Clays and Clay Minerals, Vol. 32, No. 4, 249–258, 1984.

COMPARISON OF INTERCALATION METHODS FOR DIFFERENTIATING HALLOYSITE FROM KAOLINITE

B. K. G. THENG, G. J. CHURCHMAN, J. S. WHITTON, AND G. G. C. CLARIDGE

Soil Bureau, Department of Scientific and Industrial Research, Private Bag, Lower Hutt, New Zealand

Abstract—The intercalation of formamide, potassium acetate, and hydrazine by halloysite and/or kaolinite-rich samples, with and without subsequent displacement of the interlayer species by water or glycerol/water, has been investigated. Halloysite, as such, or in mixtures with kaolinite is completely expanded by all the treatments used, thereby enabling halloysite concentrations to be determined from the basal X-ray powder diffraction (XRD) peak ratios of the appropriate complexes. The values so obtained are usually proportional to the abundance of tubes, laths, and spherules in the transmission electron micrographs of the samples. The analysis of kaolin samples (halloysite plus kaolinite) by intercalation methods is less straight forward because a proportion of the kaolinite component in the system may not expand, even after lengthy ($\geq$18 days) contact of the sample with the intercalating agent. Only prolonged immersion in hydrazine produces complete or nearly complete expansion of this component. When allowance is made for the presence of non-clay mineral components, kaolin-mineral percentages estimated from XRD peak intensity ratios of the hydrazine complexes generally agree with values derived from differential thermal analysis to within $\pm$10%. Kaolinite in mixtures with halloysite cannot be directly determined by intercalation procedures inasmuch as treatments which result in complex formation with kaolinite also expand halloysite. In such systems, kaolinite can be estimated by difference between the concentration of kaolin minerals and halloysite.

Key Words—Formamide, Halloysite, Hydrazine, Intercalation, Kaolinite, Potassium acetate, Test.

INTRODUCTION

The ability of halloysite and kaolinite to intercalate certain salts and organic compounds has been well documented (Theng, 1974; MacEwan and Wilson, 1980). Besides showing characteristic basal spacings, the interlayer complexes so formed have varying stabilities towards specific solvents, thereby providing a means of distinguishing halloysite from kaolinite in mixed systems. Intercalation methods also have the advantage over other techniques in that they may be applied to whole samples, thus obviating the need for elaborate sample fractionation and pretreatment. This is an important consideration in the routine analysis and classification of materials rich in 1:1 layer silicates, exemplified by many New Zealand soils.

Two methods that have been widely used involve treating the mineral mixtures sequentially with (1) potassium acetate and then water (Wada, 1961), or (2) hydrazine, then water, and then glycerol (Range *et al.*, 1969). In either method, washing the intercalation complex with the last solvent in the sequence (i.e., water or glycerol) causes the initially expanded kaolinite crystal to collapse to its original basal spacing (~7 Å), whereas halloysite remains expanded at a spacing characteristic of the washed complex (10–11 Å).

Although these procedures and their variants (Miller and Keller, 1963; Borovec, 1975; Wilson and Tait, 1977) have generally given qualitatively sensible results, difficulties arise in their application for quantitative or even semi-quantitative analysis (see e.g., Hewitt and Churchman, 1982). On the one hand, kaolinite complexes with potassium acetate tend to show residual interlayer expansion when the salt is leached out with water (Wiewiora and Brindley, 1969). On the other hand, complexes of halloysite and kaolinite with hydrazine are inherently unstable due to volatilization of the organic liquid from the interlayer space (Theng, 1974). In addition, complex formation normally requires prolonged contact of the sample with the intercalating agent. Even then, potassium acetate (from solution) may not be completely intercalated by the kaolinite component in the mixture. This limitation may largely be overcome by grinding the sample with the solid salt, but this mode of preparation is not recommended because it is liable to disrupt the silicate structure (Wada, 1961). Still, hydrazine is apparently capable of effecting nearly complete expansion of kaolinite, with the possible exception of the 'fire-clay' types (Range *et al.*, 1969). Hydrazine, however, suffers from the disadvantage of being highly toxic and flammable.

In studying the interactions of halloysite with a series of amides, Churchman and Theng (1984) found that formamide was rapidly and quantitatively intercalated

Copyright © 1984, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

Table 1. Source, pretreatment, and composition of samples studied.

Sample[1]	Laboratory designation	Mode of formation/ parent material	Location/source
Geologic samples			
Butchers Dam (2)	8r	Weathered schist	Central Otago, New Zealand
'Dana' kaolinite (1)	Dana 492	Unknown	Langley, South Carolina
Vaturu dam site (2)	PC1108	Unknown	Vaturu, Fiji
Matauri Bay halloysite (1)	PC1135	Altered volcanics	Northland, New Zealand
Maungaparerua (1)	PC1065	Altered volcanics	Northland, New Zealand
Te Puke halloysite (1)	PC1138	Altered volcanics	Bay of Plenty, New Zealand
Wairakei kaolinite (1)	PC184	Hydrothermal	Wairakei, New Zealand
Weathered schist (1)	PC921/1	Weathered schist	Eastern Otago, New Zealand
Soil samples			
Allendale silt loam (3)	SB 9327A, B, D	Schist loess	Eastern Otago, New Zealand
Hangawera (4)	T1 C, D, E, F	Greywacke	Hauraki Plains, New Zealand
Kainui silt loam (5)	T3 C, D, E, F, G	Loess/volcanic ash	Hauraki Plains, New Zealand
Koronivia silt loam (1)	SB 9601C	Siliceous sediments	Koronivia, Fiji
Traquair silt loam (4)	SB 9329A, B, C, D	Thin loess/schist	Eastern Otago, New Zealand
Wehenga silt loam (1)	SB 9328A	Schist loess	Eastern Otago, New Zealand
Ceramic samples			
(1)	62/1	Unknown	Unknown
(1)	62/2	Unknown	Unknown
(2)	62/38, 63/111	Unknown	Unknown
(1)	62/39	Unknown	Unknown
(1)	62/82	Unknown	Unknown
(1)	78/16	Unknown	Unknown
(1)	79/14	Unknown	Unknown
(1)	57696	Unknown	Unknown
(1)	579435	Granite/gneiss	Charleston, New Zealand
Industrial samples			
(1)	Hycast VC[2]	Unknown	Devon, England
(2)	Hymod KC, AT[2]	Unknown	Dorset, England
(1)	Hywite Alum[2]	Unknown	Devon, England

[1] (Number of samples).
[2] Imperial Chemical Industries trade names.
[3] Clay fraction refers to <2 μm e.s.d. as obtained by the method of Jackson (1956).
[4] In approximate decreasing order of occurrence—as given in Reference; C = chlorite and interlayered hydrous mica; F = feldspar; G = gibbsite; H = halloysite; K = kaolinite; M = mica-illite; Q = quartz; V = vermiculite and interstratified mica/vermiculite; S = smectite.
[5] Courtesy of W. N. E. Meredith.

into halloysites of varying composition, crystallinity, and particle shape. By contrast, kaolinite intercalates formamide very slowly and then only incompletely (Weiss *et al.*, 1963; Olejnik *et al.*, 1969). Churchman *et al.* (1984) used this difference in the behavior of kaolinites and halloysites towards formamide to provide a rapid and simple test to distinguish between the two mineral types.

It is against this background that the formamide intercalation method has been compared with those involving potassium acetate and hydrazine. This paper contrasts the application of these procedures for the semi-quantitative estimation of halloysite and kaolinite in unprocessed and fractionated clay samples.

EXPERIMENTAL

Materials

Forty-two samples, each containing appreciable amounts (>40%) of halloysite, kaolinite, or both, were examined. Ten were of geologic origin, i.e., sedimentary clay deposits and weathered rock materials, 18 were from soil, and 14 were ceramic and industrial clays (Table 1). Both unprocessed ('raw') materials and separated <2-μm fractions obtained by sedimentation after removal of organic matter and the oxides/hydroxides of iron and aluminum (Jackson, 1956) were examined.

Formamide (BDH, Laboratory Reagent), glycerol (BDH, Analar), hydrazine monohydrate (J. T. Baker, TM grade), and potassium acetate (Hopkins & Williams, General Purpose Reagent) were used as received.

Methods

X-ray powder diffraction (XRD) was the principal method used for characterizing the samples and their respective complexes. The sample was spread or sedimented on porous ceramic tiles and its XRD pattern obtained using a Philips PW1010 diffractometer with

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

Table 1. Continued.

Pretreatment[3]	Composition[4]	Reference
Whole and <0.5-μm fraction	K, C, Q	Childs *et al.* (1979)
As received	Nearly pure K	This work
Whole and clay fraction	H, K, C, M	This work
Air-dried and milled	Nearly pure H	Marsters (1978)
Air-dried and milled	K, H	Murray *et al.* (1977)
As received, moist	Nearly pure H	Hughes (1966)
Air-dried	Nearly pure K	This work
Clay fraction	K, H, M, C	Hewitt and Churchman (1982)
Clay fraction	M, V, K, C, H	Hewitt and Churchman (1982)
Clay fraction	K, H, M, V	This work
Clay fraction	H, V, K, C	This work
Clay fraction	K, H, G	This work
Clay fraction	K, V, M, C, H	Hewitt and Churchman (1982)
Clay fraction	V, M, K, C, H	Hewitt and Churchman (1982)
Air-dried and milled	K, Q, H, F	Hughes and Foster (1970)
Air-dried and milled	K, Q, F, M	Hughes and Foster (1970)
Air-dried and milled	K, Q, M, S	Hughes and Foster (1970)
Air-dried and milled	H, Q, M	Hughes and Foster (1970)
Air-dried and milled	K, Q, F	Hughes and Foster (1970)
Air-dried and milled	K, Q	This work
Air-dried and milled	H, Q	This work
Air-dried and milled	K, F, Q, M, G	This work
As mined	K, M, Q	This work
Air-dried and milled	K, M, Q	Imperial Chemical Industries, U.K.[5]
Air-dried and milled	K, M, Q	Imperial Chemical Industries, U.K.[5]
Air-dried and milled	K, M, Q	Imperial Chemical Industries, U.K.[5]

CoKα radiation and a scan rate of 2°2θ/min. The nine treatments to which each sample was subjected are detailed in Table 2. The resultant complexes with formamide, hydrazine, and potassium acetate, before and after washing with water or glycerol, were 'immediately' examined by XRD, i.e., as soon as the excess liquid had drained away but always within 60 min after placement of the liquid on the tile.

The degree of complex formation (intercalation) was assessed from the ratio of the intensity of the appropriate basal reflections. For example, for complexes with formamide or hydrazine, which show a basal spacing close to 10 Å, the degree of intercalation is given by the ratio $\alpha = I_{10}/(I_7 + I_{10})$ where I_7 and I_{10} denote the intensity of the peaks near 7 and 10 Å, respectively. On the other hand, with potassium acetate, both halloysite and kaolinite expand to a basal spacing of ~14 Å; hence, the degree of intercalation is given by the ratio $\alpha = I_{14}/(I_7 + I_{10} + I_{14})$. The validity of using peak intensities rather than peak areas in deriving α-values was checked by analyzing mixtures of a pure halloysite (Matauri Bay) and a kaolinite ('Dana') (cf. Table 1). The mixtures were prepared by grinding the minerals in proportions of 20, 40, 60, and 80% for 15 min using a Spex mixer mill. The mixtures were then sprayed with formamide (treatment 2, Table 2) and their expansion characteristics analyzed in terms of both peak intensity and peak area.

In addition to XRD, the samples were characterized by differential thermal analysis (DTA) using a Du Pont 900 instrument with alumina as reference and a heating rate of 10°C/min (in air), and by transmission electron microscopy (TEM) using a Philips EM200 instrument. DTA allowed the percentage of kaolin minerals, i.e., halloysite plus kaolinite, in each sample to be estimated independently of their intercalating properties. This percentage was determined by measuring either the intensity of, or the area enclosed by, the high-temperature (500–600°C) endotherm in the DTA pattern (Tan and Hajek, 1977; Whitton, 1978; Hewitt and Churchman, 1982). Although kaolin mineral percentages as determined by DTA may be subject to uncertainties associated with such factors as sample crystallinity and pretreatment (Mackenzie, 1970), our experience suggests that DTA is less strongly affected by such variables than is XRD. Mackenzie (1970) considered that,

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

Table 2. Treatments of samples for estimation of halloysite and kaolin minerals.

Treatment		Remarks
Number	Mode	
1	Unheated sample, moistened with water	Peak near 10 Å ascribed to hydrated halloysite with contribution from illite-mica (cf. treatment 3); peak near 7 Å indicates kaolinite and/or dehydrated halloysite.
2	Formamide spray, unheated sample (as in 1)	Dehydrated halloysite expands to ~10 Å immediately (within 1 hr) after spraying; kaolinite remains unexpanded at ~7 Å within this time interval.
3	Oven-dried at 110°C overnight	Both halloysite and kaolinite collapse to ~7 Å; any residual line near 10 Å indicates illite-mica.
4	Potassium acetate (6.5 M), 18 days immersion, unheated sample	Time scale sufficient for kaolinite component to reach maximum expansion; both halloysite and kaolinite expand to ~14 Å; residual line at ~7 Å ascribed to unexpanded kaolinite with contribution from second order basal reflection of potassium acetate complex.
5	As for 4, then washed with water until material dispersed, centrifuged	Halloysite component contracts from ~14 Å to ~10 Å while kaolinite component collapses to its original basal spacing near 7 Å.
6	Hydrazine hydrate, 25 days immersion (room temp.)[1], unheated sample	Time scale sufficient for kaolinite component to attain maximum expansion; both halloysite and kaolinite give interlayer complexes with basal spacing near 10 Å.
7	As for 6, then washed three times with water, centrifuged	Kaolinite collapses from ~10 to ~7 Å; peak near 10 Å ascribed to halloysite; any 'disordered kaolinite' remains expanded at ~10 Å[2].
8	As for 7, then sprayed with glycerol (10% v/v in water)	Halloysite remains expanded at ~10 Å; all types of kaolinite contract to ~7 Å.
9	Formamide, 28 days immersion, unheated sample	Time scale sufficient for kaolinite component to attain maximum expansion; both halloysite and kaolinite expand to ~10 Å; a residual line at ~7 Å indicates some unexpanded kaolinite.

[1] Range *et al.* (1969) used 7 days at a temperature of 65°C.
[2] Correspond to types II and III kaolinite of Range *et al.* (1969).

for most purposes, quantitative determinations could be made with sufficient accuracy using the kaolin dehydroxylation peak. Similarly, transmission electron microscopy gave an independent approximation of halloysite proportions by assuming that halloysite particles occurred only in the form of tubes, laths, and spherules (Churchman and Theng, 1984). The electron micrographs used for this purpose were obtained at a magnification of 25,000. For every sample, 4 to 19 micrographs were examined, each of which had at least 50 particles in the field of view. The abundances of tubes, laths, or spherules were noted.

With a variety of factors besides concentration affecting XRD peak intensities, peak intensity ratios do not necessarily indicate the proportions by weight of each phase present. Nevertheless, these ratios are useful for comparative purposes and are used here to estimate halloysite and kaolin percentages in kaolin-rich samples. Even then, only those minerals whose basal reflections fall within the range shown by the appropriate complexes, were accounted for by the ratios. Species such as chlorite, interlayered hydrous mica, smectite, and vermiculite were excluded from the peak intensity ratios of formamide and hydrazine complexes. Likewise, non-clay minerals (e.g., quartz), present in appreciable proportions in some of the samples, were also left out of the ratios. On the other hand, kaolin mineral percentages estimated from DTA were expressed in terms of sample weight. For this reason, the DTA values tend to be slightly greater than the corresponding kaolin percentages derived from intercalation complexes, even if the kaolinite component of the mixture was fully expanded.

RESULTS

Estimation of halloysite

The proportion or concentration of halloysite in the samples may, to a first approximation, be estimated from the ratio $\alpha = I_{10}/(I_7 + I_{10})$ of the complexes formed following treatments 2, 5, 7, and 8 (Churchman *et al.*, 1984). As noted in Table 2, these treatments caused halloysite to expand completely or to maintain its expansion against washing with water or water-glycerol. Kaolinite, on the other hand, either failed to form a complex or collapsed to its original (unexpanded) state on washing. The halloysite proportions so obtained were refined by subtracting the respective peak ratio of the sample after oven-drying (treatment 3) which represented the contribution of mica (and/or illite) to the intensity of the 10-Å line of the complex. The

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

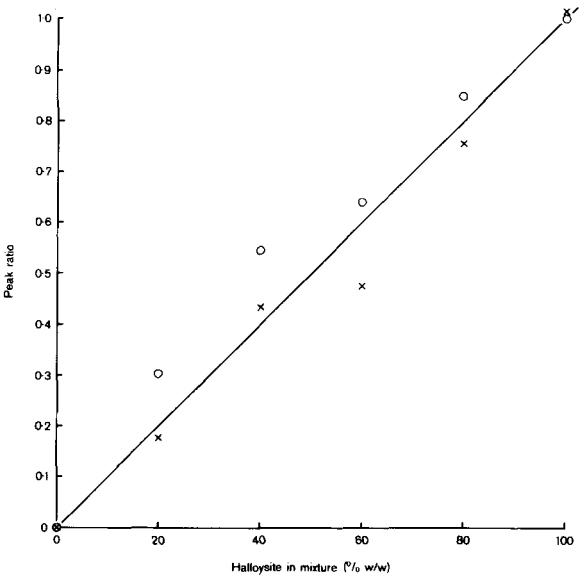


Figure 1. Variation in basal peak ratios with percentage halloysite (Matauri Bay) in synthetic mixtures with kaolinite ('Dana'); ratios refer to complexes with formamide, obtained on the basis of either peak intensity (×) or peak areas (○).

percentage of halloysite in a given sample was simply obtained by multiplying the corrected ratio by 100. Inasmuch as individual peak ratios were reproducible to ±0.1, the uncertainty in clay percentage values was ±10%.

Figure 1 shows a plot of the percentage halloysite in synthetic mixtures with kaolinite vs. the peak ratio of the respective complex after expansion with formamide (treatment 2). Each ratio obtained on the basis of either peak intensity or peak area (Churchman, 1980) corresponds closely to the respective percentage halloysite in the mixture. Although this observation may be specific to this pair of kaolin minerals, the results indicate the general equivalence of intensity and area for estimating halloysite percentages. For routine analyses, however, the use of peak intensity is preferable to the more elaborate method of measuring peak areas.

Halloysite percentages (X) for all 42 samples, as derived from the peak intensity ratios of complexes obtained by treatment 2, were correlated with percentages derived from treatments 5, 7, and 8 (Table 3). The correlations were all highly significant ($r > .85$), with the correlation between X_2 and X_5 being nearly 1:1. The equations relating X_2 to X_7 and X_2 to X_8 indicate that formamide intercalation complexes (treatment 2) gave peak ratios that underestimated halloysite percentages as compared with treatments involving hydrazine (7 and 8).

Table 4 shows the frequencies of occurrence of halloysite in electron micrographs vs. the corresponding percentages of this mineral determined by formamide

Table 3. Regression equations relating halloysite percentages (X) derived from rapid formamide (2) treatment to those obtained by washed potassium acetate (5), washed hydrazine (7) and glycerated washed hydrazine (8) treatments.

Treatment[1]	Regression equation[2]	Correlation coefficient (r)[3]	Number of samples
2 against 5	$X_2 = 1.01X_5 + 1.36$	.905	42
2 against 7	$X_2 = 0.87X_7 - 0.52$	.934	42
2 against 8	$X_2 = 0.81X_8 + 3.71$	.850	42

[1] See Table 2.
[2] Values of X are based on the clay mineral content of the samples; subscripts 2, 5, 7, and 8 refer to the respective treatments as detailed in Table 2.
[3] Level of significance $P < .001$.

intercalation (X_2). For comparative purposes, the values of X_2 are arranged into three classes of similar frequency, i.e., 0–10%, 20–50%, and 60–100%.

In view of its selective and unrepresentative nature, TEM yields only broad estimates of concentration. This attribute is confirmed by the general increase in the abundance of tubes, laths, and spherules as the percentage of halloysite in the samples increased. The relationship between these two values was more evident at low than at high halloysite percentages. Thus, for samples containing 0–10% halloysite, 122 of 137 micrographs showed <10% recognizable halloysite forms, whereas for samples with $60\% < X_2 < 100\%$, only half of the micrographs examined showed halloysite forms in the corresponding frequency class. Another 24% of micrographs gave little evidence of halloysite although from the formamide intercalation method they were apparently rich in halloysite. These micrographs were of the two Vaturu dam site samples from Fiji (PC1108, Table 1), containing aggregates of spheroidal particles. Because of their blocky appearance, individual spherules of halloysite were difficult to identify as such, illustrating the problem of relying on TEM alone to indicate the occurrence or absence of halloysite in a given sample.

Estimation of kaolin minerals

Table 5 shows kaolin-mineral percentages derived from peak intensity ratios of samples selected from

Table 4. Relationship between halloysite percentages, estimated using rapid formamide treatment, and the occurrence of distinctive halloysite forms[1] in transmission electron micrographs.

Halloysite (%)	Number of micrographs showing the occurrence of halloysite forms			Total number of micrographs examined
	<10% occurrence	20–50% occurrence	>50% occurrence	
0–10	122	15	0	137
20–50	31	45	25	101
60–100	11	12	23	46

[1] Tubes, laths, and spherules.

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

Table 5. Percentages of kaolin minerals estimated from long-term intercalation and differential thermal analysis (DTA) and kaolinite by difference between the kaolin-mineral and halloysite values.

Sample name/designation	Kaolin minerals (%)				Halloysite (%)[1]	Percentage kaolinite	
	Potassium acetate	Hydrazine	Formamide	DTA		Method (1)[2]	Method (2)[3]
Geologic clays							
'Dana' kaolinite	50	100	90	100	0	100	100
Matauri Bay halloysite	90	100	100	90	100	0	−10
Te Puke halloysite	90	100	100	90	100	0	−10
Wairakei kaolinite	20	80	40	100	0	80	100
Weathered schist	80	80	80	70	30	50	40
Soil clays							
T1 E	60	80	50	70	20	60	50
T3 C	70	90	80	65	80	10	−15
T3 G	70	80	80	80	70	10	10
SB 9329D	70	70	50	65	10	60	55
Ceramic clays							
78/16	30	70	40	60	10	60	50
79/14	80	90	90	100	70	20	30
62/1	40	80 (60)[4]	60	60	30	50 (30)[4]	30
62/2	70	90 (50)[4]	80	40	20	70 (30)[4]	20
62/39	50	80 (50)[4]	80	40	50	30 (0)[4]	−10
Industrial clays							
Hycast VC	20	60	40	40	0	60	40
Hymod AT	20	50	30	40	10	40	30
Hymod KC	20	40	20	40	0	40	40
Hywite Alum	20	70	40	70	0	70	70

[1] Estimated from rapid formamide treatment.
[2] Difference between kaolin percentage from hydrazine and halloysite percentage.
[3] Difference between kaolin percentage from DTA and halloysite percentage.
[4] Values in parentheses obtained after correcting for the quartz content.

each group in Table 1 after long-term treatment with potassium acetate solution (4), hydrazine (6), and formamide (9) (Table 2). The XRD data for the pure kaolinites suggest that only prolonged immersion in hydrazine gave complete or nearly complete expansion of the kaolinite component in the samples. On the other hand, potassium acetate apparently failed to expand kaolinite completely. The incomplete reaction with potassium acetate and the coincidence of the second-order line of the complex with the basal reflection of unexpanded kaolinite led to an underestimate of kaolin-mineral proportions. Likewise, formamide (treatment 9) did not completely intercalate the kaolinites, and, hence, the peak ratio of the complexes did not adequately reflect the concentration of kaolin minerals in a given sample.

The kaolin-mineral percentages derived from treatment 6 agree with those measured by DTA. Only for samples 62/1, 62/2, and 62/39 were the two sets of values markedly different. These are ceramic bodies which contain substantial amounts of quartz (~30% w/w) and some feldspar (<5% w/w), both of which do not contribute to the appropriate basal peak ratios of the hydrazine complexes. When the respective amounts of these constituents were allowed for, however, good agreement was obtained between the DTA and the hydrazine intercalation values.

Estimation of kaolinite

Table 5 also lists the halloysite percentages in the samples as derived from formamide intercalation (treatment 2). Values of similar magnitude (not shown) were given by treatments 5, 7, and 8 (cf. Table 3). The corresponding percentages of kaolinite were obtained by subtracting these values from the respective percentages of kaolin minerals as determined by either DTA or long-term immersion in hydrazine. As might be expected, both methods yielded comparable values for kaolinite, the quartz-rich samples being the exception for reasons stated above.

DISCUSSION

Inasmuch as halloysite expanded completely or maintained its expanded state on treatment with formamide, potassium acetate followed by water, and hydrazine followed by water or water-glycerol, any one of these intercalation methods is capable of yielding acceptable estimates of halloysite in mixtures with kaolinite. This observation applies even to unprocessed ceramic and industrial materials, thus obviating the

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

need for elaborate and time-consuming procedures of sample pretreatment often required for quantitative analysis (e.g., Al-Khalissi and Worrall, 1982).

The formamide and potassium acetate methods, however, tended to underestimate halloysite concentrations as compared with treatments involving hydrazine (Table 3). A possible explanation is that some of the samples contain disordered types of kaolinite. As Range *et al.* (1969) reported, such minerals, together with halloysite, should have remained expanded when the interlayer hydrazine was displaced by water. If so, the peak near 10 Å in the water-washed hydrazine complexes would have contained a contribution from disordered kaolinite, leading to an overestimation of halloysite. Range *et al.* (1969) also noted that the addition of glycerol to water-washed hydrazine complexes led to a collapse of both well-crystallized and disordered kaolinite; however, like halloysite, disordered kaolinite maintained its expanded state when ethylene glycol instead of glycerol was added. This finding is surprising in view of the similar manner by which both polyhydric alcohols intercalate into expanding 2:1 layer silicates (Brindley, 1966; Theng, 1974). The distinction between halloysite and disordered kaolinite, based on the respective behavior of their water-washed hydrazine complexes towards ethylene glycol or glycerol, may therefore be too fine to apply to systems in which both mineral species coexist. Certainly, the similarity in slopes of the regression lines relating X_2 to X_7 and X_2 to X_8 (Table 3) suggests that water washing of the hydrazine complexes, both with and without subsequent treatment with glycerol, gave essentially identical products.

The concentration of kaolin minerals in the samples may, in principle, also be estimated by intercalation of formamide, potassium acetate, or hydrazine over a long period of time ($\geq$18 days); however, only the hydrazine treatment appeared to give complete expansion of the kaolinite component in the samples. Formamide was generally less effective than hydrazine in this regard, whereas potassium acetate gave but limited interlayer expansion with kaolinite. (There were indications that in some instances complete expansion of the kaolinite component by hydrazine could occur within 6 days.) Plausibly, the size of the complexing agent is important in determining interlayer entry because the observed extent of intercalation, i.e., hydrazine > formamide > potassium acetate, is also the sequence of increasing molecular weight.

In studying the interactions of amides with halloysites, Churchman and Theng (1984) found that the reactivity of the mineral was influenced by its crystallinity and particle size. Table 5 shows that on every count, the Wairakei kaolinite was significantly less reactive than the 'Dana' sample, whereas by all the criteria used to assess crystallinity (Churchman *et al.*, 1984), the former is also better crystallized. This result contrasts with the behavior of halloysites for which the more-crystalline specimens generally showed a higher reactivity than their less-ordered counterparts.

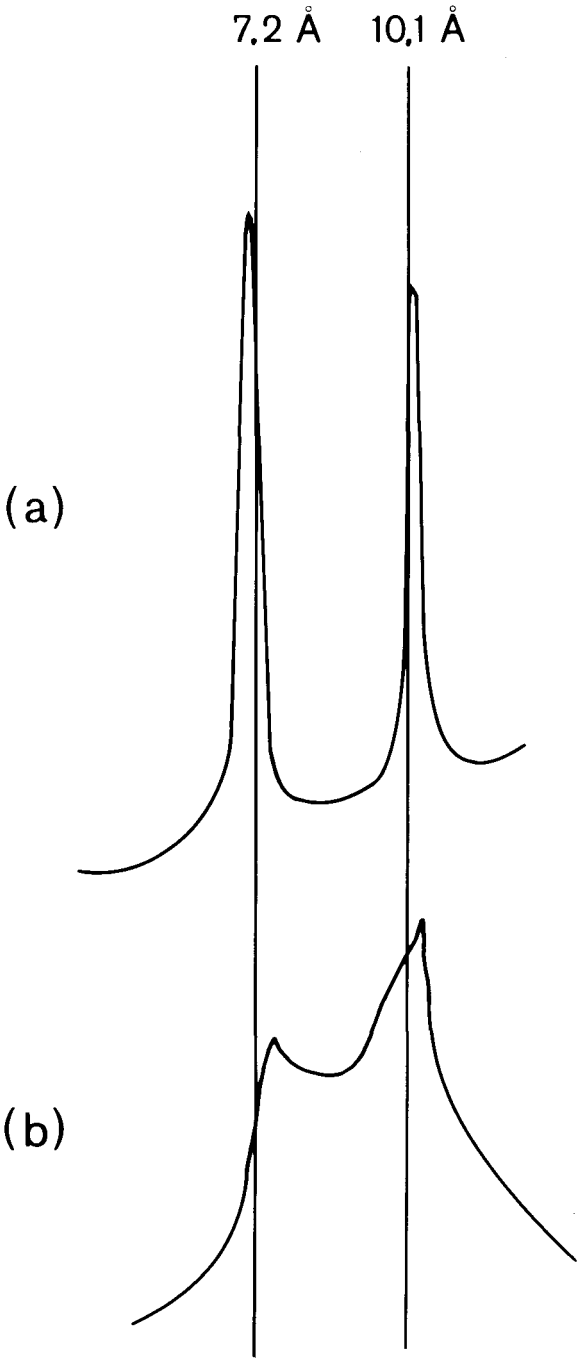


Figure 2. X-ray powder diffraction profile over the basal peak region of partially formed complexes (a) unheated kaolinite (Wairakei) after 11 days immersion in formamide; (b) oven-dried (110°C, overnight) halloysite (Te Puke) after 20-min contact with formamide.

In addition, some kaolinite-rich samples (Hymod

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

AT, Hymod KC, Hycast VC and Hywite Alum) did not intercalate potassium acetate. This failure could be due to a particle size effect, the average particle thickness of these samples being ~0.02 μm (W. N. E. Meredith, Imperial Chemical Industries, U.K., personal communication, 1983). Similarly, the Butchers Dam sample was significantly more reactive towards both formamide and hydrazine as compared with its <0.5-μm size fraction. It would therefore appear that interlayer complex formation was more difficult to achieve with smaller particles, in accord with previous observations for pure kaolinite and halloysite (Martin-Vivaldi *et al.*, 1973; Churchman and Theng, 1984). Possibly, the difficulty was due to enhanced interlayer bonding as the amount and extent of crystal growth dislocations diminish with a decrease in particle size (Chekin, 1982).

The XRD patterns over the basal peak region of partially formed complexes indicate that a qualitative difference in intercalation mechanism exists between halloysite and kaolinite. Figure 2 shows the formamide complex with Te Puke halloysite after oven-drying, which inhibits complex formation (Churchman and Theng, 1984). This complex gave a spread of reflections between 7.1 and 10.4 Å, corresponding to the basal spacings of the parent clay at one end of this range and the fully formed complex at the other. On the other hand, the complex with Wairakei kaolinite showed two discrete sharp peaks at these spacings. By analogy with partially dehydrated halloysite (Churchman *et al.*, 1972), intercalation into halloysite presumably gave rise to interstratification of fully collapsed and expanded layers within a single crystal. The validity of this analogy was confirmed by computer simulation of XRD patterns of partially formed halloysite-formamide complexes (L. P. Aldridge, Chemistry Division, D.S.I.R., New Zealand, personal communication, 1983). With kaolinite, however, segregation apparently occurred between fully expanded and nonexpanded crystals. This fundamental difference in intercalation mechanism further emphasizes the clear distinction between halloysite and kaolinite (e.g., Chukhrov and Zvyagin, 1966).

REFERENCES

Al-Khalissi, F. and Worrall, W. E. (1982) The effect of crystallinity on the quantitative determination of kaolinite: *Trans. Brit. Ceram. Soc.* **81,** 43–46.

Borovec, Z. (1975) Formation of interlayer complexes in kaolinite and metahalloysite by treatment with potassium acetate and ethylene glycol: in *Proc. 6th Conf. Clay Mineralogy Petrology, Praha, 1973,* J. Konta, ed., University of Karlova, Prague, Czechoslovakia, 67–76.

Brindley, G. W. (1966) Ethylene glycol and glycerol complexes of smectites and vermiculites: *Clay Miner.* **6,** 237–259.

Chekin, S. S. (1982) Swelling of kaolinite crystals in polar organic liquids: *Izv. Akad. Nauk SSSR, Ser. Geol.* (11), 89–99.

Childs, C. W., Goodman, B. A., and Churchman, G. J. (1979) Application of Mössbauer spectroscopy to the study of iron oxides in some red and yellow/brown soil samples from New Zealand: in *Proc. Int. Clay Conf., Oxford, 1978,* M. M. Mortland and V. C. Farmer, eds., Elsevier, Amsterdam, 555–565.

Chukhrov, F. V. and Zvyagin, B. B. (1966) Halloysite, a crystallochemically and mineralogically distinct species: in *Proc. Int. Clay Conf., Jerusalem, 1966, Vol. 1,* L. Heller and A. Weiss, eds., Israel Program for Scientific Translations, Jerusalem, 11–25.

Churchman, G. J. (1980) Clay minerals formed from micas and chlorites in some New Zealand soils: *Clay Miner.* **15,** 59–76.

Churchman, G. J., Aldridge, L. P., and Carr, R. M. (1972) The relationship between the hydrated and dehydrated states of a halloysite: *Clays & Clay Minerals* **20,** 241–246.

Churchman, G. J. and Theng, B. K. G. (1984) Interactions of halloysites with amides: mineralogical factors affecting complex formation: *Clay Miner.* **19,** (in press).

Churchman, G. J., Whitton, J. S., Claridge, G. G. C., and Theng, B. K. G. (1984) Intercalation method using formamide for differentiating halloysite from kaolinite: *Clays & Clay Minerals* **32,** 241–248.

Hewitt, A. E. and Churchman, G. J. (1982) Formation, chemistry and mineralogy of soils from weathered schist, Eastern Otago, New Zealand: *New Zealand J. Sci.* **25,** 253–269.

Hughes, I. R. (1966) Mineral changes of halloysite on drying: *New Zealand J. Sci.* **9,** 103–113.

Hughes, I. R. and Foster, P. K. (1970) The ranking of halloysites and kaolinites by moisture content measurements: *New Zealand J. Sci.* **13,** 89–107.

Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course:* Published by the author, Department of Soil Science, University of Wisconsin, Madison, Wisconsin, 991 pp.

MacEwan, D. M. C. and Wilson, M. J. (1980) Interlayer and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals and Their X-ray Diffraction,* G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 197–248.

Mackenzie, R. C. (1970) Simple phyllosilicates based on gibbsite- and brucite-like sheets: in *Differential Thermal Analysis, Vol. 1,* R. C. Mackenzie, ed., Academic Press, London and New York, 497–537.

Marsters, S. (1978) Report upon the extraction and industrial uses of halloysite: in *Proc. Ann. Conf. Australasian Institute of Mining and Metallurgy, Whangarei, New Zealand, 1978,* Australasian Inst. Mining and Metallurgy, New Zealand Branch, Whangarei, 91–100.

Martin-Vivaldi, J. L., Pozzuoli, A., Mattias, P., and Galan-Huertos, E. (1973) The swelling of layer minerals I. Interaction with DMSO and NMFA: in *Proc. Int. Clay Conf., Madrid, 1972, Additional Contributions,* J. M. Serratosa, ed., Division de Ciencias, C.S.I.C., Madrid, 455–468.

Miller, W. D. and Keller, W. D. (1963) Differentiation between endellite-halloysite and kaolinite by treatment with potassium acetate and ethylene glycol: in *Clays & Clay Minerals, Proc. 10th Nat'l. Conf., Austin, Texas, 1961,* E. Ingerson, ed., Pergamon Press, New York, 244–253.

Murray, H. H., Harvey, C., and Smith, J. M. (1977) Mineralogy and geology of the Maungaparerua halloysite deposit in New Zealand: *Clays & Clay Minerals* **25,** 1–5.

Olejnik, S., Posner, A. M., and Quirk, J. P. (1970) The intercalation of polar organic compounds into kaolinite: *Clay Miner.* **8,** 421–434.

Range, K. J., Range, A., and Weiss, A. (1969) Fire-clay type kaolinite or fire clay mineral? Experimental classification

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

of kaolinite-halloysite minerals: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1,* L. Heller, ed., Israel Univ. Press, Jerusalem, 3–13.

Tan, K. H. and Hajek, B. F. (1977) Thermal analysis of soils: in *Minerals in Soil Environments,* J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 865–884.

Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions:* Adam Hilger, London, 343 pp.

Wada, K. (1961) Lattice expansion of kaolin minerals by treatment with potassium acetate: *Amer. Mineral.* **46,** 78–91.

Weiss, A., Thielepape, W., Göring, G., Ritter, W., and Schäfer, H. (1963) Kaolinit-Einlagerungs-Verbindungen: in *Proc. Int. Clay Conf., Stockholm, 1963, vol. 1,* I. Th. Rosenqvist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 287–305.

Whitton, J. S. (1978) Differential thermal analysis: in *Methods for Mineral and Elemental Analysis,* N. Wells and R. E. Smidt, compilers, *New Zealand Soil Bur. Sci. Rept.* **10D,** D1.E1–D1.E5.

Wiewiora, A. and Brindley, G. W. (1969) Potassium acetate intercalation in kaolinite and its removal: effect of material characteristics: in *Proc. Int. Clay Conf., Tokyo, 1969, vol. 1,* L. Heller, ed., Israel Univ. Press, Jerusalem, 723–733.

Wilson, M. J. and Tait, J. M. (1977) Halloysite in some soils from north-east Scotland: *Clay Miner.* **12,** 59–66.

(Received 27 August 1983; accepted 4 March 1984)

Резюме—Исследовалось прослаивание формамида, ацетата калия и гидразина галлуазитом и/или обогащенными каолинитом образцами, с и без последующего замещения междуслойных веществ водой или смесью глицерола с водой. Использованые образцы представляли геологические, почвенные, керамические и промышленные материалы. Галлуазит, как таковой, или в смесях с каолинитом полностью расщирялся при всех примененных методах обработки, позволяя, таким образом, определить концентрации галлуазита на основе отношений пиков рентгеновской порошковой дифракции соответствующих комплексов. Полученные таким образом, величины обычно пропорциональны частоте появления трубок, пластинок и шариков в микрографах образцов, полученных при использовании трансмиссионного электронного микроскопа.

Анализ каолиновых минералов (галлуазита плюс каолинита) путем методов прослаивания является менее непосредственным, так как часть каолинитового компонента в системе может не расшириться даже после длительного (≥18 дней) контакта образца с включаемым реагентом. Только длительное погружение в гидразине приводило к полному или почти полному расширению этого компонента. После учета присутствия неглинистых минеральных компонентов процентные содержание каолиновых минералов, определенные на основе отношений интенсивности пиков гидразиновых комплексов, согласовывались с величинами, рассчитаными по дифференциальному термическому анализу, с точностью до ±10% во всех почти случаях. Каолинит в смеси с галлуазитом не может быть непосредственно олределен при помощи методов прослаивания так как методы обработки, которые вызывают образование комплкеса с каолинитом также вызывают расширение галлуазита. В таких системах количество каолинита может быть определено как разница между концентрацией каолиновых минералов и галлуазита. [E.G.]

Resümee—Es wurde der Einbau von Formamid, Kaliumacetat, und Hydrazin in Halloysit- und/oder Kaolinit-reiche Proben mit oder ohne Austausch der Zwischenschichtart durch Wasser oder Glyzerin/Wasser untersucht. Halloysit an sich oder in Mischungen mit Kaolinit wird durch alle verwendeten Methoden vollständig expandiert. Dadurch ist es möglich, den Gehalt an Halloysit aus den Verhältnissen der basalen Röntgenpulverdiffraktometer (XRD)-Peaks der geeigneten Komplexe zu bestimmen. Die derart bestimmten Werte sind im allgemeinen proportional der Menge an Röhren, Leisten und Spiralen in den transmissionselektronenmikroskopischen Aufnahmen der Proben. Die Untersuchung von Kaolinproben (Halloysit und Kaolinit) durch die Wechsellagerungsmethode ist weniger exakt, da ein Teil der Kaolinitkomponente im System u.U. nicht expandiert, selbst nach einer langen Reaktionszeit (≥18 Tage) der Probe mit dem Wechsellagerungsagens. Nur eine lange Einwirkung von Hydrazin führt zum vollständigen oder nahezu vollständigen Expandieren dieser Komponente. Wenn man die Anwesenheit von Nicht-Tonmineralkomponenten berücksichtigt, dann stimmen im allgemeinen die aus den XRD-Peakintensitätsverhältnissen der Hydrazinkomplexe geschätzten Kaolinmineralanteile mit den Werten aus der Differentialthermoanalyse mit einer Genauigkeit von ±10% überein. Kaolinit in Mischungen mit Halloysit kann durch Wechsellagerungsmethoden nicht direkt bestimmt werden, da die Methoden, die zu einer Komplexbildung mit Kaolinit führen, auch Halloysit expandieren. In diesem System kann der Kaolinitanteil aus der Differenz zwischen der Konzentration der Kaolinminerale und der von Halloysit abgeschätzt werden. [U.W.]

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press

Résumé—On a investigué l'intercalation de formamide, d'acétate de potassium et d'hydrazine par des échantillons riches en halloysite et/ou en kaolinite, avec et sans le déplacement subséquent de l'espace interfeuillet par l'eau ou le glycol/eau. Les échantillons utilisés représentent des matériaux géologiques, de sol, et céramiques industriels. L'halloysite en tant que telle, ou en mélange avec la kaolinite est complètement dilatée par tous les traitements employés, permettant de cette manière que les concentrations d'halloysite soient déterminées par les proportions des pics XRD de diffraction aux rayons-X de base des complexes appropriés. Les valeurs obtenues ainsi sont généralement proportionnelles à l'abondance de tubes, de lattes, et de sphérules dans les micrographes d'électrons à transmission des échantillons. L'analyse d'échantillons de kaolin (halloysite plus kaolinite) per des méthodes d'intercalation est moins directe parce qu'une proportion du composé kaolinite dans le système pourrait ne pas se dilater, même après que l'échantillon ait été en contact avec l'agent intercalant pendant longtemps (≥ 18 jours). Seule l'immersion prolongée dans l'hydrazine produit l'expansion complète ou presque complète de ce composé. Lorsqu'on tient compte de la présence des composés de minéraux non-argileux, les pourcentages de minéral kaolin estimés à partir de proportions d'intensité de pics XRD des complexes d'hydrazine s'accordent généralement bien avec les valeurs derivées de l'analyse thermale differentielle à $\pm 10\%$ près dans la plupart des cas. La kaolinite, dans des mélanges avec l'halloysite, ne peut pas être directement determinée par des procédés d'intercalation dans la mesure où les traitements qui resultent en la formation de complexe avec la kaolinite dilatent aussi l'halloysite. Dans de tels systèmes, la kaolinite peut être estimée par la différence entre la concentration de minéraux kaolins et halloysites. [D.J.]

https://doi.org/10.1346/CCMN.1984.0320402 Published online by Cambridge University Press