ISSN 1001—0742
Journal of Environmental Sciences Vol. 18, No. 1, pp. 90—95, 2006
CN 11—2629/X

Article ID: 1001-0742(2006)01-0090-06 **CLC number**: X513 **Document code**:A

Mineralogical characterization of airborne individual particulates in Beijing PM_{10}

LU Sen-lin[1,2,*], SHAO Long-yi[2], WU Ming-hong[1], JIAO Zheng[1]

(1. Shanghai Applied Radiation Institute, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 201800, China. E-mail: senlinlv@staff.shu.edu.cn; 2. Department of Earth Science, China University of Mining and Technology, Beijing 100083, China)

Abstract: This work mainly focuses on the mineralogical study of particulate matter(PM_{10}) in Beijing. Samples were collected on polycarbonate filter from April, 2002 to March, 2003 in Beijing urban area. Scanning electronic microscopy coupled with energy dispersive X-ray(SEM/EDX) was used to investigate individual mineral particles in Beijing PM_{10}. 1454 individual mineral particulates from 48 samples were analysed by SEM/EDX. The results revealed that mineral particulates were complex and heterogeneous. 38 kinds of minerals in PM_{10} were identified. The clay minerals, of annual average percentage of 30.1%, were the main composition among the identified minerals, and illite/smectite was the main composition in clay minerals, reaching up to 35%. Annual average percentage of quartz, calcite, compound particulates, carbonates were 13.5%, 10.9%, 11.95%, 10.31%, respectively. Annual average percentage less than 10% were gypsum, feldspar, dolomite, and so on. Fluorite, apatite, halite, barite and chloridize zinc($ZnCl_2$) were firstly identified in Beijing PM_{10}. Sulfurization was found on surface of mineral particles, suggested extensive atmospheric reaction in air during summer.

Keywords: inhalable particulate matter(PM_{10}); individual analysis; mineral composition

Introduction

Many researches demonstrated there were strong links between PM_{10}(aerodynamic diameter of particulate matter less than 10 μm) pollution and morbidity and mortality (Chapman *et al.*, 1997; USEPA, 2001; Richard, 2003). The air quality of Beijing is of great concern than ever before owing to 2008 Olympic Games to be held in Beijing. Mass concentration of Beijing PM_{10} is always higher than Chinese National Air Quality Standards (class-two is less than 150 $\mu g/m^3$) because of the locality of Beijing and rapid economic growth. There were many reports on the chemical characteristic of Beijing PM_{10}, but only a few papers concerned with mineral composition of Beijing PM_{10}, which are the major composition in Beijing PM_{10} (Shao, 2003), especially in spring season. Bulk composition of Beijing aerosol had been investigated in the last decades (Winchester *et al.*, 1981; Winchester and Bi, 1984; He *et al.*, 2001; Yao *et al.*, 2002), however, mineral airborne particles were not well studied, and mineral aerosol plays an important role in removal, deposition and transport of atmospheric pollutants, and even more, the identification of mineral assemblages of aerosol may be diagnostic of their sources (Davis and Guo, 2000; Ganor and foner, 2000). Recently, an individual analysis technology was applied in aerosol science research(Gao and Anderson, 2001). As enlightened by this study, we conducted the method on individual mineral particles in Beijing air.

The objective of the current work was to identify the mineralogy of Beijing PM_{10} and its variety in different seasons through analyzing chemical composition of individual mineral aerosol. Our mineralogical experience and experimental techniques can provide uniquely useful information for atmospheric scientist.

1 Materials and methods

1.1 Collection parameters

The urban collection site was located in northwestern Beijing around 1 km from the fourth ring road of Beijing City. The samplers were mounted on the fifth floor of the main building in China University of Mining and Technology (18.5 m high from the background), 100 m west from the Xueyuan Road(a major road in Beijing). A Negretti selective head(UK) linked to a high-volume air sampler (Laoshan Electronic Co., China) running at a flow rate of 30 L/min that was monitored using a flow meter (CT Playton Ltd. UK) during the collection. The particulate matters were collected onto polycarbonate filters (Millipore, UK, pore size 0.6 μm). The surface of this kind filter is smooth for microscopic analysis. 6—12 h PM_{10} were collected continuously for 7 d per month from April, 2002 to March, 2003. 168 samples were collected in this study. During the sample collection, temperature, humidity, wind speed and direction were also

Foundation item: The National Natural Science Foundation of China(No. 40275040) and the Shanghai Leading Academic Disciplines(No. T0105);
*Corresponding author

recorded. More than 2 samples from each month collection were randomly selected for the investigation. 48 samples were selected from the total samples.

The polycarbonate filters were weighed before and after collection with a 0.01-mg precision microbalance after preconditioning for 48 h at constant humidity(40%—42%) and temperature(20—22℃).

1.2 Scanning electron microscopy/energy dispersive X-ray(SEM/EDX)

Copper washers (3.5 mm internal diameter) were mounted on aluminum SEM stub using epoxy resin (Araldite). Approximately 1 cm^2 of the polycarbonate filter was cut and mounted onto the copper washer using epoxy resin to form a drum-like mounting(Jones and Williamson, 2001). The samples were viewed using a scanning electron microscopy (SEM) LEO453VP, equipped with an energy dispersive X-ray system (EDX) which was used for the chemical elemental analysis. The EDX spectrometer was Link ISIS spectrometer with a Si(Li) detector which allows X-ray detection from elements higher than carbonate (Z>6). The system was equipped with software and elemental weight percentage were calculated using standard atomic number, absorption, fluorescence (ZAF) corrections. Operation conditions were 20 keV accelerating voltage and 600 pA beam current with spectral acquisition time of 100 s. The diameter of spot of electron beam was 1 μm. The instrument allowed the observation of particles down to 0.5 μm. In order to reduce effectively interference from the metal sample platform and the coated materials, the filter was used without any pretreatment during the SEM/EDX measurement. Percentage of mineral particles in samples almost kept constant after 100 or 30 mineral particles were statistic, so, 30 individual mineral particles were detected in each samples. 1454 mineral particles from 48 samples of Beijing PM_{10} were analysed.

2 Results and discussion

2.1 Minerals in Beijing PM_{10}

Minerals can be identified through comparing their oxide composition with the classification in the literature (Wang *et al.*, 1982). Although "polymorphism" existed in minerals, geologists had used this method to study minerals (Kupianiuen *et al.*, 2004). Recently, some researchers used this method to investigate the airborne particulates (Gao and Anderson, 2001; Krueger *et al.*, 2004). According to the results of SEM/EDX spectra(Fig.1), there existed clay minerals, quartz, feldspar, calcite, dolomite, gypsum, ect. in Beijing air (Table 1).

Table 1 Minerals in Beijing PM_{10}

Minerals		Intensity of Si/Al	Percentage of oxidates in Beijing mineral particles, %								
			SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	MgO	Fe	SO_3
Clay minerals	Kaolinite	ca. 1	37.87—52.86	26.7—45.07	<5	<5	<5	<5	-	-	-
	Illite	ca. 2	41.94—52.57	21.23—35.99	<5	6.3—11.58	<5	<5	-	-	-
	Illite/smectite (I/S)	ca. 2—3	35.63—58.09	21.72—36.71	<5	6.3—11.58	<5	<5	-	-	-
	Chlorite	ca. 2	26.54—46.65	14.32—37.30	-	-	-	0.65—37.92	1.91—14.85	-	-
Quartz			76.62—89.66	2.40—10.75	-	<2	<2	-	<2	<2	1.15—6.18
Feldspar	Plagioclase	ca. 3	37.39—67.75	13.38—28.40	<2	<2	<2	<2	0.53—3.68	-	-
	Potussium feldspar	ca. 3	58.24—64.14	16.21—19.53	<2	12.74—3.91	<2	<2	-	-	-
Carbonates	Calcite[a]	-			-		37.92—72.56		0.98—3.36	-	0.73—19.79
	Dolomite[a]	-					32.86—53.77		13.52—39.42	-	0.73—24.19
Sulfates	Gypsum[b]	-					12.92—40.76		-	-	22.86—55.71

Notes: a. There existed SiO_2, Al_2O_3, etc.; b. there existed Na_2O, Fe_2O_3, SiO_2, Al_2O_3, etc.

The results of SEM/EDX spectra showed that clay minerals in Beijing PM_{10} consist of I/S (illite/smectite), C/S (clorite/smectite), kaolinite, smectite, illite, chlorite, etc. From these kinds of mineral combination, clay minerals in Beijing air possibly originated from cold and dry climate environment.

Quartz (Fig.1b) in Beijing PM_{10} always with rounded outline can be found in every sample. The rounded quartz particles, which observed by optical

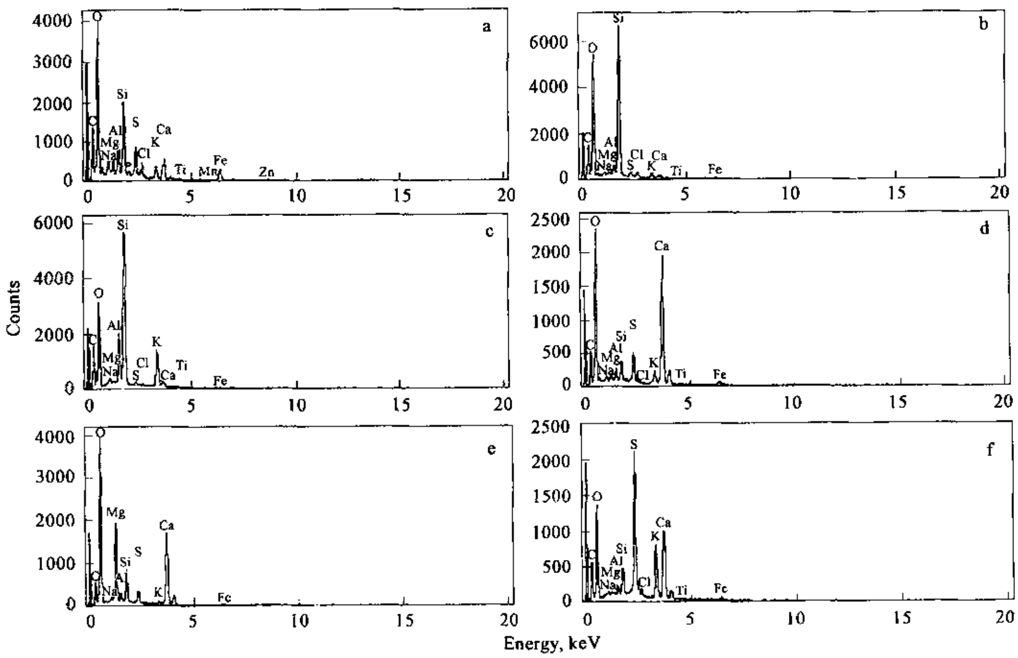

Fig.1 SEM/EDX spectra of minerals
a: Illite/Smectite; b: quartz; c: K-feldspar; d: calcite; e: dolomite; f: sulfates

microscopy, might reflect quartz particles being transported for a long distance.

Plagioclase and potassium feldspar (Fig.1c) were the main types of feldspar. The feldspar was common phase in Beijing PM_{10}.

Calcite(Fig.1d) and dolomite(Fig.1e) consisted of carbonates minerals in Beijing PM_{10}. Other kinds of carbonates, such as magnesite and siderite were also found in Beijing PM_{10}.

Individual particle analysis indicated sulfates(Fig. 1f) could be found in all the samples except April collections. Gypsum was the main form of sulfates in PM_{10} and appeared in the form of perfect strip crystal and always been absorbed on surface of other kind mineral particles. However, sulfates could not be found in Beijing surface soil and duststorm samples by using XRD analysis (Lu *et al.*, 2004). The result at least proved that sulfates in Beijing PM_{10} did not originated from the surface soil and duststorm, or not enough sulfate particles in the PM_{10} sample originated from surface soil and duststorm. On the contrary, if a number of sulfates in PM_{10} were found, it would confirm that these sulfates coming from anthropogentic sources or being the secondary particles formed in atmosphere.

During the investigation, oxides, such as hematite, corundum, rutile and lead oxide, halides represented by fluorite, halite, potassium chloride, zinc chloride, pyrite, zinc blende, apatite, barite and ilmenite were also found in Beijing PM_{10}. Although these mineral particles were founded rarely, it showed mineral composition of Beijing PM_{10} was very complex.

Besides the mineral particles mentioned above, there also existed another kind mineral particles with very complex chemical composition, it was hard to identify by the individual technology. The authors regarded it as compound particles. The compound particles might be aggregation of very tiny mineral particles or debris consisting of several minerals or other elements absorbed in the mineral particle. The similar conclusion could be found in "yellow sand" (WRINU, 1992).

2.2 Statistic of individual mineral aerosol

The statistic results showed clay mineral which mostly dominated in PM_{10} ranged 11.5%—57.5%, its annual average reached to 30.1% (Table 2). The maximum of clay percentage was 57.5% in February (2003) sample. It was probably due to many episodes of duststorm in this month. In clay minerals, I/S (illite/smectite mixed layers) was dominant components, reaching 35% , followed by C/S (chlorite/smectite mixed layers) (17%), kaolinite (14%), smectite(12%), illite(12%) and chlorite(10%). This characterization showed clay minerals could be transported easily due to its slender diameter, and also had close relationship with high frequency of wind in Beijing during spring.

The proportion of quartz mostly stayed stable in different season samples, ranged 9.3% —18.18% ,

Table 2 Different kinds of minerals content in PM_{10}

Date	Number*	Clay minerals, %	Quartz, %	Feldspar, %	Calcite, %	Dolomite, %	Gypsum, %	Other minerals, %**	Carbon particles, %	Compounds, %	Total
02 Apr.	44(2)	57.50	17.50	12.50	10.00	2.50	0	0	0	0	100
02 May	186(4)	38.40	12.21	13.37	8.72	4.07	4.65	9.98	6.98	1.74	100
02 Jun.	370(1)	22.80	10.86	6.96	4.18	3.9	8.36	9.19	12.53	21.17	100
02 Jul.	120(6)	11.50	10.62	4.42	3.54	0.88	8.85	0	37.17	23.01	100
02 Aug.	140(4)	30.50	10.17	5.08	3.39	3.39	37.74	5.08	5.08	2.54	100
02 Sept.	69(3)	21.80	10.91	5.45	29.09	7.27	9.09	0	7.27	9.09	100
02 Oct.	90(3)	14.50	17.39	5.80	14.49	4.35	11.59	0	7.25	24.64	100
02 Nov.	78(3)	52.50	16.95	5.08	3.39	1.69	1.69	0	10.17	8.47	100
02 Dec.	150(6)	27.90	9.30	16.28	3.49	5.81	12.79	0	10.46	13.95	100
03 Jan.	58(2)	20.00	12.50	5.00	7.50	5.00	12.50	7.50	20.00	10.00	100
03 Feb.	74(2)	36.40	18.18	9.09	14.54	1.82	1.82	0	3.64	14.54	100
03 Mar.	75(3)	27.00	15.88	1.59	28.54	4.76	4.76	0	3.18	14.29	100
Ave.	121(4)	30.10	13.50	7.55	10.9	3.79	9.24	2.64	10.31	11.95	
SD		14.10	3.36	4.36	9.30	1.85	9.14	2.14	9.90	8.23	

Notes: * Number of analysed particles(number of sample); ** other minerals includes fluorite(CaF_2), apatite[$Ca_2Ca_3(PO_4)_3(OHF)$], halite(NaCl), barite ($BaSO_4$) and chloridize zinc($ZnCl_2$)

annual average was 13.5%. This meant quartz could also stay in air for a long time. Feldspar in PM_{10} ranged from 1.59% to 16.28%, average was 7.55%. This results was similar with the conclusion that feldspar contributed 5.8% of Beijing PM_{10} by weight (Davis and Guo, 2000). Carbonates comprised PM_{10} from 3.39% to 29.09%, while dolomite just accounted for 0.88%—7.27%, their annual percentage was 9.3% and 1.85% respectively. Gypsum, regarding as secondary particles, could be found in Beijing PM_{10} except in April sample, varied from 0—37.74%, its annual average reached to 9.24%. Compound particles with S and Cl often occurring on the surface acc-ounted for 0—24.64% , its annual average were 11.95%. The reason of S and Cl elements absorbing on particle is needed to be studied further.

It is necessary to claim that individual analysis as a method to investigate particles in number, but semi-quantitative analysis XRD as a method to analyse particles in mass. For example, percentage of feldspar in Beijing PM_{10} was much higher than that of Gypsum by XRD method (Lu *et al.*, 2004), however, the result became different by using individual analysis. That was the reason gypsum was much more in number but much less in mass.

2.3 Comparsion of minerals with PM_{10} with other areas by SEM/EDX

Minerals in PM_{10} were studied by some researchers using SEM/EDX, the results are listed in Table 3. It showed quartz was the unique mineral in PM_{10} samples collected in different areas. It might revealed that quartz, which was the most abundance in the crust, not only been transported for a long range but also exist in the atmosphere for a long time. Compared with quartz, the other minerals in PM_{10} showed a difference. For example, clay minerals, the dominated phase in Beijing PM_{10}, could not be detected in Guiyang PM_{10}. It is possibly due to high vegetation coverage and humid climate, the soil dust contribution to airborne particles was relatively low. Sea-salt only appeared in marine atmosphere, such as in Qingdao and in South Wales PM_{10}. But in duststorm areas or duststorm reached area, such as Tel-Aviv and Beijing, mineral composition of PM_{10} seemed similar. Clay minerals, quartz, carbonates and feldspar were the main components.

Minerals in PM_{10} also reflected their origination. Kupiainen (Kupiainen *et al.*, 2003) testified that minerals, such as hornblende, biotite, muscovite, olivite, chlorite coming from the traction sand which used on the pavement aggregates.

2.4 Sulfurization on surface of mineral particles

Sulfurization on the surface of aerosol has been reported in recent years, especially on the formation of fine particles or wrapping the particle. Liu *et al* . (1994) reported that sulfates element could be found

Table 3 Minerals in PM_{10} identified by researchers by using SEM/EDX

No.	Area	Minerals	Literature
1	Beijing	Clay minerals, quartz, calcite, compound particulates, carbonates, gypsum, feldspar, dolomite, Fluorite, Apatite, Halite, Barite, chloridize zinc, ect.	This study
2	Beijing	Plagioclase, clay mineral, quartz, calcite, gypsum, Fe oxides, Ti oxides, aggregates of aluminosilicate	Shi *et al.*, 2005
3	Beijing	Clays, quartz, calcite, carbonates, aluminosilicate, chlorides, coxides, sulfates	Wang *et al.*, 1996
4	Guiyang	Silicomanganese, quartz, syngenite, calcium gypsum, sphalerite, dolomite, iron, sulfate	Xie *et al.*, 2005
5	Qingdao	Quartz, clays, feldspars, Na-rich particles (Na_2SO_4), K-S-rich particles (potassium sulfate), Ca-rich particles($CaCO_3$), Si-particles, Cr-particles(oxides), Fe-rich particles	Gao and Anderson, 2001
6	South Wales	Chlorides, sulphates (gypsum), silicates, ammonium sulphate, sea-salt, elemental and organic	Moreno *et al.*, 2004
7	Tel-Aviv	Silicates (clay, kaolinite), carbonates (dolomite, calcite), oxides (quartz, hematite), gypsum	Falkovich *et al.*, 2004
8	Finland	Quartz, k-feldspar, plagioclase, hornblende, biotite, muscovite, olivite($(Mg, Fe)_2SiO_4$), chlorite	Kupiainen *et al.*, 2004

on the surface of aerosol in marine atmosphere. This phenomena can be explained by two factors: one was particles coagulated with other parts or absorbed each other; another reason was that SO_2 had be absorbed on the surface of particles. However, sulfurization occurred on aerosol surface in the inland city air (Beijing is far away from marine area), it was reflected there existed a lot of atmospheric S elements, which implied serious air pollution in Beijing City.

Sulfurization can occur on the surface of carbonates and clay mineral particles, and even on quartz and silicates particle (Figs. 2 and 3). It always happened in summer, there the meteorological condition in Beijing is very different from Qingdao in winter reported by Liu *et al.* (1994). It meant mass concentration of SOx in Beijing atmosphere in summer was high enough for sulfurization to proceed.

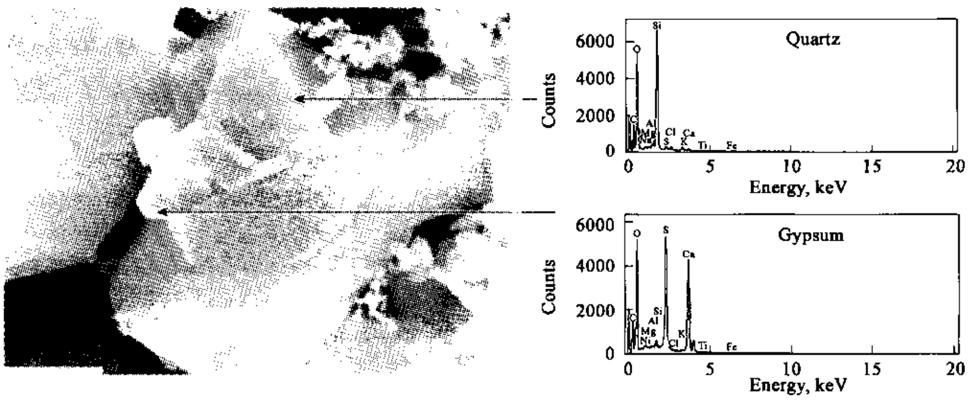

Fig.2 Sulfurization on quartz particles(secondary electronic image), scale bar 2 μm

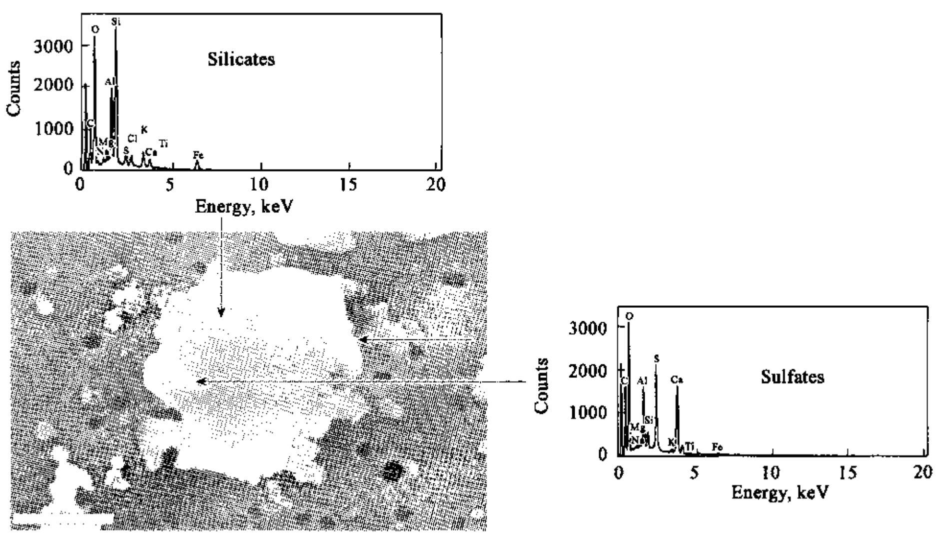

Fig.3 Sulfurization on sicilicates particles(secondary electronic image), scale bar 2 μm

3 Conclusions

SEM/EDX was proved to be an effective method for analysis of individual airborne particles. 38 kinds of minerals were identified, indicating that mineral components were very complex in Beijing PM_{10}. The Beijing PM_{10} mostly comprised clay minerals and quartz, with minor amounts of calcite, gypsum, feldspar, dolomite as well as unidentified species. Oxides, such as hematite, corundum, rutile and lead oxides, and halides represented by fluorite, halite and zinc chloride were also identified. Pyrite, zinc blende, apatite, barite and ilmenite were also found in Beijing PM_{10}. In clay minerals, I/S (illite/smectite mixed layers) was dominant components, reaching 35%, followed by illite, chlorite, C/S (chlorite/smectite mixed layers), smectite and kaolinite. Potassium feldspar and albite were dominant species in feldspar minerals, followed by anorthite and anorthoclase. Gypsum were main sulfates in PM_{10}.

Sulphur species were commonly seen on the surface of mineral particles, particularly in the summer collections. This suggested sulfurization occurred more frequently in summer than in other seasons, indicating extensive atmospheric reaction in Beijing air in summer.

Acknowledgments: The authors thank He Jinfa of Beijing Petroleum Exploitation Academe for giving direction in SEM/EDX analyses, and the reviewers for the helpful comments.

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(Received for review April 19, 2005. Accepted June 27, 2005)