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Uranium-Isotope Systematics in Groundwaters of the Rustler Formation, Northern Delaware Basin, Southeastern New Mexico

I: Principles and Preliminary Results

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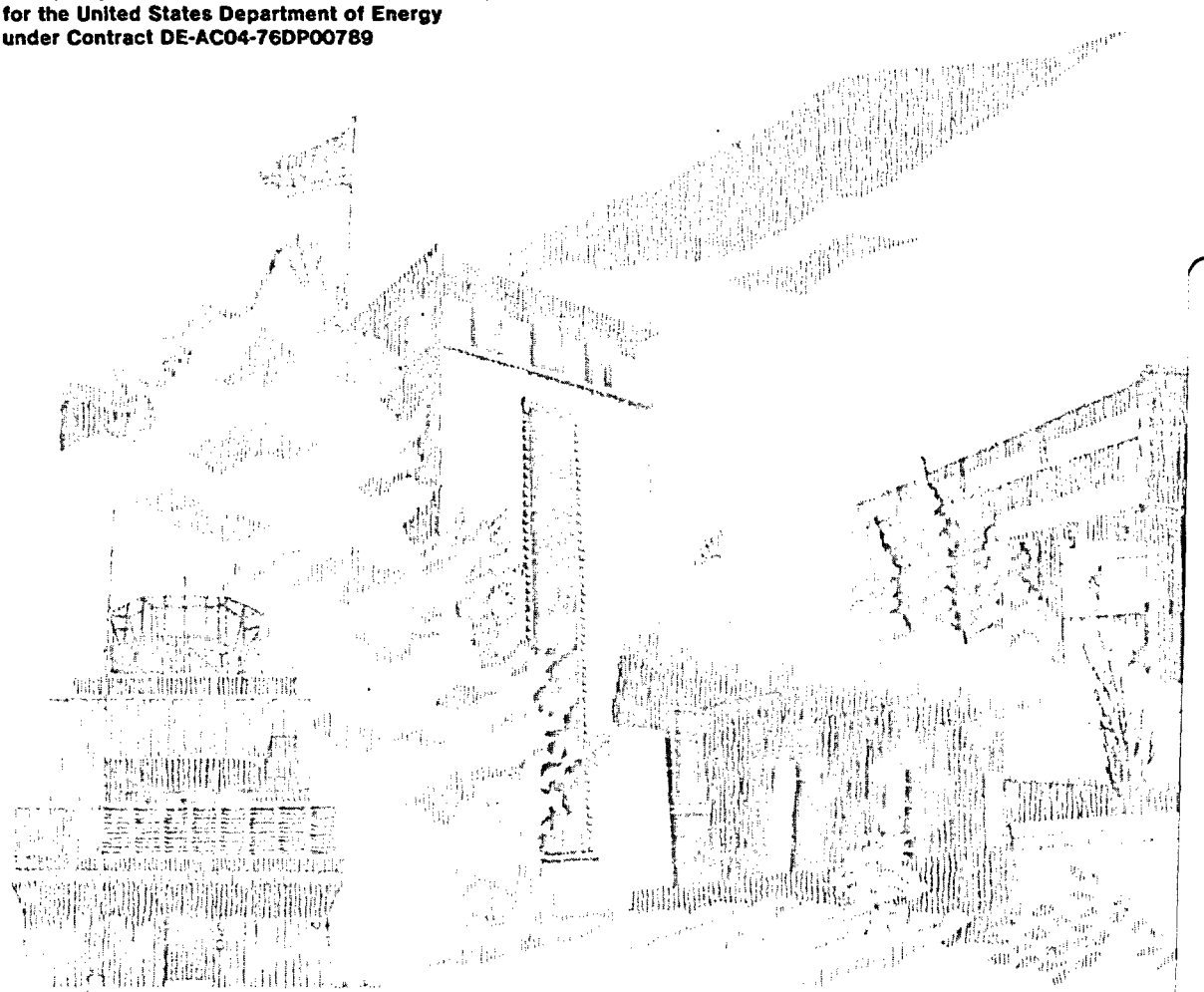

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Uranium-Isotope Systematics in Groundwaters of the Rustler Formation, Northern Delaware Basin, Southeastern New Mexico I: Principles and Preliminary Results

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ABSTRACT

Values for uranium concentration ([U]) and $^{234}U/^{238}U$ activity ratio (A.R.) have been determined for groundwaters and host rocks from the Rustler Formation near the Waste Isolation Pilot Plant (WIPP) site in the northern Delaware Basin of southeastern New Mexico. [U] varies from about 0.02 to 40×10^{-9} g/g, increasing westward across the WIPP site to Nash Draw, a dissolution valley underlain by outcrops of Rustler Formation evaporites. Large deviations from secular equilibrium (A.R. $\approx$ 1) in the groundwaters increase eastward from about 2 to 3 in Nash Draw to almost 12 in the eastern part of the WIPP site. [U] and A.R. variations cannot be completely explained by simple mixing due to congruent dissolution of uranium from rock (without isotopic fractionation). A.R. values typically increase along the flow path in a reducing environment, and the observed eastward increase in A.R. suggests a relict flow system whose dominant flow direction (eastward) was at high angles to that now observed. A westward decrease in A.R. coupled with a steady increase in [U] indicates not only that there was a change in flow direction since recharge, but that Rustler groundwater is now draining from areas of high potentiometric level and low permeability near the WIPP site, without appreciable recharge. The maximum time required for this westward drainage is about 200,000 a. The minimum time required to achieve the highest observed A.R.s during the earlier episode of eastward flow from recharge in the west is 10,000 to 30,000 a. Radiocarbon and stable-isotope studies of the Rustler Formation near the WIPP indicate that the modern Rustler flow system is not at steady state, recharge being dominated by wetter climatic conditions in the Pleistocene. Uranium-isotope studies are consistent with these results, and further suggest that present flow directions are qualitatively different from those existing at the time of recharge.

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EXECUTIVE SUMMARY

Uranium concentrations and $^{234}U/^{238}U$ activity ratios (A.R.s) have been determined for groundwaters and their host rocks from the Rustler Formation near the Waste Isolation Pilot Plant (WIPP) site, in the northern Delaware Basin of southeastern New Mexico. Aqueous total-U ([U]) concentrations range from about 0.02 to about 40×10^{-9} g/g ("parts per billion"). Large deviations from the expected secular-equilibrium A.R. value of 1 are observed in the groundwaters. West of the WIPP site, in central Nash Draw (a dissolution valley underlain by outcrops of Rustler Formation evaporites) well-mixed high-permeability hydrologic systems are developed in the Culebra dolomite member and near the contact between the Rustler and Salado Formations. This mixing has resulted in relatively uniform aqueous [U] values of ~10 ppb, and A.R. values between 2 and 3. In the southwestern part of Nash Draw, where the Culebra member carries groundwaters very near the surface, the [U] has its highest observed aqueous value of about 40 ppb. Southwestern Nash Draw is dominated by a shallow hydrologic system that is recharged by water imported for potash refining, and the high [U] and low A.R. values are consistent with a large amount of congruent dissolution, without isotopic fractionation, of uranium and other constituents from soluble evaporites.

In the Culebra groundwaters, [U] increases monotonically from east to west toward Nash Draw. The A.R. decreases westward from maximum values of 6 to 12 near the WIPP site, in the same general direction as [U] increases. Westward-decreasing A.R. contours in the Culebra mimic westward-decreasing potentiometric levels in the Magenta dolomite member of the Rustler Formation, which has lower overall permeability than the Culebra, and may thus partially preserve a record of flow direction that formerly prevailed in the Culebra. Geographic variations in [U] and A.R. in the Rustler/Salado contact mimic those in the Culebra, although the A.R. variations are smaller and the number of reliable control points, particularly near the WIPP site, is smaller. Overall, the [U] values are lower at the Rustler/Salado contact. Reliable [U] and A.R. values for Magenta waters at WIPP-25 and WIPP-27 (in Nash Draw) are similar to those of Culebra waters there, and these similarities are consistent with a well-developed degree of vertical interconnection at those points.

The evolution of [U] and A.R. distributions in confined groundwater systems, such as the Rustler near the WIPP site, is generally explained by a multi-legged path, as originally described by Osmond and Cowart (1976). As water enters an oxidizing recharge zone, congruent dissolution raises the [U], with minimal effect on A.R. As groundwater conditions become more reducing, the [U] drops. If reducing conditions prevail along the flow path, very little additional ^{238}U is introduced into solution; ^{234}U, however, becomes more concentrated in solution, due to the enhanced leachability of its parent ^{234}Th, which has damaged its local lattice environment during recoil that accompanies α-decay of its parent ^{238}U. This results in an A.R. that increases in solution downgradient along the flow path. The rate-determining step in this process is the initial decay of ^{238}U to ^{234}Th, rather than any subsequent process of decay or leaching. Buildup of A.R. proceeds until a steady-state value is reached, which depends on the initial [U], the amount of leachable uranium

provided by rock surfaces, and the time spent on the evolutionary path. If the source of rock uranium is removed or decreased in abundance, the A.R. values decrease by radioactive decay of ^{234}U back toward secular equilibrium. If oxidizing conditions are again encountered, the A.R. values decrease due to dilution of ^{234}U by uranium congruently dissolved from the host rock, which typically has an A.R. near unity.

From the eastern scarp of Nash Draw westward, [U] and A.R. relationships are consistent with ongoing congruent dissolution of uranium from the host rock. Near the WIPP site, the [U] and A.R. systematics cannot be described by such simple dissolution. Some of the high A.R. values near the WIPP site may have been lowered from initially higher values by rock dissolution and resultant dilution of ^{234}U by low-A.R. uranium, but according to the model, high A.R. values can be generated only at distal, not proximal, points along the flow path. Thus, the increase in A.R. value in a direction different from that of the modern flow direction indicates that flow at one time was generally west to east. If the present-day permeability distribution is similar to that at the time of recharge, the flow was from the higher permeability in Nash Draw toward the lower permeability near the WIPP site. The extremely high A.R. values (>6 and <12) near borehole H-5 (at the eastern boundary of the WIPP site), together with the low permeability there, are not consistent with active modern recharge east of the WIPP site, even though the potentiometric levels there are highest. The relict A.R. distributions, which at one time increased along the flow direction, indicate that the principal flow direction has since changed. Changes of principal flow direction with respect to that necessary to generate eastward increasing high A.R.s indicate that groundwater flow in the Rustler Formation is not at steady state.

Based on decay of ^{234}U, assuming no additional uptake from the rock, uranium travel time during drainage from east to west along the modern flow direction, from the WIPP site to a hypothetical discharge point in southwestern Nash Draw, is no more than 200,000 years. Westward decreases in A.R. in Nash Draw are attributable largely to dilution by dissolution and not radioactive decay. The time required for A.R. values to build up to observed values of 6 to 12 near the WIPP site, during an earlier eastward-flowing regime, depends on the initial U concentration in solution and in rock. It is not possible to achieve A.R. values greater than 3.4 using (a) the mean present-day U concentration in Culebra rock (0.9×10^{-6} g/g) and (b) the lowest aqueous Culebra U concentration (0.134×10^{-9} g/g at H-5). Using reasonable likely values of [U] at the time of recharge (0.02×10^{-9} g/g), and silty uranium-rich rock (9×10^{-6} g/g), minimum times required to achieve the Culebra A.R. values observed at the WIPP site are 10,000 to 30,000 years, regardless of recharge area. The most likely paleorecharge area for the old eastward-flowing system is to the west, where the ancestral Pecos River drainage flowed over the Rustler outcrops in Nash Draw during the Pleistocene. Rustler groundwater flow has since changed direction and is now probably draining without appreciable recharge in the site area.

Stable-isotope data reported by Lambert and Harvey (1987) indicate that modern recharge has a different isotopic composition than meteorically derived confined Rustler groundwaters. Tritium and radiocarbon data (Lambert, 1987) indicate that such waters have a minimal modern meteoric component, and have been isolated from the atmosphere

for at least 12,000 to 16,000 years. Uranium systematics reported here for the same groundwaters suggest that groundwater flow from the paleorecharge area was in a direction different from that inferred for the modern flow system from potentiometric measurements. All the available isotopic data are consistent with the interpretation that principal recharge and groundwater flow patterns and probably evaporite dissolution patterns during the Pleistocene were dominated by climatic variations that represented wetter conditions than now found in the northern Delaware Basin.

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1. INTRODUCTION

1.1 Fundamental Questions

An understanding of the geologic history of the Rustler Formation in the northern Delaware Basin of southeastern New Mexico is considered fundamental to evaluating the ability of the bedded evaporite environment at the Waste Isolation Pilot Plant (WIPP) to contain waste radionuclides for long periods of time. The Rustler is deemed important because it (1) is the uppermost evaporite-bearing unit in the Ochoan (Permian) sequence, (2) is experiencing active dissolution where it crops out in Nash Draw, 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, porous rock that carry the most abundant and regionally persistent occurrences of groundwater associated with the evaporites.

Lambert and Harvey (1987) documented the stable-isotope compositions of groundwaters in the Rustler Formation and concluded that they are of meteoric origin (ultimately derived from surface recharge). However, comparison with other meteoric groundwaters whose origins could be traced by observation and inference to infiltration of modern precipitation showed that most of the Rustler groundwaters were probably recharged under climatic conditions different from those at present. Thus, it was suggested that most of the Rustler contains "fossil" groundwater, no longer being actively recharged. The precise time of this recharge remains indeterminate, although radiocarbon measurements (Lambert, 1987) suggest that the Rustler Formation contains a significant component of groundwater isolated from the atmosphere for more than 12,000 years. Independent paleoclimatic evidence points to much wetter conditions, more conducive to recharge, at various times in the Pleistocene, ranging from 10,000 (Van Devender, 1980) to 600,000 years ago (Bachman, 1985). If indeed the meteorically derived Rustler groundwater has been isolated from the atmosphere for a time interval equivalent to the recharge age, remaining questions concerning the post-Pleistocene evolution of the groundwater and its solutes deal with processes restricted entirely to within the Rustler, rather than with questions of recharge by vertical infiltration.

The relevance of isotopic methods to these various questions for a given groundwater system depends largely on one's ability to unravel the effects of artificial contamination and natural mixing of different reservoirs in the subsurface. Previous work (Lambert, 1987) has shown that the effects of contamination and mixing may make the atmospheric-based dating methods of limited value. However, there are certain cases in which mixing phenomena may actually be of use in tracking changes in other kinds of isotope systematics in groundwater if it can be shown that the degree of natural mixing is related to another parameter, such as geographic position.

As in the case of studies related to stagnant brine reservoirs within the Castile Formation underlying the Salado (Barr et al., 1979; Lambert and Carter, 1984), specific questions need to be formulated in a groundwater "dating" attempt:

> How long has the water been where it is? (residence time)
>
> How long has the groundwater been isolated from other groundwaters that can be shown to be modern? (isolation time)

One question to which principles of uranium-isotope-disequilibrium may be relevant for **moving**, versus stagnant, groundwater is:

> How long did the groundwater take to get between various points in the system? (travel time)

This last question, posed by regulatory agencies governing radioactive waste repositories in particular (e.g., the U. S. Environmental Protection Agency and the U. S. Nuclear Regulatory Commission), is commonly expressed thusly: How long **will** [radionuclide-contaminated] water take to get from the repository to the accessible environment? An assumption fundamental to most efforts to arrive at such predictions is that the present set of measureables and observables in a given flow system, such as permeability distribution and flow directions, represents a steady state that has persisted and will persist for times **much longer** than both the time scale of regulatory interest and the response time of the system to climatic change and erosional changes in base level, and **very much longer** than water travel times within the system. This assumption may not be valid, and must be demonstrated before use in making predictions of radionuclide travel time. Implicit in inferring travel time from time-dependent observations such as isotopic measurements is the process of associating these observations with discrete points along a specific flow path. Flow paths, and more specifically, flow directions, may not be at steady state. Different sets of measurements (e.g., hydraulic versus geochemical) may yield different results, representing different "snapshots" in time. For example, the stable-isotope shift in groundwaters at the Rustler/Salado contact (Lambert and Harvey, 1987) is correlative with the amount of surviving Rustler halite (an increasing rock/water ratio) and inversely correlative with permeability. The removal of Rustler halite appears to have outpaced the consequent permeability increase and the resultant flushing of isotopically-shifted water.

1.2 Limitations and Objectives

All isotopic "dating" methods that utilize the time-dependent radioactive decay of a measurable constituent require assumptions about (1) the initial, pre-decay state of the system, (2) the consequences of mixing and contamination, whether they result in an apparent age either too old or too young, and (3) processes that alter the concentration of the measurable constituent by means other than radioactive decay. The uranium-isotope disequilibrium systematics of "dating" groundwater involve all of these assumptions. In addition, a special application entails the time-dependent **accumulation** of a measurable

constituent (^{234}U), together with its radioactive decay and other processes that tend to decrease its concentration.

Models have been developed to account for the changes in $^{234}U/^{238}U$ activity ratio (A.R.) along a flow path in a confined groundwater system under reducing conditions. Give the multitude of assumptions required in attempting to "date" a groundwater using uranium isotopes, a failure of one or more of these assumptions may invalidate the usefulness of uranium isotopes for absolute "dating." This is analogous to the role of underlying assumptions in the use of other isotopic "dating" methods, such as radiocarbon, as discussed in detail by Lambert (1987). Nevertheless, given the descriptive models for uranium-isotope fractionating along a flow path, it may still be possible to compare observed systematic behavior of A.R.s and total-U concentration ([U]) values with A.R. and concentration distributions predicted according to models. Uranium-isotope studies then assume a valuable role in allowing flow paths to be inferred according to the uranium-isotope models. Flow paths thus derived can then be compared to modern flow paths inferred from potentiometric measurements alone, and the nature and degree of transience in the flow system suggested by other geological and geochemical studies can be further evaluated. As a result, uranium-isotope studies proved a potentially valuable means not only of testing both the steady-state and transient hypotheses, but also of refining them.

1.3 Previous Work

Experimental verification of preferential leaching of ^{234}U due to α-recoil was reported by Kigoshi (1971). Buildup of ^{234}U concentrations as an effect of aging in confined waters was described by Kronfeld et al. (1975). Fundamental principles of applying U-isotope systematics in natural waters were discussed by Osmond and Cowart (1976). U-isotope disequilibrium dating was applied to pressurized brine reservoirs in evaporites by Barr et al. (1979) and Lambert and Carter (1984). Kraemer (1981) discussed U-isotope activity ratios in geopressured aquifers from the Gulf Coast. For moving groundwater systems Kronfeld et al. (1979) inferred flow patterns based on U-isotope activity ratios and total-U concentration distributions. Comparisons of calculated and observed activity ratios in moving groundwater systems were made by Andrews and Kay (1982; 1983) for the Lincolnshire limestone and the East Midlands sandstone, respectively.

As of this writing, detailed treatments of the general stratigraphy and dissolutional history of the Delaware Basin in southeastern New Mexico, and of the Rustler Formation in particular, are available from Powers et al. (1978), Lambert (1983), Bachman (1984), and Snyder (1985).

2. METHODS

The strategy used for the collection of water samples in the field was based on the desire to eliminate as much contamination as possible from drilling additives and metallic equipment put into the hole for each pump test. The criteria for collection of a uranium

sample were those developed by Barr et al. (1979) and the method used in applying these criteria was described in detail by Lambert and Robinson (1984). As shown by the data in the latter work, vertical mixing in the boreholes sampled has not been sufficient to homogenize the major solutes in vertically-stacked hydrologic units (Magenta and Culebra members of the Rustler Formation; Rustler/Salado contact), even in much of the partially dissolved and severely collapsed Rustler Formation in Nash Draw, except for probable mixing between the Magenta and Culebra water in boreholes WIPP-25 and WIPP-27. Even in southwestern Nash Draw, where partial dissolution of evaporites and complete halite removal has penetrated to the middle Salado, the Rustler/Salado contact zone contains a solute assemblage significantly different from that in the near-surface Culebra in WIPP-29. Thus, near-surface influences of wastewater dumping by local industries in Nash Draw, as discussed by Hunter (1985), may have perturbed the major and minor elements and isotope ratios in the Culebra in WIPP-29, but we consider this effect minimal elsewhere (cf. Lambert and Harvey, 1987).

Total uranium content in solution and the uranium-isotope ratio are particularly susceptible to contamination by contact of sample water with heavy metals (such as iron pipe) in a stagnant, corrosive environment. Long purging (several days) was required before sampling a system for determination of the uranium-isotope ratio, as shown by Lambert and Robinson (1984) and Lambert and Carter (1984). Barr et al. (1979) showed that during a flow test, the asymptotic approach of total iron in solution to some steady-state value correlated with a similar asymptotic approach to steady-state of total dissolved uranium concentration ([U]) and $^{234}U/^{238}U$ A.R. Lambert and Robinson (1984) documented the approach of iron to steady-state values in the pump tests of WIPP-25, WIPP-26, WIPP-27, WIPP-28, WIPP-29, and WIPP-30 over periods of hours to days. This group is commonly called the "Nash Draw" holes, because even though WIPP-30 is not within Nash Draw, one of its objectives was to provide stratigraphic data relevant to the evaporite-dissolution processes exemplified by Nash Draw, a broad dissolution valley developed in outcrops of the Rustler Formation west of the WIPP site. Although [U] and A.R. were measured in the final samples, but not in any of the intermediate serial samples from these wells, it is assumed that by analogy [U] and A.R. reached steady-state values when the total iron did. No similar sets of field measurements were made for H4, H5, and H6, but the pumping times were similar to those in Nash Draw, and it is assumed that steady-state geochemical conditions were obtained in these three holes also.

Only those boreholes are considered here that have to date supplied both reasonably representative groundwater samples and samples of dolomitic aquifer rock that appeared to have been in contact with local groundwater. In the case of the Culebra dolomite member of the Rustler Formation, the most productive horizons in the aquifer unit tend not to be recovered in coring operations, or are recovered as rubble rather than intact core; higher permeability appears correlative with higher fracture density. Mineralogical heterogeneity and lack of core cohesion made a comparably extensive sampling of "basal brine aquifer" rock at the Rustler/Salado contact impractical.

Waters from rainfall, spring discharge, and a potash mine seep were grab-sampled in containers pre-rinsed with the sampled fluid. Sampling conditions for the latter two made it impractical to obtain rock uniquely representative of that which had been demonstrably coexisting with the water.

Aqueous samples were prepared for isotope-dilution mass spectrometry in a clean room by using a modified resin-bead concentration method (described in detail by Lambert and Carter, 1984), in which the small amounts of natural uranium in water or rock (much smaller than could be α-counted) were spiked with ^{233}U and passed through an anion-exchange resin column. Uranium was eluted, the volume of solution reduced, and the small amount of solution was employed on a single resin bead affixed to the filament of a three-stage, solid-source mass spectrometer.

Rock samples, consisting largely of carbonate and sulfate minerals, were dissolved by refluxing in 8 to 10 M electronic-grade nitric acid. This treatment quantitatively dissolved all the carbonate and sulfate. The minute amount of silicate residue was dissolved in a mixture of hydrofluoric, nitric, and hydrochloric acids. The resulting aqueous solution was spiked and concentrated using the resin-bead method described above.

3. DATA AND CONFIDENCE LIMITS

The resulting data were the total uranium concentrations (as small as 10 parts in 10^{12}, or 10 parts-per-trillion) and $^{234}U/^{238}U$ A.R.s, based on the known amount of ^{233}U spike. All water samples were analyzed in duplicate, and mean values of the water-sample data are given in Table 1. The "±" value given for the Culebra water from borehole H5B is representative of the typical relative standard deviation, ±4-5 %.

The rock-sample data are given in Table 2. Replicate analyses on rocks gave pooled s values of 0.04 for both [U] and A.R.. By the method of Natrella (1963) the confidence limits at the 95% level are ±0.11 for both [U] and A.R. in rock samples. This is about ±10% of the measured values.

4. INTERPRETATION AND DISCUSSION

4.1 Principles of Uranium-Isotope Disequilibrium

In this section we describe in detail the basic principles governing the distribution of uranium concentration and isotope ratios and discuss how these principles allow age calculations to be made according to different mechanisms governing changes in A.R.s. These principles are applied to the Rustler Formation groundwaters in subsequent sections.

TABLE 1. AQUEOUS URANIUM AND $^{234}U/^{238}U$ ACTIVITY RATIOS[1]

Sample Name	[U](aq), $\times 10^{-9}$ g/g	A.R. (A_{234}/A_{238})
Rustler/Salado Contact:		
WIPP-25	1.40	2.00 ± 0.10
WIPP-26	4.46	1.36 ± 0.03
WIPP-28	3.32	1.59 ± 0.04
WIPP-29	11.6	1.68 ± 0.04
WIPP-30	0.02	2.0 ± 0.24
Culebra Member, Rustler Formation:		
H-4B	3.43	6.09 ± 0.18
H-5B	0.134 ± 0.006	11.6 ± 0.4
H-6B	5.86	3.57 ± 0.20
WIPP-25	10.22	3.12 ± 0.03
WIPP-26	10.91	3.02 ± 0.03
WIPP-27	8.69	2.87 ± 0.06
WIPP-28	5.70	2.93 ± 0.05
WIPP-29	41.4	2.19 ± 0.04
WIPP-30	1.08	8.06 ± 0.10
Magenta Member, Rustler Formation:		
WIPP-25	10.46	3.09 ± 0.06
WIPP-27	7.57	2.37 ± 0.04
Tamarisk Member, Rustler Formation:		
Surprise Spring	38	2.48 ± 0.02

TABLE 1. (continued)

Sample Name	[U](aq), $\times 10^{-9}$ g/g	A.R. (A_{234}/A_{238})
Rainfall:		
Storm, 05 May 77	0.01	1.74 ± 0.25
McNutt Potash Zone, Salado Formation:		
2L ME BT29 28 Oct 77	0.03	≈2.9

1. Where the standard deviation ("±") is explicitly tabulated, values are means of duplicate analyses of different sample aliquots. Otherwise, typical relative standard deviation in [U] is about ± 4%, as tabulated for H5B.

TABLE 2. URANIUM AND ACTIVITY RATIOS IN CULEBRA DOLOMITE[1]

Sample Name	[U], $\times 10^{-6}$ g/g	A.R. (A_{234}/A_{238})
H-4B	0.94	1.18 ± 0.02
H-5B	0.97	1.47 ± 0.04
H-6B	0.75	1.03 ± 0.04
WIPP-25	0.90	1.01 ± 0.04
WIPP-26	0.54	1.05 ± 0.02
WIPP-27	0.94	1.05 ± 0.02
WIPP-28	0.94	1.01 ± 0.04
WIPP-29	0.70	0.90 ± 0.02
	0.68	0.96 ± 0.04
	0.66	0.96 ± 0.04
WIPP-30	0.80	1.66 ± 0.04
	0.74	1.68 ± 0.07
	0.70	1.76 ± 0.10

1. Where the standard deviation ("±") is explicitly tabulated, values are means of duplicate analyses of different sample aliquots. Otherwise, typical relative standard deviation in [U] is about ± 4%, as tabulated for H5B.

4.1.1 Evolution of Uranium Concentration and A.R.

A survey of the range of uranium concentrations and A.R.s in nature has been conducted by Osmond and Cowart (1976). For surface waters, they found that total uranium concentration varied over 5 orders of magnitude, but that A.R.s are typically in the range 1-2, very close to secular equilibrium[1] (A.R. = 1). The range of [U] was similar for groundwaters, but A.R.s could be as high as 12, particularly when the [U] was below 0.1 μg/L (approximately equivalent to 0.1 parts-per-billion, or ppb). Extreme departures from uranium-isotope equilibrium (A.R. = 1), indicated by high A.R.s and associated with low [U], are particularly relevant in the Rustler Formation, since Culebra groundwaters have A.R.s as high as 11.6 and [U] values as low as 0.1 ppb.

Phenomenological models for evolving uranium systematics in groundwaters have been described in general terms by Osmond and Cowart (1976), were specifically applied to the Lincolnshire limestone by Andrews and Kay (1982), and are illustrated schematically in Figure 1. Water entering the local groundwater system moves through the oxidized recharge zone. Dissolution of uranium from the surrounding rock takes place congruently, increasing the [U] in solution with no uranium-isotope fractionation, such that the A.R. in the solution remains relatively constant near unity, which is the expected A.R. in the rock. Congruent dissolution may proceed until saturation in dominant aqueous uranium species is reached. We call the portion of an aquifer in which these conditions prevail Zone I in Figure 1. At some depth or distance along the flow path, the oxidizing agents in the recharge zone are expended, and uranium is precipitated in response to a lowering oxidation potential. This precipitation is assumed to take place without isotopic fractionation, so that the precipitation changes the A.R. in neither the precipitate nor the solution; only the total U in solution decreases. The zone in which this takes place is called the redox barrier, but may be a relatively dispersed zone in the aquifer rather than a discrete boundary. This zone is commonly the host for uranium ore deposits.

Next, as long as reducing conditions prevail in the aquifer, the [U] will remain at a relatively uniform low level, but the A.R. will generally increase in the solution. The mechanism for this entails the α-decay of ^{238}U in rock, giving ^{234}Th. The thorium nucleus recoils somewhat, causing local damage to the crystal lattice, and making the daughter thorium somewhat more leachable than the parent ^{238}U by solutions that contact the rock surface. Only the daughter thorium within a near-surface layer, having the thickness of the recoil range of thorium, is leached. The ^{234}Th leached into solution decays with a half-life of 24 d to ^{234}Pa. The ^{234}Pa in turn decays with a half-life of 1 min to ^{234}U. Thus, the rate-determining step of the recoil-leach process is the initial decay of ^{238}U with a half-life of 4.5 $\times$ 10^9 a (years), producing the leach-susceptible ^{234}Th. The recoil energy, according to

1. Secular equilibrium is achieved when the rate of decay of parent nuclei equals that of the daughter nuclei, and the half-life of the parent is much longer than that of the daughter, such that the change in number of parent nuclei is negligible during several half-lives of the daughter (cf. Friedlander et al., 1966). Hence, when the activities of ^{234}U and ^{238}U are equal, A.R. = 1.

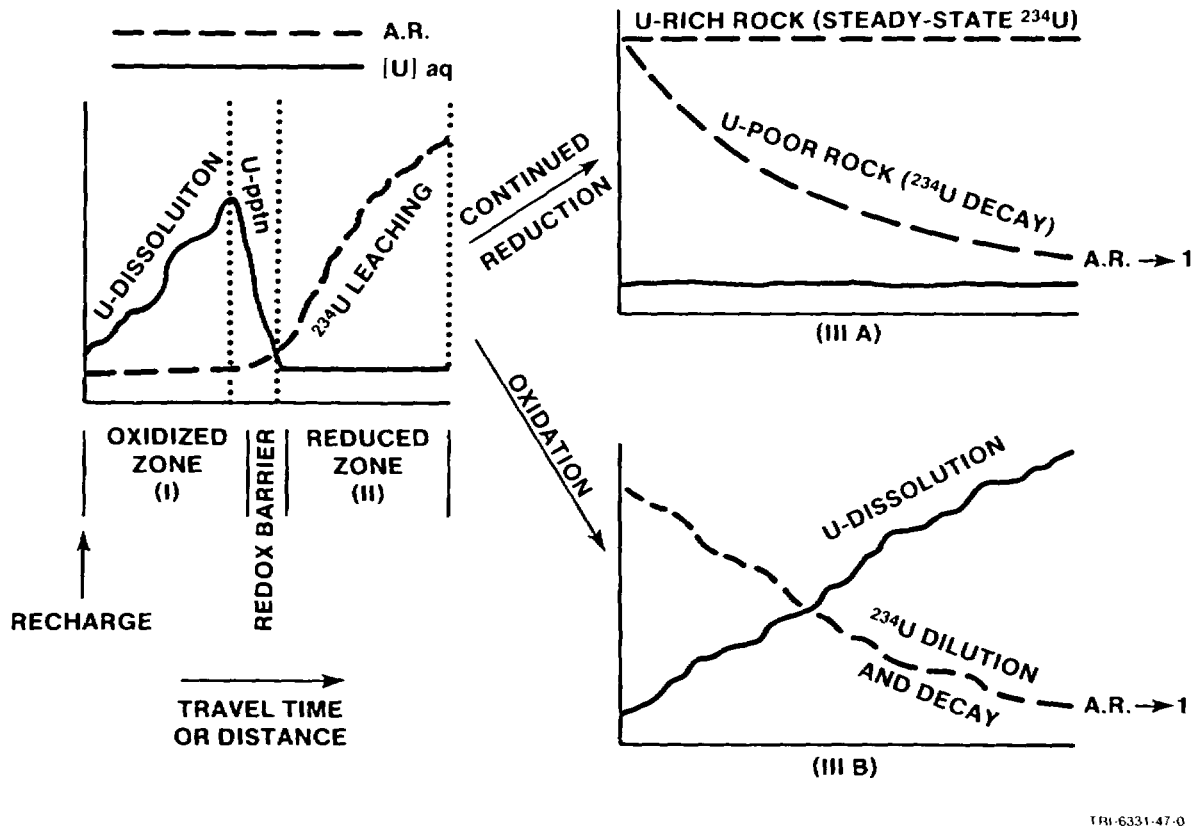

Figure 1. Schematic diagram of evolutionary paths for uranium concentrations and $^{234}U/^{238}U$ activity ratios in groundwaters. In the oxidizing recharge zone (I), uranium is congruently dissolved from rock without isotopic fractionation. When the redox barrier is reached, uranium is congruently precipitated. In the reducing zone (II), the $^{234}U/^{238}U$ A.R. increases due to preferential leaching of ^{234}Th, which has undergone recoil during the α-decay of its parent nucleus, ^{238}U. The ^{234}Th quickly decays to ^{238}U. In groundwater under reducing conditions, either the A.R. achieves a steady-state value, or else a diminished supply of leachable ^{234}Th allows the A.R. to decrease by preferential decay of ^{234}U (IIIA). Resumption of congruent dissolution of uranium from rock with a low A.R. under oxidizing conditions decreases the groundwater A.R. value by dilution while increasing the total uranium concentration (IIIB).

many workers (cf. Osmond and Cowart, 1976), is sufficient to oxidize the (IV) ion to the (VI) state. This is the only process of uranium-isotope fractionation that leads to a preferential increase in aqueous ^{234}U relative to that of ^{238}U and hence to an increase in A.R. in the solution. In Figure 1 we call the portion of the aquifer in which the aqueous A.R. increases by recoil-leach Zone II. A.R. increases mostly under the influence of reducing conditions, which probably accounts for the occurrence of high A.R. with low [U]. The A.R. trend in Zone II normally asymptotically approaches some maximum steady-state value governed by the ratio of the activity of leachable ^{234}Th in rock to that of ^{238}U in water (see Equation (9)). We have not shown the A.R. trend for Zone II as an idealized asymptote-approaching smooth curve, because in practice the moving groundwater interacting downdip with rocks of varying [U] and oxidation potential may not result in either a smooth variation of A.R. with distance or time or a fixed position for the "steady state" line.

Next, after the time-dependent buildup of A.R. values in solution, the solution may remain under reducing conditions in the aquifer (whether moving or stagnated) or may again encounter oxidizing conditions. Under continued reducing conditions, as in Zone IIIA in Figure 1, the [U] will remain at its relatively low value, limited by the solubility of uranium species. If the U-content of the rock remains constant, as would for a time be the case in a stagnant system like the brine reservoirs (cf. Barr et al., 1979; Lambert and Carter, 1984), a steady-state A.R. value is attained, representing a balance between the production and decay rates of aqueous ^{234}U. If there is less U in the rock than in that in which the A.R. evolved in Zone II, the decay rate will exceed the production rate, and the aqueous A.R. will decrease to a new A.R. value consistent with a new steady state. In very old systems where much of the uranium has already been leached from the near-surface rock layer (estimated to be about 0.03 μm thick, according to Andrews and Kay, 1982), the aqueous A.R. value will approach unity. The steady-state case is illustrated for Zone IIIA in Figure 1 by the horizontal A.R. trend, which could be considered a culmination of the processes in Zone II; hence, under constant physicochemical conditions and constant U-concentration in rock, the steady-state (horizontal) A.R. trend in Zone IIIA is simply the asymptotic limit of the increasing-A.R. trend in Zone II. The diminished ^{234}U recoil-leach rate from a rock poorer in uranium results in the decreasing trend of aqueous A.R. in Zone IIIA, also depicted in Figure 1.

Finally a high-A.R. solution may move into an oxidizing zone, regardless of its previous history. Oxidizing conditions allowing additional congruent dissolution of uranium from rock (i.e., without isotopic fractionation) would not only increase the [U], but would also decrease the aqueous A.R. by the addition of rock-derived uranium (containing both ^{234}U and ^{238}U) with an A.R. near unity. The portion of the aquifer that harbors this simultaneous increase in [U] and decrease in A.R. is depicted as Zone IIIB in Figure 1. Two different processes contribute to decreases in A.R. here: the faster radioactive decay of ^{234}U relative to that of ^{238}U, and dilution of excess aqueous ^{234}U by rock-derived uranium with A.R. = 1.

At different times in geologic history, the same part of an aquifer may be dominated by physicochemical characteristics of different zones. For example, rock that used to be

dominated by the reducing conditions of Zone II may later be exhumed by erosion, and become dominated by the physicochemical processes characteristic of oxidizing conditions in Zone I. Such a transition over geologic time scales can give rise to transients in a hydrologic system, reflected in its dissolved constituents such as uranium, just as transients have been observed in the stable-isotope ratios of the water molecules themselves (Lambert and Harvey, 1987).

4.1.2 Age Calculations

Time-dependent changes in A.R., due dominantly to radioactive decay, occur in Zones II and IIIA. Since it is not possible to use changes in A.R. as indicators of travel or residence time in those zones of oxidation (I and IIIB) where congruent dissolution dominates changes in aqueous A.R., the models for time calculations performed herein will be based on the processes we infer to be dominant in Zones II and IIIA. In Zones I and IIIB, however, uranium concentration and uranium-isotope ratios in groundwaters can be used to show relative trends; systematically and monotonically changing ratios as a function of distance in a particular direction can be used to infer a flow path, thus qualitatively yielding flow directions in the groundwater system independent of those inferred from modeling potentiometry and permeability alone.

4.1.2.1 Zone IIIA model.

By a special case of the $^{234}U/^{238}U$ disequilibrium dating model (Barr et al., 1979; Lambert and Carter, 1984), uranium travel time between points having different A.R.s can be calculated. In this model it is assumed that A.R. decreases in the direction of flow, and that exchange of uranium with rock along the flow path or at the sampling point is negligible. The special case also assumes no change in the $^{234}U/^{238}U$ ratio along the flow path due to either subsurface mixing of different groundwaters or congruent dissolution of uranium from rock. In principle this model applies to the decreasing-A.R. trend in Zone IIIA of Figure 1. It has been shown by Lambert and Carter (1984) that neglecting rock-water interactions under the conditions prevalent in Zone IIIA (confined, reducing groundwater, whether moving or stagnant) yields a minimum age, even if the recoil-leach mechanism is still somewhat active in this zone. Recoil-leaching elevates the A.R., making fluids appear spuriously young according to this model. However, adding uranium of a constant isotopic composition (by mixing, rock dissolution, or whatever) may make the calculated age spuriously old; Lambert and Carter (1984) showed how certain conditions could lead to a calculation of ages that were spuriously young (i.e., minimum ages). We shall show that spuriously old apparent groundwater ages derived from this no-leach, decay-only model occur dominantly in the higher-permeability active dissolution zone of Nash Draw rather than at the WIPP site. We shall also discuss the implications of this for calculating travel times semi-independently of physical (i.e., potentiometry/permeability) measurements alone.

Decreases in A.R. resulting from congruent dissolution of rock uranium can be superimposed on the decreases in A.R. due to radioactive decay alone. If water has acquired a

high A.R. value in Zone II or IIIA and then has moved into a Zone IIIB-like environment, calculations resulting from the use of the Zone IIIA model in Zone IIIB will yield maximum travel or isolation times. Thus, the Zone IIIA model is the simplest of our models, requiring only the measured aqueous A.R. and an inferred initial value for A.R.; it is limited in that the user must be certain that Zone IIIA conditions prevail, rather than those of Zone I or IIIB. This distinction requires a relatively constant low [U] in the groundwater for both observed and inferred initial values of A.R.. A marked increase in total U accompanying the decrease in A.R., normally attributed entirely to radioactive decay, may indicate that the decrease in A.R. is not entirely so attributable, but may be due at least in part to congruent dissolution.

4.1.2.2 Zone II model.

Refinements to Zone IIIA model-age calculations can in principle be made by taking into account exchange of ^{234}U and ^{238}U between rocks and water. Virtually all rocks and water (and, unfortunately, wellbore apparatus) contain some uranium (even if at the parts-per-billion or -trillion level), and the time required to achieve an observed $^{234}U/^{238}U$ activity ratio (which varies with time according to two different radioactive decay pathways) can in principle be determined, given some initial A.R.. The pathways are the faster radioactive decay of ^{234}U relative to ^{238}U, resulting in a decreasing A.R., and buildup of A.R. by recoil-leaching, yielding preferential buildup of ^{234}U activity in solution under suitable conditions and an A.R. that increases asymptotically toward a steady-state value governed by total aqueous U and rock U concentrations. The first pathway is the basis for the age calculation using the Zone IIIA model. The second can be used to refine the Zone IIIA model age, but requires additional detailed knowledge of the system that has fostered the growth of A.R. values. By itself, the second pathway to increasing A.R. values forms the basis of the Zone II model, based on the growth of A.R. towards steady-state. The Zone II model incorporates loss of ^{234}U by radioactive decay, as well as production of ^{234}U from the decay of ^{238}U and subsequent recoil-leaching. Even if the A.R.-buildup clock is "reset" by congruent dissolution of rock uranium, for example, calculations using the Zone II model will give minimum ages. Unfortunately, the Zone II model requires more detailed knowledge and/or inferences about the initial state of the system, particularly the initial uranium concentration in both rock and coexisting water. If there are large uncertainties in these initial values, the uncertainty in minimum travel or isolation times calculated from the Zone II model will also be large.

4.2 Rustler Uranium Concentrations and A.R. Values

The values of total dissolved uranium and $^{234}U/^{238}U$ A.R.s for Culebra waters are plotted near their corresponding well locations in Figures 2 and 3, respectively. Although control on contouring in these and following figures is not particularly tight, there is a monotonic increase in total uranium from east to west, and a monotonic decrease in A.R. in the same general direction. When the respective values are contoured, the highest A.R. values appear to emanate from H-5 and decrease toward nearby data points to the northwest,

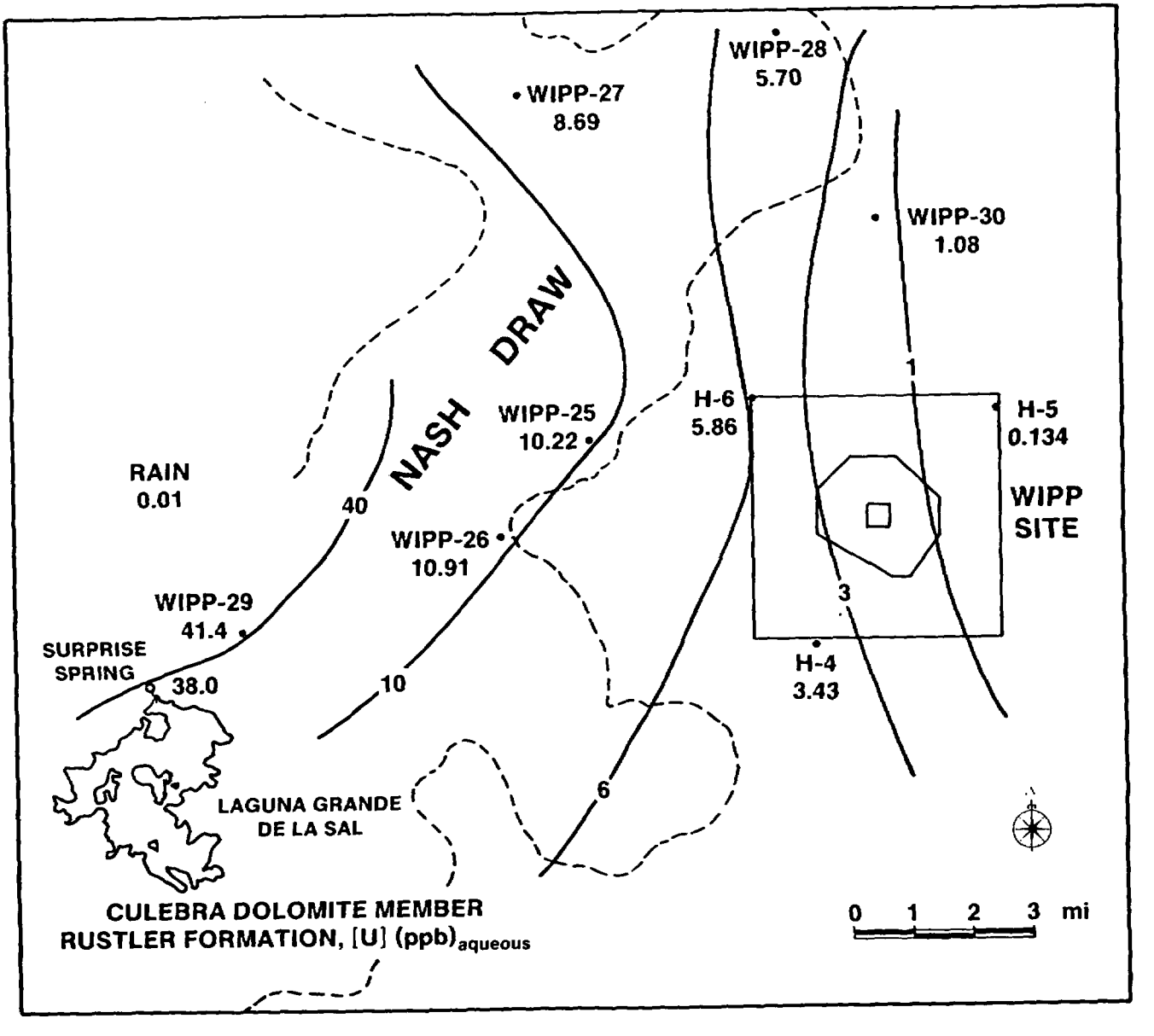

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Figure 2. Contour map of total uranium concentration in groundwater from the Culebra dolomite member of the Rustler Formation. Total-U in units of 10^{-9} g/g, or parts-per-billion (ppb) increases monotonically westward toward Nash Draw, generally along the flow path inferred from potentiometric levels.

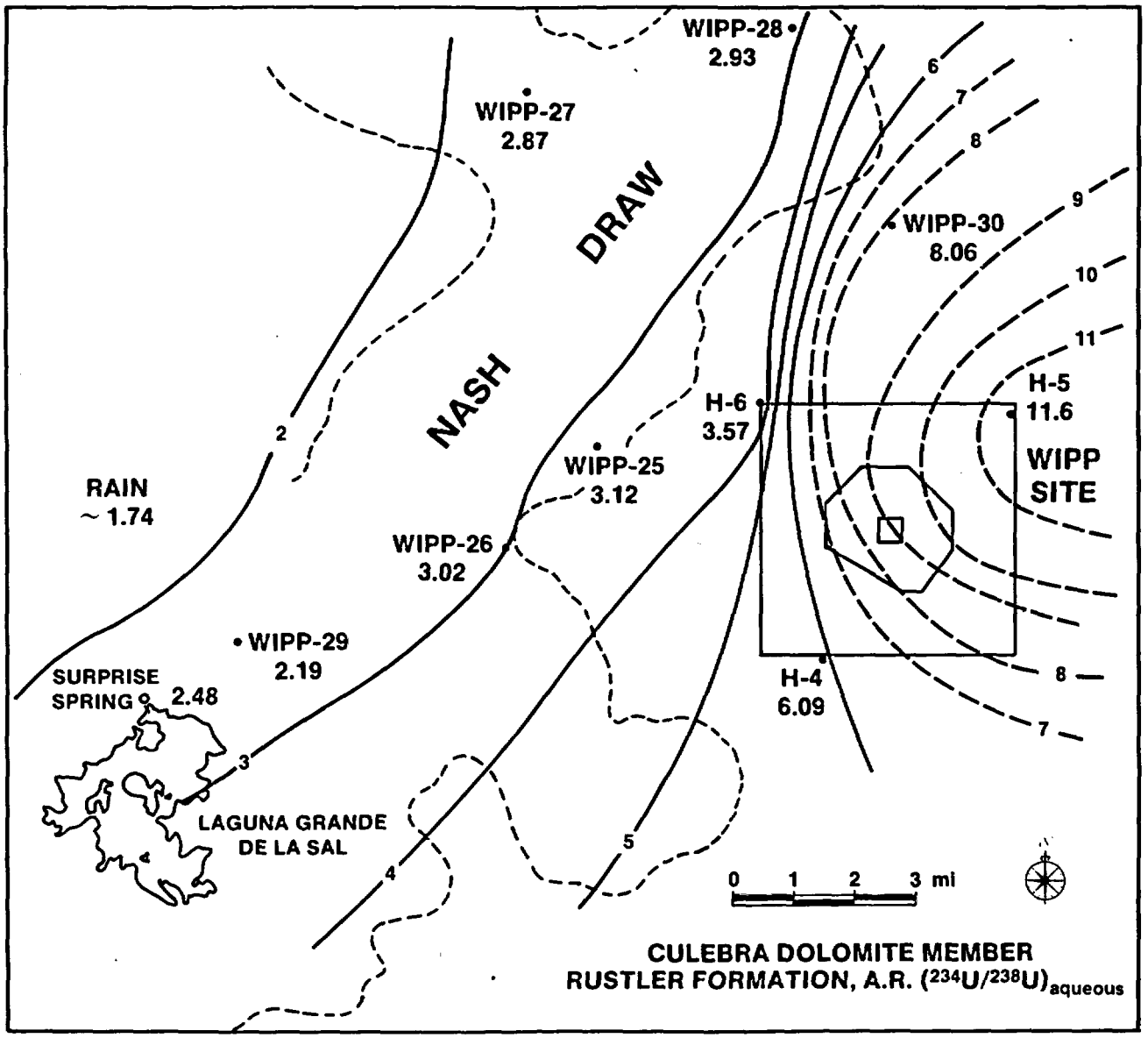

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Figure 3. Contour map of $^{234}U/^{238}U$ activity ratio (A.R.) in groundwater from the Culebra dolomite member of the Rustler Formation. A.R. decreases westward and somewhat southward toward Nash Draw, generally along the flow path inferred from potentiometric levels, from extremely high values (>6) near the WIPP site. This is inconsistent with zone II in Figure 1, but may be indicative of zone IIIB. Control on contouring east of the WIPP site is not stringent, due to the scarcity of wells suitable for sampling in the low-permeability region of the Culebra east of the WIPP site.

west, and southwest. The highest [U] values appear to emanate from the WIPP-29/Surprise Spring area and decrease toward adjacent data points. Note suggestion of a westward to southwestward component in increasing U and decreasing A.R. between H-5 and H-4. The contour patterns are generally consistent with the potentiometric contours in Figure 4 (Mercer, 1983). Thus, water moving down the potentiometric gradient over the WIPP site southward and westward toward the higher-permeability region of Nash Draw appears to be increasing in [U] and decreasing in A.R.. In comparison with Figure 1, this apparent flow pattern is consistent with the uranium systematics depicted for Zone IIIB, where oxidation and dissolution of uranium are taking place, resulting in an increasing aqueous U concentration and a decreasing A.R. Field measurements of platinum-electrode potential ("Eh") measurements reported by Lambert and Robinson (1984) and Robinson (1987) in Culebra water in Nash Draw and the western part of the WIPP site (e.g., H-4 and H-6) are significantly higher ("Eh" ≈ +0.1-0.2 V) than at H-5 ("Eh" ≈ 0.05 V). In Nash Draw permeability is higher and water occurs nearer to the surface. Thus, a westward increase in total U coupled with a decrease in A.R., while some crude measure of apparent oxidation potential increases, is consistent with Zone IIIB-type phenomena.

Since Lambert and Harvey (1987) and Lambert (1987) have shown that recharge is probably not taking place near H-5 under the present (observed) hydrologic conditions, in spite of the high potentiometric levels there, the origin of the high potentiometric levels and high A.R.s, in the eastern part of the WIPP site, are problematical under steady-state hydraulic conditions. According to the models for uranium behavior depicted in Figure 1, high A.R.s (Zone II) evolve **downgradient** from a recharge area (Zone I). Since modern flow is inferred from potentiometry (southward/westward) to be in directions opposed to those inferred from the direction of increasing A.R.s (eastward), a likely alternative is that the uranium-isotope systematics reflect a **transient** condition in the Culebra groundwater system at the WIPP site and in Nash Draw. We believe that the high A.R.s to the east accompanied by low [U] values originated in groundwater flowing down an eastward gradient that included the conditions of the "redox barrier" and Reduced Zone II in Figure 1. Since the southward/westward flow direction is now roughly reversed relative to the eastward direction required to produce high A.R.s and low [U] under the conditions of Zone II, we propose that the uranium patterns may be, like the stable-isotope ratios, relics of a former flow regime.

Another important observation about these data is that the high-U/low A.R. region around WIPP-29/Surprise Spring (hereafter called "southwestern Nash Draw," or SWND) is the only region in the study area where the Culebra is likely to receive significant amounts of modern surface-derived recharge, as shown by the stable-isotope and major solute arguments of Lambert and Harvey (1987). For comparison, the [U] and A.R. values of rain collected at nearby Carlsbad are also shown in Figures 2 and 3. Note that most of the uranium in Rustler groundwater appears to be acquired from the rock by dissolution, not introduced by the local rainfall.

A similar pattern of [U] and A.R. distributions is observed for groundwater from the Rustler/Salado contact (the "basal brine aquifer" of Robinson and Lang, 1938). The

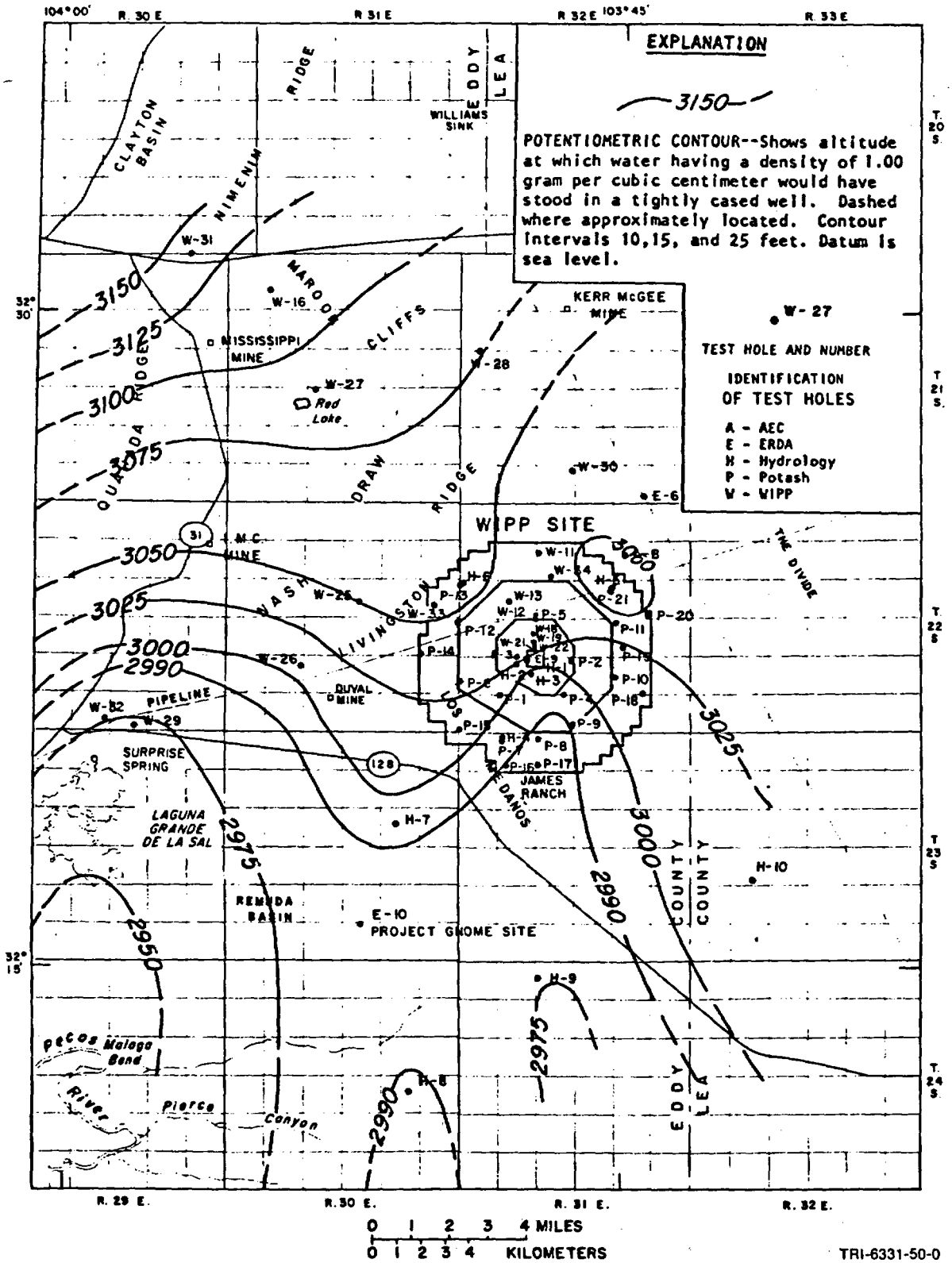

Figure 4. Adjusted potentiometric surface of the Culebra dolomite member of the Rustler Formation, as of 1982. From Mercer (1983). Area covered is the WIPP site and Nash Draw, similar to Figures 2 and 3.

contour maps are shown in Figures 5 and 6, respectively. The number of reliable control points is fewer, largely limited to the higher-permeability region of Nash Draw where the "basal brine aquifer" flow system is better developed. At the WIPP site, it is very difficult to obtain a minimally contaminated sample of water from the Rustler/Salado contact, given the eastward-decreasing permeability. Nevertheless, relationships between potentiometrically indicated flow patterns and U and A.R. trends indicate that increases in A.R. values toward the east developed in a system that at one time flowed dominantly toward the east, similar to the case of the Culebra. As shown by Mercer (1983), Lambert (1987), and Lambert and Harvey (1987), there appears to be **little** vertical homogenization of geochemical parameters by mixing, and therefore **minimal** hydraulic connection between the Culebra and the Rustler/Salado contact in the study area. Significant differences in major, minor, trace, and isotopic concentrations between the Culebra and Rustler/Salado are preserved even at WIPP-29 in SWND, where increases in Rustler permeability due to partial evaporite dissolution, collapse, and fracturing have been most profound. Included in Figures 5 and 6 are the data from the seep in the Duval Nash Draw potash mine. Although this occurrence is in the Salado and not the Rustler, its association with evaporite rock has resulted in a low [U] (0.03×10^{-9} g/g) and a somewhat elevated A.R. value (~3). These values are consistent with the low oxidation potential expected for evaporites at the Rustler/Salado contact and in the middle Salado Formation, if their contained groundwaters are governed by the conditions expected in Zone II. Overall, [U] values at the Rustler/Salado contact, even in the relatively high-permeability region of Nash Draw, are lower than in the overlying Culebra, probably reflecting the more reducing conditions (Pt-electrode "Eh" ≈ -0.4 to +0.09 V) described at the Rustler/Salado contact by Lambert and Robinson (1984), based partly on the occurrence of odoriferous reduced species.

If observed variations in A.R. are due to radioactive processes alone, one can quantitatively interpret such variations in A.R. in one of two ways (cf. Barr et al., 1979):

(1) A.R. increases with time during rock-water interactions that preferentially leach ^{234}U (Zone II), or

(2) A.R. decreases with time during the radioactive decay of ^{234}U, which is much faster than the decay of ^{238}U (Zone IIIA, U-poor rock).

Andrews and Kay (1982) showed that in some carbonate systems, once an A.R. value is established it can be difficult to carry out the preferential leaching that leads to A.R. buildup. Barr et al. (1979) showed that if one interprets the decrease in A.R. as an aging process, times can easily be calculated for such changes. Lambert and Carter (1984) showed that if one neglects any buildup of A.R. by the leaching mechanism, one obtains a minimum age from the time required for decreases in A.R. by natural decay alone; they also showed that an A.R. value will tend to level off (either by buildup or decay) after about 1 to 2 Ma in an otherwise undisturbed geological system. Unfortunately, this is also the age range in which it is difficult for the analytical method to detect statistically significant differences in A.R. values.

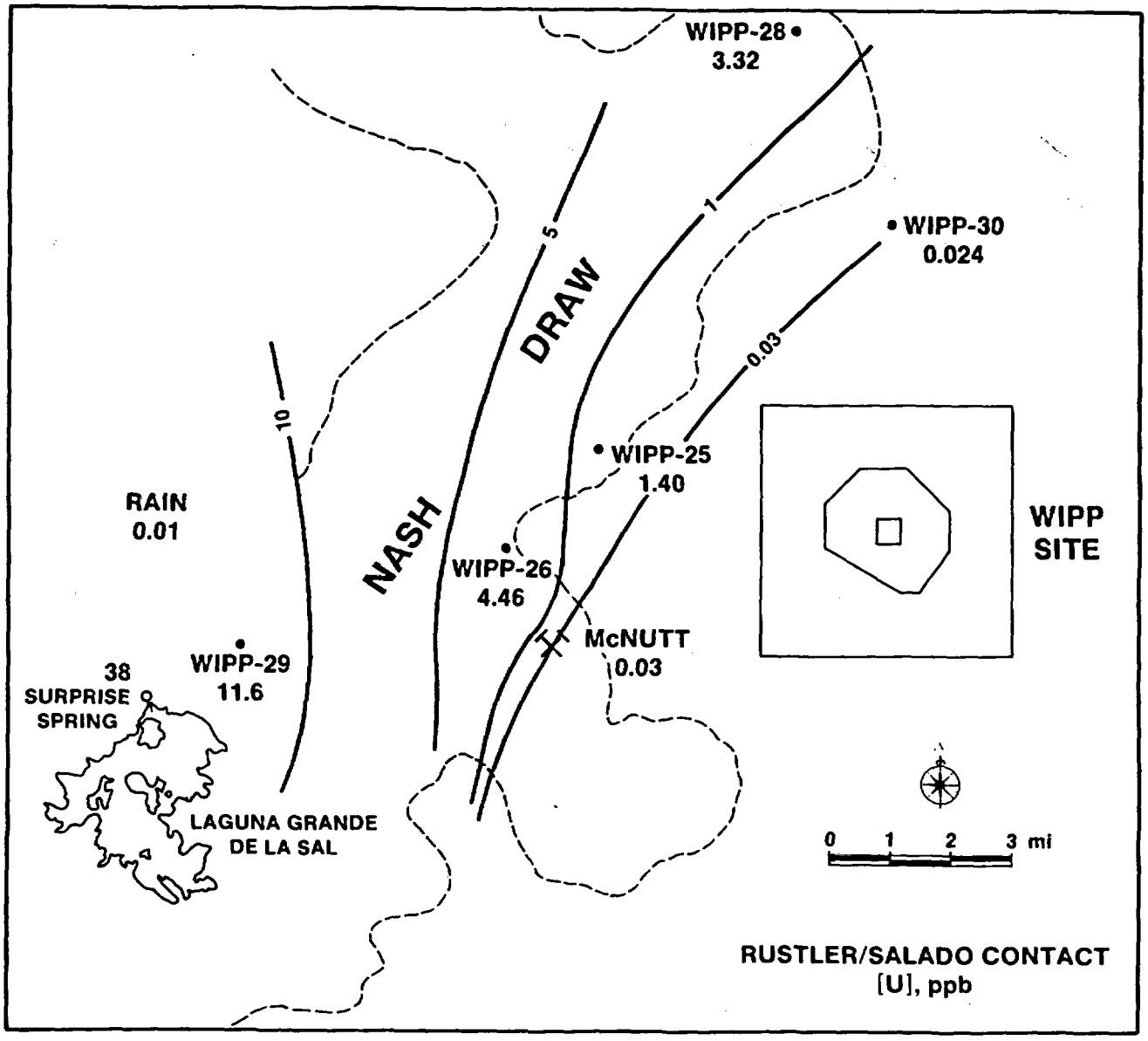

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Figure 5. Contour map of total uranium concentration in groundwater from the zone near the Rustler/Salado contact. Total-U, in units of 10^{-9} g/g, or parts-per-billion (ppb) shows patterns similar to those in the Culebra member (Figure 2), although the variation is significantly larger. These data include the smallest U-concentration found so far in meteoric groundwaters of southeastern New Mexico (0.024 x 10^{-9} g/g) at borehole WIPP-30.

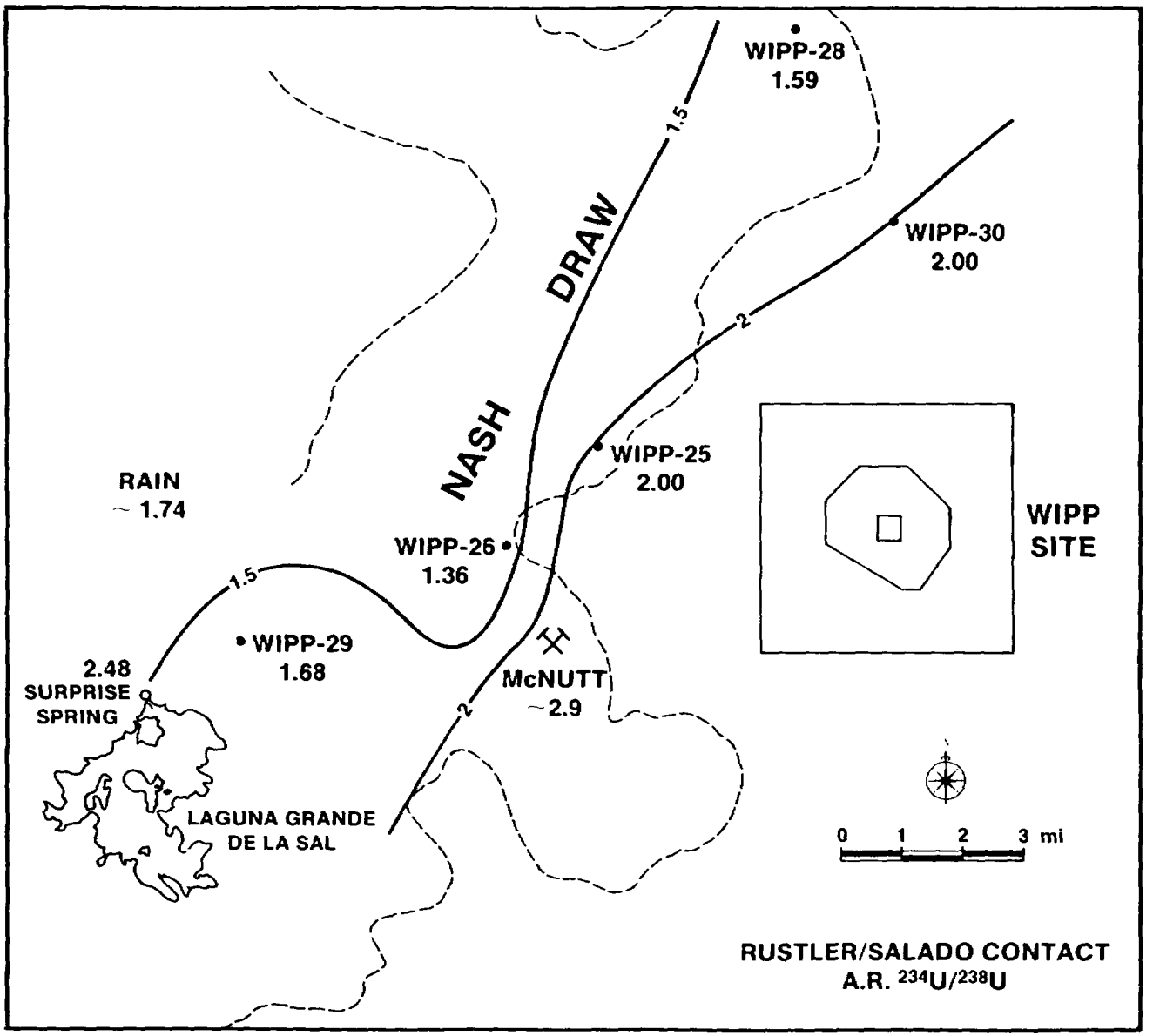

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Figure 6. Contour map of $^{234}U/^{238}U$ A.R. in groundwater from the Rustler/Salado contact. The westward-decreasing pattern of A.R. values is similar to that in the Culebra member (Figure 3), although the variation is smaller.

The Culebra aqueous uranium contours suggest (1) that the water is getting older (or leaching ^{234}U-enriched uranium from host rock) from west to east, if the A.R.-buildup (Zone II) mechanism dominates the isotopic systematics, or (2) that the water is getting older from east to west, if the radioactive-decay (Zone IIIA) mechanism dominates, or (3) that the water is congruently dissolving low-A.R. uranium from host rock (Zone IIIB). The present potentiometric surface for the Culebra indicates that water is apparently flowing from the WIPP site generally to the southwest. Furthermore, the uranium contours for the Culebra resemble somewhat the potentiometric contours for the Magenta (Figure 7). We suggest, however, that different types of coexisting values (i.e., high potentiometric level versus high A.R.) probably were established at different times, one being a relic of former hydrologic conditions.

4.3 Travel Time Calculation: ^{234}U Decay (Zone IIIA Model)

In an isotropic medium, flow paths (or, more precisely, general flow directions) can be inferred on the basis of vectors drawn perpendicular to potentiometric contours (cf. Mercer, 1983). One can infer generalizations about the relative permeability distributions (and in turn travel times) based on the separation of contour lines. However, travel time as defined by Lambert (1987) must be estimated along a specific flow path (which may be impossible to identify uniquely) and results from taking the difference in relative "ages" for two discrete points along the flow path.

Flow paths and resulting estimated travels times inferred from geochemical methods need not be unique. In general, subsurface migration of water through different rock types changes the major solute assemblage (and, perhaps, various isotopic ratios) in the aqueous phase, during rock/water interaction along the flow path. The relationship (i.e., "connectedness," albeit small) between various bodies of groundwater, based on certain geochemical parameters, may be indeterminate. This is particularly true if available data are consistent with more than one mechanism that can reasonably account for the geochemical evolution of one groundwater from another one upgradient. For example, many nearby occurrences of groundwater could be inferred sources for any local occurrence of groundwater in the Rustler (i.e., there can be a multitude of flow paths). The only defensible approach to calculating travel times with a groundwater system is to consider each occurrence to represent a local source, and then compare the concentration of time-dependent (i.e., radioactive) trace species in the groundwater with the abundance of the same species at various points along the inferred flow path downgradient.

If we take the A.R. variations simply as radioactive decay phenomena, neglecting dilution and dissolution, and try to calculate apparent "ages" under the geochemical conditions in Zone IIIA (Figure 1), we must use both an observed value of A.R. and an inferred initial value of A.R. As outlined above, we shall assume for the moment that groundwater flow in the mapped part of the Culebra in Figures 2 and 3 is uniformly connected. Thus, between every pair of adjacent A.R. values, we obtain an apparent uranium travel time, based on the equation:

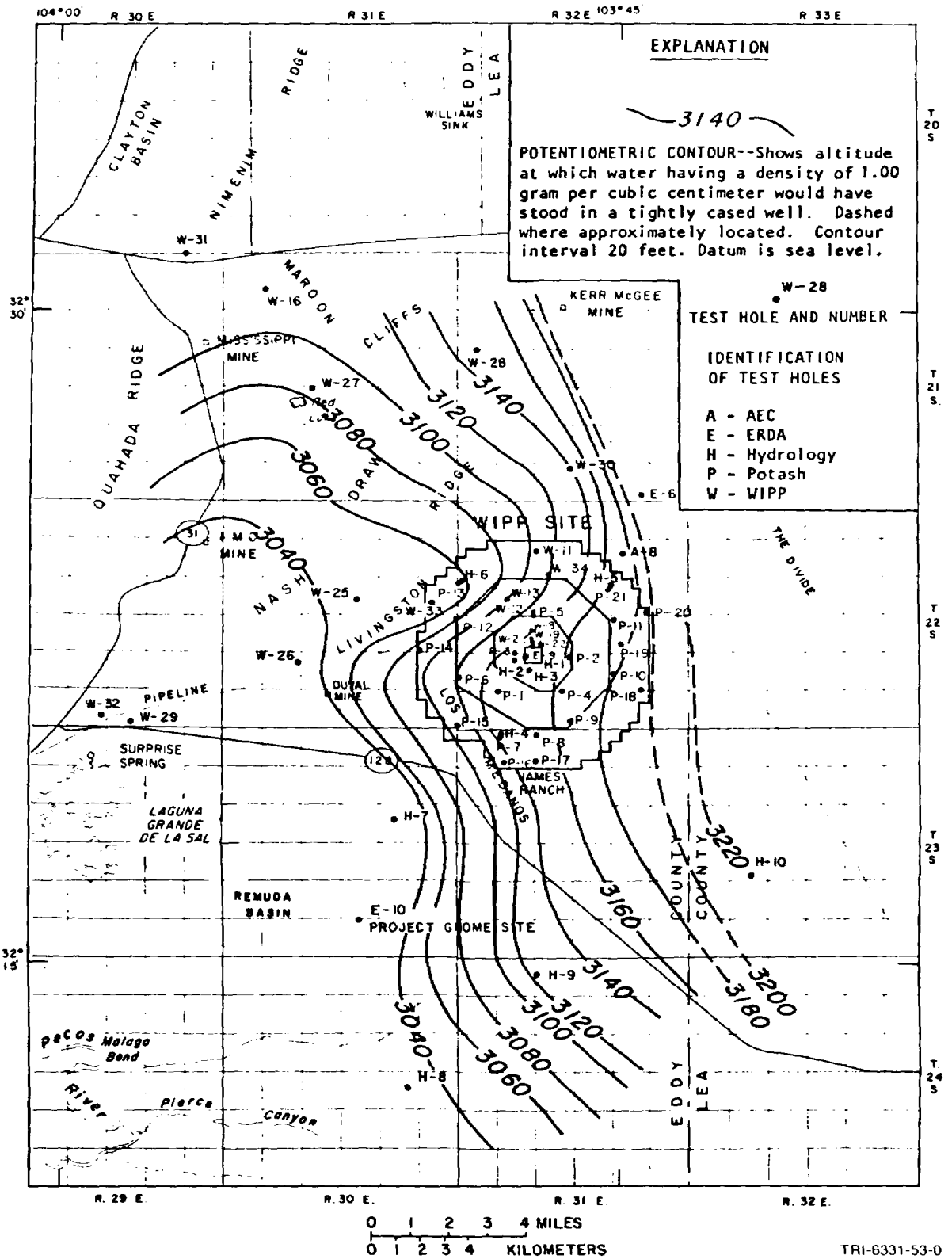

Figure 7. Adjusted potentiometric surface of the Magenta dolomite member of the Rustler Formation, as of 1982. From Mercer (1983). Area covered is the WIPP site and Nash Draw, similar to Figure 4. These westward-decreasing contours and those of westward-decreasing A.R.'s in Culebra groundwaters (Figure 3) mimic one another.

$$t = \frac{\ln \frac{A.R.(b) - 1}{A.R.(0) - 1}}{-2.806} \qquad (1)$$

where A.R.(b) is the measured (present) A.R., A.R.(0) is the inferred initial A.R., and t is the time required for the change by radioactive decay, in Ma (see Barr et al., 1979, for the derivation of Equation (1)). A sample curve for A.R. as a function of decay time, with a specific initial A.R. value, is shown in Figure 8.

The apparent uranium travel times calculated by Equation (1) from A.R. values at individual sampling points in the Culebra are given in Figure 9. Each vector in Figure 9 indicates the direction of decreasing A.R. between any two adjacent points, not necessarily an actual flow direction. Note that model uranium travel times are on the order of several tens to several hundreds of Ka. Lambert (1987) showed that the radiocarbon data, when the effects of contamination were partially mitigated by extrapolation, probably indicate times of isolation from the atmosphere in excess of 12,000 and perhaps 20,000 to 30,000 a. Note especially that the apparent uranium travel times, based on uranium decay, are longer over the WIPP site, where the permeability tends to be smaller (near H-5 and WIPP-30), than in Nash Draw where the permeability tends to be greater. This is particularly evident from the apparent uranium velocities (expressed in miles per million years, mi/Ma, and shown in square brackets in Figure 9). To the east, apparent velocities are all ~ 10 to 20 mi/Ma. In the west, apparent velocities are higher, typically on the order of 100 mi/Ma, and as high as 400 mi/Ma. Of course, these apparent uranium travel times and velocities are averages between the pairs of sampling points. If additional reliable sampling points were available between these data points, the apparent uranium travel times and velocities might prove not to be uniform over the distance of several miles separating each pair. Nevertheless, the distribution of the apparent uranium travel times seems to be divided east versus west, and generally corresponds to the permeability contrast.

There is, however, a major difficulty with closed-system travel-time calculations such as this. In particular, the Zone-IIIA model neglects the possible effects of non-radioactive processes, such as mixing and dilution, on A.R. values. These problems are discussed in the next section.

4.4 Mixing and Dilution (Zone IIIB)

One might argue that the westward decrease in A.R. is due to admixing of uranium of lower A.R. value to the west, since the total U increases in that direction. In fact, we consider here that either such admixing has actually taken place, or that some parameter is allowing a westward-increasing dissolution of uranium from rock (Section 4.6). If the first possibility is true, then the preservation of high A.R.s (>4) in the east requires that the source of admixed low-A.R. water be from the west (not the east or northeast as inferred from the modern potentiometric measurements). The greater degree of admixture in the west than in the east is consistent with the modern westward-increasing permeability distribution, because modern admixing (e.g., recharge) is more difficult in an area to the east, whose permeability is lower than anywhere else (cf. Mercer, 1983) if flow is restricted

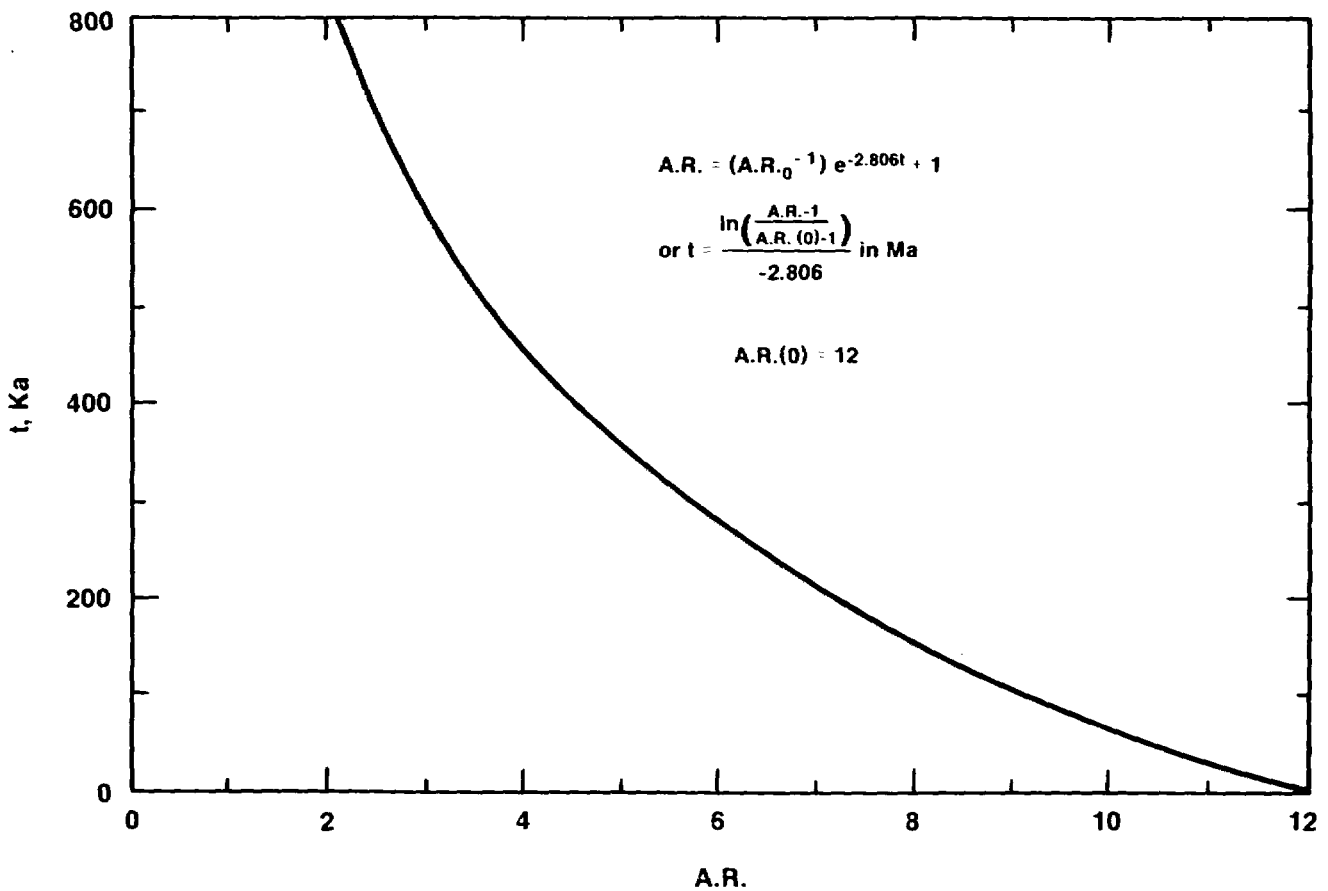

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Figure 8. Typical curve showing A.R. decay as a function of time. The only assumptions necessary to calculate minimum time required to yield a given A.R. value under this model are (1) that the initial A.R. is known (12 in this example), (2) that the only process actively decreasing the A.R. value is radioactive decay, and (3) the initial A.R. is greater than the observed A.R.

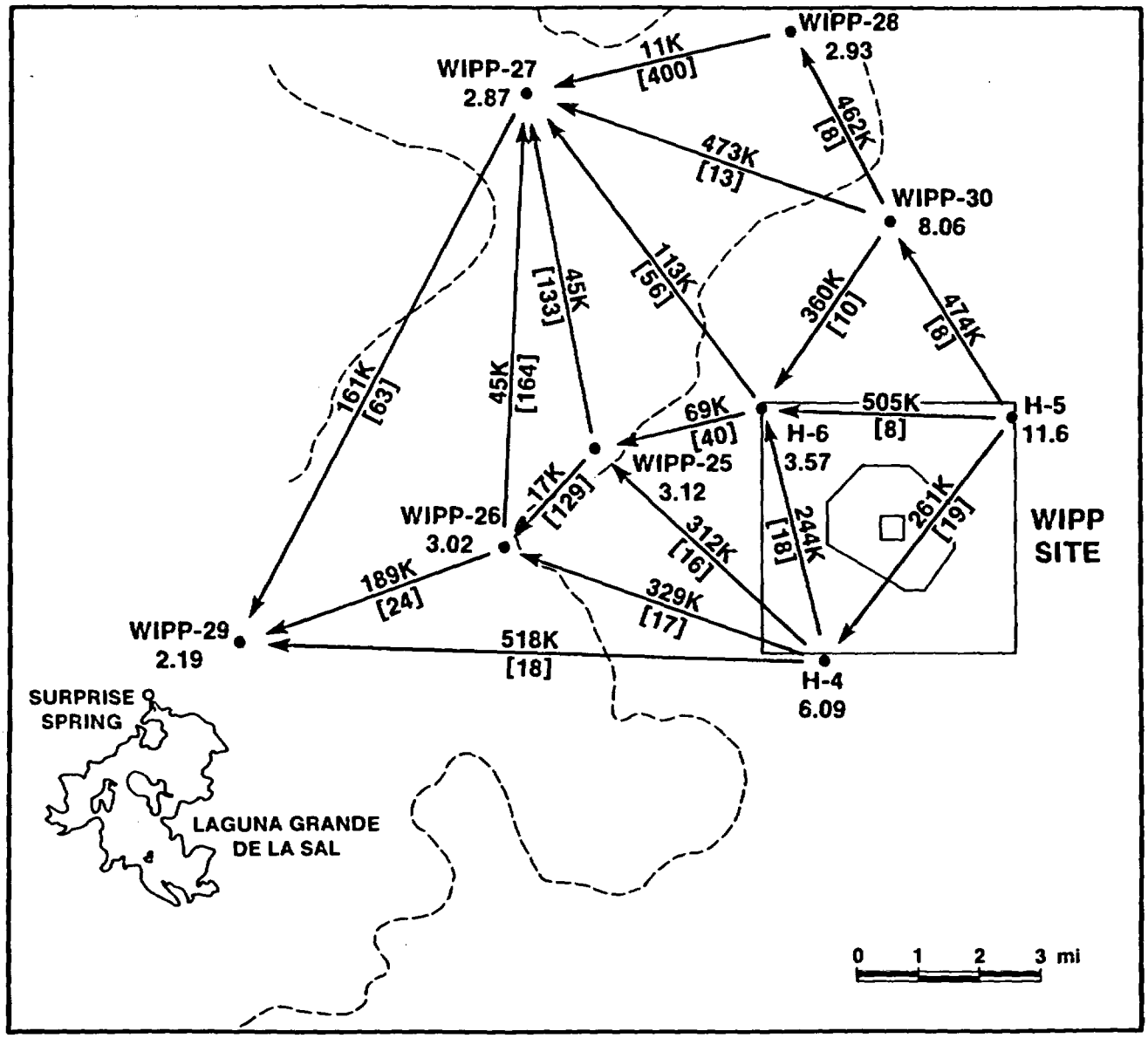

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Figure 9. Apparent travel times calculated between points of different A.R. values in the Culebra groundwater. Numbers followed by "K" along each hypothetical path between points are apparent travel times, in thousands of years, calculated from the parenthetical A.R. values at the endpoints, using the model depicted in Figure 8. Values in square brackets are calculated flow rates between points in miles per million years. Vectors indicate the direction of decreasing A.R. between any two adjacent points, not necessarily actual flow directions.

entirely within the Culebra. However, the second, more likely possibility, implies that as the uranium-poor water has moved southward/westward toward Nash Draw under the present potentiometric distribution, dissolution of uranium out of the rock (under more oxidizing conditions than at H5) has added to the total U in solution, adding uranium having an A.R. value closer to the secular equilibrium value of unity.

In order to test the mixing hypothesis, we plotted A.R. against total U in Figure 10. The theoretical relationship between A.R. and U concentration for simple binary mixing is

$$A.R._m = \frac{C_1C_2(A.R._1 - A.R._2)}{C_m(C_2 - C_1)} + \frac{C_2A.R._2 - C_1A.R._1}{C_2 - C_1} \qquad (2)$$

where C is the aqueous uranium concentration, and subscripts m, 1, and 2 refer to the mixture and mixing endmembers 1 and 2, respectively.

The Nash-Draw-type Culebra environment (which we consider here to include H-6, WIPP-25, -26, -27, -28, and -29) has A.R. values less than 5. We tried to fit a simple mixing line to the distribution of points, using endmembers with A.R. = 11.6, [U] = 0.134 ppb (taken as representing the eastern part of the WIPP site at H-5) and A.R. = 2.19, [U] = 41.4 ppb (more characteristic of evaporite-dissolution brines in SWND at WIPP-29). All of the points with intermediate [U] and A.R. values lie significantly above the resulting theoretical mixing line. Thus, the [U] and A.R. distributions throughout the Culebra are not products of simple binary mixing, but contain greater [U] than can result from simple binary mixing of fluid reservoirs. The A.R./[U] relationships, however, suggest open system conditions, incompletely communicating reservoirs within the Culebra, or three-component (rather than two-component) mixing. A westward-increasing trend in oxidation state for the Culebra is not consistent with the first alternative; potentiometric and permeability relationships are not consistent with the second. The likelihood of the third (i.e., uranium dissolving from rock) will be discussed in Section 4.6.

The best mathematical fit to all the Culebra points involving simple functions was the equation:

$$A.R. = 7.67 - 1.84 \ln [U] \qquad (3)$$

with a correlation coefficient (r) of 0.96. This indicates some relationship between A.R. and [U], but it is not one of linear mixing over the entire range of total U and A.R.. If this relationship has physical significance, it implies that A.R. varies linearly with the relative (percentage) change in [U]; thus, at higher values of [U], it requires a greater absolute change in [U] to yield the same change in A.R. that would result at low values of [U]. The resulting plot, together with the line representing Equation (3), is in Figure 11.

An obvious concern in the foregoing discussion is the admixture of uranium to solution from dissolving or leaching rock and its effect on the A.R. value, which in turn was used to

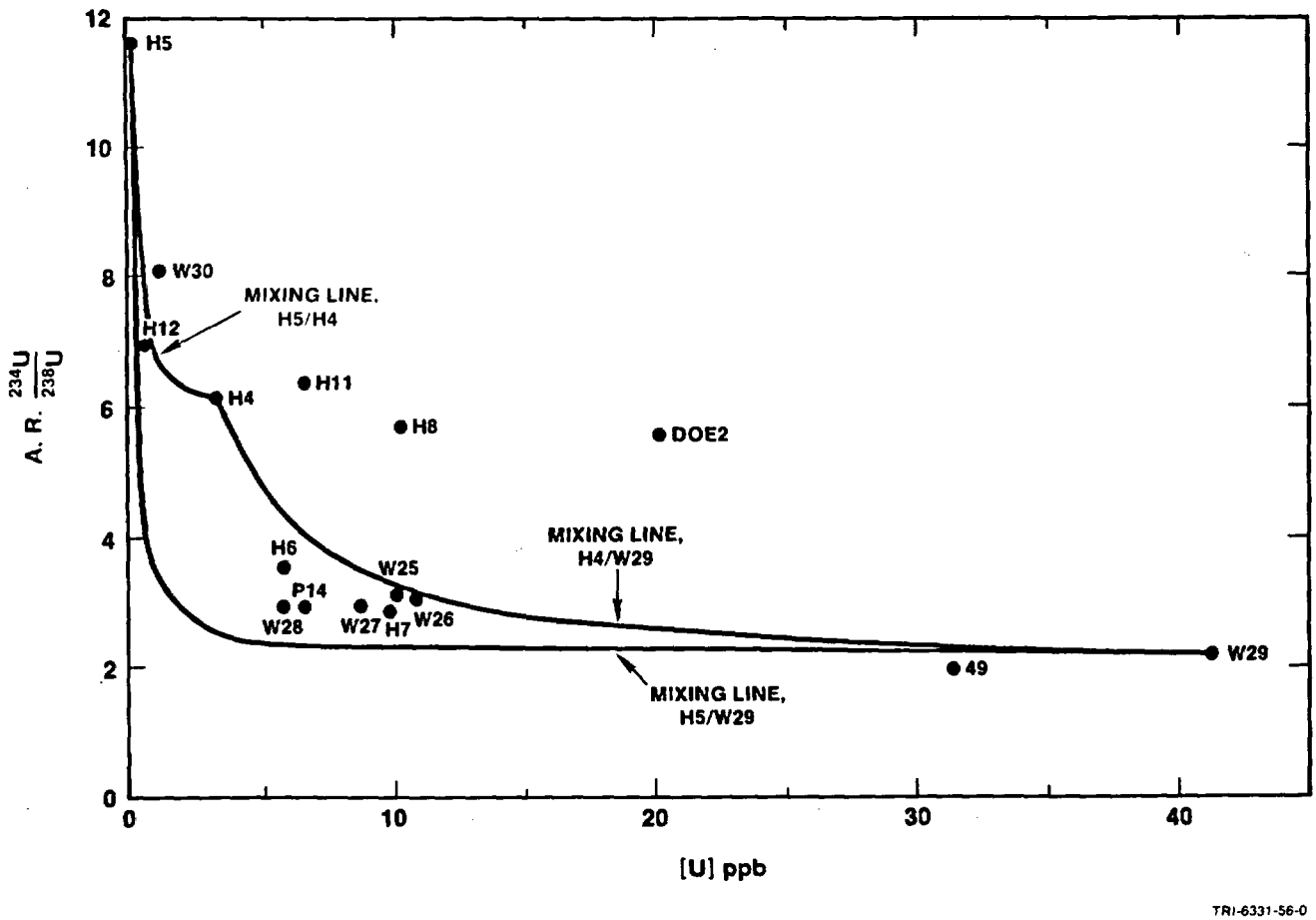

Figure 10. Linear plot of A.R. versus total U for Culebra groundwaters. A single simple binary linear mixing relationship cannot account for the observed distribution of total U and A.R. Instead, two mixing relationships are suggested, one involving endmembers similar to H4 and H5, and the other involving endmembers similar to W29 and H4.

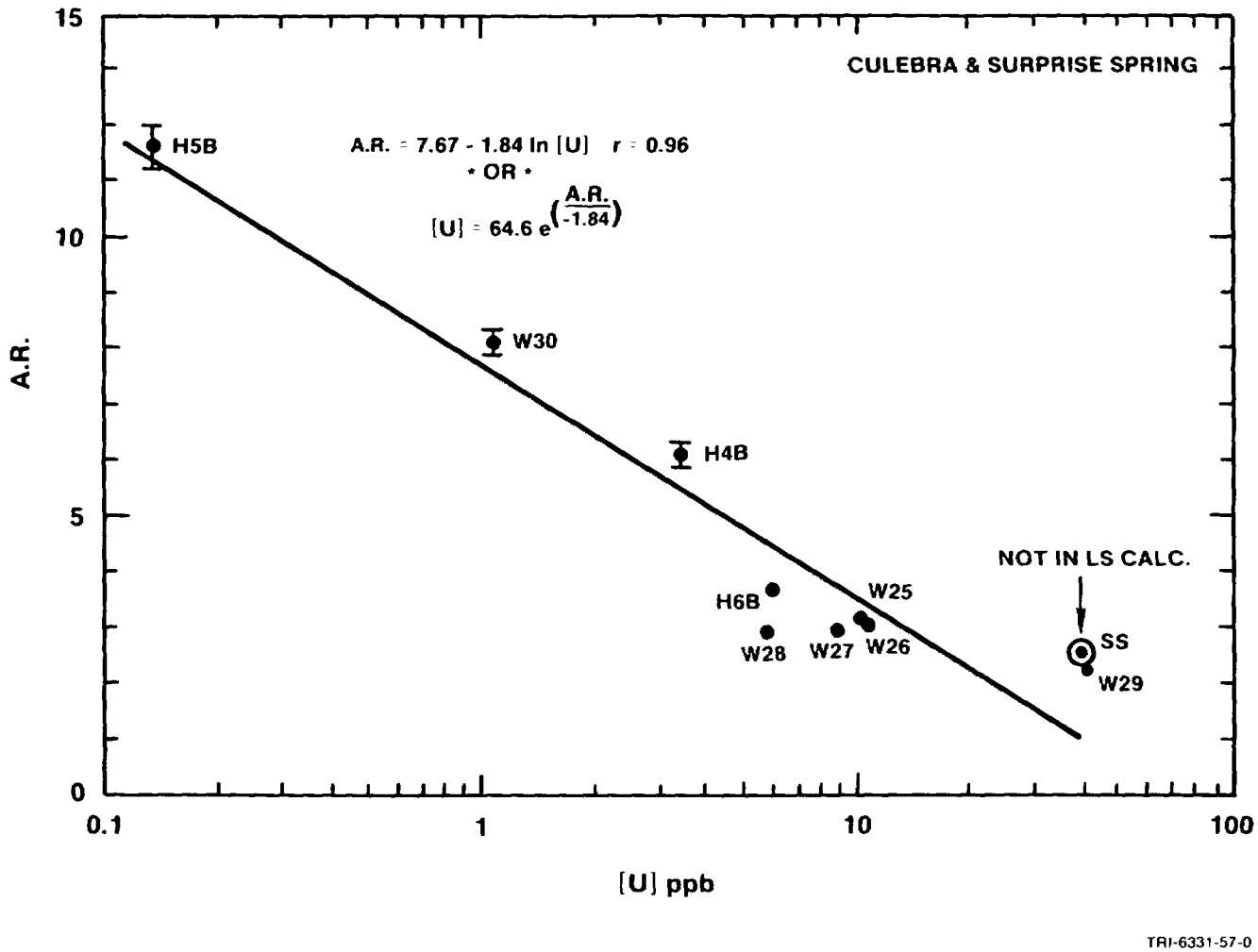

Figure 11. Semilogarithmic plot of A.R. versus total U for Culebra groundwaters. This transformation produces a linear plot, suggesting an Arrhenius-type relationship of as yet unknown nature, rather than simple binary mixing.

calculate apparent "age" (Section 4.3) using the Zone-IIIA model. Indeed, these model "ages" are dependent on the selection of two A.R. values (presently observed and inferred initial); different selections of one or the other will in general yield different results. Combining Equation (1) with Figure 12 indicates that several pairs of A.R.(b) and A.R.(0) can yield the same age, depending on the ratio whose natural logarithm forms the numerator. In our treatment in Figure 9, the five easternmost A.R. values (nearest the WIPP site) are associated with [U] values significantly less than 10 ppb. Nearly all the A.R. values (except very near the surface in SWND) are significantly greater than 2. If uranium is dissolving from rock congruently (i.e., without a change in isotopic ratio), the A.R. value contributed to solution in such dissolution would be the same as that in the rock. Previous studies of evaporites (Barr et al., 1979; Lambert and Carter, 1984) have shown that the A.R. value in evaporite rock is very near the secular equilibrium value of unity (see also Table 2). Thus, we infer that congruently adding uranium to solution decreases the A.R. value in solution. If values thus perturbed were used as A.R.(b) in the Zone IIIA model-age equation ((1)), the age would be spuriously old. It is, of course, also possible to obtain an age that is spuriously young, but Lambert and Carter (1984) have shown that in a **closed** system, the no-leaching model yields a minimum age, which is probably younger than the true age. The complication of an **open** system presented here has not previously been considered for evaporites that host a dynamic groundwater system.

In Nash Draw, A.R. values (3.12 at WIPP-25, 3.02 at WIPP-26, 2.87 at WIPP-27, and 2.93 at WIPP-28) and [U] values (10.22, 10.91, 8.69, and 5.70) at the respective sampling points are all similar to one another. This suggests some degree of homogenization of dissolved uranium within Nash Draw. If the hypothetical mixing endmember (A.R. ≈ 2) were not present, and the A.R. value of ~4 were observed instead of A.R. ≈ 3 at each of the Nash Draw wells, recalculated apparent uranium travel times between pairs would be less if A.R.(b) ≈ 4 than if A.R.(b) ≈ 3. Thus, the difference in apparent "ages" between dissolved uranium made spuriously old by dissolution of isotopically equilibrated uranium (A.R. = 1), and uranium that has been less so perturbed, could be significant. To illustrate the magnitude of this difference in the region most likely to have spuriously old apparent uranium-isotope-disequilibrium ages, we set A.R.(b) = 4 for both WIPP-25 and WIPP-26. Thus, the revised magnitudes of the apparent travel time vectors between H-4 and each of the two other wells, still using 6.09 as the A.R.(0) value at H-4 (Figure 9), are 190 Ka and 170 Ka, respectively, compared to 329 Ka and 312 Ka. Thus, in the more sensitive range of resolution of the Zone-IIIA model (where the difference between A.R.(b) and A.R.(0) is significantly greater than 1) the effect of spurious aging resulting from changing A.R.(b) by 1 is about a factor of two or less. An examination of Equation (1) shows that this sensitivity to A.R.(b) values diminishes as A.R.(0) values increase. This is illustrated in Figure 12 by the wider spacing of isochrons at higher A.R.(0) values. Thus, if perturbation of A.R.(b) values in Nash Draw by dissolution of uranium from the rock has decreased the observed A.R. values by 1, the apparent uranium travel times would be overestimated by no more than about 100 Ka. This is the maximum overestimate as long as the A.R.(b) values are greater than about ~3.

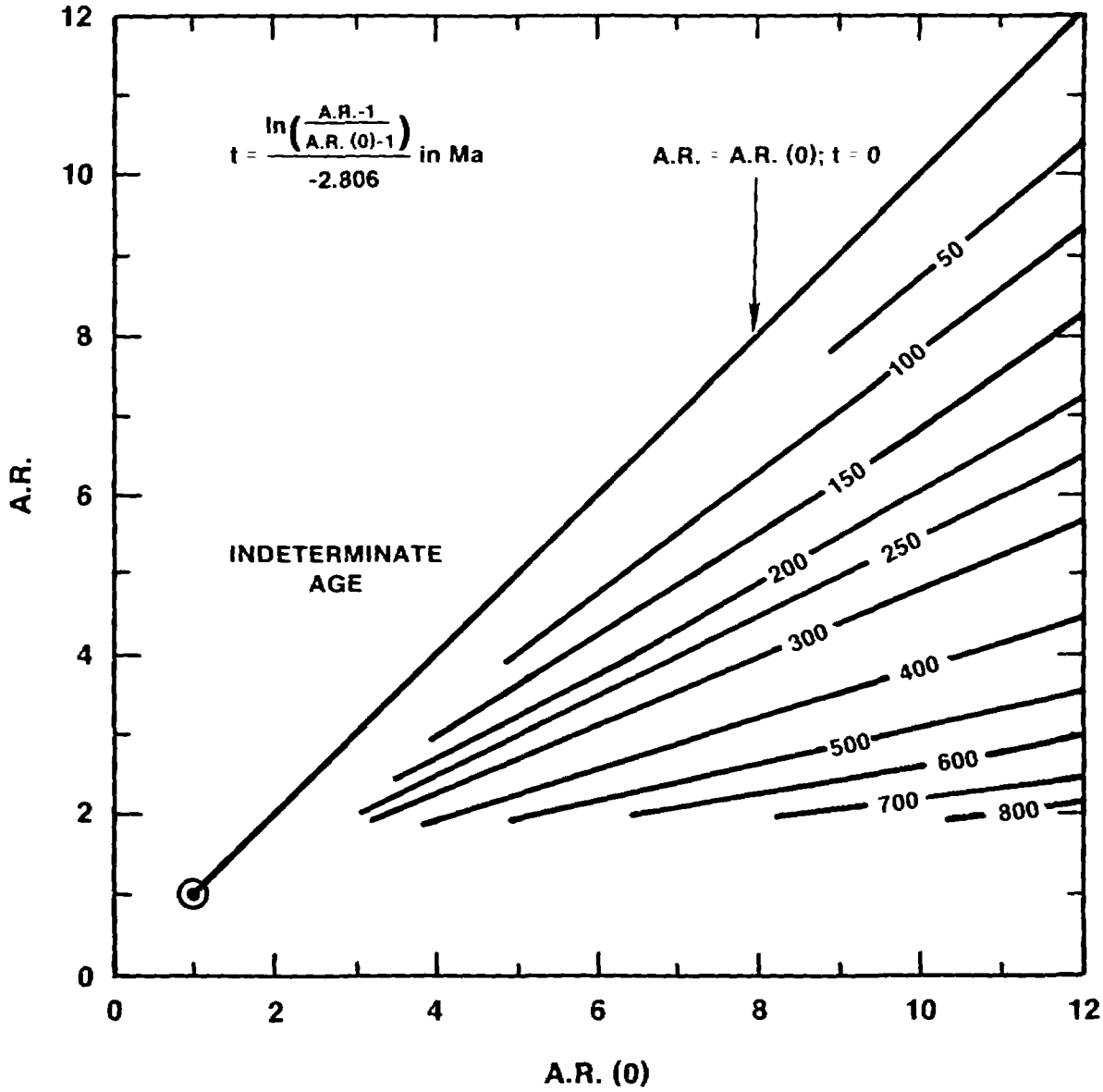

Figure 12. Arrays of initial and observed A.R. values yielding ages assuming no recoil-leaching and only radioactive decay (zone IIIA model). Isochrons are labelled in units of thousands of years. Under this model the age is indeterminate if A.R. > A.R.(0). The model is more sensitive to small age variations (isochrons are more spread out) with large A.R. values.

One could argue that the admixture of uranium introduced from the west in Nash Draw and migrating eastward is due to the ongoing admixture of oxidized high-uranium groundwater (e.g., recharge), rather than rock dissolution along the present southwestward flow path. Such a mixing process would also have progressively increased the [U], and progressively decreased the A.R. value below the level achieved by natural decay, making the apparent uranium travel time spuriously long. However, this would lead to the untenable conclusion that recharge is not only presently coming from the west and moving eastward from a zone of high permeability (Nash Draw) to a zone of low permeability (the WIPP site), but is also moving generally up the potentiometric gradient.

4.5 Evolution of the Uranium Isotope Ratio along a Flow Path

Despite the limitations on calculating uranium travel times as discussed above, we do not consider mixing and dilution of different uranium-isotope ratios a formidable obstacle to inferring flow patterns from the uranium data. Interpretation of isotopic data must of course be consistent with the observed physical hydrology of the system, if the evolution of the uranium distribution is considered contemporaneous with the modern flow system. Regardless of the quantitative relationships among time, A.R., and [U], the fact remains that A.R. decreases from east to west, and [U] decreases from west to east. Further, [U] increases in the same general direction as flow inferred from potentiometry. This may be in large part due to congruent dissolution along the flow path. Thus, if we knew the average uranium content of the surrounding soluble rocks inferred to have contributed uranium to the solution, together with the local rock/water ratios and uranium travel time between points with different aqueous U concentrations, we could calculate an instantaneous dissolution rate. Heretofore only an average dissolution rate (traditionally based on inferred geomorphological changes) has been available. If the time involved in the change in A.R. in Nash Draw is made spuriously long due to leaching and premature decreases in A.R., the apparent uranium travel time calculated from Equation (1) is a maximum and hence we derive a minimum dissolution rate. There is no known way to derive a maximum instantaneous dissolution rate from these data alone. Some hope is offered by Equation (3), whose functional form resembles an Arrhenius-type law, a familiar mathematical model used in chemical kinetics. It will be interesting to know if other solute data (Robinson, 1987), when they are interpreted for Nash Draw, obey similar Arrhenius-type correlations.

Proponents (e.g., L. J. Barrows in Chaturvedi and Channell, 1985) of the concept of unpredictably accelerated water flow in undetectable solution channels in the Rustler Formation (the so-called "karst proposition") have suggested that water flowing down the generalized regional potentiometric gradient in the Rustler originated by direct infiltration at the WIPP site, and discharges at Surprise Spring and Laguna Grande de la Sal (Figure 2) in SWND, rather than continuing onward to the Pecos River to discharge in a series of seeps in the riverbed near Malaga. The several difficulties with this proposal are summarized in Section 4.9. For the sake of argument, however, we shall assume that this intermediate discharge point actually exists, in order to calculate uranium travel times from the WIPP site to SWND.

If in the travel-time-vector grid in Figure 9 we set the travel time at WIPP-29 equal to zero, then all other travel times to that point from points northeast and east can be calculated. Again, the vectors in Figure 9 are not intended to indicate actual flow directions, simply the direction of decreasing A.R. value between any two adjacent points. If we add up all the apparent travel times between adjacent points with WIPP-29 as an arbitrary zero, we obtain the results plotted in Figure 13. The resulting contour diagram shows (1) apparent travel times from any point to WIPP-29 monotonically decreasing westward toward the surficial Rustler outcrops in western Nash Draw, (2) wide contour spacing in the high-permeability zone of Nash Draw and narrower spacing in the low-permeability zone of the WIPP site, and (3) an apparent travel time for uranium through the Culebra from the center of the WIPP site to the Surprise Spring area of SWND of about half a million years.

The A.R. decay curve as a function of time, taking t=0 for an A.R. value of 2.2, is shown in Figure 14. Note that for any given age model, greater differences in A.R. values are associated with greater apparent uranium travel times between points. This is true regardless of the exact mathematical relationship between A.R. and t.

4.6 The Effect of Dissolution

At 10 ppb, the total uranium molarity is 4.2×10^{-8}. In the Nash Draw range of "Eh", pH, and bicarbonate (cf. Lambert and Robinson, 1984), the solubility limit of uranium is probably not exceeded, since the maximum observed molarity under the Nash Draw-type conditions is 1.7×10^{-7} (corresponding to 40 ppb). Consequently, changing solution parameters are not limiting the distribution of [U] values over much of Nash Draw and the WIPP site.

Alternatively, the [U] could be related to the path length that the water has travelled, the water dissolving more uranium out of the rock as it moves along the flow path. Although halite would not be expected to provide much uranium, impure gypsum increases in abundance westward toward the more profoundly dissolved portions of the near-surface Rustler Formation, and is a ready source for additional uranium.

Neither the rock encountered by the dissolved uranium along any hypothetical flow path nor the dissolved uranium itself can be considered inert to each other. Rock-water interactions will take place in a nonsystematic way such that the equilibrium distribution of uranium between solution and coexisting rock will be locally controlled; thus, the distribution coefficient will be a constant in neither space nor time. This is a difficulty overlooked by most computer codes that calculate solute transport.

If, as Figure 13 suggests, the Culebra groundwater flow system is actually two flow systems exhibiting different physical behavior (Nash Draw versus the WIPP site area), and leaching has been taking place in both systems to various degrees, it may be possible to differentiate between decreases in A.R. due to radioactive decay and dilution of ^{234}U due to leaching of uranium of low A.R. value from the rock. After the suggestion of Osmond and Cowart (1976) for evaluating mixing phenomena in uranium-bearing groundwater systems, Figure

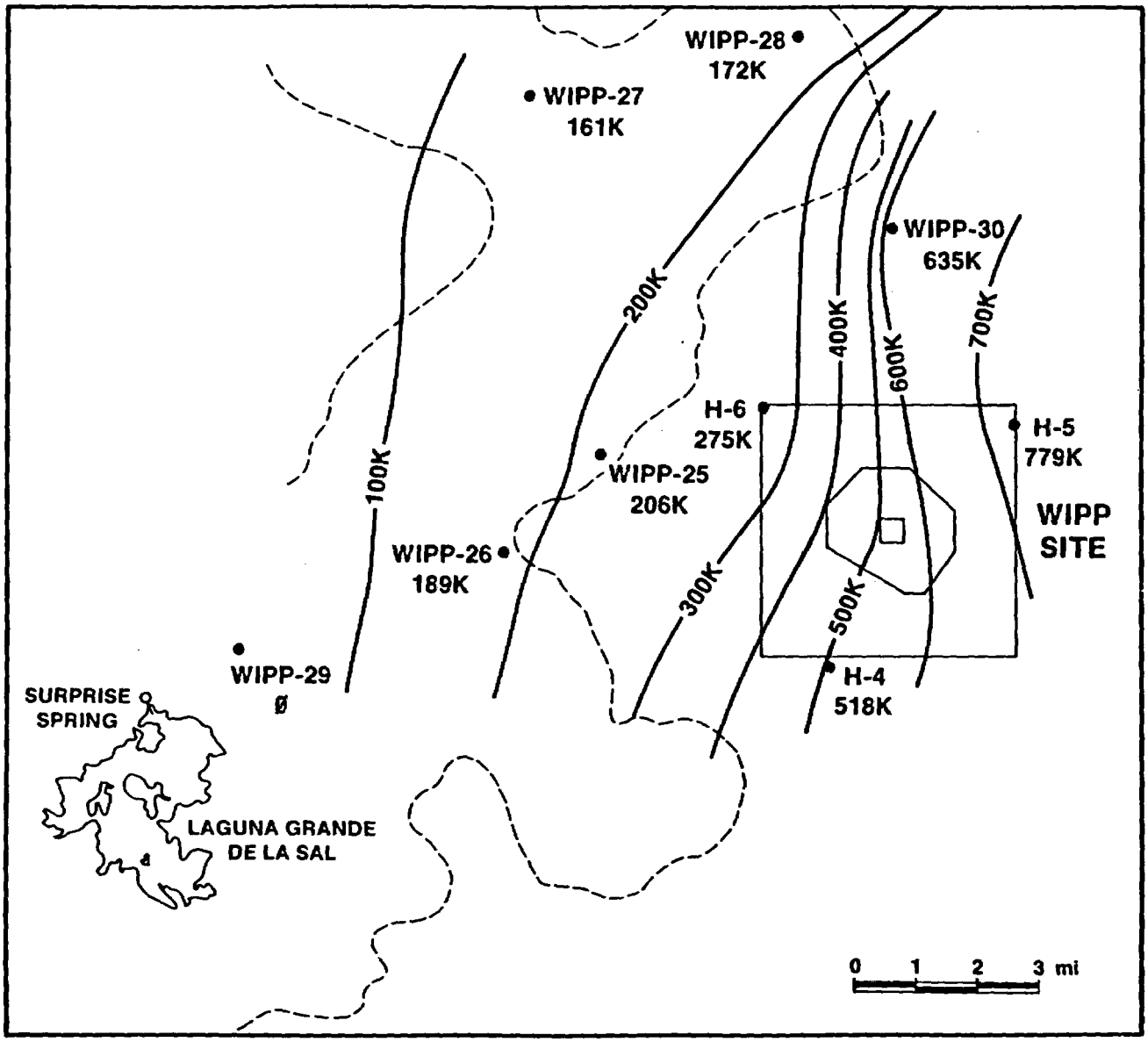

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Figure 13. Contour map of apparent uranium travel times between any point in the Culebra and Surprise Spring, calculated according to the zone IIIA model. In this treatment, the assumptions in the numerical interpretive model used to calculate apparent travel times are derived from the expected behavior of uranium and uranium isotopes entirely within zone IIIA in Figure 1. It is also assumed here that Surprise Spring is a discharge point for Culebra water, an assumption not consistent with other geochemical data.

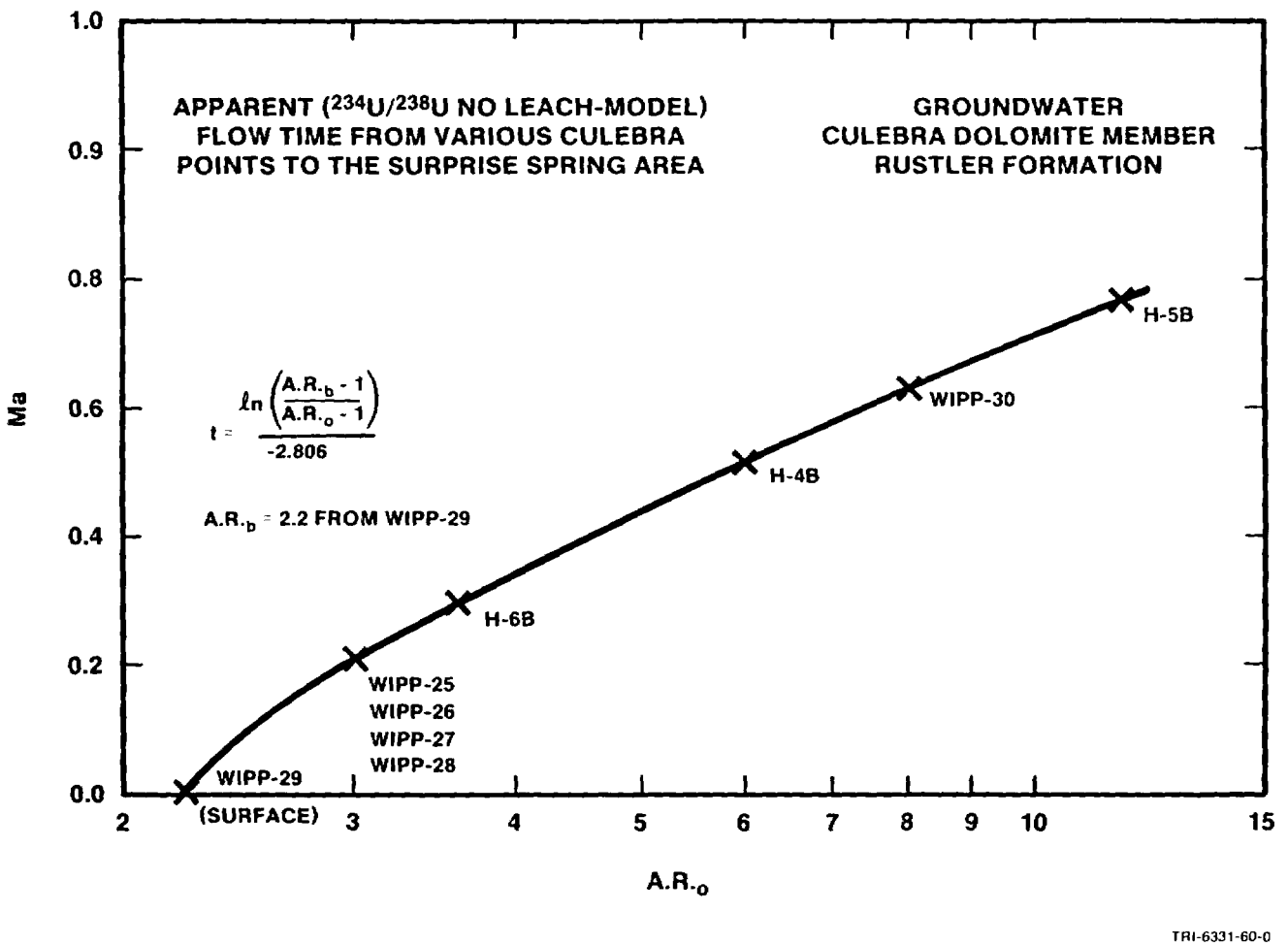

Figure 14. Hypothetical evolutionary path for uranium isotopes in the Culebra across the WIPP site and Nash Draw. Flow times from various points in the Culebra to WIPP-29 (near Surprise Spring in southwestern Nash Draw) are calculated according to the no-leach, decay-only model for uranium behavior expected in zone IIIA in Figure 1.

15 was prepared by plotting A.R. versus inverse-concentrations of total dissolved uranium (1/C), in units of inverse parts-per-billion (ppb^{-1}). The resulting distribution of data points cannot be described by a single straight line, but could be subdivided into two straight lines. H-4B appears to be common to both curves, and so was used in the calculation of both lines. One set of points (WIPP-25, WIPP-26, WIPP-27, WIPP-28, WIPP-29, H-6B, and H-4B) seems to fit the equation

$$A.R. = 1.55 + 13.40/C \qquad (4)$$

with an r value of 0.91. Another set of points (H-4B, WIPP-30, and H-5B) appears to be reasonably described by the equation

$$A.R. = 6.63 + 0.68/C \qquad (5)$$

with an r value of 0.96, even though the latter collection consists of only three points. [U] and A.R. at H-4 may represent a sort of intermediate between conditions dominating Nash Draw and those prevailing at the WIPP site.

The steep slope in Equation (4) indicates that leaching from the rock (i.e., mixing of water with an "infinite" concentration of uranium in the solid state) is probably taking place, involving an apparent A.R. value of 1.55 (at 1/C = 0) in the rock. Whereas most A.R. values in evaporites would be expected to be about 1 (Table 2), we consider this close enough to reflect the rock origin of some of the uranium in solution in Rustler groundwaters of the Nash Draw subsystem, especially since some rock A.R. values in Table 2 are close to 1.5. However, the very gentle slope (not far from zero, relatively speaking) of equation (5) indicates that dilution may have taken place, with a relatively small amount of uranium available to be dissolved, and only a small dependence of A.R. on [U]. The interpretation that congruent dissolution of rock with A.R. ≈ 6.7 has taken place is unreasonable, since A.R. values that high are generally not observed in rocks, much less the Culebra from the sampled boreholes. Thus, we can be more confident that changes in A.R. in Rustler groundwaters of the WIPP site subsystem (versus the Nash Draw subsystem) have arisen either from preferential leaching of ^{234}U, or faster radioactive decay of ^{234}U, or both, but probably not entirely from dissolution. It is not, however, outside the realm of possibility that the A.R. values of ~6 (H-4B) and ~12 (H-5B) define the ends of a mixing line. If the intermediate value of about 8 (W-30) was obtained from mixing, then less reliance can be placed on calculations of apparent age based solely on decreases in A.R. value. If the three available A.R. values at the WIPP site arose from mixing of waters, then we need to know the time required for such high A.R. values to evolve in this system. This can be done with a knowledge of the uranium concentrations and A.R. values in the host rock (Section 4.8).

Based on the information available thus far, the uranium travel time across the WIPP site in the Culebra may be no greater than 200 to 400 Ka, as indicated in Figure 13. This result is irrespective of the possibility that travel times in Nash Draw may actually be very much shorter. Given the overall low [U] values near the WIPP site, it is likely that even the

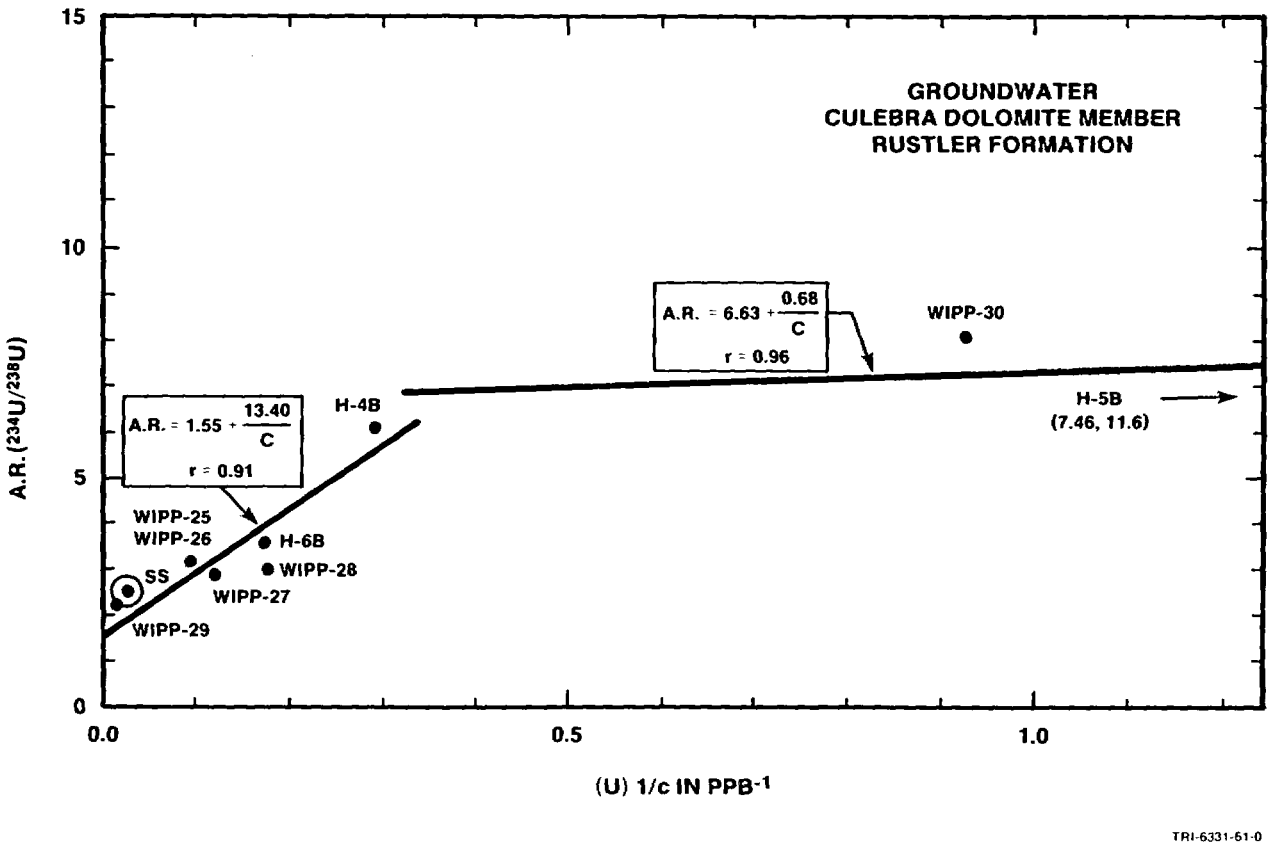

Figure 15. A.R. value versus inverse total-U concentration in Culebra groundwater. The relationship cannot be described by a single line, but the line through higher total-U concentrations (lower 1/C values) appears to describe mixing between waters in Nash Draw and a low-A.R. source of uranium such as rock. This line is considered to represent a decrease (e.g., dilution) of aqueous A.R. accompanying congruent dissolution of uranium. The source of uranium, as well as other solutes in Nash Draw waters, is taken to be evaporite rock, which has dissolved progressively from east to west across the outcrop area of the Rustler Formation evaporites in Nash Draw. The line with the flatter slope relates the waters with the highest A.R. values, and is not characteristic of domination by dissolution of rock uranium.

uranium isotope ratios at H-6B and WIPP-28 have been more influenced by processes involving mostly ^{234}U, and less influenced by congruent dissolution of uranium from host rock. Even though the closed-system inferences developed by Barr et al. (1979) and Lambert and Carter (1984) do not apply in a dynamic system such as the Culebra, it may be possible to estimate uranium travel times in some parts of the groundwater system (Section 4.8).

4.7 The Effect of Retardation

The retardation of a solute is

$$R = \frac{V_{solute}}{V_{solution}} = \frac{1}{1 + \frac{1 - p}{p} dK} \qquad (6)$$

where V is velocity, p is porosity, d is density, and K is distribution coefficient. Over a geographic area, $V_{solution}$ will vary with the permeability, p will vary with the degree of fracturing and cementation of component grains of rock, d will vary with bulk composition, and K will vary with a number of parameters dependent on both rock and solution. Dosch and Lynch (1978), Lynch and Dosch (1980), and Dosch (1980) showed that K for a solute is a function of rock/water ratio, concentration of solute, mineralogy, other solutes, and a host of intensive variables (temperature, contact time, speciation, solubility, etc.). Thus, K is not likely to be constant throughout a groundwater system; it has, however, been treated as constant in many solute-transport computer codes.

None of the known mechanisms of sorption would affect the A.R. values during a transition of uranium between the dissolved and sorbed states at any given sampling point, because any precipitation or adsorption of uranium on rock along the flow path would not be isotopically fractionated. At total mass of about 240, a difference of 4 atomic mass units (amu) does not provide a sufficient difference in the partition functions for ^{234}U species versus ^{238}U species to yield measurable physicochemical fractionation (cf. Urey, 1947). The A.R. value of any uranium precipitated along the flow path would be identical to the A.R. in solution, and the A.R. in solution would remain unchanged. Thus, any possible sorption of uranium along the flow path affects the A.R. value, and hence minimally affects the calculated apparent uranium travel time. The actual fluid velocity ($V_{solution}$ in equation (6)) is of course related to the uranium travel velocity (V_{solute}) by the factor R.

Dosch (1980) showed the multitude of variations in K for the Culebra core samples (that incidentally contain significant amounts of gypsum and/or anhydrite, as well as dolomite) under a few different conditions; the range for uranium in the +6 oxidation state (the most likely mobile state expected in Culebra groundwater), but otherwise unspecified as to complexation, was 13 to 224 mL/g. These K values were measured at far greater concentrations of total U (1, 10, or 50 ppm) than exist in the Rustler groundwaters (0.1 to 40 ppb). Such high concentrations of [U] were necessary for measurement of K with the batch method, but bear no relevance to natural conditions, and the actual K may be higher if during the laboratory measurement the sorption sites on the rock had become saturated.

We have noted that [U] values in the Culebra increase in the generalized inferred flow direction; this is opposite to the effect expected if uranium sorption were progressively taking place along the flow path. As discussed above, this trend indicates that uranium is being progressively dissolved out of the rock. The somewhat abrupt increase in [U] at Livingston Ridge may be a function of a change in lithology, uranium content, and the leachability of the rock's uranium. At the WIPP site where the Culebra is more confined, little else but the host rock can contribute uranium to the groundwater. In more highly fractured Rustler rock in Nash Draw the water is probably no longer confined to the Culebra, but probably finds its way into adjacent parts of the Forty-niner and Tamarisk gypsums to dissolve additional uranium. In SWND, even minerals in the Salado Formation may be contributing some uranium to solution, since there the evaporite dissolution has developed below the Vaca Triste siltstone in the middle Salado. This westward increase in uranium, together with the low overall [U] values, indicates that the solutions may not be saturated with respect to uranium, even in SWND. Consequently, in a dissolution-dominated system such as the unperturbed Culebra (as opposed to a sorption-dominated system such as might exist if a slug of uranium-enriched water were introduced from the outside), this preliminary treatment considers the loss of total uranium from solution due to sorption along the flow path to be more than compensated by congruently dissolved uranium. Here, regardless of the possibility that the uranium travel velocities are retarded by sorption relative to the solution particle velocity, we consider the A.R.s more a function of the amount of uranium congruently dissolved along the flow path, rather than of uranium sorption.

4.8 Travel Time Calculation: ^{234}U Buildup (Zone II)

4.8.1 Leach Rate of Recoil-^{234}Th

In the discussion of the Zone II model (Section 4.1.2), it was evident that in order to apply the model, the amount of leachable ^{234}Th ejected from the rock into solution must be known. In the chain that ultimately produces ^{234}U in solution from recoil-leached ^{234}Th,

$$\underset{4.5 \times 10^9\ a}{^{238}U \rightarrow} \; \underset{24\ d}{^{234}Th \rightarrow} \; \underset{1\ min}{^{234}Pa \rightarrow} \; \underset{2.4 \times 10^5\ a}{^{234}U \rightarrow} \; ^{230}Th, \qquad (7)$$

the decay of rock ^{238}U involves the longest half-life and is thus the rate-determining step for the buildup of A.R. values in solution. As yet no single process or combination of processes has been identified in nature, aside from leaching of recoil-generated ^{234}Th, that can give high A.R. values in solution.

We calculated the number of ^{234}Th atoms that are in the rock's interstitial water at any one time using the method documented by Andrews and Kay (1982). They gave the equation

$$N_{Th} = 0.235 \frac{\lambda_{238}}{\lambda_{Th}} \cdot {}^{238}U_s \qquad (8)$$

where λ_{238} is the decay constant for ^{238}U (1.537×10^{-10} a^{-1}), λ_{Th} is the decay constant for ^{234}Th (10.5 a^{-1}), ^{238}U is the number of atoms of ^{238}U in the mineral grain surface layer whose thickness is less than the recoil range of ^{234}Th (the "leachable layer"), and 0.235 is a constant, representing the probability of a ^{234}Th atom in the leachable layer escaping to the solution given the local geometry. For this calculation, we used the same geometry as Andrews and Kay (1982), representing mineral grains as 1 mm spheres in close packing, which gives a fractional porosity of 0.26. The surface area is about 1.56×10^{-3} m/g of rock, for a leachable volume of 4.68×10^{-5} cc/g of rock, assuming a bulk density of 2.8 to 2.9 for dolomite. Thus, 1 g of rock contains about 1.31×10^{-4} g leachable mass. Of that, 0.9×10^{-6} g/g is uranium, which is nearly all ^{238}U (Table 2); this [U] value is the mean for Culebra rock where the water A.R. values are relatively high. We assume that the high A.R. values developed in water in the presence of rock having a [U] value of $\sim 1 \times 10^{-6}$ g/g and an A.R. value ~1 to 2. Thus, the number of leachable ^{238}U atoms per gram of rock is $\sim 3 \times 10^{11}$. According to Equation (8) the number of ^{234}Th atoms present in solution at a time is slightly more than 1 per gram of rock. Since we take the fractional porosity for dolomite aquifer rock in the calculation to be 0.26 (for close-packed spheres), the steady-state concentration of ^{234}Th in solution is about 12 atoms/cc.

4.8.2 Increase in A.R. Values as a Function of Time

4.8.2.1 Principles.

The A.R. value in solution acquiring ^{234}U from recoil-leaching of the rock, as a function of time, is

$$A.R. = 1 + \frac{N_{Th} \quad \lambda_{Th} \; [1-\exp(-^{234}\lambda_U \; t)]}{\lambda_{238} N_{238}} \qquad (9)$$

where $^{234}\lambda_U$ is the decay constant for ^{234}U (2.806×10^{-6} a^{-1}), t is the time in years, and N_{238} is the number of ^{238}U atoms initially in solution before the recoil-leaching took place. Equation (9) also assumes, for simplicity, that the initial A.R. value in solution is close to unity, as would be the case in Zone I of Figure 1. N_{238} is based on the [U] value in solution, given that at A.R. values near unity the number of ^{234}U atoms relative to the number of ^{238}U atoms is very small.

4.8.2.2 A.R. evolution under native conditions.

Table 3 gives the results of calculating A.R. values as a function of time according to the Zone II model. In part A, the third column gives calculated A.R. values assuming A_{238} ($=\lambda_{238}N_{238}$) = 52.1. This value of A_{238} is based on the assumption that the lowest value for [U] in the Culebra water, at H-5B (Table 1), represents the initial aqueous [U] before any uranium may have congruently dissolved into solution from rock. Clearly, under these assumptions, it is not possible to achieve an aqueous Culebra A.R. value as high as any observed near the WIPP site (represented by H-4B, H-5B, and H-6B); the ^{234}U production rates under these conditions are too slow to allow asymptotic approach of A.R. values to

TABLE 3. CALCULATED A.R. VALUES FOR CULEBRA GROUNDWATERS[1]

t (years)	$1-\exp(-2.806\times10^{-6}t)$	A.R.s $N_{Th}=12$ ($U_s=0.9$)	A.R.s $N_{Th}=120$ ($U_s=9$)
A. Using $U_0=0.134 \times 10^{-9}$ g/g, from H-5B Culebra; $A_{238}=52.1$.			
0	0.00	1.00	1.00
5000	0.01	1.03	1.34
10000	0.03	1.07	1.67
20000	0.05	1.13	2.32
30000	0.08	1.19	2.95
40000	0.11	1.26	3.57
50000	0.13	1.32	4.17
80000	0.20	1.49	5.86
100000	0.24	1.59	6.92
170000	0.38	1.92	10.17
200000	0.43	2.04	11.39
350000	0.63	2.52	16.24
500000	0.75	2.82	19.24
550000	0.79	2.90	20.02
600000	0.81	2.97	20.69
800000	0.89	3.15	22.52
1000000	0.94	3.27	23.72
2000000	1.00	3.41	25.10
B. Using $U_0=0.024 \times 10^{-9}$ g/g, from WIPP-30 Rustler/Salado; $A_{238}=9.34$.			
0	0.00	1.00	1.00
5000	0.01	1.19	2.88
10000	0.03	1.37	4.73
20000	0.05	1.74	8.36
30000	0.08	2.09	11.89
40000	0.11	2.43	15.32
50000	0.13	2.77	18.66
80000	0.20	3.71	28.12
100000	0.24	4.30	34.01
170000	0.38	6.12	52.18
200000	0.43	6.79	58.94
350000	0.63	9.50	85.99
500000	0.75	11.17	102.74
550000	0.79	11.61	107.08
600000	0.81	11.99	110.85
800000	0.89	13.01	121.06
1000000	0.94	13.67	127.75
2000000	1.00	14.44	135.41

TABLE 3. (continued)

t (years)	$1-\exp(-2.806\times10^{-6}t)$	A.R.s $N_{Th}=12$ ($U_s=0.9$)	A.R.s $N_{Th}=120$ ($U_s=9$)
C. Using $U_0=0.01 \times 10^{-9}$ g/g, from Carlsbad rain; $A_{238}=3.89$.			
0	0.00	1.00	1.00
5000	0.01	1.45	5.51
10000	0.03	1.90	9.96
20000	0.05	2.77	18.68
30000	0.08	3.62	27.15
40000	0.11	4.44	35.39
50000	0.13	5.24	43.40
80000	0.20	7.51	66.13
100000	0.24	8.93	80.25
170000	0.38	13.29	123.88
200000	0.43	14.91	140.11
350000	0.63	21.41	205.06
500000	0.75	25.43	245.27
550000	0.79	26.47	255.70
600000	0.81	27.38	264.76
800000	0.89	29.83	289.28
1000000	0.94	31.43	305.33
2000000	1.00	33.27	323.72

1. Activity Ratios (A.R.s) calculated according to the equation

$$A.R. = 1 + \frac{N_{Th}\ 10.5\,[1 - \exp(-2.806 \times 10^{-6}t)]}{A_{238}}$$

using the indicated initial uranium concentration in solution (U_0).[1] Calculations of A.R.s are included for both the mean uranium concentration in Culebra dolomite rock near the WIPP site ($U_s=0.9 \times 10^{-6}$ g/g), and an order of magnitude more rock uranium ($U_s=9 \times 10^{-6}$ g/g).

steady-state values even as high as 3.6 (H-6B, Table 1). The maximum A.R. value under these conditions seems to be 3.4, realized in principle only after 2 Ma. Thus, either the lowest [U] value in Culebra water at H-5 does not represent the initial A_{238}, or the aqueous A.R. values near the WIPP site resulted from recoil-leaching of rocks richer in uranium than represented by the Culebra dolomite [U] values in Table 2 (all of which are less than 1 $\times 10^{-6}$ g/g), or both. One implication of this shortfall in calculated A.R. values is that the lowest observed [U] value in Culebra water represents a higher [U] value than actual initial conditions. If this is the case, the excess [U] would probably have come from congruent dissolution of rock, such as in Zone IIIB. This would have diluted the actual A.R. to the lower observed level by admixture of rock uranium with A.R. = 1. Hence, the observed aqueous A.R.s would be in part products of mixing, and the times necessary to reach the pre-mixing (higher) A.R.s would be longer than those calculated from the observed (lower) A.R.s, regardless of any other assumptions implicit in Equations (8) and (9).

Mercer and Orr (1979, p. 98) reported a "high gamma count" in the Culebra during geophysical logging of borehole P-15 (Figure 4). A spectralized gamma log (selectively sensitive to gamma-ray energies of uranium, thorium, and potassium) "indicated the anomalous zone to be an interval of naturally deposited uranium." Unfortunately, this zone was never cored, so no analyses for rock uranium could be obtained. Nevertheless, the rock [U] value at P-15 is apparently higher than that prevalent in most of the Culebra (Table 2). In the Delaware Basin, [U] values in natural occurrences have been as high as 6.6×10^{-6} g/g, in a uraninite-bearing silt from the New Mexico Room of Carlsbad Caverns (Lambert and Carter, 1984). Thus, rock [U] values an order of magnitude higher than those measured for the Culebra are not unknown in the Permian stratigraphic column. The fourth column in part A of Table 3 shows aqueous A.R. values calculated assuming that the A.R. values were generated by leaching of a rock having an order of magnitude more uranium than measured for the Culebra. A.R.-versus-time trends calculated for U-poor (Culebra) and U-rich (cavern) rock, both assuming an initial aqueous [U] represented by the lowest value observed in Culebra water, are plotted in Figure 16A. While the U-poor-rock trend never reaches aqueous A.R. values characteristic of the Culebra near the WIPP site, the U-rich-rock trend reaches those values in times between 40 and 200 Ka. This, coincidentally, occupies the interval between the minimum isolation time of the Culebra water from the atmosphere (Lambert, 1987), and the maximum drainage time calculated by the Zone IIIA (no-leach, decay-only) model. Thus, it is in principle possible to achieve the observed A.R values in times consistent with independent determinations, using the lowest observed [U] as the initial aqueous [U], but such water is required to have interacted with rock of a much higher uranium content than occurs in most of the Culebra.

4.8.2.3 A.R. evolution from a more primitive source-water.

Part B of Table 3 gives the results of aqueous A.R. calculations assuming that the initial [U] in solution was 0.024×10^{-9} g/g, as observed in the Rustler/Salado contact water from WIPP-30. This is the lowest observed value associated with the Rustler, and its A.R. (2.0) indicates that either its A.R.-buildup (Zone II) has not evolved very far, or the water is so

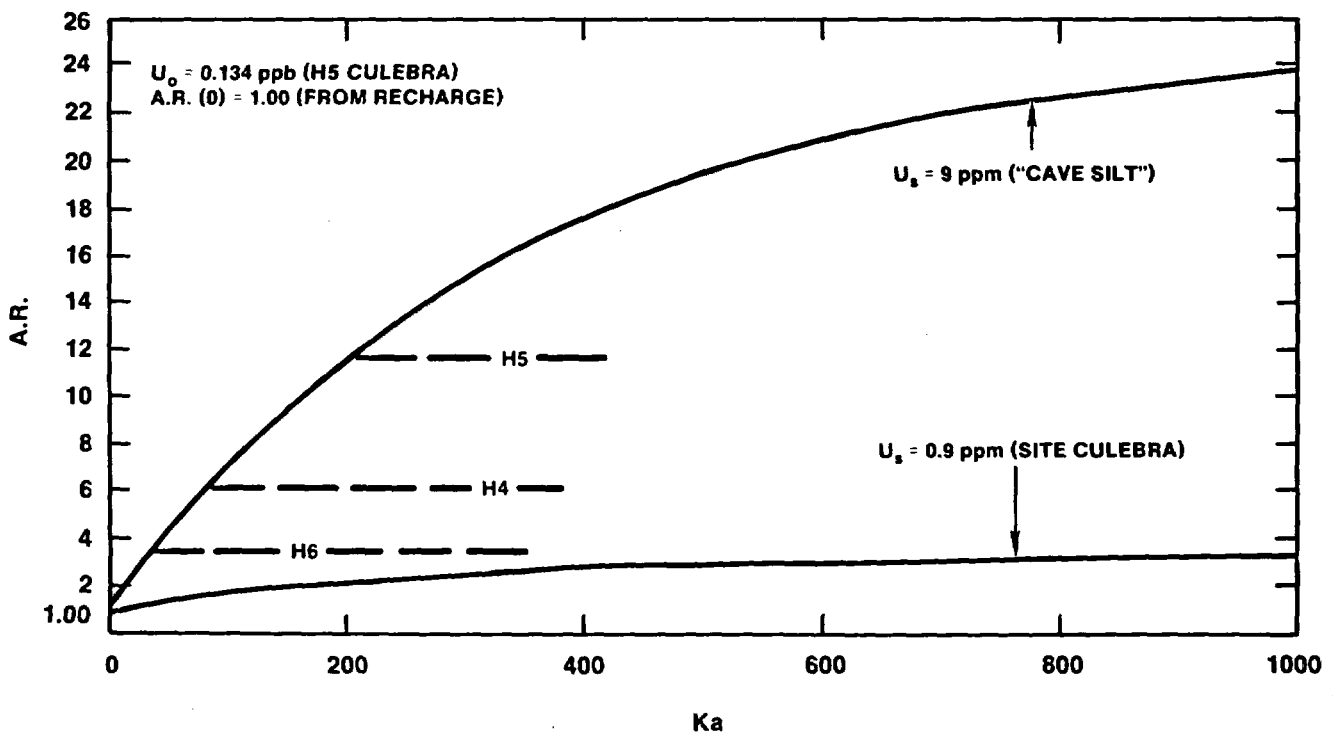

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Figure 16. Buildup of aqueous A.R. value as a function of time according to the model describing uranium behavior in Zone II. Calculated A.R. evolution curves are given for water in the presence of rock containing 0.9 x 10^{-6} g/g, represented by the mean Culebra rock total-U concentration, and rock containing an order of magnitude more uranium, similar to that in silty material elsewhere in the Delaware Basin.

16A. Times required to achieve A.R. values starting with an initial total-U concentration represented by H5 Culebra water (0.134 ppb). Note that under these conditions it is not possible to achieve the high A.R. values observed near the WIPP site (>6) if the source of leachable uranium is the mean Culebra rock with a total-U concentration of 0.9 ppm.

old that its A.R. has decayed (Zone IIIA) almost back to 1. The stable-isotope compositions of Culebra and Rustler/Salado contact waters from WIPP-30 indicate that both originated as meteoric recharge under similar climatic conditions (Lambert and Harvey, 1987), but the potentiometric levels and major solute contents indicate that hydraulic connections between them have not been significant (Mercer, 1983) on the time scale to which uranium-isotope disequilibrium is applicable (2 Ma). Given the significantly lower (by almost an order of magnitude) [U] content of the Rustler/Salado contact water, it probably contains less uranium congruently dissolved from rock than does the Culebra water confined in a layer above it. Thus, since they have similar meteoric origins, without stable-isotope shift induced by rock/water interactions, the two geochemically-distinct, superposed groundwater occurrences probably have a common origin, and may be contemporaneous. Starting with an ancestral water with a [U] similar to that of WIPP-30 Rustler/Salado, we obtain the A.R. evolutionary trends plotted in Figure 16B; trends are shown for U-rich and U-poor rock as before.

Under these conditions, with a lower initial [U], it is possible to attain the relatively high A.R. values observed near the WIPP site in finite time. The time required for A.R. values to evolve, in the presence of U-poor rock, from A.R. = 1 to A.R. values observed near the site varies between 70 Ka (H-6) and 550 Ka (H-5). The latter apparent buildup age coincides with the age of Gatuña Formation deposition, when the climate was significantly wetter, as indicated by the local high-energy stream deposits (Bachman, 1985). For A.R. evolution in the presence of U-rich rock, the observed WIPP-site A.R. levels are achieved in 10 to 30 Ka. This coincides with the range 12 to 16 Ka given by Lambert (1987) for the time of isolation of Culebra water from the atmosphere.

4.8.2.4 A.R. evolution from meteoric recharge.

Finally, for completeness, we calculated the time required to achieve the observed WIPP-site Culebra-water A.R. values starting from uranium concentrations observed in rainfall. This may represent the most primitive evolutionary path, since the initial conditions even predate entry of water into Zone I (Figure 1). It is assumed here that water left the hypothetical redox barrier with an A.R. value near unity, and an extremely low [U] (0.01×10^{-9} g/g), which we approximate by that in local rainfall (Table 1). Table 3, part C, gives the A.R. values calculated assuming such an initial [U] in water recharged to the Culebra, in contact with U-rich and U-poor rocks as before. In U-poor rock typical of the Culebra, the calculated travel time from recharge to H-5 (A.R. = 11.6) is 140 Ka, and for H-6 (A.R. = 3.57) is about 30 Ka. The respective uranium travel times (neglecting retardation) through U-rich rock are about 11 Ka and a few thousand years, as indicated by the trends plotted in Figure 16C.

4.8.2.5 Summary: The most probable evolutionary path.

In spite of the fundamental differences among the evolutionary paths for which A.R.s as a function of time were calculated above, all have certain common characteristics. First, congruent dissolution of uranium from rock (e.g., transient reversion from purely Zone II

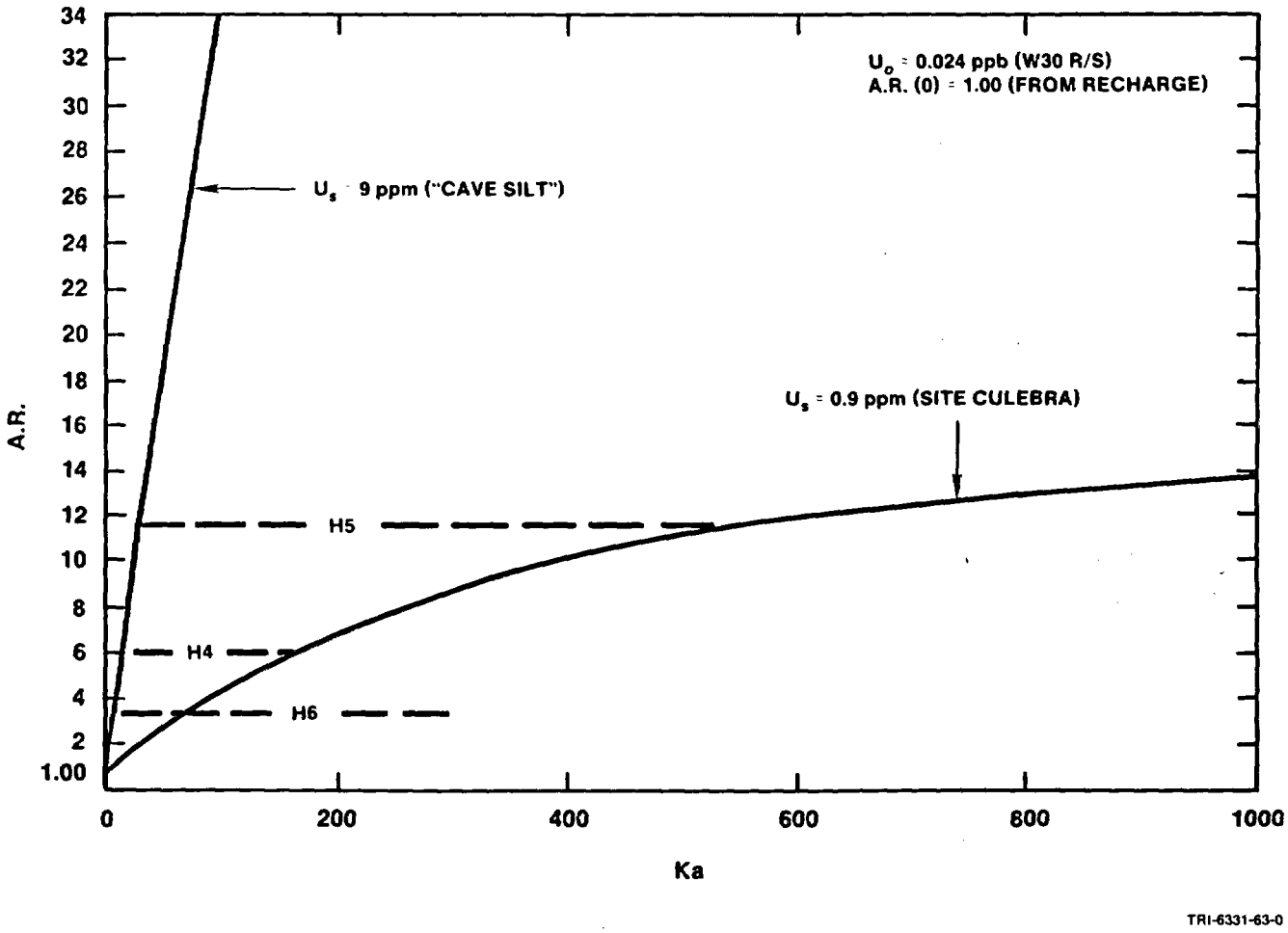

Figure 16B. Times required to achieve A.R. values starting with an initial total-U concentration represented by WIPP-30 Rustler/Salado contact water (0.024 ppb).

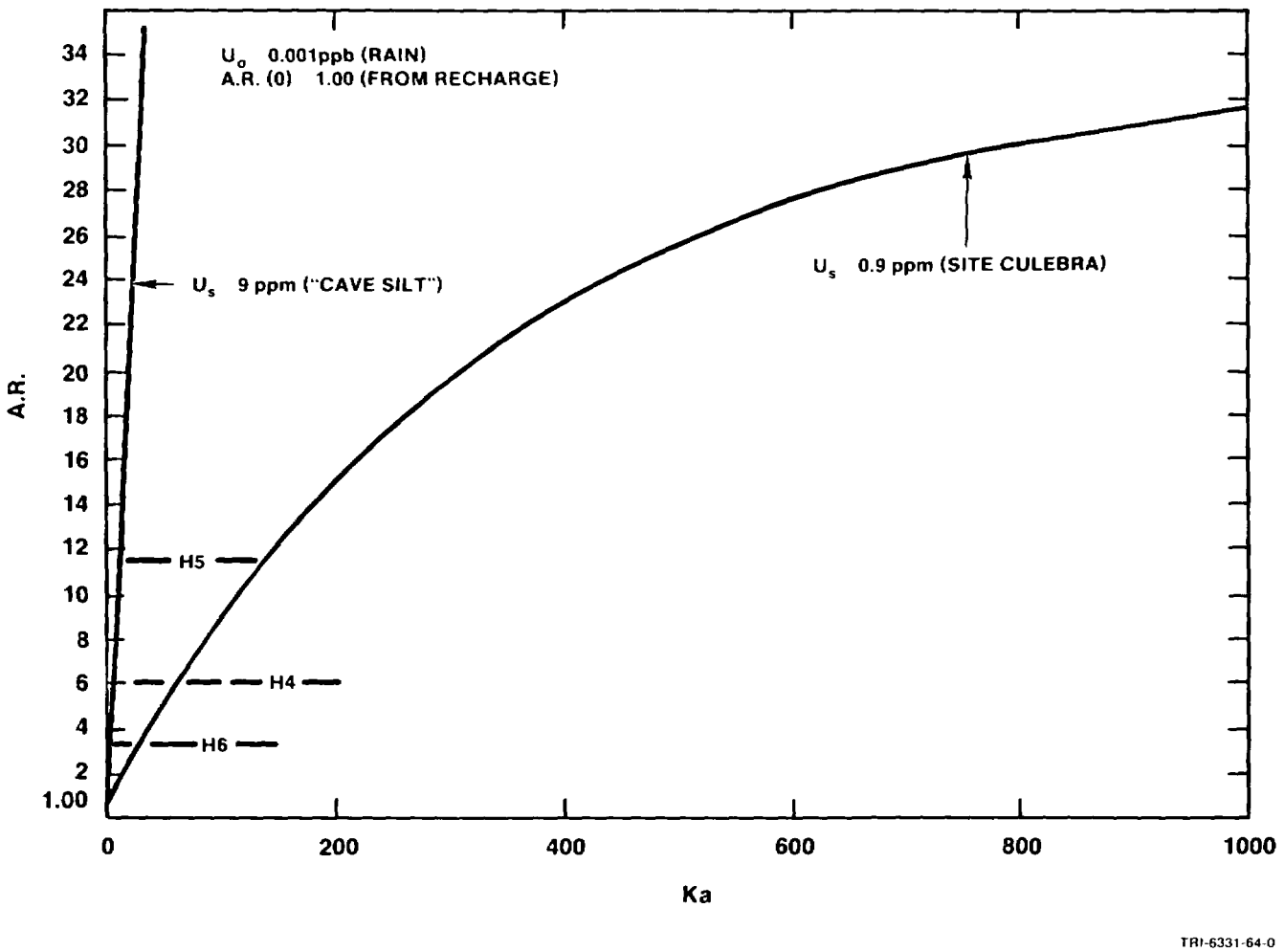

Figure 16C. Times required to achieve A.R. values starting with an initial total-U concentration represented by local rainfall (0.01 ppb).

conditions to Zone I or IIIB conditions) superimposed on the Zone II-type growth of A.R.s will add to the time required to achieve the high observed A.R. values. Thus, in the presence of any congruent dissolution competing with recoil-leaching, the times calculated by the Zone II model will be minima. Second, a major uncertainty is the U-content of the rock that actually supplied recoil-leached ^{234}U to the water and increased its A.R. along the evolutionary (i.e., flow) path. Zones of Culebra dolomite rock rubble through which the most water is likely to have flowed (Table 2) may represent a spuriously low [U] content, if such rock has already been leached of much of its original total uranium content. Leaching of uranium from the surfaces of discrete mineral grains, such as occurs in "classic" sandstone aquifers (Osmond and Cowart, 1976) and oölitic beds (Andrews and Kay, 1982), is not as useful a concept in evaporite beds. In fact, the Culebra more resembles a crystalline rock than a sediment, containing several generations of interlocking grains of calcium sulfates, as well as calcium-magnesium carbonates. We suggest that evaporite host rocks differ significantly from sandstone and oölitic aquifers, with respect to mechanisms of uranium leaching, in several ways:

- Recrystallization of sparingly soluble phases common in evaporites (e.g., sulfates) is likely to homogenize the rock, so that the concentration of uranium on surfaces is not likely to differ much from bulk rock

- Dissolution of halite underlying the Culebra has resulted in episodic collapse and fracturing, exposing new surfaces to rock/water interaction

- Sulfates, which are likely to contain appreciable uranium, are more readily dissolved outright than silicates, releasing their trace constituents, such as uranium, without isotopic fractionation, more readily than silicates.

Pockets of U-rich rock such as those apparently preserved at P-15 may represent local maxima, although the distributed uranium in the aquifer rock available to the moving groundwater was probably lower than the local deposit at P-15, but higher than that measured in more highly productive rock. Thus, we consider that 9×10^{-6} g/g, rather than 0.9×10^{-6}, may better represent the U-content of the rock whose incongruent leaching produced the high A.R.s near the WIPP site.

Aside from the U content of the rock, the other major uncertainty in calculating uranium travel times from A.R.-buildup along an evolutionary path is the original U content of the water entering Zone II. In the presence of rock with a U content of about 1×10^{-6} g/g, it is possible to generate the high A.R.s using the lowest observed [U] in the Culebra, that of H-5. This value also happens to be located furthest east along the paleoflow direction indicated by the trend of increasing A.R.s. The fact that the inferred paleoflow vector is from a region of higher permeability toward a region of lower permeability is somewhat problematical. Nevertheless, we regard this initial [U] from H-5 (~0.1 ppb) as somewhat high relative to other groundwaters with high A.R. values in a reducing zone (cf. Osmond and Cowart, 1976), so a more likely original [U] is probably represented by the low-[U] Rustler/Salado contact water at WIPP-30 (0.02×10^{-9} g/g), which may be more reducing

("Eh" ≈ -0.4 V) relative to most of the Culebra (Lambert and Robinson, 1984). Thus, even the [U] of H-5 Culebra may bear a significant Zone IIIB overprint, in which a reversal in flow direction and accompanying incipient exhumation by erosion and dissolution has made the flow system in the Culebra more oxidizing than formerly.

We perceive the most probable evolutionary path for uranium concentrations and A.R.s in Rustler groundwater to involve an extremely low initial aqueous U-concentration (<<1 ppb) interacting with rock containing about 10 ppm, an order of magnitude more uranium than represented by the measurements in Table 2. This implies that either partial dissolution has previously leached uranium from the water-bearing rock, resulting in the observed ppm-levels, or that the distribution of uranium in the Culebra is less uniform than represented in Table 2. In any case, the relatively low rock-uranium concentrations, together with the relatively high dissolved uranium concentrations, are not likely to have produced the observed high A.R.s in the groundwaters from the eastern part of the study area.

There are other uncertainties in the Zone II model-age calculations. If, for example, the porosity we assumed in Equation (8) is too high, a lower true value would decrease the time required to achieve a given A.R. value, and the calculated times would be overestimated. Conversely, a lower porosity might also decrease the leachable surface area and hence the leachable volume; under those conditions the required time would be longer, and our calculation would be an underestimate. Finally, in all the calculations herein, we do not consider the effect of retardation of aqueous uranium species, and hence we do not rigorously equate uranium travel times with groundwater travel times.

4.9 Implications: Recharge, Karst Flow, and Climatic Change

From a geological and geochemical perspective, there are several difficulties with the concept of unrestricted or uniform high-velocity groundwater recharge and flow through undetectable subterranean channels near the WIPP site. Several of these difficulties have arisen as a result of the work described herein; others have been addressed by previous work. This section contains a summary of the various geochemical limitations to rapid steady-state recharge, groundwater flow, and discharge in the Rustler system.

4.9.1 Limitations to Rapid Groundwater Flow

4.9.1.1 Geochemical heterogeneity.

Regardless of the specific numerical inputs to Equations (8) and (9), a time on the order of several thousand years is required to achieve aqueous A.R.s as high as 6 to 11, even with the most conservative of assumptions consistent with the geological and geochemical data. The uranium A.R. data, together with the stable-isotope data (Lambert and Harvey, 1987), and the radiocarbon and tritium data (Lambert, 1987) are not consistent with the premise of Chapman (1986, p. 64) that "there is a good possibility that the Rustler is currently receiving recharge" at the WIPP site. Similarly, high A.R.s are not consistent with the premise that groundwater travel times near the WIPP site are uniformly rapid, facilitated

by a regionally well-developed, fracture- and dissolution-dominated "karst" flow regime, as described by Chaturvedi and Channell (1985). A regional-scale mixing of fresh and older fluids that would be facilitated by such a phenomenon would homogenize the solutes, the uranium content, and the activity ratios. This has not been the case.

4.9.1.2 Present-day recharge at the WIPP site.

Lambert and Harvey (1987) have argued by means of stable-isotopes in Rustler groundwaters that little or no modern meteoric recharge is reaching the Rustler near the WIPP site, except in SWND where Chaturvedi and Channell (1985) and Chapman (1986) have proposed that discharge in SWND is draining the Rustler groundwater flowing from the WIPP site through Nash Draw. The interpretation of Lambert and Harvey (1987), however, is that parts of SWND may be an active local recharge area, with nearby discharge into Laguna Grande de la Sal, with little contribution from the other parts of Nash Draw, much less the WIPP site. This is consistent with the findings of Hunter (1985), indicating that a great volume of modern wastewater is dumped into SWND by local industrial operations.

4.9.1.3 The presence of evaporite karst east of Nash Draw.

Bachman (1985), by detailed mapping of geomorphic/geological features in Nash Draw and at the WIPP site, has proposed that the only true karst feature (i.e., cavernous flow structure closely associated with surficial recharge) east of Nash Draw near the WIPP site is the sinkhole at WIPP-33, which is correlated with "cavernous" zones above and below the Magenta dolomite member of the Rustler Formation at depth. Bachman (1981) also suggested that the probable discharge of the local recharge at WIPP-33 was a series of extinct springs along the east side of Nash Draw, now represented by mound- and apron-shaped gypsite deposits containing bones and teeth of extinct horses and camels of Pleistocene age. This implies that evaporite karst features large enough to be important in Rustler groundwater flow would be conspicuous, would involve distinct surface expression, and would not be obscured completely by dune sand. There is no modern discharge at the paleo-springs on the eastern edge of Nash Draw; the paleo-groundwater system probably involved more water than is available today, flowed in and dissolved the gypsic water-bearing horizons in the Rustler at and near WIPP-33 (such as the dolomitic layers), and may have involved some vein-deposition of gypsum in the Dewey Lake (cf. Lambert and Harvey, 1987). Again, the stable-isotope data show little modern recharge to the Culebra or Magenta at WIPP-25 (drilled in the middle of the chain of spring deposits), from infiltration at WIPP-33 or anywhere else along the eastern margin of Nash Draw.

4.9.1.4 The nature of evaporite karst within the Rustler.

Lee (1925) observed active recharge to sinkholes in gypsum (not dolomite) in the Rustler Formation exposed at the surface in Nash Draw. This particular instance was in the Tamarisk Member (although surficial sinkholes are also locally developed in the Forty-

niner Member), **not** the Magenta or Culebra Member. Also, massive amounts of surface-derived recharge observed pouring into these sinkholes during storms and flash floods are not characteristic of Rustler groundwater in east-central Nash Draw or the WIPP site, according to the isotopic data (Lambert and Harvey, 1987). It is entirely likely that gypsum karst forms its own local near-surface groundwater system under water-table conditions, probably discharging into Laguna Grande (Hunter, 1985, p. 49).

4.9.1.5 Evidence for confined aquifers at and near the WIPP site.

Mercer (1983) showed that the Magenta and Culebra groundwaters are confined, except locally in SWND. These conditions would be difficult to maintain if there were free and open conduits to the surface. There is a growing body of evidence to show that at WIPP-25 and WIPP-27 the Magenta and Culebra are freely connected with each other, but are not under water-table conditions. Previously observed similarities in stable-isotope ratios (Lambert and Harvey, 1987), field-measured solutes (Lambert and Robinson, 1984), and now uranium ([U] and A.R.) values (Table 1) all independently point to this possibility, and potentiometric levels and permeabilities for these two members are also similar at these two points (Mercer, 1983). This is not to say, however, that such is the case everywhere in Nash Draw. In WIPP-28 and WIPP-26, for example, the confined Culebra is a reasonably good producer of water, while the overlying Magenta is dry. The apparent drainage of the Magenta downward into the Culebra (and, by extension, the inferred drainage of some Culebra water downward into the "basal brine aquifer" of Robinson and Lang, 1938) is potentially a useful concept for explaining potentiometric head distributions and differentials at the WIPP site, as well as in Nash Draw. However, this mechanism is not rapid enough to have allowed geochemical homogenization.

4.9.1.6 Summary.

The literature contains much documentation of the genesis of observable geological and hydrological features whose origins are widely separated in geologic time. It is unreasonable to assume that all observable features are as active at the present time as they were formerly, especially when geological observation dictates otherwise. An example of such time-dependent variation in activity is the subsidence feature at WIPP-33. Chaturvedi and Channell (1985) argued that active dissolution is taking place because the depression is preserved. However, the demonstrably dominant process at WIPP-33 appears to be alluvial infilling of the depression (Bachman, 1985). The WIPP-33 feature has been proposed by Bachman (1981; 1985) as a source of the gypsum (now partially dissolved, leaving subsurface cavities) for the spring deposits along the eastern scarp of Nash Draw. Although this hypothesis has yet to be tested geochemically, the springs are not observably active now, and the faunal remains entrapped in the gypsite deposits indicate that they have not been active since the Pleistocene. The observations do not indicate that the WIPP-33 structure is totally inactive. They do, however, indicate that the present infilling rate exceeds any possible subsidence or collapse rate at WIPP-33, and that, if dissolution is still locally occurring in the gypsums adjacent to the Magenta, the fluid amounts involved are insufficient to support continued spring discharge within the eastern portion of Nash Draw.

Similarly, there are no high-energy streams in the northern Delaware Basin of southeastern New Mexico having the magnitude necessary to deposit the gravels of the widespread Gatuña Formation, which are interpreted to mark the course of the ancestral Pecos River more than 600 Ka ago when gradients were steeper, base level was higher, and there was more water available to both surface and subsurface by virtue of a wetter climate (Bachman, 1985).

The absence of karstic features east of WIPP-33 must not be taken to indicate a complete absence of active evaporite dissolution east of that point. As has already been noted, essentially all the aqueous [U] values within the Culebra appear to have been affected by evaporite dissolution, and even within Nash Draw, Rustler fluids appear to be unsaturated with respect to uranium species. Ongoing work indicates that, while most Culebra fluids appear to be approximately saturated with respect to both carbonate and gypsum, all Rustler fluids analyzed to date are undersaturated with respect to halite. Thus, it must be assumed that all Rustler fluids are presently capable of halite dissolution within the formation, even in the total absence of modern meteoric or surficial recharge.

4.9.2 Limitations to Steady-State Flow

In the isotopic record of Culebra groundwater there is evidence of groundwater that may have existed without surficial recharge for as long as tens of thousands of years (Lambert, 1987). This implies that groundwaters presently in the Culebra at the WIPP site have not resulted from modern vertical recharge. Under the assumption of steady-state confined flow, however, these fluids may result from water entering the system at some point, flowing to another point, and ultimately discharging; groundwater flow contemporaneous with recharge and discharge, all summing to zero net change in storage, is commonly called "steady state." In contrast to this traditional perception, Lambert and Harvey (1987) proposed that the Rustler groundwaters are actually draining from the rock without significant recharge at the WIPP site or anywhere else nearby, except in SWND. This work attempts to estimate the time required for uranium in Culebra water to travel eastward from an ancient recharge area in western Nash Draw in the direction of increasing A.R., since A.R. conventionally increases along the flow path (Osmond and Cowart, 1976). The flow direction has since changed in response to cessation of recharge and lowering of base level by erosion or dissolution toward the west; flow may also now be more southerly (Haug et al., 1987), toward a southeastern re-entrant of Nash Draw.

4.9.3 Flow Directions and Recharge Area

Probably one of the most obvious indicators that groundwater flow in the Culebra is not at steady-state is the distribution of [U] and A.R. We showed in Section 4.8 that it is not possible for the A.R.s observed at the WIPP site to have become as great as they are by evolving either from water having any [U] now observed in the Culebra, or in the presence of any typical Culebra rock. Superimposed on the A.R. systematics, which have a monotonic directionality over the WIPP site and Nash Draw, are the [U] systematics. While [U] monotonically increases toward the southwest in mimicry of the present general

flow direction, the A.R. values increase in a direction opposite or at least at angles to the prevailing flow. Whereas we can partially explain the westward increase in [U] and decrease in A.R. by increasing degrees of congruent dissolution of uranium from rock along the modern flow path, this does not account for the coincidence of the highest A.R. value (H-5) with the highest potentiometric levels and the lowest permeabilities. It also does not explain the origin of the high A.R. values. If the southwestward-flowing groundwater in the Culebra is progressively and congruently dissolving uranium and diluting the higher A.R. values to lower values, we suggest that the initial generation of high A.R. values arose from processes different from those now prevailing in the Culebra, perhaps under more oxidizing conditions now than formerly. We further suggest that the generation of high A.R. values took place during former geologic time intervals (e.g., the Pleistocene). For the rest of the discussion, we call the conditions under which the high A.R. values developed the "former flow system," versus the "modern flow system."

We have estimated the minimum time required for water in the former flow system to travel from the paleorecharge area (outcrops of the Rustler Formation in Nash Draw) downdip to what is now the WIPP site to be at least 10 to 30 Ka, based on the time required for A.R. values to build up from typical recharge values to those observed near the WIPP site today. This is an underestimate if the measured A.R. values were lowered from originally higher values due to congruent dissolution of uranium (as is supported by the relatively high [U] of most Culebra samples), or if intermittent episodes of A.R.-decay time are added to the time required for A.R.-buildup.

Given that A.R. values in confined systems generally increase in the direction of flow (Osmond and Cowart, 1976), and that the presently inferred flow direction in the Culebra is opposed or at least at high angles to the direction of increasing A.R. value, the groundwater flow must at one time have been in the direction of increasing A.R. value, toward the east. The occurrence of the highest A.R. value (H-5) in the region of lowest permeability suggests that H-5 may be near the eastward limit of groundwater movement in the former flow system. The most probable recharge area for the former flow system was outcrops of the Rustler Formation in what is now Nash Draw. Recharge was likely in that area many times during the Pleistocene, since Pleistocene-age high-energy stream deposits of the Gatuña Formation are preserved there (Bachman, 1985). Water from the ancestral Pecos River flowing over the Nash Draw area probably permeated the substrate by karstic processes described by Bachman (1984). With continued downcutting, evaporite dissolution, collapse, and lowering of base level, the Pecos River sought its present course further west, leaving Nash Draw. Karstification processes have continued within Nash Draw to a lesser degree since the climate became drier, but the area no longer is one of high potentiometric level. With the removal of high hydraulic potential from this area, the flow direction in the former flow system changed to become the modern flow system, flowing generally westward and southward toward Nash Draw. At present the ultimate base level for local flow within the Rustler remains unclear; it may lie within the Balmorhea-Loving Trough (cf. Lambert, 1983) southeast of the site. Hence, the system now appears to be draining, with only minimal sustained recharge entering the system (Lambert and Harvey, 1987; Lambert, 1987).

Some additional observations may relate to the drainage hypothesis: the distribution of water in the Magenta member, and the difference in potentiometric level between the Magenta and Culebra at the WIPP site. For many years (Mercer and Orr, 1979; Mercer and Gonzalez, 1981; Mercer, 1983) it has been known that the Magenta and Culebra members support potentiometric levels over much of the WIPP site that are significantly different from one another, with increasing head differences toward the east. The Magenta and Culebra heads are more similar over the western portion of the WIPP site, near Nash Draw. Furthermore, westward and northward into Nash Draw, the Magenta either does not contain any water (at WIPP-26, WIPP-28, and WIPP-30), is eroded away (at WIPP-29), or is hydraulically and geochemically indistinguishable from the Culebra (at WIPP-25 and WIPP-27). The last case is particularly anomalous, since the lobe of surviving water occurrences in the Magenta at WIPP-25 and WIPP-27 is bounded on both the northeast and southwest by dry regions. This itself severely limits the degree of uniform connectedness of the Magenta, because on the basis of field determinations of solutes (Lambert and Robinson, 1984), stable-isotopes in the water molecules (Lambert and Harvey, 1987), and now uranium (see Table 1), the Magenta and Culebra at WIPP-25 and WIPP-27 appear to be connected to each other, but function independently elsewhere. In fact, it is not obvious that the Magenta at WIPP-27 is hydraulically connected to the rest of the Magenta at WIPP-25, since the intervening area has experienced severe collapse in the Forty-niner and Tamarisk members stratigraphically adjacent to the Magenta (Bachman, 1981).

Closely related to the observed difference in Magenta and Culebra potentiometric levels is the difference in apparent flow directions inferred from potentiometric contours (Mercer, 1983): generally westward in the Magenta (until it is truncated by erosion) and generally southward in the Culebra. While the modern Culebra flow system appears to flow southward, the modern Magenta flow system appears to flow westward, in the same direction as indicated by the uranium distribution in the Culebra. Consequently, as many as three different flow directions may have developed sequentially in the Culebra at different times since the Pleistocene: (1) originally eastward, as preserved in the eastward-increasing Culebra A.R. values; (2) dominantly westward, as preserved in the westward-increasing Culebra [U] values in response to congruent dissolution, and in the westward-decreasing potentiometric levels in the Magenta; and (3) southward, as preserved in the modern potentiometric levels in the Culebra (Haug et al., 1987).

Mercer (1983) attributes the discharge from the Magenta to drainage into other Rustler members, due to an enhanced porosity of adjacent units arising from dissolution and collapse in Nash Draw. Thus, it is probably differential rates of drainage due to a profound permeability contrast, and not difference in elevation of postulated recharge areas, that accounts for the potentiometric differences between the Magenta and Culebra. Just as Mercer (1983) argued for drainage of the Magenta using physical observations, Lambert and Harvey (1987) argued for the drainage (i.e., minimal recharge) of the Culebra, based on isotopic data. The area of drainage from the Culebra into nearby units is developed farther down section than for the Magenta, because erosion by solution-and-fill (cf. Lee, 1925) has preferentially disrupted Magenta and adjacent rocks that are nearer the surface. Only where erosion has stripped the Magenta and brought the Culebra and underlying

rocks near the surface (in SWND and points west and south) could downward drainage out of the Culebra be similarly developed.

4.9.4 Paleoclimate and Drainage Time to Discharge Area

For the modern flow system that appears to be draining toward the south and west, we calculated an apparent maximum uranium travel time (and by inference, maximum travel time for groundwater) of 200 Ka from the WIPP site to a hypothetical discharge point near Surprise Spring. Based on other evidence, we do not regard SWND as a likely discharge area for Rustler groundwaters emanating from the WIPP site (Lambert and Harvey, 1987), although SWND may have been part of the recharge area for the former flow system, and may now contain a localized shallow groundwater system. A groundwater travel travel time of 200 Ka from the WIPP site may seem surprisingly long, but the possibility of such a long drainage time suggests an important consideration involving the dynamic nature of surface and subsurface hydrologic systems: the control of climate over water supply and flow.

Figure 17 tabulates the cause (climate) and effects (types of deposits and estimated elevations of base level) of changes in surface hydrology for the Quaternary Period. Several alternating cycles of wetter and drier climate are evident in southeastern New Mexico. The number and duration of these wet/dry cycles is uncertain, since the geologic record is incomplete.

Figure 17 shows that there are at least two times in the Pleistocene when the climate was significantly wetter: the interval 20 to 200 Ka BP (before present), and some interval earlier than 600 Ka BP. We shall refer to the former interval as late Pleistocene time, and to the latter as Gatuña time.

Although we do not know how far back in time (beyond 10,000 years BP) the late Pleistocene humid period extended in southeastern New Mexico (cf. Van Devender, 1980; Bachman, 1981), we know that just before this time a semi-arid to moderate climate prevailed, lasting about 150 Ka (the time span apparently covered by the formation of the Mescalero caliche and the Berino soil). Thus, the two humid periods (late Pleistocene and Gatuña time) are separated by about 150 Ka. Similarly, we do not know how long the humid Gatuña time lasted; the beginning of it may be as old as Ogallala time (Pliocene).

In any case, the apparent maximum drainage times of the Culebra from the WIPP site to Nash Draw of a few hundred thousand years could imply that the recharge event that introduced a slug of water into the Culebra and Magenta from the west had its source shut off as early as 200 Ka BP, exclusive of travel time through Nash Draw. After the cessation of that recharge, the gradient and flow directions would have reversed as base level dropped and/or the climate became too dry to support a sufficiently high potentiometric level in outcrop areas updip to the west; diminished potentiometric levels in areas of former recharge would no longer have induced a significant rate of recharge. If we assume that the source of this water was infiltration from the part of the ancestral Pecos River

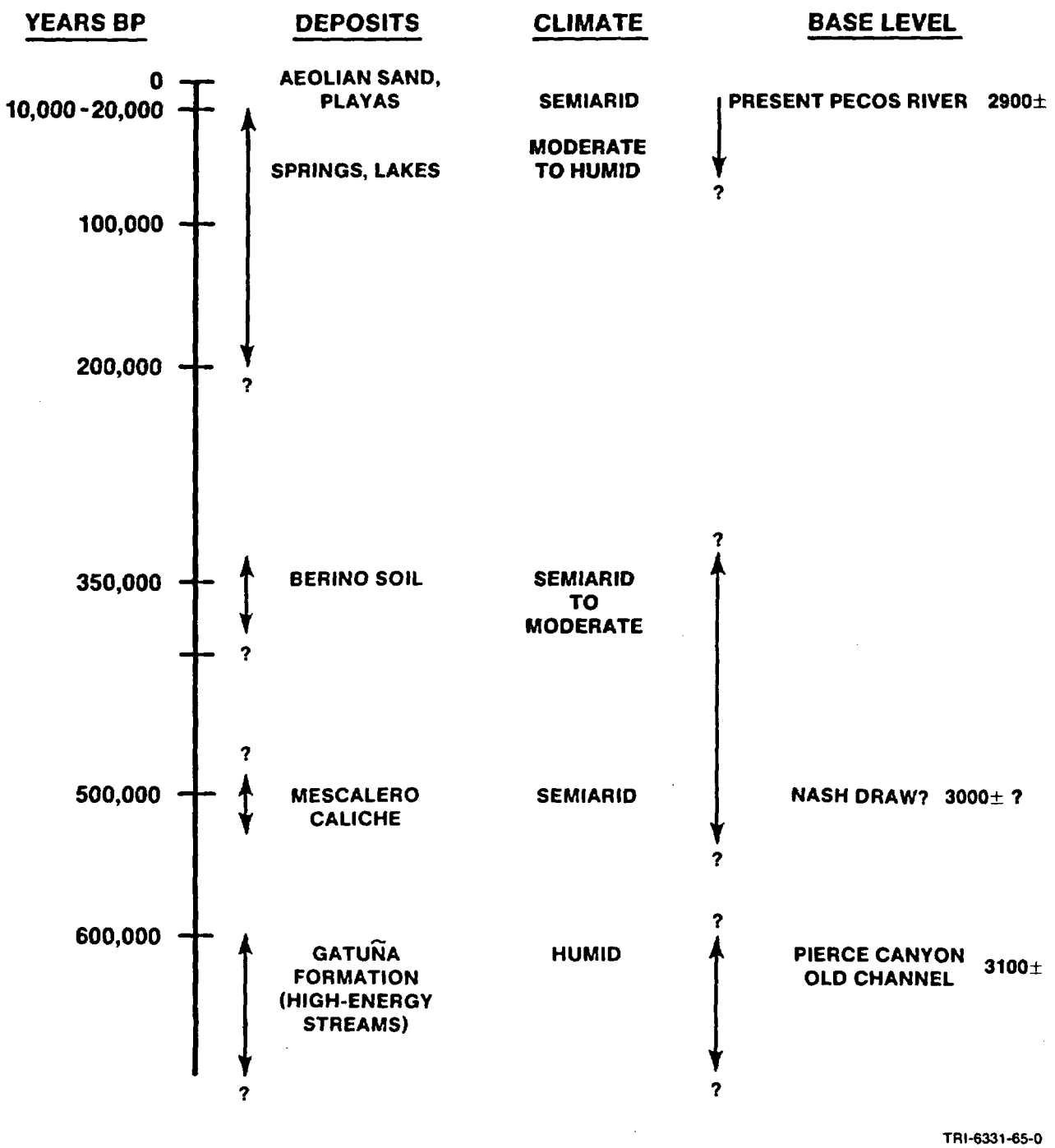

Figure 17. Diagram of variations in type of surficial deposits, climate necessary to produce them, and inferred base level at various times since the middle Pleistocene in southeastern New Mexico. Several intervals in the Quaternary have been more favorable to groundwater recharge than the present, due to a greater abundance of rainfall in the past.

system that flowed through Nash Draw over the present Rustler outcrops, and that karst-type mechanisms of recharge from riverbed to groundwater prevailed as postulated by Bachman (1984), then the drainage time between several thousand and a few hundred thousand years, based on uranium-isotope disequilibrium (i.e., travel time from recharge to the WIPP site and then back to old point of original recharge) is consistent with a major episode of recharge during the climatically wetter Pleistocene Epoch. Recharge from the west, followed by a reversal of flow and drainage back to the west, taking place at different rates in different parts of the Rustler Formation, would account for several hydrologic and geologic observations:

- Preservation of the higher potentiometric levels to the east, where there is lower permeability and no apparent modern recharge

- Preservation of significant differences in potentiometric levels between the Magenta and Culebra groundwater over much of the WIPP site (the Magenta having lower overall permeability, greater impedance to groundwater flow, and hence the higher potentiometric level)

- Preservation of a more intact evaporite section to the east, where less dissolution has apparently taken place.

This last observation is exactly the opposite of what one would expect if active recharge were coming from the east and dissolution were active there; one would normally expect the most dissolution to have taken place upgradient near the source of fresher-water recharge, and to have tapered off downgradient as the solutions become more concentrated in soluble evaporite constituents. This last premise is of course dependent on the degree of access of groundwater to the soluble evaporites, which may in turn be a function of local permeability of rock adjacent to the water-bearing unit (cf. Lambert, 1983).

5. CONCLUSIONS

In this study we have estimated the **maximum** drainage time of the Culebra along a flow path between its least permeable reaches in the east part of the WIPP site and its most permeable reaches in southwestern Nash Draw near Laguna Grande de la Sal and Surprise Spring. This time estimate, about 200 Ka, does not include any travel time in the currently high-permeability region of Nash Draw. Similarly, this time estimate does not presume any particular recharge or discharge point or mechanism; it is independent of flow direction inferred from potentiometric contours alone, but is dependent on a particular model describing uranium-isotope behavior along a flow path. The uranium contours in the Culebra indicate that some component of travel was dominantly to the west, with progressively westward-increasing values of total dissolved uranium ([U]) acquired from dissolution of uranium from rock encountered along the flow path. The [U] contours in the Culebra correspond well with the potentiometric levels in the Magenta, which are consistent with more westward flow than the significantly southward flow presently observed in

the Culebra near the WIPP site. One possible explanation is that, because of its lower permeability, the Magenta has been slower than the Culebra to readjust its potentiometric levels in response to changes in local base level due to erosion or evaporite dissolution, which have probably been responsible for the development of subsurface drainage-discharge. The uranium-concentration contours in the Culebra have not adjusted to the change in principal discharge area and dominant southward flow direction, whereas the potentiometric contours have (Haug et al., 1987).

We regard the uranium-isotope contours in the Culebra as relict indicators of a former eastward flow regime, which was established at the time when surface drainage in Nash Draw controlled groundwater recharge to the Rustler outcrops there, before the present Pecos River had lowered the base level to capture the inferred present discharge at Malaga (Robinson and Lang, 1938; Hale et al., 1954). The minimum travel time required to flow from the inferred paleorecharge areas west of the WIPP site to the area near the WIPP site, based on the time required to establish the observed high A.R. values, is about 10,000 to 30,000 years. This travel-time estimate between likely paleorecharge areas and the WIPP site is based on time required for uranium isotope A.R.s to reach values as high as 11, as observed in the less permeable portions of the Culebra at the WIPP site. This estimate is an absolute minimum, given the several processes, such as congruent dissolution of uranium from rock and mixing of aqueous uranium reservoirs, that tend to make the results of such calculations spuriously young. The time required for A.R. values to become as high as 11 is appreciably long, regardless of actual point of recharge. A sustained supply of modern meteoric water directly recharging the Rustler at the WIPP site would perturb several solution parameters, including stable-isotope ratios, tritium, and radiocarbon (Lambert and Harvey, 1987; Lambert, 1987). The perturbations to the uranium isotope A.R.s would be a sustained supply of oxygenated water, effectively "killing" the recoil-leach mechanism that allows A.R. values to build up to high levels in the reducing zone (Zone II in Figure 1), and congruent dissolution of uranium from rock, without isotopic fractionation, rapidly lowering the high A.R. values that were attained before the recoil-leach mechanism was killed (Zone IIIB in Figure 1). Such a resultant lowering of A.R. value has not been observed where the potentiometric level is highest and the permeability is lowest in the Culebra at the WIPP site (H-5). Consequently, the modern flow system is not being recharged at H-5, in spite of the high potentiometric level there, but is draining away from that area.

The minimum travel times calculated according to the Zone-II model, between the recharge area and any given point are the same, given the same inferred initial [U] and A.R. values in water and rock, regardless of the recharge area. Even if the major recharge area for the Rustler Formation is indeed Bear Grass Draw (35 to 40 miles north-northwest of the WIPP site) as proposed by Robinson and Lang (1938), the inferred initial conditions for A.R. buildup are the same, and the systematics for total uranium and A.R. evolution are the same as in Figure 1. Nevertheless, the uranium-isotope data are not consistent with travel times significantly less than 10,000 to 30,000 years from any area of Rustler recharge, given a reasonable set of inferences about the dominant geochemical conditions in an

active recharge zone. Calculated travel time is an underestimate if (1) congruent dissolution of rock uranium has prematurely lowered the aqueous A.R.s from an originally higher value while increasing [U], or (2) decay of ^{234}U has lowered the observed A.R.s from originally higher values, while minimally affecting the [U], or (3) the assumed porosity of 26% and the leachable surface area used in calculating required A.R.-buildup times are actually significantly smaller.

Changes in Culebra flow direction consistent with uranium and uranium-isotope distributions, and calculated times required to achieve the observed groundwater A.R. values indicate that the Rustler hydrology at and near the WIPP site is not at steady state on the time scale of approximately 10,000 to 30,000 years, and there are probably three general flow directions that must be considered in evaluation of the hydrologic history of the Rustler Formation during the past 10,000 to 30,000 years. These general flow directions are (1) eastward during a recharge interval at least 10,000 to 30,000 a before present, during which high values of A.R. were achieved downgradient in the groundwater system, (2) westward for some time after the cessation of recharge, the time period being sufficient to essentially establish the present [U] distributions, and (3) a recently established southern potentiometric gradient for hydraulic flow (Haug et al., 1987), especially near the WIPP site proper. The limited evidence available indicates that this last change is recent enough not to have reoriented the total-dissolved-uranium and uranium-isotope distributions.

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