THE AMERICAN MINERALOGIST, VOL. 46, JANUARY–FEBRUARY, 1961

LATTICE EXPANSION OF KAOLIN MINERALS BY TREATMENT WITH POTASSIUM ACETATE

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ABSTRACT

Grinding with K-acetate ($KC_2H_3O_2$) caused a lattice expansion to 14 Å not only for halloysite but good kaolinite, while the formation of the same complex by drying from a $KC_2H_3O_2$ solution was only observable for halloysite, hydrated or dehydrated without heat. Heating the 14 Å complex at 100° C. caused a collapse to 11.4 Å by dehydration. No comparable result was obtained for kaolinite by grinding with the other NH_4 and K salts which were effective in the formation of the halloysite complex. Also, no complex of $KC_2H_3O_2$ formed with some clay minerals, such as pyrophyllite, talc, antigorite, chrysotile, and chlorites.

The 14 Å complexes of kaolin minerals were subjected to washing with water and air-drying at R.H. 65%. The resulting spacings were 7 Å with good kaolinites, and 10 Å with halloysites, even if they had once dehydrated either with or without heat. The observed difference was interpreted in terms of the regularity in the arrangement of the structural layers affecting the orientation of interlayer water molecules.

INTRODUCTION

Generally it has been considered that the dehydration of halloysite is not reversible and the hydrated form ordinarily can not be formed again. This sometimes presents a problem in identification of 7 Å minerals in clays, and particularly in soil clays. MacEwan (1946, 1948) found that halloysite dehydrated without heat will combine with ethylene glycol, and when the product is treated with water, hydrated halloysite is regenerated. The usefulness of this method, however, is also restricted by the fact that not all forms of halloysite respond to this ethylene glycol treatment.

Earlier studies (Wada, 1958, 1959, Garrett and Walker, 1959) show that salt-halloysite complexes are obtained from the hydrated form of halloysite by drying from solutions, or by grinding with crystals of certain K, Rb, NH_4, and Cs salts. The complex-forming ability of some of these salts is suggested to be greater than that of the organic reagent. Formation of the salt complexes and regeneration of hydrated halloysite might be utilized as a criterion for differentiation of halloysite from kaolinite. The above consideration has led to the present study on the formation of the salt complex with halloysites which differ in the degree of hydration, and further with some kaolin clays.

EXPERIMENTAL

$KC_2H_3O_2$, NH_4Cl, and HN_4NO_3 were first selected as the complex-

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forming salts in view of their greater ability in the complex formation in comparison with other NH_4 and K salts. Basal spacings characteristic to each salt complex of halloysite are 14.3, 10.5, and 11.6 Å, respectively.

The following procedures were adopted for the preparation of the salt complexes.

a) Drying from solutions of complex-forming salts

An aqueous solution containing an appropriate amount of a salt was added and allowed to dry on the thin layer of a clay (-2μ) formed on a glass plate by sedimentation. In the case of halloysite, maximum intensities of the basal reflections of the salt complex were obtained when it was treated with 3 to 4 m.mols of the salt per gm. of clay.

b) Dry or wet grinding with salts

One gm. of clay (-150 mesh) was ground in an agate mortar, either mechanically or manually, with 5 to 10 m.mols of the salt. The time necessary for complete formation of the complex varies with the method of grinding, manual or mechanical, dry or wet, and the kind of the minerals and salts. The wet grinding was made in the presence of water just wetting the clay-salt mixture. The dry or mechanical grinding was 3 to 5 times as effective as the wet or manual grinding respectively, but caused considerable destruction of the crystal structure. Standing overnight (or longer) after a brief grinding has been found to be as effective in complete complex formation as longer grinding, with less destructive effect. (Andrew, Jackson and Wada, 1960.)

Results and Discussion

Halloysite

A thin layer of hydrated halloysite from Yoake, Oita, Japan (Aomine and Higashi, 1956) was dried over concentrated H_2SO_4 for two weeks. It combined completely with $KC_2H_3O_2$, but only partly with NH_4Cl and NH_4NO_3 by drying from the respective salt solutions (Fig. 1). Although MacEwan (1946, 1948) stated that halloysite gently dried without heat combined completely, or almost completely with ethylene glycol, most of it remained unaffected in this experiment. A halloysite from Bedford, Indiana, (API reference specimen), which was partly dehydrated as received, responded to the $KC_2H_3O_2$ treatment, and the hydrated halloysite was readily regenerated from the $KC_2H_3O_2$ complex by treating with water (Fig. 2). A similar result was obtained with a halloysite from Eureka, Utah.

Since the result proved that $KC_2H_3O_2$ was most effective to reopen the partly closed interlayer spaces, this treatment was tried with halloysite

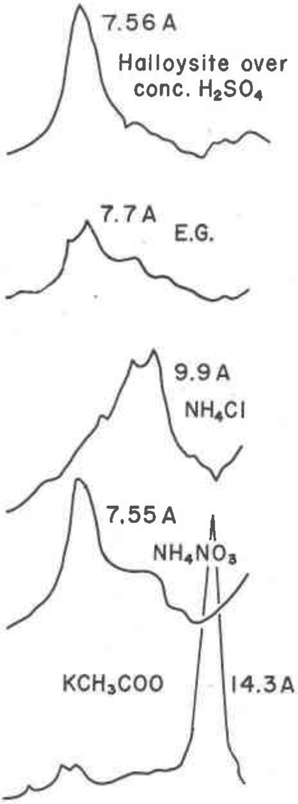
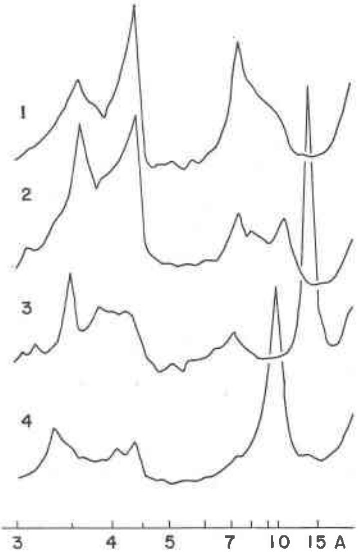


FIG. 1. Effect of pre-drying over conc. H_2SO_4 on the complex formation of the Yoake halloysite.

dehydrated by heating. The Yoake halloysite heated at 100° C. was only partly susceptible, namely, about 80 to 85% remained unaffected, while that heated at 300° C. was almost completely resistant.

After several attempts, grinding with $KC_2H_3O_2$ was found to be most effective for formation of the complex with the halloysite dehydrated by heating (Fig. 3). The time necessary for complete formation of the complex increases with the degree of dehydration, for example, 10 to 40 minutes by the mechanical grinding in the wet state. The amount necessary to obtain the well-developed complex was slightly greater (5 to 6 m.mols/g.) than that in the former drying up treatment. Treating the complex with water, the hydrated form was regenerated (Fig. 3). Therefore, in this sense, the dehydration of halloysite is reversible, and not irreversible as has been generally considered.



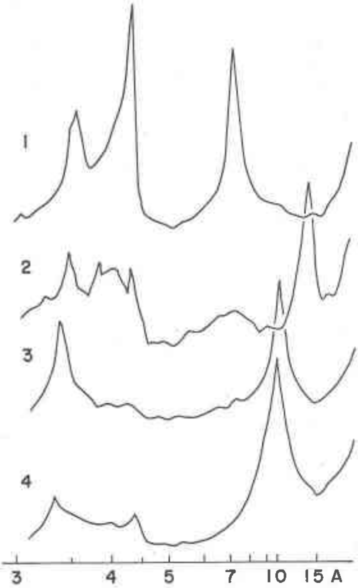


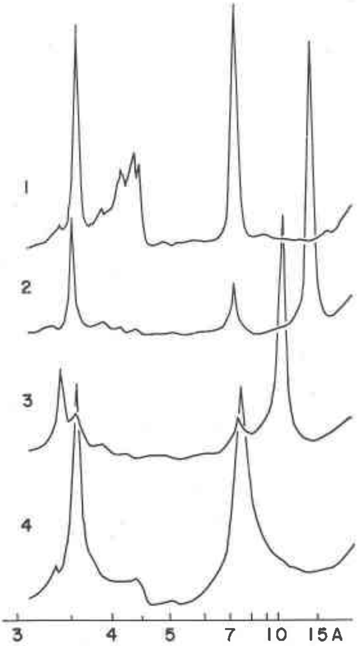
FIG. 2 (left). Bedford halloysite: natural (1); treated with ethylene glycol (2); dried from $KC_2H_3O_2$ solution (3); then, washed with water and air-dried (4).

FIG. 3 (right). Yoake halloysite: heated at 100° C. (1); ground with $KC_2H_3O_2$ (2); then, washed with 1 *N* NH_4Cl solution (3) or water (4), and dried at R.H. 65%.

Kaolinite

Complex formation by drying from the $KC_2H_3O_2$ solution was tried on a platy kaolinite from Macon, Georgia (API reference specimen), but no complex formed. Further, it was subjected to the dry grinding with $KC_2H_3O_2$. Contrary to expectation, very strong and sharp reflections appeared at 14.2, 7.1, and 3.51 Å (Fig. 4), indicating that the kaolinite structure expanded along its *c*-axis as did halloysite. A comparatively greater amount of the salt (8 m.mols/g.) was needed to produce the well-developed complex. The time necessary for complete formation of the complex was longer than that needed for metahalloysite, but partial formation was readily noticed after 20 minutes grinding.

The basal reflections for the kaolinite complex were about eight times as strong as those for the corresponding halloysite complex. This might be interpreted in terms of the higher regularity of the layer stacking and the greater number of the structural layers in the kaolinite complex. Furthermore, smoothing the surface of the specimen packed in the sample holder in x-ray analysis may produce strong orientation of the platy crystallites



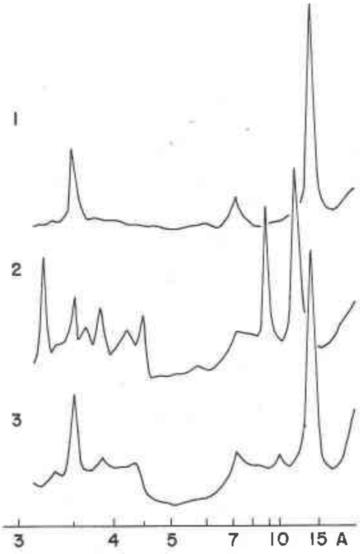


FIG. 4 (left). Georgia kaolinite: natural (1); ground with $KC_2H_3O_2$ (2); then, washed with 1 *N* NH_4Cl solution (3) or water (4), and dried at R.H. 65%.

FIG. 5 (right). Georgia kaolinite: ground with $KC_2H_3O_2$ (1); then, heated at 100° C. (2); and allowed to stand in the laboratory air for 1 hour (3).

in the sticky mass of the clay and $KC_2H_3O_2$, resulting in enhancement of the basal reflections.

An x-ray analysis was made on the clay obtained from the kaolinite complex by washing with water and air-drying. A broad peak appears at about 7 Å instead of 10 Å (Fig. 4), suggesting that there is some difference between kaolinite and halloysite in the stability with which water molecules orient between the kaolin layers. The two triplets of the original kaolinite with spacings, 2.56, 2.53, 2.50 and 2.38, 2.34, 2.29 Å, were replaced by a doublet (2.56 and 2.50 Å.) and a broader reflection at 2.34 Å. Also, a two dimensional diffraction effect appeared on the reflections corresponding to the (020) to (002) reflections of the original kaolinite. The finding indicates that the reversible penetration of $KC_2H_3O_2$ has caused a considerable modification on the disposition of kaolin layers, but it still has some distinctive structural features. These are comparable to those found for "fireclay" (Brindley and Robinson, 1946, 1947) and kaolinite ground in a ball mill for 4 to 10 weeks (Dragsdorf *et al.*, 1951), suggesting the presence of the structural layers being randomly displaced by multiples of $b_0/3$ along the b-axis.

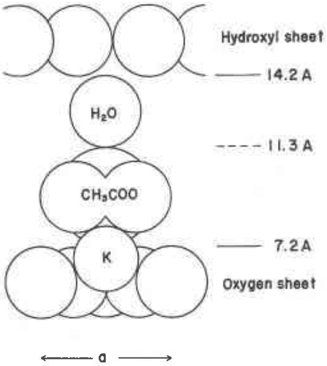


FIG. 6. A cross section of the 14 Å complex, showing a probable position of K^+, $C_2H_3O_2^-$, and H_2O.

From the foregoing, a mechanical disruption of the kaolinite structure to that of halloysite may be ruled out as a probable cause of the observed lattice expansion. It is certainly true that, in the absence of $KC_2H_3O_2$, the kaolinite structure would be considerably disrupted by only 30 minutes of dry grinding (Fig. 7). In its presence, however, the kaolinite structure may be more stable probably owing to the lubricating action of interlayer water molecules, as will be shown later. Therefore, the observed expansion to 14 Å by positive penetration of $KC_2H_3O_2$ can be considered as a potential characteristic of kaolinite, and consequently, common to all the members of the halloysite-kaolinite series.*

The effect of heating at 100° C. on the $KC_2H_3O_2$ complex is interesting in view of the configuration of the interlayer material and the preference for $KC_2H_3O_2$ in the reaction. The heating caused a collapse of the complex to 11.4 Å (Fig. 5). The reflections due to the excess salt appeared at 8.85, 4.44, 3.55, and 3.21 Å. The decrease in the basal spacing and the readiness of its restoration by allowing the heated complex to stand in the laboratory air indicates the presence of a monomolecular layer of water together with that of $KC_2H_3O_2$. The cation size was found to be of primary importance in the reaction in relation to the size of the cavity in the SiO-sheet (Wada, 1958, 1959), so $KC_2H_3O_2$ and water molecules probably are oriented in a configuration, such as that illustrated in Fig. 6, in which K^+ fits in the cavity of the oxygen hexagon and the clearance space is about equal to the sum of the CH_3 and H_2O *van der Waals* radii.

Much longer grinding of the Georgia kaolinite with NH_4Cl resulted in an appearance of a diffuse reflection at about 10 Å. The effect of mechanical destruction was found to be greater as illustrated by some of the

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* A recent study (Andrew, Jackson and Wada, 1960) has shown that dickite is also expandable upon grinding with $KC_2H_3O_2$.

rather diffuse and generally weakened (*hkl*) reflections. The partial formation of the hydrated form from the complex by washing with water may be related to this. Since the well-developed NH_4Cl complex can readily be obtained by washing the $KC_2H_3O_2$ complex with an NH_4Cl solution (Fig. 4), the result seems to indicate difficulty in the penetration into the kaolinite structure, and not the unstable nature of the resulting configuration.

The dry grinding was also tried with the following salts; NH_4NO_3, $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, K_2HPO_4, NH_4-formate, NH_4-acetate, and $(NH_4)_2$-citrate. These were effective in the formation of the halloysite complex (Wada, 1959), but none was comparable to $KC_2H_3O_2$ in the penetration into the kaolinite structure.

The reason of this preferential penetration is as yet not clear. The presence of interlayer water molecules owing to its strong deliquescent nature might have an effect in the penetration as a lubricant and/or as a stabilizing agent in the complex formation. Lubricating action of interlayer water was also assumed by Mackenzie and Milne (1953) in the explanation of the relative stability of vermiculite to grinding in comparison with muscovite. However, it alone could not account for the observed preference, because the deliquescent salts, $NH_4C_2H_3O_2$ and K_2HPO_4, fail to form the complex upon dry grinding.

Relationships of Complex Formation to Clay Structure

In view of a common peculiarity of their crystal structures, salt-complex formation was previously tried with montmorillonites as well as with halloysite (Wada, 1959), but no complex was found. The difference between both the minerals was ascribed to the differences in the density of the interlayer charge and in the atomic configuration of the interlayer surface.

Further, in this study, dry grinding with $KC_2H_3O_2$ was tried with the following minerals:

1. Pyrophyllites from Fukue, Nagasaki and Mitsuishi, Okayama.
2. Talc from Sasaguri, Fukuoka.
3. Antigorite from Sasaguri, Fukuoka (Table 1).
4. Chrysotile from Kashii, Fukuoka (Table 1).
5. Chlorites from Sanno, Fukuoka, and Okushi, Nagasaki (Shirozu, 1958).

There is no indication of the lattice expansion with these minerals. Pyrophyllite and talc were used in view of the absence of the interlayer charge and the difference in the atomic configuration at the interlayer surface. The fact that no complex formation occurred with these minerals could be attributed to their atomic configuration of the interlayer surface, namely, the oxygen and oxygen sheets in these minerals instead of the oxygen and hydroxyl sheets in the kaolin minerals. It is also evident that the absence of the interlayer charge may contribute, but it alone can not cause the penetration and orientation of the salt molecule.

Considering their structural similarity, a sharp difference in the complex formation between the kaolin and serpentine minerals is particularly interesting. So far as the 1:1 layer structure is assumed, there seems no significant difference in the strength of the interlayer bonds between both the minerals. The effect of cation substitution is practically negligible in this connection. On the other hand, the configuration of the oxygen and hydroxyl layers are different as seen in their b_0 parameters 8.93 and 9.24 Å for kaolinite and antigorite respectively, and this might affect the stability of the resulting complex. It seemed still questionable, however, that the striking difference in the complex formation could be ascribed to such a rather small difference.

TABLE 1. THE EFFECT OF DRY GRINDING ON THE *X*-RAY DIFFRACTION PATTERNS OF CHRYSOTILE AND ANTIGORITE

Chrysotile (Kashii)				Antigorite (Sasaguri)			
Before grinding		After 2.5 hrs. grinding		Before grinding		After 2.5 hrs. grinding	
d(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I
7.25	56	7.25	38	7.20	200	7.20	35
4.53	18	4.54	14				
3.64	41	3.63	26	3.60	184	3.60	22
2.62	10	2.61	8				
2.50	31	2.50	20	2.52	42	2.52	23
2.43	18	2.44	12	2.41	14	2.41	3
2.33	15	2.33	7	2.16	10	2.16	5
2.15	3			2.15	10		
1.96	5			1.81	8		
1.53	20	1.53	12	1.56	8	1.57	4
				1.54	8	1.54	4

The samples were mounted by packing into the hollow of the Al-holder and smoothing the surface. Intensities were measured from the peak height on the automatic recording chart.

In relation to this, the result of grinding of these mineral samples alone should be noted (Fig. 7). Under comparable conditions (dry, mechanical), the (001) reflections of the kaolinite, talc, and pyrophyllite markedly reduced their intensities in the first 30 minutes. At the end of 2 hours, they completely collapsed with disappearance (kaolinite) or marked blurring (talc and pyrophyllite) of all the (*hkl*) reflections. In the meanwhile, the chrysotile showed little change in the sharpness and intensity of its (001) reflection, and contrary to what expected from its hypothesized tubular structure, was reasonably stable to grinding (the Yoake halloysite completely collapsed within 1 hour). In the case of antigorite, a marked degradation was observed at first, but the (00*l*) reflection maxima remained more resistant on further grinding in comparison with the other platy materials. The coincidence of the (001) intensities of both the minerals after prolonged grinding may be meaningful, although there is no comparable agreement in other reflections (Table 1). These results seem to indicate the presence of some fundamental fiber-crystallites in these minerals, such as that suggested by Pundsack (1956) on the basis of the density measurement for massive chrysotiles.

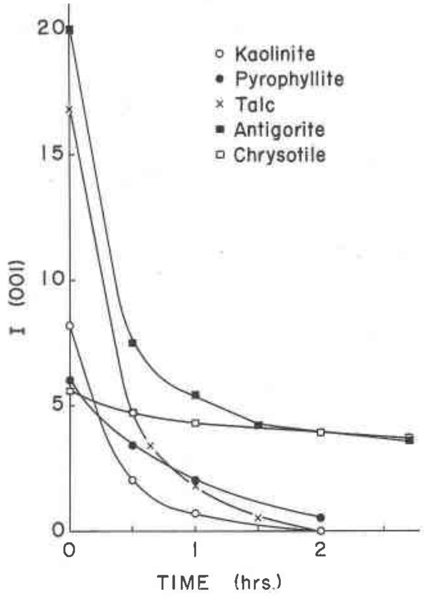

FIG. 7. Effect of dry grinding on the (001) intensities of kaolinite (Georgia), pyrophyllite (Fukue), talc (Sasaguri), antigorite (Sasaguri), and chrysotile (Kashii).

At any rate, it seems apparent that both the serpentine minerals react to grinding differently from the kaolin minerals, and this would be a cause for the inhibition of the formation of a salt complex. There may be some significant differences in their crystalline arrangement and therefore in the strength of the interlayer bonds, although this seems difficult to understand on the basis of the structural and morphological analogy between the kaolin and serpentine minerals (e.g. Bates, 1959).

The absence of the chlorite complex could be used in determination of kaolin minerals in the presence of chlorite minerals. Unfortunately, the basal-reflections of the $KC_2H_3O_2$ complex of the kaolin minerals are close to the corresponding spacings of the chlorites, but the shift of 14 Å reflection to 10 or 11 Å is easily seen by forming the NH_4Cl or NH_4NO_3 complex.

STABILITY OF WATER COMPLEX

The foregoing data suggest that the stability of the water complex derived from the $KC_2H_3O_2$ complex closely relates to its source minerals; the Georgia kaolinite forms only a very unstable water complex, while the Yoake halloysite, even after it has been heated, readily regenerates its hydrated form. If it is generally correct, the difference in the stability of the water complex would aid in differentiation of 7 Å minerals in clay materials, and provide useful informations on their genesis.

The proposed method is the following. Clay samples are subjected to wet grinding with $KC_2H_3O_2$. The resulting complexes are washed twice with water (water complex) or a 1 N NH_4Cl solution (NH_4Cl complex) by the centrifuge technique, spread on a glass plate, allowed to stand in a desiccator at R.H. 65%, and x-rayed.

Either the kaolinite or halloysite forms its NH_4Cl complex (Figs. 3 and 4), that permits a check of the formation of the complex with $KC_2H_3O_2$. Meanwhile, the stability of the water complex is much different for the minerals; no complex formed with well-crystallized kaolinites, such as those from Macon, Georgia (Fig. 4); Mesa Alta, New Mexico; and Ibuski, Kagoshima, Japan. Even a transient formation of their fully-hydrated forms could hardly be followed by x-ray analysis made while the clays were kept moistened. On the other hand, several natural hydrated and partially dehydrated halloysites (formed either by weathering of volcanic glass or by hydrothermal action) gave water complexes which were stable at R.H. 65%, even after they had been dehydrated by heating (Fig. 3).

The observed difference in the stability of the water complex derived from the $KC_2H_3O_2$ complex seems to reflect the difference in the arrangement of their structural layers that is inherited from the original minerals and is probably associated with environmental conditions of their formation. Random displacements of successive kaolin layers along both b- and a-axes in halloysite may favor relatively stable orientation of water molecules, whereas the higher degree of regularity, such as that found for the salt complex derived from kaolinite may not. It suggests that the interlayer water molecules of halloysite are in a regular crystalline array that is related in some way to the clay structure, but not in the state of two dimensional liquid.

Of all the specimens examined, the Spruce Pine kaolin (API reference specimen) is interesting in showing an intermediate character between kaolinite and halloysite, and in suggesting a possible transition from the poorly crystalline halloysite to the well-ordered kaolinite. Electron microscopic studies of this material revealed a predominance of tubular crystals (Davis *et al.*, 1950; Sand and Ormsby, 1954; Taggart *et al.*, 1955). Further, the electron diffraction studies made by Honjo and his collaborators (1954) showed that these tubular crystals have a regular structure different either from that of halloysite, or of kaolinite. The x-ray diffraction pattern shows a rather sharp (001) reflection at 7.20 Å, and two triplets with spacings at 2.56, 2.53, 2.50 and 2.38, 2.34, 2.29 Å are fairly well-separated. These x-ray characteristics are also indicative of a higher degree of crystallinity than that commonly attributed to halloysite minerals.

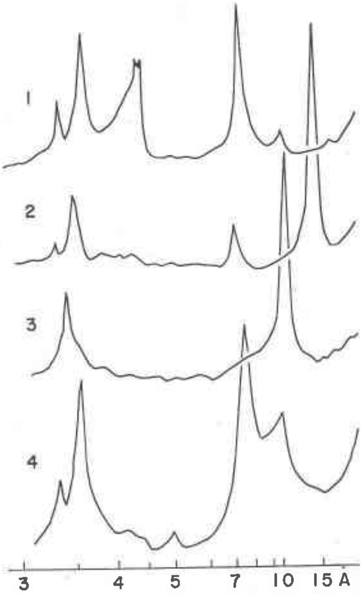

FIG. 8. Spruce Pine kaolin: natural (1); ground with $KC_2H_3O_2$ (2); then, washed with 1 N NH_4Cl solution (3) or water (4), and dried at R.H. 65%.

Partial formation of the water complex was observed by washing its $KC_2H_3O_2$ complex with water (Fig. 8), while only 15 to 20% of this material (-2μ) and even less of that included in the coarser fraction (-150 mesh) formed the complex by drying from the $KC_2H_3O_2$ solution.

Sand (1956) analyzed the material believed to be of the same origin but kept in moist conditions and gave the ratio of *hydrated halloysite*: kaolinite as approximately 7.5–6.9:1.0–2.1. In this district, all halloysites were found in the hydrated form, and not its dehydrated form. He interpreted his data to indicate that environmental conditions in weathering of feldspathic rocks that are conducive to the formation of the hydrated halloysite, have not changed appreciably since Tertiary time. On the other hand, he noted that the Spruce Pine halloysite dehydrates much more rapidly than the compact hydrothermal hydrated halloysite (personal communication). A similar observation was also made by Kerr, Kulp, and Hamilton (1950).

These data are interesting in indicating the presence of a particular kaolin mineral that is derived from its hydrated form but exhibits rather high degree of regularity in the stacking of the structural layers. As has been well-known, environmental conditions, such as humidity, temperature, and pressure cause the dehydration of halloysite (Brindley and Goodyear, 1948; Brindley, Robinson, and Goodyear, 1948). In view of the present results, it seems very probable that the dehydration of halloysite is also a function of its crystallinity, and the ready and irreversible dehydration of the Spruce Pine material might be interpreted as due to a long period of crystallization time.

CONCLUSION

Formation of the interlayer complex resulting in lattice expansion to 14 Å. by grinding with $KC_2H_3O_2$ can be considered as a potential characteristic common to all the minerals of the kaolinite-halloysite series, but not to serpentine minerals, 2:1 and 2:2 type minerals, either with or without interlayer charge. So far as tested, no well developed complex forms with other NH_4 and K salts, although the reason for this preference for $KC_2H_3O_2$ is as yet not known. Contraction of the 14 Å complex to 11.4 Å by heating indicates the presence of a monomolecular layer of water together with that of $KC_2H_3O_2$.

The water complexes of kaolin minerals could be obtained from each 14 Å complex by washing with water, and their stability has a relationship to the degree of randomness of the stacking of the structural layers. The water complexes derived from good kaolinites are far less stable, while those from poorly crystalline halloysites are stable, even if they have once dehydrated with or without heating. Differentiation between these two types of 7 Å minerals on this basis could be of considerable significance in studying kaolin minerals in clays and soil clays.

ACKNOWLEDGMENT

The author would like to acknowledge the help and encouragement received during the study from Professor S. Aomine. The research was supported in part by a grant from the Asahi Science Research Fund. API specimens were kindly furnished by Dr. T. Sudo through Professor Aomine, Ibuski kaolin and talc samples by Drs. N. Tanaka and T. Muta, serpentine and chlorite minerals by Dr. H. Shirozu, respectively. The author is also grateful to Dr. L. B. Sand who has provided the Utah halloysite and valuable informations on the Spruce Pine kaolin.

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Manuscript received April 5, 1960.