UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Notes on the Clay Mineralogy of the Retsof Salt Bed, International Salt Company Mine, Retsof, New York

by

Marc W. Bodine, Jr.[1]

Open-File Report 83-718

[1]U.S. Geological Survey
Box 25046, Mail Stop 939
Denver Federal Center
Denver, Colorado 80225

1983

CONTENTS

ILLUSTRATIONS

TABLE

Notes on the Clay Mineralogy of the Retsof Salt Bed, International Salt Company Mine, Retsof, New York

by

Marc W. Bodine, Jr.
U.S. Geological Survey
Box 25046, Denver, Colorado 80225

INTRODUCTION

This report reviews the unusual mineralogy and chemical composition of the clay-mineral assemblages in the salt mined at the International Salt Company's operation at Retsof, New York, and summarizes the evidence for their authigenic origin. Interaction between evaporite brines and aluminous siliciclastic detritus in the depositional and subsequent diagenetic environments resulted in pervasive magnesium metasomatism and clay-mineral recrystallization. More complete accounts of these relations are given in Bodine and Standaert (1977) and Bodine (*in press*).

The International Salt Company mine, commonly called the Retsof mine, is located along the northwestern margin of the Appalachian Basin at the village of Retsof (York Township, Livingston County) in western New York State, about 50 mi east of Buffalo (fig. 1). The mine is the largest underground salt mine in the free world with an 1,152-foot deep production shaft, and workings covering an area of approximately 4,900 acres with nearly 100,000,000 tons of rock having been removed since production began in 1895.

GEOLOGIC SETTING

Salt production at Retsof is from a single 3- to 4-m-thick halite bed, the Retsof salt bed, at the top of the middle member of the Vernon Shale. The Vernon Shale is the basal unit of the Upper Silurian (Cayugan) Salina Group in New York and northwestern Pennsylvania (fig. 2). Overlying the Vernon Shale are the Syracuse Formation, Camillus Shale, and Bertie Limestone, which constitute the Salina Group in the Retsof area. The Salina Group overlies the Silurian Lockport Dolomite (Niagaran) and, in turn, is overlain by the Devonian Onandaga Limestone. Evaporative concentration during deposition of the Salina Group salts in western New York State proceeded no further than halite precipitation; dolomite, anhydrite, and abundant halite are common, but soluble potash and magnesium salts are absent.

Sedimentologic features that characterize the Retsof salt bed have been interpreted by Dellwig and Evans (1969) as indicative of salt deposition in shallow water that periodically was above wave base. Cross-stratified salt beds, diffuse bedding and banding, numerous isolated rounded "shale ball" inclusions in the salt, and pervasive anhydrite admixed with halite (rather than sharp anhydrite banding so common in salts deposited in deeper water environments to the west) prompted their conclusion that considerable remixing of soft salt "mush" occurred contemporaneous with salt deposition.

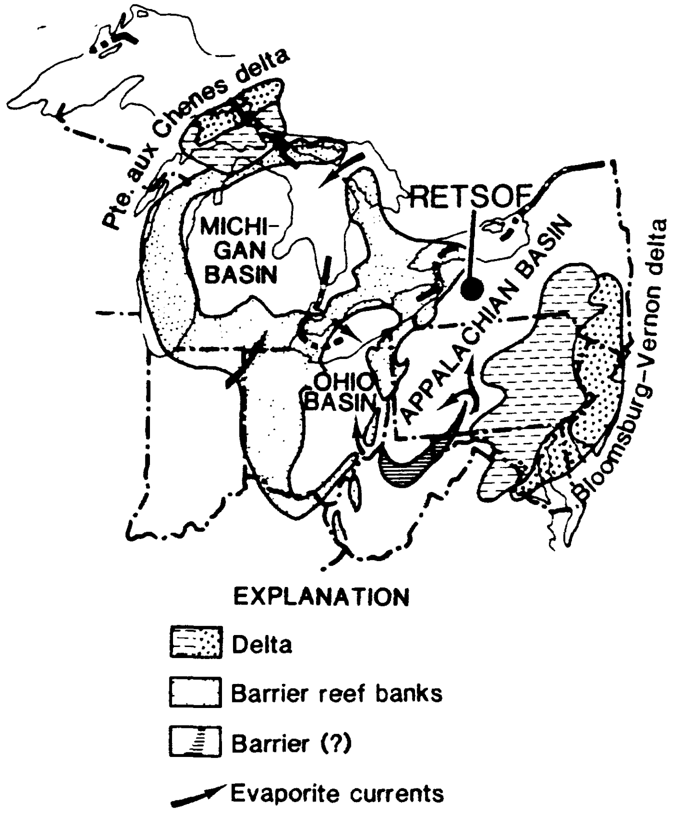

Figure 1.--Location map of the International Salt Company mine at Retsof, New York, with reconstruction of Cayugan paleogeography showing suggested Niagaran reef banks, deltas, and barriers (Alling and Briggs, 1961).

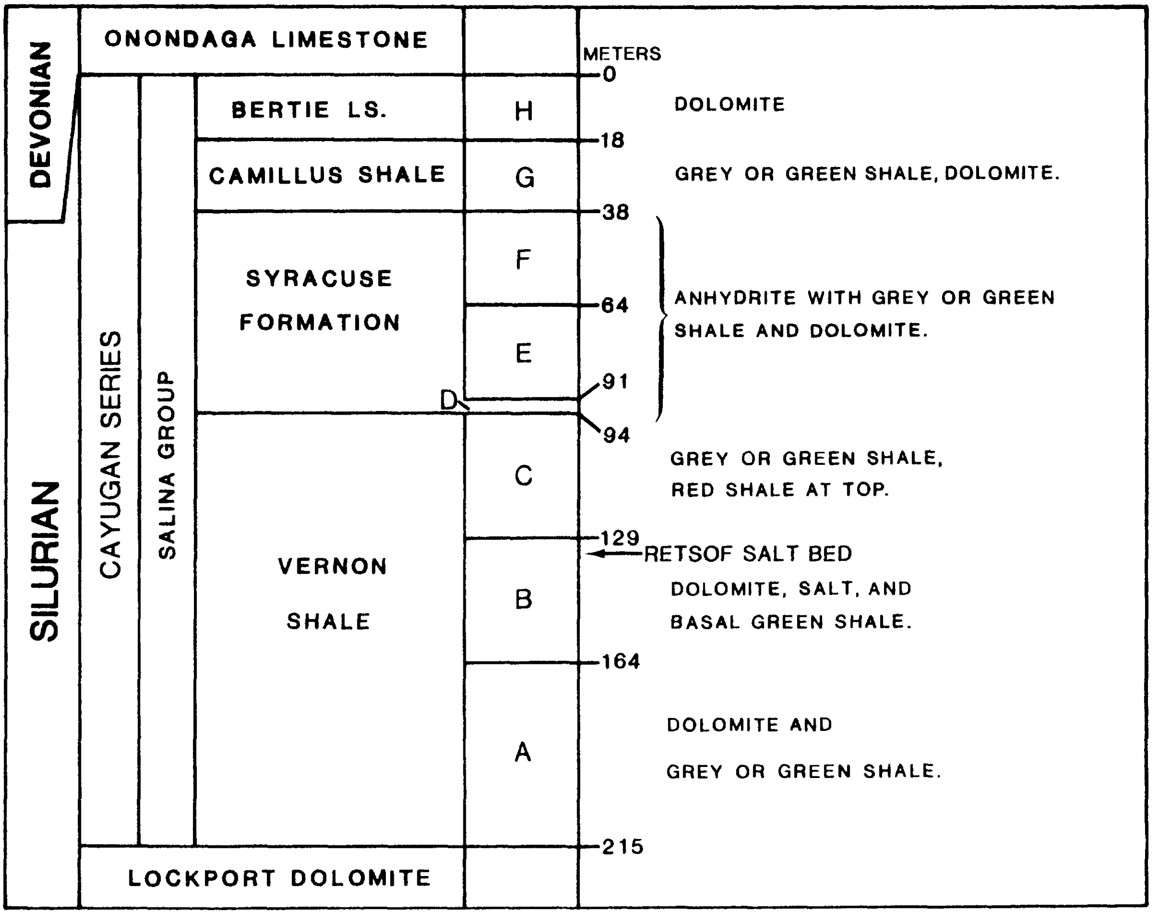

Figure 2.--Generalized stratigraphic column of Cayugan rocks from the MacDonald No.1 drill hole, York Township, Livingston County, New York, near the Retsof mine; lettered intervals signify correlation with the standard Michigan Basin section (Rickard, 1969).

Salt beds in the Vernon Shale thin rapidly and pinch out to the east with a parallel coarsening and thickening of the clastic beds. The unit grades into the deltaic beds of the Bloomsburg Formation in central and eastern Pennsylvania (fig. 1). To the west, the Retsof salt bed has been traced in the subsurface through northwestern Pennsylvania, northern Ohio, and across the Chatham sag into the Michigan Basin (Rickard, 1969), and correlates with the standard Michigan Basin section (fig. 2). General agreement exists (Alling and Briggs, 1961; Rickard, 1969) that the principal source of detritus in the Vernon Shale lay far to the east in uplands on the eastern margin of the Appalachian Basin (fig. 1); siliceous detritus in the Retsof area is fine-grained, well-weathered material that had a lengthy and complex transport history.

Other than dehydration of primary gypsum to anhydrite, little indication exists of salt diagenesis, recrystallization, or metasomatism. Bromine contents of halites from Retsof (Dellwig and Evans, 1969; Bodine, *in press*) are characteristic of a primary precipitate.

CLAY-MINERAL ASSEMBLAGES

Clay minerals and associated silicates in the Retsof salt bed occur as pervasive disseminations; diffuse streaks or bands reflecting bedding in the rock salt; and, with anhydrite and dolomite, in discrete "shale ball" inclusions in the rock salt. Clay minerals consist of illite, chlorite (clinochlore), talc, and serpentine; quartz, potash feldspar, pyrite, and minor quantities of iron oxides are associated with the clays.

Illite and chlorite are the most abundant clay minerals and occur in all samples. Microprobe analysis (Bodine and Standaert, 1977) of 106 flakes of illite from five samples yields an average structural formula of

$$K_{0.85}(Al_{1.61}Fe^{3+}_{0.20}Mg_{0.23})(Al_{0.76}Si_{3.24})O_{10}(OH)_2.$$

The illite has unusually high interlayer charge while retaining the characteristic aluminum deficiency in tetrahedral sites. Analysis of 80 flakes of chlorite from four samples yields an average structural formula of

$$(Mg_{4.51}Fe^{2+}_{0.23}Al_{1.21})(Al_{1.09}Si_{2.91})O_{10}(OH)_8$$

or a high-magnesium clinochlore. Both chlorite and illite are well crystallized as evidenced by the extraordinarily sharp and symmetrical diffraction maxima (figs. 3 and 4).

Talc occurs in most samples although generally not as abundantly as either illite or chlorite. In some samples talc is the dominant clay. It is least abundant and occasionally absent in the "shale ball" inclusions and generally most abundant in serpentine-bearing assemblages. Talc is typically well crystallized and yields sharp diagnostic reflections (fig. 3).

Serpentine is not common; it was observed as disseminated flakes in only four of the salt samples near the base of the Retsof salt bed. The bromine content in halite increases from 75-85 ppm at the base of the bed to 107 ppm at the top (Bodine, *in press*); the four serpentine-bearing assemblages are in halites with <84 ppm bromine. Serpentine appears to be restricted to salts that precipitated during or shortly after halite saturation was reached in the evaporite progression. The well-crystallized character of the clays permits

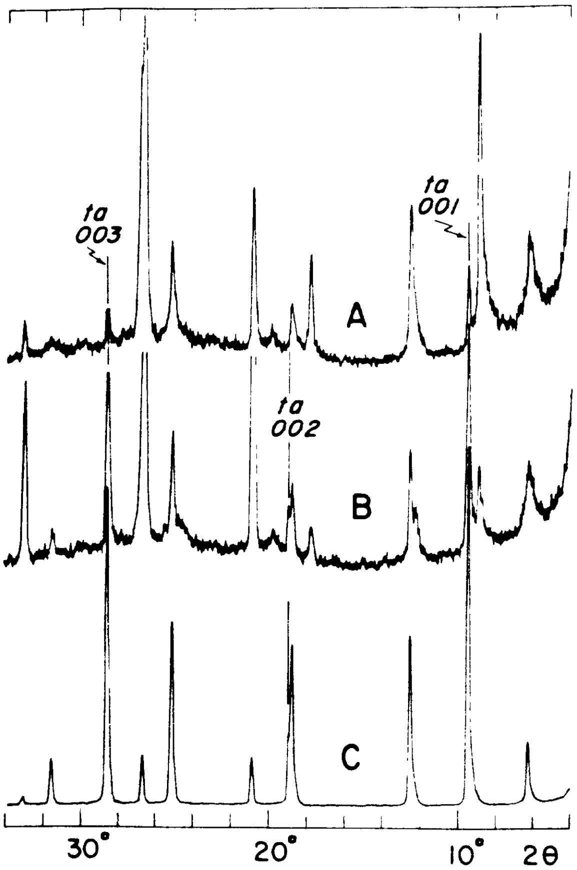

Figure 3.--X-ray (CuK_α) diffractometer traces from sedimented mounts illustrating the variable abundance of talc (ta) throughout the insoluble residues of the Retsof salt bed: A. RS-72-3 (<2µm) with substantial quartz and illite, moderate chlorite, and minor talc and pyrite (table 1, no. 2); B. RS-72-18 (<2µm) with quartz dominant, substantial talc and pyrite, moderate illite and chlorite, and minor serpentine; and C. RS-72-5 (<2µm) with talc dominant, substantial chlorite, minor quartz and pyrite, and barely detectable illite (table 1, no. 3).

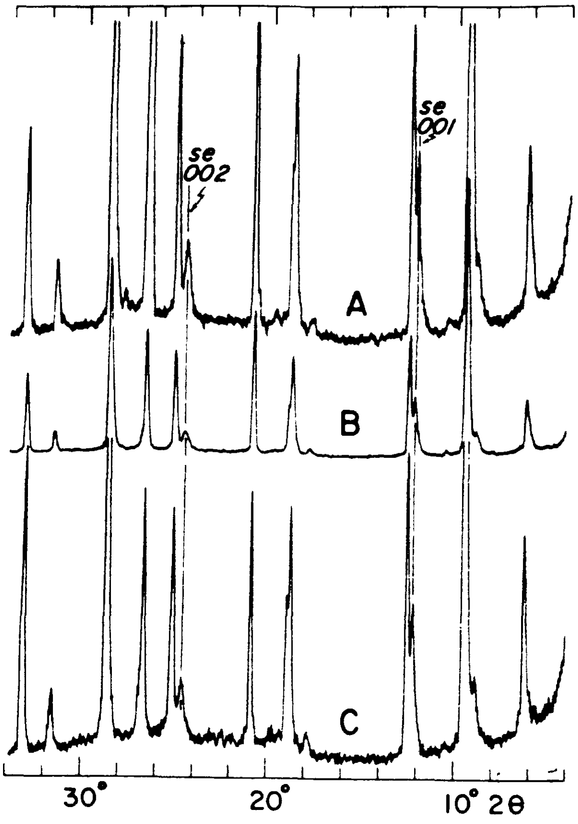

Figure 4.--X-ray (CuK_α) diffractometer traces from sedimented mounts of three serpentine-bearing, clay-size (<2μm), insoluble residues with serpentine (se) maxima forming doublets with even-numbered 001 chlorite maxima: A. RS-72-11 (table 1, no. 5); B. RS-72-12 (table 1, no. 7); and C. RS-72-16. Talc, quartz, illite, and pyrite also present in each sample.

unequivocal identification of serpentine. In the serpentine-bearing assemblage, each even-numbered 001 reflection of the more abundant chlorite appears as a well-defined doublet; the high-angle maximum of the doublet is the chlorite peak, and the low-angle maximum is the serpentine peak (fig. 4).

Quartz is present in most samples and characteristically occurs as well developed doubly terminated euhedra. Potash feldspar is also common, but not as abundant as quartz, and is characteristically euhedral. Pyrite occurs both as small individual euhedral pyritohedrons and as equally small polycrystalline spheroidal framboids. The three minerals are always fine grained--less than 50 µm in diameter and commonly smaller.

Chemical compositions of the clay-rich insoluble residues from samples of the Retsof salt bed are given in table 1; all analyses except analysis 1 were determined on the <2.0-µm fraction. The low calcium, sodium, and aluminum contents and the high magnesium and potassium contents in these assemblages are compatible with the mineralogy. Those samples with abundant talc (nos. 3, 5, and 7) and some serpentine (nos. 5 and 7) are extremely rich in magnesium and depleted in aluminum. Much of the iron in these samples occurs in pyrite as indicated by the sulfur content.

DISCUSSION

Except for illite, all clay minerals in the Retsof salt bed are trioctahedral. These clay-mineral assemblages differ distinctly from the dominance of dioctahedral clays characterizing clay-mineral assemblages in most continental and normal marine sediments. Furthermore, chlorite in the Retsof salt has an unusually high magnesium content and a correspondingly low iron content in contrast with the more ferrugenous character typical of most sedimentary chlorites (Weaver and Pollard, 1973). The common, sometimes abundant occurrence of talc, and the less common but distinctive occurrence of serpentine are also unusual. Similar mineralogic features characterize the clays in several marine evaporite successions in North America (Bodine, 1978; Bodine and Rueger, in press) and Europe (Füchtbauer and Goldschmidt, 1959; Echle, 1961; Dreizler, 1962; Lippmann and Savascin, 1969).

Chemical compositions of clay-mineral fractions are equally distinctive. Molar proportions in clay-rich residues from three North American evaporite deposits, including those from table 1, are plotted on the $KAlO_2$-Al_2O_3-MgO triangle (fig. 5A) and form a well defined compositional belt along the aluminum-poor side of the muscovite-clinochlore reference join; a nearly identical belt is generated by data for European salt clays (fig. 5B). For comparison molar proportions of average shales and of selected clay-mineral assemblages in sedimentary rocks are also plotted on figure 5B; the proximity of average shale compositions to the muscovite-clinochlore join is due, in part, to magnesium in dolomite and potassium in detrital/authigenic feldspar that contribute to the whole rock composition. The more aluminous character of normal sedimentary clay-mineral assemblages is apparent.

The consistent uniqueness of the mineralogic and chemical characteristics of clay-mineral assemblages in marine evaporite lithologies, coupled with their apparent chemical compatability with the succession of marine brine compositions (Stewart, 1963), strongly suggests that brines played the dominant role in the formation of the clay-mineral assemblages. Normal

Table 1.--Compositions (wt. %) of insoluble residues from the Retsof salt bed

[Analyst: M. Budd]

	1	2	3	4	5	6	7	8	9
SiO_2	55.9	56.1	46.7	55.6	45.4	64.2	46.8	64.8	60.4
TiO_2	0.66	0.86	0.26	0.84	0.43	0.79	0.35	0.81	0.81
Al_2O_3	17.32	15.91	7.97	10.89	6.56	13.37	7.48	13.21	14.30
Fe_2O_3*	5.75	6.04	6.84	9.05	12.18	4.75	11.16	4.84	5.29
MnO	0.07	0.06	0.05	0.05	0.05	0.08	0.08	0.05	0.07
MgO	4.32	6.06	21.4	4.30	15.6	5.33	14.4	4.00	5.67
CaO	0.12	0.17	0.12	0.21	0.32	0.14	0.40	0.50	0.14
Na_2O	0.20	0.51	0.18	0.48	0.34	0.22	0.31	0.16	0.30
K_2O	6.66	3.77	0.45	2.50	0.89	2.79	1.25	3.70	3.82
P_2O_5	0.05	0.06	0.03	0.06	0.05	0.10	0.06	0.12	0.05
S	1.87	1.30	3.13	4.34	6.73	1.25	5.87	0.78	1.10
Total	92.9	90.9	87.1	88.3	88.6	93.0	88.2	93.1	92.0

1. MB-72-2 (whole residue); 2. RS-72-3 (<2μm); 3. RS-72-5 (<2μm); 4. RS-72-9 (<2μm); 5. RS-72-11 (<2μm); 6. RS-72-11 (<2μm fraction of a 4 cm "shale ball" inclusion); 7. RS-72-12 (<2μm); 8. RS-72-15 (<2μm); 9. RS-72-20 (<2μm).

*Total Fe as Fe_2O_3

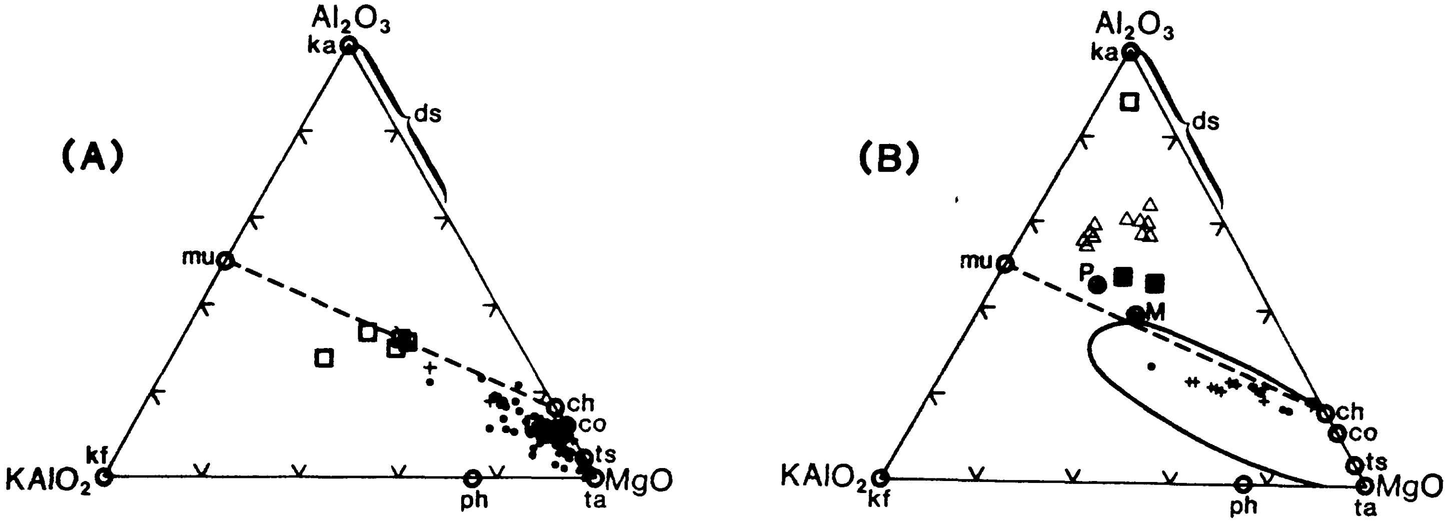

Figure 5.--Molar proportions in clay-size residues plotted on the Al_2O_3-$KAlO_2$-MgO Ternary projection of the Al_2O_3-$KAlO_2$-$NaAlO_2$-MgO-SiO_2-H_2O system. Abbreviations for idealized mineral compositions: ch - chlorite (clinochlore); co - corrensite; ds - dioctahedral smectite (montmorillonite-beidellite series); ka - kaolinite and pyrophyllite; kf - potash feldspar; mu - muscovite; ph - phlogopite; ta - talc, serpentine, and stevensite; ts - trioctahedral smectite (saponite). The dashed muscovite-clinochlore join shown for reference. A. Residues from Paleozoic North American marine evaporites: Salado and uppermost Castile Formations, Eddy County, New Mexico (solid circles); Paradox Member of the Hermosa Formation, San Juan County, Utah (crosses); and Retsof salt bed (table 1), Livingston County, New York (open squares). B. Residues from European marine evaporites: Zechstein Grauen Salzton (Niemann, 1960) near Göttingen, West Germany (crosses); and carbonate strata from the Keuper (Echle, 1961) near Göttingen (solid circles). Average whole-rock shale compositions (Pettijohn, 1975): Paleozoic (P) and Mesozoic (M). Clay-size insoluble residues from normal marine and continental strata: paleosol in lowermost Molas Formation (open square) and marine shales from the Molas Formation (solid squares) from San Juan County, Utah (Bodine and Rueger, *in press*); and Tertiary shales (Hower and others, 1976) from the Gulf Coast (open triangles). Solid boundary encloses compositions of residues plotted in A.

aluminous detritus, rich in dioctahedral clay minerals, interacted with the magnesium-rich brines upon deposition in the marine evaporite environment and, with subsequent burial, continued to interact with connate pore brines. The major results of these interactions were, except for illite, pervasive magnesium metasomatism and recrystallization of detrital aluminosilicates and quartz with conservation of aluminum to form the trioctahedral clays.

REFERENCES

Alling, H. L. and Briggs, L. I., 1961, Stratigraphy of Upper Silurian Cayugan evaporites: American Association Petroleum Geologists Bulletin 45, p. 515-547.

Bodine, M. W., Jr., 1978, Clay-mineral assemblages from drill core of Ochoan evaporites, Eddy County, New Mexico: New Mexico Bureau Mines and Mineral Resources Circular 159, p. 21-31.

Bodine, M. W., Jr., in press, Trioctahedral clay-mineral assemblages in Paleozoic marine evaporite rocks: Sixth International Salt Symposium, Proceedings.

Bodine, M. W., Jr. and Rueger, B. F., in press, Clay-mineral assemblages from the Gibson Dome No. 1 drill core, Paradox Basin, Utah (abs.): Program, Clay Minerals Society Annual Meeting, 1983.

Bodine, M. W., Jr. and Standaert, R. R., 1977, Chlorite and illite compositions from Upper Silurian rock salts, Retsof, New York: Clays and Clay Minerals, v. 25, p. 57-71.

Dellwig, L. F. and Evans, R., 1969, Depositional processes in Salina salt of Michigan, Ohio, and New York: American Association Petroleum Geologists Bulletin 53, p. 949-956.

Dreizler, Ingo, 1962, Mineralogische Untersuchungen an zwei Gipsvorkommen der Werraserie (Zechstein): Beitrage Mineralogie und Petrographie, v. 8, p. 323-338.

Echle, Wolfram, 1961, Mineralogische Untersuchungen an Sedimenten des Steinmergelkeupers und der Roten Wand aus der Umbegung von Göttingen: Beitrage Mineralogie und Petrographie, v. 8, p. 28-59.

Füchtbauer, H. and Goldschmidt, H., 1959, Die Tonminerale der Zechsteinformation: Beitrage Mineralogie und Petrographie, v. 6, p. 320-345.

Hower, John, Eslinger, E. V., Hower, M. E., and Perry, E. A., 1976, Mechanism of burial metamorphism of argillaceous sediment: Mineralogical and chemical evidence: Geological Society of America Bulletin 87, p. 725-737.

Lippmann, F. and Savascin, M. Y., 1969, Mineralogische Untersuchungen an der Lösungsrückständen eines württenbergischen Keupergipsvorkommen: Tschemaks Mineralogie und Petrographie Mitteilungen, v. 13, p. 165-190.

Nieman, Hans, 1960, Untersuchungen am Grauen Salzton der Grube "Königshall-Hindenburg," Reyerhausen bei Göttingen, Beitrage Mineralogie und Petrographie, v. 7, p. 137-165.

Pettijohn, F. J., 1975, Sedimentary rocks (3rd ed.): New York, Harper and Row, 628 p.

Rickard, L. V., 1969, Stratigraphy of the Upper Silurian Salina Group, New York, Pennsylvania, Ohio, Ontario: New York State Museum and Science Service, Map and Chart Series 12.

Stewart, F. H., 1963, Marine evaporites: U.S. Geological Survey Professional Paper 440-Y, 52 p.

Weaver, C. E. and Pollard, L. N., 1973, The Chemistry of Clay Minerals: New York, Elsevier Scientific Publishing, 213 p.