

Waste Isolation Pilot Plant

Compliance Certification Application

Reference 88

Brookins, D.G., J.K. Register, and H. Krueger. 1980.

Potassium-argon dating of polyhalite in southeast New Mexico, *Geochimica et Cosmochimica Acta* 44, 635-637.

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Potassium-argon dating of polyhalite in southeastern New Mexico

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Abstract—Polyhalite, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$, is an important mineral in many evaporites. Although its use for K-Ar dating has never been investigated, our results indicate that it is a very useful mineral for dating events ranging from the time of potash mineralization to any younger events which may have affected the evaporite. Five K-Ar dates on pure polyhalite, including two from included material and from beds distorted by the formation of a rubble chimney, yield dates between 198 and 216 Myr, in good agreement with Rb-Sr dates and the diagenetic age of the potash deposits from the same rocks. Two polyhalites mixed with sylvite gave lower dates (154 and 174 Myr) which is to be expected because of radiogenic ^{40}Ar loss from the sylvite phase. One polyhalite, formed after the intrusion of a 31 Myr lamprophyre dike, yielded 21 Myr. Collectively our results indicate that pure polyhalite is satisfactory for K-Ar dating and may provide critical age information in studies of the geologic history of the evaporite sequences.

INTRODUCTION

It is an established fact that some evaporite minerals yield K-Ar dates clearly lower than their age of formation. Sylvite, in particular, has yielded anomalously low dates due to loss of radiogenic ^{40}Ar (See discussion in DALRYMPLE and LANPHERE, 1969). Evaporite minerals from the Castile Formation of southeastern New Mexico previously dated by the K-Ar method include langbeinite, sylvite and mixtures of these two minerals (SCHILLING, 1973). Pure langbeinite yields a date of 245 ± 10 Myr which is reasonable for formation in the Late Permian, while pure sylvite yielded younger dates of 18 and 74 Myr. Two langbeinite-sylvite mixtures yielded dates of 137 and 147 Myr.

Polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$] from southeastern New Mexico is of special interest because the area is being studied for the possible storage of radioactive wastes. At the WIPP (Waste Isolation Pilot Plant) area (SAND, 1978), the evaporites contain several well defined zones rich in polyhalite. This mineral is also found sporadically distributed throughout the sequence (commonly close to sylvite, carnalite, or langbeinite zones). Polyhalite is interpreted as secondary on the basis of petrographic studies (See summary in SAND, 1978). Whether it formed at about the time of sylvite-langbeinite ore formation or much later is subject to debate.

The time of origin of polyhalite and its subsequent stability are crucial questions in any evaluation of the salt beds for radioactive waste storage. Polyhalite contains two molecules of structurally bonded water. If polyhalite was formed in very recent times, the argument can be made that the area has been sub-

jected to infiltration by aqueous fluids. If the polyhalite formed early in the history of the evaporite sequence, the opposite argument can be made because the presence of this extremely soluble mineral indicates little or no infiltration of the evaporite sequence by aqueous fluids. Although the matter of whether or not large amounts of water have penetrated the WIPP site is beyond the scope of this paper, it is important to keep in mind that polyhalite is a potentially important indicator of geologic events which may have affected the area.

REGISTER (1979; and manuscript in preparation) has independently dated sylvite-polyhalite-anhydrite from the Castile Formation potash zones at 213 ± 10 Myr by the Rb-Sr isochron method (27 data with $^{87}Rb/^{86}Sr = 0.006-329.0$ and $^{87}Sr/^{86}Sr = 0.7071-1.6412$; $\lambda = 1.42 \times 10^{-11}/yr$ for ^{87}Rb). A brief summary of this work is given by BROOKINS *et al.* (1978). Despite a 1:1 molar ratio for K:Ca in polyhalite, the Sr content of the evaporating primary brine and secondary brines was presumably so high that all polyhalite data fall between 0.7074 to 0.7082 on the $^{87}Sr/^{86}Sr$ ordinate. Because of the massive nature of the polyhalite, the fact that it appears to be undisturbed since its time of formation, and because its crystal system (trigonal) may be more favorable for radiogenic ^{40}Ar retention, it was decided to attempt to date the polyhalite by conventional K-Ar methodology.

SAMPLE PREPARATION AND ANALYSIS

Samples of the purest available polyhalite were selected from various drill cores or other available specimens. The physical characteristics and solubility of polyhalite place severe restrictions on sample preparation and purification.

Table 1. Analytical data and calculated ages

Sample	Rad. ^{40}Ar (ppm)	Rad. ^{40}Ar Total ^{40}Ar	K (%)	Age, Myr
1. E9-84	0.1803	0.907	12.42	200 \pm 7
	0.1824	0.951	12.38	
2. E9-59	0.1876	0.817	11.87	212 \pm 7
	0.1819	0.913	11.90	
3. E9-15	0.1966	0.761	12.34	216 \pm 7
	0.1949	0.775	12.35	
4. MCC-M121	0.1810	0.934	12.32	198 \pm 7
	0.1796	0.888	12.60	
5. 2S-638.2	0.1706	0.828	11.29	212 \pm 7
	0.1807	0.943	11.30	
6. E9-99	0.1452	0.897	11.62	174 \pm 6
	0.1517	0.900	11.83	
			11.71	
7. A8-18	0.1380	0.899	12.29	154 \pm 5
	0.1325	0.841	12.11	
			12.24	
			12.08	
8. MB-76-22	0.01800	0.291	12.12	21.4 \pm 0.8
	0.01813	0.343	12.16	

The selected material was very gently crushed by hand to -40/+200 mesh under dehumidified conditions.

Radiogenic argon analysis were performed in duplicate on separate aliquots of each sample using conventional K-Ar dating techniques. No heating of the samples prior to analysis was feasible because of the sensitive nature of the polyhalite structure. The argon analysis were performed statically using an AEI MS-10 mass spectrometer.

Potassium analysis were done by flame photometry after fusion of the samples with LiBO_3 .

Results of all analysis are shown in Table 1. Ages have been calculated using the constants of STEIGER AND JÄGER (1977). Descriptions and locations of the samples are given in Table 2.

RESULTS AND DISCUSSION

Five of the eight analyzed samples (Nos 1-5) yield dates in excellent agreement with the independently determined Rb-Sr date of 213 \pm 10 Myr for the same evaporite sequence (REGISTER, 1979), although not from the same samples. The K-Ar dates range from 198 \pm 7 to 216 \pm 7 Myr with an arithmetic mean of 208 Myr (Table 1).

The Salado and Castile Formations are Late Permian and therefore were deposited about 240-225 \pm 10 Myr ago. This poses a problem at first glance because the Rb-Sr and K-Ar dates are younger by some 20-30 Myr. Recent interpretations of the genesis of the potash deposits (R. Y. ANDERSON, personal communication; BROOKINS and REGISTER, unpublished data) suggest a dissolution-remobilization-final precipitation sequence. These diagenetic events probably were complete in the early-to-mid Triassic (about 210 Myr ago). Petrographic studies of the salt beds indicate extensive early diagenetic-epigenetic recrystallization. While this event has not been reliably dated, the combined Rb-Sr isochron date (Register, 1979) and the K-Ar polyhalite data (this report) agree with the suggested 210 Myr age for final crystallization.

More important is the fact that the five most reliable samples all yield dates close to 210 Myr even though the samples came both from different depths in undisturbed core (Nos 1-3) and from highly dis-

turbed zones (Nos 4, 5) taken from a polyhalite-rubble chimney exposed Corporation Mine and ite beds very near the amounts of water been of this rubble chimney be expected to have dis material would yield a halite and halite-sylvite ney appear to repres. bedded strata rather tha due to the formation c supported by the polyh

Two samples (Nos-6 contain several percent X-ray diffraction and c is known to lose ^{40}Ar 1 dates as being too you any particular 'event sequence. It should be samples are from undis in the evaporite sequ tectonic effects are evid these samples. The un dating has been mentie

In the Kerr-McGee dike yields a K-Ar a 31 Myr (See SAND, 1979 immediately adjacent to lized and second gener and other minerals som prophyre. Because the Mine have been mined ible, a sample of very (See Table 2) was obt Institute of Technology. This sample (No. 8) wi date of 21.4 \pm 0.8 Myr age of the lamprophy obtained, questions at dating could be raised with the established age 210 Myr for samples direct evidence that the a local event and appar zones.

TREMBLA 1969) and more-or-less continuou tion of the evaporite s and into the Cenozoic able geochronologic c Rb-Sr mineral dates). their hypothesis.

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The data presented ab reasons:

(1) The determined p with the Rb-Sr iso

Table 2. Sample information

Sample locations and remarks		
1. E9-84	Polyhalite (99 + %)	DH ERDA 9. 1784.2-1784.3 ft
2. E9-59	Polyhalite (99 + %)	DH ERDA 9. 1959.1-1759.8 ft
3. E9-15	Polyhalite (99 + %)	DH ERDA 9. 1215.2-1215.3 ft
4. MCC-M121	Polyhalite (99 + %)	Mississippi Chemical Corporation Mine; from area of highly distorted beds near rubble chimney (See text).
5. 28/638.2	Polyhalite (99 + %)	Mississippi Chemical Corporation Mine; from Pleistocene rubble chimney exposed in workings, sample from apparent detrital material.
6. E9-99	Polyhalite (plus sylvite-halite)	DH ERDA 9. 1499.0-1500.0 ft
7. A8-18	Polyhalite + sylvite	DH AEC 8. 1618.9-1619.4 ft
8. MB76-22	Polyhalite (99 + %)	From contact zone of recrystallized evaporate minerals with lamprophyre dike (31 Myr) from Kerr-McGee Potash Mine.

(Note: All locations are given in more detail in SAND, 1978)

turbed zones (Nos 4, 5). These last two samples were taken from a polyhalite-rich inclusion in a Pleistocene rubble chimney exposed in the Mississippi Chemical Corporation Mine and from highly distorted evaporite beds very near the rubble chimney. Had large amounts of water been present during the formation of this rubble chimney, than the polyhalite(s) would be expected to have dissolved and any newly formed material would yield a date of near 'zero' Myr. Relict halite and halite-sylvite-anhydrite in the rubble chimney appear to represent brecciated parts of original bedded strata rather than products of recrystallization due to the formation of the rubble chimney; a view supported by the polyhalite dates.

Two samples (Nos-6 and 7, Table 1) were found to contain several percent sylvite and/or sylvite-halite by X-ray diffraction and chemical analysis. Since sylvite is known to lose ^{40}Ar readily, we interpret these two dates as being too young and therefore not indicating any particular 'event(s)' affecting the evaporite sequence. It should be emphasized that these two samples are from undisturbed marker beds (No. 121) in the evaporite sequence and that no large scale tectonic effects are evident in the core above or below these samples. The unreliability of sylvite for K-Ar dating has been mentioned above.

In the Kerr-McGee Potash Mine a lamprophyre dike yields a K-Ar apparent emplacement date of 31 Myr (See SAND, 1978). The evaporite minerals immediately adjacent to this dike have been recrystallized and second generation sylvite, polyhalite, halite and other minerals sometimes fill fractures in the lamprophyre. Because the exposures in the Kerr-McGee Mine have been mined out and are no longer accessible, a sample of very pure polyhalite from this area (See Table 2) was obtained from the New Mexico Institute of Technology (courtesy of Dr M. BODINE). This sample (No. 8) was free of sylvite and yielded a date of 21.4 ± 0.8 Myr, in rough agreement with the age of the lamprophyre. If a predike age had been obtained, questions about the use of polyhalite for dating could be raised. The result corresponds well with the established age of the dike. The ages of about 210 Myr for samples one through five provide indirect evidence that the emplacement of the dike was a local event and apparently affected only the contact zones.

TREMBLA 1969) and BODINE (1978) have suggested more-or-less continuous and/or episodic recrystallization of the evaporite sequence through the Mesozoic and into the Cenozoic based on limited and questionable geochronologic data (i.e. sylvite K-Ar dates; Rb-Sr mineral dates), but our data do not support their hypothesis.

CONCLUSIONS

The data presented above are of interest for several reasons:

(1) The determined polyhalite K-Ar ages agree well with the Rb-Sr isochron age (REGISTER, 1979;

BROOKINS *et al.* 1978), suggesting that the actual last crystallization of the potash ore may have taken place in the Triassic (210 Myr) rather than in the Latest Permian. It is not clear if the polyhalites actually crystallized at about 210 Myr ago, or if the measured ages are low relative to the age of sedimentation because of a limited amount of argon loss from the polyhalites. The data indicate that no substantial recrystallization has occurred since 210 Myr ago, in disagreement with the possibility of widespread dissolution of salts through the Mesozoic-Cenozoic (TREMBLA, 1969; BODINE, 1979).

(2) Polyhalite associated with a lamprophyre dike (No. 8; Table 1) is reasonably close in age (21.4 Myr) to the dike itself (31 Myr) and confirms the age of intrusion of the dike. The nearby melt halite and post-polyhalite sylvite are probably also close to 20 Myr in age (BROOKINS and REGISTER, unpublished data).

(3) The polyhalite data refute the old statements made by several authors (DARLYMPLE and LANPHERE, 1969; FAURE and POWELL, 1972) that this mineral is not suitable for K-Ar dating. We suggest that potassic evaporite minerals may be very useful for investigating postformational events in evaporites as well as the ages of formation.

(4) Polyhalite is apparently a very useful mineral for dating by the K-Ar method. Polyhalites can and should be used for purposes of tracing diagenetic and post-formational events at the WIPP site and in other evaporites.

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