groundwater hydrology of the Rustler Formation as related to the WIPP.

2. METHODS

2.1 Origins of Samples

Locations of boreholes relevant to this work are given in Figure 1. Three water-bearing units above the main evaporite sequence are of primary interest in this study: 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, two of the boreholes allowed sampling of local water-bearing horizons in the Dewey Lake Red Beds immediately overlying the Rustler Formation. The Culebra dolomite member of the Rustler Formation appears to be the most regionally-pervasive and consistent water-producing horizon (Mercer, 1983). The detailed stratigraphy of the Rustler Formation and the general stratigraphy of the Ochoan rocks in the northern Delaware Basin of southeastern New Mexico have been described by Snyder (1985), and will not be reviewed here.

In 1980 and 1981, water samples were collected by personnel of Sandia National Laboratories. After 1981 samples were collected by Hydro-Geo-Chem, Inc., of Tucson, Arizona, a Sandia sub-contractor.



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Figure 1. Locations of boreholes and other geographic features relevant to this study, northern Delaware Basin, southeastern New Mexico.

In several boreholes core samples of the water-bearing horizons were available along with water samples. Carbon-isotope analyses of the rock in most recent contact with the water allow carbon-isotope systematics of rock-water interactions to be considered in various interpretive (dating) models. This is necessary in the case of attempted radiocarbon dating of groundwaters from carbonate aquifers. 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 drilled largely by the rotary method, and were cored through the Magenta and Culebra members only. Where the Culebra member contains significant (i.e., recoverable) amounts of water it is typically highly fractured or poorly consolidated in its water-bearing horizons, and near the WIPP site is rubblized due to a combination of high fracture density and partial dissolution of its significant calcium sulfate component (Mercer, 1983). Thus, complete recovery of intact core is not typical of the permeable horizons of the Culebra. It is more typical for loose fragments and poorly consolidated material to fall out of the the core barrel in the subsurface or after it is brought to the surface, and hence the precise depth of many fragments of Culebra from permeable zones is unknown; however, the depth of origin for most fragments can be determined within an interval of a few feet.

In any field investigation, what is proper for one set of objectives may not be consistent with optimizing the experimental design for an entirely different set of objectives. Specifically, the Nash Draw series of holes (WIPP-25 through -30) was designed to be drilled for **as complete core recovery as possible**. This commonly required the addition of organic materials such as shredded newspaper, peanut shells, cottonseed hulls, and proprietary hydropolymer mud to control lost circulation. Other holes were designed to optimize hydrologic testing, to establish maximal hydraulic communication between formation and borehole, and to minimize hydraulic communications between the formation and units above and below. Thus, none of the boreholes in this study was designed expressly for geochemical sampling to support radiocarbon dating of Rustler groundwater. The collection of samples for hydrochemical studies is largely dependent upon pre-existing hole conditions, and must be considered a "target of opportunity."

2.2 Carbon Isotopes

The methods of collection and field preservation of samples for radiocarbon analysis were reported in detail for boreholes WIPP-25 through -30 by Lambert and Robinson (1984). In 1980 these boreholes (originally 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, not all effluents from pump tests were considered suitable for radiocarbon sampling.

The principal procedure used by Lambert and Robinson (1984) for field preservation of radiocarbon samples involved the (presumed) quantitative fixation of dissolved carbon in the solid state. A 50 to 200 L sample was made basic and the inorganic carbon was precipitated as BaCO_3 ; the precipitate was sent to the laboratory for analysis. When high total dissolved solids interfered with the chemical preservation procedure, a bulk water sample (also 50 to 200 L) was sent to the laboratory. For four of the samplings, both methods were used. Similar methods were used for Culebra samples from boreholes H-4B, H-5B, and H-6C (Robinson, 1987). The methods used at wells sampled after 1981 are also given by Robinson. Basically, post-1981 bulk samples were collected in 500 mL stainless steel cylinders.

The procedure used to measure dissolved carbon (an ordinary bicarbonate/carbonate "alkalinity" titration), unless otherwise specified, was also the same as that described by Lambert and Robinson (1984). Confidence limits at the 95% level for this method were ± 5 mg/L. Many literature tabulations of radiocarbon data for groundwaters do not include the concentrations of dissolved carbon, although in this study it was necessary to know the concentration of bicarbonate and carbonate prior to applying the chemical preservation procedure in the field, in order to determine required quantities of certain reagents. Recent analytical developments appear to have made the preservation procedure unnecessary, and unfortunately the dissolved carbon concentration may no longer be routinely determined by those principally interested in radiocarbon. The usefulness of other measurements related to radiocarbon dating (in addition to PMC and $\delta^{13}\text{C}$), such as total dissolved carbon concentration, is apparent in this study.

All carbon-isotope measurements were performed by the Laboratory of Isotope Geochemistry at the University of Arizona. Samples of barium carbonate prepared in the field as described by Lambert and Robinson (1984) were acidified in the laboratory under vacuum to liberate carbon dioxide, which was then purified (over cupric oxide at 800°C to convert any carbon monoxide to carbon dioxide, over phosphorus pentoxide to remove water, and through activated charcoal to remove any remaining impurities). In some cases, the carbon dioxide was obtained from bulk water samples by acidification and nitrogen-purging after the bulk water samples had reached the laboratory. Each gas sample was then aged to allow the decay of ^{222}Rn (half-life of 3.8 days versus 5730 years for ^{14}C). The activity of ^{14}C in the gas was determined in a gas proportional counter, and expressed as percent modern carbon (PMC) relative to the ^{14}C activity in the equivalent amount of carbon dioxide liberated in the combustion of 1950 wood (containing organic carbon fixed before the era of atmospheric testing of nuclear devices). Each gas sample was counted at least twice, for at least 2000 minutes. $\delta^{13}\text{C}$ values of the carbon dioxide samples were measured using a Micromass 602C isotope-ratio mass spectrometer, and are expressed in parts per thousand (‰) relative to the Chicago Peedee Belemnite (PDB).

Water samples in 500 mL stainless-steel cylinders were treated differently. Dissolved CO_2 was extracted, incorporated into a graphite target, and analyzed with an accelerator mass spectrometer. $\delta^{13}\text{C}$ was measured on an aliquot of the CO_2 gas resulting from this extraction, as above.

Ratios of the stable carbon and oxygen 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 CO₂ collected after one hour is attributed to calcite, and CO₂ 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 three-day reaction time was sufficient to obtain reproducible δ -values, but a maximum CO₂ yield required 6 days.

2.3 Chlorine-36

All samples for ³⁶Cl were collected as described by Lambert and Robinson (1984); bulk water samples were collected in 125 mL polyethylene bottles and sent to Hydro-Geo-Chem, Inc. of Tucson, Arizona. Samples were collected from the Magenta at WIPP-25 and -27, the Culebra at WIPP-25, -26, -27, -28, -29, and -30, and the Rustler/Salado contact at WIPP-25, -26, -28, -29, and -30. Chloride was precipitated from water samples using silver ion, and was incorporated into a target and analyzed for ³⁶Cl with an accelerator mass spectrometer in the Nuclear Structure Laboratory at the University of Rochester, as arranged with Hydro-Geo-Chem.

2.4 Tritium

There were three episodes of tritium sampling:

1. Samples collected in 1980 by Sandia National Laboratories, in 4-oz clear flint glass bottles fitted with polyseal-lined screw-caps. These bulk samples were counted for tritium in a liquid scintillation apparatus as part of a preliminary screening procedure. Results were in pCi/L or dpm/L, and were not corrected for density.
2. Aliquots taken by Hydro-Geo-Chem from bulk radiocarbon samples (polyethylene jerrycans) of H-4B Culebra (may actually have been WIPP-26 Culebra), WIPP-27 Magenta, and H-5B Culebra. The first two were counted in bulk for tritium by Teledyne Isotopes, Inc. The last was analyzed for tritium by the U. S. Geological Survey using a method similar to that of the University of Miami, described below. The Teledyne results were reported in pCi/L and were corrected for density.
3. Samples collected by Hydro-Geo-Chem, 1983-1985, in 1-L brown flint glass screw-cap bottles, sealed with beeswax/paraffin. Measurements on these samples were made by the University of Miami. After distillation of the water sample, electrolytic enrichment of tritiated water, and liberation of hydrogen by reduction of water with hot magnesium, the gas was admitted to a low-level gas

proportional counter. Counting times were 6 to 20 hours. The procedure is described in detail by Ostlund and Dorsey (1977). Results were reported in tritium units (TU; 1 tritium in 10^{18} hydrogen atoms).

3. DATA AND CONFIDENCE LIMITS

3.1 Data

The alkalinity, $\delta^{13}\text{C}$, radiocarbon, and some tritium data (from Teledyne and the University of Miami) are given in Table 1.

3.2 Confidence Limits for Carbon Isotopes in Groundwaters

Table 2 contains only the raw radiocarbon data, including the $\pm 1 \sigma$ arising from the replicate counting. Standard deviations (s values) were calculated from the replicate measurements for WIPP-27 Magenta, WIPP-27 Culebra, WIPP-26 Culebra, WIPP-25 Culebra, and WIPP-25 Magenta; in each of those five cases, the number of degrees of freedom was 1. The pooled s value for 5 degrees of freedom was 1.57, which was found to be statistically representative of the 5 individual s-values, according to the M-test (Natrella, 1963). Thus, using the method of calculation given by Natrella (1963), at the 95% confidence level the double-sided confidence limits are ± 2.86 for 2 replicates and ± 4.03 for 1 replicate; at the 99% confidence level the respective limits are ± 4.48 and ± 6.33 . Note that at the 95% confidence level, the PMC values for H-9B Culebra and Pocket (the two lowest PMC values in Table 1) include zero in their confidence limits. At the 99% confidence level, the three lowest PMC values in Table 1 (H-9B Culebra, Pocket Dewey Lake, and H-4B Culebra) include zero in their confidence limits. The confidence limits are not derived from the conventional standard deviation arising from counting statistics on an individual analysis, but from replicate sampling, extraction, and counting. Indeed, counting statistics contribute to the analytical variation in PMC, and are designed to so contribute minimally. The replicate analyses show variations exceeding the variations ascribable to the measurement alone (Table 2), so the variations arising from replicate sampling, chemical preservation (in some cases), and laboratory treatment clearly outweigh the contribution of counting variation alone. Thus, the counting variation does not adequately represent the total analytical variation ("uncertainty"), and could be a minimum but not a maximum estimate of this variation.

The same set of 5 samples was used to calculate confidence limits at the 95% level for $\delta^{13}\text{C}$ values. There were also two replicates of each, giving a pooled s-value (0.71) with 5 degrees of freedom as before. Using the same T-factor as before, the double-sided confidence limits at the 95% level are $\pm 1.82 \text{ ‰}$. Again, this is much larger than the typical analytical confidence limits for $\delta^{13}\text{C}$ measurements, due to inclusion of wellbore effects that adversely influence sample homogeneity at various sampling localities.

TABLE 1. RADIOCARBON AND OTHER RELEVANT MEASUREMENTS
IN GROUNDWATERS OF SOUTHEASTERN NEW MEXICO

| Well and Date of Collection | Bicarbonate mg/L | $\delta^{13}\text{C}$ vs. PDB (‰) | PMC (type) | Tritium TU (lab) ¹ $\pm 1 \sigma$ |
|------------------------------------|---|---|---|--|
| Dewey Lake Red Beds: | | | | |
| Unger 26 Jan 84 | unk. | | | -0.08±0.07 |
| Pocket 2 Nov 83 | unk. | -3.78 | 3.67 (cyl) ² | |
| Magenta Member, Rustler Formation: | | | | |
| WIPP-25 18 Sep 80 | 180 | -6.8 -6.4 | 50.7 (bulk) ³ 49.27 (pptn) ⁴ | |
| WIPP-27 25 Sep 80 | 210 | -7.0 -9.0 | 69.6 (bulk) 67.76 (pptn) | 6.9±0.9 (Tel) |
| Culebra Member, Rustler Formation: | | | | |
| H-3B3 11 Jun 84 | | | | 0.05±0.04 |
| H-3B3 4 Feb 85 | | -79.35 | [lost] (cyl) | |
| H-4B 29 May 81 | 71 | -6.7 | 4.82 (bulk) | 2.8±0.6 (Tel) |
| H-5C 15 Oct 81 | 86 | -3.7 | 18.0 (bulk) | 0.3±0.1 (USGS) |
| H-6C 27 May 81 | 95 | -8.4 | 9.7 (pptn) | |
| H-9B ⁵ 7 Oct 83 | (USGS) 90 | -2.40 | 2.22 (cyl) | |
| H-12 11 Jan 84 25 Jan 84 | unk. | | | 0.17±0.08 0.11±0.08 |
| WIPP-25 20 Aug 80 | 210 | -7.6 -7.1 | 59.8 (bulk) 56.6 (pptn) | |
| WIPP-26 24 Aug 80 | 140 | -5.9 -5.8 | 36.2 (bulk) 33.3 (pptn) | |
| WIPP-27 5 Sep 80 | 120 | -4.3 -5.1 | 30.7 (bulk) 30.0 (bulk) | |
| WIPP-29 28 Aug 80 | 210 | -5.1 | 49.76 (bulk) | |
| WIPP-30 5-6 Sep 81 | 40 (HCO ₃ ⁻³) 17 (CO ₃ ⁻²) | | -- ⁶ | |

TABLE 1. (continued)

| Well and Date of Collection | Bicarbonate mg/L | $\delta^{13}\text{C}$ vs. PDB (‰) | PMC (type) | Tritium TU (lab) $\pm 1 \sigma$ |
|-----------------------------------|---------------------|---|-------------|---------------------------------------|
| RF-10 ⁷ 6 Oct 83 | unk. | -5.39 | 39.7 (cyl) | |
| Engle ⁸ 9 Nov 83 | 110 | -2.80 | 11.5 (cyl) | 0.03±0.09 |
| Rustler/Salado Contact Zone: | | | | |
| WIPP-26 23 Jul 80 | 270 | -7.1 | 90.7 (bulk) | |
| WIPP-28 31 Jul 80 | 170 | -4.7 | 48.5 (bulk) | |
| WIPP-29 24 Jul 80 | 200 | -4.8 | 53.4 (bulk) | |

1. Unless otherwise specified, all tritium measurements were performed by the University of Miami. USGS indicates measurements made by the United States Geological Survey. Tel indicates measurements made by Teledyne Isotopes. Samples sent to Teledyne for tritium analysis were drawn from the bulk water samples (in polyethylene jerrycans) collected for radiocarbon analysis. Teledyne received these samples, and analyzed them for tritium 10 months after sample collection. Hence, values reported here have been corrected for tritium decay between time of collection and time of measurement. There is reason to question the reliability of the mode of preservation of these samples. There is also some indication (the date of collection given as "8/24/80" on the Teledyne report) that the "H4B" tritium value may actually be from WIPP-26.

2. cyl - water samples collected in 500 mL steel cylinders, whose carbon-isotope compositions were analyzed by accelerator mass spectrometry.

3. bulk - bulk water samples (in wax-sealed polyethylene jerrycans) from which carbon dioxide was liberated by acidification and nitrogen-purging in the laboratory.

4. ppt - carbon dioxide samples obtained by acidification of the barium carbonate precipitate prepared in the field immediately following the collection of the water.

5. The bicarbonate and PMC values for this well were measured on samples collected according to different criteria, and which came from two **different** pump tests of the well.

6. "No CO₂ from 6 bottles of barium ppt."

7. These data were identified with "H.13" (and bore the same collection date as given here) by the letter of transmittal from University of Arizona to Hydro-Geo-Chem, March 1, 1984. In the transmittal of data from Hydro-Geo-Chem to Sandia, the hole identification was "RF-10", as appears here. The correct hole designation is more likely "FR-10".

8. The bicarbonate and PMC values for this well were measured on samples collected according to different criteria, and which came from two **different** pump tests of the well.

TABLE 2. CONFIDENCE LIMITS FOR RADIOCARBON MEASUREMENTS¹

| <u>Well</u> | <u>PMC ± counting (1 σ)</u> | <u>DF</u> | <u>Mean</u> | <u>S²</u> |
|--|-------------------------------------|-----------|-------------|----------------------|
| <u>WELLS HAVING TWO REPLICATE ANALYSES:</u>³ | | | | |
| WIPP-25 Magenta | 50.7 ±1.1 | 1 | 49.99 | 1.01 |
| | 49.27 ±0.79 | | | |
| WIPP-27 Magenta | 69.6 ±0.7 | 1 | 68.68 | 1.30 |
| | 67.76 ±0.71 | | | |
| WIPP-25 Culebra | 59.8 ±1.1 | 1 | 58.20 | 2.26 |
| | 56.6 ±1.0 | | | |
| WIPP-26 Culebra | 36.2 ±1.9 | 1 | 34.75 | 2.05 |
| | 33.3 ±1.0 | | | |
| WIPP-27 Culebra | 30.7 ±1.4 | 1 | 30.35 | 0.49 |
| | 30.0 ±1.2 | | | |
| <u>WELLS HAVING ONE REPLICATE ANALYSIS:</u>⁴ | | | | |
| Pocket Dewey Lake | 3.67 ±0.33 | 0 | | |
| H-4B Culebra | 4.82 ±0.96 | 0 | | |
| H-5C Culebra | 18.0 ±1.9 | 0 | | |
| H-6C Culebra | 9.7 ±1.4 | 0 | | |
| H-9B Culebra | 2.22 ±0.33 | 0 | | |
| WIPP-29 Culebra | 49.76 ±0.59 | 0 | | |
| RF-10 Culebra | 39.7 ±1.3 | 0 | | |

TABLE 2. (continued)

| <u>Well</u> | <u>PMC ± counting (1 σ)</u> | <u>DF</u> | <u>Mean</u> | <u>S</u> |
|---------------------------|-------------------------------------|-----------|-------------|----------|
| Engle Culebra | 11.5 ±1.5 | 0 | | |
| WIPP-26 Rustler/Salado | 90.7 ±1.9 | 0 | | |
| WIPP-28 Rustler/Salado | 48.5 ±1.7 | 0 | | |
| WIPP-29 Rustler/Salado | 53.4 ±1.2 | 0 | | |

1. See Natrella (1963) for a detailed discussion of the procedure used to calculate two-sided confidence limits at various levels of confidence.
2. Pooled $s = 1.57$; $df = 5$.
3. For two replicates (one degree of freedom) the confidence limits derived from the pooled S-value (note 2) are ± 2.86 and ± 4.48 PMC, at the 95% and 99% confidence levels, respectively.
4. For one replicate (zero degrees of freedom) the confidence limits derived from the pooled S-value (note 2) are ± 4.03 and ± 6.33 PMC, at the 95% and 99% confidence levels, respectively.

Some PMC and $\delta^{13}\text{C}$ values are available from both BaCO_3 -precipitate and bulk-water samples from the same unit in the same well. The analytical results differ somewhat for the two methods of carbon preservation. In subsequent discussions and calculations, preference is given to the results from the barium carbonate method, if available, as it is not known how much carbon-isotope exchange took place through the walls of the bulk-water-sample containers while bulk samples were awaiting transit to the laboratory. Several samples (WIPP-25 Magenta, WIPP-25 Culebra, WIPP-26 Culebra, and WIPP-27 Magenta) spent 6 to 7 months awaiting shipment to the laboratory, while the typical delay was 1 to 2 months. This preference also assumes that no isotopic fractionation occurred either during carbon fixation as BaCO_3 or subsequent extraction in the acidification step. In the case of WIPP-27 Magenta, for which only bulk water samples were available, the higher of the two PMC values (30.7) is given preference. Fritz et al., 1985) compared two methods of CO_2 collection for carbon isotope studies (wellhead versus downhole fixation with sodium hydroxide), showing that during the course of a sampling episode, isotopic fractionation was likely to occur, as might be expected, if sorption and fixation of an aliquot of CO_2 were incomplete. The BaCO_3 -precipitation method was designed for use in relatively dilute groundwater solutions, to maximize the probability of complete fixation. However, treatment of one sample (WIPP-30 Culebra; Table 1) resulted in no carbon fixation. The completeness of the fixation in any of the BaCO_3 samples cannot be evaluated, because no information is available regarding the quantity of CO_2 recovered from the BaCO_3 by acid-extraction in the laboratory relative to the estimated quantity of original CO_2 in each aliquot of water sampled and subjected to the BaCO_3 procedure.

Although the $\delta^{13}\text{C}$ measurement is typically reproducible to within 0.1 ‰, larger variations between replicates are observed in Table 1 for WIPP-27 Magenta ($\Delta = 2.0$ ‰), WIPP-27 Culebra ($\Delta = 0.8$ ‰), and WIPP-25 Culebra ($\Delta = 0.5$ ‰). The variation is particularly conspicuous for WIPP-27 Magenta, and accounts in part for the anomalously large confidence interval for the $\delta^{13}\text{C}$ value of dissolved carbon (± 1.8 ‰). The variation in WIPP-27 Culebra is remarkable in that the $\delta^{13}\text{C}$ measurements came from each of two identical jerrycans of bulk water. According to analyst Austin Long at the University of Arizona, (written communication, June 17, 1981):

Differences in $^{13}\text{C}/^{12}\text{C}$ are greater than expected for duplicate analyses, but the ^{13}C sampling technique is not optimized for precision, rather for normalization of any fractionation which might occur anywhere in sample processing. The $\delta^{13}\text{C}$ reported is, therefore, only an approximation of that value in the sampled water. ^{14}C values reported are not normalized by ^{13}C .

The "normalization" in the conventional usage of radiocarbon dating (shell, bone, wood, charcoal, etc.) is inappropriate for groundwaters, because evaluating the applicability of various interpretive dating models shows the critical dependence of calculated model age on a knowledge of carbon-isotope systematics, including consideration of sources and sinks of carbon in the groundwater system. Also, note the unusual relationships between the bulk and precipitate values (Table 1) for WIPP-27 Magenta and WIPP-25 Culebra; in the former the bulk sample has the higher PMC and the less negative $\delta^{13}\text{C}$, while in the latter the bulk sample has the higher PMC and the more negative $\delta^{13}\text{C}$. Thus, conventional

"normalization" for fractionation (during precipitation, extraction, or other processes) would not be able to "correct" for the differences observed in these two sets of PMC and $\delta^{13}\text{C}$ values.

3.3 Carbon Isotopes in Rock Carbonate

The $\delta^{13}\text{C}$ values of rock carbonate are given in Table 3, together with the yields in weight percent. All gas liberated in a three-day extraction period was attributable to dolomite, but the yields show that the rock was in no case pure carbonate. Extractions were also made after six days, but the resulting $\delta^{13}\text{C}$ values were not substantially different, and the carbonate yield in no case approached 100%. The $\delta^{13}\text{C}$ values of the dolomite occurrences in the water-bearing units of the Rustler Formation sampled for radiocarbon have a mean of +5.7 ‰, with a standard deviation of 0.3 ‰ for 9 degrees of freedom. The resulting confidence limits, at the 95% level, are ± 0.7 ‰. The $\delta^{13}\text{C}$ value of material potentially contributing to the total dissolved carbon is one essential input to a numerical model that provides an interpretation of radiocarbon data as groundwater ages. A subsequent discussion will explain how the assumed systematic behavior of stable carbon isotopes is used to adjust the radiocarbon values for loss during dilution and isotope exchange with host rock.

4. DISCUSSION

First, the ^{36}Cl results will be discussed in the context of Permian evaporites. Then, most of the remaining discussion will deal with radiocarbon, and the discussion of the tritium data will be deferred until a context has been developed in terms of the radiocarbon.

4.1 Chlorine-36

The ^{36}Cl values reported for Rustler groundwaters (H. Bentley, written communication) are all less than the limit of detectability for the measurement method (1 part ^{36}Cl in 10^{15} parts ^{35}Cl). This does not necessarily imply that the groundwaters have been out of contact with the atmosphere for a length of time greater than many half-lives of ^{36}Cl . Instead, it probably implies that the original level of cosmic-ray-generated ^{36}Cl has been diluted below the detection limit by dead ^{35}Cl and ^{37}Cl dissolved from the halite adjacent to the water-bearing intervals in the Rustler Formation.

A preponderance of chloride in solution derived from Paleozoic halite contradicts the fundamental assumption of this method that most chloride, including the neutron-activation product ^{36}Cl , originates from dust in the atmosphere that becomes partially activated by cosmic rays to some steady-state concentration of ^{36}Cl , to be subsequently accumulated and concentrated by raindrops that infiltrate and recharge the groundwater system. This dilution by dead chlorine is a far more stringent limitation to the applicability of this method to Rustler groundwaters than the uncertainty imposed by subsurface activation of chloride by slow neutrons released in natural fission. ^{36}Cl systematics in Quaternary

TABLE 3. STABLE-ISOTOPE COMPOSITION OF CARBONATES

| <u>Sample Name</u> ¹ | <u>Extraction</u> | <u>Yield (%)</u> ² | <u>$\delta^{13}\text{C}$</u> ³ | <u>$\delta^{18}\text{O}$</u> ⁴ |
|---------------------------------|-------------------|-------------------------------------|--|--|
| Culebra Dolomites: | | | | |
| H-4B 509/517 | 3-day | 45 (D) | 5.8 | 34.3 |
| | 6-day | 19 (D) 64 (Σ) | 5.8 | 35.1 |
| H-5B 912 | 3-day | 41 (D) | 5.3 | 33.4 |
| | 6-day | 32 (D) 23 (D) 55 (Σ) | 5.8 | 32.3 |
| H-6B 616 | 3-day | 41 (D) | 5.9 | 32.6 |
| | 6-day | 24 (D) 65 (Σ) | 6.1 | 33.9 |
| WIPP-25 461 | 3-day | 45 (D) | 5.9 | 33.4 |
| | 6-day | 44 (D) 21 (D) 65 (Σ) | 6.2 | 33.7 |
| WIPP-26 198/208 | 3-day | 48 (D) | 6.1 | 33.7 |
| | 6-day | 49 (D) 24 (D) 73 (Σ) | 5.7 | 34.3 |
| WIPP-27 307/308 | 3-day | 49 (D) | 5.4 | 33.9 |
| | 6-day | 40 (D) 25 (D) 65 (Σ) | 6.1 | 33.7 |
| WIPP-28 431 | 3-day | 42 (D) | 5.9 | 33.6 |
| | 6-day | 44 (D) 27 (D) 71 (Σ) | 5.9 | 33.4 |
| WIPP-29 35 | 3-day | 42 (D) | 5.8 | 33.2 |
| | 6-day | 52 (D) 22 (D) 74 (Σ) | 5.5 | 33.4 |
| | 3-day | 53 (D) | 5.6 | 33.8 |
| | 3-day | 52 (D) | 5.4 | 33.4 |
| | 3-day | 52 (D) | 5.4 | 33.3 |

TABLE 3. (continued)

| <u>Sample Name</u> | <u>Extraction</u> | <u>Yield (%)</u> | <u>$\delta^{13}\text{C}$</u> | <u>$\delta^{18}\text{O}$</u> |
|---------------------------|-------------------|------------------|---|---|
| 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) | | |
| 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 |

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

2. (D) = weight % dolomite; (C) = weight % calcite; (Σ) = cumulative yield after 6-day reaction.

3. ‰, versus Chicago Peedee Belemnite.

4. ‰, total oxygen versus Standard Mean Ocean Water (SMOW).

evaporites (Phillips et al., 1983; Paul et al., 1986) rely on exposure of chloride to near-surface processes regardless of the chloride source. In addition, similar limitations apply to the ^{36}Cl method as to radiocarbon. Problems of contamination (especially in the presence of chloride-rich dust locally generated by potash refineries) and mixing will only magnify the uncertainties associated with very low levels of ^{36}Cl that can be measured with modern analytical methods.

This study concludes that the ^{36}Cl method has applicability neither to the Rustler groundwaters in particular, nor to groundwaters in ancient evaporites in general. In southeastern New Mexico, the problem of locally generated, ancient-chloride-bearing dust severely restricts the applicability of the method in near-surface environments as well.

4.2 Relationships among Radiocarbon and Other Data

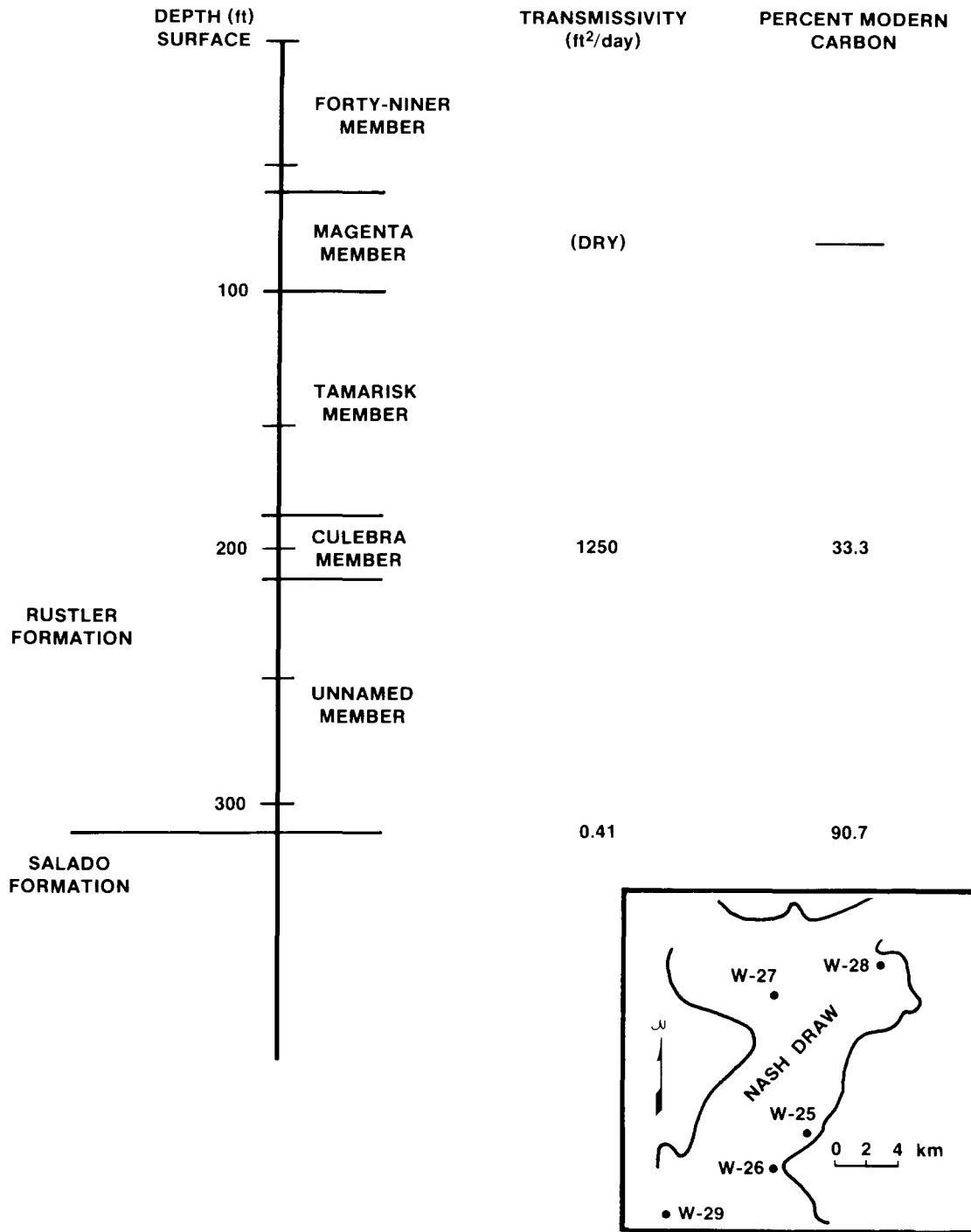
4.2.1 The Need for a Geological Context.

One objective of radiocarbon and other isotopic studies is to derive certain systematics relevant to groundwater systems, such as water origins and travel or residence times. In order for isotopic interpretations to be reliable, however, it is critical that the interpretations be consistent with local and regional geological inferences. Several specific types of inconsistency described in this section give one reason to question the validity of many of the data collected as part of this study. These inconsistencies suggest varying degrees of local contamination that cast in doubt how well many of the data actually represent unperturbed groundwater conditions.

4.2.2 Hydraulics.

A rather striking observation involves the highest PMC value of the data set, WIPP-26 Rustler/Salado. This water contains almost three times as much modern carbon (91 PMC versus 33 PMC) as water from the Culebra in the same hole, 100 feet above. This relationship is depicted in Figure 2, which also is a schematic representation of the generalized stratigraphy of the Rustler Formation. Apparently older water overlying apparently younger water is a somewhat problematical, albeit possible, geological relationship. It would be most probable if the "younger" (i.e., higher-PMC) water were in a highly transmissive zone, and the older (possibly relict) water in lower-transmissivity zones. In WIPP-26, however, the potentiometric level is higher in the upper unit (3006 versus 2960 feet above sea level). The same is true of the transmissivity (1250 feet²/day for the Culebra, versus 0.041 feet²/day for the Rustler/Salado, according to Gonzalez, 1983). If either of the superposed yet hydraulically isolated water-bearing units could be expected to show affinity with surface-derived and hence younger water, it should be the Culebra, with its significantly higher transmissivity. This observation alone suggests that individual PMC values should not be used to calculate absolute "ages", especially if such ages are not consistent with geological observations. The presence of a non-native component of dissolved modern carbon is suspected.

WIPP 26



TRI-6331-41-0

Figure 2. Generalized stratigraphy, hydraulic properties, and percent-modern-carbon (PMC) values in borehole WIPP-26. The stratigraphy is typical of all boreholes in this study, except for WIPP-29, where erosion has truncated all of the stratigraphic section above the Culebra member. Inset: location of WIPP-26 in relation to other boreholes in Nash Draw.

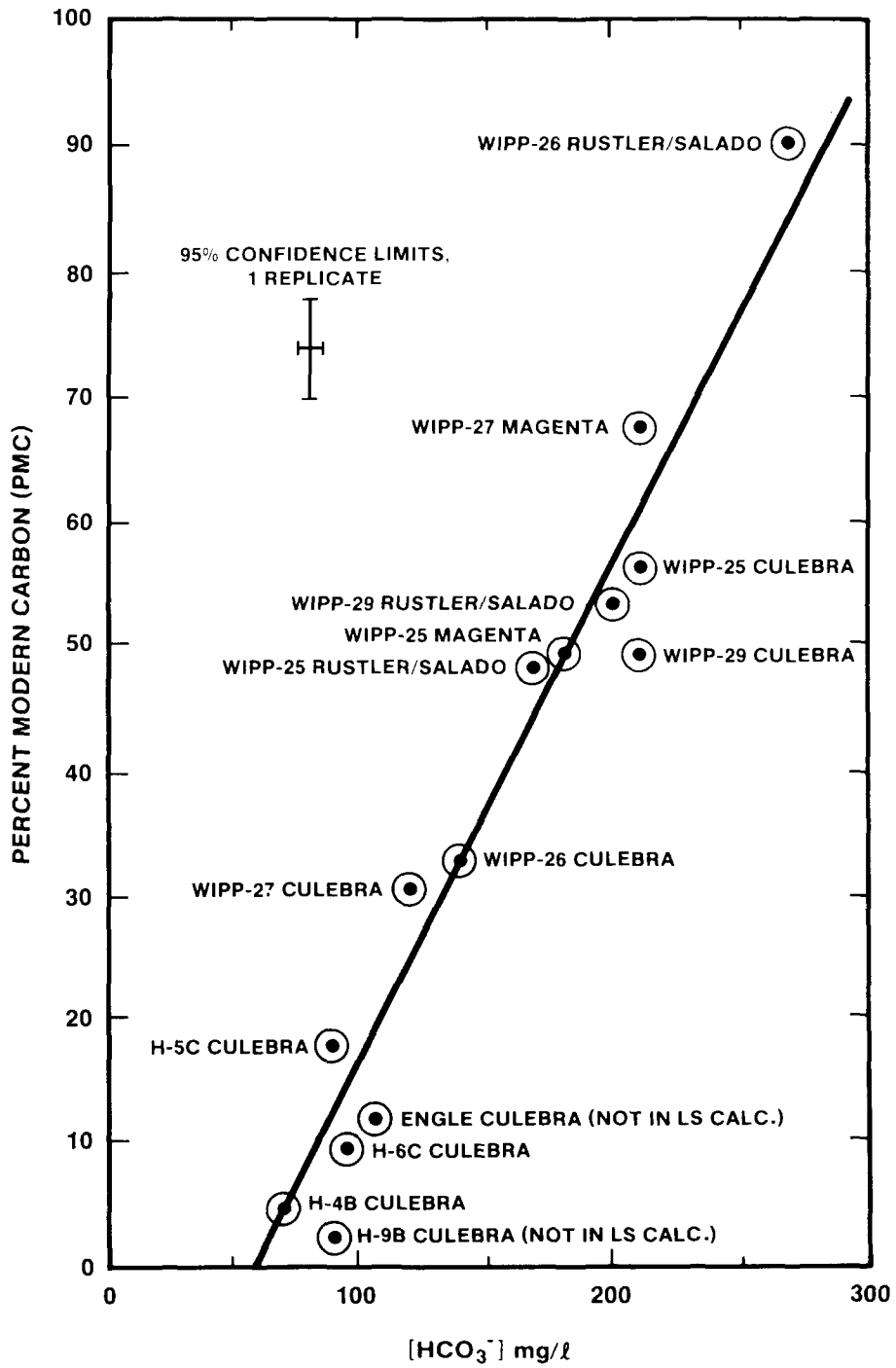
Another indication of relatively large but differing amounts of contamination is the significant difference in PMC values between the Magenta and Culebra in WIPP-25 and WIPP-27. According to Lambert and Harvey (1987), the similarities in potentiometric levels, field-geochemistry, and oxygen- and hydrogen-isotope ratios, indicate that the Magenta and Culebra members have a vertical hydraulic interconnection in these two boreholes. Laboratory determinations of major solutes (Robinson, 1987) have also shown similarities of Magenta and Culebra waters at these localities. Although it cannot be determined with absolute certainty that vertical connections at these localities are natural and not induced by drilling, the geochemical and hydraulic similarities suggest that the PMC values for Magenta and Culebra waters should also be similar at each locality. This is not the case. In WIPP-27, the PMC values differ by a factor of two. In WIPP-25, the PMC values differ by 6 to 10 PMC, a variation that significantly exceeds the confidence interval of ± 4 PMC; i.e., PMC values for the Magenta and Culebra in WIPP-25 do not statistically overlap. Also, the PMC value for the Culebra in WIPP-25 is greater than that of the overlying Magenta. Thus, at these wells, and possibly others, a non-native component of carbon has been admixed in nonconstant proportions in each of the two hydraulically connected but individually sampled horizons. The results also indicate that the time scale for vertical mixing and homogenization of fluids is long relative to the two- to three-year interval between drilling and sampling at these holes, in spite of the apparent vertical connection.

4.2.3 Speciation of Total Dissolved Carbon.

The field-measured alkalinity was taken as a close approximation to $[\text{HCO}_3^-]$, since the correction for contributions of borates, sulfides, phosphates, iron species, silica species, etc. was estimated to be very small (Lambert and Robinson, 1984; Robinson, 1987). The partitioning of total dissolved carbon among the species $\text{CO}_2(\text{aq})$, HCO_3^- , and CO_3^{2-} is related to pH, whose field accuracy was estimated by Lambert and Robinson to be ± 0.1 pH unit. Given that most confined groundwaters near the WIPP site had pH values of at least 6.9 (Lambert and Robinson, 1984), and are typically somewhat higher in the most productive zones at the WIPP site itself (Robinson, 1987), it is estimated, using the approximations based on discussions by Stumm and Morgan (1970), that greater than 90% of the total dissolved carbon in the least contaminated (e.g., lowest-carbon) groundwaters will be bicarbonate, whose concentration is taken to be approximately equivalent to alkalinity. The notable exception to this is WIPP-30 Culebra (Table 1), where $[\text{CO}_3^{2-}]$ is appreciable, due to the relatively high pH measured there (8.8; Lambert and Robinson, 1984). The possible effect of underestimating the $[\text{CO}_2(\text{aq})]$ in this approximation (total dissolved carbon $\approx [\text{HCO}_3^-]$) is to underestimate the original ^{14}C activity and therefore to underestimate the radiocarbon age calculated from models that take into account dilution of radiocarbon by dead carbon (Section 5).

4.2.4 PMC versus Bicarbonate.

In order to determine the extent of possible differential contamination, the entire data set was examined for systematic variations. Figure 3 is a plot of percent modern carbon



TRI-6331-42-0

Figure 3. PMC values plotted versus dissolved carbon as bicarbonate. The excellent linear correlation indicates mixing between two reservoirs of carbon, one with nearly 0 PMC and one with nearly 100 PMC.

(PMC) versus total bicarbonate in milligrams per liter. The bicarbonate values are from field alkalinity titrations of wellhead samples immediately after collection. At the near-neutral pH values of these samples (Lambert and Robinson, 1984) the bicarbonate concentration is taken to represent the dissolved carbon; at constant pH bicarbonate will be a constant fraction of total dissolved carbon. Thus, Figure 3 is essentially a plot of PMC versus total dissolved carbon. Note the apparent linear correlation. Engle well (Culebra) and H-9B (Culebra) data were not used in calculating the least-squares fit, because at each of these wells the sample for the PMC measurement did not come from the same pump test that provided the alkalinity measurement. Nevertheless, all the data, including Engle and H-9B, lie close to the least-squares line described by the equation

$$\text{PMC} = 0.40[\text{HCO}_3^-] - 22.2 \quad (1)$$

with a correlation coefficient (r) of 0.97. This value of r close to unity indicates an excellent fit.

A simple binary mixing relationship in PMC/bicarbonate space would have the form

$$\text{PMC}_m = \frac{C_m - C_2}{C_1 - C_2} \text{PMC}_1 + \frac{C_1 - C_m}{C_1 - C_2} \text{PMC}_2 \quad (2)$$

where PMC and C represent percent modern carbon and carbon concentration, and subscripts 1, 2, and m represent mixing components 1 and 2 and the mixture, respectively. If component 2 is water that contains virtually no ^{14}C and component 1 is entirely modern, then $\text{PMC}_2 = 0$ and $\text{PMC}_1 = 100$. Equation (2) then takes the form

$$\text{PMC}_m = 100 \frac{C_m - C_2}{C_1 - C_2} \quad (3)$$

and PMC of the mixture varies linearly with total dissolved carbon in the mixture.

The linear relationship for PMC versus bicarbonate in Figure 3 implies some sort of mixing of at least two reservoirs of carbon to produce the local PMC value in the groundwater system being sampled at each well. The linear relationship, which is independent of location, depth, or producing unit, indicates that mixing phenomena involving similar endmembers prevail at each sampling locality. The PMC values used in the correlation range from 5 to 91, spanning almost the entire theoretical range of PMC values (0 to 100). Such a wide range implies that the true PMC values of the mixing endmembers must be close to these extremes. Thus, the least squares line of Equation (1), extrapolated to 0 and 100 PMC, could describe mixing of a reservoir of 0 PMC with 56 mg/L bicarbonate, and a reservoir of 100 PMC with 305 mg/L bicarbonate.

Although no effects of ionic strength have been taken into consideration, it is interesting to note that 60 mg/L bicarbonate is the equilibrium value resulting from the dissolution of calcite in pure water in a closed system at pH 7 (Stumm and Morgan, 1970). The pH of the brines considered here was very near neutrality (Lambert and Robinson, 1984). It is easy to account for a reservoir of dissolved carbon in the Rustler, with 60 mg/L bicarbonate and

0 PMC. Carbonaceous species derived from essentially "dead" primary marine carbonate may have partially dissolved to give a basal bicarbonate concentration of about 60 mg/L in the water. These carbonates (largely dolomite) are available in at least small amounts in all of the rock units that produce water. A difficulty with a simple two-component mixing model for PMC values will be observed in the discussion below. There is no requirement for a unique high-PMC endmember.

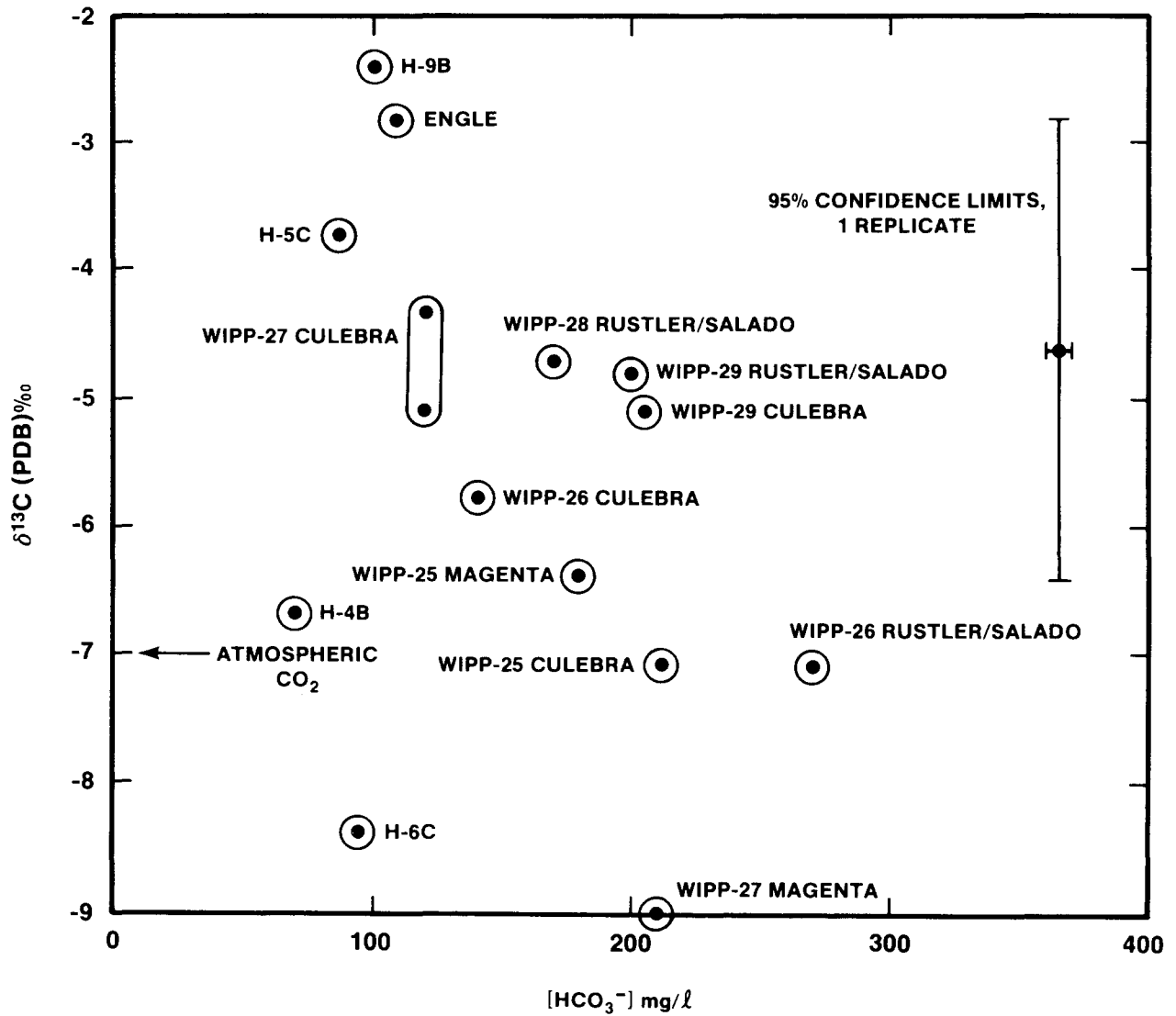
The waters with PMC values <10 have a relatively tight range of bicarbonate values (70 to 95 mg/L). This range is here interpreted as the probable basal range representative of minimally contaminated dissolved carbon in much of the Rustler. Thus, the concentration of natural (uncontaminated) dissolved carbon in Rustler groundwater is probably uniformly <100 mg/L.

4.2.5 $\delta^{13}\text{C}$ versus Bicarbonate.

It is difficult to identify a unique high-PMC reservoir. It is commonly assumed that physicochemical processes of fractionation of carbon isotopes affect both ^{13}C and ^{14}C in systematic ways. If this were the case here, similar linear relationships with bicarbonate should exist for both ^{13}C and ^{14}C , if only two reservoirs of carbon are involved. Figure 4, a plot of $\delta^{13}\text{C}$ versus bicarbonate, shows that this is not the case. One might infer from Figure 4 a generally decreasing trend in $\delta^{13}\text{C}$ with increasing bicarbonate, but this trend is not nearly so well defined as the relationship between bicarbonate and PMC. In fact, using the same well samples as in the previous treatment, the least-squares fit yields the equation

$$\delta^{13}\text{C} = -0.006[\text{HCO}_3^-] - 5.14 \quad (4)$$

with an r value of 0.22. Clearly, the relationship between $\delta^{13}\text{C}$ values and bicarbonate is not well represented by a straight line, as would be expected in the case of two mixing endmembers. As shown in Table 3, the $\delta^{13}\text{C}$ value of Rustler carbonates averages +5.7 ‰. If the foregoing argument developed from the PMC/bicarbonate relationship still held, the low bicarbonate values and the smallest PMC values would correspond with $\delta^{13}\text{C}$ values characteristic of Rustler marine carbonates (close to +6 ‰). In this case, one might interpret these mixing systematics as a pervasive reservoir of water with 100 PMC, diluted to various degrees by dead marine carbonate derived from the host rock. If so, $\delta^{13}\text{C}$ values of low-PMC samples should all be about +6 ‰. Instead, the lowest observed bicarbonate values (H-4B and H-6C) have some of the most negative $\delta^{13}\text{C}$ values in the data set (-6.7 ‰, -8.4 ‰). Also, if 100 PMC water were being diluted by dead carbon dissolved from marine carbonate, PMC would be expected to be *inversely* proportional to $[\text{HCO}_3^-]$, exactly opposite of the trend observed in Figure 3. Thus, it is concluded that the carbon with relatively low PMC values represented by the lowest bicarbonate values (Figure 3) is not entirely derived from congruently dissolved marine carbonates, but is either (1) a small amount of contamination during drilling, or (2) in part a consequence of long residence times of groundwaters whose originally high PMC values (i.e., characteristic of meteoric



TRI-6331-43-0

Figure 4. $\delta^{13}\text{C}$ values plotted versus dissolved carbon as bicarbonate. The lack of a linear correlation indicates that more than two reservoirs of carbon may be mixing to produce the observed values of bicarbonate and $\delta^{13}\text{C}$.

recharge) have decayed to low levels during their post-recharge isolation from the atmosphere, or (3) a mixture of carbon from carbonate rock, original surface-derived dissolved carbon, and contamination.

4.2.6 Sources of Introduced Carbon.

In order to identify likely sources for the dissolved carbon that have significant amounts of radiocarbon, it is necessary to consider the developmental history of the various wells that yielded the original samples. The history of sampling of the Nash Draw holes during pump tests (the water-bearing subsurface occurrences of the Magenta, Culebra, and Rustler/Salado interface units in WIPP-25, -26, -27, -28, -29, and -30) was documented in detail by Lambert and Robinson (1984). They observed that "typically, bicarbonate changed significantly during a pump test, seldom reaching steady state. This observation and the drilling history have shown that, given the nongeological sources of carbon, radiocarbon results will be difficult to interpret."

Modern carbon was introduced during the drilling and coring operations as an inescapable part of additives used during drilling and coring to control lost circulation. These additives were in the form of shredded paper, cottonseed hulls, peanut shells, and various proprietary organic additives to drilling mud (J. W. Mercer, personal communication). Evidence of the biodegradation of these nutrients included effervescence of some of the waters as they emerged from the wellhead (some hydrogen sulfide and probably carbon dioxide evolved during alkalinity titrations), a slow, perceptible, monotonic decrease in bicarbonate when other solution parameters had stabilized, and the forcible ejection of fluid from each of the holes (except for WIPP-30) during perforation. No such ejection or gas evolution took place at the time of drilling; such occurrences cause operational problems that would certainly have been reported.

It is inferred here that the introduced nutrients were forcibly injected into the rock under the downhole pressure of the drilling fluid, became entrapped in the formation during loss of circulation, and that biodegradation and accompanying gas evolution have proceeded continuously since casing and cementing. Lambert and Robinson further inferred that "biodegradation will most likely proceed for many years, thus providing a nongeological source of carbon that will be difficult to purge from the local groundwater system regardless of pumping time."

At the time the Nash Draw holes were drilled, it was not anticipated that radiocarbon measurements would be made on the groundwaters that the holes intercepted, as the holes were designed for as complete core recovery as possible in order to investigate the evaporite-dissolution process. Consequently, no documentation was preserved as to the type of material introduced to control lost circulation in each hole, and no samples of those materials exist. Even if such documentation and samples did exist for isotopic analysis, it would not be possible to determine the degree of contribution of partially metabolized nutrients to the PMC in each sample and thus correct for the contamination due to the

introduced modern organic carbon. In spite of a long history of development (and, one would suspect, purging of contaminants), even stock wells may have been perturbed by mixing phenomena.

4.2.7 Consequences of Contamination.

An increasing PMC with increasing bicarbonate is consistent with the effect of an introduced source of biogenic modern carbon mixing in various proportions with a low-PMC component of carbon native to the groundwater. If CO₂ were an admixed metabolite in the biodegradation of the introduced nutrients, this mixing would increase bicarbonate and modern carbon in direct proportion to one another, and would result in intermediate values of PMC as a linear function of bicarbonate. Since this proportionality is suggested in Figure 3, most of the modern carbon appears to have been introduced in this manner, yet it has arisen from more than one source. If the modern carbon were derived from a single source common to all the pump tests but in various proportions, linear plots of both $\delta^{13}\text{C}$ versus bicarbonate and PMC versus bicarbonate would be obtained. Figure 4 shows that this is certainly not the case for $\delta^{13}\text{C}$. Instead, it is proposed that much of the modern carbon is contaminant (which has the effect of making the apparent radiocarbon dates appear spuriously young), but that both the nature and relative amount of the source(s) of modern carbon are different for each sample.

Highly variable $\delta^{13}\text{C}$ values might result from using different additives, according to the derivation of the additives (i.e., whether their vegetable materials are derived from the Calvin- or Hatch-Slack-cycle). $\delta^{13}\text{C}$ values of organic carbon in materials used to control lost circulation would be expected to lie in the approximate range -30 ‰, the approximate lower limit for Calvin-cycle materials, to -10 ‰, the approximate upper limit for Hatch-Slack-cycle materials (Bender, 1971). Depending on the mechanisms of metabolism by various microorganisms, the specific nutrient metabolized (cellulose, lipid, protein, lignin, etc.), and the completeness of the metabolism, the respired carbon dioxide would be expected to have $\delta^{13}\text{C}$ values either somewhat greater or less than this range (Epstein, 1968), but still more depleted in ¹³C than marine carbonates, whose $\delta^{13}\text{C}$ values would be near +6 ‰ in the case of the Rustler. Vegetable derivatives such as paper, cottonseed hulls, peanut shells, and even the pine oil that was once added to H-2 (about 3/4 mile northwest of H-3) would be low-¹³C/high-PMC sources. Petroleum derivatives such as diesel oil (which is known to have been added to some holes, such as DOE-2) would be low-¹³C/low-PMC sources. The respired carbon dioxide (or other metabolite that ultimately contributes to the total bicarbonate in solution) released during metabolism (independent evidence for which was observed by Lambert and Robinson, 1984) would alter the local carbonate equilibrium, and additional carbon would be dissolved from the host rock or precipitated. The unknown degree of isotopic exchange involved in such localized rock-water interaction in the presence of a contaminant introduces yet another nonsystematic variable to govern the mixing phenomena. The extremely depleted ¹³C content of H3B3 (-79.35 ‰), for which a PMC value is not available, remains problematical. It may reflect a high degree of metabolic fractionation of carbon derived from terrestrial-type nutrients

with a $\delta^{13}\text{C}$ value less than or equal to -30‰ , or it may reflect a high degree of fractionation during some step in extraction, purification, and analysis.

Depending on the local situation at each well, there could be as many as four sources contributing dissolved carbon to the aqueous effluent: dissolved marine carbonate (high bicarbonate, high $\delta^{13}\text{C}$, low PMC), carbon dioxide dissolved at the time of recharge (low bicarbonate, low $\delta^{13}\text{C}$, originally high PMC), metabolism of "dead" organic carbon (high bicarbonate, very low $\delta^{13}\text{C}$, low PMC), and metabolism of modern organic carbon (high bicarbonate, very low $\delta^{13}\text{C}$, high PMC). Based on the roughly triangular field occupied by the data points in Figure 4, as many as three of these four probably have combined at each well to produce nonsystematic mixing that accounts for the observed range in PMC values, and for $\delta^{13}\text{C}$ values as low as -9‰ and as high as -3‰ . Furthermore, most of the dissolved radiocarbon is probably an anthropogenic contaminant superimposed on a background level of low-PMC carbon that is relatively uniform throughout the Rustler. In spite of the fact that H-4B and H-6C waters contain little modern carbon and the least bicarbonate, the possibility of their contamination (as indicated at first glance by their $\delta^{13}\text{C}$ values, which are significantly lower than dissolved marine carbonate) cannot be entirely dismissed. In fact, a petroleum derivative added to these wells could actually have decreased the net PMC while also decreasing the $\delta^{13}\text{C}$. The complete history of the development of Engle Well is not documented, but the local informal accounts indicate that it is not inconceivable for wildlife (e.g., rabbits and mice) to take refuge in an open well, die, and have their remains fall into the water, thus contributing yet another source of low $\delta^{13}\text{C}$ modern carbon to the local groundwater system.

As indicated above, the lowest PMC values appear to be part of the same two-component mixing systematics that have affected all the other waters in the data set, as seen from the direct linear variation of PMC with concentration of dissolved carbon. Furthermore, the fact that the linear variation seems to hold for the entire data set suggests that all the groundwaters have a basal background value for bicarbonate of about 60 mg/L. If these two inferences can be drawn from the linear relationship of PMC with bicarbonate, then it is likely that even the lowest PMC values of all the Rustler radiocarbon data may be contaminated with some introduced modern carbon. In spite of documentation that the H-4 and H-6 holes were drilled with "air," organic additives are still present, as air drilling commonly requires the assistance of detergent "mist" or "foam," which may become metabolized in part to CO_2 , that subsequently becomes incorporated into the carbon systematics. If indeed the ^{13}C systematics (and hence the amount of total dissolved carbon) are not governed by two-component mixing, and even though the PMC values appear to be linear combinations of a low-PMC reservoir and modern radiocarbon (100 PMC), the total carbon may have come from more than two sources, including marine carbonates. Hence, the measurable radiocarbon may have come from more than one source. This contradicts one of the fundamental assumptions in radiocarbon dating.

4.2.8 Carbon-Isotope Systematics.

In Figure 4 the $\delta^{13}\text{C}$ versus bicarbonate relationship is not linear over the entire data set. A dichotomy in carbon-isotope systematics is apparent in Figure 5, in which PMC is plotted versus $\delta^{13}\text{C}$. In this case, two independent linear relationships are readily suggested by the distribution of data points. One least-squares line was calculated for the waters with PMC < 10. Even though it is from the Dewey Lake and not the Rustler, Pocket well is included as a member of this small subset of the data for reasons that will become apparent. The equation for the least-squares line fit to the H-6C/H-4B/Pocket/H-9B data set is

$$\text{PMC} = -1.09[\delta^{13}\text{C}] - 0.72 \quad (5)$$

and the r-value is 0.92. This fit is considered adequate; it will be used in the development of subsequent discussions. The $\delta^{13}\text{C}$ value of the zero-PMC intercept of this line is -0.66 ‰, which is very close to the hypothetical value of +0.5 ‰ expected for the equilibrium $\delta^{13}\text{C}$ value of bicarbonate derived from dissolved dolomite (see Section 5.3.8).

When the least-squares calculation is done for all PMC values < 20, including the data from H-5C and Engle, the resulting equation is

$$\text{PMC} = -0.0243[\delta^{13}\text{C}] + 8.21 \quad (6)$$

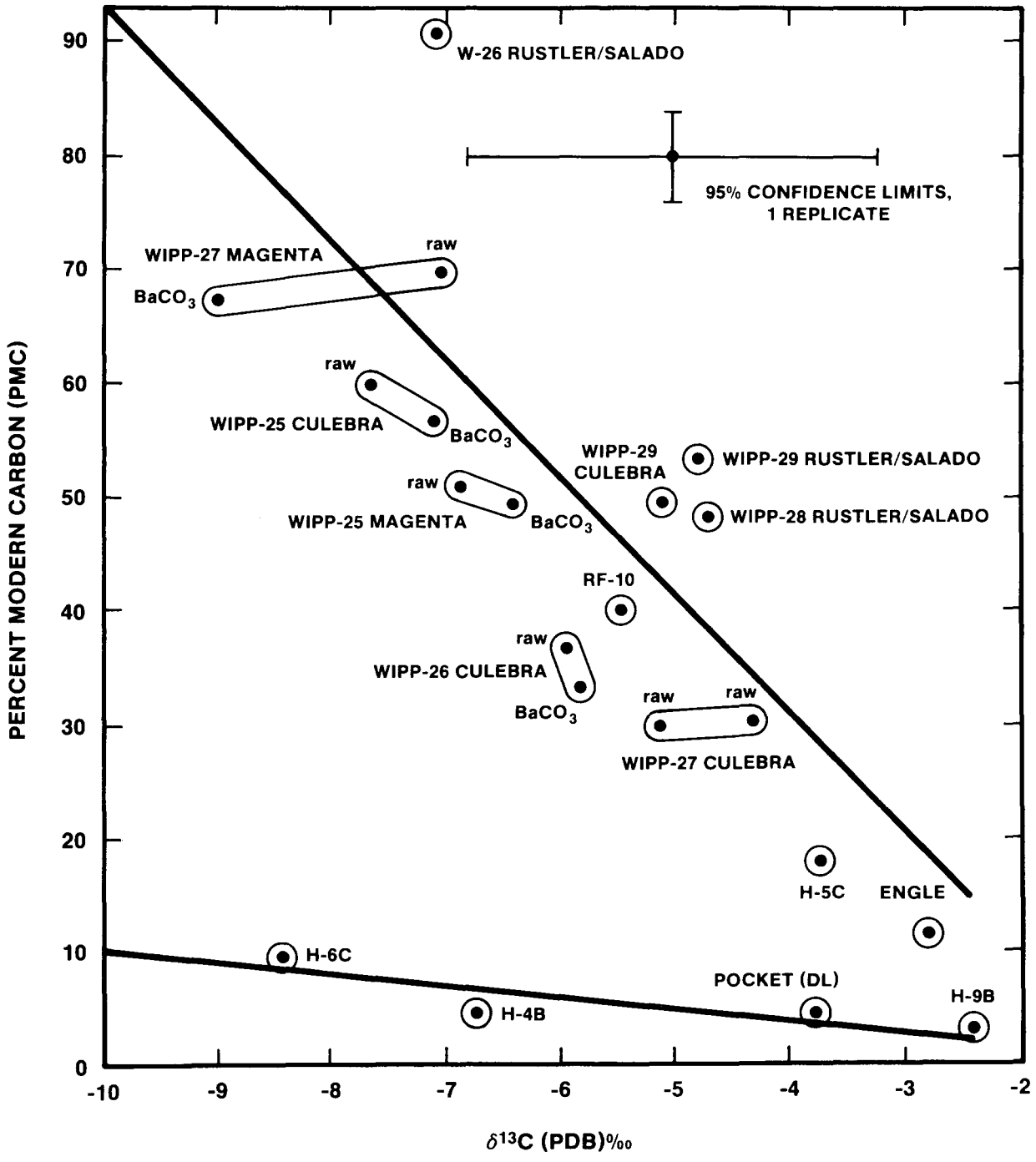
and the r-value is 0.01. This extremely low value of r by itself indicates that the fit is poor, that these six points should not be taken together, and that H-5C and Engle probably do not follow the same carbon-isotope systematics as the other four. In addition, the $\delta^{13}\text{C}$ value of the zero-PMC intercept described by this line is +338 ‰. Since no natural substances are known to have this carbon isotopic composition, this situation is clearly absurd. Hence, this numerical treatment provides additional argument why H-5C and Engle should not be included with the other four waters of low PMC value.

The equation for the least-squares line fit to the remainder of the data, including H-5C and Engle, is

$$\text{PMC} = -10.07[\delta^{13}\text{C}] - 9.80 \quad (7)$$

and the r-value is 0.79. This latter group of data, as shown in Figure 5, appears to be dominated by a different set of carbon-isotope systematics from that of the four low-PMC data. The possible significance of linear relationships in PMC/ $\delta^{13}\text{C}$ space, such as Equation (5) for the four low-PMC data, will be discussed in Section 6.2.

As indicated in Section 3.2, the three lowest PMC values are include zero in their confidence intervals at the 95% level. Thus, although the present **uncontaminated** ^{14}C content of the carbon dioxide that dissolved in the Rustler groundwaters at the time of meteoric recharge (the essential basis for the radiocarbon dating method) may now be indeterminate, it is inferred from these arguments and the apparent linear mixing relationship in Figure 3 that all the Rustler water samples have in common a significant fraction of water



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Figure 5. PMC values plotted versus $\delta^{13}\text{C}$. Two separate linear trends are indicated, one for samples with high-PMC values (greater than 10) and one for samples with low-PMC values (less than 10). The two trends appear to converge near PMC = 0 and $\delta^{13}\text{C}$ = 0.

containing low PMC at 60 mg/L total bicarbonate. The four lowest-PMC waters have $\delta^{13}\text{C}$ values significantly different from that of dissolved Permian marine carbonate, suggesting that low-PMC values have not arisen entirely by dilution with dead carbon dissolved from marine carbonate. Processes that diminish the PMC value, other than this dilution by dissolution, are (1) rock/water interaction that has diminished the aqueous PMC value while increasing or decreasing the $\delta^{13}\text{C}$ value, which could take place in a geologically short period of time, and (2) radioactive decay from originally high PMC values, requiring a much longer time. Hence, the native dissolved carbon in Rustler waters treated in this study, excluding the carbon dissolved from the host rock, probably has a very low PMC value, and may be essentially "dead" (i.e., statistically indistinguishable from zero). The four lowest-PMC waters (H-4B, H-6C, H-9B, and Pocket), which also have bicarbonate concentrations less than 100 mg/L, are considered to contain the smallest fraction of modern contaminants.

All the waters represented in Figure 3 are considered to have a common low-PMC/low-bicarbonate endmember, regardless of their varying degrees of contamination, by virtue of their linear binary mixing relationship. At least three of the lowest-PMC waters (H-4B, H-9B, and Pocket) have PMC values statistically indistinguishable from zero, according to confidence limits defined by replicate sample collections and analyses. If this low-PMC endmember is represented as a significant component in the low-PMC waters, then it is not possible to dismiss entirely the premise that the Rustler waters (over the entire sampled thickness interval and a reasonably wide geographic area) may indeed have been isolated from original atmospheric recharge for a period of time greater than the maximum age of applicability of the radiocarbon method. At one time there may have been significant natural differences in radiocarbon content in various parts of the groundwater system because of differences in times of isolation from the atmosphere as water progressed along a flow path away from a recharge point. These differences would now be imperceptible, even in the absence of contamination, since according to the foregoing assumptions all the native carbon now recoverable from the low-PMC endmember is nearly "dead."

Because of the degree of contamination and the difficulties imposed by possible mixing of waters of various age, the use of more sensitive detection methods for radiocarbon by itself will not allow interpretation of even very low PMC values as absolute ages. The difficulty lies not in measurement, but interpretation. In fact, in the words of Evans et al. (1979), "the dangers of mixing and contamination will be greatly magnified when the dating of very old waters becomes possible by methods now being developed for ^{14}C enrichment and the use of high energy accelerators for ^{14}C measurements." An example of other, more subtle implications of the ability to measure very small concentrations of radiocarbon with accelerators is provided by Barker et al. (1985). They interpreted excess ^{14}C abundances in uranium ores as possible evidence for emission from uranium-series decay. It is likely that additional sources of small amounts of radioisotopes will be discovered with accelerator mass spectrometry. All of these additional sources will tend to limit the validity of the assumptions necessary in dating groundwaters using various atmospherically generated nuclides; it may not be possible to correct for many of these additional sources, especially

in a groundwater whose history and flow path are not precisely known *a priori*. This limitation is equally applicable to "dating" waters using ^{81}Kr . In spite of the fact that it is now possible to measure very low amounts of ^{81}Kr in groundwaters (Lehmann et al., 1985), the problems of contamination, mixing, and nonuniqueness of source will be just as severe with ^{81}Kr as they are with ^{14}C .

4.3 Complications in Interpretations

All conventional groundwater-dating methods based on atmospherically generated nuclide systems require the assumptions that (a) all the nuclides of interest in the water originated in the atmosphere, and (b) there has been no artificial subsurface admixture from a modern surficial source of the nuclide. Under the conditions in waters associated with water-poor evaporites in general and the Rustler groundwaters in particular, neither of these assumptions may be valid. The assumption is also commonly made that at the time the water parted company with the atmosphere as it entered the ground, no more of the nuclide of interest entered the water, and the nuclide began to decay, with no further uptake of that nuclide from the rock. Various interpretive models have been developed to correct for dilution and for loss of radiocarbon to the rock. Given all these assumptions, an elapsed time is calculated based on the assumed initial and measured final concentrations of the nuclide of interest. It is often exceedingly difficult if not impossible to confidently demonstrate the validity of these assumptions. To the contrary, independent geological observations may show that some if not all of these assumptions are invalid. It is possible (and common) to obtain negative ages if contamination is present or if the other assumptions break down. Even if a non-negative age is obtained from a single isotopic measurement, it may not be possible from a single measurement to determine which, if any, of the assumptions have failed. Thus, radiocarbon data may not be uniquely interpretable as ages. Evans et al. (1979) have shown for carbonate aquifers in the United Kingdom that (a) mixing of various waters can also complicate the interpretation of nuclide data in terms of "age," even if the other assumptions hold, and (b) it may be impossible to apply a correction for ^{14}C loss based on ^{13}C , due to the diversity of carbon-containing rocks through which the water may have flowed. The mixing problem is particularly troublesome, since "a mixed water cannot be reliably dated because varying proportions of different components could give the same apparent age." Evans et al. also attempted to address the possibility of correcting for modern contamination on the basis of tritium.

4.4 Tritium

Tritium measurements obtained by liquid scintillation counting of samples collected from Nash Draw in 1980 as part of the preliminary screening procedure yielded only one value that was significantly above background: WIPP-29 Culebra, which was 4.5 pCi/mL. The top of the Culebra in this borehole is 12 feet below surface in the southwestern part of Nash Draw (Figure 1), a broad karst valley formed by dissolution of evaporites from the Rustler Formation where it outcrops (Bachman, 1987). Shallow occurrences of groundwater in this area, such as WIPP-29 Culebra, are profoundly influenced by surface runoff from nearby potash refining operations (Lambert and Harvey, 1987). An especially

large quantity of fission- and activation-generated nuclides (including tritium) was released to the local area in 1961 with the unintended venting of Project Gnome (about 3 miles southwest of Pocket in Figure 1), when a nuclear device was detonated within the Salado Formation as part of the Plowshare program. Thus, tritium levels as high as that of WIPP-29 Culebra would reflect that event, as well as association with near-surface processes such as runoff and evaporation. The association of WIPP-29 Culebra water with such near-surface processes is also reflected in its δD and $\delta^{18}O$ values (Lambert and Harvey, 1987). Tritium values of other waters from Nash Draw as measured in the Sandia screening process were statistically indistinguishable from background.

An obvious limitation in tritium measurements is that they do not provide any information concerning water that may have infiltrated in modern times, but **before** the time of atmospheric testing of hydrogen bombs (1954). Another limitation in interpreting tritium data is that the measured TU values are subject to the same effects of mixing and contamination as is radiocarbon. If concentrations of both ^{14}C and T as measured represent the native values (and it has been established in the foregoing discussion that the PMC values do not), one should expect a direct linear relationship of tritium with radiocarbon. This linear relationship should prevail even though carbon dioxide can interact extensively with host rock and water hydrogen does so to a lesser extent; if the carbon-isotope behavior is systematic, the extent of the rock-water interaction should vary with some function of distance along a given reaction-path. Evans et al. reported 10 TU as their highest tritium value for modern water containing 37.3 PMC. One of their oldest waters (with an apparent radiocarbon age of 26,400 years) had a significant level of tritium: 2.7 TU. They interpreted this as contamination. Isaacson et al. (1974) considered that values less than ~ 10 TU in natural waters are not conclusively indicative of a large degree of hydraulic connection with the surface .

The other available tritium measurements for Rustler groundwaters are given in Table 1. The values range from -0.08 to 6.9 TU. In the Rustler the lowest TU values (including H-3B3, H-5C, H-12, Engle, and Unger) are ≤ 0.3 TU, and statistically do not significantly differ from zero. Only one PMC value (18.0 from H-5C) is available for this group of samples. The lowest Rustler PMC value in Figure 3, 4.8 PMC at H-4B, contains 2.8 TU. Such a low PMC value, even when $\delta^{13}C$ "corrections" are applied in various model age calculations, yields a time of isolation from the atmosphere that would allow all atmospherically derived tritium to decay to virtually undetectable levels. This is additional evidence that levels of T as high as 3 TU probably represent contamination, at least with respect to tritium and probably with respect to radiocarbon.

The highest TU value in the Rustler (6.9 TU at WIPP-27) was from the western part of Nash Draw. This locality had some of the most severe losses of circulation during drilling (using hydropolymer mud as an additive) of any hole in this study. Furthermore, values as high as 7 TU in situations such as this should be no surprise, in view of the difficulties in pumping and sampling described by Lambert and Robinson (1984). Thus, nonzero tritium values from such heavily contaminated environments as this should not be uniquely interpreted to represent very young native water. Anthropogenic mixing of various reservoirs in

the subsurface can also cause groundwater mixtures having measurable tritium concentrations to appear spuriously young, as discussed in more detail by Lambert and Harvey (1987) for the Roswell Artesian Basin.

For comparison, tritium concentrations of surface water, derived largely from modern local precipitation, are significantly higher than those of confined groundwaters reported here; the absolute tritium concentration varies according to worldwide frequency of weapons testing in the atmosphere and local precipitation patterns. For example, the tritium concentration of the Pecos River near Artesia, about 30 miles north of Carlsbad, varied from 32 to 66 TU during 1974 and 1975 (Gross et al., 1976); in 1973 the tritium concentrations were as high as 130 to 140 TU along the stretch of the Pecos River between Roswell and Artesia. Thus, groundwaters having less than about 3 TU certainly do not contain a significant component derived directly from the surface since the early 1950s. Tritium values indistinguishable from zero (H-5C Culebra, H-12 Culebra, Engle, H-3 Culebra, and Unger Dewey Lake) indicate that these waters (1) were recharged before 1954, and (2) are now governed by recharge (if any) with an infiltration rate much slower than the decay rate of tritium. If the virtual absence of tritium at these localities indeed reflects a current absence of natural meteoric recharge, a significant **past** climatic event should be sought to account for the amount of meteoric water now present in the Rustler Formation.

4.5 Summary

Groundwater-dating methods based on the atmospheric generation of nuclides by cosmic rays should not be used by themselves apart from a geological context for the groundwater system in which they are to be applied. This is especially true in slow-moving groundwater systems in carbonates and evaporites where the "purging" effect (cf. Lambert and Robinson, 1984) during sampling is small and the contamination effect can be large due to the relatively small amount of natural water available in the system. An age calculation should not be made on the basis of a single nuclide measurement together with only its inferred initial value and half-life. Discussions in Section 5 will illustrate that even model-age calculations have their limitations.

Nuclide systems generated in the atmosphere from neutron-activation by cosmic rays are particularly susceptible to contamination by even small amounts of modern sources, especially organic carbon in the case of radiocarbon. Also, despite claims of very low detection limits allowed by such instruments as accelerator mass spectrometers, the overwhelming amount of ^{35}Cl and ^{37}Cl (as chloride) in Rustler waters makes inapplicable the assumption of a known initial concentration of chloride (including ^{36}Cl) that is entirely atmospheric in origin. Thus, with the breakdown of assumptions fundamental to dating models, analyses of the atmospherically-generated nuclides will do nothing to aid in the determination of flow-paths, groundwater velocity and the recharge/discharge areas.

In view of the likely effects of contamination of the Rustler, the lower limit of resolution for PMC measurements may represent the baseline value of radiocarbon in the Rustler groundwater system. Thus, the "true" age of recharge of the Rustler groundwater system at

the WIPP site and in eastern Nash Draw, in view of the possible drilling-induced carbon contamination of even low-PMC waters, may be greater than 30,000 years.

5. ATTEMPTED APPLICATION OF INTERPRETIVE MODELS

5.1 Model Process

In order to evaluate quantitatively (1) the applicability of radiocarbon geochronology to Rustler groundwater, and (2) effects of modern carbon contamination on apparent radiocarbon age, several interpretive numerical models were applied to the PMC and $\delta^{13}\text{C}$ data in Table 1. Some models were developed specifically for attempting to date groundwaters in carbonate aquifers, and impose adjustments to the PMC value to account for:

1. The dilution of original radiocarbon due to dissolution of carbonate host rock (congruent dissolution)
2. The simultaneous irreversible precipitation of radiocarbonate and coupled dissolution of dead carbon from carbonate host rock (incongruent dissolution, or isotopic exchange).

5.2 Assumptions of the Models

The fundamental premises common to several numerical models used to calculate absolute groundwater dates from radiocarbon data are:

1. That the original radiocarbon was introduced to near-surface meteoric water infiltrating through soil layers, the water dissolving carbon dioxide evolved from the oxidative decay of the soil organic matter. This organic matter is assumed to contain a steady-state amount of radiocarbon (equated to 100 PMC by some models) prevalent at the time the organisms lived, took up carbon laced with this steady-state amount of radiocarbon, and died to become incorporated into the soil humus.
2. That the $^{14}\text{CO}_2$ -bearing water, upon entering a carbonate aquifer, dissolved carbonate from the host rock, thus diluting the radiocarbon in solution below its original value (congruent dissolution). This assumption implies that contamination should be suspected if the measured PMC value exceeds the expected post-dilution value in groundwaters from carbonate aquifers.
3. That the fraction of subsequent isotopic exchange (if any) between rock carbonate and solution carbonate (or bicarbonate) is the same for ^{14}C and ^{13}C (incongruent dissolution), thus allowing one in principle to calculate ^{14}C loss during incongruent dissolution on the basis of inferred ^{13}C gain or loss. This

adjustment commonly assumes that instantaneous isotopic equilibrium governs the ^{13}C exchange. This implies that contamination should be suspected if the PMC value lies near the expected post-dilution value **and** the $\delta^{13}\text{C}$ value is significantly more positive than its expected post-dilution value (see Section 5.3). If such a combination of values is observed, this implies that ^{13}C but not ^{14}C has been exchanged between rock and water during incongruent dissolution, subsequent to dilution during congruent dissolution.

4. That once the systematics of carbonate geochemistry (entailing local rock-water interactions) are established in the aquifer, no additional carbon is introduced to the aquifer system, either artificially (by contamination) or naturally (by mixing).

Although this fourth premise is violated in many parts of the Rustler groundwater system (a concern also addressed by Evans et al., 1979, for their carbonate aquifer systems in the United Kingdom), application of numerical models will allow one to explore the effects of uncertainties in the other three premises. Some of the models considered here for their applicability make simplifying assumptions that may or may not be valid for the data resulting from this study; the applicability of some models and/or assumptions may even be indeterminate in the absence of certain geological data necessary to either confirm or deny the applicability of models or validity of assumptions. Some models may be so rigorous in their data requirements that they simply cannot be applied within the limitations of the data available in this study.

5.3 Brief Descriptions of Models

5.3.1 The Decay Equation.

The simplest expression of the time-dependence of radiocarbon concentration, arising from radioactive decay as the **only** process that decreases the PMC value, is:

$$t = 8267 \ln \frac{100}{\text{PMC}} \quad (8)$$

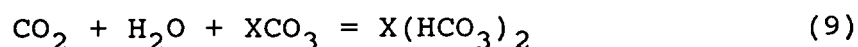
The prelogarithm factor is the "official" half-life of ^{14}C (5730 a) divided by the natural logarithm of 2. It is assumed in Equation (8) that the original activity of radiocarbon at the cessation of radiocarbon uptake was equivalent to 100 PMC. Equation (8) **must not** be used to calculate "age" of carbon dissolved in waters from carbonate aquifers using the measured PMC value of the dissolved carbon. The use of this equation entails the assumption that the system has been closed to carbon gain or loss since the time of recharge, that the PMC value has changed only by radioactive decay. This assumption is invalid in carbonate aquifers, where groundwater has dissolved aquifer carbonate, and in any system where modern contamination has been introduced.

5.3.2 Vogel (1970).

The model of Vogel (1970) is a modification of simple radioactive decay (Equation (8)), in that the initial ^{14}C activity was empirically inferred from approximately 100 measurements of PMC in groundwaters from northwestern Europe. Instead of 100 PMC, the initial radiocarbon activity used by the Vogel model is 85 PMC. Thus, the value of 100 in Equation (8) is replaced by 85. As pointed out by Fontes and Garnier (1979), this empirical value for initial radiocarbon activity in groundwater does not account for any isotope exchange reactions below the water table.

5.3.3 Tamers (1975).

The next level of complexity in radiocarbon-dating models takes into account dilution of dissolved carbon by additional carbon dissolved from mineral matter. Generally, the dissolution is described by the reaction



where X is generally Ca^{+2} and/or Mg^{+2} in carbonate aquifers. It is commonly assumed for simplicity that the radiocarbon activity of mineral carbonate in the aquifer rock is zero. Thus, instead of 100 PMC as the initial activity used in Equation (8), the appropriate value becomes

$$A_0 = \frac{m\text{CO}_2 + 0.5m\text{HCO}_3^-}{m\text{CO}_2 + m\text{HCO}_3^-} A_g \quad (10)$$

where A_0 equals initial radiocarbon activity, A_g is the radiocarbon activity of the soil CO_2 (generally equated with 100 PMC), and $m\text{CO}_2$ and $m\text{HCO}_3^-$ are the molality values of dissolved CO_2 and bicarbonate, respectively.

This method is based on pure stoichiometry of carbonate/water interactions at "normal" groundwater pH values, and was used by Tamers (1975). The Tamers model may be applicable to groundwater systems in which it can be shown that dilution by carbonate dissolution is the major nonradioactive process that diminishes radiocarbon activity in solution. Note that when $m\text{HCO}_3^- \gg m\text{CO}_2$, implying that total dissolved carbonate is represented by bicarbonate, and half the bicarbonate came from dissolved CO_2 and half from dissolved carbonate, Equation (10) reduces to

$$A_0 = 0.5A_g \quad (11)$$

which simply describes the radiocarbon dilution by congruent (stoichiometric) dissolution. This approximation also implies that the maximum PMC value (barring modern contamination) that should be observable in groundwaters from carbonate aquifers immediately following recharge is 50.

5.3.4 Pearson and Swarzenki (1974).

The model of Pearson and Swarzenki (1974) accounts for dilution of the original radiocarbon activity by dissolution as does the Tamers model, but makes no assumptions about the dissolution stoichiometry. Instead, this model assumes that the radiocarbon dilution factor is the same as the dilution factor calculated from mixing systematics involving ^{13}C . According to the Pearson and Swarzenki model, the initial radiocarbon activity to be used in the decay equation is

$$A_0 = \frac{\delta_T - \delta_c}{\delta_g - \delta_c} A_g \quad (12)$$

where δ_g , δ_c , and δ_T are the $\delta^{13}\text{C}$ values of soil CO_2 , mineral carbonate, and total dissolved carbon, respectively.

The latter two δ -values can be measured directly. As in the other models, A_g is commonly equated with 100 PMC. Radiocarbon activity of mineral carbonate is assumed to be zero. δ_g will not be known precisely if the conditions of recharge for an old groundwater cannot be observed in order to obtain a measurement. For plant cover that obeys the carbon-isotope systematics of the Calvin cycle, which is commonly the case in temperate climates, values of -25 to -26 ‰ have been used, although this is an "adjustable parameter," considering variations in climatic conditions that prevailed at the time of recharge (Fontes and Garnier, 1979).

5.3.5 Mook (1976).

The model of Mook (1976) is based on a simultaneous chemical and isotopic balance, involving isotopic exchange of carbonaceous species at equilibrium (gaseous and aqueous CO_2 , bicarbonate, carbonate, and mineral carbonate). The equation describing that balance is

$$A_0 = \frac{a}{\Sigma} A_{a0} + 0.5 \left(a - \frac{a}{\Sigma} \right) (A_{a0} + A_{\lambda 0}) + [A_{g0} (1 - 2 \times 10^{-3} \epsilon_g) - 0.5 (A_{a0} + A_{\lambda 0})] \cdot \frac{\delta_{\Sigma} - (a/\Sigma) \delta_{a0} - 0.5 [1 - (a/\Sigma)] (\delta_{a0} + \delta_{\lambda 0})}{\delta_{g0} - \epsilon_g (1 + 10^{-3} \delta_{g0}) - 0.5 (\delta_{a0} + \delta_{\lambda 0})} \quad (13)$$

where the quantities a and Σ are the concentrations of aqueous CO_2 and total dissolved carbon, respectively, ϵ_g is the $^{13}\text{C}/^{12}\text{C}$ isotopic enrichment of gaseous CO_2 relative to that of bicarbonate, in the usual isotopic per mil (‰) units, and other quantities are as previously defined. The subscripts a , λ , g , and Σ denote aqueous CO_2 , limestone, gaseous CO_2 , and total dissolved carbon, respectively. In addition, the subscript "0" denotes the state of the quantity before any of the isotopic exchange reactions have taken place. Obviously, it is not in general possible to measure values for all the required inputs to such a complex model, so simplifying assumptions and approximations are made. First, it is assumed, that initial radiocarbon activity in carbonate rock (dolomitic gypsum, in the case of the Rustler Formation) is zero. Also, it is assumed that $A_a \approx A_g$, given only a small

change in radiocarbon activity as gaseous CO₂ dissolved. These two initial radiocarbon activities must themselves be estimated, and are typically near 100 PMC. The resulting equation, after these moderately conservative approximations, becomes

$$A_0 = 100a/\Sigma + 50(1 - a/\Sigma) + [50 - 0.2\varepsilon_g] \cdot \frac{\delta_\Sigma - (a/\Sigma)\delta_{a0} - 0.5[1 - (a/\Sigma)](\delta_{a0} + \delta_{l0})}{\delta_{g0} - \varepsilon_g(1 + 10^{-3}\delta_{g0}) - 0.5(\delta_{a0} + \delta_{l0})} \quad (14)$$

Note that the isotope enrichment, ε_g , does not relate isotopic exchange between dissolved bicarbonate and mineral carbonate, but only the exchange systematics between gas and solutes. Thus, with respect to mineral carbonate, the Mook model is also a stoichiometric mixing model.

5.3.6 Fontes and Garnier (1979).

Fontes and Garnier (1979) used a multistage model that accounts for the same sorts of processes as the forgoing models, specifically dilution by dissolution, but also accounts for carbon isotope exchange between solution and mineral carbonate. The complexities increase dramatically when this consideration is added, and the limitations of the model must be evaluated relative to the geological and geochemical specifics of the groundwater system. Fontes and Garnier themselves described the limitations to their model:

The model does not apply in several hydrochemical situations. It does not apply if, for instance, significant amounts of Ca⁺² and Mg⁺² are released into the liquid phase by silicate weathering (waters with low hardness in regions of crystalline rocks), part of the SO₄⁻² content comes from the leaching of sodium sulfate (waters of endoreic basins under tropical climates), part of the SO₄⁻² content comes from the oxidation of sulfides (waters with large changes in redox potentials) and no calcium carbonate is present to buffer the formation of sulfuric acid, significant amounts of extra CO₂ may enter the system (e.g., perivolcanic CO₂, CO₂ coming from the oxidation of organic matter, CO₂ coming from sulphate reduction). These limitations of the model should be considered for any field situation with knowledge of the hydrogeologic situation and of the hydrochemical data.

Several of these limitations are present in the hydrogeochemical system of the Rustler Formation. First, since the Rustler Formation is known to contain polyhalite (Snyder, 1985), this mineral is a ready source of additional dissolved calcium, magnesium, and sulfate in addition to that of the simpler sulfates handled by the model of Fontes and Garnier. Also, oxidation/reduction phenomena attributable to biogenic activity are known in many parts of the Rustler Formation (Lambert and Robinson, 1984). Finally, there indeed is no pervasive occurrence of calcium carbonate in the Rustler Formation dolomite layers, except under special circumstances (Section 5.4.2). Because of these limitations, the model of Fontes and Garnier (1979) is mentioned here for completeness only, with no intent to calculate model radiocarbon ages from it; also, several of the data inputs it requires are not available.

5.3.7 Wigley, Plummer, and Pearson (1978).

The model of Wigley et al. (1978) stems from a detailed theoretical treatment of the behavior of carbon isotopes in carbonate aquifer systems. In its most complete form, it is probably not possible to rigorously define all its necessary data inputs, so several simplifying assumptions can be applied. Even then, the remaining data input requirements entail parameters whose values may not be uniquely measurable. A special case of the model is described by the equation

$$t = 8267 \ln \left[\frac{A_1}{A} \cdot \frac{\delta_2^{13}\text{C} - \delta^{*13}\text{C}}{\delta_1^{13}\text{C} - \delta^{*13}\text{C}} \cdot \frac{\beta \delta^{13}\text{C} - \delta^{*13}\text{C} + \frac{\epsilon_{ps}}{\Gamma}}{\beta \delta_2^{13}\text{C} - \delta^{*13}\text{C} + \frac{\epsilon_{ps}}{\Gamma}} \right] \quad (15)$$

For simplicity, A_1 is commonly equated to 100 PMC. The second multiplicative term is similar to Equation (12), in that it entails dilution by congruent dissolution, and is derived from $\delta^{13}\text{C}$ values rather than the stoichiometry implicit in Equation (10). $\delta^{*13}\text{C}$ is measured on the rock. $\delta^{13}\text{C}$ is measured in solution. A is the measured PMC. All other inputs must be inferred. In the words of Wigley et al. (1978)

This result allows us to examine individually the effects of each stage on age determination. The first term is the apparent or 'raw' age, the second term is a stage-2 adjustment factor (note that it involves $\delta_1^{13}\text{C}$ rather than the soil-gas value, $\delta_g^{13}\text{C}$) and the third term is an incongruent dissolution (stage-3) adjustment factor. Both adjustments reduce the age. The use of equation [(15)] as an adjustment formula is recommended only after careful analysis of the assumptions on which it is based. Even then the determination of suitable values for $\delta_1^{13}\text{C}$, $\delta_2^{13}\text{C}$, ϵ_{ps} , and Γ is not a simple task.

$\delta_1^{13}\text{C}$ refers to the dissolved carbon at the end of the open-system stage, involving isotopic exchange between solution and gaseous CO_2 originally entering the groundwater system. $\delta_2^{13}\text{C}$ refers to the dissolved carbon at the end of the closed-system stage involving congruent dissolution of carbonate rock, and is used as input (initial conditions) for the following stage, involving incongruent dissolution in a closed system. Γ is the ratio of the carbon input rate to the carbon output rate for a single input and a single output (e.g., dissolution and reprecipitation of mineral carbonate) during the incongruent stage. Although Equation (15) treats this quantity as a constant, this need not be the case in either time or space. ϵ_{ps} is the **additive** fractionation factor (approximately equal to the difference in $\delta^{13}\text{C}$ values) for equilibrium partitioning of ^{13}C between mineral carbonate and dissolved carbon. β is a function of the **multiplicative** fractionation factor (α ; Section 5.4.2.2) and the quantity Γ .

While the theoretical treatment of Wigley et al. (1978) is rigorous, the potential user's inability to determine "suitable" values for the many unmeasurable but required inputs makes this model of limited practical applicability in attempted radiocarbon dating of

groundwater whose history is not completely known. Many additional simplifying approximations would be required in order to reduce the number of necessary inputs to those for which values can be measured or reasonably inferred. The present degree of quantitative understanding of hydrogeochemical systematics in Rustler groundwaters probably does not allow a sufficiently rigorous evaluation of the many simplifying assumptions and approximations necessary to apply the model of Wigley et al. (1978) to attempted radiocarbon dating of Rustler groundwaters.

5.3.8 Evans, Otlet, Downing, Monkhouse, and Rae (1979).

The model of Evans et al. (1979) for radiocarbon-dating of groundwaters in carbonate aquifers is a single equation:

$$t = \frac{^{14}\text{C half-life}}{\ln 2} \ln \frac{50}{\text{PMC}} \left[\frac{(K - \delta_s^{13}\text{C})}{(K - \delta_i^{13}\text{C})} \right]^{(1 + \frac{\epsilon_{13}}{1000})} \quad (16)$$

where t is apparent groundwater age in radiocarbon years, ϵ_{13} is the temperature-dependent equilibrium fractionation factor for ^{13}C between solution and rock (expressed as the δ -difference, $\delta^{13}\text{C}_p - \delta^{13}\text{C}_s$, where subscript "s" refers to the solution and "p" to the precipitate), $K = \delta^{13}\text{C}_r - \epsilon_{13}$ (where subscript "r" refers to the rock), and $\delta^{13}\text{C}_i$ is the $\delta^{13}\text{C}$ value of the carbon in solution after the congruent dissolution stage. The derivation of the equation is given in the original paper. This model, like that of Wigley et al. (1978), adjusts for both congruent and multistage incongruent dissolution of carbonate rock. As in the Tamers model, congruent dissolution is considered to reduce the original PMC by half when the radiocarbon-laced infiltrating groundwater enters the carbonate aquifer, according to the stoichiometry implied by Equation (9). Thus, the maximum PMC value that should be found in groundwater from a carbonate aquifer according to this argument is 50. The incongruent part of the model, as before, adjusts for radiocarbon loss during the coupled dissolution and reprecipitation of carbonate rock. The incongruent dissolution results in isotopic exchange between rock and water that is reflected in a change in $\delta^{13}\text{C}$ value of dissolved carbon (and probably rock, depending on the rock/water ratio). Since the exponential expression in Equation (16) is very close to unity, Equation (15) corresponds to Equation (16) when $\beta=1$ and $\Gamma=1$. Implicit in Equation (16) is the assumption that the total dissolved carbon is changing neither concentration nor speciation along the reaction path.

5.4 Numerical Inputs to Models for Which Data Exist

5.4.1 Stable-Isotope Fractionation Factors.

The value of the $^{13}\text{C}/^{12}\text{C}$ fractionation factor between dolomite and dissolved bicarbonate is somewhat problematical. Evans et al. (1979) used $\epsilon_{13} = 2.42 \text{ ‰}$ as the equilibrium fractionation between calcite and dissolved bicarbonate. In other words, the difference

between the $\delta^{13}\text{C}$ value of the rock calcite and that of dissolved bicarbonate is 2.42 ‰. This corresponds to an actual multiplicative fractionation factor of 0.9976 (the α -value, expressed as the $^{13}\text{C}/^{12}\text{C}$ ratio of bicarbonate divided by the same ratio in calcite; defined in Section 5.4.2.2).

The equilibrium $\delta^{13}\text{C}$ difference between coexisting dolomite and calcite at ambient surface temperatures has not been determined experimentally with any success, because exchange reactions between the two phases at such temperatures are kinetically inhibited (Northrop and Clayton, 1966). In many geological occurrences of coexisting dolomite and calcite there is evidence that the calcite and dolomite formed under different conditions (Clayton et al., 1968), or that dolomite formed from a calcite precursor (Epstein et al., 1964). The available estimates for the equilibrium $\delta^{13}\text{C}$ difference between dolomite and calcite range from 2.5 ‰ (Hoefs, 1973) to about 3 ‰ (extrapolable from higher-temperature data of Northrop and Clayton, 1966). This work infers that the average of the two estimates, about 2.8 ‰, is a reasonable approximation for the dolomite-calcite $\delta^{13}\text{C}$ difference at equilibrium. This yields 0.9972 for the calcite/dolomite carbon-isotope equilibrium fractionation factor (α), and by extension, the bicarbonate/dolomite equilibrium fractionation factor (α) is 0.9948. In other words, dolomite is inferred to have a $\delta^{13}\text{C}$ value 5.2 ‰ heavier than that of dissolved bicarbonate in equilibrium with it. The resulting value of K as defined in Section 5.3.8 is 5.7 ($\delta^{13}\text{C}$ of rock) less 5.2 (the ϵ_{13} value for the system dolomite-bicarbonate), or 0.5. In spite of the uncertainties inherent in this parameter, this value of K will be used here in the numerical interpretive model. At worst, it will still represent an attempt to calculate apparent radiocarbon ages using the best available estimates for a dolomite-dominated carbonate "aquifer" rather than a calcite-dominated one.

5.4.2 The Isotopic Composition of Rock Carbonate.

5.4.2.1 The nature of the carbonates.

Bachman (1985; 1987) has argued that the presence of pedogenic Mescalero caliche covering much of southeastern New Mexico is **evidence** that water has not penetrated the caliche, or else it would have been dissolved; the presence of caliche is **not** interpreted as a **barrier** to infiltration. In several localities (Nash Draw to the west and Clayton Basin to the north of the WIPP site), caliche is indeed absent. In localities where caliche is absent and the Dewey Lake Red Beds have been eroded, various horizons of the Rustler crop out or are covered by a thin veneer of alluvium. Thus, these near-surface occurrences of the Rustler are actually more likely candidates for recharge areas than are areas where the Rustler is overlain by the Mescalero caliche and a few hundred feet of Dewey Lake Red Beds. It was on the basis of such an occurrence of Rustler rock angularly truncated by erosion near Bear Grass Draw, far to the north of the study area, that Robinson and Lang (1938) proposed that locality as a recharge area for the Rustler. More recent work by Vine (1963) and Bachman (1980; 1981) has revealed the presence of such occurrences nearer the WIPP site, in Nash Draw to the west and Clayton Basin to the north. In such Rustler outcrop areas having experienced significant infiltration and recharge, the Rustler marine

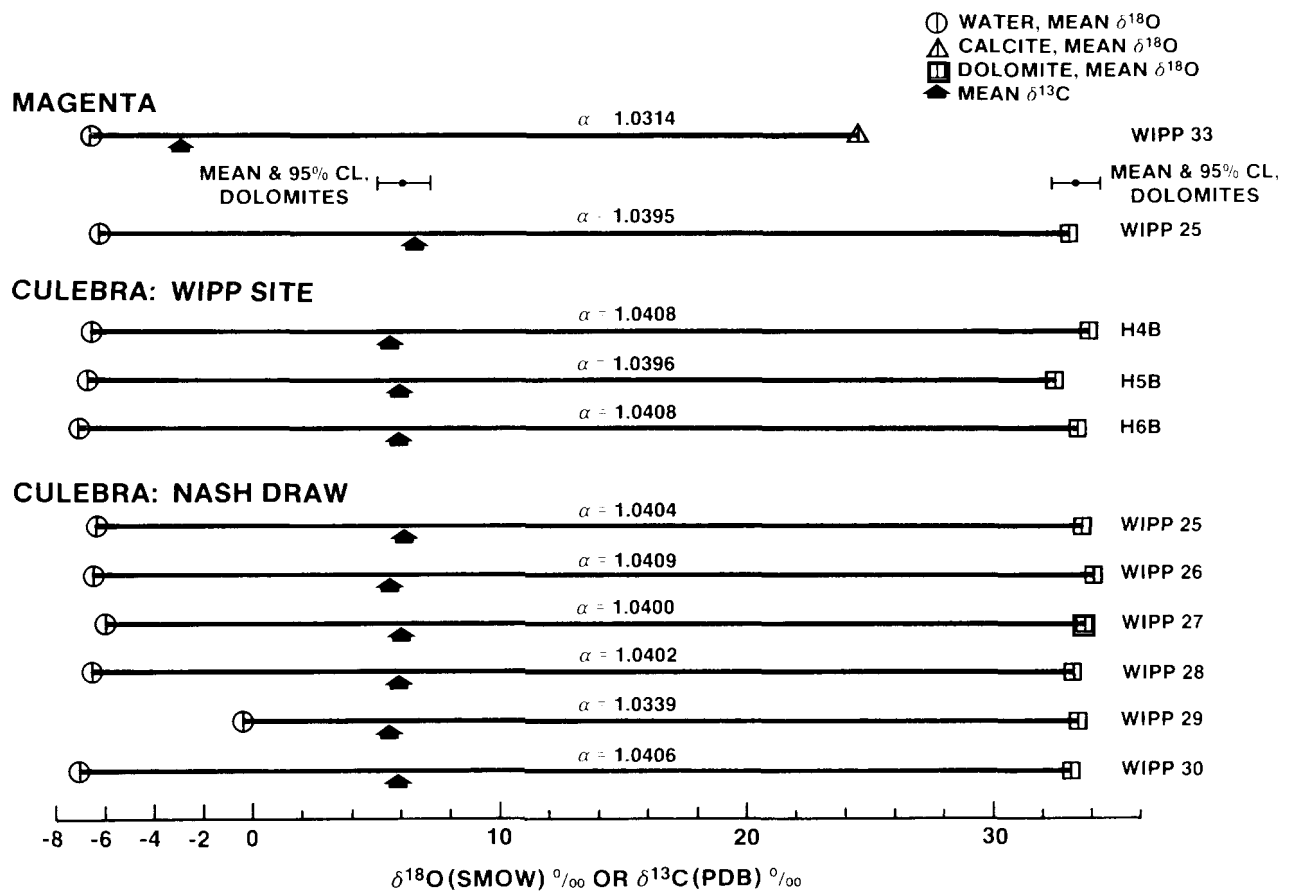
dolomite will probably be the most abundant solid carbonate. Whereas the disruption of caliche (by collapse, dissolution, etc.) generally is a precursor to the establishment of recharge conditions in this model of recharge mechanism, it is conceivable that some caliche will have dissolved at some time prior to the infiltration of the groundwater presently found in the Rustler. However, the Wisconsinian time was not the first interval climatically wet enough to dissolve caliche; it was probably the last. Nash Draw (a shallow dissolution feature developed in Rustler outcrops west of the WIPP site) is largely free of caliche (Bachman, 1980; 1981; 1985; 1987), and has experienced intervals wet enough to dissolve caliche for the past 500,000 years. The geologic record of these climatic fluctuations is incomplete, but the occurrence of several wet/dry climatic cycles in Quaternary southeastern New Mexico cannot be ruled out. Consequently, for the purposes of this study, Rustler dolomite, rather than pedogenic caliche, is selected as the congruently dissolving solid carbonate phase.

Carbonate reservoir rock was collected from several holes that produced water, emphasizing horizons 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 or a lesser degree of consolidation; such rock does not core completely, 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 presented 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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 three-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 $\delta^{13}\text{C}$ values of the respective fractions were indistinguishable. The data, including the cumulative yields, are presented in Table 3.

To facilitate the presentation, mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for replicate (3-day) analyses of carbonates are plotted with the mean $\delta^{18}\text{O}$ values of coexisting waters (Lambert and Harvey, 1987) in Figure 6. No representative water sample was available from WIPP-33 Magenta, so the plotted water $\delta^{18}\text{O}$ value is the mean of all available Magenta waters (Lambert and Harvey, 1987), which is very typical of Culebra waters also.

$\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}$ 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



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Figure 6. $\delta^{18}\text{O}$ values for coexisting carbonates and waters in the Rustler Formation. Dolomite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for both Magenta and Culebra are all very uniform (33.4 ± 1.0 and 6.1 ± 1.1 ‰, respectively). Calculated dolomite/water oxygen-isotope fractionation factors for coexisting dolomite and meteoric groundwater are between 1.0395 and 1.0409, too high to reflect isotopic equilibrium. Only calcite in the Magenta rubble from WIPP-33 appears to be at isotopic equilibrium, with typical meteoric Rustler groundwater at ambient temperature.

remarkable. Either there has been no post-depositional alteration of the carbonate isotopic composition, or such alteration has affected a large area to a precisely uniform degree. Rock samples from water-bearing horizons of the Culebra dolomite member at locations that provided radiocarbon samples (H-4B, H-5C, H-6B, WIPP-25, WIPP-26, WIPP-27, and WIPP-29) have a mean $\delta^{13}\text{C}$ value of about +5.7 ‰, as measured on CO_2 recovered at the end of the 3-day extraction (Table 3). This is the mean $\delta^{13}\text{C}$ value of dolomite that will be used in model calculations involving possible carbon-isotope exchange between the mineral dolomite and solution. The confidence limits at the 95% level for the mean of $\delta^{13}\text{C}$ values measured on the 3-day extractions are ± 0.7 ‰. The calcite $\delta^{13}\text{C}$ confidence limits are ± 0.3 ‰.

5.4.2.2 Evidence for carbonate/water isotopic exchange.

Oxygen-isotope fractionation factors for the carbonate-water coexisting pairs were calculated from the equation:

$$\alpha = \frac{\frac{\delta^{18}\text{O}(\text{calcite})}{1000} + 1}{\frac{\delta^{18}\text{O}(\text{water})}{1000} + 1} \quad (17)$$

and are given for the coexisting pairs in Figure 6. Except for WIPP-29 Culebra, whose water shows an isotope shift from the meteoric field in $\delta\text{D}/\delta^{18}\text{O}$ space (Lambert and Harvey, 1987), the observed dolomite/water fractionation factors, between 1.0395 and 1.0409, are all quite uniform. Note 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 (four orders of magnitude between H-5B and WIPP-26 in the Culebra). The small negative deviation in the rock at H-5B might be interpreted as a small amount of isotopic alteration, but its $\delta^{18}\text{O}$ 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) was outside the possible range for calcite-water, precluding a calcite precursor to dolomite formation. The dolomite-water fractionation factors observed here are even larger; thus, these dolomites did not recrystallize from a calcite precursor in isotopic equilibrium with the water presently in the dolomites ($\delta^{18}\text{O} \approx -7$ ‰). The equilibrium fractionation factor for $^{18}\text{O}/^{16}\text{O}$ partitioning between dolomite and water at ambient temperatures is not precisely known 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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 C^{13} ." Due to the uniform significant enrichment of these dolomites in ^{13}C and ^{18}O , it is tentatively proposed that their origin has been more evaporitic than biogenic. Aside from ripple-drift cross-bedding prominent in the Magenta, and the variable bedding-thickness and (probably) secondary vugs in the Culebra, both units appear to be devoid of conspicuous dominant 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 $\delta^{13}\text{C}$ 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 $\delta^{18}\text{O}$ values comparable to the Rustler had $\delta^{13}\text{C}$ values as high as the Rustler. 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 oxygen-isotope exchange with the water they presently host. Among these Rustler carbonates, the possible exception to the general absence of carbonate/water oxygen-isotope exchange 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 > 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 [~500,000 years old] 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, -2.9‰ and $+24.6\text{‰}$, respectively, for the calcite are 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 analyzable carbonate, suggests that carbonate recrystallization has taken place. The criteria of Keith and Weber (1964) indicate that the calcite is borderline between marine and fresh-water calcite, with a slight tendency toward fresh-water. The observed calcite-water $^{18}\text{O}/^{16}\text{O}$ fractionation factor, 1.0314, yields a temperature of crystallization of 11.7°C according to the equation of O'Neil et al. (1969):

$$1000 \ln \alpha = 2.78 (10^6 T^{-2}) - 3.39 \quad (18)$$

This is the only calculable temperature for any of the carbonate-water pairs in Figure 6. 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 $\delta^{18}\text{O}$ value of about -7‰ . It is not possible to uniquely determine 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 of mineral/water interaction is not itself an indicator of even relative age. If it is true that water with a $\delta^{18}\text{O}$ value of about -7‰ was responsible for the recrystallization, 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. Furthermore, oxygen-isotope equilibrium between calcite and water indicates that the calcite formed by precipitation from solution, rather than by dedolomitization in the solid state. That the calcite $\delta^{13}\text{C}$ value is so different from those of surrounding dolomites implies that the calcite $\delta^{13}\text{C}$ value was influenced by introduced aqueous carbon species rather than derived from dissolved dolomites elsewhere in the Magenta, all of which have a uniformly high $\delta^{13}\text{C}$ value, around $+6\text{‰}$. 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 record 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 dominantly involve 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 non-existent.

Whereas it is conceivable that secondary calcite was precipitated throughout the Rustler from solution isotopically similar to water now in the Rustler, this has been observed only at WIPP-33, where a solution/collapse structure has formed. Moreover, secondary

dolomite precipitation, if any, has not brought the Rustler dolomite to oxygen-isotope equilibrium with the water now present in the Rustler. If part of the dolomite had undergone the necessary dissolution and reprecipitation, the isotopic compositions would be highly variable, arising from various mixtures of primary and secondary dolomite. Either no such multiple generations of dolomite so formed have been preserved (each with a different isotopic composition), or at each locality the mixing proportions of different generations (and isotopic compositions) of dolomite have been identical, so as to produce a highly uniform isotopic composition for the dolomite. The second instance is highly unlikely. The preferred interpretation is that no dolomite has precipitated in the presence of water now in the dolomitic rock, but that dolomite is being dissolved.

In some of the following model-age calculations, a calcite phase was assumed to have precipitated during incongruent dissolution. For these cases, the $\delta^{13}\text{C}$ value was taken from the WIPP-33 calcite, which is a fresh-water value, and is inferred to be in oxygen- (and therefore carbon-) isotope equilibrium with groundwater typical of the Rustler Formation in most of the study area (cf. Lambert and Harvey, 1987).

5.4.3 Other Fundamental Parameters.

The constants used here are 5730 a for the "best" half-life of ^{14}C (differing somewhat from the "official" value of 5570 a), and 0.693 for the natural logarithm of 2.

In all model calculations that require the $\delta^{13}\text{C}$ value of original biogenic (radiocarbon-bearing) carbon dioxide from the soil in the recharge zone, this value is taken to be -26 ‰, after the usage of Evans et al. (1979). This is very close to the value of -25 ‰ used by several other authors.

The $\delta^{13}\text{C}$ value of dissolved carbon following a stoichiometric congruent dissolution step in any of the models is taken to be -10.15 ‰ ($\delta^{13}\text{C}_i$ in the model of Evans et al., 1979). This value comes from mixing equal parts of marine carbonate (+5.7 ‰) and original biogenic (radiocarbon-bearing) carbon dioxide from the soil in the recharge zone (-26 ‰) during congruent dissolution. The $\delta^{13}\text{C}$ value of marine carbonate is here taken to be +5.7 ‰. In applying some models, calculations were repeated using calcite having a $\delta^{13}\text{C}$ value of -2.9 ‰. This is done for illustrative purposes only, given that calcite with such an isotopic composition is not found in the Rustler except in small abundance at a certain locality. Where the presence of calcite was assumed in the calculations, the appropriate fractionation factor was used for $^{13}\text{C}/^{12}\text{C}$ partitioning, as recommended by the original authors of each model.

5.5 Results of Calculations

Using the PMC and $\delta^{13}\text{C}$ values from the apparently least contaminated water samples as discussed in Section 4.2.8 (H-4B, H-6C, H-9, and Pocket), together with other inputs as available from reasonable assumptions consistent with Rustler hydrogeochemistry (Section

5.3), ages were calculated from the models of Tamers (1975), Pearson and Swarzenki (1974), Mook (1976), and Evans et al. (1979). The results are given in Table 4.

Calculated ages reported in Table 4 are of two types. Single entries are model ages calculated under the assumption that all input parameters, whether analytical results or averaged global values, have deterministic values. Ranges of ages were also calculated for models that gave consistently positive finite model ages (the models of Tamers, Pearson and Swarzenki, and Evans et al.). Ranges of numbers are the maximum and minimum model ages based on the confidence limits of the analytical data. Ranges in square brackets calculated by the Tamers model result only from the confidence limits derived from the pooled- s for replicate PMC values. Ranges in square brackets calculated by the model of Pearson and Swarzenki result from the confidence limits of PMC, $\delta^{13}\text{C}_r$ (dissolved), and $\delta^{13}\text{C}_c$ (rock). Ranges in square brackets calculated by the model of Evans et al. result from the confidence limits of PMC and $\delta^{13}\text{C}_s$ (dissolved). Ranges in curly braces calculated by the model of Evans et al. result from the confidence limits of $\delta^{13}\text{C}_s$ alone, the PMC being treated as invariant. In each of the three models, virtually all the statistically-based model-age ranges overlap. The only exception is in the Evans et al. model ages for the invariant-PMC case, where there is a small gap (200 years) between the range of H-4 (13800-18000 a) and that of H-6 (10200-13600). This gap is not considered geologically significant. This exercise shows that even though the analytical variation in PMC may be taken as small (zero in the PMC-invariant case), typical replicate variations in $\delta^{13}\text{C}_s$ as small as 1 to 2 ‰ can contribute a range in model ages that spans several thousand years. Within the variations arising from replicate analyses of even $\delta^{13}\text{C}$ alone, the Evans et al. model ages are considered statistically indistinguishable, and there is no significant age gradient from north (H-6) to south (H-9) in the Culebra across the WIPP site. Also, the Evans et al. model age of the single Dewey Lake sample is statistically indistinguishable from that of the three Culebra samples.

It was inferred in Section 4.2.8 that these four water samples all follow similar carbon-isotope systematics, and that they all fall on a single reaction-path. This is suggested by their monotonic decrease in PMC coupled with a monotonic increase in ^{13}C content. If a given model does not yield calculable radiocarbon ages for all points along a reaction-path, the model does not adequately account for the processes along the path. In Table 4, some models give indeterminate ages for certain values of input parameters. All models give an indeterminate age for H-9 using calcite ($\delta^{13}\text{C} = -2.9$ ‰) as a congruently dissolving phase, because the observed $\delta^{13}\text{C}$ value of dissolved carbon in H-9 (-2.4 ‰) cannot be derived from congruent dissolution of calcite having a more negative $\delta^{13}\text{C}$ value. If H-9 represents a high- ^{13}C , low- ^{14}C endmember of the reaction path to which H-4, H-6, H-9 and Pocket belong, calcite dissolution cannot be a major contributor to diluting the ^{14}C in the other three. Dolomite in great abundance is a more likely candidate.

Similarly, the Evans et al. model gives an indeterminate age for H-9 and Pocket when incongruent dissolution of calcite is assumed. This shows that either the numerical approximations inherent in the Evans et al. model are inappropriate, or reprecipitation of calcite is not an important process in non-decay reduction of PMC. In view of the scarcity

TABLE 4. MODEL RADIOCARBON AGES FOR GROUNDWATERS¹

| Locality | PMC | $\delta^{13}\text{C}$ | Tamers (1975) ² | Pearson & Swarzenki (1974) | Mook (1976) | Evans et al. (1979) |
|--|------|-----------------------|--|----------------------------------|--------------------|--|
| ADJUSTMENTS INVOLVING DOLOMITE ($\delta^{13}\text{C}_r = +5.7 \text{‰}$; $\epsilon_{13} = 5.2 \text{‰}$): | | | | | | |
| H-4 | 4.82 | -6.7 | 19300 [14300- 34300] | 17300 [10600- 33600] | 12000 | 16100 [8700- 28700] {13800- 18000} |
| H-6 | 9.7 | -8.4 | 13600 [10700- 18000] | 12600 [8300- 18200] | 10600 | 12100 [7300- 18000] {10200- 13600} |
| H-9 | 2.22 | -2.4 | 25700 [17200 ₄ - +∞] ⁴ | 20200 [8800- +∞] | indet ³ | 14900 [-1600- +∞] {7000- 19000} |
| Pocket | 3.67 | -3.8 | 21600 [15500- +∞] | 17400 [8900- +∞] | indet | 14000 [3500- +∞] {9600- 17000} |
| ADJUSTMENTS INVOLVING CALCITE ($\delta^{13}\text{C}_r = -2.9 \text{‰}$; $\epsilon_{13} = 2.42 \text{‰}$): | | | | | | |
| H-4 | 4.82 | -6.7 | | 10100 [-1400- 28500] | indet | 3800 |
| H-6 | 9.7 | -8.4 | | 7400 [700- 14400] | indet | 4600 [-300- 18100] {2600- |
| H-9 | 2.22 | -2.4 | | indet | 13600} | indet |
| Pocket | 3.67 | -3.8 | | 500 [-∞ ₅ - +∞] | indet | indet |

1. Ages in radiocarbon years. Ranges in square brackets are calculated from the extremes of the 95% confidence limits for PMC (± 4.03) and $\delta^{13}\text{C}$ of both rock ($\pm 0.7 \text{‰}$ for dolomite; $\pm 0.3 \text{‰}$ for calcite) and dissolved carbon ($\pm 1.8 \text{‰}$) under Pearson and Swarzenki; of only dissolved carbon under Evans et al. Ranges in curly braces are calculated from the extremes of the 95% confidence limits for $\delta^{13}\text{C}$ (dissolved) only, assuming PMC and rock $\delta^{13}\text{C}$ to be invariant.

2. The model of Tamers (1975) is independent of $\delta^{13}\text{C}$ values.

3. Indeterminate, due to resulting negative argument of logarithm.

4. +∞: PMC was < 0 under conditions necessary to yield oldest age permitted by lower confidence limit.

5. -∞: $\delta^{13}\text{C}$ term was < 0 under conditions necessary to yield youngest age permitted by $\delta^{13}\text{C}$ confidence limits.

of secondary calcite in the Rustler water-bearing horizons, precipitated at isotopic equilibrium with Rustler water, the virtual absence of calcite precipitation is the preferred interpretation. The Evans et al. model yields calculable radiocarbon ages for the four waters that are inferred to be part of the same reaction-path involving dolomite; this is the case even though the evidence for incongruent dissolution of dolomite is weak.

The Evans et al. model involving incongruent dissolution of dolomite yields the youngest set of radiocarbon ages, considering all the models that yielded calculable ages for all four waters. The models that entail only congruent dissolution of dolomite (Tamers; Pearson and Swarzanki) yield greater ages, which may be closer to the true ages if dissolution, not precipitation, is the dominant mechanism governing Rustler carbonate minerals. In any case, H-4 and H-6 yield ages of several thousand years, regardless of model, and the lowest PMC value (2.22 at H-9) does not give the oldest age, as would be predicted solely from Equation (8). Variations in calculable ages produced by the various models (Tamers; Pearson and Swarzenki; Evans et al.) do not differ among themselves by more than a half-life of ^{14}C , and the estimated "true" age of these four waters is here taken to be late Pleistocene. Since the Evans et al. model using dolomite gives the youngest set of calculable ages, these ages are adopted as minimum ages of isolation from the atmosphere, of Rustler and Dewey Lake waters having $\delta^{18}\text{O}$ values more negative than -6.0‰ and δD values more negative than -45‰ (Lambert and Harvey, 1987). In the calculation of Evans et al. model ages it is implicit that a stage of incongruent dissolution (carbon-isotope exchange) has actually take place in the Rustler. In the absence of conclusive evidence of such a process (i.e., pervasive and widespread secondary carbonate deposition in equilibrium with Rustler groundwater), the actual minimum ages of Rustler groundwaters may be closer to those calculated by the model of Tamers.

5.6 Sensitivity Analysis of the Evans Model

Using only the tabulated values of PMC and $\delta^{13}\text{C}$ in solution, the ages calculated from Equation (16) (Evans et al., 1979) for all available radiocarbon and $\delta^{13}\text{C}$ data are given in Table 5. Age calculations were made on each replicate of PMC, as this exercise serves as an illustrative example of the sensitivity of the model to data inputs. Apparent radiocarbon ages range from $-7,730\text{ a}$ to $+16,100\text{ a}$. Clearly, the large negative dates (all between $-1,000$ and $-7,730\text{ a}$) are unreasonable. These are not the results expected for modern waters, as radiocarbon ages obtained by Evans et al. for demonstrably modern waters used to test the model differ from zero by only a few hundred years instead of several thousand years.

A clue to some of the possible reasons for the failure of this interpretive model in much of the Rustler Formation can be found in two of the table entries. In the case of WIPP-27 Culebra, two replicate values of $\delta^{13}\text{C}$ were obtained that differ by 0.8‰ , whereas the two replicates of PMC were identical within the confidence limits. Each $\delta^{13}\text{C}$ value was used together with the corresponding PMC value in a different age calculation; calculated ages are $-2,560\text{ a}$ for the -5.1‰ value, and $-1,120\text{ a}$ for the -4.3‰ value. The two replicate PMC values in the Magenta from WIPP-27 were also identical to one another within the confidence limits, but twice as high as the Culebra. A variation in $\delta^{13}\text{C}$ of 2.0‰ (slightly larger

TABLE 5. RADIOCARBON AGES, MODEL OF EVANS ET AL.¹

| Well | $\delta^{13}\text{C}$ (‰) All Replicates | PMC All Replicates | Apparent Age (radiocarbon years) |
|----------------------|--|---|-------------------------------------|
| Pocket Dewey Lake | -3.8 | 3.67 (cyl) ² | 14,000 |
| WIPP-25 Magenta | -6.8 -6.4 | 50.7 (bulk) ³ 49.27 (pptn) ⁴ | -3,250 -3,490 |
| WIPP-27 Magenta | -7.0 -9.0 | 69.6 (bulk) 67.76 (pptn) | -5,650 -3,460 |
| H-4B Culebra | -6.7 | 4.82 (bulk) | 16,100 |
| H-5C Culebra | -3.7 | 18.0 (bulk) | 714 |
| H-6C Culebra | -8.4 | 9.7 (pptn) | 12,100 |
| H-9B Culebra | -2.4 | 2.22 (cyl) | 14,900 |
| WIPP-25 Culebra | -7.6 -7.1 | 59.8 (bulk) 56.6 (pptn) | -3,760 -3,830 |
| WIPP-26 Culebra | -5.9 -5.8 | 36.2 (bulk) 33.3 (pptn) | -1,560 -1,000 |
| WIPP-27 Culebra | -4.3 -5.1 | 30.7 (bulk) 30.0 (bulk) | -2,560 -1,120 |
| WIPP-29 Culebra | -5.1 | 49.76 (bulk) | -5,300 |
| RF-10 Culebra | -5.4 | 39.7 (cyl) | -3,020 |
| Engle Culebra | -2.8 | 11.5 (cyl) | 2,410 |
| WIPP-26 R/S | -7.1 | 90.7 (bulk) | -7,730 |
| WIPP-28 R/S | -4.7 | 48.5 (bulk) | -5,710 |
| WIPP-29 R/S | -4.8 | 53.4 (bulk) | -6,340 |

1. $\delta^{13}\text{C} = 5.7$ ‰; $\epsilon_{13} = 5.2$ ‰ for dolomite.

2. cyl - Water samples collected in 500 mL steel cylinders, whose carbon-isotope compositions were analyzed by accelerator mass spectrometry.

3. bulk - Bulk water samples (in wax-sealed polyethylene jerrycans) from which carbon dioxide was liberated by acidification and nitrogen-purging in the laboratory.

4. pptn - carbon dioxide samples obtained by acidification of the barium carbonate precipitate prepared in the field immediately following the collection of the water.

than the confidence limits, $\pm 1.8 \text{ ‰}$) causes a variation of nearly 2,200 years in the apparent age (even though the apparent age is negative for both values of $\delta^{13}\text{C}_s$). This attests to the sensitivity of the adjustment for incongruent dissolution based on the measured value of $\delta^{13}\text{C}$ in solution. The $\delta^{13}\text{C}$ values for the entire data set vary between -2 and -9 ‰, yielding a "correction" that does not vary in a systematic way.

Variations in other parameters, such as the temperature dependence of the equilibrium fractionation factor, are of the order of a few tenths ‰, but would introduce a change in a constant that would presumably prevail with little variation throughout much of the Rustler Formation, although this would have to be laboriously and rigorously tested. Similarly, the "true" value of the dolomite-bicarbonate fractionation factor ϵ_{13} could be different from 5.2 ‰ and could vary throughout the Rustler Formation if temperature varied. Nevertheless, as illustrated by Equation (16) this effect would be small relative to, for example, the uncertainty in the original $\delta^{13}\text{C}$ value of biogenic carbon dioxide, $\delta^{13}\text{C}_i$. The selection of -10.15 ‰ as the $\delta^{13}\text{C}$ value of solution carbonate after the congruent dissolution can never be justified by observation. It is unreasonable to expect to find an organic soil horizon that has survived undisturbed since the time of original infiltration and recharge to the groundwater, even if the area of paleo-recharge could be identified and characterized. Nevertheless, the value of this parameter would have to be taken as a constant for the entire Rustler system, if physicochemical mechanisms of radiocarbon dissolution during recharge to the groundwater system were the same in the past as they are now.

The calculated model ages tabulated in Table 5 for each PMC/ $\delta^{13}\text{C}_s$ data pair treat the data as if they were single replicates at each sampling point. For five of the sampling points, a second replicate data pair yielded a substantially different date. In many studies of radiocarbon in groundwater, as at most sampling localities in this study, only a single analysis is obtained at each locality. This exercise has illustrated that a date calculated from single-replicate data should be interpreted with due caution.

5.7 Sources of Nonsystematic Carbon Behavior

There are three possible reasons for deviations of carbon isotopes from the systematics predicted by the model of Evans et al. (1979):

1. Modern contamination by introduced modern carbon dioxide.
2. Congruent dissolution of rock carbonate by acids other than carbonic.
3. Natural mixing.

As well expressed by Evans et al., there is no way of evaluating the third possibility, since literally an infinite number of mixing combinations can lead to the same numerical measurement for a solution parameter:

For example, groundwater with a measured age of say 57K years may be water of 100K years [i.e., zero PMC] with a mix of only 0.1 % of modern water. The result is little changed even if the modern component is 5K years old.

Note that the effect of small admixtures from a carbon reservoir having a different PMC is much more severe for an ultratrace constituent such as radiocarbon (average abundance = 1 in 10^{12}) than it is for small admixtures from reservoirs with different isotopic ratios (e.g., $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, D/H, $^{234}\text{U}/^{238}\text{U}$). This geochemical principle has been demonstrated in numerous geological systems, and is virtually axiomatic.

Previous discussions addressed the consequences of the first possibility (contamination), particularly in Section 4.2.4.

The relevance of the second possibility (excess acid) was not anticipated before the present investigation. One of the limiting cases encountered by Evans et al. was that of the $\delta^{13}\text{C}_s$ value being very close to that of the rock (cf. Equation (16)). At equilibrium, these two values should differ from one another according to the fractionation factor ϵ_{13} . As the value of $\delta^{13}\text{C}_s$ approaches the value of K in Equation (16), the numerator decreases while the denominator is held constant. The exponent is a number very near unity, and hence its application changes very little the expression in square brackets. If the resulting expression is very much less than unity (possibly counteracting the result of even a very low PMC), a negative logarithm can ensue, leading to a negative age. Under normal circumstances the bracketed expression should asymptotically approach unity at zero age. If the value of $\delta^{13}\text{C}_s$ becomes so positive (resulting from nonsystematic behavior) as to approach or overtake that of the rock, the expression can even become zero or negative, which causes fundamental mathematical problems when the logarithm is taken. An obvious way of obtaining a zero or negative numerator in Equation (16) is to accumulate a local transient mineral acidity that is neutralized by congruently dissolving rock carbonate, contributing additional solution carbonate with a high $\delta^{13}\text{C}$ but a low PMC value. This would make the $\delta^{13}\text{C}$ value in solution instantaneously more positive than predicted by ^{13}C exchange (incongruent dissolution) at equilibrium.

This extra step of congruent dissolution in response to mineral acidity, not handled by the model, may or may not be accompanied by additional admixing of modern carbon dioxide into the solution. One good reason it cannot be handled by any model is that the amount of this additional congruent dissolution is probably indeterminate. Again from some field observations made at the time of pumping, there is evidence for continuing, recent, local metabolism of nutrients introduced at the time of drilling. The transient presence of minor levels of hydrogen sulfide (reported by Lambert and Robinson, 1984) is evidence for (a) anaerobic microbial activity, and (b) some level of mineral acidity. Any weak acid will cause more calcium carbonate to dissolve, bringing the $\delta^{13}\text{C}$ value of total dissolved bicarbonate closer to that of the rock by simple mixing. Weak metabolic acids (such as carboxylic), may be locally present. The most common of these is acetic acid, a product of glycolysis that has entailed at least partial metabolism of alcohol. These carboxylic acids can congruently dissolve rock carbonate with or without contributing contaminant modern

carbon, nevertheless invalidating the fundamental premises of the interpretive model. The effervescence of (presumed) carbon dioxide observed by Lambert and Robinson in some waters as they exited the wellhead may be a result of this dissolution.

Once the initial congruent dissolution has taken place at the time of recharge, two effects (besides radioactive decay) may decrease the PMC value: (a) further dilution of radiocarbon by additional congruent dissolution of the rock as a result of induced transient acidity and (b) the natural approach of the $\delta^{13}\text{C}_s$ value to isotopic equilibrium with the rock (by incongruent dissolution), accompanied by loss of radiocarbon from solution. The relative importance of these processes cannot be determined, since they both can decrease the PMC by comparable amounts. Thus, the "incongruent stage" of the model of Evans et al. (1979) cannot correct for such perturbations in the systematics of carbon-isotope behavior in groundwaters of the Rustler Formation.

Since virtually all models rely on quantification of the unperturbed state of the system, it does not appear possible to correct for these variable processes. For example, the small amount of additional calcium and/or magnesium resulting from additional congruent dissolution cannot be used to correct for this additional carbon, because (a) the increment of divalent cations would be small relative to the total, perhaps comparable to or smaller than the confidence limits of the analysis, and (b) the original divalent cations concentration in the water (after the first congruent dissolution but before the second) would have to be known with uncanny precision and accuracy. Lambert and Robinson (1984) reported a large variability in both total divalent cations and calcium, and hence there is no pervasive baseline value from which to infer a small variable increment. Also, pH measured at the wellhead would not be expected to indicate in situ mineral acidity because of (a) buffering by well equipment such as iron pipe, and (b) neutralization by carbonate to liberate additional carbon dioxide in the subsurface, some of which Lambert and Robinson inferred was exsolving.

Depending on how much metabolite is produced to dissolve rock carbonate in situ, the carbon in solution will (a) be further diluted by rock carbon in a nonsystematic indeterminate way, such that the numerical model will overcorrect for incongruent dissolution (on the basis of the $\delta^{13}\text{C}$ value) by an unknown amount that can lead to large negative ages, and (b) be augmented by some indeterminate amount of modern carbon in the form of metabolic carbon dioxide, a product of the partial degradation of cellulosic nutrients that were put into the hole during drilling to control lost circulation. It can be clearly seen in Equation (16) that adding **either** dead rock-carbon or modern contaminant-carbon can give spuriously young ages. Although the reasons for both of these admixing phenomena may be related to the introduction of nutrients, their effects are expressed by different parts of the equation: the first (additional congruent dissolution) involves only addition of dead carbon from the rock; the second involves only addition of ^{14}C -laced carbon dioxide. The equation predicts that a loss of ^{14}C to the rock should be correctable by the degree of approach to closed-system $^{13}\text{C}/^{12}\text{C}$ isotopic equilibrium between dissolved and rock carbonate species. When the aquifer system is opened by a new well, this equilibration is disrupted so that the model is no longer valid. The greater the difference between the $\delta^{13}\text{C}$

in solution and its equilibrium state in the presence of rock, the less ^{14}C is predicted by the model to have been lost to the rock by incongruent dissolution. Thus, irrespective of the PMC, the adjustment made on the basis of $\delta^{13}\text{C}$ can profoundly influence the age calculation, whether or not such adjustment is justifiable by the detailed carbon-isotope systematics.

Note the range of apparent radiocarbon ages calculated from the lowest PMC value in Table 1, that of Pocket. Applying the confidence limits at the 95% level obtained from the pooled s value for the entire data set, the confidence interval of PMC values is -0.36 (here taken as 0) to 7.70. The apparent age calculated from the lower confidence limit is infinity, and that from the upper is 3500 a (Table 4). Thus, the confidence limits of the lowest PMC value (which statistically include 0) yield an age range that covers essentially the entire range of the radiocarbon method. From this simple numerical treatment alone, the fact that the lowest PMC values statistically include zero suggests that if Rustler waters with even the lowest PMC values are contaminated in a nonsystematic way, the dates calculated from PMC and $\delta^{13}\text{C}$ values treated as invariant cannot be considered true absolute maxima. This is irrespective of the source of contamination, whether introduction of modern organic material or additional anthropogenic leaching of the carbonate host rock.

5.8 Summary

The model of Evans et al. (1979) gives the youngest calculable radiocarbon ages for groundwaters thought to be minimally contaminated with drilling-introduced modern carbon, and to be part of the same carbon-isotope systematics. The numerical model of Evans et al. for calculating the radiocarbon age of groundwaters in carbonate aquifers yields the "correct" radiocarbon age only when:

1. The measured PMC value is less than 50 (i.e., there is no contamination of the water by modern carbon introduced after the initial infiltration).
2. The steady, progressive $^{13}\text{C}/^{12}\text{C}$ isotopic equilibration of the dissolved carbon with rock carbon has not been perturbed by an event that adds non-radioactive carbon dioxide to the water by instantaneous leaching (congruent dissolution) of the rock.
3. There has been no mixing of waters of significantly different age to produce the water sampled for radiocarbon measurement.

If any of these conditions have been violated, the "true" radiocarbon age is indeterminate. If independent information is not available to show that none of these conditions has been violated, a high degree of confidence should not be placed even in a positive radiocarbon date, unless (1) the data can be verified by replicate analyses, and/or (2) the date fits into a consistent regional trend with other dates.

The radiocarbon dating method cannot be applied to groundwaters without a consideration of the geological/geochemical context. Thus, contrary to the statement of Davis and DeWiest (1966, p. 141), that "¹⁴C dating of water may be more accurate than would be suggested by general geological reasoning," the geological and recent history of a groundwater system may be so complex as to violate any or all of the assumptions fundamental to the application of the method. Despite the detailed development of the method in well-characterized sandstone aquifers (cf. Pearson et al., 1983), spurious results are very likely to ensue if the method is blindly applied to other systems, especially carbonate aquifers. Radiocarbon dating of groundwater should not be attempted without a reasonably complete understanding of the carbon-isotope systematics in the groundwater system.

6. THE MINIMUM AGE OF RECHARGE TO THE RUSTLER FORMATION

6.1 Waters of Apparent Finite Age

According to Equation (16) and the data in Table 1 (treated as invariant), the only apparent radiocarbon ages that are finite and positive in Table 5 are those of H-4B (16,100 a), H-6C (12,100 a), H-9B (14,900 a), Pocket (14,000 a), Engle (2,410 a), and H-5C (714 a). This means only that the respective combinations of PMC and $\delta^{13}\text{C}$ values of the dissolved carbon in these waters have systematics that are following the assumptions in Equation (16) closely enough so that the interpretive model of Evans et al. is not overcorrecting the PMC values for the expected effects of dilution and isotopic exchange between rock and water to the extent that negative apparent ages result. In Section 4.2.8 it was argued that a different set of geochemical constraints dominates the dissolved carbon in four of the samples (H-4B, H-6C, H-9B, and Pocket) than in all the others. The fact that finite positive ages were derived from the model age calculation does not alone imply that these are true ages. As suggested in foregoing discussions the PMC and/or $\delta^{13}\text{C}$ values of even these low-PMC but variable-¹³C data may have been perturbed somewhat from their natural values by an unknown amount of contamination.

It is remarkable that Culebra water samples from H-9B and Engle only three-quarters of a mile apart (Figure 1) should yield apparent radiocarbon ages that differ by 12,500 a. In terms of major solutes these waters are identical (Robinson, 1987), and it is reasonable to assume that there is a high degree of natural hydraulic connection between these boreholes at the Culebra horizon. Based on the relatively high transmissivity of the Culebra in that region (231 feet²/day at H-9B; Gonzalez, 1983), it is reasonable to expect that if natural mixing has homogenized the major solutes, mixing should also have homogenized the PMC values so as not to preserve a gradient of 9 PMC over 1000 meters. It was shown above that the dating model of Evans et al. could correct for loss of radiocarbon, but not for excess introduced radiocarbon. It was also shown above that excess introduced radiocarbon makes age calculations spuriously young, in many cases negative. Consequently, any age calculation using models such as that of Evans et al. yields a minimum age. As also

argued above, there is the possibility that even waters with the lowest PMC values may be contaminated with introduced modern carbon, though the dating model yields a finite positive age. Hence, the maximum ("true") radiocarbon age will remain indeterminate. When two water samples in such close proximity as H-9B and Engle have such different apparent ages, allowances made for modern contamination of the higher-PMC sample suggest that more confidence be placed in the lower PMC value and hence the greater apparent age.

Even though Engle and H-9B were not used in the least-squares calculation correlating PMC with bicarbonate (Figure 3), their proximity to the least-squares line suggests that they are indeed part of the same PMC/HCO₃⁻ mixing systematics as all the other points. However, in PMC/ $\delta^{13}\text{C}$ space (Figure 5) there is reason to consider H-5C and Engle data apart from the data for H-6C, H-4B, H-9B, and Pocket. For example, note that even though the PMC values of Engle and H-6C are similar (11.5 versus 9.7), their divergent $\delta^{13}\text{C}$ values (-2.8 versus -8.4 ‰) result in apparent model ages that are very dissimilar (2,410 versus 12,100 a). Whereas the confidence intervals for the respective PMC values overlap, the confidence intervals for the respective $\delta^{13}\text{C}$ values do not. The $\delta^{13}\text{C}$ values of H-9B (-2.4 ‰) and Pocket (-3.78 ‰) are close to that of H-5C (-3.7 ‰), but H-9B and Pocket have significantly lower PMC values (2.22 and 3.67, respectively) than H-5C (18). Thus, H-5C and Engle, even with their low apparent positive ages (714 and 2410 a), are not considered to be part of the same mixing systematics as the other waters of apparent positive age (H-6C, H-4B, Pocket, and H-9), but are considered part of the mixing systematics involving a significant contribution of introduced modern (contaminant) carbon having high PMC and low ^{13}C , as discussed in Section 4.2.8. Note that all waters having apparent negative ages according to the Evans et al. model appear to be part of the mixing systematics described by Equation (7). Four of the six waters having apparent finite ages are the group that gave the least-squares fit described by Equation (5).

It is not geologically reasonable that H-5C is a recharge point, in spite of its young apparent age (714 a). Its radiocarbon is probably contaminated, and Culebra transmissivity in its vicinity (0.14 feet²/day; Gonzalez, 1983) is not conducive to active recharge, especially when other localities with transmissivities one to three orders of magnitude higher have much greater apparent ages (for example, the H-9B area, $T \approx 200$ feet²/day; apparent radiocarbon age $\approx 14,900$ a). Furthermore, the extremely low tritium content at that point (0.3 ± 0.1 TU; Table 1) is not consistent with modern active recharge in the northeast part of the WIPP site.

The four waters of significant apparent finite radiocarbon age have a mean age of 14,280 a ($s = 1690$ a). For three degrees of freedom at the 95% confidence level, the single-replicate confidence limits are ± 5360 a. Thus, the four ages in the range 12,000 to 16,000 a are statistically indistinguishable from each other. Two hypotheses consistent with this result are:

1. That major recharge of groundwaters now found in the Rustler and Dewey Lake occurred as a single "event" (i.e., over a relatively short time span) in the late Pleistocene.
2. That significant recharge to the Rustler and Dewey Lake, if sustained over a long period, effectively ceased in the late Pleistocene, and travel times from recharge point(s) to each of the four sampling points were nearly the same.

An additional test of these hypotheses is discussed below, involving the consideration of PMC and $\delta^{13}\text{C}$ values as discrete points along a reaction path, and the degree of coincidence of this reaction path with an isochron common to all four points.

PMC values, radiocarbon dates according to the model of Evans et al., and tritium-content values are given in Figure 7. The geographic distribution of Evans et al. model radiocarbon dates and tritium suggests (1) the virtual absence of modern recharge in the WIPP area east of Nash Draw, (2) the uniformity of radiocarbon dates in the Culebra (12,000-16,000 a), showing no strong north-to-south gradient, and (3) the similarity of radiocarbon model ages and tritium levels in Dewey Lake sampling localities to those in the Culebra. The geological significance of these results will be discussed below.

6.2 Natural Evolution of Carbon Isotopes

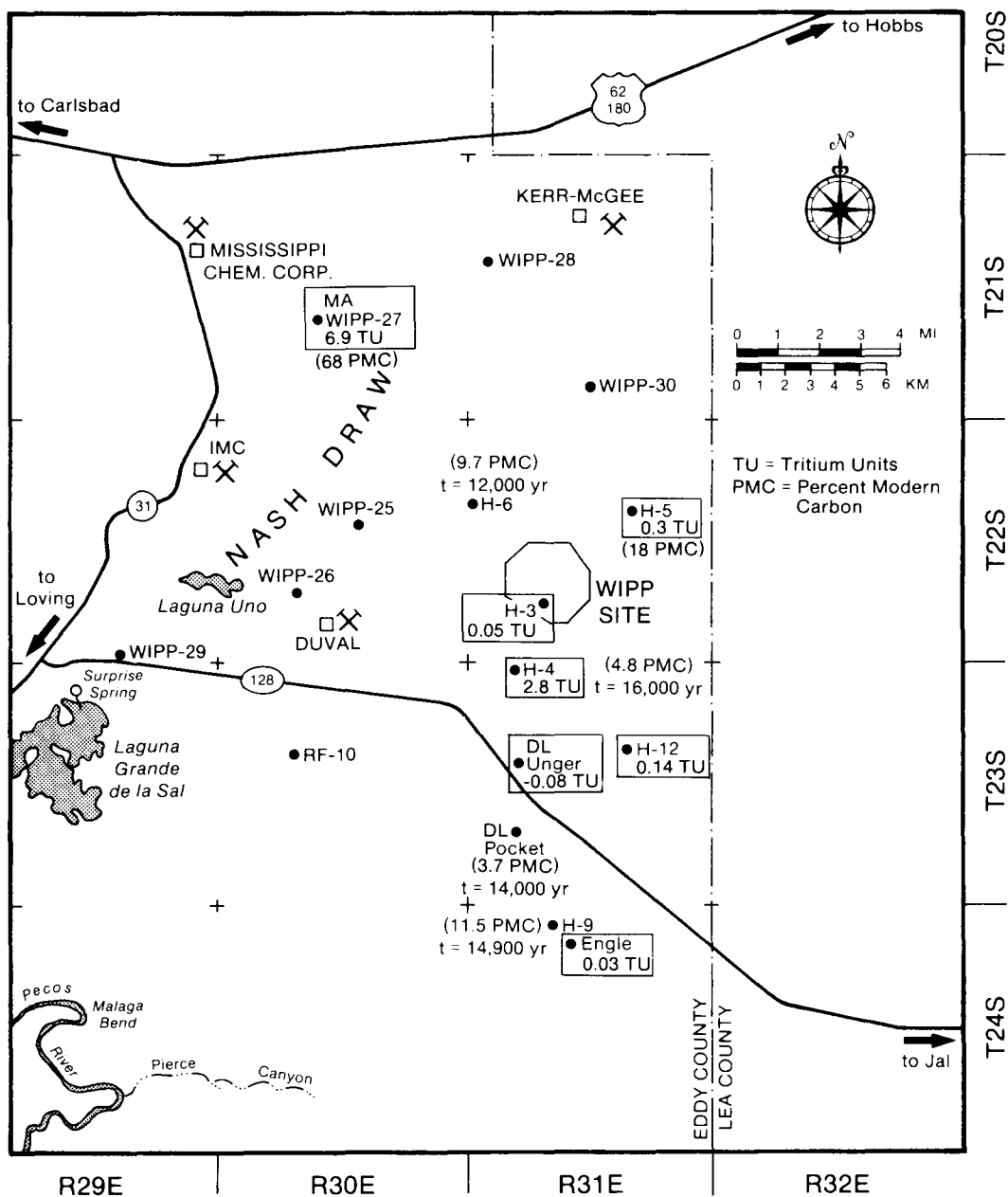
If any possible effects of contamination on H-4B, H-6C, H-9B, or Pocket are neglected, it is instructive to reconstruct in reverse the hypothetical evolutionary path of the carbon isotopes of this group. Doing so will also test the hypothesis that these waters are of approximately the same age. If these widely separated waters are of similar (late Pleistocene) age, this will strengthen the argument that either the last major recharge took place as a discrete event during a time of different climatic conditions, or the recharge ceased in response to that climatic change. Neither of these hypotheses is consistent with active recharge continuing unabated to the present. The well locations from which these waters came are spread out over a north-south distance of about 12 miles (Figure 7), and transmissivities vary by two orders of magnitude. Thus, the regional significance of a recharge event covering a relatively short time interval should not be underestimated.

Equation (16), rearranged with the approximation that the exponent $1+\epsilon_{13}/1000$, which has a value of about 1.0052, is very close to unity, becomes

$$\frac{10.65}{50} e^{t/8267} = \left(\frac{0.5 - \delta^{13}\text{C}_s}{\text{PMC}} \right) \quad (19)$$

At constant age (an assumption that could be made if original recharge of the entire groundwater system took place as a discrete event), the expression on the left side of Equation (19) is a constant. Thus, the equation is linear in PMC and $\delta^{13}\text{C}_s$, with the form

$$\text{PMC} = 0.5k - k(\delta^{13}\text{C}_s) \quad (20)$$



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Figure 7. Tritium and radiocarbon in Rustler and Dewey Lake groundwaters. DL = Dewey Lake; MA = Magenta; all others Culebra member of the Rustler Formation. Tritium units (TU) values enclosed in rectangles (all < 7 TU) indicate minimal introduction of an atmospheric component since 1950. Three Culebra and one Dewey Lake water dateable by the carbonate-aquifer model of Evans et al. (1979) have been isolated from the atmosphere from 12,000 to 16,000 radiocarbon years, indicating long residence times or long travel times from recharge areas, but providing no evidence of either modern vertical infiltration or monotonic age gradients indicating north-to-south flow.

where $k = (50/10.65)\exp(-t/8267)$, a constant for an isochron of age t .

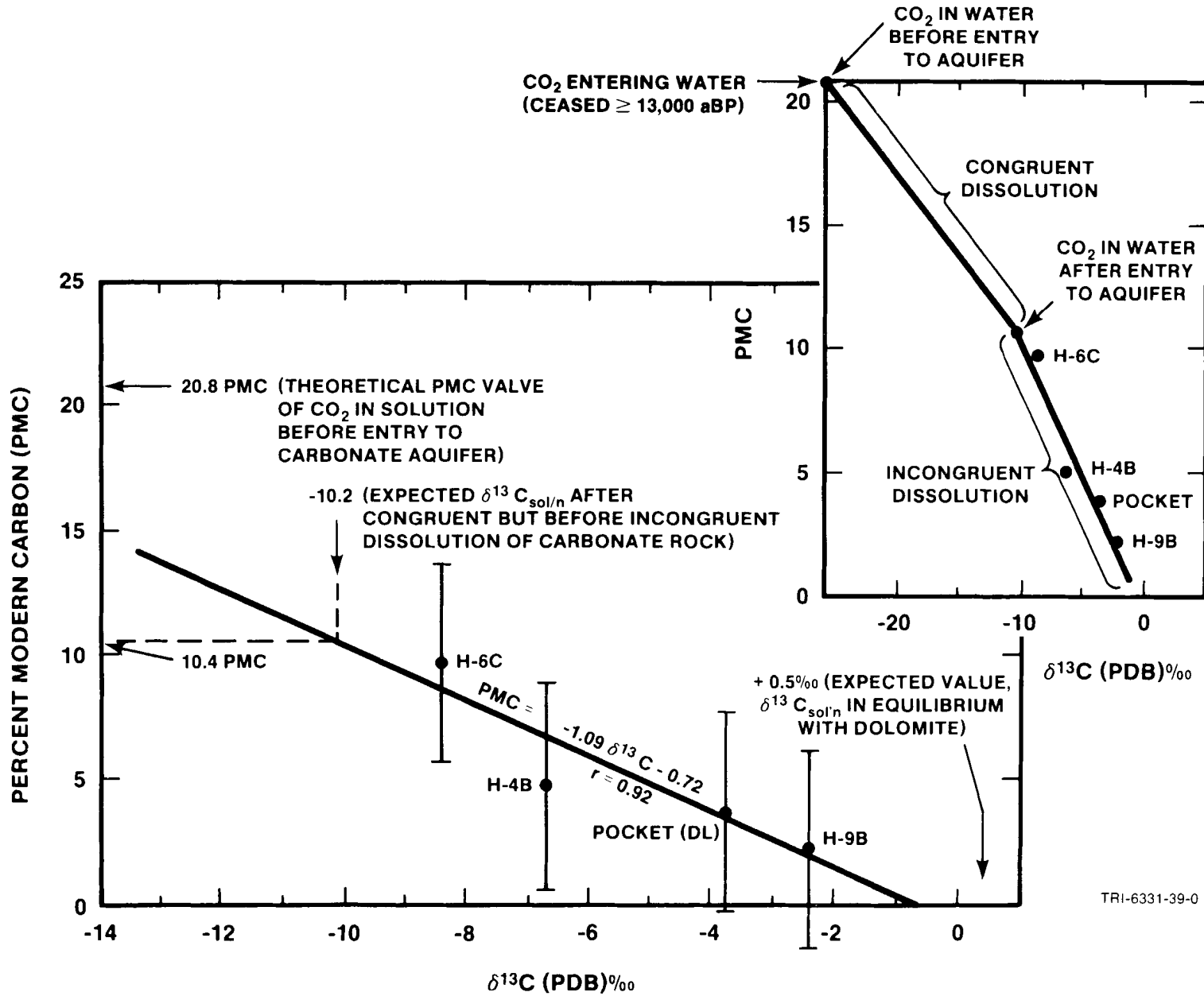
Two of the difficulties inherent in the previous calculations of model ages for individual samples from their PMC and $\delta^{13}\text{C}$ values were the uncertainties in (1) the estimated carbon-isotope fractionation factor at equilibrium between dolomite and dissolved bicarbonate, and (2) the estimated $\delta^{13}\text{C}$ value of the original dissolved biogenic carbon. Nor is it possible from Equation (19) to obtain unique values of these parameters from the slope and intercept of the straight line described by the form of equation (20). However, treating this subset of data as a group represented by a straight line is valid for the purpose of trying to deduce the evolutionary path of their carbon-isotope systematics. The attempt to reconstruct this path is shown in Figure 8.

According to the model of Evans et al. (1979), exchange of ^{14}C and ^{13}C between rock and water shifts the PMC downward (due to loss of ^{14}C to the rock) and the $\delta^{13}\text{C}$ upward (due to the approach of the $\delta^{13}\text{C}$ value of dissolved carbon to a value in equilibrium with the $\delta^{13}\text{C}$ value of the rock). Thus, the theoretical end of the equilibration path should have a $\delta^{13}\text{C}$ value of about +0.5 ‰.

The model of Evans et al. (1979) as applied here assumes that the original $\delta^{13}\text{C}$ value of the dissolved carbon at its maximum concentration should be about -10.15 ‰. At this stage, surface-derived carbon has entered the carbonate aquifer and has been diluted during congruent dissolution of carbonate rock, but isotopic exchange between rock and water during incongruent dissolution has not yet taken place. Equation (5), based on H-4B, H-6C, H-9B, and Pocket data, implies that dissolved natural carbon with $\delta^{13}\text{C}$ value of -10.15 ‰ had a PMC value of 10.4, given that this equation describes some reaction path common to all four PMC/ $\delta^{13}\text{C}$ data pairs. If the pre-dilution (i.e., pre-congruent-dissolution) PMC value is twice the post-dilution value, as governed by the stoichiometry of congruent dissolution (Equation (9)), then the PMC value of the dissolved carbon at the time it entered the carbonate aquifer was 20.8. The $\delta^{13}\text{C}$ value at that time is inferred to be -26 ‰.

It is now necessary to assume that the carbon dioxide released from the decay of natural organic matter in the soil and dissolved in downward-percolating water has the same carbon-isotope composition as the organic matter itself (i.e., that the release of carbon dioxide during decay and the dissolution of carbon dioxide into the water does not cause appreciable carbon-isotope fractionation). This allows the further assumption that 100 PMC represents the original ^{14}C content of biogenic carbon dioxide that dissolved in the water that then recharged the groundwater system in the Rustler and/or Dewey Lake, and that 20.8 represents the theoretical present-day PMC value of this material.

It is now possible to calculate the apparent age of the organic material that provided dissolved carbon to the recharging groundwater system according to the well known decay equation used in dating wood from archeological sites (Equation (8)). Again, assuming no ^{14}C gain or loss and neglecting the possible effects of modern contamination that would tend to make apparent radiocarbon ages spuriously young, and assuming that the present PMC of the infiltrated carbon would be 20.8, the calculated age of that organic matter is



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Figure 8. PMC and $\delta^{13}\text{C}$ values for waters that give finite positive apparent radiocarbon ages according to the model of Evans et al. (1979). Inset: Hypothetical reconstruction of the quantitative evolution of carbon-isotope systematics for these waters.

13,000 a. In other words, recharge to the groundwater system represented by these low-PMC values ceased at the end of the Pleistocene.

Next, an attempt was made to reconcile the slope and intercept obtained from the least-squares fit, Equation (5), with those obtained from different model ages, Equation (20). Table 6 gives the values of the constant in Equation (20) evaluated for 10, 15, 10, 25, and 30 Ka. The resulting lines generated from various values of the constant are plotted in Figure 9 along with the least-squares line fit to the four data points. The 15 Ka isochron comes closest to the least-squares line, which is consistent with the minimum age (13,000 a) empirically calculated from the carbon-isotope systematics qualitatively inferred from the interpretive model. This approximate convergence and the relatively high value of r (0.92) derived for Equation (5), suggest that the hypothesis of recharge at H-4B, H-6C, H-9B, and Pocket during a discrete event (or cessation of recharge over a short period of geological time) in the Pleistocene is consistent with the data.

Evidence for wetter local climate more conducive to groundwater recharge in the past is given by Van Devender (1980). From studying packrat middens in Rocky Arroyo northwest of Carlsbad, New Mexico (about 35 miles northwest of the study area in Figure 1), he determined that a juniper-oak community was present in the early Holocene (10,500 to 10,000 radiocarbon years ago), where now desert scrub communities exist.

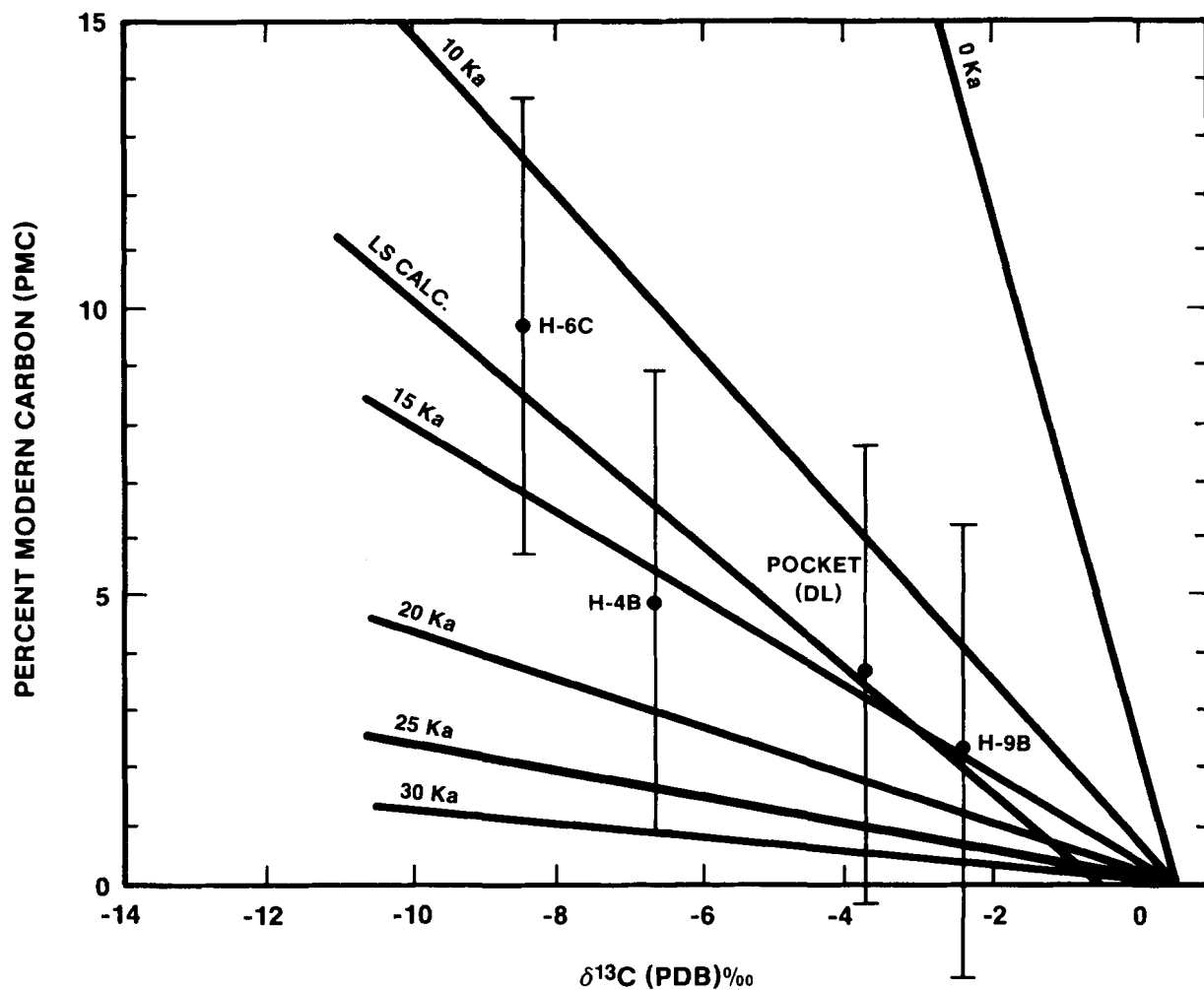
6.3 The Effects of Contamination and Mixing

The 95% confidence limits derived in Table 2 for a single replicate have been applied to the individual PMC values plotted in Figure 9. Note that the 15, 20, 25, and 30 Ka isochrons pass through the confidence intervals of H-4B and Pocket. Virtually any theoretical isochron of age > 10 Ka would pass through the confidence intervals for H-9B and Pocket, as their confidence limits include zero. Thus, the 2.2 PMC value for H-9B, while low, could nevertheless have been elevated by contamination above some indeterminate natural value. The model age calculation at such low values of PMC is highly sensitive to small variations in PMC. If H-6C, H-4B, and Pocket, for example, all were contaminated by 2 PMC, then their "natural" PMC values would be 2 PMC lower than observed. The 20 Ka isochron would then pass through the confidence intervals of all four points, and the older isochrons would pass through the confidence intervals of three of them. As seen in Figure 10, the effect of mixing a small amount of carbon from the reservoir labelled " CO_2 derived from modern organics" with a similar amount of carbon from the reservoir labelled " CO_2 derived from Pleistocene & older organics" would significantly increase the PMC, but would not necessarily change the $\delta^{13}\text{C}$ value, since the ranges of $\delta^{13}\text{C}$ values for the two reservoirs are similar. As also seen in Figure 10, the carbon-isotope systematics in the Rustler (and at least part of the Dewey Lake) groundwater system can be modeled as three-component mixing, instead of two-component mixing suggested solely by the $\text{PMC}/\text{HCO}_3^-$ relationship. The systematics at higher-PMC values are dominated by modern organics (i.e., modern contamination) and dissolved "dead" marine carbonate, while the systematics at lower-PMC values appear to be governed more by the evolutionary model similar to that of Evans et al. (1979), entailing mixing between dissolved carbon originally recharging the

TABLE 6. ISOCHRONS DERIVED FROM THE MODEL OF EVANS ET AL.¹

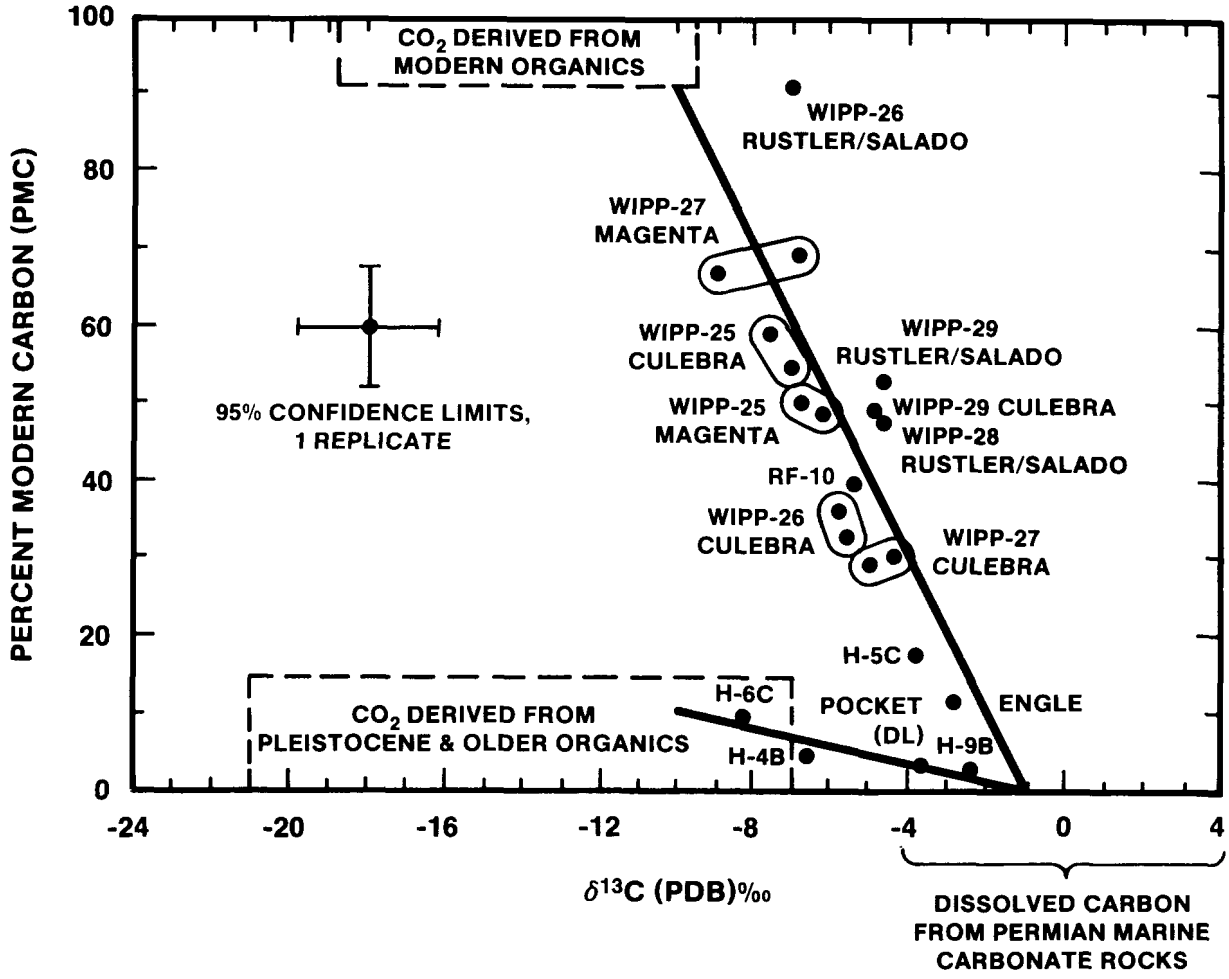
| <u>t</u> | $\frac{10.65}{50} \exp\left(\frac{t}{8267}\right) = \frac{1}{\text{const}}$ | <u>const</u> |
|----------|---|--------------|
| 10 Ka | 0.71 | 1.41 |
| 15 Ka | 1.31 | 0.76 |
| 20 Ka | 2.39 | 0.42 |
| 25 Ka | 4.38 | 0.23 |
| 30 Ka | 8.02 | 0.12 |

1. $\text{PMC} \approx [0.5]\text{const} - [\delta^{13}\text{C}]\text{const}$



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Figure 9. Radiocarbon isochrons for 10, 15, 20, 25, and 30 Ka derived from the numerical model of Evans et al. (1979). The 15 Ka isochron corresponds closely with the least-squares line calculated from the PMC and $\delta^{13}\text{C}$ values of H-6C, H-4B, and H-9B (Culebra) and Pocket (Dewey Lake). Vertical bars depict the confidence interval at the 95% level for one replicate of each PMC value (± 4.03 PMC), and in some cases encompass older isochrons as well.



TRI-6331-46-0

Figure 10. Three-component mixing as a plausible explanation for the distribution of PMC and $\delta^{13}\text{C}$ values from groundwaters in this study. This plot is very similar to that in Figure 5, but is presented at a different scale, and includes expected ranges of values for various reservoirs of carbon. Note that a small amount of high-PMC modern organic carbon introduced by artificial contamination can significantly increase the PMC values of low-PMC carbon derived from older organics, with essentially no change in $\delta^{13}\text{C}$.

groundwater system and carbon derived from the marine-carbonate host rock. A small amount of artificial mixing from modern sources in these latter systematics cannot be dismissed. This mixing is probable, in view of the locally high density of boreholes emplaced for potash-core assays, all of which have penetrated the Rustler (Powers et al., 1978). If this mixing actually took place, the true natural age of recharge of the Rustler Formation and part of the Dewey Lake Red Beds is likely to be in excess of 20 to 30 Ka, the practical limit of the radiocarbon method. At any rate, the residence time (recharge age) is probably in excess of 13,000 a.

The issue of contamination notwithstanding, waters of age 13,000 a could result from mixing of various reservoirs of different ages in various proportions. It is not possible to determine the proportions and ages of mixing reservoirs from the carbon-isotope data alone. Given the consistency between the apparent 13,000 a age for the four lowest-PMC groundwaters and their individual minimum ages calculated by the Evans et al. model (12,000 to 16,000 radiocarbon years), either the mixing proportions have been highly uniform over a widely scattered area, resulting in fortuitously uniform apparent ages, or the relatively tight range in apparent ages actually represents a recharge interval that ceased over a relatively short time period prior to 10,000 years ago.

7. CONCLUSIONS

Maximum age should not be calculated on any individual value of PMC available for the Rustler Formation groundwaters, since it is impossible to eliminate the effects of anthropogenic contamination or natural mixing for any individual value. This contamination has had the effect of raising the PMC values significantly above probable native values, and lowering the apparent age; this is exactly the opposite effect that is usually obtained in groundwater systems involving exchange of carbon species between water and host rock. If this were the usual case (i.e., if contamination due to well development had not occurred), one would expect to find a decrease in PMC with increasing bicarbonate, owing to the dilution and "sorption" of radiocarbon during carbon dissolution from the host rock. In such usual cases, the lowering of the PMC value by rock-water interactions would give a spuriously old apparent age, unless the PMC value could be adjusted for rock-water interactions.

Taken as a group, these radiocarbon data indicate mixing between a source of dead carbon, probably in the rock carbonate, and modern carbon, probably in the organic matter introduced during drilling and developing wells. There is no indication of a preponderance of original soil- or atmosphere-derived carbon dioxide at 12 of the 16 sampling localities. The most comprehensive applicable model for interpreting radiocarbon data as dates fails for most of the data because of the complex mixing phenomena. Given the highly variable climatological history of the Delaware Basin, and the fact that the area has not always been arid, the soil cannot be excluded as an important source of the original carbon dioxide introduced into the groundwater system. Thus, although much of the area is presently covered by dune sand, the generalization of Davis and DeWiest (1966, p. 141) that

"moderately accurate dating may be possible for water from desert regions where the water percolates through sandy aquifers free of carbonate and organic matter" may not apply here, since (a) the "aquifers" here are highly calcareous, and (b) the region probably was not a sandy desert at the time of recharge.

The age of the minimally contaminated carbon reservoir, based on four of the 16 sampling localities, is estimated to be at least 13,000 a and probably in excess of 20,000 to 30,000 years. These results are consistent with the hypothesis proposing that regional meteoric recharge of Rustler and some Dewey Lake groundwater effectively ceased during the late Pleistocene. The confidence limits applied to the less contaminated waters having less than about 6 PMC imply that these values statistically include zero PMC in their confidence intervals. In other words, the "age" (time of isolation from the atmosphere) of the natural carbon in these waters may exceed the limit of resolution of the radiocarbon method.

The minimum estimated age of surface-derived recharge for groundwaters in the Rustler and Dewey Lake aquifers near the WIPP site is 12 to 16 Ka, and this age range is supported by other paleoclimatic evidence (fossil packrat middens) in the region. The recharge may actually be part of an earlier Pleistocene event older than about 30 Ka, the age range of the radiocarbon method, given the possibility that even a small amount of contamination of these waters by modern carbon was introduced during well development. This contamination would make apparent radiocarbon ages spuriously young. These ages should not be used to calculate a travel time for Rustler groundwater across the WIPP site, because (a) residence times of the four least contaminated groundwaters show no coherent trends of becoming significantly younger toward some recharge point, (b) residence times (or ages of isolation from the atmosphere) of least contaminated groundwaters are statistically indistinguishable from one another, and may represent "pulse" recharge in a discrete event rather than continuous flow away from a recharge area, and (c) the relatively uniform residence times of least contaminated groundwaters may have arisen through homogenization after recharge.

There is a conspicuous dichotomy in carbon-isotope systematics between waters containing less than 10 PMC (four sampling localities having apparent radiocarbon ages of 12,000 to 16,000 years) and those containing more than 10 PMC (12 sampling localities for which one could argue that contamination had taken place during well development). The wide geographic separation (Figure 1) of sampling localities yielding model ages >10,000 a suggests that water of this apparent age was originally widespread throughout the area near the WIPP site. The mathematical relationships among the data from the contaminated wells suggest that the mechanism generating the observed PMC values has involved nonsystematic modern mixing of three carbon-reservoir endmembers: (1) ancient organic material dissolved in the water at the time of recharge, (2) carbonaceous species dissolved from the host carbonate rock, and (3) modern organic material introduced during water-well development. The last two dominate the more contaminated samples, but such samples probably contain some component of original dissolved carbon dioxide. Consequently it is concluded that the contaminated waters were derived from the original widespread Pleistocene-age waters. In some cases, insufficient time had elapsed between

well development and sampling to allow for dilution of modern contaminants to the expected 50 PMC value, which would be derived from the reaction of newly introduced carbon dioxide with host rock.

Enhanced analytical capabilities designed to allow detection of smaller amounts of radiocarbon have no bearing on the interpretability of PMC values as ages, since the effects of contamination and mixing in groundwater systems of nonuniformly low productivity cannot be precisely quantified.

Because of better ways of identifying meteoric water (D/H and $^{18}\text{O}/^{16}\text{O}$ ratios), and due to surface contamination associated with the venting of the Gnome event in the area, the usefulness of the class of weapons-generated nuclides (e.g., tritium and krypton) is limited. Furthermore, the relatively small content of native radiocarbon shows that the Rustler groundwater has been out of contact with the atmosphere for so long (at least several half-lives) that no native tritium, ^{90}Sr , ^{137}Cs , or ^{85}Kr should be observable. If significantly nonzero concentrations of these nuclides were observed, they would surely be attributable to contamination.

Because of the questionable validity of the assumptions necessary in applying radiocarbon and radiochloride dating methods in the evaporite environment of southeastern New Mexico, and because of the previously demonstrated susceptibility of these components to contamination in this groundwater system, these methods will not be pursued beyond this feasibility study with the expectation of obtaining additional or more definitive absolute dates. The available samples span the spectrum of hydrologic conditions: contaminated by potash outfall (WIPP-27 and -29), cavernous karstic porosity in Nash Draw (WIPP-25, -26 and -28), moderate permeability (H-4, H-6, Engle and H-9), and low permeability (WIPP-30 and H-5). They are also distributed north (WIPP-28 and -30, H-5 and -6), south (H-4 and -9, Engle), and west (WIPP-25, -26, -27, and -29) of the WIPP site. They include two stock wells (Pocket and Engle). They originated from four water-producing horizons: Rustler/Salado contact, Culebra, Magenta, and the Dewey Lake. Within this range of hydrologic conditions and sampling localities, the carbon-isotope systematics of four samples were sufficiently well behaved to allow the application of an internally consistent dating model. Based on this experience with sixteen different sampling localities, the probability of successful radiocarbon "dating" of the Rustler and perhaps the Dewey Lake groundwaters in the WIPP region is 0.25. As a general recommendation to those who would apply the radiocarbon method in studies of other areas, auxiliary measurements (such as concentration of dissolved carbon) should be determined in the field at the time of collection of radiocarbon sample, to allow one to test the validity of the assumption that the PMC and $\delta^{13}\text{C}$ measurements are representative of the carbon native to the groundwater.

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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

FOREIGN ADDRESSES

Studiecentrum Voor Kernenergie
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 1LO

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

Mr. D. Alexandre, Deputy Director
ANDRA
31, Rue de la Federation
75015 Paris, FRANCE

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 für Forschung und
Technologie
Postfach 200 706
5300 Bonn 2
FEDERAL REPUBLIC OF GERMANY

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

Hahn-Meitner-Institut für Kernforschung
Attn: Werner Lutze
Glienicker Strasse 100
100 Berlin 39
FEDERAL REPUBLIC OF GERMANY

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

Kernforschung Karlsruhe
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

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

Department of Earth Sciences
and Quaternary Sciences Institute
Attn: T. W. D. Edwards
University of Waterloo
Waterloo, Ontario
CANADA N2L 3G1

British Geological Survey (3)
Hydrogeology Group
Attn: G. Darling
R. A. Downing
R. L. F. Kay
Maclean Building
Crowmarsh Gifford
Wallingford
Oxfordshire OX10 8BB
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 0RA
GREAT BRITAIN

Hermann Gies
Institut für Tieflagerung, Gruppe Geochemie
Gesellschaft für Strahlen und Umweltforschung mbH
Theodor-Heuss-Strasse 4
D-3300 Braunschweig
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