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Elemental and Morphological Analyses of Atmospheric Particles from Southwestern Part of Mexico City

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The chemical composition of atmospheric particles is complex and not completely known. These can be formed by a large variety of elements and chemical compounds, both organic and inorganic, depending on their origin (Junge 1963; Warneck 1988). The chemical composition gives to the particle special characteristics which, in turn, influence its interaction with the various systems where it is involved. Such is the case, for example, of solar radiation in the atmosphere which, by interacting with a particle, can absorb it or disperse it with higher or lower intensity, depending on its size and composition, thereby allowing modification of the earth's climate (Ivlev Popova 1973; Mita and Isono 1980). Since chemical composition of aerosols depends on their source, and this composition is of great importance insofar as human health is concerned (Schroeder et al. 1987), it is of interest to carry out local studies on this subject. It is in this context in which the present study focused on the identification of chemical elements that are found in the atmospheric particles in the southwestern part of Mexico City. The samples analyzed were collected during the dry and rainy seasons, which characterize the climate of the area. The analyses were made by Scanning Electron Microscopy (SEM) and by Energy Dispersive X-Ray Analysis (EDXRA). Information is also presented regarding the morphology and size of the observed particles.

The results are presented here to aid in the chemical characterization of atmospheric aerosols, which is underway by various researchers in different parts of Mexico City (Castellanos et al. 1991; Salazar et al. 1991; Falcón et al. 1988; Rosas et al. 1990; Jauregui 1988).

MATERIALS AND METHODS

Samples were collected using a high-volume, cellulose filter- equipped sampler. The particles obtained were approximately 0.1-50 mm diameter (Trijonis 1983; McCrone and Delly 1980). Sampling was done during the period 1985-1986, and each sample represented a 24 - hr period. The sampler was located at a height of 7 m above the ground in the Observatorio de Radiación Solar, located in the southwestern part of Mexico City.

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Table 1. Characteristics of all observed aerosol particles.

#F	#P	Type of Particles	#F	#P	Type of Particles
		% - W			% - W
3	1	100.0-S	7		2.5-Si,7.8-P,50.3-S,19.9-CL,19.5-V
13		51.7-S,48.3-Ca	7		18.3-Al,51.1-Si,7.6-S,14.2-Ca,8.8-Fe
4		97.2-Si,2.8-Fe	7		18.2-Al,56.0-Si,3.2-S,11.6-Ca,11.0-Fe
6		29.4-S,70.6-Ca	7		16.2-Al,61.7-Si,12.6-K,6.9-Ca,2.7-Fe
3		37.0-S,63.0-Ca	11		19.2-Mg,7.2-Al,8.8-Si,2.1-S,62.8-Ca
7		17.2-Cl,92.8-Ca	13		16.7-Al,63.5-Si,5.0-S,7.9-Ca,6.9-Fe
7	6	99.1-Si,0.9-Fe	13		15.0-Al,44.6-Si,9.1-S,24.3-Ca,7.0-Fe
2		5.1-Al,70.4-Si,24.5-Fe	13	29	11.8-Mg,24.6-Si,9.8-S,7.4-Cl,46.4-Ca
2		11.0-S,9.2-Cl,79.8-Ca	2		12.2-Al,73.2-Si,2.9-K,0.7-Ca, 0.6-Ti,10.0-Fe
4		70.1-Si,13.2-Ca,16.7-Fe	2		14.7-Al,58.3-Si,0.3-P,9.6-K, 4.7-Ca,12.4-Fe
4		92.1-Si,3.9-K,4.0-Fe	4		10.9-Al,44.6-Si,9.8-S,1.1-Cl, 26.8-Ca,6.8-Fe
8		96.3-Si,1.23-S,2.48-Cl	6		12.7-Mg,19.7-Al,55.9-Si,3.0-S,3.1-K
8		30.1-Si,42.8-S,27.1-Cl	6		3.0-Mg,0.1-Al,1.7-Si,2.6-Cl, 92.6-Ca,5.7-Fe
3		12.8-Al,85.7-Si,1.5-Cl	10		10.6-Al,77.1-Si,2.8-S,0.7-K, 3.1-Ca,5.8-Fe
3		0.3-S,2.3-Cl,97.4-Ca	12		2.5-AL,11.0-Si,70.6-S,8.2-Cl, 5.4-Ca,2.4-V
3		23.4-Al,56.8-Si,19.8-Ca	12		10.3-Al,40.8-Si,12.6-S,4.4-Cl, 28.1-Ca,3.9-Fe
3		14.9-P,5.7-S,79.4-Ca	12		4.8-Al,30.7-Si,5.6-S,3.7-Cl, 52.3-Ca,2.9-Fe
7		10.1-Si,38.9-S,51.0-Ca	12		0.4-Mg,31.7-Si,5.8-S,3.7-Ca, 51.6-Ti,6.8-Fe
11		2.5-Si,84.2-S,13.3-V	12		15.7-Al,21.2-Si,2.6-S,3.0-Cl, 43.1-Ca,14.35-Fe
11		5.4-Si,8.4-S,86.2-Ca	12		9.0-Al,57.9-Si,1.2-S,5.5-K, 23.0-Ca,3.3-Fe
13	14	33.5-Si,65.6-S,0.9-Ti	12		2.6-Al,8.4-Si,5.9-S,6.0-Cl, 14.5-K,62.7-Ca
6		15.2-Al,67.3-Si,10.9-S,25.3-Fe	1		17.1-Al,51.9-Si,6.0-S,1.7-K, 13.9-Ca,9.5-Fe
6		10.2-Al,78.4-Si,2.7-S,5.2-Ca	1		14.0-Al,29.9-Si,7.1-S,5.1-K, 37.4-Ca,6.6-Fe
8		3.8-Si,42.0-S,6.4-Cl,47.8-K	1		8.5-Al,73.1-Si,0.4-Cl,3.3-Ca, 2.3-Ti,12.4-Fe
8		0.5-Si,79.1-S,11.8-Cl,8.6-K	3		1.8-Al,7.1-Si,0.9-S,3.2-Cl, 84.5-Ca,2.6-Fe
10		95.6-Si,2.7-S,1.2-Cl,0.5-K	5		16.1-Al,69.3-Si,0.2-S,9.4-K, 1.7-Ca,3.3-Fe
12		25.2-Mg,42.5-Si,1.5-S,30.8-Fe	5		15.4-Al,66.5-Si,0.2-S,0.6-K, 12.0-Ca,5.2-Fe
3		18.2-P,47.5-S,25.0-Ca,9.4-Fe	5		14.4-Al,52.6-Si,1.4-s,2.0-K, 16.5-Ca,13.2-Fe
5		24.9-Al,55.1-Si,19.3-Ca,0.7-Fe	9		0.4-Si,3.0-P,11.2-S,2.9-Cl, 50.0-K,32.6-Ca
7		5.8-P,70.9-S,22.7-Cl,0.6-V	11		17.0-Al,56.5-Si,6.2-S,2.9-K, 3.6-Ca,13.9-Fe
7		2.3-Si,38.6-S,48.9-Ca,10.2-Fe	11		17.9-Mg,6.7-Al,62.4-Si,4.7-S, 6.9-Ca,1.4-Fe
9		1.8-S,3.4-Cl,6.4-K,90.4-Ca	11		21.0-Al,61.0-Si,2.9-S,1.2-K, 0.1-Ca,13.8-Fe
9		82.3-Si,5.3-S,4.2-Cl,8.2-K	13		14.5-Al,43.8-Si,5.7-S,8.4-K, 20.2-Ca,7.6-Fe

Table 1. Characteristics of all observed aerosol particles. (Cont.)

#F	#P	Type of Particles	#F	#P	Type of Particles
		% - W			% - W
11		6.0-Mg,6.4-Al,11.5-Si,76.1-K	13		10.4-Si,27.4-P,16.5-S,8.9-Cl, 22.4-K,14.4-Ca
11		1.8-Si,56.6-S,25.9-Cl,15.7-V	13	27	18.4-Al,76.5-Si,1.7-S,1.2-Ca, 1.4-Ti,0.8-Fe
11		14.2-Si,10.9-S,3.2-Cl,71.8-Ca	2		2.6-Al,14.6-Si,3.2-S,1.3-Cl,1.3-K, 73.9-Ca,3.1-Fe
13	16	17.6-Al,66.4-Si,5.0-Ca,11.0-Fe	2		2.3-Al,10.2-Si,14.4-P,14.9-S, 3.8-Cl,31.7-K,22.8-Ca
4		52.3-Si,11.1-S,7.8-Cl,17.7-Ca,11.1-Fe	2		14.5-Al,47.4-Si,2.0-S,0.03-Cl, 12.7-K,14.5-Ca,8.9-Fe
4		4.1-Si,26.2-S,23.1-Cl,41.4-K,5.5-Ca	2		15.1-Al,58.7-Si,0.5-S,11.7-K, 3.2-Ca,0.4-Ti,10.5-Fe
4		51.4-Si,30.2-S,7.6-Cl,1.7-K,9.5-Ca	4		1.24-Mg,24.0-Al,53.7-Si,1.7-K, 1.8-Ca,0.5-Ti,17.0-Fe
4		51.9-Si,32.5-S,3.2-Cl,1.0-K,3.8-Ca	8		3.60-Mg,15.2-Al,49.2-Si,2.8-S, 5.6-K,1.8-Ca,21.8-Fe
6		13.8-Al,58.3-Si,1.0-S,1.7-Ca,3.4-Fe	8		4.8-Al,31.0-Si,8.0-S,4.0-Cl,2.3-K, 48.9-Ca,1.1-Fe
6		30.4-Si,14.8-S,4.9-Cl,47.0-Ca,8.7-Fe	10		3.2-Al,71.5-Si,7.4-S,2.0-Cl, 8.9-Ca,5.0-Fe
6		3.7-Si,84.3-S,8.3-Cl,3.7-V,2.9-Fe	10		4.3-Al,79.6-Si,1.1-S,0.7-Cl,1.5-K, 2.3-Ca,10.5-Fe
6		3.7-Mg,19.3-Al,53.1-Si,7.9-S,7.4-Ca	10		19.4-Al,66.6-Si,0.1-S,0.3-Cl, 2.1-K,11.1-Ca,0.5-Fe
6		6.7-Si,36.1-P,31.7-S,22.6-Cl,3.0-Ca	10		10.7-Mg,13.7-Al,32.2-Si,0.3-S, 12.2-K,3.4-Cr,27.4-Fe
8		0.6-Al,9.7-Si,34.7-S,0.6-Cl,54.4-Ca	1		2.7-Al,12.9-Si,2.6-S,1.7-Cl,6.0-K, 71.9-Ca,2.3-Fe
8		0.1-Al,2.0-Si,2.9-S,5.3-Cl,89.7-Ca	3		2.0-Al,40.3-Si,0.1-P,10.3-S, 14.1-Cl,29.0-Ca,4.1-Cr
10		14.5-Si,1.4-P,73.6-S,3.4-Cl,7.2-V	5		4.7-Al,29.5-Si,11.2-S,8.7-Cl, 14.5-K,23.0-Ca,8.3-Fe
12		13.3-Al,47.6-Si,4.3-S,7.4-Ca,27.4-Fe	5		1.9-Mg,14.5-Al,50.5-Si,3.7-S1.1-K, 16.7-Ca,11.7-Fe
12		7.2-Mg,52.9-Si,4.0-S,11.9-Ca,24.0-Fe	5		1.4-Al,45.3-Si,1.9-P,8.8-S,2.7-Cl, 31.6-Ca,8.2-Fe
1		0.3-Si,39.2-S,1.9-Cl,5.6-K,53.1-Ca	9		4.8-Al,9.9-Si,7.5-S,2.8-K,10.2-Ca, 63.9-Ti,0.9-Fe
1		33.9-Si,12.9-S,0.2-Cl,28.8-Ca,24.1-Fe	9		0.6-Al,2.7-Si,1.9-P,6.5-S,5.2-Cl, 6.7-K,33.8-Ca,42.6-Fe
3		7.6-Al,81.9-Si,6.0-S,1.5-Cl,3.0-Ca	9		0.4-Al,7.7-Si,17.5-S,12.9-Cl, 15.8-K,41.7-Ca,4.1-Fe
5		19.1-Al,61.4-Si,4.3-K,3.9-Ca,11.3-Fe	11	20	16.8-Al,45.4-Si,10.9-S,1.6-Cl, 6.4-K,12.2-Ca,6.7-Fe
5		1.8-Si,2.3-P,50.3-S,1.4-Cl,44.1-Ca	2		4.8-Al,47.7-Si,0.3-P,0.2-S,1.5-K, 11.4-Ca,2.1-Ti,32.0-Fe
7		4.8-P,63.6-S,16.5-Cl,14.4-Ca,0.7-V	8		13.2-Al,52.5-Si,0.9-P,2.9-S, 1.4-Cl,2.7-K,12.8-Ca,13.4-Fe
8		12.2-Al,51.3-Si,3.8-S,0.1-Cl, 5.2-K,2.0-Ca,6.3-Mn,19.1-Fe	1		0.9-Al,5.6-Si,9.1-P,15.3-S,6.5-Cl, 46.6-K,14.6-Ca,1.4-Fe
10		13.9-Al,48.2-Si,0.3-P,7.0-S, 2.4-Cl,2.5-K,16.2-Ca,9.6-Fe	9		9.6-Al,34.3-Si,0.8-P,6.6-S,2.9-Cl, 10.6-K,11.7-Ca,23.4-Fe
10		8.9-Al,29.8-Si,14.2-P,5.6-S, 2.0-Cl,4.6-K,31.4-Ca,3.4-Fe	9		0.5-Mg,4.8-Al,22.0-Si,3.7-S, 2.3-Cl,4.7-K,39.6-Ca22.6-Fe
10		9.2-Mg,12.1-Al,30.0-Si,0.7-S, 0.7-Cl,13.2-K,2.5-Ti,31.6-Fe	9	11	5.7-Al,40.0-Si,0.6-P,26.7-S, 3.2-Cl,6.3-K,7.1-Ca,7.4-Fe
1		12.9-Al,35.8-Si,3.4-P,6.5-S, 2.9-Cl,17.5-K,15.5-Ca,5.6-Fe	9	1	7.4-Mg,4.1-Al,53.1-Si,1.4-P,1.8-S, 1.7-Cl,4.2-K,25.5-Ca,0.9-Fe

The particle samples studied came from 30 filters, which correspond to different dates of collection, and their observation revealed a striking similarity, both morphologically and composition-wise, from sample to sample.
Due to this similarity, the results presented in this paper are based on the precise analysis of only 13 samples. In these samples, about 300 particles were analyzed, and only about 130 of these turned out to be new or unique. Table 1 shows the elemental composition (W%) of the analyzed particles, since the others showed similarity to the ones reported in this paper.

In Table 1, the items in the first and fourth columns represent the filter numbers corresponding to the observed particles. Even filter numbers stand for the dry season, and odd filter numbers for the rainy season. The second and the fifth columns represent the total number of particles whose elemental composition is of one, two, up to nine elements.

The particles to be analyzed were removed from the filter with a perfectly clean fine brush and placed in the sample holder of the SEM. To avoid overcharging the image by non-conducting particles, a metallic vacuum cover was used; the best results were obtained with Cu and Ag covers.

The samples prepared in this manner were placed in a JEOL 35 CF Scanning Electron Microscope, whose column was equipped with an Ortec System 5000 Energy Dispersive Detector. With this equipment we made the microanalysis of the observed particles and the mapping of the elements in order to know local variations in concentration.

The Ortec System 5000 is designed to make automatic, semiquantitative analysis, normalizing the results only with those elements which can be detected.

The Man-Witney-Wilcoxon (Conover 1980) test was used to determine levels of significant differences for simple and combined elements.

RESULTS AND DISCUSSION

The results indicated 13 elements were present: Mg, Al, Si, P, S, Cl, K, Ca, Cr, Ti, V, Mn, and Fe.

Table 2. Total and seasonal average of detected chemical elements (W%)

ELEMENT	TOTAL AVERAGE OF SAMPLES	DRY SEASON	RAINY SEASON
Mg	1.09	1.28	0.92
Al	6.39	6.27	6.48
Si	35.45	41.56	30.21
P	1.32	1.13	1.48
S	16.73	13.46	19.54
Cl	3.30	3.44	3.19
K	4.90	4.61	5.14
Ca	22.20	19.10	24.85
Cr	0.03	0.00	0.06
Ti	1.00	1.02	0.98
V	0.57	0.22	0.86
Mn	0.05	0.11	0.00
Fe	6.28	7.93	4.86

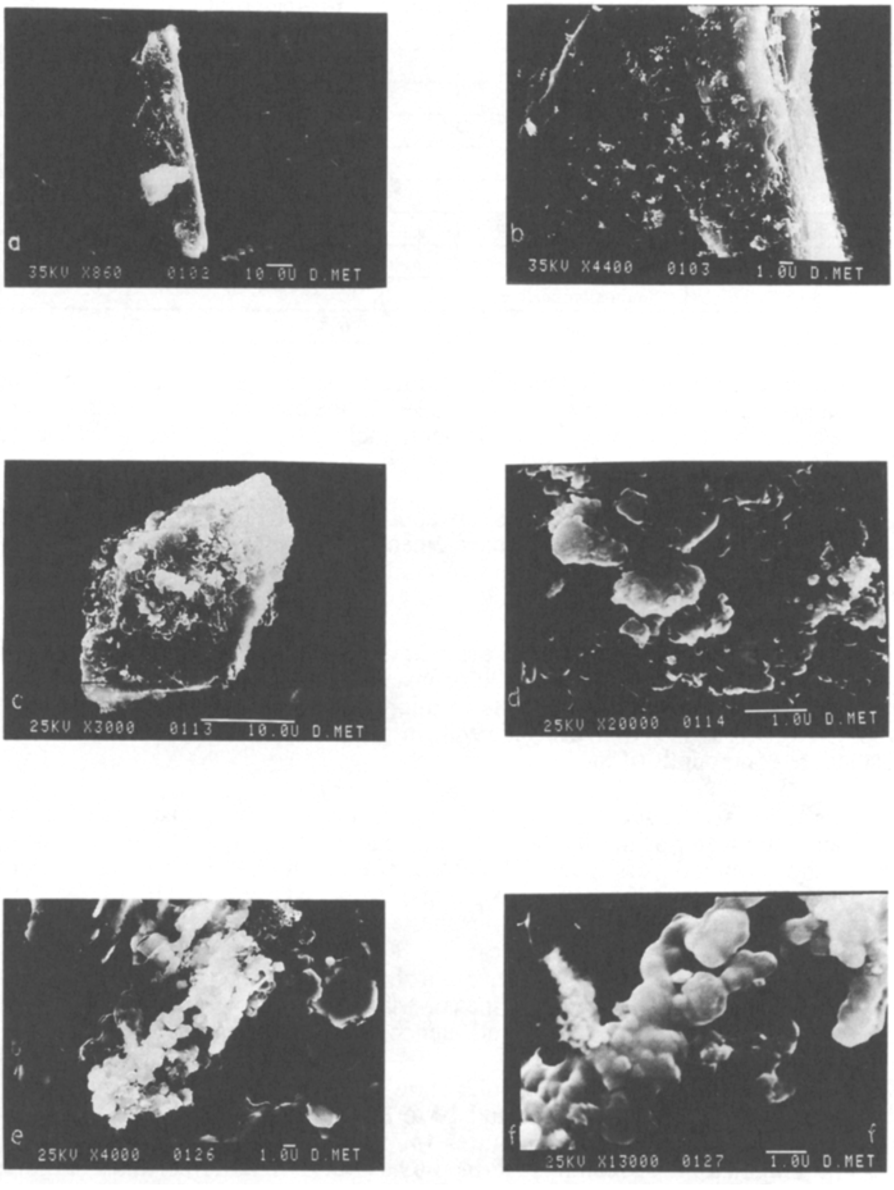

Figure 1. Gigantic particles (from 20 to 80 mm in length and 10 to 30 mm in diameter), (a, b, and d). Soil dust, 20 mm diameter (c) Agglomerates of 10-15 mm diameter (e, and f). Five or six elements were detected in all of these particles.

Table 2 presents these elements together with their average seasonal weight (percentage) and by total weight. As simple Si and Fe, and combinations of them are present abundantly in the dry season with respect to the rainy season, it is possible to say that the effect of the rain is to wash the atmosphere (Junge 1963). This can be noticed in Table 2 and 3.

Table 3. Results of the Man-Witney-Wilcoxon test for the combination of two and three elements

ELEMENTS	SIGNIFICANCE	LEVEL (Z)	OBSERVATION
Cl+Fe	significative	0.015	dry > rainy
K+Ca	non-significative	0.21	
S+Ca	significative	0.034	rainy > dry
Si+Cl	significative	0.007	dry > rainy
Si+Fe	significative	0.005	dry > rainy
Si+Fe+Cl	significative	0.003	dry > rainy
S+K	non-significative	0.26	
Si+Ca+K	significative	0.025	rainy > dry

Silicon is abundant in nature, with a tetrahedral structure susceptible to ionic interchange with other elements (Fairbridge 1972); the behavior of its combinations is represented by that of the single element, including the Si, Fe, and Cl triad (Table 3).

Significant combinations of sulphur (S) are abundant during the rainy season (Table 3), in spite of the fact that S, as a simple element, is not significant. In the presence of humidity, S reacts forming a series of compounds which cannot form during the dry season.

This, in turn, allows us to understand the behavior related to the change of seasons (Table 3). Thus, since sulphur dioxide is unstable in the atmosphere, it produces its corresponding acid,SO_3 , and salts in micro- and macro-particles (Junge and Ryan 1958; Brosset 1978; Warneck 1988) in the form of sulfates, which are the most stable compounds of S.

These particles are frequent pollutants in the atmosphere of industrialized urban areas, and they result primarily from the conversion of SO_x (gas) to SO_4 (particle) through the burning of fossil fuels (USEPA 1982). In our case, high concentrations of SO_2 have been detected in the atmosphere of Mexico City (SEDUE 1986). Thus this information indicates that the atmospheric S is of anthropogenic origin.

It can also be concluded that atmospheric chlorine in the Mexico City area is derived from the emission of combustion engines or from industrial wastes (Willison et al. 1989) since the area is continental, and, hence, it is also of anthropogenic origin.

Microscopic examination of the samples shows; (1) the presence of gigantic particles (from 20 to 80 mm in length and 10 to 30 mm in diameter), with adherent submicron-size smaller particles (Figures 1a, 1b, 1c and 1d); (2) the presence of 10-15 mm diameter agglomerates, formed by 1 mm or smaller particles (Figures 1e and 1f); and (3) the presence of individual particles of 25 to 35 mm in diameter (Figures 2c, 2d, 2e and 2f). The first two groups contain variable amounts of five or six of the 13 elements found. The third group of particles is more specific, since in this an abundance of paired elements (Si-Fe, S-Ca, Si-Cl) were detected, or some combinations of Si-Fe-Cl, and S-K-Ca, but with the predominance of one element with more than the half of its weight percentage.

The morphology of these particles was studied, with reference to the Atlas of Particles (McCrone and Delly, 1980). We observed typical crystalline forms of natural compounds (Figure 3a), anthropogenic forms of thin flakes containing Ti, S, and Si (Figure 3b).

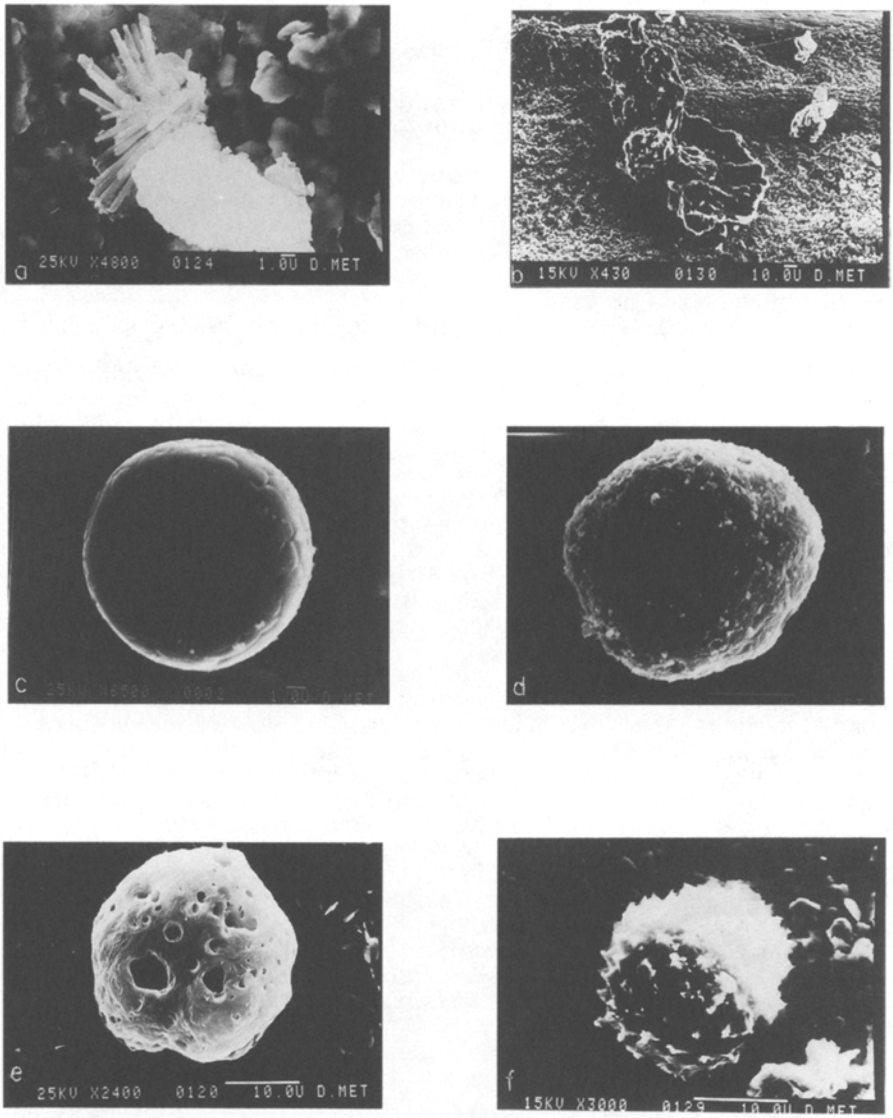

Figure 2. Crystalline aerosol particle (a). Anthropogenic form of aerosol (b). Spherical aerosol from metals processing (c). Combustion aerosols (d, e, and f)

Spherical forms typical of refinement and processing of metals with high Fe content (Figure 3c), typical forms resulting from combustion (Figures 3d, 3e and 3f), and soil dust (Figure 2c).

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