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# CLAY MINERALS IN MIXTURES: SAMPLE PREPARATION, ANALYSIS, AND STATISTICAL INTERPRETATION

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**Abstract**—A method of clay mineral sample preparation for electron microprobe analysis has been developed in which a film of clay plus 10–12 wt. % colloidal graphite is deposited on a porous ceramic disc using a specially designed suction device. Correction procedures are used to obtain quantitative elemental analyses representing the average chemical composition of the prepared sample. A statistical technique is employed to estimate the most likely proportions of clay minerals representing the known composition. Chemical compositions of clay minerals are presented in terms of five coordinates ("Si," "Al," "Mg," "K," and "Fe"). Using literature data, the chemical compositions of 13 different clay mineral groupings were defined statistically by their multivariate means and variance-covariance matrices. A correlation parameter, $\chi^2$, was calculated to compare the chemical composition of a sample with that of any mixture of the defined clay mineral groupings, the minimum $\chi^2$ indicating the best-fit mixture.

From chemical analyses of artificial mixtures only approximate clay mineral proportions could be determined when the various clay mineral groupings had been defined statistically from literature analyses. The best results were obtained when the actual compositions of the end-members forming the artificial mixtures replaced the statistical definitions. Tests of the estimation procedure on clay mineral mixtures for which chemical compositions and corresponding clay mineral proportions were found in the literature, indicate that the technique has appreciable merit.

**Key Words**—Electron microprobe, Illite, Kaolinite, Mixed layer, Montmorillonite, Quantitative mineral analysis, Statistical method.

## INTRODUCTION

The proportions of the mineral components of most rocks (the mode) can be determined reasonably accurately using optical point-counting techniques. The compositions of the individual minerals can also be determined conveniently and routinely today by means of electron microprobe analysis. The clay mineral group, however, is an exception to these generalizations, and because of their fine grain size, only the identities of most clay mineral constituents can be determined with any degree of certainty. Attempts have been made to estimate proportions of clay mineral components on the basis of X-ray diffraction intensities, but these methods are fraught with difficulties associated with the effects of crystallinity, chemical substitutions, and variable water contents, as well as the possible presence of mixed-layer structures. The problem of determining the composition of clay mineral components of rocks has proved even more intractable inasmuch as physical separation is almost impossible and the range of possible compositions varies greatly with significant departures from idealized structural formulae. Because of these problems, we know little about the chemical equilibria amongst naturally occurring assemblages of clay minerals. Many of these assemblages may represent non-equilibrium mixtures of two or more clay minerals, yet we have no means of establishing the equilibrium state of such mixtures, nor are satisfactory ways available for tracing changes in the compositions and the proportions of these minerals during maturation and diagenesis.

Many techniques have been used to obtain chemical information on clay minerals, but the only widely used means of determining the complete composition have been the classical methods of wet chemistry and the somewhat more convenient methods of X-ray fluorescence analysis. Although the latter technique is relatively rapid when modern automated instrumentation is used, both require substantial amounts of sample and are destructive (unless questionable preparation procedures utilizing pressed powders are used in the X-ray technique). In recent years, great strides have been made in perfecting the techniques of electron microprobe analysis. In particular, developments in energy dispersive X-ray analysis have permitted fully quantitative analyses of complex natural minerals to be performed routinely and in a matter of a few minutes. These techniques appear to be applicable to the analysis of clay minerals and clay mineral mixtures. An attempt was therefore made to develop a rapid and accurate method for determining the chemical composition of such clay materials and to develop a statistical technique using these data to estimate the most likely proportions of clay mineral components in the sample.

## EXPERIMENTAL

### *Preparation of samples*

The $<1$-$\mu$m fraction of each sample was used to minimize the amount of non-clay mineral impurities. This

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fraction was obtained by standard settling techniques after the sample had been dispersed, using an ultrasonic vibrator of the probe type, and repeatedly washed with distilled water to remove soluble impurities.

Uniform clay mineral films were deposited onto porous ceramic discs (Kinter and Diamond, 1956; Gibbs, 1965) using a method similar to that described by Shaw (1972). However, pure clay films could not be made conductive by the usual technique of coating with carbon (or even gold), and a modified technique involving the addition of a known amount of colloidal graphite was developed (Smith and Cavell, 1978, 1980). A suspension of colloidal graphite was prepared by dispersing Acheson "Aquadag" in distilled water, centrifuging for 1 hr and retaining only that portion which had not settled. The typical amount of graphite required to impart adequate conductivity was found to be 10–12% (by weight), but ranged from 4 to 15% depending upon the individual clay sample. The concentrations of graphite and clay sample suspensions were determined by weighing the residues from known (pipeted) volumes, oven dried at 105°C.

To prepare the analytical sample, the volume of each suspension required to produce a film of 50–60 mg total weight and containing 10–12 wt. % graphite was mixed in a small beaker and deposited onto a porous disc using the suction device shown in Figure 1. After being washed with distilled water, the disc with its clay film was removed from the holder and left to air dry for about 10 min, clay-side up. It was then placed clay-side down on a glass slide coated with a fluorotelomer (e.g., Dupont "Vydax 550"), and left to air dry completely. The weight of the ceramic disc (2.5 g) was usually sufficient to maintain compaction while drying and thereby prevent the cracking and peeling that are frequently sources of difficulty in the preparation of such films. For some of the smectites, which absorbed large amounts of water, it was necessary to add extra weight (e.g., one or two extra discs) to ensure compaction during drying. The fluorotelomer coating prevented sticking while maintaining a smooth upper surface. The electrical resistance of the film after preparation (which must be sufficiently low to allow incident electrons from the microprobe beam to leak away) was checked using an ohmeter. Values less than 5 megohms were considered satisfactory.

*Electron microprobe analysis*

Samples prepared in the above manner for microprobe analysis, can also be used for X-ray powder diffractometry. The minor amount of "colloidal" graphite produces only a very weak, broad peak which does not interfere with basal reflections from the clay mineral. A 5-mg sample prepared with a modified suction apparatus is adequate if X-ray diffraction patterns are not needed.

The quantitative, energy-dispersive microprobe technique used to analyze as many as 22 elements in such materials was described by Smith (1976); the computer software used in the data reduction step (EDATA2) was described by Smith and Gold (1979). The EDATA2 program integrates peak intensities, makes full corrections for matrix effects (atomic number, absorption, and characteristic and continuum fluorescence), and accurately calculates and subtracts background. It also strips escape peaks, makes dead-time corrections where necessary, and deals rigorously with complex possibilities for peak overlap (i.e., interference). The program determines system resolution at the time of analysis, corrects all spectra acquired for any instrument miscalibration, and takes into account possible fluctuations in probe current during acquisition.

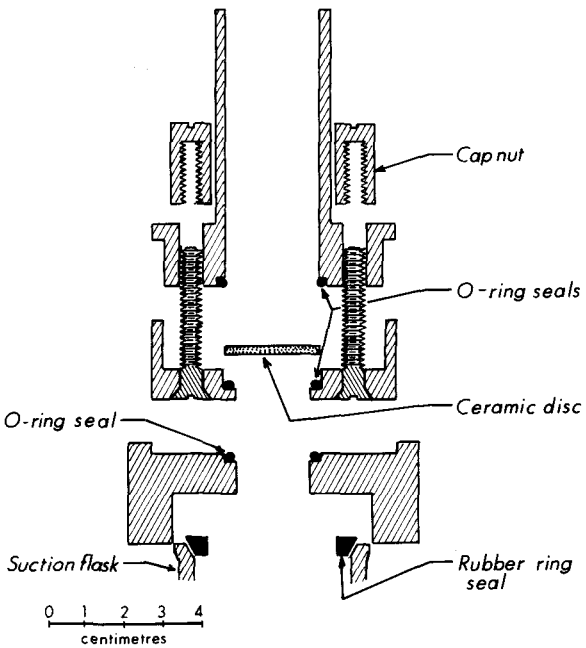



Figure 1. Exploded cross-section of suction device.

Light elements which cannot be or are not usually determined by the microprobe, but which may be present in the clay films (e.g., H, Li, C, and O) are handled by a special subroutine. The subroutine allows either the entry of a known concentration (perhaps determined by X-ray fluorescence or atomic absorption) or the calculation of the concentration from parameters such as the analytical total or a structural formula. The subroutine also allows the entry and use of two different oxidation states for elements such as iron. Adjustments to the analysis can be performed during each iteration of the correction procedure to produce a more accurate result.

The precision of the entire analytical method was tested by comparing the results of 40 replicate analyses (2 locations on each of 20 different discs) (Smith and

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Table 1. Comparison of analytical results for Fithian illite.

| | Published values | | Experimental sample | |
|---|---|---|---|---|
| | Average | Range | Wet chemical | Probe average |
| Si | 26.59 | 23.24–29.35 | 25.93 | 25.96 |
| Al | 13.95 | 10.80–17.74 | 14.01 | 14.17 |
| $Fe^{3+}$ | 3.51 | 3.15–5.48 | 2.81 } 4.34 | 4.60 |
| $Fe^{2+}$ | 0.93 | — 1.88 | 1.53 } | |
| Mn | — | — — | 0.02 | — |
| Mg | 1.32 | 0.85–1.84 | 1.58 | 1.46 |
| Ca | 0.76 | 0.12–1.66 | 1.08 | 1.86 |
| Na | 0.30 | 0.14–0.46 | 0.29 | 0.07 |
| K | 5.10 | 4.22–5.71 | 5.49 | 5.65 |
| Ti | 0.45 | — 0.62 | 0.54 | 0.46 |
| O | 47.09 | | 46.72 | 46.76 |

Weight % elements, recalculated water- and phosphorus-free to 100%.

Table 2. Source of clay mineral analyses used.

Trioctahedral chlorite: Foster, 1962, A27–A29; Deer *et al.*, 1962, 139–145.
Dioctahedral chlorite: Weaver and Pollard, 1975, 96.
Montmorillonite: Weaver and Pollard, 1975, 58–59, 64–65, 76–77; Grim and Güven, 1978, 144–148; Deer *et al.*, 1962, 232–234.
Palygorskite: Weaver and Pollard, 1975, 120, 123.
Vermiculite: Deer *et al.*, 1962, 252–253.
Celadonite: Weaver and Pollard, 1975, 48–49.
Glauconite: Weaver and Pollard, 1975, 32, 42.
Nontronite: Weaver and Pollard, 1975, 76; Deer *et al.*, 1962, 233.
Beidellite: Weaver and Pollard, 1975, 60, 76–77.
Sepiolite: Weaver and Pollard, 1975, 128.
Saponite: Weaver and Pollard, 1975, 80.
Kaolinite: Weaver and Pollard, 1975, 132, 134, 145, 146, 150–151; Deer *et al.*, 1962, 202–203.
Illite: Weaver and Pollard, 1975, 8–9; Deer *et al.*, 1962, 218–220.
Mixed-layer clays: Weaver and Pollard, 1975, 109–110, 115.

Cavell, 1980). The accuracy of the method is indicated in Table 1 by comparison of the microprobe average for a sample of Fithian illite (A.P.I. reference clay) with the wet chemical analysis[3] of identical material. Table 1 also gives the average of 7 published analyses for other samples of this clay (Weaver and Pollard, 1975). The analytical results for any clay may vary with the amount of structural, interlayer, or adsorbed water present. During electron microprobe analysis, variable amounts of this water are driven off depending on the probe current, the size of the analytical area, and the time required for the analysis. However, Smith and Cavell (1978) established that the analyses recalculated on a water-free basis do not vary. Hence, all microprobe analyses reported here and other published values have been recalculated on a water-free basis for the purpose of comparison.

Smith and Cavell (1978) used this analytical technique successfully for various homogeneous clay minerals, including members of the kaolinite, smectite, illite, and palygorskite groups; the same technique has been used without modification on clay mineral mixtures.

## STATISTICAL ANALYSIS

Previous attempts to use bulk chemistry as a basis for examining clay mineral mixtures (Pearson, 1978; Imbrie and Poldervaart, 1959; Nicholls, 1962; Miesch, 1962), have met with rather limited success due to the variability of clay compositions. Clay mineral specimens show not only a wide range of possible substitutions, but also deviations from ideal stoichiometry, variable $H_2O$ content, variations in exchangeable cations, and the ubiquitous presence of both soluble and insoluble impurities. As a means of avoiding the constraints of fixed or idealized end-member compositions, the following technique was developed to provide a more flexible statistical approach to the definition of clay mineral compositions.

Clay mineral analyses were selected from the literature (Table 2) in the following manner: (1) No duplicate analyses were used; (2) Analyses were not used if the original report expressed doubt about the sample identity or purity; (3) If the calculated structural formula showed an excess of aluminum or silicon (common impurities) over the maximum permissible for the clay mineral species to which the sample had been assigned, the analysis was not used; (4) Kaolin-group mineral analyses with more than 0.25% alkalis and analyses of chlorites with more than 0.25% $Na_2O + K_2O +$ CaO were rejected on the grounds that there is no place in the structure of these clays for these elements; (5) Smectite analyses with more than 1.0% $K_2O$ were rejected as possibly being mixed-layered smectite/illites. Similarly, illites with less than 1.0% or more than 10% $K_2O$ were rejected. All analyses reported in the compilations listed in Table 2 and not rejected for the reasons given above were used to define statistically the chemical compositions of each of the clay mineral species in terms of a group centroid and a variance-covariance matrix.

Useful individual elements or element combinations were sought which would result in the grouping of analyses of each clay mineral species about a unique centroid. On the basis of valence, structural sites occupied, and the tightness of the groupings of the data for each clay mineral, the following combinations were chosen: "Si" = $Si^{4+}$only;"Al" = $Al^{3+} + Ti^{4+}$;"Mg" = $Mg^{2+}+ Mn^{2+}$; "K" = $K^+$ only, and "Fe" = $Fe^{2+} + Fe^{3+}$. Ca and Na were not included because they produced unacceptable scatter in some of the sample groupings,

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Table 3. Centroid, variance-covariance definitions for 13 clay mineral groupings.

KEY:

CLAY MINERAL

| | centroid "Al" (ppm) | centroid "Mg" (ppm) | centroid "K" (ppm) | centroid "Fe" (ppm) |
|---|---|---|---|---|
| Al | variance-covariance | | | |
| Mg | matrix of | | | |
| K | correlation | | | |
| Fe | coefficients × $10^6$ | | | |

GLAUCONITE

| 151044 | 84643 | 134191 | 270589 |
|---|---|---|---|
| 4823 | 752 | 640 | 5197 |
| 752 | 558 | 80 | 336 |
| 640 | 80 | 504 | 483 |
| 5197 | 336 | 483 | 9457 |

CELADONITE

| 129565 | 121637 | 126928 | 188743 |
|---|---|---|---|
| 6693 | 2732 | 412 | 4792 |
| 2732 | 1785 | 119 | 1078 |
| 412 | 119 | 1193 | 63 |
| 4792 | 1078 | 63 | 5565 |

ILLITE

| 379420 | 40202 | 105660 | 40396 |
|---|---|---|---|
| 2272 | 701 | 520 | 669 |
| 701 | 415 | 190 | 230 |
| 520 | 190 | 455 | 201 |
| 669 | 230 | 201 | 788 |

MONTMORILLONITE

| 282789 | 61670 | 4071 | 32385 |
|---|---|---|---|
| 1586 | 720 | 30 | 131 |
| 720 | 746 | 21 | 159 |
| 30 | 21 | 35 | 26 |
| 131 | 159 | 26 | 781 |

VERMICULITE

| 207057 | 384199 | 286 | 59931 |
|---|---|---|---|
| 900 | 752 | 5 | 390 |
| 752 | 1177 | 4 | 347 |
| 5 | 4 | 0 | 4 |
| 390 | 347 | 4 | 657 |

BEIDELLITE

| 378266 | 16951 | 5049 | 40664 |
|---|---|---|---|
| 2091 | 516 | 81 | 981 |
| 516 | 216 | 61 | 147 |
| 81 | 61 | 31 | 31 |
| 981 | 147 | 31 | 1273 |

TRIOCTAHEDRAL CHLORITE

| 290447 | 366651 | 63 | 222330 |
|---|---|---|---|
| 8040 | 11045 | 0 | 17483 |
| 11045 | 18141 | 4 | 30823 |
| 0 | 4 | 0 | 5 |
| 17483 | 30823 | 5 | 56099 |

SAPONITE

| 98976 | 382930 | 1075 | 55041 |
|---|---|---|---|
| 2265 | 1086 | 13 | 679 |
| 1086 | 2400 | 8 | 3550 |
| 13 | 8 | 4 | 20 |
| 679 | 3550 | 20 | 6388 |

KAOLIN

| 504903 | 2434 | 357 | 6709 |
|---|---|---|---|
| 177 | 2 | 2 | 63 |
| 2 | 5 | 0 | 8 |
| 2 | 0 | 1 | 0 |
| 63 | 8 | 0 | 87 |

SEPIOLITE

| 15568 | 354437 | 0 | 58178 |
|---|---|---|---|
| 891 | 878 | 0 | 171 |
| 878 | 2500 | 0 | 2882 |
| 0 | 0 | 0 | 0 |
| 171 | 2882 | 0 | 8253 |

DIOCTAHEDRAL CHLORITE

| 608892 | 10185 | 0 | 3918 |
|---|---|---|---|
| 2464 | 638 | 0 | 40 |
| 638 | 220 | 0 | 9 |
| 0 | 0 | 0 | 0 |
| 40 | 9 | 0 | 13 |

PALYGORSKITE

| 167207 | 165669 | 2148 | 25534 |
|---|---|---|---|
| 1579 | 1124 | 58 | 84 |
| 1124 | 1159 | 28 | 95 |
| 58 | 28 | 13 | 10 |
| 84 | 95 | 10 | 320 |

NONTRONITE

| 145461 | 15769 | 2363 | 445684 |
|---|---|---|---|
| 4105 | 166 | 308 | 3162 |
| 166 | 181 | 39 | 366 |
| 308 | 39 | 28 | 279 |
| 3162 | 366 | 279 | 2803 |

Variance-covariance matrices have been corrected for sample size (N) by division by (N − 1).

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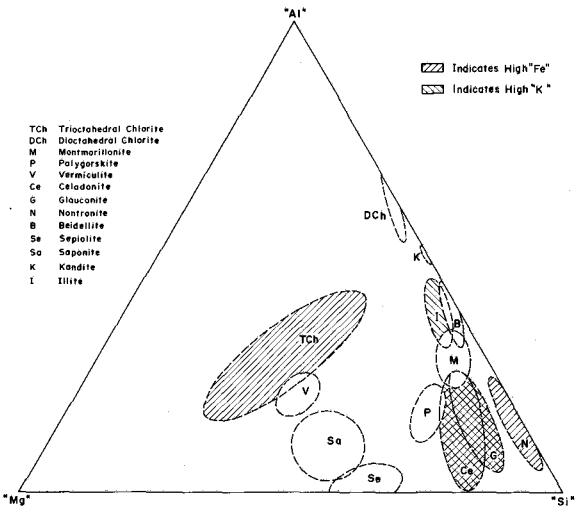



Figure 2. A diagrammatic representation of the 13 clay mineral groupings based on the statistical definitions of Table 3.

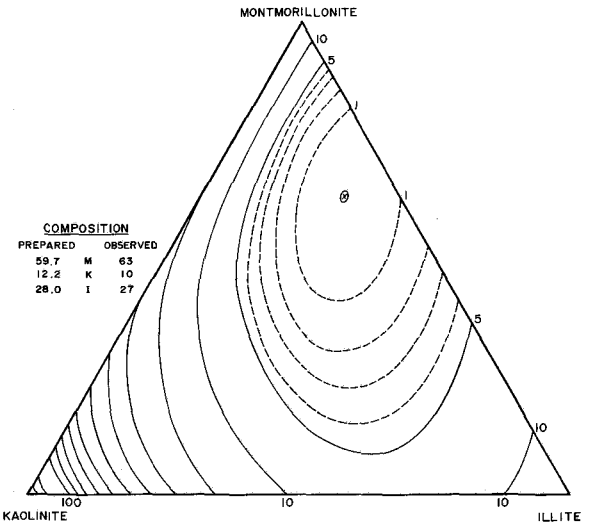



Figure 3. $\chi^2$ values obtained by plotting an analysis of sample 155 against hypothetical mixtures of three end-members.

possibly because of their presence as exchangeable cations or in impurities.

The compositional groupings of 13 clay minerals are expressed in statistical terms in Table 3. For each of four of the "elements" used, the centroid or mean value is shown as well as the variance-covariance matrix obtained by standard statistical methods. "Si" was not included because it plus two of the other "elements" in the table, "Al" and "Mg," equal unity, and one (e.g., "Si") was therfore redundant. This is a direct result of normalizing all analyses by division by the sum of the raw "Si" + "Al" + "Mg" values.

Figure 2 is a diagrammatic representation of the various clay mineral groupings based on the literature analyses. The groupings lie within a base triangle with "Si," "Al," and "Mg" as apexes and "Fe" and "K" as separate vertical axes. Groupings high in either "Fe" or "K" are shown by shading. The ellipses represent one standard deviation variation about the centroid and enclose approximately 68% of all samples within each group, if the groups are multivariate-normally distributed. This assumption was made for the illustrative purposes of this diagram, but not elsewhere in the calculations. For element proportions, which form a closed number system, multivariate normality is unlikely. The clay mineral groupings are well separated with distinct centroids and characteristic standard deviations. Only glauconite and celadonite show substantial overlap, and indeed, these two minerals may form a continuous series (Weaver and Pollard, 1975, p. 47). Figure 2 also shows clearly a separation between trioctahedral clays ("Mg"-rich) and dioctahedral clays, parallel to the "Si"-"Al" baseline. No such clear trend is evident parallel to the "Mg"-"Al" baseline (separating 1:1 from 2:1 clays) because of the increased substitution of Al for Si in vermiculites and saponites (Deer *et al.*, 1962, p. 272).

This statistical description of the clay mineral groupings is, in one sense, a "worst case," because the data taken from the literature encompass not only a broad spectrum of clay mineral parageneses but also a wide range of laboratory techniques, analysts, and errors. For a particular study a much more restricted selection of literature analyses might be more appropriate; alternatively, a series of carefully selected pure clays actually involved in the study might be used. In such cases, centroid values based on the more select population should be better and variances smaller than those shown in Table 3.

The composition of an individual sample was compared to the statistical definition of a single clay mineral group by calculating a $\chi^2$ value:

$$\chi^2 = (U - X)' \cdot S^{-1} \cdot (U - X)$$

where U is a vector of compositional values for the unknown, S is the variance-covariance matrix for the clay mineral grouping to which the unknown is being compared, and X is a vector defining the centroid of the clay mineral grouping. Because this expression involves the inverse of S, it is necessary that the leading diagonal of this matrix (the individual variance values for each variable) be entirely non-zero. A small constant was therefore added to the values in Table 3 as required. If the variables ("Al," "Mg," "Fe," and "K") were normally distributed, the probability that the sample belongs to a given group could have been assigned, but as the variables used here formed a closed number system this was inappropriate and only the $\chi^2$ values could be used. In this situation the most suitable group to which a given sample can be assigned is that which gives the lowest $\chi^2$ values.

A property of variance and of variance-covariance

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Table 4. Best estimates of two- and three-component artificial mixtures against end-members defined by literature values and against known end-members.

| Mixture number | Prepared mixture compositions | | | Mixtures determined: Using end-members defined by literature values (Table 3) | | | | Mixtures determined: Using analyzed end-member compositions | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | M | K | I | M | K | I | $\chi^2$ | M | K | I | $\chi^2$ |
| 142 | 100 | 0 | 0 | 100 | 0 | 0 | 0.17 | 100 | 0 | 0 | 0.00 |
| 143 | 0 | 0 | 100 | 17 | 0 | 83 | 0.24 | 1 | 0 | 99 | 0.00 |
| 144 | 20.5 | 0 | 79.5 | 36 | 0 | 64 | 0.18 | 22 | 1 | 77 | 0.00 |
| 145 | 51.5 | 0 | 48.6 | 62 | 0 | 38 | 0.16 | 53 | 0 | 47 | 0.00 |
| 146 | 71.9 | 0 | 28.1 | 80 | 0 | 20 | 0.13 | 74 | 0 | 26 | 0.00 |
| 147 | 0 | 100 | 0 | 11 | 89 | 0 | 0.13 | 0 | 100 | 0 | 0.01 |
| 148 | 19.6 | 80.4 | 0 | 29 | 71 | 0 | 0.12 | 20 | 80 | 0 | 0.01 |
| 149 | 49.4 | 50.6 | 0 | 60 | 40 | 0 | 0.14 | 54 | 46 | 0 | 0.01 |
| 150 | 71.5 | 28.5 | 0 | 76 | 24 | 0 | 0.15 | 73 | 27 | 0 | 0.00 |
| 151 | 20.4 | 29.3 | 50.3 | 41 | 18 | 41 | 0.12 | 23 | 27 | 50 | 0.00 |
| 152 | 32.0 | 32.8 | 35.2 | 52 | 20 | 28 | 0.12 | 37 | 28 | 35 | 0.00 |
| 153 | 51.7 | 20.4 | 27.9 | 67 | 12 | 21 | 0.12 | 54 | 18 | 28 | 0.00 |
| 154 | 19.5 | 60.0 | 20.5 | 36 | 48 | 16 | 0.11 | 23 | 57 | 20 | 0.00 |
| 155 | 59.7 | 12.2 | 28.0 | 75 | 5 | 20 | 0.13 | 63 | 10 | 27 | 0.00 |
| 156 | 16.0 | 69.9 | 14.1 | 32 | 57 | 11 | 0.12 | 19 | 66 | 15 | 0.01 |
| 157 | 15.6 | 16.0 | 68.5 | 40 | 6 | 54 | 0.14 | 18 | 16 | 66 | 0.00 |

M = montmorillonite; K = kaolinite; I = illite.

matrices is that they, as well as centroids, are additive. Thus, a statistical definition may be obtained for any hypothetical mixture of statistically defined clay minerals by taking the necessary proportions of the end-member values. Furthermore, the $\chi^2$ test may be used to compare the composition of an unknown with that of any postulated mixture or series of mixtures to determine a 'best fit.' As an illustration, in Figure 3 illite, kaolinite, and montmorillonite have been chosen as three components. Hypothetical mixtures covering the entire range of compositions in the triangle were generated at 1% intervals, and the composition of test sample 155 compared with each. The $\chi^2$ values obtained are shown as contours which reach a minimum representing the best estimate of the composition of sample 155. In practice such testing was carried out using simple 'hill-climbing' computer techniques.

## RESULTS AND DISCUSSION

To test the procedure described, a series of sixteen, 2- and 3-component synthetic, mechanical mixtures of kaolinite, illite, and montmorillonite, chosen from the A.P.I. reference series, was prepared. Microprobe analyses were performed on the pure end-members and on each of the mixtures. The statistical procedures outlined were then used to obtain a 'best' (minimum $\chi^2$) estimate of the proportions of the 3 clay minerals in each of the artificial mixtures. In Table 4, the prepared composition of each sample is compared with the composition estimated from the analyses by means of the statistical parameters obtained from the literature data.

In general, although the results are encouraging, there is a consistent bias of about 20% towards montmorillonite at the expense of kaolinite and illite, even in the case of pure end-members. The reason for divergence between the actual (prepared) and the estimated compositional values is the discrepancy between the compositions of the real clays used and the literature group definitions. This difference can be demonstrated quite clearly if the statistical procedure is repeated replacing the literature centroids by the actual values for the clay minerals used, while retaining the literature-based variance-covariance matrices. This change results in estimated compositions closely approaching the actual compositions and $\chi^2$ values tending to zero (also shown in Table 4), compared to 0.1–0.2 when literature values were used.

In practice, the identities of the clay mineral components of a mixture may not be known and must be determined by some other technique, such as an X-ray powder diffraction pattern of the same sample as prepared for microprobe analysis. Particularly where only small amounts of one or more of the components are present, an incorrect choice may be made for the components of the test triangle, but this is not critical. Figure 4 illustrates that where an incorrectly chosen end-member was actually absent from the sample, the approach remained entirely appropriate. The $\chi^2$ values reach a minimum at the edge of the triangle between the two clay minerals present.

Table 5 illustrates other results obtained using one incorrect component in the test triangle. Here, illite has been replaced by chlorite. In 2-component mixtures, where both components (here kaolinite and montmorillonite) are present in the test triangle, the results are identical to those shown earlier, the lowest $\chi^2$ values falling on the edge between the 2 components present. However, where one component (illite) present in the

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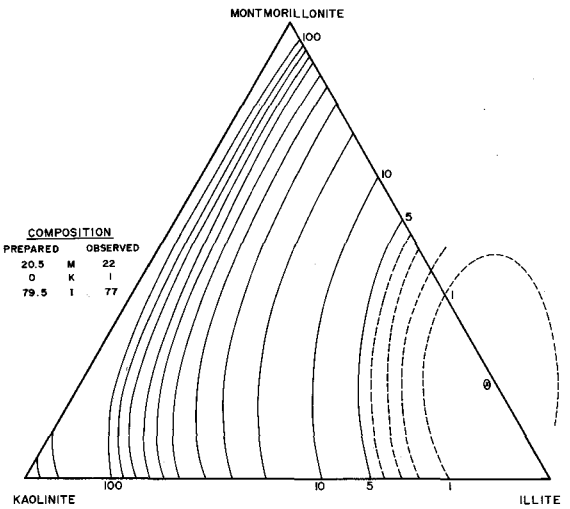



Figure 4. $\chi^2$ values obtained by plotting an analysis of sample 144 against hypothetical mixtures of three end-members.

3-component sample was not present in the test triangle, the extremely high $\chi^2$ values show that the results are meaningless and that a different suite of clays should be chosen for the test triangle. Clearly, it should be possible to choose the most appropriate clay components using the computer program, on the basis of the position in compositional space of the analytical data. Furthermore, such a choice need not be limited to three components. Testing with 4-component mixtures could readily be accomplished.

Apart from the ubiquitous mechanical mixtures of clay minerals, natural examples also include many mixed-layer clays. The procedures described here should be suitable for estimating the proportions of the interlayered species. Table 6 shows estimates of the proportions of illite and montmorillonite in a series of natural mixed-layer clay minerals, estimated by X-ray powder diffraction methods (Weaver and Pollard, 1975). Also shown are the proportions statistically estimated using the chemical data for these samples reported in the same publication. Again, literature-based statistical parameters have been used, and the discrepancies between the results are comparable to those in Table 4 where these parameters were also used. It will be noted that although kaolinite was one available component, it was invoked in only one case which, possibly significantly, was annotated as "hydrothermal" in Weaver and Pollard (1975).

The results obtained for another series of natural mixed-layer clays (Weaver and Pollard, 1975) are shown in Table 7. These are reputedly regularly interlayered montmorillonite/chlorite. The three components of the test triangle were chosen as montmorillonite, dioctahedral chlorite, and trioctahedral chlorite. Again, the actual component clay mineral compositions are unknown but the use of the literature-based statistical parameters produced reasonable results. The $\chi^2$-values obtained for samples 2, 3, and 7 are high, and it is uncertain whether the poor fit reflects inadequacies in the reported chemical analyses or substantial deviations of the actual clay mineral compositions from the litera-

Table 5. Best estimates of 2-component artificial mixtures using incorrect selection of end-members.

| Mixture number | Prepared mixture composition | | | Determined mixture composition | | | |
|---|---|---|---|---|---|---|---|
| | M | K | I | M | K | C | $\chi^2$ |
| 142 | 100 | 0 | 0 | 100 | 0 | 0 | 0.17 |
| 143 | 0 | 0 | 100 | 98 | 0 | 2 | 44.62 |
| 144 | 20.5 | 0 | 79.5 | 99 | 0 | 1 | 26.51 |
| 145 | 51.4 | 0 | 48.6 | 99 | 0 | 1 | 9.55 |
| 146 | 71.9 | 0 | 28.1 | 100 | 0 | 0 | 2.60 |
| 147 | 0 | 100 | 0 | 11 | 89 | 0 | 0.13 |
| 148 | 19.6 | 80.4 | 0 | 29 | 71 | 0 | 0.12 |
| 149 | 49.4 | 50.6 | 0 | 60 | 40 | 0 | 0.14 |
| 150 | 71.5 | 28.5 | 0 | 76 | 24 | 0 | 0.15 |

M = montmorillonite; K = kaolinite; I = illite; C = chlorite.

Table 6. Estimates of montmorillonite/illite mixed-layer clay proportions.

| XRD estimates | | | Statistical estimates | | | |
|---|---|---|---|---|---|---|
| M | K | I | M | K | I | $\chi^2$ |
| <10 | 0 | >90 | 0 | 0 | 100 | 0.77 |
| 10 | 0 | 90 | 11 | 0 | 89 | 1.18 |
| 15 | 0 | 85 | 2 | 0 | 98 | 0.90 |
| 20 | 0 | 80 | 9 | 0 | 91 | 0.92 |
| 30 | 0 | 70 | 39 | 0 | 61 | 0.44 |
| 33 | 0 | 67 | 30 | 0 | 70 | 0.53 |
| 40 | 0 | 60 | 29 | 0 | 71 | 0.38 |
| 45 | 0 | 55 | 41 | 0 | 59 | 1.28 |
| [1]50 | 0 | 50 | 17 | 43 | 40 | 0.22 |
| 60 | 0 | 40 | 71 | 0 | 29 | 0.29 |

M = montmorillonite; K = kaolinite; I = illite. Analyses and XRD data from Weaver and Pollard (1975).
[1] Hydrothermal alteration.

Table 7. Estimates of montmorillonite/chlorite mixed-layer clay proportions.

| Literature estimates | | | Statistical estimates | | | |
|---|---|---|---|---|---|---|
| M | $C_2$ | $C_3$ | M | $C_2$ | $C_3$ | $\chi^2$ |
| 50 | 0 | 50 | 45 | 0 | 55 | 0.73 |
| 50 | 0 | 50 | 58 | 0 | 42 | 9.06 |
| 50 | 0 | 50 | 45 | 0 | 55 | 2.86 |
| 50 | 0 | 50 | 26 | 0 | 74 | 0.42 |
| 50 | 0 | 50 | 29 | 0 | 71 | 0.25 |
| 50 | 50 | 0 | 33 | 54 | 13 | 0.07 |
| 50 | 50 | 0 | 48 | 52 | 0 | 2.66 |

M = montmorillonite; $C_2$ = dioctahedral chlorite; $C_3$ = trioctahedral chlorite. Analyses and literature estimates from Weaver and Pollard (1975).

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ture-based centroid values. Sample 1 appears to be a 1:1 clay, but samples 4 and 5, which have moderate $\chi^2$ values, are probably 1:3 rather than 1:1 clays. Sample 6, with a very low $\chi^2$ value, appears to involve all three components and not to be a simple mixed-layer clay.

## CONCLUSIONS

Accurate analyses of clay minerals and clay mineral mixtures can be obtained using a specially developed, energy-dispersive electron microprobe technique. The analytical data from mixtures can be interpreted by computer programs which use simple statistical procedures to obtain a best estimate of the proportions of the possible clay mineral components in the mixture. Precise estimates of these proportions can be obtained when the compositions of the individual clay mineral components are known. Less precise estimates can be obtained using average compositions and statistical measures of compositional variations based on available analyses published in the literature.

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**Резюме**—Разработан метод подготовления образцов глинистых минералов для анализа путем рентгеновского микроанализатора. Фильмы глины и 10–12% по весу коллоидального графита осаждаются на пороватом керамическом диске при помощи специально конструированного всасывающего прибора. Процедуры коррекции используются для качественных эдементных анализов, представляющих средний химический состав подготовленных образцов. Статистическая техника используется для определения более вероятных пропорции глинистых минералов, представляющих известный состав. Химические составы глинистых минералов представлены как функции пятп координат ("Si," "Al," "Mg," "K," и "Fe"). Используя дитературные данные был определен статистически химический состав 13 различных группировок глинистых минералов на основании их многовариантных средних и вариантных-ковариантных матриц. Параметр коррелиции, $\chi^2$, был подсчитан для сравнения химического состава образца с составом любой смеси определенных группировок глинистых минералов; минмиум $\chi^2$ соответствовал самому лучшему подбору смеси.

Только приблизительные пропорции глинистых минералов можно определить из данных химических анализов искусственных смесей, в то время когда различные группировки глинистых минеролов были определены статистически по литературным данным. Самые лучшие результаты былы получены когда действительные составы конечных членов, формирующих искусственные смеси, заменяли статистические определения. Проверка оценивающей процедуры на смесях глинистых минералов, для которых химические составы и соответствующие пропорции глинистых минералов были найдены в литературе показывают, что эта техника имеет большое значение. [E.G.]

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**Resümee**—Es wurde eine Methode zur Probenaufbereitung von Tonmineralen für Mikrosondenanalysen entwickelt, bei der ein Film von Ton mit 10–12 Gew.-% kolloidalem Graphit auf eine poröse Keramikscheibe aufsedimentiert wird, wozu eine speziell entworfene Absaugvorrichtung verwendet wird. Korrekturvorgänge werden verwendet, um quantitative Elementanalysen zu erhalten, die den Durchschnittschemismus der präparierten Probe darstellen. Ein statistisches Verfahren wird benutzt, um die wahrscheinlichsten Tonmineralverhältnisse aus der gegebenen Zusammensetzung abzuschätzen. Die chemische Zusammensetzung der Tonminerale werden durch fünf Koordinaten ("Sr," "Al," "Mg," "K," und "Fe") dargestellt. Indem Ergebnisse aus der Literatur verwendet wurden, wurden die chemischen Zusammensetzungen von 13 verschiedenen Tonmineralgruppen statistisch definiert und zwar durch ihre Multivariatmittelwerte und ihre Varianz-Kovarianz-Matrizen. Ein Korrelationsparameter, $\chi^2$, wurde berechnet, um die chemische Zusammensetzung einer Probe mit der einer Mischung aus den definierten Tonmineralgruppen zu vergleichen, wobei das kleinste $\chi^2$ die best passendste Mischung anzeigt.

Aus den chemischen Analysen von künstlichen Mischungen konnten nur ungefähre Tonmineralverteilungen bestimmt werden, wenn die verschiedenen Tonmineralgruppen statistisch aus den Literaturanalysen definiert wurden. Die besten Ergebnisse wurden erzielt, wenn man die tatsächliche Zusammensetzung der Endglieder, die die künstlichen Mischungen bildeten, anstelle der statistischen Daten verwendete. Tests dieses Auswerteverfahrens an Tonmineralmischungen, deren chemische Zusammensetzung und entsprechende Tonmineralverhältnisse in der Literatur angegeben sind, zeigen, daß diese Methode beachtliche Vorzüge hat. [U.W.]

**Résumé**—Une méthode de préparation d'échantillon de minéral argileux pour l'analyse microprobe d'électrons a été dévelopée dans laquelle un film d'argile plus 10–12% au poids de graphite colloïdale est deposé sur un disque de céramique poreux au moyen d'un dispositif à ventouse crée spécialement. Des procédés de correction sont employés pour obtenir des analyses quantitatives d'éléments représentant la composition chimique moyenne de l'échantillon préparé. Une technique statistique est employée pour estimer les proportions les plus vraisemblables des minéraux argileux représentant la composition connue. Les compositions chimiques des minéraux argileux sont présentées en fonction de cinq coordonnées ("Si," "Al," "Mg," "K," et "Fe"). En employant les données de la littérature, les compositions chimiques de 13 groupes differents de minéraux argileux ont été définis statistiquement par leur moyenne multivariat et par leurs matrices de variance-covariance. Un paramètre de correlation, $\chi^2$, a été calculé pour comparer la composition chimique d'un échantillon avec celle de n'importe quel mélange des groupes de minéraux argileux définis, le minimum $\chi^2$ indiquant le mélange chimiquement le plus proche de l'échantillon.

A partir d'analyses chimiques de mélanges artificiels, seules des proportions approximatives de minéraux argileux pouvaient être déterminées quand les groupes de minéraux argileux avaient été définis statistiquement à partir des analyses provenant de la littérature. Les meilleurs resultats ont été obtenus lorsque les compositions actuelles des membres extrêmes formant les mélanges artificiels remplaçaient les definitions statistiques. Des tests de procédés d'estimation des melanges de minéraux argileux pour lesquels des compositions chimiques et des proportions de minéraux argileux correspondants avaient été trouvées dans la littérature, indiquent que la techique a un mérite appréciable. [D.J.]

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