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MINES BRANCH INVESTIGATION REPORT IR 71-19

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CLAY MINERALOGY OF A SAMPLE OF SYLVITE ORE FROM THE DUVAL CORPORATION MINE, SASKATOON, SASKATCHEWAN

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by

R. S. DEAN

MINERAL PROCESSING DIVISION

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Mines Branch Investigation Report IR 71-19

CLAY MINERALOGY OF A SAMPLE OF SYLVITE ORE
FROM THE DUVAL CORPORATION MINE,
SASKATOON, SASKATCHEWAN

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R. S. Dean*

- - -

SUMMARY OF RESULTS

A sample of reddish sylvite-halite ore from the Middle Devonian Prairie Evaporite Formation of Saskatchewan contained a narrow greenish-grey seam, which consisted largely of anhydrite. Clay minerals constituted only a minor proportion of this layer.

Similar clay mineral suites, consisting of illite, chlorite, septechlorite and vermiculite, in roughly equal proportions, occurred within the grey seam and within the residue of the red salt. Similarities were evident between this assemblage and authigenic clay mineral suites from other evaporite deposits containing high proportions of Mg-rich phases.

Quartz, monoclinic K-feldspar, dolomite, hematite and anatase were also identified within the sample.

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PART I

INTRODUCTION

On September 2, 1970 a specimen of "potash ore with clay seam" weighing approximately 1 kilogram was submitted to the Mineral Processing Division by Dr. V.F. Hollister, Manager of Exploration, Duval Corporation, Vancouver, British Columbia. The sample had been collected within the Company's mine, "approximately 1000 feet east of the main shaft", which is located near the town of Vanscoy, 6 miles southwest of Saskatoon, Saskatchewan (Twp. 36, Range 6, West of 3rd Meridian). The principal "potash" mineral is sylvite (KCl) and the ore horizons are part of the Prairie Evaporite Formation of the Elk Point Group of Middle Devonian age. These deposits have been described in some detail by Goudie (1) and Gorrell and Alderman (2).

The Duval sample consisted of massive, reddish, coarse-grained evaporite minerals and contained a somewhat irregular seam of greenish-grey "clay" several millimeters thick. The distribution of the red colouring of the salts appeared to be gradational within the sample as a whole and was generally concentrated within the outermost 1-mm portion of individual evaporite grains.

It was requested that a mineralogical study be made of the clay mineral fraction of the sample and, in particular, the grey "clay" seam. The widespread occurrence of such bands, partings, and inclusions has been noted within these (1, p. 7) and other (3, p. 47) evaporite deposits. The investigation was assigned Laboratory Number MP-MIN-1411.

PROCEDURE

A Guinier-deWolff four-sample X-ray powder camera was used to examine a ground portion of the red saline material, a part of the grey seam (removed with a dental drill), and the washed, water-insoluble residues of these. This preliminary investigation served to identify the major constituent of the grey seam as anhydrite.

A portion of the sample weighing approximately 300 grams was subsequently placed in a large water-filled beaker. When solution of the salts was apparently complete, it was noted that the grey seam either remained as a single layer or was separated into fairly large cohesive fragments, whereas the residual red material was widely dispersed. A mechanical separation of the grey and red residues was accomplished without difficulty by decantation. Both residues were washed repeatedly with demineralized distilled water, recovered by centrifugation (when necessary), and re-dispersed by magnetic stirring. The dithionite-citrate reduction method of Mehra and Jackson (4) was used to remove free iron oxides from the red residue which turned grey following this treatment.

The fragments of the grey seam residue were stirred vigorously in distilled water for several hours in order to disaggregate the anhydrite cement as much as possible. The suspension which, at that point, contained 2 to 3 grams of anhydrite-rich residue was diluted to approximately 50 ml, and 50 ml of concentrated (fuming) hydrochloric acid was quickly added with constant stirring. Exactly one minute later, the acidified suspension was neutralized by pouring it into a large volume (excess) of sodium bicarbonate solution. The anhydrite-free residue was recovered by centrifugation and washed. Calcium carbonate, precipitated during the bicarbonate neutralization, was subsequently removed by treatment with an excess of 2% acetic acid.

The grey seam residue was washed repeatedly with demineralized distilled water, as was the residue from the free iron-oxide removal treatment of the dispersed red material. Following each washing, the clays were collected by centrifugation for 5 minutes at 9000 rpm in a Sorvall SS-3 Superspeed Centrifuge equipped with a 200-ml-capacity HB-4 swing-bucket rotor. Re-dispersion of the samples was effected by the use of a magnetic stirring rod within each centrifuge tube. Portions of both treated clays were examined with the Guinier X-ray powder camera.

The minus 5-micron size fraction (equivalent settling diameter) was separated by centrifugation from a portion of the suspension which had been derived from the grey seam. Preliminary X-ray diffractometer scans revealed

few differences between the minus 5-micron clay and the unfractionated sample, hence the suspensions were re-combined and all subsequent work performed upon unfractionated material.

Oriented clay mineral mounts were prepared by drying dilute suspensions of the treated grey seam and (formerly) red clays on borosilicate glass slides at approximately 50°C. These were scanned with a North American Philips High-Angle X-Ray Diffractometer under conditions approximating 0% and 100% relative humidity. The differing humidity conditions were obtained by sealing the sample chamber window with thin polyethylene film and introducing either a stream of dry nitrogen gas or nitrogen which had been bubbled through hot (60°C) distilled water. Prior to each examination, the mounts were allowed to equilibrate overnight under humidity conditions approximating those under which the analyses were to be made. The instrumental settings for these (and all other) diffractometer scans were as follows: CoK α radiation with Fe filter; full-scale deflection - 400 counts; time constant - 8; scanning speed, 0.5° 2 θ per minute; 1° slits; proportional-counter detector with pulse-height analyser.

Following the scans at 100% relative humidity, the oriented mounts were sprayed with ethylene glycol using a DeVilbiss Nebulizer. Spraying was continued until the clay surface was coated with a slight excess of liquid, visible as a thin film. The glycolated mounts were subsequently allowed to equilibrate overnight in a sealed container partially filled with glycol-saturated paper tissue. In scanning these mounts with the X-ray diffractometer, glycol-saturated tissue was also placed within the sealed sample chamber and the chamber interior was sprayed with glycol mist.

Both mounts were subsequently subjected to consecutive 30-minute heat treatments at 300, 450, 580, 650, and 725°C. Following each heating stage, the mounts were cooled in a dessicator and scanned with the diffractometer in a dry nitrogen atmosphere.

Portions of the two clay residues were also boiled for one hour in concentrated (fuming) hydrochloric acid, collected by centrifugation, and washed several times with distilled water. Oriented mounts of the acid-treated clays were scanned with the X-ray diffractometer under air-dry conditions, and other portions of the same residues were examined with the Guinier X-ray powder camera.

RESULTS

The mineralogical data obtained from the Guinier X-ray powder photographs (Table 1) indicated that the grey "clay" seam actually consisted largely of evaporite minerals and contained only a small proportion of layer silicates. The latter were concentrated for study by the one-minute hydrochloric acid treatment, which dissolved the grey seam anhydrite, and by the removal of free iron oxide (hematite) from the red residue of the coarse salt crystals. The X-ray diffractograms of the clays thus treated are shown in Figures 1 and 2.

TABLE 1

Mineralogy of the Non-Clay Fraction of the
Duval Sylvite Ore (Guinier Camera Data)*

Mineral	Grey "Clay" Seam			Red Salt	
	Whole	Water Residue	1-Min HCl Sol Residue	Whole	Water Residue
Sylvite	D	-	-	A	-
Halite	C	-	-	D	-
Anhydrite	B	A	-	-	-
Quartz	E	D	B	G	B
K-Feldspar	-	G	C	-	C
Dolomite	F	E	-	-	D
Hematite	-	-	-	-	C
Anatase	-	-	G	-	G
Total Clay Minerals	E	D	A	G	A

*Mineral abundances estimated from "A" (very abundant) to "G" (trace)

The scans of both residues at 0% relative humidity (Scan 1) are virtually identical, except for the absence of the 2.88Å dolomite reflection from the acid-treated grey seam material (Figure 2).



Figure 1. X-ray diffractograms of oriented mounts of water-insoluble fraction of red salt crystals; free iron oxides removed.

Scan 1 - 0% relative humidity (dry N₂ gas)

Scan 2 - 100% relative humidity

Scan 3 - Ethylene glycol saturated

Scan 4 - Boiled for 1 hour in concentrated HCl; air-dry

<u>Illite</u>	- 9.9, 4.97, 3.34 Å
<u>Chlorite</u>	- 14.1, 7.07, 4.71, 3.53 Å
<u>Septechlorite</u>	- 7.13, 3.58 Å
<u>Vermiculite</u>	- (Scan 2) 14.8 Å
<u>Quartz</u>	- 4.26, 3.34 Å
<u>K-Feldspar</u>	- 3.78, 3.23 Å
<u>Dolomite</u>	- 2.88 Å

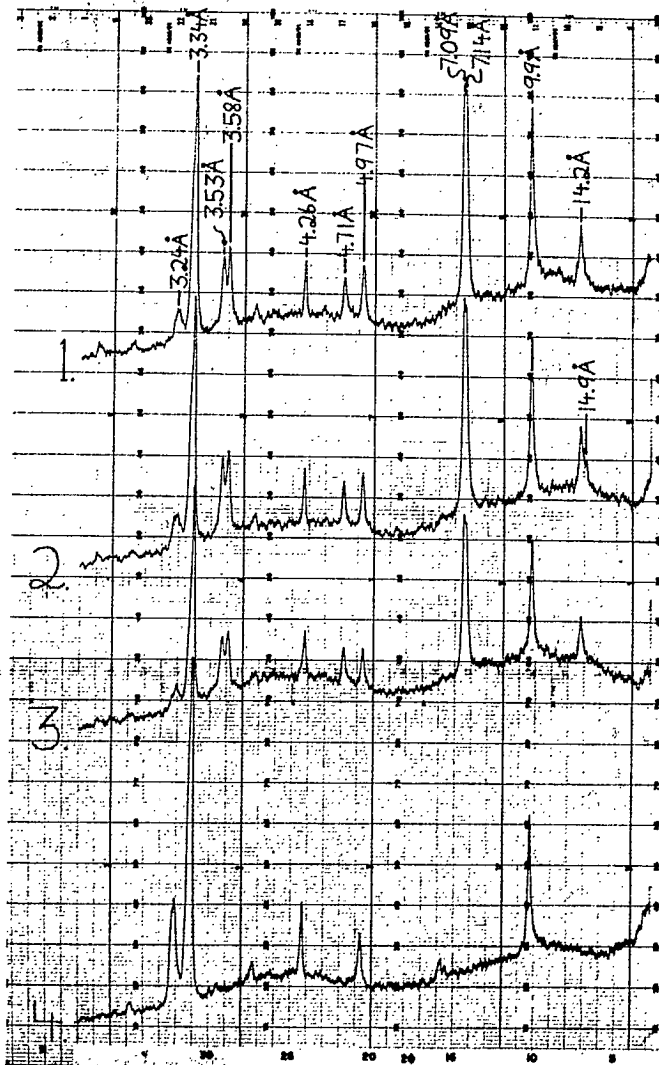


Figure 2. X-ray diffractograms of oriented mounts of grey seam residue. Anhydrite removed by 1-minute HCl treatment.

- Scan 1 - 0% relative humidity (dry N₂ gas)
- Scan 2 - 100% relative humidity
- Scan 3 - Ethylene glycol saturated
- Scan 4 - Boiled for 1 hour in concentrated HCl; air-dry

<u>Illite</u>	- 9.9, 4.97, 3.34 Å
<u>Chlorite</u>	- 14.2, 7.09, 4.71, 3.53 Å
<u>Septechlorite</u>	- 7.14, 3.58 Å
<u>Vermiculite</u>	- (Scan 2) 14.9 Å
<u>Quartz</u>	- 4.26, 3.34 Å
<u>K-Feldspar</u>	- 3.24 Å

The diffractograms in Figures 1 and 2 also reveal an unusual characteristic of both samples - the occurrence, in roughly similar proportions, of both normal (14\AA) and 7\AA chlorite. The 14\AA chlorite yielded a first-order basal reflection at $14.1 - 14.2\text{\AA}$ and integral higher orders at 7.07 , 4.71 , and 3.53\AA whereas the 7\AA mineral yielded 001 and 002 reflections at 7.13 and 3.58\AA respectively. The identity of the latter material as a type of chlorite, rather than a kaolin, was established beyond question by the boiling hydrochloric acid treatment (Figures 1 and 2, Scan 4) which resulted in the complete elimination of all 7 and 3.5\AA reflections. Following Nelson and Roy (5), the 7\AA chlorite may be referred to as "septechlorite".

Differences in the thermal stability of the two chlorite phases were brought to light by the heating tests. The replacement, following the 580°C heat treatment, of the 14\AA chlorite basal reflection series by a single intense reflection at 13.9\AA (Figures 3 and 4, Scan 3), indicates that 'brucite' layer dehydroxylation was well advanced at that temperature (6). According to Grim and Johns (7, p. 87) and to many more recent studies, 500 to 600°C is the usual range within which this reaction occurs among chlorites from ancient sediments. In contrast, little change was evident in the septechlorite basal reflections following the same treatment, although the chamosite examined by Nelson and Roy (5, p. 339) was decomposed under similar conditions.

The most conspicuous difference between the grey seam and disseminated red clay diffractograms was noted in the 100% relative humidity scans (Figures 1 and 2, Scan 2) where a sharp and intense 14.8\AA reflection appeared only in the red clay residue scan. The expansion properties of this phase were unusual in that the 14.8\AA peak was replaced by a diffuse $12.8 - 14\text{\AA}$ band following glycol saturation (Figure 1, Scan 3). This suggested the formation of interstratified mixtures of layers which were, on the whole, more contracted than the 14.8\AA expansion which had been achieved with water vapour. The expandable material was tentatively identified as vermiculite.

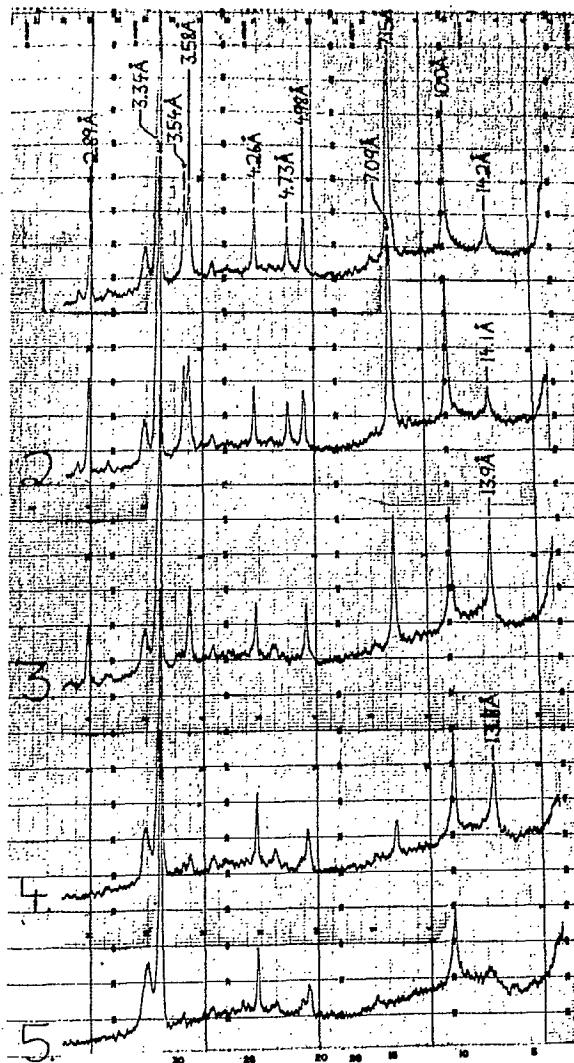


Figure 3. X-ray diffractograms of oriented mounts of water-insoluble fraction of red salt crystals; free iron oxides removed.

- Scan 1 - Heated for 30 minutes at 300°C; dry N₂ gas
- Scan 2 - Heated for 30 minutes at 450°C; dry N₂ gas
- Scan 3 - Heated for 30 minutes at 580°C; dry N₂ gas
- Scan 4 - Heated for 30 minutes at 650°C; dry N₂ gas
- Scan 5 - Heated for 30 minutes at 725°C; dry N₂ gas

<u>Illite</u>	- 10.0, 4.98, 3.34 Å
<u>Chlorite</u>	- 14.2, 7.09, 4.73, 3.54 Å; (Scan 3) 13.9 Å
<u>Septechlorite</u>	- 7.15, 3.58 Å
<u>Quartz</u>	- 4.26, 3.34 Å
<u>Dolomite</u>	- 2.89 Å



Figure 4. X-ray diffractograms of oriented mounts of grey seam residue. Anhydrite removed by 1-minute HCl treatment.

- Scan 1 - Heated for 30 minutes at 300°C; dry N₂ gas
- Scan 2 - Heated for 30 minutes at 450°C; dry N₂ gas
- Scan 3 - Heated for 30 minutes at 580°C; dry N₂ gas
- Scan 4 - Heated for 30 minutes at 650°C; dry N₂ gas
- Scan 5 - Heated for 30 minutes at 725°C; dry N₂ gas

<u>Illite</u>	- 10.0, 4.98, 3.34 Å
<u>Chlorite</u>	- 14.2, 7.09, 4.72, 3.53 Å; (Scan 3) 13.9 Å
<u>Septechlorite</u>	- 7.16, 3.57 Å
<u>Quartz</u>	- 4.26, 3.34 Å

The presence, within both residues, of a high proportion of trioctahedral layer silicates was confirmed by the Guinier X-ray powder patterns. Prominent 02 and 06 reflections were recorded at 4.6 and 1.54 \AA but both lines disappeared after treatment with boiling hydrochloric acid, the dioctahedral (illite) reflections remaining unaffected. No difficulty was encountered in distinguishing the 1.54 \AA layer silicate reflection from the quartz 211 reflection which occurs at the same spacing, as the latter was clearly visible as a sharp line lying within the broad band representing the former.

PART II

INTRODUCTION

The diffractometer and X-ray powder data indicated that the non- evaporite constituents of the grey "clay" seam resembled very closely, in both mineralogy and layer silicate crystallinity, the hematite-free residue of the coarse salt crystals. In view of these similarities, the distribution of vermiculite seemed anomalous, as this phase appeared to be virtually confined to the red clay residue (compare Figure 1, Scan 2 with Figure 2, Scan 2). It could therefore be suspected that the 1-minute hydrochloric acid treatment to which the grey seam material had been subjected in order to dissolve anhydrite had resulted in the decomposition or dissolution of the vermiculite. A further investigation of this possibility was indicated, not only to establish the correct mineralogy of the grey seam, but also to provide further data on the susceptibility of certain clay minerals to attack by acids.

PROCEDURE

The very high anhydrite content of the grey "clay" seam precluded the study of vermiculite within the untreated grey material. As an alternative, the resistance to acid attack of the vermiculite within the dispersed "red clay" was investigated.

An aliquot was taken from the iron oxide-free "red clay" suspension which had yielded the 14.8\AA vermiculite reflection shown in Figure 1, Scan 2. This was subjected to a 1-minute 1:1 hydrochloric acid:water treatment identical to that previously utilized to remove anhydrite from the grey seam. The solution was neutralized as before, the clay recovered by centrifugation, and washed several times with demineralized distilled water. An oriented mount was prepared, and this was scanned with the X-ray diffractometer under conditions approximating 0 and 100% relative humidity and following saturation with ethylene glycol.

RESULTS

The diffractograms of the treated "red clay" are illustrated in Figure 5. These show no evidence of the prominent 14.8\AA reflection which was obtained from the original material (Figure 1, Scan 2), hence it may be presumed that the vermiculite did not survive the 1-minute acid treatment. Alternatively, it could be supposed that the vermiculite had collapsed irreversibly to about 10\AA with acid treatment, as indicated by the apparent increase in intensity of the 9.9\AA reflection in Figure 5, Scan 2 over that in Figure 1, Scan 2. However, intensity comparisons involving other reflections on the same scans, such as the $9.9/3.58\text{\AA}$ peak height ratios, suggest that this may simply be part of a general increase in layer silicates basal reflections from the acid-treated clay (Figure 5) mount.

It is therefore highly probable that vermiculite was not confined to the dispersed red clay but was originally also present in equivalent proportions within the layer silicate fraction of the grey "clay" seam. On the basis of this assumption, the mineralogy of the layer silicate fraction (reported as "Total Clay Minerals" in Table 1) of both red and grey samples is as follows:

- (1) Illite (dioctahedral)
- (2) Chlorite (trioctahedral)
- (3) Septechlorite (trioctahedral)
- (4) Vermiculite (probably trioctahedral)

The four phases occur in roughly comparable proportions.

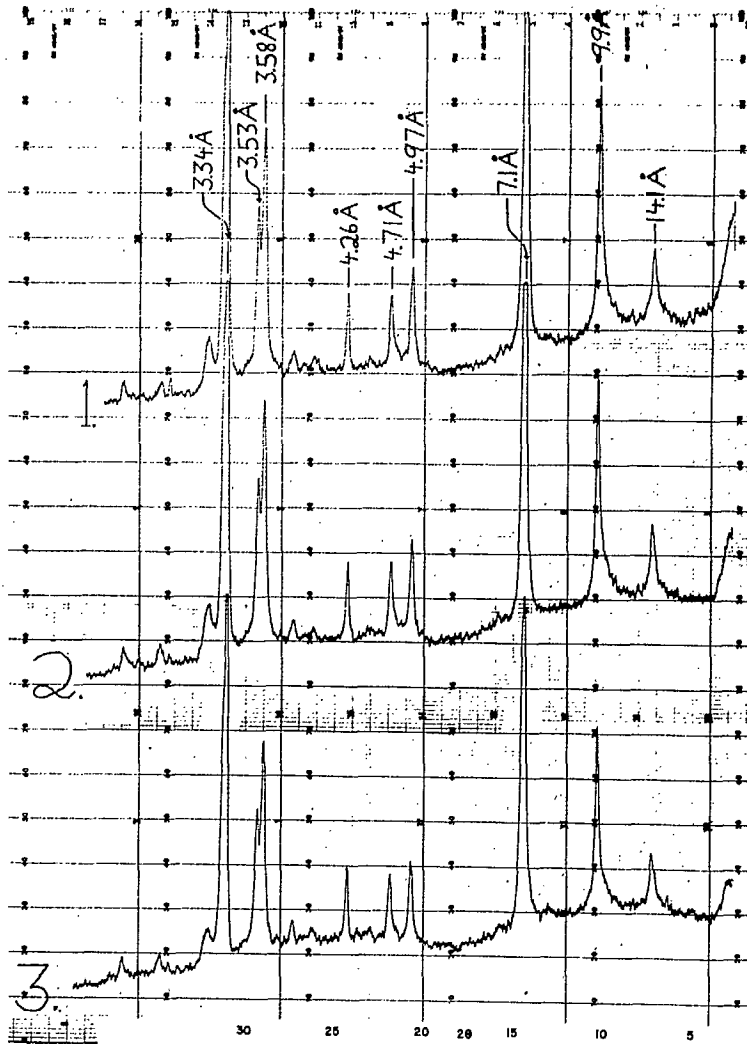


Figure 5. X-ray diffractograms of oriented mounts of water-insoluble fraction of red salt crystals; free iron oxides removed; 1-minute HCl treatment.

Scan 1 - 0% relative humidity (dry N_2 gas)

Scan 2 - 100% relative humidity

Scan 3 - Ethylene glycol saturated

<u>Illite</u>	- 9.9, 4.97, 3.34 \AA
<u>Chlorite</u>	- 14.1, 7.1, 4.71, 3.53 \AA
<u>Septechlorite</u>	- 7.1, 3.58 \AA
<u>Quartz</u>	- 4.26, 3.34 \AA

DISCUSSION

The identification of anhydrite as the major constituent of the grey "clay" seam within the Duval ore sample agrees with the observations of Droste (3, p. 47), who has noted a generally low clay mineral content within such layers. If maintained, this low total content of layer silicates should minimize the potential physical hazards connected with the expansion and/or contraction of the vermiculite phase upon wetting or drying.

Previous investigations have indicated that the clay minerals within ancient saline deposits either may represent the contributions of the source areas (to the same degree as do shale clay minerals) or may consist of authigenic Mg-rich and, to a lesser extent, K-rich layer silicates. Among the former are the the illite-chlorite suites identified by Harrison and Droste (8) and Lounsbury (9) from, respectively, the gypsum-anhydrite deposits of the lower St. Louis limestone (Mississippian) of southwestern Indiana and the halite-anhydrite-gypsum deposits within the Salina Formation (Silurian) near Detroit. The diffractograms of the Salina clays illustrated by Lounsbury (9, pp. 59-61) were, in fact, quite similar to those obtained by Brady and Dean (10) in adjacent southern Ontario from the underlying Ordovician Queenston Formation and the overlying Devonian Hamilton shale.

Authigenic clay mineral suites from within evaporite deposits have frequently been found to consist of layer silicates having an unusually high Mg content. The formation of abundant authigenic chlorite has been noted by Pundeer (11) in shaly clay within the Permian Zechstein evaporites of Germany. Regular interstratifications of chlorite and "swelling chlorite" (in glycerol or glycol) layers, known as corrensite, have been reported from several evaporite deposits including unspecified localities within the Devonian of western Canada (3, p. 48). In some instances, such as within the Permian Salado Formation of New Mexico studied by Grim et. al. (12), this type of magnesian layer silicate may constitute the bulk of the clay mineral fraction within certain argillaceous bands.

The clay minerals within the Duval sample would appear to include a large authigenic fraction, as suggested by the unusually high proportions of trioctahedral phases - chlorite, septechlorite, and (probably) vermiculite. The latter mineral is thought to be trioctahedral because of the extreme ease by which it is decomposed by hydrochloric acid.

The occurrence together of chlorite and septechlorite has been observed by several authors, one of the best-documented investigations being that of the Recent sediments of Loch Etive, Scotland, by Rohrllich et al. (13). Worthy of note in this study is the interpretation of the septechlorite (chamosite) as authigenic and the chlorite as detrital. A similar interpretation might also be tentatively applied to the Duval clay, in which the 14\AA chlorite may be too rich in iron to be considered as an alteration product of Mg-rich saline solutions. Although complicated by septechlorite interference, the relative intensities of the chlorite basal reflections do suggest a certain Fe content (14) as does its merely "average" thermal stability (15). In contrast, the much greater thermal stability of the septechlorite indicated strongly that this was a Mg-rich variety (16, p. 134; 17, p. 221).

Possibly, the illite and 14\AA chlorite, and similar assemblages reported from elsewhere within these deposits by Droste (3, p. 48), represent the unmodified or regional clay mineral suite whereas the septechlorite and (possibly) vermiculite are products of local authigenesis effected by highly saline solutions rich in dissolved magnesium. Why authigenesis should result in the formation of a 7\AA rather than a 14\AA chlorite is not obvious. This may, however, be related to the fact that the Al-deficient Mg-rich "end members" among the chlorites (i.e., the serpentine minerals) occur as 7\AA rather than 14\AA types. The 14\AA chlorite could be detrital or it might have been formed during another diagenetic episode by the alteration of ferro-magnesian detrital minerals such as biotite (18, pp. 181-186).

In order to dissolve anhydrite, the finely divided grey seam material was treated for 1 minute with a 1:1 mixture of concentrated (fuming) hydrochloric acid and water at room temperature, which was then immediately neutralized with sodium bicarbonate solution. Although it is known that hydrochloric acid at this concentration will attack and eventually decompose many trioctahedral clay minerals (18, p. 130), it might be supposed that the rate of this reaction would be considerably slower than those involving finely divided anhydrite, gypsum, or

dolomite. The nearly complete decomposition of the clay vermiculite by the above treatment illustrates the dangers involved in the use of strong acids on clay minerals, for however brief a period. This particular vermiculite might serve as a useful test material for other sample preparation procedures involving acid treatments.

An alternative to the use of hydrochloric acid in the removal of calcium sulphate minerals is the lengthy sodium chloride solution treatment outlined by Dreizler (19, pp. 323-324). Apart from its time-consuming aspects, this procedure would probably result in the alteration of trioctahedral 10\AA layers to vermiculite (20). The possibility that the varied trioctahedral clay mineral suites within evaporite deposits could include mica cannot, of course, be ignored.

CONCLUSIONS

(1) The grey "clay" seam within the Duval sylvite ore sample consists principally of anhydrite, with lesser halite and sylvite. Quartz, clay minerals, and dolomite occur in decidedly smaller quantities.

(2) The clay mineral fraction within both the grey seam and the insoluble residue of the coarse red salt consists of roughly equal proportions of four phases: illite, chlorite, septechlorite and vermiculite. Chlorite, septechlorite, and, probably, vermiculite are trioctahedral.

(3) The septechlorite and vermiculite are possibly of authigenic origin. The septechlorite has a high thermal stability, hence it is probably rich in magnesium. The vermiculite is very readily decomposed by hydrochloric acid.

ACKNOWLEDGEMENTS

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