

# RAPID DISSOLUTION OF ALLOPHANE AND KAOLINITE-HALLOYSITE AFTER DEHYDRATION

*by*

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## ABSTRACT

Differential dissolution in NaOH solution was investigated as a means of purification of clay. It was discovered that a large quantity of allophane and free alumina and silica were dissolved from clay preparations in 0.5 N NaOH solution by boiling for as little as 2.5 min, provided the ratio of clay weight to solution volume was kept less than 100 mg to 100 ml. Reprecipitation of dissolved silica occurred if a more prolonged digestion or higher sample to solution ratio was employed. Also, prolonged digestion in the NaOH solution (for 80 min) dissolved as much as 50 percent of kaolinite (Merek) and 25 percent of Wyoming montmorillonite, but only a small quantity of these crystalline minerals was dissolved during the 2.5 min digestion period. Subsequent dithionite-citrate-bicarbonate treatment removed the released iron. Marked improvement of x-ray diffraction patterns of the clays resulted. This rapid and selective dissolution of allophane and free oxides greatly improves the quantitative analysis of crystalline minerals by conventional methods.

After dehydroxylation at 500°C, kaolinite and halloysite became amorphous and also dissolved by the same differential dissolution procedure. Heat-stable (aluminous) montmorillonite and chlorite were only slightly dissolved by this treatment. The selective removal of the 1:1 layer aluminosilicates greatly improves the quantitative analysis of the remaining crystalline components of clays by conventional methods.

## INTRODUCTION

Differential dissolution techniques have been used for many years in the field of clay mineralogy. Strong inorganic acids individually or mixed, followed by NaOH solution to dissolve the released SiO<sub>2</sub>, are used to dissolve the nonquartz fraction so that the content of quartz can be determined (Jackson, 1956, p. 524). Digestion in warm dilute HCl has been employed to dissolve chlorites (Brindley and Robinson, 1951; Oda, 1954). Chlorite (Brindley, Oughton and Youell, 1951) or kaolinite (Steger, 1953) dissolved readily in HCl after heating these minerals at 500°C. Heating minerals to their decomposition temperature seems to have a marked effect on the subsequent acid extraction treatment. The amount of aluminum extracted by sulfuric acid digestion is a function of the preheating temperature and mineral species (Pask and Davies, 1945).

While acids have been used to dissolve crystalline components differentially, alkaline reagents have been used to dissolve amorphous aluminosilicate, free silica, and free alumina. Boiling clays in a dilute Na<sub>2</sub>CO<sub>3</sub> solution is a widely accepted practice to facilitate complete dispersion of clay particles by dissolution of amorphous cementing materials (Jackson, 1956, p. 72)

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consisting of finely divided films of precipitated  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and aluminosilicate (Jackson, Whittig and Pennington, 1950); however, dissolution of more resistant amorphous aluminosilicate materials is generally incomplete because of slow rate of the reaction and because of the solution becoming saturated. Only small amounts of silica and alumina were dissolved in

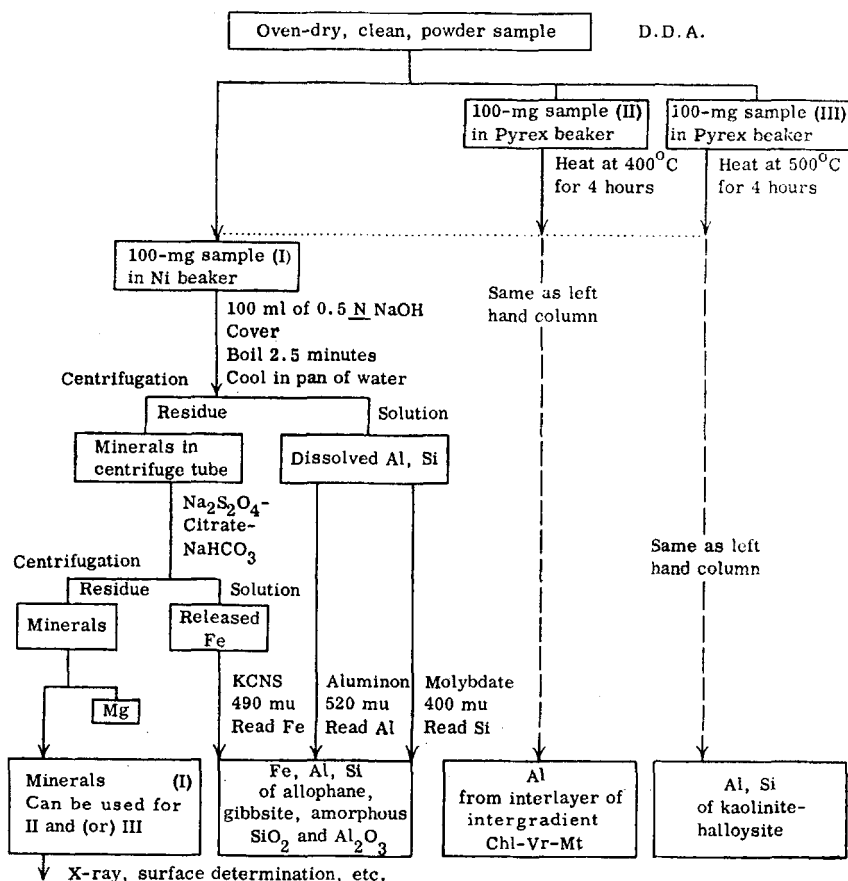


FIGURE 1.—Flow sheet for differential dissolution of allophane, gibbsite, amorphous silica and alumina; interlayer aluminum of intergradational vermiculite-montmorillonite-chlorite; and kaolinite-halloysite.

$\text{Na}_2\text{CO}_3$  solution from a highly weathered ferruginous humic latosol soil of Hawaii which contained an appreciable amount of amorphous aluminosilicate relics; the same material released considerable amounts of silica and alumina during alternate HCl and NaOH digestions (Whittig, 1954). Dehydroxylated kaolinite was quite resistant to treatment in  $\text{Na}_2\text{CO}_3$  solution (Hislop, 1944). Boiling a clay sample in 0.5 N NaOH solution rapidly dissolved free alumina or free silica from montmorillonitic samples (Foster, 1953).

## PROCEDURE

The procedure (flow sheet, Fig. 1) developed to dissolve allophane, gibbsite, free alumina and free silica, interlayer aluminum of the so-called intergradient vermiculite–montmorillonite–chlorite (Dixon and Jackson, 1959), and kaolinite–halloysite by differential dissolution is described first and then the experimental results on which it is based are presented. One objective is to obtain the other layer silicate minerals, free of these materials, for other types of analysis.

*Dissolution of allophane and free alumina and silica.*—An oven-dry, iron oxide-free (Jackson, 1956, p. 57), powder sample (weighing 100 mg) is placed in a Ni beaker, 100 ml of 0.5 N NaOH is added, and the suspension is brought to boiling rapidly and boiled for exactly 2.5 min. (The total heating time is approximately 5 min.) The beaker content is immediately cooled in a water bath to room temperature and the supernatant liquid is removed by centrifugation. The dissolved Si and Al are immediately determined (Jackson, 1958, pp. 296–300). (On standing, aluminosilicate may precipitate.) The iron oxide released (still remaining in the residue) is dissolved by the  $\text{Na}_2\text{S}_2\text{O}_4$ –citrate–bicarbonate method (Jackson, 1956, p. 57; Mehra and Jackson, 1959) and the Fe is determined (Jackson, 1958, p. 169) in the supernatant solution.

*Extraction of interlayer aluminum of intergrades.*—A 100 mg sample, free of gibbsite, is heated in a 50 ml Pyrex beaker at 400°C for 4 hr (Dixon and Jackson, 1959), which dehydroxylates interlayer aluminum of intergradient vermiculite–montmorillonite–chlorite, and this Al is then extracted in NaOH in exactly the same way as for allophane, and the Al is determined.

*Dissolution of kaolinite and halloysite.*—A 100 mg sample, free of gibbsite, is heated in a 50 ml Pyrex beaker at 500°C for 4 hr. The dehydroxylated kaolinite and halloysite are dissolved in NaOH in the same way as for allophane and the Al and Si are determined.

## EXPERIMENTAL RESULTS

*Differential Dissolution of Allophane*

The white allophane of Ross and Kerr (1934), which had a high cation exchange capacity delta value (Aomine and Jackson, 1959) typical of the more reactive type of allophane, dissolved rather completely from the oven-dried preparation (Table 1), as did the allophane (White, 1953) weathered from halloysite. The undissolved portion of the latter showed a 7 Å peak of halloysite concentrated by removal of allophane. Significantly lower amounts of elements were dissolved after the 500°C heating of the original samples, indicating that some portion of the allophane or free oxides was made less soluble by the process of heating at 500°C. The allophanic clay of Kuroishibaru Ando soil (Japanese volcanic ash soil) released 90 percent of its total constituents from the oven-dried preparation, and the amount dissolved was not greatly influenced by the 500°C heating treatment, indicating very little kaolinite–halloysite present and very little interaction of the allophane with

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TABLE 1.—ANALYSIS OF TOTAL AND DIFFERENTIALLY DISSOLVED ELEMENTS FROM ALLOPHANIC SAMPLES

Sample	Total Elemental Analysis (%)			Differentially Dissolved (%)			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	110°C		500°C	
				SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Allophane <sup>1</sup> (Ross and Kerr)	30.2	42.0	0.14	(a) 29.4	38.3	27.6	32.5
				(b) 29.7	37.8	27.6	33.0
Allophane <sup>2</sup> Lawrence Co., Ind.	28.5	41.8	0.07	(a) 28.8	36.5	25.6	31.0
				(b) 28.4	36.9	23.8	29.2
Allophanic Soil Clay (Kuroishibaru <sup>3</sup> )	25.5	31.4	5.8	20.4	29.4	22.1	28.1

(a) and (b) represent duplicate samples.

<sup>1</sup> Sample kindly furnished by Dr. C. S. Ross of the U.S. Geol. Survey, Washington, D.C.

<sup>2</sup> Sample kindly furnished by Dr. W. A. White of the Illinois State Geological Survey, Urbana, Illinois.

<sup>3</sup> Sample kindly supplied by Dr. S. Aomine, Kyushu University, Fukuoka, Japan.

heat. Upon x-ray examination, the residue revealed the presence of vermiculite and chlorite which could not be detected in the x-ray diffraction pattern of the bulk sample (Fig. 2).

*Solubility of Kaolinite and Montmorillonite in NaOH*

*Effect of pretreatment temperature.*—The striking similarity in the x-ray diffraction patterns of allophane and dehydroxylated kaolinite and halloysite (Fig. 3) suggests that these three materials might behave alike in dissolution properties in NaOH solution. A series of 100 mg samples of kaolinite (Merck) and montmorillonite (Wyoming) were heated for 2 hr in a muffle furnace at various temperatures and subjected to the NaOH procedure. Dissolution of kaolinite followed exactly the same course as dehydroxylation (Fig. 4); a sharp break occurs at 500°C where almost complete dissolution takes place. The amount of montmorillonite dissolved is almost negligibly more after 500° preheating than after 110°C preheating; appreciable amounts dissolve only after reaching dehydroxylation preheating temperatures. It appears that dissolution follows the same function of temperature as dehydroxylation and concurrent structure disruption.

*Effect of concentration of NaOH solution.*—The optimal concentration of NaOH solution was tested by keeping the sample-to-reagent ratio identical but varying the NaOH concentration from 0.05 to 0.5 N. Dissolution of dehydroxylated kaolinite is directly related to the logarithm of concentration of NaOH (Fig. 5). Slight deviation from the line at 0.5 N NaOH is due to

complete dissolution of the 100 mg kaolinite sample. The 0.5 N solution, however, appeared to be near optimal for rapid dissolution of dehydroxylated kaolinite and other amorphous materials. This logarithmic relationship does indicate that repeated treatments with less concentrated NaOH solution,

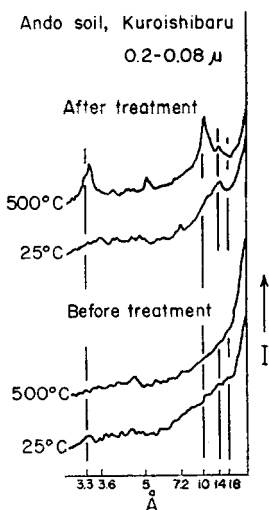


FIGURE 2.—x-Ray diffraction patterns of Kuroishibu clay sample, 0.2–0.08  $\mu$ , Ando soil, Japan (intensity,  $I$ , is on a log scale).

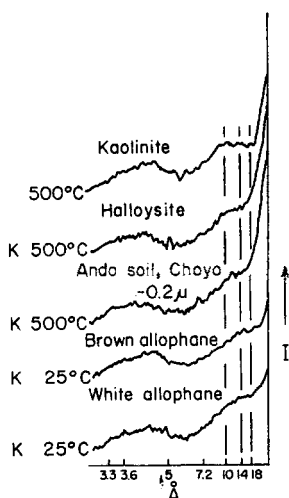


FIGURE 3.—x-Ray diffraction patterns of allophanes, halloysite and kaolinite (intensity,  $I$ , is on a log scale). Data of Aomine and Jackson (1958) except kaolinite (H-saturated).

for example three times with 0.2 N, might be applied just as effectively although the procedure becomes more complex.

*Effect of sample size.*—Samples ranging from 0.1 to 2.0 g were dehydroxylated and treated by the above procedure. Dissolution followed a logarithmic

curve and reached a maximum at approximately the 0.8 g level, above which the solution became saturated with respect to aluminosilicate (Fig. 6). An identical result was obtained with other kaolinite specimens, that is, 130 mg of silica in the presence of 110 mg of alumina was the upper limit for 100 ml

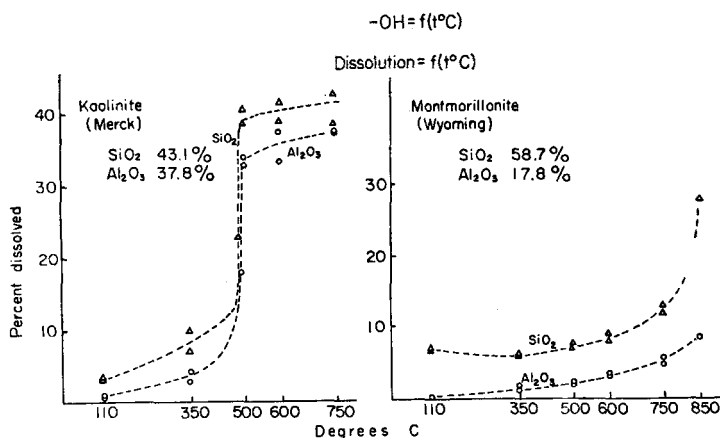


FIGURE 4.—Dissolution in 0.5 N NaOH of kaolinite (Merck) and montmorillonite (Wyoming) as a function of preheating temperature.

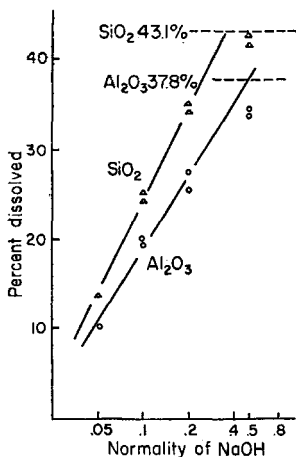


FIGURE 5.—Dissolution of dehydroxylated kaolinite (Merck) as a function of the concentration of NaOH. (Dashed lines indicate total present.)

of the reagent. A 0.1 g sample of dehydroxylated kaolinite was dissolved completely. A 0.2 g sample was largely dissolved also. A lower percentage of the sample was dissolved as the saturation point of the solution was approached with greater sample size. The sample size should be sufficiently small, of the order of from 100 to 150 mg/100 ml of 0.5 N NaOH, to be taken completely into solution.

*Effect of time of digestion.*—To determine the stability of kaolinite and montmorillonite in the NaOH involving the high ratio of solution to solid adopted in the procedure, the time of digestion was varied (Table 2). As much as 50 percent of kaolinite and 25 percent of montmorillonite dissolved during 80 min of boiling. A striking feature exhibited in the tests using montmorillonite (Table 2) is that 2.5 min of boiling extracted more silica than 5 min of boiling, indicating that some dissolved silica was reprecipitated. A test was made to determine if 100 mg of dehydroxylated kaolinite would be

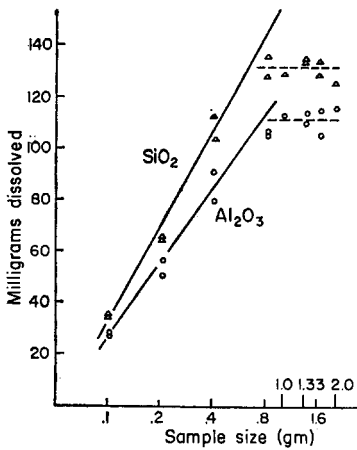


FIGURE 6.—Dissolution of dehydroxylated kaolinite (Baker) as a function of sample size. (Dashed lines indicate saturation of the solutions.)

dissolved in the presence of various amounts of montmorillonite (Wyoming) or chlorite (Cartersville, Ga.). The unheated montmorillonite hindered the dissolution of the heated kaolinite (Table 3), again indicating that the unheated montmorillonite helps induce reprecipitation of silica. The mont-

TABLE 2.—EFFECT OF 0.5 N NaOH BOILING TIME ON KAOLINITE AND MONTMORILLONITE DISSOLUTION, EACH ON A SEPARATE SAMPLE

Boiling Time (min)	Kaolinite (Merck)		Montmorillonite (Upton, Wyo.)	
	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>
2.5	3.34	0.82	6.93	0.29
5	5.32	2.63	3.66	0.52
10	7.83	3.72	4.93	0.81
20	10.3	8.8	n.d.	n.d.
40	15.3	12.4	10.3	3.1
80	25.0	18.3	15.7	5.5
Total in Sample	43.1	37.8	58.7	17.8

n.d. = not determined.

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TABLE 3.—DISSOLUTION OF KAOLINITE MADE AMORPHOUS BY PREHEATING TO 500°C AS AFFECTED BY THE PRESENCE OF VARYING ADDED AMOUNTS OF MONTMORILLONITE OR CHLORITE

	Crystalline Mineral (mg) Added to 100 mg of Kaolinite					
	0	25	50	100	200	400
<i>Untreated Montmorillonite added to Heated Kaolinite</i>						
%SiO <sub>2</sub>	39.5	43.1	42.7	41.1	36.8	32.7
%Al <sub>2</sub> O <sub>3</sub>	33.5	32.8	31.6	31.7	27.6	23.6
<i>Montmorillonite added to Kaolinite and Heated together at 500°C</i>						
%SiO <sub>2</sub>	39.5	39.2	43.5	42.0	43.9	52.5
%Al <sub>2</sub> O <sub>3</sub>	35.5	32.6	36.0	33.7	30.8	34.6
<i>Chlorite added to Kaolinite and Heated together at 500°C</i>						
%SiO <sub>2</sub>	39.5	41.0	41.2	40.9	42.8	—
%Al <sub>2</sub> O <sub>3</sub>	33.5	36.7	36.8	34.8	36.0	—

morillonite heated together with the kaolinite (the usual procedure) did not hinder a satisfactory recovery of dehydroxylated kaolinite, although the dissolution of the small amount of amorphous silicate from the montmorillonite is noted. The chlorite did not interfere (Table 3) with recovery of the kaolinite, indicating a high stability of chlorite.

To avoid breakdown of crystalline materials and also to avoid reprecipitation of dissolved silica, the 2.5 min boiling period was adopted. Very little of either kaolinite or montmorillonite was dissolved during that time, while the amorphous substances present were dissolved completely. This short boiling period gives satisfactorily reproducible results (Table 1).

*Differential Dissolution of Mineral Specimens  
and Soil Clays*

The procedure for differential dissolution of amorphous materials and kaolinite worked out above was applied to a number of clay specimens (Table 4) and soil samples (Table 5). The kaolinite specimens released an appreciable amount of silica and alumina at 110°C, and more than 70 percent of the total constituent dissolved after 500°C heating, concentrating micas and other 2 : 1 layer silicates in the residue.

The 110°C halloysite sample showed a very large amount of dissolved silica and alumina, indicating the presence of a fairly large amount of allophane, and also the presence of gibbsite was verified by x-ray diffraction and differential thermal data. After dehydroxylation at 500°C, a larger amount of the sample dissolved but dissolution was nevertheless incomplete. A 110°C sample was freed from gibbsite and allophane by four successive applications of the NaOH procedure; then the purified halloysite dissolved like kaolinite after 500°C preheating (Table 4). Interference by gibbsite is



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TABLE 4.—ANALYSIS OF TOTAL AND DIFFERENTIALLY DISSOLVED ELEMENTS FROM MINERAL SPECIMENS

Sample	Total Elemental Analysis (%)			Differentially Dissolved (%)			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	110°C		500°C	
				SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Kaolinite (Merck)	43.1	37.8	n.d.	3.34	0.74	39.5	33.5
Kaolinite (Baker)	46.6	32.4	2.9	n.d.	n.d.	35.1	27.9
Kaolinite Delaware, Pa.	46.8	34.5	0.8	6.98	4.14	38.0	29.3
Kaolinite McNamee Mine	45.8	33.1	0.7	3.50	1.95	33.0	29.2
Halloysite Bedford, Ind.	37.2	37.0	0.7	17.2	21.7	27.5	29.3
Purified <sup>1</sup>	41.8	32.0	0.5	—	—	40.9	26.9
Chlorite Cartersville, Ga.	30.8	19.7	3.5	n.d.	n.d.	1.0	0.3
Vermiculite Colorado	n.d.	n.d.	n.d.	n.d.	n.d.	11.2	3.1

<sup>1</sup> Same sample purified by four successive applications of allophane dissolution n.d. = not determined.

quite evident and its removal is necessary before the 500°C preheating treatment. The chlorite showed very high stability (Table 4). The vermiculite sample, being an iron-rich 2:1 layer aluminosilicate, dehydroxylated partially at 500°C, and dissolved accordingly.

The relatively pure montmorillonitic clays from dark magnesium clays of Hawaii contained large amounts of allophane-like materials (Table 5). After 500°C preheating, these clays released the kaolinite component as well as a fair amount of nontronite as indicated by the chemical analysis of the specimens and a high silica-alumina ratio of the portion dissolved. The kaolinitic samples from a low humic latosol of Hawaii also released a large amount of silica and alumina at 110°C (Table 5). After heating at 500°C they dissolved almost completely leaving a small trace of 2:1 layer silicate minerals showing that the samples were mainly kaolinite-halloysite. The montmorillonitic clays from the same profile sampled underneath a basaltic boulder also contained a large amount of allophane. Approximately 30 per cent of the sample was extracted as kaolinite-halloysite (and a small quantity of nontronite).

## DISCUSSION

A method of this type usually suffers greatly from a lack of specificity of the reagent. However, with the recommended procedure, amorphous

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TABLE 5.—ANALYSIS OF TOTAL AND DIFFERENTIALLY DISSOLVED ELEMENTS FROM SOIL CLAYS

Soil Samples	Total Elemental Analysis (%)			Differentially Dissolved (%)					
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	110°C			500°C		
				SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
<i>Dark Magnesium Clays of Hawaii<sup>1</sup> (Montmorillonitic)</i>									
No. 2—0.08 μ	56.1	16.5	11.2	9.8	1.79	n.d.	19.2	5.66	n.d.
No. 2—0.2–0.08 μ	52.2	14.8	15.1	7.6	1.43	n.d.	19.6	7.20	n.d.
No. 36—0.08 μ	46.2	18.8	17.6	12.2	4.19	n.d.	21.8	8.95	n.d.
No. 53—0.08 μ	51.9	19.2	12.6	10.9	3.25	n.d.	22.4	8.09	n.d.
<i>Low Humic Latosol of Hawaii<sup>1</sup></i>									
Exf-1 (Kaolinitic)									
2–0.2 μ	37.4	32.0	8.3	9.7	4.30	4.8	34.6	28.7	6.3
0.2–0.08 μ	38.2	34.0	5.4	11.4	5.40	2.8	37.2	33.1	4.3
Exf-5 (Montmorillonitic)									
2–0.2 μ	41.0	20.4	12.8	10.4	2.70	2.8	28.0	15.7	6.2
0.2–0.08 μ	35.8	15.5	12.6	10.1	2.70	3.1	24.1	10.7	4.6

<sup>1</sup> These soil samples were collected under the supervision of Dr. G. D. Sherman, University of Hawaii.  
n.d. = not determined.

materials dissolve completely whereas highly crystalline layer silicates are attacked only an insignificant amount. The method largely depends on the relative strength of chemical bond which ties the structure together and on the reaction rate as controlled by specific surface. For this reason, the smaller size fraction may undergo a considerable amount of dissolution as particles approach the lower limit of crystallinity with increasing surface for reaction.

Heat-instability of certain minerals creates another problem. As pointed out earlier, iron-rich 2 : 1 layer silicates, particularly nontronite, dehydroxylate partially at 500°C and are dissolved accordingly in the NaOH solution. Determination of the difference in planar specific surface and elemental analysis for iron released are needed to measure the nontronite dissolution.

The preheating temperature, however, should be high enough to disrupt the kaolinite-halloysite component so that the subsequent NaOH treatment will remove it completely. A sharp break for kaolinite dissolution at a preheating temperature of 500°C suggests that the control of temperature is extremely critical. A variation of a few degrees in temperature within a furnace space is common and therefore it is advisable that a slightly higher temperature, for example, 525°C, be employed in practice. It is conceivable also that shorter preheating at a still higher temperature may preserve the nontronite fraction better and further studies are being conducted on this.

Changes observed on x-ray diffraction patterns resulting from application of the procedure are of great diagnostic value. The x-ray diffraction pattern of the allophanic sample from an Ando soil may lead one to conclude that the sample is 100 percent allophane (Fig. 2). Peaks of vermiculite and chlorite were identified only after removal of allophane which constituted 90 percent of the sample. The kaolinitic x-ray diffraction patterns of samples from the low humic latosol of Hawaii also showed marked improvement through removal of allophane. Also, the presence of mica in some kaolinite samples could be positively proved only after dissolution of the kaolinite present. The differential dissolution technique may be employed to great advantage, since the x-ray diffraction pattern often does not reveal the presence of an appreciable quantity of crystalline minerals in allophane, nor a really considerable amount of amorphous materials in crystalline samples.

### CONCLUSIONS

The proposed differential dissolution procedure is rapid, simple and quantitative, through simple analysis of dissolved elements. The procedure requires no special type of equipment nor rare reagents. The removal of allophane, free alumina and silica, and kaolinite-halloysite should greatly improve the accuracy of quantitative analysis of the remaining components of clays by conventional methods. Removal of the 1 : 1 layer aluminosilicates should be particularly helpful in evaluation of the 7 Å spacing in terms of chlorite, vermiculite, and antigorite in the remaining portion of the sample.

### ACKNOWLEDGMENTS

This contribution from the Department of Soils, University of Wisconsin, was supported in part by the University Research Committee through a grant of funds from Wisconsin Alumni Research Foundation.

### REFERENCES

- Aomine, S. and Jackson, M. L. (1959) Soil allophane determination by cation-exchange delta value : *Proc. Soil Sci. Soc. Amer.* In press.
- Brindley, G. W., Oughton, B. M. and Youell, R. F. (1951) The crystal structure of amesite and its thermal decomposition : *Acta Cryst.*, v. 4, pp. 552-557.
- Brindley, G. W. and Robinson, K. (1951) The chlorite minerals : in *X-ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, pp. 173-198.
- Dixon, J. B. and Jackson, M. L. (1959) Dissolution of interlayers from intergradient soil clays after preheating at 400°C : *Science*, v. 129, pp. 1616-1617.
- Foster, M. D. (1953) Geochemical studies in clay minerals. III. The determination of free silica and free alumina in montmorillonite : *Geochim. Cosmochim. Acta*, v. 3, pp. 143-154.
- Hislop, J. F. (1944) The decomposition of clay by heat : *Trans. Brit. Ceram. Soc.*, v. 43, pp. 49-51.
- Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course* : Published by the author, Dept. of Soils, University of Wisconsin, Madison, Wis., 991 pp.
- Jackson, M. L. (1958) *Soil Chemical Analysis* : Prentice-Hall, Englewood Cliffs, N.J., 498 pp.

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- Jackson, M. L., Whittig, L. D. and Pennington, R. P. (1950) Segregation procedure for the mineralogical analysis of soils : *Soil Sci. Soc. Amer., Proc.*, v. 14, pp. 77-81.
- Mehra, O. P. and Jackson, M. L. (1959) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate : This volume.
- Oda, Saburo (1954) x-Ray investigations on clays in Manchuria. IV. On the chemical composition of the iron chlorite in aluminous shales : *J. Chem. Soc. Japan (pure chem. sect.)*, v. 75, pp. 1320-1323.
- Pask, J. A. and Davies, B. (1945) Thermal analysis of clays and acid extraction of alumina from clays : *U.S. Bur. Mines Tech. Paper* 664, pp. 56-78.
- Ross, C. S. and Kerr, P. F. (1934) Halloysite and allophane : *U.S. Geol. Survey, Prof. Paper* 185-G, pp. 135-148.
- Steger, W. (1953) Quantitative chemical determination of muscovite in clays : *Clay Min. Bull.*, v. 2, p. 23. (Abstract.)
- White, W. A. (1953) Allophanes from Lawrence County, Indiana : *Amer. Min.*, v. 38, pp. 634-642.
- Whittig, L. D. (1954) Crystalline and x-amorphous mineral weathering products in some soils of temperate and tropical origin : Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin.