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INTERCALATION METHOD USING FORMAMIDE FOR DIFFERENTIATING HALLOYSITE FROM KAOLINITE

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Abstract—A rapid and simple test to distinguish halloysite from kaolinite in mineral mixtures has been developed based on differences in the rate and extent of formamide intercalation. With halloysite, complex formation was both rapid (<1 hr) and complete, whereas no significant intercalation occurred with kaolinite until at least 4 hr after contact with formamide, and then the process may not have been complete. Unheated halloysite formed complete complexes with formamide regardless of the interlayer hydration state of the mineral. The test, however, was inconclusive for halloysite that had been oven-dried at 110°C, although some water may still have been present in the interlayer space. The extent of formamide intercalation by kaolinite was likely influenced by sample crystallinity, and the rate of complex formation was enhanced by the addition of up to 10% v/v water to the system. Nevertheless, the formamide test unambiguously differentiated halloysite from kaolinite. N-methylformamide, which yields complexes with a basal spacing of 10.9 Å, could be substituted for formamide (basal spacing = 10.4 Å) for samples containing appreciable amounts of illite-mica.

Key Words—Formamide, Halloysite, Intercalation, Kaolinite, N-methylformamide, Test.

INTRODUCTION

In mixtures with kaolinite, hydrated halloysite can easily be identified by its 001 (basal) reflection near 10 Å in the X-ray powder diffraction (XRD) pattern. In the absence of other clay minerals, the quantity of kaolinite and hydrated halloysite may also be estimated from the intensity or area of the 7- and 10-Å peaks, respectively. If the mixture contains some illite or mica, prior drying at 110°C is required to indicate the presence of hydrated halloysite. This pretreatment weakens the 10-Å reflection and increases the 7-Å reflection, arising from both kaolinite and (dehydrated) halloysite. Halloysite, however, readily loses its interlayer water even under ambient conditions of temperature and humidity (Churchman, 1970). Inasmuch as this process is irreversible, it is often difficult to differentiate halloysite from kaolinite by XRD in samples in which the halloysite component may already be largely dehydrated.

In suggesting a definition of halloysite, Churchman and Carr (1975) pointed out that halloysite may be distinguished from kaolinite on the basis of the number, position, and sharpness of characteristic peaks in their XRD and infrared (IR) patterns, as well as by the asymmetry of the differential thermal analysis (DTA) peaks. Such differences, however, are too subtle to be useful in situations where halloysite and kaolinite occur together. A common method of differentiation relies on electron microscopy, halloysite being recognizable by its tubular shape whereas kaolinite appears as platy, polygonal particles (Beutelspacher and Van der Marel, 1968). Indeed, this morphological distinction is being used as a diagnostic criterion for halloysite in some soil classification systems, including *Soil Taxonomy* (Soil Survey Staff, 1975). Besides requiring expensive instrumentation and technical expertise, the information gained from both transmission and scanning electron microscopy is often ambiguous (see e.g., Keller *et al.*, 1980) because halloysite can occur in a variety of particle shapes (Dixon, 1977; Kirkman, 1981; Sudo *et al.*, 1981; Churchman and Theng, 1984). In addition, the possibility of kaolinite adopting an acicular or tubular morphology cannot be altogether discounted (Brindley and de Souza Santos, 1966; Churchman and Carr, 1975).

In studying the intercalation of amides by various halloysites, Churchman and Theng (1984) showed that complex formation with formamide was rapid and complete, irrespective of differences in crystallinity, morphology, and iron content among the clay samples. In the present paper, the factors influencing the rate and extent of formamide intercalation by halloysite, kaolinite, and mixtures of these minerals have been examined with the objective of developing a rapid, routine test for differentiating between these two minerals. In the following paper Theng *et al.* (1984) compare several intercalation methods for the semi-quantitative estimation of halloysite and kaolinite in raw and processed clay samples.

MATERIALS AND METHODS

The samples examined in this study were obtained from a variety of sources and are described in detail in Table 1, along with their locations, pretreatments,

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

Sample[1]	Laboratory designation	Mode of formation/ parent material	Location/source
Geologic samples			
'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
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			
Hangawera (1)	T1 E	Greywacke	Hauraki Plains, New Zealand
Kainui silt loam (3)	T3 C, D, G	Loess/volcanic ash	Hauraki Plains, New Zealand
Traquair silt loam (1)	SB9329B	Thin loess/schist	Eastern Otago, New Zealand
Ceramic samples			
(1)	62/1	Unknown	Unknown
(1)	62/2	Unknown	Unknown
(1)	63/111	Unknown	Unknown
(1)	78/16	Unknown	Unknown
(1)	79/14	Unknown	Unknown
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] Grouping, name, (number of samples).
[2] Imperial Chemical Industries trade name.
[3] Clay fraction refers to <2 μm e.s.d. as obtained by the method of Jackson (1956).
[4] In approximate decreasing order of abundance—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.

and mineralogical composition. Intercalation complexes with formamide (d(001) = 10.4 Å) and N-methylformamide (d(001) = 10.9 Å) were prepared using 'Purum grade' reagents from Fluka AG under varying conditions of sample pretreatment, reaction time, and reagent dilution with water. The following experimental procedures were used:

(1) The samples, before and after oven-drying (110°C, overnight), were spread on porous ceramic tiles and examined by X-ray powder diffraction (XRD) within 60 min;
(2) The samples were prepared as in (1) but sprayed with an aerosol of formamide prior to XRD examination;
(3) Two pure kaolinites ('Dana' and Wairakei) and several kaolinite-rich samples (62/2, 78/16, Hymod KC, Hycast VC, and Hywite Alum) were immersed in formamide from 1 hr to 28 days;
(4) Formamide containing 2, 5, and 10% v/v water was added to the 'Dana,' Wairakei, and 62/2 samples and allowed to react for as long as 24 hr;
(5) Formamide and N-methylformamide were reacted with the 'Dana,' Hymod AT, and Traquair soil B horizon (SB 9329B) samples for 1, 2, and 4 hr.

The reaction products from procedures (3), (4), and (5) were examined by XRD, scanning over the basal reflection region at a rate of 2°2θ/min using a Philips PW1010 diffractometer and CoKα radiation. The degree or extent of intercalation was estimated from the ratio $I_{10}/(I_7 + I_{10})$, where I_{10} and I_7 represent the basal peak intensity of the complex (d ~ 10 Å) and of the unexpanded kaolin component (halloysite plus kaolinite) (d ~ 7 Å), respectively.

Figure 1 illustrates the changes that occurred in the XRD patterns (over the basal peak region) of halloysite, a synthetic mixture of halloysite and kaolinite, and kaolinite on immediate treatment (within 60 min) with formamide. The degree of intercalation (α) was obtained as shown. Providing that intercalation was complete, this ratio also gave the proportion of halloysite and kaolin minerals in the samples, after allowing for the contribution of mica or illite to the 10-Å line (Theng *et al.*, 1984) (*vide infra*).

Sample crystallinity was assessed from either the XRD patterns (obtained at a scan rate of 0.5°2θ/min) using the Hinckley (1963) method and the procedure of Hughes and Brown (1979) or the ratio of the hydroxyl stretching bands at 3690 and 3620 cm^{-1} in the IR spectrum of oven-dry samples (Parker, 1969). Crystallinity was also estimated from the endotherm peak temperature of DTA patterns recorded with a DuPont

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Table 1. Continued.

Pretreatment[3]	Composition[4]	Reference
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)
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	K, H, M, V	This work
Clay fraction	H, V, K, C	This work
Clay fraction	K, V, M, 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	K, Q	This work
Air-dried and milled	H, 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]

900 instrument using alumina as reference and a heating rate of 10°C/min (in air) (Churchman and Theng, 1984).

RESULTS AND DISCUSSION

Effect of interlayer water on intercalation by halloysite

Inasmuch as hydrated halloysite may be regarded as an interlayer complex with water, the extent of interlayer hydration of the halloysite component in a given sample may be estimated from the ratio $I_{10}/(I_7 + I_{10})$. Here, I_7 and I_{10} denote the intensity of the basal lines near 7 and 10 Å, given by the fully dehydrated and hydrated forms of the mineral, respectively. Thus, this ratio is zero for fully dehydrated halloysite and unity when the clay is completely hydrated. The data in Table 2 indicate that the extent of hydration of the parent halloysite samples varied over the entire range from 0 to 1. Irrespective of its initial hydration state, however, halloysite was apparently capable of forming complete interlayer complexes with formamide. This capability is evident from the close correspondence between halloysite percentages obtained by formamide expansion and those derived by washing the respective potassium acetate complexes with water, a treatment specific for halloysite (Wada, 1961; Theng *et al.*, 1984). Besides being quantitative, formamide intercalation was rapid, occurring within less than 60 min after contact between the sample and the reagent during which time kaolinite, as exemplified by the 'Dana' specimen, showed no measurable expansion.

Effect of oven-drying on intercalation by halloysite

As might be expected, previous drying at 110°C generally led to a decrease in halloysite expansibility by

Table 2. Formamide intercalation by halloysite and halloysite-containing samples in relation to their interlayer hydration status.

Sample[1]	Degree of interlayer hydration[2]	Halloysite (%)[3]	Degree of formamide intercalation[4]
Te Puke halloysite	1.0	100	1.0
T3G (Kainui soil)	0.6	70	0.7
Matauri Bay halloysite	0.5	90	1.0
T3C (Kainui soil)	0.4	80	0.8
62/1 (Ceramic clay)	0.3	50	0.3
Vaturu dam, whole sample (Fiji dam)	0.2	60	0.6
Vaturu dam, clay fraction (Fiji dam)	0.1	60	0.6
Weathered schist	0.1	30	0.3
79/14 (Ceramic clay)	0	80	0.7
T1E (Hangawera soil)	0	20	0.2

[1] Samples arranged in decreasing order of degree of hydration. Samples described in Table 1.

[2] From peak intensity ratios of unheated parent samples (cf. Figure 1).

[3] Estimated from peak intensity ratios of water-washed potassium acetate complexes and expressed on the basis of clay mineral content (Theng *et al.*, 1984).

[4] From peak intensity ratios of complexes formed on immediate contact with formamide (Figure 1); the corresponding halloysite percentages may be obtained by multiplying these values by 100.

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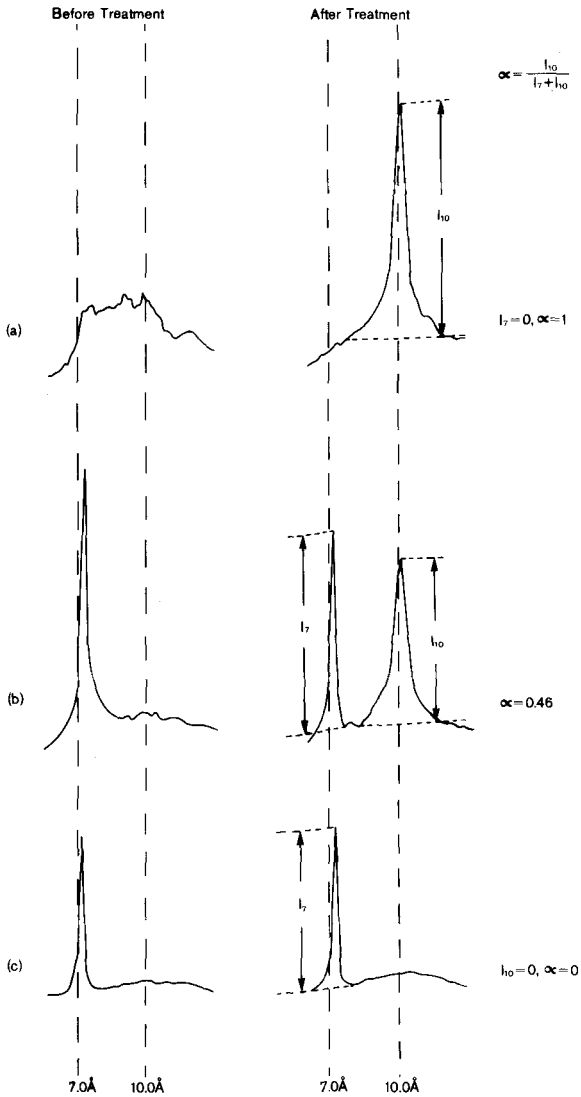


Figure 1. X-ray powder diffraction patterns of basal-peak region of (a), halloysite (Matauri Bay); (b), a synthetic mixture of halloysite (60%) and kaolinite (40%); (c), kaolinite ('Dana') before and after immediate (20–30 min) treatment with formamide, showing the calculation of basal peak intensity ratios. Note that the halloysite sample was initially partially dehydrated.

formamide because more energy was apparently required for interlayer penetration (Table 3). The data in Table 3 show that the extent of this decrease was variable and unrelated to the concentration of halloysite in the samples. Notably, the propensity of pure halloysite, e.g., the TePuke and Matauri Bay samples, for complexing formamide was least affected by oven-drying. The reason for these observations is not obvious, although the presence of other clay species and non-clay minerals in the samples as well as factors relating to the particle size and crystallinity of the halloysite component may be involved.

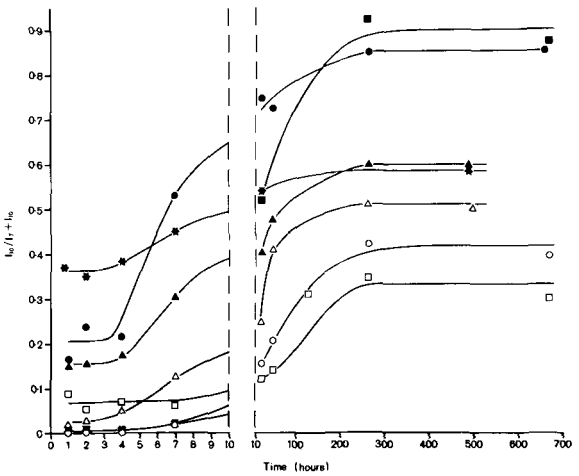


Figure 2. Effect of contact time on formamide intercalation (complex formation) by kaolinite and kaolinite-containing samples (cf. Table 4). ○ = sample 78/16; ■ = 'Dana' kaolinite; △ = Hywite Alum; □ = Wairakei kaolinite; ▲ = Hycast VC; ● = sample 62/2; ★ = Hymod KC.

It is interesting to compare the reactivity towards formamide of sample T1E before and after oven-drying. With reference to Table 2 the halloysite component of this sample in the unheated state was apparently already fully dehydrated because its XRD pattern was closely similar to that of the oven-dry material. Yet, in terms of formamide intercalation, the unheated sample was significantly more reactive. Inasmuch as the determination of halloysite in mixtures with kaolinite is based on the ability of the former mineral to

Table 3. Effect of oven-drying[1] on formamide intercalation by halloysite and halloysite-containing samples.

Sample[2]	Halloysite (%)[3]	Degree of intercalation[4]	
		Before oven-drying	After oven-drying
Te Puke halloysite	100	1.0	0.7
Matauri Bay halloysite	90	1.0	0.8
T3C (Kainui soil)	80	0.8	0
T3G (Kainui soil)	70	0.7	0.1
T3D (Kainui soil)	60	0.8	0
62/1 (Ceramic clay)	50	0.3	0.1
Weathered schist	30	0.3	0.2
T1E (Hangawera soil)	20	0.2	0
63/111 (Ceramic clay)	10	0	0.1
'Dana' kaolinite	0	0	0

[1] 110°C, overnight.

[2] Samples arranged in order of decreasing halloysite concentration.

[3] Estimated from peak intensity ratios of water-washed potassium acetate complexes and expressed on the basis of clay mineral content (Theng *et al.*, 1984).

[4] From peak intensity ratios of complexes formed on immediate contact with formamide (Figure 1); the corresponding halloysite percentages may be obtained by multiplying these values by 100.

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Table 4. Sample crystallinity vs. percentage of kaolinite capable of being expanded by formamide.

Sample[1]	Kaolinite		Crystallinity indexes			
	Total[2] (%)	Expansible by formamide[3] (% of total)	Hinckley (1961)	Hughes and Brown (1979)	Parker (1969)	DTA endotherm peak (°C)[4]
Pure kaolinites						
Wairakei kaolinite	100	40	0.97	34.2	1.33	620
'Dana' kaolinite	100	90	0.71	17.6	1.34	575
Kaolinitic samples						
78/16 (Ceramic clay)	50	30	0.97	15.7	1.58	595
Hywite Alum (Industrial clay)	70	50	0.46	10.8	1.52	575
Hymod KC (Industrial clay)	40	20	0.20	7.8	1.08	565
Hycast VC (Industrial clay)	40	60	0.30	10.1	1.32	570
62/2 (Ceramic clay)	20	80	0.71	9.9	1.30	590

[1] Samples arranged in order of increasing expansibility by formamide.
[2] Difference between the percentage kaolin minerals (halloysite plus kaolinite), determined by differential thermal analysis, and the percentage halloysite, estimated from peak intensity ratios of complexes on immediate contact with formamide (Theng *et al.*, 1984).
[3] From peak intensity ratios of complexes at maximum (plateau) expansion after long-term immersion in formamide (cf. Figure 2).
[4] Churchman and Theng (1984).

expand completely on immediate contact with the intercalating agent, the formamide method does not appear to be applicable to samples which have undergone oven-drying.

Effect of reaction time on intercalation by kaolinite

Figure 2 shows plots of peak intensity ratios vs. immersion period for pure kaolinite and kaolinite-rich samples containing different proportions of halloysite and/or mica-illite. Because the halloysite component in the samples should have expanded completely on immediate contact with formamide, and the contribution of mica-illite to the intensity of the 10-Å peak should not have varied with time, peak ratios at 1-hr immersion in formamide may be regarded as starting points or baseline values of these plots. This assumption is justified by the data for the 'Dana' and Wairakei samples which, being pure kaolinites, showed a zero baseline. No change was detected in baseline value before at least 3 hr of immersion, indicating a negligible interlayer uptake of formamide during this period. On the other hand, the kaolinite-rich samples gave rise to a finite baseline which may be ascribed to the presence of mica in the Hymod KC, Hycast VC, and Hywite Alum samples (Theng *et al.*, 1984) and to the expansion of the halloysite component.

The near constancy of the baselines up to 4 hr of contact time suggests that little, if any, formamide was intercalated by the kaolinite component of the samples within this time interval (cf. Table 5). By the same token, the increase in peak intensity ratios beyond 4 hr, followed by a steep rise between 20 and 40 hr of reaction time may be ascribed to the interlayer uptake of formamide by kaolinite or the kaolinite component. Differences between samples in the rate and extent of intercalation are a reflection more of variations in kaolinite reactivity than of concentration. This is well illustrated by comparing the curves for the 'Dana' and Wairakei samples, both of which consist of relatively pure kaolinite. Another feature of Figure 2 is that the equilibrium (or plateau) peak ratios, reached after some 10 days of immersion in formamide, were always less than unity, the maximum value attainable if complete expansion had occurred. The 'Dana' and 62/2 samples came close to this maximum, their XRD patterns showing a small residual line near 7 Å due to unexpanded kaolinite. Apparently, the other samples in the group only 'partially' expanded in the sense that only a proportion of the kaolinite crystals or particles was capable of intercalating formamide. This proportion, as estimated from the respective plateau peak ratio, is listed in Table 4 together with the corresponding crystallinity indexes. The unexpanded portion of the kaolinite component in each sample was presumably associated with the fine (<0.5 μm) fraction (Theng *et al.*, 1984).

In studying the intercalation of amides by halloysite, Churchman and Theng (1984) found that complex formation is facilitated by an increase in sample crystallinity. Comparing the reactivity towards formamide of the Wairakei and 'Dana' samples with their respective crystallinity, as measured by the various indexes (Table 4), suggests that the above relationship could apply to kaolinite but in the inverse sense. Thus, the well-crystallized Wairakei kaolinite was apparently much less expanded by formamide than was the relatively poorly ordered 'Dana' kaolinite. With the possible exception of the Hymod KC sample, which has a relatively high mica-illite content, this dependence of reactivity on

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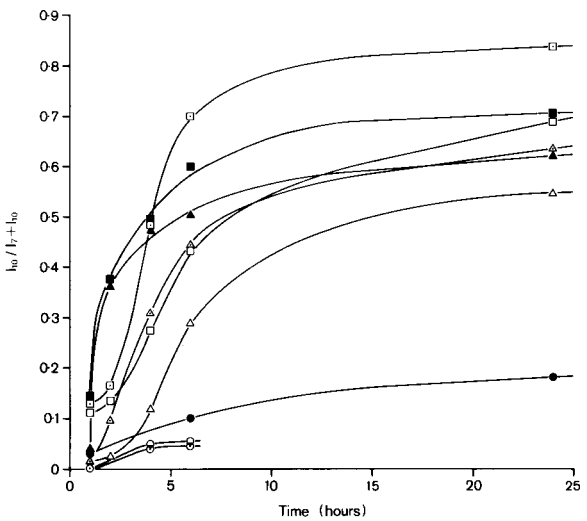


Figure 3. Effect of adding different amounts of water to the system on formamide intercalation. Circles = Wairakei kaolinite; triangles = 'Dana' kaolinite; squares = sample 62/2. ○, △, □ = 2% v/v water; ⊙, ◬, ⊡ = 5% v/v water; ●, ▲, ■ = 10% water.

crystallinity also extends to the kaolinite-rich samples. Even the most reactive among these samples, however, failed to intercalate formamide after a contact time of 1 hr. This slow rate of intercalation contrasts sharply to the behavior of halloysite which expands completely on immediate contact with the organic liquid (Theng *et al.,* 1984).

Effect of water on formamide intercalation

Figure 3 illustrates the effect of water on the rate of formamide intercalation by 'Dana' and Wairakei kaolinite and a kaolinite-rich sample (62/2). Comparison with Figure 2 clearly shows that the addition of water to the system (up to 10% v/v of formamide) markedly accelerated interlayer complex formation. This observation accords with the earlier finding by Olejnik *et al.* (1970) and may be explained in terms of the disruptive effect of water on the liquid structure of formamide. The influence of water on reaction rates generally increased with an increase in the amount added as exemplified by the 'Dana' kaolinite. The results for the Wairakei kaolinite were less striking because of its low reactivity towards formamide, whereas for the 62/2 sample, the effect at 5% v/v exceeded that at 10% v/v beyond a contact time of 4 hr. What seems clear, however, is that even at 10% v/v water little, if any, expansion took place within 1 hr of contact between sample and the formamide-water solution. The formamide test may therefore be applied without ambiguity to field-moist samples rich in halloysite and/or kaolinite.

Comparison of formamide with N-methylformamide

Table 5 compares the peak intensity ratios for complexes of the 'Dana' kaolinite and two kaolinite-rich samples (SB 9329B soil clay and Hymod AT) with formamide and N-methylformamide after the specified reaction times. In accord with the data of Figure 2, the extent of formamide intercalation by all three samples remained essentially constant within 4 hr of contact with the organic liquid although individual peak ratios varied between samples. A slight expansion of the SB 9329B and 'Dana' samples appeared to occur, though the magnitudes of changes in ratios were always insignificant. The significantly higher peak ratios recorded for the Hymod AT sample may have been due to the presence of halloysite (~10%) and mica (~30%), both of which have a basal reflection near 10 Å, coincident with that for the formamide complex. Mica, however, should not have interfered with the peak ratio analysis of N-methylformamide complexes with either halloysite or kaolinite, both of which give basal spacings at 10.9 Å (Churchman and Theng, 1984). High mica contents could account for the lower ratios observed for the Hymod AT-N-methylformamide complexes relative to their formamide counterparts.

Like formamide, little, if any, intercalation of N-methylformamide was noted within 1 hr of contact time. In contrast to formamide, however, some intercalation of N-methylformamide apparently occurred with the kaolinite-rich samples after 4 hr reaction. Thus, by limiting the time of analysis to 1 hr or less, N-methylformamide may be used as an alternative to

Table 5. Comparison of formamide and N-methylformamide as an intercalating agent for kaolinite and kaolinite-containing samples.

Sample	Peak intensity ratio						Kaolinite[2] (%)
	Formamide			N-methylformamide[1]			
	1 hr	2 hr	4 hr	1 hr	2 hr	4 hr	
'Dana' kaolinite	0	0	0.04	0	0	0.02	100
SB 9329B (Soil clay)	0.05	0.06	0.08	0	0.10	0.36	80
Hymod AT (Industrial clay)	0.46	0.43	0.41	0	0.11	0.17	40

[1] From the ratio $I_{10.9}/(I_7 + I_{10} + I_{10.9})$.

[2] Difference between the percentage of kaolin minerals (determined by DTA) and the percentage of halloysite (estimated by immediate expansion with formamide) (Theng *et al.,* 1984).

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formamide. The latter reagent, however, is preferable for routine purposes because it is less toxic and cheaper than N-methylformamide. Nevertheless, N-methylformamide is a useful intercalating agent for detecting small concentrations of halloysite in a matrix of kaolinite and mica because the basal spacing of its complex is sufficiently far removed from the mica line in the XRD pattern.

FORMAMIDE INTERCALATION TEST FOR HALLOYSITE AND KAOLINITE

The following procedure is currently used routinely by the New Zealand Soil Bureau for differentiating halloysite from kaolinite in mixed systems:

(1) Prepare a thick aqueous slurry of the unknown clay sample; place about 2 ml of this slurry on a porous ceramic tile (40 × 20 mm).

(2) When the excess water has drained away, obtain an X-ray powder diffraction pattern of the dried clay by scanning over the 10- and 7-Å peak region, establishing the background on either side of these peaks.

(3) Spray the sample with an aerosol of formamide, using any convenient spray bottle, and obtain an XRD pattern of the complex after 20–30 min, but always within 1 hr of spraying. Halloysite, if present, gives rise to a peak at 10.4 Å, whereas kaolinite does not expand beyond 7.2 Å. The relative proportions of halloysite and kaolinite in the sample are related to their respective peak intensities.

(4) To allow for the presence of illite-mica, prepare a sample of the clay on a tile and heat it in an oven at 110°C for at least 15 min. After cooling the sample, obtain its XRD pattern as above. The heat treatment does not affect the position of the illite-mica basal reflection near 10 Å but causes the halloysite complex with formamide to collapse to ~7 Å. Subtract the intensity of the 10-Å peak from that obtained in step (3).

(5) Determine the total concentration of kaolin minerals (halloysite + kaolinite) by differential thermal analysis as described by Theng *et al.* (1984). By way of illustration, if this concentration is 80% w/w and the ratio of the intensity of the 10.4- to the 7.2-Å peak, from steps (3) and (4), is 75:25, the percentages of halloysite and kaolinite in the sample are 80 × 75/100 = 60 and 80 × 25/100 = 20, respectively. The error involved in these estimates is ±10%.

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Резюме—Разработан быстрый и простой опыт для отличения галлуазита от каолинита в смесях минералов на основе разниц в скоростях и размере прослойки формамида. В случае галлуазита формирование комплексов было и быстрое (<1 часа) и полное, тогда как в случае каолинита значительная прослойка не появлялась по крайней мере 4 часа после контакта с формамидом и еще потом процесс мог быть не завершенным. Неподогретый галлуазит образовывал завершенные комплексы с формамидом несмотря на межслойное гидрационное состояние минерала. Однако нельзя было сделать выводы из опыта с галлуазитом, сушенным в печи при 110°C, хотя некоторые количество воды могло присутствовать в межслойном пространстве. На размер прослойки формамида с каолинитом, вероятно, влияла кристалличность образцов, а скорость образования комплекса увеличивалась при добавлении к системе до 10% воды (по объему). Тем не менее опыт с формамидом без сомнения отличал галлуазит от каолинита. N-метилформамид, который дает комплексы с основным расстоянием 10,9 Å мог бы быть заменен формамидом (основное расстояние = 10,4 Å) в случае образцов, содержащих значительные количества иллита-слюды. [E.G.]

Resümee—Es wurde ein schneller und einfacher Test zur Unterscheidung von Halloysit und Kaolinit in Mineralgemengen entwickelt, die auf der unterschiedlichen Geschwindigkeit und dem unterschiedlichen Ausmaß des Einbaus von Formamid beruht. Bei Halloysit geht die Komplexbildung sowohl schnell (<1 Stunde) als auch vollständig vor sich, während bei Kaolinit bis mindestens 4 Stunden nach dem Beginn der Einwirkung von Formamid kein bemerkenswerter Einbau geschieht, und auch dann ist der Prozess nicht vollständig. Nicht erhitzter Halloysit bildet vollständige Komplexe mit Formamid unabhängig vom Hydratationsstadium der Zwischenschicht. Der Test war jedoch für Halloysit, der bei 110°C im Trockenschrank getrocknet wurde, nicht eindeutig, obwohl noch eine gewisse Menge Wasser in der Zwischenschicht enthalten gewesen sein könnte. Das Ausmaß des Formamideinbaus durch Kaolinit wurde wahrscheinlich durch die Kristallinität der Probe beeinflußt, und die Geschwindigkeit der Komplexbildung wurde durch die Zugabe von bis zu 10% v/v Wasser zum System erhöht. Dennoch kann man durch den Formamidtest eindeutig Halloysit von Kaolinit unterscheiden. N-methylformamid, mit dem Komplexe mit einem basalem Schichtabstand von 10,9 Å gebildet werden, kann anstelle von Formamid (Basis abstand 10,4 Å) bei Proben mit größeren Mengen Illit-Mica verwendet werden. [U.W.]

Résumé—Un test rapide et simple a été développé pour distinguer l'halloysite de la kaolinite dans des mélanges minéraux, basé sur les différences d'allure et d'étendue d'intercalation de formamide. Avec l'halloysite, la formation de complexe était à la fois rapide (<1 heure) et complète, tandis qu'aucune intercalation significative ne s'est produite avec la kaolinite jusqu'à au moins 4 heures après le contact avec la formamide, et alors il est possible que le procédé n'ait pas été complet. L'halloysite non-chauffée a formé des complexes avec la formamide sans égards à l'état d'hydration interfeuillet du minéral. Aucune conclusion n'a cependant pû être tirée du test pour l'halloysite qui avait été sechée au four à 110°C, quoiqu'il est possible que de l'eau ait encore été présente dans l'espace interfeuillet. L'étendue de l'intercalation de formamide par la kaolinite était probablement influencée par la cristallinité de l'échantillon, et l'allure de la formation du complexe a été encouragée par l'addition au système de jusqu'a 10% v/v d'eau. Il n'empêche que le test de formamide a differencié sans ambiguités l'halloysite de la kaolinite. La formamide N-méthyle, qui produit des complexes avec un espacement de base de 10,9 Å, pourrait être substituée à la formamide (espacement de base = 10,4 Å) pour des échantillons contenant des quantités appréciables d'illite/mica. [D.J.]

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