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THE COMPOSITION OF KAOLINITE—AN ELECTRON MICROSCOPE MICROPROBE STUDY

W. B. JEPSON and J. B. ROWSE

Central Laboratories, E.C.L.P. & Co. Ltd., St. Austell, Cornwall, U.K.

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Abstract—Electron microscope microprobe analysis (EMMA) has been applied to the determination of the elemental compositions of the kaolinite particles (Mg, Al, Si, K, Ti and Fe) contained in the 0·2–0·3 μm e.s.d., the 0·9–1·0 μm e.s.d. and the 1·9–2·0 μm e.s.d. fractions of an English kaolin and an American kaolin. Particles with masses as small as 10^{-13} g were analysed. An EMMA-4 instrument (A.E.I. Ltd.) equipped with linear fully focussing spectrometers was used. The ratio method of analysis was employed. The operating procedures used to obtain the required high experimental precision in the measurement of Al:Si atom ratio are discussed.

Statistical analysis of the results gives the estimated mean and spread of the Al:Si atom ratios. In the English kaolin the mean Al:Si atom ratio differs from the ideal 1:1 at the 0·05 significance level. There is evidence for a variation in composition from kaolinite particle to kaolinite particle in the 1·9–2·0 μm fraction of each kaolin. In the 0·9–1·0 μm fractions, the mean Fe:Si atom ratio was close to 0·002 showing the presence of iron in the kaolinite structure. The mean K:Si ratio was about 0·002 which would be equivalent to 1 unit muscovite layer associated with a 0·175 μm thick kaolinite particle. In the American clay the Ti:Si atom ratio was 0·002 suggesting that some 12 per cent of the 'titania' found by conventional chemical analysis was associated with the kaolinite particles either as titania itself or as an isomorphous substituent.

INTRODUCTION

Kaolinite is always found in association with ancilliary minerals which can include one or more of anatase, feldspar, hydrated iron oxide, mica, montmorillonite, quartz and rutile. The amounts of these ancilliary minerals can be estimated from, for example, the results of XRD analysis and selective chemical dissolution. Such data may be combined with results obtained from chemical analysis and used to calculate, after making various assumptions, the elemental composition of the kaolinite. Whilst such a calculation invariably indicates deviations from the ideal formula $Al_2Si_2O_5(OH)_4$, and the presence of other elements, one can never be certain that these deviations are not due to experimental inaccuracies (Weaver and Pollard, 1973).

There is strong evidence from Mössbauer and ESR investigations (Malden and Meads, 1967, 1974; Angel and Hall, 1972) that some ferric iron is present as a substituent in the kaolinite structure and that it occupies octahedral sites. The amount of iron actually substituting is not revealed by either technique. There have been claims that titanium isomorphously substituted in the kaolinite structure can be distinguished from that present in associated crystalline titania minerals. Weiss and Range (1966) used X-ray diffraction to estimate the amount of pseudo-anatase formed upon heating the kaolinite above 450°C and identified this with titanium present in the original kaolinite structure. Dolcater *et al.* (1970) selectively dissolved the crystalline titania minerals in hydrofluotitanic acid.

This paper describes an application of electron microscope microprobe analysis (EMMA) to the determination of the elemental compositions of individual kaolinite particles. An English kaolin and an American kaolin, each representative of the best available materials in terms of mineralogical purity, were used. Individual particles were analysed by the EMMA technique for the elements Al, Si, Mg, Fe, K and Ti. Particular attention was paid to experimental precision in the measurement of Al:Si atom ratios.

THE EMMA TECHNIQUE

Analyses were carried out with the commercial instrument EMMA-4 (A.E.I. Ltd.) which combines the functions of a high resolution electron microscope and a microprobe analyser. The kaolin is mounted on a carbon film supported on a grid as in conventional electron microscopy. When the instrument is used in its analytical mode an extra lens, called a mini lens, is energized. A single particle is chosen for analysis by direct observation of the image on the fluorescent screen of the microscope. The electron beam is then focussed onto the particle. The emitted X-rays pass out of the microscope column at a take-off angle of 45° through two opposite windows into a pair of linear fully focussing spectrometers each offering a choice of one of four diffracting crystals. The crystals used were potassium hydrogen phthalate for Mg Kα, mica for Al Kα, pentaerythritol for Si Kα and K Kα, and lithium fluoride for Ti Kα and Fe Kα. Windows of cast nylon film, 1000 Å thick, are used to minimise intensity losses through absorption. The characteristic X-ray intensities are measured with gas flow proportional counters. The micrographs in Fig. 1 illustrate the application of the technique

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by showing a particle of estimated mass 10^{-12} g before and after analysis.

Hall (1971) has reviewed the quantitative aspects of electron microscope microprobe analysis. The characteristic X-ray intensities I_1 and I_2 from a "thin" specimen containing atoms 1 and 2 respectively are related to the atom fractions X_1 and X_2 by

$$\frac{I_1}{I_2} = k\frac{X_1}{X_2}. \qquad (1)$$

Provided that the X-ray intensities are measured simultaneously the ratio I_1/I_2 is independent of fluctuations in probe current. The constant k allows for differences in ionization cross section, stopping power and spectrometer efficiency for the two elements. For equation (1) to be valid X-ray absorption and X-ray fluorescence in the specimen should either cancel or be negligible; this is a partial definition of "thin". The constant k is determined using a standard containing elements 1 and 2 in a known atom ratio.

In the present work silicon was used as the reference element so that equation (1) becomes

$$\frac{I}{I_s} = k_s\frac{X}{X_s} \qquad (2)$$

where the subscript s refers to silicon. The constant k_s is affected by instrumental conditions and increases with atomic number, from about 0·5 for Mg + Si to about 4·4 for K + Si (Rowse *et al.*, 1974).

EXPERIMENTAL

Materials

An English kaolin from St. Austell, Cornwall, U.K. and an American clay from Washington County, Georgia, U.S.A. were used. They were part of larger batches (*ca.* 250 kg) which had been prepared for surface chemical studies following the procedures described by Bidwell *et al.* (1970) Particle size distribution curves are given in Fig. 2. Table 1 shows mineralogical analyses determined by XRD and elemental analyses determined by conventional wet chemical methods. The hydroxyl contents were calculated from isothermal TG measurements made in flowing dry air; it was assumed that all adsorbed water had been lost when the sample reached constant weight at 300°C and that all lattice water had been lost when the sample reached constant weight at 950°C. The correction for weight loss through burning off of organic carbon was negligible. Ion exchange capacities, by the ammonium acetate method (Mackenzie, 1950), were 3·9 m-equiv./100 g and 4·3 m-equiv./100 g for the English and American clay respectively.

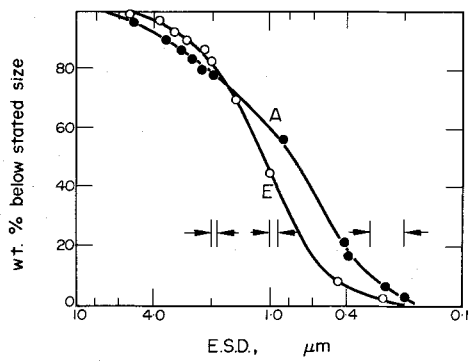


Fig. 2. Particle size distribution curves for the two clays. Curve E, ○—English clay; Curve A, ●—American clay. The fractions used for EMMA investigation are indicated.

Table 1. Chemical and mineralogical analyses of the two clays

	Analysis (wt.%)	
	English Clay	American Clay
SiO_2	46.2	45.2
Al_2O_3	39.2	39.2
Fe_2O_3	0.23	0.17
TiO_2	0.09	1.21
CaO	0.06	0.06
MgO	0.07	0.08
K_2O	0.21	0.02
Na_2O	0.09	0.03
L.O.I. (300–950°C)	13.8	13.3
Total:	99.15	99.27
Mica	1 - 2	Trace
Anatase	0	1 - 2

Three sized fractions with equivalent spherical diameters (e.s.d.) between 0·2 and 0·3 μm, 0·9 and 1·0 μm and 1·9 and 2·0 μm were prepared in an ultracentrifuge (Superspeed 40, M.S.E. Ltd., Crawley, Sussex) using a modified zonal rotor at speeds up to 10^4 rev/min as appropriate. The clay was deflocculated at pH 7 with sodium polyacrylate. A minimum of 5 cuts was made. A part of each fraction was reserved for EMMA investigation. The remainder was flocculated with strontium chloride and sufficient hydrochloric acid to reduce the pH to 4·5. After filtering, washing and drying, the clay was analysed by wet chemical

Table 2. Chemical analyses for the sized fractions from each clay

(a) English Clay.

Element Ratio	Atom Ratio in Stated Fraction (e.s.d.)			95% Confidence Limits
	0.2 - 0.3 μm	0.9 - 1.0 μm	1.9 - 2.0 μm	
Na:Si	0.003	0.0004	0.0004	± 0.0021
Mg:Si	0.0027	0.002	0.0033	± 0.001
Al:Si	0.987	0.993	0.998	± 0.0129
K:Si	0.0071	0.001	0.012	± 0.003
Ca:Si	0.001	0.0007	0.0014	± 0.0014
Ti:Si	0.0017	0.0008	0.0036	± 0.0005
Fe:Si	0.0042	0.0026	0.0064	± 0.0001
Fe:Si*	-	0.0024	-	± 0.0001
OH:Si	1.88	1.97	1.98	± 0.036

(b) American Clay.

Element Ratio	Atom Ratio in Stated Fraction (e.s.d.)			95% Confidence Limits
	0.2 - 0.3 μm	0.9 - 1.0 μm	1.9 - 2.0 μm	
Na:Si	0.0003	0.0009	0.0003	± 0.0021
Mg:Si	0.002	0.002	0.002	± 0.001
Al:Si	1.041	1.019	1.014	± 0.0134
K:Si	0.0003	0.0009	0.0003	± 0.0021
Ca:Si	0.0025	0.0027	0.002	± 0.0015
Ti:Si	0.0291	0.0178	0.0171	± 0.0010
Fe:Si	0.0036	0.0032	0.0043	± 0.0001
Fe:Si*	-	0.0030	-	± 0.0001
OH:Si	2.06	2.07	2.03	± 0.036

* After reaction with excess sodium dithionite.

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methods. Results are expressed in Table 2 as atom ratios. The indicated spreads are for 95 per cent confidence limits. In further experiments, a part of each 0·9–1·0 μm fraction was reacted with excess sodium dithionite (Mitchell and Mackenzie, 1954) at pH 4. Only about 6 per cent of the total iron was removed.

For the English clay (Table 2) the spread of values for Ca and Ti each contain zero. The K:Si and Fe:Si atom ratios decrease at first (compare the 1·9–2·0 μm fraction with the 0·9–1·0 μm fraction) and then increase again in the finest fraction reflecting perhaps an increase in the concentration of mica there. For each fraction the range of values for Al:Si atom ratio include the ideal value of 1:1.

For the American clay (Table 2) the range of values for Na and K contain zero. Ca is present in each fraction and the Ti content is high, reflecting the anatase detected by XRD. Each Al:Si atom ratio and two of the three OH:Si mole ratios exceed the ideal values. When the chemical analyses are expressed in the conventional way, a deficiency of SiO_2 is indicated. Thus the 0·9–1·0 μm fraction analysed 44·9 wt. per cent SiO_2 compared with the ideal value of 46·6 wt. per cent. This deficiency is partially eliminated if allowance is made for the anatase present in the sample.

Specimen preparation

The development and verification of standards for EMMA have been described in detail elsewhere (Rowse *et al.*, 1974). The preparation of an Al + Si standard is quoted as an illustrative example. A gibbsite (<0·5 μm e.s.d.) slurry and a silica (<0·5 μm e.s.d.) slurry were mixed in proportions appropriate for an Al:Si atom ratio of about 1:1. One part of the mixture was filtered, dried and its Al:Si atom ratio determined by chemical analysis. The other part was dried, embedded in resin and sections about 1200 Å thick were cut with an ultramicrotome. One or more of the sections were mounted side by side on an electron microscope grid carrying a Formvar film and then vacuum coated with a carbon film.

Specimen preparation followed the technique used in these laboratories for conventional electron microscopy. A suspension of the deflocculated kaolin at about 0·1 wt. per cent solids was diluted with an equal volume of methanol and sprayed through a microspray onto a freshly cleaved mica surface. Carbon was then evaporated onto the mica, and the carbon film (together with the clay particles) was floated off on water and transferred to the electron microscope grid. For measurements of Al:Si atom ratios, a high experimental precision was required and it was preferred to mount the standard on one half of the grid and the specimen on the other half of the same grid. With this technique, the particles were covered with a second carbon film.

Instrumental conditions

Each kaolinite particle was analysed with an accelerating voltage of 60 kV, a maximum probe current

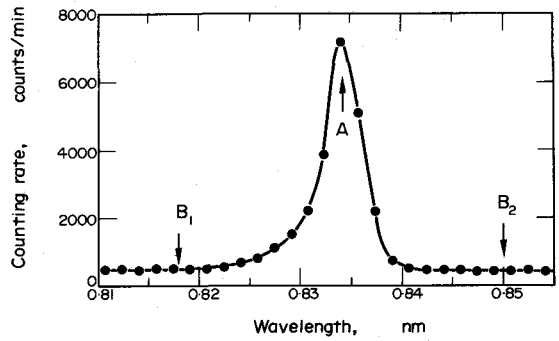


Fig. 3. The measured Al Kα peak. Counting rate is plotted against wavelength. The letters A, B_1 and B_2 are referred to in the text.

of 80 nA and a probe area just sufficient to cover the particle. The shape of the probe was adjusted using the stigmator controls of the instrument. Each standard was measured using the same accelerating voltage but with a probe current of 300 nA and a probe diameter of 60 μm. Because more than 10^4 particles in the standard were simultaneously irradiated, the recorded characteristic X-ray intensity ratio could be identified with the atom ratio determined from the chemical analysis of the bulk standard.

One spectrometer was reserved for measurement of Si Kα intensity. The other spectrometer was used to measure the Kα intensities from the other element or elements. Figure 3 shows the curve of counting rate vs wavelength for Al Kα radiation. It was important at the start of a run to establish the optimum spectrometer settings for each sought element (position A in Fig. 3) and to check these periodically making adjustments as necessary. Counting rates were corrected for continuum background (Bremsstrahlung) using the mean of the counting rates measured on either side of the peak. Thus for Al Kα the background was taken as the arithmetic mean of the counting rates B_1 and B_2 shown in Fig. 3. For kaolinite particles in the 0·9–1·0 μm size fraction, the peak to background ratio was 22:1 for Al Kα radiation and 120:1 for Si Kα radiation. Counting rates for peak-plus-background and for background are given in Table 3. They apply to a kaolinite particle in the 0·9–1·0 μm e.s.d. size fraction with the elements at the stated atom ratios.

The probe current used for particle analysis was a compromise between the desire for high counting rates (and hence precision) and specimen stability.

Table 3. Counting rats for peak-plus-background and for background. Values are for a kaolinite particle in the 0·9–1·0 μm fraction with the elements at the indicated atom ratios

Element	Element:Si atom ratio	Counting Rate (c.p.m.)	
		Peak + Background	Background
Mg	0.0025	206	194
Al	1	4920	218
Si	(1)	9070	75
K	0.002	210	160
Ti	0.002	36	31
Fe	0.0025	188	137

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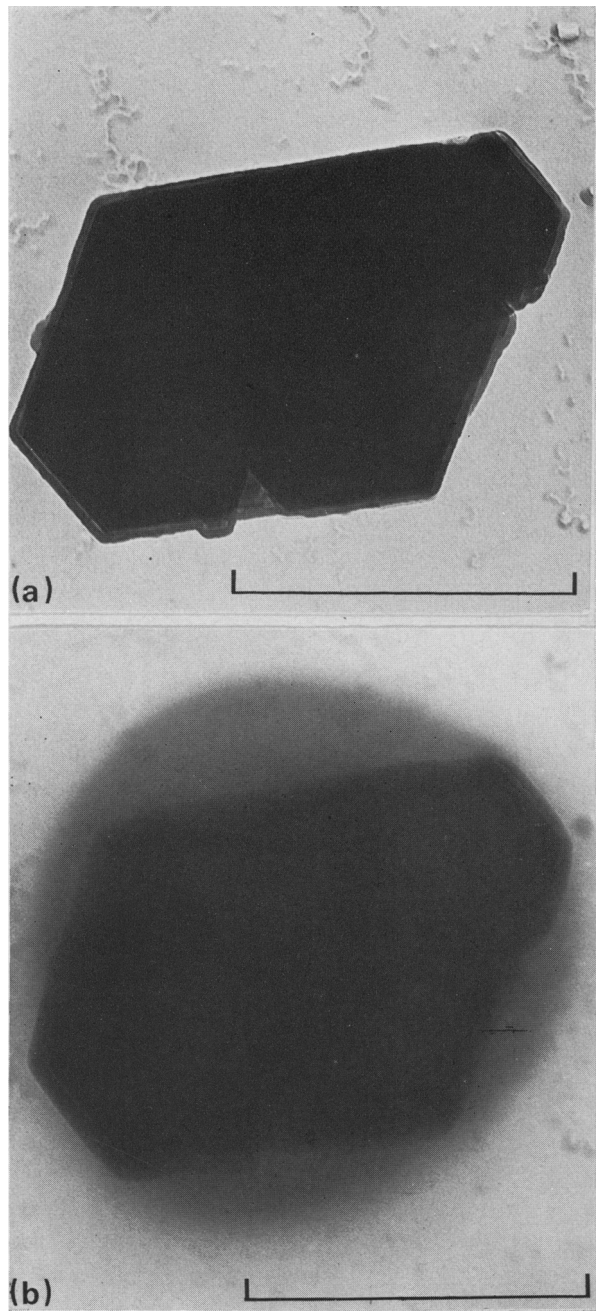


Fig. 1. Electron micrographs showing a particle (a) before analysis, and (b) after analysis.

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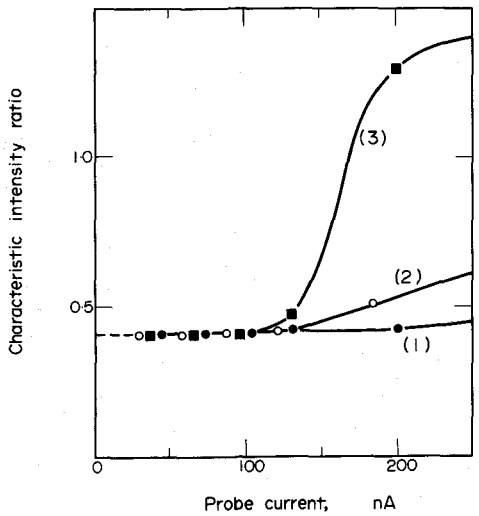


Fig. 4. The effect of probe current on characteristic intensity ratio, Al:Si. The curves 1, 2 and 3 were obtained with three different kaolinite particles.

Figure 4 shows a graph of Al:Si intensity ratio vs probe current for three different kaolinite particles representing the range of thicknesses. Measurements were sequential, each experimental point representing a counting period of 40 sec. For probe currents up to 100 nA, I/I_s was constant and independent of time. For greater values, I/I_s increased, probably through volatilization of silicon monoxide formed by the reaction of dehydroxylated kaolinite with deposited carbonaceous material. The increase was greatest with the thickest particle (curve 3). In the measurements described below the probe current was always less than 80 nA.

There was no indication of potassium migration (Hodson and Marshall, 1971) or loss using the K + Si standard or when analysing the specimen.

The validity of equation (2) was tested by making experiments with a mica flake having a stepped section. The results are shown semilogarithmically on an exaggerated scale in Fig. 5 as Al:Si intensity ratio vs $100\,Q/Q_o$ where Q and Q_o are the transmitted and incident probe currents respectively. Log(100 Q/Q_o) is approximately proportional to specimen thickness.

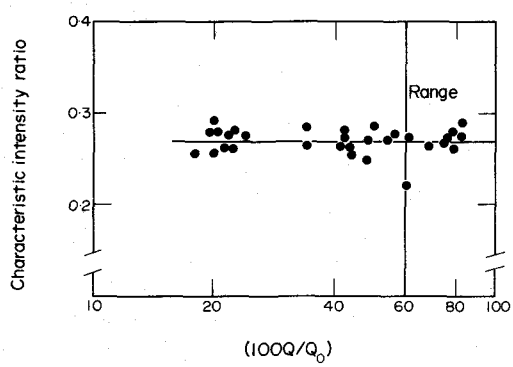


Fig. 5. Experiments with a stepped mica flake. The characteristic intensity ratio, Al:Si, is plotted against $100\,Q_o/Q$. Particle thicknesses were within the indicated range, $60 < 100\,Q/Q_o < 100$.

Over the indicated range (Fig. 5) of values of Q/Q_o for the kaolinite particles, the Al:Si intensity ratio measured on the mica flake was constant. This finding is consistent with previous work with EMMA-4 (Nissen *et al.*, 1973; Lorimer and Champness, 1973). Calculations using tabulated X-ray absorption coefficients (Jenkins and De Vries, 1967) show that deviations from equation (2) are likewise negligible for the other elements of interest. Considering Fe as a substituent in kaolinite at a fixed Fe:Si atom ratio then for two particles, 0·1 and 0·2 μm thick, the recorded Fe:Si intensity ratios would differ by only 1·5 per cent.

RESULTS AND DISCUSSION

Measurements of Al:Si *atom ratios*

Al:Si atom ratios were measured for each of the three fractions prepared from the English and American clays. It was necessary to complete the measurements on a given fraction within one run to avoid errors which would otherwise have been incurred through instrumental variations between shutdowns. Hexagonal particles with well-defined 120° corners were selected for analysis. Alternate measurements were made on the particles and on the same area of standard. At least 60 and usually 100 particles were analysed; not less than 5000 counts were recorded for the Al Kα radiation and about 10,000 counts were recorded for the Si Kα radiation. Counting rates on the standard generally exceeded those on the particles by a factor of at least four. Spectrometer peaking was checked after every 10 measurements.

The results for the 1·9–2·0 μm fraction of the English clay (100 particles) and for the standard (100 replicate measurements) are shown on an exaggerated scale in Fig. 6 as Al:Si intensity ratio vs analysis sequence. The slopes of the two lines were not significant at the 0·05 level showing the absence of any long term instrumental instability. The statistical analysis of the data is described using these results.

A χ^2-test (Chatfield, 1970) showed that the data for particles and standard could be represented by normal distribution curves. These are shown in Fig. 7 superimposed on the histograms. The curve for the standard had a mean intensity ratio $(I/I_s)_{st}$ of 0·470 and a standard deviation s_{st} of $0{\cdot}013_2$. In physical terms the experimental values show a spread because the generation of X-ray photons is a random process and because there are random instrumental variations. The curve for the specimen had a mean intensity ratio of $(I/I_s)_{sp}$ of 0·473 and a standard deviation s_{sp} of $0{\cdot}018_7$. There is now a third possible contribution to the spread: a compositional variation between the kaolinite particles. An F-test (Chatfield, 1970) was used to compare the variance s^2_{st} of 0·000174 with the variance s^2_{sp} of 0·000350. It showed that the difference between the two values was significant even at the 0·01 level. If the curve of normal distribution for compositional variation alone (i.e. the curve for the

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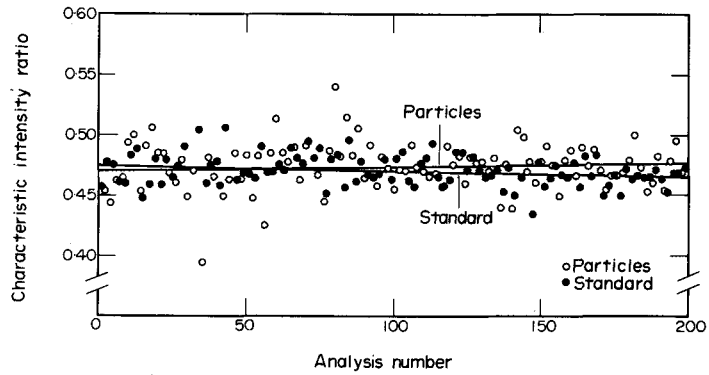


Fig. 6. Analysis of the 1·9–2·0 μm fraction of the English clay. The characteristic intensity ratio Al:Si is plotted against analysis number. ○—Particles. ●—Standard.

particles minus the curve for the standard) has a s.d. of s_p then

$$s_{sp}^2 = s_{st}^2 + s_p^2. \quad (3)$$

Substitution gives s_p as between 0·0119 and 0·0149 for 95 per cent confidence limits: these values are equivalent to 2·5 and 3·1 per cent of the mean value of $(I/I_s)_{sp}$. It might be argued that this result arises from a dependance of I/I_s on particle thickness. Such an effect would be more pronounced with the larger particles, being magnified by surface roughness and variable orientation. This can be dismissed. A rough calculation (Jenkins and De Vries, 1967) shows that I/I_s decreases by only 0·01 for an increase in particle thickness of 0·2 μm.

Application of equation (2) to the specimen and standard gives

$$(X/X_s)_{sp} = (X/X_s)_{st} \frac{(I/I_s)_{sp}}{(I/I_s)_{st}} \quad (4)$$

where $(X/X_s)_{sp}$ and $(X/X_s)_{st}$ are atom ratios in specimen and standard respectively. Sections cut from a single preparation of standard were used for all six sets of measurements: chemical analysis gave $(X/X_s)_{st}$ as 1·017 ± 0·017. Insertion of the appropriate values in equation (4) gives $(X/X_s)_{sp}$ as 1·024 with a spread of ±0·017 for 95 per cent confidence limits.

The data for the other five sets of measurements were treated in a like manner. The F-test showed that there was no difference at the 0·05 significance level between s_{sp}^2 and s_{st}^2 for the data appropriate to the experimental runs on both 0·2–0·3 μm fractions and both 0·9–1·0 μm fractions. This does not prove an absence of compositional variation but merely indicates that no useful conclusions can be made without analysing many more particles. For the 1·9–2·0 μm fraction of the American clay s_p lay between 3·6 and 4·5 per cent of the mean value of $(I/I_s)_{sp}$ for 95 per cent confidence limits.

Values of $(X/X_s)_{sp}$ are listed in Table 4. The spreads for the English clay do not include the ideal Al:Si atom ratio of 1:1 at the 95 per cent confidence level. For the American clay the converse holds. The EMMA values and the chemical values, reproduced in Table 4, differ at the 95 per cent confidence level for four of the six fractions (English 0·9–1·0 μm and 1·9–2·0 μm; American 0·2–0·3 μm and 0·9–1·0 μm). The discrepancy, if real, means that particles with an Al:Si atom ratio different from 1:1 are present in the kaolins and that such particles were not included in the population sample chosen for EMMA investigation.

Table 4. Mean Al:Si atom ratios determined by EMMA. Values calculated from chemical analysis are included for comparison

		Al:Si atom ratio	
Clay	Fraction (μm)	EMMA	Chemical Analysis
English	0.2 - 0.3	0.973 ± 0.019	0.987 ± 0.0129
	0.9 - 1.0	0.962 ± 0.018	0.993 ± 0.0129
	1.9 - 2.0	1.024 ± 0.017	0.998 ± 0.0129
American	0.2 - 0.3	0.997 ± 0.018	1.041 ± 0.0134
	0.9 - 1.0	0.997 ± 0.019	1.019 ± 0.0134
	1.9 - 2.0	1.008 ± 0.018	1.014 ± 0.0134

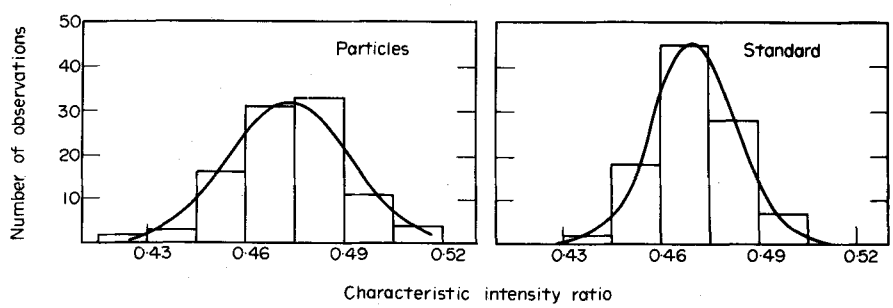


Fig. 7. The data of Fig. 6 are plotted as histograms with curves of normal distribution superimposed.

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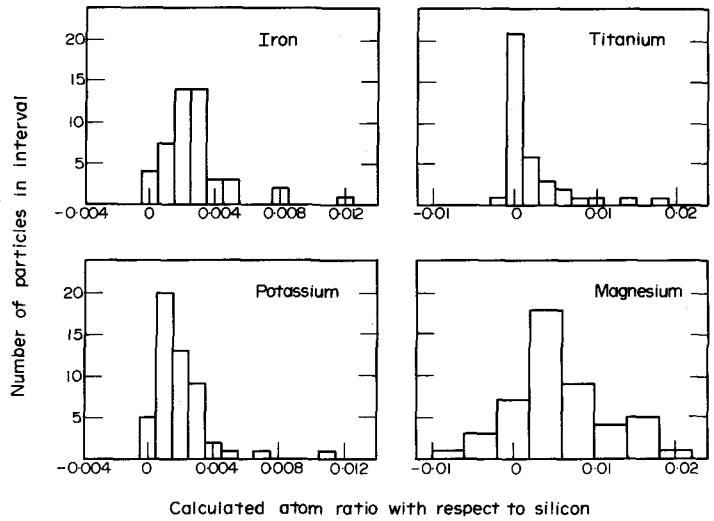


Fig. 8. Histograms showing the atomic ratios Fe:Si, Ti:Si, K:Si and Mg:Si in the 0·9–1·0 μm fraction of the American clay. Note the different scales on the abscissae.

Measurement of minor element concentrations

The 0·9–1·0 μm sized fractions from each clay were examined to determine the amounts of Fe, Ti, K and Mg relative to Si associated with the kaolinite particles. Separately mounted binary standards and the specimen were accommodated in the sample rod. Approximately 50 particles from each clay were examined. Because of the low counting rates (Table 3) the analysis was particularly time-consuming: at least 45 min were needed to complete the analysis of one particle. One consequence of the long analysis time was the build up of contamination on the specimen with an attendant increase in background counting rate.

(a) *American clay*. The experimental values for the atom ratios with respect to Si of Fe, Ti, K and Mg are shown as histograms in Fig. 8. The calculation of atom ratios from intensity ratios followed the example given above. The mean atom ratios with their 95 per cent confidence limits are given in Table 5 and compared with the values from the chemical analysis of the bulk fraction.

Referring to Fig. 8, it is seen that the distribution of Fe:Si atom ratios was wide: the mean was 0·00248 with a s.d. 0·00188. This represents a coefficient of variation of 75 per cent which is about a factor of three greater than would have been expected from instrumental and counting variations alone. Comparison with the value from chemical analysis shows that most of the iron must be associated with the kaolinite. Also, most of the iron must be occupying structural positions and not confined to the surface as a coating since only 6 per cent of the total was removed on reacting with an excess of sodium dithionite.

Table 5. Mean Mg:Si, K:Si, Ti:Si and Fe:Si atom ratios determined by EMMA for the 0·9–1·0 μm fraction of the American clay

Element Ratio	Atom Ratio	
	EMMA	Chemical Analysis
Mg:Si	0.00246 ± 0.00200	0.002 ± 0.001
K:Si	0.00186 ± 0.00044	0.0009 ± 0.0021
Ti:Si	0.00221 ± 0.00140	0.0178 ± 0.0010
Fe:Si	0.00248 ± 0.00053	0.0032 ± 0.0001

The results for Ti:Si atom ratios are of particular interest. Because XRD analysis showed between 1 and 2 wt. per cent anatase, a disparity between the results of the EMMA investigation and the value derived from chemical analysis of the whole sample was to be expected. Isolated titania particles were identified and their iron contents measured. What is surprising is that as much as 12 per cent of the total titania is associated with the kaolinite. In a further experiment a 0·75–1·0 μm sized fraction was prepared after first stirring a suspension of the deflocculated clay at about 75 wt. per cent solids under conditions of shear sufficient to give a temperature rise of about 20°C in 4 min. Four cuts were made. The fraction was flocculated, filtered and dried. It was then stirred at 75 wt. per cent solids as above and fractionated to give a 0·9–1·0 μm sized fraction. Four cuts were again made. Analysis of the fraction gave 0·90 wt. per cent TiO_2 corresponding to a Ti:Si atom ratio of 0·0153 compared with 0·0178 for the fraction (Table 2) prepared with the vigorous stirring omitted. The difference is not statistically significant. EMMA measurements were made on 50 kaolinite particles contained in this new fraction. The mean Ti:Si atom ratio was 0·00355 ± 0·0018 which agrees with the earlier value of 0·00221 ± 0·0014 (Table 5). If this titanium is present as very small titania particles attached to the surfaces of the kaolinite particles there can be little detachment as the kaolinite particles rub against each other during the vigorous stirring.

The K:Si atom ratios are shown in Fig. 8. Naïvely it might have been expected that perhaps one particle in every several hundred would have been mica so that the failure to find such a particle after examining only 50 clay particles is not unreasonable. What is surprising is that many of the kaolinite particles showed a finite K:Si atom ratio. The spread was

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0·00186 ± 0·00044 which is consistent with the spread of 0·0009 ± 0·0021 determined by chemical analysis though now the experimental errors are larger. Methods of sample preparation not involving a mica substrate have given similar results so that a false conclusion through contamination of the kaolinite particles by mica during specimen preparation can be discounted. Also, it was confirmed that there is no detectable potassium when the Al + Si standard is examined by EMMA. The mean K:Si ratio given above is equivalent to 1 unit muscovite layer associated with about 250 unit kaolinite layers. (A particle, 0·2 μm thick, contains 280 unit kaolinite layers).

The histogram in Fig. 8 for Mg:Si atom ratio is seen to contain a significant proportion of negative values. If the true Mg:Si atom ratio was zero then the whole population of experimental values would include an equal number of positive and negative values. The estimated spread here was 0·00246 ± 0·00200 which shows within the 95 per cent confidence limits that some magnesium is associated with some of the kaolinite particles.

Graphs of the K:Si atom ratio versus the Fe:Si and the Ti:Si atom ratios and of the Fe:Si atom ratio versus the Ti:Si atom ratio showed no correlation. For example, a particle with a high Fe:Si ratio did not have a high K:Si ratio.

(b) *English clay.* With the English clay every particle within one grid square excluding the few obviously undersized particles present, was analysed. This avoided any possible bias towards the more regularly shaped particles. The results are shown as histograms in Fig. 9 and as spreads of values in Table 6. The broad conclusions made above for the American clay again apply: a spread in the Fe:Si atom ratios and potassium again apparently associated with many of the kaolinite particles. No individual mica particles were found. The spread of values for Mg:Si atom ratio, 0·00438 ± 0·0155, included zero at the 95 per cent confidence level. There was no correlation between the three atom ratios.

Table 6. Mean Mg:Si, K:Si and Fe:Si atom ratios determined by EMMA for the 0·9–1·0 fraction of the English clay

Element Ratio	Atom Ratio	
	EMMA	Chemical Analysis
Mg:Si	0.00438 ± 0.0155	0.002 ± 0.001
K:Si	0.00185 ± 0.00139	0.001 ± 0.003
Fe:Si	0.00137 ± 0.00100	0.0026 ± 0.0001

Of the 50 particles analysed there was one particle which was atypical, being low in each of K, Si, Mg, Fe and Al. Its identity was not established.

CONCLUSIONS

The present study has shown that with proper attention to operating procedures and choice of standards, the technique of electron microscope microprobe analysis can be applied to the elemental analysis of individual clay particles with masses approaching 10^{-14} g. Because most clay particles are platelike and can be prepared for study with their smallest dimension perpendicular to the electron beam, the simple ratio method expressed by equation (1) is applicable and the lengthy corrections applied in normal probe analysis are unnecessary. The technique is capable of giving results of high precision, about 3 per cent as a coefficient of variation, provided that the sought elements are present in sufficient amounts to give adequate counting rates.

The Al:Si atom ratios of the kaolinite particles contained in three sized fractions of an English kaolin and three sized fractions of an American clay have been measured. Statistical analysis of the results shows that for each 1·9–2·0 μm fraction, the Al:Si atom ratio does vary from kaolinite particle to kaolinite particle; the coefficient of variation was 2·8 per cent for the English clay and 4·1 per cent for the American clay. It was not possible to make any definitive statement about compositional variation from kaolinite particle to kaolinite particle for the

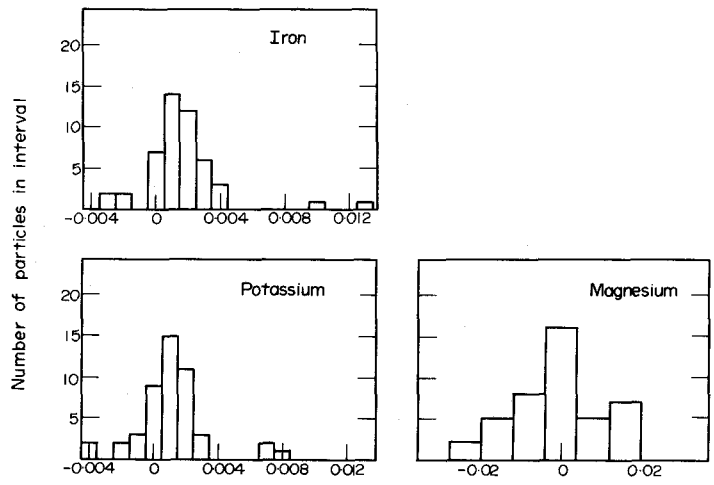


Fig. 9. Histograms showing the atomic ratios, Fe:Si, K:Si and Mg:Si in the 0·9–1·0 μm fraction of the English clay. Note the different scales on the abscissae.

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other sized fractions (0·2–0·3 μm and 0·9–1·0 μm) from each clay. The mean Al:Si atom ratio for each fraction has been estimated together with its range of values for 95 per cent confidence limits. The values for the English clay, unlike those for the American clay, do not include the ideal Al:Si atom ratio of 1:1 at the 95 per cent confidence level (Table 4). The validity of these conclusions on compositional deviations is reinforced by a current study of the composition of the "kaolinite" present in certain ball clays. EMMA investigation of the "kaolinite" particles contained in a Dorset ball clay gives a mean Al:Si atom ratio of 0·924 with a spread of ±0·023 for 95 per cent confidence limits. Specifically for the 0·2–0·3 μm and 0·9–1·0 μm fractions, the mean Al:Si atom ratios are less than unity. Any replacement of Si by Al in the kaolinite structure would give an Al:Si atom ratio *greater* than unity. From the data of Table 2 it is readily seen that the reduction in Al:Si atom ratio through isomorphous replacement of Al by Fe is negligibly small. The most reasonable interpretation is one in terms of an excess of silica: whether this is present as a gel coating (Jones and Uehara, 1973) or as discrete particles attached to each kaolinite particle is conjecture.

Measurement of the minor element concentration in the kaolinite present in the 0·9–1·0 μm fractions of each clay has confirmed the conclusion from Mössbauer and ESR measurements (Angel and Hall, 1972; Malden and Meads, 1967, 1974) that iron is present as a substituent in the kaolinite structure. Unexpectedly the spread in Fe:Si atom ratio was wide (Fig. 8 and 9) reflecting perhaps the large samples of matrix used to prepare the clays. It would be of interest to investigate the kaolinite extracted from a single feldspar pseudomorph in English matrix; here the Fe:Si atom ratio might show a smaller variation. Some 12 per cent of the titanium detected by chemical analysis in the American clay is associated with the kaolinite particles. It was not possible to reduce this value by stirring the suspension of clay prior to fractionation under conditions such that the kaolinite particles rubbed against each other. The value is not dissimilar from that found by Dolcater *et al.* (1970) for a similar clay, after selective dissolution of the free titania in hydrofluotitanic acid. It might be interpreted by them and by Weiss and Range (1966) as present as an isomorphous substituent in the kaolinite structure although there is no confirmatory evidence on this point. The kaolinite particles contained in the 0·9–1·0 μm fractions of both the English and American clays have a statistically significant K:Si atom ratio. The potassium may be present as a mica interlayer (Range *et al.*, 1969) to the extent of about one unit muscovite layer for every 250 unit kaolinite layers.

The analytical sensitivity for magnesium was small. There was some indication of its presence in the kaolinite contained in the 0·9–1·0 μm fraction of the American clay but not in the same fraction of the English clay.

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