X tia

URANIUM ISOTOPE DISEQUILIBRIUM
IN GROUNDWATERS OF SOUTHEASTERN NEW MEXICO
AND IMPLICATIONS REGARDING AGE-DATING OF WATERS

by

G. E. Barr
Steven J. Lambert
(Sandia Laboratories)

and

Joel A. Carter
(Oak Ridge National Laboratory)

URANIUM ISOTOPE DISEQUILIBRIUM IN GROUNDWATERS OF SOUTHEASTERN NEW MEXICO AND IMPLICATIONS REGARDING AGE-DATING OF WATERS

G. E. BARR, S. J. LAMBERT
Sandia Laboratories, Albuquerque, New Mexico, USA
J. A. CARTER
Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

ABSTRACT

Regional exploration of bedded salt for a radioactive waste repository in the Delaware Basin (Permian, New Mexico, USA) included boreholes into the evaporites and associated rocks. One such hole, ERDA No. 6, encountered an accumulation of saturated $NaCl-Na_2SO_4$ brine accompanied by H_2S-rich gas. This fluid and fluids from other boreholes elsewhere in the area have been characterized geochemically according to solute content, $^{18}O/^{16}O$ and D/H ratios and natural actinide content. Deviations from the equilibrium $^{234}U/^{238}U$ activity ratio (α) of 1.0 were found in all water samples. These deviations are used to affirm the isolation of ERDA No. 6 and to establish bounds on the age of the ERDA No. 6 fluid.

A mathematical model for the age of ERDA No. 6 water intrustion was formulated in terms of the following variables: initial α-value (α_0) of the brine precursor waters, zero order kinetic rate constants of leaching of ^{234}Th and ^{238}U from the rocks, and degree of leaching of ^{234}Th from the rocks. The model allows calculation of α-values of brines as a function of time, leach rate and α_0. Various combinations of α_0's, leach fractions and leach rates indicate that the leach rate must be low. If no leaching is assumed and the α_0 is the highest known α from the nearby Capitan Reef ($\alpha_0 = 5.2$ at present), the fluid is older than 880,000 years. ERDA No. 6 brine has undergone more profound rock/fluid interactions, reflected in its solutes and stable isotopes, compared with younger meteoric Capitan waters.

1. INTRODUCTION

1.1 History

Regional exploration of bedded salt deposits for a radio-active waste repository in the Delaware Basin (Permian, New Mexico) included boreholes into the evaporites and associated rocks. These rocks contained various amounts of fluids, already described [1]. Although the halite deposits of the Ochoan Epoch are the prime target of consideration for waste storage, the older rocks of the Guadalupian Epoch are included in the present study, because of the Capitan reef, a body of cavernous limestone which encircles the Basin. The Capitan not only is the dominant rock in the Carlsbad Caverns, but also supplies potable water to the city of Carlsbad. Therefore, it is appropriate to consider possible connections between the Capitan and accumulations of water found in pockets in the evaporites. Brine and gas pockets are known to occur in the Carlsbad district potash mines and in the Castile Formation (anhydrite and halite) underlying the Salado Formation.

One exploration hole, ERDA No. 6, drew national attention [2], when it encountered an accumulation of saturated NaCl brine laced with Na_2SO_4, accompanied by H_2S-rich gas at 826 m below the surface. Discovery of this artesian fluid, together with bedding-plane dips in the host Castile Formation exceeding 70°, led to abandonment of that immediate site. Geophysical investigations showed that this and other occurrences of brine and gas were associated with closed structure contours drawn for the Castile Formation. These structures, restricted to a narrow strip of evaporites near the reef have been termed "salt anticlines" [3]. Core from the fluid-producing zone of ERDA No. 6 consisted of gray laminated anhydrite whose fractures were filled with massive crystalline white anhydrite (Plate 1). While fluid accumulations are not rare in evaporites, the possible use of the region for radioactive waste disposal requires attention to the origin of this particular type of accumulation. In the extreme cases, the fluid originates directly from water from the Capitan Reef, or the water was entrapped in the Castile Formation at the time of evaporite deposition in the Permian. In the first case, the water would have an age little older than Capitan waters. In the second case, the water would be in excess of 230 million years old.

1.2 Implications

Indeed, the very presence of the ERDA No. 6 accumulation of fluid poses several questions:

1. How long has the water been confined in the pocket?

2. Does the time of the water's intrusion correspond to any significant known geologic events?

3. What is the source of the water?

4. How long has this pocket been disconnected from nearby aquifers such as the Capitan Reef, if it ever was connected?

5. What are the limits to rates of influx (if any) or recharge and discharge (if any) of this fluid pocket?

6. To what degree does the ERDA No. 6 occurrence (or any other in the area) represent a flowing system?

7. Which radiometric clock should be used to age-date the water and what should be taken as initial conditions for age-dating?

2. ANALYTICAL APPROACH

2.1 General Geochemistry of Groundwaters

A number of groundwaters from the Delaware Basin have been characterized in terms of their general geochemistry with respect to their host rocks [1]. In terms of solutes, the waters from below the fresh-saline interface in the Capitan were similar to each other. In addition the shallow ($\leq$300 m depth) waters were similar to one another and all deep ($\geq$1000 m depth) waters were similar to one another. The ERDA No. 6 water was unique in its solute content, indicative of pronounced disequilibrium between solution and host rock and also between solution and associated gas phase.

In terms of D/H and $^{18}O/^{16}O$ ratios, Capitan and shallow waters all are similar and are of meteoric origin. (Carlsbad Caverns waters are also of meteoric origin, but are not related to other waters in the Capitan.) Deep water stable isotope ratios are similar to one another, and are not characteristically meteoric. ERDA No. 6 has uniquely non-meteoric isotopic ratios among those of Delaware Basin waters. No waters were found which represent original evaporite mother-liquor.
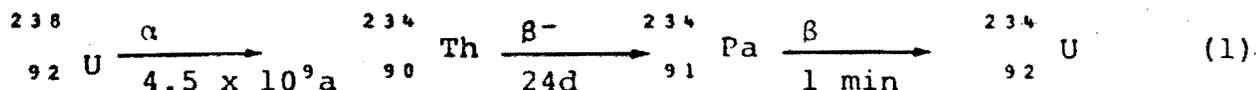
2.2 Experimental Procedures

In spite of the evidence that this fluid has experienced strong interactions with rock [1], radioisotopes were examined to establish that the ERDA No. 6 fluid was not of relatively recent origin. Plutonium concentration was determined by isotope dilution employing a spike of ^{244}Pu. The actual measurement was made on a three-stage thermal emission solid source mass spectrometer equipped with pulse counting for ion detection. The instrument has a very high abundance sensitivity (10^7) and low background, allowing for the determination of

precise isotopic ratios on small samples amounting to 0.1 to 1 nanograms of plutonium. The plutonium concentration of the ERDA No. 6 brine was found to be less than 10^{-15} grams per gram, corresponding to the lower limit of analytical detectability. The absence of plutonium suggests the brine has been isolated at least since 1945, a date corresponding to the first atmospheric detonation of nuclear weapons.

Carbon 14 was measured in the CO_2, which amounted to 55% of the total gas collected from ERDA No. 6. Carbon 14 content was counted in a gas proportional detector whose efficiency was calibrated with the NBS oxalate standard. The result was the same as the background, which was about 2 counts per minute in a 1.5 liter detector at 2 atmospheres pressure. From this it was concluded either that the brine is older than about 30,000 years or possibly that carbonates in the host rock have diluted the carbon in the system with non-radioactive carbon.

The disequilibrium of the activity of ^{234}U relative to ^{238}U in natural waters has been attractive as an indicator of the age of groundwaters [4]. ^{234}U and ^{238}U are related by the decay scheme:

$$^{238}_{92}U \xrightarrow[4.5 \times 10^9 a]{\alpha} {}^{234}_{90}Th \xrightarrow[24d]{\beta^-} {}^{234}_{91}Pa \xrightarrow[1\ min]{\beta} {}^{234}_{92}U \qquad (1)$$

It has been proposed that excess ^{234}U builds up in confined waters as an aging effect as a result of the alpha-recoil of ^{234}Th, which ejects ^{234}Th out of the host rock crystal lattice into the water [5,6]. From a knowledge of decay constants and initial activity ratio α_0 ($\alpha = {}^{234}U/{}^{238}U$ activity ratio), time of confinement is calculated. It cannot be assumed, however, that the earth's natural abundance ratio, $\alpha = 1.00$, is a priori valid for a confined rock-water system. The water carried in with it an initial uranium concentration and original activity ratio, α_0. The water ultimately comes to thermodynamic equilibrium with its host rock and may leach or even deposit ^{234}U and ^{234}Th. Uranium concentrations and α-ratios of rocks and waters in this study were determined by isotope dilution mass spectrometry, described above. Figure 1 shows the locations of principal water samples of this study. Table I shows uranium concentrations and values of α for various waters.

3. RESULTS AND DISCUSSION

The overleaf of Plate 1 shows the variations of U content and α in anhydrite of rock core taken from the zone which produced fluid in ERDA No. 6 (826 m, 2709 ft depth). Table I results show that in ERDA No. 6, both U concentration and α vary with time, until U concentration falls asymptotically to about 2 parts in 10^9, and α rises asymptotically to about 1.35. In the early part of a several-hour flow test, water samples were

found to be contaminated with drill mud and spallations from metal pipe. By 1400 hours not only had the uranium reached steady state values, but the iron concentration had fallen from 260 parts in 10^6 (1130 hours) to a steady value of 5 parts in 10^6 (1400 hours), indicating the flushing out of drilling-introduced contaminants. Thus, the later samples are probably representative of the fluid accumulation.

The total variation in α among all water samples is relatively small (1.2 to 5.2). In contrast, absolute uranium content in the waters of Table I varies by more than two orders of magnitude. Similarly, rock material illustrated in Plate 1 shows a wide variation in U content: 1 to 2 parts in 10^6 for "original" laminated gray anhydrite down to 20 to 30 parts in 10^9 in the secondary white anhydrite fracture filling only a few centimeters away.

4. APPLICATION OF THE URANIUM ISOTOPE DISEQUILIBRIUM MODEL

If N_2 is the amount of ^{234}U present in a phase, and N_1 is the amount of ^{238}U, the change in ^{234}U content with time in the brine is

$$\left(\frac{dN_2}{dt}\right)_{brine} = \lambda_1 N_1 - \lambda_2 N_2 + Q_1 + Q_2, \tag{2}$$

in which Q_1 is the rate of release of ^{234}Th (the parent of ^{234}U) from the rock, Q_2 is the rate of release of ^{234}U from the rock and λ_1 and λ_2 are decay constants for ^{238}U and ^{234}U, respectively. Release rates Q_1 and Q_2 can be modeled in the fashion of Kigoshi [5], who studied the release of ^{234}Th from zircon powder. He gave the accumulated activity of ^{234}Th in solution after time t as

$$(\lambda_{Th} N_{Th})_{brine} = 1/4 \ L \ S\rho \ (N_{238} \ \lambda_1)_{rock} \ (1 - e^{-\lambda_{Th} t}), \tag{3}$$

in which λ_{Th} is for ^{234}Th, L is the recoil distance of ^{234}Th in decay scheme (1) above, S is the surface area of parent rock, ρ is its density, and N_{238} is expressed as the number of ^{238}U atoms per gram of rock. Thus, the activity of ^{234}Th in the brine is related to the activity of ^{238}U in the rock by a proportionality constant, and, of course, the time-dependent term. When t >> 24 days, (3) can be approximated as

$$(\lambda_{Th} N_{Th})_{brine} \approx f_1 \cdot (\lambda_1 N_1)_{rock}, \tag{4}$$

in which f_1 is now the leach fraction of ^{234}Th, incorporating $1/4 \ L \ S\rho$ in (3). In general, ^{238}U activities in rock and co-existing brine will not be equal, but will be related by a distribution coefficient r, which is theoretically an equilibrium constant, neglecting the kinetics of dissolution and

precipitation:

$$(\lambda_1 \ N_1)_{rock} = r \ (\lambda_1 \ N_1)_{brine} \tag{5}$$

In actual fact, the time required to achieve chemical equilibrium between rock and brine might be very long relative to the half-life of ^{234}Th. Q_1 now becomes

$$Q_1 = r \cdot f_1 \cdot (\lambda_1 \ N_1)_{brine} \tag{6}$$

Similarly, the amount of ^{234}U released is dependent on the decay of its precursor ^{238}U, and on the equilibrium ratio r, and on the leach fraction for ^{234}U, f_2:

$$Q_2 = r \cdot f_2 \cdot (\lambda_1 \ N_1)_{brine} \tag{7}$$

In addition, some fraction, f_3, of the ^{238}U will be leached from the rock,

$$\lambda_1 \ N_1 \rightarrow r \cdot f_3 \cdot (\lambda_1 \ N_1)_{brine} + (\lambda_1 N_1)_{brine} \tag{8}$$

Now, equation (2) becomes:

$$\left(\frac{dN_2}{dt}\right)_{brine} = (\lambda_1 \ N_1)_{brine} \left[1 + r \ (f_1 + f_2 + f_3)\right] - \lambda_2 \ N_2 \tag{9}$$

If f is defined as a composite leach fraction $(f_1 + f_2 + f_3)$, the solution to (9) is:

$$N_2(t) = \frac{\lambda_1}{\lambda_2 - \lambda_1} \ (1+fr) N_1(t) + N_1(t=0) \ \frac{\lambda_2 N_2(t=0)}{\lambda_1 N_1(t=0)} \ \frac{\lambda_1}{\lambda_2} \ (1+fr) \ e^{-\lambda_2 t} \tag{10}$$

which allows us to express the solution in terms of $\alpha = \frac{\lambda_2 N_2}{\lambda_1 N_1}$:

$$\alpha_{brine} = \frac{\lambda_2}{\lambda_2 - \lambda_1} \ (1 + fr) + \left[\alpha_0 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \ (1 + fr)\right] e^{-(\lambda_2 - \lambda_1)t} \tag{11}$$

and since $\lambda_2 \gg \lambda_1$

$$\alpha_{brine} \approx 1 + fr + \left[\alpha_0 - 1 + fr\right] e^{-\lambda_2 t} \approx \alpha_b \tag{12}$$

The corresponding equation for the rock is:

$$\left(\frac{dN_2}{dt}\right)_{rock} = \lambda_1 \ (1 - f) \ (N_1)_{rock} - \lambda_2 \ (N_2)_{rock} \tag{13}$$

Since for a closed system, the $^{234}U/^{238}U$ equilibrium activity ratio is 1.000, the solution to (13) is:

$$N_2(t)_{rock} = \frac{\lambda_1}{\lambda_2-\lambda_1}(1-f)N_1(t)_{rock} + \frac{\lambda_1}{\lambda_2}N_1(0)_{rock}e^{-\lambda_2 t}$$

$$- \frac{\lambda_1}{\lambda_2-\lambda_1}N_1(0)_{rock}(1-f)e^{-\lambda_2 t} \tag{14}$$

which in terms of α is

$$\alpha_{rock} = \frac{\lambda_2}{\lambda_2-\lambda_1}(1-f) + e^{-(\lambda_2-\lambda_1)t} - \frac{\lambda_2}{\lambda_2-\lambda_1}(1-f)e^{-(\lambda_2-\lambda_1)t} \tag{15}$$

The approximation $\lambda_2 \gg \lambda_1$ reduces the equation (15) to

$$\alpha_{rock} \approx 1 - f + f\,e^{-\lambda_2 t} \approx \alpha_r \tag{16}$$

Let us now assume that the geochemical conditions (i.e. U content and α) observed in the ERDA No. 6 rock-fluid assemblage represent equilibrium conditions. This requires the mutual consistency of equations (12) and (16), and that

$$f = \frac{(\alpha_0 - 1)(\alpha_r - 1)}{\alpha_b - \alpha_0 + r(\alpha_r - 1)}. \tag{17}$$

Anhydrite found in the veins is the most recently formed phase in the core, and using the U values from 2709.4 white anhydrite (U = 33 parts in 10^9, α = 1.04; Plate 1 overleaf), and the averages of the last two ERDA No. 6 brines in Table I, (U = 2.01 parts in 10^9, α = 1.35) equation (17) gives rise to the plot in Figure 2. Note the prominent singularity at α_0 = 2.01, and that $\alpha_0 \leq 1.971$ at f = 1 (corresponding to 100% leaching, and $\alpha_0 \geq 2.052$ at f = -1 (corresponding to all the uranium in the rock having precipitated from the brine).

Solving equation (12) for t, we obtain an expression for the age of the brine:

$$t = \frac{\ln\left(\dfrac{\alpha_b - 1 - fr}{\alpha_0 - 1 - fr}\right)}{-\lambda_2}. \tag{18}$$

For values of $\alpha_0 \leq 1.971$, negative ages result. Only for values of $\alpha_0 \geq 2.052$ are realistic ages obtained. This result implies that there has been minimal leaching from the rock. Furthermore, it suggests rather than precipitation of uranium has occurred from brine to rock which is consistent with reducing conditions implied by the presence of H_2S.

Clearly, the amount of precipitation which has occurred (negative leaching), is related to the original α at the time of closure of the rock-fluid system.

Values of α for nearby waters in the Capitan limestone (Table I) which by proximity afford the most likely ultimate source of water for the ERDA No. 6 brine pocket, mostly have α values in excess of 1.35. In addition, the ERDA No. 6 brine is not saturated in $CaSO_4$ [1], and is not likely to have been responsible for the precipitation of substanial amounts of vein anhydrite. Furthermore, the limited volume of the brine pocket [7] could not realistically be expected to dissolve and reprecipitate anhydrite in veins to the extent observed in the core. Therefore, the α_0 of the ERDA No. 6 brine must have been larger than 2.052, with very little interaction with the reservoir rock.

5. MODEL AGES BASED ON NO LEACHING

Values of α and α_0 will in this model allow an age determination of a water to be made. The highest value thus far determined is 14.2, the result of isotope dilution mass spectrometry on a sample from Israel supplied by J. Kronfeld. Its α value was 10.1 ± 1.6 by alpha-spectroscopy [6]. In addition, the occurrence of waters elsewhere in the Delaware Basin (Table I) suggests that a reasonable α_0 value might be 5.14 (in the Capitan limestone), the highest thus far found in the Basin. If the ERDA No. 6 brine represents water escaped from the Capitan, and its α_0 was on the order of 5, Figure 2 shows that its interaction with the ERDA No. 6 reservoir rock (fractured Castile anhydrite) precipitated less than 6% of the rock's uranium from the brine.

Neither total concentration nor isotopic composition of uranium in the ERDA No. 6 brine was inherited through interaction with the Capitan limestone, for the ERDA No. 6 brine contains substantially more uranium than the Capitan waters (Table I) presently do. Likewise, uniformity in the stable isotope composition of Capitan waters [1] shows that the peculiar stable isotope composition of ERDA No. 6 water cannot have arisen by interaction with the Capitan limestone. Composition of stable and unstable isotopes in ERDA No. 6 brine might have arisen from interaction between water and rocks encountered by the water as it moved from the Capitan to its ERDA No. 6 environment.

In its simplest form, equation (18), under conditions of no interaction between ERDA No. 6 brine and its reservoir rock, reduces to:

$$t = \frac{\ln\left(\dfrac{\alpha_b - 1}{\alpha_0 - 1}\right)}{-\lambda_2} \tag{19}$$

which very nearly corresponds to the combination of the solutions to the equations

$$\frac{dN_1}{dt} = - \lambda_1 N_1$$

$$\frac{dN_2}{dt} = - \lambda_2 N_2 + \lambda_1 N_1$$

for which

$$t \approx \frac{\ln\left(\frac{\alpha_b - 1}{\alpha_0 - 1}\right)}{- \lambda_2 + \lambda_1} \quad . \tag{20}$$

The above conclusions allow limits to be assigned to the age of confinement of the ERDA No. 6 brine, and also to ages of waters in the Capitan. Equation (2) differs from equation (19) only by the approximation that

$$\frac{\lambda_2}{\lambda_2 - \lambda_1} \approx 1,$$

since $\lambda_2 = 2.806 \times 10^{-6} a^{-1}$ for ^{234}U

and $\lambda_1 = 1.537 \times 10^{-10} a^{-1}$ for ^{238}U.

Figure 3 shows the family of curves obtained from equation (20), using observed values of α from Table I, and various values for α_0. The model ages indicated on Figure 2 for the ERDA No. 6 brine are less than those in Figure 3 because 4 to 5 percent interaction between brine and rock (uranium precipitation) involves loss of uranium from solution by means other than radioactive decay. There is no evidence for any degree of chemical equilibrium between ERDA No. 6 rock and fluid. If we realistically limit f (Figure 2) to have a value between -0.02 and -0.05, the minimum age of the ERDA No. 6 occurrence is 570,000 years ($\alpha_0 = 6$). If in actual fact, as the data of Kronfeld et al (1975) suggest, maximum α_0 values are universally in the range 10 to 15, the age is between 800,000 and 1,000,000 years. According to the no-interaction model, (Figure 3), water could have escaped from the Capitan ($\alpha_0 = 5.14$) into the brine pocket 880,000 years ago. The highest α_0 value (14.2) confirmed by isotope dilution mass spectrometry gives an age of 1,300,000 years.

If the Carlsbad area (near the Pecos River) is a major recharge area for much of the Capitan reef, and if Carlsbad water ($\alpha_0 = 5.14$) is the basis for age-dating other waters in the Capitan, ages between 300,000 and 1,100,000 years are obtained. The maximum α_0 (14.2) would imply that Capitan waters are at least 400,000 years old.

6. IMPLICATIONS AND CONCLUSIONS

A mathematical model based upon analytical data has showed that the ERDA No. 6 occurrence of brine can be age-dated by the uranium-disequilibrium method. Combinations of leach fractions and ages could be derived, and the interaction between rock and fluid was indicated to be minimal. If the brine pocket was once connected to the Capitan Reef, the most productive aquifer in the region, such connection was severed at least 500,000 years ago, and probably more than 900,000 years ago. The brine pocket has been stagnant ever since, and there is little evidence to indicate that chemical equilibrium has been established among the solid, liquid and gaseous phases involved in the brine pocket.

Even though the α value of the ERDA No. 6 brine was close to those of nearby meteoric waters taken from the northern apex of the Capitan Reef, these α values are far removed from those of more remote meteorically-derived saline Capitan waters from the east and west arms of the reef (Carlsbad No. 7 and Shell No. 28). In fact, the remote waters appear to be younger than apex waters (Hackberry and Middleton), implying that ground-water flow in the reef is indeed toward the apex and recharge is in the east and west part of the reef.

Fresh and saline Capitan Reef waters have retained their meteoric D/H and $^{18}O/^{16}O$ ratios, even though the ages of some of them are comparable to that of ERDA No. 6. Although reef apex waters and ERDA No. 6 brine are radiometrically similar, the solutes and stable isotopes of ERDA No. 6 reflect a more profound rock/fluid interaction than Capitan waters have experienced. This interaction, however, is more likely to have taken place in rocks between the Capitan and the brine pocket than in the brine pocket itself.

The ERDA No. 6 reservoir rock has not replenished ^{234}U to the brine in spite of long contact. Furthermore, uranium mobility into the white recrystallized anhydrite from the gray laminated anhydrite was shown to be very low in this anoxic environment.

Dating by the uranium-disequilibrium method is not necessarily dependent on a closed system, and bounds on ages can be assigned. Requirements for $^{234}U/^{238}U$ dating include: α values of fluid and rock, leach rate, and knowledge of a value for original activity ratio, α_0. The α value for the rock is necessary to evaluate the degree of rock-fluid disequilibrium. The leach rate might be negligible even in a closed system. A unique solution to an age-dating problem, however, requires knowledge of initial conditions, just as in the case of the well-established uranium-lead and carbon 14 age-dating techniques.

ACKNOWLEDGEMENT

REFERENCES

[1] Lambert, Steven J., "The geochemistry of Delaware Basin groundwaters" (New Mexico Bur. Mines and Min. Res. Circ. 159, in press, 1978).

[2] Boffey, Philip M., Radioactive waste site search gets into deep water, Science 190 (1975) 361.

[3] Anderson, Roger Y., and Powers, Dennis W., "Salt anticlines in the Castile-Salado evaporite sequence, northern Delaware Basin, New Mexico" (New Mexico Bur. Mines and Min. Res. Circ. 159, in press, 1978).

[4] Osmond, J. K., and Cowart, J. B., The theory and uses of natural uranium isotopic variations in hydrology, Atomic Energy Review 14 (1976) 621.

[5] Kigoshi, Kunihiko, Alpha-recoil thorium-234: dissolution into water and the uranium-234/uranium-238 disequilibrium in nature, Science 173 (1971) 47.

[6] Kronfeld, J., Gradsztajn, E., Müller, H. W., Radin, J., Yaniv, A., Zach, R., Excess ^{234}U: an aging effect in confined waters, Earth Planetary Sci. Letters 27 (1975) 342.

[7] Griswold, George G., Site selection and evaluation studies of the Waste Isolation Pilot Plant (WIPP), Los Medaños, Eddy County, New Mexico, Sandia Laboratories, SAND77-0946 (1977).

TABLE I

URANIUM CONCENTRATIONS AND ISOTOPIC RATIOS IN DELAWARE BASIN WATERS

Sample	U Concentration	α ($^{234}U/^{238}U$)	$\delta^{18}O$(SMOW) ‰	δD(SMOW) ‰
Shell	0.60 parts in 10^9	2.75	−7.7	−56
Middleton	0.54 parts in 10^9	1.81	−7.5	−55
Hackberry	0.02 parts in 10^9	1.22±0.05	−6.5	−46
Carlsbad 7	0.05 parts in 10^9	5.14	−7.9	−54
ERDA 6 1140 hr.	89 parts in 10^9	1.11±0.04		
ERDA 6 1212 hr.	4.8 parts in 10^9	1.26±0.05		
ERDA 6 1445 hr.	2.14 parts in 10^9	1.37±0.07	+10.3	0
ERDA 6 1520 hr.	1.88 parts in 10^9	1.33±0.07		
ERDA 6 Drill Mud	67.2 parts in 10^9	1.19		
Brine Lake (Mud Ingredient)	56.3 parts in 10^9	2.04		

FIGURE CAPTIONS

Figure 1:   Map of a portion of the Delaware Basin (southeast New Mexico, west Texas) showing locations of holes whose fluids were sampled for $^{234}U/^{238}U$-disequilibrium age-dating. The brick-pattern shows the surface projection and outcrop of the Capitan reef limestone. (from Hiss, 1975)

Figure 2:   Graph of the equation $f = \dfrac{(\alpha_o - 1)(\alpha_r - 1)}{\alpha_b - \alpha_o + r(\alpha_r - 1)}$

for the ERDA No. 6 assemblage of rock and brine, in which $r = 16.42$, $\alpha_r = 1.04$, $\alpha_b = 1.35$.

Uranium disequilibrium ages for the brine are shown according to the equation

$$t = \frac{\ln\left(\dfrac{\alpha_b - 1 - fr}{\alpha_o - 1 - fr}\right)}{-\lambda_2}$$

Note that the ERDA No. 6 assemblage is indicative of uranium deposition ($f < 0$) rather than uranium leaching.

Figure 3:   Uranium disequilibrium ages as a function of original $^{234}U/^{238}U$ ratio, for Deleware Basin groundwaters. These curves are derived from a model involving no exchange of uranium between rock and water.
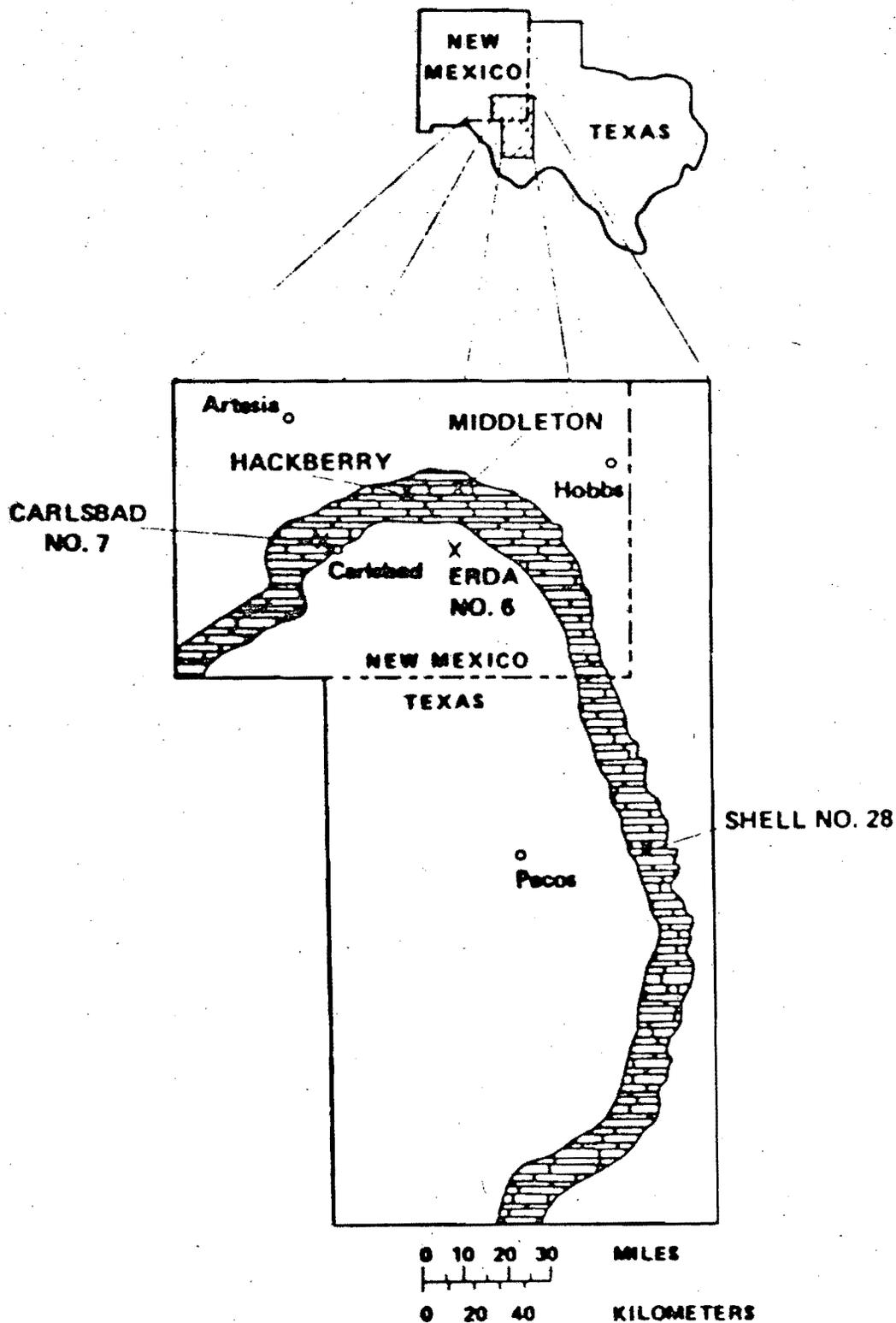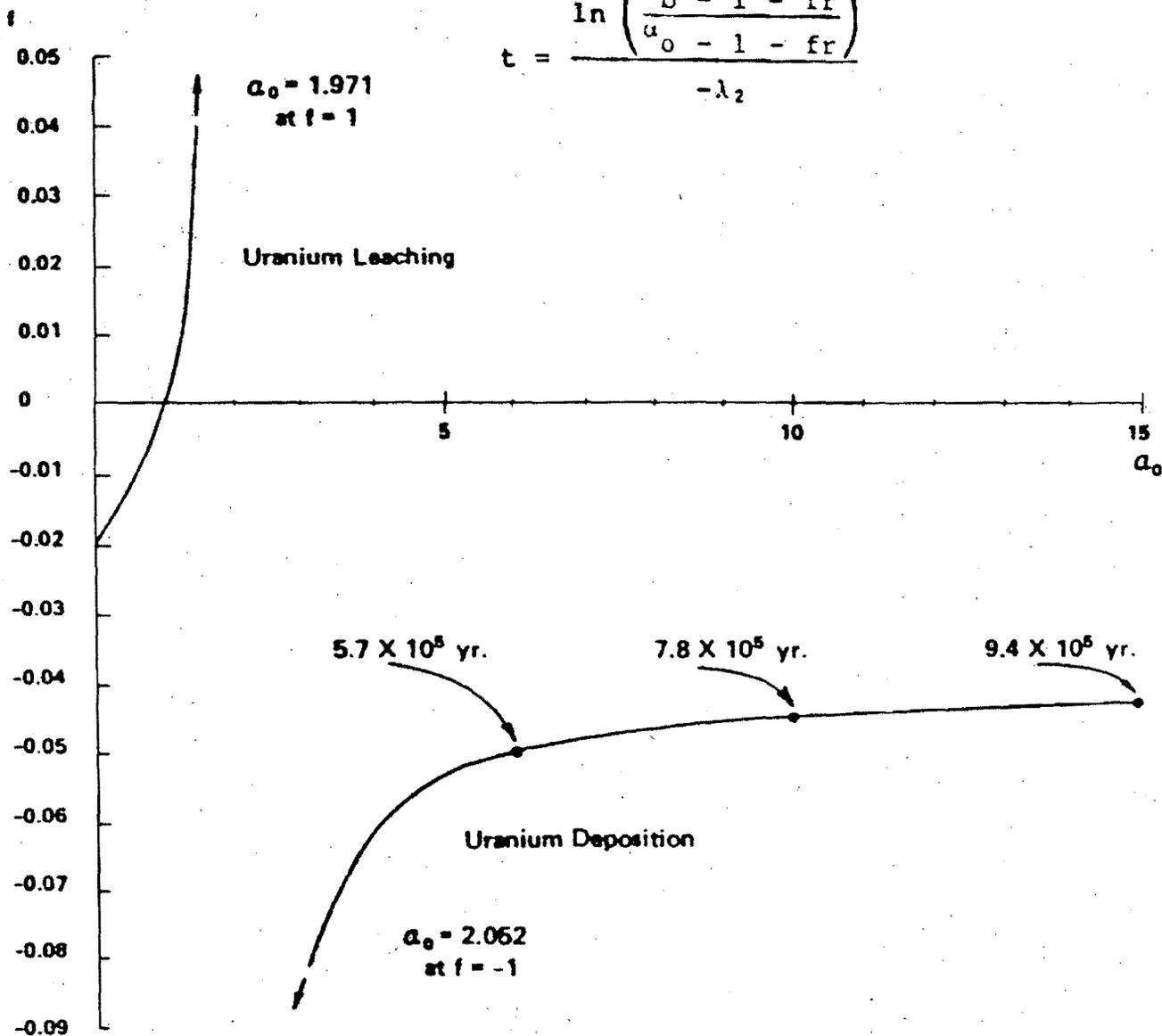
Figure 1: Map of a portion of the Delaware Basin (southeast New Mexico, west Texas) showing locations of holes whose fluids were sampled for $^{234}U/^{238}U$-disequilibrium age-dating. The brick-pattern shows the surface projection and outcrop of the Capitan reef limestone. (from Hiss, 1975)

Figure 2: Graph of the equation $f = \dfrac{(\alpha_o - 1)(\alpha_r - 1)}{\alpha_b - \alpha_o + r(\alpha_r - 1)}$

for the ERDA No. 6 assemblage of rock and brine, in which $r = 16.42$, $\alpha_r = 1.04$, $\alpha_b = 1.35$.

Uranium disequilibrium ages for the brine are shown according to the equation

$$t = \frac{\ln\left(\dfrac{\alpha_b - 1 - fr}{\alpha_o - 1 - fr}\right)}{-\lambda_2}$$

$\alpha_o = 1.971$ at $f = 1$

Uranium Leaching

$\alpha_o = 2.062$ at $f = -1$

Uranium Deposition

5.7×10^5 yr. 7.8×10^5 yr. 9.4×10^5 yr.

Note that the ERDA No. 6 assemblage is indicative of uranium deposition ($f < 0$) rather than uranium leaching.
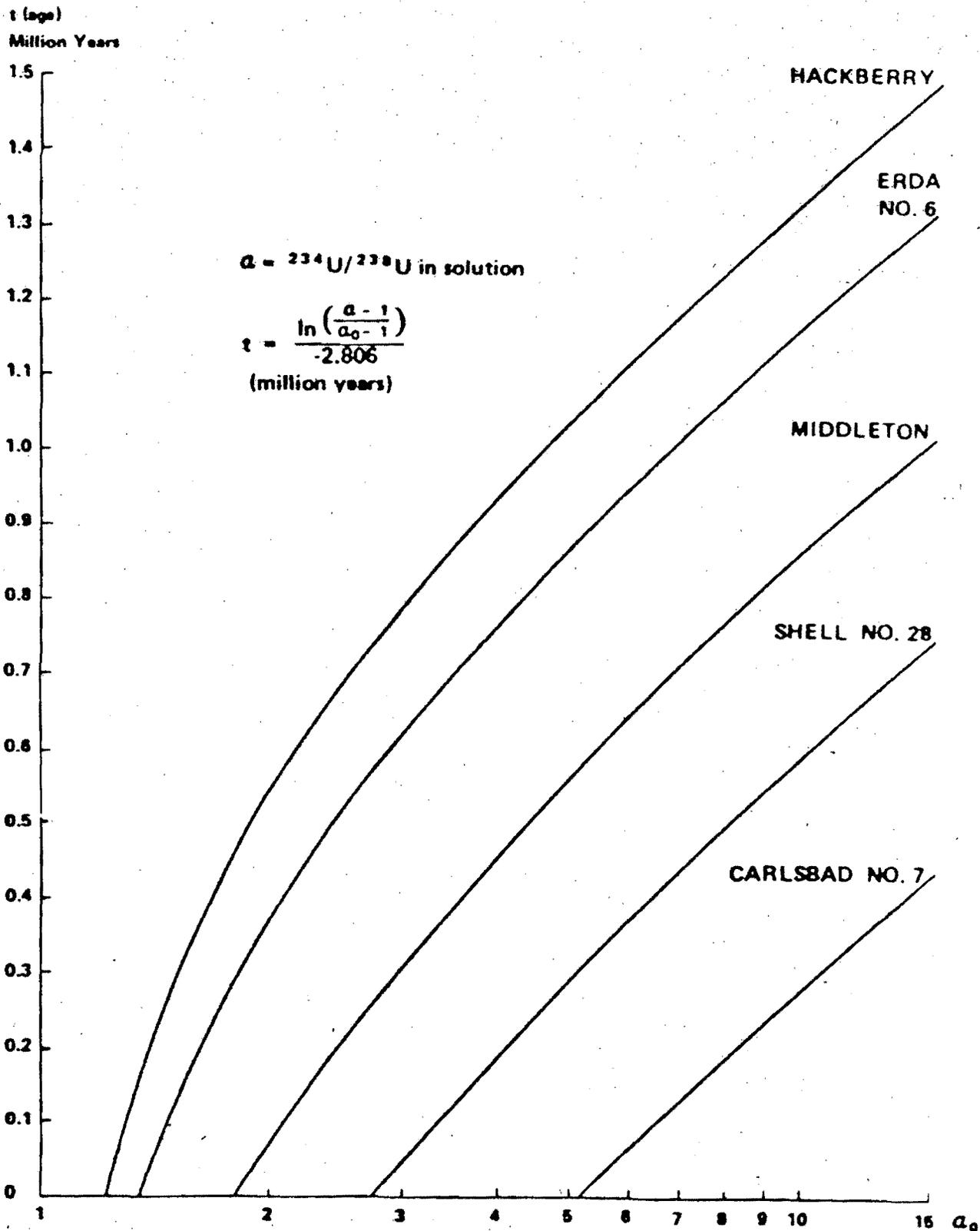
Figure 3: Uranium disequilibrium ages as a function of
           original $^{234}U/^{238}U$ ratio, for Deleware Basin
           groundwaters.   These curves are derived from a
           model involving no exchange of uranium between
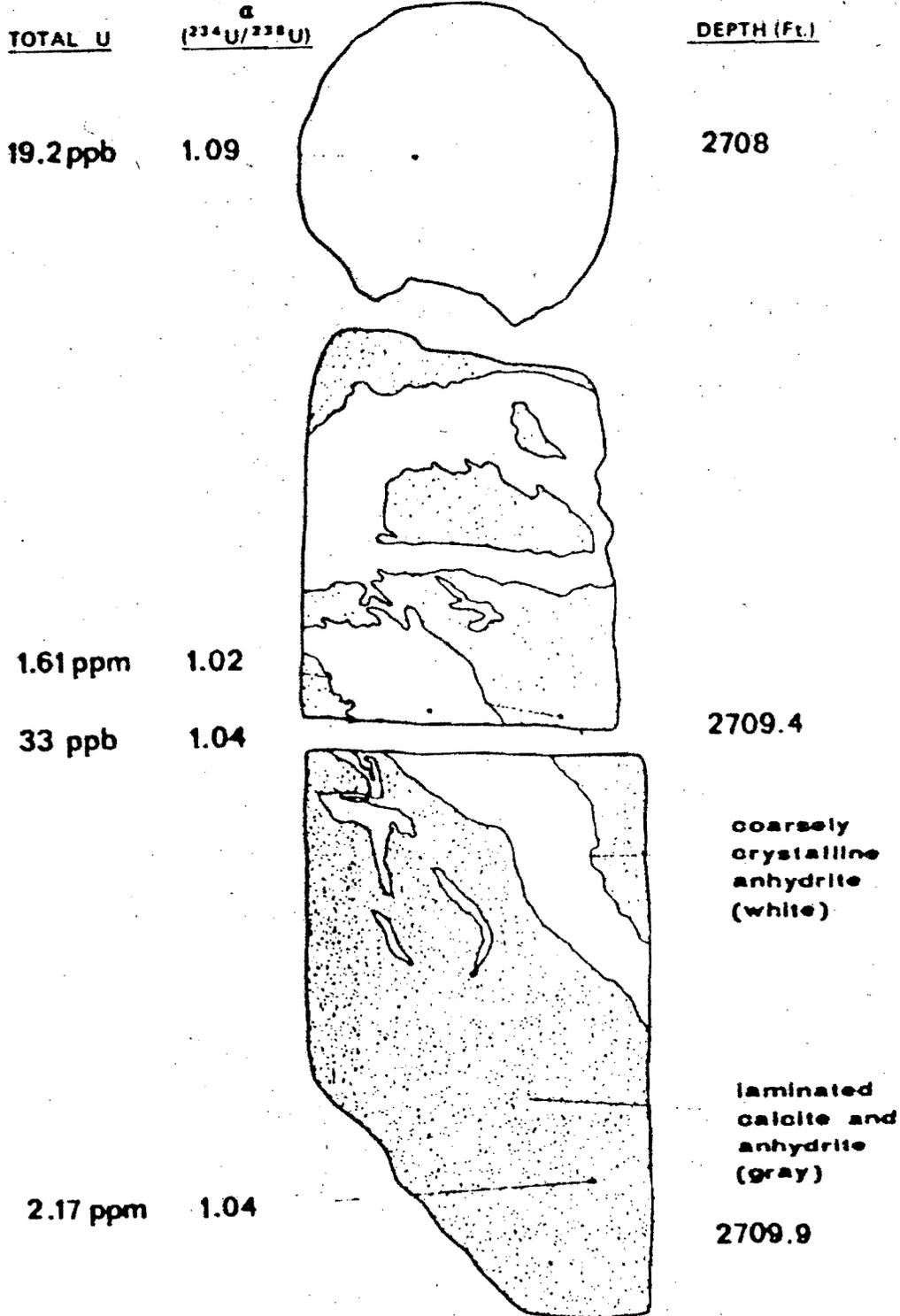   rock and water.

PLATE CAPTION

Plate 1 and Overleaf: Core fragments from Castile amhydrite serving as host rock for the ERDA No. 6 brine reservoir. Depths of origin, uranium contents and $^{234}U/^{238}U$ ratios are given in the overleaf for various parts of the core fragments.

TOTAL U	α $(^{234}U/^{238}U)$		DEPTH (Ft.)
19.2 ppb	1.09		2708
1.61 ppm	1.02		
33 ppb	1.04		2709.4
			coarsely crystalline anhydrite (white)
			laminated calcite and anhydrite (gray)
2.17 ppm	1.04		2709.9

Plate 1 and Overleaf: Core fragments from Castile amhydrite serving as host rock for the ERDA No. 6 brine reservoir. Depths of origin, uranium contents and $^{234}U/^{238}U$ ratios are given in the overleaf for various parts of the core fragments.

FULL SCALE-mm

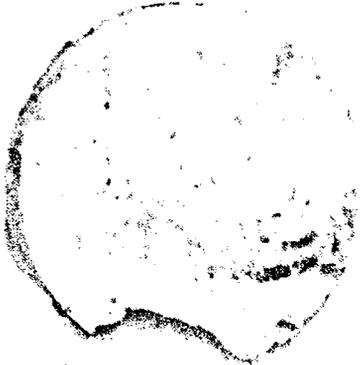0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220

PLATE 1