

CLAY MINERAL STUDIES OF THE LOWER PERMIAN HAVENSVILLE SHALE IN KANSAS AND OKLAHOMA

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Abstract—Analyses of samples of the Havensville Shale, collected from six localities in Kansas and northern Oklahoma, showed that the distribution of clay minerals and chemical variations in the clay minerals were related to changes in the sedimentary facies. The major clay mineral assemblages were: (1) illite, mixed-layer illite-montmorillonite, and regularly interstratified chlorite-vermiculite in the shaly facies of northern and central Kansas, (2) montmorillonite, illite and mixed-layer illite-montmorillonite in the calcareous shale and algal limestone facies of southern Kansas, and (3) kaolinite, illite and mixed-layer illite-montmorillonite in the sandy facies of northern Oklahoma. Differential settling and transportation of clay detritus were the major factors in the pattern of distribution of the clay minerals. Regional differences were noted in the abundance of 2M illite polymorphs, the K/Rb ratio and the illite 001/002 intensity ratio. Some structural variations and chemical differences among the clay minerals were consequences of modifications during deposition in different environments and diagenesis.

INTRODUCTION

The problems of recognizing a sedimentary environment by the clay mineral assemblage in a rock have been adequately discussed in a recent paper by Keller (1970). Based on our present knowledge of clay mineral-environmental relationships, it appears that a trend of environmental changes may be inferred from a lateral sequence of clay mineral assemblages. Weaver (1964), among others, has recognized a trend of clay mineral assemblages with broad changes in the depositional environments. The primary purpose of the present paper was to describe the distribution and characteristics of clay mineral assemblages in the Lower Permian Havensville Shale of Kansas and northern Oklahoma across a distance of over 200 miles. Hattin (1957) described the depositional environment of the Havensville Shale and reported several sedimentary facies along the north-south direction. The clay mineral data thus can be evaluated in terms of the depositional environment of the Havensville Shale. Stindl (1965) and Stindl and Twiss (1968) made a similar study of the clay mineral-environmental relationship of the Lower Permian Cottonwood Limestone in Kansas and Oklahoma. Results of the present work, therefore, provide additional data for an understanding of the clay mineral-environmental relationship and an evaluation of the origin of clay minerals in the Lower Permian rocks of Kansas and adjacent areas.

The Havensville Shale is a member of the Lower Permian Wreford Limestone (Fig. 1). Throughout

northern Kansas the Havensville Shale, ranging in thickness from 14 to 20 ft., consists dominantly of shale interbedded with a few argillaceous limestones. In southern Kansas and northern Oklahoma the unit, having an average thickness of 7 ft., primarily contains sandstones and sandy limestones. The Havensville Shale becomes very thin, attaining a thickness of about 3 ft., above a reef-like structure in the Three-mile Limestone member of the Wreford Limestone in south-central Kansas. Paleogeographic reconstruction of the Permian basin in Kansas and northern Oklahoma favors the existence of Arbuckle and Oklahoma highlands to the south and low-lying lands to

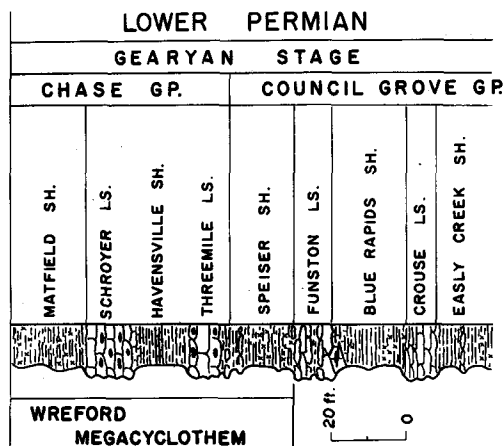


Fig. 1. Stratigraphic column indicating a portion of the Lower Permian section of Kansas and Oklahoma.

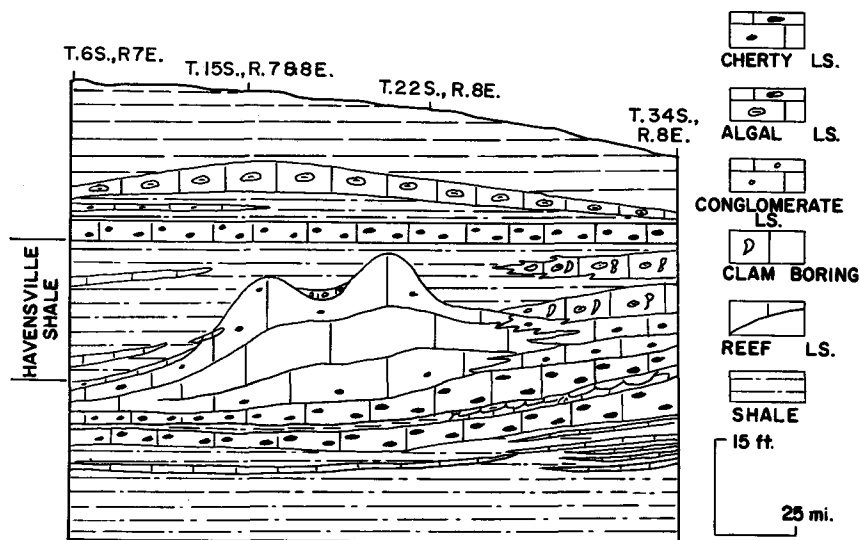


Fig. 2. Relationship of sedimentary deposits in the Wreford Megacyclothem.

the north. Based on the recurrence of lithologic types with characteristic fossils, Hattin (1957) recognized the members of the Wreford Limestone as a part of the "Wreford Megacyclothem". The relationship of sedimentary deposits in the megacyclothem is indicated in Fig. 2. Paleontological evidence tends to indicate that the sea in this region remained shallow during much of the Early Permian time. Since delicate morphological features of many organisms are often preserved over the entire area of study, the depth of burial of the Havensville Shale appears to be shallow and the regional difference in the burial diagenesis tends to be minimal.

ANALYTICAL PROCEDURES

Samples collected from six stratigraphic sections covering a distance of approx. 200 miles in a north-south direction were chosen for the clay mineral analysis. Locations of samples analyzed are shown in Fig. 3. Each sample of shales was broken into small chips, which were then digested in distilled water followed by stirring in a blender for a few minutes to

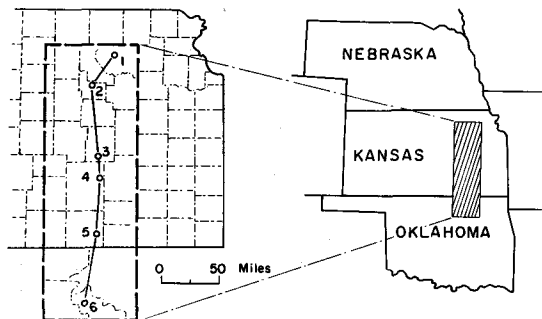


Fig. 3. Location of samples from Kansas and Oklahoma. Sample designations and locations are: 1-HP, Pottawatomie Co., Kans.; 2-HG, Geary Co., Kans.; 3-HCh, Chase Co., Kans.; 4-HB, Butler Co., Kans.; 5-HC, Cowley Co., Kans.; 6-W, Pawnee Co., Okl.

facilitate disaggregation. In case of hard and dense limestones, crushed samples were treated in 0.5 M acetic acid for complete dissolution of the carbonates. Less than 2- μ m fractions were then separated from each of the dispersed and disaggregated suspensions by the standard sedimentation process. A portion of slurry of the clay fraction was placed on glass slide for X-ray powder diffraction of oriented samples, while the remaining slurry was evaporated for random powder X-ray powder diffraction and analysis for K and Rb contents.

All clay mineral determinations were made with a Norelco diffractometer and Cu K α radiation. Each of the oriented samples was analyzed in its untreated condition, after glycol treatment and after heat treatment at 450 and 600°C. A semi-quantitative analysis of clay minerals was made following a method outlined by Biscaye (1965).

Polymorphic forms of illites present in the clay aggregate were determined after digestion of the less than 2- μ m fractions in 6N HCl to eliminate interference from chlorites and carbonates in the X-ray powder diffraction pattern. The identification of polymorphic forms was based on the X-ray powder diffraction data given by Yoder and Eugster (1955). A method by Reynolds (1963) was adopted for semi-quantitative estimation of relative abundances of the polymorphs. The intensities of 2.58 and 3.00 Å reflections were measured directly from diffractograms. The 3.00 Å reflection was attributed solely to 2M, whereas 2.58 Å was assigned to combined 1M_d, 1M and 2M reflections. The presence of 1M polytype was checked by the 3.66 Å reflection.

Potassium and rubidium content of the clay fractions were determined by X-ray fluorescence spectrometry. Rb was determined with a molybdenum tube, which provided the primary radiation, and a lithium fluoride crystal. Standards used in the Rb measurements were samples of the Havensville clays whose

Rb content had been determined by a mass spectrometric isotope dilution analysis. For potassium analysis samples were fused in a mixture of La_2O_3 and $\text{Li}_2\text{B}_4\text{O}_7$ and pellets were made from the fused materials following the suggestion by Rose *et al.* (1963). Each pellet was then analyzed for potassium content with a Norelco X-ray fluorescence spectrometer equipped with a chromium tube and an EDT crystal. A standard curve was obtained from analysis of samples which covered a range of 1–6% potassium.

CLAY MINERAL IDENTIFICATION

Illite, montmorillonite, chlorite, mixed-layer illite-montmorillonite, kaolinite and mixed-layer chlorite were major clay minerals recognized in less than 2- μm fraction clays of the Havensville Shale. Some of their characteristic X-ray diffraction maxima are illustrated in Fig. 4. Illite was identified by basal reflections at 10.0, 5.0, 3.3 and 2.5 Å. Neither glycol solvation nor heating up to 600°C caused any significant changes in the *d*-spacings. Montmorillonite was identified by its 001 reflection at 14.0 Å, which readily expanded to 17 Å by glycol solvation. It seemed to have a low layer charge as revealed by the contraction of the layer to 12 Å upon potassium saturation and the expansion of the potassium saturated layers in ethylene glycol. Differentiation of montmorillonite from vermiculite was achieved by magnesium saturation and glycerol solvation. Chlorite reflections occurred at 14.0, 7.0, 4.7 and 3.5 Å. Neither glycolation nor heating up to 600°C had any effect on the positions of the diffraction maxima of the chlorite. Kaolinite

was determined by its reflections at 7.2 and 3.6 Å, which overlapped with chlorite reflections. Persistence of the reflection under acid treatment, slow scanning and heating to 600°C accompanied by decrease in the intensity of the reflection were useful in the differentiation of kaolinite 002 reflection from chlorite 004 reflection.

Mixed-layer illite-montmorillonite was recognized from a diffuse and broad reflection at 11 Å. Upon ethylene glycol solvation the reflection shifted to nearly 14 Å. The interstratification was judged to be random for the lack of higher order reflections. Both heating to 450°C and potassium saturation shifted the reflection to 10 Å. The relative abundance of each component could not be determined because of the general diffuse nature of the reflection.

Two types of mixed-layer chlorite-expandable clays, one with regular interstratification and the other with partially random interstratification, were recognized. Regular interstratified chlorite-expandable clays were characterized by reflections at 14.7, 9.7, 7.3 and 4.9 Å, for untreated air-dried samples. Upon glycolation, the diffraction maxima appeared at 15.7, 7.8, and 5.2 Å. Reflections at 23.0, 11.8 and 7.9 Å appeared on heating to 600°C. Magnesium saturated samples generally showed an increase in intensity of 14.7 Å reflection and exhibited no shift in the *d*-spacing upon glycerol solvation. Thus a vermiculite-like layer was recognized in the regularly interstratified chlorite-expandable clay minerals. The partially random mixed-layer chlorite-expandable clays produced reflections in the range of 14.2 to 14.5 Å for air-dried samples. Upon ethylene glycol solvation the *d*-spacing ranged from

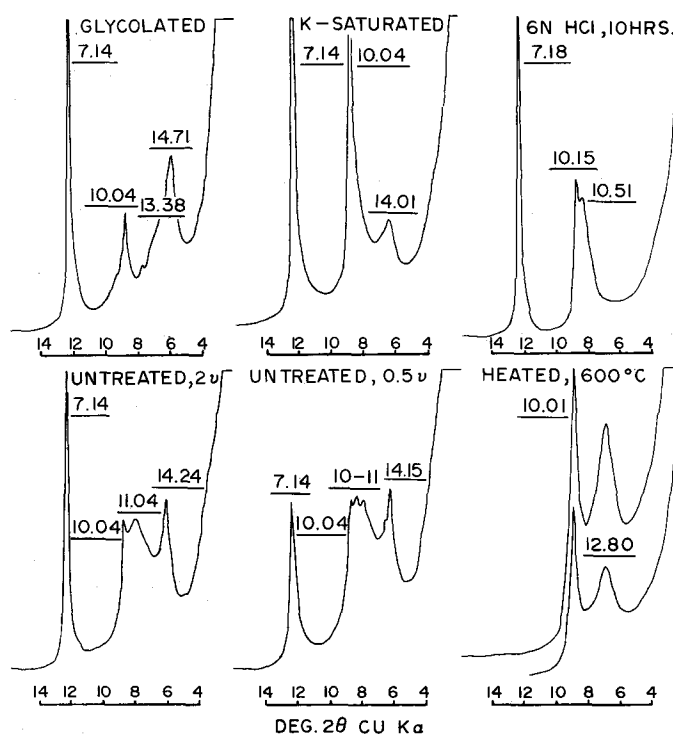


Fig. 4. Typical X-ray powder diffraction patterns of major clay minerals in the Havensville Shale.

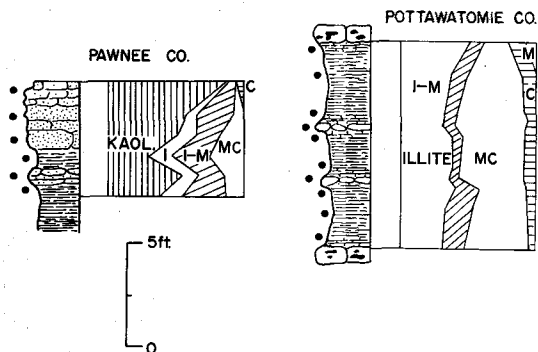


Fig. 5a. Vertical variation of clay minerals in the Havensville Shale in Pawnee Co., Oklahoma (Kaol., Kaolinite; I, Illite; I-M, Mixed-layer illite-montmorillonite; M-C, Random mixed-layer chlorite; C, Chlorite).

Fig. 5b. Vertical variation of clay minerals in the Havensville Shale in Pottawatomie County, Kansas (I, Illite; I-M, Mixed-layer illite-montmorillonite; MC, Regular mixed-layer chlorite; C, chlorite; M, Montmorillonite).

14.8 to 15.2 Å. A weak, broad reflection of 12.4–13.4 Å appeared at 450°C. Further heating to 600°C the X-ray diffraction pattern showed a prominent reflection at 12 Å. Higher order reflections of the mixed-layer chlorite-expandable clays under various treatments could not be determined from the diffraction pattern. Magnesium saturation and glycerol solvation seemed to indicate the association of vermiculite-like layers in the mixed-layer assemblage.

DISTRIBUTION OF CLAY MINERALS

The difference in the type and abundance of clay minerals is readily apparent from the distribution of clay minerals in the Havensville Shale in Pawnee County, Oklahoma and Pottawatomie County, Kansas which were the two most remote areas of the present investigation (Figs. 5a, b). In Pawnee County, Oklahoma, kaolinite was the dominant clay mineral, with smaller amounts of illite, mixed-layer illite-montmorillonite and partly random mixed-layer chlorite-expandable clays. In Pottawatomie County, Kansas, the clay mineral composition was characterized by 40–45% illite, 40–50% regularly interstratified chlorite-vermiculite, 10–15% mixed-layer illite-montmorillonite, and a very small quantity of montmorillonite and chlorite.

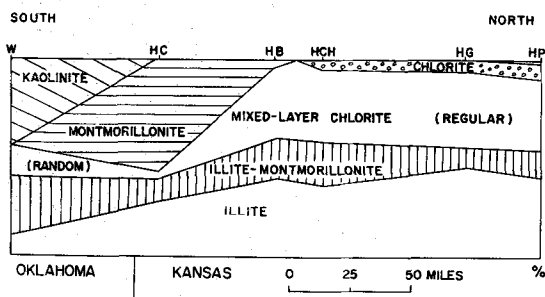


Fig. 6. Lateral distribution of clay minerals in the Havensville Shale.

The lateral distribution of clay minerals was determined from the clay mineral composition of the Havensville Shale studied in six localities covering a distance of approx. 200 miles. Figure 6 presents the nature and trend of clay mineral distribution across this distance from northern Kansas to northern Oklahoma. Illite in the northernmost localities at Pottawatomie and Geary Counties of Kansas made up nearly 40% of the clay minerals, whereas at Pawnee County, Oklahoma, it amounted to approximately 25%. Mixed-layer illite-montmorillonite, which constituted nearly 10% in the northern localities, represented approx. 20% of the clay minerals in the southern localities. Montmorillonite was found to be abundant at Cowley County of Kansas, where its average content was estimated to be 60%. In Oklahoma and northern counties of Kansas the montmorillonite was present only in trace quantities. Discrete chlorite generally constituted a small fraction of the clay minerals. An average of 5% chlorite occurred in the northern localities, whereas only a trace amount could be found in the southern areas. Mixed-layer chlorite-vermiculite in the northern localities consisted of regularly interstratified minerals and generally comprised 30–40% of the clay minerals. In the southern localities the mixed-layer chlorite-expandable clays, averaging 10% of the clay, was partially randomly interstratified and exhibited very weak resistance to heat treatment. Kaolinite was abundant in the southernmost area of investigation and was absent in the northern localities. In Pawnee County, Oklahoma, the kaolinite constituted approx. 40% of the clay minerals.

K/Rb ratio, illite polytype and illite 001/002 intensity ratio

Illites were dioctahedral, having 060 reflections at 1.50–1.51 Å. Table 1 presents the K and Rb contents, the abundances of illite polymorphs and the illite 001/002 intensity ratio for clay samples of different localities. Much of the K and Rb contents in the samples could be attributed to their presence in the illite and mixed-layer illite-montmorillonite minerals. It is apparent from the data that the samples in the southern localities at Pawnee County, Oklahoma and Cowley County of Kansas seem to have an average K/Rb ratio of 154, which is less than the corresponding value of 211 for the samples in the northern localities of Kansas.

Both 1M₁ and 2M polytypes of illite were noted in the clay samples of the Havensville Shale. The 2M polymorph made up an average of 45% illite in the northern localities and an average of 15% illite in the southern localities. Figure 7 shows that the 2M content increases with decreasing abundance of mixed-layer illite-montmorillonite. The 2M content seemed to increase with the increasing K/Rb ratio of the clays (Fig. 8). The illite 001/002 intensity ratio for clay samples of the northern localities, having an average value of 2.9, appeared higher than that for

Table 1. K and Rb concentrations and 2M contents of the Havensville Shale

Sample	Locality	K (%)	Rb (ppm)	K/Rb	%2M	Illite 001/002
W-4	Pawnee Co., Oklahoma	1.44	106	136	—	2.0
W-3	Pawnee Co., Oklahoma	0.44	29	152	—	1.5
W-2	Pawnee Co., Oklahoma	2.48	137	181	17	2.1
W-1	Pawnee Co., Oklahoma	1.93	110	175	—	2.3
WGC	Pawnee Co., Oklahoma	3.53	242	146	13	2.0
HC-7	Cowley Co., Kansas	2.14	174	146	12	2.0
HC-6	Cowley Co., Kansas	1.93	159	121	13	1.9
HC-4	Cowley Co., Kansas	1.43	77	186	33	1.7
HC-2	Cowley Co., Kansas	2.36	181	130	34	1.8
HC-1	Cowley Co., Kansas	2.80	171	164	25	2.1
HB-7	Butler Co., Kansas	3.66	190	193	27	2.4
HB-6	Butler Co., Kansas	3.36	203	166	25	2.3
HB-5	Butler Co., Kansas	2.37	142	167	26	2.9
HB-4	Butler Co., Kansas	3.93	177	222	23	2.7
HB-1	Butler Co., Kansas	3.59	186	193	30	2.8
HCH-5	Chase Co., Kansas	3.78	145	261	36	3.4
HCH-4	Chase Co., Kansas	3.71	148	251	33	3.0
HCH-3	Chase Co., Kansas	3.56	143	249	63	3.1
HCH-2	Chase Co., Kansas	3.44	146	236	40	2.7
HCH-1	Chase Co., Kansas	3.42	147	233	39	3.0
HP-14	Pottawatomie Co., Ks.	3.91	185	211	55	2.9
HP-10	Pottawatomie Co., Ks.	3.93	182	216	48	3.0
HP-8	Pottawatomie Co., Ks.	3.78	185	204	33	2.8
HP-5	Pottawatomie Co., Ks.	4.08	188	217	—	2.9
HP-4	Pottawatomie Co., Ks.	3.98	222	179	38	3.0
HP-1	Pottawatomie Co., Ks.	3.96	208	190	47	3.1

clay samples of the southern localities where the average value was estimated to be 2.0.

DISCUSSION

The trend of clay mineral distribution in the Havensville Shale reflects broad changes in the sedimentological environment. The rocks of the Havensville Shale in northern Oklahoma belonged to a near-shore facies and in northern Kansas represented an off-shore facies (Hattin, 1957). The near-shore facies is marked by abundant kaolinite, high illite to mixed-layer illite-montmorillonite ratio, and low montmorillonite and partially random mixed-layer chlorite-expandable clays. The clay mineral assemblage in the off-shore facies is represented by absence or trace

amounts of kaolinite and montmorillonite, high illite to illite-montmorillonite ratio and abundant regularly interstratified chlorite-vermiculite. Abundant montmorillonite was found in the Havensville Shale in an area shoreward behind a carbonate mound of the underlying Threemile Limestone (Hattin, 1957). The area is also considered to be a part of the Greenwood shoal recognized by Imbrie *et al.* (1959). Thus, in conformity with facies changes across the sedimentary basin, three major clay mineral assemblages had been recognized, which include illite and regularly mixed-layer chlorite-vermiculite in the northern shaly facies, montmorillonite in the calcareous shaly and

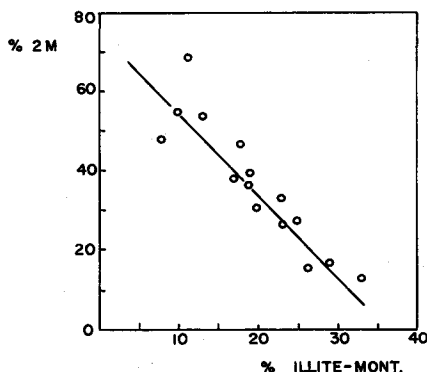


Fig. 7. Relationship between the 2M illite content and the percent illite-montmorillonite.

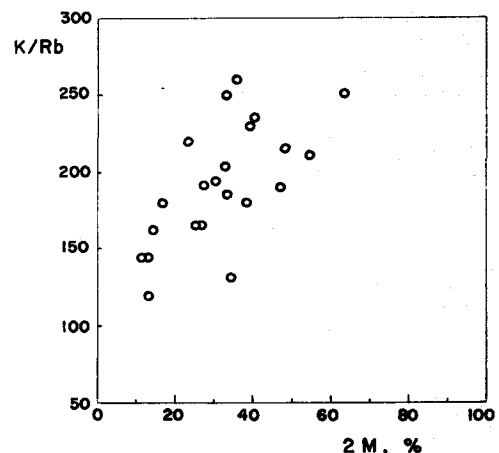


Fig. 8. Relationship between 2M illite content and K/Rb ratio.

agal limestone facies, and kaolinite with partially random interstratified chlorite-vermiculite in the southern sandy facies.

Illite and mixed-layer illite-montmorillonite are abundantly present throughout the area of investigation. There appears no lithologic preference for the illites. Nor are these minerals preferentially located in any particular area of the sedimentological basin. Chaudhuri and Lee (1972) established a detrital origin of the illites and mixed-layer illite-montmorillonites based on their Rb-Sr dates of 320-390 m. y. Whereas $1M_d$ illite was more abundant to the south than that to the north, the Rb-Sr date was slightly higher for the southern samples than that for the northern samples. This relationship between the age and the $1M_d$ illite argues strongly against the authigenic origin of the illites.

Kaolinite is concentrated in the southern sandy facies of the Havensville, while being absent in the seaward shaly facies. Such a limited distribution of kaolinite may be attributed either to slow diagenetic alteration under marine condition (Grim, Dietz and Bradley, 1949), or to more rapid flocculation of it in a near-shore environment. Kaolinite may be converted to illite during diagenesis. Velde (1965) reported the conversion of kaolinite in presence of excess K to $1M_d$ mica within a diagenetic pressure-temperature condition. For the present study there was no evidence of any significant difference in the diagenetic pressure-temperature condition between the kaolinite-containing sediment and the kaolinite-free sediment of the Havensville Shale to account for the observed distribution of the kaolinite. Also, contrary to the expected trend, $1M_d$ polytype content was less in the kaolinite-free sediment than in the kaolinite-bearing sediments. Furthermore, $1M_d$ illites appear to be detrital in origin. Since kaolinite in the Havensville Shale was found to occur only in rocks of the near-shore facies, a rapid flocculation of it would be a likely process responsible for the limited distribution.

Differential settling tendencies of clay minerals may have been a causative factor in the localized concentration of montmorillonite. The deposition of montmorillonite took place in the shallow marine environment behind a calcareous organic mound of the Threemile Limestone. Adsorption of organic material and cation fixation by the montmorillonites in the shoreward environment may have produced a high degree of coacervation and facilitated rapid settling of these clay minerals.

Cation exchange and fixation by the clay mineral detritus during sedimentation in the marine basin and diagenesis also may have played a major role in the variation of structural and chemical characteristics of the clay minerals across the basin. Since K and Rb generally have a coherent relationship, the K/Rb ratios of clay minerals are useful in the evaluation of the degree of structural modifications of the clay minerals during deposition and diagenesis. If the

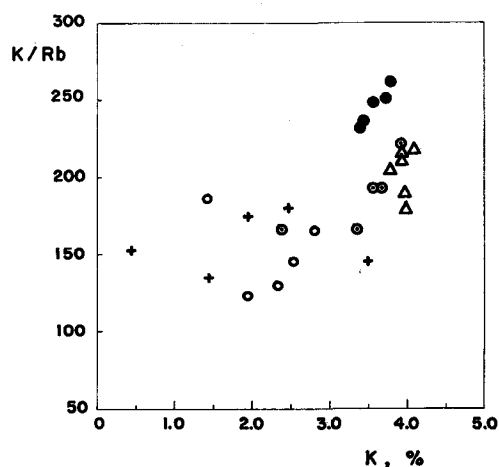


Fig. 9. Variation of K/Rb ratio with K content of the clay minerals in the illite.

K/Rb ratios are primarily inherited from source rocks, then the observed differences in the ratio for clay minerals in the Havensville Shale may be attributed to the effect of differential transportation and settling of illites having different K/Rb ratios. The high K/Rb ratio for clay mineral assemblages may also be related to the presence of illites that could have formed authigenic minerals, such as microcline or mica, having high K/Rb ratios (Reynolds, 1963). Since there is a lack of evidence to suggest any great regional difference in the burial diagenesis, and the K/Rb ratio increases with increasing $2M$ illite, the effects of authigenic minerals appear minimal in determining the K/Rb ratios of the clay minerals in the Havensville Shale. As shown in Fig. 9, the K/Rb ratios tend to increase with increasing K content. Consequently, the adsorption of K by degraded illites during deposition and diagenesis may explain the high K/Rb ratio of minerals in the offshore facies. The K adsorption may also partly account for the seaward increase in the illite to mixed-layer illite-montmorillonite ratio. In the absence of K-Ar ages the proper role of the K adsorption can not be evaluated.

Increase in illite 001/002 ratios may be related either to partial weathering of illites, and consequent decrease in K content, or to high iron content which weakens the (002) intensity. Weaver (1965) showed that the illite 001/002 intensity ratio generally increases with decreasing K. Since the illites in the Havensville Shale generally indicate an increase in the 001/002 intensity ratio with increasing K/Rb ratio, and therefore with increasing K content, the higher 001/002 intensity ratios of samples from the off-shore facies to the north than those of the sample from the near-shore facies to the south may be related to their high iron content. The illites with high iron content may assume considerable charge deficiency in the lattice resulting from reduction of iron in the diagenetic environment. Consequently, there will be some diagenetic adsorption of K to satisfy the lattice charge. This adsorption of K derived from a source

having a high K/Rb ratio may account for the positive correlation between the 001/002 intensity ratio and the K/Rb ratio of the illites.

Chlorite and mixed-layer chlorite distributions are strongly facies dependent. They are abundant in the off-shore facies, while being present in small amounts in rocks of the near-shore facies. Thus a selective transportation of these minerals may be suggested to explain their present distributions. Both the random mixed-layer chlorite in the near-shore facies and the regular mixed-layer chlorite in the off-shore facies could have formed from the weathering of chlorite. Alternatively, the adsorption of magnesium during deposition and diagenesis by expandable minerals transported to the off-shore environment may have been a causative factor in the formation of the regularly interstratified chlorite-vermiculite minerals. Since the distribution of these minerals is limited to the rocks of the off-shore facies and they are equally abundant in both the shales and the limestones, at least a part of these chlorite-vermiculite were the product of the environment of deposition and diagenesis.

The clay mineral distribution in the Havensville Shale thus establishes a distinct clay mineral-environmental relationship. Lateral variations in the clay mineral assemblage were the consequence of differential settling and transportation of the clay detritus and reflect broad changes in the environment of deposition of the Havensville Shale. Change in the clay mineral composition within a major sedimentary facies, such as the off-shore facies, appeared to be less distinct. The X-ray and chemical characteristics of the clay minerals provide information on the extent to which structure and composition of minerals have been progressively modified during their seaward transport. The negative correlation between the 2M illite content and the percent mixed-layer illite-montmorillonite content, which decreases in the off-shore direction, may be explained in terms of very subtle selective dispersion of the illites in the sedimentary depositional basin. However, the positive correlation between the 2M illite content and the K/Rb ratio signifies that the increase in 2M content in the off-shore environment is most likely to be accompanied by structural modifications of the illites with incorporation of varying amounts of potassium in the deposit-

ional basin. The increase in K/Rb ratio may have resulted from adsorption of K by the illites because of the possible reduction of iron during diagenesis resulting in a charge deficiency of the lattice. The high K/Rb ratio, and possibly the evolution of regularly interstratified chlorite-vermiculite minerals in the off-shore clay samples were the likely diagenetic modifications in the clay mineral assemblage of the Havensville Shale.

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