

## SIMPLIFIED, COMPLETE CsCl-HYDRAZINE-DIMETHYLSULFOXIDE INTERCALATION OF KAOLINITE

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**Abstract**—The coarse (2–0.2  $\mu\text{m}$ ) and fine (<0.2  $\mu\text{m}$ ) size fractions of several soil and reference kaolinite samples were completely intercalated and expanded to 11.2 Å using a simplified CsCl-hydrazine-dimethylsulfoxide (DMSO) treatment. Rapid equilibration of the clay in hot (80°C) hydrazine monohydrate and hot (100°C) DMSO, and the use of ceramic tile mounts, limited the sample pretreatment time to only 15 min. The fine size fraction of kaolinite may be X-rayed immediately after pretreatment, though analysis of the sample 2 or 12 hr after pretreatment produced more intense, sharp basal reflections. This difference may be due to a better ordering of the DMSO-kaolinite complex with time and to a drying of the excess DMSO. The coarse size fraction of kaolinite did not entirely expand to 11.2 Å when analyzed immediately after pretreatment. A 9.6-Å peak was also present and possibly represents a mixed layering of expanded and nonexpanded kaolinite layers. The larger crystals seem to require additional time for the reaction to become complete as evidenced by the presence of an intense, sharp 11.2-Å peak and absence of the 9.6-Å peak when the coarse clay was analyzed 2 or 12 hr after sample pretreatment. Kaolinite particles <50  $\mu\text{m}$  did not react completely even when they were analyzed 24 hr after pretreatment. Therefore, this technique should be limited to <2- $\mu\text{m}$  particles.

**Key Words**—Dimethylsulfoxide, Expansion, Intercalation, Kaolinite, X-ray powder diffraction.

### INTRODUCTION

It is often desirable to differentiate kaolinite from chlorite or serpentine-group minerals when they are present in the same sample. Four ways to differentiate these phases by X-ray powder diffraction (XRD) have been used: (1) Various (hk $l$ ) reflections are used for random powder mounts; however, this method requires that the phases of interest have (hk $l$ ) reflections intense enough for identification; (2) The slight differences in positions of the basal reflections near 3.6 Å of the three mineral phases are used for preferentially oriented mounts; however, these peaks are commonly broad, and resolution may be impossible; (3) The sample is treated with hot HCl to dissolve the more labile chlorite, thereby concentrating the more resistant kaolinite. This treatment, however is not entirely selective for chlorite and may be destructive to other phases; (4) The kaolinite is intercalated and expanded, thus separating its basal reflection from those of serpentine-group minerals and chlorite which do not expand; however, expansion is commonly incomplete and the intercalation techniques are time-consuming.

Many intercalation techniques have been used to characterize kaolinite by XRD (Range *et al.*, 1969) and, by expansion of the kaolinite structure, to distinguish the first order basal reflection of this mineral from the second order basal reflection of chlorite and the first (or second) order basal reflection of serpentine-group minerals (Wada and Yamada, 1968; Abdel-Kader *et al.*, 1978; Jackson and Abdel-Kader, 1978; Lim *et al.*, 1981). Most methods have not been successful in expanding all types of kaolinite or have failed to

expand all of the kaolinite in a given sample, particularly in the fine clay fraction (<0.2  $\mu\text{m}$ ). Recently, Jackson and Abdel-Kader (1978) completely intercalated several kaolin-group minerals (kaolinite, halloysite, and dickite), including the fine particle sizes, by first dry-grinding the sample with CsCl and then successively intercalating the sample with warm (65°C) hydrazine monohydrate (85%) and warm (90°C) dimethylsulfoxide (DMSO). The final kaolinite-DMSO complex gave a distinctive 11.2-Å spacing which is different from all other phyllosilicates. Unfortunately, the Jackson and Abdel-Kader (1978) method often produces decreased XRD intensities of basal reflections, possibly due to the breakage of crystals during grinding and to the poor preferential orientation of crystals after mounting. Lim *et al.* (1981) reported that the basal reflection intensities can be maximized by minimizing the grinding time, by washing the clay slurry in concentrated KOAc solutions immediately after the hydrazine treatment, and by washing the clay-DMSO complex with 99% methanol prior to mounting the specimen onto a glass slide.

The CsCl-hydrazine-DMSO procedure was tested in our laboratory with several kaolinite samples and gave results identical to those of Jackson and Abdel-Kader (1978). Their method, however, and the method of Lim *et al.* (1981) require two days before XRD data can be obtained. This may limit the usefulness of these techniques when time is an important factor in analysis. The objective of the present paper is to present a simplified CsCl-hydrazine-DMSO intercalation procedure that will rapidly expand all types of kaolinite

Table 1. Kaolinite samples used in this study.

Sample	Size fractions ( $\mu\text{m}$ )	Source
Twiggs County, Georgia, kaolinite	<0.2, 2-0.2	Ward's Natural Science Establishment
Poorly crystalline (KGa-2), Georgia kaolinite	<0.2, 2-0.2	Clay Minerals Society Repository
Bath, South Carolina, kaolinite	<0.2, 2-0.2	American Petroleum Institute
Murfreesboro, Arkansas, kaolinite	<0.2, 2-0.2	American Petroleum Institute
Ikom, Nigeria, soil B horizon	<0.2	Calvert, 1981
Conroe, Texas, soil B horizon	<0.2	Calvert, 1981
Benin, Nigeria, soil B horizon	<0.2	Calvert, 1981

and differentiate them from the nonexpanding chlorite and serpentine-group minerals.

### MATERIALS AND METHODS

Four reference kaolinite samples and three kaolinite samples from soils were studied (Table 1). After dispersion of these samples in pH 10  $\text{Na}_2\text{CO}_3$  with an ultrasonic probe, each kaolinite sample was fractionated at the 2- $\mu\text{m}$  and the 0.2- $\mu\text{m}$  limiting diameters using a centrifuge. The suspensions were flocculated with 1 N  $\text{MgCl}_2$  and washed in distilled water and ethanol until free of chlorides, as ascertained by the  $\text{AgNO}_3$  test. They were then dried overnight at 110°C.

The dried kaolinite samples were treated by two intercalation methods. The first treatment, the hydrazine-DMSO treatment of Jackson and Abdel-Kader (1978), assessed the ability of the clays to form an intercalation complex. This procedure is identical to the CsCl-hydrazine-DMSO treatment of Jackson and Abdel-Kader (1978), except that the samples were not previously ground in CsCl. The second treatment was a modified CsCl-hydrazine-DMSO method that used the same principles as the original method described by Jackson and Abdel-Kader (1978), except that it required much less time. Approximately 50 mg of dry clay was ground with 250 mg of CsCl for 3 min in a Wig-L-Bug mixer (if this mixer is unavailable, the grinding method outlined by Lim *et al.* (1981) may be used). The mixture was transferred to a 50-ml centrifuge tube along with 5 ml of preheated, 85% hydrazine monohydrate (80°C in a water bath). This slurry was gently mixed, and the suspension was maintained in a water bath at 80°C for 5 min. The suspension was then poured through a ceramic tile under suction (Figure 1) until all of the hydrazine passed through the sample. Immediately, two, 5-ml increments of preheated DMSO (100°C in a boiling water bath) were successively passed through the sample. The tile was then removed from the suction device, smoothed by smearing with a spatula if necessary (adding a drop of hot DMSO if too dry, smoothing, then applying suction to remove excess DMSO), and immediately X-rayed. Several samples were also X-rayed 2 hr and 12 hr after mounting on the ceramic tile, resmoothing and again applying suction to the sample immediately before analysis.

Each preferentially oriented clay sample was scanned from 5° to 15°2 $\theta$  on a Siemens D500 diffractometer with  $\text{CuK}\alpha$  radiation. Diffractograms of randomly oriented kaolinite samples were obtained by backfilling the powdered samples and scanning from 2° to 35°2 $\theta$ .

### RESULTS AND DISCUSSION

#### *Fine (<0.2 $\mu\text{m}$ ) kaolinite samples*

It is important to assess the intercalation ability of the kaolinite samples used in this study. The ability of kaolinite to intercalate is generally related to particle size and crystallinity (Jackson and Abdel-Kader, 1978). The soil kaolinites seem to have thinner particles (broader line width for the basal reflections at 7.15 and

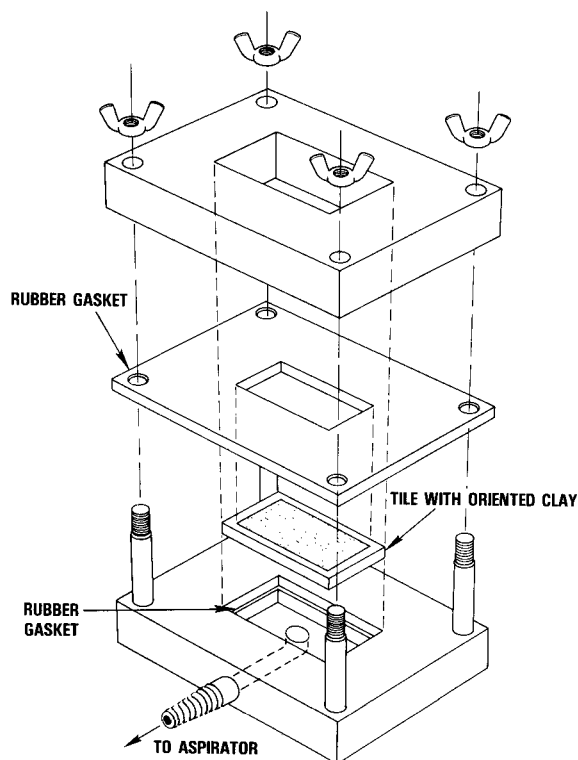


Figure 1. Suction device for mounting preferentially oriented clay samples on ceramic tile.

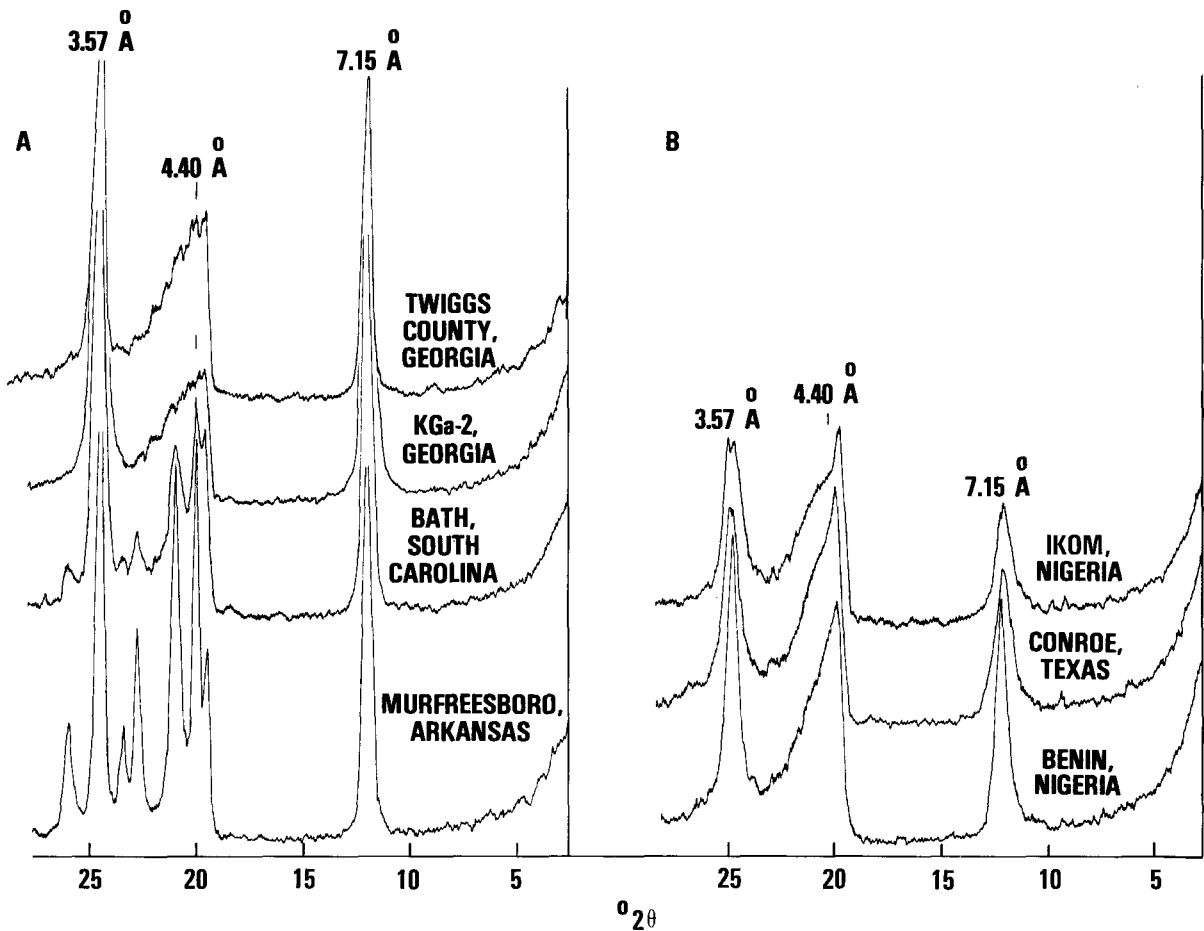


Figure 2. Random powder X-ray diffractograms of fine ( $<0.2 \mu\text{m}$ ) kaolinite samples. A = reference kaolinite samples; B = soil kaolinites. Note the broader line widths for the basal reflections and the generally poorer crystallinity of the soil kaolinites ( $\text{CuK}\alpha$  radiation).

3.57 Å) and generally poorer crystallinity (poorer resolution of the closely spaced 02/ and 11/ reflections near 4.40 Å) than do the reference kaolinite samples (Figure 2). All kaolinite samples were only partially expanded by the hydrazine-DMSO treatment (Figure 3). In fact, the soil kaolinite samples almost completely resisted expansion. These reactions are not unlike those observed by Jackson and Abdel-Kader (1978).

Although kaolinite resisted intercalation by the hydrazine-DMSO method, the results in Figure 4 indicate that the modified CsCl-hydrazine-DMSO procedure is as successful as the original CsCl-hydrazine-DMSO procedure proposed by Jackson and Abdel-Kader (1978). The modified method, however, takes approximately 15 min rather than the 2 days required for the original method. A small, residual 7-Å peak was observed in some samples after intercalation. The magnitude of this peak was negligible and may have represented chlorite in some samples. These results indicate

that the modified CsCl-hydrazine-DMSO treatment completely expands kaolinite and separates its basal reflection from any chlorite or serpentine basal reflection that might superimpose. No evidence of intercalation or expansion was noted for any of the serpentine or chlorite minerals examined in this laboratory which agrees with the results of Jackson and Abdel-Kader (1978).

Unfortunately, the basal reflections of the treated clays were weak and broad, particularly after the modified CsCl-hydrazine-DMSO treatment. Lim *et al.* (1981) attribute such results to crystal breakage and poor preferential orientation. We noted, however, that equilibration of the sample 2 or 12 hr after mounting on the ceramic tile produced sharp and intense peaks, thereby making the technique more sensitive (Figure 5). This intensification may have been due to a greater ordering of the DMSO in the kaolinite interlayer with time and to a drying of the excess DMSO.

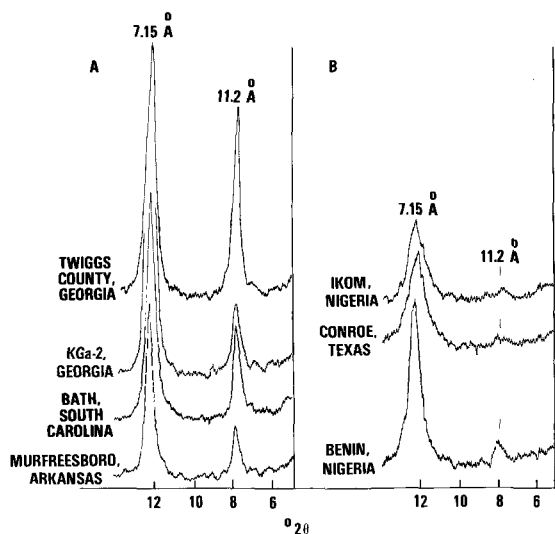


Figure 3. X-ray diffractograms of fine ( $<0.2 \mu\text{m}$ ) kaolinite samples after the hydrazine-DMSO intercalation. A = reference kaolinite samples; B = soil kaolinites. Note the incomplete intercalation of each sample, particularly the soil kaolinites ( $\text{CuK}\alpha$  radiation).

#### Coarse ( $2\text{--}0.2 \mu\text{m}$ ) kaolinite samples

The coarse kaolinite fraction should have expanded readily with the modified  $\text{CsCl}$ -hydrazine-DMSO treatment because coarse kaolinite particles generally intercalate more readily than do fine kaolinite particles (Jackson and Abdel-Kader, 1978). The coarse fraction did not immediately intercalate and expand to  $11.2 \text{ \AA}$  after the treatment (Figure 6), probably due to the inability of the DMSO to react rapidly with large crystals (small surface area). In all of the samples investigated, a second peak near  $9.6 \text{ \AA}$  was observed immediately after intercalation. This peak may indicate an incomplete intercalation, with some layers in the crystal being completely intercalated and others not (mixed layering). The  $9.6\text{-}\text{\AA}$  peak merged with the  $11.2\text{-}\text{\AA}$  peak with time, however, and the latter peak intensified. Within approximately 2 hr the excess DMSO reserved in the porous tile reacted with the kaolinite creating a completely expanded phase.

#### $<50\text{-}\mu\text{m}$ kaolinite samples

Preliminary testing of the  $<50\text{-}\mu\text{m}$  fraction of several kaolinite samples indicated that only a portion of the kaolinite was completely intercalated and expanded after a 24-hr equilibration using the modified  $\text{CsCl}$ -hydrazine-DMSO procedure. These coarse kaolinite particles resisted intercalation probably because of the inability of the intercalating compounds to react with portions of the large kaolinite particles. Additional grinding or long equilibration times might have pro-

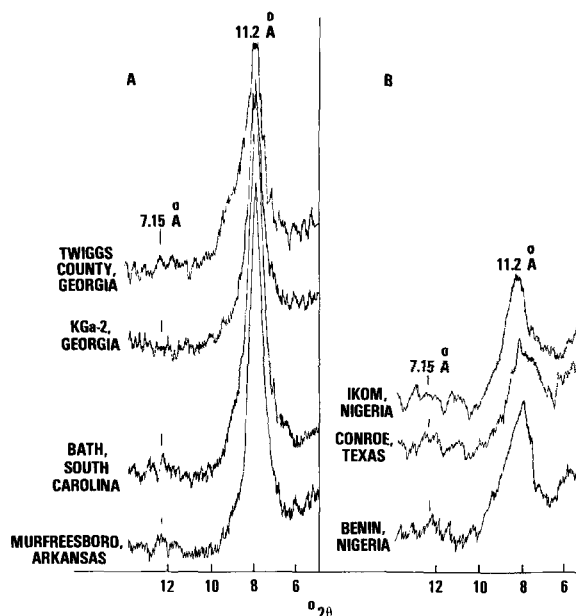


Figure 4. X-ray diffractograms of fine ( $<0.2 \mu\text{m}$ ) kaolinite samples analyzed immediately after the modified  $\text{CsCl}$ -hydrazine-DMSO intercalation. A = reference kaolinite samples; B = soil kaolinites. Note the complete intercalation of all kaolinite samples, though the soil kaolinites give fairly broad, weak reflections ( $\text{CuK}\alpha$  radiation).

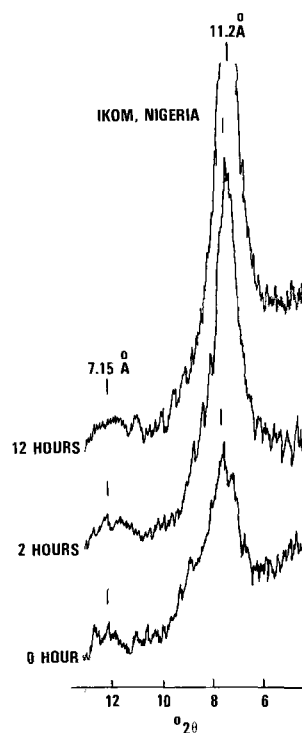


Figure 5. X-ray diffractograms of a fine ( $<0.2 \mu\text{m}$ ) kaolinite sample analyzed immediately after the modified  $\text{CsCl}$ -hydrazine-DMSO intercalation and after equilibrating for 2 hr and for 12 hr. Note the intensification of the  $11.2\text{-}\text{\AA}$  peak with time ( $\text{CuK}\alpha$  radiation).

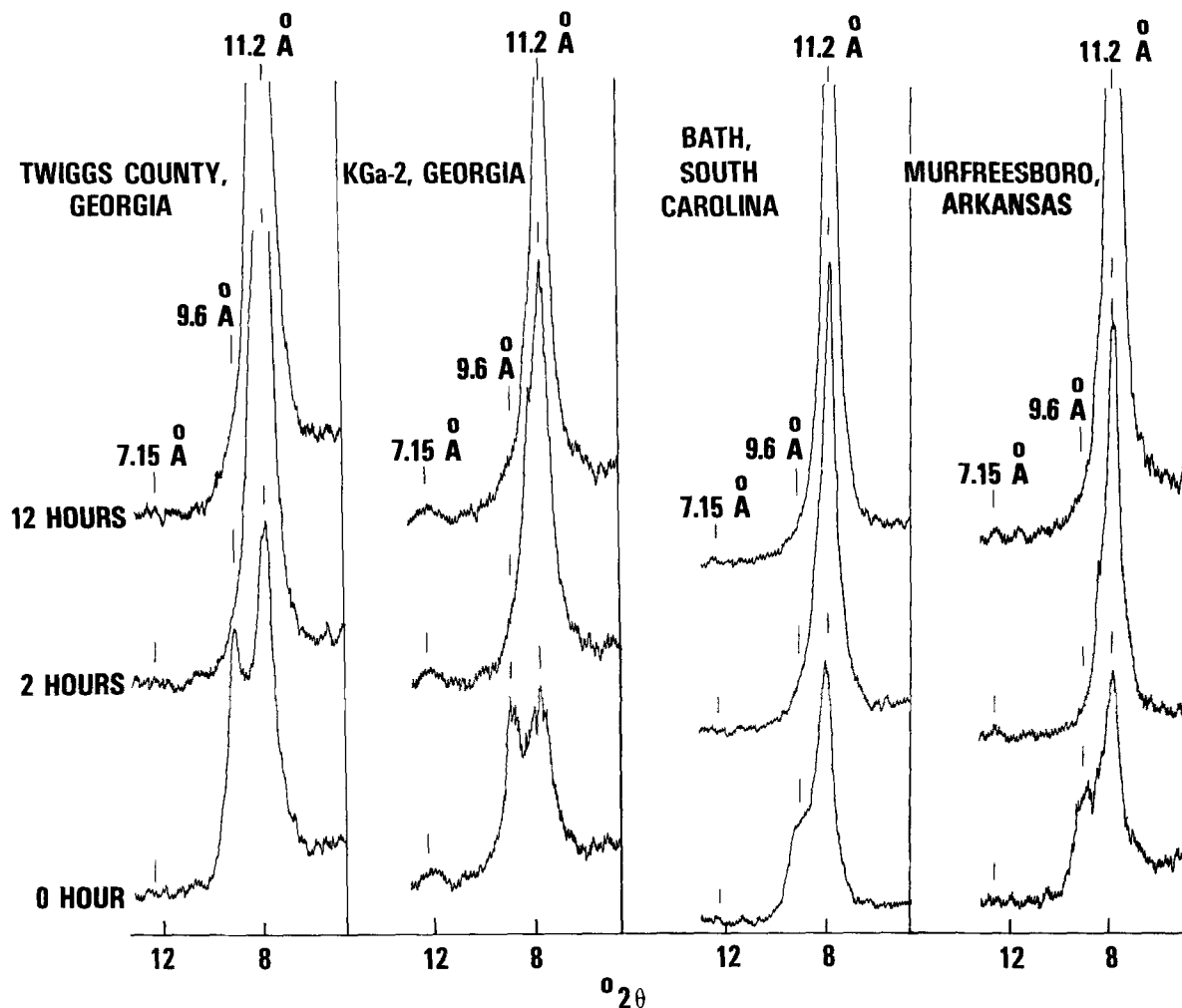


Figure 6. X-ray diffractograms of coarse (2 to 0.2  $\mu\text{m}$ ) kaolinite samples analyzed immediately after the modified CsCl-hydrazine-DMSO intercalation and after equilibrating for 2 hr and for 12 hr. Note the incomplete expansion of the kaolinite immediately after the treatment. With time, however, the intercalation and expansion become complete and well ordered, and the 11.2- $\text{\AA}$  peak intensifies ( $\text{CuK}\alpha$  radiation).

noted a complete reaction, but these options were generally not desired. The upper size-limit of rapid intercalation still needs to be examined; therefore, the modified CsCl-hydrazine-DMSO technique should be confined to  $<2\text{-}\mu\text{m}$  particles.

### CONCLUSIONS

A complete intercalation and expansion of kaolinite to 11.2  $\text{\AA}$  resolved the basal reflections of kaolinite from those of chlorite and serpentine-group minerals in samples containing these phases. To ascertain the presence or absence of kaolinite in samples ( $<2\ \mu\text{m}$ ) containing chlorite and/or serpentine-group minerals, samples should be treated by the modified CsCl-hy-

drazine-DMSO method (mounted on a ceramic tile substrate) and allowed to equilibrate for a minimum of 2 hr or preferably overnight, before XRD analysis. The presence of an 11.2- $\text{\AA}$  peak positively identifies kaolinite. The residual 7- $\text{\AA}$  peak represents chlorite and/or serpentine. Inasmuch as  $<2\text{-}\mu\text{m}$  particles only have been successfully intercalated, this technique should be limited to particles of this size.

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**Резюме**—Грубозернистая (2–0,2  $\mu\text{m}$ ) и мелкозернистая (<0,2  $\mu\text{m}$ ) фракции нескольких почв и образцовые каолиниты были полностью переслоинны и набухли до 11,2 Å при использовании упрощенной обработки CsCl-гидразино-диметилдисульфоксиом (ДМСО). Быстрое уравнивание глины в горячем (80°C) моногидрате гидразина и горячем (100°C) ДМСО, а также использование керамических кафельных оправ ограничивало время обработки до 15 минут только. Мелкозернистая фракция каолинита может быть исследована при помощи порошковой рентгеновской дифракции непосредственно после обработки, хотя анализ образца через 2 или 12 часов после обработки дает более интенсивные и острые основные линии. Это различие может быть результатом лучшего упорядочения комплекса ДМСО-каолинит со временем и высушения избытка ДМСО. Грубозернистая фракция каолинита не набухла полностью до 11,2 Å, если анализирована непосредственно после обработки. Дифракционная линия 9,6 Å также присутствует и она, вероятно, является результатом переслаивания набухшего и ненабухшего каолинита. Кажется, что кристаллы большего размера требуют дополнительного времени, чтобы реакция закончилась, что вытекало из присутствия интенсивной, острой линии 11,2 Å и отсутствия линии 9,6 Å, если грубозернистая фракция глины анализировалась через 2 или 12 часов после обработки образца. Частицы каолинита размером <50  $\mu\text{m}$  не реагировали полностью даже через 24 часов после обработки. Поэтому эта техника должна использоваться для частиц размером <2  $\mu\text{m}$ . [E.G.]

**Resümee**—Die grobe (2–0,2  $\mu\text{m}$ ) und die feine (<0,2  $\mu\text{m}$ ) Kornfraktion mehrerer Bodenproben und der Vergleichskaolinitprobe wurden vollständig auf 11,2 Å expandiert, wozu eine vereinfachte Behandlung mit CsCl-Hydrazin-Dimethylsulfoxid (DMSO) verwendet wurde. Da der Ton mit heißem (80°C) Hydrazinmonohydrat und heißem (100°C) DMSO rasch ins Gleichgewicht gebracht und Keramikkplättchen als Träger verwendet wurden, hat sich die Vorbehandlung der Proben auf 15 Minuten verkürzt. Die feine Kornfraktion von Kaolinit kann unmittelbar nach der Vorbehandlung röntgenographisch untersucht werden, obwohl diese Untersuchung zwei oder zwölf Stunden nach der Vorbehandlung intensivere und schärfere Basis-reflexe liefert. Dieser Unterschied dürfte auf eine bessere Ordnung des DMSO-Kaolinit-Komplexes im Laufe der Zeit und auf die Trocknung des überschüssigen DMSO zurückzuführen sein. Die gröbere Kornfraktion von Kaolinit war bei einer unmittelbar nach der Vorbehandlung durchgeführten Untersuchung noch nicht vollständig auf 11,2 Å expandiert. Ein 9,6 Å-Peak war ebenfalls vorhanden, der eine Wechsellagerung von expandierten und nicht expandierten Kaolinitlagen darstellt. Größere Kristalle scheinen eine zusätzliche Zeit zu benötigen, damit die Reaktion vollständig abläuft. Dies geht aus dem Auftreten eines intensiven und scharfen 11,2 Å-Peaks und aus der Abwesenheit des 9,6 Å-Peaks hervor, wenn man den größeren Ton zwei oder zwölf Stunden nach der Probenvorbehandlung untersucht. Kaolinitteilchen <50  $\mu\text{m}$  hatten noch nicht vollständig reagiert, wenn man sie vierundzwanzig Stunden nach der Vorbehandlung untersucht. Daher sollte man die Anwendung dieser Methode auf die Fraktion <2  $\mu\text{m}$  beschränken. [U.W.]

**Résumé**—Les fractions de grosse taille (2–0,2  $\mu\text{m}$ ) et de taille fine (<0,2  $\mu\text{m}$ ) de plusieurs échantillons de sol et de référence de kaolinite ont été complètement intercalées et dilatées à 11,2 Å, en utilisant un traitement CsCl-hydrazine-diméthylsulfoxide (DMSO) simplifié. L'équilibration rapide de l'argile dans du monohydrate d'hydrazine chaud (80°C) et du DMSO chaud (100°C), et l'emploi de cadres de montage en tuile céramique a limité le temps de prétraitement de l'échantillon à 15 min seulement. La fraction de kaolinite de taille fine peut être radiographiée immédiatement après le prétraitement, quoique cette analyse de l'échantillon faite 2 ou 12 heures après le prétraitement a produit des réflexions de base plus intenses et nettes. On peut attribuer cette différence à une plus longue durée de temps causant un meilleur rangement du complexe DMSO-kaolinite et au séchage du DMSO en excès. La fraction de kaolinite de grosse taille ne s'est pas dilatée entièrement à 11,2 Å lorsqu'on l'a analysée immédiatement après le prétraitement. Un sommet à 9,6 Å était aussi présent et représente possiblement un ensemble de couches mélangées de couches de kaolinite dilatée et non-dilatée. Les cristaux les plus grands semblent exiger plus de temps pour que la réaction soit complète, comme le met en évidence la présence d'un sommet intense et net à 11,2 Å et l'absence d'un sommet à 9,6 Å lorsque l'argile à gros grains était analysée 2 ou 12 heures après le prétraitement de l'échantillon. C'est pourquoi cette technique devrait être limitée aux particules <2  $\mu\text{m}$ . [D.J.]