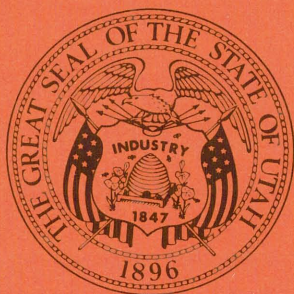


THE ORIGIN OF
PYROPHYLLITE - RECTORITE
IN SHALES OF NORTH CENTRAL UTAH

by G. V. Henderson



Utah Geological and Mineralogical Survey

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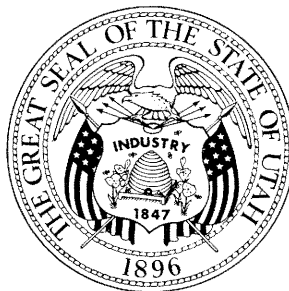
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UTAH GEOLOGICAL AND MINERALOGICAL SURVEY
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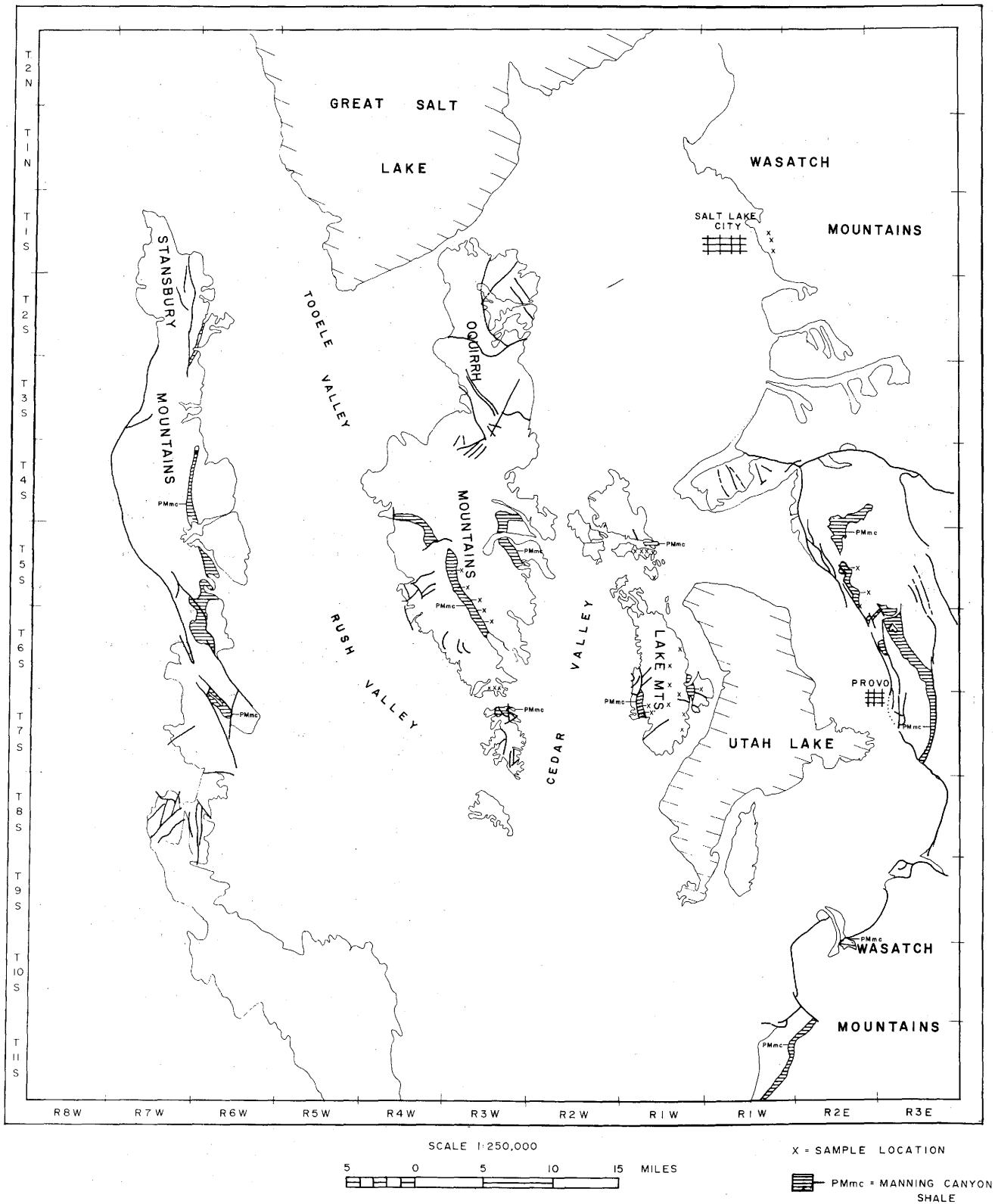


Figure 1. Index map.

THE ORIGIN OF PYROPHYLLITE-RECTORITE IN SHALES OF NORTH CENTRAL UTAH

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G. V. Henderson¹

ABSTRACT

Pyrophyllite is widespread in pelitic rocks of the Manning Canyon shale in north central Utah; association of this mineral with other clay minerals, especially rectorite, is related to origin. The regular mixed-layer clay mineral rectorite seems to form as a result of the alteration of muscovite-paragonite during late stages of diagenesis and represents an intermediate metastable phase in the mineral paragenetic sequence. Pyrophyllite subsequently formed from the alteration of rectorite during advancing metamorphism and is the stable end member of the clay mineral assemblage.

Structural interpretation of rectorite found in the Manning Canyon shale shows a regular, alternating sequence consisting of a fixed layer of 9.6 Å and an expandable layer varying from 10 Å to 17 Å. With ethylene glycol saturation in the natural state a basal reflection of 26.60 Å is recorded.

INTRODUCTION

The presence of pyrophyllite in pelitic rocks of Mississippian-Pennsylvanian age in north central Utah has been known for many years, but the origin of this mineral and its association in a rather unique suite with other clay minerals has not been studied or explained in detail.

Mineralogical analysis of shales, clays and associated limestone samples from the Manning Canyon Formation reveals that a long-spacing, regular mixed-layer clay mineral typical of rectorite or allevardite occurs with pyrophyllite throughout much of the formation.

The stratigraphic relationships of pyrophyllite-rectorite and a wide geographic distribution indicate that origin cannot be attributed entirely to hydrothermal activity and that diagenesis and prograde regional metamorphism must be considered in any theory of origin.

The primary objectives of this study are to determine the origin of pyrophyllite in these shales and limestones and to study the relationships between pyrophyllite-rectorite and the associated clay minerals illite, chlorite, kaolinite and gibbsite. X-ray

diffraction, petrographic and differential thermal analysis (DTA), and electron microprobe data are combined with chemical and geological data in an attempt to meet these objectives. Among the most significant contributions of this study are (1) the positive identification of rectorite in this shale-clay sequence and (2) evidence concerning its origin and association with pyrophyllite.

The widely disseminated nature of pyrophyllite in the Manning Canyon shale over a large geographic area is related to the origin of this mineral, and the occurrence of rectorite with pyrophyllite in unmetamorphosed shales indicates clay mineral paragenesis.

An index map showing the area of study, sample locations and general geologic setting is shown in figure 1.

GEOLOGY

General

Most of the samples studied in this investigation were taken from the Manning Canyon shale which is exposed in outcrops throughout north central Utah. Miscellaneous spot samples were collected from other Paleozoic shales in Salt Lake, Tooele, Utah and Weber counties. This study is centered on the Manning Canyon Formation because of (1) the unique mineralogic association of clay minerals present, (2) abundance of the minerals pyrophyllite-rectorite in the formation and (3) the apparent variation of depositional environment reflected in the sequence of sedimentary rocks in this formation.

The area studied includes the southern part of the Oquirrh Range, the Wasatch Front Range from Ogden to Provo, the Lake Mountains west of Utah Lake and parts of the highly faulted Traverse Range.

Mesozoic rocks are absent in the study area and Cenozoic rocks are not well documented. The Paleozoic sequence of rocks is well exposed in north central Utah and is important in documenting the history of the Great Basin (Bissell and others, 1959). For regional studies of the geology, refer to Gilluly (1932) and Proctor and others (1959).

Stratigraphy of the Manning Canyon Shale

In his study of the systemic boundaries in Mississippian and Pennsylvanian rocks of north central Utah, Moyle (1959) stated that the Manning Canyon shale, at the type locality in Manning Canyon of the

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Oquirrh Mountains, bridges the Mississippian-Pennsylvanian time boundary and reflects considerable variation in depositional environment. The formation consists predominantly of carbonaceous shale and interbedded limestone, with a few beds of quartzite, siltstone and mudstone. Five measured sections of the formation show an average thickness of 1,500 to 1,600 feet (Moyle, 1959).

The Manning Canyon shale is bounded at its base by the ridge-forming Upper Mississippian Great Blue Limestone and at its top by limestone of the Lower Pennsylvanian Oquirrh Formation.

The type area for the formation is in the Oquirrh Mountains (Manning Canyon), Utah (Gilluly, 1932, p. 31). Moyle refers to this type locality in Manning Canyon, sec. 4, T. 7 S., R. 3 W., but calls the section in Soldier Canyon, sec. 33, T. 5 S., R. 4 W., the type section.

Lithology

The lithologic composition of the Manning Canyon shale, as shown by Moyle (1959, p. 65), consists of 60 percent shales, 34 percent limestones and 2 percent mudstones and miscellaneous. Clay-shales predominate in the basal 600-700 feet of the formation (Moyle).

In general, the shales vary from red to brown silty units to light grey to black paper-thin shales and clays. The black shales are carbonaceous and Moyle (1959) noted that some areas may be considered petroleum source rocks. He also noted that hydrothermal alteration is evident throughout the formation, but he believes it is of minor importance.

Significant work could be done on zonation of the Manning Canyon Formation through a study of the mixed-layer clay minerals present. Weaver (1956) indicated that although mixed-layer clays are generally quite sensitive to environmental changes, they can be used in the zonation of thick sections of sedimentary rocks.

Environment of Deposition

Moyle (1959) suggests that the environment of deposition is nearshore, suggesting shallow epineritic to infraneritic conditions. Sediments may have been deposited on an unstable shelf directly adjacent to the deeper zones of the geosyncline. The nature of the black shales indicate deposition farther from shore under reducing conditions or in a lagoonal environment.

The study of clay minerals in the Manning Canyon shale verifies Tidwell's (1962) postulate of nearshore and lagoonal or euxinic type environments of deposition. The original clay minerals in the sediments appear to have been illite and chlorite. Con-

ditions favoring the formation of illite are (1) adequate amounts of silica in solution, (2) the presence of Ca^{++} , Mg^{++} and Fe^{++} ions, (3) alkaline conditions, (4) potassium in solution in concentrations high enough to effect appropriate cation exchange and (5) a deficit of positive electrical charge inside the three-layer illite structure. Alternate wetting and drying cycles of the weathering system would aid in the fixation of potassium in the clay mineral structure. The apparent presence of chlorite in the original sediments of the Manning Canyon Formation would fit well in the chemical system with the formation of illite. Its origin is controversial but it generally coexists with illite in marine conditions which are alkaline, favoring the formation of illite-chlorite rather than kaolinite. Kaolinite does not usually form in the presence of carbonate materials.

Studies by Glass and others (1956) and Grim (1951) of the clay minerals in Mississippian-Pennsylvanian sediments of the Illinois Basin indicate that the clay minerals illite and chlorite were the most abundant clay minerals in the unweathered portions of the ancient sediments.

Environmental interpretation of the Manning Canyon shale is somewhat difficult because of the complex system of clay minerals in the sediments. It is difficult to isolate the effects of depositional environment from those of source area contribution and post-depositional history. The physicochemical characteristics of the mineral assemblage in the sediments indicate a pH of about 7 to 8 in a marine environment; the presence of pyrite, however, as well as the great abundance of organic matter in some of the shales would imply reducing conditions with negative Eh values.

Bissell (1962) states that sediments which accumulated in the Oquirrh and Lake Mountain areas may have been derived from the western Utah highland along the southwest border of the embayment. The northern part of the embayment probably received sediments from the highland in northeast Nevada and northwest Utah. Moyle (1959) states that much of the Manning Canyon sediment may have been eroded from the emerging Emery uplift of east central Utah. The Uncomphagre uplift far to the southeast may also have provided some sediment for the Manning Canyon shale embayment. The mixed-layer clays and pyrophyllite appear to have developed from the original illite-chlorite clay minerals.

METHODS OF STUDY

Sample Preparation

A total of 130 samples from the Manning Canyon Formation and associated stratigraphic units in the study area were collected and ground to -100 mesh. Samples of limestones containing clay were also ground so that clay mineral constituents could be leached from them for detailed study.

Samples were prepared for X-ray diffraction analysis as $-2\ \mu$ oriented slides, bulk powder packs and smear slides of bulk samples. Oriented slides of $-2\ \mu$ material were prepared by placing approximately 5 g of ground clay in a 50-ml beaker filled with distilled water. The clay suspensions were repeatedly washed and stirred until total dispersion was attained and all soluble salts were removed. The $-2\ \mu$ fraction of each sample was then removed with a pipette, placed on a glass slide and evaporated to dryness at room temperature.

Smear slides were prepared for determination of bulk mineralogical composition of the entire sample by placing approximately 0.5 g of powdered clay on a glass slide, adding a few drops of distilled water and smearing the clay over the slide with a spatula to form a paste (Gibbs, 1967).

Powder packs of the bulk sample were used for qualitative determination of nonclay minerals in the sample. Standard powder pack holders were packed with a -100 mesh sample and pressed firmly into position with a clean glass slide.

Size Separation

Size separations of selected samples were made with a Model K International centrifuge and by hydrometer-pipette methods.

Rectorite appeared stronger on X-ray traces of size fractions in the 30-50 μ range and weaker in the smaller fractions which contained abundant pyrophyllite, chlorite and illite. Ehlmann (1958, p. 24) states that pyrophyllite was concentrated in the coarser size fractions. He found that the 32-74 μ fraction usually contains at least 90 percent pyrophyllite and the $-1\ \mu$ fractions are usually free of pyrophyllite.

It was extremely difficult to obtain size separations of $-1\ \mu$ and $-2\ \mu$ material because of the high carbon content of the black shales. In general, size fractionations down to $-0.5\ \mu$ and $-1\ \mu$ in diameter showed persistence of pyrophyllite in the smaller sizes.

Pre-analysis Treatment

Most of the clay and shale samples contained large amounts of carbonaceous material. This high carbon content is indicated by high "loss on ignition" figures (10-12 percent) and from low temperature ashing results of five samples which showed an average of from 3 to 5 percent carbon.

Removal of carbon from the samples helped increase the intensity and clarity of X-ray diffraction lines. This was especially true where splits or overlapping diffraction peaks were evident. Removal of carbon, which acts as a bonding agent between clay particles, also facilitated dispersion and size fraction-

ation of the clays. Cold Clorox treatments worked satisfactorily and provided a good method for removal of carbon, but extended treatments with strong solutions of Clorox saturate the clays with Na^+ ions and must be used with caution. X-ray traces of five samples treated in a low-temperature ashing device at approximately $150^\circ\ \text{C}$ (Gluskoter, 1967) showed an increase in anhydrite content of the clays and did not seem to help with dispersing problems. The soluble sulfate salts in the raw clay samples dehydrated upon heating and formed crystals of anhydrite.

X-ray Analysis

X-ray diffraction analysis was done using a North American Phillips (Norelco) X-ray diffractometer with nickel filtered copper radiation. A 1-degree beam split and 0.003-inch detector slit were used. In general, patterns were run at a scanning rate of 2 degrees 2θ per minute, but for more detailed analytical work, a scanning speed of $\frac{1}{2}$ degree 2θ per minute was sometimes used. The X-ray unit was operated at 35 KV and 15 MA. The relative humidity in the laboratory ranged from 50 to 60 percent.

Three X-ray traces were obtained for all clay samples; traces of powder pack-bulk samples, traces of samples treated with ethylene glycol and traces of samples heated to $350^\circ\ \text{C}$ for 1 hour. Rectorite samples were studied from additional traces of material heated $650^\circ\ \text{C}$ for 3 hours. The limits of accuracy of the data, according to Gibbs (1967), should be ± 10 percent for 2 degrees 2θ per minute fast scan and ± 5 percent for $\frac{1}{2}$ degree 2θ per minute slow scan.

Quantitative data in this report are based on calculations using relative intensities (peak area) of the basal (00 ℓ) reflections of each clay mineral constituent in the sample. Intensities were measured in terms of counts per second. Percentages of minerals determined by X-ray analysis in the samples from Manning Canyon are shown in appendix A.

Quantitative determinations of clay minerals are particularly difficult because of (1) orientation effects, (2) compositional variations, including stratification of the clay minerals and (3) variations in crystal perfection. In particular, the variations in composition and crystallinity of clay minerals make unlikely the development of a precise quantitative X-ray method that will be applicable to all clays.

Bradley and Grim (1961) reviewed the variety of clay mineral analysis techniques available, discussed the problems of composition and crystallographic variability, and emphasized the importance of selecting as a standard a clay with crystallographic properties similar to those of the mineral to be assessed in the sample. The major problem in working with the usual complex mixtures of clays found in nature is the determination of the diffracting power of each of the

QUANTITATIVE FORMULAS USED	
% Chlorite	$= A(C_4^*) / .42 \times A(I_1^*)$
% Kaolinite	$= A(K_2^*) / .42 \times A(I_1^*)$
% Illite	$= 1$
% Montmorillonite	$= a(I_1^*) - A(I_1^\theta) (1.2) / 4 \times (AI_1^\theta) (1.2)$
% Mixed-layer + montmorillonite	$= (.84)(A \times I_1^*) - (AI_1^\theta) / (AI_1^\theta)$
% Mx	$= (Mx + Mont) - (Mont)$
<u>For Smear Slides</u>	
% Pyrophyllite	$= A(P_4^*) / 3A(I_2^\theta)$
<u>For <2μ slides</u>	
	$A(P_4) / A(I_2)$
Explanation:	
* = Heated Trace	(K ₂) = Kaolinite (002)
θ = Glycolated Trace	Mont = Montmorillonite
A = Area of Peak = (Peak Height x Peak Width at 1/2 Peak Height)	(Mx) = Mixed-Layer Material
(C ₄) = Chlorite (004)	(P ₄) = Pyrophyllite (004)
	(I ₁) = Illite (001)

Figure 2. Standardization of Norelco X-ray diffractometer for quantitative clay mineral determinations.

clay minerals in the sample under study. These diffraction factors have often been assumed or calculated, or an approximation has been determined by using as standards clays with seemingly similar properties. Gibbs (1967) noted in reviewing the techniques available for the quantitative analysis of a series of clay samples that it was obvious that none of the available techniques have fully overcome the problems of variability of composition and crystallinity of the clay minerals.

The quantitative X-ray diffraction analysis of the clay minerals in the samples of this study was based on the use of illite as a standard. This mineral was present in all samples and seemed to fit the qualifications listed for a good standard: (1) low mass absorption, (2) medium to high intensity which allows use of small amounts with a resulting low dilution of the sample and (3) the ability to produce a wide range of reflections without interfering with those of the minerals under study. All clay mineral peak heights on X-ray diffractometer traces were compared with the illite peak height intensity on a ratio basis. The ratios used for comparing illite with chlorite, kaolinite, montmorillonite and mixed-layer clays were worked out by the Clay Minerals Technology Section of the Illinois Geological Survey and are used as standard calculations for clay mineral determinations by the Illinois Survey (figure 2). The accuracy of the calculations are ±10 percent. All data included in this report are considered to be semi-quantitative, and except for percentages of pyrophyllite, are based on the calculations listed below. Data on the relative amounts of pyrophyllite in the samples from Manning Canyon were obtained using a technique described on the following pages.

Numerical values obtained from the calculations of the quantity of the mineral components are relative and are used strictly as a guide in this study to show the increases and decreases of one mineral with respect to another.

In the case of a mixed-layer material, although glycol traces of rectorite show a sharp distinct reflection at 26.6 Å (3.6° 2θ), calculations were based on the difference between the intensity of the 10 Å illite (001) peak on a glycolated trace and that of the same reflection on a heated trace. All mixed-layer material collapsed to 10 Å upon heating to 340°C for 1 hour.

The ratios listed below are for the standardization of clay mineral data obtained using the Norelco X-ray diffractometer at the Illinois Geological Survey where all samples were analyzed. Ratios were calculated for peak areas and used for quantitative work.

Ratios determined: (For <2 μ oriented slides)

Heated traces (350° C for one hour)

$$\frac{\text{Chlorite (004)}}{\text{Illite (001)}} \text{ Kaolinite (002)} = .42$$

$$\frac{\text{Chlorite (004)}}{\text{Kaolinite (002)}} = 1.0$$

Pyrophyllite (004): Illite (002) = 1:1

Ratios determined: (For smear slides)
Pyrophyllite (004): Illite (002) = 3:1

The relative percent of quartz in the entire sample (material >2 μ in diameter) was determined by running various standard mixtures of quartz-kaolinite on the diffractometer and plotting the percentage composition of the mixture against peak height at a scale setting of 250 counts per second, using the technique outlined below:

1. Different percentages of -200 mesh quartz and a -2 μ illite-kaolinite mixture were batched by weight and thoroughly mixed.
2. Powder packs of quartz-clay mixtures were run on the diffractometer at 2° 2θ per minute and at a slower scan speed of ½° 2θ per minute. All mixtures were repacked and rescanned 3 times. The peak heights are plotted against percent of quartz in figure 3.

The linearity of the results for clay-quartz mixtures is good up to 50 to 55 percent, but beyond this point the curve deviates. None of the samples used in this study contains more than 30 percent free quartz; the accuracy of the standard calibration curves are therefore within the limits of acceptability.

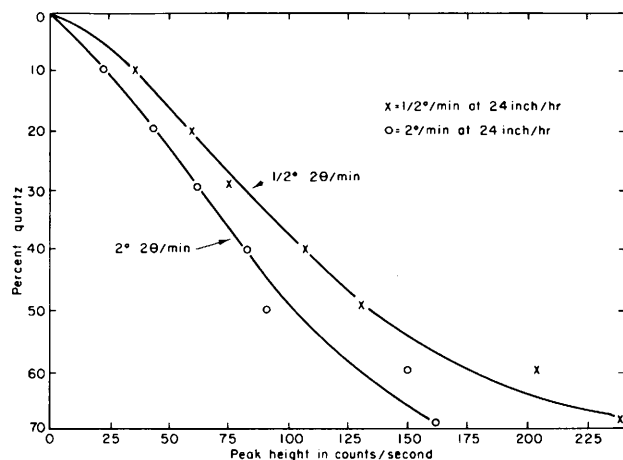


Figure 3. Diffraction intensity of quartz in a kaolinite-illite mixture. Points represent the intensity of the 101 quartz peak at $20.9^\circ 2\theta$.

The method of calibration used is outlined by Brown (1961, p. 493) who gives the following equation for a standard binary mixture of quartz and feldspar:

$$\frac{I_p}{I_q} = \frac{K_p}{K_q} \cdot \frac{W_p}{W_q}$$

Where I = Intensity ratio of components p and q

W = Weight ratio

K = Constant for any particular reflection from components p and q .

The following curve was plotted from standard mixtures of 200-mesh quartz in a kaolinite-illite mix. Marblehead illite was used as an internal standard.

An experimental procedure was established to compare the relative amount of pyrophyllite in a system containing illite, chlorite, kaolinite, montmorillonite and mixed-layer clays. Pyrophyllite has low absorption and high crystallinity and therefore produces sharp distinct basal reflections at low 2θ angles of 9.6° , 19.4° and 29.6° . This mineral occurs as large well-developed crystalline particles compared to the less well-crystallized and smaller particles of kaolinite, chlorite and illite. The setting rates for pyrophyllite compared to the other clay mineral in water are different because of the larger particle size, especially where montmorillonite is concerned. This causes problems in sample preparation of $<2\mu$ oriented slides for X-ray diffraction studies and was noted by Gibbs (1967). Several sample preparation techniques were tried without success. Size separation techniques using centrifuge and hydrometer failed to provide good separation of particle sizes for each clay mineral. The mixed clays proved to be unseparable and no pure samples of any of the clays could be

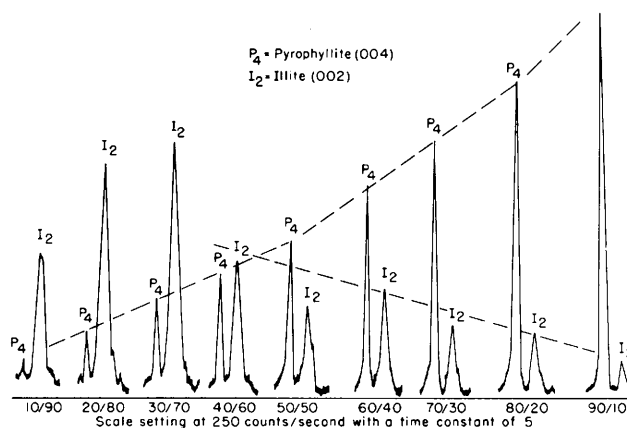


Figure 4. Actual X-ray diffraction traces of $<2\mu$ samples of pyrophyllite/illite mixes showing linear relationship between the two clays.

obtained. Some relatively pure pyrophyllite was found, however, in veins at the limestone shale contacts.

Using $<2\mu$ marblehead illite and vein pyrophyllite sized to $<2\mu$, a series of mixtures with desired percentages of each mineral component was dried in an oven for 24 hours and batched by dry weight. Oriented slides were made and scanned on the diffractometer at $2^\circ 2\theta$ per minute. Peak height and peak areas (peak height "x" peak width at $\frac{1}{2}$ peak height) were determined and approximate ratios of pyrophyllite to illite established. The relative diffraction intensities of various pyrophyllite-illite mixes are shown plotted against peak areas in figures 4 and 5. Each mixture was run three times to substantiate reproducibility and a linear plot of the ratios was obtained. Here again the plot of ratios becomes non-linear (as it does with quartz-kaolinite mixtures) as percentages of pyrophyllite/illite greater than 70/30 are attained. The data were reproducible and the accuracy could be established with ± 10 percent.

Calculations for determining ratios of pyrophyllite/illite mixes are shown in table 1. Peak areas were calculated from X-ray diffractometer traces of the mixes shown. The actual X-ray traces from which data were taken are shown in figure 4. Note the linearity of the plot for pyrophyllite in the mixes and the deviation of the illite traces when the mixes reach 50 percent illite.

The relative percent of pyrophyllite in a given sample was determined by comparing the (004) pyrophyllite peak with that of a standard illite peak, either (001) or (002). Figure 5 shows a plot of the ratios for $<2\mu$ oriented slides and figure 6 represents the same data $>2\mu$ material on smear slides. Figure 7 shows a plot of the ratios for the same two clay minerals using peak heights instead of peak areas for

Table 1. Calculations for determining approximate ratios of pyrophyllite (004) reflections and illite (002) reflections (data taken from X-ray diffraction traces shown in figure 7).

Percent Composition of Mixture (P/ILL)	Actual Ratio (P/ILL)	Ratio of Peak Areas ^{a/}	Normalized	Calculated Ratio ^{b/}
10/90	1:9	4/24	$4 \times 9 = 36/24$	1:1
20/80	1:4	9/57	$9 \times 4 = 36/57$	1:1.7
30/70	1:2.33	15/61	$15 \times 2.33 = 35/61$	1:1.7
40/60	7:1.5	23/34	$23 \times 1.5 = 34/34$	1:1
50/50	1:1	20/18	$20 \times 1 = 20/18$	1:1
60/40	1.5:1	28/20	$20 \times 1.5 = 28/25$	1:1
70/30	2.33:1	32/15	$15 \times 2.33 = 32/30$	1:1
80/20	4:1	36/18	$18 \times 4 = 36/72$	1:2
90/10	9:1	46/9	$9 \times 9 = 46/81$	1:2

a. Peak area determined by taking peak height times peak width at $\frac{1}{2}$ peak height.
b. Calculations rounded off to approximate ratio.

smear slides. Note the obvious linearity for pyrophyllite and the slight deviation from a linear relationship for illite.

Electron Microprobe Study

An electron microprobe was used to determine the Al_2O_3 , SiO_2 and FeO content and distribution in 3 samples. The instrument used was an (ARL) EMX-SM electron microprobe (Applied Research Laboratory) using a 100-150 μ diameter beam operated at 15 KV. Adjustments of the scanning electron beam were made to fit the specimen. All data were obtained by use of a digital recorder and automatic printout sheet. A strip chart recorder using an integrated signal (counts/5 sec) printed out data automatically on chart paper and magnetic tape for computer evaluation. Strip chart traces of the electron beam scan were also obtained for each sample. All microprobe analyses were done at the Materials Research Laboratory.

Petrographic Examination

A petrographic study of the clays, shales and limestones found in the study area was made to aid in establishing the distribution and origin of pyrophyllite. A Leitz Ortholux microscope equipped with an automatic 35 mm Orthomat camera was used for all photomicrography.

Forty thin sections of clays and shales were prepared. The minerals were impregnated with an epoxy resin before the sections were ground in oil to petrographic thickness.

Pyrophyllite is easy to distinguish from kaolinite and other clay minerals under the microscope because of its higher birefringence. Pyrophyllite was

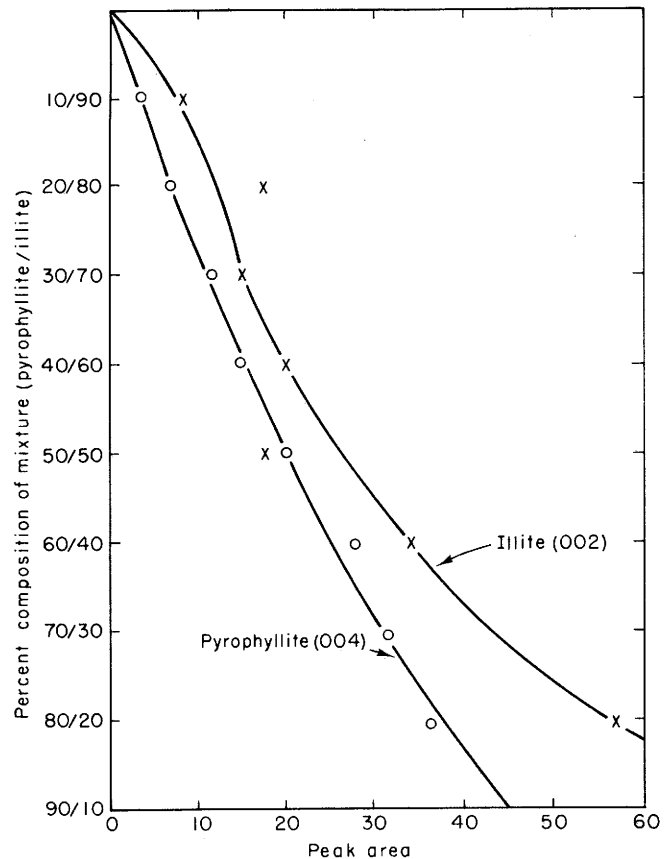


Figure 5. Plot of pyrophyllite (004)-illite (002) peak area ratios for $<2 \mu$ oriented slides.

easy to detect in thin section because of its large well-developed crystalline form and predominance in large-crystalline aggregate. Chlorite was identified by grinding the sample material, leaching the $<2 \mu$ clay fraction with dilute acetic acid and running X-ray patterns of the clay-size material.

PRESENTATION AND DISCUSSION OF DATA

General-Mineralogy

Experimental work confirms the presence of at least seven different clay minerals in the shale-limestone sedimentary sequences. The presence of such a multicomponent system of clay minerals is indicative of the complex nature of the sediments in this area. Both detrital and authigenic minerals are present. The most abundant clay minerals were illite, rectorite and pyrophyllite. Kaolinite and montmorillonite are less abundant and are probably less important in explaining the origin of rectorite-pyrophyllite. Chlorite appears to be of two polymorphic types; one occurs in the clay-shales, and the other is found in disseminated particles in the interbedded limestones. The latter is indicative of a chlorite-vermiculite type of mixed-layer clay mineral.

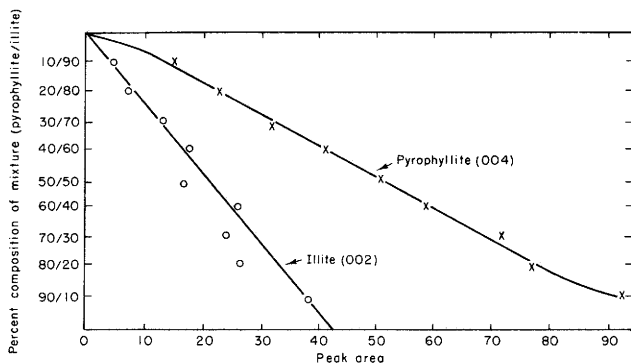


Figure 6. Plot of pyrophyllite (004) and illite (002) peak area ratios for smear slides. Approximately 3:1 ratio.

Kaolinite occurs in most of the samples but is limited in quantity to a very small percent in relation to the other clay minerals. Montmorillonite is present in "micro-boudinage"-type structures in the tightly folded portions of the clay beds and may represent small isolated lenses or beds of ash. Gibbsite ($\text{Al}(\text{OH})_3$) occurs as vein-filling material in the fractured limestones surrounding the clay-shale beds. Quartz is a common constituent in all samples. Some aragonite occurs in a small number of samples, and Na-Ca zeolites occurred in many of the samples studied.

A list of samples with their location and mineralogy is given in appendix B. Also given is a summary of semi-quantitative mineralogical data denoting the average composition of (1) the entire samples, (2) the $<2\mu$ clay fraction, (3) the $<2\mu$ fraction of the hard indurated black fissile shales and (4) the $<2\mu$ fraction of those samples taken from areas showing some hydrothermal activity and a high degree of deformation.

Rectorite

Ehlmann (1958) and Henderson (1968) describe the presence of mixed-layer clay minerals in some Paleozoic shales of northwest Utah.

Ehlmann (1958, p. 18) stated that the dark grey and black shales of the Manning Canyon Formation generally contain mixed-layer illite montmorillonite clay that shows a layering ratio of 7:3. Ehlmann pointed out that the blackest shales appeared to contain most of the well-crystallized mixed-layer clays.

Previous Studies

The first to recognize and name the clay mineral rectorite were Brackett and Williams in 1891. Caill  re (1934) worked with a regular mixed-layer, long-spacing clay mineral ($\pm 25 \text{ \AA}$) from Allevard, France, and proposed the name allevardite which is still in use by some authors today. The first person

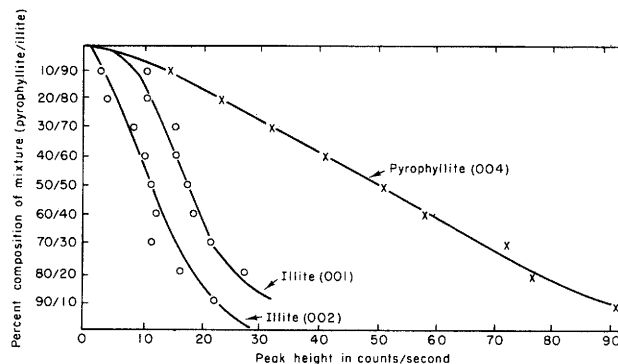


Figure 7. Plot of pyrophyllite (004) and illite (001) and (002) peak heights for smear slides.

to recognize and discuss the structure of this long-spacing mineral in detail was Bradley in 1951. He noted that the mineral was a complex, regularly stratified layer-type hydrous aluminosilicate related to the better known mica-like minerals. His interpretation was that this unusual mineral consists of contiguous pairs of pyrophyllite-like units separated by paired layers of water molecules. He described the layering as an alternation of 1 pyrophyllite unit (a fixed layer) with 1 vermiculite unit (an expandable layer). The specimen Bradley studied was predominantly monomineralic and provided excellent structural data. The fundamental periodicity or basal $d(001)$ spacing with ethylene glycol saturation in the natural state was $26.46 \text{ \AA} \pm .02 \text{ \AA}$.

Other investigators using progressively improved analytical data who have made significant studies of a regular mixed-layer clay mineral of the rectorite-allevardite type since Bradley's original work in 1951 are Heysteck (1954), Brindley (1956), Brown and Weir (1963), Kodama (1966), Cole (1966) and Hamilton (1967). All of these authors reported the mineral to be of the allevardite or rectorite type, with a basal (001) spacing of about 26.5 \AA on glycol saturation. The chart in table 2 compares the various structural interpretations of allevardite-rectorite.

All previously reported rectorite-allevardite type clay minerals except Bradley's were reported from countries other than the United States.

- | | |
|-----------|---|
| Bradley: | A rectorite from Garland County, Arkansas |
| Brindley: | An allevardite from Allevard, France |
| Kodama: | A rectorite from Baluchistan, Pakistan |
| Hamilton: | A rectorite-allevardite type mineral from New South Wales |
| Cole: | An allevardite-like mineral from Surges Bay, Tasmania |

Table 2. Summary of basal spacings $d(001)$ of rectorite from Arkansas (Bradley), Pakistan (Kodama), Utah (Henderson; Brown and Weir) and France (Brindley).

Condition of Specimen	$d(001)$ Å				
	Bradley	Kodama	Brown and Weir	Brindley	Henderson
Air-dry (natural state)	23.95	23.87 ± 0.17	24.9	24.62 ± 0.05	25.34
Air-dry (Na ⁺ saturation)		22.22 ± 0.17	22.0		22.2
Glycerol + natural state		27.39 ± 0.05	27.2		
Ethylene glycol + natural state	26.46 ± 0.02		26.5	26.47 ± 0.06	26.60
After heating (600°C for 3 hours)	19.5 ±	19.3	19.6	19.09 ± 0.02 ^{a/}	19.6 ^{b/}
After heating (350°C for 1 hour)					19.48
Air-dry (after treatment in HCl)				22.00 ± 0.05	22.0
Ethylene glycol (after treatment in HCl)					26.6

a. 450°C for 24 hours.
b. 500°C for 1 hour.

It is interesting to note that Bradley considers this long-spacing clay mineral to consist of two pyrophyllite-like layers, or one 17 Å vermiculite and one 9.3 Å pyrophyllite-like layer, plus water layers, to give a repeat distance of ±25 Å for a basal (001) spacing, with interlayer cations in the vermiculite swellable layer. Brindley's interpretation (1956) was that the 26 Å basal spacing resulted from pairs of mica-like layers equal to 20 Å linked by 0.7 Å ions of K⁺, Ca⁺⁺ per cell plus 1, 2 or 3 layers of water. He stated that swelling takes place via the pyrophyllite-like uncharged interlayer region, and that the mica-like layer does not swell. Brindley made no preference concerning K⁺ or Ca⁺⁺, but stated that either could occur, and in some cases both could be present in the structure.

Brown and Weir (1963) explained that their data showed allevardite-rectorite to be made up of pairs of dioctahedral 2:1 type layers. They noted that alternate layers are mica-like and montmorillonite-like. The mica-like layers, which do not swell, contain about 1.7 univalent cations (but predominantly Na⁺ rather than K⁺ ion) per unit cell layer; the montmorillonite-like layers, which swell, have about 0.7 univalent cations per unit cell layer. The above authors studied 3 allevardites and 1 rectorite and concluded that they were all the same mineral. Their data showed a basal spacing for air-dried material at 19.5 Å ± 1 Å and a spacing of 26.4 Å ± 1 Å after ethylene glycol saturation. Their study also showed that agreement on the nature of the interlayer region could not be reached and that they had no good explanation for the swelling of the mineral. Probably the most important conclusion reached concerning the consistency of the rectorite-type mineral was that it is made up of pairs of dioctahedral 2:1

type layers and that alternating layer regions absorb water (and some organic liquids) leading to swelling. Brown and Weir's results also showed that the kind of exchangeable cations lie in the expanding interlayer region.

Brown and Weir (1963) showed that allevardite and rectorite were, in fact, the same mineral and that rectorite had priority in name. Bradley (personal communication) also stated that the name rectorite should have preference over the much used term allevardite.¹ It is suggested, therefore, that the mixed-layer clay mineral noted by Ehlmann in 1958 and later identified by Henderson (1968) be called rectorite. The data to be presented show that this mixed-layer clay mineral relates directly to all the definitions and qualifications proposed for rectorite-allevardite by previous authors as reconciled by Brown and Weir.

The mineral described by Kodama (1966) probably compares closely with the clay mineral rectorite examined in this study. He maintains that experimental evidence from his sample of rectorite from Pakistan substantiates Brown and Weir's conclusions that rectorite is made up of pairs of mica-like (nonexpandable) and montmorillonite (expandable) layers. The Fourier transform of glycerol-solvated Mg⁺ rectorite from Pakistan gave a regular sequence with a mixing ratio of 1:1 and a mica-like layer thickness of 9.2 Å. Kodama divides the expandable layers into beidellite-like and montmorillonite-like layers. His most important conclusions are that rectorite consists of a regularly alternating sequence of paragonite-like layers and expandable layers having beidellitic and montmorillonitic compositions. Of even greater significance is Kodama's conclusion that the specific name rectorite should be confined to a regular intrastratification of Na⁺ mica (paragonite) and montmorillonite, as judged from the chemical data of the original rectorite from Garland County, Arkansas (Bradley, 1951).

Hamilton's work in 1967 on an allevardite-type clay mineral from a Permian sandstone at Maitland, New South Wales, shows it to be a 2:1 mica-montmorillonite structure with a slightly imperfect regular interstratification. His Fourier transform analysis and synthesis of 00 ℓ X-ray diffraction data indicates a complete alternation in the stacking and a strong development of the 1:1 allevardite-type layer sequence. He notes that the structure is mica-like, with a predominantly tetrahedral layer charge of -1.48 per unit cell. The interlayer cations are K⁺, Ca⁺⁺ and Na⁺. The Na⁺ ions, which are almost completely exchangeable, are believed to be concentrated in the montmorillonite interlayers. He placed the K⁺ and Ca⁺⁺ ions in the nonswelling layers, but also in small concentrations on the montmorillonite exchange site.

¹Multiple name usages in these cases are in a sense comparable with the introduction of separate names for Na⁺-montmorillonite and Ca⁺⁺-montmorillonite.

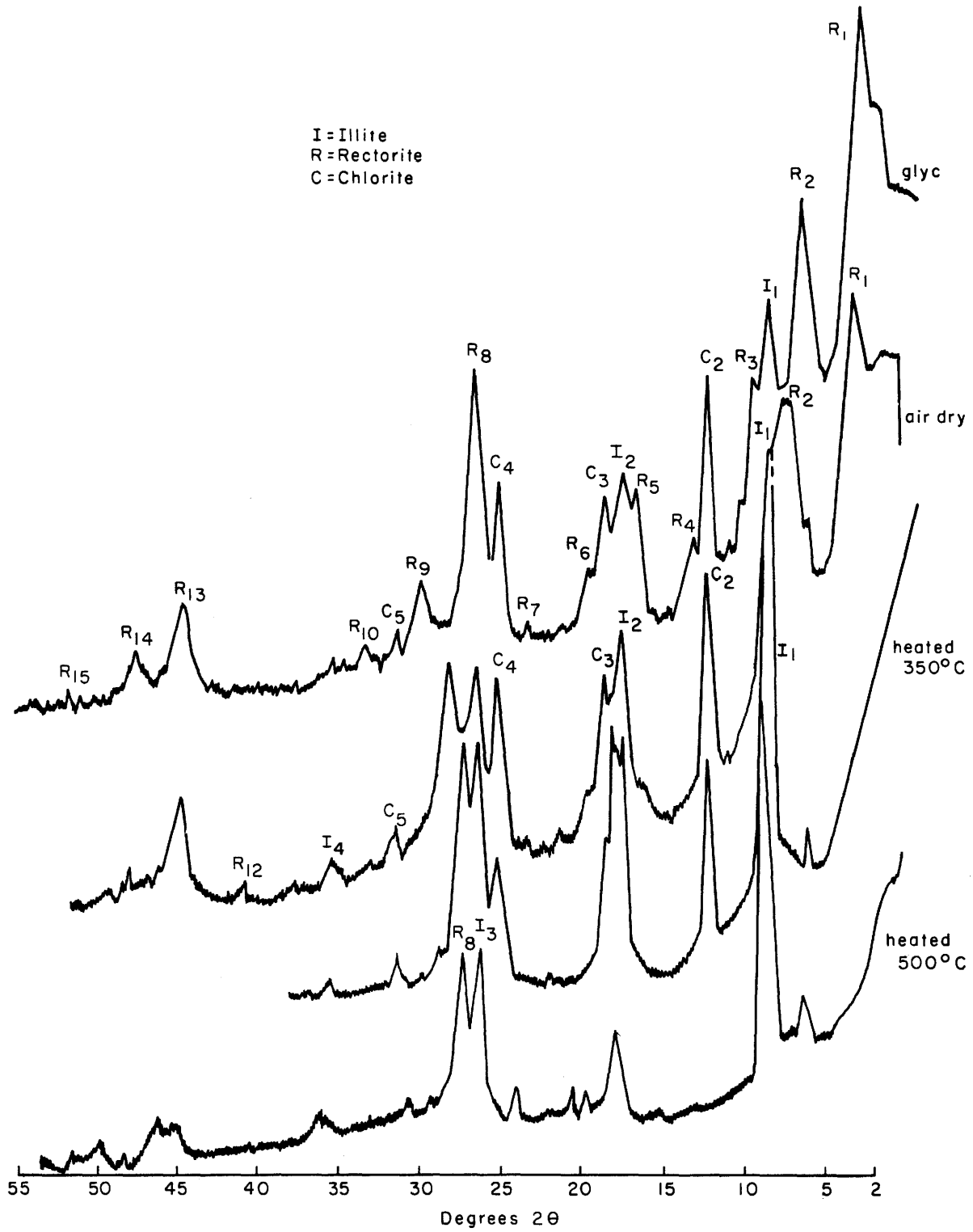


Figure 8. X-ray diffraction traces of <math>< 2 \mu</math> sample of rectorite from Utah (Manning Canyon Shale).

The Nature of Rectorite in Utah Shales

Only rectorite samples showing a sharp basal spacing at $3.6^\circ 2\theta$, and from 12 to 14 orders of $d(00\ell)$ spacings were selected for detailed study. Although many light-colored shales containing pyrophyllite also showed good rectorite traces, most of the detailed structural work was done with samples taken from outcrops of black carbonaceous shale throughout the Manning Canyon Formation. Two samples were selected from the type locality in Manning Canyon in secs. 9 and 10, T. 6 S., R. 3 W., four were taken from the Beverly Hills area, secs. 7, 8 and 9, T. 5 S., R. 1 W., and two from the Lake Mountain area, secs. 38, T. 5 S., R. 1 W. This represents a geographical area of 200 to 300 square miles.

The rectorite in the Manning Canyon shales shows a regular alternation of a nonexpandable mica-

like layer with a swellable montmorillonite-like layer. Studies of $d(00\ell)$ X-ray diffraction data have shown that there is an essentially complete alternation in the stacking sequence and that a 1:1 (rectorite-type) later sequence is strongly developed. The basal (001) reflection for a sample air-dried at room temperature is 25.34 \AA , and with ethylene glycol saturation in the natural state a basal reflection of 26.60 \AA is recorded (figure 8). All data compare favorably with Bradley's original rectorite from Garland County, Arkansas, and with Kodama's rectorite from Baluchistan, Pakistan.

A sample of Bradley's Arkansas rectorite was obtained by the author and analyzed on the same diffractometer to substantiate similarities or differences in structural parameters (figure 9). Structural interpretation of the alternating sequences of the Utah and Arkansas samples showed a remarkable similarity (table 3). The suggested structure for the Utah rectorite is one fixed layer of 9.6 \AA and an

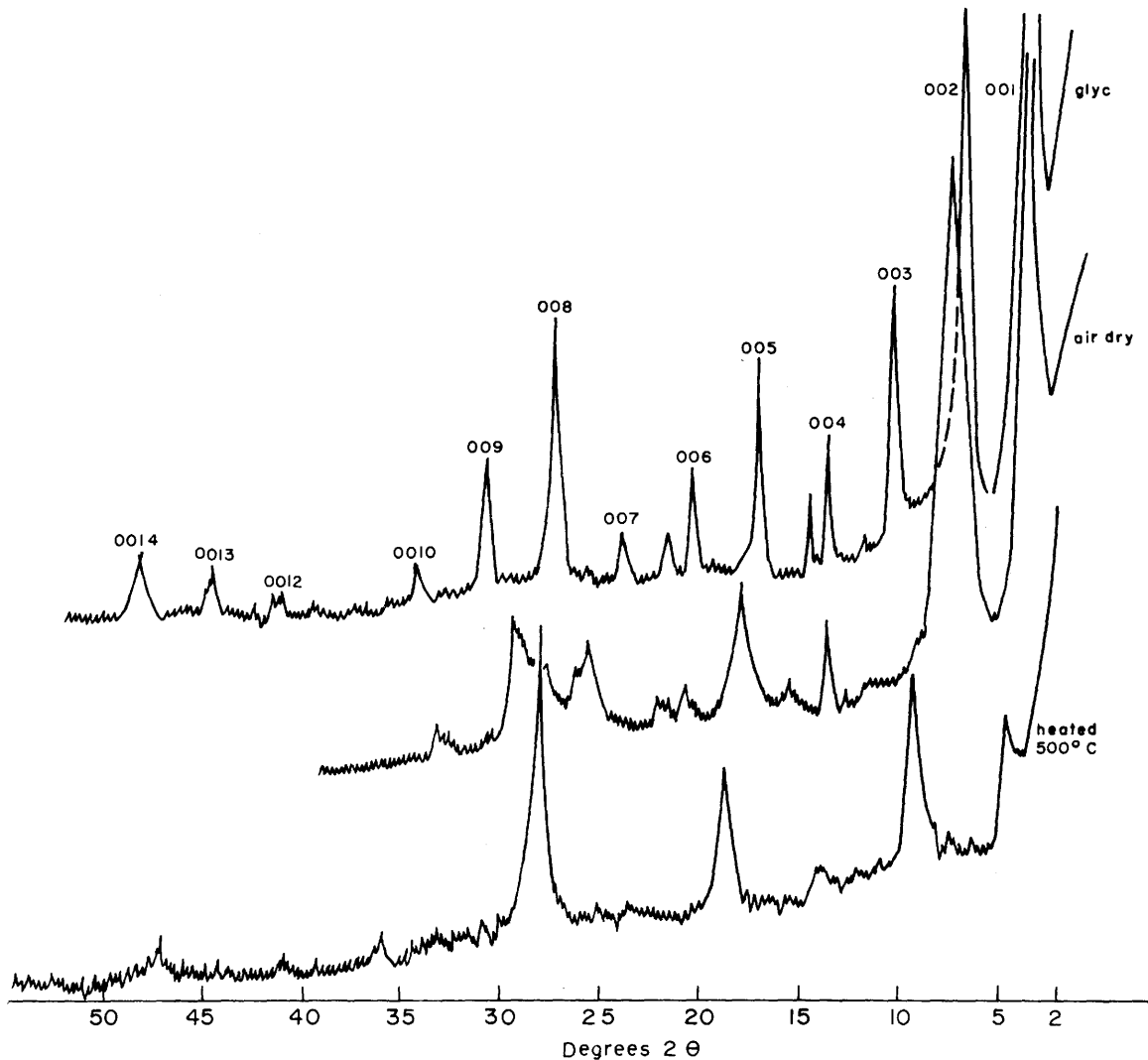


Figure 9. X-ray diffraction traces of $<2 \mu$ sample (oriented) of rectorite from Arkansas.

expandable layer, varying from 10 Å to 17.0 Å. The 9.6 Å fixed layer would fit the structure of paragonite, a Na⁺ mica as suggested by Kodama (1966), rather than the 9.2 Å first suggested by Bradley (1951) or the 10 Å muscovite suggested by Brindley (1956). The 9.6 Å fixed layer also fits the structural interpretation of Bradley.

The rectorite noted in the samples studied in this investigation would fit Kodama's definition, as the chemical analysis of most samples show a high Na⁺ content (see chemical analysis of pyrophyllite samples, table 15). The definition of the 9.6 Å paragonite layer (a sodium muscovite) also helps substantiate the definition of a rectorite.

Detailed mineralogic studies of the clay minerals by the author confirm the general observations of Ehlmann but modify some analytical details. Also, the presence of a regular mixed-layer, long-spacing clay mineral in the Paleozoic shales instead of the previously reported random mixed-layer clay mineral is proven. It appears to have a well-defined structure in the black highly carbonaceous shales of the Manning Canyon Formation. The data show that this long-spacing mineral is not necessarily restricted to black shale units but is moderately abundant in light grey pyrophyllite-bearing shales, and also occurs in the multicolored light brown to tan shales throughout the Manning Canyon Formation.

All previously reported rectorite shows a fibrous ribbonlike morphology. The rectorite from Utah could not be separated from the other mineralogical constituents for study of its morphology and chemical analysis, but electron micrographs of the clay size fraction of several black shale samples show good hexagonal crystals among amorphous masses of clay material. This suggests that the Utah rectorite is not fibrous but occurs as pseudo-hexagonal crystals.

X-ray Data

Data from X-ray investigations of the basal (001) reflections of the mixed-layer clay mineral rectorite are shown in tables 4-12. The 2θ positions of all peaks observed on X-ray traces and the calculated $d(00\ell)$, $d(001)$ and $1/d(00\ell)$ values for each treated sample are listed. $1/d(00\ell)$ values were calculated for use in the plot of (00 ℓ) spacings shown in table 13. Observed intensities are noted for convenience of comparison. This chart shows in graphic form the regular alternation of (00 ℓ) spacings of Utah and Arkansas rectorite. The (00 ℓ) spacings are plotted as a function of $1/d(00\ell)$. The height of the line above base represents the observed intensity $[I(00\ell)]$ of each line.

A $d(001)$ basal spacing of 26.60 Å was recorded for the Utah samples saturated with ethylene glycol; several Na⁺ saturated samples had $d(001)$

Table 3. Summary of the structural interpretations of the clay mineral rectorite from Arkansas and Utah.

Arkansas Rectorite (Bradley)	Utah Rectorite (Henderson)
(a) Air-dry = 23.95 Å 9.6 Å = 23.95 Å 13.35 Å	(a) Air-dry = 25.34 Å 9.6 Å = 25.34 Å 15.74 Å
(b) With glycol = 26.46 Å ± 0.02 9.6 Å = 26.5 Å 17.0 Å	(b) With glycol = 26.60 Å 9.6 Å = 26.6 Å 17.0 Å
(c) Heated = 19.11 Å 9.6 Å = 19.2 Å 9.6 Å	(c) Heated to 350° C = 19.48 Å 9.6 Å = 19.6 Å 10.00 Å
	(d) Heated to 500° C = 19.60 Å 9.60 Å = 19.60 Å 10.00 Å
	(e) Na ⁺ saturated (air-dry) = 22.2 Å
	(f) HCl treatment (air-dry) = 22.0 Å (glycol) = 26.6 Å

spacings of 22.0 Å. Samples heated at 500° C for 1 hour show a collapse of this structural dimension to 19.60 Å, and after heating at 350° C for 1 hour, a collapse to 19.48 Å.

Tables 4 through 9 represent the structural data for rectorite from Utah, and tables 10, 11 and 12 represent X-ray data for Arkansas rectorite.

Discussion of Data

The rectorite in the Manning Canyon shale appears to be in two distinct forms: a paragonite layer and a thick swellable layer, and the other a paragonite layer and a thin swellable layer. It is very likely that a large amount of elemental carbon found in the shales accounts for the variation in the thickness of the swellable layers. The carbon probably burns off only partially at 350° C (the temperature to which most of the samples were heated), and it is completely gone from samples heated to 500° C (figure 8). Walker (1967) in his studies of carbon coatings on vermiculites and other clay minerals demonstrated the effect carbon can have on X-ray traces of clay minerals.

The amount of carbon in the Manning Canyon shale is almost three times that in clays in Walker's studies. X-ray traces of heated samples (especially those heated to 500° C) show a clean split at 26.6° 2θ showing rectorite moving up to 27.5° and leaving the illite (003) and quartz peaks at their usual position of 26.4° and 26.6° respectively (figure 8).

Table 4. (00ℓ) X-ray diffraction data for Utah rectorite.

(Untreated - air-dry sample <2μ material)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)	1/d(00ℓ)
1	3.60°	24.52 Å	24.52 Å	.04078
2	7.20	12.26	24.52	.08156
3	10.80	8.173	24.51	.1223
4	14.60	6.066	24.26	.1648
5	18.50	4.795	23.97	.2085
6	22.50	3.951	23.70	.2531
7	25.80	3.453	24.17	.2896
8	29.10	3.065	24.52	.3262
9				
10	36.60	2.452	24.52	.4078
11				
12	44.28	2.043	24.51	.4894
13	48.20	1.886	24.51	.5302
14				
		Average = 24.33 Å		

Table 5. (00ℓ) X-ray diffraction data for Utah rectorite.

(Blender treated - air-dry sample <2μ material)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)
1	3.6°	24.5 Å	24.5 Å
2	7.35	12.0	24.0
3	10.40	8.5	25.5
4	16.3	5.43	27.15
5	19.7	4.72	23.6
6	21.3	4.17	25.02
7			
8	28.25	3.156	25.25
9	31.6	2.83	25.47
10	35.5	2.527	25.27
11			
12	41.0	2.20	24.2
13	44.8	2.02	26.26
		Average = 25.34 Å	
		9.60 Å } = 25.34 Å	
		15.74 Å }	

Table 6. (00ℓ) X-ray diffraction data for Utah rectorite.

(Ethylene glycol saturation)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)	I obs	1/d(00ℓ)
1	3.33°	26.6 Å	26.6 Å	100	.03759
2	6.67	13.24	26.24	- 90	.07552
3	9.85	9.02	27.06	+ 50	.1086 (1102)
4	13.25	6.695	26.7	+ 50	.1494
5	16.75	5.29	26.45	- 40	.1890
6	20.0	4.44	26.64	+ 20	.2252
7	23.5	3.78	26.45	- < 5	.2646
8	26.67	3.34	26.72	+ 50	.2994
9	30.16	2.96	26.64	+ 20	.3378
10	33.5	2.677	26.77	+ < 5	.3745
11					
12	42.0				
13	44.75	2.023	26.30	- 10	.4943
14	47.75	1.903	26.64	o 10	.5255
		Average = 26.60 Å _{Kα1}			
		Mean d(001) = 26.60 Å ±			
		9.6 Å } = 26.6 Å = Paragonite + Swellable Layer			
		17.0 Å }			

Table 7. (00ℓ) X-ray diffraction data for Utah rectorite.

(Na⁺ saturation)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)
1	3.8°		23.0 Å
2	8.0	11.04 Å	22.1
3	12.3	7.19	21.6
4	16.1	5.50	22.0
5	19.75	4.49	22.45
6	25.0		
7	28.1	3.17	22.19
			Average = 22.2 Å

Table 8. (00ℓ) X-ray diffraction data for Utah rectorite.

(Heated at 350° C for 1 hour)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)
1			
2			
3			
4	18.2°	4.874 Å	19.49 Å
5			
6	27.6	3.231	19.38
7	32.0	2.796	19.57
			Average = 19.48 Å
			9.60 Å } = 19.48 Å
			9.88 Å }

Table 9. (00ℓ) X-ray diffraction data for Utah rectorite.

(Heated at 500° C for 2 hours)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)
	4.5°	19.60 Å	19.60 Å
	6.4	13.6	
2	18.05	4.91	
	27.4	3.25	
	35.66	2.515	
4	36.20	2.47	
	46.6	1.95	
Completely collapsed paragonite			
2	18.1	4.9	9.82
3	27.4	3.25	9.75
5	46.6	1.95	9.75
			Average Paragonite = 9.6 (or Muscovite = 9.9)
			(2) 9.82 } = 9.80
			(3) 9.75 }
			(4) 9.88 }
			(5) 9.75 }
			9.6 Å Paragonite
			9.9 Å Muscovite

Table 10. (00ℓ) X-ray diffraction data for rectorite from Garland County, Arkansas.

<2μ sample heated at 500° C (2 hours)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)	I obs	1/d(00ℓ)
1	4.4°	20.082 Å	20.08 Å	80	.04803
2	9.3	9.509	19.02	90	.1051
3	14.0	6.325	18.96	10 B	.1581
4	18.25	4.860	19.40	50	.2057
5	24.6	3.618	18.09	< 5	.2763
6	28.0	3.186	19.11	100	.3138
7	32.8	2.730	19.11	< 5	.3663
		Average = 19.11 Å			

Table 11. (00ℓ) X-ray diffraction data for rectorite from Garland County, Arkansas.

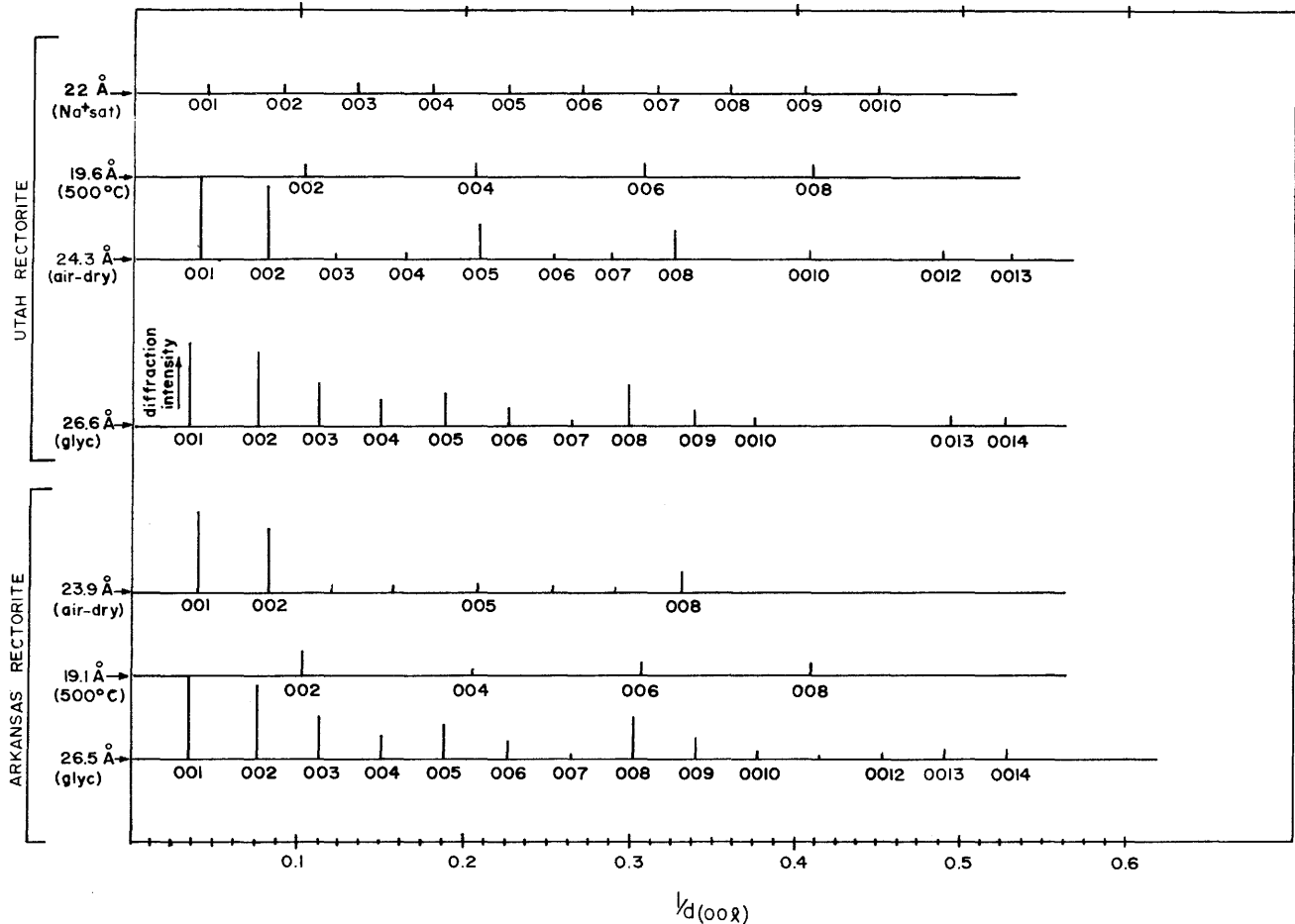
Air-dry samples <2μ (15 hours)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)	I obs	1/d(00ℓ)
1	3.70°	23.879 Å	23.87 Å	100	.04189
2	7.40	11.946	23.92	90	.08371
3					
4	14.2	6.236	24.94		.15966
5	18.5	4.795	23.97		.20855
6	22.5	3.951	23.70		.25310
7	26.0	3.426	23.98		.2918
8	29.6	3.017	24.13		.3314
9	34.4	2.606	23.45		.3837
		Average 23.95 Å			

Table 12. (00ℓ) X-ray diffraction data for rectorite from Garland County, Arkansas.

(Ethylene glycol treated <2μ sample)
Cu Kα (λ = 1.5418 Å) radiation

00ℓ	2θ	d(00ℓ)	d(001)	I obs	1/d(00ℓ)
1	3.37°	26.77 Å	26.77 Å	100	.03749
2	6.67	13.24	26.48	90	.07552
3	10.00	8.838	26.51	50	.1131
4	13.37	6.617	26.47	25	.1511
5	16.75	5.288	26.44	40	.1891
6	20.10	4.414	26.48	20	.2265
7	23.55	3.774	26.42	<5	.2649
8	26.95	3.305	26.44	50	.3025
9	30.38	2.940	26.46	25	.3401
10	33.85	2.646	26.46	<5	.3779
11					
12	40.90	2.204	26.45	<5	.4537
13	44.45	2.036	26.47	10	.4911
14	48.10	1.890	26.46	10	.5291
		$26.46 \text{ Å } K_{\alpha 1}$ $26.48 \text{ Å } K_{\alpha 2}$ Mean d(001) = $26.46 \pm 0.02 \text{ Å}$ $\left. \begin{matrix} 9.6 \text{ Å} \\ 17.0 \text{ Å} \end{matrix} \right\} = 26.5 \text{ Å}$			

Table 13. Plot of $1/d(00\ell)$ values for rectorite from Arkansas and Utah showing regularity of layer sequence.

Because the Manning Canyon shale is not monomineralic but contains some kaolinite or dickite, chlorite, pyrophyllite and muscovite, it was impossible to obtain a good chemical analysis of the rectorite. No attempt was made to develop a structural formula for this material since it would be difficult to distribute the cation populations correctly without additional information. The chemical data for Utah rectorite (table 14) were taken from samples showing the highest percentage of mixed-layer material and the lowest percentage of other clay minerals.

Various techniques were used in attempts to isolate the rectorite from the other clay minerals. Size separations were made of several samples, but chlorite and illite persisted in the smaller size fractions down to 0.1μ . The 1μ and 2μ fractions were treated with hot 1N and 5N HCl for periods of $\frac{1}{2}$ to 1 hour to destroy the chlorite. This technique was generally successful in destroying most of the chlorite, leaving illite and rectorite. X-ray diffractometer traces also show increased resolution of the clay peaks after acid treatment. Size fractionation data show that rectorite occurs primarily in the larger size

fractions (16μ - 32μ). This is contrary to Kodama's work in which he isolated his mixed-layer material into 0.5μ to 0.1μ size fractions.

In summary, the extensive X-ray data supported by chemical data clearly show that this unusual mineral, occurring in the Manning Canyon shale, is a regularly stratified mixed-layer clay mineral of the allevardite or rectorite type. Structural interpretations emphasize a regular layering of the clay minerals.

Spot checks of the electron density plots for this rectorite show that it fits perfectly the curves proposed by Hamilton (1967) and Brindley (1956). All experimental evidence also supports conclusions by Bradley (1951), Brindley (1954), Kodama (1967), Brown and Weir (1963) and others, that rectorite is made up of pairs of mica-like (nonexpandable) and montmorillonite (expandable) layers.

Pyrophyllite

Pyrophyllite has the same structure as talc with Al^{+++} completely replacing Mg^{++} . The structure is a 2:1 layered structure in which a sheet of octahedrally

Table 14. Chemical analysis of Manning Canyon (black) shales containing rectorite.

Component	Percent Composition		
	Sample 1	Sample 2	Sample 3
SiO ₂	50.07	50.72	48.0
Al ₂ O ₃	23.19	24.43	32.6
Fe ₂ O ₃	7.80	7.35	3.4
TiO ₂	1.06	1.06	1.2
CaO	3.25	2.20	1.0
MgO	1.21	2.08	1.0
Na ₂ O	.55	.86	.6
K ₂ O	.70	1.98	
P ₂ O ₅	.53	.34	
MnO	.11	.08	
L.O.I.	<u>11.46</u>	<u>8.90</u>	<u>12.0</u>
TOTAL	99.93	99.96	99.8
(Carbon)	2.36	.89	

1. Black carbonaceous clay in floor of open pit mine, secs. 8 and 9, T. 5 S., R. 1 W. (in the floor of the Clinton Clay mine).
2. Weathered black paper shale (fissile), sec. 7, T. 5 S., R. 1 W. (west of the Clinton Clay mine).
3. Black shale—unaltered, sec. 9, T. 6 S., R. 1 W. (Mercer Canyon).

coordinated Al⁺⁺⁺ ions is sandwiched between two sheets of linked SiO₄ tetrahedra. In contrast to muscovite, there is little or no substitution of Si by Al, and the pyrophyllite layers are electrically neutral.

Nature of Pyrophyllite in Utah Shales

The occurrence of pyrophyllite in shales in northwest Utah was reported by Crawford and Buranek (1948) and Hyatt (1956) and was studied later by Ehlmann (1958) and Henderson (1968), who agree that its wide geographic distribution and disseminated nature in the shales and limestones throughout the Lake Mountains Range and its occurrence in widely distributed areas of the Oquirrh and Traverse ranges and along the Wasatch Front support the conclusion that diagenesis must be considered in any studies of origin. The fact that pyrophyllite occurs in shales and limestones that are practically

untouched by metamorphism or hydrothermal activity as well as in sedimentary rocks that have undergone some degree of deformation (tight folding and faulting) makes it difficult to rule out the theory of a diagenetic origin. Because hydrothermal activity is apparent in places in the highly deformed shales and limestones, metamorphism must also be considered.

The mineral assemblage of samples containing pyrophyllite also includes kaolinite, illite, montmorillonite, chlorite and gibbsite. Some evidence of primary mineral alteration to zeolites is also present within the area studied.

Pyrophyllite occurs in 90 percent of the 130 shale-clay samples studied and represents an average of 20 percent of the -2 μ material of all samples (see figure 25). In the black-brown unaltered shales, the average -2 μ material was ± 17 percent pyrophyllite, and in the areas showing some degree of alteration or strong deformation, it represents ± 40 percent of the clay fraction. A summary of quantitative data appears in the appendix. Its occurrence is unusual in that it is not restricted to any specific stratigraphic unit, except that it appears to be more strongly developed in the Manning Canyon Formation and is found over a large geographic area. Pyrophyllite was found in Cambrian shales along the Wasatch Front. The occurrence of pyrophyllite in the Utah shales is probably related to composition and permeability of the sedimentary rocks involved. Genesis is discussed in detail in the section on origin of pyrophyllite-rectorite.

Pyrophyllite occurs in several different arrangements throughout the area studied:

1. As disseminated booklets and aggregates developed with the mass of clay-shale beds.
2. As vein fillings along fracture zones where it forms well-crystalized masses of pure pyrophyllite. In some masses of pure pyrophyllite is associated with and appears to grade into gibbsite (Al₃(OH)₃) near the center of the fracture zone.
3. As individual randomly scattered booklets or "eyes" in highly carbonaceous fine-grained limestones surrounding the shale beds.
4. In highly altered shales where activity of hydrothermal solutions is evident, and in black to brown shales where no alteration other than some surface oxidation has taken place.

Probably the most striking feature concerning the occurrence of pyrophyllite in this area is the fact that it is not restricted to any stratigraphic zone or to areas of strong deformation, but it is present in pelitic sediments with a geographic distribution of several hundred square miles.

In studying the association of pyrophyllite with other clay minerals in the area, it was found that the

Table 15. Samples of pyrophyllite from study area and pyrophyllite from Nagano Prefecture, Japan, Mariposa County, California, and Robbins, North Carolina.

Lake Mountain, Utah			Mariposa County, California			Nagano, Japan			Robbins, North Carolina	
\bar{A}	I/I ₁	hKl	\bar{A}	I/I ₁	hKl	\bar{A}	I/I ₁	hKl	\bar{A}	I/I ₁
9.30	80	002	9.14	40	002	9.21	60	002	9.5	46
4.575	60	004	4.57	50	004	4.58	50	004	4.68	11
4.395	20	110,021	4.15	20	111,112	4.40	20B	110,021	4.43	86
4.17	15	112,111	3.87	5	113,002	4.17	15B	112,111	4.15	34
3.33	5	113	3.34	20-40	113	3.08	100	006	3.07	100
3.04	100	006	3.04	100	006	2.97	2	115,114	2.56	57
2.52B	15	132,200	2.52	20	132,200	2.59	5	130	2.42	72
2.404	20	204,132	2.40	40	204,132	2.55	10	200,132	2.34	6
2.292	5	008	2.29	20	008	2.44	15	202,132	2.15	23
2.14	5	206,134	2.14	10-20	206,134	2.31	5	008	2.06	23
2.08	5	204	2.07	10	204	2.17	5	134,204	1.89	6
2.05	5	136	2.04	10	136	2.09	5	206	1.83	11
1.88	2	136	1.88	5	136	2.07	5	136	1.68	11
1.862	5		1.83	40	010	1.895	2	136	1.64	17
1.830	20	010	1.64	20-40	138	1.848	15	010	1.58	6
1.69	2	208	1.621	10-20	2010	1.692	5	208	1.49	40
1.640	5	138	1.567	0.25	208	1.650	10B	138	1.43	6
1.577	5		1.522	1	012	1.542	5	012	1.38	11
1.490	10	060	1.485	2-3	060,332 334	1.492	10	060		
1.437	2	1310	1.463	0.5-1	062,330	1.475	2	062,332		
1.380	10	2010	1.432	0.5	1310	1.437	2	1310		
1.368	10	1312	1.419	0.5	2012	1.388	10	2010		
1.33	5	338,066	1.377	3	2010	1.373	10	1312		
			1.362	3	1312					
1.31	5	0014 1312	1.344	0.5	344					
			1.328		338,066					
1.280	5	206,262	1.307	1-2	0014 206,262					
1.266	5	264,400	1.264	1-2	264,400					

Table 16. Chemical analysis of three shale samples containing pyrophyllite from the Clinton mine in the Beverly Hills district.

Component	Percent		
	Sample 106	Sample 107	Sample 118
SiO ₂	64.47	64.44	64.08
Al ₂ O ₃	23.27	23.49	25.70
Fe ₂ O ₃	0.76	0.74	0.93
TiO ₂	1.00	0.96	1.26
CaO	0.14	0.15	0.03
MgO	0.31	0.28	0.08
Na ₂ O	4.98	5.06	0.39
K ₂ O			0.77
	<u>94.93</u>	<u>95.12</u>	<u>93.26</u>
Ign. Loss	<u>4.46</u>	<u>4.46</u>	<u>6.55</u>
	99.39	99.58	99.81

abundance of rectorite is inversely proportional to that of pyrophyllite (figure 26). There is very little literature available on such an association of clay minerals. Pyrophyllite occurs everywhere that rectorite was found except in the samples taken near Five Mile Pass, secs. 34, and 35, T. 6 S., R. 3 W., and near the Salt Lake County gravel pits on Wasatch Boulevard in Salt Lake City, T. 2 S., R. 1 E. The rectorite-pyrophyllite association appears to be restricted to the Manning Canyon Formation.

X-ray Data

Randomly oriented powder patterns of vein pyrophyllite from the Lake Mountain area in Utah show that the Utah pyrophyllite is well-ordered material. X-ray traces of randomly oriented samples of Utah and North Carolina pyrophyllite are shown for comparison purposes in figures 10, 11 and 12. Samples of pyrophyllite from La Rioja Province, Argentina, and Robbins, North Carolina, were also analyzed. The North Carolina sample is the same material used for the standard API 49 studies. Oriented slides of -2μ material showed strong basal $d(00\ell)$ spacings at (002)=9.21 Å; (004)=4.57 Å; (006)=3.04 Å; (008)=2.29 Å and (0010)=1.83 Å. Table 15 shows the X-ray data for pyrophyllite from Utah, California, North Carolina and Japan for purposes of comparison.

Chemical Data

Table 16 is a chemical analysis of three shale samples containing pyrophyllite from the Clinton mine in the Beverly Hills district,¹ secs. 8 and 9, T. 5 S., R. 1 W. The Na₂O content indicates the presence of rectorite.

Differential Thermal Analysis (DTA)

Differential thermal curves for three selected samples of vein-type pyrophyllite taken from the Lake Mountain area are compared with a disseminated-type pyrophyllite-bearing clay from the Clinton region in figure 13.

All of the curves show broad endothermic peaks between 550° and 650° C and are typical of pyrophyllite. Dehydroxylation is slow because of the structural fit of OH⁻ ions and because no excess cations or water are inherent in the structure. The small splits visible in the endothermic peak are probably the result of free quartz in the sample material or of the presence of impurities.

Grim (1968, p. 290) shows a broad endothermic peak for North Carolina pyrophyllite between 800°-900° C and a sharp endothermic peak at about 200° C. Van Der Marel (1956) showed DTA curves for pyrophyllite and made special note of the fact that $<2\mu$ material had a broad endothermic peak between 600°-700° C, whereas coarser-powdered material showed a broad endothermic peak between 700°-800° C. He noted also the influence of particle size, disordered structure, ion substitution and other factors that influence the shape and intensity of the thermal curves of clay minerals.

Chlorite

The mineral chlorite identified in this study appears to be of two different types. One type, found in the clay-shales, seems to be a natural trioctahedral Mg⁺⁺ chlorite with a standard unit cell c-dimension of 14.0 Å. The other type, found in limestones interbedded with the shales, shows some peculiar characteristics. It appears to be similar to a chlorite-vermiculite mixed-layer clay and has a smaller unit cell c-dimension than regular trioctahedral chlorite (table 17).

X-ray Data

The smaller (d) spacings shown for chlorite in sample CLN 130 and 131 suggest that it is either a dioctahedral type material or has some replacement of Al⁺⁺⁺ for Mg⁺⁺ in the brucite layer, causing a reduction in the c-dimension. It is also possible that the brucite layer has been replaced by a gibbsite layer, accounting for the smaller unit cell dimension.

Grim (1968, p. 102) noted that various numbers of the chlorite group differ from each other in the kind and amount of substitutions within the

¹Chemical analysis was done in 1965 by International Pipe and Ceramics Corporation Laboratories. These data are published with their permission.

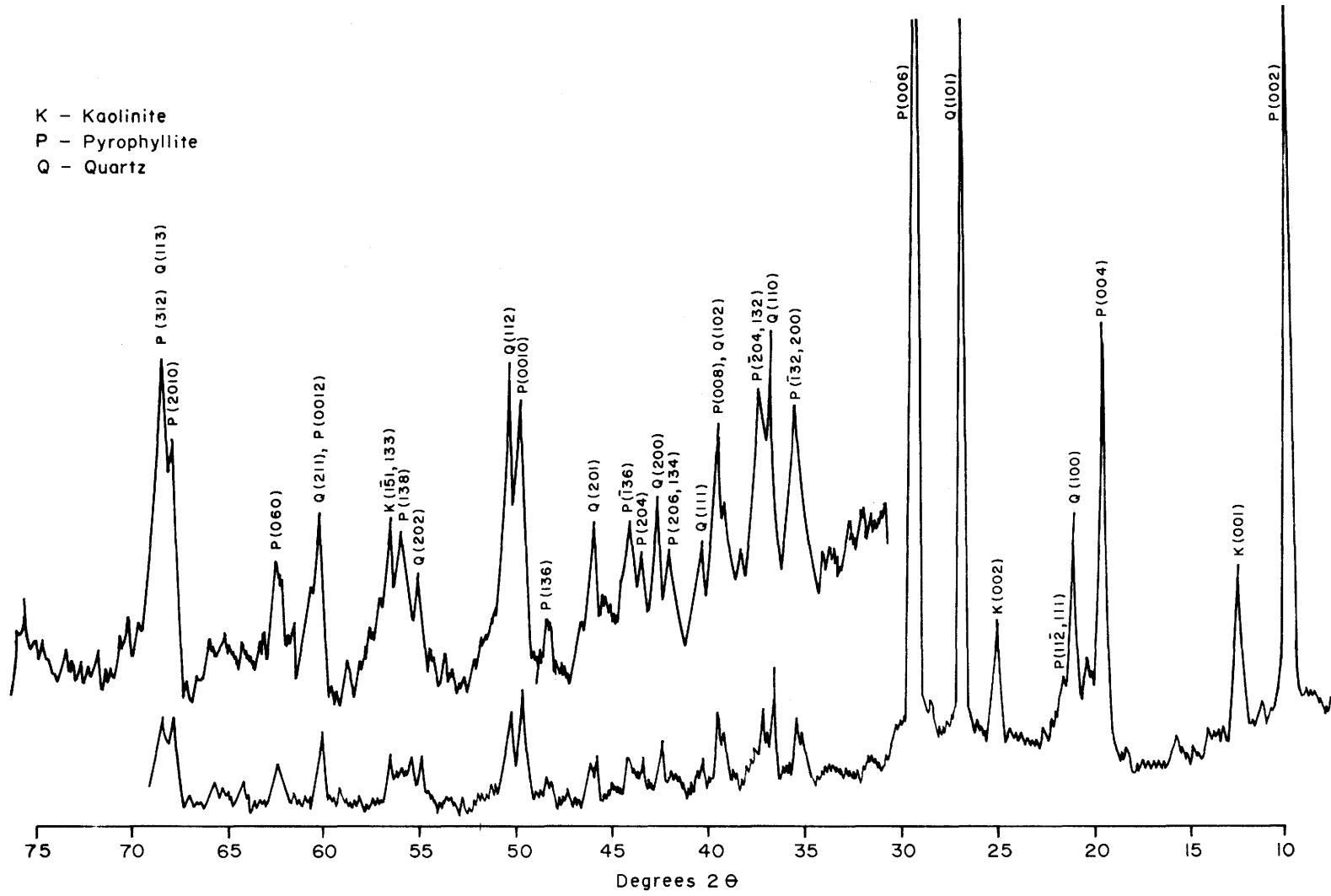


Figure 10. X-ray diffraction trace of bulk sample Lake Mountain No. 221.

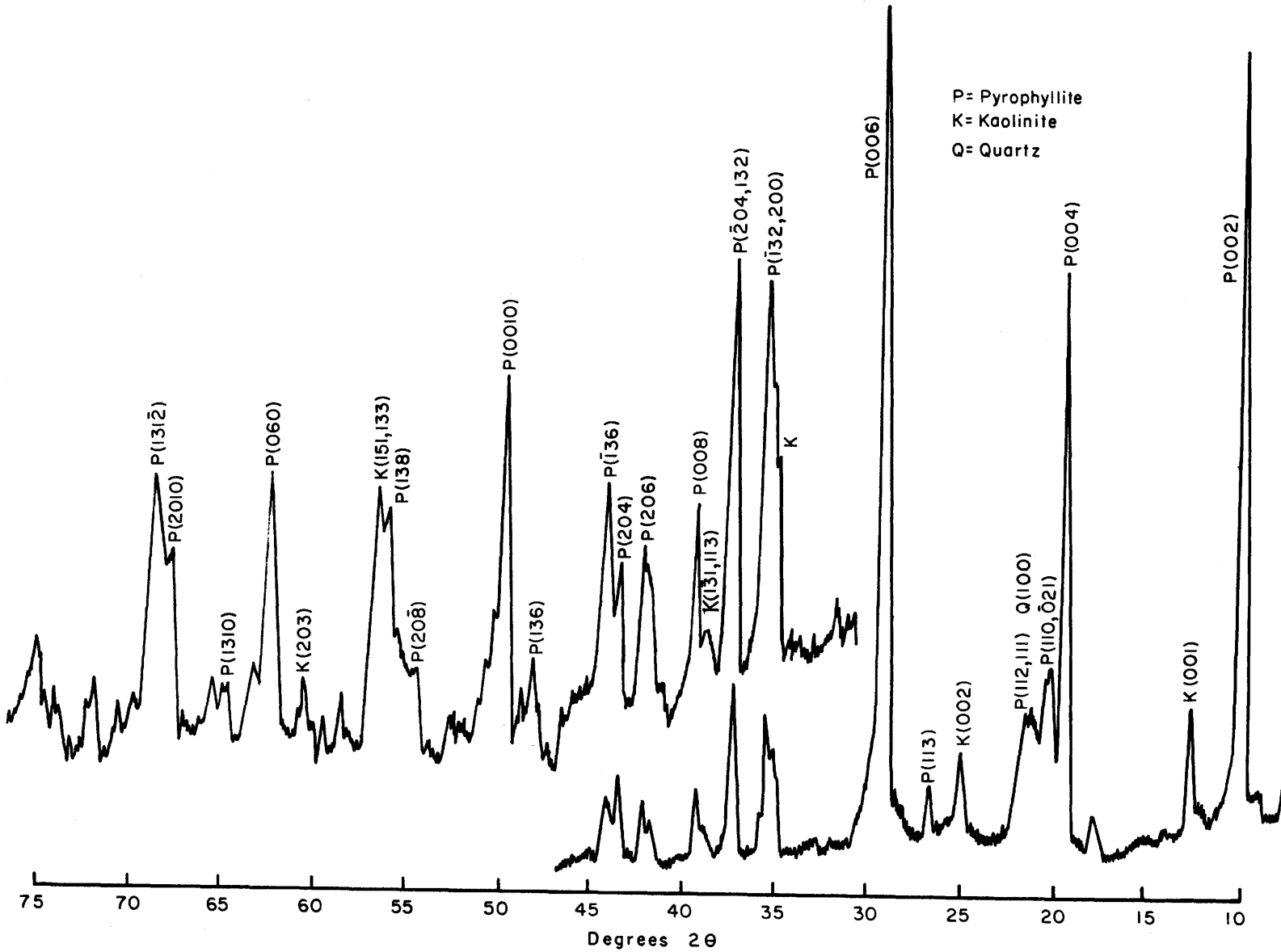


Figure 11. X-ray diffraction trace of bulk sample Lake Mountain No. 202.

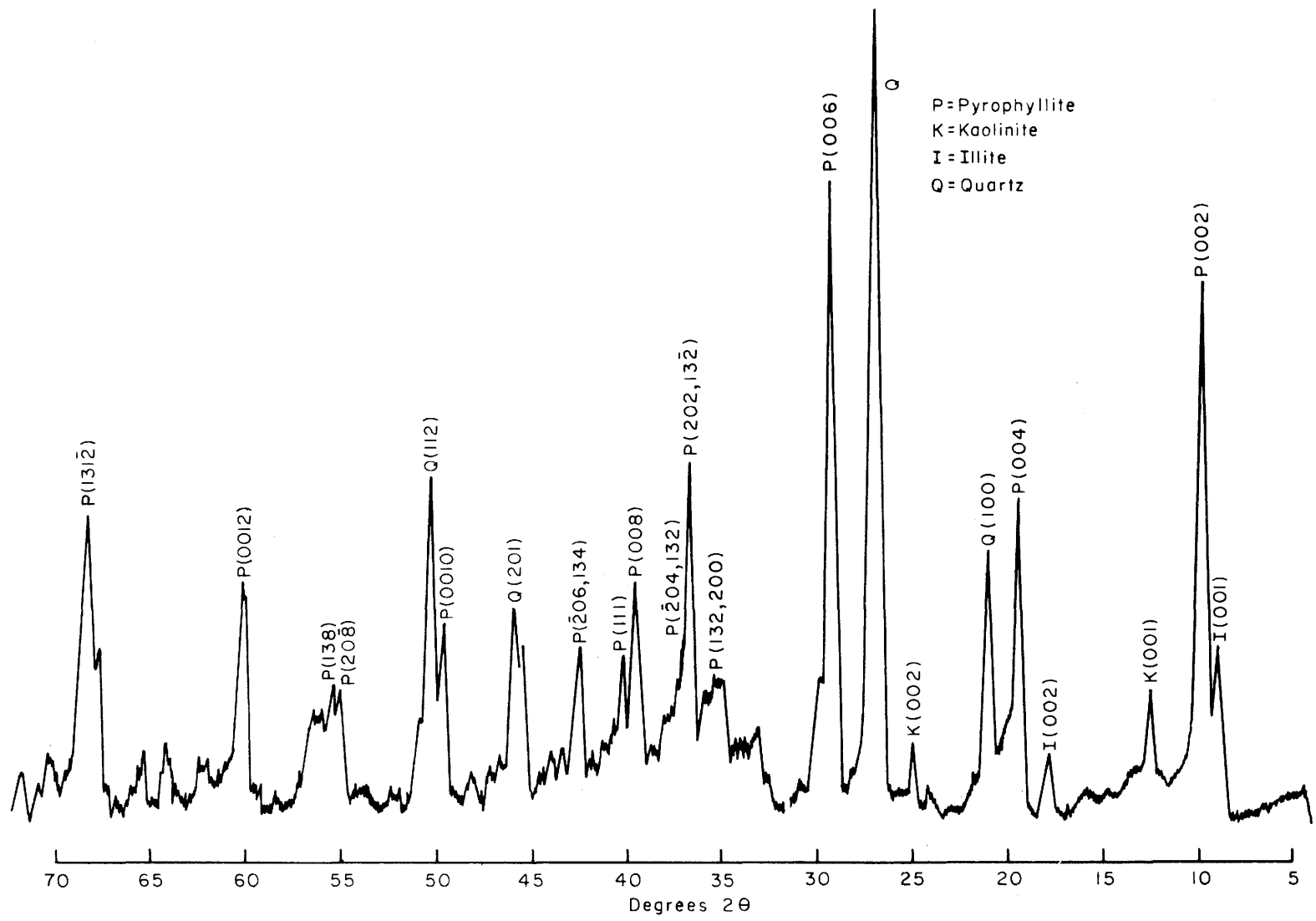


Figure 12. X-ray diffraction trace of sample API 49, Robbins, North Carolina (bulk pack of pulverized commercial grade material).

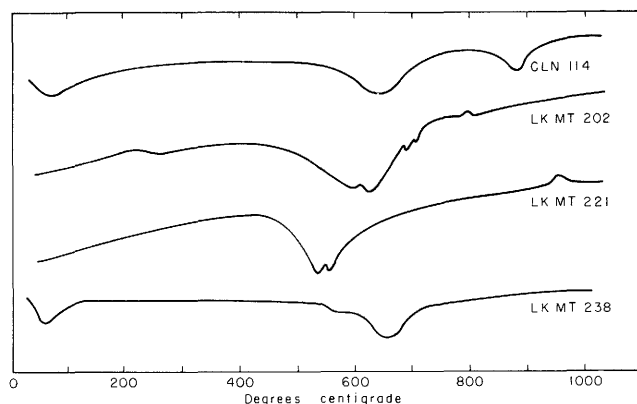


Figure 13. Differential thermal analysis curves of pyrophyllite samples from Utah.

brucite layer. Brindley (1961) pointed out that the basal spacing of chlorites varied from about 14.1 to 14.35 Å as the layer charge per unit cell decreased from 1.5 to about 0.5.

Sudo and others (1954) noted the possibility of a dioctahedral chlorite which contained pyrophyllite-like and gibbsite-like layers. They also identified chlorite containing a gibbsite layer interleaved between two adjacent silicate layers. This lattice had a c-dimension of 14.0 Å. One of the interesting things about Sudo's studies was that he attributed the origin of the gibbsite layer in the chlorite structure to the acid condition in a highly aluminous system of rocks. Albee (1962) and others have shown that the basal spacing for chlorite decreases with Al^{IV} content. Since the samples studied in this investigation are highly indicative of an aluminous system, it seems reasonable to assume that some replacement by Al^{IV} has taken place in the structure; this substitution probably accounts for the smaller unit cell dimension.

Some chlorite samples show a slight reduction of peak heights on X-ray traces when heated as low as 320° C for 1 hour (figures 14, 15) and a further reduction when heated to 480° C for 1 hour. X-ray traces also show that the chlorite is almost entirely gone when heated to 540° C for 1 hour (figures 16, 17). There appears to be a slight shift in the basal reflections from glycolated to heated traces in some samples.

Weaver (1956) noted in his studies of chlorite-vermiculite mixed-layer clays that when the sample is heated to 400° C, approximately 50 percent of the layers collapse to 10 Å and the resulting X-ray curve has peaks at 12.6 Å (10 Å/14.142 Å), 8.0 Å, 4.90 Å and 3.49 Å which are average values obtained by interaction of the 14.2 Å (00 ℓ) series. He reported that when the sample is heated to 550° C and the OH^- is removed from the chlorite interlayer positions, the second, third and fourth order chlorite reflections are destroyed and the curve contains only an 11.6 Å reflection formed by the 10 Å and 13.8 Å (with the loss of OH^- , the chlorite shrinks from 14.2 Å to approximately 13.8 Å).

Upon heating, the basal reflections of some of the samples show a change in intensity, with the (001) reflection getting larger or broader as the (002) and (003) reflections get smaller (figure 14). Brindley and Ali (1950) attribute this progressive change in basal reflections in chlorite to the gradual breakdown of the brucite layer while the mica layer remains unaffected.

The chlorite traces shown in figures 15 and 16 appear to fit Weaver's (1956) conclusions for a mixed-layer chlorite-vermiculite type clay mineral.

Table 17. X-ray data for three samples of chlorite from limestone stringers.

Sample	(d)Å										
	Glycol				Heated (320° C)				Heated (480° C)		
	001	002	003	004	001	002	003	004	001	002	003
CLN 130 (Chlorite)	13.59	7.08	4.64	3.49	13.59	6.10	4.72	3.52	Split	7.13	Split
CLN 131 (Chlorite)	13.81	7.02	4.69	3.50	13.81	7.02	4.69	3.50			
CLN 139 (Chlorite- Pyrophyllite Rectorite ^{a/})		7.02		3.37		6.95	3.49			7.15	3.45

a. Rectorite is partially destroyed at 320° C and completely destroyed at 480° C.

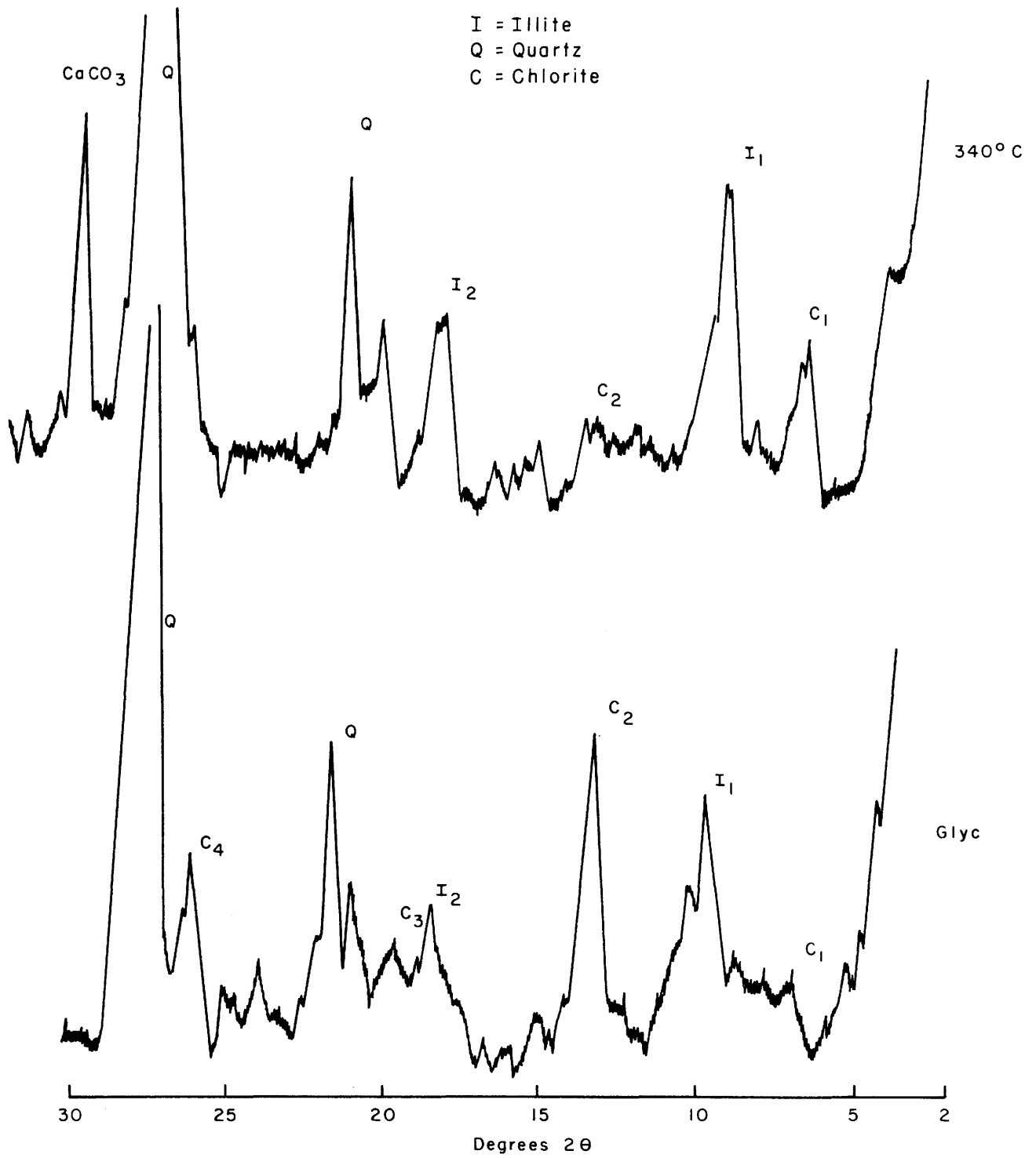


Figure 14. X-ray traces of smear slide of sample No. 605 containing chlorite, illite and quartz.

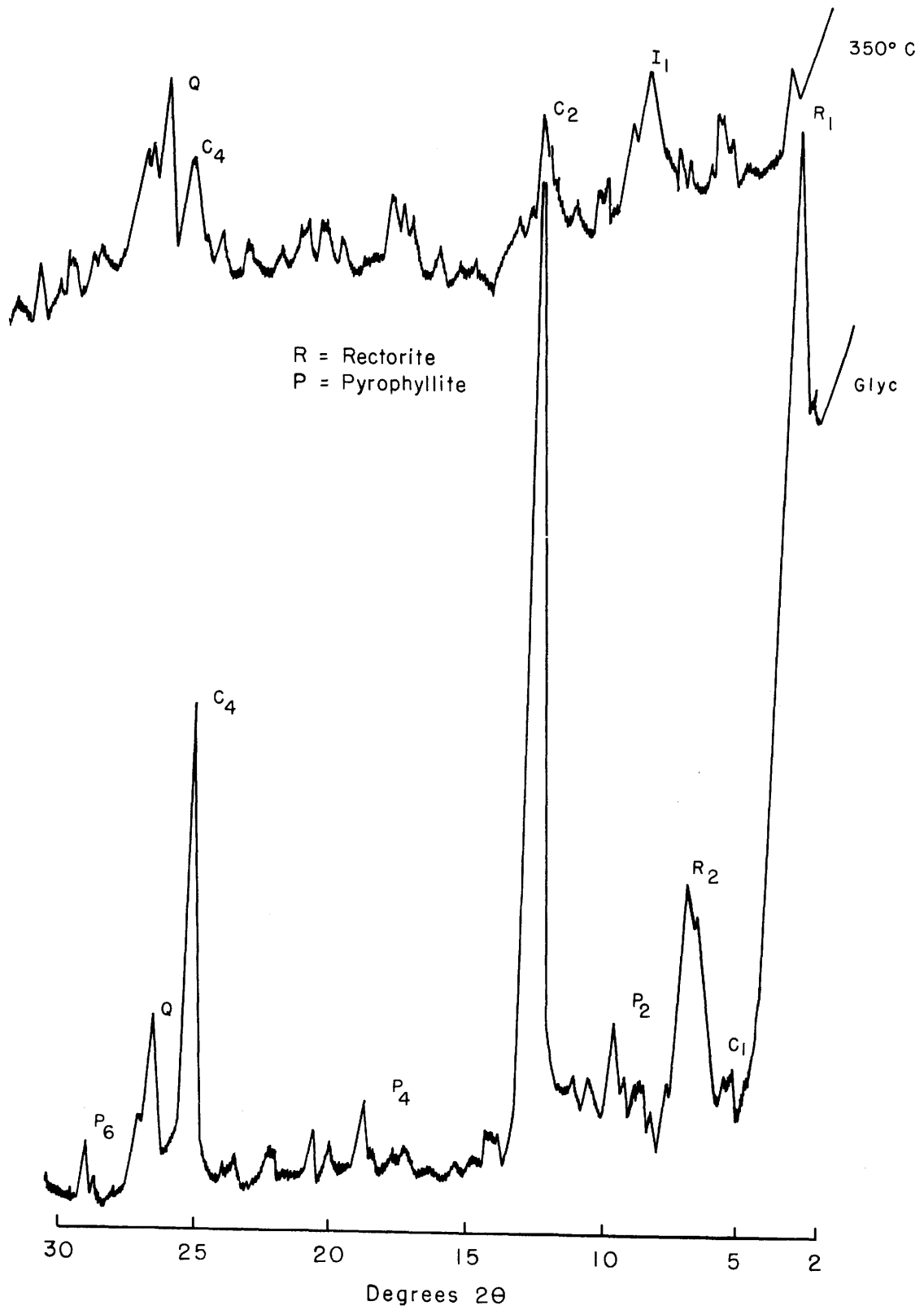


Figure 15. X-ray traces of $<2\mu$ slide of sample No. 139 containing rectorite, chlorite and pyrophyllite.

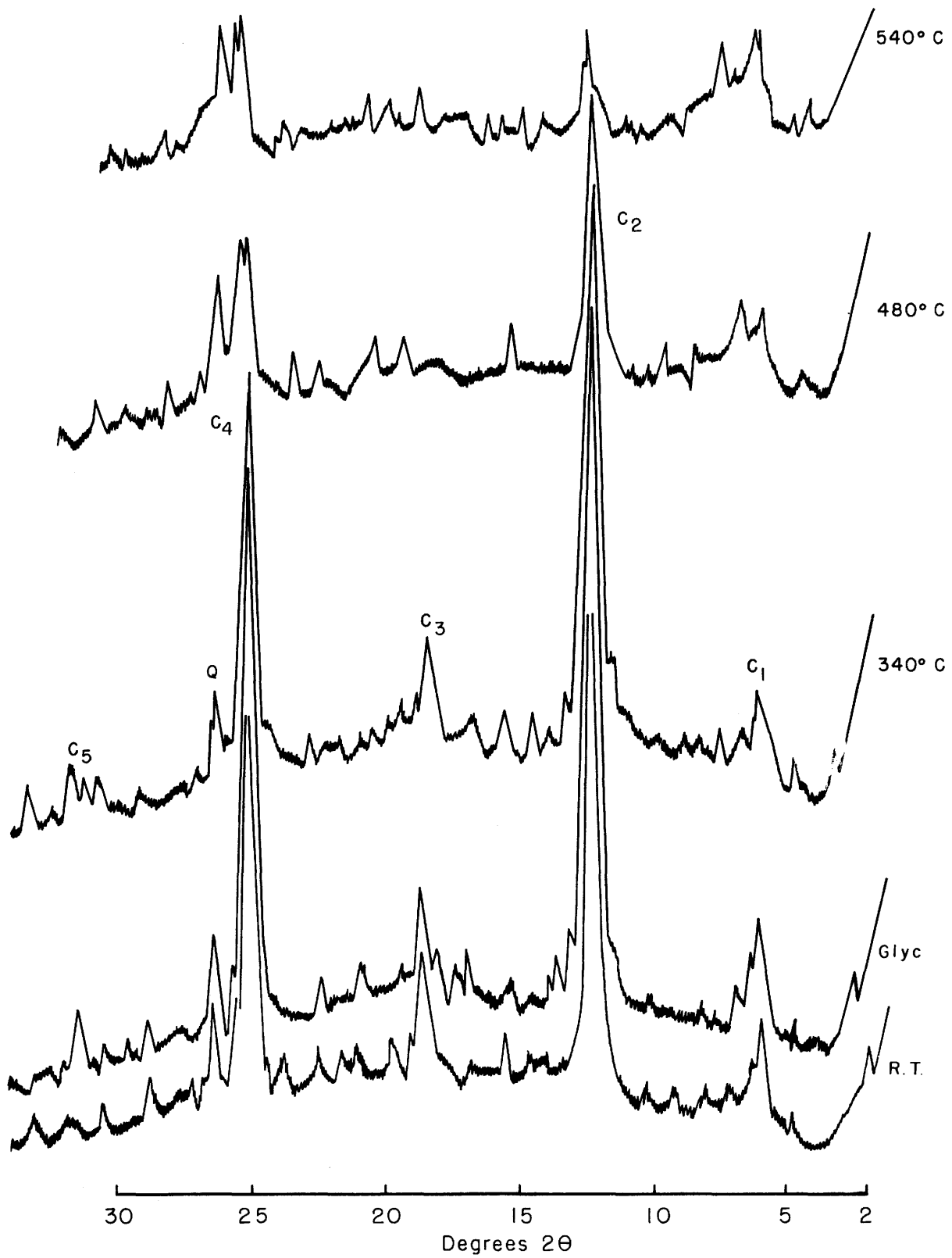


Figure 16. X-ray traces of $2\ \mu$ slide of sample No. 130 containing chlorite.

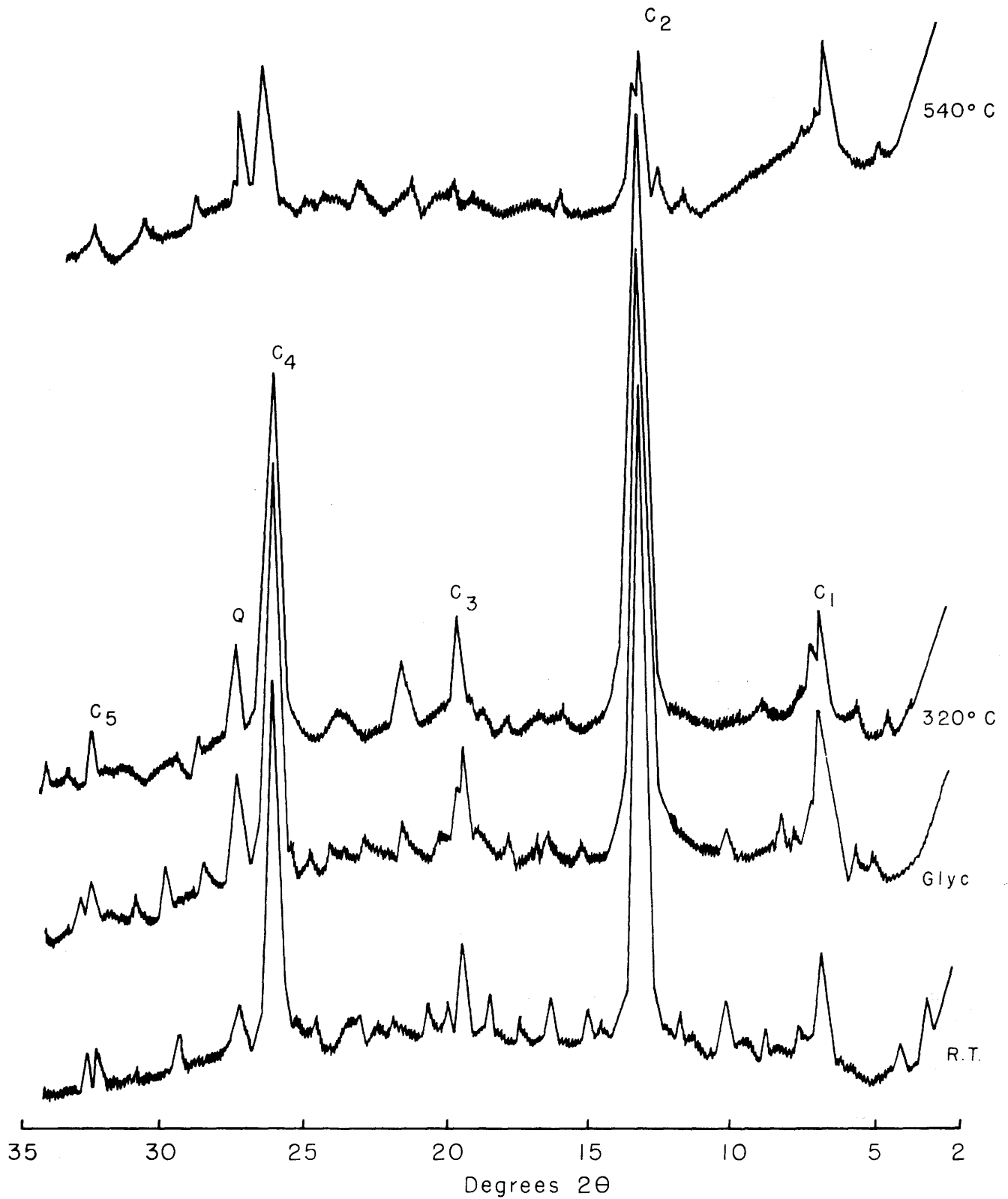


Figure 17. X-ray traces of <math><2\ \mu</math> slide of sample No. 131 containing chlorite.

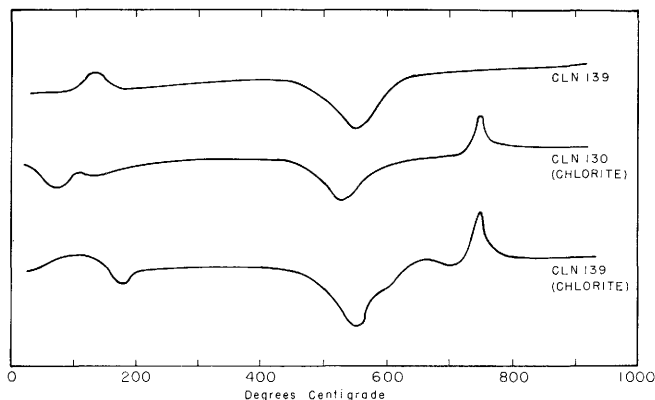


Figure 18. Differential thermal analysis curves of clay leached from limestone samples.

Differential Thermal Analysis

DTA was used to confirm the identification of chlorite leached from some of the limestones interbedded with shales in the study area. The curves shown in figure 18 represent three different samples of clay, all leached from limestones in the area of the Clinton Clay Mines, secs. 8 and 9, T. 5 S., R. 1 W., Utah County, Utah.

Samples CLN 130 and 131 represent a chloritic clay leached from limestone stringers 3-4 inches thick, interbedded with vertical shales in the Clinton area. Sample CLN 139, also leached from limestone stringers in this area, is mostly rectorite and chlorite with some pyrophyllite.

All three DTA curves show a good endothermic reaction between 500° and 600° C. The two pure chlorite samples show a distinct sharp exothermic peak at about 750° C. The low-temperature endotherms for the chlorites indicate the presence of some interlayer or adsorbed water. The OH⁻ or hydroxyl water is lost in the endotherm at 550° C for all three clays. Sample 131 shows a possible second endothermic peak at about 625° C which could represent a second stage of dehydroxylation. The exothermic peaks at about 750° C represent nucleation of a new phase.

The curves for samples 130 and 131 look very similar to those shown by Grim (1962, p. 93) for a chlorite-vermiculite mixed-layer clay mineral.

Gibbsite

The identification of the mineral gibbsite in small veins within the fractured limestones is significant in that it is associated with pyrophyllite and possibly shows some gradation to this hydrous aluminosilicate. The presence of gibbsite (Al(OH)₃) as a pure material in these small veins indicates that some hydrothermal solutions were active and moved through microfractures in the shales and limestones during deformation. Gibbsite is usually found as a low-temperature hydrothermal mineral in veins or

cavities in aluminum-rich igneous rocks and it is not difficult to visualize its presence under similar conditions in sediments which have undergone low-grade metamorphism. Gibbsite is the stable form at lower temperatures in the system Al₂O₃·H₂O.

X-ray traces and a DTA curve of this mineral are shown in figures 19 and 20 and confirm its presence in fractures and veins near the shale-limestone contacts.

Petrography

Photomicrographs not included in this paper show how pyrophyllite occurs and developed in the Manning Canyon shale and associated limestones. Pyrophyllite is present in approximately 90 percent of the samples studied and was found as vein or fracture filling material and as disseminated booklets in clay shales and limestones. It was distinguished from other minerals in thin section by its large well-formed booklets and by its high birefringence.

Radiographs of limestone samples found in areas of extensive folding and faulting show a unique microfold structure (figure 21). X-ray diffraction traces of the clay material found in the small folded seams (samples were ground and the clay-size material was removed by leaching) showed the clay material to be predominantly pyrophyllite with small amounts of illite.

Petrographic studies of thin sections show well-developed crystals of pyrophyllite in dark bands within the limestone samples. The development of pyrophyllite mainly in the dark bands (apparently bands of high carbon content in the limestone) suggests that its origin may be controlled by carbon content in the sediments.

Electron Microprobe Data

The relative percentages of Al₂O₃, SiO₂ and FeO were calculated from microprobe data for two clay-shale samples and one limestone sample.

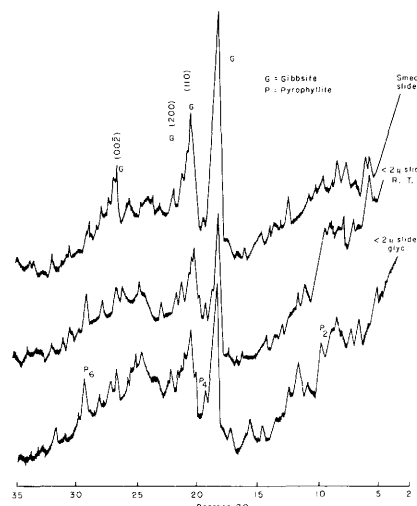


Figure 19. Differential thermal analysis curve of gibbsite from limestone sample.

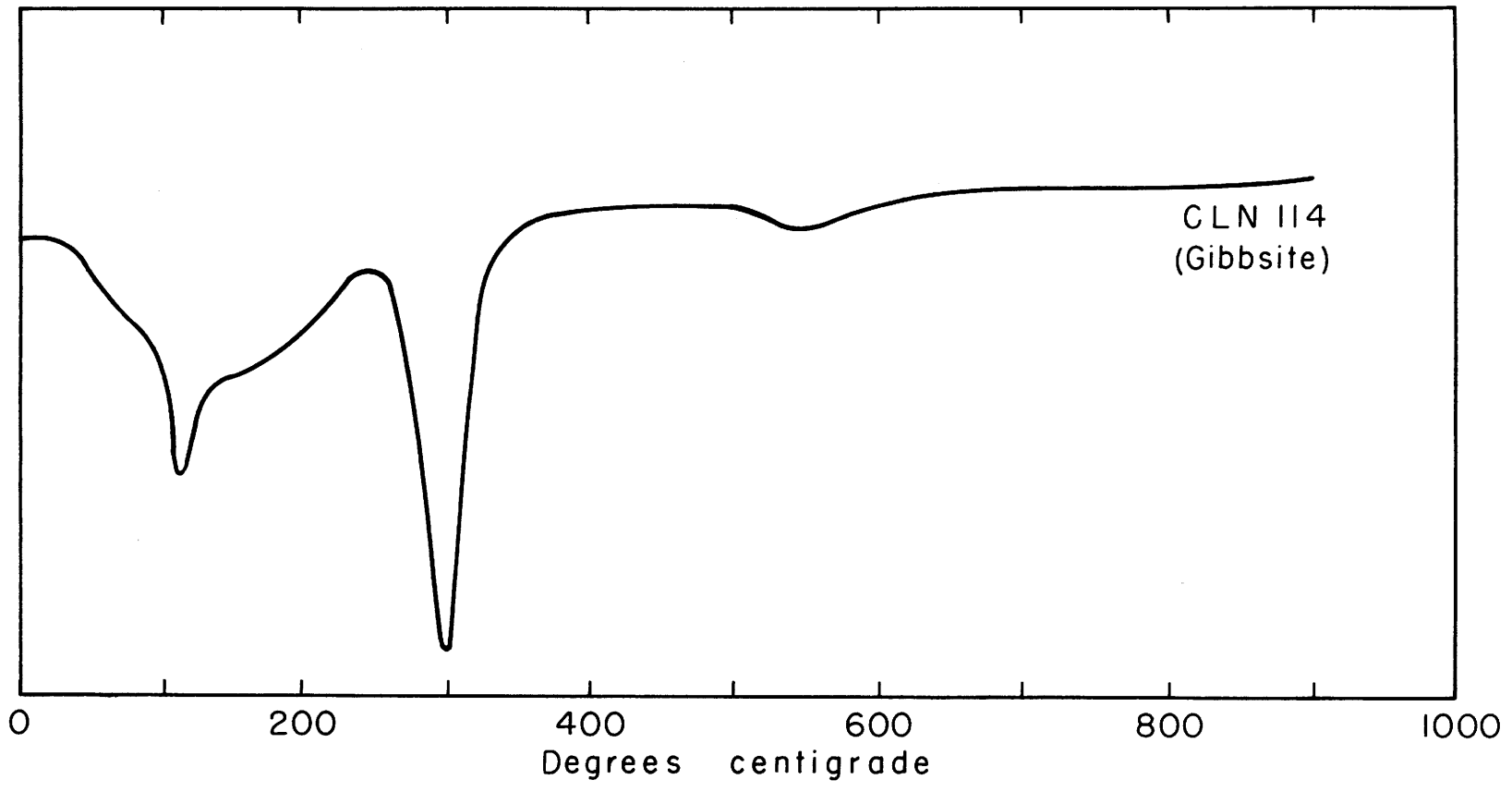


Figure 20. X-ray traces of <math><2 \mu</math> and smear slide of gibbsite with a trace of pyrophyllite.

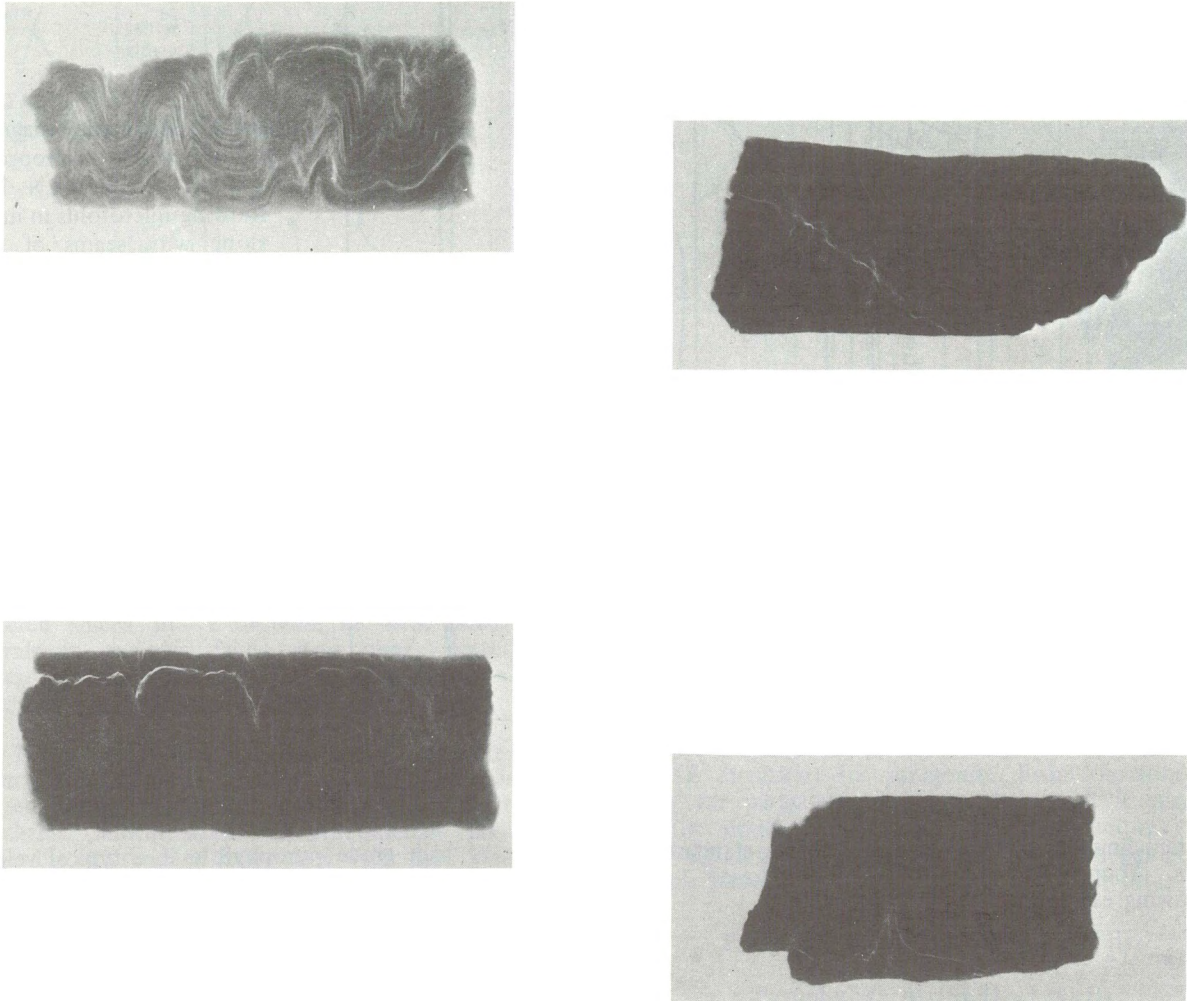


Figure 21. Radiographs of limestone sample No. 138 showing intricately folded structure. Small seams are clay minerals consisting mostly of pyrophyllite with some rectorite and chlorite (60KV5 MA. KWA film).

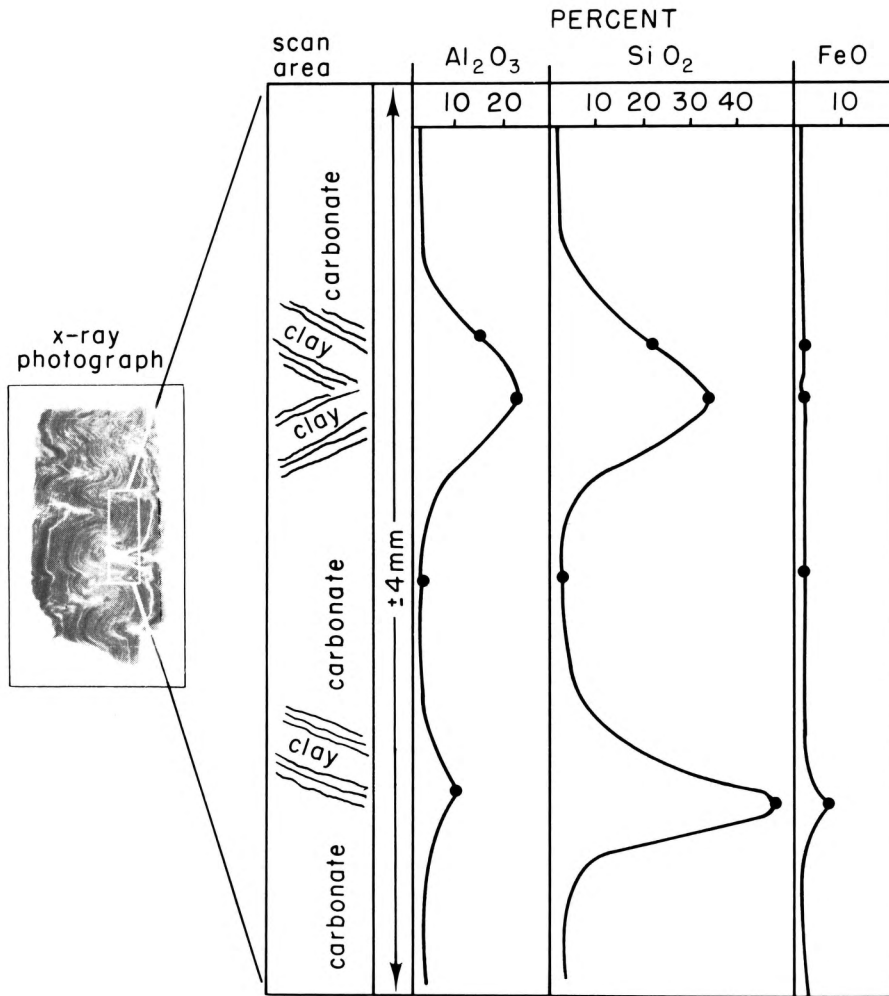


Figure 22. Schematic diagram of electron microprobe scan of sample CLN 138 showing microfolds in limestone with seams of red clay. X-ray data of 2μ material from thin red seams show 25 percent illite and 75 percent pyrophyllite.

Microcline and actinolite were used as standard materials. Abundance computations were based on the following equation:

Relative percent =

$$\frac{\text{Average counts / 5 sec (sample)}}{\text{Average counts / 5 sec (standard)}} \times (\text{Percent of each material in standard})$$

Schematic diagrams of the three samples analyzed are shown in figures 22, 23 and 24.

The small clay bands in the microfolds of the limestone (figure 21) appear to contain abundant pyrophyllite. A plot of microprobe data, figure 22, shows that the highest Al_2O_3 and SiO_2 content, indicative of pyrophyllite, are found in these red clay seams. In figure 23, the microprobe data support the

presence of high grade pyrophyllite in a typical vein-type occurrence. In figure 24, the brown zones represent a smaller degree of alteration and smaller amounts of pyrophyllite.

ORIGIN OF PYROPHYLLITE AND RECTORITE

The mineral pyrophyllite is widespread in pelitic rocks of north central Utah, and its association with other clay minerals, especially rectorite, is probably related to its origin. That such a relationship does exist is evident from semiquantitative analysis of X-ray data. The relative percent composition of the clay-shales plotted in the histogram and schematic diagram in figures 25 and 26 indicates an inverse relationship between the amounts of rectorite and pyrophyllite present in a sample. These data also show a definite correlation between the clay minerals

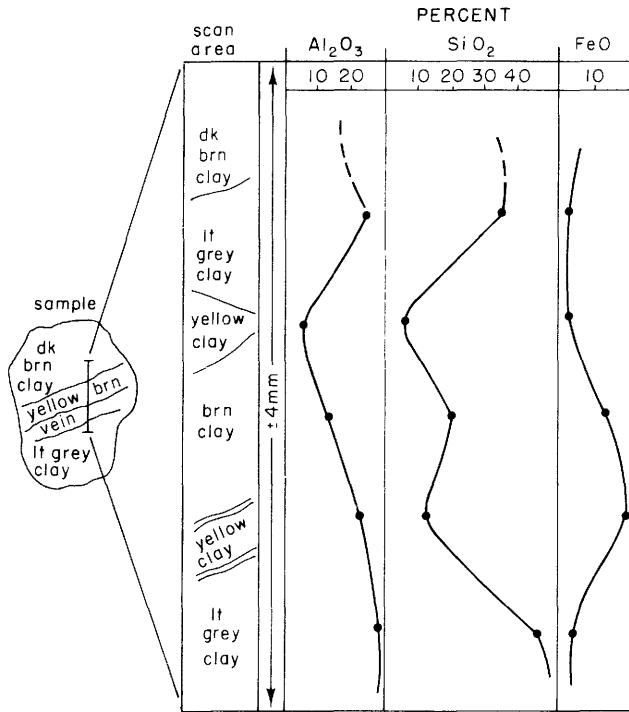


Figure 23. Electron microprobe scan of sample Lake Mountain No. 202. Scan covers area from dark brown clay across fracture to light gray clay. Typical of "vein" pyrophyllite zone.

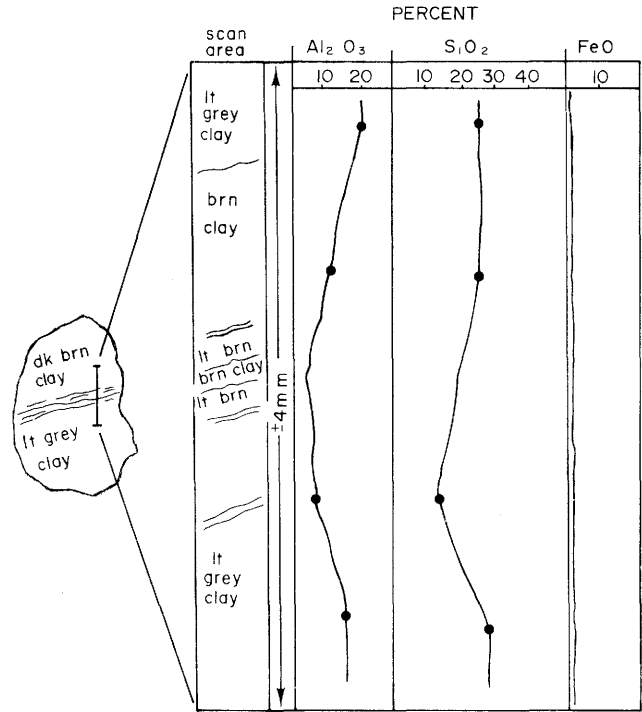


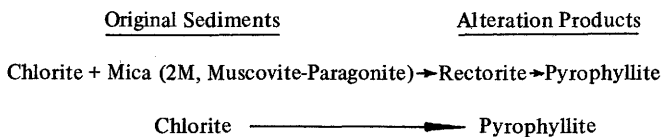
Figure 24. Electron microprobe scan of sample CLN 103. Light gray massive pyrophyllite zone.

in unaltered shales and those in altered clay-shales. The trend shows high chlorite and illite content in unaltered shales and a decrease in these same clay minerals in samples taken from areas that have undergone some deformation or a high degree of alteration.

It is clear that chlorite and illite were the primary clay minerals present during deposition of the sedimentary sequence of interbedded limestones and shales. Chlorite is also the predominant clay mineral in the interbedded limestones with illite, rectorite and pyrophyllite present in lesser amounts.

Post-depositional alteration of the clay minerals in this area is difficult to determine because of the complexity of the mineral assemblage and their stratigraphic and mineralogic relationships.

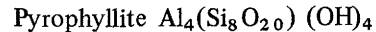
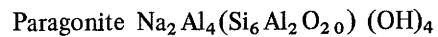
The paragenesis of the formation for the clay mineral assemblage appears to be as follows:



The regular mixed-layer clay mineral rectorite probably formed from the alteration of the sodium

mica (paragonite) or illite, followed by later formation of the 2:1 sheet silicate pyrophyllite from rectorite. Pyrophyllite could also have developed directly from the alteration of chlorite.

The structure of paragonite is similar to that of muscovite (2M, polymorph), except for the substitution of Na^+ for K^+ , which results in a smaller unit cell (Z direction) for paragonite. From the formulas given for paragonite and pyrophyllite, it is easy to see the similarities in their 2:1-type structures. The only differences are the presence of Na^+ in paragonite and the increase in Si^{+4} over Al^{+3} in pyrophyllite.



The evidence suggests that rectorite, being a high lattice charge clay mineral (expandable and therefore readily susceptible to alteration, with a high cation ion exchange capacity), yielded to the more stable form of 2:1-type clay mineral pyrophyllite. It is a little difficult, but not impossible, to imagine the sequence of formation going from a stable material like pyrophyllite to a metastable mixed-layer clay mineral like rectorite. Rectorite, then, probably represents the metastable phase in the clay mineral alteration and pyrophyllite represents the stable end product of alteration. The removal of Na^+ from the paragonite structure is not difficult to explain, but some substitution of Si^{+4} for Al^{+3} would have to

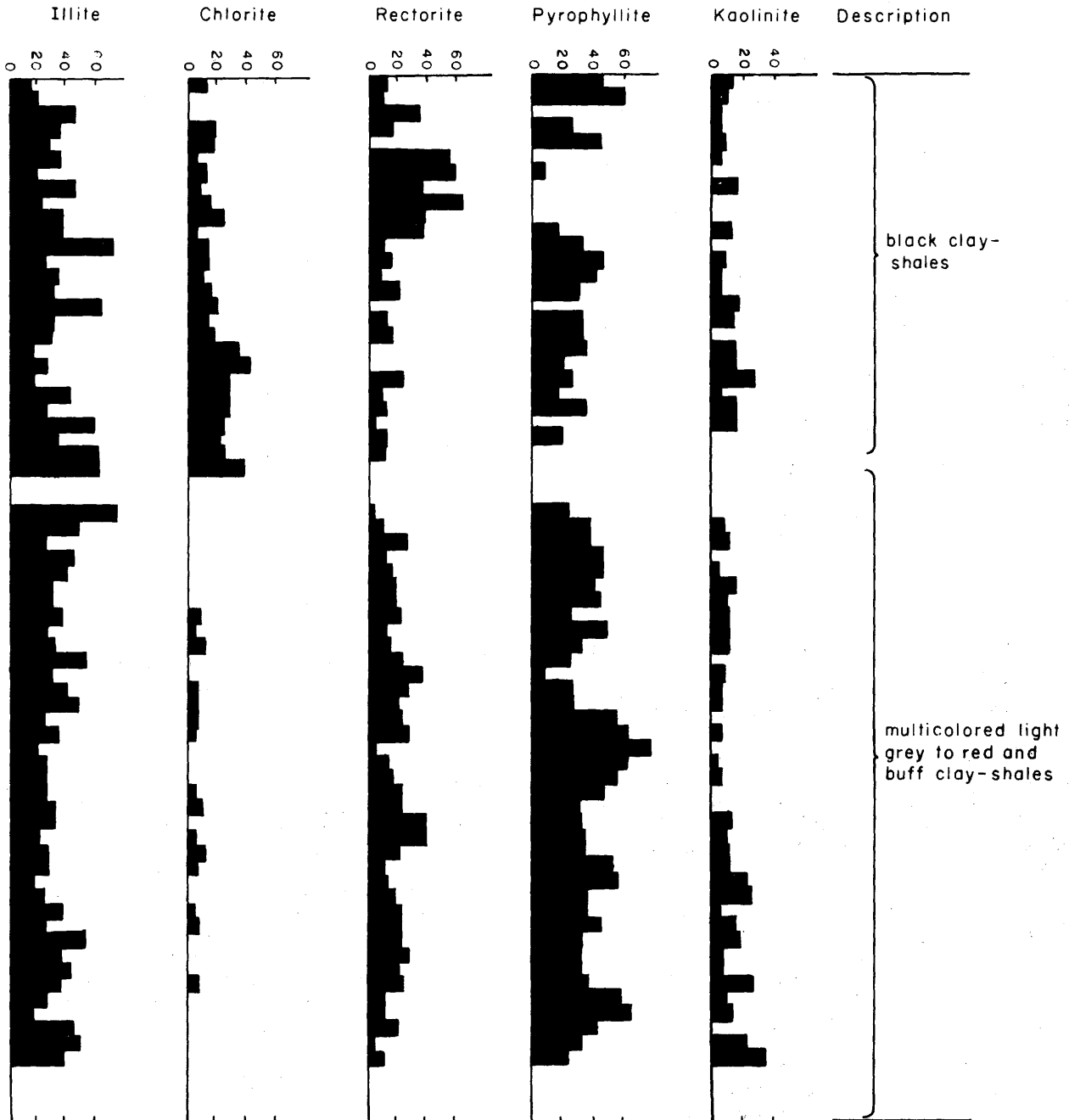


Figure 25. Histogram showing contrasting abundance of $< 2 \mu$ clay fraction of samples.

take place to form pyrophyllite. Iiyama and Roy (1963) in their studies of the system $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ indicate that randomly stacked mixed-layer phases were formed at 1Kb pressure in the temperature range from 450° to 575° C, whereas at higher pressure, regular mixed-layers tended to form.

There is no literature available concerning a clay mineral assemblage such as that described above, i.e. the sequence of alteration products, rectorite to

pyrophyllite. The hypothesis is, however, substantiated by the work of several authors who have studied the geochemistry of mixed-layer clay minerals. Zen (1962, p. 1056) concluded that mixed-layer clays must represent metastable phases in clay mineral assemblages. Krauskopf (1967) noted that the mixed-layer clay minerals represent a metastable intermediate material formed in the course of weathering.

In the case of mixed-layer clay mineral rectorite in this assemblage, pressures of at least 1 to 2Kb

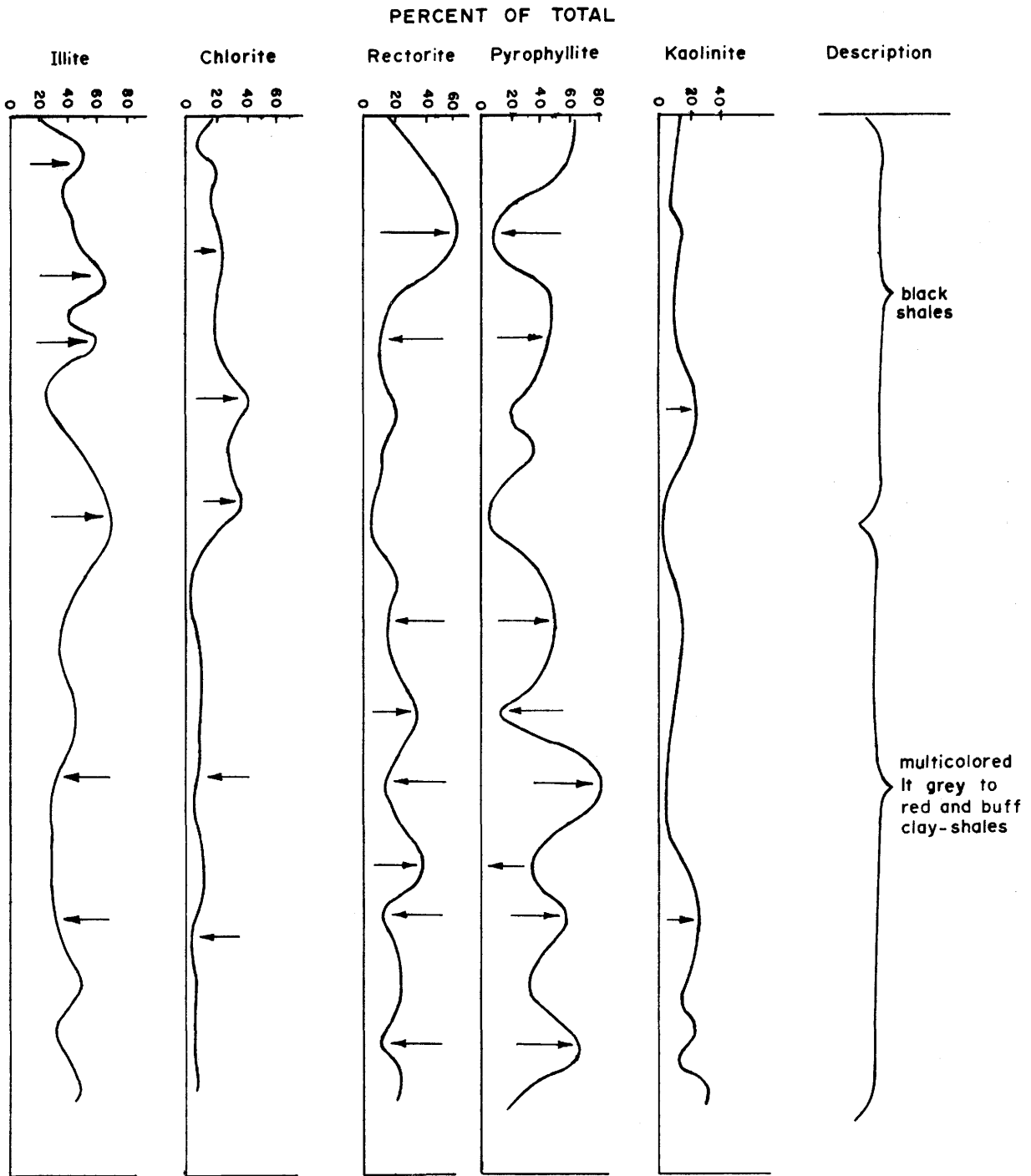


Figure 26. Generalized diagram showing contrasting abundance of the clay minerals in samples (overlay of histogram—figure 25).

must have had some influence on the formation of a regular rather than an irregular layer-stacking sequence.

Experimental work by Roy and Osborne (1954), Eskola (1939), Goldschmidt (1922) and others on the geochemistry and formation of py-

rophyllite attribute its origin to hydrothermal activity in an aluminous system low in silica and at temperatures above 400° C. There is increasing evidence, however, that the lower limits of formation of pyrophyllite are somewhat less than previous syntheses indicated. Evidence exists that the mineral can and does form during low-grade regional meta-

morphism and possibly during later stages (high-grade) of diagenesis (Millot, 1954; Biscaye, 1965; Beuf, 1966, and others). The greatest controversy in synthesis work on pyrophyllite formation lies in establishing its lower limits of formation. Most authors agree that this mineral can form at temperatures much lower than that used by synthesis work (400° C). Roy and Osborne (1954) stated that pyrophyllite is the stable phase above 420° C under varying H₂O pressures and that it is obtained as the only crystalline phase from 1:4 Al₂O₃:SiO₂ gels at equilibrium. They also concluded that pyrophyllite would be expected to crystallize only in the temperature range of 420° C to 575° C when excess H₂O is present, but that it is no doubt a stable phase at much lower temperatures and will form if sufficient water is present to convert the mixture to higher hydrates.

Velde (1968) noted that the infrequent occurrence of pyrophyllite in more evolved sedimentary rocks and low-grade metamorphic facies of pelitic rocks is probably the result of chemical controls in the bulk composition of these rocks. He believes that the oxidation-reduction state of the iron minerals in the sediments controls the bulk composition of the silicate system, and therefore the formation of pyrophyllite.

Turner and Verhoogan (1960) noted in their studies of chemical changes accompanying hydrothermal metasomatism of feldspars, that pyrophyllite originates in silica-systems under conditions the same as for kaolinite (neutral solutions free of alkali metals or in acid solutions containing alkali metals) except that pyrophyllite forms at temperatures upward from 400° C. At lower temperatures (below 400° C) its formation depends upon the alkali concentration of the active solutions whether zeolites or kaolin are formed.

Field observations and laboratory test data show that the origin of rectorite and pyrophyllite in the study area is associated with low grade metamorphism (prograde) and late stages of diagenesis. The author prefers to use Winkler's (1965) definition of regional (burial) metamorphism and diagenesis:

Burial metamorphism: Regional (burial) metamorphism bears no genetic relationship to orogenesis nor to magmatic intrusions. The rock formations accumulating in a geosynclinal basin gradually subsided to so profound a depth that the temperatures there sufficed to bring about reactions between the minerals of the sediments. Temperatures of the order of ±300° C were probably realized at the beginning phases of metamorphism and ending phases of diagenesis.

Diagenesis: Comprises all changes taking place in a sediment between sedimentation and the onset of metamorphism, save those caused by weathering.

Turner and Verhoogan (1960) defined the lowest temperature regional metamorphism as being represented by the zeolitic facies. This facies probably represents a transition between late diagenesis and the beginning of regional metamorphism. Winkler (1965) defines the mineral paragenesis in the sub-facies (quartz-albite-muscovite-chlorite) of the greenschist facies. In this sub-facies he notes that the most frequent minerals present in pelitic rocks are muscovite+quartz+chlorite±paragonite±pyrophyllite. The clay mineral assemblage found in the area of this study would appear to fit the paragenesis outlined by Winkler for the low-temperature zone of regional metamorphism. This assemblage would probably represent the zeolitic facies or lower sub-facies of the greenschist facies of metamorphism. X-ray traces of several samples show the presence of zeolites, mostly the Na⁺, Ca⁺⁺ variety of zeolite, phillipsite. Local areas show some higher degree of metamorphism (areas of strong deformation) producing hydrothermal solutions.

The working hypothesis advanced by the author in the approach to the study of the origin of pyrophyllite-rectorite can be divided into three general explanations:

1. The formation of pyrophyllite-rectorite by hydrothermal alteration of the clay-shales during metamorphism. The plumbing for the hydrothermal solutions was probably created by strong deformation in local areas of interbedded limestones and shales.
2. The formation of rectorite-pyrophyllite during late stages of diagenesis or prograde regional metamorphism.
3. The formation of pyrophyllite-rectorite during late stages of diagenesis and low-grade regional (burial) metamorphism with concurrent hydrothermal solutions active in localized area.

Origin by metamorphism with concurrent formation of hydrothermal solutions seems unlikely because it does not fit the entire picture. This theory accounts for the formation of pyrophyllite in localized areas in the sedimentary rocks that have undergone strong deformation (fault zones, etc.), but the surrounding limestones show little signs of metamorphism. This lack of visible evidence of metamorphism in the limestones indicates that solutions formed must have been cool and traversed mostly through the clay-shale beds. The presence of pure gibbsite in small veins near the limestone-clay-shale contact verifies the fact that solutions were highly aluminous. Gibbsite can and usually does form at low temperatures. The first theory does not account for the fact that pyrophyllite and rectorite are found in abundance in clay-shales that have not been subjected to hydrothermal activity. Rectorite and pyrophyllite are found in clay-shales that appear to show nothing more than diagenetic changes, surface weathering or

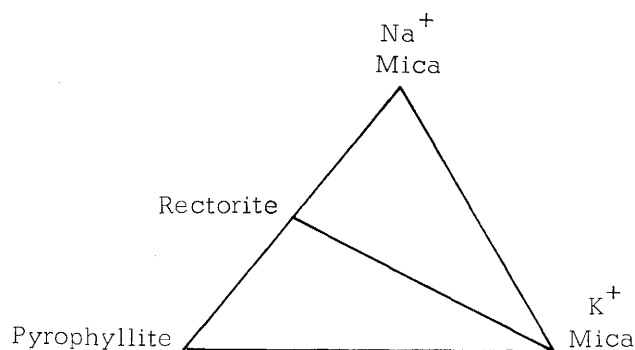


Figure 27. Proposed schematic phase diagram of the system pyrophyllite-paragonite-muscovite-rectorite.

oxidation. Also it is not likely that rectorite, found associated with pyrophyllite, would have formed from hydrothermal solutions.

The second explanation does account for the widespread distribution of pyrophyllite-rectorite in comparatively unaltered clay-shales but does not explain the increase in relative percentages of pyrophyllite in areas of high deformation compared to those areas showing no deformation.

Probably the best explanation for the formation of rectorite-pyrophyllite in the clay-shales is a combination of the first two theories into No. 3 above. Rectorite could have formed in late stages of diagenesis (alteration of illite or paragonite) with subsequent formation of pyrophyllite by prograde metamorphism. Hydrothermal solutions probably developed in isolated areas such as the Lake Mountains and Beverly Hills regions where there is field evidence of strong local deformation (folding and faulting). This deformation probably created the plumbing (permeability) within the sedimentary rock sequence that allowed hydrothermal solutions to migrate through the clay-shales. Migration and concentration of highly aluminous solutions probably followed or was concurrent with deformation.

The identification of pyrophyllite, muscovite and rectorite in the samples suggest a chemical phase system not often found in nature. The author's definition of the structure of (paragonite+expandable layer) is probably the key to this system.

The mineralogical associations described appear to support Eugster and Yoder's (1955) work on the Join muscovite-paragonite system. This system shows a subsolidus with low Na^+ solubility in muscovite and low K^+ solubility in paragonite. It seems logical that this same interpretation can be applied to the partitions in an alkali-deficient province, as proposed in figure 27. There can be a muscovite-rectorite partition with low Na^+ and a muscovite-pyrophyllite partition with no Na^+ and kaolinite-pyrophyllite partition with deficient K^+ as suggested in figure 28.

All three minerals, pyrophyllite-paragonite-muscovite, are compatible under these conditions and should coexist. This system is representative of low to moderate conditions of metamorphism. A regular alternating arrangement of Na^+ mica and pyrophyllite layers appears to be characteristic of the rectorite in this area.

There is one other factor that should be considered, and that is that many of these samples contain as much as 4 to 5 percent organic carbon. The carbon in this province could be the agent that keeps the rectorite from becoming a paragonite, or in other words controls the Na^+ content.

Velde's (1968) hypothesis sheds some light on the formation of pyrophyllite in sedimentary rocks. His theory concerning the control of the formation of kaolinite and pyrophyllite in sedimentary rocks by the oxidation-reduction state of iron minerals present seems to fit the theory of low-temperature metamorphism and diagenesis proposed by this author. The gradual destruction of organic molecules during progressive metamorphism can effect the silicate phases by providing a means for changing the effective bulk composition of the silicate system. Certainly, the high carbon content of the Manning Canyon shales would be a ready source of reducing agents in the system.

CONCLUSIONS

The clay mineral rectorite occurs in significant abundance in the Manning Canyon shale in northern Utah; it is especially well developed in the black highly carbonaceous paper-thin shales. Rectorite did not occur in shales sampled from other formations in the area studied, but other mixed-layer clays were present.

The author proposes that the regular mixed-layer clay mineral rectorite probably formed from the alteration of muscovite-paragonite during late stages of diagenesis (considerable burial pressures) and represents the metastable phase of mineral paragenesis. The mineral pyrophyllite formed from the

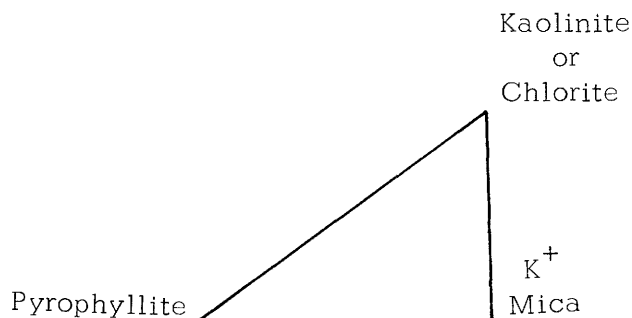


Figure 28. Proposed schematic diagram of third dimension plane in the system chlorite or kaolinite-pyrophyllite-muscovite.

alteration of rectorite during prograde metamorphism and represents the stable end-member of the clay mineral assemblage.

Since rectorite is so widespread, its association with pyrophyllite and mica can probably be attributed to the high organic carbon content of the shales which controls the paragonite-muscovite phase.

The predominance of a regular, rather than irregular, mixed-layer sequence in this material can probably be attributed to the extreme burial pressures to which the Paleozoic shale has been subjected.

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APPENDIX A

Quantitative X-ray data showing
relative percentages of clay minerals

Location	Average Composition in Percent of Entire Sample (< 2 μ)					
	Qtz	Ill	Pyr	Rect + Mx	Kaol	Chl
Beverly Hills	5	36	31	13	6	9
Lake Mountain	5	33	36	14	6	9
Manning Canyon	10	35	± 10	7	-	40
Pleasant Grove	26	2	18	2	9	39
Five Mile Pass	32	38	-	16	6	-
Cottonwood	33	48	20	-	-	-
	Average Composition in Percent of <2 μ Clay Fraction					
Beverly Hills	5	38	26	19	8	7
Lake Mountain	5	25	42	18	9	7
Manning Canyon	5	54	2	22	-	20
Pleasant Grove	-	27	24	11	15	30
Five Mile Pass	-	72	-	22	7	-
Cottonwood	-	44	27	3	25	-
	Average Composition in Percent of < 2 μ Clay Fraction: Indurated Black Paper-thin Shales Showing No Alteration					
All Locations	-	37	17	23	6	16
	Average Composition in Percent of <2 μ Clay Fraction: Light Grey and Multicolored Clay-Shales from Areas Showing A High Degree of Deformation					
All Locations	-	32	40	15	9	4

APPENDIX B

Sample location and mineralogy

Clay Minerals		County	
Kaolinite	K	Utah	U
Chlorite	C	Tooele	T
Illite	I	Salt Lake	SL
Pyrophyllite	P	Weber	W
Rectorite	R		
Mixed-layer (Undifferentiated material)	MX		

Sample No.	Relative Percent of Clay Minerals						Description	Location			
	I	P	R	K	C	Mx		County	Section	Range	Township
100			(Chlorite)		100		U	8	1W	5S	
101							U	8	1W	5S	
102							U	8	1W	5S	
103	25	37	27	10			U	8	1W	5S	
104	47	37	9	6			U	8	1W	5S	
105	72	23	4				U	8	1W	5S	
106	42	46	11				U	8	1W	5S	
107	38	44	13	4			U	8	1W	5S	
108	27	40	17	14			U	8	1W	5S	
109	29	43	17	9			U	8	1W	5S	
110	36	25	20	10	8		U	8	1W	5S	
111	25	48	11	10	4		U	8	1W	5S	
112	30	32	13	10	12		U	8	1W	5S	
113	25	50	20			5	U	8	1W	5S	
114			(Gibbsite)				U	8	1W	5S	
115	31	31	13	17	7		U	8	1W	5S	

Appendix B continued

Sample No.	Relative Percent of Clay Minerals						Description	Location			
	I	P	R	K	C	Mx		County	Section	Range	Township
116	27	51	15		5		Sooty black sh.	U	8	1W	5S
117	52	25	22				Lt. grey, brn. shale	U	8	1W	5S
118	35	35	22	2	4		Lt. grey, soft shale	U	8	1W	5S
119	39	24	26	5	5		Red, brn., grey shale	U	8	1W	5S
120	45	26	19	4	4		Lt. grey sh.	U	8	1W	5S
121	19	61	10	9			Multicolored shale	U	8	1W	5S
122	46		34	5	14		Black, fissile shale	U	8	1W	5S
123	26	42	14	10	8		Red, plastic clay	U	7	1W	5S
124	44		33	16	7		Brn., indurated shale	U	8	1W	5S
125	22		62		16		Brn., indurated shale	U	8	1W	5S
126	38		38		23		Brn., indurated shale	U	8	1W	5S
127	64		35	tr			Lt. grey sh.	U	8	1W	5S
130			(Chlorite)		100		Limestone	U	8	1W	5S
131			(Chlorite)		100		Limestone	U	8	1W	5S
132			25		75		Limestone	U	8	1W	5S
133	23	43	20	5	7		Black, soft clay	U	8	1W	5S
134							Volcanic rock (latite)	U	9	1W	5S
135							Volcanic rock (latite)	U	9	1W	5S
136							Volcanic rock (latite)	U	9	1W	5S
137							Volcanic rock (latite)	U	9	1W	5S
138	25	75					Limestone (highly folded microstructure)	U	8	1W	5S

Appendix B continued

Sample No.	Relative Percent of Clay Minerals						Description	Location			
	I	P	R	K	C	Mx		County	Section	Range	Township
139			(Chlorite)		100		Carb. limestone	U	8	1W	5S
140							Carb. limestone	U	8	1W	5S
141	61	18		11	9		Lt. grey clay	U	8	1W	5S
142	40		40	20			Red, silty clay	U	8	1W	5S
143	100						Yellow, silty clay	U	8	1W	5S
144	31	19	10	20	18		Limestone	U	8	1W	5S
145							Siliceous limestone	U	8	1W	5S
150	36	27	15	3	18		Black fissile shale	U	8	1W	5S
151	15	36	tr	15	32		Caliche	U	8	1W	5S
152	34		54	5	5		Black fissile shale	U	8	1W	5S
153	56		4	18	21		Brn., black fissile sh.	U	8	1W	5S
154	16	44	13	12	15		Sooty black sh.	U	8	1W	5S
200	30	30	30		9		Brn., black fissile sh.	U	12	1W	7S
201	25	46	9	7	12		Limestone	U	12	1W	7S
202		80		20			White vein of pyrophyllite in limestone	U	12	1W	7S
203	33	41	8	6	10		Brn., black sh. with white veins of pyrophyllite	U	12	1W	7S
204							Brn., black sh. with white veins of aragonite	U	12	1W	7S
205	30	30	20	5	14		Brn., shale, silty	U	12	1W	7S
206	25	61	11	3			Multicolored shale	U	33	1W	5S
207	25	55	15	5			Multicolored shale	U	33	1W	5S
208	25	46	21	tr	6		LS-SH contact	U	33	1W	5S

Appendix B continued

Sample No.	Relative Percent of Clay Minerals						Description	Location			
	I	P	R	K	C	Mx		County	Section	Range	Township
209	33	63	27	5	4		Multicolored shale	U	33	1W	5S
210	22	54	12	5	5		Multicolored shale	U	33	1W	5S
211	18	35	38	4	4		Lt. grey, soft clay	U	33	1W	5S
212	26	52	7	9	5		Lt. grey, soft clay	U	33	1W	5S
213	27	34	18	10	10		Lt. grey, soft clay	U	33	1W	5S
214							Limestone	U	33	1W	5S
215							Carbonaceous limestone	U	33	1W	5S
216							Limestone	U	12	1W	7S
217	13	53	11	22			Lt. grey shale with seams of pyrophyllite	U	5	1W	7S
218	37	23	35		5		Brn. indurated shale	U	1	1W	7S
219	30	32	12	12	12		Brn., black ind. shale	U	1	1W	7S
220	28	45	9		16		Black ind. sh.	U	1	1W	7S
221	23	36	15	25			Lt. grey clay	U	1	1W	7S
222	13	64	9	13			Lt. grey clay	U	1	1W	7S
223	(100% Pyrophyllite)						Lt. grey clay	U	1	1W	7S
224	29	32	38				Multicolored clay	U	30	1W	6S
230	35	30	25	10			Black shale	U	33	1W	5S
231	(100% Montmorillonite)						Lt. grey, porous-tuff	U	33	1W	5S
232	(100% Montmorillonite)						Lt. grey, porous-tuff	U	33	1W	5S
233	40	32	18	9			Lt. grey sh.	U	33	1W	5S
234	29	9	33	27			Red clay	U	33	1W	5S
235							Limestone silty, sandy	U	33	1W	5S

Appendix B continued

Sample No.	Relative Percent of Clay Minerals						Description	Location			
								County	Section	Range	Township
	I	P	R	K	C	Mx					
236							Carbonaceous limestone	U	33	1W	5S
237	23	58	8	9			White clay seam in red clay	U	33	1W	5S
238	(100% Pyrophyllite)						Lt. grey clay with white seams	U	12	1W	7S
239	18	78	4				Lt. brn. shale	U	12	1W	7S
240	50	50					Concretionary tuff material in "boudinage structure" montmorillonite	U	12	1W	7S
241	41	41	18				Black fissile sh.	U	12	1W	7S
242							Siliceous limestone	U	12	1W	7S
243	30	41	14	6	8		Silty shale	U	12	1W	7S
244	25	31	32	4	7		Black fissile sh.	U	12	1W	7S
245							Punky lt. grey sh. - siltstone	U	12	1W	7S
246	36	36	20	4	4		Lt. grey clay with white seams	U	12	1W	7S
300	47	31		21			Hard, indurated brn., grey sh.				
301	34	20		35		9	Hard, indurated brn., grey sh.				
302	30	25		30		15	Hard, indurated brn., grey sh.				
303	50	31		18			Hard, indurated brn., grey sh.				
400	72			9		18	Lt. grey clay-shale	T	10	3W	7S
401	72			8		20	Lt. grey clay-shale	T	10	3W	7S
402	100						Lt. grey clay-shale	T	10	3W	7S
403	44			6		49	Lt. grey clay-shale				
500				100			White and lt. tan clay	U	27	3W	6S

Appendix B continued

Sample No.	Relative Percent of Clay Minerals						Description	Location			
								County	Section	Range	Township
	I	P	R	K	C	Mx					
501							Limestone	U	27	3W	6S
600	25	19	2	14	40		Black clay-shale	U	22	2E	5S
601	15	25	22	11	27		Brn., black clay-shale	U	22	2E	5S
602	41	15	9	6	26		Brn., black clay-shale	U	16	2E	5S
603	25	35	11	13	28		Brn., black clay-shale	U	16	2E	5S
700	100			tr			Pink shale	U	13	2W	11S
701	100			tr			Lt. grey sh.	U	13	2W	11S
702	100			tr			Pink and grey sh.	U	13	2W	11S
800							Black, brn. shale	U	10	2W	5S
801							Black, brn. shale	U	10	2W	5S
802							Black, brn. shale	U	10	2W	5S
803	36	26	33	4			Black, brn. shale	U	10	2W	5S
804	28	15	54	3			Black, brn. shale	U	10	2W	5S
900							Ash	T	5	4W	6S
901							Ash	T	5	4W	6S
902	20	7	58		10		Black indur. fissile sh.	T	30	4W	5S
903	70		12		12		Red silty sh.	T	30	4W	5S
904	60		13		22		Black fissile shale	T	36	4W	5S
905	60	tr	tr		37		Dark brn. sh.	T	36	4W	5S
906	60	tr	tr		40		Black soft plastic clay	T	36	4W	5S

UTAH GEOLOGICAL AND MINERALOGICAL SURVEY

103 Utah Geological Survey Building
University of Utah
Salt Lake City, Utah 84112

THE UTAH GEOLOGICAL AND MINERALOGICAL SURVEY since 1949 has been affiliated with the College of Mines and Mineral Industries at the University of Utah. It operates under a director with the advice and counsel of an Advisory Board appointed by the Board of Regents of the University of Utah from organizations and categories specified by law.

The survey is enjoined to cooperate with all existing agencies to the end that the geological and mineralogical resources of the state may be most advantageously investigated and publicized for the good of the state. The *Utah Code, Annotated, 1953 Replacement Volume 5, Chapter 36, 53-36-2*, describes the Survey's functions.

Official maps, bulletins, and circulars about Utah's resources are published. (Write to the Utah Geological and Mineralogical Survey for the latest list of publications available).

THE LIBRARY OF SAMPLES FOR GEOLOGIC RESEARCH. A modern library for stratigraphic sections, drill cores, well cuttings, and miscellaneous samples of geologic significance has been established by the Survey at the University of Utah. It was initiated by the Utah Geological and Mineralogical Survey in cooperation with the Departments of Geology of the universities in the state, the Utah Geological Society, and the Intermountain Association of Petroleum Geologists. This library was made possible in 1951 by a grant from the University of Utah Research Fund and by the donation of collections from various oil companies operating in Utah.

The objective is to collect, catalog, and systematically file geologically significant specimens for library reference, comparison, and research, particularly cuttings from all important wells driven in Utah, and from strategic wells in adjacent states, the formations, faunas, and structures of which have a direct bearing on the possibility of finding oil, gas, salines or other economically or geologically significant deposits in this state. For catalogs, facilities, hours, and service fees, contact the office of the Utah Geological and Mineralogical Survey.

THE SURVEY'S BASIC PHILOSOPHY is that of the U. S. Geological Survey, i.e., our employees shall have no interest in Utah lands. For permanent employees this restriction is lifted after a 2-year absence; for consultants employed on special problems, there is a similar time period which can be modified only after publication of the data or after the data have been acted upon. For consultants, there are no restrictions beyond the field of the problem, except where they are working on a broad area of the state and, here, as for all employees, we rely on their inherent integrity.

DIRECTORS:

William P. Hewitt, 1961-
Arthur L. Crawford, 1949-1961