EEG-18

ORIGIN OF THE BRINES NEAR WIPP FROM THE DRILL HOLES ERDA-6 AND WIPP-12 BASED ON STABLE ISOTOPE CONCENTRATIONS OF HYDROGEN AND OXYGEN

Peter Spiegler

Dave Updegreaff

Environmental Evaluation Group
7007 Wyoming Boulevard NE, Suite F-2
Albuquerque, New Mexico 87109

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FOREWORD

The purpose of the Environmental Evaluation Group (EEG) is to conduct an independent technical evaluation of the potential radiation exposure to people from the proposed Federal radioactive Waste Isolation Pilot Plant (WIPP) near Carlsbad, in order to protect the public health and safety and ensure that there is minimal environmental degradation. The EEG is part of the Environmental Improvement Division, a component of the New Mexico Health and Environment Department -- the agency charged with the primary responsibility for protecting the health of the citizens of New Mexico.

The Group is neither a proponent nor an opponent of WIPP.

Analyses are conducted of data concerning the proposed site, the design of the repository, its planned operation, and its long-term stability. These analyses also include assessments of reports issued by the U.S. Department of Energy (DOE) and its contractors, other Federal agencies and organizations, as they relate to the potential health, safety and environmental impacts from WIPP.

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Robert H Neill

Robert H. Neill
Director

EEG STAFF AND CONSULTANTS

(1983)

James K. Channell, Ph.D., P.E., Environmental Engineer
Lokesh Chaturvedi, Ph.D., Engineering Geologist
Jo Anna DeCarlo, Secretary
Stuart Faith, M.S., P.E., Consulting Geochemist
Luz Elena Garcia, B.B.E., Administrative Secretary
Marshall S. Little (1) M.S., Health Physicist
Jack M. Mobley, B.A., Scientific Liaison Officer
Robert H. Neill, M.S., Director
Kenneth R. Rehfeldt, M.S., Hydrologist
Norma I. Silva, Administrative Officer
Peter Spiegler (1) (2), Ph.D., Radiological Health Analyst
Robbe Tucker, M.L.S., Librarian

---

(1) Certified, American Board of Health Physicis
(2) Certified, American College of Radiology

SUMMARY

Pathways which might alter the isotopic compositions of deuterium and oxygen-18 in meteoric waters, seawaters, and in hydration waters in gypsum to the isotopic compositions of brines encountered at ERDA-6 and WIPP-12 are discussed. Present geologic conditions do not favor the alteration of the isotopic compositions of waters that exist near the WIPP site to those of the brines by these pathways. It is concluded that the brines encountered at ERDA-6 and WIPP-12 are probably derived from ancient ocean waters that have been isotopically enriched in oxygen-18 by exchange interaction with rock. The dehydration of gypsum as a process of origin of these brines cannot be ruled out.

1. INTRODUCTION

This report represents an independent analysis by the Environmental Evaluation Group of the isotopic compositions of hydrogen and oxygen of the brines encountered at ERDA-6 and WIPP-12. The data used in this analysis are published in the "Data File Report ERDA-6 and WIPP-12 Testing" (ref. 1) and in a preliminary analysis of the data (ref. 2). This analysis is limited to these two isotopic compositions in a manner similar to other studies published in the literature that determine the origin of brines from such data. White (ref. 3) has expressed the opinion that these two isotopic parameters provide the most diagnostic data for determining the origin of waters. It is recognized however that the major and minor element chemistry compositions are relevant data for determining the origin of fluids. An independent analysis of such data by the EEG will be published in a subsequent report.

The material in this report is organized into the following four sections:

- Data
- Mechanisms to produce isotopic composition of brines
- Possible site from which brine originated
- Discussion

The first section presents the data and a brief discussion of the geologic formations near the WIPP site. The second section looks at four pathways which could alter the isotopic compositions of meteoric water or seawater to those of the brines. The third section discusses how the pathways could alter the isotopic composition of waters near the WIPP site to those of the brines. In the discussion, the emphasis is on analyses of similar data published in the scientific literature and on the most likely pathway suggested by the data. Since the conclusions derived from isotope analysis should be consistent with those derived from the major and minor element chemistry of the host rock and the brine, these conclusions should be considered preliminary.

2. DATA

The data (Table 1) and the isotopic concentrations of meteoric waters, seawaters, hydration waters in gypsum, and waters encountered near the WIPP site (ref. 4) have been replotted on Figure 1. The area and shape of the evaporation field for seawater must be considered as an approximation because it is dependent upon variables internal to the evaporating system such as temperature, humidity, water composition, surface kinetics, and ambient and transport parameters. The looping arrows at the end of the lines bounding the seawater evaporation field indicate the trend discussed in reference 5; i.e., in the presence of high salt concentrations, the heavy isotope content of the residual brines increases at first to a maximum value and then decreases. A two sided t-test indicates that the isotopic compositions of the ERDA-6 and WIPP-12 brines are different from each other at the 1.5×10^{-5} level of significance. For this reason the ERDA-6 and WIPP-12 isotopic data are separated by the ellipses shown on Figure 1.

The Rustler Formation consists primarily of anhydrite, rock salt, clastics and two water-bearing dolomitic units, the Magenta Dolomite Member and the Culebra Dolomite Member. The Salado Formation, which underlies the Rustler Formation, is the bedded salt formation in which the WIPP repository would be located. This formation contains small pockets of brine, generally associated with clay seams, which have occasionally been encountered in potash mines. The Castile Formation is located beneath the Salado Formation. It consists primarily of alternating layers of anhydrite and halite. The ERDA-6 and WIPP-12 brine pockets have been encountered in fractures at the base of the upper anhydrite layer of the Castile Formation. The Capitan Limestone is a water-bearing limestone formation that encircles the Delaware Basin. At the WIPP site the Castile Formation is at a depth comparable to the Capitan Limestone. The Capitan Limestone outcrops to the southwest of the WIPP site in the Guadalupe Mountains. The Bell Canyon Formation which contains limestone, siltstone, shale, and water bearing sandstone strata is located beneath the Castile Formation.

Table 1

δD and δ^{18}O values of brines from ERDA-6 and WIPP-12

Isotopes	Number of sample points	Minimum	Maximum	Average(3)	Standard Deviation
ERDA-6(2)					
δD(1)	16(4)	-8	+0.5	-4.6	2.32
δ^{18}O(1)	16(4)	9.02	9.93	9.51	0.24
WIPP-12(2)					
δD(1)	20(5)	-4	+1	-1.1	1.43
δ^{18}O(1)	18(5)	10.04	11.23	10.63	0.32

(1) $\delta x = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 10^3$

x = δD, R = D/H, Standard = SMOW
x = δ^{18}O, R = ^{18}O/^{16}O, Standard = SMOW
units are in permil.

(2) ERDA-6 data taken from Table 6.7-C7, Reference 1.
WIPP-12 data taken from Table 12.20-C9, Reference 1.

(3) average = arithmetic mean, taken over the number of sample points.

(4) Analysis of 8 split samples were performed.

(5) Analyses of 10 split samples. Two 18-oxygen data points lost due to contamination.
Analyses of samples performed by Global Chemistry.

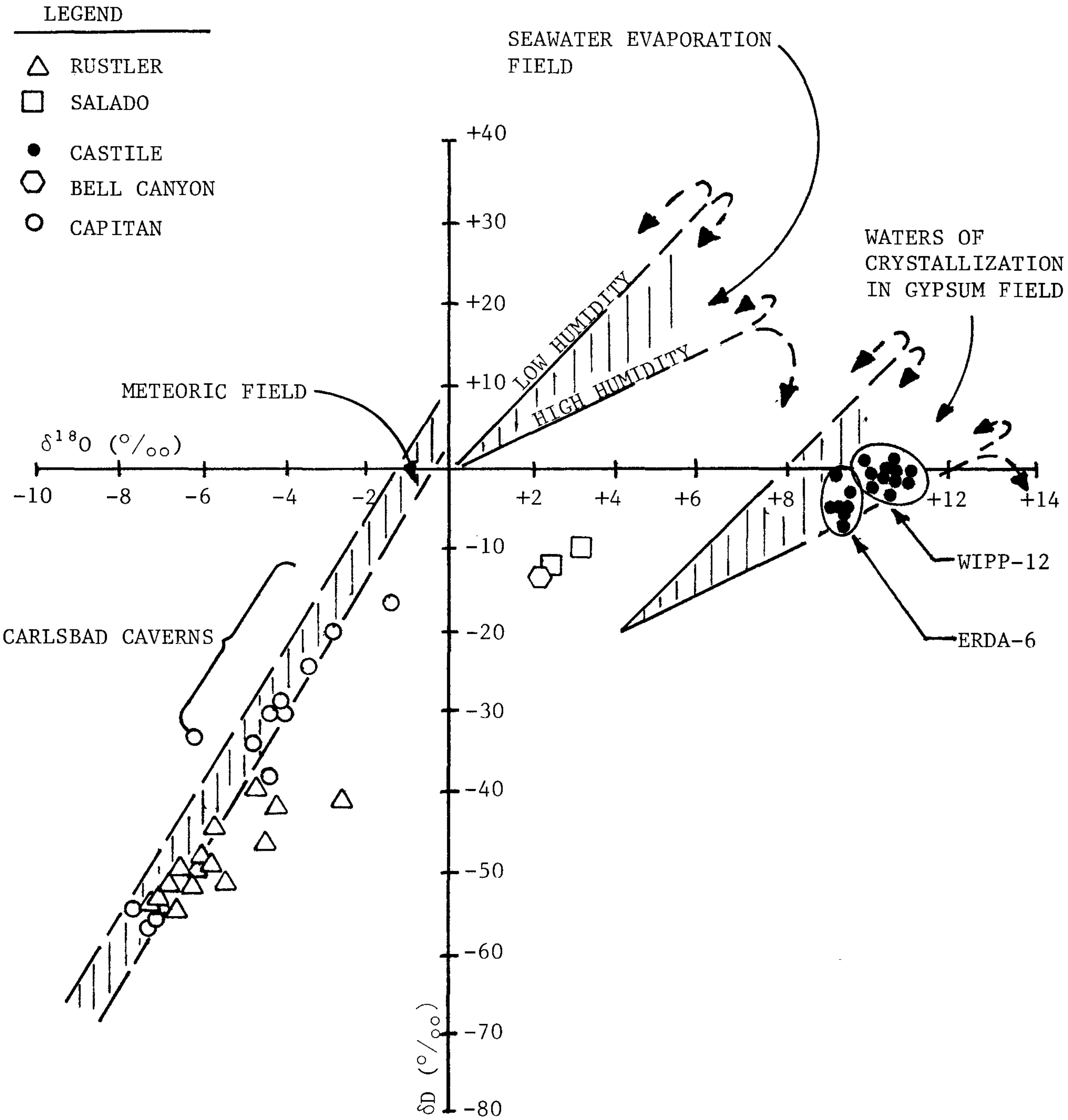

Figure 1. Isotopic compositions of the water/brine from the Delaware Basin.

3. MECHANISMS TO PRODUCE ISOTOPIC COMPOSITION OF BRINE

3.1 Alteration of Trapped Seawater

The pathway for alteration of trapped seawater is illustrated in Figure 2 by the arrow labeled 1. It requires two processes: a process that substantially increases the $\delta^{18}O$ value to about 10 permil and a process that slightly decreases the δD value to the -1 to -5 permil range. The increase in $\delta^{18}O$ could be attributed to maintaining the water in contact with a large carbonate or anhydrite reservoir for a long time. In the preceding sentence the word "large" implies an excess or overabundance of carbonate relative to water such that the isotopic composition of oxygen in the rock is not altered substantially subsequent to establishment of equilibrium. The word "long" implies that there has been enough time for the exchange reaction to reach equilibrium. Based on these assumptions, it is possible to use the following equilibrium relationship to describe the calcite-water system (ref. 6):

$$\Delta_{\text{calcite-water}} = \delta^{18}O_{\text{calcite}} - \delta^{18}O_{H_2O} = (2.78 \times 10^6)T^{-2} - 3.4 \qquad (1)$$

where T is the temperature in °K. Equation 1 is reported to be valid over the 0 - 800 °C temperature range. It follows that the rock-brine mixture must be at temperatures of 70 °C if the $\delta^{18}O_{\text{calcite}}$ values are 30 permil, which is the value in fresh marine sediments. Higher temperatures will be necessary if the $\delta^{18}O_{\text{calcite}}$ value is less than 30 permil. The analogous equation for an anhydrite-water system is (ref. 6)

$$\Delta_{\text{anhydrite-water}} = \delta^{18}O_{\text{anhydrite}} - \delta^{18}O_{H_2O} = (3.88 \times 10^6)T^{-2} - 3.4 \qquad (2)$$

However, it is reported to be valid only over the 100-500 °C temperature range. It follows from Equations 1 and 2 that, for a given temperature, the Δ for anhydrite-water is much greater than the Δ for calcite-water. Therefore, it is much more difficult to attribute the high $\delta^{18}O$ value of the water in the brines to an exchange reaction between anhydrite and water. The slight decrease in the δD value could be attributed to several mechanisms: 1) shale ultrafiltration (ref. 7), which requires the assumption that the brines migrated to their present site from distant locations and, in their path of

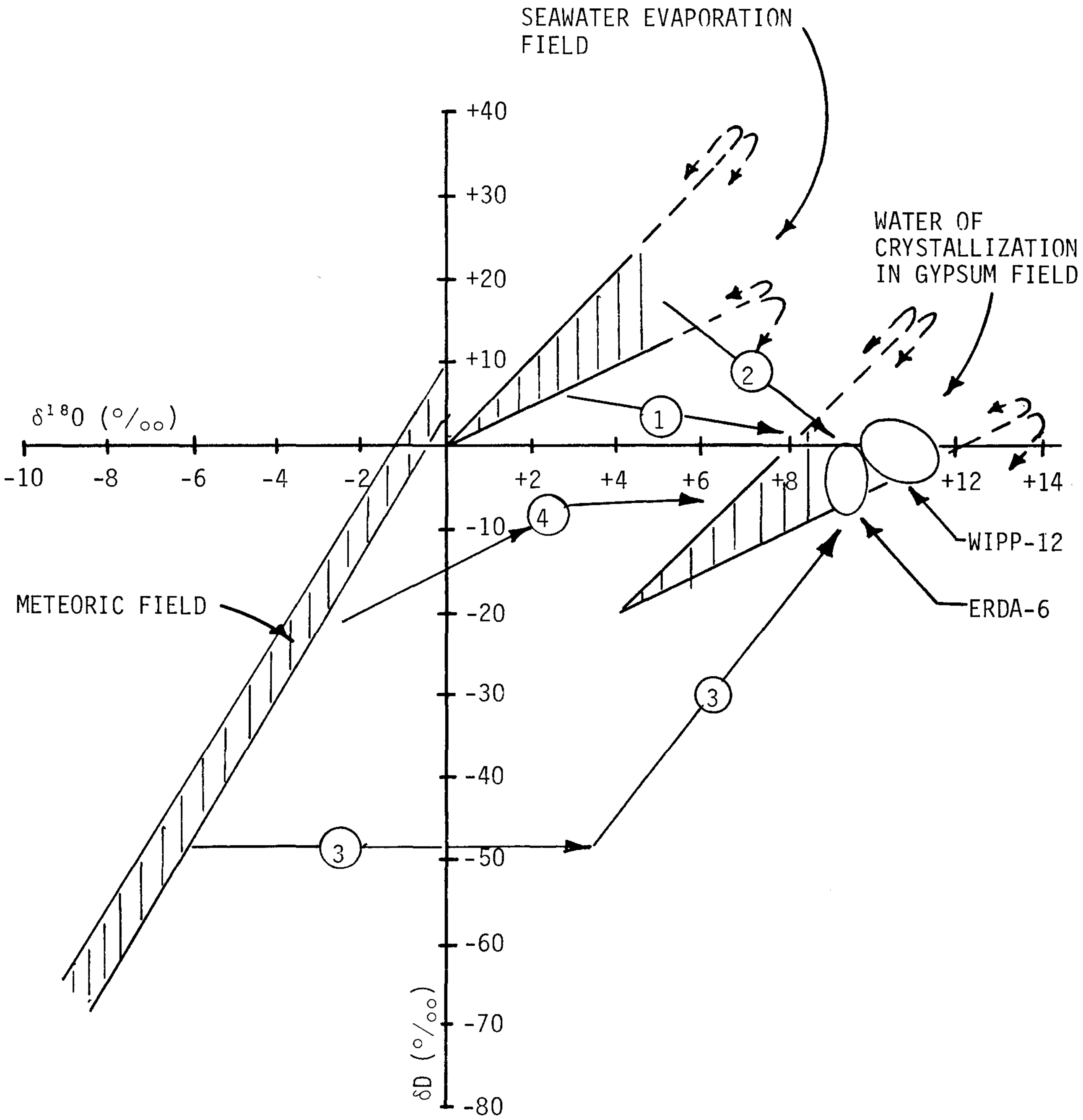

Figure 2. Pathways which could alter the isotopic composition of meteoric water or seawater to those of the brines.

travel, passed through shale barriers; 2) mixing of seawater with a small amount of meteoric water; 3) highly evaporated seawater (see looping of the δ-diagram evaporation curve in ref. 5). Explaining the origin of the brines as trapped seawater does not imply that the seawater was originally trapped in the Castile Formation. The seawater may have been trapped in an adjacent formation such as the Capitan Limestone Formation and migrated to its present location through fractures in the anhydrite layers which have since become sealed.

3.2 Gypsum Dehydration

The pathway for gypsum dehydration is illustrated in Figure 2 by the arrow labeled 2. The pathway has been proposed by Sofer (ref. 8) who has studied extensively the isotopic composition of the system: water + anhydrite → gypsum. Gypsum is known to fractionate 18-oxygen and deuterium with a fractionation factor (α) of 1.004 and 0.980 respectively. If gypsum precipitates from concentrated seawater, the bound water would possess an isotopic range shown approximately by the second wedge-shaped field (ref. 2). The water resulting from gypsum dehydration would have a composition that falls within the second wedge. This assumes that any further isotopic exchanges between the water and the anhydrite are neglected. It is possible that post conversion exchange reactions with other minerals will affect the $\delta^{18}O$ values of the waters in the brine. The extrapolation also assumes that the isotopic composition of the ocean water at the time of gypsum precipitation was identical to the isotopic composition of present day seawater. For the ancient Permian ocean, this correspondence is uncertain.

3.3 Mixing of Meteoric Water with Trapped Seawater

Mixing of meteoric water with seawater is a likely process reported for substantially increasing the δD value of meteoric water (ref. 9). In such a process it must be assumed that the isotopic composition of the brines is the result of mixing local meteoric water of recent origin with trapped seawater. The pathway for this assumption is illustrated in Figure 2 by the arrow labeled 3, which starts from the values of local meteoric water. The δx value for the mixture of meteoric water and evaporated seawater is obtained from the following relationship

$$\delta x_{mix} = \frac{y_{sw}\,\delta x_{sw} + y_{mw}\,\delta x_{mw}}{y_{sw} + y_{mw}} \qquad (3)$$

where y_{sw} is the number of parts of evaporated seawater in the mixture, y_{mw} is the number of parts of local meteoric water in the mixture, and x stands for either D or ^{18}O. Equation 3 can also be solved for y_{sw}:

$$y_{sw} = y_{mw}\,\frac{\delta x_{mw} - \delta x_{mix}}{\delta x_{mix} - \delta x_{sw}} \qquad (4)$$

As an example we use the following input values:

δD_{mw} = -50 permil; $\delta^{18}O_{mw}$ = -7.5 permil.
δD_{sw} = +10 permil; $\delta^{18}O_{sw}$ = +4 permil.
δD_{mix} = -5 permil.
y_{mw} = 1.

With the input data for deuterium, the solution of equation 4 yields y_{sw} = 3. With the input data for oxygen, the solution of equation 3 yields $\delta^{18}O_{mix}$ = 1.1 permil.

For this example, a second process that increases the $\delta^{18}O$ value from 1.1 permil to +10 permil is needed. As in section 3.1, the increase in the $\delta^{18}O$ value could be attributed to maintaining the water in contact with a large carbonate reservoir at an elevated temperature.

The δx_{sw} values used in the sample calculations pertain to highly evaporated seawater. For δx_{sw} values of present seawater, the calculated values for y_{sw} would be greater. The mixing hypothesis, therefore, implies that brines are mostly seawater.

3.4 Meteoric Water and Evaporation

The pathway for this hypothesis is illustrated in Figure 2 by the arrows labeled 4. It is assumed that the origin of the water in the brines is local meteoric water. The increase in δD and $\delta^{18}O$ by evaporation from the recharge area or at depth is indicated by the arrow pointing to the upper right corner. However, the mechanism is not plausible during transport of water from one aquifer to another. The mechanism might be possible in large underground openings such as caverns. It could be argued that evaporation could increase the δD value of waters from the Carlsbad caverns to that of the Castile brines. A second mechanism that increases the $\delta^{18}O$ value is also needed (horizontal arrow). As indicated in sections 3.1 and 3.3, the second mechanism could be achieved by maintaining the water in contact with a large carbonate reservoir at elevated temperatures.

4. POSSIBLE ORIGIN OF BRINE

4.1 Bell Canyon Formation

The waters of the Bell Canyon Formation have a δD value of -13 permil and a $\delta^{18}O$ value of 2.2 permil. Lambert (ref .10) concludes that the Bell Canyon Formation waters are presently in isotopic equilibrium with the calcite cement of the Bell Canyon Formation at a temperature of 54 °C. His conclusion is based on measured $\delta^{18}O$ values of the Bell Canyon Formation water (2.2 permil) and the Bell Canyon calcite cement (25.1 permil). Lambert also calculates a molar calcite to water ratio of 1.88. This ratio is based on the assumption that the Bell Canyon water was originally local meteoric water which had a $\delta^{18}O$ value of -7 permil and that the calcite cement was of marine origin which has a $\delta^{18}O$ content of 30 permil. The small calcite to water ratio suggests that the Bell Canyon Formation cannot be considered a large carbonate reservoir with respect to its water content.

It could be hypothesized that the ERDA-6 and WIPP-12 brines contain water of the Bell Canyon Formation that moved upward into the Castile Formation. The hypothesis requires that the isotopic composition of the Bell Canyon Formation waters be altered by additional 18-oxygen exchange with calcite cement or by evaporation (pathway 4). Equilibrium between the 18-oxygen of the water and of the calcite cement (ref. 10) precludes further exchange reaction in the Bell Canyon Formation. A travel path through a large carbonate reservoir at elevated temperatures from the Bell Canyon Formation to the upper anhydrite of the Castile Formation is also not plausible because there are no large quantities of calcite in the Castile Formation. A mechanism such as either mixing the Bell Canyon Formation water with evaporated seawater or an interaction of the water with clay minerals might be necessary to slightly increase the δD value. The evaporation of Bell Canyon water requires an explanation for evaporation at depth, which does not seem possible. Because of the above considerations, the hypothesis that the brines of ERDA-6 and WIPP-12 could have come from the Bell Canyon Formation in recent geologic times is not considered plausible.

4.2 Salado Formation

The Salado Formation contains small amounts of brines whose water have isotopic compositions similar to the water of the Bell Canyon Formation. However, it is not possible to hypothesize a travel path at elevated temperatures through a large carbonate reservoir from the Salado Formation to the Castile Formation because of the lack of calcite in the Castile Formation and the Salado Formation. Also, it is necessary to hypothesize a mechanism that would cause the brine to move downward through a medium that has an extremely low permeability. Because of the above considerations, the hypothesis that the brines of ERDA-6 and WIPP-12 could have come from the Salado Formation is not considered plausible.

4.3 Capitan Limestone

The waters of the Capitan Limestone have isotopic compositions similar to meteoric waters. Further, since the Capitan Limestone abuts the area of the brine reservoirs, it is tempting to hypothesize that the brines originated from there. Evaporation of meteoric water (pathway 4) could be used to link the origin of the brines to waters of the Carlsbad Caverns. However, the caverns are about 30 miles away from the area of the brine pockets. The northern part of the reef is much closer to the brine reservoir area. The water in the northern part of the Capitan Limestone has δD and $\delta^{18}O$ values of about -50 permil and -7 permil, respectively. Pathway 3 is the only mechanism that could alter the isotopic composition of these waters to that of the Castile brines. As discussed in sections 3.1 and 3.3, the pathway would require a path of travel through a large carbonate reservoir with temperatures of 70 °C, assuming the carbonate reservoir contains calcite with a $\delta^{18}O$ value of 30 per mil and additionally large amounts of trapped seawater. A path of travel with such conditions is not present today. Therefore, it is not plausible to hypothesize that the brines at ERDA-6 and WIPP-12 could have come from the Capitan Limestone to the north of the brine encounters in recent geologic times.

4.4 Anhydrite of Castile Formation

The brines of the Castile Formation are located in the uppermost anhydrite layer. It is, therefore, tempting to hypothesize that they resulted from the dehydration of gypsum. The mechanism has been discussed in section 3.2. Several extrapolations, based on geological and geochemical data, must be made to test this hypothesis. Therefore, it is not possible, on the basis of isotopic composition data alone, to determine if the brines resulted from gypsum dehydration.

5. DISCUSSION

A comprehensive study of the values of δD and $\delta^{18}O$ in oil field brines from the Illinois, Michigan, and Alberta basins and from the Gulf Coast has been published by Clayton et al. (ref. 11). The data led Clayton, et al. to the following conclusions: (a) the waters are predominantly of local meteoric origin, (b) the deuterium content has not been greatly altered by exchange or fractionation processes; (c) extensive oxygen exchange has taken place between water and reservoir rocks. In an earlier paper, Clayton (ref. 12) had shown in the laboratory that the oxygen isotopic exchange between water and calcite was much more rapid than between water and silicates. Therefore, Clayton et al., (ref. 11) suggested that the exchange of oxygen between water and limestones would be the dominant factor in determining the $\delta^{18}O$ value in oil field brines. Their analysis of the $\delta^{18}O$ values of the brines, based on the bottom hole temperature of the wells, supports this suggestion. Later, Hitchon and Friedman (ref. 9) again analyzed the δD and $\delta^{18}O$ values of oil and gas field brine of the Western Canada sedimentary basin. They hypothesized that the observed isotopic ratios are the result of mixing of surface water and diagenetically modified seawater accompanied by a process which enriches the heavy oxygen isotope. The hypothesis of mixing seawater and other waters to explain the origin of waters with unusual isotopic composition has been endorsed by White et al., (ref. 13) who interpret certain mineral waters of the California coast range as waters of connate and metamorphic origin, derived from reaction of ancient ocean waters and marine sediments. Isotopic compositions of formation waters from the geopressured and normally pressured zones from the Northern Gulf of Mexico Basin have been reported by Kharaka, et al. (ref. 14). The pressurized zones are located in the Corpus Christi and Houston-Galveston area. On a δ-diagram the isotopic composition of these formation waters fall on a trend that passes through SMOW and away from the meteoric waters of the area. Because of the stable isotope data and the fluid potentials, the authors conclude that these formation waters are of connate origin representing the original marine water of deposition. Kharaka and Carothers (ref. 15) have also studied the isotopic composition and chemical data of oil field waters from the North Slope of Alaska. They conclude that the waters are meteoric in origin but that recharge took place in Miocene or earlier times. Ref. 15 also has a literature survey and a discussion on the isotopic composition of ocean water through geologic time. While unanimity is lacking in estimates of the isotopic composition of oceanic water in the past, the available data suggests that δD and $\delta^{18}O$ values of water of the ancient Permian sea did not differed by more than a few permil from the values of present oceanic water.

In this report, the various hypotheses cited in the literature for explaining the origin of brines based on the isotopic composition of water have been applied to the data obtained from the testing of ERDA-6 and WIPP-12. In an analysis of the 1975 ERDA-6 data, citing the work of Clayton, et al., Lambert (ref. 4) had stated that the isotopic composition of the ERDA-6 brine with its history of cation exchange, had resulted in a brine with a history similar to that of oil-field brines of Alberta and the Gulf Coast. When entered on the δ-diagram plot of Clayton et al. (Figure 3) the data for ERDA-6 and WIPP-12

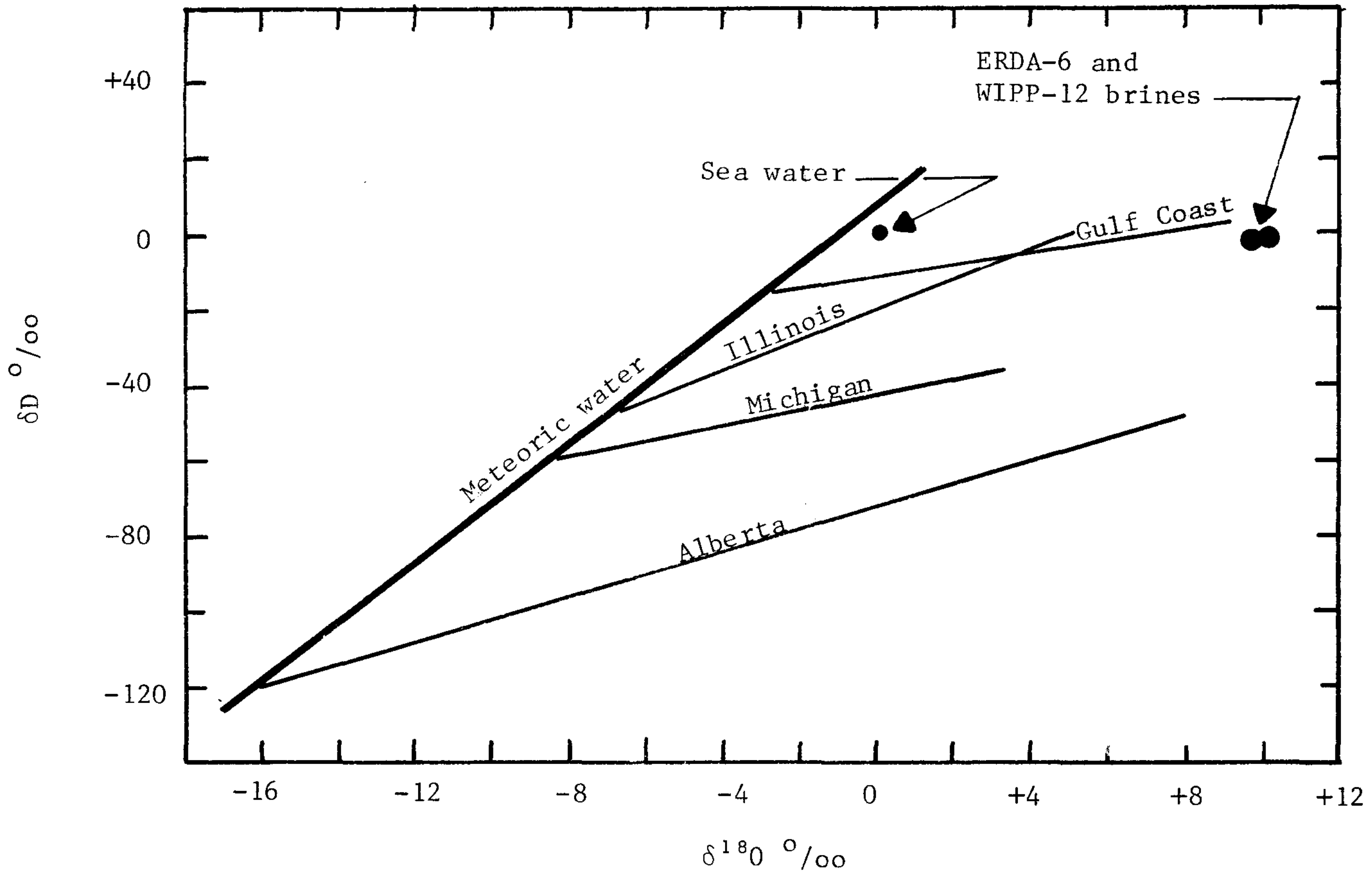

Figure 3. Isotopic composition of brines studied by Clayton et al. and of Castile brines.

indeed fall on the line joining the Gulf Coast brine. However, they are farther away from the lines joining the data of the Illinois, Michigan, and Alberta brines. For the brines of the Gulf Coast, the conclusion by Clayton, et al. (ref. 11) that their origin is local meteoric water is perhaps questionable. In the Gulf Coast area, the δD and $\delta^{18}O$ values of meteoric water and seawater are very close, and with the scatter in the data, it is not possible to use the δD and $\delta^{18}O$ versus total dissolved solid plots to indicate that the waters in the brines are of meteoric origin. Also, Kharaka, et al. (ref. 14), concluded that the formation water from the geopressured and normally pressured zones from the Northern Gulf of Mexico basin were connate waters representing the original marine water of deposition. In section 3.3, the hypothesis that the origin of the ERDA-6 and WIPP-12 brines might be the result of mixing local meteoric water and seawater was studied, but the sample calculation indicated that the mixture would be mostly seawater. The work of Sofer suggests that the brines could have resulted from the dehydration of gypsum. However, the hypothesis requires several extrapolations, and it can only be evaluated carefully by examining the chemical composition of the anhydrite rock and of the brines. Even if the gypsum dehydration hypothesis is accepted, it implies that we are dealing with water that has been isolated from other waters since Permian times and the origin of which is ancient ocean water.

The hypotheses that the brines could have originated from waters of the Bell Canyon Formation or Capitan Reef in recent geologic time were studied in sections 4.1 and 4.3. The hypotheses did not seem plausible. The aquifers that flow through these formations were probably created with the tilting of the Delaware Basin as a unit. Prior to the tilting, the formations may have carried substantial quantities of trapped seawater.

In summary, it is concluded that the brines encountered at ERDA-6 and WIPP-12 are probably derived from ancient ocean waters that have been isotopically enriched in oxygen-18 by exchange interaction with rock. The dehydration of gypsum as a process of origin of these brines cannot be ruled out.

REFERENCES

1. D'Appolonia Consulting Engineers, Inc. Data File Report. ERDA-6 and WIPP-12 Testing. Waste Isolation Pilot Plant, Westinghouse Electric Corp. Project No NM 78-648-811A/812B, 7 vols., February 1982.

2. Black, S.R., Coons, W.E., Olsen, R.L., and Popielak, R.S., Draft ERDA-6 and WIPP-12 Testing. Interim Data Analysis (April 1982). Waste Isolation Pilot Plant (WIPP). U.S. Department of Energy, Albuquerque, (TME 3153) July 1982.

3. White, D.E., Diverse origin of Hydrothermal Ore Fluids, Econ. Geol., 69, p. 954-973, 1974.

4. Lambert, S.J., Geochemistry of Delaware Basin Groundwaters, New Mexico Bureau of Mines and Mineral Resources, Circular 159, p. 33-38, 1979.

5. Sofer, Z. and Gat, J.R., The Isotopic Composition of Evaporating Brines: Effect of the Activity Ratio in Saline Solutions, Earth and Planetary Science Letters, 26, p. 179-186, 1975.

6. Faure, Gunter, Principle of Isotope Geology: New York, John Wiley and Sons, 1977.

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

8. Sofer, Zwi, Isotopic composition of Hydration Water in Gypsum, Geochimica et Cosmochimica Acta, 42, 1141-1149, 1978.

9. Hitchon, B., and Friedman, I., Geochemistry and Origin of Formation Waters in the Western Canada Sedimentary Basin-I. Stable Isotopes of Hydrogen and Oxygen, Geochimica et Cosmochimica Acta, 33, p 1321-1349, 1969.

10. Lambert, S.J., Interim Report: Dissolution of Evaporites in and Around the Delaware Basin, Southeastern New Mexico and West Texas, Sandia National Laboratories, Report SAND81-0461, p. 117-118, 1982.

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

12. Clayton, R.N., Oxygen Isotope Fractionation in the System Calcium Carbonate-Water, J. Chem. Phys., 30, p. 1246-1250, 1959.

13. White, D.E., Barnes, Ivan, and O'Neil, J.R., Thermal and Mineral Waters of Nonmeteoric Origin, California Coast Ranges, Geol. Soc. America Bull., 84, p. 547-560, 1973.

14. Kharaka, Y.K., Carothers, W.W., and Brown, P.M., Origin of Waters and Solutes in the Geopressured Zones of the Northern Gulf of Mexico Basin, Proc., 53rd Annual Conf., Soc. Petrol. Engineers of AIME, Preprint paper SPE 7505, 1978.

15. Kharaka, Y.K. and Carothers, W.W., Oxygen and Hydrogen Isotope Geochemistry of Deep Basin Brines, in The Handbook of Environmental Isotope Geochemistry, P. Fritz and J. Ch. Fontes, Editors, Elsivier Scientific Publishing Co., Amsterdam, Vol. II, (to be published).