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A Review of WIPP Repository Clays and their Relationship to Clays of Adjacent Strata*

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ABSTRACT

The Salado Formation is a thick evaporite sequence located in the Permian Delaware Basin of southeastern New Mexico. This study focuses on the intense diagenetic alteration that has affected the small amounts of clay, feldspar, and quartz washed into the basin during salt deposition. These changes are of more than academic interest since this formation also houses the WIPP (Waste Isolation Pilot Plant). Site characterization concerns warrant compiling a detailed data base describing the clays in and around the facility horizon. Further, because of their diagenetic history, the minerals indigenous to the Salado also provide a natural analog for the fate of sand-bentonite backfills that may be used in sealing the facility.

An extensive sampling effort was undertaken to address these programmatic issues as well as to provide additional insight regarding diagenetic mechanisms in the Salado. Seventy-five samples were collected from argillaceous partings in halite at the stratigraphic level of the Waste Isolation Pilot Plant (WIPP). These were compared with twenty-eight samples from cores of the Vaca Triste member of the Salado, a thin clastic unit at the top of the McNutt potash zone, and with a clay-rich sample from the lower contact of the Culebra Dolomite (in the overlying Rustler Formation). These settings were compared to assess the influence of differences in brine chemistry (i.e., halite and potash facies, normal to hypersaline marine conditions) and sediment composition (clays, sandy silt, dolomitized limestone) on diagenetic processes.

X-ray diffraction analyses and electron microscopy identified a clay similar to corrensite from all three stratigraphic horizons. Authigenic quartz and potassium feldspar were found in both Vaca Triste samples and in those from the WIPP. The feldspar occurred in greater abundance in the Vaca Triste samples than in those from the WIPP horizon. Fluid inclusion compositions from halite in the Vaca Triste were compared with those from the WIPP repository horizon. The solution speciation/mineral solubility code EQ3NR was used to calculate ionic activities of relevant species in WIPP and Vaca Triste brines. In both cases, the predicted assemblage was consistent with

the observed mineralogy.

We propose a diagenetic interpretation in which the original, detrital clays reacted with magnesium-rich brines to produce a suite of Mg-rich, mixed-layer species. By-products of these reactions were authigenic quartz and K-feldspar. The dissolution of plagioclase, kaolinite, and fine-grained, detrital illite probably contributed components precipitated in the authigenic phases.

Of programmatic concern it was found that: a) clays exposed in the repository workings resemble those occurring throughout the rest of the Salado; b) though corrensite or similar mixed-layer phases always predominate, the proportions of corrensite, chlorite, and illite in the clay vary from place to place in individual strata; and c) bentonite-sand backfills will probably undergo significant mineralogic changes if exposed to WIPP brines for a geologically significant span of time.

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1 INTRODUCTION

1.1 *Objectives*

The primary objective of this study is to compare the diagenetic alteration of silicate minerals from different evaporite environments. Samples representative of halite-facies depositional conditions came from the lower part of the Salado Formation, part of the Permian evaporite section in the Delaware Basin, southeastern New Mexico (Fig. 1). These samples were collected in conjunction with ongoing site studies for the Waste Isolation Pilot Plant (WIPP), an underground DOE repository for the disposal of transuranic nuclear waste. In addition to halite, the diagenesis of silicate minerals is relevant to WIPP performance because (1) characterizing the clays that result from such changes is a prerequisite to radionuclide transport studies, and (2) the mechanisms responsible for these changes may also affect components used in backfilling or sealing the repository.

The lower Salado also contains small but variable amounts of an assortment of clays. In contrast, the Vaca Triste member of the Salado Formation is a thin unit of silty sandstone containing only a small amount of clay. Unlike the lower Salado, this unit was deposited at the conclusion of a potash-facies stage of the evaporite sequence. Finally, a single clay sample from a mudstone immediately below the Culebra Dolomite was also included in the study to further broaden the range of diagenetic settings sampled.

These depositional environments were sampled in order to compare the effects of bulk sediment composition and brine chemistry on their respective diagenetic histories. In order to make this comparison, the mineralogy of each unit was characterized by x-ray diffraction and by scanning and transmission electron microscopy. In addressing the composition of diagenetic fluids, we analyzed fluid inclusions from halite cement in the Vaca Triste. No fluid inclusions were available from the clay unit immediately below the Culebra. These results were then compared with previously-described fluid inclusion compositions from the WIPP repository horizon (Stein and Krumhansl 1988).

1.2 Background

A considerable body of data on brines from Permian salt in New Mexico and west Texas now exists (Holser 1963; Lambert 1978; Roedder *et al* 1987), including the WIPP fluid compositions reported in our earlier work (Stein and Krumhansl 1988). The WIPP data are the result of extensive sampling and analysis of fluid inclusions in the salt, "weeps" on freshly-excavated exposures within the repository, and brines seeping into boreholes in the repository floor. The measured WIPP fluid compositions are consistent with the "halite-facies" compositional range according to Holser (1963), and isotopic analyses (Knauth and Beeunas 1986) from WIPP fluid inclusions are also consistent with this interpretation.

From textural and mineralogical evidence from WIPP horizon samples, we suggested (Stein and Krumhansl, 1988) that two suites of diagenetic reactions may have determined the observed brine compositions. One set of reactions probably occurred early in the depositional sequence. One is the formation of polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$), possibly as a consequence of brines reacting with gypsum or anhydrite. Another is the precipitation of magnesite ($MgCO_3$) by reaction of a Mg-rich brine with either biogenic or inorganic $CaCO_3$. Both of these reactions significantly displace the K and Mg concentrations from values expected from simple seawater evaporation. K-Ar dates in excess of 200 million years obtained from polyhalites from the WIPP site (Brookins 1980) support the assumption that this phase probably formed early in the diagenetic history of the Delaware Basin sediments.

The second group of slower reactions affected the silicate minerals. These reactions most likely involve detrital clays (possibly illite or chlorite), which are altered by interaction with Mg-rich brines. Bodine (1978, 1983) and others (Braitsch 1971; Harville and Fritz 1986; Palmer 1987; Fisher 1988) have examined clays from the Paradox, Palo Duro, Appalachian, and Delaware Basins as well as from other evaporite deposits. Their observations indicate that clay diagenesis appears to have certain elements that are common to all of these environments - *e.g.*, Mg uptake by various detrital clays

resulting in an assemblage typically consisting of illite plus an assortment of Mg-rich, poorly-ordered, randomly-interstratified clays.¹

In sediments from the Delaware Basin in southeastern New Mexico, the presence of authigenic quartz in association with such clays suggests that both were produced by the same diagenetic processes. The widespread occurrence of Eocene cherts in marine sediments, formed by recrystallization of biogenic opal, implies that the kinetics of quartz crystallization at 25 °C are significantly slower than those of sulfate or carbonate precipitation. Hence, it is likely that clay diagenesis was contemporaneous with burial and that these reactions accompanied basin subsidence and persisted throughout the remainder of the Permian. This is consistent with late Permian isotopic ages for both the Salado authigenic clays and polyhalite (Brookins and Lambert 1987; Brookins 1980).

The presence of authigenic feldspars in evaporite environments is also pertinent to the following discussion. Braitsch (1971) refers to the occurrence of authigenic potassium feldspar in evaporites of the Rhine valley and the Zechstein Basin. More recently, Mossman *et al* (1982), in an examination of clays from Middle Devonian Prairie Formation evaporites, reported the presence of potassium feldspar possibly "of diagenetic origin." To date, little speculation has been offered to explain the occurrence of potassium feldspar in evaporite deposits, particularly as its formation relates to the geochemical conditions in a hypersaline environment. In contrast, albite is suggested to be the most commonly-occurring authigenic feldspar in evaporites, due to the abundance of Na (Kastner and Siever 1979); however, these authors also indicate that K-spar may be expected to form in a potash facies environment.

2 STRATIGRAPHY AND LITHOLOGY

The Salado Formation is part of the upper Permian Ochoa Series in west Texas and southeastern New Mexico. The Salado is divided into unnamed lower and upper units

¹An assemblage containing well-ordered, well-crystallized chlorite plus illite has been reported from Silurian salts in the Appalachian Basin (Bodine 1983).

separated by the McNutt potash zone. The underlying Castile Formation is composed of thick anhydrite-halite sequences and is thought to have a deep-water origin (Dean and Anderson 1978). In contrast, the Salado Formation was formed in relatively shallow water (Lowenstein 1982; Adams 1944). Lowenstein (1988) presents an excellent discussion of evidence for this interpretation based primarily on mineralogy and sedimentary textures, from which he defines two types of depositional cycles, both supporting a shallow-water origin. The Type I depositional sequence contains anhydrite-polyhalite beds (consistent with a shallow lagoonal environment at or below gypsum saturation), syndepositional halite textures similar to those observed in modern lagoons and salt pans, and siliciclastic sedimentation. The Type II cycles yield similar mineralogy and textures as Type I but without evidence for the continuous existence of a body of brine, i.e., deposition during periods of subaerial exposure.

2.1 *The Rustler Formation*

Overlying the Salado is the Rustler Formation, which marks the final stage of filling in the Delaware Basin during the Late Permian and the transition back to non-evaporite sedimentation. The Rustler Formation is primarily composed of reddish-brown siltstone and silty sandstone containing varying amounts of gypsum, halite, and anhydrite.

Two dolomite marker beds are present: the uppermost is the Magenta, at a subsurface depth of 200 m at the WIPP site. The lower dolomite is the Culebra. In the vicinity of the WIPP site, this unit is approximately 6 m thick and its uppermost contact lies at a subsurface depth of about 232 m, or 413 m above the repository. Clays from a sample of dark gray-brown mudstone immediately below the Culebra were analyzed for this report. The Culebra is an aquifer lying above the WIPP and much attention has been given to release scenarios involving radionuclides transported through this unit. Consequently the nature of the clays in adjoining strata are of programmatic concern.

The Culebra Member itself is a dolomitized limestone, possibly of stromatolitic origin. It was probably formed as a consequence of limestone alteration by hypersaline brines containing high concentrations of Mg and K. Magnesium-rich clays such as

clinochlore, Mg-berthierine, and trioctahedral mixed-layer chlorite/smectite have been reported throughout the Rustler Formation (Glenn, 1986; Brookins *et al*, 1989).

2.2 *The Vaca Triste Member (Potash Facies)*

In the vicinity of the WIPP site, subsurface depth to the Vaca Triste is between ~390 m and ~450 m, approximately 255 to 195 m above the WIPP facility horizon. At borehole WIPP-32, approximately 18 km west of the WIPP site, the Vaca Triste occurs at 84 m depth, reflecting the general eastward dip of the strata in this region. In his discussion of sedimentation in the Delaware Basin, Adams (1944) notes the occurrence of multiple episodes of clastic deposition; at the time of deposition of the Salado, the sediment source apparently was to the northwest. In this description, the Vaca Triste is a thin, flat-lying, widespread, fine-grained, sandy unit. It has been adopted in the literature as a stratigraphic marker due to its regional extent, and it is unique in that it is the only siliciclastic marker bed to be described from the Salado.

Adams (1944) states that the Vaca Triste is "rarely more than 10 feet thick"; as observed in the cores examined in this study, taken at distances of 20 km or less from the WIPP site, the Vaca Triste ranges from approximately 1 to 4 m in thickness. The Vaca Triste appears as a reddish-brown layer in the cores, primarily composed of unconsolidated sand containing variable amounts of argillaceous and polyhalitic halite. Vaca Triste mineralogy consists primarily of quartz, halite, K-feldspar, polyhalite, hematite, gypsum, anhydrite, and clays. X-ray diffraction studies (this work) show the clays to be predominantly mixed-layer types (chlorite-saponite) with lesser amounts of discrete chlorite and illite.

The McNutt Potash horizon immediately beneath the Vaca Triste consists of eleven distinct zones enriched in potassium and magnesium minerals. Of these, five have been mined for potassium. Each zone reflects a period of extreme evaporation, during which brines developed relatively high concentrations of chloride, sulfate, potassium and magnesium. Between evaporation episodes, the basin temporarily flooded with fresh seawater. Some of the bittern salts then dissolved, forming other concentrated brines,

which in turn altered the primary evaporite minerals to form the secondary phases comprising the bulk of the ore (Harville and Fritz 1986). Dissolution-reprecipitation textures, as well as the low and variable bromide content of the Salado halite, also suggest repeated episodes of dissolution and reprecipitation (Holser 1966; Roedder *et al* 1987; Lowenstein 1988). Such evidence of post-depositional alteration abounds throughout the upper Permian sequence. Consequently, because of their proximity to the McNutt Potash Zone, it is presumed that the Vaca Triste sediments were exposed to potash-facies brines even though the latter unit does not contain potash minerals.

2.3 WIPP Horizon (*Halite Facies*)

At a subsurface depth of 645 m, within the WIPP facility, the Salado Formation lithology is primarily halite, with minor amounts of anhydrite, polyhalite, gypsum, magnesite, quartz, clays (principally mixed-layer saponite-chlorite, with lesser chlorite and illite), and trace amounts of K-feldspar. Total insoluble residues in the WIPP salt in the vicinity of the repository average approximately 5 weight percent (Stein 1985). In this part of the stratigraphic section, clays can occur as discrete layers from less than one to a few centimeters thick; finely-disseminated clays are also dispersed uniformly through the halite. It has been postulated (Lowenstein and Hardie 1985; Bodine 1978) that the discrete clay layers are formed by dissolution of halite containing dispersed clay during an incursion of fresh seawater. It is also thought that strata containing disseminated clays were formed during periods of relative desiccation in the basin (the "ephemeral salt pan-saline mudflat complex" of Lowenstein 1988).

3 SAMPLING AND ANALYSIS

Within the WIPP repository, 75 samples (a few tens of grams each) were taken from two distinct clay-rich layers that are approximately parallel, laterally continuous throughout the exposed strata in the mine, and separated by a vertical distance of approximately 2 m. These clay layers (shown in Figure 1 as clay F and the argillaceous

unit below the orange, polyhalitic band) range in thickness from a few cm to several cm, and vary in color from greenish-gray to reddish-brown. Samples were taken in two drifts over large lateral distances, approximately 600 m in a N-S trending drift, and 950 m in the E-W direction. Sample locations are shown on the map in Figure 2. A hand specimen of Rustler clay was also collected in the process of excavating the air intake shaft.

The Vaca Triste Member is not accessible in any of the underground exposures in the WIPP. However, twenty-eight samples of this unit, weighing approximately 500 g each, were obtained from six 10 cm diameter cores taken in the Delaware Basin as part of the WIPP site characterization program (Fig. 3). Preparation and analysis of samples from both the Vaca Triste cores and from the WIPP repository were performed as described in the following sections.

3.1 *Mineralogy*

3.1.1 *Analytic Techniques*

A variety of techniques was employed to gather the data presented in this paper. In general, samples were prepared by first washing to remove water-soluble salts, and then disaggregating the residue with an ultrasonic probe operating at about 250 watts. Differential settling was used to separate the clays from coarser-grained minerals (principally K-feldspar, quartz, anhydrite, and polyhalite). The anhydrite and polyhalite were then removed using the EDTA method described by Bodine and Fernald (1973). Clays were examined using routine x-ray diffraction techniques. Samples were sedimented onto glass slides that were either glycolated or heated to 250, 500, or 650 °C. Typical diffraction patterns resulting from this treatment are shown in Figure 4.

Adsorbed Mg^{2+} was removed from selected clay samples by saturating the exchange sites with Ca^{2+} . These samples were then examined by analytic transmission electron microscopy (AEM). Elemental compositions were quantified using the thin-foil data reduction technique developed by Romig (1983). The coarse-grained fraction was ex-

amined with a scanning electron microscope (SEM) equipped with an X-ray energy dispersive analytic attachment. In addition, samples with abundant quartz and feldspar were examined by cathodoluminescence (for evidence of overgrowths and compositional zoning), and the feldspar was analyzed with high precision X-ray diffraction (to establish the degree of Al-Si ordering).

Finally, the cation exchange capacity was determined on a subset of the samples collected. Each sample was first washed free of soluble salts. Next, the exchange sites were saturated with Ca^{2+} by repeatedly washing the samples with 0.5 N CaCl_2 . The clay was then rinsed free of residual calcium chloride. Finally the absorbed Ca^{2+} was removed by repeatedly washing the clay with 0.5 N MgCl_2 . Ca^{2+} in this final wash was analyzed by D. C. plasma emission spectroscopy and compared with the initial weight of the clay to yield an exchange capacity.

3.1.2 Results

1. K-Feldspar: The feldspar grains, as analyzed by the SEM energy dispersive unit, contained only Al, K and Si. No feldspars of other composition were observed. Precision X-ray diffraction analysis of the K-feldspar from ERDA6-1284 was used to determine Al/Si ordering by measuring the difference between $2\theta_{131}$ and $2\theta_{1\bar{3}1}$ reflections (Sipling and Yund 1974). The occupancy factor determined by this difference, a spacing of $0.09^\circ 2\theta$, is 0.25, indicating a degree of disorder for this K-feldspar that is comparable to sanidine. Such disorder is unusual in a low-temperature feldspar, as most previously reported sedimentary feldspars are highly ordered (Kastner and Siever 1979).

Crystal morphology of the K-spar ranged from euhedral to smoothly rounded. Throughout the following discussion, the criteria used to distinguish between "detrital" and "authigenic" are purely visual observations made by scanning electron microscopy; the former tend to be generally smooth and rounded, and usually show some evidence of chemical corrosion (*e.g.*, angular or linear etch pits). The

latter have sharply-defined corners and flat crystal faces that are generally free of pits and crevices indicative of chemical weathering. As these samples were never exposed to any solutions other than distilled, deionized water, it is unlikely that sample preparation procedures introduced any of these features. In the Vaca Triste samples, the K-spar commonly appeared as large (several tens of microns), well-developed, euhedral crystals (Fig. 5a). Only rarely were smoothly rounded, presumably detrital, grains of K-spar observed in the Vaca Triste samples (Fig. 5b). In contrast, feldspars from the WIPP repository horizon were frequently rounded in appearance and usually showed evidence of chemical corrosion. Infrequently, euhedral faces and crystallites growing on apparently detrital K-spar surfaces were also observed.

In addition, five samples of the Vaca Triste from AEC-8 core (1469.0', 1470.0', 1472.0', 1473.8', and 1479.4') were mounted in epoxy, polished, and examined by cathodoluminescence. These samples were selected because their examination by SEM showed a high proportion of euhedral, presumably authigenic, feldspar crystals. In contrast to previous studies of authigenic, non-luminescent, sedimentary feldspars (Kastner 1971), the K-feldspars in these samples all luminesced a uniform, bright, blue-violet without showing any evidence of overgrowths or compositional zoning. In similarly prepared polished grain mounts, no evidence of compositional zoning was observed in samples from either formation using the SEM X-ray analyzer.

2. Quartz: In samples from the WIPP horizon, quartz occurs as large (several hundred microns to a few mm in length) euhedral, doubly-terminated bipyramids (Fig. 6). Quartz in the Vaca Triste samples was similar in appearance, although rounded and corroded grains were more commonly observed than in the WIPP repository samples. We note here that samples from *both* the WIPP and the Vaca Triste contain both quartz and K-feldspar (although the latter phase was observed more frequently in Vaca Triste samples). In both stratigraphic hori-

zons, both of these phases show etched and rounded grains as well as evidence of authigenic growth (i.e., euhedral crystallites on detrital surfaces).

3. Clays: The $< 2 \mu\text{m}$ clay fraction was characterized principally by routine X-ray diffraction, although compositions of selected samples were obtained by analytical transmission electron microscopy (Table 1). In general, the X-ray diffraction patterns of clays from the Vaca Triste were indistinguishable from those found in the WIPP repository horizon, though the proportion of clay in the water-insoluble residue was generally much smaller in the Vaca Triste samples. A typical diffraction pattern for a glycolated clay (sample from WIPP) is shown in Fig. 4a with all major peaks identified. A comparison of the patterns of the observed mixed-layer clays with synthetic diffraction patterns (Reynolds, 1980) provides insight into the nature of the principal authigenic phase in the Salado samples. The peak position at $2.8^\circ 2\theta$ ($31.5\text{\AA}$) is explained by assuming a stacking sequence containing approximately equal proportions of trioctahedral chlorite and trioctahedral smectite layers. This peak is smaller than the main peak at $5.7^\circ 2\theta$ ($15.5\text{\AA}$), suggesting that either the amounts of smectite and chlorite in this stacking sequence are *not* equal, or that the layers do not alternate in a regular manner, as in a stoichiometric corrensite. Variations of this nature probably also explain why, from location to location, the $2.8^\circ 2\theta$ peak varies from being a prominent feature of the diffraction pattern to being barely discernible. The effects of dehydration at 250, 500, and 650°C on a clay sample are illustrated in Figure 4b-4d. Both corrensite and chlorite peaks are significantly reduced by the heating process, while the illite peak remains prominent throughout the temperature range to which this sample was exposed.

The large number of samples from the WIPP permit an estimate of the degree of lateral heterogeneity in individual strata throughout the mine. This was accomplished by measuring relative peak heights of the three principal clays (corrensite at $15.5\text{\AA}$, illite at $10\text{\AA}$, and chlorite at $7.1\text{\AA}$) for each sample, and then evaluat-

ing the three possible peak height ratios (mixed-layer/chlorite, mixed-layer/illite, and illite/chlorite). Bar graphs show these ratios and the underground sample locations (Fig. 7).

Neither of the principal clay-bearing strata in the WIPP show significant systematic mineralogical variation over the area sampled. Although within any given layer the proportions of the three clays vary from place to place, these changes appear to be random. One poorly-defined trend, however, is the apparent enrichment of corrensite in the upper clay than the lower clay. Both the mixed-layer/illite and mixed-layer/chlorite ratios are higher in the upper clay, while the illite/chlorite ratio shows no comparable trend. Thus, the corrensite enrichment in the upper clay does not occur predominantly at the expense of just one of the other clays.

Results of the analytical transmission electron microscopy are shown in Table 1. In interpreting this data it must be noted that the exchangeable cations normally on the clay were replaced with Ca^{2+} . This was done because in naturally-occurring clays, Mg^{2+} occurs both as a fixed constituent in the lattice and as an exchangeable cation. Therefore the exchangeable Mg^{2+} was removed so that it would be possible to derive structural formulas from the chemical analyses.

The clay fraction consisted of a mixture of morphologic and compositional groups (Fig. 8) that usually included most, not all, of the following:

- small, pseudo-hexagonal plates of magnesite;
- irregular platelets up to several microns in diameter. The AEM analyses showed that these platelets were relatively low in Fe (3.1 to 4.4 weight percent); the average ratio of Fe to K in this material was ~ 0.67 (using averages of the weight percents in Table 1). These platelets were tentatively identified as detrital illite.
- irregular platelets similar in appearance to the detrital illite(?), with higher

Fe content (20.0 to 28.4 weight percent); the average Fe:K ratio in these platelets is ~5.9 (from Table 1). These were tentatively identified as chlorite.

- a fine-grained material having no discernible morphology at a resolution of 300Å. In a spot by spot analysis the material may or may not give an electron diffraction pattern characteristic of a well crystallized material—hence the distinction between amorphous and crystalline fines made in Table 1. It is noteworthy that in the clay found below the Culebra dolomite the proportion of amorphous fines was so small as to preclude obtaining an analysis of the material. This material is compositionally uniform (by AEM analysis), in comparison to the illite and chlorite platelets, and probably represents the corrensite (mixed-layer chlorite-saponite) that appears prominently in the X-ray diffraction patterns of Salado samples. The X-ray diffraction patterns also suggest that the mixed-layer phase consists of a nearly 1:1 mixture of chlorite and saponite. The following formula is constructed from this 1:1 ratio and the bulk compositions determined from the AEM data for this material:

This formula is similar to that presented by Bodine (1983) for a corrensite-like structure.

Cation exchange capacity is another parameter needed to fully characterize mixed-layer clays. The results of calcium exchange determinations are shown in Table 2. For reference, the exchange capacity of the idealized corrensite formula just given is 43 meq/100 g. Evidently, for even a single stratigraphic unit the exchange capacity varies from place to place. The samples of upper WIPP clay also show a consistently higher exchange capacity than those from the unit below it. This is consistent with the X-ray diffraction results that yielded a higher proportion of the corrensite-like phase in the upper unit. However, the data are insufficient to rule out the possibility that the

corrensite in the upper unit, in fact, has a higher exchange capacity than the corrensite of the lower unit.

3.2 *Brine Chemistry: Fluid Inclusions*

3.2.1 *Techniques*

The Vaca Triste unit, as exposed in the cores sampled for this study, is composed of reddish-brown, coarse to fine-grained sandstone in which large (up to 3 cm) halite crystals are intergrown. Sampling was limited to these two cores because they were the only ones available containing halite crystals with fluid inclusions in sufficient quantity and of adequate size for sampling and analysis using our technique (described in Stein and Krumhansl 1988). Brines from 11 fluid inclusions were extracted from large halite crystals in cores from AEC-8 (sample #1476.1) and ERDA-6 (sample #1289). Fluid inclusions in Vaca Triste halite were of two apparently primary types: numerous very small (generally $\leq 10 \mu\text{m}$) inclusions in parallel growth bands of chevrons, and larger (up to a few mm on an edge) inclusions in clear, colorless, possibly recrystallized halite.

Fluids from the largest inclusions in the salt were extracted using a pin vise, a #65 drill bit, and a 25-gauge needle attached to a preweighed, 5 ml syringe. Amounts of brine extracted in this manner from these inclusions typically ranged from 15 to 75 mg. These samples were diluted with distilled, deionized water and analyzed for major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) by D.C. plasma emission spectroscopy; major anions (Cl^- , Br^- , SO_4^{2-}) were analyzed by ion chromatography. Results are presented in Table 3. Although limited in number, enough analyses of fluid inclusions were obtained from the Vaca Triste halite to provide a basis for comparison with previously-obtained analyses of inclusions taken from WIPP halite.

3.2.2 *Results*

The fluid inclusions from Vaca Triste halite comprised two compositional groups: one, high in Na, low in Mg, and with Br concentrations close to the detection limit

(approximately 200 ppm) in high-Cl brines. The other compositional group was low in Na, high in Mg, and with Br of the order of 2 parts per thousand. The latter group is similar to the Group I fluid inclusions from the WIPP that were reported in our earlier work (Stein and Krumhansl 1988), with the weight ratio K:Mg less than ~ 0.2 . Potassium concentrations are about the same in both groups of Vaca Triste inclusions (13 and 16 parts per thousand), and slightly higher than the average K values reported from the WIPP fluid inclusions (7 to 10 parts per thousand). However, one important difference between WIPP and Vaca Triste inclusion fluids is the extremely high Mg content ($\text{Mg} > 70 \text{ ppt}$) of three samples of the latter. For comparison, the mean value for the Group I inclusions from the WIPP was only 45 ppt Mg.

4 DISCUSSION

The technical goals of this study are 1) to relate the presence of authigenic quartz and K-feldspar from two different stratigraphic horizons within the Salado Formation to the abundance and type of clay minerals present; 2) to identify possible alteration pathways responsible for the observed diagenetic mineralogy; and 3) to discuss the consequences of increasingly concentrated evaporite brines on silicate diagenesis. Since the formation brines played a key role in each of these processes, we begin by first discussing the evolution of fluid compositions in both stratigraphic horizons.

4.1 *Fluid Inclusion Analyses*

In their examination of seawater evaporation, McCaffrey *et al* (1987) report weight percent ratios for Na/Cl and K/Mg around 0.15 and 0.3, respectively, for the point at which both ratios decrease rapidly with continued evaporation, corresponding to the transition from halite to potash-facies deposition. Our interpretation of fluid inclusions from the lower Salado Formation with high Mg relative to K and low Na relative to Cl is that they formed locally, in isolated pockets of highly concentrated brines (Stein and Krumhansl 1988). Overall, however, the preponderance of the fluid inclusions examined

in that study are in the halite-facies compositional range. Because the brines from some of the Vaca Triste fluid inclusions appear to be similar in composition, we propose that they originated in a similar manner. However, the high magnesium content of some of the Vaca Triste brines relative to those from the WIPP suggests that the former may have evolved well into the potash facies. This hypothesis is supported by a comparison of the the WIPP brines with those of the Vaca Triste on the Jänecke diagram (Braitsch, 1971) shown in Figure 9. A number of the Vaca Triste brines plot in fields compatible with sylvite, carnallite, or both, while the balance of the WIPP brines plot in the kainite field. In addition, a number of the Vaca Triste brines lie near the leonite-glaserite-sylvite triple junction. These are the same brines (Table 3) that are characterized by anomalously low concentrations of bromine and magnesium, and unusually high K/Mg and Na/Cl ratios. It is possible that these compositions originated when fresh seawater flooded the basin after the conclusion of the last episode of potash facies deposition. In summary, three types of brines may have been involved in diagenetic processes in the Salado: those typical of normal halite-facies conditions, those characteristic of potash-facies deposition, and a Na-K-rich brine formed by dissolution of bittern salts by undersaturated seawater.

4.2 *Clay Reactions*

Any diagenetic interpretation of Delaware Basin sediments is non-unique due to a number of sources of uncertainty; therefore any diagenetic model is necessarily somewhat speculative. It is not possible to characterize the original detrital components, especially the compositions of detrital clays, due to their alteration by later diagenetic processes. Neither the evaporite brine composition nor the extent of reaction with clastics during the evaporative process can be established with certainty. The fluid inclusion analyses are of limited usefulness because neither the conditions under which they were trapped, nor the extent to which their compositions may have been modified by diagenetic processes, is known. However, these solutions provide the only available source of information on the fluids that may have been involved in the diagenetic

process. Finally, there is much uncertainty in the deduction of reaction pathways and mechanisms, in the thermodynamic data for clay minerals, and in the calculations of ionic activities. Hence, any predicted "equilibrium" assemblages must be considered at best as only approximate.

We summarize briefly here the potentially relevant processes with examples, noting, however, that the compositional variability of the argillaceous component of both reactants and products precludes writing specific reactions. The principal diagenetic silicates observed in both the Vaca Triste and WIPP samples are authigenic quartz and K-feldspar, and Mg-rich mixed layer clays. Dissolution of detrital quartz has obviously occurred, and certain common sedimentary components are missing—plagioclase, feldspar and certain clays (*e.g.*, kaolinite, bentonite)—or observed only rarely (*e.g.*, chemically and mechanically weathered grains of olivine, pyroxene, or amphibole). These observations suggest that reactions may be written in which silica is either produced or consumed; Mg^{2+} and K^+ , both of which are presumably present in abundance in the associated brine, may be produced, consumed, or exchanged; and Fe may be oxidized or reduced. No evidence is present to suggest that brine pH was ever sufficiently extreme as to cause significant mobilization of aluminum; however, it is likely that Al is partitioned into one or more newly-formed phases during diagenesis. To illustrate the mass balance constraints on transforming an illite typical of an evaporite basin (Bodine 1983; Table 4) to produce clinochlore, corrensite, or amesite, we have written the following equations:

Corrensite may also form by alteration of albite, which perhaps accounts for the

apparent absence of detrital plagioclase feldspars in the Salado samples, *e.g.*:

Bodine and Madsen (1985) suggested a two-step mechanism for authigenic corrensite formation. The first step produces a magnesium-enriched smectite and consumes Mg^{2+} and quartz. The smectite then undergoes further diagenesis to produce both corrensite and quartz. This process is consistent with our SEM observations of abundant euhedral (presumably authigenic) quartz crystals and very few rounded (presumably detrital) quartz grains in the WIPP repository horizon samples. In this lithology, it is plausible that the abundance of clays (as well as Mg^{2+}) relative to detrital quartz resulted in the consumption of all of the latter phase. In contrast, the Vaca Triste contains much siltier material; there the ratio of clays to detrital quartz may have been lower. With more available quartz relative to reactive clays, a portion of the detrital quartz grains should be preserved. We observed that rounded, presumably detrital, quartz grains are *more* common, and euhedral, authigenic quartz *less* abundant in the Vaca Triste samples than in those from the WIPP.

Results of the AEM analyses of the Salado clays further constrain the possible diagenetic interpretations. Compositions (Fig. 10) of the illitic component vary consistently along a trend away from those typical of "normal" terrestrial illite (Bodine 1983), and toward more magnesium-rich clays such as saponite. The morphology of the illite suggests that the origin of this phase was probably detrital, rather than resulting from *in situ* diagenetic reactions, as suggested by Bodine and Madsen (1985). The discrete chlorite identified in the samples also has an irregular morphology suggestive of a detrital origin. In contrast, the predominant mixed-layer phase ("corrensite") is extremely fine-grained, lacks a distinct morphology (*e.g.* the formless gray material making up most of the background in Fig. 8), and is probably formed diagenetically. A plausible formation mechanism is the reaction of brine with detrital illite (Eq. 2). A diagenetic origin for this phase is also consistent with its apparent compositional

homogeneity (shown in Figure 10), as determined by AEM, in contrast to the illite and chlorite.

The post-depositional alteration of illite in evaporites has been the object of considerable speculation (*e.g.*, Bodine 1983; Sass *et al* 1987; Glenn 1986). Our observations of this phase in Salado halite are consistent with their interpretations. The residual detrital illite appears to have survived post-burial diagenesis morphologically and structurally intact. However, analyses of even the coarsest grain size indicate alteration toward a more Mg-rich composition. The illite compositions shown in Figure 10 are displaced directly toward the Mg corner of the plot and slightly outside the illite field. Furthermore, the AEM analyses suggest that the finest-grained fraction of the original detrital clays was affected to a greater degree by these reactions. The apparent consumption of detrital quartz can be explained by the two-step reaction mechanism of Bodine and Madsen (1985) in which the formation of a poorly-crystallized trioctahedral smectite/saponite is followed by more ordered species such as corrensite.

Age determinations can also be used to interpret the existence of residual, primary illite in the Salado sediments. Brookins and Lambert (1987) report a Rb/Sr isochron with a date of 428 Ma for the insoluble residue fraction of samples from the WIPP horizon. These samples consisted primarily of smectite (possibly with some corrensite), illite (possibly with some mixed-layer smectite/illite), and chlorite. Brookins and Lambert found that the coarsest clay size fraction was dominated by illite (presumably detrital), while the finer size fractions contained the Mg-rich, mixed-layer species, which are assumed to be diagenetic. It seems probable that the abundance of the detrital component relative to the Mg-rich fraction produces the pre-Permian date. Similar results have been reported from clays in the Palo Duro Basin (Fisher 1988).

In more recent work, Brookins *et al* (1989) describe isotopic analyses on size fractions of clays from impure evaporites of the Rustler Formation, overlying the Salado. The Rb/Sr isochron obtained from the <0.1 and <0.5 μm fractions yielded an age of 250 $\pm$ 15 Ma for these clays. Mineralogy of these samples consisted of Mg-rich, mixed-layer

clays.² Again, an increase in illite abundance with increasing grain size was found.

Although clay alteration may have contributed to the production of potassium feldspar, the scarcity of K-spar in the WIPP samples suggests that this contribution is negligible. Alternatively, authigenic K-spar, present in abundance in the siltier Vaca Triste sediments, may have been produced simply by alteration of detrital plagioclase, conserving both Al and Si:

4.3 Hypothetical Mineral Assemblages

The solution speciation/mineral equilibrium code EQ3NR (Wolery 1983) was used to compute the activities of the principal ions in solution (Na^+ , K^+ , and Mg^{2+}) relevant to the evaporite and silicate mineral reactions. These activities were then used to determine the predicted coexisting phases.

Solution compositions used as input to this code were taken from previous work on intergranular brine compositions at the WIPP site (Stein and Krumhansl 1988), and the fluid inclusion analyses from the Vaca Triste samples in Table 3. These compositions, together with the calculated activities and activity coefficients, are presented in Table 5.

For the EQ3NR calculations, the silica activity is assumed to be at saturation with respect to quartz, based on the abundance and apparent authigenic origin of this phase in the samples examined in this study. The pH was arbitrarily assumed to be equal to 7.0. Field pH measurements in a Tunisian evaporite basin were reported to decrease from 7.4 to 6.6 as evaporation increased (Gueddari *et al* 1983), so a pH of 7.0 is a reasonable approximation. Several factors may have a potentially large effect on measurement of pH in brine; comprehensive discussions may be found in Krumhansl (1989) and Sonnenfeld (1984). For the purpose of these calculations, it is

²Note that Clay P (Table 1), representative of these Rustler Formation clays, is similar in composition to the Salado Formation Mg-rich clays.

sufficient to note that brine pH measurements are affected to a significant extent by large ionic activity coefficients, hydrolysis of Mg^{2+} , and formation of ionic complexes. Initial EQ3NR runs were made with two alkalinity values, at molarities of 0.0138 M (L. Brush, pers. comm.), and 0.0561 M, using measurements from WIPP brines (Deal *et al* 1989). Calculated activities appear to be relatively insensitive to alkalinity. When the alkalinity is changed by a factor of 4, the EQ3NR activity ratios change only by ± 0.001 (except for $\frac{a_{\text{Mg}^{2+}}}{a_{\text{H}^+}^2}$, by ~ 0.003 .)

As seen in the activity diagrams for $\log \frac{(a_{\text{Na}^+})}{(a_{\text{H}^+})}$ vs. $\log \frac{(a_{\text{K}^+})}{(a_{\text{H}^+})}$ (Fig. 11-a), these fluids are consistent with stability of microcline. For $\log \frac{(a_{\text{Mg}^{2+}})}{(a_{\text{H}^+}^2)}$ vs. $\log \frac{(a_{\text{K}^+})}{(a_{\text{H}^+})}$ (Fig. 11-b), these solutions plot close to the phlogopite- or muscovite-microcline two-phase boundaries (Bowers *et al* 1984).³ Phlogopite has the idealized formula $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. Within the context of the limited number of phases considered in compiling these diagrams (Bowers *et al* 1984), it may be considered to be a reasonable substitute for any Mg-rich trioctahedral sheet silicate of the TOT type. Alternatives would be a Mg-rich 1:1 sheet silicate in the form of 14Å clinocllore (*e.g.*, $\text{Mg}_3\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$) or even non-magnesium-containing minerals such as kaolinite (*i.e.*, Al-rich TO-TO structure), muscovite (*i.e.*, Al- and K-rich TOT structure), or tektosilicates such as K-feldspar, and albite.

The code EQ3NR is limited by the approach used to calculate activity coefficients and may not be appropriate for the high ionic strength Salado brines. Therefore, the results presented here must be taken as only an approximation. The code EQ3NR uses the extended Debye-Hückel equation of Helgeson (1969), which is generally regarded as unreliable for ionic strengths greater than one molal (Wolery 1983). Typically, mean activity coefficients for the common salts (*e.g.*, NaCl, KCl, MgCl_2) initially decrease and then increase with increasing ionic strength. At higher ionic strengths than those corresponding to this minimum value, the extended Debye-Hückel approach fails to capture this increase. Thus the activities computed here, using EQ3NR for an ionic

³In *situ* pressure at the level of the WIPP repository probably never exceeded a few hundred bars and the temperature probably never was above 60°C (Bodine and Madsen 1985)

strength of ~5 molal, the approximate concentration of the Salado Formation brines, are probably systematically low, possibly by as much as an order of magnitude (e.g., for Mg). Alternative methods for activity-coefficient calculations, appropriate for higher ionic strengths, would move the data plotted in Figure 11 upward and to the right. The net effect on the predicted mineral assemblage would, however, be small, as these data would still fall in the K-spar field (Fig. 11-a) and well into the phlogopite field (Fig. 11-b).

Saturation indices (SI) are calculated by EQ3NR as the log of the ion activity product divided by the equilibrium constant for a dissolution reaction. The calculated SI values from the WIPP brine samples are consistent with deposition of evaporite minerals under halite-facies conditions. The EQ3NR calculations also support the probable exposure of Vaca Triste sediments to potash-facies brines. For the WIPP horizon fluids, the phases calculated to be at or above saturation are calcite, aragonite, halite, dolomite, magnesite, and huntite. Results of the EQ3NR calculations indicate that the Vaca Triste fluid inclusions were at or above saturation for these phases plus gypsum, anhydrite, glauberite, kainite, kieserite, sylvite, carnallite, syngenite, polyhalite, and bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). The occurrence of some assortment of these minerals is consistent with a potash-facies origin, as well as with the mineralogy predicted by a Jänecke projection of the Vaca Triste fluid inclusion compositions (Fig. 9). For comparison, the WIPP data are also shown.

5 PROGRAMMATIC APPLICATIONS

These observations and results are relevant to the needs of the WIPP project in the areas of site characterization and backfill stability. With regard to the first, we found that the same three clays (chlorite, illite, and corrensite) comprise the bulk of the argillaceous material in both the upper and lower Salado units sampled for this study. At the stratigraphic horizon of the WIPP, the proportions of these clays were found to vary from place to place, and certain strata generally contained slightly more corrensite

than others. Ion exchange capacities were consistent with these mineralogic variations. None of these differences, however, were very large. Thus, until sophisticated radionuclide transport models evolve, it is valid to model clay seams using spatially invariant sorptive properties.

The question of whether a backfill would be mineralogically stable is more difficult, as many variables are involved. Various mixtures of sand, salt, and bentonite have been proposed as candidate materials. The results presented in this study show that eventually these materials will be transformed into a suite of minerals whose sorptive and mechanical properties differ significantly from that of the original backfill. Plagioclase feldspar in the backfill sand is consumed to produce either clays or potassium feldspars. Quartz in the sand will also be consumed as bentonite undergoes the first stage of reactions that, in the end, produce corrensite. The second stage of this same process may then liberate quartz, probably forming tiny euhedral crystals similar to those found ubiquitously in argillaceous halite in the Salado. Since similar minerals were found in a variety of diagenetic environments ranging from halite- to potash-facies, this eventuality would not be averted by postulating the influx of brines differing somewhat in composition from those presently found in WIPP weeps. The eventual alteration of the backfill cannot be avoided by changing the clay used in the backfill, either, since all the differing argillaceous materials entering the basin have apparently reacted to form the same distinctive suite of Mg-rich clays. In short, the rationale behind using bentonite-sand backfills lies in their present desirable properties and what is presumably a very slow transformation rate, rather than in their ultimate mineralogic stability.

6 SUMMARY AND CONCLUSIONS

The observed silicate mineralogy in samples from the Vaca Triste potash-facies siliciclastic unit, and from the halite facies lower in the Salado Formation, at the level of the WIPP repository, resulted from the complex interaction between halite- and potash-facies brines with the detrital mineral assemblage. A possible, though non-unique, set of reactions is proposed for the formation of authigenic quartz, K-feldspar,

and a corrensite-like, mixed-layer clay. The principal mechanisms appear to consist of Mg uptake by detrital clays such as smectite, kaolinite, and possibly the finer-grained illite. Free silica may be released during the latter stages of this process. Simultaneous alteration of other detrital silicates (quartz, clays, plagioclase feldspars) may also occur and contribute to the formation of authigenic quartz and K-spar. Some components liberated during these reactions may also contribute to the formation of the observed corrensite.

The Vaca Triste samples contained more K-spar, a greater proportion of which appeared to be authigenic, than the WIPP samples. The WIPP samples, on the other hand, contained more authigenic quartz and, only rarely, rounded, detrital grains. The latter were more abundant in the Vaca Triste sediments. We attribute these differences primarily to the significantly different proportions of clays to other silicate minerals in these two units, rather than to the transition from halite- to potash-facies conditions. The apparent consistency between fluid compositions and calculated mineral assemblages suggests that these diagenetic reactions may be considered to approach, if not attain, equilibrium, at least for the formation of quartz and microcline. Finally, the overall similarity in clay compositions in the halite-facies WIPP horizon and in the potash-facies Vaca Triste sediments is significant. This observation implies that clay minerals undergoing diagenesis in a hypersaline environment react with a concentrated brine to form a particular suite of compositions which is then quite insensitive to further increases in brine concentration.

In terms of programmatic concerns, two generalizations seem warranted: 1) indigenous Salado clays probably resemble those found in the repository for significant distances beyond the boundary of the excavation, and 2) given sufficient brine and time, backfill materials (along with many other components used in sealing the repository) will undergo significant mineralogic transformations. With regard to this second matter, conventional wisdom (by analogy with silicate reactions in deep-sea sediments) suggests that such changes would be "slow" even by geologic standards. However, until data are available for quantifying the rates of these reactions, their possible relevance

to the issue of backfill longevity cannot be completely dismissed.

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Figure 1: Stratigraphy of the Delaware Basin in the vicinity of the WIPP site and detailed repository horizon stratigraphy.

Figure 2: Underground map of WIPP showing locations of clay samples.

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Figure 3: Map of the Delaware Basin in the vicinity of the WIPP site showing location of cores from which Vaca Triste samples were taken.

Figure 4: X-ray diffraction patterns of a WIPP clay sample: A. glycolated; B. heated to 250°C for one hour; C. heated to 500°C for one hour; D. heated to 650°C for one hour.

a.

b.

Figure 5: a. Authigenic K-spar from AEC8-1476.1. Scale bar = 1 μ ; b. Rounded, detrital K-spar from AEC8-1470.0. Scale bar = 10 μ m.

Figure 6: Scanning electron micrograph of authigenic quartz from AEC-8-1470.0. Scale bar = 100 μm .

Figure 7A: Upper clay, illite (10Å)/chlorite (7Å)

Figure 7B: Upper clay, mixed-layer (15.5Å)/illite (10Å)

Figure 7C: Upper clay, mixed-layer (15.5 Å)/chlorite (7Å)

Figure 7D: Lower clay, illite (10Å)/chlorite (7Å)

Figure 7F: Lower clay, mixed-layer (15.5Å)/chlorite (7Å)

Figure 8A: Clay A - from WIPP core sample ERDA601276.6. Scale bar = 0.5 μm

Figure 8B: Clay B - large platelets with low Fe content (presumably degraded Illite), from WIPP core sample ERDA5-1276.6. Scale bar = 0.5 μ m

Figure 8C: Clay F - O Drift, upper clay. Scale bar = 1.0 μm

Figure 8D: Clay G - from core sample WIPP34-1439.8. Scale bar = 10. μ m

Figure 8E: Clay M - Drift, lower clay; scale bar = 1.0 μ . Hexagonal platelets are magnesite

Figure 8F: Clay M - O Drift, lower clay, large platelet with high Fe content; scale bar + 1.0 μm

Figure 8G: Clay P - unnamed clay below Culebra dolomite; scale bar = 1.0 μm

Figure 9: Jänecke diagram (Braitsch, 1971) with (a) Vaca Triste and (b) WIPP fluid inclusion data. Abbreviations for compositional fields are: bl, bloedite; c, carnallite; bi, bischofite; ks, kieserite; hx, hexahydrite; le, leonite; k, kainite. * denotes seawater composition.

Figure 10: Triangular diagram showing WIPP clay compositions, determined by analytical electron microscopy (data from Table 1). Other Mg silicate compositional fields, as shown, are taken from literature values. R is the ratio of all the iron atoms in the clay to all those of aluminum, silicon, and magnesium, without regard to the atomic site being occupied.

Figure 11: Activity diagrams (after Bowers *et al*, 1984) with activities calculated by EQ3NR, Table 5, for WIPP and Vaca Triste brines. Diagrams are for 1 bar, 25°C. A. $\log a_{Na^+}/a_{H^+}$ vs. $\log a_{K^+}/a_{H^+}$; B. $\log a_{Mg^{2+}}/a_{H^+}^2$ vs. $\log a_{K^+}/a_{H^+}$

Sample	Si	Mg	Al	K	Ca	Ti	Fe
<u>Amorphous Fines</u>							
Clay A	45.4	37.8	13.5	0.0	1.3	0.0	2.1
Clay F	42.9	42.6	12.0	0.2	0.7	0.0	1.6
Clay G	42.7	38.6	13.3	0.6	1.0	0.0	3.9
Clay M	46.0	38.6	11.9	0.7	0.8	0.0	2.0
<u>Crystalline Fines</u>							
Clay A	42.0	37.8	14.9	1.2	1.1	0.0	3.0
Clay F	42.1	41.0	13.4	0.3	0.9	0.0	2.2
Clay G	43.5	38.6	13.3	0.7	1.0	0.0	3.1
Clay M	46.0	39.4	11.9	0.4	0.7	0.0	1.8
Clay P	42.9	39.0	13.4	0.9	1.2	0.0	2.7
<u>Large Platelets, low Fe</u>							
Clay A	50.7	7.8	31.2	5.8	0.0	0.0	4.4
Clay F	52.0	6.9	33.0	3.9	0.0	0.4	3.7
Clay G	51.7	7.0	31.1	6.8	0.0	0.0	3.4
Clay M	52.3	9.2	29.9	5.2	0.0	0.4	3.1
Clay P	50.1	7.2	31.1	5.3	0.0	0.4	5.4
<u>Large Platelets, high Fe</u>							
Clay A	32.4	18.2	19.4	5.0	0.0	0.9	24.1
Clay F	33.1	16.4	17.9	4.1	0.1	1.9	26.6
Clay G	32.3	17.0	20.5	1.4	0.2	0.1	28.4
Clay M	37.2	17.7	17.6	6.2	0.0	1.4	20.0
Clay P	38.2	21.9	17.7	1.5	0.8	0.4	19.6

Table 1: Average compositions of WIPP clays from analytical transmission electron microscopy (given as weight percent). Letters designate sample locations: A, ERDA6-1276.6; F, 0 Drift, upper clay; G, WIPP34-1439.8; M, 0 Drift, lower clay; and P, unnamed clay below the Culebra Dolomite, Rustler Formation. Amorphous and crystalline fines are probably composed of corrensite-like materials. No amorphous fines were observed in Clay P. Large platelets, low Fe are tentatively ascribed to degraded detrital illite and large platelets, high Fe are probably detrital chlorites.

Sample	Exchange Capacity (meq/100 g)
<u>Rustler Formation</u>	
Unnamed Unit Below Culebra (Clay P)	31
<u>Vaca Triste Member, Salado Formation</u>	
ERDA6-1276.6-1277.2 (Clay A)	43
WIPP34-1439.8-1441.1 (Clay G)	38
WIPP32-268.1-268.3	42
AEC8-1476.1	13
<u>WIPP Repository (lower Salado Formation)</u>	
G Drift, 60 ft., lower clay	30
G Drift, 60 ft., upper clay	44
G Drift, 1260 ft., lower clay	30
G Drift, 1260 ft., upper clay	45
G Drift, 1060 ft., lower clay	18
G Drift, 1060 ft., upper clay	35
O Drift, S1800, lower clay (Clay M)	29
O Drift, S1800, upper clay (Clay F)	44

Table 2: Cation exchange capacities of selected clays (in meq/100 g)

Ca	Mg	K	Na	Cl	Br	SO ₄	charge balance
0.9	8.5	12.0	89.4	176.6	n.d.	12.5	0.94
0.4	75.8	9.7	20.5	231.7	2.7	10.2	1.09
n.d.	6.2	9.3	97.7	182.1	n.d.	11.6	0.93
0.3	49.2	33.3	42.7	200.5	1.8	54.5	0.99
n.d.	73.9	9.4	15.4	229.1	2.7	9.5	1.04
n.d.	72.1	16.8	30.3	252.8	2.4	9.1	1.04
n.d.	46.2	16.5	37.6	200.4	1.5	14.3	0.98
0.4	53.0	15.3	51.8	237.2	1.6	11.4	1.01
n.d.	42.4	11.7	53.7	200.0	1.3	12.8	1.03
n.d.	7.5	20.9	98.8	191.5	n.d.	11.6	0.97
0.3	7.0	11.4	81.8	156.5	n.d.	12.0	0.95

Table 3: Compositions of fluid inclusions from Vaca Triste samples (in parts per thousand); n.d., not detected. Charge balances are expressed as equivalents of positive charge divided by equivalents of negative charge.

Clay	Composition
illite	$K_{0.87}(Al_{1.61}Fe_{0.20}^{3+}Mg_{0.23})(Al_{0.76}Si_{3.24})O_{10}(OH)_2$
clinochlore	$(Mg_{4.51}Fe_{0.23}^{2+}Al_{1.20})(Al_{1.09}Si_{2.91})O_{10}(OH)_8$
corrensite	$Na_{0.34}K_{0.02}(Mg_{7.59}Fe_{0.25}^{2+}Al_{0.95})(Al_{0.88}Si_{7.12})O_{20}(OH)_{10}$
amesite	$(Al_{0.994}Fe_{0.33}^{3+}Mg_{1.637})(Al_{0.994}Si_{1.006})O_5(OH)_4$

Table 4: Average compositions of typical evaporite clays. The illite, clinochlore, and corrensite compositions are composites from Bodine, 1983; the amesite, from Deer *et al*, 1966.

Sample	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log \frac{a_{Na^+}}{a_{H^+}}$	$\log \frac{a_{Mg^{2+}}}{a_{H^+}^2}$	Log Activity Coefficients ($\log \gamma$)						
				Na	Mg	K	Ca	HCO ₃	CO ₃	SO ₄
<u>WIPP</u>										
Weeps	5.7504	6.9431	12.9948	-0.6133	-0.9905	-0.9367	-1.2387	0.1492	-0.9655	-0.5220
Group I	5.3435	6.5618	13.3494	-0.5731	-0.9521	-0.9434	-1.2399	0.1311	-1.6017	-0.5320
Group II	5.5750	6.8820	13.1445	-0.5579	-0.9393	-0.8710	-1.1909	0.0748	-1.2804	-0.6531
<u>Vaca Triste</u>										
Group I	5.6177	7.0353	12.5650	-0.7162	-1.0630	-1.0670	-1.3294	0.2427	-0.3762	-0.2669
Group II	4.9485	6.3354	13.4038	-1.0527	-1.1739	-1.8595	-1.8388	0.1332	-0.4638	1.0872

Table 5: Calculated activities from EQ3NR; pH and alkalinity fixed at 7.0 and 0.0138

M, respectively.

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