method of obtaining the derivative should be indicated and the units of the ordinate specified.

When reporting DTA traces, these specific details should also be presented:

10. Sample weight and dilution of the sample.

11. Identification of the apparatus, including the geometry and materials of the thermocouples and the locations of the differential and temperature-measuring thermocouples.

12. The ordinate scale should indicate deflection per degree Centrigrade at a specified temperature. Preferred plotting will indicate upward deflection as a positive temperature differential, and downward deflection as a negative temperature differential, with respect to the reference. Deviations from this practice should be clearly marked.

Members of the Committee on Standardization of ICTA are: Professor C. Mazieres (France), Professor T. Sudo (Japan), Mr. R. S. Forsyth (Sweden), Mr. H. G. Wiedemann (Switzerland), Dr. I. S. Rassonskaya (U.S.S.R.), Mr. C. J. Keattch (United Kingdom), and Dr. P. D. Garn (United States). Other delegates to the Committee include Professor L. G. Berg (U.S.S.R.), Dr. R. C. Mackenzie (United Kingdom), Dr. J. P. Redfern (United Kingdom) and Dr. S. Gordon (United States). The Chairman is Dr. H. G. McAdie from Canada.

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Laboratory processing of halloysite*

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INTRODUCTION

CLAY mineral analysis commonly involves X-ray diffractometry, yet no standards exist for preparation of the clay samples. Previous work clearly has shown that mounting techniques and preparation methods can affect X-ray results (Fenner, 1967; Figueiredo, 1965; Gibbs, 1965; Keller *et al.*, 1966; Parrish, 1960; Schultz, 1955; and Takahashi, 1957). Equipment and techniques used should be reported on to prevent results of sample preparation from being attributed to the minerals investigated.

We found that preparation differences change the X-ray diffraction peak intensities for samples, usually increasing the intensity up to a point in the comminution, and then decreasing the intensity. This change in intensity was caused primarily by decreasing particle size and sorting changes. Our methods did not bring about the amorphous state that Figueiredo (1965) achieved by other means. Mounting procedures also affect the results of X-ray diffractometry by influencing particle orientation within the clay sample. More electron microscope work is necessary; as more data are accumulated, possible standardization of analytical procedures for working with clay minerals (Fenner, 1966) can be proposed. Such standardization should ultimately serve as a means of communication rather than as a restriction among researches.†

Samples

API Project 49 reference samples no. 12 (Bedford, Indiana) and 13 (Eureka, Utah) were used in this study; their origin is discussed elsewhere (Wheeler and Burkhardt, 1950, p. 87).

Kerr *et al.* (1950) recognized two halloysite varieties. Both of our samples were placed in the 7 Å, $2H_2O$ group (their Table 7, p. 12). The $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ structures and their tubular morphologies were described or explained in several conflicting reports (*e.g.*, Alexander *et al.*, 1943; Bates *et al.*, 1950; Miller and Keller, 1963; Pundsack, 1958), but the question of structure vs. morphology—hence more detailed classification—has not yet been resolved to the satisfaction of all authors (*e.g.*, Brindley and Santos, 1966; Chukhrov and Zvyagin, 1966). According to the classification scheme preferred by Brindley and Santos (their p. 8), our samples are halloysites—at least in part; the many platy grains also found would have to be considered kaolinites under their classification scheme.

*Modification of presentation entitled Halloysite Response To Preparation For X-Ray Diffractometry, given at the 16th Annual North American Conference on Clay Minerals.

†The Organisation de Coopération et de Développement Économiques (OECD) has recently embarked upon a project to create an information bank on availability of reference materials, and to make a study of the characterization of fourteen specimens of non-metallic minerals (including clays) utilizing ten categories of standardized measuring methods (unpublished documents for OECD by Fripiat and Jelli, 1967, and OECD Secretariat, 1968).

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All are 7 Å minerals. According to the AIPEA Nomenclature Committee's proposed classification scheme (Mackenzie, 1967, p. 3), these samples are 1 : 1 kaolinite-serpentine minerals.

Techniques

We observed affects of comminution by ultrasonification and different grinding methods, using various preparation times.*

The ultrasonifier microtip was immersed directly into a test tube containing 1 g of sample and 10 ml of distilled water, and a cold water bath was prepared to prevent a large rise in temperature within the test tube. The time of treatment was varied from 1 to 36 hr and both samples were treated. In addition, 4 g of sample 12 were subjected to both manual and mechanical grinding, and an 8 g specimen of sample 13 was wet-ground in a mechanical mortar and pestle for 4 hr. After removing a small quantity of the sample for examination purposes, grinding was continued for a total time of 24 hr.

Three mounting methods for X-ray diffraction were used: (1) sample pellets were produced under 20,000 psi pressure, (2) packed powder slides were manually prepared in Philips aluminum powder holders, (3) slides were made from gravity-settled clay suspensions in distilled water. All samples used in this phase of the study were untreated, except for manual crumbling of the raw material.

Results of the laboratory work were observed by electron-microscopic inspection and by noting changes in intensity, position, and base width of four X-ray diffraction peaks (7·4 Å, 4·41 Å, 4·34 Å, and 3·62 Å) of the samples. Although X-ray diffraction patterns for halloysite are relatively poor, these four peaks show up well and are easily measured; they coincide with the strongest lines listed by Molloy and Kerr (1961, p. 592–593) for these reference samples.

OBSERVATIONS AND DISCUSSION

Comminution changed absolute and relative X-ray peak intensities differently for different treatments. No real *d*-spacing shifts were observed at any point during ultrasonification. None of the four peaks studied were lost at any time, but peak intensities decreased; peak bases did not broaden, but the diminished peaks did so at their tops.

The increase and subsequent decrease in peak intensity observed with treatment time can be accounted for by first a narrowing of particle-size range, then single grain fragmentation and cleavage, and some destructuring with the little line broadening that does occur. For sample 12, where the initial sample particle-size was <50 mesh (297 μ) and >100 mesh (147 μ), normalized peak intensities dropped to 42–60 per cent of the maximum after 36 hr of treatment (Fig. 1a). For sample 13, only the < 325 mesh (44 μ) particle-size fraction was used. Although the initial particle size was smaller, the results were nearly the same (Fig. 1b) and even less reduction of intensity was shown for the basal peak.

Short-period dry grinding produces essentially the same results as short-period ultrasonification, and ultimately achieves the same goal, but grinding takes much longer to accomplish similar qualitative changes. Hence, agreeing with Fenner (1967) and Figueiredo (1965), it seems that for small samples of relatively pure non-lithified clay samples, ultrasonification may the best method of comminution to use; it efficiently results in a generally uniform size-distribution of constituent particles.

Dry grinding for 4 hr enhanced peak intensities, nearly equally so for mechanical and manual grinding treatments (Fig. 1c). Diffraction results for wet grinding showed increased intensities for the basal 7·4 Å peak and the 3·62 Å peak, and reductions in the other two peaks (Fig. 1d) – probably the effect of differential grinding ease with various grain sizes and crystal directions in fluid medium.

Our methods generally enhanced orientation of grains, hence (00*l*) reflections; this was a sought-after bias. The difference in basal peak intensities shown for different mounting techniques thus reflects the extent of particle orientation.

Normalized peak intensities vary according to the mounting method used for X-ray analysis. Basal reflections are compared in Fig. 1e, and are normalized to pressed pellet maxima, where intensity was found to be the greatest. Intensities for the oriented specimens were 52 and 62 per cent of the pressed pellet intensities, respectively, for samples 12 and 13. The basal peak intensities for the powder slides were 39 per cent of the pellet intensities for both samples.

The compressive force used in pellet making orients most surficial particles. The gravity-settled suspension slide surface is rougher and has particles less well oriented, hence basal peak intensities are lowered. Gibbs' (1965) work may help explain the apparent disagreement with the observations of Fenner (1967). In the gravity-settling technique, larger grains will settle out first – this causes an unrepresentative and uneven upper surface to be presented to the X-rays if some of the larger and earlier deposited grains are not flat or do not land uniformly on the substrate. If this is the case, later deposited grains – in such a thin agregate thickness – will tend to parallel the uneven surface formed below. Fenner's results imply that the suspensions he used had a shorter grain-size span than those studied here. The powder slide has the roughest surface and the least oriented particles; it thus shows greatly reduced peak intensities.

Albedo and reflectance reduction with increasing ultrasonic treatment is as yet unaccounted for; no other treatment created a similar affect. The initial sample had a white color and the sample treated for 36 hr became a medium grey. Using 1½ in. diameter flat spots of dried powder sample on a black matte surface, reflectance

*Equipment used included: Carver laboratory press and piston of 1 in² area; Fisher No. 155 electric alumina mortar and pestle with scraper and 0·28 kg on grinding arm; Branson No. S-110 ultrasonifier, at maximum vibration at about 7·5 A d.c.; Philips X-ray diffractometer and panel, with Ni-filtered CuK radiation, 1° slits, scanned at 2°2θ/min by a scintillation detector with 0·5 sec time constant, and at 35 kV with 20 mA current, strip chart speed of 1/2"/min; Siemens Elmskop I electron microscope at 80 kV; and, Sekonic No. 86 lightmeter for reflectance measurements.

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values were measured with a light-meter. Using an arbitrary linear scale ranging from 5·5 to 18·5, reflectance values varied from 7, for the 36-hr ultrasonified sample, to 8·7, for the untreated sample (Fig. 2). Future work should reveal whether the changes result from wear of the titanium-steel tip of the ultrasonifier.

Halloysite 12 is made up of sheets with some tubes. Further work should help determine, more precisely, the nature of the platy grains (7 Å halloysite or kaolinite?), and whether any of these grains can be made to curl or uncurl by appropriate treatment (*e.g.*, Weiss and Russow, 1965; Weiss and Thielepape, 1965), especially for treatments used in some laboratories as routine preparation methods for X-ray analysis. Figure 3a shows this sample before treatment, and Fig. 3b shows it after 36 hr of ultrasonification. Ultrasonification has reduced the average particle size. The similarity to Fig. 9 of Beutelspacher and Van der Marel (1966, p. 22) is striking (despite origin and compositional differences), although the more apparent "cauliflower" aspect of some of our grains remains unexplained. Note that some of the tubular particles – which appear to be in the minority – on our Fig. 3b seem to show the polygonal prism structure shown in 1966 by Chukrov and Zvyagin. We do not, however, have cross-sections to prove this.

Results for sample 13 are inconclusive, but seem to show that there is little real external change among grains.

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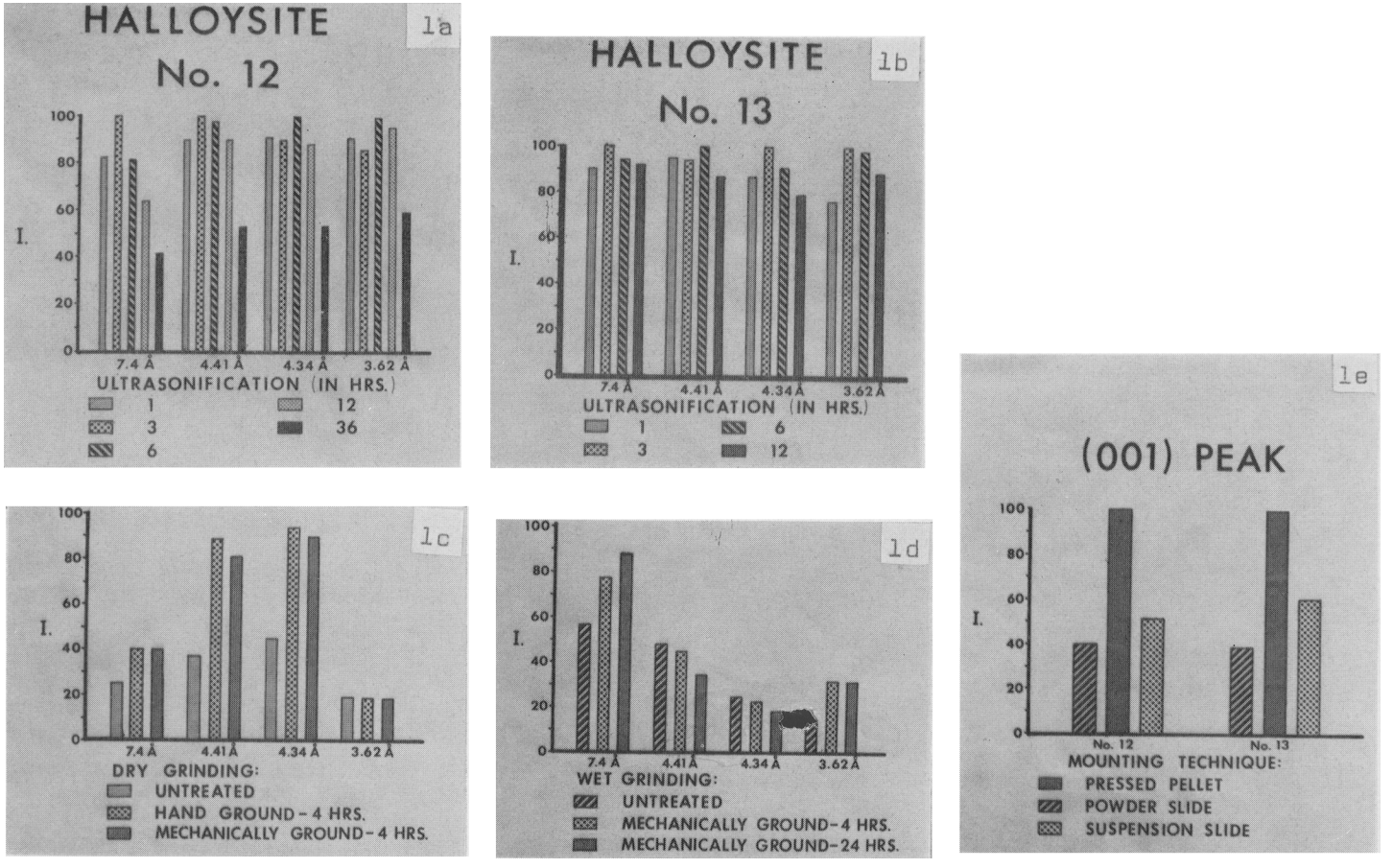
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Fig. 1. (a) Affect of ultrasonification on peak intensities, sample 12. I = peak intensities, normalized to highest value for a given reflection; (b) Affect of ultrasonification on peak intensities, sample 13. I = peak intensities, normalized to highest value for a given reflection; (c) Affect of dry grinding, sample 12. I = detector counts/sec/2; (d) Affect of wet grinding, sample 13. I = detector counts/sec/4; (e) Affect of mounting technique on basal X-ray reflection, normalized to pressed pellet method.

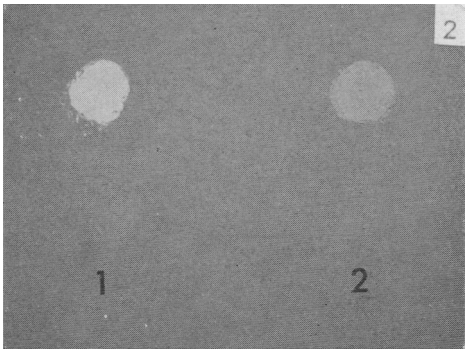


Fig. 2. Albedo differences incurred during ultrasonification; specimen 1 is untreated, specimen 2 has been ultrasonified for 36 hr.

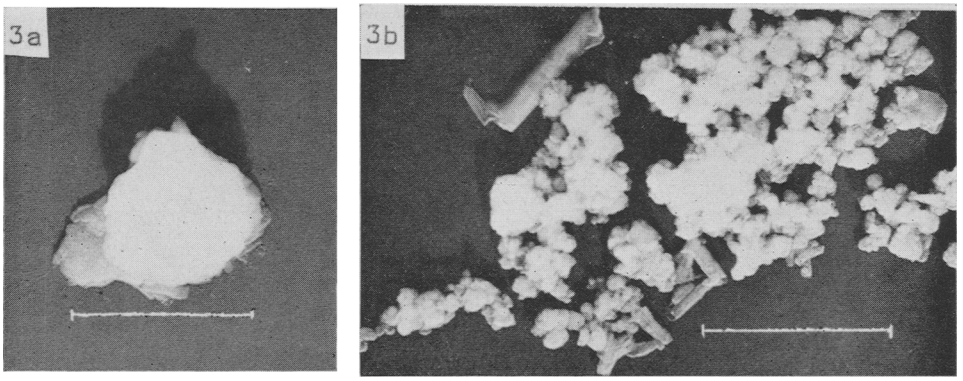


Fig. 3. (a) Halloysite 12, untreated. Cr-shadowed. Marking is 1 μ. Flat halloysite (?) or kaolinite (?); (b) Halloysite 12, after 36 hr ultrasonification. Cr-shadowed. Marking is 1 μ. Note prism shape of long grain.

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