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GEOCHRONOLOGIC STUDIES NEAR THE WIPP SITE, SOUTHEASTERN, NEW MEXICO

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ABSTRACT

The U.S. Department of Energy's Waste Isolation Pilot Plant (WIPP) site is currently being investigated for pilot storage of defense-generated radioactive waste. A critical facet of the overall study is the question as to whether the rocks have remained closed systems with respect to their bulk chemistry and isotopic composition since formation in the Late Permian as opposed to episodic or more-or-less continuous recrystallization during the post-Late Permian. Early attempts at K-Ar dating of sylvites mixed with other salts yielded inconclusive results, primarily because sylvite is not well suited for K-Ar study due to loss of radiogenic ^{40}Ar. Rb-Sr study of sylvites (Register and Brookins, 1980) yields a 214 ± 15 m.y.B.P. (million years before present) isochron indicating closed system conditions to Rb and Sr since latest Permian or earliest Triassic. Pre-200 m.y.B.P. K-Ar dates have also been determined for pure langbeinites and polyhalites (Brookins and others, 1980a). When mixed with sylvite, age lowering results. The Rb-Sr systematics of eolian clay minerals known to have interacted with the evaporite brine yield a poorly defined isochron of 390 ± 77 m.y.B.P., but the apparent date does indicate that the clay mineral-brine interactions were not so severe as to completely rehomogenize Sr isotopes despite the clay mineral alteration. A 34 ± 1.5 m.y.B.P. lamprophyre dike intrudes the evaporite sequence some 70 km north of the WIPP site. Contact effects, including recrystallization of polyhalite, are restricted to within 10 m of the dike. Finally, polyhalite inclusions in one rubble chimney yield a pre-200 m.y.B.P. age indicating no major recrystallization effects due to this disturbance of the evaporite sequence. Collectively, the geochronologic studies argue for pre-200 m.y. B.P. formation of the evaporite minerals and stability of the rocks since that time.

INTRODUCTION

The age of the Salado and Castile formations, Ochoa Series, is given as Late Permian (Walter, 1953). The post-diagenetic history of the evaporites from the WIPP site area has been summarized in SAND (1978). The rocks, described in more detail elsewhere in this volume (Mercer and Gonzalez, this volume), consist of interbedded halites and anhydrite with smaller, but economically significant, interbeds of K-rich minerals such as sylvite and langbeinite. Polyhalite and other less common evaporite minerals are locally abundant. The evaporites have a low regional dip to the east. The only major structural disturbances of the evaporite sequence are in the vicinity of igneous dikes which intrude the evaporites some 70 km from the WIPP site and at local rubble chimneys of Pleistocene age (see SAND, 1978 and Anderson, this volume, for discussion of these features).

One of the important questions concerning use of these evaporites for the possible storage of radioactive waste is whether or not these rocks have, except very locally (i.e., near the dikes or rubble chimneys), remained chemically and isotopically closed to elemental migration since their deposition. The age of deposition (discussed later in this paper) must be between 235 and 240 m.y.B.P. although epigenesis and potash ore-zone formation may not have been complete until 220-215 m.y.B.P. (see discussion in Brookins and others, 1980a). To answer this question of closed versus open system conditions, the University of New Mexico has undertaken a geochronologic study of the evaporites by the K-Ar and Rb-Sr geochronologic methods (see Faure, 1977, for discussion of these methods).

Previous dating attempts (Schilling, 1973; Tremba, 1969) are discussed below. Our studies include carefully selected samples from large drill cores and from mine-wall samples. Some samples (e.g., lamprophyre and contact zone evaporite) have been provided by U.S. Geological Survey (USGS) personnel (i.e., M. C. Bodine, J. Calzia, W. Hiss). In addition, pure and impure samples of several evaporites were used for the study. In some instances impure samples were intentionally selected to test for causes of age lowering. Preparation of samples for both K-Ar study and Rb-Sr study are described in Register (1979), Brookins and others (1980a), and Brookins (1980a, b). Detailed mineralogic and X-ray information for the samples used is given in Register (1979), Brookins and others (1980b), and Register and others (1980).

Polyhalites were given special attention for two reasons: (1) they contain two structurally bonded moles of water per mole of mineral; and (2) if they formed more or less continuously throughout the Mesozoic and Cenozic, as proposed by Bodine (1978), then the problem of availability of water becomes important. Water, if available, would cause perturbations of isotopic systematics and, more important, could cause brines to form near warm radioactive waste canisters. Hence, it is imperative to know if the water was only available during the final stages of epigenesis or, alternatively, if unknown sources of water have been responsible for polyhalite formation (and therefore, available for other mineral reactions as well) much later than evaporite formation.

PREVIOUS GEOCHRONOLOGIC STUDIES

Several geochronologic studies have been carried out at or near the WIPP site (Table 1). Schilling (1973) reported K-Ar ages for langbeinite, sylvite, and mixtures of the two minerals. The one pure langbeinite analyzed yielded 245 ± 10 m.y.B.P., two langbeinite-sylvite mixtures yielded 137 and 147 m.y.B.P., and two sylvites yielded 18 and 74 m.y.B.P. Since sylvites easily lose radiogenic (*) ^{40}Ar, the 245 m.y.B.P. langbeinite age is considered the most reliable. This age is within the stated limits of error for the Triassic-Permian boundary given as 235 ± 5 m.y.B.P. by Webb and McDougall (1967).

In addition, igneous dikes which cut the evaporites some 70 km from the WIPP site have yielded K-Ar ages of 32.2 ± 1.0 and 34.4 ± 1.3 m.y.B.P. (Calzia and Hiss, 1978). Two additional dates of 34.4 ± 1.3 and 34.7 ± 1.4 m.y.B.P. (Brookins, 1980a) have confirmed these dates, and their significance will be discussed below.

Tremba (1969) attempted Rb-Sr age determinations for several evaporite samples. His results, discussed in more detail later in this paper, indicate evaporite formation at 230 ± 10 m.y.B.P. and also a

Table 2. Rb-Sr age determinations (A) and $^{87}Sr/^{86}Sr$ initial ratios (B) for selected samples in evaporites of Permian Basin, southeastern New Mexico. Locations for samples are given in the sources cited; m.y.B.P. = million years before present. Ages are calculated by methods of York (1969).

A. Rb-Sr Isochrons	*Age (m.y.B.P.)*	*Source*
Evaporite minerals	129 ± 5	Tremba (1969)
Evaporite minerals	120 ± 28	Tremba (1969)
Evaporite minerals: composite	230 ± 240	Tremba (1969)
41 evaporite minerals	199 ± 20	Register (1979)
32 evaporite minerals	214 ± 15	Register and Brookins (1980)
Evaporite whole rocks	171 ± 36	Register (1979)
Clay minerals in evaporites	390 ± 77	Register and others (1980)
B. $^{87}Sr/^{86}Sr$ Initial Ratios	*Value*	
Calculated for 41 point isochron	0.7076 ± 0.0014	Register (1979)
Calculated for 32 point isochron	0.7093 ± 0.0007	Register and Brookins (1980)
30 data on $^{87}Sr/^{86}Sr$ axis	0.7084 ± 0.0014	Register (1979)
Calculated from whole-rock isochron	0.7113 ± 0.0016	Register (1979)
Calculated from clay-mineral isochron	0.7112 ± 0.0049	Register and others (1980)
Permian seawater:		
i) Selected fossils	0.7073	Peterman and others (1970)
ii) Marine limestones	0.7078	Brass (1973)
iii) Anhydrites, polyhalites	0.7076 ± 0.0003	Register (1979)

evidence for a "mid-Cretaceous" event affecting the evaporites. Further, Tremba's (1969) model age, based on large, composite samples, yields a 230-240 m.y.B.P. age which, based on the 32 point isochron of Register and Brookins (1980) is more likely.

RADIOMETRIC K-Ar AGES FOR POLYHALITES FROM THE WIPP SITE

Brookins and others (1980a) have investigated polyhalites ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) by the K-Ar method to see if this mineral is suited for geochronologic study. Unlike sylvite, used by Register and Brookins (1980) for Rb-Sr isochron work, polyhalite is extremely Sr-rich relative to Rb; thus, the $^{87}Rb/^{86}Sr$ ratios are too small and restricted in range for Rb-Sr isochron work. Other workers (see discussion in Brookins and others, 1980a) have stated that polyhalites probably are not suited for K-Ar work, but their reasoning was speculative. Polyhalite is of extreme importance in evaporite sequences because it is commonly interpreted as secondary in origin, and at least one author (Bodine, 1978) has suggested that polyhalite has formed more-or-less continuously from pre-200 m.y.B.P. to very recent times. This period of polyhalite formation would require that water be present in that two moles of water are required for each mole of polyhalite formed. According to Bodine's (1978) ideas, sources of water would have to be present at numerous times throughout the Mesozoic and Cenozoic. The presence of water in the WIPP site area would pose many uncertainties about availability of water to interact with radioactive wastes should the wastes be placed in the evaporites.

A more fundamental question is whether the polyhalite formed early in the history of the evaporites or late if the polyhalite is secondary. To address this and other questions, 19 polyhalites have been selected for study. These include very pure polyhalites, polyhalites mixed with halides, and one polyhalite from the dike contact zone which was mentioned earlier in this paper.

Brookins and others (1980a) reported K-Ar ages for eight polyhalites, including five very pure polyhalites, two polyhalite-halide mixtures, and one polyhalite in the lamprophyre dike contact zone. The data are shown in Table 3. The five pure polyhalites yield a range in K-Ar ages from 198 to 216 m.y.B.P. (mean=208 m.y.B.P.) while the two impure polyhalites yield lower ages of 154 and 174 m.y.B.P. Brookins and others (1980a) attribute the lower ages to the presence of the halides which could cause loss of $*^{40}Ar$ by presence of small amounts of sylvite or K-bearing halite or, possibly, by loss of $*^{40}Ar$ from halide-filled fractures in the polyhalite. The polyhalite in the dike contact zone yields a date of 21.4 m.y.B.P. which is significantly lower than the 34 m.y.B.P. age of the dike. This dike-related material, too, is mixed with sylvite and halite and their genetic relationships are not well known.

More recently, Brookins (1980b) has reported K-Ar ages for four additional polyhalites, three of which were chosen to purposely include halide minerals while the fourth was a pure polyhalite. The pure polyhalite yields 209 ± 7 m.y.B.P. while the impure polyhalites range from 183 to 187 m.y.B.P. Still more recently, Brookins (unpublished information submitted to Sandia Laboratories) has obtained K-Ar ages for three pure polyhalites, one polyhalite-clay mixture, and three halide-bearing polyhalites. The pure polyhalites yield a range of ages from 195 to 205 m.y.B.P. and the polyhalite-clay mixture also yields 205 m.y.B.P. The three polyhalite-halide samples range from 181 to 183 m.y.B.P.

The 10 pure polyhalites plus the one polyhalite-clay mixture yield an average age of 205 ± 5 m.y.B.P., and, exclusive of the two

Table 3. K-Ar radiometric ages for polyhalites sampled from evaporites in Permian Basin, southeastern New Mexico. Age given in million years before present (m.y.B.P.).

Sample	Age (m.y.B.P.)	Source
A. Pure Polyhalites		
E9-15a	216 ± 7	Brookins and others (1980a)
E9-59	212 ± 7	Brookins and others (1980a)
E9-84	200 ± 7	Brookins and others (1980a)
MCC-RC	212 ± 7	Brookins and others (1980a)
MCC-121a	198 ± 7	Brookins and others (1980a)
E9-15b	209 ± 7	Brookins (1980b)
E13-1	201 ± 7	Brookins (unpublished information submitted to Sandia Laboratories)[1]
E13-7 (plus clay)	205 ± 7	Brookins (unpublished information submitted to Sandia Laboratories)[1]
E13-11	205 ± 7	Brookins (unpublished information submitted to Sandia Laboratories)[1]
E13-12a	195 ± 7	Brookins (unpublished information submitted to Sandia Laboratories)[1]
B. Impure Polyhalites (polyhalite plus halite ± sylvite ± anhydrite)		
E9-99	174 ± 6	Brookins and others (1980a)
A8-18	154 ± 15	Brookins and others (1980a)
E9-84b	184 ± 6	Brookins (1980b)
E9-91	187 ± 7	Brookins (1980b)
MCC-121b	183 ± 6	Brookins (1980b)
E13-2b	183 ± 6	Brookins (unpublished information submitted to Sandia Laboratories)
E13-3	183 ± 6	Brookins (unpublished information submitted to Sandia Laboratories)
E13-12b	181 ± 6	Brookins (unpublished information submitted to Sandia Laboratories)
C. Polyhalite in Lamprophyre Dike Contact Zone		
MB7622	21.4 ± 0.8	Brookins and others (1980a)

[1]E13 samples are from drill core next to ERDA-9 at the center of the WIPP site. Locations of other samples are given in the sources cited.

polyhalites dated at 154 and 174 m.y.B.P., the other six samples yield an average age of 183.5 ± 4 m.y.B.P.

One sample (MCC-RC) is from a rubble chimney exposed in a local mine (Mississippi Chemical Mine) where the beds adjacent to the chimney are highly distorted and from which samples MCC-121a (pure polyhalite) and MCC-121b (polyhalite+halides) were taken. If the polyhalite represented newly formed material in the rubble chimney, it should yield a near-zero age. If it is a xenolith affected by partial dissolution, it should yield an age significantly younger than 200 m.y.B.P., and if it represents true xenoliths, then an age of near 200-210 m.y.B.P. would be expected. We consider it especially noteworthy that MCC-RC and MCC-121a yield ages of 212 and 198 m.y.B.P. (Table 3). The fact that MCC-121b yields a lower age of 183 m.y.B.P. is presumably due to loss of $^{*40}Ar$ due to the presence of halides. More important is that the amount of water in the rubble chimneys must have been extremely small; otherwise, xenoliths of halite, anhydrite, and the polyhalite would have been dissolved. If dissolution were prevalent, the textures should show reprecipitated material interlayered with clay-oxide-hydroxide minerals and as void fillings. The evaporite minerals appear to be xenoliths; however, as there is no well defined textural evidence to support the dissolution-reprecipitation model. Instead, the xenoliths are randomly oriented and are highly fragmented on a local scale; some of the banded rubble consists of broken fragments of xenolithic material instead of optically continuous, new generation material. Thus, the age and textural evidence argue against these chimneys as conduits for large amounts of water to enter the evaporite sequence. Further discussion on this matter may be found in SAND (1978).

Brookins (1980c; unpublished report submitted to Sandia Laboratories) has proposed that the post-200 m.y.B.P. ages are due to halide minerals mixed with the polyhalite. An attempt to determine if there is any correlation between age lowering and Na_2O content is shown in Figure 1; the hypothesis being tested is that of Na_2O as proportional to total halide (i.e., sylvite, halite, and potassium-bearing halite). Two distinct curves (A and B) are shown in Figure 1. Curve A is determined for polyhalites with sylvite amounts greater than halite while curve B is for polyhalites with halite amounts greater than sylvite. Both curves show an apparent age lowering with increasing Na_2O content, but at this time the curves are considered only preliminary. If curve B is considered, then it is interesting to test possible ways of age correction for the 21.4 m.y.B.P. polyhalite from the lamprophyre dike contact zone (Table 3), with a Na_2O content of 1.63 percent. If an equation of the type:

$$\frac{\Delta T_1}{T_{f_1}} = \frac{\Delta T_2}{T_{f_2}}$$

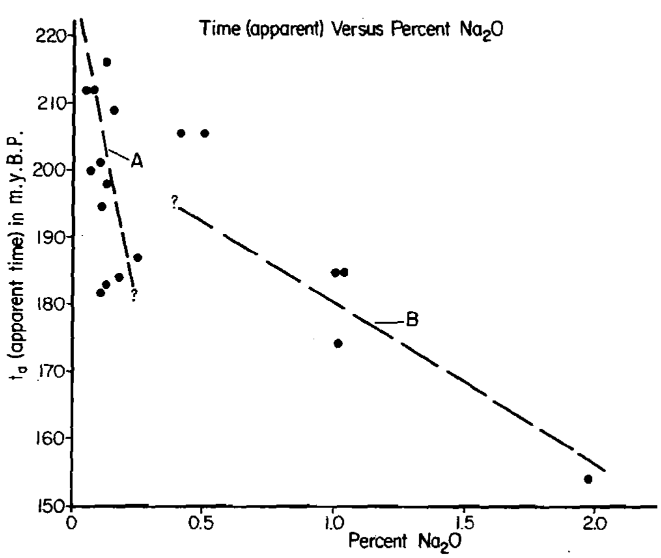

Figure 1. Time (apparent) versus percent Na_2O for early stage polyhalite. Curve A is determined for polyhalites with sylvite amounts greater than halite, and curve B is determined for polyhalites with halite amounts greater than sylvite. Time given in million years before present (m.y.B.P.).

is considered where T_f refers to the age of polyhalite formation and ΔT is the age lowering that is proportional to Na_2O (percent) content, then from the above equation and setting T_1 = 225 m.y.B.P., T_2 = 34.4 m.y.B.P., and ΔT_1 = 63 m.y., ΔT_2 is calculated at 8.3 m.y. This correction, applied to sample MB7622 (Table 3) yields an apparent date of 29.7 m.y.B.P. which is much closer to the emplacement age of the dike. While somewhat speculative, the method shows promise pending future work.

Of additional interest is curve A in Figure 1. Extrapolation to the ordinate indicates a formational age of approximately 240 m.y.B.P. which is in much better agreement with the age of the Late Permian than that obtained by the 214 ± 15 m.y.B.P. Rb-Sr isochron. Finally, it should be mentioned that recent work (S. J. Lambert, oral commun.) has reported that some polyhalite previously thought to be of secondary origin is in fact primary (i.e., petrographic examination shows that it is pre-carnallite formation and not post-carnallite as previously reported). Use of newly calculated ΔG_f^o (standard Gibbs free energy) data for polyhalite (Brookins, unpublished information submitted to Sandia Laboratories) shows that polyhalite is stable with respect to carnallite and to sylvite + anhydrite for ideal conditions. Collectively, all data reported in this paper suggest formation of polyhalite early in the evaporite's history except for the dike contact-zone material. These data in turn, of course, implies that the structurally bonded water in the polyhalites was available from the last brines accompanying epigenesis and was not related to some later Mesozoic-to-Cenozoic sources of water.

CONCLUSIONS

The conclusions drawn from this study are summarized below.

(1) The evaporites of the WIPP site, southeastern New Mexico, are Late Permian based on geologic evidence. Model K-Ar dates (Schilling, 1973; and this study) and model Rb-Sr dates (Tremba, 1969) indicate closure of evaporite minerals to radiogenic daughter element loss between 230-245 m.y.B.P.

(2) Pure evaporite minerals yield a 214 ± 15 m.y.B.P. isochron (Register and Brookins, 1980); these data may indicate end of diagenetic effects concomitant with potash ore formation.

(3) Pure polyhalites yield an average K-Ar date of 205 m.y.B.P. while impure polyhalites yield two groups of samples with post-200 m.y.B.P. and pre-154 m.y.B.P. dates: (a) samples with sylvite ± halite which extrapolate to a possible formational age of 235 m.y.B.P. (fig. 1), and (b) samples with halite ± sylvite which apparently fall on a poorly defined line intersecting the age axis (fig. 1) at about 215 m.y.B.P. Use of this last curve for polyhalite in the contact zone of a 34.4 m.y.B.P. lamprophyre dike allows a 21.4 m.y.B.P. date to be corrected to 29 m.y.B.P. although this method is considered preliminary.

(4) A lamprophyre dike cuts the evaporites some 70 km from the proposed WIPP site. Contact effects are restricted to within 10 m of the contact where exposed in the Kerr-McGee Potash Mine (Brookins, 1980d). Further, dike samples yield identical ages from samples taken from the center of the dikes and at its edge; trace elements have not migrated from the dike into the evaporite (Brookins, 1980d).

(5) Clay mineral separates from detrital material yield a 390 ± 77 m.y.B.P. Rb-Sr isochron which indicates lack of complete rehomogenization of the clay minerals with the brines (Register and others, 1980). The 390 m.y.B.P. may be a minimum date for detrital material.

(6) During this study no geochronologic evidence has been obtained to support either a mid-Cretaceous event (Tremba, 1969) or continuous polyhalite formation throughout the Mesozoic and Cenozoic (Bodine, 1978). Rather, it is proposed that the evaporites have remained chemically and isotopically closed systems since 200 m.y.B.P. This, in turn, attests to the great stability of the evaporites and supports their potential for the disposal of radioactive wastes at the WIPP site.

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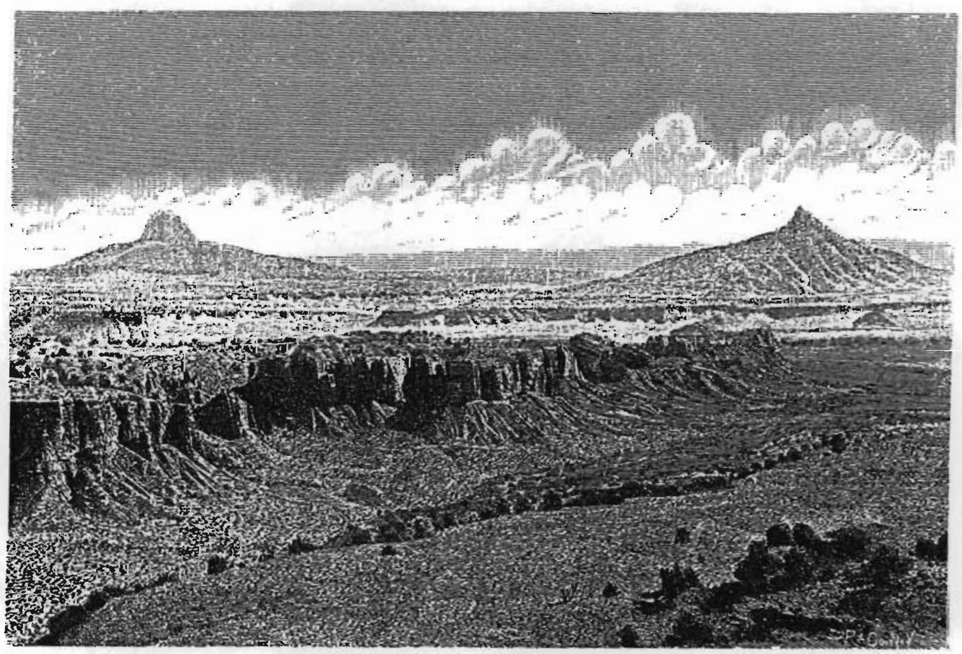

Two large necks, the more distant one being the Cabazon; Cretaceous mesas in the foreground. Photographed on wood. (From U.S. Geological Survey, Sixth Annual Report, 1885.)