3/18-90 8S ①

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for the United States Department of Energy
under Contract DE-AC04-76DP00789

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Authigenic Clay Minerals in the Rustler Formation, WIPP Site Area, New Mexico*

Douglas. G. Brookins[1], Steven J. Lambert[2], and David B. Ward[1]

ABSTRACT

Transuranic waste is planned for disposal in the Late Permian evaporites of the Delaware Basin, southeastern New Mexico, at the WIPP Site. The disposal horizon is located in the bedded halite of the Salado Formation, which is overlain by the impure halite-anhydrite(gypsum)-siltstone-mudstone of the Rustler Formation. The Rustler Formation also contains two dolomite members, the Magenta and Culebra, which transmit water. The Culebra Member is suspected to have actively interacted with waters at time(s) from the Late Permian to the present, and it is important to assess the reactivity of these waters in conjunction with WIPP stability.

We have investigated the Rb-Sr systematics of clay minerals from the Culebra Member and elsewhere in the Rustler Formation. By separating the less than 0.125 μm size material we are able to deal with presumed true authigenic clay minerals. The authigenic fraction is especially sensitive to chemical and isotopic exchange with waters, and an episodic exposure to a large amount of water will reset the clay minerals to such a time. Our data yield 259 ± 22 Ma Rb-Sr isochron, which is consistent with the Late Permian age of the Rustler Formation. This age demonstrates that age-determining cations in these clay minerals have preserved their isotopic and chemical integrity since the Late Permian.

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* This paper has been accepted for publication in the Proceedings of the Materials Research Society (Scientific Basis for Radioactive Waste Disposal), but may differ from its present form when it is published therein.

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INTRODUCTION

The marine evaporites of the Delaware Basin consist of thickly bedded sequences of anhydrite-halite (Castile Formation), halite (Salado Formation), halite with mudstones and sulfates (Rustler Formation), and sandy red beds (Dewey Lake Formation), all of which were deposited in the Late Permian. The Castile Formation is gypsified near the surface. The WIPP repository is located 2150 feet below the surface in the halites of the Salado Formation. Overlying the Salado Formation is the Rustler Formation which contains two dolomite members, the Culebra and Magenta; both are low-permeability water-bearing units. From previous studies it is thought that the Culebra dolomite has contained meteoric water at various times since the Late Permian (1). This is of concern because if this inflow has been in geologically recent time, then a potential pathway might exist for meteoric water to come into contact with the repository rocks.

We have chosen to investigate a response of minerals to groundwater using the Rb-Sr geochronologic method on size fractions of clay minerals separated from Rustler Formation rocks and especially from Culebra Member samples. Samples of clay mineral-bearing material from zones of suspected evaporite dissolution in the Rustler Formation (2) were investigated as well. In previous studies, we examined selenite veinlets from these same cores, and presented Sr isotopic evidence for their in situ origin as opposed to some extrinsic source (3). Yet the clay minerals may be an independent indicator of Post-Permian meteoric water influxes. The clay minerals throughout the evaporite section consist of detrital phases, commonly illitic (4) which have interacted with fluids in the evaporites to form a new generation of corrensite, saponite, and mixed layer varieties. The detrital phases typically yield pre-Permian ages of 300 to 400 Ma (3,5).

The key indicator of clay/water interaction is here considered to be the timing of the clay mineral alteration. If geochronology indicates that the new generation of corrensite, saponite, etc. formed in the Late Permian or very shortly thereafter, then this would indicate little fluid effect on Rb-Sr systematics of these clay minerals since (roughly) 230 Ma ago. Alternatively, if these new clay minerals have formed at one or several times, or even continuously, *since* the Late Permian, this will be reflected in their mineral ages, and such a result may not support certain aspects of the integrity of some WIPP minerals. A Rb-Sr age greater than or equal to Late Permian, however, does not preclude the possibility that meteoric water has been in post-Permian contact with the clays, without the achievement of threshold conditions necessary to reset the Rb-Sr dates.

SAMPLING AND METHODOLOGY

Samples of the Rustler Formation were taken from the WIPP core-storage facility at the site near Carlsbad, New Mexico in June 1988. Samples were selected by visual inspection of the core after identifying likely targets from the drill core log records. Each sample was inspected by at least two persons at the time of collection. The visual descriptions and depths for each sample are given in Table 1.

Samples selected were treated for clay mineral separation as follows: Approximately 3 g of bulk sample was suspended in 80 ml of acetic acid-sodium acetate buffer (27 ml glacial acetic acid and 82 g sodium acetate mixed with 1000 ml deionized water) by treatment with an ultrasonic dismembrator for five minutes. The acetate buffer dissolves any carbonate and sulfate minerals which may be present without structurally damaging the delicate clay minerals (6). The samples flocculated after disaggregation allowing decantation of most of the acetate buffer. Next, they were re-suspended in 200 ml deionized water and centrifuged at 2600 rpm for 45 minutes. The supernatant water was decanted and the process repeated until each sample ceased to flocculate. The samples were then re-suspended a final time and centrifuged according to standard methods to collect the desired size fraction (7). Because the desired size fraction was that material which did not settle during centrifuging, the supernate was decanted and flocculated by adding 5 ml of 10% KCl solution. After final centrifuging and decanting, the samples were re-suspended in a few ml deionized water, transferred to small beakers, and evaporated to dryness on a hotplate in a Class 100 clean hood.

Where only small amounts of material were in the -2 μm fraction, only -2 μm size material was collected. When larger amounts were apparent, then collections were made at -1 μm, -0.5 μm, and -0.125 μm. Ideally, -0.125 μm material offers the best possibility of yielding representative authigenic clay minerals (8).

Spikes enriched in ^{87}Rb and ^{84}Sr were added to aliquots of each clay-mineral separate, which were then digested in HF and vycor-distilled $HClO_4$. After evaporation they were redissolved in deionized HCl and Rb and Sr fractions were separated from other cations by ion exchange chromatography. The samples were analyzed using a VG 354 thermal ionization mass spectrometer. Replicate analyses on a variety of samples gave the following analytical precisions (1 standard deviation, 13 degrees of freedom): Rb concentration -- 0.55%, Sr concentration -- 0.60%, ^{87}Sr/^{86}Sr -- 0.047%, ^{87}Rb/^{86}Sr -- 0.84%. Internal precisions (1 standard error) of mass spectrometer analyses were typically better than the following values: Rb concentration -- 0.07%, Sr concentration -- 0.06%, and ^{87}Sr/^{86}Sr -- 0.0013%. The data for Rb, Sr, ^{87}Sr/^{86}Sr, and ^{87}Rb/^{86}Sr are presented in Table 2.

Isochrons were calculated using York's (9) algorithm as implemented by one of us (D.B. Ward) on an MS-DOS personal computer. Errors in ^{87}Sr/^{86}Sr are assumed to be uncorrelated with errors in ^{87}Rb/^{86}Sr. All isochrons presented here are scatterchrons because actual scatter of data about each regression line exceeds that which would be expected due to analytical error alone. Reported confidence intervals incorporate this excess uncertainty by assuming such scatter is normally distributed and proportional to analytical errors. The degree of excess scatter is reflected in the mean square of the weighted deviates (MSWD), which has an expected value of unity and follows the $F(n_1,n_2)$ distribution where n_1 is the degrees of freedom of the regression (equal to the number of points included in the isochron minus 2) and n_2 is the degrees of freedom of analytical replicates (equal to 13 for this work). *A priori* confidence limits, based solely on analytical precision, are multiplied by MSWD to give scatterchron confidence limits. All regression errors are reported at the 95% confidence level.

RESULTS AND DISCUSSION

The Rb-Sr isochrons for differing clay-size fractions are shown in Figures 1-3. Figure 1 shows the composite Rb-Sr isochron for all samples in the -2 µm fraction (Table 2A, B, C, D). The apparent scatterchron age is 288 ± 30 Ma with an intercept on the $^{87}Sr/^{86}Sr$ axis of 0.7073 + 0.0027. There is considerable excess scatter about this scatterchron, and the clay minerals from different size fractions fall in somewhat distinct domains. This will be discussed below.

The -0.5 µm material is plotted in Fig. 2, where the apparent age of this scatterchron is 278 ± 45 Ma. Excess scatter here is still considerable and, though less than for the composite isochron of Fig. 2, the age overlaps the -2 µm and -0.125 µm ages.

The -0.125 µm material is plotted in Fig. 3. There the apparent age is 259 ± 22 Ma, in much closer agreement with the Late Permian age of the host evaporites. This size fraction exhibits least excess scatter and is also much richer in corrensite, saponite, and mixed layer corrensite-saponite than either the -0.1 or -0.5 µm fractions, both of which are more illitic and smectitic.

The original geochronologic study on clay minerals from the WIPP area was conducted by Register (5) and summarized later by Brookins (10). The Rb-Sr dates of -2 µm material were used in all these studies; their use was based on the assumption that this size material contains only the supposed authigenic fraction of clay minerals. Morton (11) has shown, however, that in many sedimentary rocks, diagenetic effects reset detrital clay mineral Rb-Sr systematics and one often has to use a size fraction very much less than 2 µm. His work suggests 0.1 µm or smaller.

The dates reported in these early studies (5,10) are 390 ± 77 Ma; the authors also noted a great deal of scatter in the data. As the samples used in these studies were from many locations, including potash mines, drill cores, etc., it is not surprising that such scatter was obtained. Of interest, though, is that the 390 ± 77 Ma date is significantly pre-Late Permian, attesting to the detrital nature of the clay minerals. All the samples were from the Salado Formation.

That residence in the evaporites had not been sufficient to reset the Rb/Sr systematics of the clay minerals was consistent with other independent studies (12,13). Later, we studied the -2 µm fraction of clay minerals and oxyhydroxide minerals from clay horizons in the WIPP repository rocks which revealed an Rb-Sr isochron age of 428 ± 7 Ma and K-Ar dates ranging from 362 to 390 Ma for clay mineral separates (3). These dates are consistent with the earlier work (12,13). This 428 Ma date is interpreted as the age of essentially unperturbed clay minerals of detrital origin in the Salado Formation--where the clay mineral assemblages are dominated by smectites with lesser amounts of illites and small amounts of chlorite (4). In the Rustler Formation samples the clay minerals contain smectites mixed with corrensite, saponite, and, in the -2 and -1 µm fractions mixed layer varieties. The proportion of smectite decreases rapidly with decreasing grain size so that in the -0.125 µm fraction the assemblage is dominated by corrensite, saponite, and mixed layer varieties.

The results presented in this report, however, are different. The -2 or -1 μm fractions are too few in number (n=4) for any meaningful treatment. The -0.5 μm material (n=11), however, shows a pre-Late Permian date, but this date is significantly younger than the detrital clay mineral dates from Salado Formation clay minerals at the WIPP repository (3). The -0.125 μm fraction (n=13) yields an even younger date, and this 259 ± 22 Ma figure is in agreement with the Late Permian.

These results argue that the detrital clay minerals in the Rustler Formation, and especially in the Culebra Member, were subjected to Rb-Sr isotopic resetting during the Late Permian, and this is reflected in truly authigenic clay minerals formed at the expense of detrital material at that time. Thus, the fine-grained material is more representative of the authigenic fraction than the coarser grained samples, and this is clearly demonstrated by our data (Table 2; Figs. 1-3).

This study also allows us to address the role of water infiltrating into the evaporites. If meteoric or other waters were pervasive continuously from the Late Permian to the present, then the clay minerals would have continuously reacted to reflect that abundance. If so, a complete scatterchron enveloping near-zero Ma to greater than 400 Ma would probably result. Yet, the data show a fair fit to the Rb-Sr isochrons suggesting that while water was available and sufficient to perturb Rb-Sr systematics, this resetting took place during sedimentation-diagenesis, probably terminating in the Late Permian as well. All of the independently obtained geochronologic data are consistent with such an interpretation (10). At the same time, the data also support the idea that the Rustler rocks were more likely to interact with waters than the underlying Salado rocks, hence the Rustler clay minerals may have been reset to a larger degree than the others. This problem is currently being pursued through a similar analysis of the Salado Formation. Thus the degree of resetting of the Rb-Sr systematics of the clay minerals in the post-Permian is not extreme.

It is estimated that a water-rock ratio of 100 to 10,000 is required to significantly affect Rb-Sr systematics of ocean bottom materials and assumes very low concentrations of Rb as well as very high concentrations of Sr both consistent with the brine chemistry of the Delaware Basin evaporites (15,16). Further, the evaporites in general show preservation of original sea water Sr isotopic composition and independently argue against large amounts of waters passing through the evaporites in the post-Late Permian (16). Yet the scatter about the isochrons suggests that one of the possible explanations for the observed variations in the data may be the effects of waters in the post-Late Permian (16). While data for modern meteoric waters are not available as yet, data for surface calciferous sediment are (4), which suggest a ^{87}Sr/^{86}Sr ratio close to 0.709 to 0.710 (16). Another explanation for at least some of the scatter is that the detrital clay minerals reacted at different rates and to different degrees of completion during the alteration to corrensite-saponite, and that local open system conditions were present as well. This could also easily account for the scatter noted. Again, however, any significant post-Late Permian interactions with any high Sr fluid would severely affect the clay minerals as described above. In the absence of such excessive age lowering, it appears that the water-rock ratios in the post-Late Permian were insufficient to affect the overall isotopics of the clay minerals (this report) and the evaporites (4,16).

The paleohydrologic implication of the results of the present study is that availability of waters for pronounced reaction with clay minerals in the evaporites was restricted to pre-200 million years ago. Again, this implication is consistent with previous geochronologic and isotopic work (3,4).

CONCLUSIONS

1. The -0.125 μm clay minerals from the Rustler Formation yield a Rb-Sr isochron age of 259 ± 22 Ma, which is consistent with the Late Permian age of the formation.

2. Coarser grained material yields pre-Late Permian dates of 278 ± 45 Ma (-0.5 μm clay minerals) and 288 ± 30 Ma (all fractions finer than 2 μm). We interpret these dates to indicate incomplete resetting of detrital clay minerals.

3. The clay mineral Rb-Sr ages do not appear to have been affected by post-Permian interaction with waters, but this does not preclude all such contact, which may be reflected in properties other than Rb-Sr age (14,16). The causes for the scatter in the isochrons are not yet resolved.

4. Our geochronologic work conducted to date is consistent with the thesis that appreciable amounts of waters have not entered into and reacted with the evaporites of the Rustler Formation to the same degree as in the Late Permian.

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Acknowledgments

Financial support of this work was from Sandia National Laboratories (Contract 05-7510). The U.S. Dept. of Energy (Grant DE-FG05 - 84ER5161) provided funding to D. G. Brookins for the mass spectrometer used in this study. Laboratory assistance was provided by C. R. Bryan, D. Milligan, and A. Johnson. J. Binder prepared the manuscript.

Table 1. Sample Locations and Macroscopic Descriptions

Sample	Drill Hole	Depth (feet)	Unit/Description
060188-03	W12	813.2	Rustler just above Culebra; gypsiferous mudstone
060188-05	W13	726.5	Culebra; clay seam
060188-06	W13	705	Culebra; mudstone
060188-07	W13	714	Culebra; surface clay on dolomite
060188-10	W25	473	Culebra; mudstone
060188-12	W25	475	Culebra; dark gray mudstone
060188-13	W25	530	Rustler; green-to-red mudstone
060188-14	W25	534	Rustler; gray mudstone
060188-16G	W26	215	L. Rustler; breccia -- green mudstone clasts
060188-16R	W26	215	L. Rustler; breccia -- red mudstone matrix
060188-18	W27	321.3	Culebra; mudstone -- green
060188-19	W27	321.3	Rustler; mudstone -- red
060188-20	W27	319.5	Rustler; mudstone
060188-21	W27	322.33	Rustler; red mudstone
060188-22	W28	450	Rustler; gray mudstone
060188-23	W28	448	Rustler; gray mudstone
060188-25	W29	45	Basal Culebra; clay seam
060188-27	W29	43.5	Culebra; clay seams in dolomite
060188-32	W32	27.6	Magenta; argillaceous dolomite
060188-33	W32	50.8	Rustler; oxidized mudstone
060188-37	W32	68	Culebra; argillaceous dolomite
060288-38	W32	89.5	Culebra; very argillaceous dolo.
060288-39	W32	90.5	Culebra; very argillaceous dolo.
060288-41	W32	86	Culebra; argillaceous dolomite with minor siltstone
060288-42B	W33	581.7	Rustler just below Culebra; mudstone
060288-43	W33	579.4	Culebra; green-gray siltstone
060288-46	W34	862.3	Rustler just below Culebra; argillaceous dolomite with some siltstone
060288-47	W34	836.1	Culebra; argillaceous siltstone in dolomite with minor organic (?) matter

Table 2. Rb-Sr Data from Rustler Formation Clays

Sample ID	Sr(ppm)	Rb(ppm)	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
A. < 0.125 μm				
060188-16G	29.90	29.70	0.71733	2.877
060188-16R	42.81	35.16	0.71554	2.378
060188-18	15.49	28.04	0.72731	5.248
060188-19	21.13	41.57	0.72957	5.704
060188-20	20.57	47.68	0.73284	6.723
060188-21	15.73	14.14	0.71773	2.603
060188-22	27.78	57.50	0.72925	6.001
060188-23	24.97	58.59	0.73115	6.805
060188-25	15.13	13.28	0.71712	2.543
060188-27	16.53	17.27	0.71941	3.026
060188-33	26.91	33.10	0.72247	3.564
060288-42B	19.75	27.93	0.72314	4.098
060288-46	23.56	62.77	0.73767	7.731
B. < 0.5 μm				
060188-3	19.12	65.46	0.75172	9.948
060188-5	31.28	73.38	0.73564	6.806
060188-7	27.04	105.19	0.74994	11.302
060188-10	25.15	72.17	0.74398	8.332
060188-12	39.16	81.41	0.73275	6.030
060188-13	56.88	98.94	0.73049	5.044
060188-14	55.84	94.79	0.72923	4.922
060288-38	26.30	57.58	0.73222	6.350
060288-39	17.51	57.38	0.74562	9.517
060288-41	34.22	54.08	0.72615	4.581
060288-43	29.19	64.58	0.73262	6.417
C. < 1.0 μm				
060188-6	44.87	107.63	0.73748	6.961
060188-32	66.72	96.54	0.73193	4.196
D. < 2.0 μm				
060188-37	40.44	18.50	0.71324	1.324
060288-47	34.66	69.23	0.73272	5.793

Figure 1. Rb–Sr isochron from WIPP clays, including all fractions finer than 2 µm.

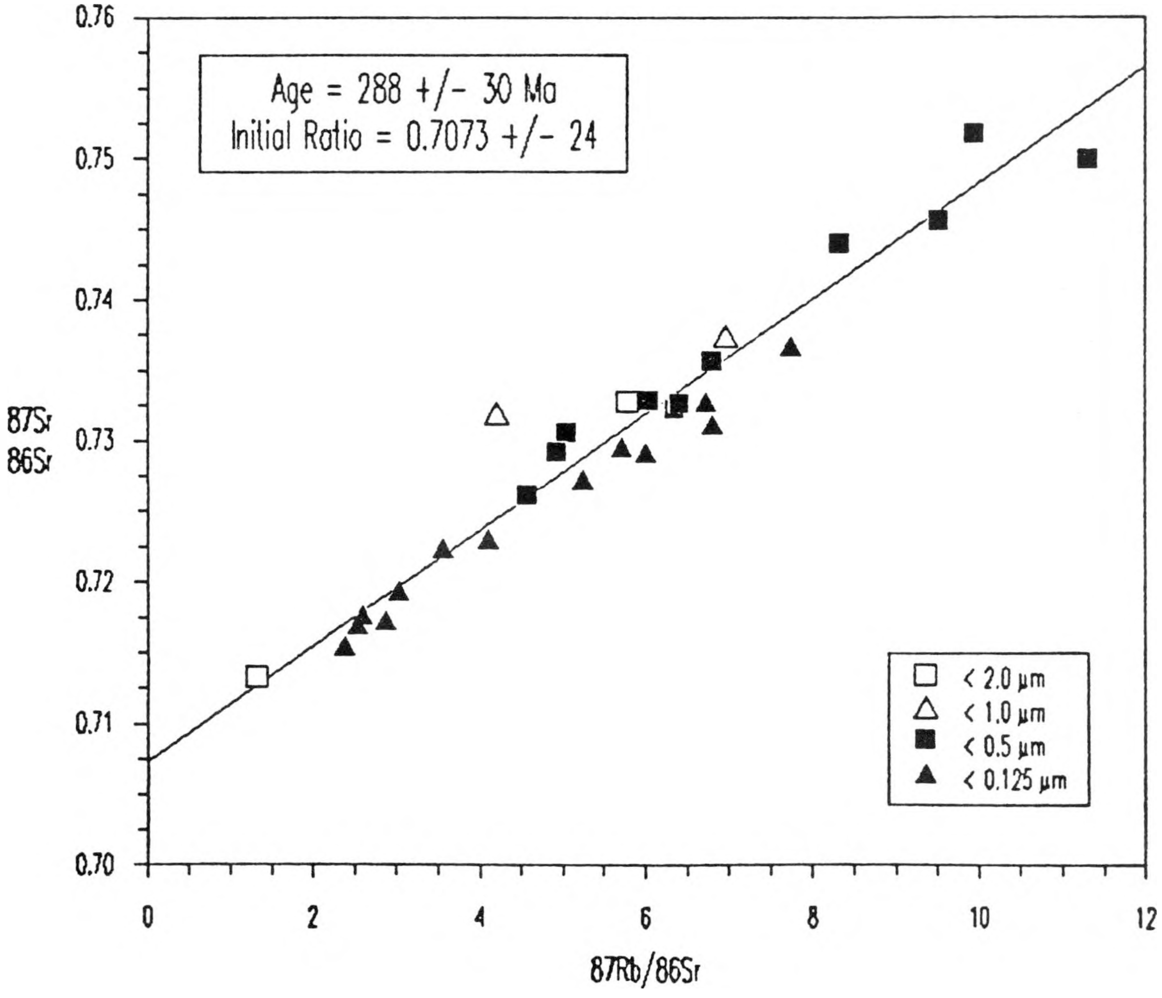

Figure 2. Rb–Sr isochron on WIPP clays: < 0.5 μm fractions only.

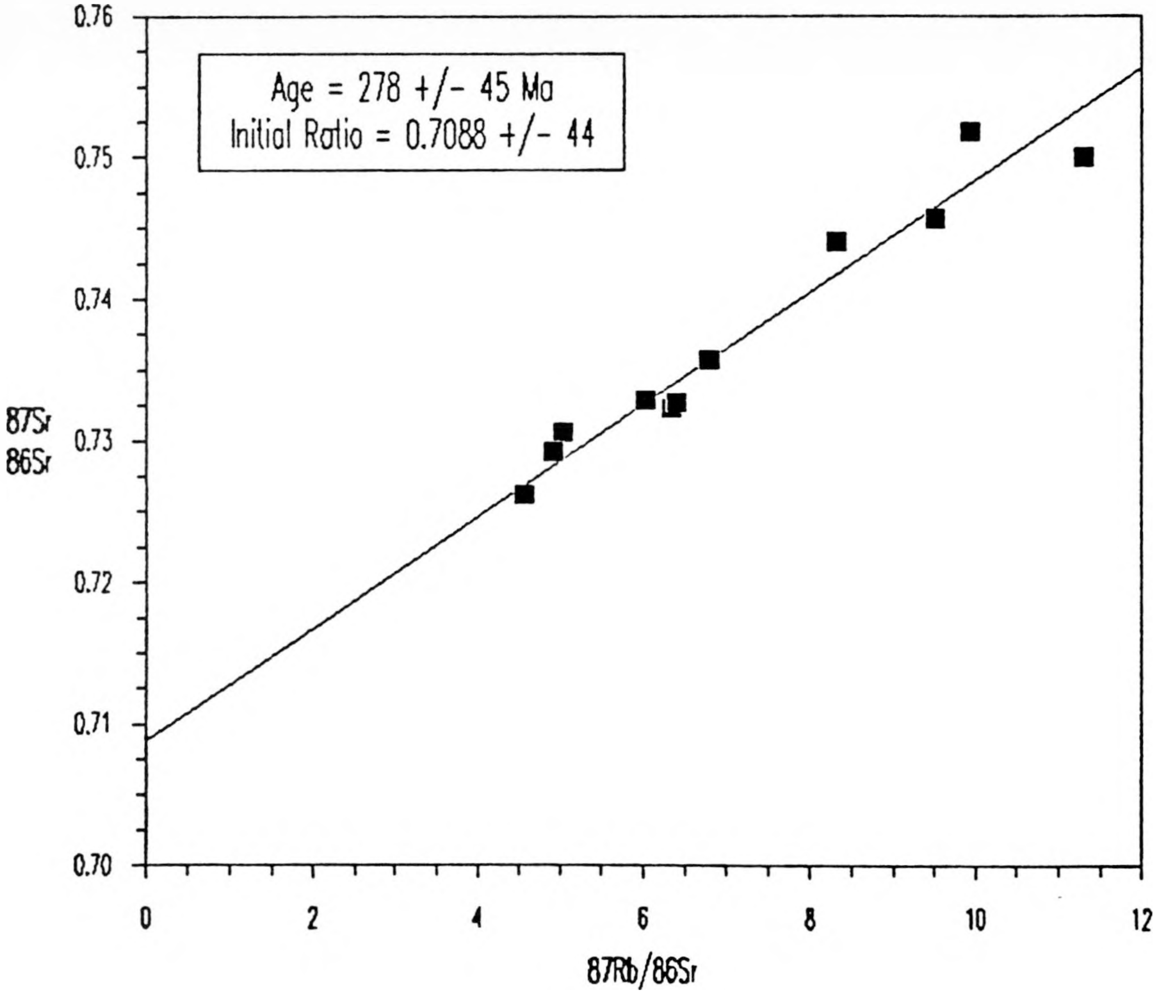

Figure 3. Rb-Sr isochron on WIPP clays: < 0.125 μm fractions only.