

NOTE

EFFECT OF CHLORINE IN CLAY-MINERAL SPECIMENS PREPARED ON SILVER METAL-MEMBRANE MOUNTS FOR X-RAY POWDER DIFFRACTION ANALYSIS

Key Words—Chloride, Instrumentation, Silver membrane mount, Thermal treatment, X-ray powder diffraction.

Silver metal-membrane filters are commonly used as substrates in the preparation of oriented clay-mineral specimens for X-ray powder diffraction (XRD). They are relatively unaffected by organic solvent treatments and specimens can be prepared rapidly. The filter mounts are adaptable to automatic sample changers, have few discrete reflections at higher 2θ angles, and, because of the high atomic number of silver, produce a relatively low overall background compared with other membrane filters, such as cellulose (Poppe and Hathaway, 1979). The silver metal-membrane filters, however, present some problems after heat treatment if either the filters or the samples contain significant amounts of chlorine. At elevated temperature, the chloride ions react with the silver substrate to form crystalline compounds. These compounds change the mass-absorption coefficient of the sample, reducing peak intensities and areas and, therefore, complicating the semiquantitative estimation of clay minerals. A simple procedure that eliminates most of the chloride from a sample and the silver metal-membrane substrate is presented here.

EXPERIMENTAL AND RESULTS

Silver filters commonly contain small concentrations of chlorine introduced during the manufacturing process. The 30–60-min 400°C heat treatment used during a standard clay mineral analysis to collapse smectite, vermiculite, and mixed-layer clay minerals, produces distinct changes in both the composition and texture of silver metal-membrane filters (Figure 1). As silver oxide decomposes at about 230°C, the silver converts to a face-centered cubic structure (Guy, 1951) or, in the presence of chloride ions, reacts to form cerargyrite (AgCl). The cerargyrite crystals are typically anhedral, but internally possess an ordered face-centered cubic structure. The heat-related effects observed in the filters are enhanced if saltwater (35‰) is passed through the filters prior to the treatments. XRD analyses of blank, untreated filters (Table 1) show that the intensity of cerargyrite peaks increases by an average of 46% after the filters are heated to 400°C. XRD patterns of the saltwater-rinsed blank filters and of Holocene marine

sediment mounted on silver metal-membrane filters also show a corresponding decrease in halite (NaCl) peak intensities with a relative increase in cerargyrite. For example, the major halite peak shifts from 2.82 Å toward 2.77 Å, the main cerargyrite peak (Figure 2), when the sample is heated to 400°C. Structural changes in the filter are slight at this temperature, but include a 10% reduction in filter thickness that results from recrystallization of the filter matrix and the formation of the cerargyrite.

Standard clay mineral analyses also involve a 550°C heat treatment which is used to destroy palygorskite, sepiolite, and the kaolin-group minerals. The chemical and textural changes initiated in the filters during the 400°C treatment become more pronounced after the filters are heated to 550°C. At this higher temperature the filters extensively recrystallize and cerargyrite continues to grow until the chlorine is depleted. These phenomena are evidenced by the complete shift from the 2.82-Å halite peak to the 2.77-Å cerargyrite peak (Figure 2).

To study these heat-induced effects further, scanning electron microscopy (SEM) and energy-dispersive X-ray spectrographic (EDX) analyses were performed on subsamples of an in-house marine sediment standard. The clay fraction was separated by centrifuge, split, and suction-mounted onto silver metal-membrane filters; the specimens were then subjected to the standard heat treatments. The calculated average relative weight composition of the sample was 61.6% illite, 21.1% chlorite, 12.6% kaolinite, 4.0% mixed-layer clay minerals, and 0.7% smectite. EDX analyses of the clay removed from the filters show that the concentration of silver in the sample increased from below the detection limit in the air-dried samples to the point where a silver compound was a major component in the samples heated to 550°C.

DISCUSSION AND SOLUTION

Clay-mineral specimens prepared from marine or evaporitic sediments commonly contain significant concentrations of halides. If the chlorine in both the silver filter and that associated with the bound and

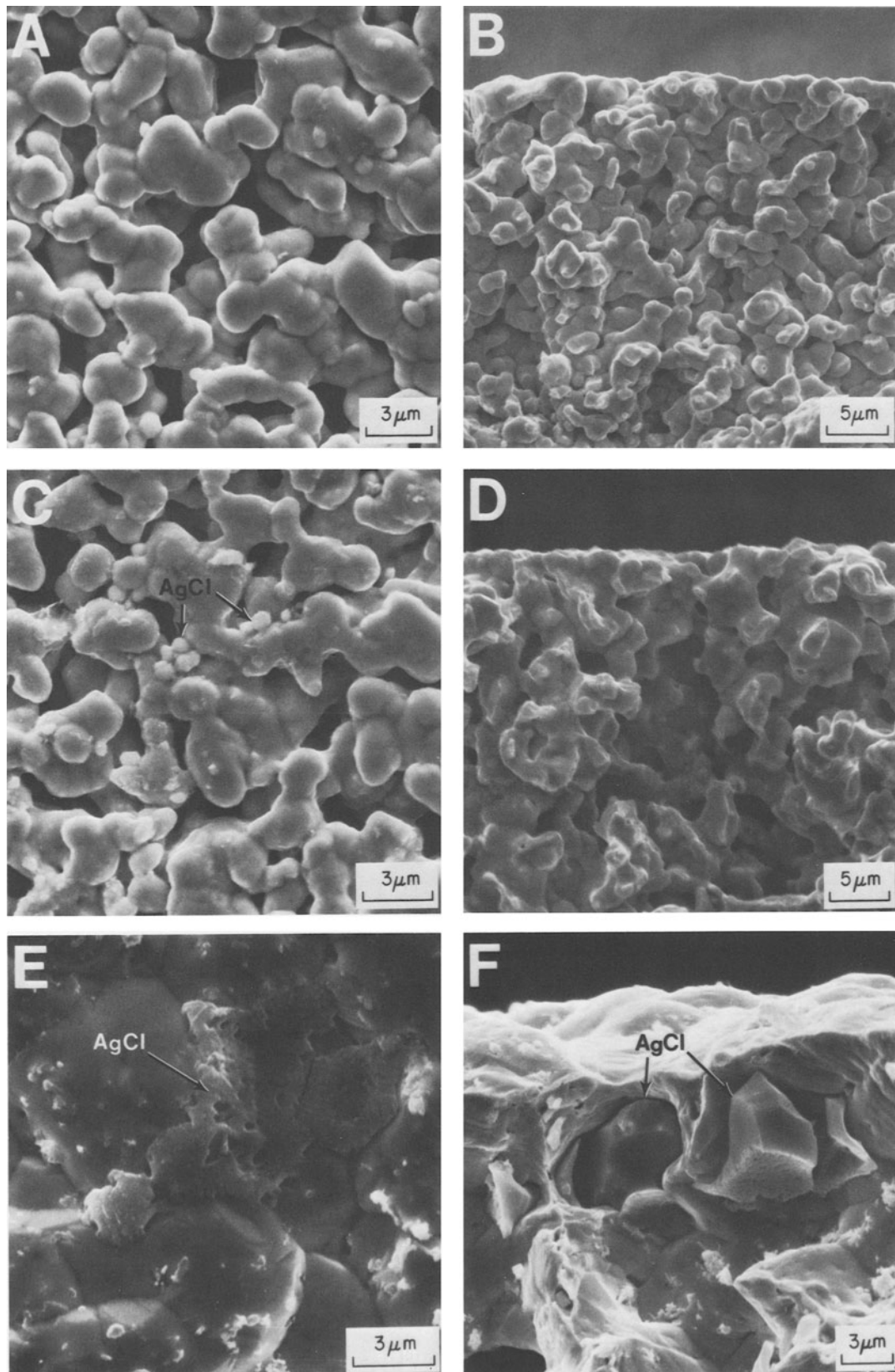


Figure 1. Scanning electron micrographs of silver metal-membrane filters. (A) Surface of an untreated filter. (B) Cross section of an untreated filter. (C) Surface of a saltwater-rinsed filter heated to 400°C. Note slight alteration of surface texture and presence of nodular chloride-enriched silver and/or cerargyrite. (D) Cross section of a filter heated to 400°C. (E) Surface of a

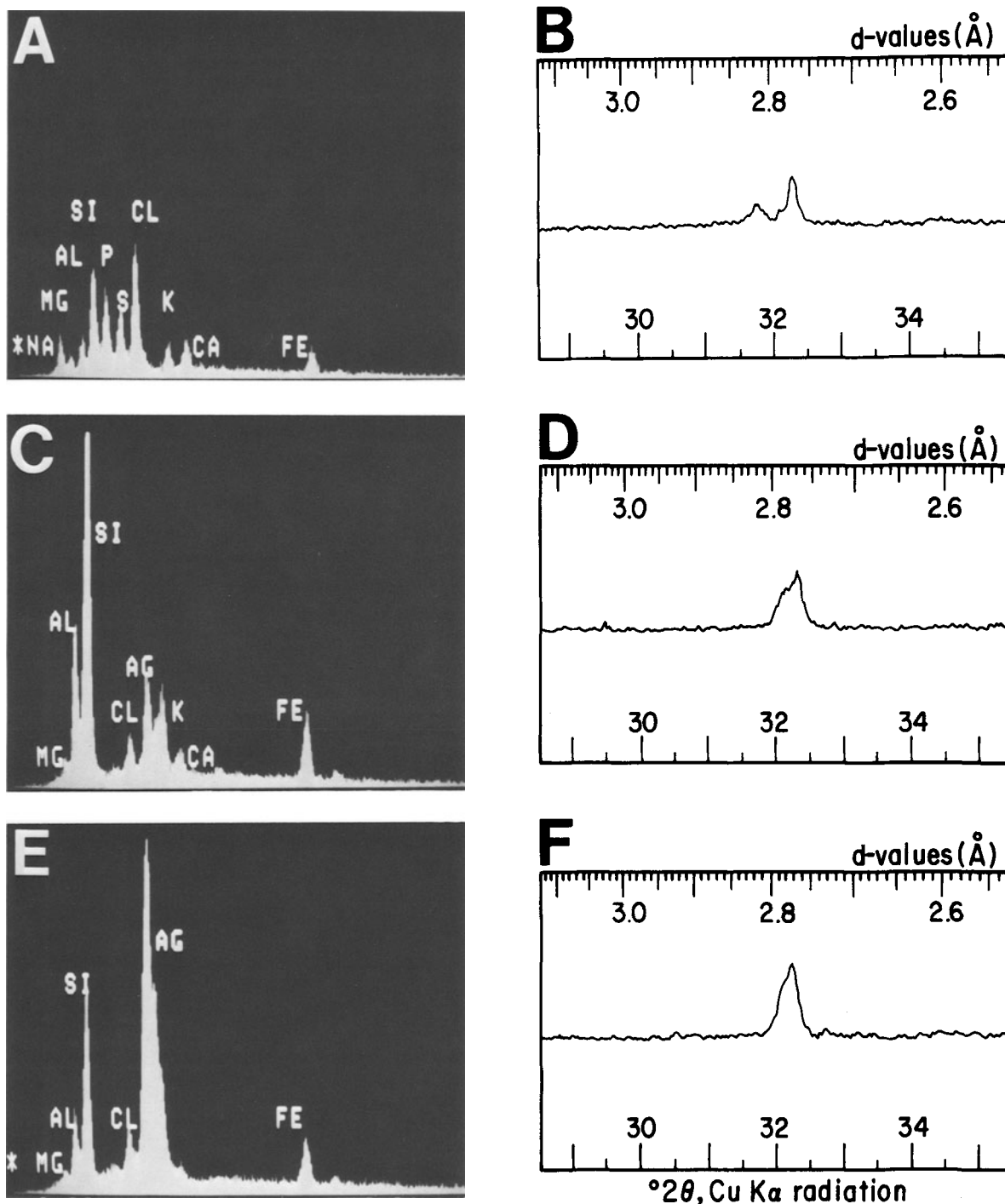


Figure 2. Energy-dispersive X-ray analyses (EDX) of clay-mineral specimens mounted onto silver metal-membrane filters, heat treated, and subsequently removed for analysis and X-ray powder diffraction (XRD) profiles of blank, saltwater-rinsed silver metal-membrane filters subjected to the corresponding treatments. (A) EDX spectra of an air-dried sample. (B) XRD profile of the 2.82-Å halite and 2.77-Å cerargyrite peaks from an air-dried filter. (C) EDX spectra of a sample heated to 400°C. Note increase in the relative amount of silver. (D) XRD profile of filter heated to 400°C; note that the 2.82-Å peak has shifted position and decreased in intensity, whereas the 2.77-Å peak has increased in intensity. (E) EDX spectra of a sample heated to 550°C. Analysis shows a further increase in amount of silver present. (F) XRD profile of filter heated to 550°C. The halite peak has disappeared, and the cerargyrite peak has increased in intensity.

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filter heated to 550°C showing recrystallization. Encrustations on the surface are cerargyrite. (F) Cross section of filter heated to 550°C showing chemical compaction due to recrystallization and subhedral grains of cerargyrite.

Table 1. X-ray powder diffraction data for silver metal-membrane filters and clay-mineral specimens.¹

Sample	% AgCl change air-dried to 400°C	% AgCl change 400°C to 550°C	% AgCl change air-dried to 550°C	% NaCl change air-dried to 400°C	% Kaolinite change air-dried to 400°C
Blank filter untreated					
1	44	64	136	NA	NA
2	47	179	293	NA	NA
3	47	134	221	NA	NA
Blank filter NaCl rinse					
1	121	114	323	(55)	NA
2	230	20	289	(61)	NA
3	340	23	440	(38)	NA
Marine sediment untreated					
1	1979	NA	NA	(72)	(54)
2	425	NA	NA	(78)	(62)
3	1325	NA	NA	(64)	(57)

¹ Data show the percentage increase or (decrease) in peak area determined from the 3.20-, 2.77-, and 1.96-Å cerargyrite peaks; the 2.82-Å halite peak; and the 7.17-Å kaolinite peak after various heat treatments. NA = not analyzed.

unbound waters of the clay sample is not removed prior to XRD analysis, the chlorine may react with the silver to form cerargyrite producing errors in the estimates of clay minerals. Silver ions, especially in the presence of chloride, are exceedingly mobile in solids (Fyfe, 1964). Under conditions of elevated temperature, such as those used for the heat treatments in standard XRD analyses of clay minerals, the silver ions diffuse through crystals of silver chloride and sodium chloride, whereas the chloride ions remain immobile. This mechanism permits the silver ions to migrate from the filter into the overlying sample. Silver chloride will, therefore, replace crystals of sodium chloride via solid solution, without any change in structure. This process is evidenced by the simultaneous reversal in XRD intensities of halite and cerargyrite observed in heated vs. unheated samples and the increasing concentrations of silver found in the heated samples of clay-mineral specimens from SEM and EDX analyses. The absence of Na in the EDX analyses of the 400°C and 550°C specimens (Figure 2) does not suggest that the Na was removed, but rather that the higher atomic weight of

silver may have depressed the spectra of the lighter sodium.

Any chlorine inherent in the silver filters may be removed by rinsing the mount in 5–10 ml of dilute (10%) aqueous ammonium hydroxide (NH₄OH) before the sample is suction-mounted onto the filter. Soluble salts associated with unbound water in the sample can be removed by rinsing with distilled water after the specimen is mounted onto the filter. We recommend the following procedure: (1) rinse with ammonium hydroxide in the filtration device to remove any silver chloride present in the filter, (2) rinse the filter with 20 ml of distilled water to remove the ammonium hydroxide and any residual chlorine, (3) suction-mount the clay specimen onto the filter, and (4) rinse the specimen with 5–10 ml distilled water to remove any free saline water from the sample. Rinsing with ammonium hydroxide after the sample has been mounted on the filter is less desirable because of the greater time necessary to pass this solution through a partially clogged filter.

Bound water within the clay minerals, especially smectite, may also contain significant concentrations of chlorine that can not be removed prior to XRD analysis; however, removing the chloride inherent in the silver metal-membrane filter or present in the unbound water of the sample will minimize, if not eliminate, any noticeable effect.

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