GEOCHRONOLOGIC STUDY OF CLAY MINERALS FROM WIPP: IMPLICATIONS FOR SITE STABILITY

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ABSTRACT

Clay minerals are common constituents of the Late Permian evaporites of the Delaware Basin, southeastern New Mexico. The WIPP site is located within these rocks in the bedded halites of the Salado Formation. Clay-rich seams in the Salado Formation and in dolomite members of the overlying Rustler Formation are of concern as sources or pathways for possible meteoritic water transport to stored TRU wastes at WIPP.

We have investigated the clay minerals of these seams to test their stability in the presence of natural waters. Using Rb-Sr geochronologic methods on successively finer grain size fractions, we find that there is a pronounced age lowering. The minus two micron (-2.0 μm) fraction for Rustler and Salado clay minerals reflects their detrital origin and yields isochrons of 300 to 400 Ma. The finest fractions yield 258 $\pm$ 22 Ma for the Rustler (-0.32 μm), and 304 $\pm$ 18 Ma for the Salado (-0.125 μm), ages much closer to the K-Ar ages of 230 Ma on primary polyhalites in the WIPP rocks than to ages of the detrital clay fractions. The detrital clay minerals are dominantly illites, whereas the finer fractions show development of corrensite, saponite, and chlorite formed during diagenetic reactions. Since all the Rb-Sr ages are older than Late Permian, we interpret our results to date the end of significant water-clay mineral interactions in the Late Permian. This interpretation is consistent with other Sr isotopic and K-Ar studies.

INTRODUCTION

The marine evaporites of the Delaware Basin consist of thickly bedded sequences of anhydrite-halite (Castile Formation), halite with minor anhydrite and clay interbeds (Salado Formation), halite with shale and Ca-sulfates (Rustler Formation), and sandy redbeds (Dewey Lake Formation), all of which were deposited in the Late Permian. The WIPP repository is located 2,150 feet below the surface in the halites of the Salado Formation. The overlying Rustler Formation contains two dolomites (Culebra and Magenta Members) which are low-permeability water-bearing units. Previous studies have indicated that the Culebra Member 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 times, then a potential pathway might exist for meteoric water to come into contact with the repository rocks. In addition, argillaceous rocks in the Salado Formation have been suggested as possible sources of water due to dewatering accompanying clay mineral-brine interactions (2,3).

We have chosen to investigate the response of clay minerals in WIPP-area rocks to water by applying Rb-Sr geochronologic techniques. Based on previous studies (2,3,4) we note that the K-Ar method, while useful for dating some primary and secondary evaporite minerals, is suspect when dealing with complex mixed-layer clays such as saponite-corrensite assemblages due to loss of radiogenic ^{40}K. Since the finest size fractions of clay minerals are more susceptible to chemical ion exchange and other processes than are coarser fractions, we have conducted our Rb-Sr work on various clay size fractions from -2.4 μm to -0.125μm. Samples were obtained from the Salado Formation and from the Culebra Member of the Rustler Formation, with emphasis on clay bearing horizons. In the Salado Formation, care was taken to approximate or directly sample the repository depths. In addition, samples of clay-mineral-bearing material from zones of suspected evaporite dissolution were included from the Rustler Formations (5). In previous studies we found that selenite veins from these cores show evidence for *in situ* origin as opposed to some extrinsic source (2). However, the clay minerals may still be independent indicators of post-Permian meteoric water influxes. While many of the clay minerals are of detrital origin, a large amount of authigenic (and/or diagenetic ?) clay minerals are present as well. Often these latter clay minerals formed at the expense of detrital clay minerals.

The detrital clay minerals are characterized by illites and illite-smectite mixed-layer assemblages. The authigenic clay minerals are characterized by saponite, corrensite, $\pm$ chlorite $\pm$ magnesite assemblages. This group of minerals requires an abundance of water and/or brine for formation; hence it is critical to know if these reactions occurred early or late in the history of the WIPP evaporites. If early, then the necessary aqueous phases are readily explained by diagenetic reactions involving Permian sea water; if late, then this implies a significantly younger, and possibly extrinsic, source of water being introduced into the evaporites. This last option would cast doubt on the integrity of the WIPP site evaporites.

SAMPLING AND METHODS

Samples of the Salado and Rustler Formations were taken from the core storage facility at the WIPP site near Carlsbad, New Mexico. 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.

Samples from the Rustler Formation 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 ($\sim$1.5 M acetate ion, pH$\approx$5) and then treated 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 of 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.

Because of the abundant sulfates present in the Salado samples, these were treated somewhat differently. Instead of using acetate buffer, evaporitic sulfate and carbonate was removed by boiling in 200 ml 0.2 M Na-EDTA solution (adjusted to pH 11 with NaOH) for four hours followed by ultrasonic disaggregation for three minutes (8). The samples flocculated, allowing most of the EDTA solution to be decanted. Re-suspension in additional EDTA solution diluted any leftover Ca-EDTA the may have been created while boiling the clays. EDTA was again decanted after flocculation and centrifuging. Clays were repeatedly rinsed and centrifuged, first with 200 ml deionized water plus 1 ml 2.5 N HCl (to facilitate flocculation), and then with just deionized water until flocculation ceased.

Where only small amounts of material were present in the coarsest fraction (-2.4 μm for Rustler, -2.0 μm for Salado samples), it was not further subdivided. When larger amounts were apparent, then collections were made at successively finer sizes (-1.2 and -0.32 μm for Rustler, -0.50 and -0.125μm for Salado samples). Ideally, -0.125 μm material offers the best possibility of yielding representative authigenic clay minerals (9).

Spikes enriched in ^{87}Rb and ^{84}Sr were added to aliquots of each clay-mineral separate, which were then digested in HF and low-temperature-distilled HClO$_4$. After evaporation they were dissolved 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 spectrometric analyses were typically better than the following values: Rb concentration —0.07%, Sr concentration —0.06%, ^{87}Sr/^{86}Sr —0.0013%. The Rb and Sr data are presented elsewhere (Brookins, in prep.). All required constants for data reduction and isochron calculations were obtained from the literature (10,11,12).

Isochrons were regressed using the algorithm of York (13) with weights inversely proportional to σ^2 errors in ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr. To perform these calculations, a program (Isochron v. 4.0) was written for MS-DOS computers using Borland's Turbo-C compiler and libraries (program available on request). Two regression models are used (cf. 14): model 1, based on analytical errors only; and model 3, in which the scatter in ^{87}Sr/^{86}Sr is adjusted so that the root mean square of the weighted deviates ($MSWD^{1/2}$) is equal to unity. The model 1 treatment is appropriate for isochrons in the strict sense (15), whereas model 3 accommodates excess scatter in the data (that which is not attributable to the analytical process) by assuming ^{87}Sr/^{86}Sr was not uniform at the time of closure of a suite of samples. The amount of excess scatter is called *geologic scatter* and is reported at the 1σ level.

Both models report scatter in age and initial ratio at the 95% confidence level; model 1 uses a small-sample *t*-multiplier based on the degrees of freedom of the determination of analytical precision (15), whereas model 3 uses t for n-2 degrees of freedom (where n = number of points in the regression) because the uncertainty for each point is determined from the data themselves rather than externally. For the case that $MSWD^{1/2} > 1$, model 1 uses it as an additional multiplier of the 95% confidence interval, effectively decreasing analytical precision to the extent required to explain the observed scatter. Model 1 also calculates the probability that the data do indeed fit the regression line within the limits specified by analytical precision, a probability reported here as the *significance*. If $MSWD^{1/2} >> 1$, *significance* $<5\%$, and analytical precision drastically under-estimates the scatter inherent in the data set; model 3 has been used here for such data sets.

RESULTS

Three Rb-Sr isochrons for differing clay-size fractions from the Rustler Formation are shown in Fig. 1. Size separations for Rustler clays did not strip the fines from a given size fraction; e.g., the -2.4 μm fraction contains all material finer than 2.4 μm and not just the size fraction between 2.4 and 1.2 μm. Figure 1a shows the composite Rb-Sr model 3 isochron (scatterchron) for all Rustler clay samples ana-
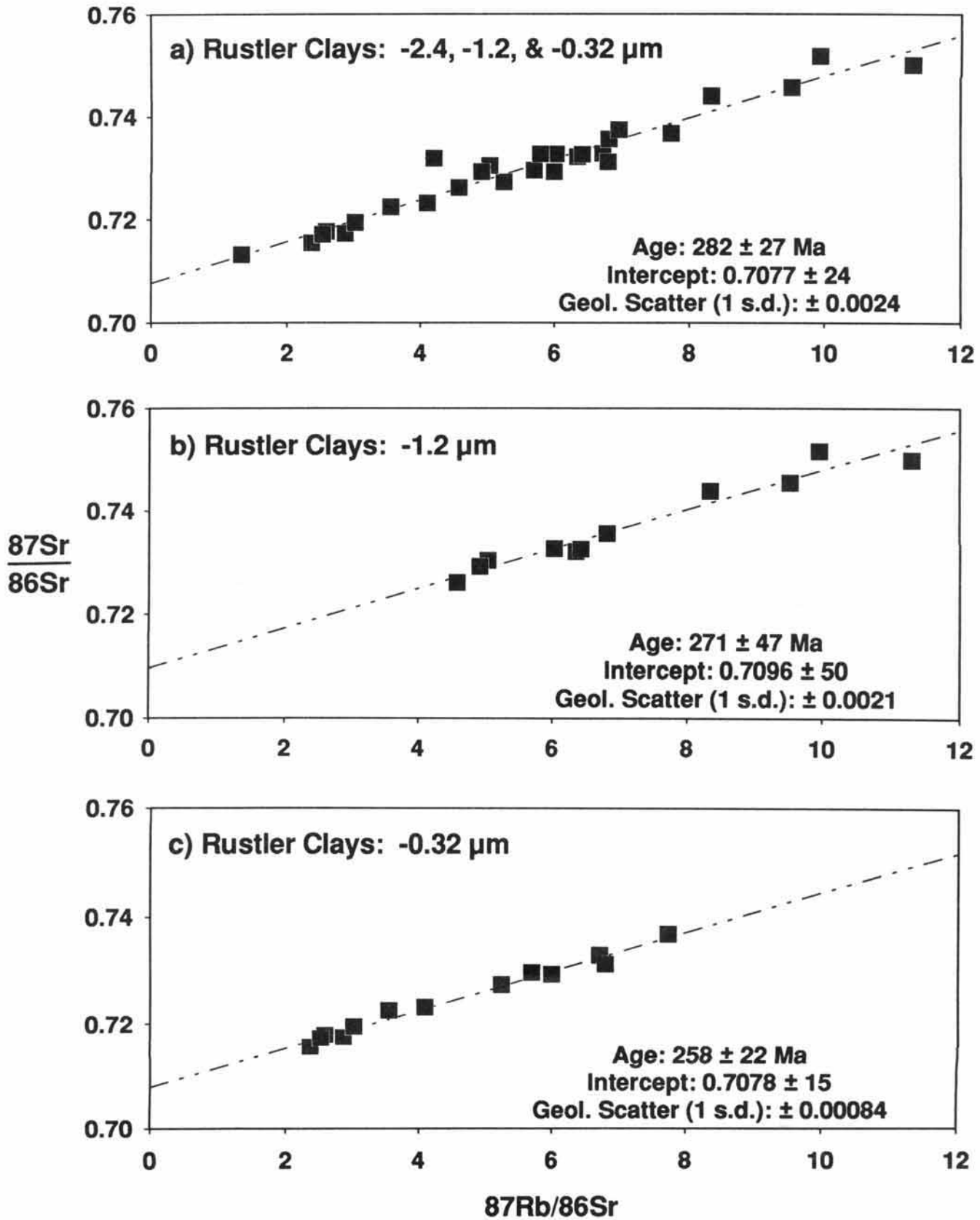
Fig. 1 Clay-mineral isochrons from the Rustler Formation. All of these are model 3 isochrons (scatterchrons), exhibiting scatter beyond that attributable to analytical variability. The amount of such excess is reported at the 1σ level as *geologic scatter*. a) Composite isochron of all size fractions. b) Clays finer than 1.2 μm. c) Clays finer than 0.32 μm.

lyzed. The apparent age is 282 ± 27 Ma with an initial ratio $((^{87}Sr/^{86}Sr)_0)$ of 0.7077 ± 24 and excess (*geologic*) scatter of ± 0.0024 (1σ). This degree of *geologic scatter* is quite large (cf. analytical scatter of ± 0.000018 (1σ)), and clay minerals from different size fractions fall in somewhat distinct domains. Figure 1b shows only the $-1.2\mu m$ clays, which give a model 3 isochron with an age of 271 ± 47 Ma, $(^{87}Sr/^{86}Sr)_0$ of 0.7096 ± 50, and *geologic* scatter of ± 0.0021 (1σ); this isochron does not differ significantly in age or intercept from the composite isochron. Figure 1c shows only the -0.32 μm clays, which give a model 3 isochron with an age of 258 ± 22 Ma, $(^{87}Sr/^{86}Sr)_0$ of 0.7078 ± 15, and geologic scatter of ± 0.00084 (1σ). This isochron gives an age slightly younger than the first two and in close agreement with the Late Permian age of the host evaporites. Inherent *geologic* scatter is also much smaller, reduced by nearly a factor of three over the amount seen in the first two isochrons.

Figure 2 shows three isochrons from differing clay size fractions from the Salado Formation. The separation procedure for these samples did strip the fines, so that only particles within the designated size intervals are present. Figure 2a, based on clays between 2.0 and $0.5 \mu m$, is a true (model 1) isochron giving an age of 409.9 ± 9.5 Ma, $(^{87}Sr/^{86}Sr)_0$ of 0.70694 ± 72, $MSWD^{1/2}$ of 2.40, and *significance* of 0.51. Clays between 0.5 and $0.125 \mu m$ are plotted in Fig. 2b, and give a model 3 scatterchron with an age of 371 ± 28 Ma, $(^{87}Sr/^{86}Sr)_0$ of 0.7075 ± 24, and *geologic scatter* of ± 0.0015 (1σ), significantly younger but also more scattered than the coarse clays of Fig. 2a. For the fine fraction ($-0.125 \mu m$), excess scatter once again requires the use of model 3 (Fig. 2c), resulting in a scatterchron age of 306 ± 15 Ma, $(^{87}Sr/^{86}Sr)_0$ of 0.7083 ± 16, and geologic scatter of ± 0.00011 (1σ).

The Salado ages show the same trend as those from the Rustler, becoming younger in finer clay fractions. All of the Salado ages, however, are older than those of the Rustler samples, and the two coarser Salado fractions show less geologic scatter than similar fractions from the Rustler Formation.

DISCUSSION

The original geochronologic study on clay minerals from the WIPP area was conducted by Register (4) and summarized by one of us (16). The Rb-Sr dates of $-2.0 \mu m$ material were used in these studies; use of this size fraction was based on the assumption that this material contains only the supposed authigenic fraction of clay minerals. Morton (17) has shown, however, that in many sedimentary rocks, diagenetic effects reset detrital clay-mineral Rb-Sr systematics, so that one often has to use a size fraction much smaller than $-2.0 \mu m$. His work suggests $-0.1 \mu m$ or smaller.

The dates reported in these early studies of Salado clays (4,16) 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.

More recently, we studied the $-2.0 \mu m$ fraction of clay minerals and oxyhydroxide minerals from clay horizons in the WIPP repository rocks, and obtained a Rb-Sr age of 428 ± 7 Ma and K-Ar dates ranging from 362 to 390 Ma for clay mineral separates (2). These dates are consistent with the earlier work (18,19). This 428 ± 7 Ma date is interpreted as a younger end-member age of detrital origin in the Salado Formation. The actual age of detrital material may be older, but cannot be determined precisely because of incomplete separation of detrital from authigenic clays.

In subsequent work, clay minerals from the Rustler Formation were investigated in detail. We find that the clay minerals in the Rustler Formation can be distinguished by the size fraction analyzed. The coarser ($-2.4 \mu m$) fraction is richer in illite and smectite than in saponite and corrensite, and yields a Rb-Sr isochron age of 282 ± 27 Ma with considerable scatter (Fig. 1a), whereas the finest fraction ($-0.32 \mu m$) yields a Rb-Sr isochron age of 258 ± 22 Ma with significantly less scatter (Fig. 1c). These ages are statistically distinct at the 89% confidence level, suggesting a trend toward younger ages with decreasing grain size. Even the youngest date, however, is no younger than the Late Permian. We interpret these ages to argue that clay mineral resetting, and thus the ready availability of waters and/or brines, was a common feature of the Late Permian but not of some younger period of time.

Our most recent work, summarized here, again examines clay minerals, this time from the repository-bearing Salado Formation (Milligan, in prep.). Our Rb-Sr ages show that the $-2.0, +0.50 \mu m$ fraction yields 409 ± 10 Ma and the $-0.125 \mu m$ fraction 306 ± 15 Ma. These ages confirm the trend toward younger ages with decreasing clay size concomitant with formation of more saponite-corrensite in the finer fractions. These data argue that while there has been resetting of the original detrital clay minerals, no resetting has been significant enough to reset the Rb-Sr systematics to even a Late Permian date. We also argue that this resetting in the rocks of the Salado Formation occurred in the Late Permian, because polyhalites from the clay mineral horizons yield Late Permian ages (~ 230 Ma).

The ages for clay minerals from the Salado Formation are of interest for several reasons. First, the Salado Formation has almost certainly been much drier than the overlying Rustler Formation since the Late Permian, a fact attested to by the less extensive resetting of detrital clays in the Salado. Further, clay ages may constrain the age of secondary selenite veins common in both units, which yield isotopic
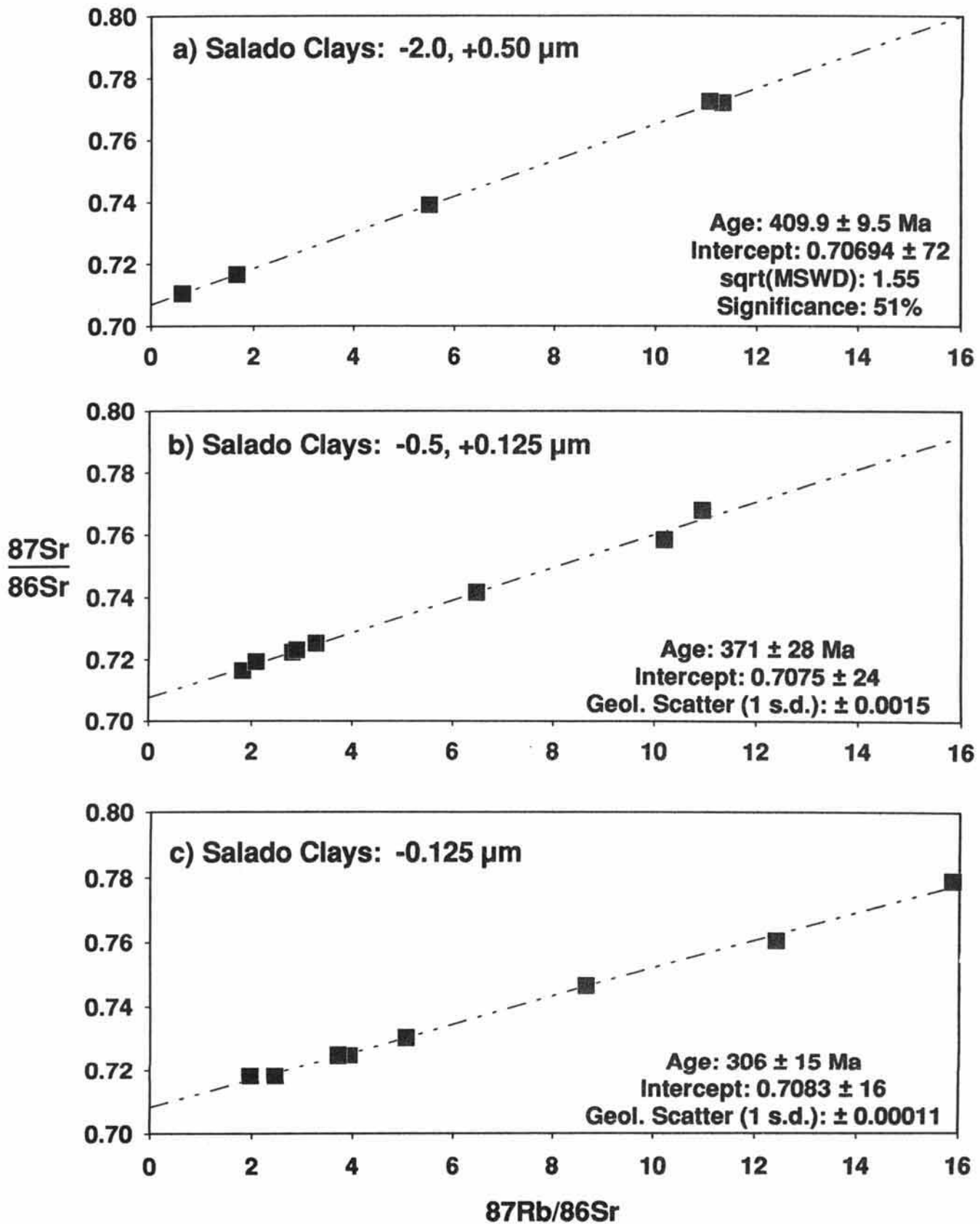
Fig. 2. Clay-mineral isochrons from the Salado Formation. a) Clays between 2.0 and 0.5 µm; a model 1 isochron with a probability of 0.51 that the observed scatter is attributable solely to analytical variability. b) Clays between 0.5 and 0.125 µm; a model 3 isochron (scatterchron). c) Clays finer than 0.125 µm; also a model 3 isochron.

data indicating a local source of Sr bearing waters, in agreement with lack of evidence for large scale penetration of the units by extrinsic waters since the Late Permian (3). Third, the ages are also in agreement with trace element data (Cl,U, etc.) suggestive of lack of major meteoric water influx since the Late Permian (3). Finally, since the partially reset clay minerals of the Salado Formation are types with fairly high cation exchange capacities, they should serve as excellent getters for mobilized constituents from wastes stored at WIPP.

Our results are consistent with the hypothesis 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 samples (Figs. 1,2).

This study also allows us to address the role of water infiltrating into the evaporites. If meteoric or other foreign 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 good fit to the Rb-Sr isochrons suggesting that while water was available and sufficient to perturb Rb-Sr systematics, this resetting took place during diagenesis, which probably terminated in the Late-Permian as well. All of the independently obtained geochronologic data are consistent with such an interpretation (16). At the same time, the data also support the idea that Rustler rocks were more likely to interact with waters than the underlying Salado rocks, leading us to infer that Rustler clays may have been reset to a larger degree than the others. 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 (17), assuming very low concentrations of Rb as well as very high concentrations of Sr, both consistent with the brine chemistry of the Delaware Basin evaporites (20,21). 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 (21). Yet the scatter about the Rustler 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 (21). While data for modern meteoric waters are not available as yet, data for surface calciferous sediments (3) suggest a $^{87}Sr/^{86}Sr$ ratio close to 0.709 to 0.710 (21). A variable

mixing of Sr from Late Permian clays and meteoric waters with such ratios might explain much of the observed scatter. Another explanation for at least some of the scatter is that the detrital clays reacted at differing rates and to differing 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 noted scatter. 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 (3,21).

The paleohydrologic implication of the present study is that availability of waters for pronounced reaction with clay minerals in the evaporites was restricted to pre-200 Ma, an implication consistent with previous geochronologic and isotopic work (2,3).

CONCLUSIONS

Our conclusions reached from this study are as follows: 1) The -0.32 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 from the Rustler Formation yields pre-Late Permian dates of 271 ± 47 Ma (-1.2 μm) and 282 ± 27 Ma (all fractions finer than 2.4 μm), dates which reflect incomplete resetting of detrital clay minerals. 3) The -0.125 μm clay minerals from the Salado Formation yield a Rb-Sr isochron age of 306 ± 15 Ma, older than Late Permian. 4) The 0.5 to 0.125 μm clay minerals from the Salado Formation yield an isochron age of 371 ± 28 Ma, and the 2.0 to 0.5 μm fraction 410 ± 9.5 Ma. Both dates show a clear detrital influence, but the finer fraction shows evidence for resetting due to the clay-mineral/water interactions. 5) The clay-mineral Rb-Sr ages do not appear to have been affected by post-Permian interactions with water, but this does not preclude all such contact, which may be reflected in properties other than Rb-Sr age (20,21). The causes for the scatter in the isochrons are not yet resolved. 6) Our geochronologic work conducted to date is consistent with the thesis that appreciable amounts of water 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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