THE AMERICAN MINERALOGIST, VOL. 45, JANUARY-FEBRUARY, 1960

X-RAY DIFFRACTION STUDY OF ORIENTATION IN THE CHATTANOOGA SHALE*

E. N. SILVERMAN AND THOMAS F. BATES,† *The Pennsylvania State University, University Park, Pa.*

ABSTRACT

An x-ray diffraction technique has been used to obtain a quantitative measure of the degree of orientation of the (001) planes of 10 Å illite and mica flakes in fifty-eight samples from a drill core taken from the Chattanooga shale. Thin sections cut perpendicular to the bedding are placed on the x-ray spectrometer in such a position that, upon rotation of the section in its own plane, the geiger counter records all diffraction from mica flakes with (001) perpendicular to the plane of the section. Analysis of the resulting curve, using the Chi-square statistic divided by the area under the curve, gives an "orientation index" for each specimen which is reproducible and independent of the amount of 10 Å material present.

An evaluation of the data with respect to the uranium content of the samples shows that there is no significant correlation between the concentration of the element and this particular measure of the texture of the rock. This supports other evidence which indicates that the uranium was precipitated during deposition of the sediment and that the distribution of uranium has not been affected by movement of solutions during or followng compaction.

The technique is applicable to the study of lattice orientation of any sufficiently fine-grained mineral in natural or synthetic substances.

INTRODUCTION

The problem of obtaining precise quantitative measurements of the textural characteristics of various materials is an important one which has been studied by many workers using many different techniques. For the study of preferred orientation in fine-grained crystalline substances, x-ray diffraction methods have proved most satisfactory and the application of x-ray spectrometer techniques has greatly simplified the procedures involved (Klug and Alexander, 1954, p. 580). The present paper describes the application of one of these x-ray spectrometer techniques to the problem of precisely measuring the degree of orientation of the (001) plane of the 10 Å micaceous minerals in fifty-eight samples of Chattanooga shale. The orientation values are then evaluated statistically in relation to the uranium content of the samples to determine whether the distribution and concentration of this element is significantly related to this particular measure of texture. Since it was established, as part of the study, that the preferred orientation of the (001) plane of the micas is

* Contribution No. 58-4, Mineral Industries Experiment Station, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

† Technologist, U. S. Steel Corp., Applied Research Laboratory, Monroeville, Pennsylvania and Professor of Mineralogy, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

parallel to the micro and megascopic laminations referred to as bedding, conclusions can be drawn in terms of megascopic as well as microscopic aspects of the rock.

TECHNIQUES

Since the *x*-ray diffraction technique used for the measurement of degree of orientation may easily be applied to any fine-grained material, cer-

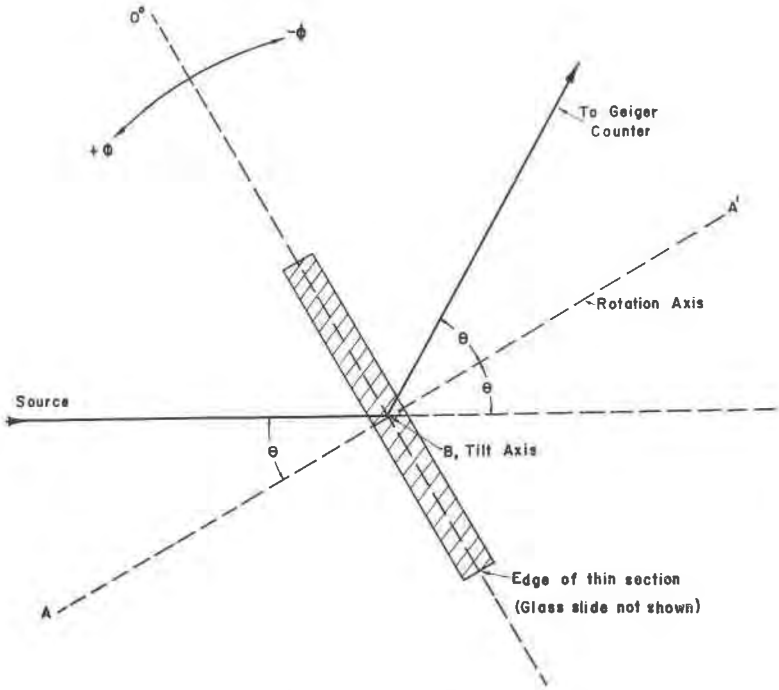

FIG. 1. Relationship of rotation and tilt axes to sample and source.

tain details of the procedure are included herein. For a more extensive discussion of instrumentation, *x*-ray optics, and pole figure diagrams, reference should be made to Decker, Asp and Harker (1948) and Schulz (1949).

A thin section of the sample is mounted on the spectrometer so that the angle θ between the incident beam and the perpendicular to the plane of the section is equal to the Bragg angle for diffraction from the particular set of planes of atoms to be studied (4.37°θ for the (001) planes of mica and illite using Ni filtered CuKα radiation). The geiger counter is set at the 2θ angle for the same set of planes (see Fig. 1). An appropriate sample holder permits rotation of the thin section in its own plane about axis AA′ and also rotation (herein referred to as "tilt") about the spectrometer axis (B) which passes through the center of the thin section. As pointed out in the references noted, most of the three dimensional orientation pattern of any given set of lattice planes can be measured by rotation of the thin section about axis AA′ at each of a series of tilt positions (in this case from $\phi = +25°$ to $-25°$).

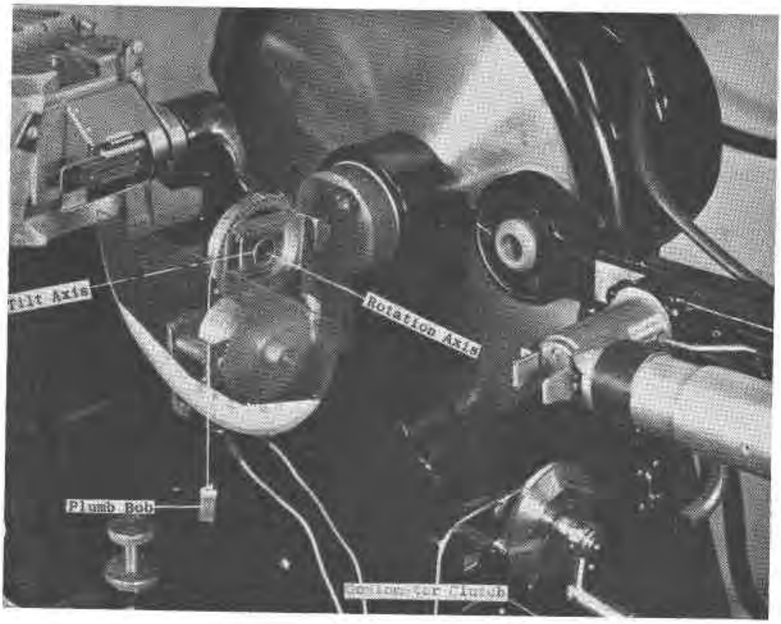

FIG. 2. Arrangement of sample and sample holder on x-ray spectrometer.

The present study was carried out on a North American Philips high angle recording spectrometer fitted with a 0.5 divergence slit and a .006° scatter slit. The arrangement of the sample holder and sample is pictured in Fig. 2. Rotation of the sample is produced by the one RPH motor seen below the sample holder. The sample holder assemblage, consisting of holder, motor, protractor and plumb bob is attached to a $\frac{5}{8}''$ diameter shaft which replaced the shaft of the ordinary sample holder on the goniometer axis. The rotating holder is so positioned that the tilt axis passing through the center of the thin section coincides with the goniometer axis. Positioning of the sample at a particular tilt angle is accomplished by manual rotation of the entire specimen holder assemblage before clamping the $\frac{5}{8}''$ shaft in position. The angle of tilt is measured by the position of the plumb line on the protractor.

The thin section can be seen mounted on the near side of the sample holder. The rock slices are cut with a diamond saw and mounted for grinding on standard microscope slides using Biggs R-313 bonding agent.* This cement permits removal of the completed 20μ thin section from the microscope slide by soaking in water. The section is then transferred to another slide with a hole in the center large enough so that no glass will be in the path of the diffracted *x*-ray beam.

Since the object of the research described here was to compare samples on the basis of the perfection of orientation of the mica particles having the (001) pole in a plane containing the normal to the bedding plane of the rock (as megascopically determined), no attempt was made to measure and plot the entire "pole figure." However, in order to determine whether or not there was a significant difference between the slope of the megascopically defined bedding plane and the slope of the surface containing the greatest number of (001) mica planes, a preliminary experiment was run on each of four Chattanooga shale samples using two thin sections cut perpendicular to each other and to the bedding. Each section was investigated by changing the tilt angle ϕ by increments of one degree from zero to plus and minus 25° and rotating the thin section about AA′ in each of the resulting 51 tilt positions.

The variation in the intensity of the (001) mica reflection demonstrated that although the preferred orientation of the mica flakes is in the bedding plane of the sample, a departure of a few degrees in any direction from the plane of the bedding did not result in a significant decrease in peak intensity. On the basis of this experiment it was assumed that in cutting the thin sections of other samples the measurement of the 90° angle between the megascopically-defined bedding plane and the direction of cut was not highly critical, particularly since the samples were to be compared on the basis of the degree rather than the direction of the preferred orientation.

Analysis of Patterns

Figure 3 shows resulting tracings from two samples: (A) in which the 10 Å mica has a high degree of preferred orientation in the plane examined; and (B) in which a larger amount of mica has less preferred orientation.

As is the case in any *x*-ray diffraction pattern, the intensity at any

* C. H. Biggs Company, 2233 Barry Avenue, Los Angeles, California.

point is equal to the background intensity plus that due to the 10 Å mica. The background intensity was measured, under the same transmission conditions used for all other work, by traversing the 10 Å reflection from higher to lower values of 2θ (in the same manner as that used for the usual "reflection" pattern), measuring the background on each side of the (001) peak, and interpolating for the background intensity beneath the peak. A line representing this background is then drawn (as b and b′ in Fig. 3); the area between the lines (a and b; and a′ and b′) represents the radiation due to the (001) reflection from the 10 Å mica flakes brought into diffracting position as the thin section is rotated 180° in its own plane.

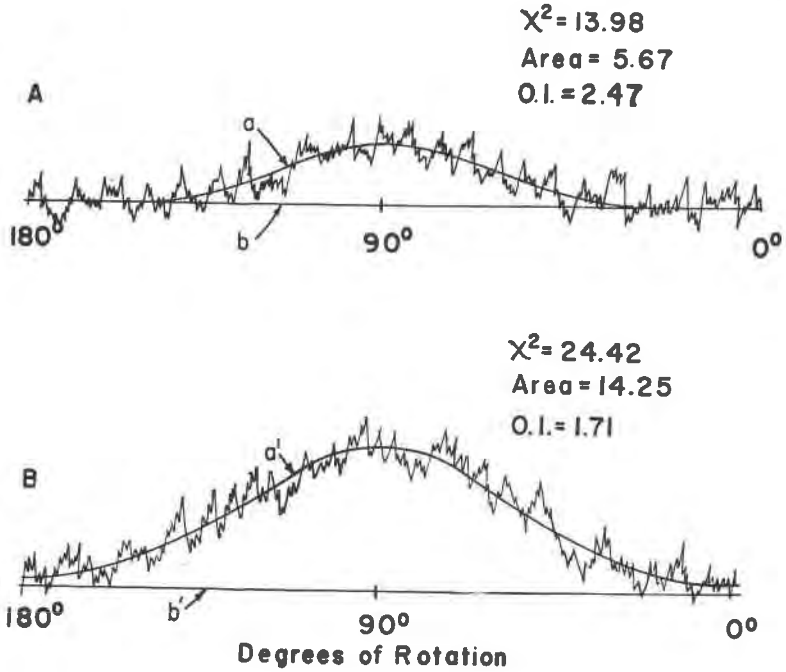

FIG. 3. Representative orientation curves.

To obtain a quantitative measure of the degree of orientation from the curves, the Chi-square statistic (χ^2) was used (Snedecor, 1946, p. 16). Chi-square is commonly employed to test goodness of fit of an observed to a theoretical distribution by comparing the two distributions, class by class. In the present case each diffraction pattern of the type shown in Fig. 3 is converted into a histogram containing 30 classes and the intensity of the curve above background is measured at the midpoint of each class. These values are summed and divided by 30 to find the expected value, and the absolute difference between each observed value and the expected value is squared. χ^2 is found by dividing the sum of the squared difference by the expected value.

Since it can be shown that the χ^2 value is dependent upon the area under the curve as well as the shape of the curve and since the area in turn is dependent upon the quantity of mica in the proper positions to diffract, a correction must be applied if the final value is to relate directly to degree of orientation of the mica independent of the amount present. Theoretical calculations having shown that the diffracted intensity from the 10 Å mica should vary linearly with the quantity of this material present, it was determined that the proper correction could be made by dividing the χ^2 value by the area between the curve and the background line. The resultant value is referred to as the orientation index: O.I. $=\chi^2/\text{Area}$. In the example illustrated in Fig. 3, for A and B, respectively, the χ^2 values are 13.98 and 24.42, the areas are 5.67 and 14.25, and the resulting orientation indices are 2.47 and 1.71. This indicates that curve A represents a better degree of orientation than is represented by curve B. The fact that the samples differ in amount of mica, as shown by the differences in areas under the curve, does not alter the conclusion that the smaller amount of mica in A has a higher degree of preferred orientation than does the larger amount in B.

Study of the Shale

The samples of Chattanooga shale studied were selected from a drill core designated as YB-19 and taken by the U. S. Bureau of Mines from the Youngs Bend area of central Tennessee.

The Chattanooga shale in this area has been divided into five stratigraphic units by the United States Geological Survey (Table I).

An important consideration in determining the number of samples needed was the fact that the data would be used in an analysis of variance designed to test for differences between stratigraphic units. Since in analysis of variance it is desirable to have at least two degrees of freedom

Table I. Chattanooga Shale Core YB-19

Stratigraphic Unit	Thickness	No. of Samples Studied
Top Black	4.46′	10
Upper Gray	2.13′	3
Middle Black	7.66′	15
Middle Gray	9.11′	20
Lower Black	6.25′	10

associated with a source of variation, at least three samples were needed from each stratigraphic unit. Consequently, sixty samples were taken from the thirty-foot core, in order to insure that the random selection would yield at least three samples from the thinnest lithologic unit, namely the 2.13′ thick Upper Gray member.

Sample numbers were determined by taking those numbers in a random number table that fell within the range of the core footage until 60 samples had been obtained. Thus, the possibility of operator bias with respect to choice of samples was eliminated. In practice, 58 of the 60 samples taken from the core were investigated, two being too small. The number of samples taken from each unit is shown in Table I.

An uncovered thin section cut perpendicular to the bedding (as determined by a contact goniometer) was prepared from each sample. The orientation index together with the fluorimetrically-determined uranium content of each sample is given in Table II.

The data have been statistically analyzed in order to provide answers to each of the following questions:

1) Are the orientation indices normally distributed?
2) Are the stratigraphic units significantly different on the basis of the orientation index?
3) Is there a significant correlation between orientation index and uranium content?

Distribution of orientation indices

To provide an answer to the first question the orientation indices, with a mean of 2.117 and a standard deviation of 0.65, were arranged in a frequency distribution. This distribution was tested for goodness of fit to a normal distribution with the same mean and standard deviation and yielded a χ^2 value of 8.625. The probability of obtaining such a value by chance alone indicates that the observed distribution is not significantly different from a normal distribution.

Lithologic variation

The variances of the orientation indices of the five lithologic units were shown to be homogeneous following a method outlined by Bartlett (Snedecor, 1945, p. 250). It was also shown, by employing a completely randomized analysis of variance, that there are no significant differences between the mean orientation indices of the stratigraphic units.

Correlation of orientation index and uranium content

A quantitative evaluation of the degree of association between the two variables was made by employing the correlation coefficient (r) statistic. The calculated correlation coefficient is 0.143, a value not sig-

TABLE II. ORIENTATION INDICES AND URANIUM CONTENT OF 58 SAMPLES OF CORE YB-19

Sample No.	O.I.	%U	Sample No.	O.I.	%U
152.1	1.645	.0091	167.2	1.747	.0005
152.4	2.317	.0076	167.8	2.769	.0021
152.7	2.003	.0115	168.0	3.392	.0016
153.1	2.295	.0108	168.5	1.667	.0010
153.8	3.421	.0086	169.0	2.495	.0009
154.0	1.615	.0073	169.5	2.342	.0010
154.5	2.071	.0087	170.1	2.336	.0000
155.1	1.686	.0089	170.5	1.445	.0002
155.7	2.872	.0097	171.1	2.101	.0007
156.4	2.182	.0044	171.3	2.729	.0001
157.3	1.549	.0036	171.9	2.296	.0006
158.1	2.011	.0022	172.1	2.307	.0010
158.5	0.600	.0023	172.8	1.878	.0007
159.0	2.466	.0040	173.4	2.533	.0008
159.2	2.688	.0055	173.9	1.717	.0003
159.5	1.283	.0056	174.2	1.651	.0007
159.9	1.413	.0057	174.5	1.507	.0009
160.2	1.714	.0037	174.8	1.395	.0002
161.5	2.075	.0051	175.2	1.833	.0014
162.1	1.399	.0071	175.8	1.921	.0012
162.6	1.550	.0068	176.1	2.408	.0020
163.2	2.882	.0047	176.7	3.188	.0019
164.1	2.006	.0071	177.0	2.572	.0038
164.4	2.104	.0063	177.3	2.084	.0032
165.0	2.468	.0070	177.7	2.699	.0055
165.3	3.224	.0071	179.0	2.687	.0046
166.0	1.993	.0057	179.9	2.089	.0027
166.2	3.603	.0039	180.7	2.137	.0017
166.8	1.755	.0014	181.5	0.015	.0005

nificant at the conventional 5% level. This indicates little or no association between uranium content and the degree of orientation of illite and mica in these samples of the Chattanooga shale.

SUMMARY AND CONCLUSIONS

Fifty-eight samples of the Chattanooga shale were studied by an x-ray diffraction technique designed to measure the degree of orientation of the (001) planes of the 10 Å micaceous minerals from thin sections cut perpendicular to the bedding. An orientation index was calculated for each sample by dividing the Chi-square statistic (used to evaluate the shape of the curve) by the area between the curve and background (to remove the effect of amount of mica present).

Statistical evaluation of the orientation indices showed that they are normally distributed and that there are no significant differences between the mean orientation indices of the five stratigraphic units represented in the drill core studied.

The correlation of this particular measure of the texture of the rock with the amount of uranium in the samples is not significant. These data agree with the results of other studies of uranium distribution in this rock which indicate that, except at weathered surfaces, there is no evidence of uranium concentration along bedding planes or microscopic laminations. Such evidence supports the hypothesis that the uranium was emplaced during deposition of the shale and that the distribution of the element has not been affected by solution movement during or after compaction.

The technique used to measure degree of orientation of the mica in these shale samples can be applied to the study of thin sections of any rock in which the mineral to be evaluated is of sufficiently fine grain size to permit representative sampling by the *x*-ray beam. Micaceous minerals are particularly well suited because the (001) lattice plane is directly and simply related to external morphology and thereby to processes which affect the orientation of the particles.

Acknowledgments

The authors wish to thank Dr. G. W. Brindley for his advice regarding details of the *x*-ray procedure and Dr. J. C. Griffiths for assistance in the statistical evaluation of the data. Fluorimetric determinations of the uranium content of the samples were made by Mr. Robert O'Neil.

This research is part of a study of the mineralogy and petrography of uraniferous shales and lignites supported by the Division of Research of the United States Atomic Energy Commission.

References

Decker, B. F., Asp, E. T. and Harker, D. (1948), Preferred orientation using a geiger counter x-ray diffraction goniometer, *J. Appl. Phys.* **19,** 388–392.

Klug, H. P. and Alexander, L. E. (1954), *X*-ray diffraction procedures, Wiley, New York.

Schulz, L. G. (1949), Determination of preferred orientation in flat transmission samples using a geiger counter *x*-ray spectrometer, *J. Appl. Phys.* **20,** 1033–1036.

Snedecor, George W. (1946), Statistical methods. The Iowa State College Press, Ames, Iowa.

Manuscript received April 9, 1959.