RELEVANCE OF DIFFERENT INTERCALATION TESTS FOR DISTINGUISHING HALLOYSITE FROM KAOLINITE IN SOILS

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Abstract—The expandabilities of kaolin-group minerals in different horizons in 10 soils from New Zealand and Fiji were measured immediately after the application of formamide and after the sequential application of hydrazine, water, and glycerol (HWG treatment). The expandabilities of these minerals in some of the soil samples with dimethylsulphoxide (DMSO) and after long-term (4-day) formamide treatments were also measured. The abundance of characteristic halloysite shapes was determined from electron micrographs of selected samples. The expandabilities of several non-soil kaolinite samples with the DMSO and HWG treatments were also measured.

The expansion of kaolin-group minerals showed the same trends within almost all profiles, whether determined using formamide (by the immediate-formamide treatment) or glycerol (by the HWG treatment). Except where both treatments led to complete intercalation, the HWG treatment always caused more expansion of kaolin-group minerals than obtained immediately after formamide application. The HWG treatment expanded some non-soil kaolinite samples, but well-crystallized kaolinite was not affected by this treatment. The DMSO treatment expanded kaolin-group minerals in the soils to a similar extent as the HWG treatment and also expanded well-crystallized kaolinite. The degree of expansion resulting from the immediate-formamide treatment matched abundance of typical halloysite particle shapes more closely than the degree of expansion given by the other intercalation treatments. The degree of expansion immediately following formamide application could be diminished, if the samples were heated at 40 ± 5°C.

Key Words—Expansion treatment, Halloysite, Intercalation, Kaolinite, Soil clay.

INTRODUCTION

Several studies have found a decrease in the abundance of halloysite relative to that of kaolinite with an increase in degree of weathering of soils or with increasing proximity to the surface of soil profiles (Shimuzu, 1972; Eswaran and Wong, 1978; Calvert *et al.,* 1980; Hughes, 1980; Hewitt and Churchman, 1982). Hence, it is tempting to infer that halloysite transforms to kaolinite with weathering. The apparently continuous series of X-ray powder diffraction (XRD) patterns of Ross and Kerr (1934) and Brindley and Robinson (1946) showing increasing order from halloysite to highly crystalline kaolinite also suggest a natural progression between halloysite and kaolinite. A genetic relationship between halloysite and kaolinite, however, is difficult to demonstrate because of confusion over the best method to use to distinguish halloysite from kaolinite. Because soil kaolinite usually gives a poorly defined XRD powder diffraction pattern for randomly oriented samples, similar to that of halloysite (Churchman and Gilkes, 1989; Dixon, 1989), these patterns cannot be used to differentiate the two minerals in soils. Generally, morphology or intercalation reactions are used for this purpose (Churchman and Carr, 1975;

Churchman *et al.,* 1984). Particle shapes have often been used to distinguish halloysite from kaolinite; however, some studies have identified halloysite in shapes (i.e., platy) that are usually typical of kaolinite and kaolinite in shapes (i.e., tubular) that commonly characterize halloysite (see review by Churchman and Carr, 1975). Hence, distinctions based on particle shapes could be misleading.

On the other hand, the prior intercalation of halloysite with a water monolayer ensures that halloysite intercalates polar compounds more easily than kaolinite, which did not previously contain interlayer water (Churchman and Carr, 1975). Range *et al.* (1969) differentiated halloysite from kaolinite on the basis of relative intercalation ability towards hydrazine followed first by water, and then by glycerol, hereafter known as the HWG treatment. Halloysite expanded to a basal spacing of 11 Å as a result of this treatment, whereas kaolinite retained a 7-Å spacing. Churchman *et al.* (1984) developed a rapid treatment with formamide to make this same distinction. Theng *et al.* (1984) showed that results from the formamide treatment correlated well with those from the older, washed-acetate treatment of Wada (1961) and that they were consistent with electron microscopy results. The distinctions based on the formamide treatment, however, were not well correlated with those using the HWG treatment (Page, 1984; Theng *et al.,* 1984). Intercalation of dimethyl-

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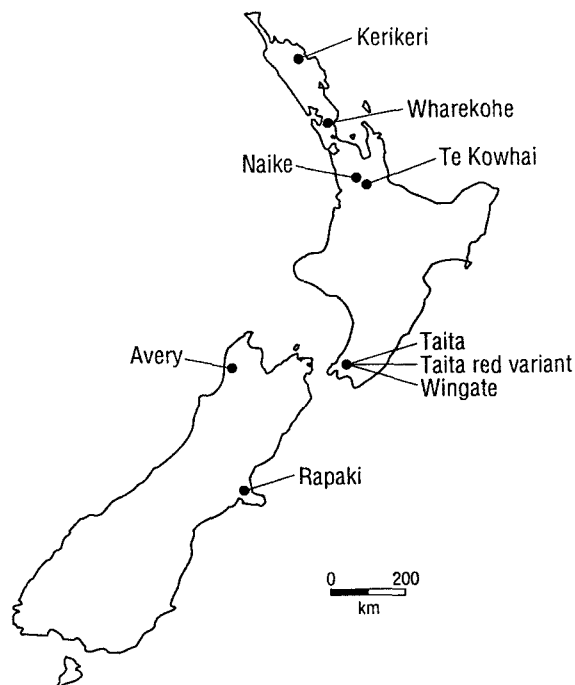
Figure 1. Map of New Zealand showing locations of nine soils used in the study.

sulphoxide (DMSO) has also been used as part of a procedure to distinguish kaolin-group minerals from other phyllosilicates (Jackson and Abdel-Kader, 1978; Calvert, 1984). Halloysite intercalated DMSO "almost completely" (Anton and Rouxhet, 1977), whereas different kaolinite samples intercalated DMSO to different extents (Olejnik *et al.,* 1968; Anton and Rouxhet, 1977). The uptake of this compound into halloysite proceeded more rapidly than its uptake into kaolinite (Olejnik *et al.,* 1968). A comparison with the intercalation of formamide by the kaolin-group minerals (Churchman *et al.,* 1984) suggested the possible use of DMSO for distinguishing halloysite from kaolinite.

This present study compares the relative contents of halloysite and kaolinite in different horizons from each of several weathering profiles based on the relative abilities of kaolin minerals to expand with formamide and HWG treatments. It also examines the abilities of these kaolin-group minerals to intercalate DMSO, and compares the effects of DMSO on standard kaolinite samples having different crystallinities to establish the range of reactivities with DMSO that can be shown by this mineral.

MATERIALS AND METHODS

Clay fractions containing kaolin-group minerals were separated from nine New Zealand soils (Figure 1) and a soil from Fiji. The Fiji soil was obtained from the Koronivia Research Station of the Department of Agriculture, Viti Levu. These soils cover a wide range of

locations, parent materials, climates, and other soil-forming factors (Table 1). In all, 68 different horizons were studied.

The soils were treated with hydrogen peroxide and sodium citrate-dithionite-bicarbonate (Jackson, 1956) to remove organic matter and iron oxides, respectively. The clay (<2 μm) fractions were extracted from the soils by centrifugation. These fractions were dried from aqueous suspensions on the top of an oven (at 40 $\pm$ 5°C) and lightly ground.

X-ray powder diffraction (XRD) analyses were made with a Philips PW 1710 diffractometer using CoKα radiation and step scanning in steps of 0.05° 2θ at a rate of 3° 2θ/min. The analyses of each sample on a glass slide were made after: (1) redispersing the air-dried sample in water by ultrasonification; (2) as in (1), but spraying with a 10% solution of glycerol in water and equilibrating for at least 16 hr; and (3) treating the air-dry sample with hydrazine, then water, and then glycerol (HWG treatment). The analyses were also made on each sample on a ceramic tile after: (4) sedimenting the ultrasonified sample onto a tile; (5) as in (4), but after adding formamide drop-wise to cover the sample completely, then examining the sample immediately (i.e., within 1 hr) (immediate-formamide treatment); and (6) as in (5), but after equilibrating for 4 days with formamide retained in the porous tile.

Undried samples from most of the original suspensions of the clay fractions were also examined after treatments 4 and 5 to investigate differences in the immediate formamide expansion that might have been brought about by drying the clays. Ten of the dry clay fractions were also examined after the dropwise addition of dimethyl sulfoxide (DMSO) to cover the samples on ceramic tiles. XRD analyses of the DMSO-treated samples followed contact periods of from 1 hr to 11 days, in order to determine the time taken for maximum expansion.

Peak heights for the 10-Å reflections from formamide-treated samples were obtained by subtracting the heights of peaks for spacings at or near 10 Å for samples sedimented onto ceramic tiles (treatment 4) from those for samples subjected to the immediate- and 4-day formamide treatments (treatments 5 and 6). Peaks for 10-Å spacings from samples prior to formamide treatment probably derived from micaceous phases. The peak heights for the 11-Å reflections from HWG-treated samples were obtained by subtracting the heights of peaks corresponding to spacings near 11 Å for samples subjected to glycerol-only treatments (treatment 2) from those for samples subjected to the HWG treatment (treatment 3). The peak heights for the 11-Å reflections from DMSO-treated samples were obtained by subtracting the heights of peaks near 11 Å for samples sedimented on ceramic tiles (treatment 4) from those of samples subjected to DMSO treatments. Interstratified minerals containing mica or

Table 1. Characteristics of New Zealand and Fiji soils containing kaolin-group minerals.

Name of soil (Soil Bureau Nos.)	Depths sampled (cm)	No. of horizons sampled	Parent material	Soil classification	
				Soil taxonomy[1]	New Zealand[2]
Taita (10000 A–F)	0–111	6	Greywacke colluvium over greywacke rock	Typic Hapluhumult	Yellow-brown earth
Taita red variant (9991 A–G)	0–140	7	Greywacke colluvium over greywacke rock	Typic Hapluhumult	Yellow-brown earth
Koronivia (9601 C, D)	26–68	2	*In situ* siliceous sedimentary rock	Epiaquic Kandihumult	n.a.
Wharekohe (9525 A–H)	0–151	7	Weathered greywacke	Typic Albaquult	Podzol
Wingate (9986 A–H)	0–125	8	Greywacke-derived loess over colluvium	Typic Hapluhumult	Yellow-brown earth
Rapaki (9998 A–F)	0–100	6	Basaltic lava + loess	Typic Hapludoll	Brown granular loam
Kerikeri (9539 A–G)	0–145	7	Strongly weathered basalt	Typic Hapluhumult	Brown loam
Naike (9579 A–I)	0–181	9	Volcanic ash (andesite/rhyolite)	Typic Kandihumult	Brown granular loam
Te Kowhai (9433 A–F)	0–100	6	Rewashed rhyolitic volcanic material	Mollic Haplaquept	Gleyed yellow-brown loam
Avery (9894 E–K)	55–139	7	Granite	Histic Sideraquod	Podzol

[1] Soil Survey Staff (1987).
[2] Taylor and Pohlen (1970).
n.a. = not applicable.

chlorite layers probably gave rise to 11-Å reflections from samples prior to DMSO treatment (Churchman, 1980). The degree of expansion following complex formation (intercalation) or hydration was assessed from the ratios of the peak heights of the basal reflections for the expanded phases (at 10 or 11 Å) to the sum of heights of these peaks and those for the unexpanded phase at 7 Å.

The abundance of tubular particles (including laths and other elongated particles) in 11 clay fractions that had been redispersed by ultrasonification was assessed from transmission electron micrographs obtained with a Philips EM200 electron microscope. Confirmation of the shapes was made using the higher resolution of a Philips EM400T electron microscope.

RESULTS

Table 2 gives the response of the kaolin-group minerals (i.e., kaolinite and halloysite) in each of the 10 soil profiles to the immediate-formamide and HWG treatments as they were applied to previously air-dried samples. The clay and kaolin-group mineral contents, as estimated using an X-ray sedigraph (Hendrix and Orr, 1970) and differential thermal analyses (Hewitt and Churchman, 1982), are also listed. The degree of expansion, whether produced by the immediate-formamide or HWG procedures, either decreased towards the surface or was constant throughout each profile, except in the Wharekohe samples, in which degrees of expansion were high at the base of the profile, decreased

towards its center, and then increased towards its surface. The degree of expansion with HWG was always greater than that with formamide.

The data in Table 3 show that even gentle heating at $40 \pm 5°C$ decreased the expansion by formamide of some of the samples, although heating often brought about no change beyond experimental error (± 0.1). Decreases usually occurred for samples that were highly expandable with formamide. Even so, the greater degrees of expansion achieved with formamide before gentle heating were still usually less than those achieved by the HWG treatment (Table 2). The HWG treatments were carried out on samples that had been air-dried with gentle heating (at 40°C). The formamide treatment was as effective as the HWG treatment only if complete or near-complete intercalation took place (i.e., in most of the Naike profile and the lower two horizons of the Te Kowhai profile).

Table 4 shows the maximum expansion of several samples with DMSO compared with those produced by the immediate-formamide, 4-day-formamide, and HWG treatments. The extent of DMSO intercalation (as given by degree of expansion) increased with time; at the maximum (after 7 days), it was similar, within experimental error (± 0.1), to that produced by the HWG treatment.

Table 5 shows the degree of expansion of several kaolinite samples by DMSO compared with that produced by the HWG treatment. The expansion of kaolinite samples was determined more precisely than

Table 2. Response of kaolin-group minerals in soils to (immediate) formamide and HWG[1] intercalation tests.

Soils from sedimentary materials

Largely weathered in situ | **from Loess**

Sample (Soil Bureau Sample Nos.)	Taita (10000) Clay (%)	Kaolin (%)	Form-amide	HWG	Taita Red Variant (9991) Clay (%)	Kaolin (%)	Form-amide	HWG	Koronivia (9601) Clay (%)	Kaolin (%)	Form-amide	HWG	Wharekohe (9525) Clay (%)	Kaolin (%)	Form-amide	HWG	Wingate (9986) Clay (%)	Kaolin (%)	Form-amide	HWG
A	35	60	0.3	0.7	25	53	0.2	0.8	51	88	0.0	0.4	7	35	0.1	0.6	20	55	0.1	0.8
B	51	57	0.2	0.7	26	50	0.2	0.8	68	80	0.1	0.4	6	65	0.0	0.5	14	57	0.1	0.8
C	67	55	0.3	0.5	26	55	0.2	0.8					4	32	n.d.	n.d.	15	57	0.1	0.7
D	68	65	0.4	0.6	40	55	0.2	0.9					14	53	0.0	0.3	18	50	0.1	0.8
E	56	68	0.5	0.7	55	50	0.6	0.8					34	76	0.0	0.2	37	60	0.1	0.8
F	41	55	0.4	0.9	49	73	0.7	1.0					47	85	0.0	0.1	46	65	0.1	0.8
G	46	55	0.6	0.9	60	75	0.7	0.9					34	80	0.0	0.3	71	60	0.2	0.8
H													61	90	0.2	0.7	65	53	0.1	0.8
I																	n.d.	50	0.0	0.7

Soils from igneous materials

Basalt | **Andesite/rhyolite** | **Rhyolite** | **Granite**

Sample	Rapaki (9998) Clay (%)	Kaolin (%)	Form-amide	HWG	Kerikeri (9539) Clay (%)	Kaolin (%)	Form-amide	HWG	Naike (9579) Clay (%)	Kaolin (%)	Form-amide	HWG	Te Kowhai (9433) Clay (%)	Kaolin (%)	Form-amide	HWG	Avery (9894) Clay (%)	Kaolin (%)	Form-amide	HWG
A	24	55	0.1	0.6	54	40	0.0	0.3	53	70	0.5	0.8	25	60	0.2	1.0	3	35	0.1	0.5
B	23	60	0.0	0.7	56	44	0.0	0.2	87	65	0.7	0.8	26	60	0.4	1.0	53	76	0.2	0.5
C	21	55	0.1	0.8	60	50	0.0	0.2	81	93	0.8	0.9	35	70	0.3	1.0	32	72	0.2	0.6
D	27	45	0.0	0.8	61	49	0.0	0.2	88	88	0.5	1.0	19	65	0.5	1.0	43	50	0.2	0.7
E	21	55	0.0	0.7	61	44	0.0	0.3	87	90	0.7	1.0	10	63	0.5	1.0	22	78	0.2	0.7
F	5	55	0.4	1.0	55	54	0.2	0.8	77	88	0.7	1.0	7	62	0.4	1.0	15	74	0.4	0.8
G					43	77	0.3	0.9	66	95	0.6	1.0					11	66	0.4	0.9
H									63	93	0.8	1.0								
I									63	100	0.9	1.0								

Degree of expansion[2]

[1] HWG = Sequential treatment with hydrazine, water, and glycerol.
[2] Degree of expansion given by ratio of height of 001 peak for expanded kaolin-group phase to sum of heights of 001 peaks for kaolin-group minerals.
n.d. = not determined.

Table 3. Effect of prior heating (at 40°C)[1] on expansion of soil clay fractions by formamide.

Soil																	
	Taita (10000)		Taita Red Variant (9991)		Wharekohe (9525)		Wingate (9986)		Rapaki (9998)		Kerikeri (9539)		Naike (9579)		Te Kowhai (9433)	
Sample	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
A	0.1	0.3	0.2	0.2	0.4	0.1	0.0	0.1	0.1	0.1	0.0	0.0	0.7	0.5	0.6	0.2
B	0.1	0.2	0.2	0.2	0.3	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.9	0.7	0.6	0.4
C	0.3	0.3	0.3	0.2	0.2	n.d.	0.1	0.1	0.2	0.1	0.0	0.0	1.0	0.8	0.7	0.3
D	0.2	0.4	0.3	0.2	0.2	0.0	0.2	0.1	0.2	0.0	0.0	0.0	1.0	0.5	0.8	0.5
E	0.3	0.5	0.6	0.6	0.2	0.0	0.4	0.1	0.5	0.0	0.2	0.0	1.0	0.7	1.0	0.5
F	0.5	0.4	0.8	0.7	0.1	0.0	0.3	0.1	0.7	0.4	0.4	0.2	1.0	0.7	1.0	0.4
G	0.6	0.6	0.8	0.7	0.0	0.0	0.3	0.2			0.4	0.3	1.0	0.6		
H					0.6	0.2	0.4	0.1					1.0	0.8		
I							n.d.	0.0					1.0	0.9		

Heading: B = before; A = after.
[1] ±5°C.
[2] As in Table 2.
n.d. = not determined.

for most of the soil kaolins (Tables 2–4), because the XRD peaks for kaolinite and its intercalates are stronger and sharper than those for halloysite (Theng *et al.*, 1984). Different kaolinite samples were expanded to different extents by DMSO. The Hymod Kc and the 62/2 samples, which are poorly crystalline according to both the Hinckley (1963) and Hughes and Brown (1979) indexes, expanded more than did some of their well-crystallized counterparts, such as the 78/16 and Wairakei samples. Samples of a poorly (KGa-2) and well-crystallized kaolinite (KGa-1) were largely resistant to expansion by intercalation. Hence, no clear relationship was found between the degree of expansion by DMSO and either of the two indexes of crystallinity. The degree of expansion by DMSO always exceeded that by HWG. None of the kaolinite samples were expanded to any substantial extent by HWG (no ratio > 0.1), and four of the six kaolinites underwent no expansion with HWG treatment.

Table 6 shows the frequency of occurrence of particle

Table 4. Expansion of soil kaolins with dimethylsulphoxide (DMSO) compared with that obtained immediately upon formamide application (<1 hr), long-term (4-day) formamide, and sequential treatments with hydrazine, water, and glycerol (HWG treatment).

	Degree of expansion[1]			
Sample	DMSO (7 days)	Formamide (<1 hr)	Formamide (4 days)	HWG
10000 B	0.9	0.2	0.2	0.7
10000 F	0.8	0.4	0.5	0.9
9601 C	0.5	0.0	0.1	0.4
9525 F	0.3	0.0	0.0	0.1
9986 A	0.7	0.1	0.1	0.8
9986 H	0.7	0.1	0.1	0.8
9998 A	0.8	0.1	0.1	0.6
9539 A	0.1	0.0	0.0	0.3
9579 A	0.9	0.5	0.6	0.8
9894 F	0.4	0.2	0.3	0.5

[1] As in Table 2.

shapes usually considered to be characteristic of halloysites (tubes and spheres) in electron micrographs of various clay fractions. These frequencies are expressed as ratios of total percentage occurrence of kaolin-group minerals, as determined by differential thermal analyses. They are compared in Table 6 with degrees of expansion from the immediate-formamide and HWG treatments, both after air-drying with gentle heating of the samples. The estimates of halloysite based on abundance of appropriate shapes in electron micrographs were commonly similar to those based on expansion by intercalation on immediate-formamide treatment. The expansion by HWG treatment always overestimated halloysite compared with the amount indicated by the abundance of appropriate shapes in electron micrographs. Both the top- and sub-soils of the Wingate profile, 9986A and H (Figures 2 and 3) yielded very large HWG-expandabilities and very low abundances of characteristic halloysite shapes. Other similar examples are the Te Kowhai topsoil 9433A (Figure 4), the lowest Kerikeri subsoil horizon 9539F, and the two uppermost Taita horizons 10000A and 10000B. In contrast, the Kerikeri topsoil 9539A (Figure 5) and the Koronivia subsoil 9601C, both of which contained little or no particles having halloysite shapes, showed only limited expansion following the HWG treatment.

DISCUSSION

Kaolin-group minerals from horizons towards the surface of several of the profiles expanded to a lesser extent than those from horizons lower in the profiles after intercalation of both formamide (by the immediate-formamide treatment) and glycerol (by the HWG treatment) (Table 2). This trend indicates a decrease in the proportion of halloysite present relative to that of kaolinite. The opposite trend in the Wharekohe profile (i.e., an increase in extent of intercalation of polar compounds towards the surface) is consistent with the parent materials for the uppermost horizons of this soil

Table 5. Degree of expansion of kaolinite samples after 7-day treatment with dimethylsulphoxide (DMSO) compared with their expansion by a sequential treatment with hydrazine, water, and glycerol (HWG treatment).

Sample	Source[2]	Crystallinity		Degree of expansion[1]	
		Hinckley (1963) index	Hughes and Brown (1979) index	DMSO	HWG
Hymod KC	ECC International Ltd., United Kingdom	0.1	8	0.41	0.09
KGa-2	The Clay Minerals Society, Source Clays Repository	0.3	8	0.03	0.00
62/2	Pottery and Ceramics Research Association, New Zealand	0.5	10	0.20	0.00
78/16	Pottery and Ceramics Research Association, New Zealand	0.8	15	0.06	0.00
KGa-1	The Clay Minerals Society	0.8	40	0.02	0.00
Wairakei	New Zealand Soil Bureau (sample PC184)	1.0	29	0.09	0.02

[1] As in Table 2.
[2] Further details given in Churchman *et al.* (1984).

originating from eroded sediments (J. S. Whitton, Division of Land and Soil Sciences, DSIR, Lower Hutt, New Zealand, personal communication). The much lower percentages of clay in samples at the top of this profile compared with those at its base bear out this explanation. Although no trend was apparent in the expansion of kaolin-group minerals within the Wingate profile (Table 2), the expansion by formamide of kaolin in clays before air-drying showed a steady increase towards the surface of the profile (Table 3). There was no change in expansion of kaolin-group minerals within some of the other profiles.

Because the same tendencies were shown with both the immediate-formamide and HWG treatments, the question remains as to which is the more appropriate test for distinguishing halloysite from kaolinite. In the samples examined, the occurrence of characteristic halloysite shapes from TEM closely matched the degree of expansion immediately upon application of formamide. On the other hand, the abundance of these shapes was usually much lower than the proportion of halloysite estimated from the HWG test data. In some samples, however, expansion by the immediate-form-
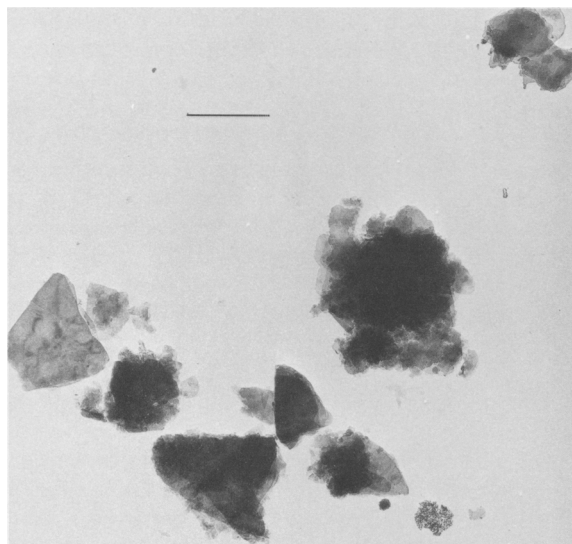

Figure 2. Transmission electron micrograph of Wingate topsoil 9986A clay fraction (55% kaolin-group minerals, 0.1 formamide-expandable, 0.8 expandable after hydrazine-water-glycerol treatment) showing relationships between morphology of kaolin-group minerals and their expandabilities. Ratios denote expandable layers as a proportion of kaolin-group minerals present. Scale = 0.5 μm.
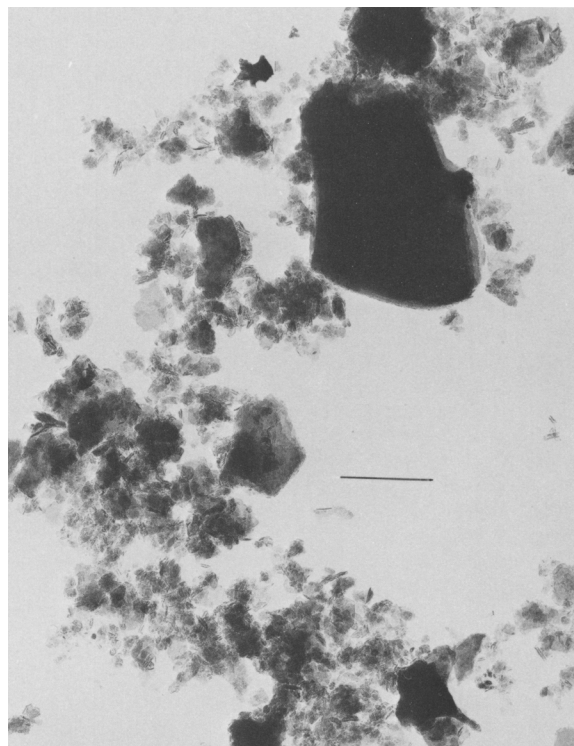

Figure 3. Transmission electron micrograph of Wingate subsoil 9986H clay fraction (53% kaolin-group minerals, 0.1 formamide-expandable, 0.8 expandable after hydrazine-water-glycerol treatment) showing relationships between morphology of kaolin-group minerals and their expandabilities. Ratios denote expandable layers as a proportion of kaolin-group minerals present. Scale = 0.5 μm.
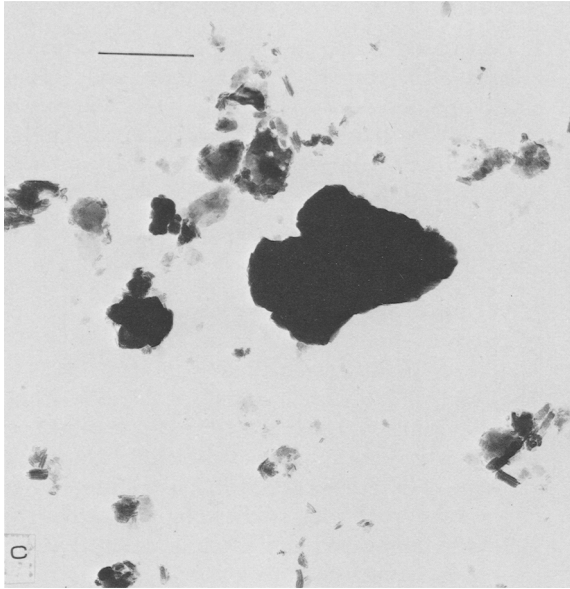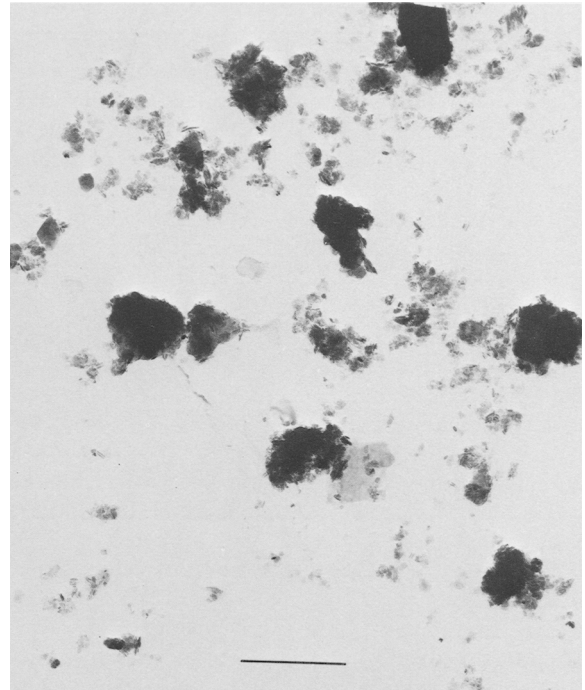
Figure 4.   Transmission electron micrograph of Te Kowhai topsoil 9433A clay fraction (60% kaolin-group minerals, 0.2 formamide-expandable, totally expandable after hydrazine-water-glycerol treatment) showing relationships between morphology of kaolin-group minerals and their expandabilities. Ratios denote expandable layers as a proportion of kaolin-group minerals present. Scale = 0.5 μm.

Figure 5.   Transmission electron micrograph of Kerikeri topsoil 9539A clay fraction (40% kaolin-group minerals, 0 formamide-expandable, 0.3 expandable after hydrazine-water-glycerol treatment) showing relationships between morphology of kaolin-group minerals and their expandabilities. Ratios denote expandable layers as a proportion of kaolin-group minerals present. Scale = 0.5 μm.

amide treatment decreased if the samples had been dried before the treatment (Table 3). The expansion of undried samples by the immediate-formamide treatment also indicated more halloysite than implied by the abundance of characteristic halloysite shapes in many of these soil clays (e.g., samples 9539F, 9579A,

9579B, 9579I, 9986H, and 9433A). Even so, estimates from electron micrographs were inaccurate because of the difficulty of distinguishing many shapes, especially if the particles were agglomerated. The halloysite estimates from electron micrographs are therefore likely to be low.

The soil clays were expanded by DMSO to a similar extent as by HWG (Table 4). Non-soil kaolinite samples did not expand with the HWG treatment to any substantial extent (Table 5); however, all of these standard kaolinite samples were partially expanded by DMSO. Churchman *et al.* (1984) showed that prolonged treatment of some kaolinite samples with formamide produced intercalates. The soil kaolins examined here, however, expanded no more with formamide on long-term (4-day) treatment than with immediate treatment of undried samples (cf. Tables 3 and 4). Formamide does not expand kaolinite immediately (Churchman *et al.,* 1984). Furthermore, unpublished tests in our laboratory on nine soil samples used in Page's (1984) study have shown that iron removal by citrate-dithionite-bicarbonate (CDB) treatment had no effect on the expansion of kaolin-group minerals by formamide. This result validates comparisons between CDB-treated soil samples and untreated standard kaolinites. Hence, although all samples listed in Table 4

Table 6.   Abundance of tubular and spheroidal particles in soil clay fractions in relation to the expansion of their constituent kaolin-group minerals immediately upon formamide application and after sequential treatment with hydrazine, water, and glycerol (HWG treatment).

Sample	Ratio of tubes and spheres to total kaolin-group mineral content[1]	Particles counted	Degree of expansion[2]	
			Formamide	HWG
9539 A	0.1	416	0.0	0.3
9539 F	0.2	443	0.2	0.9
9579 A	0.4	615	0.5	0.8
9579 B	0.7	110	0.7	0.8
9579 I	0.7	849	0.9	1.0
9986 A	0.1	289	0.1	0.8
9986 H	0.1	630	0.1	0.8
9433 A	0.2	451	0.2	1.0
9601 C	0	546	0.0	0.4
10000 A	0.1	449	0.3	0.7
10000 B	0.1	265	0.2	0.7

[1] Total kaolin-group mineral content estimated from differential thermal analyses.
[2] As in Table 2.

contained kaolinite, none of the kaolinite present was expanded by long-term treatment with formamide. Thus, both the DMSO and HWG treatments were more effective than the formamide treatment for intercalating kaolinite in the soil clay samples listed in Table 4.

On the basis of their expansion with a particular intercalating agent, the division between expandable and non-expandable kaolin-group minerals depends on the intercalating agent used and the procedure by which it is applied. One procedure, involving a sequential treatment with CsCl, hydrazine, and then DMSO, appears to intercalate all kaolinite completely (Jackson and Abdel-Kader, 1978; Calvert, 1984). The immediate-formamide treatment, however, has given halloysite contents which closely match those from the older washed-acetate test of Wada (1961) and which are also reasonable in relation to particle shapes (Churchman *et al.*, 1984). Churchman and Gilkes (1989) showed that a tubular 'kaolin' may have derived from the strong or prolonged dehydration of halloysite, at least in deeply weathered materials in Western Australia. This tubular 'kaolin' is not expandable by formamide (immediately upon application), but may be expandable by HWG. Hence, expansion immediately upon application of formamide provided a reasonable test for halloysite in Churchman and Gilkes' (1989) study.

If a non-tubular kaolin-group mineral expands only after an HWG treatment, it cannot reliably be identified as halloysite. Use of this test alone to indicate halloysite would mean that the kaolin-group minerals in samples such as 9986A, 9986H and 9433A (Figures 2–4) consist entirely of halloysite. Even so, the kaolin-group minerals in these three samples differ from those in sample 9539A, for example, because of their greater expandability on HWG treatment. The behavior of the kaolin-group minerals in samples 9986A, 9986H, and 9433A is more like that of halloysite than is that of the kaolin-group minerals in sample 9539A. This behavior could be explained by prior intercalation with interlayer water of the kaolin-group minerals in the three former samples. The residual effect of this water, however, is much weaker than is expressed in a dehydrated halloysite *per se*. The HWG treatment possibly leads to intercalation of some kaolinite samples (by glycerol), because these kaolinite samples formed from halloysite by dehydration in the first place. Churchman and Gilkes (1989) showed that kaolin-group minerals that are expandable by HWG treatment, but not by immediate-formamide treatment, represent intermediate products in the gradual change within a weathering profile from a dominantly halloysite mineralogy at the base to a strongly kaolinite mineralogy nearer the soil surface. Their results are consistent with those from the present study, which indicates that HWG expands kaolinite derived from halloysite.

SUMMARY AND CONCLUSIONS

1. The degrees of expansion of kaolin-group minerals, as measured immediately after formamide application and also after a sequential hydrazine-water-glycerol (HWG) treatment generally showed similar trends with proximity to the surface of 10 soil profiles. Expansion with both treatments decreased in several of the soils and was unchanged in all but one of the others.

2. The expansion of kaolin-group minerals by the HWG treatment was always greater than that obtained immediately with formamide, unless the samples were fully expandable with formamide.

3. The HWG procedure expanded some kaolin-group minerals that could be characterized as kaolinite by other means, but did not expand highly crystalline kaolinite. These HWG-expandable kaolinite samples were more similar in intercalation behavior to halloysite than were other kaolinite samples. They may have formed from halloysite by dehydration, possibly followed by structural and/or morphological changes.

4. DMSO was at least as effective as the HWG treatment in expanding soil kaolinite, but, unlike the HWG treatment, it also produced considerable expansion of even highly crystalline kaolinite.

5. The degree of expansion immediately upon formamide treatment usually matched the abundance of characteristic halloysite particle shapes more closely than the other intercalation tests.

6. Halloysite abundances were underestimated if they were measured by expansion immediately upon formamide application if the samples had been heated previously, even at only 40°C.

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