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KAOLINITE : NMF INTERCALATES

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Abstract—Bulk and size-fractionated kaolinites from seven localities in Australia as well as the Clay Minerals Society Source Clays Georgia KGa-1 and KGa-2 have been studied by X-ray diffraction (XRD), laser scattering, and electron microscopy in order to understand the variation of particle characteristics across a range of environments and to correlate specific particle characteristics with intercalation behavior. All kaolinites have been intercalated with N-methyl (NMF) after pretreatment with hydrazine hydrate, and the relative efficiency of intercalation has been determined using XRD. Intercalate yields of kaolinite : NMF are consistently low for bulk samples that have a high proportion of small-sized particles (i.e., <0.5 μm) and for biphased kaolinites with a high percentage ($>60\%$) of low-defect phase. In general, particle size appears to be a more significant controlling factor than defect distribution in determining the relative yield of kaolinite : NMF intercalate.

Key Words:—Defect distribution, Intercalates, Kaolinite, N-methyl formamide, Particle size.

INTRODUCTION

There has been a steady growth of interest in the formation and structure of kaolinite intercalation compounds since the first observations that certain inorganic salts could penetrate the interlayer of kaolin group minerals (Wada, 1959a, 1959b). The extensive range of compounds known to intercalate with kaolinite include 1) inorganic salts such as potassium acetate (Wada, 1961) and sodium chloride (Thompson *et al.*, 1992); 2) organic salts (Theng, 1974) and, more recently, long-chain fatty acids (Sidheswaran *et al.*, 1990); and 3) small, highly polar organic molecules (e.g., DMSO, formamide, acrylamide, and urea as in Olejnik *et al.*, 1968). Most of these species can be intercalated directly, but some require the use of an entraining agent such as hydrazine, DMSO,or ammonium acetate. In addition to the above broad categories of intercalates, a number of larger, polar organic molecules (e.g., *n*-octylamine, benzadine, and glycerol) can also be intercalated by the use of such entraining agents (Weiss *et al.*, 1963). Wada (1961) also demonstrated that halloysite, which itself can be considered a kaolinite : H_2O intercalate, was significantly more reactive with respect to intercalation than kaolinite. Subsequently, a larger number of species were shown to form stable halloysite intercalates (Carr and Chih, 1971) than that for kaolinite. More recent work on kaolinite 8.4 Å hydrate has shown that this is also more reactive than kaolinite and readily produces intercalates with molecular species which do not react with kaolinite (Costanzo and Giese, 1990).

To date, the principal applications of kaolinite intercalates have been twofold. Firstly, the formation of intercalation compounds to distinguish the different types of clays: china clays, ball clays and fire clays (Fernandez-Gonzalez *et al.*, 1976). Secondly, the quantitative formation of kaolinite intercalate (Wada and Yamada, 1968; Gonzalez Garcia and Sanchez-Camazano, 1968) has been used to discriminate kaolin-group minerals from other minerals via powder X-ray diffraction (XRD), e.g., chlorites and serpentines which display XRD peaks at ~7 Å, the basal spacing for 1:1 layer silicates. In each of these applications, the degree of intercalation by a given intercalant or process is crucial to its success. The intercalation rate for reaction of N-methylformamide (NMF) in (aqueous and non-aqueous) solution with kaolinite has been described by Olejnik *et al.* (1968 and 1970) and a general discussion of intercalation mechanism(s) has been presented for large, polar molecules. This study examines the variability of intercalation yield for the kaolinite-NMF reaction for nine kaolinites with various microstructural and morphological properties. These properties not only differ from one bulk kaolinite sample to another, but also differ between separate particle size fractions within a given kaolinite. The kaolinite-NMF intercalation is well known and serves as a reference point for other intercalation reactions with highly polar molecules.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Analytical Reagent-grade hydrazine hydrate and NMF were used for all intercalation experiments. Samples of kaolinite were chosen from both commercial

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and undeveloped Australian deposits covering both residual and sedimentary types of geological environments. In addition, two well-characterized Source Clays, Georgia kaolinite KGa-1 and KGa-2, from the Clay Minerals Society repository were included as reference materials. Both bulk and size-fractionated kaolinite samples were used in this study.

Particle size fractionation

Well-dispersed kaolinite samples were prepared by adding 100 ml of ultra-pure water to 5 g of kaolinite and then placed in an ultrasonic container for 15 min. Three ml of 10% Calgon solution were added to this slurry as an antiflocculant. The aqueous suspension was then separated into 6 size fractions: >2 μm, 0.6–2 μm, 0.5–0.6 μm, 0.4–0.5 μm, 0.3–0.4 μm, and <0.3 μm following the method outlined by Tanner and Jackson (1947). The study by Mackinnon *et al.* (1993) describes a method for estimation of the size range(s) for each fraction using a laser scattering technique. Each size fraction was dried in an oven at 120°C and subsequently weighed on a Metler balance to provide a value for the wt. % fraction of the bulk sample. In general, only data for three size fractions (>2 μm, 0.5–0.6 μm and 0.3–0.4 μm) are presented in this paper.

Synthesis

Preparation of kaolinite-NMF intercalation compounds. For this investigation, the intercalation of kaolinite by NMF was chosen for several reasons: 1) Previous intercalation studies have used NMF (e.g., Olejnik *et al.*, 1970); 2) NMF has a relatively high intercalation yield (e.g., >50%) for most kaolinites; 3) kaolinite : NMF intercalate is amenable to formation by vapor phase exposure, which is a much cleaner and more reproducible synthesis than immersion in liquid NMF (Thompson and Cuff, 1985); and 4) kaolinite : NMF intercalate is very stable at room temperature and gives a well-ordered intercalate with sharp basal reflections. The kaolinite was pretreated with hydrazine hydrate as this is known to enhance the intercalate yield (Theng, 1974; Thompson, 1984).

Five ml of hydrazine hydrate solution were pipetted onto 0.5 g of kaolinite in a small petri dish, allowed to soak into the clay for a few seconds and then stirred thoroughly with a spatula. The resulting kaolinite-hydrazine hydrate intercalate was spread out over the surface of the petri dish and dried in an oven at 60°C for 1 h. The dry kaolinite-hydrazine hydrate intercalate was scraped off the surface of the petri-dish and gently crushed to form a fine powder. Each dish of powder was then exposed to NMF fumes overnight (~15 hr) in an oven at 60°C. For each sample, the time period for reaction with NMF was constant. A guide to the degree of intercalation was obtained for each sample by comparison of powder XRD peak heights. XRD mounts were examined between 7° and 13° 2θ to determine the approximate percentage of kaolinite intercalated with NMF via the formula (Theng, 1974):

$$\text{Intercalation ratio} = \frac{\text{Intensity (001) Intercalate}}{\text{(Intensity (001) kaolinite} + \text{Intensity (001) Intercalate)}}$$

Characterization

X-ray powder diffraction patterns were collected from random mounts of all starting materials on a Siemens D5000 goniometer with graphite monochromater and Cu Kα radiation operating at a scan speed of 0.5° 2θ per minute with a step size of 0.02° 2θ. For each kaolinite sample, XRD peak parameters were used to describe the structural state of the mineral. Thus, both the Hinckley index (HI; as in Hinckley, 1963) and the defect parameters of Plançon and Zacherie (1990) were determined. Definitions for these defect parameters and the proposed types of defects in kaolinites are based upon models derived from careful analysis of well-characterized kaolinites by Plançon *et al.* (1989). The low-defect model assumes that the condition applies for kaolinites with a HI > 0.43, while a kaolinite with two defect distributions (a "biphase" kaolinite) contains both a low-defect and a high-defect phase. The high-defect phase has a distribution of C layers and a high proportion of t_2 translation defects (i.e., lattice translations from one layer to the same type of layer, as in Plançon *et al.*, 1989) and has a calculated HI value of 0.3.

An understanding of defect structures and the definition of structural parameters in kaolinites (Bookin *et al.*, 1989; Plançon *et al.*, 1989; and Plançon and Zacherie, 1990) is based upon a consistent suite of kaolinites initially studied by Brindley *et al.* (1986). The success of the method outlined by Plançon and Zacherie (1990) in defining the defect structures of kaolinites using parameters derived from powder XRD patterns is compared in their Table 1 (Plançon and Zacherie, 1990). The authors showed in their study that only kaolinites with very low abundances of defects or of low-defect phase are difficult to characterize with a high degree of reproducibility. Thus, as with this study, the reproducibility of these structural data is good and statistically significant (Plançon and Zacherie, 1990).

Scanning electron microscopy (SEM) was undertaken with two instruments: a JEOL 6400F and a JEOL 890F both equipped with field emission guns. In general, both SEMs were operated at low accelerating voltages (i.e., <5 kV) as the majority of samples were examined without a conductive coating. The JEOL 6400F SEM was equipped with a Link ultra-thin window Si(Li) EDS and Moran Scientific Analyser.

Particle size distributions for each sample were ob-

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tained by laser scattering of dispersed bulk samples. In general, this technique is the preferred method for particles >0.1 μm provided an appropriate model is used for the scattering of light from small particles. Details of these size distribution methods are given by Mackinnon *et al.* (1993). Particle size distributions for the range 0.1–80 μm were determined by laser scattering in a flow-through cell using a Malvern Mastersizer E with samples stirred in a 25 ml water suspension containing 3 ml of 10% Calgon solution. On average, greater than 10^5 particles were measured by this laser scattering technique per sample analysis (Mackinnon *et al.*, 1993). In cases where replicate analyses of a specific parameter have been determined (e.g., HI values), the mean value is reported with an estimated standard deviation to the last significant figure given in parentheses. For example, the notation 0.99(2) indicates a mean value of 0.99 with an estimated standard deviation of 0.02.

RESULTS

Bulk samples

Particle morphology. SEM micrographs from bulk samples of each Australian kaolinite are given in Figure 1. For all samples, the left-hand figure shows a typical area observed at the same screen magnification on the SEM (~1000×), while the right-hand figure contains a higher magnification SEM image of individual particles in order to demonstrate typical particle morphologies. Variations between deposits in kaolinite morphology are clearly visible in Figure 1. For example, the Weipa sample (Figures 1A and 1B) is composed predominantly of well-formed euhedral pseudohexagonal platelets whilst the Birdwood sample (Figures 1I and 1J) is a mixture of fine particles and large vermiform booklets. In Figures 1G and 1H, Mt. Hope shows large, irregular crystallites with pitted surfaces (arrowed), while Figures 1E and 1F show thick "chunky" euhedral pseudohexagonal platelets (arrowed) of the Lal Lal Dyke. The Kingaroy sample contains fine-grained particles as well as large (>3 μm) booklets of kaolinite plates (Figures 1C and 1D) while Pittong Pit shows large embayed particles (Figures 1K and 1L). In all cases, these morphologies are influenced by the depositional environment of formation of the particular kaolinite as implied in an earlier study by Lombardi *et al.* (1987).

Particle size distribution. Particle size distributions for bulk samples obtained by laser scattering are illustrated in terms of volume percentages in Figure 2. The distribution of particle sizes varies significantly with each deposit sampled. A nominal quantitative measure of these particle size distributions is given by the parameters d_{90}, d_{50}, and d_{10}, which are equivalent spherical diameters for the 90%, 50%, and 10% portions of the volume distribution. In addition, the parameter "span," which is given by the relationship;

$$\text{span} = (d_{90} - d_{10})/d_{50}$$

gives a measure of the range of size values for a bulk sample. The parameters d_{90}, d_{50}, and d_{10} as well as span are listed in Table 1 for all nine bulk kaolinites examined in this paper.

Table 1. Particle size parameters* for bulk kaolinites.

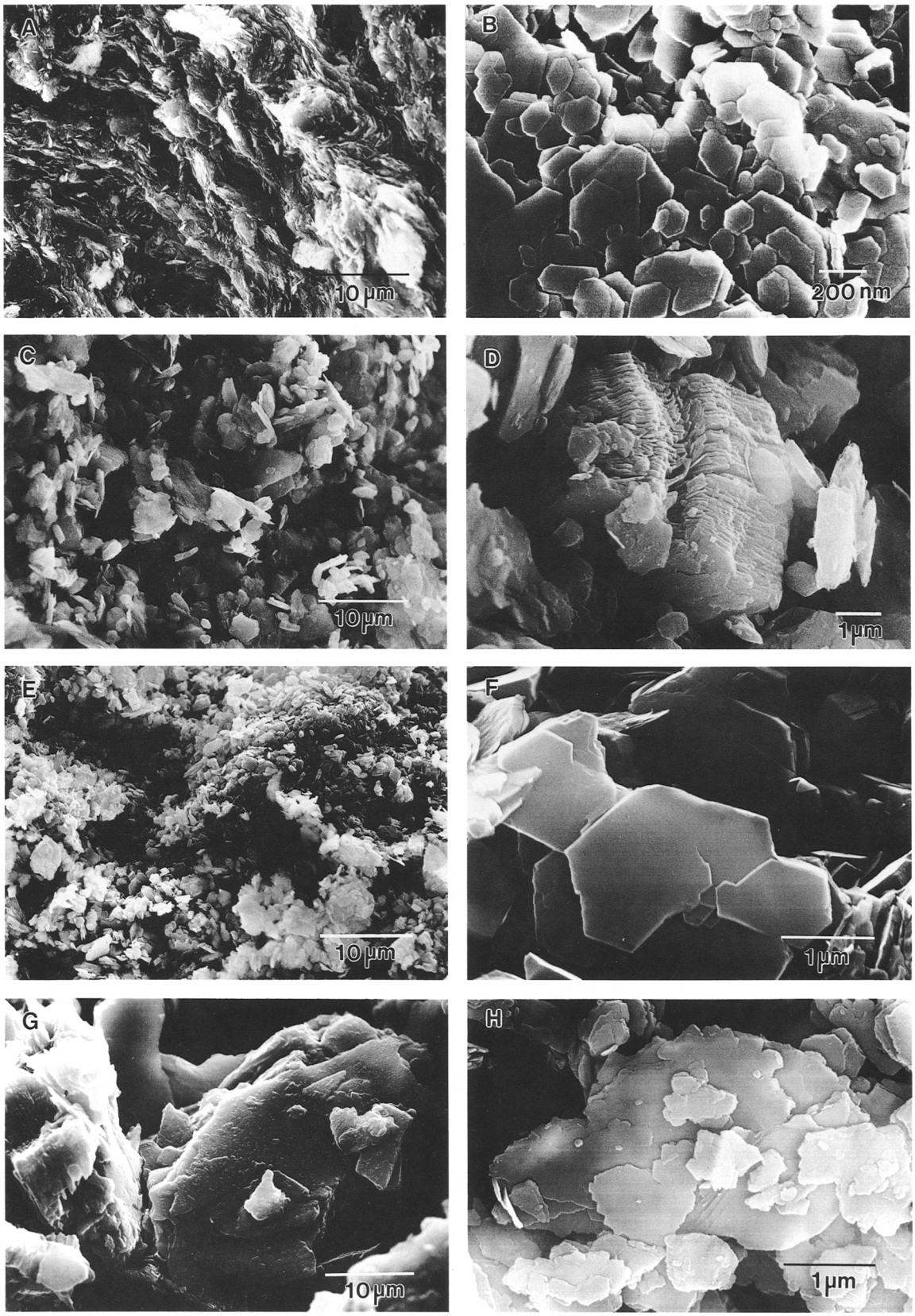
Sample	d_{90}	d_{50}	d_{10}	Span
Weipa	10.7	2.6	0.3	4.1
Georgia KGa-2	13.1	3.0	0.4	4.5
Kingaroy	13.1	4.3	1.2	2.6
Pittong Pit	9.6	3.1	0.4	3.0
Mt. Hope	54.9	14.4	3.2	3.6
Birdwood	4.5	1.1	0.3	4.0
Lal Lal Pit	17.4	3.2	0.8	6.8
Lal Lal Dyke	14.0	1.9	0.4	7.3
Georgia KGa-1	22.3	3.4	0.5	6.8

* Values, except for span, are in micrometers. All parameters determined by laser diffraction using techniques in Mackinnnon *et al.* (1993). d_{90}, d_{50}, and d_{10} are equivalent spherical diameters for particles at the 90%, 50%, and 10% levels of the particle size distributions shown in Figure 1. See text for details.

The Weipa and Kingaroy samples show similar size distributions between about 1 μm and 2 μm, but for sizes smaller than 1 μm, the proportion of smaller particles increases for the Weipa sample. The curve for Mt. Hope shows that this sample is very coarse grained with 50% of particles by volume (i.e., the modal average) greater than 14.4 μm. Ninety percent of the Mt. Hope particles are less than 54 μm and only 10% are less than 3.3 μm. On the other hand, the Birdwood deposit contains a high percentage of small particles with 90% less than 4.5 μm in size. The modal average for this deposit by volume is very small at 1.1 μm. Modal averages in decreasing order for the other deposits are Kingaroy 4.3 μm, Lal Lal Pit 3.2 μm, Pittong Pit 3.1 μm, Weipa 2.6 μm and Lal Lal dyke 1.9 μm.

X-ray diffraction indices. Estimates of crystallinity and defect distribution, via the Hinckley Index and the parameters calculated by Plançon and Zacherie (1990), respectively, are given for bulk kaolinite samples in Tables 2 and 3. These tables show XRD indices for single-phase kaolinites (Table 2) and for biphase kaolinites (Table 3) according to the definitions given by Plançon and Zacherie (1990) as noted in the Experimental Materials and Methods section. Both single-phase kaolinites from Weipa and Georgia (KGa-2) show HI values for the bulk samples that indicate, in general, a poorly crystalline kaolinite structure (Hinckley, 1963). As shown in Table 2, the Plançon and Zacherie (1990) analysis of the XRD profile indicates that the mean thickness of kaolinite crystallites in the basal dimen-

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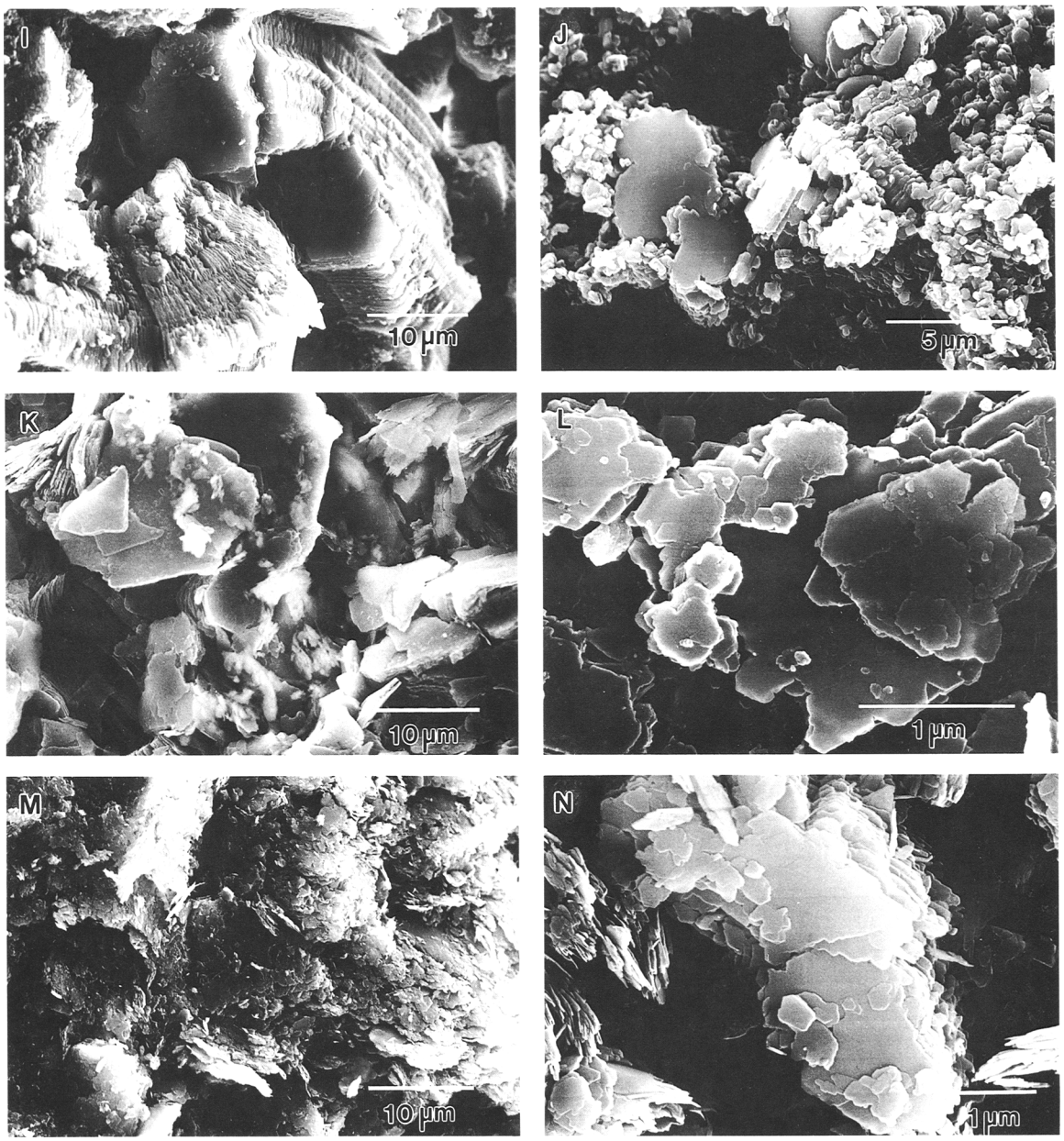
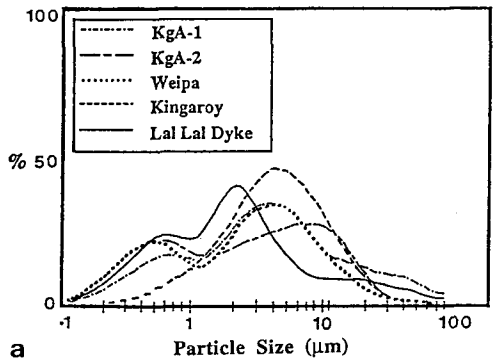


Figure 1. SEM images of typical bulk kaolinite samples from seven Australian localities. Images on the left have been obtained at the same magnification, while those on the right at higher magnifications highlight typical particle morphologies. Localities for each sample are (A, B) Weipa; (C, D) Kingaroy; (E, F) Lal Lal Dyke; (G, H) Mt. Hope; (I, J) Birdwood; (K, L) Pittong Pit; and (M, N) Lal Lal Pit.

sion is larger in Weipa (~51 layers) than in the KGa-2 sample (~33 layers).

For the biphased kaolinites, all HI values for bulk samples indicate that they are well-ordered rather than poorly crystalline and that all Australian samples have higher degrees of crystallinity than the well-characterized KGa-1 sample. Using the analysis by Plançon and Zacherie (1990), KGa-1 has a lower proportion of low-defect phase present in the bulk sample (~27.9%) than that determined in any of the Australian biphase kaolinites. The bulk samples from Lal Lal Dyke and Birdwood show the highest proportion of low defect phase (ldp), at 78.8% and 67.5%, respectively. In this case, these high values of %ldp compare favorably with the higher values of HI for these bi-phase samples. The bulk sample from Kingaroy shows the highest value for HI (1.59), but shows an intermediate level of ldp (46.1%). HI values for both KGa-1 and KGa-2 listed in Tables 2 and 3 are the average of three repeat analyses on 5 g portions of a bulk source clay. The averaged

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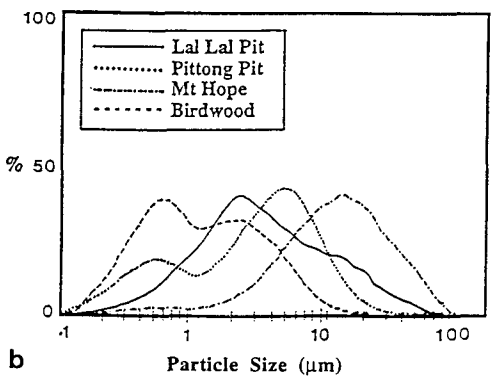


Figure 2. Particle size distributions for bulk samples of nine kaolinites determined by laser scattering: a) KGa-1, KGa-2, Weipa, Lal Lal dyke and Kingaroy samples; and b) Lal Lal Pit, Pittong Pit, Mt. Hope, and Birdwood samples.

values for these bulk samples determined in this study are 0.99(2) and 0.33(6), respectively.

Intercalation yields. The relative yield for intercalation of NMF with bulk kaolinite varied for reactions involving single-phase and biphase kaolinites. For example, intercalation of NMF with both the Weipa and KGa-2 samples gave yields of 79% and 70%, respectively (see Table 2). However, as shown in Table 3, all biphased bulk kaolinites except for the Birdwood sample, showed intercalation yields >90%.

Size fractionated kaolinites

Hinckley Index vs *particle size.* The calculated Hinckley Indices for three size fractions of all samples vary

Table 2. Structural parameters and intercalation yields for bulk, single-phase kaolinites.

Sample	HI	M	Wc	δ	p	% NMF yield
Weipa	0.61	51	0.04	0.03	0.23	79
Georgia KGa-2	0.33(6)	33	0.02	0.04	0.35	70

Table 3. Structural parameters and intercalation yields for bulk, biphase kaolinites.

Sample	HI	% Idp	% NMF yield
Georgia KGa-1	0.99(2)	27.9	94
Lal Lal Pit	1.24	38.6	92
Mt. Hope	1.40	46.5	95
Pittong Pit	1.42	55.3	94
Birdwood	1.49	67.5	69
Lal Lal Dyke	1.54	78.8	92
Kingaroy	1.59	46.1	95

significantly between each deposit, and, in some cases, within size fractions of the same deposit, as shown in Tables 4, 5, and 6. Three samples, KGa-2, Pittong Pit and Birdwood, show relatively minor variations in HI with particle size and differ little from the bulk values, although in each of these, slightly lower values were recorded in the finer size fraction (i.e., 0.3–0.4 μm). The Mount Hope sample shows a steady decrease in HI value as the particle size decreases. A similar trend is observed for the sample from the Lal Lal dyke. The Kingaroy, Weipa, and KGa-1 samples show the greatest range of HI values and, accordingly, the greatest variation from the bulk sample average value. Samples from Weipa and Kingaroy both show a sharp increase in HI value for the >2.0 μm size fraction compared with the HI value for the bulk sample. For example, the bulk HI value for the Weipa sample is 0.61 while that for the >2.0 μm fraction is 0.94. In addition, the HI values for each size fraction in Weipa decrease considerably with decrease in size (e.g., 0.94, 0.44, and 0.39 for each fraction, respectively). In contrast, KGa-1 shows a decrease in HI value in the >2.0 μm size fraction compared with the bulk value while HI values for the smaller size fractions increase to values greater than the bulk sample (1.19 and 1.25, respectively).

Defect structure and particle size. Tables 4, 5, and 6 summarize the basic parameters that describe the defect structure of each size-fractionated sample according to the analysis of Plançon and Zacherie (1990). Using this analysis, the samples can be divided into

Table 4. Structural parameters and intercalation yields for size-fractionated, single-phase kaolinites.

Sample	HI	M	W_c	δ	p	% NMF yield
Weipa						
>2.0 μm	0.94	51	0.04	0.02	0.14	93
0.5–0.6 μm	0.44	50	0.02	0.03	0.32	86
0.3–0.4 μm	0.39	33	0.02	0.04	0.35	33
KGa-2						
>2.0 μm	0.38	51	0.04	0.03	0.35	73
0.5–0.6 μm	0.42	33	0.02	0.03	0.32	77
0.3–0.4 μm	0.35	50	0.02	0.04	0.35	50

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Table 5. Structural parameters and intercalation yields for size-fractionated, intermediate kaolinites.

Sample	HI	Phases	M	Wc	d	p	% ldp	% NMF yield
Pittong Pit								
>2.0 μm	1.46	2	—	—	—	—	51.4	100
0.5–0.6 μm	1.41	1	36	0.0	0.0	0.0	—	92
0.3–0.4 μm	1.41	2	—	—	—	—	53.4	80
Kingaroy								
>2.0 μm	1.80	2	—	—	—	—	61.5	100
0.5–0.6 μm	1.29	1	50	0.0	0.20	0.60	—	96
0.3–0.4 μm	1.18	2	—	—	—	—	42.6	82

three distinct groups: 1) single phase kaolinites in all size fractions, such as KGa-2 and Weipa (Table 4); 2) biphased kaolinites with a single-phase component in one size fraction, such as Pittong Pit and Kingaroy (Table 5); and 3) biphased kaolinites in all size fractions, such as KGa-1, Lal Lal Pit, Mt. Hope, Birdwood and Lal Lal Dyke (Table 6). In samples determined as single phase, the proportion of dickite-type layers (W_c) is negligible.

The parameter, p, constructed by Plançon and Zacherie (1990) is comparable to HI values and indicates the proportion of translation defects between layers in a single defect phase kaolinite. This parameter is given by the change in HI value relative to the variations of stacking in adjacent kaolinite layers and can be evaluated for single-phase kaolinites. In both the Weipa and the KGa-2 samples, variations in the value of p are minimal, except for the >2.0 μm fraction of the Weipa kaolinite, which shows the lowest proportion of translation defects (0.14). In single-phased samples, the mean number of layers in kaolinite particles can also be determined by the parameter, M, which is directly related to the half-width at half-maximum of the 002 reflection (Plançon and Zacherie, 1990). Thus, KGa-2 shows two distinct thicknesses for different size fractions: 33 layers for the 0.5–0.6 μm fraction and approximately 50 layers in the >2.0 μm and the 0.3–0.4 μm fractions. The Weipa sample has an average of 50 layers in the larger-sized fractions, while particles in the smaller-sized fraction (0.3–0.4 μm) contain only 33 layers.

Table 6. Structural parameters and intercalation yields for size-fractionated, biphase kaolinites.

Sample	HI	% ldp	% NMF yield
KGa-1			
>2.0 μm	0.84	25.7	95
0.5–0.6 μm	1.19	43.3	90
0.3–0.4 μm	1.25	44.6	53
Lal Lal Pit			
>2.0 μm	1.33	33.4	100
0.5–0.6 μm	1.40	44.3	99
0.3–0.4 μm	1.02	37.4	78
Mt. Hope			
>2.0 μm	1.38	52.4	100
0.5–0.6 μm	1.31	51.3	94
0.3–0.4 μm	1.15	44.9	74
Birdwood			
>2.0 μm	1.48	66.7	89
0.5–0.6 μm	1.49	65.5	77
0.3–0.4 μm	1.35	59.0	44
Lal Lal Dyke			
>2.0 μm	1.35	51.5	100
0.5–0.6 μm	1.44	52.9	91
0.3–0.4 μm	1.20	51.7	86

Biphased kaolinites are considered mixtures of high- and low-defect phases (Plançon and Zacherie, 1990) and the amount of low defect phase is represented by the column %ldp in Tables 5 and 6. The percentage low defect phase represents the percentage of low defect kaolinite in biphased samples and varies considerably between deposits and within the different size fractions of a given deposit. For example, Birdwood shows a steady decrease in %ldp as particle size decreases, while KGa-1 shows an increase in %ldp as particle size decreases. However, Lal Lal Dyke shows a relatively constant set of values (~52%) in all three size fractions. The Kingaroy sample shows a relatively high 61.5% ldp in the >2.0 μm fraction compared with 42.6% in the 0.3–0.4 μm fraction. In general, the percentage of low defect phase ranges between 40% and 60% over all samples. No clear trend in the relationship between particle size and %low defect phase is apparent in Tables 5 and 6.

Intercalation yields. The percentage of NMF intercalate yield for each size fraction, as well as the corresponding bulk samples, are summarized in Figure 3. For all samples except KGa-2 and Birdwood, the >2.0 μm size range gave high yields (i.e., >90%) of kaolinite : NMF. Even in kaolinites giving the poorest intercalation yield for bulk samples (i.e., KGa-2 and Birdwood), the best yield was achieved in the 0.5–0.6 μm or the >2.0 μm size range. In addition, for size-fractionated samples, intercalation yield decreased with decreasing particle size as shown in Figure 3. On the other hand, intercalation yields were improved in at least one size-separated fraction of all samples when

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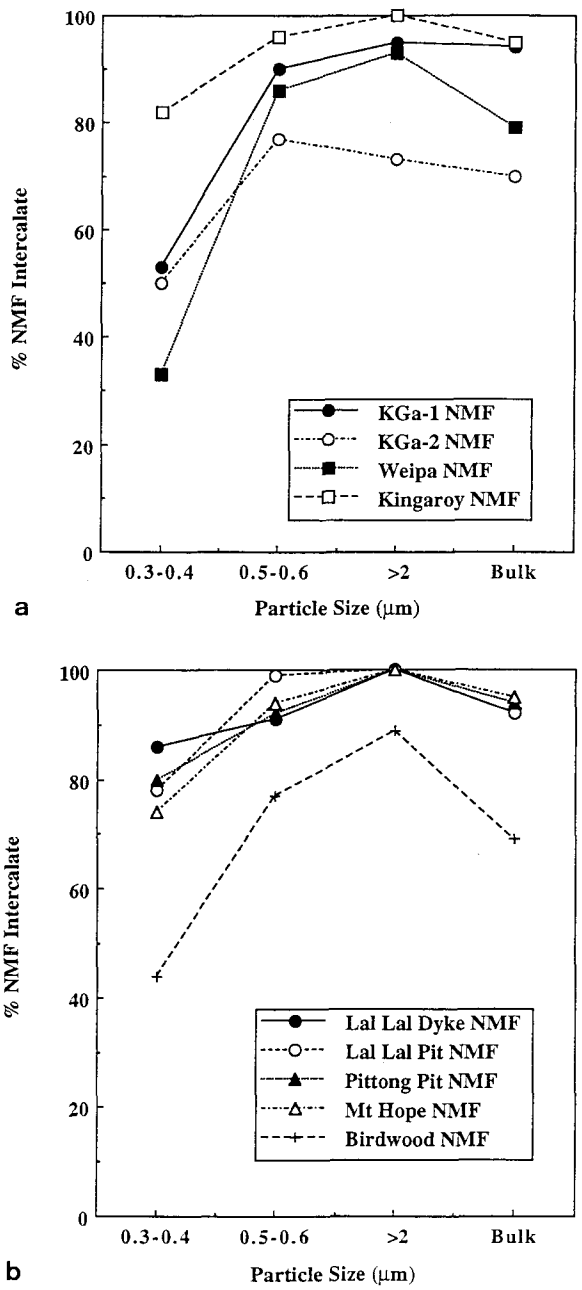


Figure 3. Percentage intercalate yield (for kaolinite : NMF intercalate) for selected size fractions and the bulk samples of nine kaolinites in this study.

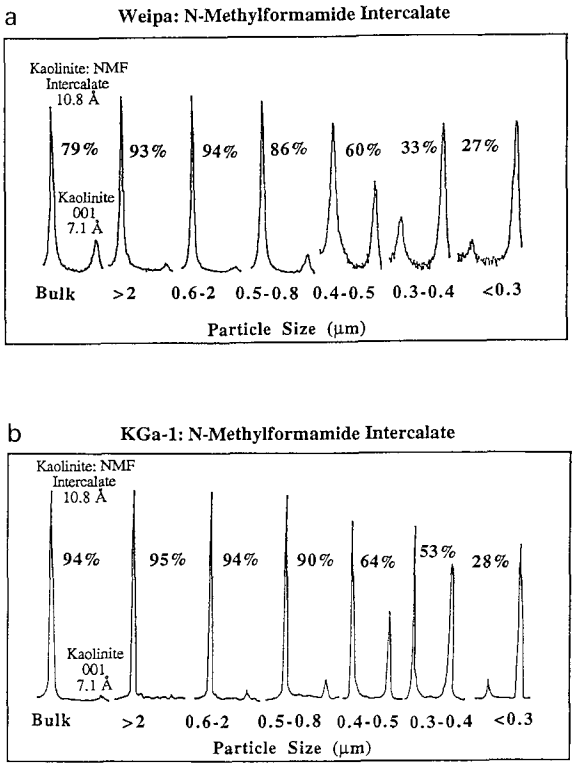


Figure 4. Two examples of XRD profiles obtained on kaolinite : NMF intercalates for: a) Weipa and b) Georgia KGa-1 samples. The relative intensities of the intercalate peak and the kaolinite (001) peak indicate the percentage yield of intercalated product for each bulk and size-separated sample.

compared with the intercalation yield of the bulk sample. This effect is also graphically illustrated in Figure 4, which shows XRD traces for the (001) basal spacing of the intercalate and the (001) basal spacing for kaolinite in samples KGa-1 and Weipa for the six separated sizes of each sample. For KGa-1, KGa-2, Birdwood, and Weipa samples, yields less than 55% are obtained in the 0.3–0.4 μm fraction. Nevertheless, in other samples such as Pittong Pit, Lal Lal Dyke, and Mt. Hope, yields >70% were attained in the 0.3–0.4 μm size fraction using the same intercalation methods.

DISCUSSION

Bulk samples

For the bulk kaolinites used in this study, there is an apparent relationship between the relative crystallinity, as defined by HI, and the relative intercalation yield determined by XRD of the product resulting from vapor phase exposure of kaolinite to NMF. For example, samples Weipa and KGa-2, both of which are single phase kaolinites and show the lowest HI values for bulk samples, result in low intercalation yields compared with all other samples except that from Birdwood. On the other hand, Birdwood has a very high HI value (1.49) but shows a high concentration of particles in the <2 μm range (see Figure 2 and Table 1). In comparison, both Weipa and KGa-2 show distributions which favor the smaller particle sizes (e.g., <2 μm) but retain a significant proportion of particles with sizes >10 μm. Alternatively, the defect characterization methods of Plançon and Zacherie (1990) reveal a distinction between single-phase and biphase kaolinites, which compares favorably with the relative in-

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tercalation yield. That is, both Weipa and KGa-2, which show the lowest intercalation yields, are also single-phase kaolinites.

For KGa-1, the "highly crystalline" sample, the degree of intercalation with NMF is high (94%) and suggests, in comparison with the data for KGa-2 and Weipa, that HI values, or degree of crystallinity, may influence the intercalation yield. In an early study of "crystallinity" *vs.* bulk physical properties, Murray and Lyons (1956) noted a similar relationship for the paper-coating quality of kaolinites with an empirical estimate of crystal perfection based upon XRD traces and electron micrographs. That is, (empirically) defect-free kaolinites provide high quality paper-coatings. Using HI values, a similar general relationship between crystallinity and intercalation yield may be considered valid for all kaolinites examined in this study, although the data for Birdwood are an exception. However, with the development of parameters that describe defect types and distribution (Plançon and Zacherie, 1990), this relationship between a bulk property (e.g., intercalation yield) and crystallinity does not appear to hold true in detail as no well-defined trend can be observed for the variation of %ldp with intercalate yield.

Hassanipak and Eslinger (1985) also obtained replicate analyses of HI value for bulk samples of KGa-1 and KGa-2 using the same methods as applied in this study. In both cases, HI values for bulk samples of KGa-1 and KGa-2 show similar values when determined in two different laboratories. The average HI values for three replicates performed by Hassanipak and Elsinger (1985) on KGa-1 and KGa-2 are 0.89(2) and 0.28(3), respectively. The averaged values for the same bulk samples determined in this study are 0.99(2) and 0.33(6), respectively. HI values for KGa-1 determined by these two studies are significantly different at the 95% confidence interval of a Students' t-test (i.e., they differ by 5× the estimated standard deviation), but the values are, nevertheless, of similar magnitude and considerably different to values determined for the poorly ordered sample, KGa-2. For KGa-2, the estimates of HI by both laboratories are equivalent at the 95% confidence level of a Students' t-test.

Variations in HI values for the same sample may be due to minor inhomogeneities in crystallographic properties of particles within the deposit. Data from this work and that of Lombardi *et al.* (1987) indicate that such variations may occur within different size fractions of the sample and, thus, differences in HI values may reflect a predominance of specific size fraction(s) within a particular bulk sample. Alternatively, these data indicate that, at an individual particle scale, the Source Clay KGa-1 shows a degree of heterogeneity in crystallographic properties.

Size-fractionated kaolinites. The above general relationships for bulk kaolinites infer that an investigation of the variation in intercalation yield with particle size and crystallinity may provide some insight into this intercalation reaction. Previous investigations on the variation of HI (or "crystallinity index") with particle size for a wide range of kaolinites have been inconclusive, in part because HI is an empirical concept with minimal crystallographic basis (Plançon and Zacherie, 1990; Hinckley, 1963) and partly because particle size has been imprecisely determined in many earlier studies. Variations in crystallographic parameters with particle size have been assessed for few kaolinites to date. This lack of data is perhaps due to the difficulty of obtaining precise estimates of particle size in the <2 μm range, although Tanner and Jackson (1949) developed useful methods that are quite reproducible (Mackinnon *et al.*, 1993).

The studies by Brindley *et al.* (1986) and Plançon *et al.* (1989) defined an empirical parameter termed, PSI, which gave an approximate, single-parameter measure of particle size. However, this parameter defines a "bulk" particle size that cannot be readily compared between samples from different investigators or methods of analysis and, in comparison to more recent work, is only a crude guide to the particle size distribution in the samples studied. The work by Hassanipak and Eslinger (1985) used size-fractionated kaolinites from various locations in the Tertiary and Cretaceous Georgia kaolins as well as bulk samples from the Source Clays respository. Hassanipak and Eslinger (1985) provide HI values (their "crystallinity index") for these Georgia kaolins in the size ranges <0.5 μm, 0.5–1.0 μm and 1.0–2.0 μm using sedimentation methods similar to those in this study. Over 65 samples from these Georgia kaolins were subjected to detailed study (including precise dating and location), but there appears to be great variation in the HI value with size and no apparent relationship between HI value and particle size (Hassanipak and Eslinger, 1985).

In all cases except for KGa-1, HI values decreased or remained relatively constant with decrease in size. In some cases, such as the Weipa and Kingaroy samples, this decrease in HI value is quite pronounced (e.g., for Weipa from 0.94 to 0.39, for the >2 μm and the 0.3–0.4 μm fractions, respectively). In comparison, the relative intercalation yield decreases with decrease in particle size for all samples including KGa-1. Thus, empirically, for all samples studied except KGa-1, the HI value appears to be related to relative intercalation yield for size-fractionated kaolinites as well as that in bulk samples. However, a plot of HI value and intercalate yield for these size-fractionated samples (Figure 5) does not reveal any well-defined trend. This lack of a well-defined trend is presumably attributable to other effects such as specific defect types and the relative proportion of defect types in a size fraction (e.g., the particle size distribution of high-defect and low-defect phases in a biphase sample) influence intercalate yield

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in a manner that cannot be determined from the available data. In addition, the relatively high values for intercalate yield for all biphased kaolinites in the >2 μm fractions tend to inhibit the development of linear trends for these data.

An indication that there may be a variation in the defect distribution for kaolinites over specific size ranges is shown in Table 5 in which, within a single sample, biphase and single-phase kaolinites dominate a particular size fraction. Both the Pittong Pit and the Kingaroy samples show the presence of single-phase kaolinites in the 0.5–0.6 μm fractions while the >2 μm and 0.3–0.4 μm fractions contain bi-phase kaolinites. The heterogeneous nature of kaolinite defect structures with particle size has not previously been described and highlights the very complex nature of kaolinites and their relationship(s) between structure and bulk physical properties.

Further indication of the complexity of these minerals and the poor correlation between structural parameters and intercalate yield is shown in a comparison of data for intercalation of NMF with KGa-1 and KGa-2. The smaller size fractions (0.3–0.4 μm) for both samples show comparable intercalate yields (~50% and 53%, respectively), yet their HI values differ markedly (HI ~ 1.25 and ~0.35, respectively). Similarly, fine-size fractions of the Weipa and Birdwood samples show poor intercalate yields (<50%), yet Birdwood has a high HI value for this size fraction (1.35) and Weipa shows a very low HI value (0.39). Clearly, particle crystallinity (HI value or the parameters defined by Plançon and Zacherie, 1990) is not the only factor that may influence the intercalation of NMF in kaolinites.

Particle size distribution also appears to play an important part in the relative efficacy of intercalation reactions with kaolinites. In general, a bulk sample of kaolinite with the majority of particles in the small size fraction appears to have a lower intercalate yield (e.g., KGa-2 and Weipa). For biphased kaolinites, the proportion of fine-grained particles present in a sample may strongly influence the intercalate yield. For example, 90% of the particles in Birdwood are <4.5 μm size; while for KGa-1, only 50% of particles are <3.4 μm in size (see Table 1). Again, the intercalate yields for bulk samples are considerably different: ~70% and ~95%, respectively. Other biphased kaolinites have relatively low proportions of the smallest size fraction (i.e., <0.4 μm) as well as modal d_{50} values greater than 2 μm. In these cases, the intercalate yields for bulk samples are relatively high (i.e., >90%). For all samples, there also appears to be a particle size at which intercalate yields remain low (i.e., <90%). That is, for all samples, the 0.3–0.4 μm size fraction showed consistently low intercalation yields irrespective of the defect distribution within individual particles. This observation implies that for very small particles (i.e., <2 μm size), particle size becomes a dominant influence in the intercalation reaction.

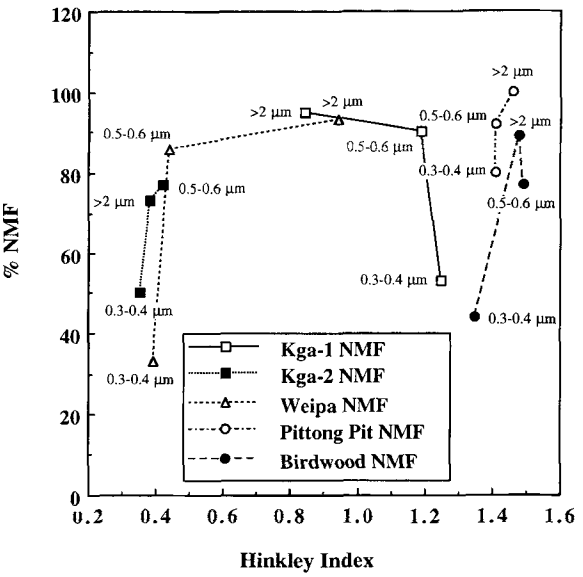


Figure 5. Plot of percentage intercalate yield *vs.* Hinckley Index for selected size fractions of five kaolinites examined in this study.

CONCLUSIONS

This detailed study of nine kaolinites indicates that a wide range of particle sizes, shapes, and defect distributions have been observed for bulk samples from widely different geological environments. Each of these bulk kaolinites have been intercalated with NMF via an intermediate reaction with hydrazine hydrate. In general, bulk, biphased, well-ordered kaolinites (high HI values) show better intercalation yields than bulk, single-phased, poorly ordered kaolinites with low HI values. However, particle size also appears to be a predominant factor in this intercalation reaction in that kaolinites <0.4 μm do not show high intercalation yields. For size-fractionated samples, well-defined relationships between particle size fraction, crystallinity or intercalation yield could not be determined. For bulk or size-fractionated samples, a relationship between intercalate yield and defined defect parameters (Plançon and Zacherie, 1990) is not apparent.

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