

## ELECTRON-MICROSCOPICAL IDENTIFICATION OF COAL FLY ASH AT A REMOTE SITE IN THE NORTHEASTERN UNITED STATES

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### ABSTRACT

Individual microparticles collected before, during and after an episode of high sulfate concentration at Whiteface Mountain, NY (26-30 July 1983) were characterized by scanning, transmission and high-voltage electron microscopy. Consistent with findings from an earlier episode, submicrometer spheres common in coal fly ash were abundant during the high-sulfate period but were absent before or after the episode. Minerals identified in iron-rich spheres by electron diffraction were magnetite, maghemite, and hematite. Equally abundant at the same time were silicon spheres which were probably glass since they yielded no diffraction patterns. Also common in high-sulfate samples were submicrometer spheres composed of varying proportions of iron, silicon, aluminum, potassium, calcium and titanium. No evidence of particles from oil combustion was observed. Additional support for coal combustion as the source of the high-sulfate concentration was given by Mn/V ratios which were consistent with air from the coal-burning Midwest rather than the oil-burning East Coast. Prevailing meteorologic conditions also indicated air flow from the Midwest. Preliminary evaluation of a new chemical signature, V/Ni ratio, is also presented. Although observed ratios were also consistent with coal rather than oil combustion, additional evaluation of this tracer is needed.

### INTRODUCTION

It is widely assumed that the industrial Midwest, because it has the highest  $\text{SO}_2$  emissions, is largely responsible for the widespread acid-stressed conditions in the Northeast. Indeed, studies that related daily sulfate concentration ( $[\text{SO}_4^{2-}]$ ) with backward air trajectories at Whiteface Mountain, NY, have invariably found that the highest  $[\text{SO}_4^{2-}]$  were associated with air masses passing through the Midwest (1,2,3). While trajectory-based studies themselves do not unequivocally prove this assumption, more recent investigations have shown with increasing clarity that coal-burning in the industrial Midwest is indeed the major source of  $\text{SO}_4^{2-}$  aerosols reaching the acid-stressed Adirondack region. Husain *et al.* (4) used samples collected at 6-hour intervals from a network of sites to trace high- $\text{SO}_4^{2-}$  air masses from the Midwest across New York State. These air masses retained Mn/V ratios characteristic of the Midwest ( $>> 1$ ) even after traveling more than 500 km. Conversely, when trajectories passed through coastal regions, Mn/V ratios were distinctly lower ( $< 0.5$ ), consistent with the region's dependence on oil. Although the Mn/V ratio technique has some limitations (5), it can be a very useful indicator of air mass history, particularly when used in conjunction with other tracers. Most recently, electron microscopy (EM) was used to identify coal fly ash in a high- $\text{SO}_4^{2-}$  air mass at Whiteface Mountain (6). Both the meteorology and the Mn/V ratios indicated a midwestern origin for this air mass. The combination of microparticle identification, meteorology and chemical tracers has provided the clearest fingerprint to date of the sources of  $\text{SO}_4^{2-}$  in northern New York.

During the summer sampling campaign in 1983 a second high- $\text{SO}_4^{2-}$  episode was observed at Whiteface Mountain. EM analysis of samples collected during this episode are presented and discussed along with the measurement of selected trace metals in simultaneous high-volume samples.

### EXPERIMENTAL

During summer 1983 airborne particulate samples were collected with high-volume pumps on Whatman 41 filters at the summit of Whiteface Mountain (WFM), at Mayville (MAY) in the southwestern corner of New York, at Alexandria Bay (AXB) on

the northeastern shore of Lake Ontario, and at West Haverstraw (WHV) in the lower Hudson River Valley (Figure 1). While the first three sites are rural, WHV is a suburban site located near the metropolitan New York City area. This site was selected primarily to characterize East Coast aerosols because of its proximity to two oil-burning power plants. Samples were collected for 6-hour intervals at WFM and MAY and for 12-hour intervals at WHV and AXB. These were analyzed for  $\text{SO}_4^{2-}$  by ion chromatography and for Al, Mn, V, and Ni by atomic absorption spectrophotometry as detailed elsewhere (4). Microparticles were collected simultaneously with the high-volume samples at WFM on carbon-coated Nuclepore filters in an automatic dichotomous sampler (6). These filters with collected particles were transported in airtight containers to the lab where a thin carbon film was vacuum evaporated over the collection surface to immobilize the particles and to reduce excess charge produced by the electron beam. In addition to the EM analyses performed on the earlier samples (6), sections of filter were shadowed with Au-Pd at an angle of  $\sim 30$  degrees to allow 3-dimensional interpretation of particle morphology by transmission EM (7).

During the period of interest (26-30 July 1983), air flow across New York State was dominated by a slow-moving high-pressure system from the Great Lakes. Although air trajectories are not available at this time, this pattern in the past has produced air flow from the Midwest across the state and is generally associated with high- $\text{SO}_4^{2-}$  periods in upstate New York (8). This high centered over southern Pennsylvania early on 27 July may produce air flow from the Midwest at MAY while AXB and WFM should be under the influence of Canadian air. By the next day, the high had moved off the coast of Virginia, where it remained stationary for two days (Figure 1). A cold front with a large mass of leading showers was trailing the high. (The leading edge of the showers can be seen in the upper left hand corner of Figure 1.) During 28 July, precipitation began in the western part of the state and by the next day, was widespread throughout the upstate area.

## RESULTS

### Chemistry

On 27 July [ $\text{SO}_4^{2-}$ ] began to increase throughout the state, first at MAY and 12 hours later at AXB and WFM (Figure 2). This is consistent with the beginning of midwestern air flow on the backside (western edge) of the high pressure system. At AXB and WFM, maximum concentrations, 46 and 49  $\mu\text{g}/\text{m}^3$  respectively, were observed in the afternoon of 28 July but decreased dramatically on 29 July when precipitation was widespread throughout the state. The onset of precipitation is also indicated by the trace metal data. Al concentrations at WFM, for example, were  $\sim 340$   $\text{ng}/\text{m}^3$  during the peak [ $\text{SO}_4^{2-}$ ] period but decreased abruptly to 90  $\text{ng}/\text{m}^3$  for the first sample on 29 July. Such an abrupt decrease is consistent with the washout of aerosols. At MAY [ $\text{SO}_4^{2-}$ ] leveled off at  $\sim 25$   $\mu\text{g}/\text{m}^3$  for 30 hours beginning with the first sample on 28 July. However, the leading edge of showers shown in Figure 1, which began affecting the western part of the state on the 28th, may have significantly affected the [ $\text{SO}_4^{2-}$ ]. The variations in trace metal concentrations are consistent with this assumption. [ $\text{SO}_4^{2-}$ ] at WHV also peaked in the last sample on 28 July, but the concentration was much lower, 15  $\mu\text{g}/\text{m}^3$ . Because this site was much closer to the center of the high, it may very well have been influenced by air from a different area than the upstate sites. This has been the case in episodes previously studied (4).

The ranges of Mn/V ratios (crustal corrected as described earlier (4)) are shown in Figure 2. Throughout the episode, Mn/V ratios at the three upstate sites were consistently  $> 2$ . While [ $\text{SO}_4^{2-}$ ] was  $> 20$   $\mu\text{g}/\text{m}^3$  at MAY, Mn/V ratios ranged from 3.3 to 21 and averaged 11. At WFM during the peak [ $\text{SO}_4^{2-}$ ] period, Mn/V ratios averaged 6 which is within the range of values observed at MAY although only about half the mean. Larger ratios at MAY compared to WFM are, however, consistent with previous data (4,6). At both sites the Mn/V ratios are clearly within the range for midwestern air and much too high to suggest any significant influence from heavy oil-burning areas. At AXB, Mn/V ratios were only slightly  $> 2$ , much lower than at WFM. While [ $\text{SO}_4^{2-}$ ] were comparable at the two sites, AXB

had much higher V concentrations. Although the Mn/V ratios at AXB were within the range of coal-burning regions, the fact that the ratios were much lower than at WFM suggests a larger influence from oil-combustion at AXB. However, since the highest V concentration was only 6.7 ng/m<sup>3</sup> and Mn/V ratios do remain >2, the high-[SO<sub>2</sub>-] period still seemed to be dominated by coal-combustion aerosols.

While Mn/V ratios at WHV have been included for completeness, its proximity to oil-burning power plants precludes the usefulness of Mn/V ratios as tracers at this site (5). As in previous studies (4,6), Mn/V ratios at WHV were almost invariably <0.5 as expected. On 28 July the Mn/V ratio increased to 0.53. Since it is generally around 0.2, this indicates that a component from some coal-combustion source may be present.

To reinforce the Mn/V ratio data we also considered V/Ni ratios in these samples. V/Ni ratios are different in coal and oil fly ash. [V] is markedly enriched in oil fly ash while [Ni] is also enriched, not to the extent of V (9). In contrast, [Ni] is increasingly enriched with decreasing particle size in coal fly ash whereas [V] is not (10,11). Henry and Knapp (12) analyzed 6 oil fly ash samples and 6 coal fly ash samples and found average V/Ni ratios to be 5.2 and 1.2 respectively. Analysis of the data of Davison *et al.* (11) reveals that V/Ni is very low (<0.5) in coal fly ash which is less than 2 μm. This is the particle size range expected to be transported long distances.

V/Ni ratios are shown in Figure 2. At WHV on 26-27 July, the V/Ni ratio averaged 3.0. This site is strongly influenced by oil emissions ([V] averaged 30 ng/m<sup>3</sup>) and the V/Ni ratio is approaching that measured in oil fly ash. During the [SO<sub>2</sub>-] episode, however, the ratio averaged 1.6 and returned to near 3 on the 30th. The decreased V/Ni ratios are consistent with increased influence from coal-burning regions during the high-SO<sub>2</sub>- period. At WFM, episodic ratios averaged 1.2 and nonepisodic ratios averaged 1.3, near that for coal, again indicating that oil-combustion aerosols were not dominant at these times. V/Ni ratios at MAY and AXB were similar to WHV with nonepisodic ratios averaging 2.1 and 2.4 respectively and episodic ratios averaging 1.4 and 2.0. At none of the sites was the episodic V/Ni ratio large enough to be associated with purely oil-fired combustion products and, except at WFM where the ratio was already near that of coal, the V/Ni ratio decreased during the high-SO<sub>2</sub>- episode, as expected for increased contributions from coal-burning areas. Consistent with Mn/V ratios, V/Ni ratios were higher at AXB than WFM during the episode supporting the earlier conclusion that AXB has an oil-derived aerosol component. AXB is on the St. Lawrence Seaway, approximately 100 km NE of a large oil-burning power plant on the southeast shore of Lake Ontario. While further study is needed, this data suggests that V/Ni ratios may provide another useful indicator of coal and oil combustion emissions.

#### Microparticles

More than 200 particles collected at WFM in the fine fraction (<2.5 μm) on 27 July I and IV, 28 July II, III and IV and 29 July I (where I=0000-0600 h, II=0600-1200 h, III=1200-1800 h, IV=1800-2400 h) were characterized by electron diffraction (ED), energy-dispersive x-ray spectroscopy (EDXRS) and morphology with transmission and high-voltage EM.

The most abundant particles were S-rich particles, usually much smaller than 0.8 μm. These particles were electron translucent and occasionally the S x-ray peaks were accompanied by much smaller K, Ca or Fe x-ray peaks. Interesting morphological features were highlighted by Au-Pd shadowing (Figure 3). S particles collected on 27 July IV ([SO<sub>2</sub>-]=6 μg/m<sup>3</sup>) and 29 July I ([SO<sub>2</sub>-]=29 μg/m<sup>3</sup>) were dome shaped and generally larger than in other periods. Those collected on 28 July II and III ([SO<sub>2</sub>-]=14 and 41 μg/m<sup>3</sup> respectively) were not flattened, but rather had cluster morphologies similar to N in Figure 3b. Ferek *et al.* (7) revealed that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> collected on SiO films with an impactor had cap-like morphologies. Particles were collected in the present study at a face velocity orders of magnitude lower than that encountered with an impactor. Hence, the S-rich clusters seen by us were probably (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

clusters which had retained their solid morphology rather than being flattened by high-velocity impaction. Ferek *et al.* also found that  $H_2SO_4$  impacted on  $SiO$  films formed a large central drop with multiple satellite droplets. This phenomenon had been reported earlier by Frank and Lodge (13), who concluded that this was caused by dehydration of the  $H_2SO_4$  on the hydrophobic  $SiO$  rather than by impaction forces. One reason that cap-like spheres with satellites were not seen by us might be that the carbon film used for collection was less hydrophobic than  $SiO$  and thus satellite formation was not favored during desiccation. Furthermore, our samples were given a second carbon coat soon after collection and this probably slowed desiccation and certainly prevented changes in morphology during any subsequent desiccation/oxidation. Hence the dome-like spheres were probably  $H_2SO_4$ . This hypothesis is reinforced by the bubbling seen within these domes during electron-beam heating. This bubbling was not evident in the clusters thought to be  $(NH_4)_2SO_4$ . The S particles collected during the peak  $[SO_4^{2-}]$  ranged from clusters to domes, with small domes often concentrated around the 0.4  $\mu m$  pores (Figure 3b). This collection pattern is not unusual for smaller particles which have insufficient inertia to be impacted uniformly on the filter face but have too much inertia to pass over the lip of the pore (14). These small domes are morphologically similar to the  $H_2SO_4$  and their contents did bubble in the electron beam. The collection of the smaller  $H_2SO_4$  near the pores during peak  $[SO_4^{2-}]$  as compared to the collection of the larger  $H_2SO_4$  between the pores in the earlier and later samples may indicate a less aged  $SO_4^{2-}$  component in the aerosol during the peak period (15).

Spheres similar to those seen in the episode one month earlier and identified as coal fly ash (6) were less numerous than the  $SO_4^{2-}$  particles. The total number of spheres is larger than shown in Figure 4 because spheres in clusters were often too small or too agglomerated to allow individual enumeration. The abundance of these spheres varied dramatically, ranging over more than two orders of magnitude. Spheres were almost absent before the episode but were abundant during the high- $SO_4^{2-}$  period. A strictly quantitative relationship between  $[SO_4^{2-}]$  and fly-ash particles was not expected because of opposing forces during transport: fly ash spheres could only decrease during transport because of sedimentation whereas  $[SO_4^{2-}]$  could increase because of  $SO_2$  oxidation.

All spheres and sphere clusters were  $< 1 \mu m$ . This would suggest a distant source in that supramicrometer spheres would have settled out during extended transport. Their spherical morphology points to combustion evolution, e.g., cooled silicate and metal droplets.

The abundance of spheres composed primarily of Fe (and called ferrospheres after Lauf (16)) generally followed  $[SO_4^{2-}]$  but peaked 12 hours earlier. Whereas magnetite ( $Fe_3O_4$ ) was the most common ferrosphere mineral in the episode studied earlier, maghemite ( $\gamma-Fe_2O_3$ ) was the most abundant mineral in ferrospheres in this episode (Figure 5a,b). Magnetite (or Fe-rich spinels) and hematite ( $\alpha-Fe_2O_3$ ) were also present. These minerals have been commonly reported in coal fly ash studies (17,18,19). The x-ray spectra of these spheres occasionally revealed traces of Mn, Zn, Si, K, Ca, Cr or Se. The first-row transition metals are possibly isomorphous substitutions in the spinel structure (19) whereas Se may be a surface-enriched volatile as reported by others (11).

Spheres composed primarily of Si were as abundant as the ferrospheres and their numbers correlated with  $[SO_4^{2-}]$ . In addition to the Si x-rays, these spheres often yielded smaller x ray peaks of Fe, K, Ti, Al, Mn, Zn, Cd or Se. Like the Si spheres collected one month earlier, these did not yield diffraction patterns, again making them likely candidates for the glass spheres found in coal fly ash (16,19).

Spheres which did not fit neatly into the Fe or Si group usually were composed of a mixture of Al, Si, Fe and/or Ti. One sphere (Figure 5c) was identified by its EDXRS and ED as mullite ( $3(Al_2O_3) \cdot 2SiO_2$ ), a high-temperature mineral found in coal fly ash (16,17,19). Fe has been previously identified in mullite coal

fly ash (19). The mixed-element sphere in Figure 5d is the largest sphere collected and identified at WFM.

The above spheres are typical of coal fly ash but have not been characterized in oil fly ash. Oil fly ash is generally platy or honeycombed carbon which is enriched in V and Ni (9,12,20). A few particles collected before, during and after the episode yielded very small V x-ray peaks but these peaks were not associated with a specific particle type or elemental combination. Hence microparticle analysis provides no evidence of an increase of oil fly ash during the elevated  $[SO_4^{2-}]$  period.

Common, though never abundant, were Si-rich fragments which were identified as quartz, K feldspars and plagioclase (Figure 4). These ranged in size from slightly less than 1  $\mu m$  to 3  $\mu m$ . Abundance varied only a little more than an order of magnitude. These were most likely local crustal fragments since the three identified mineral groups are the most common minerals in the Adirondack region (21).

Pb-rich particles ranging from 0.1 to 1.0  $\mu m$  were detected in the episodic samples. These Pb x-ray peaks were always associated with larger S peaks and  $PbSO_4$  was the most commonly identified mineral. Br x rays were not seen with any of these Pb particles but the more volatile Br may have been lost by aging or by the heat of the electron beam. These particles were seen only when  $[Pb]$  exceeded 30  $ng/m^3$  and the concentration of Pb particles correlated closely with  $[Pb]$ .

#### CONCLUSION

The variety of evidence outlined above demonstrated that  $SO_2$  emissions from the industrial Midwest rather than emissions in the Northeast were the major source of a high- $SO_4^{2-}$  episode in the acid-sensitive regions of New York State. The movement of the high-pressure system during this episode was identical to previous meteorological conditions when trajectory analyses revealed flow of air masses from the Midwest across the state. Mn/V ratios were distinctly midwestern during this episode. V/Ni ratios reinforced the interpretation of Mn/V ratios and hold promise as another regional signature. The mineralogy, morphology and elemental composition of spheres collected during the episode were typical of coal fly ash but not of oil fly ash. The submicrometer size range of these spheres pointed to a distant source. While this coal fly ash was virtually absent before the episode, it became abundant when  $[SO_4^{2-}]$  increased.

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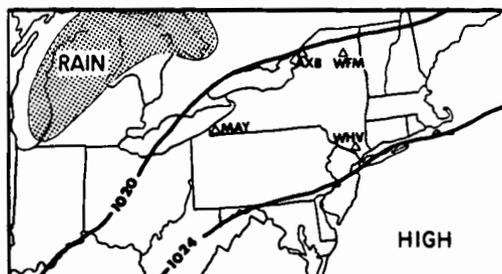


Figure 1. Simplified surface meteorologic conditions in the northeastern United States at 0730 EST on 28 July 1983. Sampling sites are Mayville (MAY), Alexandria Bay (AXB), Whiteface Mountain (WFM) and West Haverstraw (WHV).

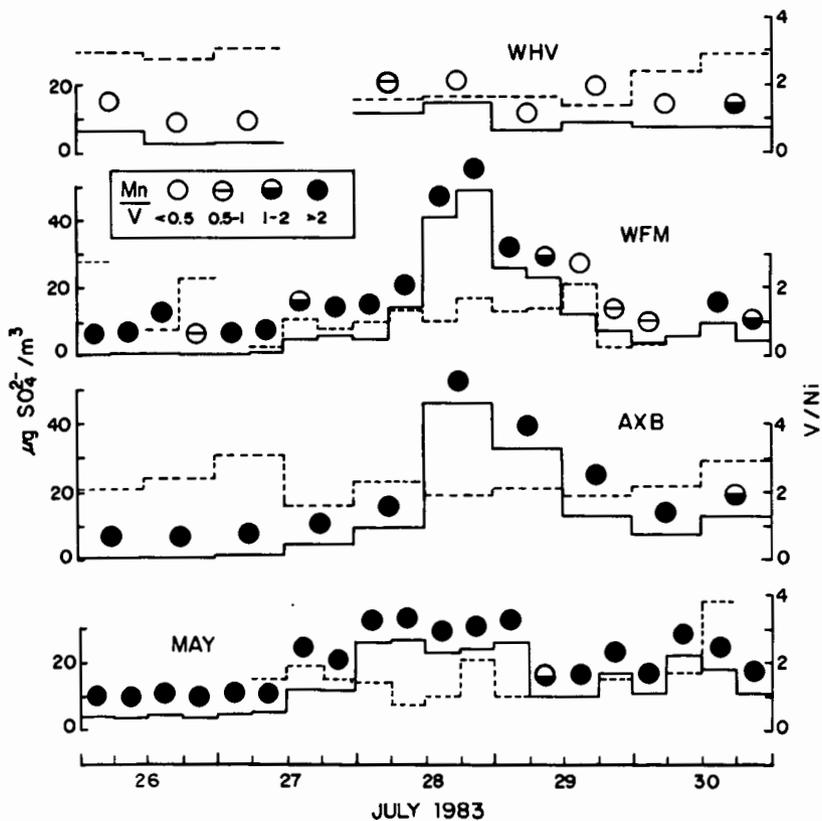


Figure 2. Sulfate concentrations (solid bars), V/Ni ratios (dashed bars) and Mn/V ratios at four sites in New York State. Metal ratios omitted for samples with one or both metals below detection limit or with excessive crustal correction.

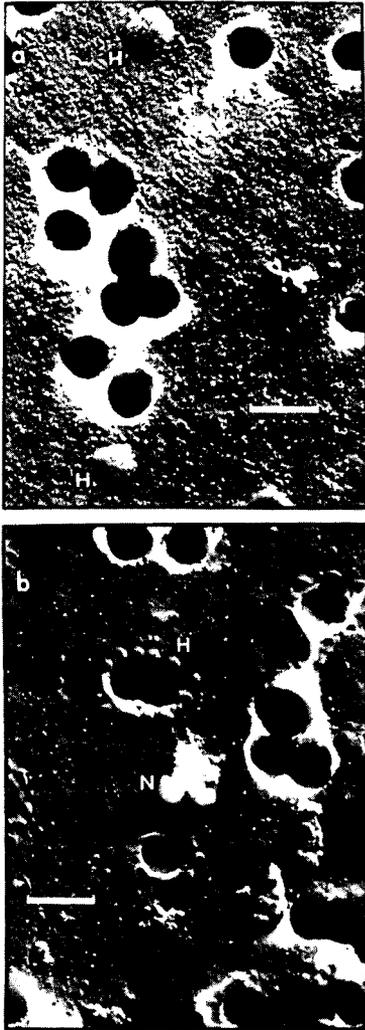


Figure 3. Transmission electron micrographs of sulfate particles collected on Nuclepore filters at WFM and shadowed with Au/Pd. (a) 27 July IV 1983. H denotes cap-like particles which are probably  $H_2SO_4$ . (b) 28 July IV 1983. N denotes cluster which is probably  $(NH_4)_2SO_4$ .

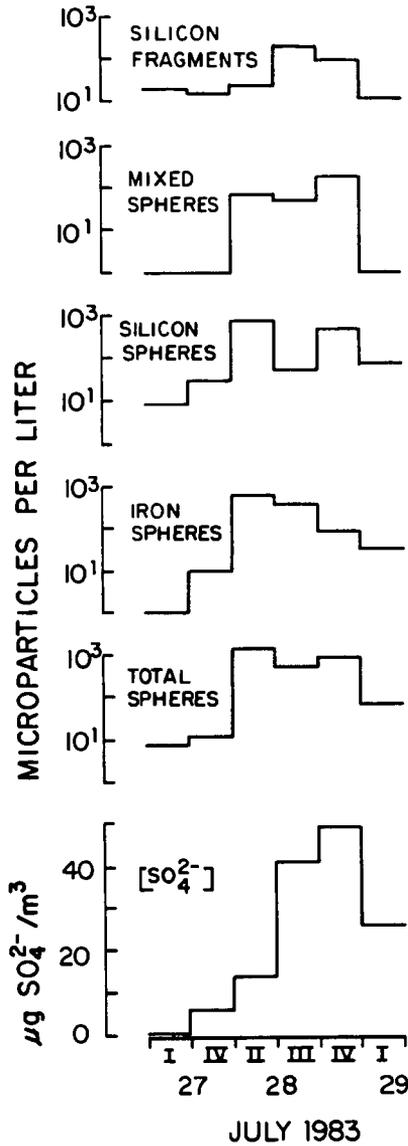


Figure 4. Sulfate and microparticle concentrations at WFM during selected periods from 27-29 July 1983.

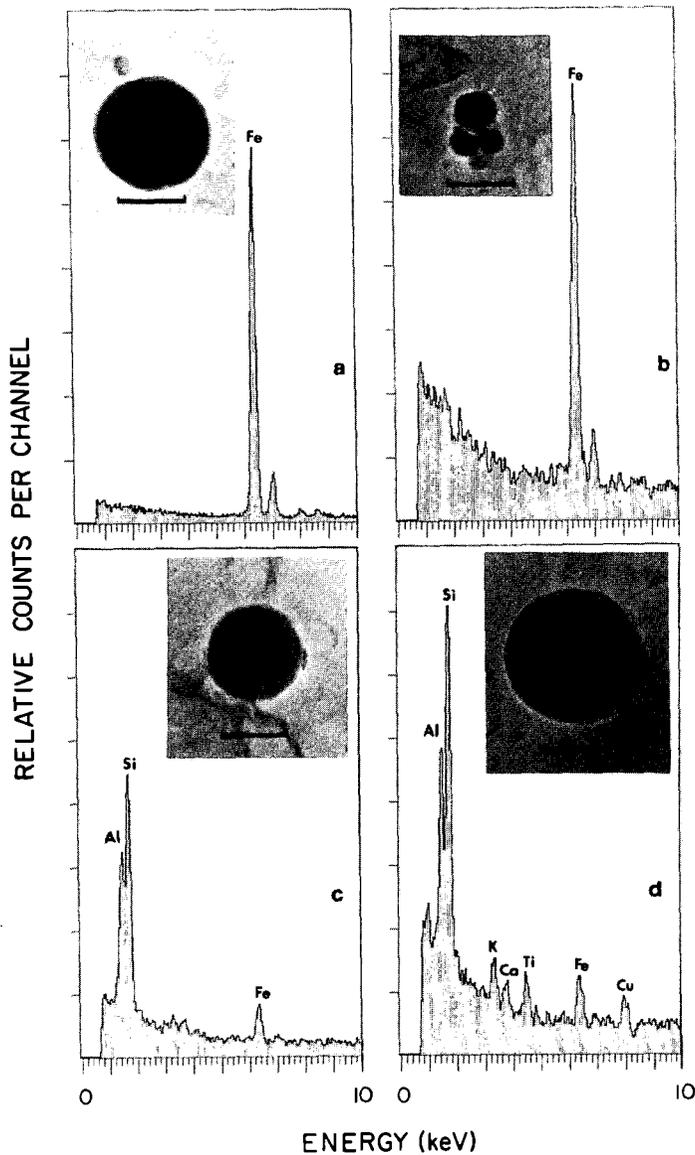


Figure 5. High-voltage electron micrographs and x-ray spectra of microparticles collected at WFM in 1983. Scale bar equals 0.5  $\mu\text{m}$ . (a)  $\gamma\text{-Fe}_2\text{O}_3$ , sphere collected 28 July II. (b)  $\gamma\text{-Fe}_2\text{O}_3$ , sphere cluster collected 28 July IV. (c) Mullite sphere collected 28 July IV. (d). Mixed-element sphere collected 28 July III.