

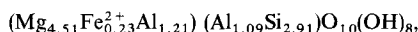
## CHLORITE AND ILLITE COMPOSITIONS FROM UPPER SILURIAN ROCK SALTS, RETSOF, NEW YORK

M. W. BODINE, Jr.\* and R. R. STANDAERT†

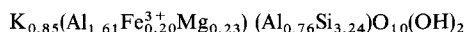
Department of Geological Sciences, State University of New York, Binghamton, NY 13901, U.S.A.

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**Abstract**—Chlorite and illite are the major clay minerals in silicate assemblages from a rock salt bed in the Vernon Formation (Upper Silurian) at Retsof, New York. Textural features and Br content of the salt indicate precipitation from shallow marine brine with no subsequent postdepositional recrystallization. Sample mounting procedure for electron microprobe analysis involves clay particle dispersion, sedimentation, and transferral to a planar silver print surface. The 001 face of the flake, rather than the conventional polished plane, constitutes the analyzed surface. Microprobe analysis of the chlorite (80 grains from four samples) yields a mean aggregate Mg-rich clinocllore composition of



which is relatively uniform among grains and among samples. Its unique composition when compared with normal shale chlorites suggests an authigenic origin in the marine evaporite environment. Illite (106 grains from five samples) has a mean aggregate composition of



with little variation among samples. The illite is distinctly less degraded than normal shale illite suggesting some recrystallization occurred in the hypersaline environment. Extensive compositional variation among illite flakes within each sample may reflect alteration of several different detrital micaceous minerals. The term *hyperhalmyrolysis* is introduced to denote mineral reactions which occur in the marine hypersaline environment.

Diagenesis effected improved crystallinity and undoubtedly involved isochemical recrystallization of the bulk silicate assemblage. Metasomatism of the assemblage during diagenesis, however, appears to be negligible.

### INTRODUCTION

Chlorite and illite are the most abundant clay minerals in Paleozoic evaporite rocks (Droste, 1963). Their common occurrence has been well documented throughout the German Zechstein (Braitsch, 1958; Füchtbauer and Goldschmidt, 1959; Dreizler, 1962; Pundeer, 1969), the German Keuper (Lippmann and Savascin, 1969), the Austrian Haselgebirge (Bodine, 1971), the Michigan basin Upper Silurian (Lounsbury, 1963), the western New York Upper Silurian (Bodine, Fernald, and Standaert, 1973), and the southeastern New Mexican Permian (Grim, Droste, and Bradley, 1960). Yet, the origin of this association remains controversial; the fundamental question—whether the chlorite and illite represent primary detrital accumulates or authigenic alteration products of degraded detrital clay assemblages—has not been resolved satisfactorily. Nor is it likely to be resolved until adequate compositional data for each of the two clays become available.

We analyzed four chlorite and five illite populations in seven samples of an Upper Silurian rock salt at the Retsof Mine in western New York. The mean composition of each population was determined by analysis of at least 17 individual flakes with the electron microprobe. Each of the clays is well crystallized and each has a nearly constant composition throughout the suite of analyzed samples. Mean compositions of both are distinctive and differ appreciably from those in normal marine pelitic rocks, but are compositionally compatible with our conclusion of a metasomatic origin in the marine hypersaline environment. Each chlorite population displays relatively minor compositional variation among individual flakes suggesting an approach toward equilibrium with the brine. Illite populations, on the other hand, revealed considerable compositional variation among the analyzed flakes in each sample which we tentatively attribute to less complete recrystallization of several detrital micaceous and mica-clay minerals.

This report is the first of two examining the geochemistry and mineralogy of the silicate assemblage in the Retsof salt bed. The second paper (Bodine and Standaert, in preparation) will document the occurrence of serpentine in some samples and discuss the genesis of the serpentine-talc-quartz and talc-quartz

\*Present address: Department of Geoscience, New Mexico Institute of Mining and Technology, Socorro, NM 87801.

† Present address: Continental Oil Co., 1755 Glenarm Place, Denver, CO 80202.

associations in terms of the total silicate assemblage and chemical composition of the silicate-rich insoluble residue.

### GEOLOGIC SETTING

Our samples were collected from the Retsof salt bed in the International Salt Company mine at Retsof, New York. Retsof is located in the western part of the state in northwestern Livingston County (York Township) about 8 km northwest of Geneseo, 42 km southwest of Rochester, and 80 km east of Buffalo. The mine is situated toward the western margin of the Appalachian Basin (Dellwig and Evans, 1969) which was a site of extensive evaporite deposition during the Upper Silurian throughout western and central New York and northern Pennsylvania. Many workers have investigated the stratigraphic, sedimentologic, and paleogeographic features of this evaporite succession; the most recent and applicable to our report include Alling and Briggs (1961), Dellwig and Evans (1969), Kreidler (1957), Rickard (1969), and Treesh and Friedman (1974).

The Retsof bed is a 3–4 m thick rock salt unit at the top of the middle member of the Vernon Formation and is the only rock salt mined at Retsof. The Vernon Formation is the basal unit of the Salina Group throughout New York and northwestern Pennsylvania (Rickard, 1969). In the Retsof area the formation is divided into three members: an upper and a lower clastic member, each consisting chiefly of green and grey shale and dolomitic shale with thin interbeds of red shale, with a middle member consisting of a number of thinly interbedded rock salt beds, anhydrite, dark grey shale, dolomitic shale, and dolomite. Near Retsof the formation has a total thickness of 120 m; the middle member is 35 m thick and contains an aggregate salt thickness of 15 m (Rickard, 1969). The salt beds thin and pinch out a few tens of kilometers east of Retsof. They persist to the west; the Retsof salt bed, for example, can be traced continuously in the subsurface through northwestern Pennsylvania, northern Ohio, across the Chatham sag and into the Michigan Basin (Rickard, 1969). The upper and lower members grade eastward into clastic sequences with proportionally more red shale which interfingers with and is correlative to the deltaic beds of the Bloomsburg Formation in central and eastern Pennsylvania. West of Retsof these shaley members of the Vernon Formation thin and pinch out east of the Michigan Basin. Alling and Briggs (1961), Rickard (1969), and Treesh and Friedman (1974) agree that the principal source of the detrital components in the Vernon Formation near Retsof lay far to the east in the uplands forming the eastern margin of the Appalachian basin; the detritus which reached the Retsof area consisted of fine, relatively well-weathered, terrigenous detritus which most likely had endured a rather complex history of transport.

Sedimentologic features and the depositional paleoenvironment of the Retsof salt bed within the mine workings have been discussed by Dellwig and Evans (1969). The rock salt, 3–4 m thick, is underlain and overlain by dark grey, somewhat massive, dolomitic shale which is a characteristic lithology of the middle member of the Vernon Formation. The salt is typically diffusely bedded or banded with thicknesses of individual layers ranging between <1 and 50 cm. The thicker beds commonly show cross-stratification. Bedding features are due principally to variations in the amount of dark grey silicate inclusions in the salt and secondarily to variations in grain size of the halite. The thin, sharp anhydrite–halite banding or “varving”, so common in the deep-water salts of the Michigan Basin is absent; in the Retsof bed the anhydrite and carbonate minerals are disseminated throughout the rock salt. The Retsof bed also contains numerous discrete rounded inclusions of dark grey dolomitic shale, or “shale balls” (Dellwig and Evans, 1969), which range from <1 to 100 cm in diameter; some of the shale inclusions are fragmental and angular.

Dellwig and Evans (1969) attribute these features to remixing of soft evaporite “mush” by wave action and current turbulence suggesting a subaqueous, but shallow environment of deposition. The “shale balls” formed on the bottom through current transport of fragments of semilithified clastic material. Rickard (1969) arrives at similar conclusions based on his elegant study of drill core data and subsurface gamma log records. He has constructed models related to clastic sedimentation rates, evaporite mineral accumulation rates, subsidence rates, and stratigraphic thicknesses from which he has calculated water depths. His calculations give depths of 10–25 m during periods of salt deposition in the Retsof area.

### SAMPLE DESCRIPTION

We selected seven specimens from our collection of the Retsof salt which contained either abundant chlorite, illite, or both in the insoluble fraction. They represent the major lithologic variations within the salt bed and are distributed throughout its stratigraphic interval. At the same time we avoided samples which exhibited features that might be attributed to significant postdepositional salt recrystallization or mobilization. The samples are from two 3 m vertical profiles through the Retsof salt bed some 500 m apart. The location, stratigraphic position, lithologic description, bromine content in halite, and the relative abundance of the silicate minerals in the insoluble fraction are summarized in Table 1. The silicate assemblages within each of the seven analyzed fractions were determined by X-ray powder diffraction (Figure 1). Chlorite, illite, talc, and quartz occur in each <2  $\mu\text{m}$  fraction. Potash feldspar occurs in some <2  $\mu\text{m}$  fractions and in all >2  $\mu\text{m}$  fractions. Serpentine, the only other silicate identified, occurs

Table 1. Characteristics of rock salt samples containing the analyzed clays from the Retsof mine

Sample	Br(ppm) in halite	Silicate mineralogy*						Stratigraphic position and lithologic description
		Chlorite	Illite	Talc	Serpentine	K-feldspar	Euhedral quartz	
								<i>Bay 5, West</i>
MB-72-2	79	[++]	[++]	+	-	++	++	20 cm above base; massive, 50-cm thick, unbanded, light grey rock salt with no "shale ball" inclusions, medium-grained (2-5 mm), somewhat cloudy halite crystals.
RS-72-5	80	[+++]	+	+++	-	+	+	180 cm above base; indistinctly banded, light grey rock salt with few small (<0.5 cm), rounded "shale ball" inclusions; medium-grained, cloudy halite crystals.
RS-72-9C	82	+	[+++]	++	-	+	+++	240 cm above base; distinctly banded (gradational), dark grey rock salt with small-to-moderate (0.5-4 cm) "shale ball" inclusions; medium-grained, cloudy halite crystals.
								<i>Bay 4, West</i>
RS-72-11	82	++	[+]	+++	+	+	++	35 cm above base; massive, 40 cm-thick, unbanded, light grey rock salt with few moderate-to-large "shale ball" inclusions (1-15 cm); medium-grained, cloudy halite crystals.
RS-72-18	82	[+++]	+	+++	+	+	+	130 cm above base; light-to-dark grey, distinctly banded (gradational), cross-stratified rock salt with few small "shale ball" inclusions; medium-grained, cloudy halite crystals.
RS-72-15	86	+	[+++]	+	-	+	+++	150 cm above base; diffusely banded, dark grey rock salt with abundant, small-to-large (0.5-50 cm) "shale ball" inclusions; moderately coarse (5-10 mm), cloudy halite crystals.
RS-72-20	97	[++]	[++]	+	-	++	++	Top of rock salt, 305 cm above base; well banded (gradational) dark grey rock salt with abundant small-to-moderate "shale ball" inclusions (some angular); coarse-grained (>10 mm), cloudy halite crystals.

\* Silicate abundances: +++ dominant, ++ major, + minor, - not detected; [ ] analyzed in this study. Silicate mineral abundances from diffraction results for total unsized silicate fraction.

in two of these samples. Pyrite is the only nonsilicate occurring in the insoluble fraction and it was identified in all samples; iron oxide minerals appear to be

absent or are present in such low abundances that they remain undetected by X-ray diffraction.

Electron micrographs of the <2  $\mu\text{m}$  fraction from RS-72-5 illustrate the well-defined crystalline character of the clay particles (Figure 2). Many of the flakes exhibit euhedral to subhedral crystal outlines (Figure 2A) and are distinctly flakelike with planar 001 surfaces; many flakes are large and commonly attain diameters of >20  $\mu\text{m}$  (Figure 2B). Since the flakes have effective spherical diameters of <2  $\mu\text{m}$ , these larger particles, and undoubtedly many of the smaller flakes, must be extremely thin. Electron micrographs of the >2  $\mu\text{m}$  fraction demonstrate the euhedral character of the associated quartz (Figure 3A) and pyrite (Figure 3B).

#### PROCEDURE

After coarse crushing, a weighed split of each rock salt sample was leached with an excess of demineralized water to dissolve the halite host. This was centrifuged repeatedly, decanted, and rewashed to remove all traces of dissolved halite from the residue. The leachates were combined and retained for bromine analysis; the residue was dried, reweighed, and suspended in a boiling EDTA solution in order to separate the "acid-soluble" salts (sulfate and carbonate minerals) following the procedure of Bodine and Fernald (1973). Again, after repeated centrifuging, decanting and washing to remove EDTA and dissolved solid components from the insoluble residue, the suspension was dried and reweighed. A split of this fraction was resuspended in water, thoroughly disaggregated with an ultrasonic probe, and separated into the >2, 2.0-0.5 and <0.5  $\mu\text{m}$  (effective spherical diameter) fractions with timed centrifugations. Oriented diffractometer mounts of these fractions

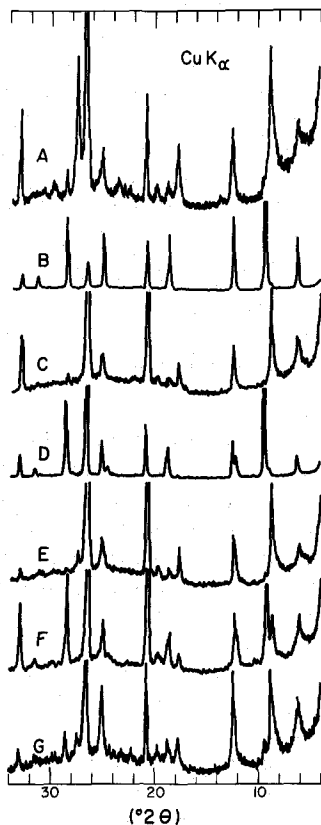


Fig. 1. Diffractometer traces from oriented (sedimented) samples of the silicate-rich residue from Retsof rock salts which were analyzed in this study: A. MB-72-2; B. RS-72-5; C. RS-72-9; D. RS-72-11; E. RS-72-15; F. RS-72-18; G. RS-72-20. Size fraction: 2.0-0.5  $\mu\text{m}$  (effective spherical dia).

were prepared by pipetting several drops of each suspension onto glass slides and air-drying.

Mounts for microprobe analysis were prepared from the 2–0.5  $\mu\text{m}$  fraction. A few drops of the suspension were diluted with water and an oriented mount was prepared by the same method which was used to prepare the diffraction mount. A coat of silver print was applied to a clean glass slide, dried slightly, and pressed against the dried oriented sample mount. The two slides were carefully separated which transferred some particles of the sample to the “tacky” thin film of silver print. Some of the individual clay flakes adhered to the silver-print surface with their 001 faces parallel to the plane of the mount. If such an exposed 001 face was planar with no, or widely spaced cleavage steps or other surface imperfections, its characteristics in the microprobe would be identical to those of a conventionally polished surface. After the silver print dried, the mount was carbon-coated in a vacuum evaporator; it was then ready for insertion into the microprobe. Similar mounts, but with an aluminum coating, were prepared for scanning electron microscopic examination.

#### Bromine analysis

Bromine content in the halite was determined from the weighed rock salt dissolved in water; we followed the advice of Schwerdtner (1963) and used the procedures given by Kolthoff and Elving (1961).

#### X-ray powder diffraction

Only basal spacings from oriented mounts are presented since the polymineralic character of the assemblages (which always included pyrite as well as the silicates) prevented assignment of general *hkl* reflections; this precluded polytype determinations and  $b_0$  measurements in both chlorite and illite. The diffraction traces were recorded at  $2^\circ 2\theta/\text{min}$  scanning speed with a Norelco diffractometer equipped with a curved crystal monochromator.

#### Electron microprobe

Our samples were analyzed on an Applied Research Laboratories EMY-SM microprobe at an output voltage of 15 Kv, an emission current of 120  $\mu\text{A}$ , and a beam current of 0.24  $\mu\text{A}$ . The smallest possible beam diameter ( $\sim 2 \mu\text{m}$ ) was used for analyzing chlorite but was slightly enlarged for analyzing illite as well as the muscovite and phlogopite standards in order to minimize potassium migration and loss. All grains, except for an occasional illite flake, remained stable and virtually unchanged after repeated exposure to the beam.

Our analyses are restricted to isolated grains which were clearly visible, remained in focus throughout both their long and short dimensions, and were largely free of surface imperfections, inclusions, overgrowths, and fracture or cleavage steps. Using these precautions we analyzed only planar 001 surfaces which were essentially normal to the beam and not

Table 2. Chemical analyses (weight %) of minerals used as microprobe standards

	Chlorite, Vermont	Muscovite, Maine	Phlogopite, Ontario
SiO <sub>2</sub>	31.8	45.7	40.9
TiO <sub>2</sub>	0.02	0.04	1.28
Al <sub>2</sub> O <sub>3</sub>	15.7	32.2	14.0
Fe <sub>2</sub> O <sub>3</sub>	—	4.4*	0.83
FeO	3.24†	—	1.17
MnO	0.07	0.46	0.03
MgO	33.1	—	24.3
CaO	—	—	0.11
Na <sub>2</sub> O	—	0.54	0.30
K <sub>2</sub> O	0.12	9.78	10.0

Analyst: Max Budd, S. U. N. Y. Binghamton.

\* Total Fe recast as Fe<sub>2</sub>O<sub>3</sub>.

† Total Fe recast as FeO.

partially imbedded in the substrate. Because of the platy and well-crystallized morphology of these minerals we were able to find many such grains, some with surface diameters of  $> 10 \mu\text{m}$  (Figure 2B).

Coarsely crystalline mineral specimens from our collections were used as internal standards. These were coarsely ground and visible contaminants were removed by hand-picking under a stereomicroscope. The standards were then finely ground ( $< 300$  mesh) and split. One split was analyzed using conventional rapid analysis procedures (Table 2) and the second split was prepared for use in the microprobe using the same mounting procedures as for the clay samples. Homogeneity of the standards was determined by making traverses across a large number of grains with the microprobe. Constant counting rates for the major elements (Si, Al, Fe, Mg, and, where appropriate, K) along individual traverses and from grain to grain were our criteria for sample homogeneity.

Chemical compositions were determined using the straight proportionality relationship,

$$\left( \frac{\text{Wt \%}_{\text{(oxide)}}}{\text{Average counts per unit time}} \right)_{\text{sample}} = \left( \frac{\text{Wt \%}_{\text{(oxide)}}}{\text{Average counts per unit time}} \right)_{\text{standard}}$$

A total of five 2-sec counts of chlorite and four 1-sec counts of illite were taken at each location on a single flake; at least two, normally three such locations were counted on each flake. For each mineral analyzed in each sample at least 17 and up to 29 different flakes were counted. Similar counting procedures were used on the standards and counts on the standard were made both before and after each unknown grain was counted. Because the ferrous-ferri ratio cannot be evaluated with our equipment we have arbitrarily assigned the total iron in chlorite as FeO and that in illite as Fe<sub>2</sub>O<sub>3</sub>. This seemed reasonable in light of published analytical data for these minerals (Weaver and Pollard, 1973; Deer, Howie, and Zussman, 1963).

In order to evaluate our mounting procedure, which omitted conventional polishing techniques, we analyzed our muscovite and chlorite standards with the microprobe and used the analyzed phlogopite as



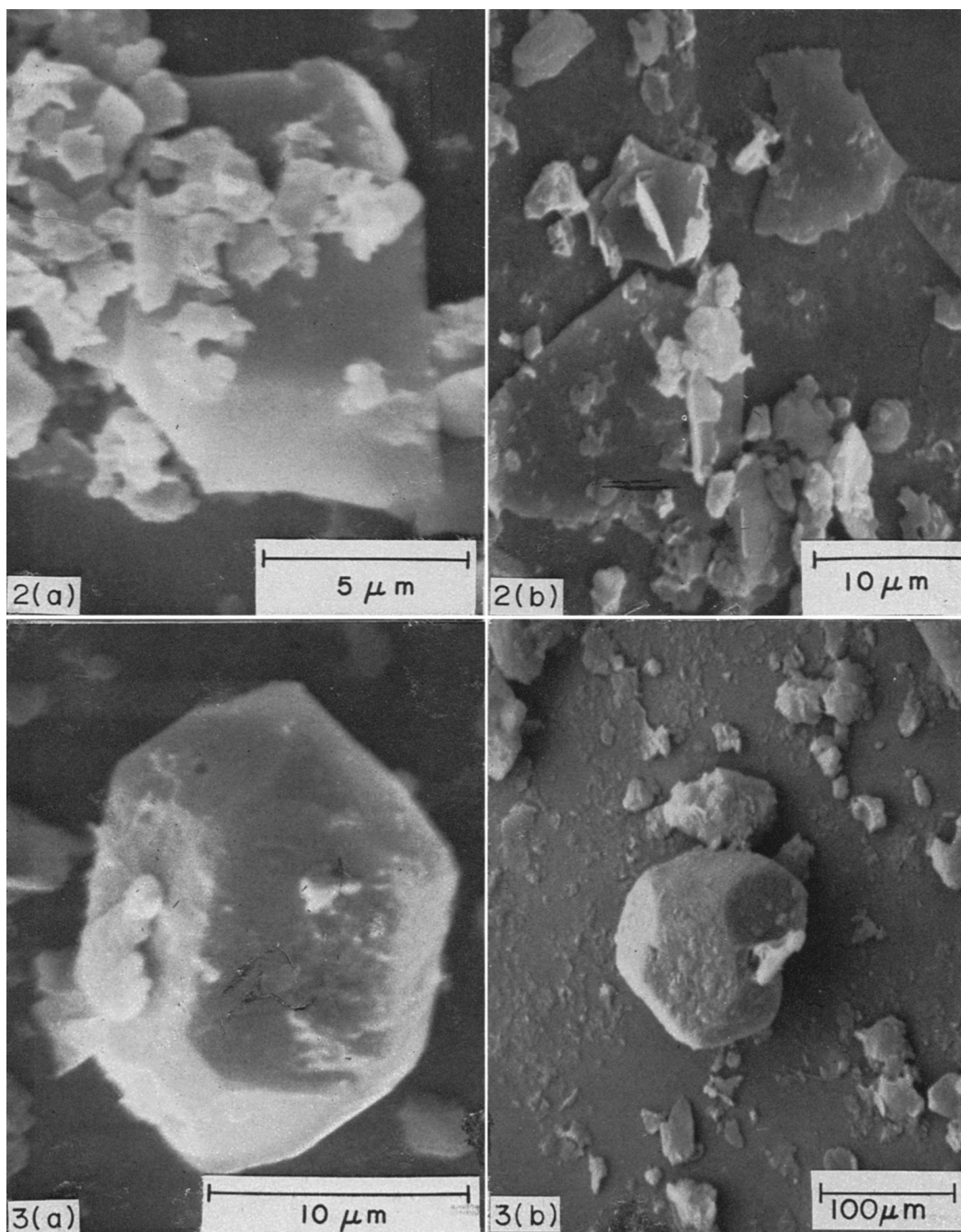


Fig. 2. Scanning electron micrographs of the 2.0–0.5 μm (effective spherical diameter) fraction from the silicate-rich residue in RS-72-5: (a) Large phyllosilicate flake with flat 001 surface and many smaller flakes; (b) Several large phyllosilicate flakes with largest (>15 μm) showing cleavage steps, overgrowths, and a surface contaminated with fine phyllosilicate debris.

Fig. 3. Scanning electron micrograph of the > 2 μm (effective spherical diameter) fraction from the silicate-rich residue in RS-72-5: (a) Small euhedral quartz crystal; (b) relatively large malformed pyritohedron of pyrite.

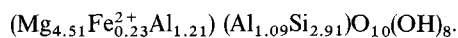
the microprobe (Table 2) standard. We mounted and counted each in the previously described manner and compared the microprobe results for the chlorite and muscovite with the results of their bulk analyses in Table 2. The muscovite was analyzed for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total Fe as  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$ ; the chlorite was analyzed for each of these components except  $\text{K}_2\text{O}$  and reporting total Fe as  $\text{FeO}$ . In no case were the discrepancies greater than 10% of the amount present and only began to approach this great a discrepancy, that is >5% of the amount present, when that particular oxide constituted  $\ll$ 5% of the phase (e.g.  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  in muscovite and  $\text{FeO}$  in chlorite). Based on these observations we are only reporting analytical results for the major elements in each phase.

Our weight percent values for each grain did not total 100 and left remainders of up to 16%. We attribute this to the presence of bound water ( $\text{H}_2\text{O}+$ ) and small amounts of the oxides of minor components ( $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , etc.). When the analytical results were recast to appropriate structural formulas we have assumed an ideal number of  $(\text{OH})$ 's to yield the proper stoichiometries. We were gratified that nearly all our data contained remainders which were only slightly in excess of the amount of bound water required to generate the correct bound-water stoichiometry of the particular phase. The small portion of the remainder which could not be attributed to bound-water most likely represents the cumulative abundances of quantitatively undeterminable minor oxides, analytical error, or, as suggested by Hower and Mowatt (1966), excess water as lenses of trapped water in illite.

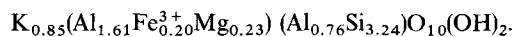
## RESULTS

The chlorite and illite from these seven samples are very well crystallized minerals and show narrow, sharp, well defined diffraction maxima (Figure 1). Microprobe analysis results yield distinctive, but uniform compositions for each mineral throughout the analyzed samples. The mean aggregate chlorite composition, recast as atom proportions in its structural

formula is a Mg-rich clinocllore:



Similarly recast data generate a mean aggregate illite composition of



Results for the individual grains of chlorite within a single sample show limited compositional variation from grain to grain. However, within each illite population there is relatively broad compositional variation among individual grains.

The results of the bromine analyses, ppm Br in halite, are given in Table 1. These values agree closely with Retsof data reported by Dellwig and Evans (1969) from the same salt bed.

## Chlorite

X-ray diffractometer traces from oriented powder mounts of the chlorite-bearing samples are given in Figure 1. The chlorite maxima, although well developed and reasonably sharp as compared with the data from many sedimentary chlorites, are broader than those from metamorphic (greenschist) chlorites. The 001 reflection at  $6.2^\circ 2\theta$  (14.3 Å), in particular, is noticeably broadened. No shifts in spacing are observed after ethylene glycol saturation and heat treatment results only in anticipated sharpening of all basal maxima and greatly enhancing 001 intensity. The relative intensities of the basal spacings and the value of the  $c_0$  dimension (14.32 Å) qualitatively suggest a chlorite with high magnesium, low iron, and relatively low aluminum content (Brindley, 1961).

Results of the microprobe analysis of the four chlorite populations are given in Table 3 as the mean chlorite composition in each analyzed sample. The mean composition and standard deviation were calculated from individual grain analyses. The four mean chlorite compositions show remarkably narrow compositional variations—far narrower than the variation within any single population. The four mean compositions were recast as atom proportions in the chlorite structural formula (Table 3). The six octahedral sites

Table 3. Microprobe analyses of chlorites from the Retsof salt bed

Number of grains	MB-72-2 20	RS-72-5 20	RS-72-18 20	RS-72-20 20
Weight %				
$\text{SiO}_2$	30.7 ± 0.9	30.7 ± 1.1	30.6 ± 1.1	30.2 ± 0.6
$\text{Al}_2\text{O}_3$	20.5 ± 1.1	20.6 ± 0.6	20.2 ± 0.7	20.9 ± 0.5
Fe as FeO	2.9 ± 0.5	2.9 ± 0.2	3.0 ± 0.2	2.9 ± 0.2
MgO	31.2 ± 1.4	31.9 ± 1.1	32.2 ± 0.6	32.0 ± 0.6
Total	85.3	86.1	86.0	86.0
Atom proportions per formula unit (atoms/14 oxygens)				
Tetrahedral				
Si	2.94	2.91	2.91	2.87
Al	1.06	1.09	1.09	1.13
Total	4.00	4.00	4.00	4.00
Octahedral				
Al	1.25	1.21	1.17	1.21
$\text{Fe}^{2+}$	0.23	0.23	0.24	0.23
Mg	4.44	4.50	4.56	4.53
Total	5.92	5.94	5.97	5.97

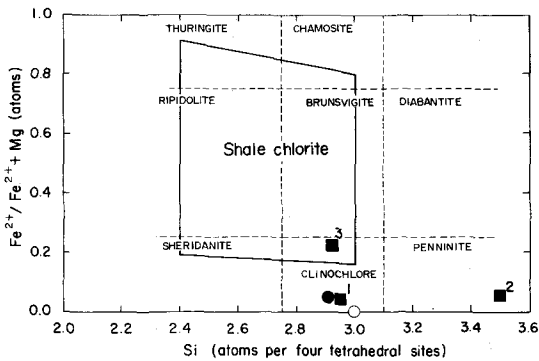


Fig. 4. Compositional classification of the chlorite minerals (Foster, 1962) with heavy boundaries outlining the probable limits of most "shale chlorite" compositions as determined from X-ray diffraction data (Weaver and Pollard, 1973); ○ stoichiometric endmember Mg-clinocllore. Chlorites associated with marine evaporites: ● average of four clinocllore samples from Retsof, N.Y. (this study); ■ chlorites from other marine evaporite localities, (1) clinocllore from the German Zechstein, Königshall-Hindenburg (Braitsch, 1971), (2) penninite from the German Zechstein, (?)Werra (Braitsch, 1971), and (3) clinocllore from an altered melaphyre, Austrian Haselgebirge, Hallstatt (Bodine, 1971).

include the three sites in a trioctahedral layer silicate structure (talc) and the three interlayer (brucite) sites. The chlorites are extremely magnesium-rich and iron-poor ( $Fe/Mg + Fe \cong 0.05$ ), contain relatively low amounts of tetrahedral aluminum ( $Al/Al + Si = 0.27$ ) and have octahedral aluminum to tetrahedral aluminum ratios somewhat greater than unity (1.07–1.08). The four chlorites are high Mg clinocllore

when following the standard compositional classification of chlorites (Figure 4) after Foster (1962). The compositions are compatible with qualitative compositional interpretation of the diffraction data.

Composition of the individual flakes comprising each of the four populations have been recast to atom proportions in the chlorite structural formula and plotted on Figure 5. The points cluster closely around their mean values defining each of the four aggregate compositions. Those very few points which do deviate markedly from their respective clusters have been flagged to permit comparison from one set of compositional variables to the other; the parenthetical values with each of the deviant points are the sum of the octahedral site occupancy which consistently total substantially less than six in the deviant flakes. We believe that the relatively small number of anomalous points, their extreme deviation from other points, and their tendency to depart markedly from trioctahedral chlorite stoichiometry are indicative of either analytical error or the presence of foreign inclusions in these flakes.

*Illite*

The illite diffraction maxima (Figure 1) are sharp, well defined, and only slightly broadened indicating good crystallinity. The 001 reflection (10.0 Å) is partially-to-completely obscured in those specimens which contain abundant talc and only a small proportion of illite (Figure 1). Although saturation with ethylene glycol reveals no apparent mixed-layer character, the slight asymmetry or high angle bulge

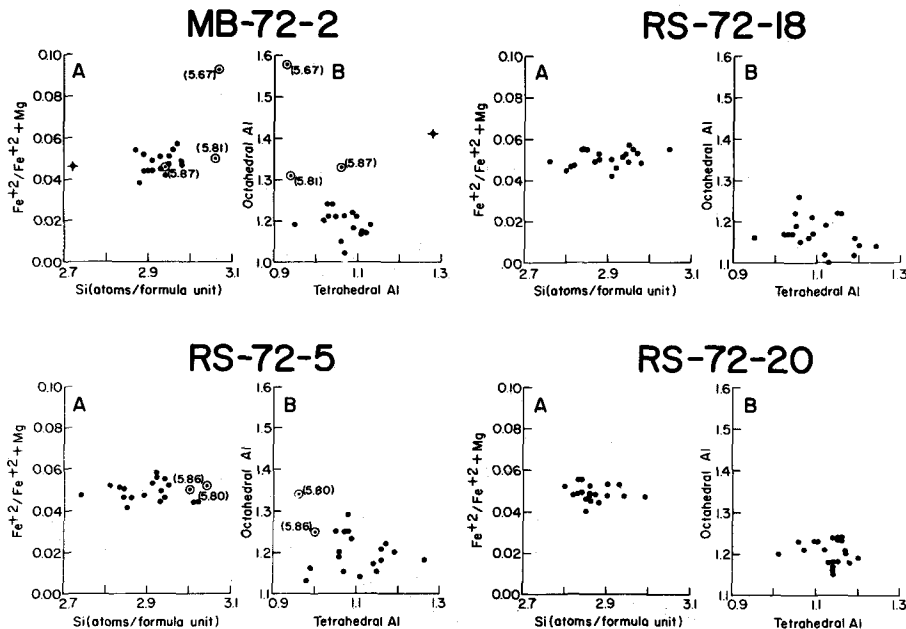


Fig. 5. Compositions of individual chlorite flakes within each of the four analyzed Retsof samples: A. Number of tetrahedral Si atoms per formula unit (Si/four sites) and mole fraction  $Fe^{2+}/(Fe^{2+} + Mg)$  in octahedral sites; B. Number of tetrahedral Al atoms and octahedral Al atoms per formula unit ( $Al^{IV}/four\ sites$  and  $Al^{VI}/six\ sites$ ). Selected data points have been flagged (○ and ●) to permit correlation between A and B; values in parentheses are the anomalously low total octahedral occupancy values per formula unit (atoms/six sites).

Table 4. Microprobe analyses of illites from the Retsof salt bed

Number of grains	MB-72-2 28	RS-72-11 21	RS-72-9C 21	RS-72-15 19	RS-72-20 17
<b>Weight %</b>					
SiO <sub>2</sub>	46.8 ± 2.3	46.5 ± 1.5	47.2 ± 1.6	45.2 ± 1.5	47.5 ± 1.2
TiO <sub>2</sub>	OBS*	OBS	OBS	OBS	OBS
Al <sub>2</sub> O <sub>3</sub>	28.7 ± 2.6	28.8 ± 3.6	29.0 ± 3.3	28.9 ± 3.1	30.0 ± 2.8
Fe as Fe <sub>2</sub> O <sub>3</sub>	3.5 ± 1.6	4.1 ± 2.1	4.6 ± 1.8	3.7 ± 1.5	3.5 ± 1.6
MnO	OBS	OBS	OBS	OBS	OBS
MgO	2.1 ± 0.6	2.2 ± 0.6	2.2 ± 0.7	2.2 ± 0.6	2.4 ± 0.7
CaO	—	—	—	—	—
Na <sub>2</sub> O	OBS	OBS	OBS	OBS	OBS
K <sub>2</sub> O	9.3 ± 0.6	9.6 ± 0.5	9.8 ± 0.4	9.3 ± 0.3	9.8 ± 0.6
Total	90.4	91.2	93.8	89.3	93.2
<b>Atom proportions per formula unit (atoms/11 oxygens)</b>					
<b>Tetrahedral</b>					
Si	3.27	3.24	3.24	3.21	3.23
Al	0.73	0.76	0.76	0.79	0.77
Total	4.00	4.00	4.00	4.00	4.00
<b>Octahedral</b>					
Al	1.63	1.60	1.58	1.63	1.63
Fe <sup>3+</sup>	0.18	0.22	0.24	0.20	0.18
Mg	0.22	0.23	0.23	0.24	0.25
Total	2.03	2.05	2.05	2.07	2.06
<b>Interlayer</b>					
K	0.83	0.85	0.86	0.85	0.86

\* OBS presence detected with the microprobe but low abundance (<1%) precludes quantitative analysis.

of the 10 Å spacing is indicative of up to 10–15% expandable layers (Hower and Mowatt, 1966). The relatively high intensity of the 002 reflection (5.0 Å) suggests that octahedral iron content is low and that the illite is a well-crystallized dioctahedral, aluminum-rich mica-clay.

Microprobe results for illite (Table 4) yield mean compositions which are nearly identical among the

five samples. The mean aggregate sample compositions, when recast to atom proportions in the muscovite structural formula (Table 4) define a clay with relatively high interlayer cation content (0.83–0.86) which is almost exclusively potassium. The octahedral site only slightly exceeds dioctahedral stoichiometry (2.03–2.07) and consists chiefly of aluminum. The tetrahedral aluminum content (0.73–0.79), although

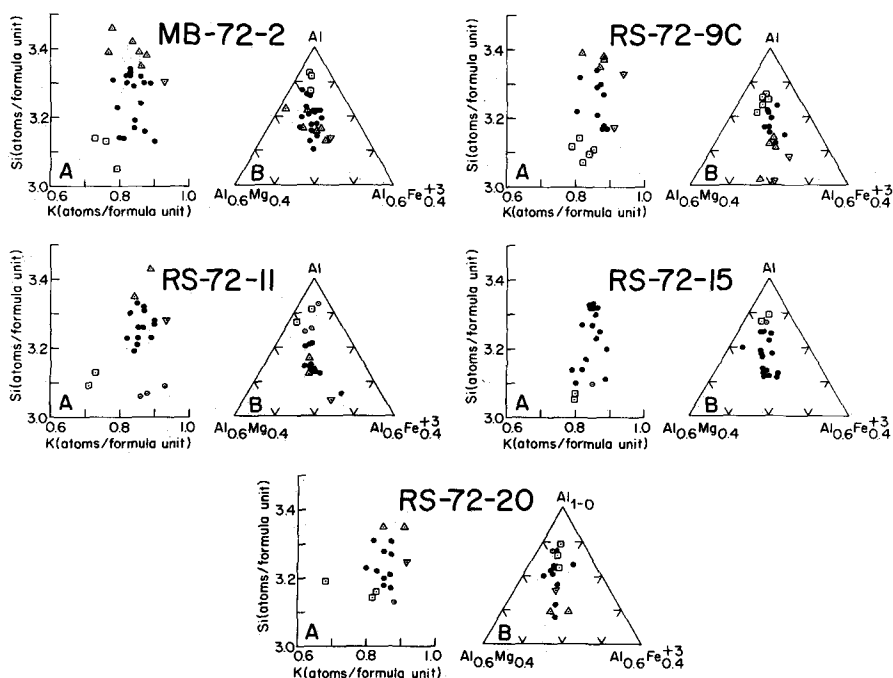


Fig. 6. Compositions of individual illite flakes within each of the five analyzed Retsof samples: A. Number of tetrahedral Si atoms per formula unit (Si/four sites) and number of interlayer K atoms (K/four tetrahedral sites) per formula unit; B. Al–Fe<sup>3+</sup>–Mg proportion in the octahedral layer. Selected points have been flagged (□△▽○) to permit correlation of compositional variation between A and B.



lower than in stoichiometric muscovite, is higher than that found in most analyzed illites (Weaver and Pollard, 1963). The Retsof illites approach sericite in composition.

The compositions of the individual analyzed grains, which have been recast into atom proportions in the muscovite structural formula and plotted on Figure 6, clearly demonstrate the extensive compositional variation among the flakes within each specimen. As observed with the chlorites there are clusters surrounding the specimen's mean illite composition, but the clusters are not nearly as tightly packed and represent smaller proportions of the sample populations. Some anomalous points have been flagged on Figure 6 which permits correlation from one diagram to the other. Because of the number and extent of individual deviations among the illite flakes it becomes difficult to attribute these anomalous compositions to analytical error or the possible presence of inclusions.

#### DISCUSSION

Since we are proposing that the chemistry of the marine hypersaline environment played a dominant role in fixing the composition of these clays we are introducing the term *hyperhalmyrolysis*. *Hyperhalmyrolysis* applies to those mineral reactions which occur in the marine evaporite environment from the time of a mineral's deposition or precipitation in the brine to the time of its burial and isolation from the surface brine environment. This usage conforms to Berner's (1971) use of the term *halmyrolysis* denoting analogous phenomena within the normal marine environment.

Throughout this discussion the terms *hyperhalmyrolysis* and *diagenesis* specify the geologic environment in which the process occurred: phenomena occurring in the surficial marine evaporite environment and those occurring in the succeeding postdepositional environment after burial respectively. We are also considering the silicate fraction as a recognizable subsystem within the total evaporite rock assemblage. Thus, a *metasomatic* process involves compositional alteration of the silicate assemblage as opposed to an *isochemical* process in which the bulk composition of the silicate subsystem remains essentially unchanged. The more general terms, e.g. *alteration*, *authigenesis*, *recrystallization*, denote only the appropriate modification of the silicate subsystem without specifying the presence or absence of bulk compositional change and the geologic environment in which the phenomena occurred.

The bromine content in the halites (Table 1) is similar to values reported by Dellwig and Evans (1969) and further substantiate the primary character of the halite and its origin from an evaporating marine brine (Braitsch and Herrmann, 1963; Holser, 1966). Throughout both profiles there is a slight increase in the bromine content in halite upwards suggesting a slight progressive increase in the salinity of the brine.

#### Chlorite composition and genesis

Our data strongly suggest that the chlorite in the Retsof salt bed is reasonably homogeneous with a composition that does not vary appreciably among the four samples (Table 3) and falls within the Mg-rich region of the clinocllore field (Figure 4). Within each sample individual flake compositions (Figure 5) generate relatively small scatter, and this scatter appears to reflect analytical error or contamination rather than significant compositional variation.

The chlorites from the Retsof salt have distinctive compositions when compared with compositions of chlorite from shales. Weaver and Pollard (1973) define a range of composition for sedimentary chlorites which we have delineated as the "shale chlorite" region in Figure 4. The Retsof chlorites fall well outside of the "shale chlorite" region and plot adjacent to the low-iron extreme of the clinocllore field and close to the low-iron projection of the Si-maximum limit of the "shale chlorite" region. The chemical distinctiveness and uniformity of the Retsof chlorites lead us to the conclusion that the chlorite is authigenic, presumably hyperhalmyrolytic, and not simply accumulation and subsequent diagenetic metasomatism of unreconstituted detrital chlorite. The relatively narrow scatter of individual flake compositions throughout the Retsof salt (Figure 7A) further supports this interpretation.

The Retsof chlorite composition appears to be compatible with halite-saturated marine evaporite brines. Magnesium activity would be approximately an order of magnitude greater than in seawater (Braitsch, 1962) while activities of dissolved aluminum and ferrous iron species would probably not be significantly greater than in seawater. Activities of the ferrous iron species would be buffered by ferrous sulfide equilibria, pH, Eh (Garrels and Christ, 1965), and

Table 5. Atom proportions per formula unit (atoms/14 oxygens) of chlorites from marine hypersaline rocks

	1	2	3	4
Tetrahedral				
Si	2.95	3.5	2.92	2.91
Al	1.05	0.5	1.08	1.09
Total	4.00	4.0	4.00	4.00
Octahedral				
Al	0.85	0.1	1.29	1.21
Ti	—	—	0.04	—
Fe <sup>3+</sup>	0.2	0.4	0.19	—
Fe <sup>2+</sup>	0.2	0.3	0.95	0.23
Mg	4.7	5.2	3.31	4.51
Total	5.95	6.0	5.78	5.95

1. Chlorite ("amesite") in carnallite from the Königshall-Hindenberg mine, Germanv (Zechstein) after Braitsch (1971).

2. Chlorite (pennine) in kieserite-sylvite-halite from (?)Werra, Germany (Zechstein) after Braitsch (1971).

3. Chlorite (clinocllore) from altered basalt tuff in rock salt, Hallstatt, Austria (Haselgebirge) after Bodine (1971).

4. Mean composition of chlorite (clinocllore) from four samples of rock salt, Retsof, N.Y. (Salina Group) from this study.

would be similar to that in many anoxic marine bottom environments; aluminum activities would be determined by the same aluminum hydroxide and Al-bearing silicate mineral equilibria (Helgesen *et al.*, 1969) which operate in seawater. The resulting high  $a_{\text{Mg}^{2+}}/a_{\text{Fe}^{2+}}$  and  $a_{\text{Mg}^{2+}}/a_{\text{Al}^{3+}}$  in the evaporite brine would promote the high Mg/Fe and Mg/Al values observed in the Retsof chlorites, and the latter ratio would, in turn, require high Si/Al in the chlorite in order to maintain charge balance within the chlorite structural formula.

Chlorite compositions from three other marine hypersaline occurrences (Table 5) also have been plotted on Figure 4 and, in general, comply with the same compositional restrictions. With one exception (Hallstatt) these chlorites also fall outside the "shale chlorite" region of Figure 4 and each lies close to, or in one case (Werra), well beyond the Mg-rich projection of the Si-maximum boundary of the "shale chlorite" region.

The Königshall-Hindenberg chlorite (Table 5, column 1 and Figure 4, no. 1) occurs in a canallite-bearing primary evaporite assemblage (Braitsch, 1971) and differs from the Retsof chlorite only by having slightly lower octahedral Al and correspondingly greater Mg content. These differences may reflect its origin in brines with the appreciably higher Mg activities associated with the carnallite and magnesium sulfate salt crystallization segment of progressive evaporation of sea water.

The Werra chlorite (Table 5, column 2 and Figure 4, no. 2) occurs in diagenetically recrystallized (metamorphosed) potash salt assemblage with abundant sylvite; the chlorite (Braitsch, 1971) contains substantially more tetrahedral Si and less Al, and somewhat more iron, principally as  $\text{Fe}^{3+}$ , but practically no Al in the octahedral sites when compared to the Retsof

chlorite. These differences may reflect exposure to diagenetic fluids at elevated temperatures accompanying recrystallization and metasomatism of the primary salt assemblage; increased Eh may have promoted the  $\text{Fe}^{3+}$  substitution for Al and higher temperature may allow the Si-maximum boundary to progress well into the penninite field.

The Hallstatt chlorite (Table 5, column 3 and Figure 4, no. 3) occurs as an alteration product of basaltic tuffs which were deposited in a halite-producing marine evaporite brine (Reinold, 1965 and Bodine, 1971); the chlorite is somewhat richer in  $\text{Fe}^{2+}$  and correspondingly depleted in Mg than the Retsof chlorite, but in other respects is essentially the same. Its occurrence as an alteration product of a pyrite-free but ferrous iron-rich rock undergoing recrystallization in an Mg-rich brine may well account for this variation but yet generate a composition close to the Si-maximum boundary of the "shale chlorite" region.

#### Illite composition and genesis

The illite fractions in each of the five analyzed specimens from the Retsof salt bed have similar mean compositions (Table 4); however, unlike the chlorite compositions, the individual flakes within each sample exhibit extensive compositional variation (Figure 6) and generate relatively large standard deviations for each mean composition (Table 4). When histograms relating selected compositional variables to cumulative grain populations of illite and chlorite are compared inhomogeneities in the illite population become readily apparent (Figure 7).

Rather than attribute the compositional variation among the illite flakes to analytical error or the presence of foreign inclusions, which becomes exceedingly difficult in light of the narrow scatter of the chlorite compositions (Figure 7), we conclude that the data re-

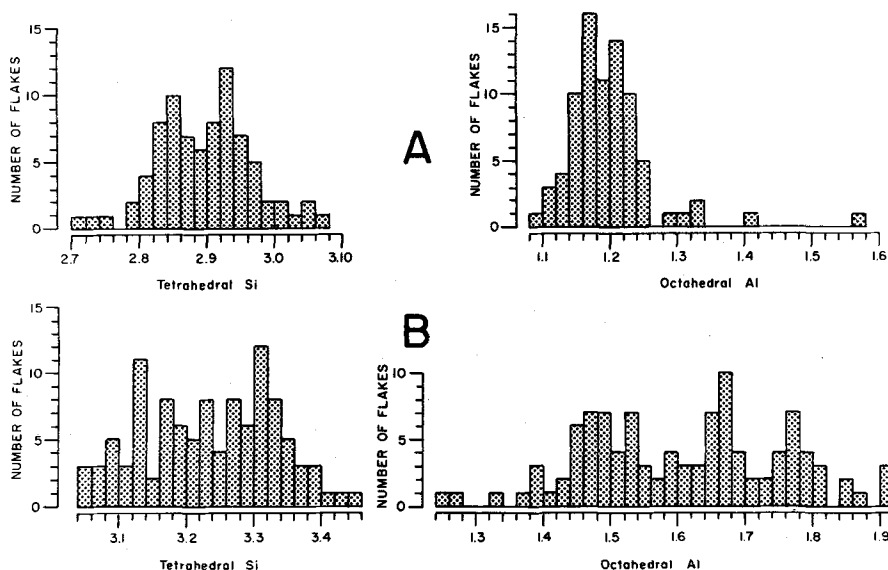


Fig. 7. Histograms of the distribution of the Si content in tetrahedral sites ( $\text{Si}/\text{four tetrahedral sites}$ ) and Al content in octahedral sites ( $\text{Al}^{\text{VI}}/\text{two or six octahedral sites}$ ) in the individual analyzed Retsof clay flakes: A. Chlorite (80 flakes); B. Illite (106 flakes).

Table 6. Atom proportions per formula unit (atoms/11 oxygens) in arbitrarily defined compositional groups of the Retsof illite

	1	2	3	4	5
Tetrahedral					
Si	3.26	3.10	3.12	3.28	3.41
Al	0.74	0.90	0.88	0.71	0.63
Total	4.00	4.00	4.00	4.00	4.00
Octahedral					
Al	1.61	1.74	1.78	1.43	1.52
Fe <sup>3+</sup>	0.20	0.15	0.13	0.35	0.20
Mg	0.24	0.18	0.17	0.24	0.30
Total	2.05	2.07	2.08	2.02	2.02
Interlayer					
K	0.85	0.87	0.77	0.89	0.83
Number of samples	5	5	5	5	3
Number of flakes	57	9	17	15	7

1. Hypersaline illite
2. Muscovitic illite
3. Stripped muscovitic illite
4. Ferromagnesian illite
5. Siliceous illite

flect real compositional inhomogeneity within each illite population. Although the compositional relations in the illite population are far too widely and diffusely scattered to define discrete compositional varieties of illite we have found it worthwhile to subdivide the illite fraction into five ill-defined compositional groups, each of which includes considerable compositional variation. These groups are shown in Figure 8 and hereinafter are referred to as *hypersaline illite*, *muscovitic illite*, *stripped muscovitic illite*, *ferromagnesian illite*, and *siliceous illite*. These terms are purely descriptive and have no validity other than specifying compositional variation within the Retsof illite population. The mean composition of each group, expressed in terms of atom proportions in the muscovite structure, is given in Table 6. The groups are defined on the basis of the following general relationships: *hypersaline illite*, the dominant composition with a relatively sericitic chemistry; *muscovitic illite*, an illite with high tetrahedral and octahedral Al content, high K, and relatively low Fe and Mg, which most closely approaches the muscovite end member stoichiometry; *stripped muscovitic illite*, similar to the

*muscovitic illite* but with significantly reduced K content; *ferromagnesian illite*, high Fe and Mg content with Fe > Mg, and generally high K content; and *siliceous illite*, relatively low tetrahedral Al content with correspondingly high Si.

On Figure 9 we have plotted the mean illite compositions of each of the five Retsof samples (Table 4), the mean compositions and compositional limits of each of the five arbitrary compositional groups (Table 6 and Figure 8), and the 29 illite and eight sericite analyses compiled by Weaver and Pollard (1973). Since the Retsof analyses do not include water and the minor oxides and since total Fe is arbitrarily assigned to Fe<sub>2</sub>O<sub>3</sub> we have recalculated these previously published analyses to yield atom proportions in the anhydrous muscovite formula on the basis of 11 oxygen atoms per formula unit after deleting the minor oxide constituents and assigning total Fe and Fe<sub>2</sub>O<sub>3</sub>.

The Retsof illites are compositionally distinct from most illites compiled by Weaver and Pollard (1973). The most striking feature is the more sericitic character of the Retsof illites: a greater proportion of occu-

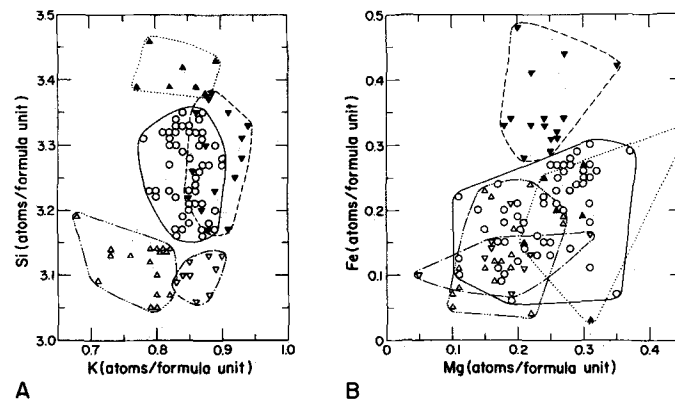


Fig. 8. Compositions of the five arbitrarily defined compositional groups of analyzed Retsof illite flakes (106 flakes): ○ *hypersaline illite* (58 flakes); ▽ *muscovitic illite* (9 flakes); △ *stripped muscovitic illite* (17 flakes); ▾ *ferromagnesian illite* (15 flakes); ▲ *siliceous illite* (7 flakes). A. Number of Si atoms (Si/four tetrahedral sites) and interlayer K atoms per formula unit; B. Number of Fe<sup>3+</sup> atoms (Fe<sup>3+</sup>/two octahedral sites) and Mg atoms (Mg/two octahedral sites) per formula unit.

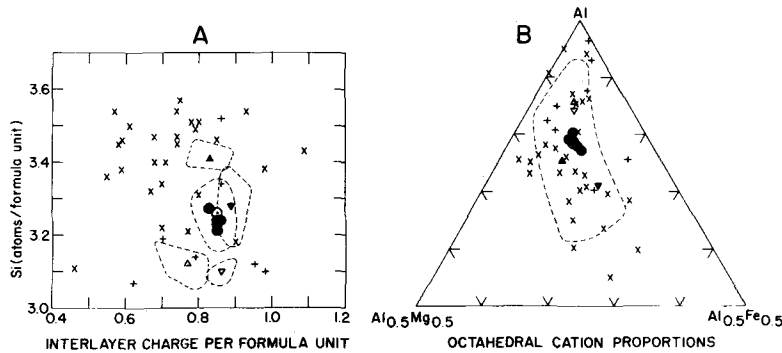


Fig. 9. Illite compositions. Published analyses from Weaver and Pollard (1973):  $\times$  illite;  $+$  sericite. Retsof illites: mean of total specimen population of each of the five samples (Fig. 6); mean of each arbitrarily defined compositional group from the total analyzed flake population— $\circ$  hypersaline illite,  $\nabla$  muscovitic illite,  $\triangle$  stripped muscovitic illite,  $\blacktriangledown$  ferromagnesian illite,  $\blacktriangle$  siliceous illite. A. Number of Si atoms (Si/four tetrahedral sites) and total interlayer cation charge per formula unit; dashed boundaries are compositional limits of each arbitrarily defined compositional group. B. Al-Fe<sup>3+</sup>-Mg atom proportions within the octahedral layer; dashed boundary is compositional limit for total Retsof illite flake population.

pied interlayer cation sites, an overwhelming proportion of K to other interlayer cations, greater tetrahedral Al content, and, to some extent, relatively high Al/Fe + Mg proportions in the octahedral layer (Figure 9). We attribute these features to metasomatic recrystallization of detrital micaceous clays and micas in which there is at least a partial approach toward equilibrium between illite and the hypersaline brine.

The relatively high interlayer cation site occupancy in the Retsof illite may reflect the brine's high  $a_{K^+}/a_{H^+}$  (Hemley, 1958), and the exclusivity of K in these sites can be attributed to somewhat increased  $a_{K^+}/a_{Na^+}$  and substantially increased  $a_{K^+}/a_{Ca^{2+}}$  in halite-producing brines (Braitsch, 1971) when contrasted with normal seawater and most terrestrial water. Formula unit charge balance is then maintained by concomitant decrease of tetrahedral Si/Al. The resultant composition is similar to those of many analyzed sericites (Weaver and Pollard, 1973) as shown on Figure 9.

Yet if the Retsof illites did develop their sericitic composition through reaction of micaceous detritus with the hypersaline brine and reach or closely approach equilibrium, only one homogeneous sericitic illite composition would be expected. We propose that the wide compositional variation among the individual Retsof illite flakes indicates that complete equilibrium was not achieved. The variety of mica and mica-clay detrital particles, representing provenance and weathering history at the source, underwent limited metasomatism in the brine and only approached equilibrium. This resulted in a heterogeneous sericitic illite assemblage in which each variety of micaceous detritus retained modified relicts of its earlier composition.

#### *Hyperhalmyrolysis and diagenesis*

Our interpretation of the illite and chlorite compositions have thus far been restricted to a consideration of mineral reactions involving chemical exchange with primary marine evaporite brines—hyperhalmyrolysis.

We also have suggested that the high degree of crystallinity displayed by these minerals reflect post-depositional recrystallization of poorly crystallized clays as some function of depth of burial, temperature, and time—diagenesis. We must then also consider the possibility that the chemistry of these minerals and that of the bulk silicate assemblage were imposed diagenetically through reaction with migrating pore fluids—pore fluids whose compositions may well have been drastically different from those of the primary marine evaporite brines. We believe that no such diagenetic metasomatism has occurred and that the bulk silicate assemblages have remained essentially isochemical since shortly after initial burial.

Evaporite rocks are dense with a tightly interlocking fabric. This results in their characteristic low permeability and generally low porosity. The small amount of static pore fluid would contain an almost insignificant amount of dissolved species (except Na) when compared with the amounts of such components in the silicate fraction. The abundance of the Mg-rich clinocllore along with talc and occasional serpentine creates a highly anomalous chemistry for a pervasive but highly disseminated pelitic assemblage in an evaporite host and bespeaks of reasonably effective isolation from normal pore fluids. In the Retsof salt bed the primary texture and composition of the halite precludes diagenetic halite dissolution and recrystallization; this feature effectively eliminates the likelihood of extensive pore-fluid migration. Only within the primary evaporite environment can we visualize an infinite brine reservoir with which chemical exchange can proceed pervasively to generate an assemblage with such a unique bulk chemistry.

At the same time we acknowledge that some local chemical exchange accompanying recrystallization undoubtedly occurred between various minerals during diagenesis. Thus, for example, one or more poorly crystallized Mg-rich clay species with excess silica which had crystallized metastably during hyperhal-

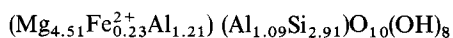


myrolysis (e.g. poorly-crystallized "protochlorite", randomly interlayered chlorite-smectite, or a trioctahedral vermiculitic or smectitic mineral, etc.) might have formed in the evaporite environment then re-crystallized diagenetically into a well-crystallized and stable chlorite-quartz assemblage. In this manner some local exchange could have occurred between solid phases during diagenesis but yet the bulk chemistry of the silicate assemblage, which had been imposed during hyperhalmyrolysis, would have been preserved to yield the distinctive compositional varieties of common rock-forming sedimentary minerals which we have described. Such isochemical recrystallization is analogous to that observed in the burial diagenesis of normal marine argillaceous sediments in the Gulf Coast (Hower *et al.*, 1976).

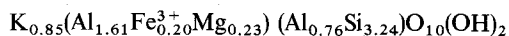
#### Summary of conclusions

1. Analysis of individual clay flakes with the electron microprobe appears to yield valid results for the major constituents.

2. Chlorite flakes in the Retsof salt bed have a reasonably homogeneous composition throughout the four analyzed samples and generate a mean aggregate high-Mg clinocllore composition of



3. Illite, on the other hand, displays wide compositional variation among individual flakes within each sample. Yet, the mean composition of the illite fraction among five samples is nearly constant and generates a mean aggregate composition of



4. The Retsof chlorite is compositionally distinct from normal shale chlorites but appears to be compositionally compatible with marine evaporite brines suggesting a metasomatic hyperhalmyrolytic origin probably followed by moderate to extensive isochemical recrystallization during diagenesis.

5. Illite is substantially more sericitic than most normal shale illites and is compositionally compatible with and suggestive of some metasomatic recrystallization in the evaporite environment. The wide compositional variation among individual flakes may reflect an origin from several detrital micaceous minerals with each having generated a somewhat distinctive illite composition.

6. The dominant diagenetic effect appears to be structural ordering and essentially isochemical recrystallization. It appears unlikely that significant metasomatism of the bulk silicate assemblage could have occurred during diagenesis.

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