Waste Isolation Pilot Plant

Compliance Certification Application

Reference 87

Brookins, D.G. and S.J. Lambert. 1987.
Radiometric dating of Ochoan (Permian) evaporites, WIPP site, Delaware Basin, New Mexico, USA, 84: Materials Research Society. Ed. 771-780.

Submitted in accordance with 40 CFR §194.13, Submission of Reference Materials.

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WESTINGHOUSE ELECTRIC CORPORATION
WASTE ISOLATION DIVISION
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CARLSBAD, NM 88221

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PAGE: 1 of 4

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PAYMENT TERMS: 1% 10 NET 30 DAYS
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1	71510-00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS. ANDERSON, R.Y., DEAN, W.E., KIRKLAND, JR., D.W., AND SNIDER, H.I. 1972 PERMIAN CASTILE VARVED EVAPORITE SEQUENCE, WEST TEXAS AND NEW MEXICO. GEOLOGICAL SOCIETY OF AMERICA BULLETIN, VOL. 83, PP. 59-86	10.00000	EA	38.000	EA	380.00
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3	71510-00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS. DACHMAN, G.O., 1976 CENOZOIC DEPOSITS OF SOUTHWESTERN NEW MEXICO AND AN OUTLINE OF THE HISTORY OF EVAPORITE DISSOLUTION. JOURNAL OF RESEARCH, U.S. GEOLOGICAL SURVEY, VOL. 4, NO.2, PP. 135-149. NO LONGER AVAILABLE PER USGS	10.00000	EA	10.000	EA	100.00
4	71510-00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS. BROOKINS, D.G. AND S.J. LAMBERT. 1987 RADIOMETRIC DATING OF OCHOAN (PERMIAN) EVAPORITES, WIPP SITE, DELAWARE BASIN, NEW MEXICO, USA, 84: MATERIALS RESEARCH SOCIETY. ED. 771-780	10.00000	EA	22.000	EA	220.00
5	71510-00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS. BROOKINS, D.G., J.K. REGISTER, AND H. KRUEGER. 1980 POTASSIUM-ARGON DATING OF POLYHALITE IN SOUTHWEST NEW MEXICO, GEOCHIMICA ET COSMOSHIMICA ACTA 44, 635-637. PERGAMON PRESS, JOURNALS DIV MAXWELL HOUSE, FAIRVIEW PARK ELMSFORD, NY 10523 (914) 592-7700	10.00000	EA	18.000	EA	180.00
6	71510-00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS. CHOPPIN, G.R. 1983 SOLUTION CHEMISTRY OF THE ACTINIDES RADIOCHIMICA ACTA. VOL. 32 43 53 ACADEMIC PRESS 1250 6TH AVE. SAN DIEGO, CA 92101 (619) 699-6328	1.00000	EA	16.000	EA	16.00
7	71510 00123 PUBLICATION, BOOKS, BOOKLETTES, PAMPHLETTS. SEE NOTE FOR SPECS.	10.00000	EA			00

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RADIOMETRIC DATING OF OCHOAN (PERMIAN) EVAPORITES, WIPP SITE, DELAWARE BASIN, NEW MEXICO, USA

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ABSTRACT

We have attempted radiometric dating of halide-sulfate salts and clay minerals from the Delaware Basin, New Mexico, USA, as part of geochemical study of the stability of the evaporite sequence at the WIPP (Waste Isolation Pilot Plant--a US DOE facility) site. We undertook this dating to determine: (1) primary age of evaporite genesis or time(s) of recrystallization, (2) if previously undated evaporite minerals (leonite, polyhalite, kieserite) give useful data, and (3) if the detrital clay minerals have been radiometrically reset at any time following their incorporation into the evaporite medium. We have shown earlier that polyhalites can indeed be successfully dated by the K-Ar method, and once corrections are applied for admixed halide minerals, dates of 210-230 Ma for the Delaware Basin are obtained. Rb-Sr isochrons from early stage sylvites-polyhalites- anhydrites yield 220 ± 10 Ma, even when some sylvites yield lower K-Ar dates due to loss of $^{40}Ar^*$. K-Ar dates on leonites and kieserites are also low due to $^{40}Ar^*$ loss, but their Rb-Sr dates are higher. Detrital clay minerals from the Delaware Basin collectively yield a highly scattered isochron (390 ± 77 Ma), but samples from a local area, such as the WIPP Site, give a much better age of 428 ± 7 Ma. These dates show that the interaction between the clay minerals and the evaporitic brines was insufficient to reset the clay minerals Rb-Sr systematics. In a related study, we note that a dike emplaced into the evaporite at 34 Ma had only very limited effect on the intruded rocks; contact phenomena were all within 2 m of the dike. All of our geochemical (radio-metric and trace element) studies of the WIPP site argue for preservation of the isotopic and chemical integrity of the major minerals for the past 200 Ma.

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INTRODUCTION

The dating of evaporites by conventional geochronologic methods has been a problem of some concern for many years (See discussion in Brookins [1]). K-Ar dating of sylvite has yielded spurious results [2], for example, and it has been questioned whether or not any evaporite minerals preserve their original isotopic signatures [2,3]. We have undertaken a study of the evaporite minerals of the bedded evaporite sequence in southern New Mexico to test whether or not reliable ages could be obtained, and for other reasons (given below). The units we have worked with include the Salado and Castile Formations, which are described in detail in Powers et. al. [4] and in Register [5]. The U.S. Department of Energy plans to store transuranic radio-active wastes in the Salado Formation, and our studies have been in large part to carry out geochronologic measurements to test mineral and rock isotopic characteristics in the area. Our samples have been obtained from drill core and underground workings at the site (WIPP; Waste Isolation Pilot Project) and from core and potash mine workings in the surrounding area. The reader is referred to [4] for geographic details and other background information.

The age of the Salado and Castile formations, Ochoa Series, is given as Late Permian [4]. The rocks 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. Structural disturbances of the evaporite sequence occur in the vicinity of igneous dikes which intrude the evaporites some 10 km from the WIPP site, [18] and at local rubble chimneys commonly and erroneously called "breccia pipes") [19] of Pleistocene age, and near the Capitan Limestone at the basin margin [18].

One of the important questions concerning use of these evaporites for the 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 Ma, although epigenesis and potash ore-zone formation may not have been complete until some time later. To answer this question of closed versus open system conditions, we have undertaken study of the evaporites by the K-Ar and Rb-Sr geochronologic methods.

PREVIOUS GEOCHRONOLOGIC STUDIES

Several geochronologic studies have been carried out of samples taken at or near the WIPP site. Schilling [6] reported K-Ar ages for langbeinite, sylvite, and mixtures of the two minerals. The one pure langbeinite analyzed yielded 245 ± 10 Ma, two langbeinite-sylvite mixtures yielded 137 and 147 Ma, and two sylvites yielded 18 and 74 Ma. Since sylvites easily lose radiogenic (*) ^{40}Ar, the 245 Ma 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 Ma [7].

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 Ma [8]. Two additional dates of 34.4 ± 1.3 and 34.7 ± 1.4 Ma [9] have confirmed these dates.

Tremba [10] attempted Rb-Sr age determinations for several evaporite samples. His results indicate evaporite formation at 230± 10 Ma and also a possible "mid-Cretaceous" event at about 120-130 Ma. A more detailed study has been completed by Register [5] which has been reported elsewhere [11,12].

RECENT STUDIES

Brookins and others [13] have reported K-Ar ages for pure polyhalite and polyhalite-halide mixtures, and additional polyhalites have also been studied [11].

The Rb-Sr studies [5,12,14,15] are of importance in discussing the origin and stability of the evaporites of the Salado Formation. These studies (Table I) show that unaltered evaporite minerals (e.g., sylvite, langbeinite, polyhalite, anhydrite) yield a 199 ± 20 Ma isochron with initial $^{87}Sr/^{86}Sr = 0.7076 \pm 0.0014$, based on 41 samples. Nine of these samples fall off the $^{87}Sr/^{86}Sr$ axis and some show values in excess of 0.712 indicating that they have incorporated Sr with relatively high $^{87}Sr/^{86}Sr$ after initial crystallization. The 32 remaining samples yield an age of 214 ± 15 Ma with initial $^{87}Sr/^{86}Sr = 0.7093 \pm 0.007$ [12]. This age is considered more reliable than the 199 Ma date. The 214 ± 15 Ma date is low, however, compared to the 235 ± 5 Ma date for the Triassic-Permian Boundary. Because some polyhalite dates cluster between 212-216 Ma (see discussion below), it has been suggested that final epigenetic effects may not have been complete until some 20 Ma after original evaporite formation.

Alternatively, the loss of $^{87}Sr^*$ due to some geologic event in the Triassic cannot be ruled out. What is noteworthy, however, is that the majority of dates previously reported for reliable samples yield ages in excess of 200 Ma.

An earlier attempt at dating evaporite whole rocks [5] in the northern Delaware Basin reports a date of 171 ± 36 Ma with initial $^{87}Sr = 0.7113 \pm 0.0016$ for 18 samples, 15 of which fall on or very close to the ordinate. These samples contain admixed clay minerals and oxide-hydroxide coating, and the samples are considered marginal at best for Rb-Sr reconnaissance work.

Tremba [10] has suggested, based on limited data, perturbations of the Rb-Sr systematics of evaporite minerals of the Salado Formation at 129 ± 5 Ma and 120 ± 28 Ma. Register [5] has questioned Tremba's data because (1) the samples are very few in number; (2) in one "apparent isochron" only four of five data were used, and the fifth sample falls well above the isochron and would drastically increase the age but no reason is given for it being discarded; and (3) lack of tectonic evidence for a "mid-Cretaceous" event affecting the evaporites. Further, Tremba's model age, based on large, composite samples, yields a 230-240 Ma, which, considering the 32 point isochron of [12], is more likely.

Table I. Rb-Sr age determinations for selected samples in evaporites of the Delaware (Permian) Basin, southeastern New Mexico. Locations for samples are given in the sources cited; Ma = Million years before present.

Rb-Sr Isochrons	Age (Ma)	Source
Evaporite minerals	129 ± 5	[10]
Evaporite minerals	120 ± 28	[10]
Evaporite minerals: composite	230 ± 240	[10]
41 evaporite minerals	199 ± 20	[5]
32 evaporite minerals	214 ± 15	[12]
Evaporite whole rocks	171 ± 36	[5]
Clay minerals in evaporites	390 ± 77	[12]
WIPP site clay minerals	428 ± 7	[18]

RADIOMETRIC K-Ar AGES FOR POLYHALITES FROM THE WIPP SITE

Brookins and others [13] have investigated polyhalites ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) from the middle and upper Salado Formation by the K-Ar method to see if this mineral is suited for geochronologic study. Polyhalite is of extreme importance in evaporite sequences because it is commonly interpreted as secondary in origin, and at least one author [16] has suggested that polyhalite has formed more-or-less continuously in the Delaware Basin from pre-200 Ma to very recent times. This period of polyhalite formation would require that water be continuously available since two moles of water are required for each mole of polyhalite formed. According to Bodine's [16] ideas, sources of water would have to be present at numerous times throughout the Mesozoic and Cenozoic. The continued presence of abundant water in the WIPP area would pose many uncertainties about availability of water to interact with radioactive wastes.

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 were studied. These include very pure polyhalites, polyhalites mixed with halides, and one polyhalite from the dike contact zone mentioned earlier in this paper.

Brookins and others [13] 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 (Table II). Five pure polyhalites yield a range in K-Ar ages from 198-216 Ma (mean=208Ma) while the two impure polyhalites yield lower ages of 154 and 174 Ma. Brookins and others [13] 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 ages or mechanisms of $^{40}Ar^*$ loss are not known. The polyhalite in the dike contact zone yields a date of 21.4 Ma which is significantly lower than the 34 Ma age of the dike. This dike-related material, too, is mixed with sylvite and halite and their genetic relationships are not well known. Brookins [11] 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 Ma while the impure polyhalites range from 183 to 187 Ma. Brookins [1] obtained K-Ar ages for three more pure polyhalites, one polyhalite-clay mixture, and three halide-bearing polyhalites. The polyhalites yield a range of ages from 195 to 205 Ma and the polyhalite-clay mixture also yields 205 Ma. The three polyhalite-halide samples range from 181 to 183 Ma. In summary, the 10 pure polyhalites, plus the one polyhalite-clay mixture, yield an average age of 205 ± 5 Ma, and, exclusive of the two polyhalites dated at 154 and 174 Ma, the other six samples yield an average age of 183 ± 4 Ma. One sample (MCC-Rc, Table II) 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 other samples were taken. If the polyhalite represented newly formed materials 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 Ma, and if it represents true xenoliths, then an age of near 200-210 Ma would be expected. It is noteworthy that all polyhalites in the chimneys yield ages of 212 and 198 Ma. 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, but the evaporite minerals appear to be xenoliths as there is no well-defined textural evidence to support the dissolution--reprecipitation model. Collectively, all data summarized 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, imply that the structurally bonded water in the polyhalites was available from the last brines accompanying epigenesis and is not related to some later Mesozoic-to Cenozoic sources of water.

Additional evaporite minerals from the IMC Mine have been studied by the Rb-Sr and K-Ar methods [17]. The data are given in Table III. The samples include very well-crystallized sylvite, secondary leonites, langbeinites, kieserite, and an authigenic sample of sylvite-halite with disseminated talc-magnesite. Langbeinites yield Rb-Sr and K-Ar dates in excess of 175 Ma. The kieserite sample yield an anomalously old Rb-Sr date (250 Ma), but a very young K-Ar date (103 Ma). The young K-Ar date is in part a reflection of the poor quality of this mineral for K-Ar work, due to its hygroscopic nature, and possible loss of $^{40}Ar^*$ by diffusion. The leonite is clearly a secondary mineral, and it yields an extremely young K-Ar date of 12 Ma. The 78-109 Ma Rb-Sr dates may be due to loss of $^{87}Sr^*$ from the leonite; alternately, it may have crystallized somewhere in the Mid-Cretaceous, although geological evidence to support this hypothesis is lacking. The sylvite is of interest because both the K-Ar and Rb-Sr model dates are near 180 Ma, which makes it the oldest sylvite K-Ar age (but youngest Rb-Sr age) yet determined from this area. Why some sylvites yield dates as young as few Ma, and this one is as old as 180 Ma, is unknown, and will be the subject of future studies.

Table II. K-Ar radiometric ages for polyhalites sampled from evaporites in the Delaware (Permian) Basin, southeastern New Mexico. Age given in million years before (Ma). (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.)

Sample	Age (Ma)	Source
A. Pure Polyhalites		
E9-15a	216 ± 7	[13]
E9-59	212 ± 7	[13]
E9-84	200 ± 7	[13]
MCC-Rc	212 ± 7	[13]
MCC-121a	198 ± 7	[13]
E9-15b	209 ± 7	[11]
E13-1	201 ± 7	[18]
E13-7 (plus clay)	205 ± 7	[18]
E13-11	205 ± 7	[18]
E13-12a	195 ± 7	[18]
B. Impure Polyhalites (polyhalite plus halite ± sylvite ± anhydrite)		
E9-99	174 ± 6	[13]
A8-18	154 ± 15	[13]
E9-84B	184 ± 6	[11]
E9-91	187 ± 7	[11]
MCC-121b	183 ± 6	[11]
E13-2b	183 ± 6	[18]
E13-3	183 ± 6	[18]
E13-12b	181 ± 6	[18]
C. Polyhalite in Lamprophyre Dike Contact Zone		
MB7622	21.4 ± 0.8	[13]

Table III. New Rb-Sr and K-Ar dates for selected IMC mine evaporites*

Sample	Description	Age-Method
IMC-1	Magnesite-talc-Sylvite-halite	183 ± 15 Ma (Rb-Sr) 304 ± 12 Ma (K-Ar)
IMC-2A,2B	leonite $K_2Mg(SO_4)_2 \cdot 4H_2O$	78 ± 15 Ma (Rb-Sr) 109 ± 15 Ma (Rb-Sr) 12.6 ± 0.5 Ma (K-Ar)
IMC-3A,3B	Langbeinite $K_2Mg_2(SO_4)_3$	173 ± 15 Ma (Rb-Sr) 205 ± 12 Ma (Rb-Sr) 202 ± 7 Ma (K-Ar) 188 ± 6 Ma (K-Ar)
IMC-4	Kieserite ($MgSO_4$)	260 ± 20 Ma (Rb-Sr) 103 ± 5 Ma (K-Ar)
IMC-5A,5B	Sylvite (KCl)	180 ± 12 Ma (Rb-Sr) 177 ± 12 Ma (Rb-Sr)

*Source: Brookins et al., [17]. All Rb-Sr dates are calculated assuming initial $^{87}Sr/^{86}Sr$ = 0.71.
Samples collected by N. Rempp, IMC mine.

CLAY MINERALS (AND INSOLUBLE RESIDUES OF LEACHED SALT SAMPLES)

Register and Brookins [12] first studied clay minerals from the WIPP area evaporites and report a date of 390 ± 77 Ma for samples from a wide variety of locations. They are careful to point out that the 390 Ma date is significant only to demonstrate that the clay minerals were not reset to a Late Permian date by reactions with evaporitic brines. More recently the authors have collected a series of clay seam samples from the underground working at the WIPP site, and these are reported below. Two types of samples were used for study; those in which enough clay (and iron oxyhydroxide) minerals were present for mechanical separation, and those in which an attempt was made to separate clays by dissolution of the salt samples. In addition, one sample (WP-5) contained enough polyhalite for hand separation. The attempt at concentrating sufficient insoluble, uncontaminated material by dissolution did not work well. X-ray data show that the samples so treated contain moderate amounts of gypsum, halite, anhydrite, and their chemistry indicates the presence of significant amounts of K, presumably derived from the evaporite salts. This excess K is attributed as a possible factor as to why the K-Ar dates shown in Table IV for the insoluble residues range from 55 to 114 Ma. These dates are interpreted as having no significance at all.

The K-Ar dates for the clay minerals (± oxyhydroxide minerals) separated by hand yield dates from 365-390 Ma, in agreement with the Rb-Sr work [12]. These dates are offered as evidence that the K-Ar systematics of these clay minerals were not completely reset to age of evaporite mineral formation when entrapped in the evaporitic brine environment.

Rb-Sr dates were determined in the UNM Geology Department Geochronology Laboratory. The data are given in Table V and Figure 1. The methods used for the study include standard dissolution methods for silicate-oxide assemblages, involving: dissolution in HF, deionized water, cooling, filtering, and separation of Rb and Sr by ion exchange chromatography using 2.2 N HCL as eluant. ^{84}Sr-enriched and ^{87}Rb-enriched spikes were added to the samples prior to dissolution. After the ion exchange procedure, samples were fused in quartz beakers, cooled and stored. Samples were loaded onto a rhenium filament and isotopic data obtained using a Nier-design 12-inch, 90-degree sector thermal ionization mass spectrometer. All ^{87}Sr/^{86}Sr values were normalized to ^{86}Sr/^{88}Sr = 0.1194. Six runs on Eimer and Amend Standard $SrCO_3$ during the course of this study yielded ^{87}Sr/^{86}Sr = 0.70803 ± 0.00005 (one sigma).

Table IV. Potassium-Argon Age Determinations

Sample	^{40}Ar* (ppm)	K (%)	^{40}40Ar*/^{40}Ar	t (Ma)[2]
FH-6B-C	0.02195	0.0694	0.387	378 ± 15
	0.02007	0.741	0.526	
FH-45-C,O	0.02755	0.904	0.753	390 ± 15
	0.02583	0.860	0.657	
FH-42-I	0.005177	0.147	0.053	88.7 ± 5.3
	0.001335	0.197	0.087	
		0.273		
FH-32-C	0.02272	0.769	0.744	387 ± 15
	0.02305	0.757	0.757	
FH-27-C	0.02315	0.821	0.659	365 ± 14
	0.02259	0.806	0.546	
FH-27-I(P)	0.001913	0.491	0.125	55.5 ± 3
	0.001873	0.475	0.138	
FH-27-WR	0.000898	0.045	0.164	324 ± 20
	0.000555	0.050	0.193	
	0.002236	0.057	0.415	
	0.001311		0.334	
FH-26-C	0.02783	0.931	0.548	382 ± 15
	0.02516	0.860	0.492	
FH-6A-I	0.09240	6.687	0.894	187 ± 7
	0.1056	7.245	0.795	
	0.08967	6.987	0.790	
FH-4-I	0.005578	0.634	0.243	114 ± 5
	0.004565	0.684	0.173	
	0.006156		0.195	

Ma = millions of years before the present; I = insoluble residue; C = clay mineral separate; O = oxide minerals; P = polyhalite.

Table V: WIPP Site Rb-Sr Data Summary

Sample	Rb(ppm)	Sr(ppm)	^{87}Sr/^{86}Sr	^{87}Rb/^{86}Sr
FH4ins	10.96	9041.0(1)	0.7072(8)	0.00351
FHGAins	0.54	3481.7(1)	0.7076(3)	0.00045
FH6Bins	42.18	58.3(6)	0.7199(9)	2.0937
FH26wr	0.15	1.2(2)	0.7083(0)	0.35576
FH27ins	2.55	7449.1(4)	0.7080(5)	0.00099
FH32wr	0.45	1.76(6)	0.7130(0)	0.74016
FH40ins	11.41	4129.5(3)	0.7073(5)	0.00799
FH42ins	40.57	83.7(3)	0.7159(9)	1.40306
FH45ins	48.17	42.0(2)	0.7271(0)	3.32312
WIPP1ins	46.31	25.1(4)	0.7405(7)	5.34694

notes: ins = insoluble, wr = whole rock

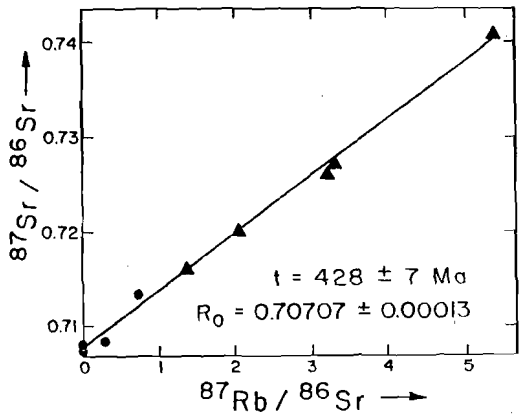

Figure 1. Rb-Sr isochron for clay minerals (Δ) and oxy-hydroxide minerals (o) (See text for discussion).

DISCUSSION

Previous work shows a clustering of dates of clay minerals from the Delaware Basin, both by Rb-Sr and K-Ar, between about 330 and 430 Ma. Surprisingly, the insoluble residues from the samples of this study define a fairly good isochron with a 428 Ma. date. These dates are well within the limits of uncertainty of previously reported K-Ar and Rb-Sr dates. The importance of the 428 Ma isochron is that, again, the Rb-Sr systematics of the samples were largely unaffected by their diagenetic residence time in the evaporitic brines.

The original interpretation of these pre-Permian dates, by Brookins and others [13] and Brookins [1] was for an aeolian origin for the clay minerals, and lack of re-setting of their K-Ar and Rb-Sr isotopic systematics due to incorporation into, and reaction with, the evaporitic brines. The 390 ± 77 Ma Rb-Sr isochron for clay minerals from several locations (Register, [5] was badly scattered, and no quantitative comments concerning provenance, and thus extent of diagenetic reaction, could be made). The isochron of figure 1, however, is much more linear (i.e. the error on the age is only 7 Ma and the error on the initial intercept only ± 0.00013). Since the samples used for this study are all from the WIPP mine, then problems of mixed provenance, etc. may have been avoided. For example, if samples with different prehistories, including different initial ratios, are homogenized at some time, t, then several parallel isochrons may result, all of the same age. This cannot be ruled out for the samples reported by Register [5]. The data of this study also suggest, but do not unequivocally prove, that there may have been a 400-450 Ma source area for the clay minerals which dominated the input. Since, in theory, source areas could have included everything from earlier in the Permian to the Precambrian, this is surprising, and should be pursued for the purposes of paleogeology.

CONCLUSIONS

Based of the forgoing data and discusaion of the proceeding pages, the conclusions of this work are:

(1) Sylvite is a suitable mineral for Rb-Sr age determination, either for model ages or for use in isochron construction.

(2) Polyhalite is suitable for K-Ar age determinations. Admixed halide minerals cause apparent age lowering, but can be corrected for.

(3) The detrital nature of clay mineral-oxyhydroxide mineral assemblages from the evaporite sequence is confirmed by both K-Ar and Rb-Sr study. These minerals were not reset to the time of sedimentary-diagenesis (Late Permian to Early Triassic) despite their residence in/with evaporite brines.

(4) Provenance for the detrital clay minerals is not resolved. The clustering of 400 Ma dates is difficult to explain in terms of either aeolian or flood sources.

(5) Some evaporite minerals are not well suited for Rb-Sr and/or K-Ar work, including leonite, kieserite and halite.

(6) Sylvite generally yields low and variable K-Ar dates, but at least one yields 180 Ma. The mechanism for $^{40}Ar^*$ loss from sylvite is not known.

(7) The fact that Rb-Sr isochron and individual dates and K-Ar (corrected) polyhalite and langbeinite dates all cluster at or in excess of 200 Ma shows that the evaporites from the Salado Formation at and near the WIPP have not been recryatallized regionally, and probably not locally, post 200 Ma.

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LABORATORY AND MODELLING STUDIES OF SODIUM BENTONITE GROUNDWATER INTERACTION

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ABSTRACT

According to the present Finnish concept sodium bentonite will be used as a buffer material in the repository for high-level waste. Experimental and theoretical studies treating the effect of bentonite upon the chemical conditions in a repository have been initiated with the object of specifying the chemistry of the near field.

Sodium bentonite was let react with water under anaerobic conditions at 25°C for 540 days, during which time six fluid samples were extracted for the chemical analysis of 15 chemical species. The generated fluid phase was alkaline (pH = 9...10) and contained a high amount of bicarbonate. Also a low redox-potential was measured. The fluid phase chemistry was investigated using the geochemical code PHREEQE. Calcite saturation was observed in all fluid samples.

A modelling of sodium bentonite interaction with water based on the main mineral components of bentonite was also performed with PHREEQE. A fairly good agreement between experimental results and model calculations was observed.

INTRODUCTION

In Finland, the current main option for the management of spent fuel is the direct disposal of spent nuclear fuel in granitic bedrock. The concept is based on multiple barriers. The chemical conditions in the repository and nearfield will thus be determined by the interaction between the groundwater and the bedrock, buffer and backfill materials and waste canisters. In order to get a more realistic description of the chemical conditions in the repository for the assessment of the corrosion of canister materials, the dissolution of spent fuel and speciation and transport of radionuclides, the possible effects of the buffer material sodium bentonite must be taken into account.

Groundwater chemistry in granitic bedrock has been studied extensively during the last years in the framework of site investigation programmes in Sweden, Switzerland and Canada. The first results from a deep test borehole in Finland are now available [1]. In addition, factors affecting the groundwater composition in Finnish bedrock have been evaluated [2].

There are very few reported results on the chemical effects of sodium bentonite. The reported experiments concern mainly the swelling behaviour, mineral alteration and leachability of bentonite. In order to get information on the changes in the groundwater chemistry due to sodium bentonite, experimental and theoretical studies were initiated.