Quantitative Interpretation of Mineralogical Composition from X-ray and Chemical Data for the Pierre Shale
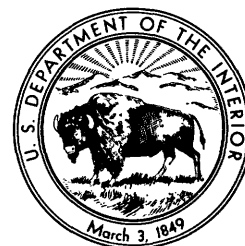
Quantitative Interpretation

of Mineralogical Composition

from X-ray and Chemical

Data for the Pierre Shale

By LEONARD G. SCHULTZ

ANALYTICAL METHODS IN GEOCHEMICAL
INVESTIGATIONS OF THE PIERRE SHALE

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

CONTENTS

ILLUSTRATIONS

TABLES

QUANTITATIVE INTERPRETATION OF MINERALOGICAL COMPOSITION FROM X-RAY AND CHEMICAL DATA FOR THE PIERRE SHALE

By LEONARD G. SCHULTZ

ABSTRACT

Quantitative X-ray determinations for total amounts of clay, quartz, feldspar, carbonate, and other minerals common in the Pierre Shale are based on heights of peaks on diffractometer traces of unoriented powder samples. Conversion factors are derived from X-ray analyses of prepared mixtures, from weight loss due to solution by dilute acid of carbonate minerals in Pierre samples, and from comparison of X-ray and chemical data for Pierre samples. Proportions of kaolinite, chlorite, illite, montmorillonite, and mixed-layer clay are interpreted from the relative sizes of basal reflections from oriented clay aggregates.

Repeated analyses indicate that variations in (1) sampling, (2) sample preparation, (3) machine response, and (4) interpretation by the operator all affect the precision of the X-ray determinations. Inconsistency of interpretation has the greatest effect on the determination of the clay minerals. If a mineral is present in an amount greater than 15 percent of the sample, the precision of its determination generally is ±10 percent. Minerals present in amounts of a few percent or less are not consistently detected. Comparison of chemical analyses for carbon dioxide and alumina and quantitative interpretations for carbonate minerals and total clay, respectively, indicates accuracy of the X-ray interpretations to be generally about the same as the precision.

Calculations of mineral compositions from chemical analyses are based, in part, on the X-ray data. The amounts of apatite, barite, pyrite, and of sulfate and carbonate minerals are calculated from their essential constituents; X-ray data for these minerals serve only to indicate the variety of sulfate or carbonate minerals to be calculated. X-ray quantitative data and mineral compositions for quartz, cristobalite, feldspars, zeolite, kaolinite, chlorite, and illite determine the amounts of chemical constituents assigned to each of these minerals; X-ray and chemical data, and, to some extent, necessary assumptions determine the composition for minerals that are extremely variable, such as chlorite, illite, and feldspar. The remaining chemical constitutents, amounting to about half of most samples, are assigned to montmorillonite and mixed-layer clay. The composition assigned to these two minerals is expressed as a combined structural formula. The structural formula partly determines which montmorillonitic clays contain interlayer gibbsite- or brucitelike structures. The rationality of the structural formula and the extent of agreement between the X-ray-mineralogical and chemical-mineralogical calculations check the gross accuracy of the calculations for individual samples of Pierre Shale.

INTRODUCTION

The geochemical investigation of the Pierre Shale is a continuing study (Tourtelot, Schultz, and Gill, 1960; Rader and Grimaldi, 1961; Tourtelot, 1962) which will attempt to relate data on mineralogical and chemical composition of a large body of fine-grained sedimentary rocks to their physical and lithologic characteristics and to their stratigraphic and geographic positions. Because much of the Pierre Shale is fairly homogeneous, such an investigation requires reasonably precise quantitative data and knowledge of the accuracy and reproducibility of the data.

Quantitative analyses based on X-ray diffraction data have been described for clay minerals by numerous investigators (Talvenheimo and White, 1952; Johns, Grim, and Bradley, 1954; Degens, Williams, and Keith, 1957; Weaver, 1958; Jarvis, 1958; Sudo, Oinuma, and Kobayashi, 1961; and others). The author (1960) described general methods used by him for analyses of some aluminous clay minerals. X-ray methods also have been used for quantitative analyses of other minerals in samples, as for example, the quartz determinations reported by Rex and Goldberg (1958), the determinations of minerals in bauxite by Black (1953), and the determinations of feldspar, quartz, and calcite in prepared mixtures by Mitchell (1960). Schmalz and Zen (1959) used X-ray diffraction techniques for quantitative evaluation of both clay and other minerals in modern sediments from the Peru-Chile Trench. Descriptions of methods for complete X-ray quantitative mineralogical analyses of sedimentary rocks that have a clay mineral suite as complex as that of the Pierre Shale, however, have not previously been published.

This report describes techniques of X-ray analyses used in the investigations of the Pierre shale, presents data on the reproducibility and accuracy of the results, and describes the calculations used to assign chemical constituents to the minerals identified in each sample.

The chemical analyses used in parts of this report will be presented in a subsequent report.

X-RAY ANALYSIS

SAMPLE PREPARATION AND TREATMENT

Two types of mounts were made from each sample for X-ray analysis. An unoriented mount was prepared by packing a finely ground powder into a holder, and a oriented aggregate was prepared by using the porous tile technique of Kinter and Diamond (1956). An X-ray diffraction trace was run of the powder, and four traces were run of the oriented aggregate in the following order: (1) dried at room temperature, (2) glycol treated, (3) heated at 300°C for half an hour, and (4) heated at 550°C for half an hour. Traces were run by using nickel-filtered copper radiation generated at 40 kilovolts and 20 milliamperes, 1° beam slit and a 0.006-inch detector slit, and scanning at 2° per minute. Uniform response of the X-ray machine was maintained by periodic alinement checks and calibration with a standard sample. Before preparation of the oriented aggregate, the calcareous samples were first treated with cold 1N (normal) hydrochloric acid and washed with distilled water; they were then treated like the noncalcareous samples. Samples containing abundant organic material were treated either with warm 10 percent hydrogen peroxide or 5 percent chlorox and then washed in distilled water.

INTERPRETATION

WHOLE ROCK DATA

The abundance of nonclay minerals is interpreted from the size of the strongest diffraction peak for each mineral on the X-ray trace of the unoriented powder. Diffraction peaks and intensity factors used in interpreting mineral percent from peak size are shown in table 1. Most of the intensity factors shown in table 1 are derived from several diffractometer traces of prepared mixtures in which the concentration range of each mineral is similar to its concentration range in the Pierre Shale. Minerals in prepared mixtures used to develop the intensity factors came from Pierre material, insofar as possible. For example, the diluting agent in the mixtures was a Pierre bentonite composed entirely of montmorillonite which had a chemical composition reasonably close to that of the clays in the Pierre Shale; it therefore had an absorption factor similar to the clays in the Pierre Shale. If sufficiently pure Pierre materials were not available, as for quartz and feldspar, the materials used in the prepared mixtures were as similar as possible to the Pierre minerals in composition and particle size. Because an internal standard was not used, some control was lost over absorption effects. However, as will be discussed later, absorption apparently does not cause much variation in diffracted X-ray intensities within the concentration range of minerals

common in the Pierre Shale; by not using an internal standard, a diluting effect on diffracted intensities is avoided as is interference between reflections from the internal standard and the dozen or so minerals in the Pierre Shale.

Clinoptilolite is used as defined by Mumpton (1960) because in the Pierre Shale this mineral is stable when heated at 550°C for half an hour.

Peak intensities for the different varieties of feldspar vary with the chemical composition of the feldspar. The intensity factors in table 1 correspond to oligoclase, because this variety apparently is the most common in the Pierre Shale. Further refinement of the factor for feldspar seemed unwarranted, because in the small amounts commonly present in the Pierre Shale, the variety of feldspar could not be determined consistently.

Although the intensity factors recorded in table 1 would probably be different if other X-ray equipment were used, they are included here for comparative purposes.

TABLE 1.—*Factors for X-ray quantitative interpretation of minerals in the Pierre Shale*

Minerals	Peak position in degrees 2θ (CuKα radiation)	Intensity factor in counts per second per 100 percent
Quartz (SiO₂)	26.6	2,000
Disordered cristobalite (SiO₂)	21.8	570
Plagioclase (oligoclase)	28.0	1,000
K-feldspar (KAlSi₃O₈)	27.5	1,000
Calcite, pure (CaCO₃)	29.4	1,000
Calcite, mixed [1] (CaCO₃)	29.6–30.0	500
Dolomite, pure (CaMg(CO₃)₂)	31.0	1,000
Siderite, mixed [2] (FeCO₃)	31.7–31.9	[3] 600
Rhodochrosite, mixed [4] (MnCO₃)	[5] 30.8–31.5	300
Gypsum (CaSO₄·2H₂O)	11.6	1,500
Jarosite [6] (KFe₃(OH)₆(SO₄)₂)	29.1	[3] 550
Alunite (KAl₃(OH)₆(SO₄)₂)	30.0	750
Pyrite (FeS₂)	33.1	[3] 250
Clinoptilolite [7] (Na₂Al₂Si₁₀O₂₄·7H₂O)	10.0	800
Clay minerals [8]	19.9	100(150)
	34.6	60(60)
	61.9	30(40)

[1] Mg⁺², Fe⁺², or Mn⁺² substitution.
[2] Ca⁺², Mg⁺², or Mn⁺² substitution.
[3] In amounts less than 10 percent.
[4] Ca⁺², Mg⁺², or Fe⁺² substitution.
[5] Commonly a very broad peak.
[6] Probably extensive substitution of H⁺¹ for K⁺¹.
[7] Some K⁺¹ and Ca⁺² substitution.
[8] Values in parentheses are for bentonite. See text for explanation of these three values.

CARBONATE MINERALS

Intensity factors for calcite and dolomite (table 1) are based on determinations of acid-soluble carbonate and X-ray measurements for 58 samples of calcareous shale and marlstone, and 5 carbonate nodules from the Pierre Shale (fig. 1). The amount of acid-soluble carbonate was determined by weight loss resulting from repeated treatment with 1N hydrochloric acid until effervescence stopped. X-ray patterns that were run before and after the acid treatment indicated that all the carbonate minerals had been removed and that no minerals other than carbonates were discernibly affected by the
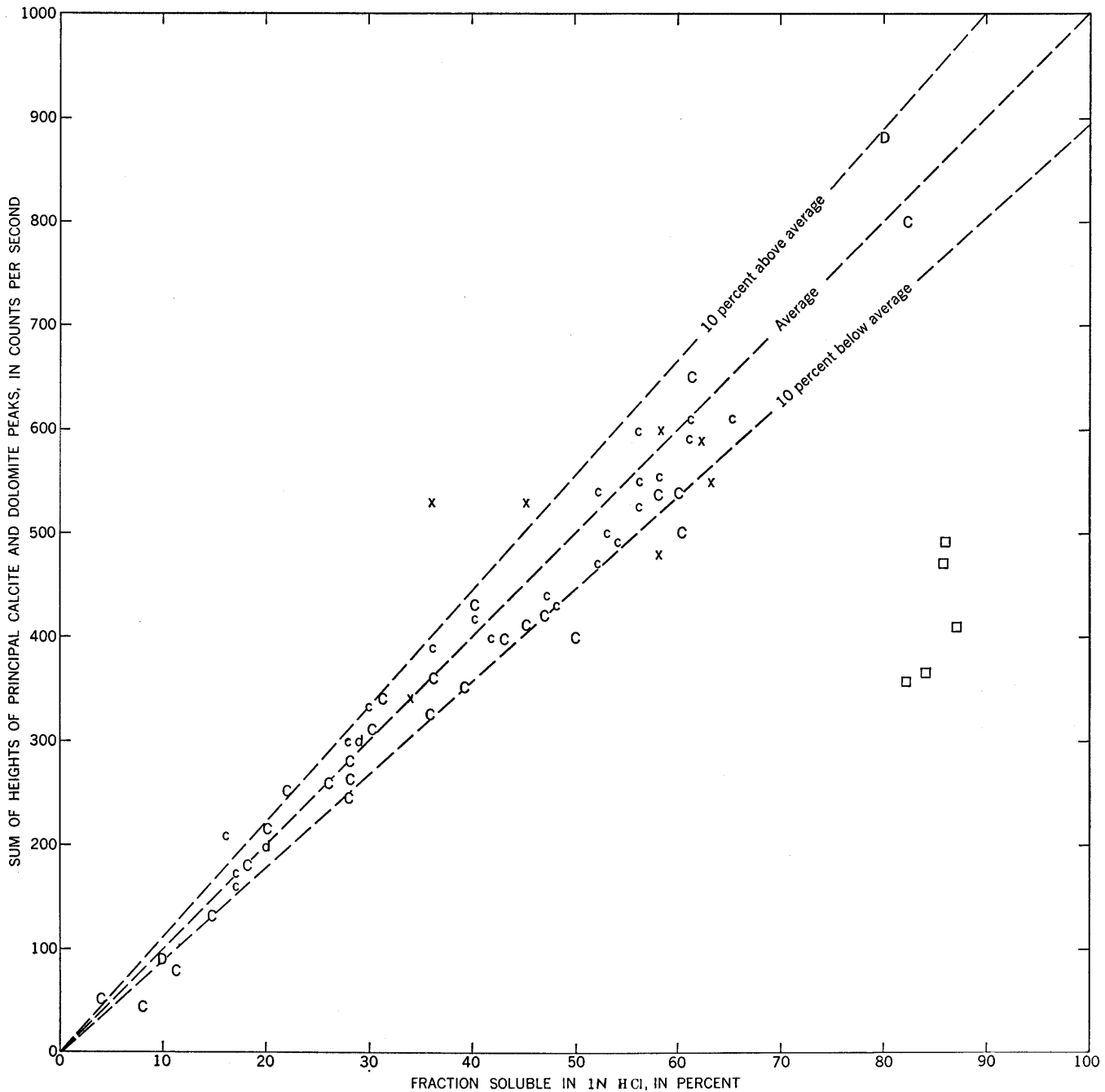
FIGURE 1.—Relation between principal carbonate X-ray peak heights and acid-soluble carbonate for 63 samples from the Pierre Shale. D, dolomite only; d, mostly dolomite; x, dolomite and calcite in about equal amounts; c, mostly calcite; C, calcite only; □, calcite from a concretion with extensive substitution of magnesium, iron, and manganese ions.

acid treatment used. The proportion of calcite and dolomite in each sample estimated from the relative intensities of their principal peaks is indicated by the symbols on figure 1. Regardless of the proportions of calcite and dolomite, the intensity sum of their principal peaks is almost linearly related to the total amount of acid-soluble carbonates. Thus, the fine-grained but pure calcite and dolomite common in many samples of Pierre Shale give principal diffraction peaks

of about the same intensity for a given amount of material; with the X-ray equipment used, the intensity of the principal peak can be divided by 1,000 cps (counts per second) to give a carbonate value that generally will be accurate within 10 percent of the amount stated (fig. 1). The fact that the strongest diffraction peaks of calcite and dolomite are of nearly equal intensity agrees generally with the results of Tennant and Berger (1957) and Gulbrandsen (1960).

An intensity factor of 1,000 cps is not applicable to the carbonate minerals composing concretions (fig. 1). The carbonates in concretions gives relatively broad X-ray peaks that are shifted from their normal positions; for a given amount of this mixed carbonate, the height of the principal peak is about half of that expected for a pure calcite (fig. 1). Although this intensity relation for X-ray diffraction peaks of calcite from concretions is shown by only five samples on figure 1, its general applicability is confirmed by observations of many traces of nodules that are composed predominantly (80–90 percent) of carbonate minerals, but for which solubility data are not available. Chemical data indicate extensive substitution of iron, magnesium, and, in some samples, manganese for the calcium in such carbonate. In table 1 and throughout this report, the modifier "mixed" is used to distinguish carbonates having extensive substitution from "pure" carbonates having an ideal chemical composition.

DISORDERED CRISTOBALITE

Cristobalite in the Pierre Shale gives a few broad X-ray peaks close to the strongest peaks of well-crystallized cristobalite. It apparently is similar to the opal of Franks and Swineford (1959, fig. 4) and to the beta cristobalite of Levin and Ott (1933). Yet, the term "opal" seems inappropriate because "opal" generally connotes a hydrous amorphous silica mineral, whereas the material in the Pierre is crystalline and produces a distinct X-ray pattern. Beta cristobalite seems inappropriate because the term "beta," though variously used, generally implies a high temperature form, whereas material like that in the Pierre apparently has not resulted from high temperatures. In this paper, the term "disordered cristobalite" indicates the presence of distortions in the crystal lattice that produce the characteristic broad X-ray peaks. According to Franks and Swineford (1959), the distortions in such material are caused by a small amount of alumina, water, and alkalies stuffed into the cristobalite crystal lattice.

The intensity factor in table 1 for disordered cristobalite in the Pierre Shale was determined empirically, because no pure samples of cristobalite known to be identical with that in the Pierre Shale were available for prepared mixtures. Two considerations were involved in the determination of the intensity factor for cristobalite: (1) the amount of material unaccounted for after percentages of other mineral components had been calculated, and (2) for chemically analyzed samples, the amount of silica left over after an appropriate amount had been assigned to clay and quartz. For example, partial X-ray and chemical analyses of a sample are as follows:

X-ray analysis:	*Percent*
Clay minerals	55
Quartz	7
Plagioclase	1
	63

Chemical analysis:	*Percent*
SiO₂	70.2
Al₂O₃	10.8
	81

The only mineral detected on the X-ray trace other than the three listed is disordered cristobalite, whose principal peak at 21.8° 2θ is 200 cps high. Clay minerals, quartz, and plagioclase constitute 63 percent of the sample; therefore the remaining 37 percent must be mostly disordered cristobalite. The general formula for converting X-ray peak intensity into percent of cristobalite is

$$\frac{\text{peak height (cps)}}{\text{intensity factor (cps) per 100 percent}} = \text{percent cristobalite;}$$

for the sample above, the intensity factor (cps) per 100

$$\text{percent} = \frac{200 \text{ cps}}{37 \text{ percent}} = 540.$$

The silica and alumina values also can be used to derive an X-ray intensity factor for cristobalite in the following way: The average ratio of weight percent silica to alumina of clays in the Pierre Shale is about 2.6; therefore, in the sample containing 70.2 percent silica, 10.8 percent alumina, and 7 percent quartz, about 28 percent of the silica (10.8×2.6) should be in the clay minerals, 7 percent in quartz, and the remaining 35 percent silica can be assigned to cristobalite. From the inferred amount of 35 percent cristobalite, an X-ray intensity factor of 570 cps $\left(\frac{200 \text{ cps}}{35}\right)$ is calculated.

Both the difference method and the chemical method generally indicate the 570-cps value given in table 1 as an appropriate intensity factor for disordered cristobalite in the Pierre Shale. The amount of cristobalite in one sample, as calculated from X-ray analysis, was subsequently checked by the solubility test of Hashimoto and Jackson (1960). As shown in table 8, the X-ray determination of 35 percent obtained by using the intensity factor of 570 cps is in good agreement with the solubility test in which 34.8 percent dissolved silica and 0.85 percent dissolved alumina are reported. Some solution of components other than cristobalite may have occurred, but the X-ray determination gives a figure that must be nearly correct and that cannot be obtained as conveniently in any other way.

TOTAL CLAY MINERALS

A direct determination of intensity factors for clay minerals in the Pierre Shale was not possible, because all the shale samples contain other components. The only reasonably pure clays are in the bentonites, and diffraction characteristics of these are not typical of the shales in general. There was no assurance that clays used in mixtures intended to approximate the Pierre would be similar to the clays actually in the Pierre. Therefore, the intensity factor for total clay minerals was obtained by difference; samples of Pierre Shale containing in most part only clay and quartz were used. For example, if X-ray data indicated that a sample contained 20 percent quartz and 2 percent feldspar and if no other reflections were perceived except for the clays, then the clay reflections were assumed to represent 78 percent of the sample. A large number of such analyses gave fairly consistent relations between the sizes of the peaks shown on table 1 and the apparent total amount of clays in each sample. Basal reflections were not used because of the considerable effect of any slight preferred orientation on these reflections, a factor which has much less effect on the intensity of the non-basal reflections. Three nonbasal reflections common to most clay minerals in shale samples from the Pierre were used (see table 1); most significance was given to the amount calculated from the peak at about 19.9° because this peak is the largest of the three and most easily measured. This amount was modified if the 34.6° and 61.9° peaks gave appreciably different but apparently valid amounts of clay. For example, if the 19.9° peak indicated 70 percent clay, but both of the other two peaks indicated 60 percent, then 65 percent clay minerals was reported. Consideration of three peaks also made possible the elimination of any one peak with which reflections from other minerals interfered.

Intensity factors used for total-clay in shales cannot be used for bentonites because the montmorillonite in bentonites generally gives bigger peaks than do the clay minerals in the shales. Therefore, the numbers in parentheses in table 1 were used to evaluate the total amount of clay minerals in bentonites.

The system for determining total clay in samples of Pierre Shale will not be applicable to all possible mixtures of clay. For example, highly kaolinitic samples will give peaks higher than the clay minerals in the Pierre; if factors listed in table 1 were used for such kaolinitic clays, an unrealistic total amount, perhaps 150 percent clay, might be calculated. The particular dual system for shales and bentonites listed in table 1 is appropriate only for material very similar to the Pierre Shale.

Because of the many considerations involved in the determination of the intensity factors for total clay minerals and cristobalite, their quantitative determinations are probably the least accurate. Accordingly, amounts of total clay and cristobalite have been rounded to the nearest 5 percent.

A figure for the total amount of clay minerals in each sample might have been obtained by assuming that clay composed that portion of each sample not assigned to nonclay minerals. This method probably would give a figure for total clay in most samples as accurate or more accurate than could be derived by using the intensity factors listed in table 1. Derivation of total amount of clay by using the X-ray intensity factors in table 1 for all samples has the advantage of indicating which of the hundreds of samples of Pierre Shale analyzed give sums for total minerals present that are so low as to indicate something unusual, such as the presence of amorphous material. Almost all samples give totals between 90 and 105 percent. Sums within this range are interpreted as normal variations caused by the inaccuracies of the methods used and as being free of appreciable amounts of components amorphous to X-rays.

Absorption of X-rays can influence intensity relations greatly in some samples. However, most Pierre samples are composed of reasonably uniform proportions of silicate minerals; the X-ray peak intensity relations observed from most prepared mixtures indicate that absorption has little effect upon the nearly linear relation between mineral percent and diffraction intensities within the concentration ranges in which the different minerals commonly occur in the Pierre Shale. The most extensive variation common in the mineralogy, chemistry, and, thus, in the absorption of Pierre samples probably involves the amount of carbonate minerals, but even in this variation no drastic deviation from linearity is observed (figs. 1 and 6). Exceptions to linearity are provided by samples having high iron contents, in which high absorption of copper radiation by the iron reduces expected intensity for all peaks and adjustments in intensity factors are necessary. Such samples, however, are not common from the Pierre Shale.

CLAY FRACTION DATA

CLAY MINERALS PRESENT

Clay minerals in samples of Pierre Shale analyzed from South Dakota and adjacent areas are classified as kaolinite, chlorite, illite, montmorillonite, and mixed-layer clay. X-ray diffractometer traces of pure clay minerals from or similar to those in the Pierre Shale are shown in figure 2. The following criteria are used to identify the clay minerals:

1. Kaolinite is characterized by a series of basal X-ray diffraction peaks at about 7A, 3.5A, and so forth. Judged from the shape of the 7A peak (Schultz, 1960, fig. 2), kaolinite in the Pierre Shale appears to be of a moderately well crystallized variety.

2. Chlorite is characterized by a series of basal X-ray diffraction peaks at about 14A, 7A, 4.8A, 3.5A, and so forth. Heating at 550°C for half an hour causes a change in the chlorite structure, hence the 14A reflection increases greatly in size and the other basal orders almost disappear.

3. Illite is characterized by a series of X-ray diffraction peaks at 10A, 5A, 3.3A, and so forth that are not appreciably affected by either glycol or heat treatment. Illite is used as a general or group term for the micalike clay of partly uncertain species and undeterminable polymorph that generally gives fewer and broader X-ray reflections than ideal mica, but that shows no significant change in the 10A spacing after mild heat or glycol treatment. The illite in the Pierre Shale is predominantly a dioctahedral aluminous variety. However, materials fitting the above description of illite may include some micalike clays other than the usually dominant disordered muscovitelike clay, and may include a small amount of undetected mixed layers. For example, analyses by optical methods revealed small amounts of glauconite and biotite that were included with illite in the X-ray analyses of some samples.

4. Montmorillonite is characterized by its expanding lattice. When dried under ordinary room conditions, montmorillonite having sodium as the exchange ion frequently has one molecular layer of water and a basal spacing of about 12.5A; when calcium or magnesium is the exchange ion, it frequently has two molecular water layers and a c-axis spacing of about 15.5A (Grim, 1953, p. 57). After glycol treatment, montmorillonite exhibits a series of basal X-ray peaks at 17A, 8.5A, 5.7A, 4.2A, 3.4A, 2.8A, and so forth. When heated at 300°C for half an hour, volatilization of all adsorbed water or ethylene glycol causes a decrease in the basal spacing to about 10A. The montmorillonite in the Pierre Shale gives the X-ray pattern of a dioctahedral aluminous variety.

5. Mixed-layer clay in the Pierre Shale is characterized by a broad basal X-ray diffraction peak near 17A on the trace of the glycolated sample (fig. 2), indicating that montmorillonite layers are most abundant. Complete collapse of the c-axis spacing to about 10A after heat treatment of most samples indicates that the only other common layers are illite, because only illite and montmorillonite give c-axis spacings of about 10A after being heated at 300°C. In only a few samples does a c-axis spacing of greater than 10A after heating indicate presence of a brucitelike interlayered component of moderate thermal stability that prevents collapse to 10A at 300°C but that will collapse at 550°C. The mixed-layer clays of the Pierre Shale are dioctahedral aluminous varieties.

COMPARISON OF X-RAY PEAK SIZES

The relative sizes of the X-ray diffraction peaks from the basal planes of the clay minerals in the 7 to 17A range provide the basis for calculating the relative amounts of the different clay minerals. For some calculations, peak area is used and for others, peak height. Methods for measuring peak size and comparing intensities, which were previously derived (Schultz, 1960), are:

1. The peak area is considered to be the sum of five measurements of the height above the baseline. One measurement is at the peak position (called peak height) and the other four are at ½° intervals on either side of the peak position. For example, in the symmetrical peak illustrated in the lower left corner of figure 3, the height above baseline at the peak position is 10 divisions, the height above baseline at ½° and 1° 20 on the left side of the peak position is 1½ divisions and ½ division, and the height above baseline at ½° and 1° on the right side of the peak position is 2 divisions and ½ division; the total of these 5 measurements, 14½ divisions, is considered a measure of the peak area. The size of the divisions is immaterial, because all measurements of the basal clay peaks are used on a relative basis only. In practice, the one-tenth-inch grid on the recorder paper is used as convenient division. For notably asymmetrical peaks (fig. 3, lower left corner), one peak flank measurement is made on the steep side of the peak and three are made on the less steep side. The determination of peak area thus requires consideration of peak shape.

2. The baseline indicates where the trace would be if the mineral producing the diffraction peak were absent. The position of the baseline depends upon the intensity of background radiation and upon radiation reflected from other minerals having closely similar lattice spacings. The exact position of a baseline below critical clay mineral peaks is, to some extent, subject to the personal judgment of the interpreter.

3. After heating at 300°C, all the clay minerals common in the Pierre Shale give X-ray reflections
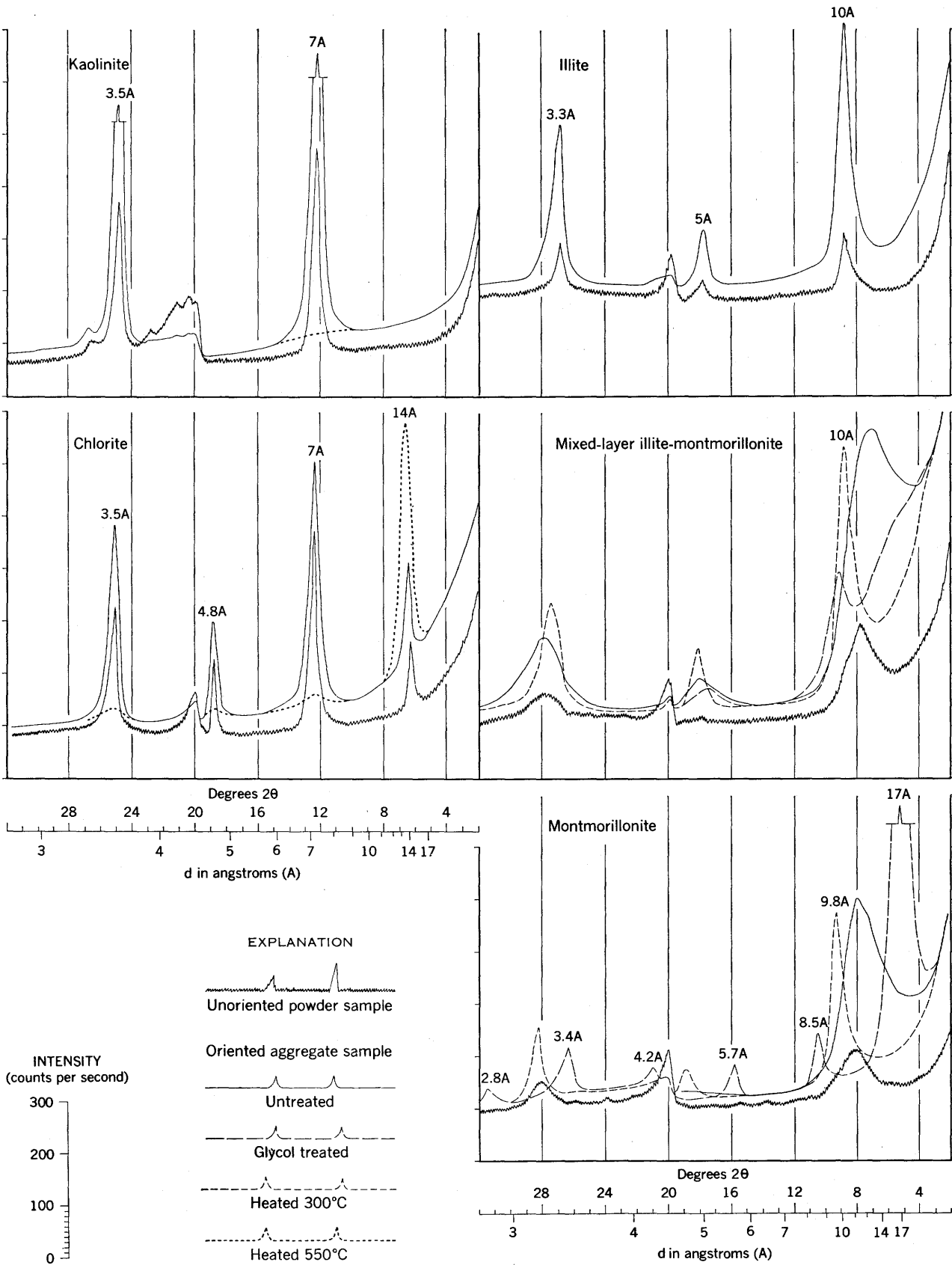
FIGURE 2.—X-ray diffractometer traces of clay minerals representative of those in the Pierre Shale (CuK α radiation).

from their basal planes at about either 7A (kaolinite and chlorite) or 10A (illite, mixed-layer clay, and montmorillonite) (fig. 2). Therefore, with suitable correction, an initial division into these two groups of clay minerals can be made by comparing the relative areas of the 7A and the 10A peaks after the sample has been heated at 300°C.

4. In their collapsed state after 300°C heating, aluminous illite, montmorillonite, and mixed-layer illite-montmorillonite give 10A X-ray peaks of about the same area for equal weights of material.

5. The ratio of peak areas of the 7A and 10A reflections for equal amounts of kaolinite and collapsed illite, montmorillonite, or mixed-layer illite-montmorillonite ranges from 1:1 for poorly crystallized kaolinite to 2:1 for well-crystallized kaolinite; the ratio for kaolinite of an intermediate degree of crystallinity is intermediate between 1:1 and 2:1. The sharpness of the 7A kaolinite peak as expressed by its area:height ratio can be used to evaluate the crystallinity of kaolinite.

6. The ratio of heights of the 17A peak of glycolated montmorillonite to the 9.8–10A peak of collapsed montmorillonite generally is between 4 and 5 for the sample mounts used; an average value of 4.5 is used.

A relation of peak intensity to crystallinity similar to that for kaolinite may exist also between illite and well-crystallized mica. Well-crystallized mica, however, is not a significant component in the Pierre Shale; thus, only the poorly crystallized illitic type of clay mineral need be considered.

Application of these factors to the quantitative interpretation of X-ray data are discussed on pages C9–C12 and are shown in table 2. The basis and methods of quantitative interpretation of the amounts of kaolinite and chlorite are discussed in the following section.

ESTIMATION OF KAOLINITE AND CHLORITE

Differentiating between kaolinite and chlorite is one of the most common difficulties in X-ray identification of clay minerals. The difficulty arises from coincidence of the basal reflections of kaolinite with those of chlorite at about 7A and 3.5A (fig. 2). The problem is important in this study because the Pierre Shale commonly contains small amounts of both kaolinite and chlorite. The (002) reflection of kaolinite and the (004) reflection of chlorite at about 3.5A are never resolved on diffraction traces of samples from the Pierre Shale; hence, the solution of Grim, Bradley, and White (1957, fig. 2) is not applicable. The thermal stability of the two minerals in the Pierre Shale is such that the intensity changes of the X-ray peaks occur at about the

same temperature, and the solution of Johns, Grim, and Bradley (1954) is not applicable. Kaolinite and chlorite in the Pierre Shale commonly occur in such small amounts that the (003) reflections of kaolinite at 2.38A and of chlorite at about 4.8A are not both seen, thus, the solution of Weaver (1958, p. 271) also is not helpful.

The factor for determining the total kaolinite and chlorite was derived in the following manner. In samples containing no chlorite, the shape of the 7A peak indicates that kaolinite in the Pierre Shale has a fairly uniform intermediate degree of crystallinity which should give a 7A peak having an area about 1.4 times that of the 10A peak of the illite and collapsed montmorillonite or mixed-layer illite-montmorillonite (Schultz, 1960, fig. 2; see also item 5, p. C8 of this report). The shape of the 7A peak for samples containing both kaolinite and chlorite is about the same as for samples containing only kaolinite; thus the crystallinity of the kaolinite is apparently similar to that of the chlorite. According to Weaver (1958, p. 271), the 7A peaks of kaolinite and chlorite, which presumably possess similar crystallinity, are of about equal intensity. Therefore, for all Pierre Shale samples the size of the 7A peak was divided by 1.4 and the quotient was then compared with the size of the 10A peak in order to estimate the relative quantities of the minerals producing these two X-ray reflections.

The method formulated for evaluating the relative amounts of kaolinite and chlorite in samples of Pierre Shale is based on a comparison of X-ray traces of oriented aggregates before and after they were treated with warm 6N hydrochloric acid for 16 hours and after they were heated at 300° C and 550° C for half an hour. Twenty-eight samples in which chlorite composed more than 5 percent of each were studied. In no sample was a 14A chlorite peak observed after the acid treatment, but in all the samples, a 7A kaolinite peak remained. Because orientation in the aggregates differed in the slides prepared before and after the acid treatment, peak-size comparisons were all relative to the 10A peak after heating at 300°C; minerals causing the 10A peak apparently were not appreciably affected by the acid treatment. For the 28 samples so studied, the amount of the decrease in height of the 7A peak due to removal of chlorite by acid treatment averaged two-thirds (ranged between one-half and one) of the height of the chlorite peak at 14A after heating at 550° C and before treating with hydrochloric acid. Therefore, for a sample of the Pierre Shale, the part of the 7A peak that is attributed to reflections from chlorite is calculated by multiplying the height of the 14A peak obtained after heating the sample at 550° C by the factor two-thirds (or dividing by 1.5). The remainder of the 7A peak

height is attributed to kaolinite. For example, if a sample gives a 7A peak that is 12 units high and a 14A peak (after heating at 550°C) 9 units high, then 6 units (9÷1.5) of the 7A peak height would be attributed to chlorite and the other 6 units to kaolinite; the two minerals would be calculated as being equally abundant.

In most samples of the Pierre, kaolinite and chlorite are generally present in small amounts, and one of these minerals is calculated to be no more than twice as abundant as the other. Within this range, differences in the relative abundance of kaolinite and chlorite may be due only to inaccuracy in measuring the usually small 7A and 14A peaks. The differences are considered to be significant only where the total amount of kaolinite and chlorite is more than a few percent and where one mineral is more than twice as abundant as the other.

As the Pierre investigation continues, samples may be found which contain large amounts of either kaolinite or chlorite that is of considerably different crystallinity than that in the fine-grained offshore facies investigated so far. If this happens, appropriate changes can be made in the factors used for the quantitative interpretation of kaolinite or chlorite. In the samples which have been investigated to date (1960), however, kaolinite and chlorite occur in such small amounts and appear to be sufficiently uniform in grain size and crystallinity that a variable comparison factor is not justified.

EXAMPLES OF INTERPRETATION

Figure 3 shows quantitative interpretations of the X-ray diffractometer traces of three samples that illustrate the known range of mineral composition in the Pierre Shale. Sample 259543 (fig. 3B) will be discussed in greatest detail because it is most typical of much of the Pierre Shale.

The minerals in sample 259543 for which diffractometer peaks are noted other than the clay minerals are quartz, feldspar, clinoptilolite, and possibly pyrite. By dividing the measured height of the 26.6° quartz peak in counts per second by 2,000 $\frac{cps}{100\ percent}$ (from table 1), the amount of quartz is determined to be 16 percent. The 2-percent value for feldspar is similarly derived by dividing the measured height of the 28.0° feldspar peak by 1,000 $\frac{cps}{100\ percent}$. On the basis of the 28.0° peak position rather than the 27.5° one (table 1), the feldspar is determined to be mainly a plagioclase rather than a potassium feldspar. The 1-percent clinoptilolite is interpreted from the small peak at 10.0°; although such a small peak might be considered to be of questionable significance, it is here interpreted as clinoptilolite because the same peak is

seen on the X-ray traces of the oriented aggregate and because no other mineral now known to occur in the Pierre Shale gives an X-ray peak in this position. Pyrite is listed as questionably present in this sample because of the very small size of the 33.1° peak and because no other pyrite peak can be distinguished. The value of 75 percent for total amount of clay is derived from the 19.9° clay peak; the values for total clay from the 34.6° peak and the 61.9° peak are in fairly close agreement. The 94-percent total of minerals determined is within the range normally expected. Of the undetermined 6 percent, 1.5 percent is known to be organic matter and the remaining 4.5 percent probably is caused mostly by using a value for total clay that is slightly too low.

Relative amounts of the different clay minerals in sample 259543 are determined by using the procedure listed in table 2. The clay mineral fraction is calculated to be comprised of 4 percent kaolinite, 3 percent chlorite, 17 percent illite, 33 percent montmorillonite, and 43 percent mixed-layer illite-montmorillonite. Each of these relative amounts may be multiplied by 75 percent (the proportion of total clay minerals) to determine their proportion in the total sample.

Amounts and proportions of minerals for samples 259574 (fig. 3A) and 259550 (fig. 3C) are calculated in a similar fashion. Inasmuch as no 17A peak is shown on the glycol trace for sample 259574 (fig. 3A), no montmorillonite is recorded. The very large 17A peak for glycolated sample 259550 (fig. 3C) corresponds to an unusually large amount of montmorillonite; although the height of the 17A peak for sample 259550 is twice that for sample 259543, the amount of calculated montmorillonite is not twice as much. The large peaks obtained from the oriented aggregate of sample 259550 are, in part, due to a very high degree of preferred orientation of the clay flakes. The large peaks near 12.5A on the untreated traces for samples 259543 and 259550 indicate that much of the montmorillonite in these samples contains one layer of hydration water, this single layer in turn suggests that sodium probably is the most abundant exchangeable cation.

The method of differentiating montmorillonite and mixed-layer clay may be unrealistic, because all the material producing the broad 17A peak in samples like no. 259543 (fig. 3) might be interpreted as entirely mixed-layer clay rather than as a combination of montmorillonite and mixed-layer clay. Pure, unmixed montmorillonite having a 17A reflection as strong as that shown for sample 259543 should produce a series of reasonably sharp basal reflections at submultiples of the 17A(001) spacing—8.5A(002), 5.7A(003), 4.2A(004)
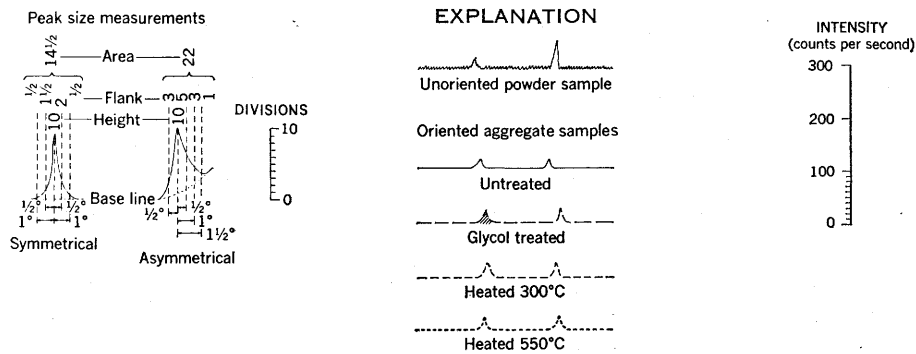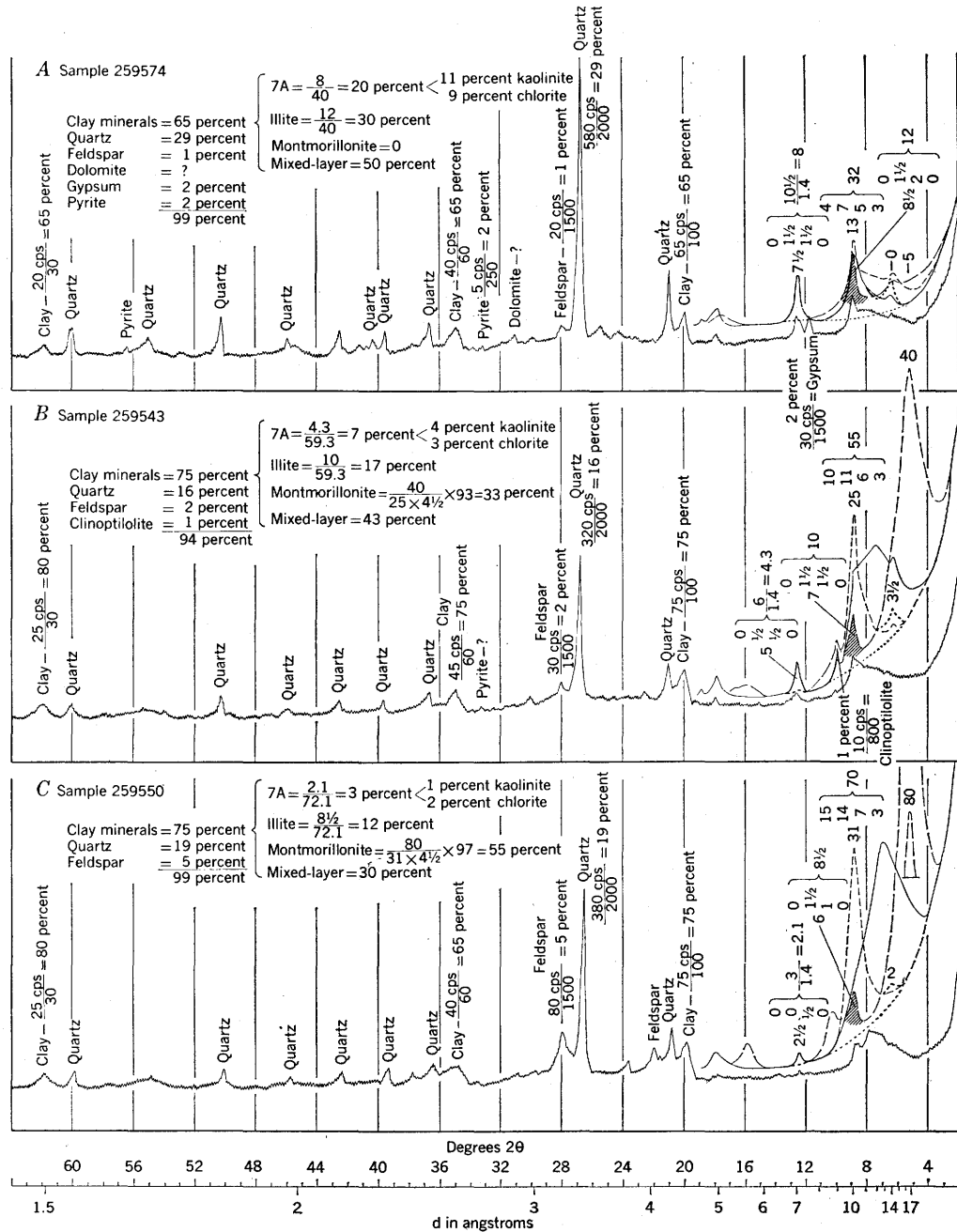
FIGURE 3.—Examples of quantitative evaluation of X-ray diffractometer traces of three samples of Pierre Shale (CuK α radiation). Illite peak at 10A is shaded.

TABLE 2.—*Procedure for calculation of relative amounts of clay minerals in the Pierre Shale*

General procedure	Calculations for sample 259543 (fig. 3B)
1. Measure the areas of the 7A, the 10A glycol, and the 10A 300°C peaks; measure the heights of the 7A, the 10A 300°C, the 14A 550°C, and the 17A glycol peaks	7A peak height=5; peak area=6. 10A glycol peak area=10. 10A 300°C peak height=25; peak area=55. 14A 550°C peak height=3½. 17A glycol peak height=40.

2. Corrected 7A peak area $=\dfrac{\text{7A peak area}}{1.4}$ ---------- Corrected 7A peak area $=\dfrac{6}{1.4}=4.3$.

3. Kaolinite+chlorite (percent) =

$$\dfrac{\text{corrected 7A peak area}}{\text{corrected 7A peak area}+\text{10A 300°C peak area}}\times100$$ ------ Kaolinite+chlorite $=\dfrac{4.3}{4.3+55}\times100=7$ percent.

4. Chlorite (percent) =

(kaolinite+chlorite) $\times\dfrac{\text{14A 550°C peak height}}{1.5\times\text{7A peak height}}$ ---------- Chlorite $=7$ percent $\times\dfrac{3½}{1.5\times5}=3$ percent.

5. Kaolinite (percent) = (kaolinite+chlorite) − chlorite --------- Kaolinite $=7$ percent -3 percent $=4$ percent.

6. Illite (percent) =

$$\dfrac{\text{10A glycol peak area}}{\text{corrected 7A peak area}+\text{10A 300°C peak area}}\times100$$ ---- Illite $=\dfrac{10}{4.3+55}\times100=17$ percent.

7. Montmorillonite (percent) =

$$\dfrac{\text{17A glycol peak height}}{4½\times\text{10A 300°C peak height}}\times(100-\text{kaolinite}-\text{chlorite})$$ - Montmorillonite $=\dfrac{40}{4½\times25}\times93=33$ percent.

8. Mixed-layer clay (percent) $=100-$ (kaolinite+chlorite+illite +montmorillonite) ------------------------------- Mixed-layer clay $=100-(4+3+17+33)=43$ percent.

and so forth. Such higher order basal reflections, though commonly noted for bentonite samples, are generally not observed for the shale samples, or, if present, they are very broad, small, and shifted slightly from their theoretical positions. According to Weaver (1956, fig. 1), interlayering of 10–20 percent of nonexpanding layers with montmorillonite produces very little shift in the first basal reflection at 17A. Such scant mixed-layering apparently shifts the higher order basal reflections more than the 17A(001) reflection. Probably the most notable effect, however, is the broadening and decrease in intensity of all the basal reflections. If mixed-layering is accompanied by dilution with several other minerals as it is in the Pierre Shale, the higher order basal reflections commonly are not clearly seen. Thus, the first basal reflection at 17A is the only consistently usable criterion for evaluating the expandable clay. However, if only the position of the 17A reflection is considered and is interpreted as evidence that all the expanding clay is unmixed montmorillonite, then the quantitative values give no indication of any difference between the expanding clay in shale samples like 259543 or 259550 (fig. 3) and the montmorillonite in the bentonite samples (fig. 2). In contrast to the shales, the bentonites generally produce a series of sharp basal re-

flections at 17A, 8.5A, 5.7A, and so forth. On the other hand, if broadness of the 17A reflection peak and weakness or slight shifting of higher order basal reflection peaks are interpreted as indicating that all the expandable clay is mixed layered, then the interpretation provides no basis for differentiating the expanding clay in a sample like 259543 from that in sample 259574 (fig. 3), even though the diffractometer patterns for the two samples are quite different. Both samples would be reported as containing abundant mixed-layer clay but no montmorillonite.

The sharpness and relative height of the 17A reflection are the most notable differences observed between most X-ray patterns from samples of Pierre Shale; in some manner the quantitative X-ray interpretation should express these differences. The means by which they have been expressed is by reporting both mixed-layer montmorillonite-illite and theoretically pure montmorillonite in relative amounts that depend on the sharpness or relative size of the 17A reflection. If no distinct 17A reflection is perceived, as in sample 259574 (fig. 3), then no montmorillonite is reported, and all the increase in size of the 10A reflection after heating at 300°C is attributed to mixed-layer clay. Relatively large 17A reflections, as in samples 259543 and 259550

(fig. 3), result in proportionately large amounts of reported montmorillonite; nevertheless, in both these samples some reported mixed-layer clay serves to differentiate the partially expanding clay in these samples from the completely expanding montmorillonite common in the bentonite beds.

Some discretion must be used in calculating the ratio of montmorillonite to mixed-layer clay, because several factors may affect the 17A : 10A ratio of 4.5 : 1 normally expected for montmorillonite in the Pierre Shale. First, the 4.5 : 1 ratio is an average; thus, for example, if a 4.0 : 1 ratio is measured but the X-ray pattern shows a good, sharp sequence of basal orders all in the proper positions for montmorillonite, then the expanding clay is interpreted as being entirely montmorillonite, regardless of the deviation of peak heights from the ideal 4.5 : 1 average. Second, a very thin oriented aggregate of pure montmorillonite produces a 17A : 10A ratio considerably in excess of the expected 4.5 : 1 ratio, because, as the diffraction angle increases from the 17A to the 10A positions, increasingly more of the X-ray beam penetrates through the sample instead of being diffracted by it. In such an example, however, the thinness of the sample is readily observed and a fairly good sequence of basal orders is still produced by the glycol-treated slide; the clay can therefore be reasonably interpreted as montmorillonite, regardless of the abnormally high 17A : 10A ratio. Third, a thick oriented aggregate of exceptionally well oriented montmorillonitic clay will produce extremely strong X-ray reflections which saturate the geiger counter for the 17A peak and cause an abnormally low 17 : 10A peak-height ratio. In such instances, the sharpness and relative intensities of the higher order basal reflections can be used to estimate the extent of mixed-layering in the montmorillonite; moreover, the intensity of the X-ray beam reaching the sample can be reduced in order to reduce the intensity of the diffracted beam until it is within the linear range of the detector.

REPRODUCIBILITY

Four variables affect the reproducibility of quantitative values as determined from the X-ray diffractometer studies. They are:

1. Interpretation: inconsistencies in measurement of peak size.
2. Machine: variations in response of the X-ray diffractometer equipment.
3. Sample preparation: variations in packing of the unoriented powder and in the degree of preferred orientation of the oriented aggregates.

4. Sampling: differences in pieces of sample selected for analysis.

Repeated analyses that are intended to indicate the importance of each of these four variables are given in table 3.

Quantitative values determined from X-ray traces of powders of five different pieces of the same sample are recorded in column 1 of table 3, and the clay-mineral analyses from the oriented aggregates prepared from the same five pieces are recorded in column 2; all four variables enter into the values in columns 1 and 2. The oriented aggregates used for columns 3, 4, and 5 of the table are made from the same minus-2 micron fraction from each of the three different samples in order to eliminate any sampling error. Data in column 3 are from five oriented aggregates prepared from the same clay-water slurry; the first three variables enter into the tabulated quantitative values. Data in column 4 are from five different groups of X-ray traces made from a single oriented aggregate; the first two variables enter into these values. Data in column 5 are from five different interpretations of the same diffractometer traces made over a period of several days; only the first variable (interpretation) enters into these values.

The means, standard deviations ($\sqrt{\dfrac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$;

n=number of determinations; x=calculated value), and coefficients of variation ($\dfrac{\text{standard deviation} \times 100}{\text{mean}}$ from each group of five determinations are also given in table 3. In the lower part of the table, the standard deviations and coefficients of variation are totaled for each of the clay minerals and for all five clay minerals combined.

The standard deviations for the five determinations of each of the individual clay minerals in each of the three samples vary considerably (table 3). The total of the three standard deviations for each clay mineral, however, generally decreases from column 2 to column 5 of the table, and the total of the standard deviations for all five clay minerals decreases consistently. The magnitude of this decrease is an approximate measure of the influence of each of the four previously mentioned variables on the reproducibility of the quantitative values. Each of the four variables introduces some uncertainty, but inconsistent interpretation of peak size seems to cause the largest variation in the calculated values.

Part of the inconsistency of interpretation is caused by slight differences in placement of the baseline below

TABLE 3.—*Repeated X-ray analyses, in percent, of three samples of Pierre Shale*

[?, presence doubtful, calculated as zero. Variables: a, interpretation; b, X-ray machine; c, sample preparation; d, sampling]

Whole sample

Sample	1 (variables a–d)							2 (variables a–d)					Total
	Total clay	Quartz	Feldspar	Pyrite	Dolomite	Gypsum	Clinoptilolite	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	
259547	65	30	1	?	?	1	--------	9	7	29	55	--------	--------
	65	30	1	0	?	0	--------	10	7	30	53	--------	--------
	70	31	2	?	?	0	--------	11	7	30	52	--------	--------
	65	31	1	3	?	0	--------	8	8	27	57	--------	--------
	70	30	2	4	?	?	--------	8	7	27	58	--------	--------
Mean	67	30.4	1.4	1.4	.4	.2	--------	9.2	7.2	28.6	55.0	--------	--------
Standard deviation	2.7	.6	.6	2.0	.9	.5	--------	1.3	.4	1.5	2.6	--------	--------
Coefficient of variation	4	2	43	140	225	250	--------	14	6	5	5	--------	--------
259543	80	14	2	?	--------	--------	1	6	5	19	43	27	--------
	75	14	2	1	--------	--------	?	3	6	19	46	26	--------
	70	17	1	0	--------	--------	0	5	4	18	47	26	--------
	75	15	2	?	--------	--------	0	5	3	18	45	29	--------
	75	16	2	0	--------	--------	2	6	3	17	45	29	--------
Mean	75	15.2	1.8	.2	--------	--------	.6	5.0	4.2	18.2	45.2	27.4	--------
Standard deviation	3.5	1.3	.5	.4	--------	--------	.9	1.2	1.3	.8	1.5	1.5	--------
Coefficient of variation	5	9	28	200	--------	--------	150	24	31	4	3	5	--------
259550	75	20	5	--------	--------	--------	--------	3	2	14	31	50	--------
	80	16	3	--------	--------	--------	--------	2	2	15	33	48	--------
	80	16	3	--------	--------	--------	--------	2	1	11	32	54	--------
	75	17	9	--------	--------	--------	--------	2	2	12	32	52	--------
	80	18	10	--------	--------	--------	--------	2	2	12	29	55	--------
Mean	78	17.4	6.0	--------	--------	--------	--------	2.2	1.8	12.8	31.4	51.8	--------
Standard deviation	2.7	1.7	3.3	--------	--------	--------	--------	.5	.5	1.6	1.5	2.9	--------
Coefficient of variation	.3	10	55	--------	--------	--------	--------	23	28	13	5	6	--------
Total of standard deviations for three samples								3.0	2.2	3.9	5.6	4.4	19.1
Total of coefficients of variation for three samples								61	65	22	13	11	172

Minus-2 micron fraction

Sample	3 (variables a–c)						4 (variables a–b)						5 (variable a)					Total
	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	
259574	7	5	24	64	------	------	8	5	21	66	------	------	7	6	25	62	------	------
	8	5	25	62	------	------	8	6	24	62	------	------	8	5	24	63	------	------
	8	6	23	63	------	------	7	7	22	64	------	------	7	6	24	63	------	------
	7	6	25	62	------	------	7	6	25	62	------	------	7	7	25	61	------	------
	6	7	21	66	------	------	7	6	25	62	------	------	7	6	24	63	------	------
Mean	7.2	5.8	23.6	63.4	------	------	7.4	6.0	23.4	63.2	------	------	7.2	6.0	24.4	62.4	------	------
Standard deviation	.8	.8	1.7	1.7	------	------	.5	.7	1.8	1.8	------	------	.5	.7	.5	.9	------	------
Coefficient of variation	11	14	7	3	------	------	7	12	8	3	------	------	7	12	2	1	------	------
259543	3	2	11	49	35	------	2	3	14	47	33	------	3	2	13	46	36	------
	4	2	11	49	34	--------	3	2	13	47	35	--------	2	3	14	45	36	------
	3	2	10	49	36	--------	3	2	13	47	35	--------	3	3	15	44	35	------
	3	2	11	49	35	--------	3	3	13	45	36	--------	2	3	15	47	33	------
	2	3	14	47	33	--------	3	2	13	46	36	--------	2	3	14	45	36	------
Mean	3.0	2.2	11.4	48.6	34.6	--------	2.8	2.4	13.2	46.4	35.0	--------	2.4	2.8	14.2	45.4	35.2	------
Standard deviation	.7	.4	1.5	.9	1.1	--------	.4	.5	.4	.9	1.2	--------	.5	.4	.8	1.1	1.3	------
Coefficient of variation	23	18	13	2	3	--------	14	21	3	2	3	--------	21	14	6	2	4	------
259550	1	1	10	30	58	--------	1	1	12	27	59	--------	1	1	11	30	57	------
	1	1	11	30	57	--------	2	?	10	29	58	--------	1	2	10	31	56	------
	1	1	8	36	54	--------	1	0	10	30	59	--------	1	1	9	31	58	------
	1	0	9	33	57	--------	1	1	9	30	58	--------	1	1	8	32	58	------
	1	1	12	27	59	--------	1	1	10	30	57	--------	1	2	10	32	55	------
Mean	1.0	0.8	10.0	31.2	57.0	--------	1.2	0.6	10.4	29.2	58.2	--------	1.0	1.4	9.6	31.2	56.8	------
Standard deviation	.0	.4	1.6	3.4	1.9	--------	.4	.5	1.1	1.3	.8	------	.0	.5	1.1	0.8	1.3	------
Coefficient of variation	0	50	16	11	3	--------	33	83	11	4	1	--------	0	36	11	3	2	------
Total of standard deviations for three samples	1.5	1.6	4.8	6.0	3.0	16.9	1.3	1.7	3.3	4.0	2.0	12.3	1.0	1.6	2.4	2.8	2.6	10.4
Total of coefficients of variation for three samples	34	82	36	16	6	174	54	116	22	9	4	205	28	62	19	6	6	121

1. Five different splits, unoriented powder.
2. Five different splits, oriented aggregate.
3. Five different oriented aggregates from one split.
4. Same oriented aggregate, rerun five times.
5. Same X-ray diffractometer traces, interpreted five times.

the X-ray peaks being measured. Figure 4 illustrates the importance of baseline placement in repeated analyses of the same set of X-ray traces; the two interpretations are the first and second listed for sample 259543 in column 5 of table.

The long baseline below the 7A, the 10A-300°C, and the 17A-glycol peaks is constructed by use of a french curve. Even if the low-angle portions of the glycol and the 300°C traces do not exactly coincide as shown on figure 4, the 300°C trace is still a useful parallel guideline for construction of a baseline for the glycol trace. Nevertheless, the baseline was placed slightly lower in the first than in the second interpretation and resulted in differences in measured sizes of the 7A, 10A-300°C, and 17A-glycol peak sizes. The baselines below the 10A-glycol peak and the 14A-550°C peak are sketched in freehand. Differences in the measured peak sizes of the two interpretations are small, but nevertheless they are large enough to explain much of the variability reported in column 5 of table 3.

Coefficients of variation in table 3 fluctuate much more than the standard deviations. The very small amounts of kaolinite and chlorite in some of the samples cause most of this variation. For example, the coefficient of variation of 50 percent for chlorite in sample 259550, column 3, is caused by a difference of only 1 percent in one of the determinations. In such a case, the coefficient of variation has little meaning.

High variation in determinations for pyrite, dolomite, gypsum, and clinoptilolite in column 1 of table 3 indicates that in small amounts these minerals are not consistently detected.

The importance of the amount of material sampled to the consistency of the X-ray quantitative determinations is illustrated in figure 5 by plotting the coefficients of variation for total clay, quartz, feldspar, and the clay minerals in columns 1, 2, and 3 of table 3 as functions of the average amount of each component calculated to be present. For minerals composing more than 15 percent of the sample, any one single determination likely will be within 10 percent of the average of five repeated determinations. The reproducibility is less for amounts smaller than 15 percent.

This generalization will apply to most, but not all, samples of Pierre Shale. For example, some bentonite and some highly bentonitic shale samples contain rela-

First interpretation:

$7A = \dfrac{3.9}{78.9} = 5 < \begin{array}{l} 3 \text{ percent kaolinite} \\ 2 \text{ percent chlorite} \end{array}$

$\text{Illite} = \dfrac{10\frac{1}{2}}{78.9} = 13 \text{ percent}$

$\text{Montmorillonite} = \dfrac{50}{29 \times 4\frac{1}{2}} \times 95 = 36 \text{ percent}$

Mixed-layer = 46 percent

Second interpretation:

$7A = \dfrac{3.5}{73.5} = 5 < \begin{array}{l} 2 \text{ percent kaolinite} \\ 3 \text{ percent chlorite} \end{array}$

$\text{Illite} = \dfrac{10}{73.5} = 14 \text{ percent}$

$\text{Montmorillonite} = \dfrac{48}{28 \times 4\frac{1}{2}} \times 95 = 36 \text{ percent}$

Mixed-layer = 45 percent

EXPLANATION

Base lines, first interpretation

Base lines, second interpretation

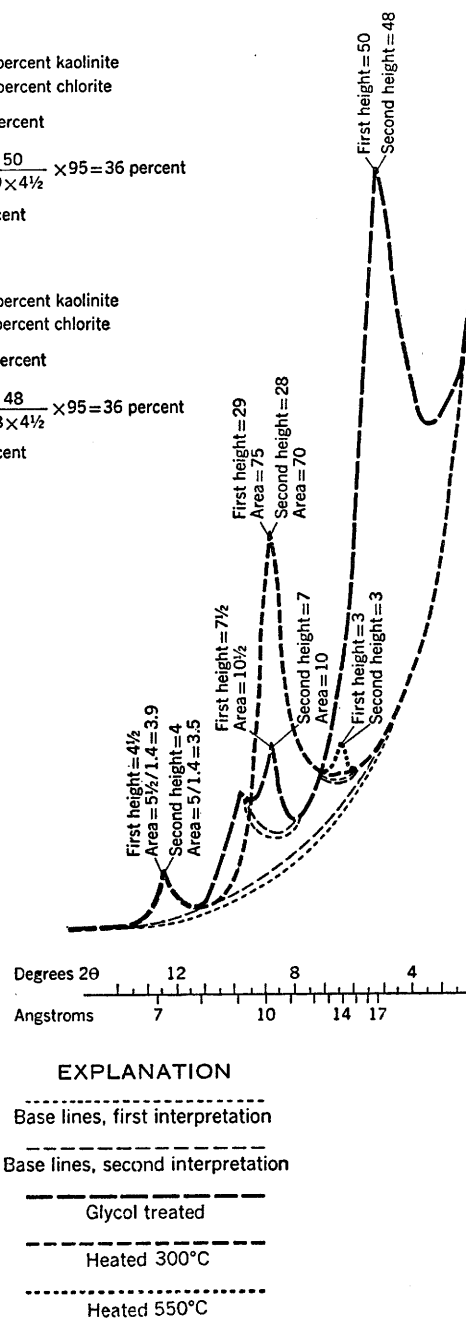Glycol treated

Heated 300°C

Heated 550°C

FIGURE 4.—The effect of baseline position on quantitative interpretation of X-ray diffractometer traces. The two interpretations illustrate derivations of the percentages in first two horizontal rows for sample 259543, column 5, table 3.

tively large particles of feldspar that in the powder samples readily orient parallel to cleavage faces. The reproducibility of X-ray intensity relations for feldspar in these samples may be considerably outside the expected limits unless the samples are especially ground or unless averages of several repeated runs are used. Sample 259550 (table 3) illustrates this. The general similarity of most values in table 3, however, shows that most minerals in the Pierre Shale are sufficiently fine-grained that they behave like ideal powders for diffraction studies. This fine-grained characteristic is also illustrated by the uniform results from repeated analyses made for calcite and quartz each in 11 samples, as shown in table 4.

An additional indication of the consistency of the X-ray quantitative mineralogical determinations is shown by the eight sets of duplicates in table 5. At the time the samples were analyzed, the duplicates were not known as such. The consistency of the mineralogical values is generally what would be expected from the standard deviation and coefficients of variation from tables 3 and 4 and from figure 5. As in table 3, the values given in table 5 indicate that small amounts of nonclay minerals are not consistently detected in the X-ray analyses—for example, alunite in sample 259549 and its duplicates, and calcite and pyrite in sample 259568 and its duplicate.
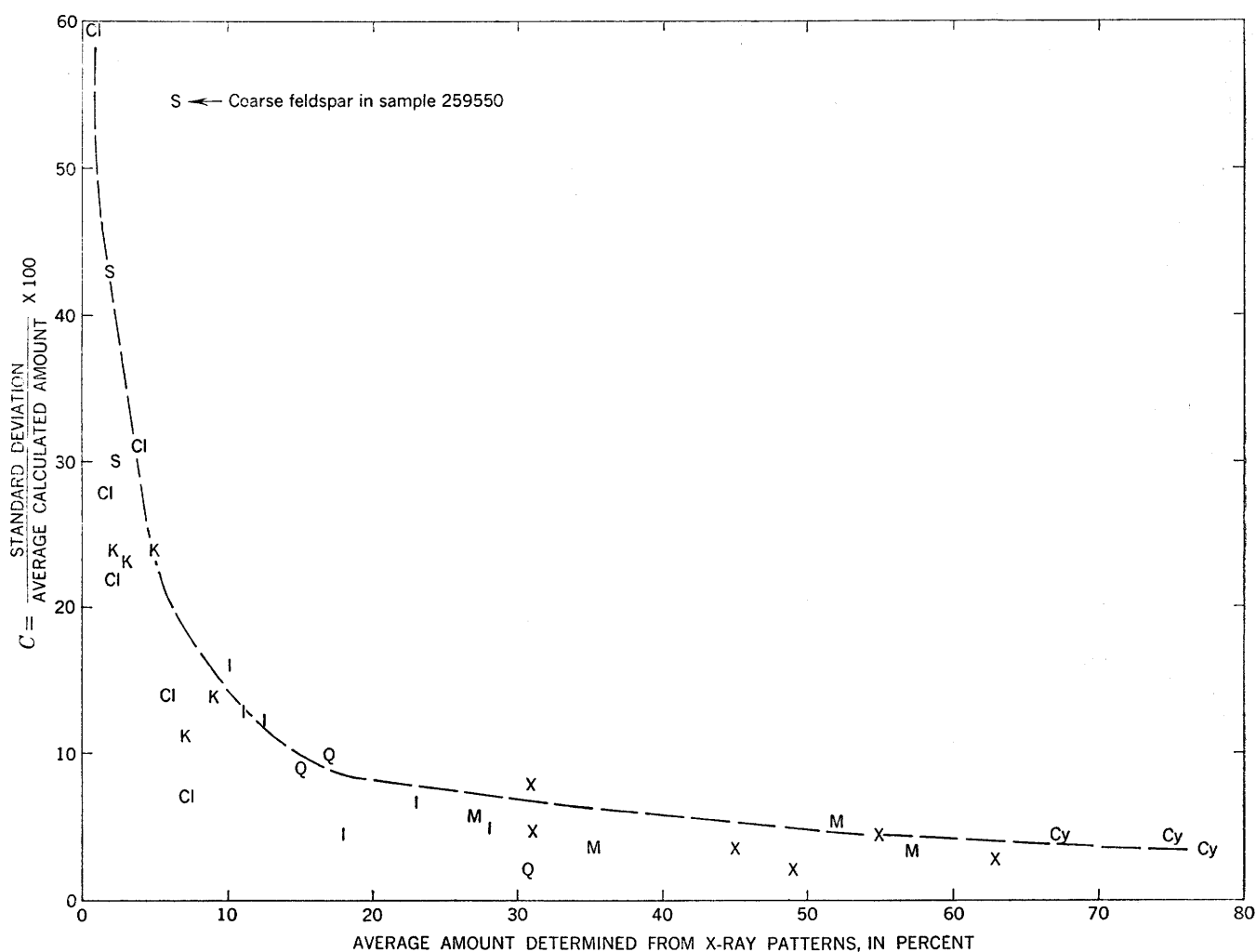

FIGURE 5.—Relation between coefficient of variation (C) and the average amount of each mineral determined from X-ray patterns. Cy, total clay minerals; Q, quartz; S, feldspar; K, kaolinite: Cl, chlorite; I, illite; X, mixed-layer clay; M, montmorillonite. Data from table 3.

TABLE 4.—*Repeated X-ray analyses, in percent, for calcite and quartz in samples of Pierre Shale*

Sample	Determinations	Calculated values ± standard deviation (range of determinations in parentheses)	Coefficient of variation
Calcite			
S57-32-6	5	55±3.0 (53-60)	5.5
S57-35A-2	11	43±1.5 (41-45)	3.5
S57-35A-3	11	42±1.0 (41-44)	2.4
S57-35C-1	11	44±1.0 (41-44)	2.3
S57-34-1	11	28±2.2 (26-32)	7.8
S57-34-2	6	41±1.9 (39-43)	4.6
S57-34-3	6	21±1.3 (20-23)	6.2
S57-35D-5N	6	47±1.5 (44-48)	3.2
S57-35E-2	6	47±5.0 (40-50)	10.5
S57-30-7	6	88±3.5 (84-93)	4.0
To57-1-3	5	65±2.0 (62-66)	3.1
Average			4.8
Quartz			
S57-35B-1	5	12±1.8 (11.0-12.5)	15.0
S57-35A-2	6	6±0.4 (5.5-6.5)	6.7
S57-35A-6	6	18±1.0 (17.0-19.5)	5.6
S57-34-3	6	13±0.8 (12.0-14.0)	6.2
S57-35D-3	5	19±1.5 (17.5-21.0)	7.9
S57-35D-5	6	16±0.8 (15.0-16.5)	5.0
S57-35D-6	6	21±1.0 (19.5-22.5)	4.8
S57-35E-2	6	12±0.3 (11.5-12.0)	2.5
S57-35E-3	6	12±0.5 (11.5-12.5)	4.2
G57-4-26L	5	37±1.0 (35.0-37.5)	2.7
S57-35A-3	6	1±0.2 (1.0-1.5)	[1]20.0
Average			6.1

[1] Not included in average.

LONG-TERM REPRODUCIBILITY

Results illustrated in table 3 were obtained from carefully prepared samples having good orientation of the oriented aggregates; all samples were treated in exactly the same manner and run on the same Norelco X-ray machine during a 3-month period in late 1958 and early 1959. In contrast, X-ray data for the Pierre study, as a whole, have been obtained over a period of several years by using two different machines and three goniometers. To determine if the reproducibility indicated in table 3 could be maintained under these conditions, three additional sets of analyses of the same group of three samples were obtained under less ideal conditions (table 6). The first set of analyses were run in November 1957 on one X-ray machine, and the two additional sets were run in 1960 on each of two goniometers mounted on another machine. Even when pyrite, dolomite, gypsum, and clinoptilolite are excluded from consideration because they occur as such small amounts and when an average of the standard deviations for each mineral in the three samples is used (table 7), less than half of the determinations are within one standard deviation of the mean for each mineral reported in table 3. Because maintenance of the same degree of reproduci-

TABLE 5.—*X-ray mineralogical analyses in percent, of unknown duplicate samples*

[Figures in parentheses are calculated from chemical analyses and are not included in total. ?, presence of the mineral doubtful]

Constituent	Set 1 259533	259597 (duplicate)	Set 2 259549	259596 (duplicate)	259599 (duplicate)	259603 (duplicate)	Set 3 259553	259604 (duplicate)	Set 4 259565	259598 (duplicate)	Set 5 259568	259601 (duplicate)	Set 6 259580	259600 (duplicate)	Set 7 259582	259602 (duplicate)	Set 8 259586	259605 (duplicate)
Clay minerals:																		
Montmorillonite	43	41	7				34	35	35	30	22	19	24	25	25	28	35	30
Mixed-layer	37	37	39	49	48	43	29	34	28	34	38	39	39	42	40	37	48	53
Illite	17	16	42	35	36	41	21	17	25	26	21	23	25	22	22	22	12	11
Chlorite	?	4	?				6	6	6	7	9	7	7	5	5	8		
Kaolinite	3	2	12	16	16	16	10	8	6	3	10	12	5	6	8	5	5	6
Whole rock:																		
Total clay minerals	45	45	45	40	40	35	40	35	70	70	70	65	70	70	65	60	80	80
Quartz	4	5	12	14	13	9	9	6	22	21	25	21	19	22	19	21	19	19
Cristobalite	35	30																
Feldspar:																		
Predominantly potassium feldspar																		
Predominantly plagioclase									4	4		3	3	4	2	2	2	3
Undertermined	1	1		?	?													
Calcite							35(40)	42(40)			2(2½)	?(2)				2(1)		
Dolomite									0(½)	?(1)	?		3(5)	8(5)	?(1½)	2		
Rhodochrosite	13(14)	10(13)																
Gypsum			6(4)	3(4)	3	5												
Jarosite			8(2)	5(15)	5	5											0(1)	?(1)
Alunite			?	?	2	?												
Pyrite	1(1)	2(1)	15(18)	20(7)	20(4)	20(4)	4(4)	2			0(1)	1			10(8)	15(3)		
Clinoptilolite								1?										
Total	99	93	[1]86	82	83	74	88	87	96	95	99	90	95	104	96	102	101	102

[1] Also contains 12 percent organic matter.

bility requires that two-thirds of the values be within one standard deviation, the short-term reproducibility was not maintained under the conditions in which data for the Pierre study have been accumulated.

The probable increase in variability due to lapse of time and use of different apparatus was estimated by trial and error adjustment of the standard deviations to the point that the required two-thirds of the determinations for each mineral in table 6 came within one empirical standard deviation on each side of the mean-values given in table 3. Significant differences between the empirical and average standard deviations (table 7) are the larger empirical standard deviations for montmorillonite, mixed-layer clay, and, to a lesser extent,

illite. The empirical standard deviation for total clay seems to be fortuitously and unrealistically low. The other empirical standard deviations, however, are believed to be more applicable to the quantitative mineralogical data for the Pierre Shale than are the generally lower standard deviations from table 3. The empirical standard deviations, however, still generally give coefficients of variation that are close to the 10 percent figure previously mentioned in reference to figure 5.

The high empirical standard deviations for some of the clay minerals (table 7) probably result mostly from slight differences in goniometer alinement. Variations in the electronic circuits and X-ray tubes probably are not important because these factors should cause increased variability for all minerals equally, not mostly creased variability for all minerals equally, not mostly

for montmorillonite, mixed-layer clay, and illite. In fact, inasmuch as quantitative determinations of the different clay minerals depend on relative peak sizes all determined within one or two days, long-term variation in electronic components should have the least effect on determinations for these clay minerals. On the other hand, slight variations in goniometer alinement have the greatest effect in the low-angle region of the measured montmorillonite, illite, and mixed-layer clay reflections. Thus, goniometer alinement would seem to be the most important cause of the increased variability in table 6, as compared with that in table 3. Increase in variability of interpretation over a long period of time also may have some effect.

TABLE 6.—*Repeated X-ray analyses, in percent, of three different splits each of three samples of Pierre Shale over a period of 2 years*

Sample	Date run	Whole sample												Minus-2 micron fraction				
		Unoriented powder							Oriented aggregate					Oriented aggregate				
		Total clay	Quartz	Feldspar	Pyrite	Dolomite	Gypsum	Clinoptilolite	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite
259574	Nov. 1957	65	29	1	2	?	2	------	11	9	30	50	------	6	7	32	56	------
	Jan. 1960	65	32	2	1	4	2	------	10	8	31	51	------	9	7	26	58	------
	----do	65	31	1	?	2	2	------	8	7	30	55	------	9	5	21	65	------
259543	Nov. 1957	75	16	2	?	------	------	1	4	3	17	43	33	3	2	15	47	33
	Jan. 1960	75	16	3	?	------	------	2	4	3	14	40	32	4	2	10	58	26
	----do	75	16	2	?	------	------	1	3	4	17	47	36	3	2	10	54	31
259550	Nov. 1957	75	19	5	------	------	------	------	1	2	30	55	------	1	?	12	30	64
	Jan. 1960	80	17	3	------	------	------	------	1	1	14	29	54	1	1	7	32	59
	----do	80	17	2	------	------	------	------	2	1	10	41	46	1	1	8	37	53

TABLE 7.—*Different standard deviations derived from repeated analyses of three samples of Pierre Shale*

	Total clay	Quartz	Feldspar	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite
Average standard deviation (from table 3)	3.0	1.2	1.4	0.8	0.6	1.4	1.9	1.9
Empirical standard deviation (for long-term use)	2.5	1.0	1.0	1.0	1.0	2.0	5.0	5.0

ACCURACY—COMPARISON WITH CHEMICAL ANALYSIS

The reproducibility of quantitative values derived from X-ray diffractometer traces is not, of course, an indication of the accuracy of the values. However, the accuracy of the quantitative X-ray analyses of some of the minerals can be checked by calculations from chemical analyses.

SULFIDE, SULFATE, AND CARBONATE MINERALS

In samples of Pierre Shale, acid-insoluble sulfur reported as sulfide sulfur probably is present in pyrite;

acid-soluble sulfur reported as sulfur trioxide may be present in gypsum, jarosite, or rarely alunite; and carbon dioxide may be present in calcite, dolomite, or rarely siderite, or rhodochrosite. X-ray patterns determine which of the possible minerals is present. Relations between the values derived from X-ray data and values calculated from chemical analyses are shown in figure 6; duplicate samples (table 5) are not included. Minerals recorded as questionably present from the X-ray analyses are plotted at 0.5 percent, and chemically derived values of less than 0.5 percent are plotted together as 0.0–0.25 percent. Of the three mineral groups represented in figure 6, the X-ray and chemical determinations are in best agreement for the carbonates. Agreement of values for the sulfate and sulfide minerals is not good, but where these minerals are present in appreciable amounts, the chemical and X-ray determinations generally agree within a factor of two.

The lack of agreement between amounts of sulfate and sulfide minerals determined by X-ray methods and amounts calculated from chemical analyses (fig. 6) may also be due to error in the chemical analyses. The value
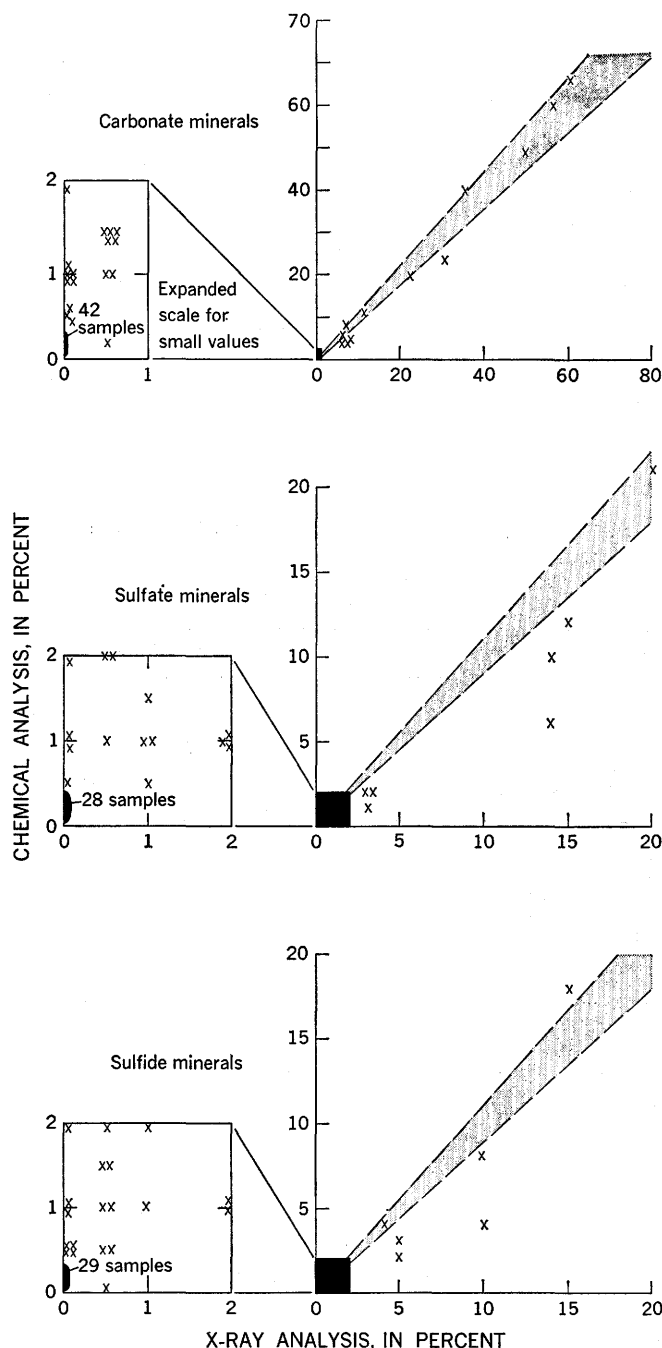
FIGURE 6.—Comparison of quantitative determinations of carbonate, sulfate, and sulfide minerals derived by X-ray methods and by chemical analysis. Points that fall within shaded areas on graphs represent differences of less than 10 percent between amounts determined by X-ray and chemical methods.

determined for ferrous oxide in the presence of organic matter such as occurs in most samples of Pierre Shale is uncertain, and the amount of ferric iron is assumed to be the difference between total iron and ferrous iron. These less dependable chemical determinations may limit the amount of pyrite and jarosite that can be calculated from the chemical analyses (such as sample 259549 and its duplicates, table 5). Therefore, only the

graph of the carbonate minerals (fig. 6) may reflect the accuracy of the X-ray determinations.

ALUMINA

Nearly all of the alumina in samples of Pierre Shale occurs in the clay minerals. Feldspar is the only other alumina-containing mineral found in most samples, and it rarely exceeds a few percent of any sample; in such amounts of feldspar, the alumina content is less than 1 percent. The chemical composition of the different clay minerals is not the same. However, the proportions in which the clay minerals occur are fairly constant for most samples of Pierre Shale. Kaolinite and chlorite compose only a few percent of the clay-mineral fraction of most samples although kaolinite may constitute as much as 10 to 15 percent of this fraction in a few samples. Illite commonly composes 15 to 25 percent of the clay-mineral fraction. Montmorillonite and mixed-layer clay are the dominant clay minerals. The montmorillonite, illite, and mixed-layer clays are the common aluminous varieties. Therefore, theoretically, the amount of alumina should bear a fairly consistent relation to the total clay content in each sample and should provide a rough check on the reliability of the X-ray-determined values for total clay.

Values for total clay and alumina are compared in figure 7. If the middle dashed line in figure 7 represents the average alumina content for a given percentage of total clay in the Pierre Shale, most of the points plot outside the limits expected from either the 3.0-percent average or the 2.5-percent empirical standard deviation for total clay shown in table 7. However, about two-thirds of the samples plot within the 10 percent coefficient of variation indicated by figure 5. Furthermore, some of the scatter of points on figure 7 may be caused by different clay-mineral composition of the samples. Of the clay minerals. in the Pierre Shale, the relative amounts of kaolinite and montmorillonite should have the most pronounced effect on the alumina content (fig. 7). Samples having unusually high montmorillonite: kaolinite ratios should have relatively low alumina content, because kaolinite contains 40 percent alumina, whereas montmorillonite like that in the Pierre probably contains only about 16 to 20 percent. As expected (fig. 7), the more kaolinitic samples (low montmorillonite: kaolinite ratio) are generally plotted above the average alumina content, and the more montmorillonitic samples are plotted below the average.

Figure 8 shows an evaluation of the relative importance of errors in total clay values and of the effect of different proportions of the clay minerals as causes for
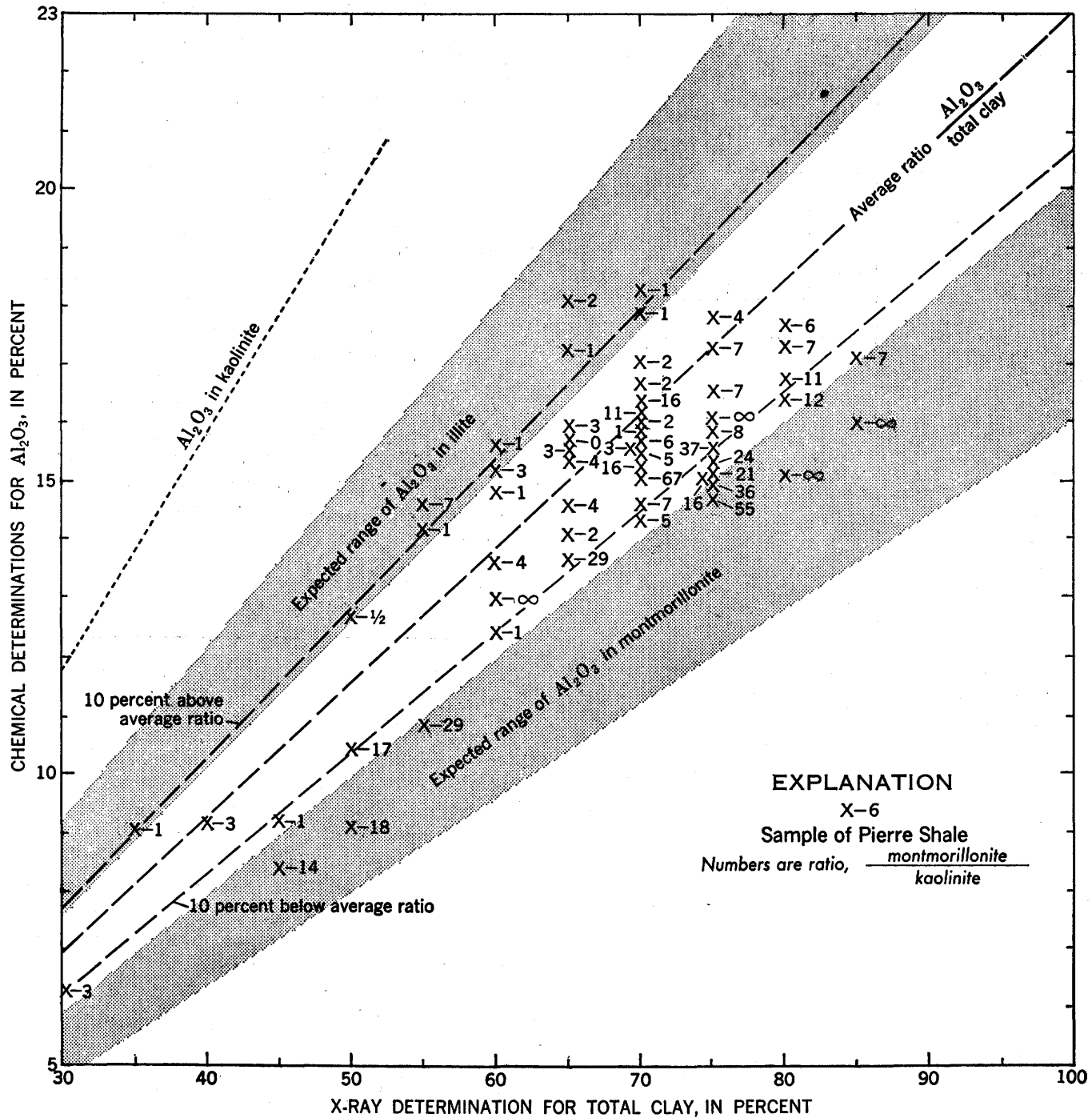
scatter of points on figure 7. A theoretical amount of alumina for each sample is calculated by multiplying the determined amount of each significant alumina-bearing mineral by an alumina content assumed to be reasonable for that mineral. The amount of each clay mineral in the sample is the product of its proportion in the clay fraction and the amount of total clay in the sample. For example, the alumina content shown in figure 8 for sample 259543 (fig. 3) is calculated as follows:

Calculation of alumina from X-ray data

[Total clay is 75 percent (rounded) of whole sample]

Mineral	Percent of total clay (1)	Percent of whole sample (2; 1×75 percent)	Alumina	
			Percent of mineral (3)	Percent of whole sample (2×3)
Clay minerals:				
Montmorillonite	33	24	18	4.46
Mixed-layer clay	43	32	20	6.45
Illite	17	13	27	3.44
Chlorite	3	2	17	.38
Kaolinite	4	3	40	1.20
Feldspar		2	22	.44
Total	100			16.37
Total alumina determined from chemical analyses				15.92

The points on figure 8 are scattered much less than they are on figure 7, and they more realistically portray the probable accuracy of determinations for total clay. Even if all the scatter of points on figure 8 is attributed to error in the total clay determinations, the indicated accuracy clearly is within the coefficient of variation of 10 percent previously mentioned in reference to figure 5.

An additional conclusion may be derived from figure 8, namely, that errors in total clay values probably cause the greatest observed deviations from the ideal 1:1 ratio of chemically determined alumina and alumina calculated from X-ray data. Two of the three samples that give alumina values of more than 10 percent in excess of the chemically determined alumina (plot below shaded area, fig. 8) have a total of minerals calculated from X-ray that is in excess of 100 percent; obviously, for some mineral in these samples the determination is too large. In these samples, inasmuch as determined feldspar is only 1 to 2 percent, determined amounts cannot possibly exceed the true amounts sufficiently to explain the abnormally high alumina calculated from X-ray data. The determinations that must be high are those for the only other common alumina-bearing minerals in these samples, the clays.

On the other end of the scale, the total amount of minerals determined for the four samples that are plotted farthest above the ideal 1:1 ratio (fig. 8) is 88 to 90 percent. The 10 to 12 percent of these samples not determined probably is not amorphous silica, for silica alone would not affect the alumina calculations. It probably is not feldspar either, because, if it were, the 2 to 4 percent feldspar determinations for these samples would correspond to true values of 12 to 16 percent; an error of this magnitude for all four samples is extremely unlikely. The only remaining common alumina-bearing minerals that can be responsible for the 10 to 12 percent deficiency in the total sample and the deficiency of about 2 percent in alumina calculated from X-ray data are the clays.

LOWER LIMITS OF DETECTION

Data in table 3 and figure 5 suggest that generally a mineral must be uniformly distributed in a sample in amounts of 2 percent or more before it is consistently detected in the X-ray analyses. In no sample is the mineral detected if present in amounts of less than 0.5 percent. These lower limits of detection depend to some extent upon the inherent diffracting ability of the different minerals (see table 1). To be consistently detected, a mineral must give a peak height of about 5 to 10 cps above background. Quartz, for example, tends to give large peaks and may be consistently detected in amounts of only 1 percent, whereas the lower limit of detection for pyrite generally is 2 percent or greater. Interference of X-ray reflections from other minerals also may raise the lower limit of detection. For example, either plagioclase or clinoptilolite could mask the main X-ray peak for a small amount of cristobalite, and a combination of X-ray diffraction peaks from illite and gypsum can hide the two main peaks of jarosite.

MINERALOGICAL OCCURRENCE OF PRINCIPAL CHEMICAL ELEMENTS

CALCULATIONS DESCRIBED IN THE LITERATURE

Calculation of the mineralogical composition of a rock from its chemical composition was first proposed by Cross, Iddings, Pirsson, and Washington (1903). By their system, generally known as the CIPW System, a chemical analysis is used to calculate a theoretical mineral composition called the norm of the rock. The norm includes minerals of simple chemical composition that may have crystallized from a magma having the chemical composition of the rock. Minerals having complex and variable chemical compositions like the micas, garnets, and aluminous amphiboles and pyroxenes are not included as norm minerals. The calculated norm may or may not agree closely with the actual (modal) mineralogical composition of the rock. CIPW normative calculations have been widely applied to igneous rocks.

Krumbein and Pettijohn (1938, p. 490–492) indicated the possible value of chemical analyses in identifying minerals in fine-grained sedimentary rocks and gave an example of the calculation of the norm of a graywacke. They assumed that the constituents occurred in minerals like kaolinite or amesite to which they ascribed simple, fixed chemical compositions. They also pointed out that the calculations were only as appropriate as were the assumptions underlying them.

Such an approach has been more fully explained by both Miesch and Nicholls. Miesch (1962) calculated the possible range of the gross mineral composition of
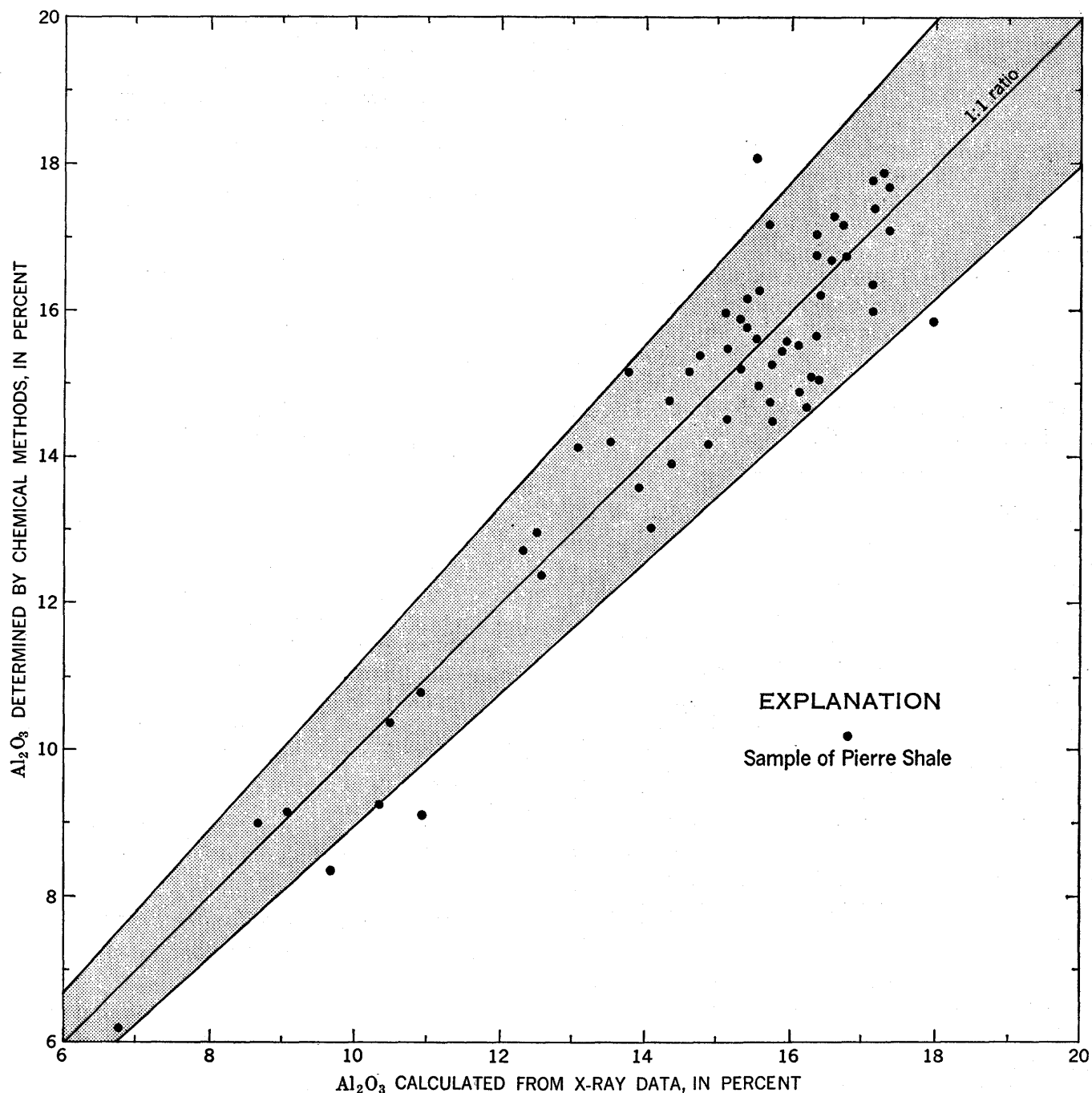
FIGURE 8.—Comparison of chemical determinations for alumina and calculations for alumina from X-ray data. Points that fall within shaded area represent differences of less than 10 percent between amounts determined by X-ray and chemical methods.

rocks from chemical composition and known mineral occurrence of some of the chemical constituents. Nicholls (1962) proposed a scheme for recalculating chemical analyses first into normative formulae representing ideal muscovite, paragonite, kaolinite, magnesian antigorite, and iron antigorite, which in turn may be regrouped into normative minerals of more probable chemical composition such as illite, chlorite, and kaolinite.

Imbrie and Poldervaart (1959) described a method for the calculation of mineral composition from chemical analyses of sedimentary rocks which contain minerals of complex and variable composition, including montmorillonite, illite, and chlorite. In the shale studied by them, these minerals were carefully determined, using several analytical techniques. Once the norm minerals were determined and the chemical compositions of these minerals were assumed, the amounts

of each norm mineral in the individual samples were determined by rigidly following a sequence of steps and allotting the chemical elements to the different norm minerals. This method obtained a good agreement between norm values, amounts of insoluble residues, and X-ray quantitative values for percent of carbonates, quartz, and total clay minerals (Imbrie and Poldervaart, 1959, tables 5 and 6). However, there was little agreement between the norm calculations and X-ray values for the various clay minerals.

A good agreement between X-ray mode and chemical norm for a sample containing mainly muscovite, chlorite, and plagioclase was obtained by Zen (1960, p. 135). The investigated rocks were sufficiently coarse grained that optical properties and chemical composition of individual minerals could be determined. Such is not true for samples of Pierre Shale.

PIERRE SHALE

The objective of the chemical-mineralogical calculations for the Pierre Shale is to allot the chemical constituents as realistically and accurately as possible to minerals known to occur in each sample. This objective allows a comparison of X-ray and chemical data to make sure they are not conflicting, and facilitates a study of compositional similarities and differences between groups of samples.

Most of the chemical constituents in the Pierre Shale can occur in several minerals, and many of these minerals in the Pierre may vary in composition. For example, alumina occurs in feldspar, in all five of the clay minerals, and also in clinoptilolite or alunite in a few samples. In fact, all the chemical components that commonly amount to more than 1 percent in the analyses of Pierre Shale have multiple mineralogical occurrences. Therefore, X-ray data are used to help assign the proper amount of the more common elements to minerals; the X-ray data are used not only to help identify minerals present in individual samples, but also to determine the amounts of several of the minerals calculated from the chemical analysis.

The moderate variation in the mineralogical composition of the Pierre Shale permits some procedures and assumptions about chemical composition of minerals that would not be justified for all sedimentary rocks. The composition of minerals which make up only a minor part of the Pierre Shale does not need to be known as accurately as does the composition of the major mineral constituents.

BASIS OF CALCULATIONS

Minerals in the Pierre Shale are divided into three groups on the basis of the method used for calculating their amounts and compositions.

In the first group, a unique constituent in the chemical analysis is the primary basis for calculating the abundance of the mineral. This group contains minerals such as pyrite, apatite, and the carbonate minerals. X-ray data aid in determining exactly the composition of the minerals in this group that are somewhat variable, such as apatite and the carbonates, but the X-ray determinations have little or no relation to the amount of the minerals calculated.

The second group includes minerals, such as kaolinite, the feldspars, illite, and chlorite, that have no unique chemical constituent to determine their abundance. Compositions of some of the minerals are almost unvariable, but the compositions of others may be highly variable, and assumptions have to be made. Because most of the minerals in this group that vary considerably in composition are present in Pierre samples only in small amounts, the effect of assumed chemical formulae in the overall calculations is small. The X-ray data provide the only basis for distributing the chemical elements in such minerals.

The third group of minerals contains montmorillonite and mixed-layer illite-montmorillonite, both of which may vary considerably in chemical composition. These minerals commonly make up half or more of most samples of Pierre Shale, and any errors in assumed chemical composition would have considerable effect on the overall chemical calculations. Therefore these two minerals are grouped together, and all chemical elements not assigned to other minerals are assigned to them.

Frequent reference to plate 1 may help the reader to understand the following discussion of the individual minerals.

CHEMICAL COMPOSITION OF MINERALS

MINERALS CALCULATED PRIMARILY FROM CHEMICAL ANALYSES

APATITE

Apatite is the principal mineral in some concretions in the Pierre Shale, but in the shale itself, apatite is detected only rarely by X-ray techniques. Petrographic examination of thin sections and heavy mineral separates reveals apatite in some shale samples in amounts too small to be detected by X-ray analysis. Small amounts of phosphate also may be adsorbed on the clay minerals.

In the Pierre Shale, the common range for chemically determined phosphorous pentoxide is about 0.05 to 0.30 percent, and most determinations are in the smaller end of this range. For the chemical-mineralogical calculations, phosphorous pentoxide in amounts less than 0.5 percent is disregarded because it is of uncertain mineralogical occurrence, and because if phosphorus having

appropriate amounts of other constituents is calculated as apatite, the remaining amount of calcium in many samples is insufficient for other determined calcium-bearing minerals. In amounts of 0.5 percent or greater, phosphorous pentoxide is calculated as apatite. X-ray and chemical data indicate that apatite in the Pierre Shale is a carbonate-fluorapatite similar to that described by Altschuler, Clarke, and Young (1958, p. 49). In chemical calculations for the Pierre Shale, apatite is assumed to contain 55 percent calcium oxide, 38 percent phosphorous pentoxide, 4 percent fluorine, and 3 percent carbon dioxide. Errors introduced by this procedure will not significantly affect most calculations, as apatite generally is at most a very minor component in the Pierre Shale.

PYRITE (FeS₂)

Pyrite has a relatively simple and unvarying chemical formula. It is the only sulfide mineral known to occur in the Pierre Shale; thus, the amount of pyrite can be calculated from the amount of acid-insoluble sulfur reported as sulfide sulfur, in the chemical analysis, unless there is reason to consider the effects of barite on the determination of insoluble sulfur.

BARITE (BaSO₄)

Most sulfate minerals are soluble under the conditions by which acid-soluble sulfur is determined. The amount of acid-soluble sulfur is subtracted from the amount of total sulfur to give a value for acid-insoluble sulfur. Barite, however, is insoluble under conditions by which acid-soluble sulfur is determined and, therefore, if barite is present, its sulfur is reported with acid-insoluble sulfur as sulfide sulfur. Unless suitable corrections are made, the amount of sulfur in barite will be used in calculating the amount of pyrite.

Although in a few places barite occurs as nodules in the Pierre Shale, in the shale itself it has not been recognized either petrographically or on X-ray traces. The commonly reported range for barium oxide in the Pierre Shale is 0.02 to 0.2 percent; most determinations are in the smaller end of this range. In such small amounts, barium oxide is disregarded in the chemical-mineralogical calculations. If reported in amounts of 0.5 percent or greater, barium oxide is calculated as barite and an appropriate correction is made in the amount of acid-insoluble sulfur. In the great majority of samples, the amount of barium is so small that errors in this procedure will not appreciably influence the calculations.

GYPSUM (CaSO₄·2H₂O)

Unless X-ray or other data indicate presence of other sulfate minerals, all acid-soluble sulfur reported as sul-

fur trioxide in the chemical analyses and the necessary amounts of calcium oxide and water are assigned to gypsum. Where calculated to be present in amounts of 2 percent or more, gypsum is invariably indicated by the X-ray patterns.

JAROSITE

Jarosite is not present in most samples of Pierre Shale, but where present, it may compose several percent of the sample. In small amounts, it is best detected by the presence of a yellow powder on the hand specimen.

The theoretical chemical formula of jarosite is $KFe_3(OH)_6(SO_4)_2$. Within it, extensive substitutions are possible (Hendricks, 1937); sodium and hydrogen most commonly substitute for potassium, and aluminum may substitute for the iron.

X-ray patterns of the jarosite in the Pierre Shale show c-axis measurements slightly smaller than those reported by Warshaw (1956) for jarosite, indicating that the jarosite in the Pierre contains some sodium or hydrogen substituting for potassium. Furthermore, several samples of Pierre having abundant jarosite contained only one-third to two-thirds of the potassium oxide needed to explain the sulfate reported in the chemical analysis as ideal jarosite. In a semiquantitative spectrographic analysis of a nearly pure jarosite separated from the Pierre Shale, 1 to 2 percent sodium oxide was reported; this is not enough sodium to make up for the deficiency in potassium in most jarosite-bearing samples. The fact that only samples containing jarosite have determinations for water-soluble sulfate in excess of 1 percent indicates that jarosite in the Pierre is slightly soluble in water. Yet, these same samples yield not enough water-soluble potassium and sodium to explain the water-soluble sulfate as a sodium jarosite. All the dissolved solutions, however, give a pH of 2 to 4, which is lower than any of the pH values determined for samples without jarosite. Apparently, appreciable numbers of hydrogen or hydronium (H_3O^+) as well as sodium ions substitute for potassium ions in jarosite in the Pierre Shale.

For chemical calculations of the Pierre Shale, jarosite is assumed to have the composition $(K_{1/2}Na_{1/6}H_{1/3})Fe_3(OH_6)(SO_4)_2$. Inaccuracies in this assumed composition may cause considerable error in the chemical calculations for a few samples, but inasmuch as most samples contain no jarosite, the assumption only rarely enters into the calculations.

ALUNITE [KAl₃(OH₆)(SO₄)₂]

Alunite, the aluminous analogue of jarosite, is found in a few samples of Pierre Shale. Its X-ray pattern closely matches that of a pure alunite. Where alunite

is indicated by X-ray or other data, it is calculated as having the ideal chemical composition.

WATER-SOLUBLE SALTS

Amounts of water-soluble calcium, magnesium, sodium, potassium, sulfate, and iron were determined for 65 samples. The most abundant soluble ions commonly are sodium and sulfate. A good correlation between reported water-soluble calcium and the presence of gypsum reflections on X-ray traces indicates that water-soluble calcium comes from gypsum; it is so assigned in the calculations. If water-soluble sulfate, potassium, and sodium apparently come from jarosite, they are so assigned. Water-soluble salts in amounts over 0.5 percent that have no obvious mineral affinity are listed simply as water-soluble ions. In amounts below 0.5 percent, which are most common, the water-soluble components are disregarded. For most samples, errors caused by using such a procedure will be small.

CARBONATE MINERALS

Calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] in samples of shale from the Pierre have compositions near those of the ideal end members. Unless a carbonate other than calcite is indicated by the X-ray data, all carbon dioxide reported in the chemical analysis is calculated as calcite. If both calcite and dolomite are indicated, carbon dioxide is calculated as calcite and dolomite in proportions indicated by the X-ray analysis.

All siderite and rhodochrosite in the Pierre, as well as calcite in nodules or concretions from the Pierre, are mixed carbonates having extensive substitutions of calcium, magnesium, ferrous, and manganese ions. Chemical analyses indicate that ratios of weight percents of $CaO:MgO:FeO$ are generally about $35:2:3$ for the mixed calcite and about $3:2:15$ for siderite.

All fresh shale samples from the Pierre having manganese oxide values of over 0.1 percent contain appreciable carbon dioxide, and X-ray data usually indicate either siderite, calcite, or rhodochrosite. Therefore, although small amounts of manganese may occur in the clay mineral structures, amounts in excess of 0.1 percent probably occur as carbonate and they are so assigned. Rhodochrosite in the Pierre is of a highly mixed variety. Most of the rhodochrosite is composed of slightly more than half maganese carbonate; the remaining part is composed of calcium and iron carbonate in about equal amounts and magnesium carbonate in smaller amounts. In siderite, amounts of manganese oxide range from 0.5 percent to nearly 10 percent, and, in mixed calcite, amounts of manganese oxide are as high as 5 percent. Therefore, no common or general ratio for manganese oxide in these minerals can be given.

The procedure adopted for mixed carbonates in the chemical-mineralogical calculations for the Pierre Shale is to assign manganese oxide below 0.1 percent to the clay minerals, and to assign manganese oxide in excess of 0.1 percent to the carbonate mineral indicated to be present by X-ray data. The carbon dioxide not combined with manganese is combined with calcium, magnesium, and ferrous iron oxide in the ratios of $2:1:2$ for rhodochrosite, $3:2:15$ for siderite, and $35:2:3$ for mixed calcite. Where necessary, these ratios are adjusted to accommodate the chemical analyses of the individual samples.

The aforesaid procedures for pure calcite and dolomite should cause little error in the chemical-mineralogical calculations. The procedures for the mixed carbonates can cause greater error. Fortunately, pure calcite and dolomite are the common carbonates in most shale samples from the Pierre; mixed carbonates are rare.

MINERALS CALCULATED PRIMARILY FROM X-RAY DATA

FELDSPAR

Assignment of chemical elements to feldspar is dependent on the X-ray data. Where the composition of plagioclase in the Pierre can be determined, it is commonly 20–40 percent anorthite. Therefore, if plagioclase is determined to be the dominant feldspar, the elements are assigned in ratios corresponding to a composition of 30 percent anorthite which is comprised of 61 weight-percent silica, 25 weight-percent alumina, 6 weight-percent calcium oxide, and 8 weight-percent sodium oxide. If potassium feldspar is dominant, the elements are assigned in the ratios of 65 percent silica, 18 percent alumina, and 17 percent potassium oxide, a composition corresponding to the ideal formula of $KAlSi_3O_8$. If the dominant type of feldspar is not determined, as commonly happens where only 1 to 2 percent feldspar is indicated, then half is assumed to be plagioclase and half is assumed to be potassium feldspar, and the elements are assigned in ratios of 63 percent silica, 22 percent alumina, 3 percent calcium oxide, 4 percent sodium oxide, and 8 percent potassium oxide.

Because most feldspar values are small, errors due to inappropriate assumptions for chemical composition will also be small.

CLINOPTILOLITE ($Na_4KAl_{5.5}Si_{30.5}O_{72} \cdot 19H_2O$)

The assumed formula for clinoptilolite is simplified from a formula—$(Mg_{.12}Ca_{.19}Na_{3.78}K_{1.08})_{5.18}Al_{5.49}Si_{30.5}O_{72} \cdot 19H_2O$—given by Mason and Sand (1960, p. 346). Inasmuch as this mineral is generally present only in small amounts in the Pierre Shale, slight deviations

from the assumed composition will not seriously affect the chemical calculations.

QUARTZ

Quartz (SiO_2) is present in all samples of Pierre Shale. Amounts of silica assigned to quartz are determined from the X-ray data. Errors in the X-ray value for quartz can be of considerable importance because quartz is fairly abundant (15 to 20 percent of most samples), occurs in all shale samples, is a notably troublesome mineral in quantitative X-ray analysis, and because all the error is concentrated in one chemical constituent. Errors of even a few percent are significant.

CRISTOBALITE

Cristobalite of the disordered variety that occurs in the Pierre Shale probably contains small amounts of alkalies, alumina, and water (Franks and Swineford, 1959). Because the impurities probably compose only 1 to 2 percent of the cristobalite, they are disregarded in the chemical calculations. Of considerable significance, however, is the absolute accuracy of the X-ray-determined value for percentage of cristobalite. As for quartz, all the error is concentrated in one constituent—silica. Cristobalite, however, occurs only in a tenth of the chemically analyzed samples.

KAOLINITE

Kaolinite [$Al_4Si_4O_{10}(OH)_8$] contains about 40 weight-percent alumina, 46 percent silica, and 14 percent water. Because of its nearly invariable chemical composition and the small amounts in which it occurs, kaolinite probably causes very little error in the chemical calculations.

CHLORITE

Chlorite varies widely in chemical composition. The most common variation is in the amount of aluminum substitution and in the relative amounts of iron and magnesium.

Theoretically, alumina may compose from zero to eight ions per unit cell of trioctahedral chlorite. However, "chlorite" minerals such as antigorite and amesite having a minimum and maximum amount of aluminum substitution, respectively, have been shown to have a 7A c-axis spacing corresponding to the kaolinite structure, and, therefore, they are not true chlorites. The chlorite in the Pierre has the 14A c-axis spacing of a true chlorite, and therefore, has a quantity of aluminum between the theoretical maximum or minimum amount. Chlorite in the Pierre is assumed to have a median number of four aluminum ions per unit cell.

The relative intensities of the basal reflections indicate that chlorite in the Pierre is not a highly ferruginous variety (Brindley, 1951, p. 187). Yet, if no fer-

rous iron is assumed to substitute for magnesium, when mineralogical-chemical calculations are made, most samples containing more than average amounts of chlorite have deficiencies of magnesia and unusually large excesses of ferrous iron; the anomalies thus created disappear if ferrous iron oxide and magnesia are assumed to occur in equal weight percents. Inasmuch as ferrous iron oxide commonly amounts to only 1 to 2 percent in most analyses of Pierre Shale, this oxide is particularly sensitive to errors in assumed composition, even of minerals that, like chlorite, rarely exceed 5 percent of the sample.

The assumed composition of chlorite in the Pierre Shale is 29 percent silica, 17 percent alumina, 21 percent magnesia, 21 percent ferrous iron oxide, and 12 percent water; it corresponds approximately to a structural formula of $(Mg_5Fe_3Al_2)(Al_2Si_6)O_{20}(OH)_{16}$.

ILLITE

The composition of illite is of considerable importance in the chemical calculations, because it commonly composes 10 to 15 percent of the samples of Pierre Shale. The composition of illite is variable (Grim, 1953, p. 372). However, X-ray patterns and petrographic data show clearly that most illite in the Pierre is a dioctahedral aluminous muscovitelike variety; the number of possible variations in the chemical composition are therefore greatly reduced. The formula used for illite in the Pierre Shale—

$$K_{1.2}(Al_{3.0}Ti_{0.1}Fe_{0.4}^{+3}Fe_{0.1}^{+2}Mg_{0.4})_{4.0}(Al_{1.1}Si_{6.9})O_{20}(OH)_4—$$
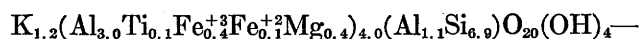
is an average from the literature (Grim, 1953, p. 372, table D, Nos. 1, 2, 5, 6, 7; Whitehouse and McCarter, 1958, p. 86, e and f; Foster, 1954, p. 390) for illites apparently similar to that in the Pierre Shale; the composition also reflects the preponderance of magnesia and ferric iron over ferrous iron in most samples of Pierre Shale. The assumed chemical formula for illite corresponds to 7 weight-percent potassium oxide, 2 percent magnesia, 1 percent ferrous iron oxide, 4 percent ferric iron oxide, 1 percent titanium dioxide, 27 percent alumina, 53 percent silica, and 5 percent water.

MINERALS CALCULATED FROM CHEMICAL CONSTITUENTS NOT OTHERWISE ASSIGNED

Montmorillonite and mixed-layer illite-montmorillonite in the Pierre Shale can have variable chemical composition, particularly in the interlayer cations. Because these two clays are quantitatively the most important in Pierre Shale, even small errors in their assumed chemical compositions would cause significant errors in the chemical calculations. Furthermore, these two clays calculated from the X-ray analyses may actually represent a single entirely mixed-layered entity,

the proportions of the different types of layers varying from one sample to the next. (See discussion on p. C9–C11.) Therefore, instead of using a fixed chemical formula for either mineral, all chemical elements not assigned to other minerals are assumed to occur in one of these two clay minerals. The chemical elements so assigned to montmorillonite and mixed-layer illite-montmorillonite are then calculated into a combined structural formula according to the method of Ross and Hendricks (1945). This method has been explained clearly by Kelley (1955) and is briefly illustrated under "Example of chemical-mineralogical calculations."

The calculated structural formulas for montmorillonite and mixed-layer illite-montmorillonite in the Pierre Shale are useful not only as a check on the overall accuracy of the X-ray data and the approximate validity of assumptions in the chemical calculations, but also as a basis for evaluating the variations in composition of these minerals through the Pierre Shale. The second use, of course, presupposes satisfactory results from the first.

EXAMPLE OF CHEMICAL-MINERALOGICAL CALCULATIONS

The chemical-mineralogical calculations used for the Pierre Shale are illustrated by the worksheet reproduced as plate 1. Data for sample 259543 were used for plate 1 and were used also for figure 3B and table 2. The worksheet includes space for tabulating chemical analysis, water soluble ions, pH, and X-ray quantitative data; chemical compositions assumed for minerals in the Pierre Shale are listed, and spaces are provided for assignment of chemical constituents to the different minerals. Not all the spaces are needed for recording data obtained from sample 259543, but all may be necessary for recording data from other samples of Pierre Shale. Most of the calculations are performed on the basis of weight percentages instead of the usual molar proportions because X-ray quantitative values used in parts of the calculations were made in terms of weight percents. The structural formula for montmorillonite and mixed-layer illite-montmorillonite is calculated using the last five columns and is entered in the skeletal formula at the top of the worksheet.

On plate 1, the numbers in parentheses represent the amount of each constituent remaining after calculation of each successive mineral; for example, in the third column, 1.43 percent ferrous iron oxide remains after 0.94 percent is assigned to pyrite. No apatite, barite, or water-soluble ions were calculated because amounts of phosphorous pentoxide, barium oxide, and determinations of water-soluble cations were all below the 0.5 percent limit previously mentioned. No jarosite, alunite, or dolomite were calculated, because these minerals were

not detected in the X-ray analysis. Amounts of pyrite, gypsum, and calcite were calculated by multiplying the chemical determinations for sulfide sulfur, sulfur trioxide, and carbon dioxide, respectively, by the factors listed at the top of the columns for each of these minerals (for example, FeO in pyrite=1.12×0.84=0.94 percent). For pyrite, the sum of the constituents do not equal the total amount of the mineral calculated, because the oxygen of the ferrous oxide does not occur in the pyrite. Amounts of oxides assigned to the feldspars, clinoptilolite, quartz, cristobalite, kaolinite, chlorite, and illite are the products of the X-ray modes for these minerals (listed in the row below the mineral names) and their assumed chemical compositions (listed at the top of each column). The amounts of the clay minerals are the products of the relative amounts of each clay and the total clay (for example, kaolinite=0.04×75=3 percent).

Chemical constituents not assigned after calculation of illite are assumed to occur in the only two minerals in the Pierre Shale not yet calculated—montmorillonite and mixed-layer illite-montmorillonite. A combined structural formula for these two clay minerals is calculated in the columns to the right as follows:

1. Cation equivalents are calculated by dividing the weight percent of each oxide by the result of the molecular weight of the oxide divided by the cations per molecule (pl. 1, fifth column from the right).

2. Charge equivalents are the product of the cation equivalents multiplied by the valence of each cation. Charge equivalents are totaled at the bottom of the column. A total of 44 positive charges is needed to balance the 44 negative charges $[O^{-2}_{20} (OH^{-1}, F^{-1})_4]$ in each unit cell of montmorillonite or mixed-layer illite-montmorillonite. A factor (f) was derived by dividing 44 by the sum of the charge equivalents $(44/3.156=13.94)$. (Note: If hydrogen ions are subsequently calculated in interlayer positions, the factor (f) must be adjusted to compensate for the charge on the H^{+1} ions; $f' = \dfrac{44 - H^{+1}}{\text{sum of charge equivalents.}}$)

3. The number of each of the cations per unit cell is the product of the factor (f) and the cation equivalents.

4. Cations are assigned to the three different structural positions as indicated at the top of plate 1, with enough Al^{+3} ions substituting for Si^{+4} to fill all eight tetrahedral positions. Possible occurrence of aluminum, magnesium, or hydrogen in interlayer positions is discussed later.

DISCUSSION

The structural formula calculated in plate 1 is typical of the formulas calculated for montmorillonite and mixed-layer clay in the Pierre Shale. The formula is close to that expected for a dioctahedral, aluminous montmorillonitic clay. For all samples calculated, the most consistent discrepancy is that the determinations for total octahedral cations are commonly slightly below 4 per unit cell; in a very few samples silicon ions exceed the theoretical limit of eight per unit cell. Both discrepancies could result from assigning too much silica to the montmorillonitic clay. Significantly, the calculated total of octahedral cations for bentonites, which contain no quartz, generally is very close to 4. At least part of the deficiency of octahedral cations in montmorillonite and mixed-layer clay of the shale samples may result from assignment of insufficient SiO_2 to quartz, and a consequent excess of SiO_2 assigned to the clay. Possibly, the fine-grained quartz in the Pierre Shale is surrounded by poorly crystallized layers of silica. Gordon and Harris (1955) suggested that such silica coatings would cause X-ray modes for quartz that are about 12 percent too low. For the Pierre Shale, such an error would result in quartz determinations that generally are about 2 percent low (that is, a determination of 16 percent quartz would probably represent about 18 percent silica).

Several analyses for amorphous silica in samples of Pierre Shale were made using the method of Hashimoto and Jackson (1960). The first two samples in table 8 seemed to contain excess amorphous silica, because the calculated structural formula for their montmorillonite and mixed-layer illite-montmorillonite had more than 8 silica molecules per unit cell. The third sample in table 8 was analyzed to determine the approximate accuracy of the cristobalite determination. The last group of samples in table 8 includes two of shale and one of bentonite (259537). These three samples were assumed to be controls having little or no amorphous silica because they caused no difficulties in the chemical-mineralogical calculations.

The dissolved silica and alumina for the control samples may be in part due to solution of crystalline silicates; for sample 259569 the silica-alumina ratio is about that expected for the clays in the Pierre Shale. The important fact shown by the table is that, although a few percent amorphous silica may be undetected (as possibly in sample 259535), the chemical-mineralogical calculations are sufficiently precise to identify samples like 259561 and 259563 that apparently contain fairly large amounts of material amorphous to X-rays.

TABLE 8.—*Amorphous silica and alumina, in percent, in Pierre Shale*

[Analyses by E.C. Mallory using method of Hashimoto and Jackson (1960; sample boiled 2½ minutes in ½N NaOH, leachate analyzed by light transmission)]

Sample	Dissolved SiO_2	Dissolved Al_2O_3
Shale samples apparently containing amorphous SiO_2 assigned to clay minerals		
259561	17.40	0.68
259563	9.76	.61
Shale sample containing 35 percent cristobalite determined by X-ray		
259529	34.80	0.85
Control samples		
259535	4.48	0.39
259537	2.60	.39
259569	1.68	.58

The theoretical interlayer charge of an ideal mica is 2 per unit cell. The interlayer charge of montmorillonite and mixed-layer clays, like those in the Pierre Shale, theoretically should be from a third to about two-thirds or possibly three-fourths of the interlayer charge of mica. The total of the charge on the potassium, sodium, and calcium ions calculated to occur in interlayer positions of mixed-layer clay and montmorillonite from samples of Pierre Shale are plotted as dots and squares on figure 9. Most of the Pierre samples plot within the theoretically reasonable field that is represented by the shaded area on figure 9. Other samples plot outside the shaded area for several reasons. For example, the bentonite sample having a calculated total of 1.17 interlayer charges per unit cell contains several percent biotite for which no correction was made. The abnormally high calculated interlayer charge results from 0.35 potassium ion per unit cell, most of which actually occurs in biotite. Therefore, the shaded area is not extended to include this sample. Some of the other samples of shale that are plotted above the shaded area contain unusually small amounts of montmorillonite and mixed-layer clay; others plotted above the shaded area contain water-soluble cations or sulfate in unknown quantities. Calculated structural formulas for these samples therefore are less reliable than most, and they are not included in the shaded area on figure 9. If the shaded area had been extended to include them, its projected upper limit would exceed the maximum possible interlayer charge of 2 per unit cell.

A considerable group of samples also are plotted below the shaded area on figure 9. For example, three of the bentonite samples, which are composed almost entirely of montmorillonite and therefore afford very little room for errors in chemical constituents assigned

to other minerals, have totals of interlayer charge from 0.17 to 0.42 per unit cell. Such totals are much below the reasonably expectable minimum. The low totals for interlayer charge plotted on figure 9 generally are related to two features: the occurrence of interlayer brucite- or gibbsite-like structures in the clay minerals and the pH of the sample slurry.

Brucite- or gibbsitelike layers in some of the clays represented on figure 9 are indicated in the X-ray traces by incomplete collapse of the first basal reflections after the samples are heated at 300°C for half an hour (fig. 10). Additional heating at 550°C for half an hour generally causes these interlayer structures to break down, and the clay layers collapse to a 10A spacing. Thus, the interlayer structures are not as stable as the brucite layer of chlorite which maintains

a basal spacing near 14A after heating at 550°C for half an hour.

The method used to calculate structural formulas (pl. 1) assigns all magnesium and aluminum to octahedral or tetrahedral positions within the clay lattice. If some magnesium or aluminum actually occurs in interlayer positions, the usual procedure would produce an abnormally high total for cations in octahedral positions and also an abnormally low total for interlayer cations and the charge on those cations. These high and low totals occur for several of the Pierre samples. For example, the bentonite sample having only 0.33 positive interlayer charge per unit cell (fig. 9) has a calculated total of 4.31 octahedral cations as compared with an ideal number of 4.0 octahedral cations. Therefore, in the chemical-mineralogical calculations
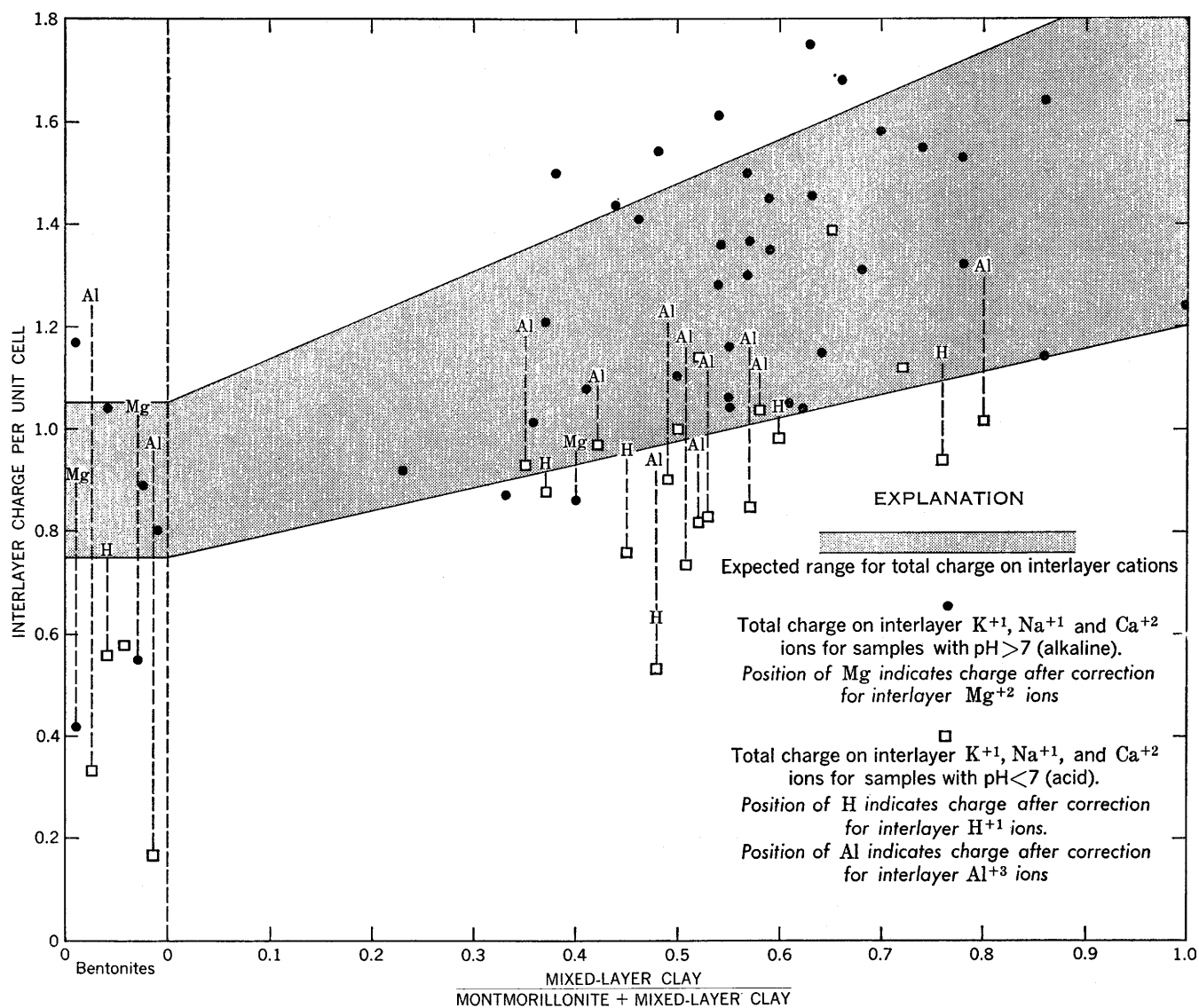

FIGURE 9.—Total charge on interlayer cations of montmorillonite and mixed-layer clay in the Pierre Shale.
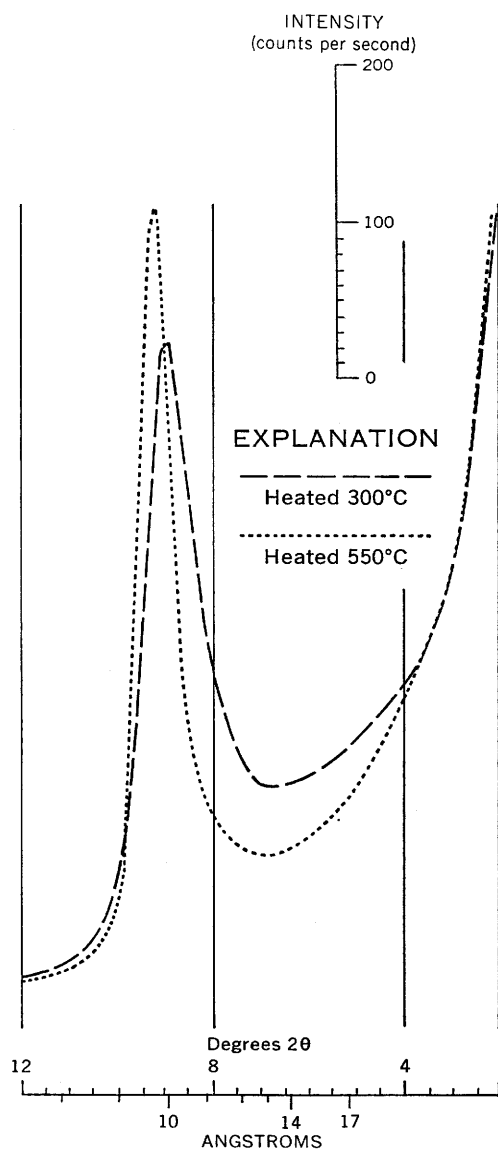
FIGURE 10.—Effect of brucite- or gibbsitelike inter-
layers on the X-ray diffractometer traces of
montmorillonitic clay.

for the Pierre Shale, if a sample contains detectable
brucite- or gibbsitelike interlayers, and if the calcu-
lated total of octahedral cations exceeds 4.0, enough
magnesium or aluminum is transferred into interlayer
positions to reduce the total of octahedral cations to 4.0.

Both interlayer hydrogen (or hydronium) and
aluminum ions may occur in clays having a low pH;
the hydrogen ions are the cause and the aluminum ions
are the effect of the acid condition. However, only the
aluminum will form gibbsitelike interlayer structures
that prevent complete collapse to a basal spacing of
about 10A after heating at 300°C for half an hour.
Therefore, if X-ray data indicate an interlayer struc-
ture and if a low pH denotes that the clay is acid, then

aluminum ions are transferred in the structural formula
to interlayer positions. If the pH shows that the clay
is alkaline, the interlayer structure is assumed to be
brucitelike and magnesium is transferred to interlayer
positions. Such transfers generally increased the total
interlayer charge until they were within the expected
range shown on figure 9. For one bentonite sample, the
aluminum transfer caused the total interlayer charge to
exceed the expected range, probably because the charges
on some of the interlayer aluminum ions are balanced
by interlayer OH^{-1} ions for which no attempt was made
to compensate.

All but one of the samples that showed no evidence of
brucitelike or gibbsitelike interlayers, but which were
plotted below the shaded areas of figure 9, have low
pH. These samples probably contained interlayer hy-
drogen (or H_3O^+) ions that were not included when the
structural formula was calculated by the usual method.
The amount of the interlayer hydrogen was determined
by assuming sufficient interlayer hydrogen to increase
the interlayer charge to the minimum expected total
indicated by the shaded area on figure 9.

The aforesaid procedures for the calculation of inter-
layer magnesium, aluminum, and hydrogen ions will
not produce corrections in every situation where small
amounts of these ions actually occur in the exchange
positions. Scant available data indicate that magne-
sium ions frequently compose about 10 percent of the
total exchangeable cations. Because no magnesium
generally is calculated in interlayer positions, exchange-
able magnesium in small amounts is assigned to octa-
hedral positions. However, in the one sample having
calculated interlayer magnesium for which exchange
data are available, magnesium ions composed 41 percent
of the exchangeable cations. Thus, the adopted proce-
dure generally will indicate the presence of interlayer
magnesium, aluminum, and hydrogen ions where they
compose a major proportion of the interlayer cations,
and the resulting structural formulas will give a more
accurate picture of the occurrence of elements in the
minerals of the Pierre Shale.

The calculated structural formulas for montmoril-
lonite and mixed-layer clay are by no means perfect.
They contain a residuum of all errors made in the
chemical analysis, the interpretation of the X-ray data,
and the assignment of chemical elements to other miner-
als, as well as small errors in assignment of the remain-
ing cations to the three structural positions of the mont-
morillonite and mixed-layer clay. Nevertheless, the
formulas are still useful for comparison among samples
handled by uniform methods, and they indicate the
major features of distribution of elements in the clay
lattices.

CONCLUSIONS

The accuracy and the reproducibility that can be expected for the quantitative determinations of mineral abundance derived from X-ray diffraction traces of samples of the Pierre Shale seem to be of the same order of magnitude. Most determinations, if greater than about 15 percent, are accurate within 10 percent of the stated value. However, unless precautions are taken, a few errors in determinations can be made that are considerably greater than the usual limits of error. Poor reproducibility of the feldspar determination in one sample illustrated the need for careful hand grinding and homogenization or repeated analyses of samples containing relatively coarse particles. Machine grinding produced uniformity, but also produced a considerable change in crystallinity and diffraction properties of some minerals. In making comparisons, consideration must be given to which minerals in which types of samples are likely to be most in error. Comparisons are best made on the basis of groups of samples rather than between individual samples. If determined values for amounts of minerals in groups of samples are consistently different, then differences smaller than 10 percent probably are significant.

Structural formulas calculated for the montmorillonite and mixed-layer clay also should be interpreted with caution, and due regard should be given to the many factors which enter into their calculation. They also are best compared as groups rather than as individual samples.

LITERATURE CITED

Altschuler, Z. S., Clarke, R. S., Jr., and Young, E. J., 1958, Geochemistry of uranium in apatite and phosphorite: U.S. Geol. Survey Prof. Paper 314-D, p. 45–90.

Black, R. H., 1953, Analysis of bauxite exploration samples—an X-ray diffraction method: Anal. Chem., v. 25, no. 5, p. 743–748.

Brindley, G. W., ed., 1951, X-ray identification and structures of clay minerals: ed. 1, London, The Mineralogical Society (Clay Minerals Group), 345 p.

Cross, Whitman, Iddings, J. P., Pirsson, L. V., and Washington, H. S., 1903, Quantitative classification of igneous rocks, based on chemical and mineral characters, with a systematic nomenclature: Chicago, University of Chicago Press, 286 p.

Degens, E. T., Williams, E. G., and Keith, M. L., 1957, Geochemical criteria for differentiating marine from freshwater shales, pt. 1 of Environmental studies of Carboniferous sediments [Pa.]: Am. Assoc. Petroleum Geologists Bull., v. 41, no. 11, p. 2427–2455.

Foster, M. D., 1954, The relation between "illite," beidellite, and montmorillonite, in Swineford, Ada, and Plummer, N. V., eds., Clays and clay minerals: Natl. Research Council Pub. 327, p. 386–397.

Franks, P. C., and Swineford, Ada., 1959, Character and genesis of massive opal in Kimball member, Ogallala formation, Scott County, Kansas: Jour. Sed. Petrology, v. 29, no. 2, p. 186–196, 5 figs.

Gordon, R. L., and Harris, G. W., 1955, Effect of particle-size on quantitative determination of quartz by X-ray diffraction: Nature, v. 175, no. 4469, p. 1135.

Grim, R. E., 1953, Clay mineralogy: New York, McGraw-Hill Book Co., 384 p.

Grim, R. E., Bradley, W. F., and White, W. A., 1957, Petrology of the Paleozoic shales of Illinois: Illinois Geol. Survey Rept. Inv. 203, 35 p., 5 figs.

Gulbrandsen, R. A., 1960, A method of X-ray analysis for determining the ratio of calcite to dolomite in mineral mixtures: U.S. Geol. Survey Bull. 1111-D, p. 147–152.

Hashimoto, I., and Jackson, M. L., 1960, Rapid dissolution of allophane and kaolinite-halloysite after dehydration, in Swineford, Ada., ed., Clays and clay minerals: Internat. Ser. Mons. Earth Sci., v. 5, p. 102–113.

Hendricks, S. B., 1937, The crystal structure of alunite and the jarosites: Am. Mineralogist, v. 22, no. 6, p. 773–784.

Imbrie, John, and Poldervaart, Arie, 1959, Mineral compositions calculated from chemical analyses of sedimentary rocks: Jour. Sed. Petrology, v. 29, no. 4, p. 588–595.

Jarvis, N. L., 1958, A method for the quantitative determination of clay mineral mixtures by X-ray diffraction and its application to four soils of southeastern Kansas: Ann Arbor, Mich., Dissertation Abs., v. 18, no. 4, p. 1181–1182, Univ. Microfilms Libr. Cong. Card Mic 58–1262, 92 p.

Johns, W. D., Grim, R. E., and Bradley, W. F., 1954, Quantitative estimations of clay minerals by diffraction methods: Jour. Sed. Petrology, v. 24, no. 4, p. 242–251.

Kelley, W. P., 1955, Interpretation of chemical analyses of clays, in Pask, J. A., and Turner, M. D., eds., Clays and clay technology: California Div. Mines Bull. 169, p. 92–94.

Kinter, E. B., and Diamond, Sidney, 1956, A new method for preparation and treatment of oriented-aggregate specimens of soil clays for X-ray diffraction analysis: Soil Science, v. 81, no. 2, p. 111–120.

Krumbein, W. C., and Pettijohn, F. J., 1938, Manual of sedimentary petrology: New York, Appleton-Century-Crofts Inc., 549 p.

Levin, I., and Ott, Emil, 1933, X-ray study of opals, silica glass, and silica gel: Zeitschrift für Kristallographie, v. 85, p. 305–318, 6 figs. [in English].

Mason, Brian, and Sand, L. B.. 1960, Clinoptilolite from Patagonia—the relationship between clinoptilolite and heulandite: Am. Mineralogist, v. 45, nos. 3–4, p. 341–350.

Miesch, A. T., 1962, Computing mineral compositions of sedimentary rocks from chemical analyses: Jour. Sed. Petrology, v. 32, no. 2, p. 217–225.

Mitchell, W. A., 1960, A method for quantitative mineralogical analysis by X-ray powder diffraction: Mineralog. Mag., v. 32, no. 249, p. 492–499.

Mumpton, F. A., 1960, Clinoptilolite redefined: Am. Mineralogist, v. 45, nos. 3–4, p. 351–369.

Nicholls, G. D., 1962, A scheme for recalculating the chemical analyses of argillaceous rocks for comparative purposes: Am. Mineralogist, v. 47, no. 1, p. 34–46.

Rader, L. F., and Grimaldi, F. S., 1961, Chemical analyses for selected minor elements in Pierre shale, in Analytical methods in geochemical investigations of the Pierre shale: U.S. Geol. Survey Prof. Paper 391-A, p. A1–A45.

Rex, R. W., and Goldberg, E. D., 1958, Quartz contents of pelagic sediments of the Pacific Ocean: Tellus, v. 10, no. 1, p. 153–159.

Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: U.S. Geol. Survey Prof. Paper 205–B, p. 23–79 [1946].

Schmalz, R. F., and Zen, E-An, 1959, Quantitative modal analysis of sediments by X-ray diffraction, in Sears, Mary, ed., Internat. Oceanog. Cong. preprints [Washington, Aug. 13–Sept. 12, 1959]: Washington, D.C., Am. Assoc. Advancement Sci., p. 485–486.

Schultz, L. G., 1960, Quantitative X-ray determination of some aluminous clay minerals in rocks, in Swineford, Ada, ed., Clays and clay minerals: New York, Pergamon Press, p. 216–224.

Sudo, T., Oinuma, K., and Kobayashi, K., 1961, Mineralogical problems concerning rapid clay mineral analysis of sedimentary rocks: Carolinae Univ. Acta, Geologica Sup. 1, p. 189–219, Praque.

Talvenheimo, Gerhardt, and White, J. L., 1952, Quantitative analysis of clay minerals with the X-ray spectrometer: Anal. Chem., v. 24, no. 11, p. 1784–1789.

Tennant, C. B., and Berger, R. W., 1957, X-ray determination of dolomite-calcite ratio of a carbonate rock: Am. Mineralogist, v. 42, nos. 1–2, p. 23–29.

Tourtelot, H. A., 1962, Preliminary investigation of the geologic setting and chemical composition of the Pierre Shale, Great Plains region: U.S. Geol. Survey Prof. Paper 390, 74 p.

Tourtelot, H. A., Schultz, L. G., and Gill, J. R., 1960, Stratigraphic variations in mineralogy and chemical composition of the Pierre Shale in South Dakota and adjacent parts of North Dakota, Nebraska, Wyoming, and Montana, in Short papers in the geological sciences: U.S. Geol. Survey Prof. Paper 400–B, p. B447–B452.

Warshaw, Charlotte M., 1956, The occurrence of jarosite in underclays: Am. Mineralogist, v. 41, nos. 3–4, p. 288–296.

Weaver, C. E., 1956, The distribution and identification of mixed-layer clays in sedimentary rocks in Swineford, Ada, ed., Clays and clay minerals: Natl. Res. Council Pub. 456, p. 385–386.

———1958, Geologic interpretation of argillaceous sediments, Pt. 1, Origin and significance of clay minerals in sedimentary rocks: Am. Assoc. Petroleum Geologists Bull., v. 42, no. 2, p. 254–271.

Whitehouse, U. G., and McCarter, R. S., 1958, Diagenetic modification of clay mineral types in artificial sea water, in Swineford, Ada, ed., Clays and clay minerals: Natl. Research Council Pub. 566, p. 81–119.

Zen, E-An, 1960, Metamorphism of Lower Paleozoic rocks in the vicinity of the Taconic range in west-central Vermont: Am. Mineralogist, v. 45, nos. 1–2, p. 129–175.

O