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# NOTES

## An improved X-ray method for detecting small quantities of palygorskite in clay mineral mixtures

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### INTRODUCTION

THE IDENTIFICATION of small quantities of palygorskite in clay mineral mixtures may be difficult, especially in the presence of illite. Nevertheless it is sometimes critical, in view of the importance of correct identification of clay minerals in sediments and particularly the identification of presumably autigenic clay minerals.

An X-ray method for this purpose has been proposed by Heller (1961). The present method is simpler and can also be applied to samples rich in montmorillonite. It is based on the fact that heating palygorskite to about 150°C produces a marked increase in the intensity of the (110) peak, 8·4° 2$\theta$ CuK$\alpha$ (Nathan, 1969). Heating at this temperature produces no changes in the diffraction pattern of other clay minerals in this vicinity, except for montmorillonites and halloysite. Montmorillonite causes a similar increase, which is also due to dehydration. This can be avoided by pretreating with an organic reagent which penetrates the montmorillonite interlayers, but is too bulky to enter the palygorskite structure, e.g. a quarternary ammonium compound. The effects of heat on organo-montmorillonite complexes of this type have been studied by McAtee and Concillio (1959) and Chou and McAtee (1969). Halloysite gives rise to the opposite effect, a marked decrease in intensity. The present method is therefore not suitable for samples containing halloysite. However the probability of finding a halloysite, illite and palygorskite mixture in a sediment is very small.

### EXPERIMENTAL

*Materials.* The standard samples used were from Ward's reference clay minerals, (1) Montmorillonite No. 25, Upton, Wyoming. (2) Kaolinite No. 4, Macon, Georgia. (3) Illite No. 35, Fithian, Illinois. (4) Palygorskite (Attapulgite) No. 44, Attapulgus, Georgia. (5) Halloysite No. 12 Bedford, Indiana.

The organic reagent used was di-coco dimethyl ammonium chloride, a commercial product of Armour Industrial Chemicals (Arquad 2C–75). The per cent "R" groups of average composition are octyl 8, decyl 9, dodecyl 47, tetradecyl 18, hexadecyl 8, octadecyl 10, 75% active chemical in 25% isopropanol and water.

*Method.* 100 mg of the clay sample is thoroughly mixed with 0·5 ml of the organic reagent. It is then washed at least twice with ethyl alcohol or carbon tetrachloride and subsequently dispersed in methyl ethyl ketone (3 ml). Several drops of the suspension are allowed to dry on a glass slide, thus producing an oriented film. The slide is placed on a stationary diffractometer set at 8·4° 2$\theta$ for CuK$\alpha$ radiation. When the recorder has had sufficient time to stabilise, the sample is heated to about 150°C with a resistance wire mounted in front of an elongated water-cooled elliptical mirror. Current was supplied by an adjustable autotransformer. Temperature was measured by a chromel–alumel thermocouple in contact with the sample, and was maintained at 150°C for several minutes, the heating is then cut off and the sample allowed to cool under ambient conditions.

### RESULTS AND DISCUSSION

The results obtained with the standard specimens and mixtures of standards are presented in Fig. 1. Recorder tracings of samples containing palygorskite show a clear increase after heating and decrease on cooling, while all other samples except halloysite give rise to a straight line. The sensitivity of the method is limited since less than 5% palygorskite cannot be unequivocally identified. However, even 1% palygorskite can sometimes be detected but the results in this case are not reproducible. While the temperature of 150°C is not critical, no appreciable effects are produced by small quantities of palygorskite below 140°C, and above 180°C organo-montmorillonites collapse.

Complete elimination of excess organic material is critical, because this gives extraneous diffraction effects on heating.

Comparison of the results of heating samples before and after treatment with the organic reagent provides a test for the presence of montmorillonite (Fig. 2). The method can also be used to differentiate between palygorskite and mixed-layer minerals (Fig. 3).

Other organic materials of sufficient size could probably also be used to prevent interference of montmorillonite, but small organic molecules e.g. ethylene glycol are not suitable since they obstruct the dehydration of palygorskite as well as that of mortmorillonite.

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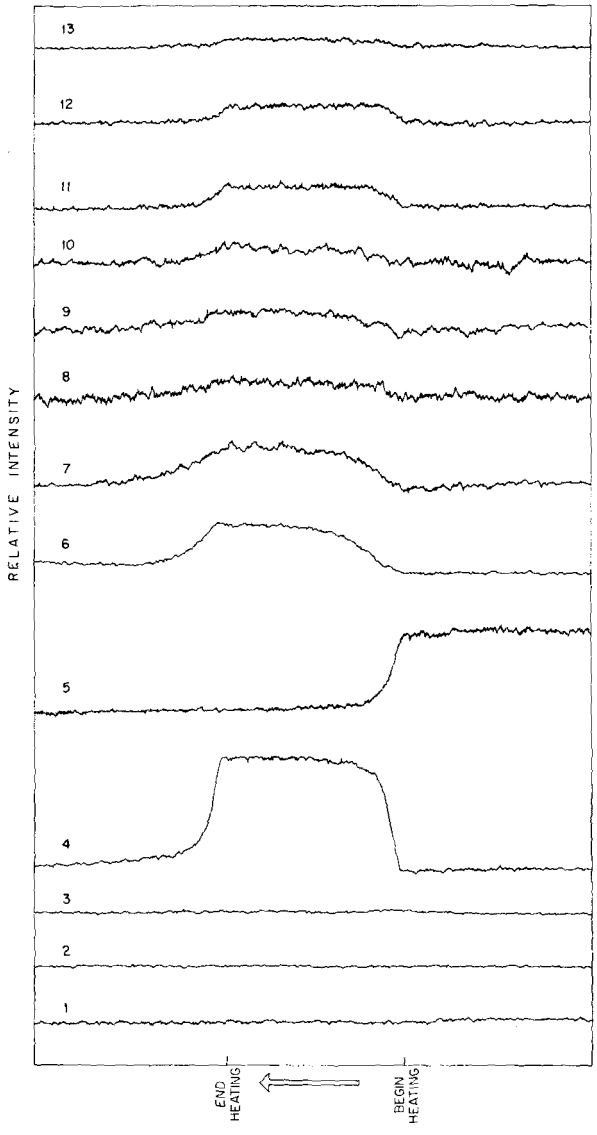



Fig. 1. Recorder tracings of stationary samples at 8·4° 2$\theta$ (CuK$\alpha$ radiation), before, during, and after heating to about 150°C. 1. 100% Kaolinite; 2. 100% Montmorillonite; 3. 100% Illite; 4. 100% Palygorskite; 5. 100% Halloysite; 6. 75% Illite, 25% Palygorskite; 7. 75% Montmorillonite, 25% Palygorskite; 8. 90% Illite, 10% Palygorskite; 9. 90% Montmorillonite, 10% Palygorskite; 10. 30% Illite, 30% Montmorillonite, 30% Kaolinite, 10% Palygorskite; 11. 95% Kaolinite, 5% Palygorskite; 12. 95% Illite, 5% Palygorskite; 13. 99% Illite, 1% Palygorskite. Samples 1–10 were run at the same sensitivity (3000 C.P.S. full scale). Samples 11–13 were run at a higher sensitivity (1000 C.P.S. full scale).

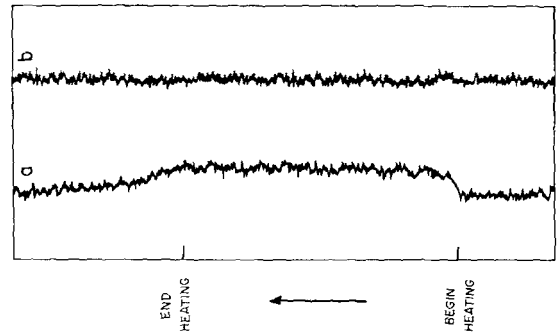



Fig. 2. Recorder tracings of a stationary sample at 8·4° 2$\theta$ (CuK$\alpha$ radiation), before, during, and after heating to about 150°C. 99% Illite, 1% Montmorillonite—(a) Untreated; (b) After organic treatment.

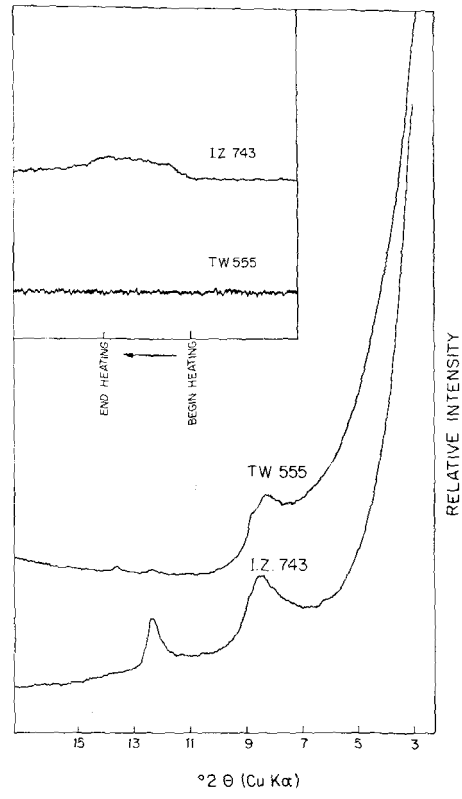



Fig. 3. Diffractograms and recorder tracings (same as Figs. 1 and 2) of two samples. T.W. 555 a Paleozoic clay from the Negev (mixed layer and illite); I.Z. 743 a Neogenic clay from Mount Sdom (palygorskite, illite and kaolinite).

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## Biodegradability factor in organic-clay sorption*

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THIS laboratory is concerned with the role of clay minerals of colloid dimensions in natural water systems as potential condensation nuclei for transport of organic substances. Research involves dilute aqueous systems of $\mu$g/l to mg/l concentrations of sorbent and sorbate. Preliminary results were unpredictably variable despite careful laboratory procedures. Eventually, this was attributed to contamination by biological organisms which utilized the organic carbon source. The purpose of this communication is to document this biological effect.

The C-14 tagged organic sorbates included phenol, substituted phenol and several fatty acids. The clay minerals were a highly-purified sodium montmorillonite and sodium kaolinite. Their preparation and characterization have been described (Luh and Baker, 1970a). Cation exchange capacities are 115 and 17 m-equiv. per 100 g and surface areas (as measured by the BET nitrogen sorption technique) are 78·2 and 21·3 m²/g respectively. Kaolinite mean particle diameter is 0·2 $\mu$ with 96 per cent <0·6 $\mu$. Montmorillonite particulates are estimated to be of comparable size. Figure 1 depicts the instability of selected, nonsterilized phenol solutions ranging in initial concentration from 12·5 to 200 mg/l. Instability rates of such blanks varied from sample to sample but losses are especially severe as initial organic concentration decreases. Loss from the 12·5 mg/l phenol solution was 35 per cent after 4 days.

Once biodegradation was suspect the following sterile procedures were adopted in making sorption experiments. All glassware, dilution water, clay suspensions and chemical stock solutions were sterilized. Sterile techniques were practiced in sample preparation. Solutions were prepared in 60 ml, serum-stoppered bottles. The stoppers were boiled for 2 hr and then rinsed with sterilized, deionized water prior to use. A 38 ml volume of solution containing the organic chemical was first added to the sample bottle. A suspension of clay was prepared separately. These solutions and all blank samples carried through the test series were adjusted to the desired pH by 4N NaOH or 4N HCl. The organic- and clay-containing solutions were sterilized for 15 min at 121–126°C. After the solutions cooled, 2 ml of clay suspension or 2 ml of dilution water in the case of blanks were added to the 60 ml sample bottle. Transfer was by sterile, disposable plastic syringes using 7·6 cm long, 19 gauge hyperchrome stainless steel needles. The

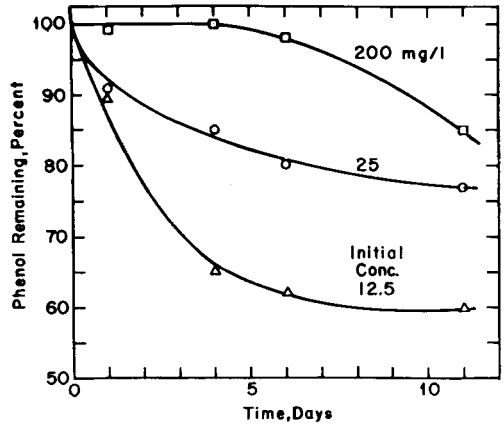



Fig. 1. Instability of unsterilized phenol solutions initial concentration: △, 12·5 mg/l; ○, 25 mg/l; □, 200 mg/l.

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