

# DIFFERENTIATION BETWEEN ENDELLITE- HALLOYSITE AND KAOLINITE BY TREATMENT WITH POTASSIUM ACETATE AND ETHYLENE GLYCOL

*by*

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## ABSTRACT

Halloysite and endellite yield 10 Å basal spacings after grinding with potassium acetate (using a modification of Wada's procedure) and washing with water and ethylene glycol, whereas the basal spacing of kaolinite, similarly treated, remains at 7 Å. The technique applies satisfactorily to sedimentary and hydrothermal halloysites, various commercial kaolins, ball clays, flint and plastic fire clays, and artificially prepared mixtures of halloysite and kaolinite. Similar responses to the treatment by both laboratory-dehydrated endellite (thereby collapsed to 7 Å) and naturally occurring halloysite add support to the concept that endellite is a progenitor of halloysite.

## INTRODUCTION

Wada (1961) and Andrew, Jackson and Wada (1960) reported that clay minerals of the kaolin group were expanded to approximately 14 Å along the *c*-axis by grinding or soaking in potassium acetate. After the KOAc was washed out, kaolinite returned to its characteristic 7 Å spacing, according to them, whereas wet halloysites contracted to about 10 Å. We have included the addition of ethylene glycol, after washing, to the procedure described by Wada, and applied it to a variety of kaolins obtained from diverse origins, commercial uses, and geographic locations. Halloysites and endellites are changed to a 10 Å spacing when ethylene glycol is added to the washed, wet clays after KOAc treatment, but similarly processed kaolinites continue to yield a 7 Å spacing. In this report, the term endellite refers to the 4H<sub>2</sub>O variety of the randomly stacked member of the kaolin group, following the usage of Alexander *et al.* (1943), and halloysite to its 2H<sub>2</sub>O polymorph. The observation that laboratory-dried endellite and naturally occurring halloysite exhibit similarities in basal expansion after processing is interpreted, as others have suggested before, as evidence that most halloysites originated as endellites.

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## EXPERIMENTAL WORK

Using Wada's experiments as a starting point, several variations in treatment were tried and a standardized procedure, as follows, was adopted.

A small sample (usually 2 g) of clay was ground with an equal weight (about 10 mm per gram of clay) of potassium acetate for 20 min in a Fisher mechanical mortar-and-pestle grinder, and allowed to stand overnight. After X-raying, the clay-KOAc sample was washed by shaking several times with distilled water, and ethylene glycol was added to the clay (not allowed to dry), and it was again X-rayed, either on porous tile or in a conventional X-ray specimen holder. After additional experience with the variety of clays studied, and different humidities, we now recommend using slightly less KOAc, say 0.7 to 0.8 g KOAc per g of clay, and either grinding by hand or maintaining a close watch on the mechanical grinder to guard against "balling up" of the clay-KOAc mixture, which may pick up moisture from the air and then tend to escape grinding.

To compare naturally occurring endellite (10 Å) and its dehydrated product with naturally occurring halloysite (7 Å), Indiana endellite, which had been collected and maintained in a moist condition, was dehydrated in a series of samples at room temperature, and for a minimum of 4 hr at 100°, 200°, 300°, and 400°C. This series of samples was processed and X-rayed along with naturally occurring halloysite.

Furthermore, kaolinite from Dry Branch, Georgia, was mixed in a series at 20 percent intervals with Indiana endellite previously dehydrated at 105°C for 18 hr, and X-rayed after processing. In detail, the clay fractions of the 20 percent series were ground together in the Fisher grinder for 10 min after weighing, further mixed by vigorous shaking in 200 ml of water for 4 hr on a mechanical shaker, then dried at 100°C, mixed and ground with KOAc for 10 min, washed free of KOAc, solvated with glycol, and X-rayed. Results of the several experiments are tabulated below.

## DISCUSSION OF DATA

In Table 1 are recorded the basal spacings of 24 kaolin minerals arranged in general sequence from endellite through halloysite, kaolinite, dickite, and various fire clays and other commercial clays. Wet endellites yielded a 10 Å spacing (nos. 1 and 3), and other samples of endellite (nos. 7 and 8), partly dehydrated on the outcrop but stored wet after collection, yielded a band of reflections between 7 Å and 10 Å similar to that which may be developed when endellite undergoes dehydration during X-raying if not protected from drying. Endellite that has been dried, and halloysite, yield basal spacings from 7.1 to 7.4 Å. All the samples after being ground with KOAc, then washed with water, and solvated with ethylene glycol, yielded spacings in the range 10.4–10.9 Å (Fig. 1). Hydrothermally altered halloysite (nos. 6 and 9) exhibited the same behavior as did those minerals of sedimentary origin (nos. 1, 4, 7, 8).

TABLE 1.—KAOLIN CLAYS PROCESSED WITH POTASSIUM ACETATE AND ETHYLENE GLYCOL

Clay	Basal Spacing in Å.U.				Source
	Before processing	Clay-KOAc mixture	Water washed	Et. glycol solvated	
1. Indiana endellite, maintained wet	10	13.9	9.7	10.4-10.8 broad peak	Bedford, Indiana; collected wet on the outcrop and stored with excess water in sealed glass jars.
2. Indiana endellite, dried 100°C (no. 1)	7.3	13.8	9.8	10.9	Material from no. 1, crushed and dried overnight at 100°C.
3. Mexico endellite, dried 100°C	7.2 (10, wet) 7.1-7.4	13.8	—	10.6	Near Oyamel, Michoacan; collected wet and stored with excess water.
4. Indiana halloysite, API-12b	7.1	14.0-14.2	—	10.7	Bedford, Indiana; original API Reference clay 12b.
5. Colorado halloysite, API-29	7.1	13.9	—	10.6	Wagon Wheel Gap; API Reference clay 29.
6. Utah halloysite, API-13	7.3	14.0	—	10.8	Eureka; hydrothermal origin, original API Reference clay 13.
7. Idaho halloysite-endellite, AD-1, 100°C	7.3 (7-10, wet)	14.0	—	10.9	Partly dehydrated on exposed outcrop, Latah County (Ponder and Keller, 1960).
8. Idaho halloysite-endellite, SC-1, 100°C	7.1 (7-10, wet)	13.9	—	10.4-10.6	Partly dehydrated on exposed outcrop, Latah County (Ponder and Keller, 1960).
9. Mexico halloysite	7.1	13.9	—	10.7	Near Etizatlán (west of Guadalajara), Jalisco; hydrothermal origin (Keller, this volume).
10. Georgia kaolinite, API-3	7.2	14.0	—	7.2	Macon; original API Reference clay 3.

11. Cornwall kaolinite, API-114a	7.2	14.1	—	7.0-7.6	St. Austell, England; original API Reference clay 114a.
12. Bavaria kaolinite, API-127a	7.2	14.0	—	7.1-7.4	Amberg district, Oberpfalzercwald; original API Reference clay 127a
13. Zettlitz kaolinite	7.15	13.8	—	7.2 (broad)	Near Carlsbad, Czechoslovakia; international reference kaolinite.
14. Colorado dickite, API-14	7.1	14.0	—	7.2	Ouray; original API Reference clay 14.
15. Mexico dickite, API-15a, no. 1	7.2	13.9	—	7.1 & 10.7	San Juanito, Chihuahua; original API Reference clay 15a, no. 1.
16. Missouri hard flint fire clay	7.1	14.0	—	7.1	(Kaolinite) Bueker pit, near Owensville (Keller, Westcott, and Bledsoe, 1954).
17. France hard flint fire clay	7.2	13.8	—	7.1	(Kaolinitic) Near Olliers (Var) east of Marseilles, collected 1960 (W. D. K.) from deposit described by Halm (1952).
18. Missouri soft flint fire clay	7.2	14.0	—	7.1	(Kaolinite-fire clay mineral?) Gleize clay pit, near Bland
19. Missouri dark semi-flint fire clay	7.2	13.8	—	7.1	(Kaolinite-fire clay mineral) Mexico, Mo., clay pit of Mexico Refractories Co. (Kaiser Aluminum Co.), Mexico, Mo.
20. Missouri light semi-flint fire clay	7.2	13.9	—	7.2	(Kaolinite-fire clay mineral, sparse illite) Mexico, Mo., clay pit of A. P. Green Fire Brick Co., Mexico, Mo.
21. Missouri semi-plastic fire clay	7.2	13.8	—	7.1	(Kaolinite-fire clay mineral) Fulton clay pit of A. P. Green Fire Brick Co., Mexico, Mo.
22. Missouri light semi-plastic fire clay	7.2	14.0	—	7.1	(Fire clay mineral and illite) Mexico, Mo., clay pit of Mexico Refractories Co. (Kaiser Aluminum Co.), Mexico, Mo.
23. Scotland semi-plastic fire clay	7.2	14.0	—	7.1	Semi-plastic to semi-flint fire clay (kaolinite-fire clay mineral), Bonnybridge.
24. Germany plastic fire clay	7.2	13.9	—	7.1	(Kaolinitic) Ramsbach (S.E. of Bonn).
25. Tennessee ball clay	7.2	13.8	—	7.0	(Kaolinitic) Near Paris, Tenn.

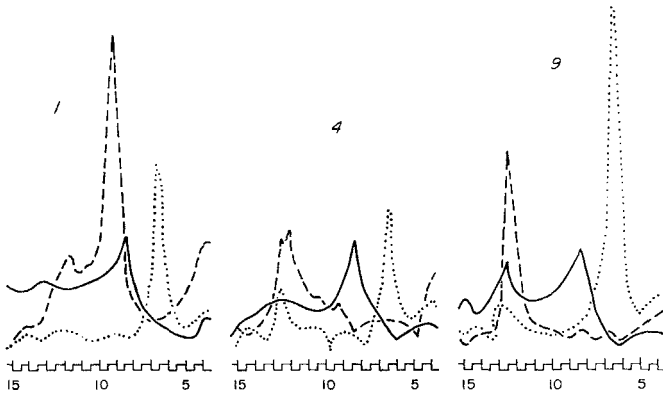


FIGURE 1.—Smoothed X-ray diffractograms; Ni-filtered Cu radiation. (1) Endellite, Bedford, Indiana. (4) Halloysite, Bedford, Indiana. (9) Halloysite, Eztatlán, Jalisco, Mexico. Dashed line, untreated clay; dotted line, clay-KOAc mixture; solid line, KOAc treated, washed, ethylene glycol.

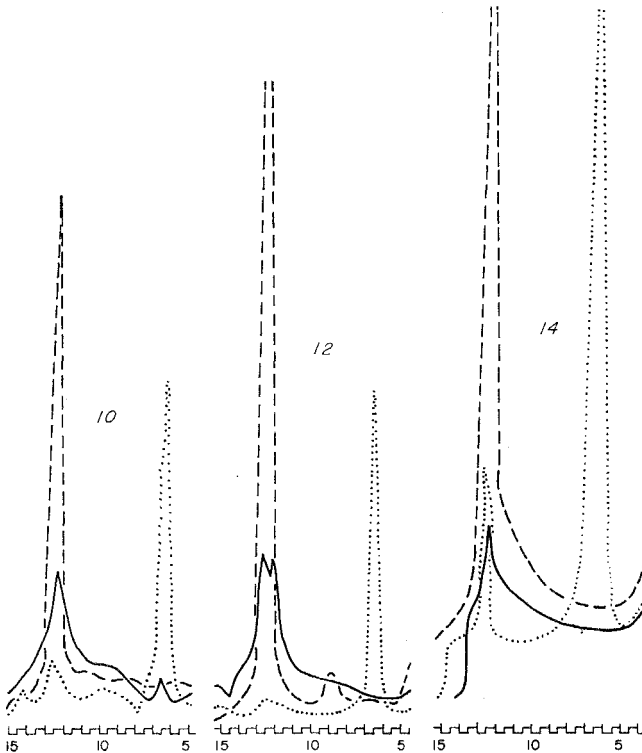


FIGURE 2.—Smoothed X-ray diffractograms; Ni-filtered Cu radiation. (10) Kaolinite, Macon Co., Georgia. (12) Kaolinite, Hirshau, Bavaria. (14) Dickite, Ouray, Colorado. Dashed line, untreated clay; dotted line, clay-KOAc mixture; solid line, KOAc treated, washed, ethylene glycol.

Kaolinites and dickites (nos. 10–15) show little to no change in basal spacing (from 7.1–7.2 Å to 7.0–7.6 Å) upon washing and solvating in ethylene glycol (Fig. 2). Dickite from San Juanito, Chihuahua, Mexico (no. 15), exhibits a small 10.7 Å peak after solvating in glycol, and this response is interpreted as being due to intermixed halloysite. The differential thermalgrams of San Juanito dickite presented in API Project 49 show the endothermic dehydroxylation peak of the dickite ranging from about 425° (Spiel *et al.*, 1945) to 500° (Kerr, Kulp and Hamilton, 1949). The API discussion on the thermalgrams of the San Juanito clay attributes its uncommonly low temperature of dehydroxylation to admixture of nacrite, but we believe that

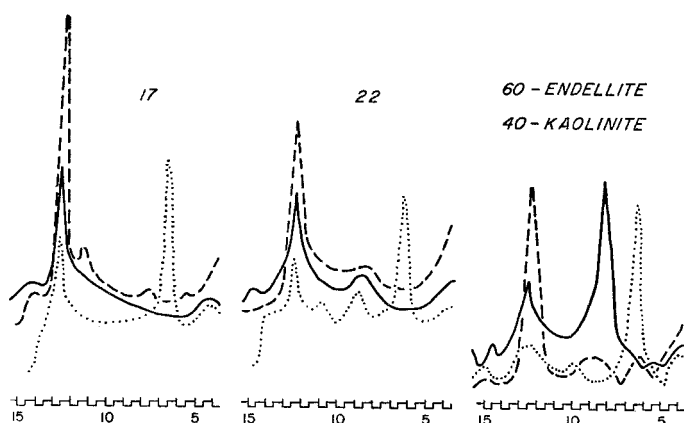


FIGURE 3.—Smoothed X-ray diffractograms; Ni-filtered Cu radiation. (17) Flint fire clay, Olliers, France. (22) Semi-plastic fire clay, Mexico, Missouri. Mixture, 60 endellite-halloysite, 40 kaolinite. Dashed line, untreated clay; dotted line, clay-KOAc mixture; solid line, KOAc treated, washed, ethylene glycol.

the low dehydroxylation temperature of our *specific* specimen probably is due to halloysite.

Hard flint fire clay (nos. 16 and 17) which yields a diffractogram of kaolinite behaves like kaolinite toward KOAc and ethylene glycol (Fig. 3). If halloysite were present in considerable amount in flint clay (as was erroneously identified in some older investigations) the halloysite should manifest itself by the KOAc-glycol processing (as will be shown below). Soft flint clay and semi-flint, semi-plastic, and plastic fire clays, including ball clay (nos. 18–25), respond to KOAc-glycol processing as does kaolinite (Fig. 3); thus the fire clay mineral of the kaolin group behaves more like kaolinite than like endellite.

The meaning of spacings recorded at approximately 14 Å by mixtures of clay and potassium acetate is beyond the objective of this report. Quite obviously some reaction occurs between halloysites and KOAc which

facilitates hydration and solvation of ethylene glycol by the clay, but interaction, if any, between the other polymorphs of kaolin with potassium acetate is obscure and questionable (personal communications from several participants in the 10th Conference).

In Table 2 are recorded data tracing the response of Indiana endellite to KOAc-glycol after, or under, different conditions of dehydration. Crushed

TABLE 2.—DEHYDRATED INDIANA ENDELLITE PROCESSED WITH POTASSIUM ACETATE AND ETHYLENE GLYCOL

	Basal spacing in Å.U.			
	Untreated	Clay-KOAc mixture	Water washed	Et. Glycol solvated
Room dry, approx. 1 week	7-10 (band)	13.9	9.9	10.4-10.8
Room dry, longer than 10 years (Bedford halloysite)	7.1-7.4	14.0-14.2		10.7
Heated 100° C, 4 hr	7.3	13.8	9.8	10.9
		"normal" peak heights		
Heated 200° C, 4 hr	7.1-7.3	13.6		10.4
		one-third "normal" peak heights		
Heated 300° C, 4 hr	7.1	13.7	10.2	10.6
		barely detectable peaks		
Heated 400° C, 4 hr	7.2	no reflections		—

endellite dehydrates and collapses gradually, in terms of mass properties, under ordinary room temperatures and humidities. When it is collected in the collapsed, dehydrated condition on the outcrop it is ordinarily classified as halloysite. This type of clay, which has dried further in an open storage cabinet for more than 10 years, is represented in the second sample in Table 2. Its response, and that of endellite dehydrated at 100° C for 4 hr, to KOAc-glycol are similar. Endellite heated to 200° C for 4 hr, although exhibiting a normally intense 7 Å peak before processing, yields peaks only one-third as intense with KOAc and ethylene glycol than when heated to 100° C. The 10.6 Å peak remaining after glycolation of the clay heated to 300° C is small.

Endellite heated to 400° C for 4 hr retains the 7.2 Å peak, but this part of the structure disappears when the clay is mixed (ground for 20 min) with KOAc, and glycolated.

The conclusions and inferences drawn from the data in Table 2 are that Bedford, Indiana, halloysite represents dehydrated endellite, and it is probable that most halloysite in nature had endellite as its antecedent.

In Table 3 are shown the relative areas above background of the 10 Å peak from artificial mixtures of Georgia kaolinite and Indiana halloysite

TABLE 3.—AREAS OF 10 Å PEAKS IN MIXTURES OF KAOLINITE AND ENDELLITE DEHYDRATED AT 100° C AND PROCESSED WITH KOAc AND ETHYLENE GLYCOL

Percent	{ kaolinite	100	80	60	40	20	0
	{ endellite	0	20	40	60	80	100
Relative area under 10 Å peak		100	78	60	49	29	0

Kaolinite, Dry Branch, Georgia.

Endellite, Bedford, Indiana.

(endellite dehydrated at 100° C) after processing and solvating in ethylene glycol (Fig. 3). Although the recorded areas are in good agreement for 80 and 60 percent halloysite (dehydrated endellite), and not very bad for 40 and 20 percent, we believe they are deceptively better than would be obtained from natural mixtures, as is usually the case. A preliminary run on these mixtures, where insufficient attention was paid to uniformity of grinding, resulted in a reversal of the magnitude of the 60 and 80 percent records. Therefore, we consider this method to be useful qualitatively, but it is semiquantitative only when particular care is given to assure uniform particle size and processing.

#### SPECULATION ON THE ORIGIN OF ENDELLITE VS. KAOLINITE

The identification and occurrence of endellite and halloysite are being reported with increasing frequency in recent years, and interest in the question, "What differentiates the origin of endellite and kaolinite?" likewise arises more frequently. Sand (1956) observed the formation of both of these minerals in the Appalachian region, and concluded as follows:

No matter what the intensity of leaching, even where the feldspars alter completely to hydrated halloysite, the primary muscovite mica always alters to kaolinite . . . explained only on the basis of structural control. . . . A rock low in mica yields a clay high in content of hydrated halloysite. . . . River terraces apparently are favorable locations for the formation of extensive deposits of hydrated halloysite. Good drainage effects a thorough leaching of potash and inhibits the formation of secondary mica.

We wish to draw on two points in Sand's conclusions. The structural control imposed by mica on the origin of kaolinite may govern the course of argillation if the alteration of feldspar is first to mica, either by surface



transition as proposed by DeVore (1959), or energywise as described by Garrels (1957).

Under other conditions, we speculate that the presence of significant concentration of soluble, i.e. mobile, potassium in the chemical system in which the clay is *formed* may conduce to the production of endellite—as Sand noted where the leaching of potash occurred. In further support of the speculation about potassium being important in halloysite–endellite formation, we note that Ross and Kerr (1934, pp. 142–143) found alunite (K-containing) to be a common associate of halloysite, as follows:

Alunite has been found associated with halloysite, studied in the preparation of this report, in specimens from five localities—Liege, Belgium; Lawrence County, Ind.; Newton County, Ark.; Hart County, Ky.; and Leakey, Real County, Tex.

One of us (W.D.K.) has observed alunite to be the most common accessory mineral, except quartz, occurring with the halloysite fire clays in Mexico. Moreover, potassium ions were released, i.e. dissolved, in unexpectedly high concentration during the laboratory hydrolysis of pulverized clay from Mexico halloysite sample 9, as shown by Keller (this Volume) in a study of the origin of that clay. It was not determined if the dissolved potassium came from the clay mineral itself, or possibly from minor associated alunite not detectable by physical means of mineral identification.

Reasoning from Wada's demonstration that KOAc and some other compounds of K can facilitate hydration of halloysite, it is but a short step in speculation to ask if the presence of soluble K, perhaps in small amount or perhaps in sulfuric acid solution, present in the chemical system in which kaolin-type clay is formed, may not implement the crystallization of an expanded, hydrated endellite. The alumina and silica, dissolved in an aqueous system in which K was mobile, would occur in relative disorder and might precipitate to become poorly ordered endellite. In contrast to this condition, the structural and crystal energy inherited from mica where K is relatively immobile could implement therefore the genesis of kaolinite, rather than endellite, where mica (even from feldspar) preceded it.

An alternative proposal, equally speculative, in which K is not critical to the reaction, may be that endellite is formed where sulfuric acid is active, but that kaolinite is formed in an environment where SO<sub>4</sub> ions are essentially lacking. This would accord with our observation that the alunitic halloysite in Mexico originated in the presence of sulfuric acid, and with those of Ross and Kerr (1934, p. 144), who state that it “seems highly probable that the halloysite in at least six of the localities from which material considered in this paper was obtained was the result of the action of waters containing sulphuric acid”.

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