THE NATURE OF SOIL KAOLINS FROM INDONESIA AND WESTERN AUSTRALIA

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Abstract—Purified soil kaolins from Indonesia and Western Australia were characterized using analytical TEM, XRD, TGA and chemical analysis. The Indonesian kaolins, formed from tuff, consist of a mixture of tubular kaolin crystals with relatively low Fe concentrations and platy kaolin crystals with higher Fe concentrations. Western Australian kaolins also contained tubular and platy crystals but showed no systematic relationship of crystal morphology with Fe content. The coherently scattering domain (CSD) size of the Indonesian samples (5–6 nm for 001, *i.e. c* axis dimension) is remarkably consistent and is approximately half of the value for the Western Australian kaolins (9.7–13.4 nm), and both are much smaller sizes than values for the reference kaolins (15.6–27.8 nm). Coherently scattering domain sizes derived from the Scherrer equation are approximately twice the values obtained from the Bertaut-Warren-Averbach Fourier method but the results show the same pattern of variation. For the Indonesian, Western Australian and reference kaolins, the N_2-BET surface area ranges 59–88, 44–56 and 5–28 m^2/g; the dehydroxylation temperatures range 486–499, 484–496 and 520–544°C, the mean cation exchange capacities (CEC) are 9.4, 5.0 and 3.5 meq 100 g^{-1} and the surface densities of charge range 0.10–0.14, 0.08–0.10 and 0.04–0.12 C/m^2. The properties of the Western Australian kaolins and Indonesian kaolins differ substantially, but kaolins within each group have similar properties. These results suggest that soil kaolin properties may be characteristic of a particular pedoenvironment and that a systematic study of kaolins in different pedoenvironments is required.

Key Words—Analytical TEM, Soil Kaolin, XRD.

INTRODUCTION

Large proportions of the world's population and agricultural activity occur on red soils (ferruginous tropical soils, ferralitic soils, oxisols, ultisols) in the tropics. These soils commonly have a clay fraction consisting mostly of kaolinite, halloysite and other minerals of the kaolin subgroup. These soils have low pH, low available P and high P fixation capacity, Al toxicity, deficiencies of N, Ca, Mg, K and micronutrients, low cation and anion exchange capacities and poor soil structure. Many of these properties relate, directly or indirectly, to the dominant kaolin mineralogy (Schwertmann and Herbillon, 1992).

The mineralogical, chemical and physical properties of kaolin can vary greatly but the nature and occurrence of these variations for soil kaolin and the influence of kaolin properties on soil properties are largely unknown. The structure, chemical and surface chemical properties of soil kaolins are remarkably different from properties of standard reference kaolins. For example, the Fe concentration of soil kaolins (typically, $Fe_2O_3 \approx 2.5\%$) is consistently greater than that of mineralogical reference kaolins ($Fe_2O_3 \approx 0.5\%$). It is unknown whether the presence of Fe in soil kaolins causes the low degree of structural order (poor crystallinity) or whether it merely accompanies the increase in lattice disorder and

morphological complexity of soil kaolins (Stone and Torres-Sanchez, 1988).

The properties of kaolin may serve as indicators of pedogenic processes and soil environment. This research is focused on identifying the properties of soil kaolins from Indonesia and Western Australia and comparing them with the properties of reference kaolins. For convenience, the term kaolinite is applied to crystals with a platy morphology and halloysite is applied to crystals with cylindrical morphology. The term kaolin is used to refer to kaolinite and halloysite collectively.

MATERIALS AND METHODS

Representative soil kaolins were selected for the present study on the basis of studies conducted on soil kaolins from Indonesia and Western Australia (Siradz, 2002; Singh, 1991). Six Indonesian and seven Western Australian soil clay samples were chosen because they represented a wide range of Fe concentrations and both X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigation showed they contained no, or very little, other clay-size minerals. A group of reference kaolins was included for comparison.

The Indonesian kaolins are from soils developed on volcanic tuff in southern Sumatra, west and central Java. The kaolins from south western Australia are from *in situ* or colluviated deeply weathered Precambrian crystalline rocks, largely granite and gneiss with intrusions of dolerite dykes. The West Australian samples included in this study have been investigated

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previously using a variety of analytical procedures (Singh and Gilkes, 1992a; St Pierre *et al.*, 1992; Singh and Gilkes, 1995).

The reference kaolins were: Georgia Kaolin Co. kaolinites, #1460, #1261 and #MP5, API project 49 (API, 1951) kaolins #4 from Oneal Pit, Macon, Georgia and #9 from Canada Del Camino, Mesa Alta, New Mexico (obtained from Wards Reference Minerals); an English China Clay kaolin identified as from Blackpool Pit, and Goomalling (Western Australia) kaolinite from a lateritic pallid zone over granite.

The clay fractions were obtained from soils by dispersing the <2 mm fraction of the soil in 0.01 M NaOH and collecting the <2 μm fraction by sedimentation. Organic carbon was removed from the soils using H_2O_2 (Gee and Baulder, 1986). Free Fe oxides were removed from the kaolins (clay fraction) by a series of dithionite-citrate-bicarbonate (DCB) extractions following the procedure of Mehra and Jackson, (1960).

TEM and EDS

Well-dispersed samples of kaolins, on carbon film, were investigated using a Philips 430 transmission electron microscope operated at 300 kV. Energy dispersive spectra (EDS) for well-separated single crystals were collected at 500–1500 counts per second for 100 live seconds. Elemental compositions of these crystals were calculated using the thin film method (Lorimer, 1987; Jepson and Rowse, 1975). The k-factors used were derived from the spectra of standard minerals and confirmed by reference to the spectra of well characterized kaolinites.

X-ray diffraction

The XRD patterns of the kaolin samples were obtained using CuKα radiation with a Philips PW 3020 diffractometer equipped with a diffracted-beam graphite monochromator. The XRD patterns were interpreted with the aid of Winfit and XPAS analytical software allowing calculation of a range of crystallographic parameters, including coherently scattering domain (CSD) size and strain (Krumm, 1999; Singh and Gilkes, 1992b). Random powder patterns were obtained from 5–70°2θ to identify minerals other than clay minerals and to determine the degree of order of the kaolinite via the HB index (Hughes and Brown, 1979). Basally oriented clay samples were prepared on ceramic plates and XRD patterns from 3–30°2θ were obtained after various pretreatments to aid identification (Brown and Brindley, 1980). Accurate measurements of *d*-values were made using both quartz and octacosane as internal standards (Brindley and Wan, 1974). For size and strain analysis, XRD patterns of basally oriented clay samples were obtained using step scans with relatively long count times of 5 s/0.02°2θ step. Instrumental peak broadening was determined by the measurement of reflections of LaB_6 and octacosane.

Other properties

Cation exchange capacity (CEC) was measured following the method of Rayment and Higginson (1992), which uses 0.01 M silver thiourea solution at pH 4.7 to displace the exchangeable cations. Thermogravimetric analysis (DTGA) was carried out using a Perkin Elmer TGS-2 thermogravimetric system with ~8 mg samples heated in air at 10°C/min. Dehydroxylation temperature was taken to be the maximum of the first derivative trace. Surface area was measured using the N_2-BET method (Aylmore *et al.*, 1970) with a Micromeritics Gemini III 2375 surface area analyzer.

RESULTS AND DISCUSSION

TEM and EDS

Electron micrographs of representative kaolins are shown in Figure 1. These clearly demonstrate the small size and different morphologies of the crystals of the soil kaolins relative to standard kaolins. In contrast to the mineral standard kaolins which consist mostly of large euhedral pseudo-hexagonal crystals, the Indonesian kaolins consist of small poorly-defined tubes and subhexagonal plates whereas the Western Australian kaolin is mainly composed of small anhedral plates. Some Western Australian soil kaolins contain tubular crystals. The crystal size, as indicated by the width of crystals in micrographs, varies from 0.02 to 0.07 μm for the Indonesian kaolins, 0.06 to 0.12 μm for the Western Australian kaolins and is 0.37 and 0.18 μm for the GMP5 and G1460 reference kaolins.

Molar ratios Al/Si and Fe/Si of the kaolins as determined by X-ray fluorescence (XRF) on bulk samples and EDS on single crystals are shown in Table 1. The Fe concentration (% Fe_2O_3) for each sample is listed along with other properties in Table 2. The molar Al/Si ratio of bulk samples was generally <1.00 which may be due to Fe substitution for Al but the presence of minor amounts of contaminant quartz, observed in the XRD patterns, could also influence this value. A feature of the Indonesian and Western Australian kaolins is their high but variable Fe concentration. The average Fe concentration is 2.51% with a range of 1.52–3.72% Fe_2O_3 for the Indonesian kaolins, and 2.56% with a range 2.16–3.34% for the Western Australian kaolins. These Fe_2O_3 concentrations are similar to those from other tropical and highly weathered soils, *e.g.* Nigeria, 1.86%; Rwanda, 2.32%; Cuba, 1.52% (Mestdagh *et al.*, 1980).

The Indonesian kaolinites contain major amounts of a tubular mineral that does not expand on formamide treatment and may be tubular kaolinite (Churchman and Gilkes, 1989). However, for convenience, the term kaolinite is applied to crystals with a platy morphology and halloysite is applied to crystals with cylindrical morphology.
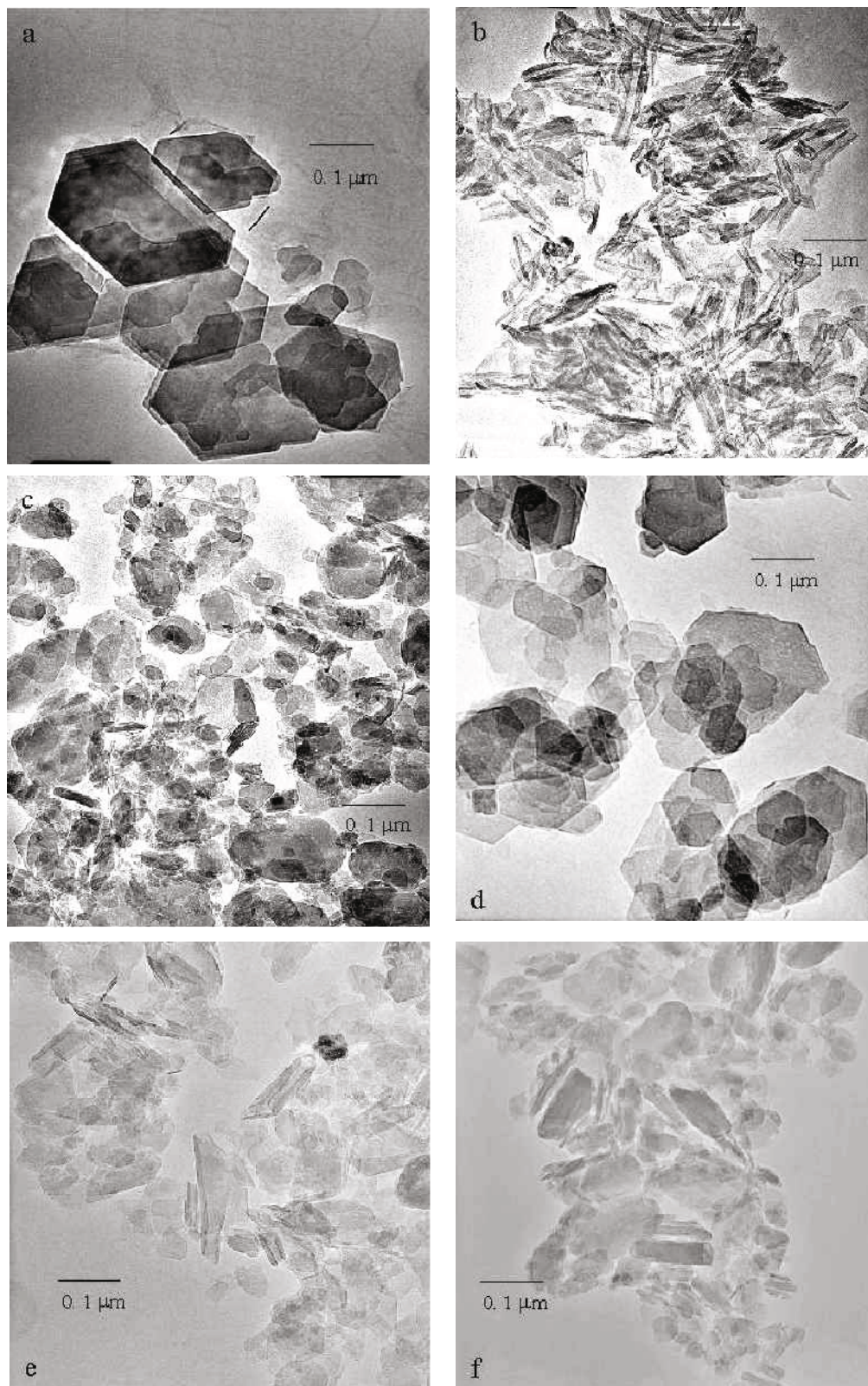
Figure 1. Electron micrographs of representative kaolins: (a) reference kaolin GMP5; (b) Indonesian kaolin B14; (c) Western Australian kaolin 175; (d) reference kaolin G1460; (e) Indonesian kaolin A11; and (f) Western Australian kaolin 239.

Table 1. Molar Al/Si and Fe/Si ratios of kaolin samples determined by XRF and EDS.

Sample	Al/Si			100 Fe/Si		
	XRF Bulk	EDS analysis Plates	Tubes	XRF Bulk	EDS analysis Plates	Tubes
Indonesian kaolins						
A11	0.938	0.981(19)	0.984(30)	5.73	4.4(5)	1.9(6)
A33	0.926	1.036(20)	0.973(28)	6.66	5.6(4)	2.1(4)
A42	0.974	1.035(13)	0.957(36)	4.60	6.1(6)	3.5(5)
B14	0.982	1.061(15)	1.042(21)	3.00	5.4(6)	2.6(3)
C51	0.970	0.961(11)	0.957(15)	4.32	5.5(7)	3.4(4)
C62	0.980	1.009(19)	0.985(28)	4.60	4.7(4)	3.8(4)
Western Australian kaolins						
124	0.995	0.988(17)	1.042(24)	3.82	4.0(6)	5.5(3)
150	0.981	0.969(14)	0.979(15)	4.29	6.2(5)	6.5(4)
167	0.984	0.996(23)	0.983(25)	4.29	5.6(4)	6.1(9)
169	0.987	0.996(41)	0.999(40)	4.41	6.1(8)	5.9(6)
175	1.002	0.967(18)	1.099(20)	3.88	2.7(4)	2.8(5)
235	0.960	0.984(15)	0.998(23)	4.86	6.4(8)	6.1(6)
239	0.936	0.962(26)	0.999(40)	5.84	6.3(7)	4.9(7)
Reference kaolins						
G1460	0.947	0.965(15)	n.p.	1.48	1.3(1)	n.p.
G1261	1.012	0.920(9)	n.p.	0.40	0.52(4)	n.p.
GMP5	0.939	0.989(12)	n.p.	0.68	0.5(1)	n.p.
New Mexico	0.941	0.925(16)	n.p.	0.76	0.96(16)	n.p.
Oneal Pit	0.957	0.973(20)	n.p.	0.68	0.60(8)	n.p.
CCBlk	1.042	1.051(6)	n.p.	0.72	0.60(8)	n.p.
Goomalling	0.976	0.937(8)	0.918(9)*	1.28	1.00(12)	0.92(16)*

* Laths rather than tubes

Table 2. Properties of soil and reference kaolin samples.

Kaolin	% Fe_2O_3	d-value 001 (Å)	% Tubes	HB Index	001 CSD size (nm) Scherrer	B.W.A.*	Strain %	Dehydroxylation Temp°C	CEC meq/100 g	N_2-BET m²/g	SCD C/m²
Indonesia											
A11	2.62	7.194	40−50	5.8	11.3	5.5	0.073	499	10.7	73	0.14
A33	3.72	7.210	<5	7.1	10.8	5.3	0.126	490	11.2	68	0.16
A42	2.66	7.218	40−50	6.8	13.7	5.7	0.130	495	6.1	59	0.10
B14	1.52	7.201	>95	4.5	8.1	5.0	0.185	497	10.1	88	0.11
C51	2.15	7.262	60−70	4.1	10.6	5.3	0.067	486	8.8	n.d.	n.d.
C62	2.54	7.191	50−60	5.3	10.3	6.0	0.122	486	9.5	76	0.12
Western Australia											
124	2.16	7.195	<5	5.8	24.4	11.2	0.107	488	5.2	56	0.09
150	2.48	7.286	<5	5.5	19.3	11.1	0.097	496	4.9	47	0.10
167	2.43	7.211	<5	5.6	21.0	10.5	0.101	492	5.0	49	0.10
169	2.53	7.211	<5	6.1	23.4	9.7	0.177	488	4.2	50	0.08
175	2.23	7.193	<5	6.2	27.7	11.9	0.081	488	5.4	55	0.10
235	2.81	7.205	<5	5.0	23.3	13.4	0.090	488	4.4	44	0.10
239	3.34	7.193	<5	4.8	21.0	9.5	0.111	484	4.8	55	0.08
Reference											
G1460	0.89	7.148	0	18.9	26.6	15.6	0.094	520	3.2	25	0.12
G1261	0.25	7.160	0	32.6	43.4	17.1	0.099	531	3.9	10	0.38
GMP5	0.42	7.132	0	34.2	47.6	26.8	0.124	546	0.4	5	0.07
New Mexico	0.43	7.148	0	60.5	43.1	16.0	0.078	554	4.6	13	0.34
Oneal Pit	0.41	7.142	0	19.8	32.2	19.0	0.123	531	11.7[†]	16	0.70[†]
CCBlk	0.42	7.160	0	26.3	48.8	27.8	0.036	540	0.5	11	0.04
Goomalling	0.75	7.173	0	5.9	20.8	16.0	0.080	530	3.5	28	0.12

n.d. not determined due to lack of sufficient sample
* Bertaut-Warren-Averbach method
[†] The high CEC (and SCD) of the Oneal Pit reference kaolin is probably due to significant quantities of smectite present in the sample

For Indonesian kaolins the amount of halloysite present is inversely related to the amount of Fe in the bulk clay (Table 2). Thus A33 with 3.72% Fe_2O_3 contains almost no crystals with tubular morphology, while B14 with 1.52% Fe_2O_3 contains almost no plates; other samples lie between these extremes both in Fe concentration and tube abundance. The Western Australian samples consist of mostly subhedral to rounded platy kaolinite with smaller numbers of elongate laths and tubes, displaying a continuum of sizes and shapes between plates, laths and tubes. The reference samples consist predominantly of hexagonal plates of kaolinite, although the Goomalling pallid zone kaolin also contains elongated laths and halloysite.

The elemental compositions of the individual crystals with distinct morphologies were determined by EDS in the TEM. For each of the soil kaolin samples, 50 kaolinite plates and, where present, 50 halloysite tubes or laths were analyzed by EDS. In most of the reference samples the dominant morphology was platey, so only plates were examined. The average molar Al/Si and Fe/Si ratios for each sample and morphology are presented in Table 1. For the Indonesian kaolins the halloysite tubes contain considerably less Fe than the plates. The tubes and plates have average Fe/Si molar ratios of 0.029 and 0.053. This result is consistent with those of Tazaki (1982), who demonstrated that tubular halloysites occurring with Fe containing crinkly film and spheroidal halloysites in weathered volcanic ash were nearly free of Fe. Similarly, Kawano *et al.* (1997) demonstrated the progressive development of halloysite-like curled domains with decreasing Fe concentration in the early stages of weathering of volcanic glass. The Al concentration of tubes is slightly greater than that of plates, suggesting that there is isomorphous substitution of Fe for Al. The Western Australian soil samples show no systematic difference in Fe concentration with morphology of kaolin crystals, which is consistent with the findings of an earlier study (Singh, 1992).

The variation in the Fe content of the single crystals in each sample is indicated by the values of standard deviation in Table 1. The standard deviation in the Fe/Si ratio for reference kaolins is 7−16% and a large part of this is due to the instrumental variability in the Fe measurement as the EDS counts for $FeK\alpha$ were typically several hundred and several to tens of thousands for $SiK\alpha$. The standard errors of Fe/Si for the reference kaolins are 2.5−5%. The standard error of the ratios Al/Si and Fe/Si were determined from the relationship given in equation 1, derived from the first-order terms in the Taylor series expansion of the ratio *a/b* (where *a* and *b* are the number of counts above background for each element).

$$SE(a/b) \supset \sqrt{\frac{b^2(SEa)^2 \quad a^2(SEb)^2}{b^4}} \qquad (1)$$

where $SEa = \sqrt{a}$ and $SEb = \sqrt{b}$.

The standard deviations of the ratios for soil kaolins are typically 9−16% for Fe/Si and 2% for Al/Si and the associated standard errors are 1.5% and 0.4%.

The quite small range of Fe concentrations in the bulk soil kaolins (*i.e.* 100 Fe/Si 3.00−6.66) is mostly associated with quite small differences in the compositions of individual crystals (*i.e.* 100 Fe/Si 2.7−6.4 for plates, 1.9−6.5 for tubes) and is remarkable considering the very great differences in the total Fe content of the clay fraction before free Fe was removed by DCB treatment ($\approx 1-10\%$ Fe_2O_3). It would appear that the Fe content of kaolin minerals in soils is not directly related to the Fe content of the soil, as was also found by Muller and Calas (1989) in their study of kaolins from some African tropical soils. This consistent result may indicate that the kaolin structure readily accommodates amounts of Fe equivalent to 100Fe/Si of 3.00−6.66, but little further substitution will occur, irrespective of the Fe content of the soil. This level of substitution of Fe^{3+} for the smaller Al^{3+} ion may sufficiently expand the size of the octahedral sheet in the kaolin structure so as to better accommodate the larger attached tetrahedral sheet (Bailey, 1989).

Examination by EDS in the TEM of high-contrast particles showed them to be small crystals of TiO_2, probably anatase (Weaver, 1976). These particles are present in most of the samples, although they were more abundant in the Western Australian samples. One Indonesian sample, C62, also contained traces of Fe sulfide with an Fe:S composition ratio <1. The Fe sulfide in the sample was probably formed during the DCB extraction to remove free Fe oxides.

X-ray diffraction

The XRD patterns showed the soil clay samples to consist of kaolin with minor amounts of quartz and occasionally very minor amounts of anatase. The mineral kaolins were similar to the XRD pattern of the Oneal pit sample also showing the presence of minor amounts of smectite. The Hughes and Brown (HB) index of crystallinity was calculated from random powder patterns of the kaolin samples (Hughes and Brown, 1979). The HB index is a convenient measure of crystallinity or degree of order in soil kaolins as the Hinkley (1963) index cannot be determined due to the absence of discrete 110 and 111 reflections. The HB index for Indonesian kaolins (range 4.5−7.1, mean 5.3) is similar to the HB index of soil kaolins from Western Australia (range 3.1−10.7, mean 5.4), Nigeria (range 4.3−13.7, mean 8.0), and Queensland (range 3.4−8.6, mean 5.9) (Singh and Gilkes, 1992a; Hughes and Brown, 1979; Koppi and Skjemstad, 1981). Several workers have suggested that high Fe concentration is inversely related to structural order (Mestdagh *et al.*, 1980; Brindley *et al.*, 1986). This does not apply to these soil kaolins as there is no single relationship for all kaolins or for any of the three subsets

of kaolins (Figure 2). The Indonesian sample A33 which has the highest Fe concentration has the highest degree of order (HB index = 7.1), and sample B14 with the lowest Fe concentration, has a low degree of order (HB index = 4.5). Indeed for Western Australian kaolins there is a tendency for crystallinity (HB Index) to decrease with increasing Fe content and a reverse trend for Indonesian kaolins. Hughes and Brown reported that their index is very sensitive to the presence of disordered kaolin with the measured HB index of Pugu K kaolinite falling from 44.0 to 11.2 with the addition of only 20% of Eureka halloysite. Thus the HB index is smallest for the Indonesian kaolins with the most halloysite, and as the disordered halloysite contains less Fe than kaolinite there is a negative relationship between Fe concentration and HB index. Mestdagh *et al.* (1980) did not determine the halloysite content of their samples so it is not possible to determine if their kaolins of low crystallinity contained halloysite. The Goomalling pallid zone kaolin also has a low HB index, due in part to the presence of halloysite while having a relatively low Fe concentration.

The accurate measurement of the spacings of the 001 reflection was made using octacosane and quartz as internal standards for samples oriented on ceramic plates. The basal spacings of the Indonesian kaolins (mean 7.216 Å) are similar to those of Western Australian kaolins (mean 7.206 Å) and all are slightly greater than those of reference kaolinites (mean 7.152 Å), as expected for Fe-containing kaolins. The apparent increase in basal spacings of kaolinite following broadening of the 001 basal reflection and change of the interference function due to small crystal size was predicted by Trunz (1976), and has been observed by Koppi and Skemsted (1981) for Queensland kaolinite. No shift in the 001 spacings was observed for the kaolins after treatment with glycerol, indicating that interstrati-fied smectite was not present in detectable amounts. The tubular mineral present in these samples was not expanded by formamide treatment and thus can be classed as tubular kaolinite using the criteria of Churchman and Gilkes (1989).

Basal spacings and the size of coherently scattering domains (CSD) estimated from the 001 reflections of the kaolins via the Scherrer equation (Klug and Alexander, 1974) are presented in Table 2. The CSD sizes of the Indonesian kaolins (mean 10.8 nm) are considerably smaller than those for the Western Australian kaolins (mean 22.9 nm). When all kaolins are considered together there seems to be an inverse relationship between CSD size and Fe content but this is spurious because the data report on three different populations of samples. For the Western Australian kaolins, CSD size does appear to decrease systematically with increasing Fe_2O_3 concentration. There is no similar relationship for the Indonesian or reference kaolins.

The CSD size calculated from the Scherrer equation is an approximation as it assumes all crystals in the sample to have the same CSD size. In practice, different distributions of sizes will affect the value of CSD obtained (Drits *et al.*, 1997). Use of Fourier methods to analyze diffraction data may overcome this deficiency. Winfit (Krumm, 1999), a Windows program for XRD analysis was used to determine crystal data using full profile shape analysis. Fourier analysis (after Bertaut, 1950; Warren and Averbach, 1950) of Pearson-VII functions fitted to the 001 and 002 reflections of kaolins was used to determine strain-corrected CSD sizes and lattice strain (Table 2). Lattice strain data from Winfit for all kaolins are also given in Table 2 and there seem to be no systematic differences between groups of samples. These values of strain (0.036−0.18%) are small and are much smaller than values (0.8−2.06%) reported for illite and illite-smectite from sedimentary rocks (Árkai *et al.*, 1996; Drits *et al.*, 1998; Eberl *et al.*, 1998). Amigo *et al.* (1994) found no internal strain in the 001 direction of kaolins they examined. We expected that there may have been a positive relationship between crystal size and strain or perhaps a negative relationship between Fe content and strain due to better fitting of the octahedral and tetrahedral sheets releasing strain. However, strain values for soil kaolins do not appear to be systematically related to other properties, *e.g.* coherently scattering domain size or Fe concentration (Figures 3 and 4).

The CSD size for the Indonesian samples (5−6 nm for 001, *i.e.* *c* axis dimension) is remarkably consistent and is approximately half of the value for the Western Australian kaolins (9.7−13.4 nm), and much smaller than for the reference kaolins (15.6−27.8 nm). The TEM micrographs (Figure 1) show that this is also true for the width and length dimensions of the kaolins, which are approximately orthogonal to the *c* axis. The values of CSD size obtained from the Scherrer equation are
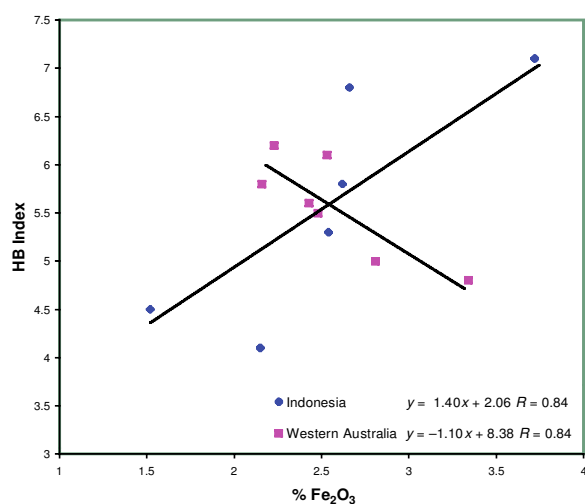

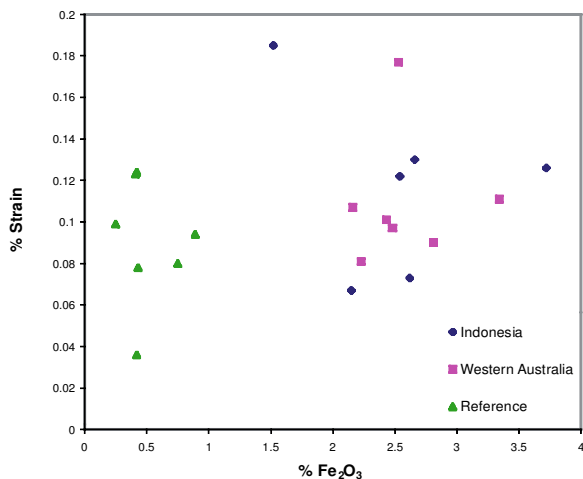
Figure 2. HB Index *vs*. Fe concentration for soil kaolins.
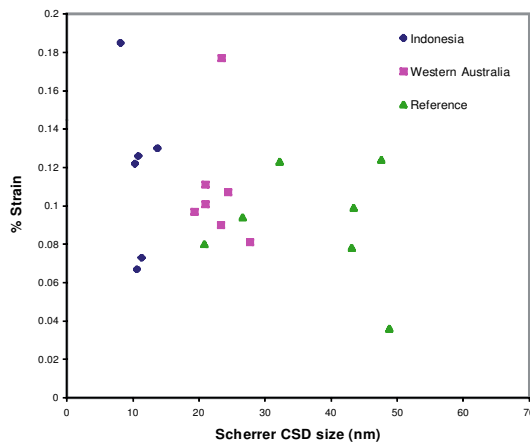
Figure 3. % Strain *vs*. Fe concentration.

Figure 4. % Strain *vs*. Scherrer CSD size.

approximately twice the values obtained from the Warren and Averbach method but the results obtained show the same pattern described above. The sizes (CSD) of the Western Australian kaolins and Indonesian kaolins are similar within each group but differ systematically between groups indicating that kaolin size and morphology are characteristic of a particular pedoenvironment. Amigo *et al.* (1994) used the Bertaut-Warren-Averbach method to determine the CSD size of kaolins and obtained values of 7.3–25 nm for Cretaceous kaolins and values of 77 and 113 nm for two industrial kaolins.

An alternative application of the Bertaut-Warren-Averbach method in which Fourier coefficients are obtained directly from the shape of the XRD peaks, without prior profile fitting, was also used to determine CSD sizes. The alternative program, Mudmaster (Eberl *et al.*, 1996), yielded similar results to Winfit, *c.f.* kaolin

A33, 5.3 *vs*. 5.3 nm; kaolin #150, 11.0 *vs*. 11.1 nm and kaolin G1261, 17.3 *vs*. 16.4 nm. There are assumptions made in using the Bertaut-Warren-Averbach technique which other authors (Lanson and Kübler, 1994), suggest may lead to inaccuracies particularly in cases where CSD sizes (thicknesses) are small (<5 nm). The CSD sizes obtained for the Indonesian kaolinites, ~5–6 nm. Árkai *et al.* (1996) found that different XRD methods; Bertaut-Warren-Averbach, Scherrer, Voigt and variance, yielded substantially different values. However, trends were well established by all methods including measurement by TEM.

The CSD size distribution of the samples was investigated using Mudmaster as the fitting of Pearson-VII functions to peak shapes used in Winfit artificially determines the domain size distribution. All the samples investigated had approximately log-normal
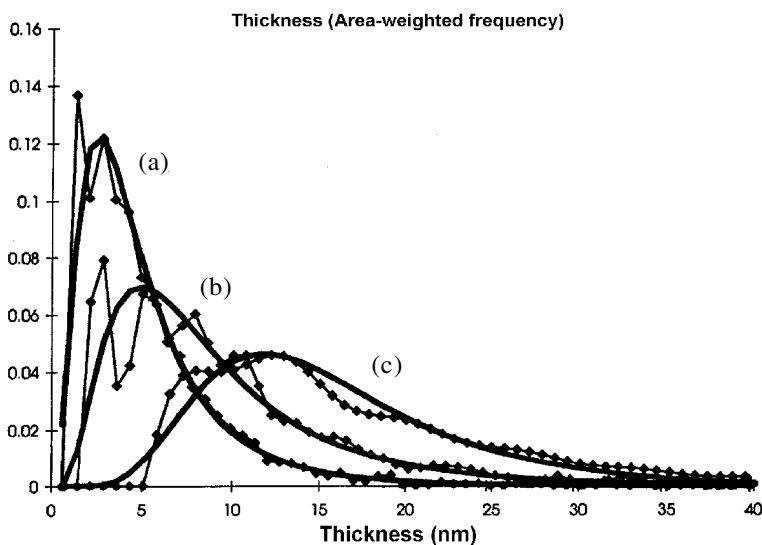

Figure 5. Relative distributions of CSD sizes for typical kaolins: (a) Indonesian kaolin A33; (b) Western Australian kaolin 175; and (c) reference kaolin G1460.

CSD size distributions (Figure 5). Log-normal size distributions are usual for clay minerals and have been reported for kaolins, illite and illite-smectite using Fourier methods of analysis (Eberl *et al.*, 1990; Drits *et al.*, 1998; Eberl *et al.*, 1998).

Other properties

The N_2-BET surface area measurements of the kaolins show that the surface area of the Indonesian kaolins is large and tends to decrease from 88 m^2/g to 59 m^2/g, generally with increasing Fe concentration. The surface areas of the Western Australian kaolins are smaller and largely remain constant with increasing Fe concentrations at 44−56 m^2/g. The increased surface area is consistent with the smaller crystal size of the Indonesian kaolins. The reference kaolins have much smaller surface areas of 5−28 m^2/g. Surface areas calculated from the CSD sizes of the kaolins, calculated from the Scherrer equation, yield values of 54−91 m^2/g, 27−38 m^2/g and 15−36 m^2/g for Indonesian, Western Australian and reference kaolins, similar to the values provided by N_2-BET surface area measurements. Surface areas calculated from the CSD sizes of the kaolins, calculated from the Bertaut-Warren-Averbach method, yield values of 123−148 m^2/g, 55−78 m^2/g and 28−47 m^2/g for Indonesian, Western Australian and reference kaolins. These values are larger than the values provided by N_2-BET surface area measurements. The calculated surface areas do not consider the edges, shapes or disorder of the kaolin crystals, factors which could be significant in determining the surface areas of these soil kaolins.

Values of dehydroxylation temperature, taken as the maximum of the DTGA trace, for Indonesian kaolins (486−499°C) and West Australian kaolins (484−496°C) are similar and are 20−50°C lower than values for reference kaolins (520−544°C). Figure 6 shows that there is no systematic variation in dehydroxylation temperature with degree of order for the soil kaolins. The reduction in the dehydroxylation temperature for soil kaolins relative to mineral kaolins is probably mostly a consequence of small crystal size and lower degree of order and has been observed previously (Singh and Gilkes, 1992a; Smykatz-Kloss, 1975). Other factors are also likely to be involved as Goomalling kaolin closely resembles Western Australian soil kaolins with respect to CSD size and strain values but the dehydroxylation temperature is 40°C higher. However, this sample does have a smaller surface area than the Western Australian soil kaolins and thus more closely resembles the other reference kaolins.

The CECs for the Indonesian kaolins (mean 9.4 meq 100 g^{-1}, range 5.2−12.9 meq 100 g^{-1}) are approximately double those for the Western Australian kaolins (mean 5.0 meq 100 g^{-1}, range 2.91−7.62 meq 100 g^{-1}) which are greater than the CECs for the reference kaolins (typically 3.5 meq 100 g^{-1}, range 0.4−4.6 meq 100 g^{-1}, (excluding the sample from the Oneal Pit which contained smectite)). Cation exchange capacity also increases with Fe concentration for the Western Australian kaolins and with tube concentration (and hence inversely with Fe concentration) for the Indonesian kaolins. The CEC appears to be primarily related to crystal size. Koppi and Skemsted (1981) reported values of 9.3−30.5 meq 100 g^{-1} for Queensland soil kaolins and Ma and Eggleton (1988) reported values of 16−34 meq 100 g^{-1} for thin (15 nm) poorly-ordered kaolins of secondary origin. The CEC increases with increasing surface area as measured by N_2-BET (Figure 7). The relationship obtained for CEC *vs.* surface area is of relatively high statistical significance ($R^2 = 0.74$) and is not improved by the inclusion of other variables, such as CSD size, Fe content or disorder into multivariate relationships.
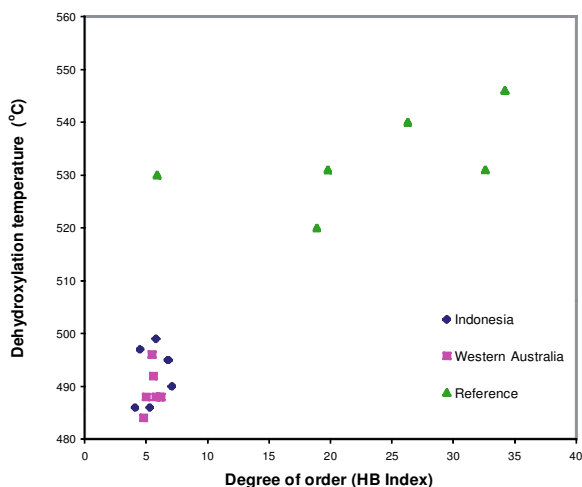

Figure 6. Dehydroxylation temperature *vs.* degree of order (HB Index) for all kaolins.
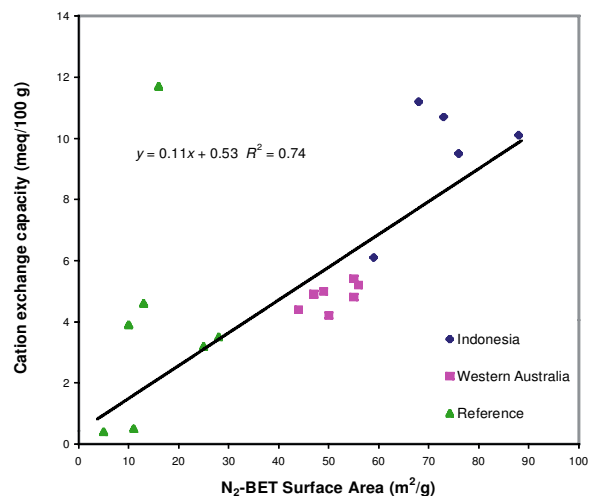

Figure 7. CEC *vs.* surface area.

The surface charge density (SCD) of the kaolins calculated from their CEC and surface area (van Olphen, 1963) ranges from $0.10-0.16$ C m^{-2} for all Indonesian kaolins, $0.08-0.10$ C m^{-2} for the Western Australian kaolins and $0.043-0.38$ C m^{-2} for the reference kaolins. The values for the soil kaolins are comparable with those found by Bolland *et al.* (1976) of $0.072-0.14$ C m^{-2} and Newman (1987) of $0.15-0.2$ C m^{-2} for kaolinite and are similar to values for moderate to high-charge smectites. The slightly higher values of CEC for halloysites of tubular morphology are probably caused by some exchangeable cations residing as salt in the tubes (Ma and Eggleton, 1998) and this may also explain the slightly higher SCD values found for the Indonesian kaolins. The wide range of values for the reference kaolins possibly reflects their wide variety of origins and impurities.

CONCLUSIONS

Several mineralogical, chemical and physical properties of soil kaolins from Indonesia, Western Australia and reference mineral kaolins have been determined. The influence of structural Fe on the properties of the kaolins remains unclear. The kaolins contain small amounts of Fe and cause and effect relationships of Fe concentration with a poor degree of order and small crystal size could not be identified. The low concentration of Fe in kaolin, the complexity of soil from which the kaolins were obtained and the effects of preconcentration and extraction methods might also need to be considered.

For the Indonesian kaolins, the high Fe concentration samples generally consist of crystals with a platy morphology and the low Fe concentration samples consist of crystals with tubular morphology; most samples have intermediate Fe concentrations and consist of a mixture of platy and tubular crystals. The statistical relationships of properties with Fe concentration of the bulk sample can therefore be misleading as the Fe concentration of the bulk sample is largely a function of morphological composition of the kaolins.

The small range of Fe concentrations in the bulk soil kaolins and small differences in the compositions of individual crystals is remarkable compared to the large differences in the total Fe content of the clay fraction from which they were obtained. It would appear that the Fe content of kaolin minerals in soils is not directly related to the Fe content of the soil.

Although different methods of determining the thicknesses of crystals yield different results and each method has apparent weaknesses, the trends revealed are similar. The CSD sizes of the Western Australian kaolins and Indonesian kaolins are similar within each group and suggest that kaolin morphology is characteristic of a particular pedoenvironment. Indeed this apparent capacity of kaolin minerals to provide a distinctive finger-print for a particular pedoenvironment may provide a useful tool in the study of transported materials and paleosols.

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