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(WITH TWO PLATES)

Summary

Amorphous silico-aluminas of varying composition prepared by simultaneous precipitation from aluminium nitrate and sodium silicate solutions were found to be heterogeneous by analysis in the electron microprobe. Exceptions were samples of Si/Al atomic ratio 1.5, which showed no heterogeneity for varying conditions of preparation. Silico-aluminas prepared by the co-hydrolysis of ethyl orthosilicate and aluminium isopropoxide were more heterogeneous, and their heterogeneity showed a greater variation with composition. The technique was able to establish heterogeneity of compositions but it was not certain whether homogeneity of the samples in the microprobe represented the homogeneity of composition in view of the large number of particles that appear to make up the aggregates. The most likely explanation of the heterogeneity is thought to be the presence of a matrix of variable composition surrounding the particles. Two out of five natural allophanes showed no evidence of heterogeneity.

Introduction

ALLOPHANES are naturally occurring hydrous amorphous silico-aluminas which do not have a well defined chemical composition. For this reason it is conceivable that there will be a range of composition for different particles within a sample. Rodrique and Declerk (1975) using a transmission electron microscope with an X-ray spectrometer attachment, have shown that for some synthetic silico-aluminas this indeed appears to be the case. Jepson and Rowse (1975) also reported a small variation in the composition of kaolinite from particle to particle in the 1.9–2.0μm size fraction. Since the interpretation of many characteristics of amorphous silico-aluminas assumes that each particle has the same composition, it is important to determine whether the results of Rodrique and Declerk (1975) are generally true for amorphous silico-aluminas. In the present study an electron microprobe has been used to compare natural allophane with synthetic amorphous silico-aluminas formed under various conditions of preparation, and to attempt to establish some guidelines for preparing amorphous silico-aluminas of homogeneous composition.

Materials and Methods

Preparation of samples

Synthetic silico-aluminas can be prepared in several ways. They can be prepared from co-hydrolysis of organic reagents such as aluminium isopropoxide and ethyl

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orthosilicate, co-precipitation of inorganic Al and Si salts, co-gelation of Si and Al gels, impregnation of a Si or Al gel with a solution of the other salt, or extensive grinding of alumino-silicate minerals. In the present study, co-precipitation of the inorganic salts using a simultaneous mixing technique was used. It was thought that such simultaneous mixing gave the greatest likelihood of producing an homogeneous product.

Batch A Samples of amorphous silico-aluminas containing 90, 80, 60, 50, 20 and 10 mol per cent Si/(Si + Al) were prepared by co-precipitation from sodium silicate with aluminium nitrate. Sodium silicate was prepared from silica (Merck, extra pure) dissolved in an equivalent amount of NaOH. All reagents used were of A.R. grade. The two reagents were added simultaneously using a multichannel Ismatec constant speed pump flowing at 180 ml per h into a magnetically stirred 2 litre plastic beaker containing 100 ml of deionised water. The pH was held constant at 7.0 ± 0.5 by dropwise addition of HNO_3 or NaOH when necessary. The whole experiment was carried out at 20 ± 2 °C. The suspension was allowed to age for 0.5 h and then was freeze-dried, washed in deionised water to a conductivity of less than 30×10^{-6} siemens m^{-1} and freeze-dried again. The first freeze drying was found to facilitate washing of the product and to reduce the probability of crystallisation occurring during washing. The same procedure was carried out for two co-precipitates of silica and ferric hydroxide (Batch A), the samples containing 50 and 80 mol per cent Fe/Si + Fe).

Batch B Samples containing 60 mol per cent Si were prepared under a variety of conditions of reagent concentration, precipitation pH and ageing time. The method was the same as for Batch A, but two reagent concentrations of 0.6M Na_2 SiO_3 with 0.4M $Al(NO_3)_3$ and 0.06M Na_2 SiO_3 with 0.04M $Al(NO_3)_3$ were used. The pH was held constant at 5.5, 7.0, or 8.5 and the suspension was allowed to age for 1, 10 or 40 days. One sample was removed from the reaction mixture halfway through precipitation. Two further samples containing 80 mol per cent Si/(Si + Al) were prepared at the high and the low reagent concentration, pH 7.0, and aged for 40 days (Batch B).

Batch C Two silico-alumina samples, C1 and C2, prepared by the co-hydrolysis of aluminium isopropoxide and ethyl orthosilicate followed by drying at 60 °C, were supplied by Dr. A. Herbillon, through Mr. H: Geering.

All synthetic samples were examined for crystallinity, and found to be amorphous both to X-rays and electrons. Chemical analysis of the samples was carried out by atomic absorption spectrometry after total dissolution in 1 M NaOH.

Batch D Samples of the naturally occuring amorphous silico-alumina, allophane, were supplied by Professor K. Wada (weathered pumice from Kitakami, Japan), Professor N. Yoshinaga (volcanic ash from Kumamoto, Japan, samples 1058, 1059), Dr. K. Norrish (volcanic ash from Imaichi, Japan) and Dr. B. Theng (volcanic ash from Tongariro, New Zealand). They were dispersed at pH 10, with the exception of Professor Wada's sample which was already dispersed in acidified dilute NaCl (see Henmi and Wada, 1976), and the 2–5μm fraction was collected by sedimentation. The fraction samples were examined by X-ray diffraction using Co-Kα radiation. The Kitakami sample was found to be completely amorphous, the Kumamoto and Tongariro samples contained a little feldspar, and the Imaichi sample contained small amounts of both feldspar and hornblende.

The kaolinite which was to be used as the standard was collected from Greenbushes, W. A. It has a Si/Al ratio of 1.0 and had been pre-treated to remove any

hydrous aluminium oxide from the surface (Bolland, 1975). Results of X-ray diffraction indicated that the kaolinite was moderately well ordered and contained no impurities.

Microprobe analysis

The instrument was an SEM-Q scanning electron microprobe manufactured by A.R.L. Ltd., equipped with three wavelength dispersive spectrometers with proportional counters. The analysing crystals used were penta erythritol for silicon, and rubidium acid phthalate for aluminium. Spectrometers were aligned using pure oxide standards and were always within 0.00030 nm. of the published values. The beam diameter was approximately 2 μm with an accelerating voltage of 15 kV and a probe current of 20 nA.

Samples were prepared for analysis by placing a carbon coated copper grid for three minutes under a drop of suspension of a sample which had been ultrasonically dispersed in n-butanol. The grid was subsequently washed in methanol and coated with a 20 nm thick layer of copper. The grids were glued onto brass studs and mounted onto the sample stage. A sample of kaolinite was prepared similarly with each batch for use as a standard. The sample stage was driven until a particle aggregate in the range 1–5 μm was lined up under the electron beam using the display screen, taking care to move only the sample stage and not the spectrometers. The grid was then moved into optical focus under the beam by vertical adjustment of the sample stage. The spectrometers aligned for Al and Si radiation were then set to count until the Al count reached 20,000, a process taking roughly 20 seconds. Background counts were made on the specimens after every 10 particles had been analysed, the counts being taken either side of the peak and averaged to allow for a sloping background. Background counts off the specimens were similar to background counts on the peak. A pulse height analyser was not used, as a good signal to background ratio was obtained. Fifty to 100 particles of each sample were counted, using 25 to 50 of each standard. The kaolinite standard was analysed before and after every sample to provide a calibration factor for converting the Si/Al count ratio to a Si/Al composition ratio and as an estimation of the spread of the ratios due to instrumental variation. The Si/Al count ratio for kaolinite with a composition ratio Si/Al = 1.0 was used to convert count ratios to composition ratios.

Statistical analysis

Heterogeneity in the samples was determined by comparison of the variances of the sample data to the variance of the kaolinite standards analysed on the same day. The variances were compared using an F test, on the assumption that the kaolinite standard was homogeneous. Because of a slight non-normality of the data and the dependence of the variance on the mean, a log transformation was used on the data. The significance of the F value is given by the probability P. For complete details of the statistical method see the Appendix.

Results

Preliminary experiments to determine the likely precision of the results indicated nine possible sources of error, seven of which are overcome by using an internal standard and a standardised procedure. The other two relate to the

properties of the sample. They are

(i) The instrumental reproducibility of the Si and Al counts was estimated on five particles by repeated counting 10–20 times. The coefficients of variation (CV) of the raw data for each particle were 1.6, 1.9, 2.8, 1.8 and 1.3 per cent, giving a mean variation of 1.9 per cent.

(ii) To check whether the Si/Al count ratio varied linearly with the Si/Al composition ratio, a range of geochemical standards of accurately known composition was examined whose Si/Al ratios varied from 0.5 to 3.0 (Pyman *et al.*, 1978). The results showed a good linear relationship between Si/Al composition and intensity ratios and demonstrated that there is no apparent effect of sample matrix on the Si/Al ratio. Consequently kaolinite has been used as the standard throughout these experiments.

(iii) The error involved in aligning the beam on the edge rather than the centre of a particle was checked. Repeated counting of two kaolinite particles in which the beam was positioned on a different part of the particle each time resulted in CVs of 1.6 per cent and 2.5 per cent. This is a similar variation to that in 1 above, and is thus not a significant source of error. The beam diameter is approximately 1 μm, so that surface roughness effects on aggregates of 1–5 μm diameter can be expected to be small since almost the whole of the aggregate will be excited wherever the incident beam strikes. Furthermore, micrographs of the samples and standards show that they lie fairly flat, and this would help to minimise the effect of a changing take-off angle.

(iv) A considerable error was involved during alignment of the particles in the beam if the beam rather than the sample stage was moved. Using the beam anywhere within 10 μm of the centre of the stage resulted in a CV for kaolinite of 13 per cent, whilst moving the sample stage only and keeping the beam in the centre of the screen throughout the analysis resulted in a CV of 6 per cent for the same sample.

(v) The use of copper as a conductive coating is a contributing factor to the need for a standard. It has been used because an even all round coating can be obtained, which is harder to obtain when carbon is used as the coating. However, there will be some differential adsorption of radiation by the copper due to the high mass absorption coefficients. It is thought that a large proportion of the variation in values for both standard and sample is due to variations in the thickness of the particles and to this use of a copper coating. The average CV of the raw data of 29 kaolinite analyses was 6.6 per cent and 5.0 per cent using transformed data. Jepson and Rowse (1975) in a detailed microscope microprobe analysis of kaolinite managed to maintain a reproducibility of 3 per cent using a carbon coating and a very narrow particle size range. No variation in composition from kaolinite particle to kaolinite particle, as found by Jepson and Rowse (1975) was detected for our kaolinite.

(vi) Kaolinite standards were analysed before and after every sample to minimise errors resulting from changing beam conditions since it was found that the mean kaolinite Si/Al ratio varied significantly. This was believed to be due to the varying thickness of the kaolinite particles as well as to instrumental variation. On the assumption that this extra variation in the standard averaged to zero, kaolinite analyses have been pooled for each day of analysis.

(vii) The error due to volatilisation of silica, reported by Rodrique and Declerk (1975) for their silica-aluminas, was thought to be minimal as repeated counting of 25 particles showed no detectable decrease in the Si count rate.

The two sources of error relating to the sample are the tendency of the particles to move away from the electron beam and the collapse of the particles to form small balls. Both these phenomena were observed for all the samples except the kaolinite standards. An accumulation of negative charge on the particle and an incomplete conducting layer at the base of the particles, resulting in heating, could cause these effects. On closer inspection, it was found that the Si/Al ratio remained constant all the time that a particle was moving away from the beam even though each count rate was decreasing rapidly. For collapsing particles, not only did the ratio remain constant throughout the collapse, but the count rate frequently increased. Since neither the Si nor Al count rate ever decreased during collapse, the collapse is not due to volatilisation of silica, as found by Rodrique and Declerk (1975). Loss of structural water due to heating by the electron beam is a likely cause of the collapse. Despite the constant silica/alumina ratio, there may be a small error associated with counts for these particles as the matrix effects of the collapsed particles will be different from the rest of the sample.

The overall reproducibility of the method was found to be reasonable, although not as good as that of Jepson and Rowse (1975). However, in view of the greater size range of particles studied, necessary in order to be able to obtain good count rates on the synthetic samples, this is not surprising. The coefficient of variation of samples analysed on several different occasions was no greater than would be expected from the variations themselves. The following results are typical: SiAl 60:40 (5.0 per cent, 5.0 per cent, 8.6 per cent), C(1) (20 per cent, 23 per cent, 18.3 per cent, 19.8 per cent, 21.5 per cent), Imaichi allophane (11.0 per cent, 12.6 per cent, 15.9 per cent, 16.0 per cent).

Properties of the synthetic silico-aluminas

The results for the synthetic silico-aluminas of varying composition are shown in Table 1. Each result, expressed as the variance of the transformed data, is the average of duplicate grids, and where two or more results appear for one sample these results were a new pair of grids done on separate occasions. The transformed pooled variance of the kaolinite standards analysed on that day is reported for comparison. The only sample to appear at all homogeneous, that having the Si/Al

TABLE 1

Varying composition of synthetic silica alumina (Batch A) and synthetic silica iron (Batch A'); F and P defined in Appendix

*Sample**	*Sample variance*	*Pooled std. variance*	*F*	*P*	*Probe Si/Al ratio*	*Chem Si/Al ratio*
Batch A						
SiAl 80:20	.0113	.00209	5.4	.0000	3.59	3.73
SiAl 60:40	.0051	.00204	2.5	.0003	1.51	1.50
SiAl 50:50	.0115	.00190	6.0	.0000	1.23	1.26
SiAl 20:80	.0389	.00190	20.5	.0000	0.21	0.25
SiAl 10:90	.0235	.00260	9.0	.0000	0.097	0.11
Batch A'						
SiFe 50:50	.0285	.0031	9.2	.0000	–	–
SiFe 20:80	.0315	.0031	10.2	.0000	–	–

*Composition expressed as mol % Si/(Si + Al) : Al/(Si + Al).

TABLE 2

Variability of composition of silica aluminas prepared under various conditions. Batch B; Si/Al ≃ 1.50; Batch B′; Si/Al ≃ 4.0

Sample	*pH of prep^n*	*Time of ageing (days)*	*Sample variance*	*Pooled std. variance*	*F*	*P*	*Probe Si/Al ratio*	*Chem Si/Al ratio*
Batch B								
1	7.0	1	.00418	.00209	2.0	.0296	1.32	1.42
2	8.5	1	.00424	.00225	1.9	.0399	1.21	1.42
3	5.5	1	.00419	.00225	1.9	.0399	1.25	1.42
4	7.0	40	.00332	.00275	1.2	.225	1.28	1.42
5	8.5	40	.00476	.00275	1.7	.0149	1.32	1.42
6	5.5	40	.00202	.00275	0.7	.9124	1.35	1.42
Batch B′								
7*	7.0	40	.0170	.00405	4.25	.0000	3.85	–
8*	7.0	40	.0300	.00405	7.50	.0000	3.82	–

*Samples 7 and 8 were prepared at high and low reagent concentrations respectively. See text.

ratio of 1.5, was examined in more detail to establish whether the homogeneity results more from some special property of a Si/Al ratio of 1.5 or is perhaps due more either to coincidence or to the method of preparation. Samples of Si/Al ratio 1.5 were prepared under a variety of experimental conditions outlined in the method section (Batch B). Each one was then examined in the probe. The results, shown in Table 2, showed that whatever the conditions of preparation, the samples were not significantly different from the kaolinite standards. Results for the other combinations of pH, ageing time and reagent concentration (not shown), gave similar results. Analysis of a sample of the same ratio that was removed from the reaction in the middle of the precipitation process also showed no heterogeneity, indicating that there appears to be no significant ageing process affecting the particle composition.

To establish the uniqueness of the Si/Al ratio of 1.5, different preparations of a sample thought to have a heterogeneous composition were also examined. Samples of Si/Al ratio of 4.0 prepared at pH 7.0, two reagent concentrations and aged for forty days, were examined in the probe. The results for the two sets of conditions given in Table 2, show from the P values that the sample variances are still significantly greater than for the kaolinite standards. This reinforces the conclusion that the homogenetiy of samples of Si/Al ratio 1.5 is due to the composition and not to the method of preparation.

The results for the two samples prepared by the co-hydrolysis of ethyl orthosilicate and aluminium isopropoxide (Batch C) are shown in Table 3 and their distributions are shown in Fig. 1. Both samples clearly possess considerable heterogeneity although D'Agostino's (1971) test showed both to be normally distributed. Our sample C(2) (CV of raw data 20 per cent) shows a smaller variation than a sample of Rodrique and Declerk (1975) (33 per cent), prepared by a similar co-hydrolysis method, whilst sample C(1) (CV of raw data 40 per cent) suggests that the heterogeneity increases towards higher Si content, as well as towards higher Al content. Both the results of Rodrique and Declerk and our Batch C show a greater variation than samples prepared by the simultaneous mixing method used for Batches A and B.

TABLE 3

Variability of silica aluminas prepared by cohydrolysis of the alkoxides (Batch C) and of natural allophanes (Batch D)

Sample	*Sample variance*	*Pooled std. variance*	*F*	*P*	*Probe Si/Al ratio*	*Chem Si/Al ratio*
Batch C						
C(1)	.0430	.00204	21.1	.0000	.241	.230
C(2)	.1480	.00161	91	.0000	3.80	3.54
Batch D						
Kitakami	.0058	.00190	3.1	.0000	0.67	0.65
Tongariro	.0044	.00260	1.7	.0730	0.59	0.58
1058	.0630	.00382	16.5	.0000	0.98	0.98
1059	.0040	.00382	1.0	.4859	0.97	1.01
Imaichi	.0210	.00309	6.8	.0000	0.92	0.90

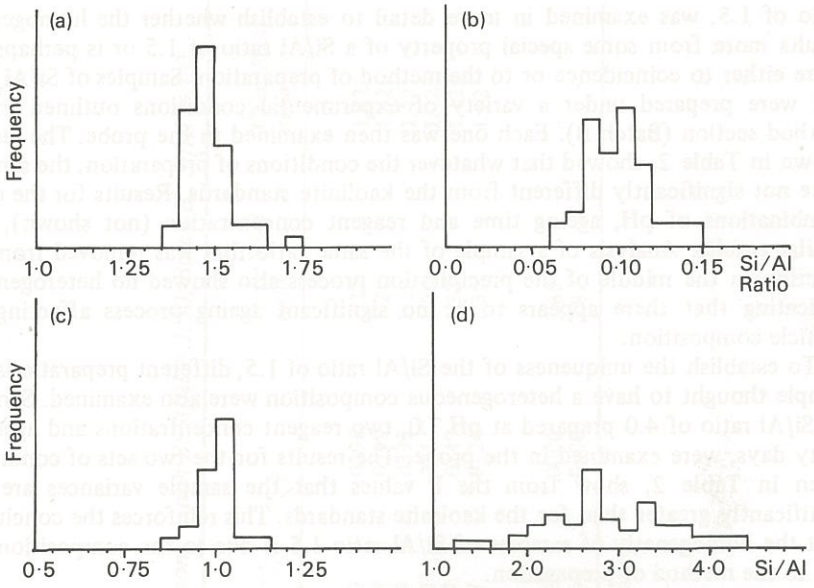

FIG. 1. Histograms showing distributions of (a) SiAl 60.40, (b) SiAl 20.80, (c) typical kaolinite standard, (d) sample C(2).

Properties of the natural silico-aluminas

The results of the analysis of natural allophanes are shown in Table 3. The distribution of the Tongariro and 1059 samples are not significantly different from those of the kaolinite standard even using the F test at the 95 per cent level, and can be considered homogeneous at the level of measurement used. The Kitakami sample appeared to be heterogeneous, but its F value of 3.1 was borderline. The Imaichi and 1058 clays have reproducibly broader distributions than the kaolinite standards, but it would be premature to conclude that these samples are heterogeneous, due to the possibility of small concentrations of feldspar present with a different Si/Al ratio. The Kitakami sample was also analysed for iron in the aggregates. Iron oxide was not removed from the sample prior to analysis as it was thought that the extraction of iron might affect the Si/Al ratio. The iron content varied randomly from 0 to 60 per cent from aggregate to aggregate with an average content of 11 per cent. Although the iron could be expected to differentially absorb some of the Al and Si radiation, the effect is unlikely to be large as the variance of the Kitakami sample was small.

Discussion

So far, it has been implicit that the term 'heterogeneous' refers to the particular particle fraction analysed in the microprobe. Examination of the sample by transmission electron microscopy (Plate I) suggested that for all the types of sample under study, the particles analysed were aggregates of much smaller primary particles. Furthermore, surface areas determined by nitrogen adsorption on the 2–5 μm fraction (not presented here) were similar to the areas of the unfractionated material, indicating that both are made up of large numbers of extremely small

primary particles. In this discussion the term 'primary particle' has been used because although the particles may not all be discrete but joined together by some means, it is possible to see particles as small as 3 nm diameter in the electron microscope, and to identify centres of high electron density in aggregates such as shown in Plate I. The primary particle is thus considered to be the smallest identifiable unit in the sample, having a diameter in the range 3–20 nm. The primary particle has been more clearly identified in natural allophanes, and has been quoted as having an average diameter of 50 nm (Kitagawa, 1971). An aggregate, which is the unit analysed in the probe and contains large numbers of primary particles, has a diameter of 1–5 μm.

Assuming that the aggregates analysed in the microprobe comprise many primary particles, the term heterogeneity takes on a different meaning. The heterogeneity no longer applies directly to the sample because it is not the primary particles that are being analysed, but instead is an indication of the composition of the aggregate. To take the extreme case, if the material is made up of equal amounts of pure silica and pure alumina primary particles mixed in a random fashion, and assuming each distribution is approximately normal, statistically no heterogeneity would be apparent in any aggregate containing more than about five hundred primary particles, above which the expected CV is less than 5 per cent. Thus the results for the samples of Si/Al ratio of 1.5 (Batch B) do not exclude the possibility that the smaller primary particles making up the aggregate may still differ in composition whilst the aggregates themselves appear homogeneous. Results that indicate heterogeneity, such as those for the co-hydrolysed samples of Batch C, show unambiguously that these samples cannot be homogeneous. Put simply, it is surprising that any heterogeneity can be found when the aggregates analysed contain many thousands of particles.

At least two possible explanations are apparent as to how aggregates can be both heterogeneous and contain large numbers of primary particles: (1) particles of different composition have some preferred mode of aggregation, or (2) the particles of either uniform or variable composition are joined in a matrix of variable composition, the matrix then determining the heterogeneity. Preferred aggregation is thought to be less likely, first because some simple arrangement such as Si- or Al-rich particles conglomerating separately would lead to a bimodal distribution, which has never been observed even for the co-hydrolysed samples. Secondly, any aggregation based on the effects of charge would be likely to bring the negatively charged silica-rich particles in contact with the positively charged alumina-rich particles, thus tending to reduce the heterogeneity. The matrix hypothesis is supported by the fact that amorphous silico-aluminas are difficult to disperse. Examination of electron micrographs taken at very high magnification on a Siemens 101 of one such sample (Plate II) using a decontamination device, supports the suggestion that the aggregate may consist of a continuous matrix. Further work to determine the structure of these aggregates is in progress.

When a comparison is made between the results of the simultaneous precipitation method used here (Table 1), the method involving co-hydrolysis of the alkoxides (Table 3), and the results of Rodrique and Declerk (see Fig. 2), it can be seen that the simultaneous precipitation method produces the least heterogeneity. The comparison is only qualitative firstly because the CVs of the raw data have been used in order to match up with Rodrique and Declerk's results and secondly because it is not possible to compare F values quantitatively. Furthermore, com-

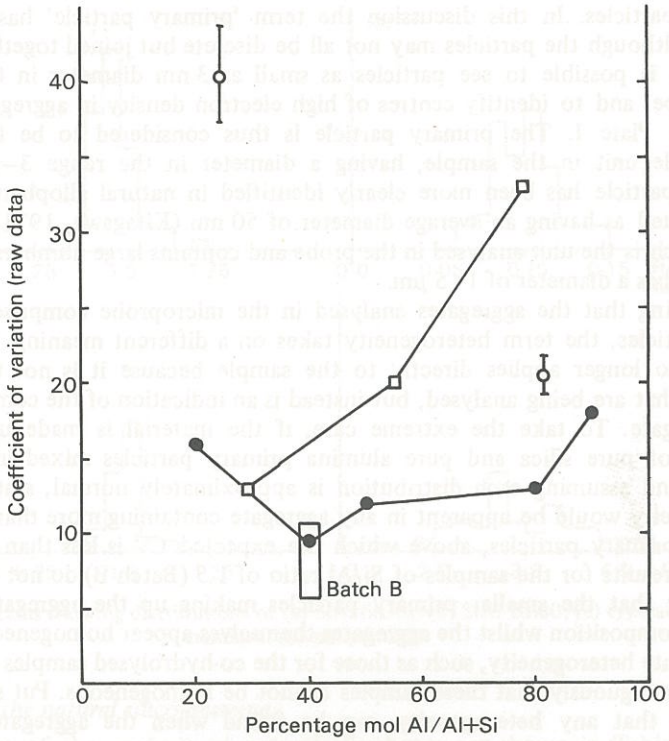

FIG. 2. Comparison of data with data of Rodrique and Declerk (1975). • Batch A, ○ Batch C, □ Rodrique and Declerk data.

parison of the CV of raw data, CV of transformed data, the variances and the F values, show rather different variations, although all are agreed on a minimum at Si/Al = 1.5. Although there is one sense in which this result may be spurious, namely that the number of particles in the alkoxide aggregates may be less, this is unlikely, since the BET nitrogen surface area of these samples was of the order of 150 m^2/g. This difference in heterogeneity between the simultaneous precipitation and alkoxide co-hydrolysis method is likely to be due to the use of completely different methods, although Table 2 shows how little difference variations within a method made to the simultaneously precipitated samples. It has been argued (Cloos *et al.*, 1969) that the structure of the alkoxide prepared samples is largely determined by the polymerised aluminium counter ions, whereas this would not be the case for our samples in which Na^+ is the counter ion. Samples prepared by these two methods might be considered to be different materials.

Although it has already been mentioned that this study is not definitive in that only the assignment of heterogeneity is unambiguous, and that a large error is involved when taking ratios of variances, the apparent homogeneity of samples of Si/Al ratio 1.5 (Batch B) under different preparative conditions is striking. The significance was enhanced by the preparation of heterogeneous samples of Si/Al ratio 4.0 (Batch B) which, under the same varied conditions, did not show any homogeneity (Table 2). A trend towards a minimum heterogeneity at Si/Al ratio- $\simeq 1.5$ can also be seen for Rodrique and Declerk's samples and our alkoxide

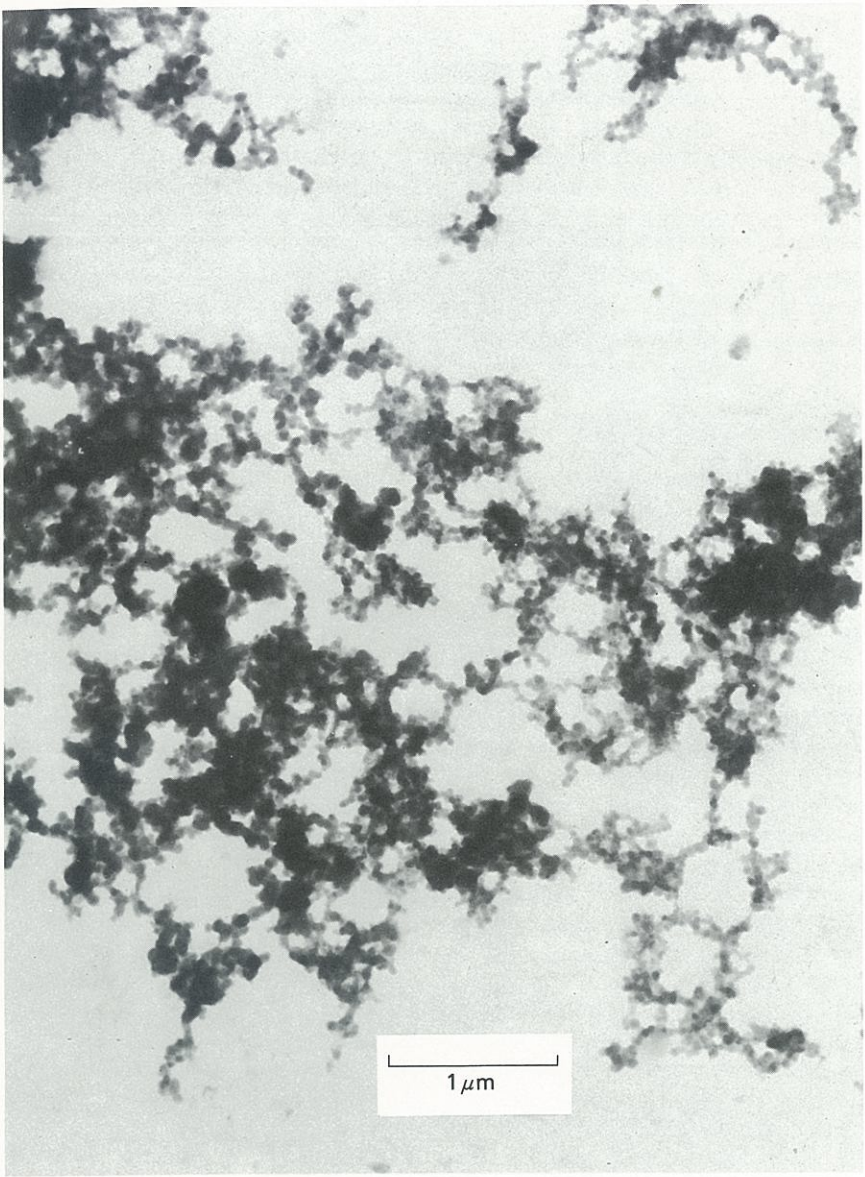

PLATE I. Electron micrograph of SiAl 60.40. Magnification x 30,000.

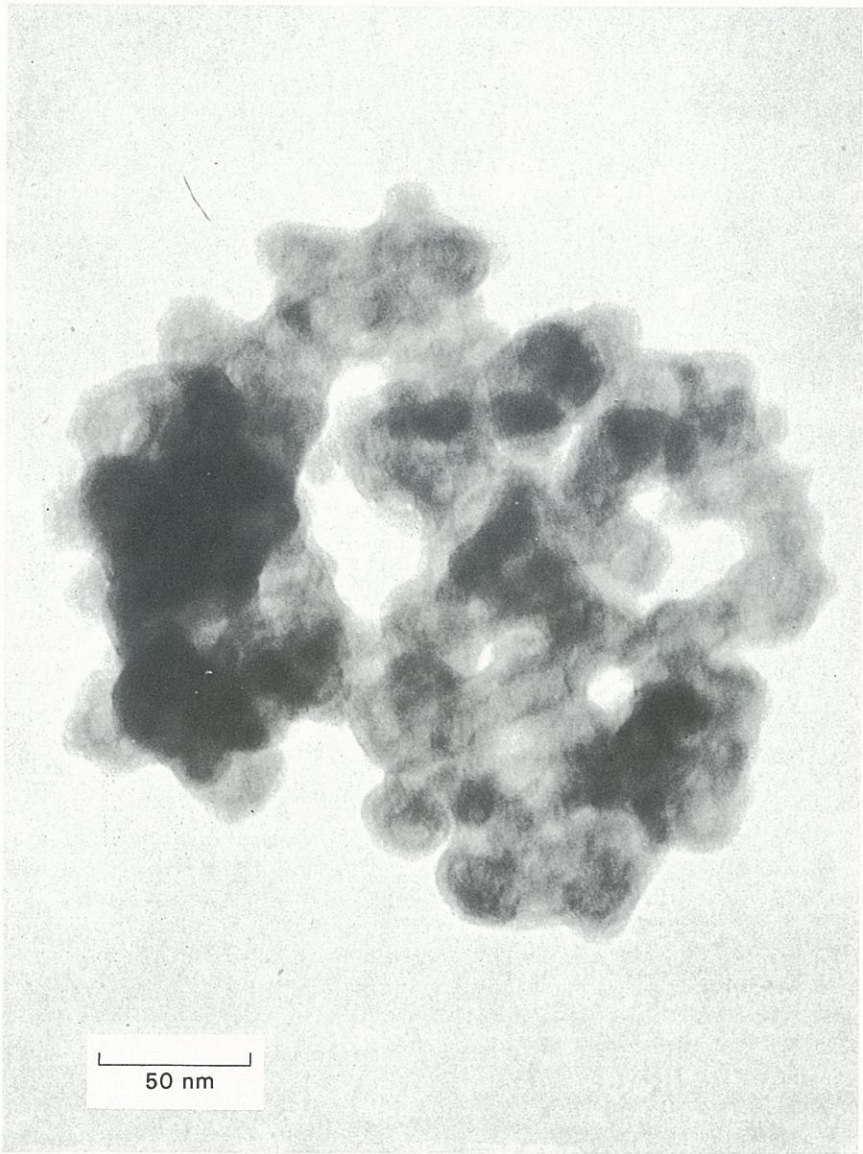

PLATE II. Electron micrograph at high magnification of SiAl 10.90. Magnification x 550,000.

prepared samples (Fig. 2), although in view of the comments made above on the difference in preparation, such agreement should be treated with caution.

The explanation for this apparent homogeneity can be sought in one of two areas. Either a structural explanation can be sought, or there is a statistical explanation in which the minimum around Si/Al 1.5 does not represent true homogeneity. In the accepted picture of the character of silico-aluminas, isomorphous substitution is considered to play a dominant role. This substitution is thought to extend up to a maximum at about Si/Al = 1.0 and thereafter de-mixing into separate phases is thought to occur. If this view is correct, one would expect the samples to be homogeneous up to Si/Al = 1, and thereafter be heterogeneous. However, the heterogeneity of the high Si samples of both Batch A and Batch C appears to show that this is not the case. An alternative explanation may lie in the preparative method used. Since it is known that the hydrolysis of silicate is slower than that of Al^{3+} (Wada and Kubo, 1975) at higher Si concentrations a random coating of SiO_2 may be deposited over the initial coprecipitate. The variations within such a coating could account for the variation at high Si content.

Two statistical explanations of the results are also possible. In the first place, the level of distinction between homogeneity and heterogeneity based on comparison of the samples with the kaolinite standards may be inappropriate due to the variation within the standards, the sensitivity of the F test to 'wild' observations, and to factors outside the scope of the statistics such as the difference in structure between kaolinite and amorphous materials and the difference in states of aggregation. It was noticeable that the F values were sensitive to the variance of the kaolinite standard which varied more than was anticipated. However, the consistency of the results on the synthetic samples prepared by the different methods (Batch B) and the wide range of F values found are sufficient for the F test to be thought usable. Furthermore, test analyses of two SiFe samples (50:50 and 20:80) which were known from DTA work to be heterogeneous showed highly significant F values (Batch A′). A second partial explanation may lie in the precision of the Si and Al counts. At the extreme ratios the precision on the smaller count will be poor thus contributing to the overall variation of the sample. The magnitude of this error can be calculated (Liebhafsky *et al.*, 1960). The standard counting error is at a minimum of 1.3 per cent at 70 per cent Si, rising to 1.5 per cent at 90 per cent Si and to 3.2 per cent at 10 per cent Si. The increase in error at low Si content is larger because the Si count rate is less than the Al count rate. Although this can be seen to be a contributing factor towards the heterogeneity at low Si content, it will not contribute at high Si content. Consequently, any explanation for the apparent homogeneity at Si/Al = 1.5 should be sought for in structural rather than statistical terms. At present the simplest explanation that can be offered is that a matrix formed by demixing of Al at high Al content, and secondary precipitation of Si at high Si content, lead to heterogeneity at all compositions except where a balance between these two effects occurs. This is presumed to be in the region Si/Al $\simeq$ 1.5.

With the natural allophanes, all the Si/Al ratios are within the range proposed by Wada (1967) in his structural model of allophane. The results on the five samples, of which two appeared homogeneous, lead to two conclusions. First, even though allophanes are well known to have a range of composition, individual allophanes can have an homogeneous composition throughout the sample. The presence of a small amount of feldspar in one of the homogeneous samples suggests either that its concentration was too small to be detected in the probe or that it has the same

Si/Al ratio as the allophane. Secondly, the observation that the other three allophanes appeared to be heterogeneous could mean either that the samples are really heterogeneous in the 1-5 μm range, or more likely, in view of the fact that two allophanes have already been found to be homogeneous, it is the impurities in the other three that are causing the heterogeneity. Indeed it is remarkable that two out of the five allophanes should be found to appear homogeneous, in view of the complexity of SiAl mixed oxides and of the soil system.

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Appendix

A preliminary investigation of the data revealed that some of the ratios were unusually large or small. The mean and standard deviation are extremely sensitive to such 'outliers' and consequently it is desirable to use more robust measures (Hampel, 1973). The estimators used were the mean and standard deviation after trimming. Such estimators are known to be more efficient.

The distribution of the Si/Al ratio for the kaolinite standards was investigated using histograms and probability plots (Wilk and Gnanadesikan, 1968) which indicated that the distribution was not symmetric but had a positive skewness. Also variance *versus* mean plots indicated that the standard deviation σ of the ratio was linearly related to the mean μ. Both of these occurrences seem reasonable if the Si and Al counts are assumed to follow a Poisson distribution, since then the Si/Al ratio obtained by waiting until the Al count reached a certain fixed number has a negative binomial distribution which is non-symmetric and in which the mean and standard deviation are related according to

$$\sigma = k\sqrt{\mu(1 + \mu)} = k\sqrt{[(\mu + \tfrac{1}{2})^2 - \tfrac{1}{4}]}$$

where k is a constant. For moderately large μ, σ is approximately linear in μ.

Since the aim is to compare variances, this dependence of σ on μ should be eliminated before valid comparisons can be made. The coefficient of variation proved to be a good qualitative measure of the difference between samples and as a more precise step a transformation was sought, which both stabilised the variance and gave reasonable normality. Normality is required to make the subsequent F-tests valid. Theoretical considerations indicated that the log transformation would be appropriate. This transformation was applied on the data and the transformed samples appeared approximately normal as judged by a Q-Q probability plot and D'Agostino's omnibus test for Normality (D'Agostino, 1971). Furthermore, variance *versus* mean plots indicated a stable variance. Thus the log transformation satisified both the requirements of stabilising the variance and giving reasonable normality and was used throughout the analysis.

Initially we intended to do bulk comparisons of the variances but Bartlett's test revealed a day-to-day instrumental variation thus making comparisons on samples taken far apart in time impossible. The variation of the kaolinite standards was also larger than was anticipated. It was assumed that this variation was due to factors affecting the standard and not the sample, such as particle thickness, and that it averaged to zero. To minimise this variation the standard variances have been

pooled for each day of analysis rather than using the standards analysed before and after each sample.

Comparisons were performed by an F test of the sample ratio to the pooled estimate of the standard variance and the results appear in Tables 1–3. The P values are the probabilities of exceeding the observed ratio under the null hypothesis of equal variance.

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