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NOTE

PARTICLE ASSOCIATION IN SMECTITE SOLS BY TRANSMISSION ELECTRON MICROSCOPY

Key Words—Fluorhectorite, Particle association, Smectite, Sols, Tactite, Transmission electron microscopy.

INTRODUCTION

Particle association in clay suspensions has been studied extensively (Swartzen-Allen and Matijevic, 1974), but although experimental data exist describing these suspensions, information about particle association within such systems has been obtained only indirectly. Models describing various types of particle association have been proposed, and the experimental data have been used to discriminate between models (Swartzen-Allen and Matijevic, 1974; van Olphen, 1977). Although this approach has been useful in understanding clay suspensions, direct observations confirming such proposed types of particle association have been reported only once (Shomer and Mingelgrin, 1978).

The examination of small particles in the electron microscope can reveal important details of external form and structure, however, the preparation procedures present a number of problems. Directly applying a suspension of fine particles onto a substrate frequently results in aggregation with the particles concentrated at the drop edge. Such aggregations impede the evaluation and falsify the results, e.g., of particle size analysis. Better dispersions can be obtained by spraying (atomizing) the suspension onto the substrate, but neither of the above procedures retains the particle relationships present in the suspension or allows the particle orientation to be controlled.

Embedding the suspension in agar retains the particle relationships of the suspension and also allows the orientation of the particles to be controlled. This controlled orientation allows direct observations of particle association and particle thickness to be made.

MATERIALS AND METHODS

Two synthetic fluorine-containing smectites were prepared using the glass-ceramic process described by Beall *et al.* (1980, 1981). One was similar to lithium fluorhectorite, in that it was a 2:1 trioctahedral phyllosilicate having magnesium and lithium in the octahedral layer and lithium as the interlayer cation. The other smectite was similar to a fluorsaponite. The glass-ceramic was batched to yield a 2:1 trioctahedral sheet silicate having magnesium and vacancies in the octahedral layer and sodium as the interlayer cation.

These smectites were swelled in deionized water using several types of mechanical agitation. The final solids concentration of the sols (i.e., dispersions of solid particles having colloidal dimensions in a liquid, wherein the solid particles do not settle within an extended period of time) so formed ranged from 4.5 to 11.0% solids by weight.

The use of synthetic smectites having only one type of interlayer cation resulted in only one type of cation being present in the aqueous phase of the sol. The smectite particles did not settle at these solids concentrations.

The samples were prepared for transmission electron microscopy (TEM) examination by placing 1 or 2 drops of the sol on a microscope slide. Several drops of 2% aqueous agar at 50°C were then quickly deposited around the drops of the sol and allowed to solidify (15 sec to gel, 60 sec to solidify completely). Once the agar had solidified, 3–5-mm squares were cut out of the sol-agar interface region and dehydrated in a graded water/acetone series of 20, 30, 50, 70, 90, and 100% acetone. Dehydration was followed by infiltration and embedment in Spurr's hard epoxy (Spurr, 1969). This procedure has been routinely used in the biological sciences for encapsulating cell pellets (Ryter and Kellenberger, 1958) and isolated cells (De Haller *et al.*, 1961). It previously had been applied to clay suspensions (Shomer and Mingelgrin, 1978).

The epoxy embedments were trimmed with a razor blade to form a trapezoid having its longest side 1.5 mm. Sections 2-μm thick were cut on an LKB Ultratome IV (LKB Instruments, Rockville, Maryland) us-

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Figure 1. Transmission electron micrograph of cross-sections of Li-fluorhectorite particles in a 10 wt. % sol.

Figure 2. Transmission electron micrograph of cross-sections of Li-fluorhectorite tactoids in a 10 wt. % sol.

Figure 3. Transmission electron micrograph showing a cross-section of a suspended tubular particle of Li-fluorhectorite particles in a 10 wt. % sol.

Figure 4. Transmission electron micrograph of ribbon formed from Li-fluorhectorite platelets in a 10 wt. % sol.

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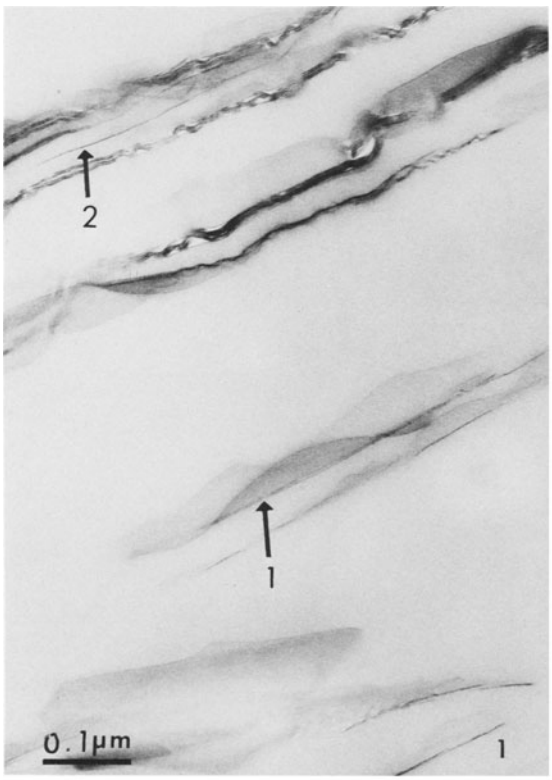

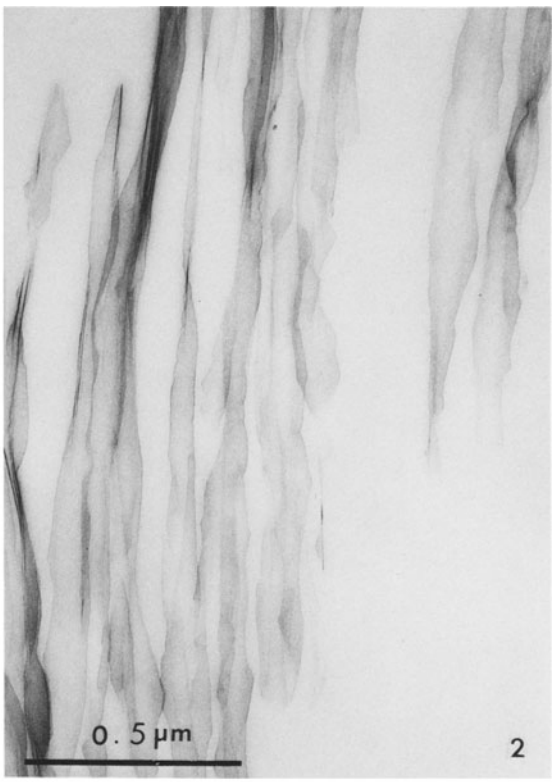

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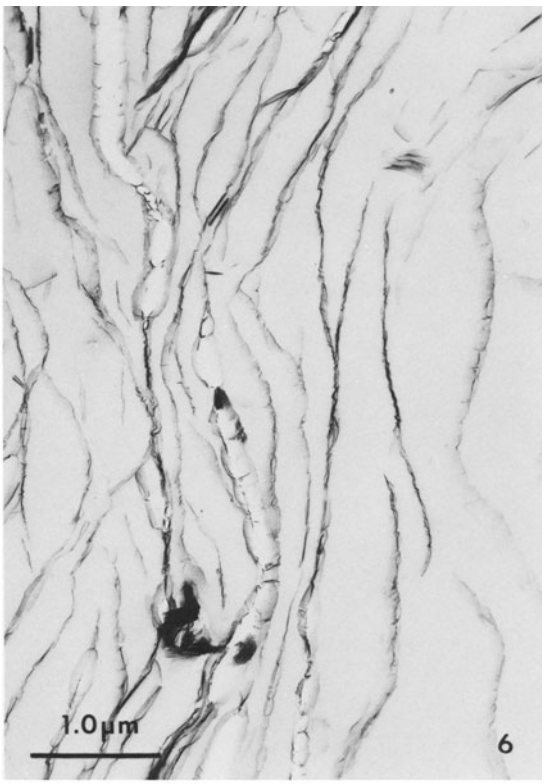

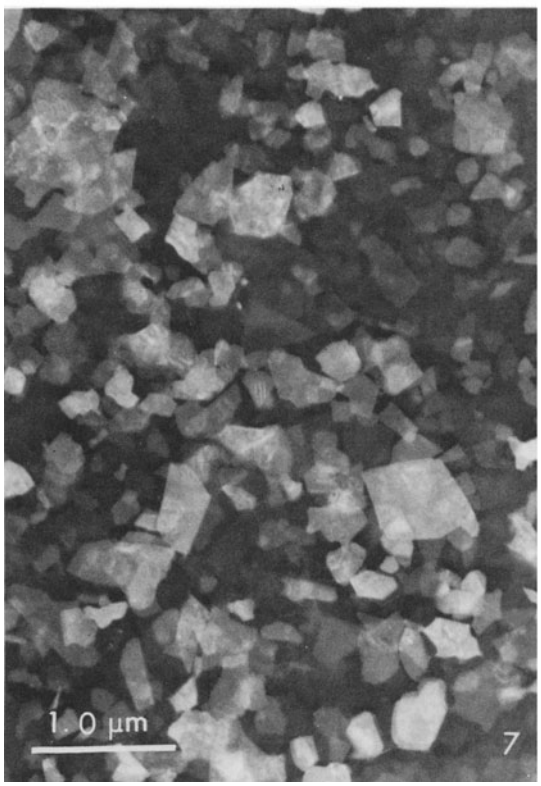

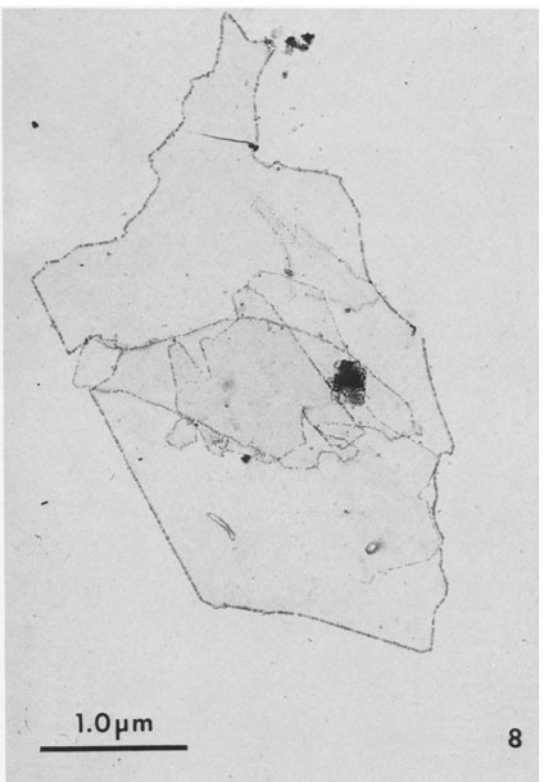

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ing glass knives, stained with 1% toluidine blue in 1% aqueous borax solution for light microscopy. Once the area of interest was determined by optical microscopy of the thick section, the trapezoid was trimmed to 0.5 mm on its longest side for ultrathin sectioning. Ultrathin sections (700–900 Å) were cut using a DuPont diamond knife, collected on 300-mesh copper grids, and examined in either a JEOL 100CX STEM or a Zeiss EM-109 TEM.

The preparation of the sample in Figure 7 consisted of diluting the sol in ethanol. The sample was spray mounted onto a carbon-coated grid using an EFFA spray mounter (Ernest F. Fullam, Inc., Schenectady, New York).

Gold decoration of the sample in Figure 8 was done by making the suspension slightly basic (pH 7.2–7.4) with LiOH and then heating the solution to 60°C. Seven drops of 1% choloroauric acid ($HAuCl_4$) were added to the solution while stirring. Several milliliters of formaldehyde were added until the solution turned pink indicating the formation of gold particles 100–200 Å in diameter. The solution was then diluted in ethanol and spray mounted as described previously.

RESULTS

Figure 1 shows a representative cross-section of Li-fluorhectorite particles in a 10 wt. % sol. Individual silicate sheets 10-Å thick can be distinguished. The particle at the center of the micrograph (arrow 1) is a tactoid (i.e., particles orientated parallel to one another at distances on the order of 100 Å) composed of two, 10-Å thick phyllosilicate layering separated by about 20 Å. Arrow 2 indicates a single silicate layer in a partially delaminated tactoid. The Li-fluorhectorite tactoids in the sols observed were composed of fewer than ten silicate sheets. The silicate sheets were somewhat flexible, and particle sizes ranged upwards from 0.25 μm with most of the particles being 3 to 5 μm in diameter.

The interplatelet spacing within a tactoid was commonly less than 100 Å. Platelets having face-to-face orientation and interplatelet spacings greater than 1300 Å were observed (Figure 2). These aggregates were interpreted as packets of tactoids (one to five unit cells thick) with face-to-face association.

Tubular structures were also present (Figure 3) in which silicate sheets appeared to have curled on themselves. The tubes were hollow, and the tube wall was less than ten unit cells thick. The tubular structure could not have resulted from drying as the samples were never dried. Therefore, the structures were present in the sol. The mechanism of formation is not known.

Ribbons of Li-fluorhectorite platelets observed in a 10 wt. % sol (Figure 4) apparently resulted from overlap of the platelets by face-to-face association. The similarity in the platelet size and shape suggest that the ribbons resulted from the delamination of a crystallite of the original glass ceramic. The ribbons are present in the sol and also cannot be the result of drying.

Figures 5 and 6 are transmission electron micrographs of Na-fluorsaponite sols having solids concentrations of 4.5 and 7.6 wt. %, respectively. The tactoids are composed of three or fewer silicate sheets and overlap in a face-to-face association to form aggregate sheets. The aggregate sheets have interacted to form an extended array of particles. They appear to have interacted over distances of several micrometers through edge-to-edge association; however, closer inspection shows that face-to-face association predominates at the contact points between particles. The extended array appears to have formed by branching as the silicate sheets partially delaminated from the tactoid. Another aggregate sheet appears to have formed as further face-to-face association occurred from that branch point.

DISCUSSION

Figure 7 is a dark-field electron micrograph of the dispersed Li-fluorhectorite particles. Figure 8 is of the same material decorated using a colloidal gold sol. Particle sizes range from 0.1 to 7 μm in diameter, with the particle shapes and sizes readily observed using these techniques. Little information could be obtained on the thickness of the particles or on the type of particle association in the sol by spraying the samples. The platelets were too thin for shadowing techniques to provide accurate measurements of particle thickness.

The sample preparation used for Figures 7 and 8 resulted in significant changes in the particle orientations from those in the sol. The relative particle orientation in the sol was preserved by fixing the sol in agar. Thin sections of the sol-agar-epoxy matrix were suitable for observing particle cross-sections.

No flocculating or dispersing agents were added to the sols. The only electrolyte present was contributed by the interlayer cations in the water-swelling fluor-

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Figure 5. Transmission electron micrograph showing particle association within a fluorsaponite sol (4.5 wt. %).

Figure 6. Transmission electron micrograph of a particle network in a fluorsaponite sol (7.6 wt.%).

Figure 7. Dark-field electron micrograph of dispersed Li-fluorhectorite particles.

Figure 8. Transmission electron micrograph of dispersed Li-fluorhectorite decorated using a colloidal gold sol.

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smectites. If all of the interlayer cations went into solution, the electrolyte concentration of the sols discussed was 0.08 to 0.2 M.

CONCLUSIONS

The procedure used in the present study permits samples of sols and suspensions to be prepared for TEM examination, which have solids concentration too low for freeze-drying techniques to yield representative samples. The time required for "fixing" the sample is rapid; therefore, the distortion of the sample characteristics due to preparation should be minimized. The embedded sample can be oriented so that ultrathin sections can be obtained with numerous orientations.

The modes of particle association observed within unflocculated clay suspensions were quite varied. The particles existed either as isolated platelets one unit cell thick or as aggregate particles formed by partial face-to-face overlap of platelets. The thickness of the aggregate particles was typically three to five unit cells. These aggregate sheets also formed tubular structures and ribbons. The particle networks observed for fluorsaponite sols arose from interactions between the aggregate sheets.

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