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METHOD OF ANALYSIS AND PRECISION OF X-RAY
DIFFRACTION DATA FROM OHIO SHALE

By
Richard W. Carlton

October 1978

Work Performed Under Contract No. EY-76-S-05-5200

Division of Geological Survey
Ohio Department of Natural Resources
Columbus, Ohio

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Prepared for

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, West Virginia

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ABSTRACT

Sample preparation and methods of calculation used by the Division of Ohio Geological Survey in its mineralogic and physical characterization of the Upper Devonian black shales are described. Our methods of sample mounting, used in conjunction with a Philips automatic sample changer (ASC), enable us to analyze a large number of samples by x-ray diffractometry. Because of the time saved with an ASC, we can scan each sample twice and increase the precision of our data. The reproducibility of our x-ray data, expressed as relative deviation, ranges from about ± 2 to $\pm 10\%$ in samples for which the percent total integrated intensity (%TII) is above 6%.

INTRODUCTION

The Ohio Division of Geological Survey is conducting mineralogical studies of the Upper Devonian black shale sequence in Ohio. The investigation is part of an extensive study of the Devonian-age black shales found in the Appalachian basin and involves numerous state, federal, and private institutions and organizations.

The purpose of this paper is to make known the methods of analysis I have developed for use in our x-ray investigations and to show the precision of the data for representative Ohio Shale samples.

Since publication of Johns, Grim, and Bradley's (1954) study of Recent sediments from the Gulf of Mexico, many investigators have attempted to quantify, by many different methods, clay mineral data obtained by x-ray analysis.

Unfortunately, different x-ray diffraction equipment and instrumental settings, mounting techniques, sample treatment, and differences in crystallinity and composition of clay minerals all contribute to differences in precision and accuracy of the results.

Gibbs (1965) reported on seven mounting techniques for clays and found that all had precision of $\pm 10\%$ of the mean.

Schultz (1964), in his wholerock analysis of Pierre Shale samples, reported that, by use of his methods and for minerals comprising more than 15% of the sample, any single determination would be within $\pm 10\%$ of the mean 68% of the time. Pierce and Siegel (1969) reported on the precision and accuracy of five different methods of calculation for the same set of clay samples. They concluded that the results obtained by the different methods were significantly different, although each method appeared internally to be acceptably precise.

Because of the large number of variables which can affect the precision and accuracy of clay mineral studies, comparisons of results obtained by different investigators must be made with extreme care. Pierce and Siegel (1969) suggested that areas of peaks measured be reported. This eliminates errors introduced by various methods of calculation. Renton (1977) used uncorrected x-ray diffraction data in the form of percent total integrated intensity (%TII). In four out of five of the methods studied by Pierce and Siegel, peak areas are determined before further calculations are performed. If investigators reported, in addition to weighted peak percentages, the peak areas and the particular peaks measured, better data comparison could be made.

SAMPLE PREPARATION, WHOLE ROCK

Two samples, each approximately one-half inch thick are cut from the core. In most cases the two samples are cut parallel and adjacent to each other. One of the two samples is used for petrographic and density studies. The other is used for chemical and x-ray analysis. The sample for x-ray is crushed to minus 10 mesh and then is pulverized in a ceramic-plate pulverizer to minus 18 mesh (fig. 1). A 15-g split of the minus 18 mesh material is placed in a SPEX mill tungsten carbide vial. This split fills the vial approximately one-third full. Methyl alcohol is added to the top of the vial, and the slurry is ground for 10 minutes by use of a half-inch-diameter tungsten carbide ball. This grinding procedure reduces 94% of the sample to minus 120 mesh (0.125 mm). The slurry is set aside overnight and allowed to evaporate to dryness. After drying, the sample is rehomogenized by lightly crushing the dry cake with a pestle and sieving through an 80-mesh screen. A 5-g split of this is used in the x-ray analysis. The remaining 10 g is used for various chemical analyses. A 0.2 g split is obtained from the 5-g x-ray sample and carefully handground to minus 325 mesh. This material is used in the x-ray analysis of the whole-rock. The remaining 4.8 g is used in the <2 μ m fraction x-ray analysis described later.

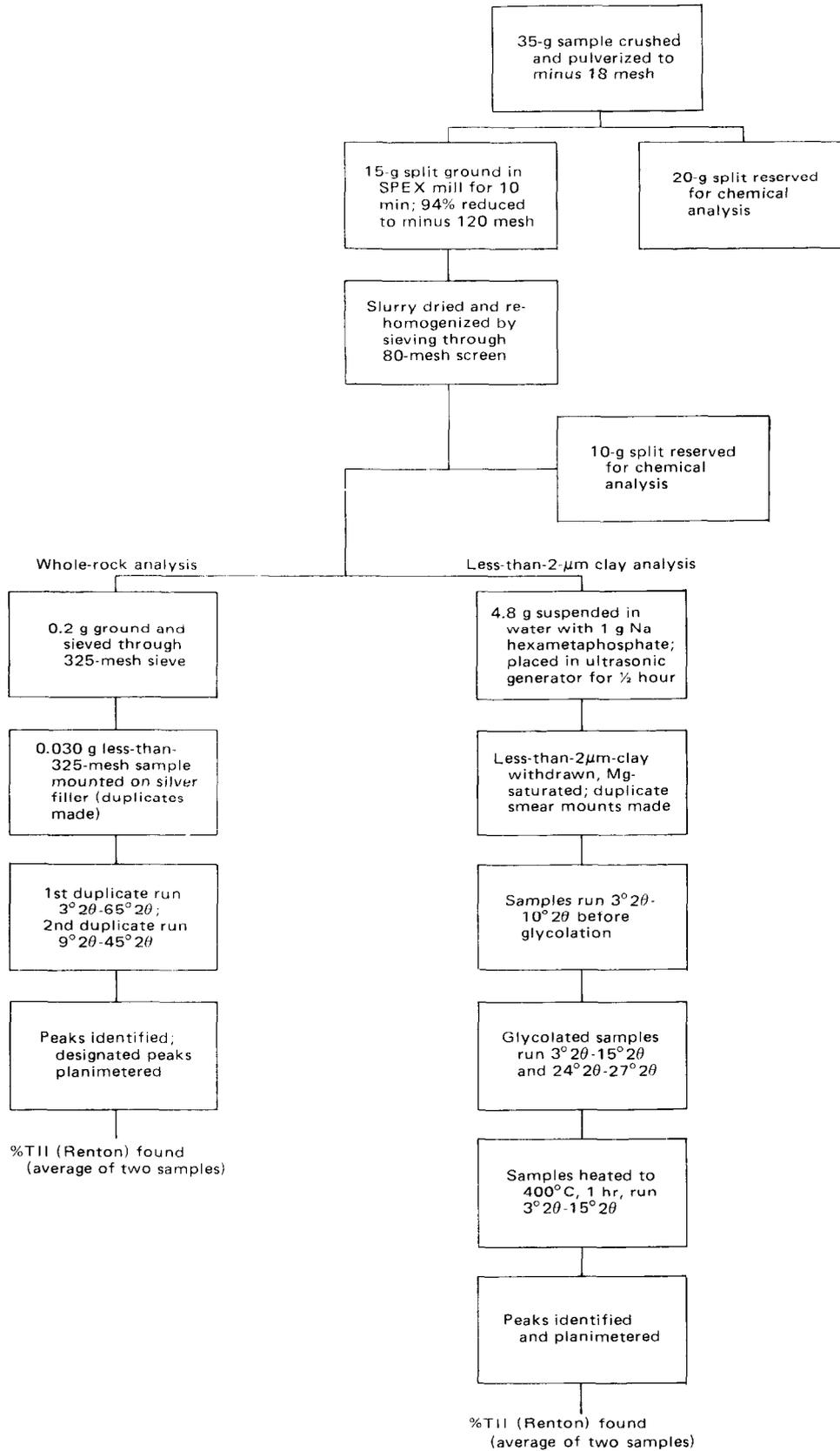


FIGURE 1.—Outline of method used in preparing samples.

A 30 mg sample of the minus-325 mesh material is mounted on a silver filter (Selas Flotronics Membrane) 25 mm in diameter with 0.45- μ m pores. Duplicate sample mounts are made. The silver filter is placed in a Gelman filter funnel connected to an aspirator. The mount is made by suspending 30 mg of the sample in about 5 ml of methyl alcohol and quickly pouring the suspension onto the silver filter while the suspension is under vacuum. Fewer than 5 seconds are required to draw the alcohol through the filter. The upper portion of the filter funnel (the portion containing the silver filter mount (SFM) is detached from the vacuum flask and oven dried at 60°C. After drying, the SFM is glued with Canada balsam to a slightly modified sample holder normally used with a Philips automatic sample changer (ASC). The sample holders used with the ASC have a rectangular hole into which powdered samples can be packed. A metal clip fits on the back to keep the sample from falling out. In our modified holders, a circular depression 0.005-inch deep and slightly greater in diameter than the silver filter is drilled directly over the rectangular hole. The round silver filter mounts are glued into these depressions, loaded into the ASC, and scanned without further attention. When the scan is completed, the SFM can be removed from the holder by applying isopropyl alcohol, which readily dissolves the Canada balsam.

Granular substances such as quartz, pyrite, and calcite cannot be mounted in the way described without the surface being disrupted by vibrations produced by the ASC. The addition of 10% clay or some other binding material is sufficient to overcome this problem. The Ohio Shale samples generally contain a natural clay binder and were not affected by vibrations from the ASC.

The layer of sample coating the silver filter is thin enough to insure that the x-ray beam can penetrate and produce a nearly full-scale silver peak at $38.15^\circ 2\theta$. Ohio Shale sample OH01L000 (table 1) has a calculated average linear absorption coefficient of 89.1/cm and a grain density of 2.25 g/cm³. Thirty mg of this sample spread over an area of 286.52 mm² (effective filtration area of the silver filter) has a thickness of about 46.5 μm . Pore space is disregarded in these assumptions because of negligible attenuation effect on the x-ray beam (Gibbs, 1965).

The calculated fraction of the total diffracted intensity of $\text{CuK}\alpha$ radiation for this sample at $38^\circ 2\theta$ and contributed by a surface layer of 46.5 μm is about 92% (fig. 2, and Cullity, 1959, p. 271). Therefore, about 8% of the x-ray beam is diffracted by the silver filter lying below the 45.5- μm

TABLE 1.--*Identification of wells mentioned in text*

Well code no. (alternate code or name)	County	Sample depth (ft)
OHO1 (Chillicothe test core)	Ross	
OHO1L000		123.0
OHO1L030		182.0
OHO1L080		279.5
OHO1L090		301.5
OHO1L170		460.5
OHO3 (R-109)	Washington	
OHO3L001		3491.0
OHO3L021		3528.2
OHO3L031		3555.5
OHO3L091		3680.9

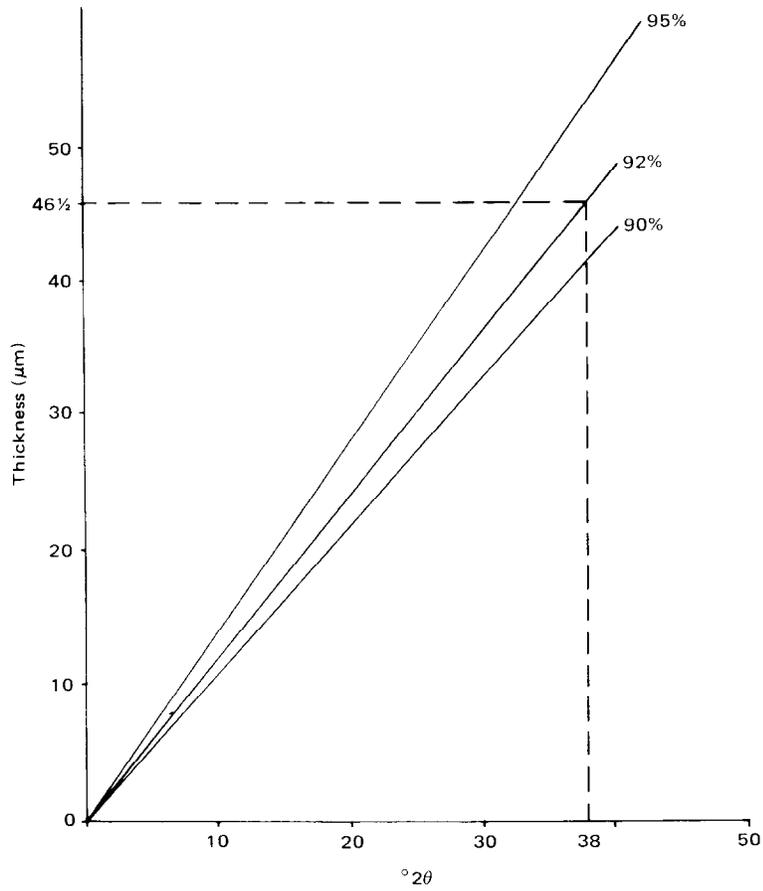


FIGURE 2.—Percent of the total diffracted intensity contributed by a surface layer about $46\frac{1}{2}$ μm thick. The surface layer has a density of 2.25 g/cm^3 and a linear absorption coefficient of $89.1/\text{cm}$. The 2θ angle is 38° and the radiation is $\text{CuK}\alpha$.

shale layer. This is enough of the total diffracted intensity to produce a silver peak from 50% to 100% full scale. If desired, this method of mounting can be used to determine mineral weight percent. A method is currently being studied by the Ohio Division of Geological Survey to enable determination of mineral weight percent by utilization of the relative intensity of the silver peak.

SAMPLE PREPARATION, CLAY

The $<2\text{-}\mu\text{m}$ clay samples are prepared from the approximately 4.8 g of the SPEX-round split referred to earlier. After dispersing with 1 to 2 g of sodium hexametaphosphate and waiting the appropriate length of time for material greater than $2\ \mu\text{m}$ to settle 4 cm, the $<2\text{-}\mu\text{m}$ suspension is siphoned off and filtered. All samples are Mg-saturated with 1N MgCl_2 solution and then smeared onto a round cover glass 0.875 inch in diameter. This mount is then glued into the depression in the ASC holder with Canada balsam. The samples are placed in a glycol atmosphere for approximately 16 hours at 60°C . Glycolation can be performed either before or after mounting in the holder, but we remove the glass smear mount from the holder prior to heating at 400°C . After heating, the mount is recemented into the ASC holder in exactly the same position as before, so that the measured 10\AA peak intensity

is affected only by the heat treatment and not by intensity changes caused by rotation of the sample.

METHOD OF ANALYSIS, WHOLE ROCK

Duplicate whole-rock x-ray mounts are made in manner previously described. One duplicate is scanned from $3^{\circ}2\theta$ to $65^{\circ}2\theta$ and the other from $9^{\circ}2\theta$ to $57^{\circ}2\theta$. The longer scan is examined carefully, and all peaks are identified. Designated peaks, shown in table 2, are planimetered on both scans if they appear on the x-ray diffraction patterns. For each pattern, each plantimetered area is divided by the total area of all the peaks measured on that particular pattern to obtain the %T11 (see Renton, 1977). The %T11 values for the duplicate patterns are then averaged.

The %T11 values for the clay minerals in the whole-rock analysis are determined by use of two nonbasal reflections at about $19.9^{\circ}2\theta$ and $35.1^{\circ}2\theta$. The peak at $19.9^{\circ}2\theta$ represents kaolinite plus mica, and the peak at $35.1^{\circ}2\theta$ represents chlorite plus mica. The relative proportion of the $19.9^{\circ}2\theta$ peak attributed to kaolinite is found by the following method:

$$(19.9^{\circ}2\theta \text{ peak area}) (\% \text{ kaolinite in } <2 \mu\text{m clay})$$

$$(\% \text{ kaolinite in } <2 \mu\text{m clay} + \% \text{ mica in } <2 \mu\text{m clay})$$

$$= \text{peak area attributed to kaolinite}$$

TABLE 2. Designated peaks for whole-rock mineral analysis

Mineral	Peak position in $^{\circ}2\theta$ (CuK α)
Kaolinite	19.9
Chlorite	35.1-35.5
Mica	19.9
Quartz	20.8
K-feldspar	26.9 to 27.8
Plagioclase	27.8 to 28.1
Calcite	29.4
Dolomite/ankerite	31.0-30.8
Pyrite	56.3
Marcasite	52.0
Carbonate fluorapatite	33.3
Fluorapatite	32.3
Siderite	32.1*
Barite	25.89**
Anhydrite	25.5

*This siderite peak can interfere with a fluorapatite peak at about $31.96^{\circ}2\theta$.

**This barite peak can interfere with a marcasite peak.

TABLE 3. Sample treatment and instrumental settings for clay analysis

Run	Replicate	Scan length $^{\circ}2\theta$	Mg-saturated	Glycolated	Heated 1 hr. at 400 $^{\circ}$ C	54% relative humidity ¹	0% relative humidity ¹	Chart speed	Goniometer speed	Counts/sec.
1	A ₁	3-10	X			X		1"/min	1	1000
2, 3	A ₁ , A ₂	3-15	X	X		X		1"/min	1	1000
4, 5	A ₁ , A ₂	3-15	X		X		X	1"/min	1	1000
6	A ₁ , A ₂	24-27	X	X		X		1"/min	1/2	500

¹ Either 0% relative humidity or 54% relative humidity air is pumped into the chamber formed by the radiation shield.

The remaining peak area at $19.9^{\circ}2\theta$ represents the mica peak area.

The chlorite peak area is found in the following manner:

(peak area at $35.1^{\circ}2\theta$) (% chlorite in $<2 \mu\text{m}$ clay)

(% chlorite in $<2 \mu\text{m}$ clay + mica in $<2 \mu\text{m}$ clay)

= peak area attributed to chlorite

The remaining peak area at $35.1^{\circ}2\theta$ represents mica and is not used in determining %T11 because the mica peak has already been determined from the $19.9^{\circ}2\theta$ peak.

METHODS OF ANALYSIS, CLAYS

Duplicate smear mounts are made for each sample. The first is run from $3^{\circ}2\theta$ to $10^{\circ}2\theta$ and is used only for the purpose of comparing the sample in the unglycolated state with the glycolated sample (table 3). The second and third scans, from $3^{\circ}2\theta$ to $15^{\circ}2\theta$, are duplicate patterns from which the %T11 values are determined. Areas are measured for the 10\AA mica and 7\AA kaolinite/chlorite peaks. In the fourth and fifth runs, duplicate samples previously used in the second and third runs are heated for one hour at about 400°C , and the 10\AA mica peak is measured. The difference between the heated and nonheated 10\AA mica peak is attributed to collapsible mixed-layer clay. The mixed-layer clay measured in this manner does not necessarily represent the total mixed-layer clay in the sample.

However, the dominant mixed-layer clay in these samples appears to be randomly interstratified montmorillonite-illite which is accounted for by this method of measurement. The sixth scan, run from $24^{\circ}2\theta$ to $27^{\circ}2\theta$, is used to differentiate between chlorite at $24.85^{\circ}2\theta$ and kaolinite at $25.13^{\circ}2\theta$ and to determine the relative proportion of chlorite and kaolinite in the 7\AA kaolinite/chlorite peak.

The %Tll of chlorite is found in the following manner:

$$\frac{3.54\text{\AA} \text{ chlorite peak area}}{3.54\text{\AA} \text{ chlorite peak area} + 3.58\text{\AA} \text{ kaolinite peak area}} \times 100 = \text{relative \% chlorite}$$

Then the
 (relative % chlorite) (7\AA kaolinite/chlorite peak area) = peak area attributed to chlorite.

The kaolinite peak area can be found by difference or by the same type of calculation used to determine peak areas for the chlorite. The percent chlorite, kaolinite, mica, or mixed-layer clay is found by dividing the respective areas of each mineral by the total peak area. That is:

$$10\text{\AA} \text{ peak area} + 7\text{\AA} \text{ peak area} + (10\text{\AA} \text{ heated peak area} - 10\text{\AA} \text{ unheated peak area}) = \text{total peak areas.}$$

Two other commonly accepted methods of differentiating kaolinite and chlorite have been tried on our samples. Four

<2- μm clay samples were immersed in 6N HCl overnight at 60°C so that all chlorite was destroyed. A number of subsamples of each of the acid treated samples were smeared onto glass disks and heated for three hours at various temperatures (fig. 3A). The data indicate that all four samples had significant amounts of kaolinite present after the samples were heated 3 hours at about 478°C. Three out of the four had no kaolinite left after heating at 500°C, and one sample was heated to 550°C for 3 hours before all kaolinite was destroyed.

In order to see if 3 hours was actually necessary to destroy kaolinite when the sample was heated to 500°C, two acid treated subsamples were subjected to heat for various lengths of time (fig. 3B). The data indicate that if 500°C heat is used in the heat treatment, samples must be heated at least 3 hours, and that some samples, even when heated to 500°C for 3 hours will still contain some kaolinite. However, heating at 550°C for 1 hour destroys all kaolinite in the samples.

Heat treatment is in some cases used to distinguish between kaolinite and chlorite. The heat destroys the kaolinite and leaves the chlorite. However, heat treatment can affect the intensities of chlorite reflections and in some cases completely

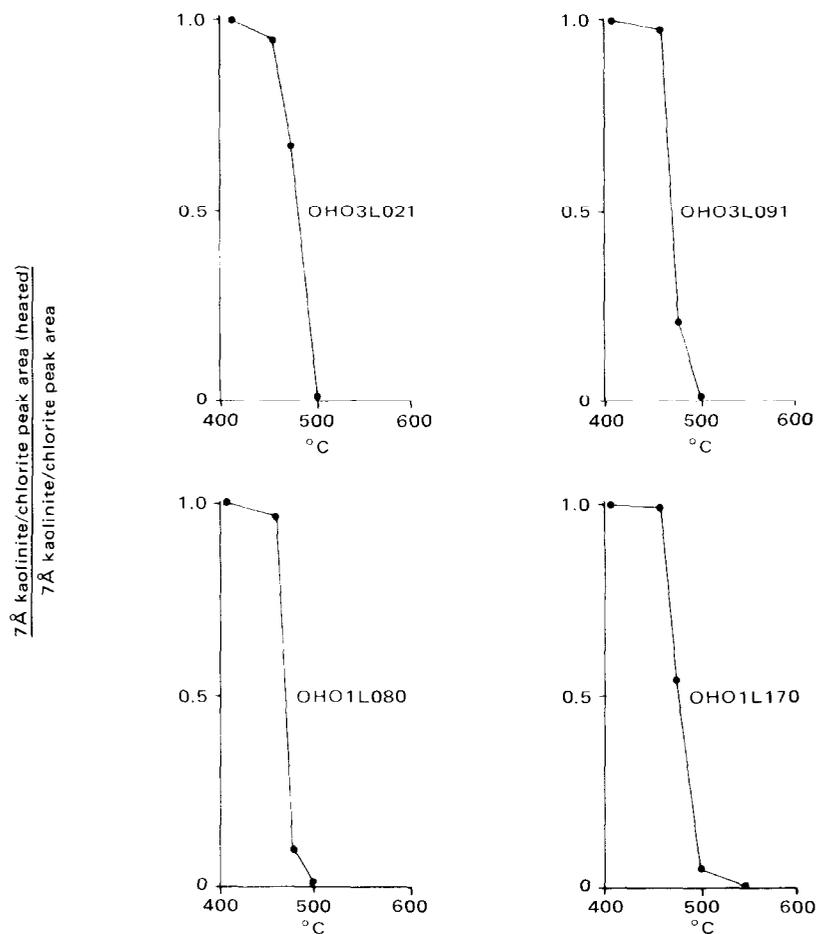


FIGURE 3A.--Acid-treated samples heated for 3 hours at 408°, 455°, 502°, and 550°C. In 3 of the 4 samples kaolinite was destroyed after the sample had been heated for 3 hours at 500°C.

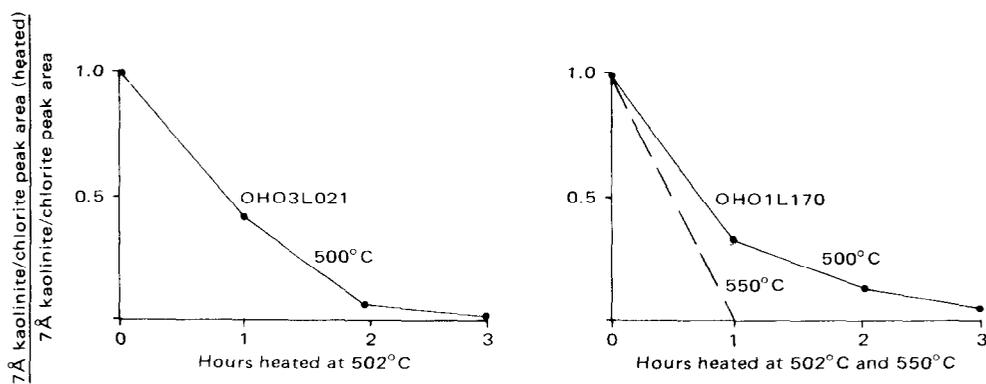


FIGURE 3B. -Acid-treated samples heated at 500° and 550°C for 1, 2, and 3 hours.

destroy the chlorite (Johns, Grim, and Bradley, 1954; Brindley, 1961). Ohio Shale sample OH01L030 is an example of a shale in which the chlorite peaks in the unheated non-acid treated samples are very distinct (fig. 4), but, when the samples are heated to 550°C for 1 hour, the chlorite peaks are obviously altered. If the heated sample is scanned only across the 7Å and 3.5Å chlorite peaks, the sample would appear to have no chlorite because the two peaks are missing after heating. The 14Å chlorite peak must be scanned in order to confirm the presence of chlorite by heat treatment, because heat treatment enhances the 14.2Å line and decreases the second-, third-, and fourth-order chlorite lines (Brindley, 1961); methods which attempt to quantify chlorite after heat treatment are probably not reliable.

An alternative method for determining %T11 kaolinite and chlorite is to acid treat the sample and compare the 7Å peak before and after acidizing. The area lost after acid treatment is considered to represent the chlorite peak area. This method is time consuming; in order for smear mounts to be acid treated they must be resuspended and resmeared. This means the 7Å peak may change area as a result of the resmearing. This problem can be overcome by using the 10Å mica peak as an internal standard and by using ratios.

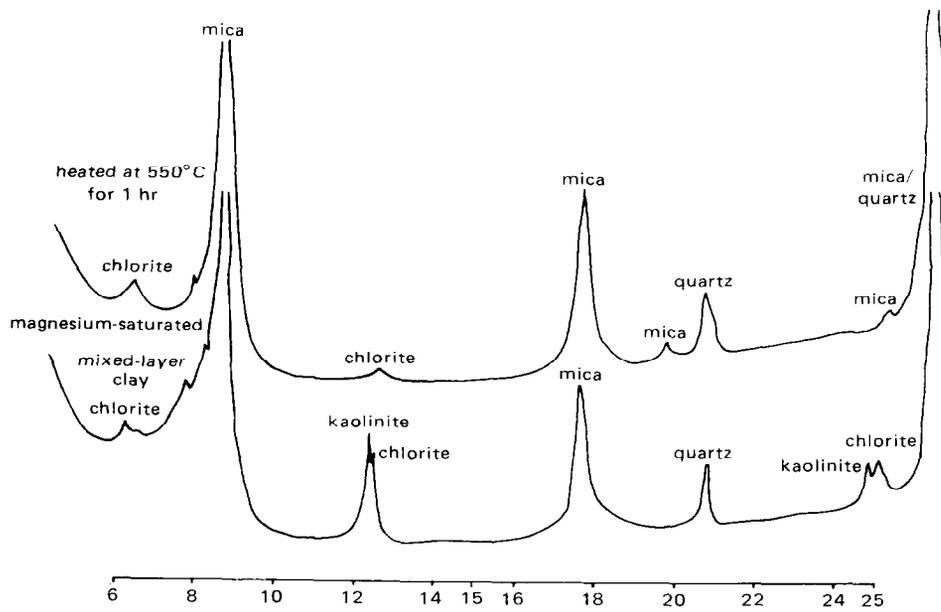


FIGURE 4.-X-ray diffraction pattern of the <2-μm clay of sample OH01L030 before and after heating.

PRECISION TESTS

The precision of our x-ray diffraction analysis depends on a number of variables. The largest errors are probably due to instrument characteristics and settings, sample preparation error, operator error, and sampling error (Cubitt, 1975; Pierce and Siegel, 1969; Gibbs, 1967; Krumbein, 1934). Error due to differences in chemical and structural makeup of the minerals in any single study is probably small unless there are great differences in crystallinity or structure of clay mineral species being investigated.

Sampling error, which is a function of the homogeneity of the sediment, of the precise locality in which the sample is collected, and of the manner in which it is collected (Krumbein, 1934), is not evaluated in our study. Instrumental, sample preparation, and human error (mainly from drawing base lines, smoothing peaks, and planimentering peak areas) are accounted for in our precision data.

Three whole-rock samples and one clay sample were each subdivided into 10 subsamples; each subsample was x-rayed and the %T₁₁ for designated peaks determined. The %T₁₁ for each mineral in the subsamples was randomly paired for each sample and averaged so that five sets of data were obtained (table 4). For each of the four samples the mean, standard deviation,

TABLE 4.—Precision data

Ohio shale sample	Mineral	Peak measured ($^{\circ}2\theta$)	%TII (average of two scans)					Mean	Standard deviation	Relative deviation
OHO1L090 (whole rock)	Clay	19.9	20	18	19	22	20	19.8	1.48	7.5
	Quartz	20.8	44	45	45	45	46	45	0.71	1.6
	K-feldspar	26.9-27.8	12	11	11	10	12	11.2	0.84	7.5
	Plagioclase	27.8-28.1	18	17	18	18	15	17.2	1.30	7.6
	Fe-sulfide	33.1	8	9	9	8	8	8.4	0.55	6.5
OHO3L031 (whole rock)	Clay	19.9	15	19	18	18	18	17.6	1.52	8.6
	Quartz	20.8	34	33	35	34	33	33.8	0.84	2.5
	K-feldspar	26.9-27.8	5	4	4	4	4	4.2	0.45	10.7
	Plagioclase	27.8-28.1	14	15	14	14	14	14.2	0.45	3.2
	Calcite	29.4	19	17	16	16	18	17.2	1.3	7.6
	Dolomite	31.0	11	10	11	11	11	10.8	0.45	4.2
	Fe-sulfide	33.1	2	3	1	2	2	2.0	0.71	35.5
	Phosphate	33.3	3	2	1	3	3	2.4	0.89	37.1
OHO1L001 (whole rock)	Clay	19.9	5	6	5	5	5	5.2	0.45	8.7
	Quartz	20.8	7	6	6	6	6	6.2	0.45	7.3
	K-feldspar	26.9-27.8	1	0	1	0	1	0.6	0.55	91.7
	Plagioclase	27.8-28.1	2	2	1	2	2	1.8	0.45	25.0
	Calcite	29.4	68	69	69	67	69	68.4	0.89	1.3
	Dolomite	31.0	5	3	5	5	4	4.4	0.89	20.2
	Siderite	32.1	14	14	14	15	15	14.4	0.55	3.8
OHO3L091 (clay)	Mica		60	58	62	59	62	60.2	1.78	3.0
	Mixed-layer clay		9	12	10	11	11	10.6	1.14	10.8
	Kaolinite/chlorite	12	29	30	28	29	26	28.4	1.51	5.3

and relative deviation (standard deviation/mean) for the five sets of data for each mineral were determined. In the whole-rock analyses, x-ray peaks for the different minerals present range from very small to off scale. The precision expressed as relative deviation is poor when dealing with these small peaks.

Figure 5 shows the relationship between relative deviation and %T11 for all four of the samples studied in the precision tests. The "best-fit" line through the points has a correlation coefficient of +0.87, indicating a significant relationship between the %T11 and the relative deviation. The curve indicates that, in cases in which our method of averaging two scans for each determination is used, %T11 of about 40% will generally be within about $\pm 2\%$ of the mean of 5 determinations. On the other hand, the reproducibility is only about $\pm 10\%$ in cases where the peaks are small and make up only 6% to 7% of the total peak areas measured.

The %T11 values for minerals such as pyrite or K-feldspar generally have very high relative deviations. For example, pyrite in table 4 has a mean %T11 of 2 and a relative deviation of $\pm 36\%$. These data are still useful because even at this level of reproducibility 2%T11 pyrite can generally be distinguished from 4%T11 for pyrite.

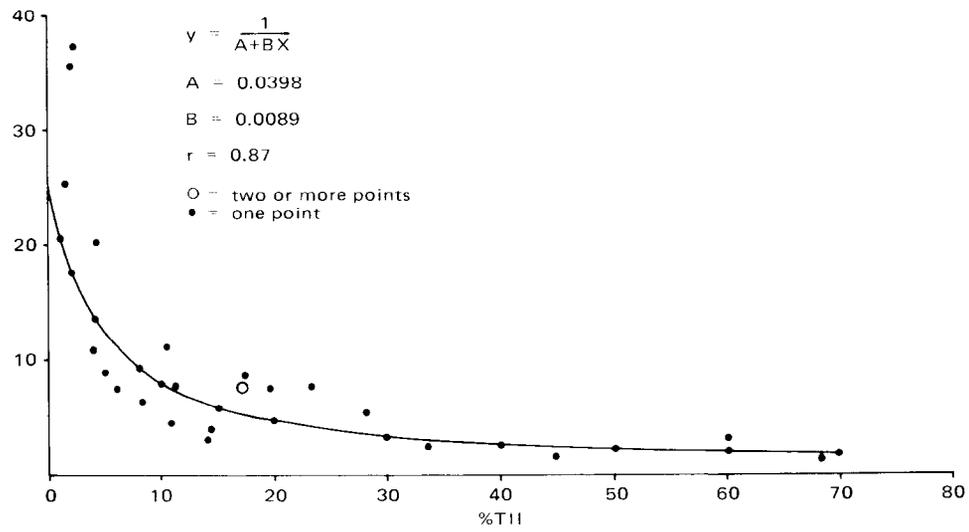


FIGURE 5. - Relationship between relative deviation and %TII determined from x-ray analysis. Data points taken from precision data (table 3).

CONCLUSIONS

The ASC combined with the silver-filter and smear-on-glass disk mounting techniques allow large numbers of whole-rock analyses to be performed. This allows us to scan each sample at least twice, increasing precision.

In the whole rock analysis designated peaks for each mineral are measured and compared to the total peak measured for the sample. More uniform x-ray data between investigators could be obtained if similar diffraction peaks are measured and %T₁₁ calculated.

The reproducibility of our x-ray data, expressed as relative deviation, ranges from about ± 2 to $\pm 10\%$ in samples for which %T₁₁ is above 6%.

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