

Single-particle Characterization of Aerosol Particles Collected Nearby a Lead Smelter in China

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ABSTRACT

China has been a top producer and exporter of refined lead products in the world since the year 2000. After the phasing-out of leaded gasoline in the late 1990s, non-ferrous metallurgy and coal combustion have been identified as potential major sources of aerosol lead in China. This paper presents the single particle analytical results of ambient aerosol particles collected near a lead smelter using a scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX). Aerosol particle samples were collected over a 24-hour period, starting from 8 pm on 31 May 2002, using a high volume TSP sampler. For this near source sample, 73 particles among 377 particles analyzed (accounting for 19.4%) were lead-containing particles mixed with other species (S, Cl, K, Ca, and/or C), which probably appeared to be from a nearby lead smelter. Lead-containing particles of less than 2 μm size in the near source sample were most frequently encountered with the relative abundances of 42%. SEM-EDX analysis of individual standard particles, such as PbO, PbS, PbSO₄, PbCl₂, and PbCO₃, was also performed to assist in the clear identification of lead-containing aerosol particles. Lead-containing particles were frequently associated with arsenic and zinc, indicating that the smelter had emitted those species during the non-ferrous metallurgical process. The frequently encountered particles following the lead-containing particles were mineral dust particles, such as aluminosilicates (denoted as AlSi), SiO₂, and CaCO₃. Nitrate- and sulfate-containing particles were encountered frequently in 2-4 μm size range, and existed mostly in the forms of Ca(NO₃,SO₄)/C, (Mg, Ca)SO₄/C, and AlSi+(NO₃,SO₄). Particles containing metals (e.g., Fe, Cu, and As) in this near source sample had relative abundances of approximately 10%. Although the airborne particles collected near the lead smelter contained elevated levels of lead, other types of particles, such as CaCO₃-containing, carbonaceous, metal-containing, nitrates, sulfates, and fly-ash par-

ticles, showed the unique signatures of samples influenced by emissions from the lead smelter.

Key words: Lead-containing particle, Low-Z particle EPMA, Single particle analysis, Lead smelter

1. INTRODUCTION

The main sources of airborne lead particles in the atmosphere can be divided into anthropogenic and natural sources. The reported anthropogenic sources include vehicle exhaust, coal combustion, metallurgical industry, cement industry, etc (Zhang *et al.*, 2009; Tan *et al.*, 2006; Wang *et al.*, 2000). The lead particles from these sources appeared predominantly in the fine fraction (Zhang *et al.*, 2009; Murphy *et al.*, 2007; Sun *et al.*, 2006; Tan *et al.*, 2006; Wang *et al.*, 2006). Fine particles can penetrate easily and be absorbed in the blood vessels of human lungs because of their small size and large surface area, respectively, possibly leading to a range of diseases (Nemmar *et al.*, 2010; Löndahl *et al.*, 2007; Donaldson *et al.*, 2001; Oberdorster, 2001; Schwartz, 2001; Seaton *et al.*, 1995). Lead can adversely affect the health of humans, particularly children, even at trace levels (Bowers and Beck, 2006; Papanikolaou *et al.*, 2005; Hilary, 2001; Winneke *et al.*, 1990; Fulton *et al.*, 1987; Yule *et al.*, 1981). Therefore, considerable effort has been made to reduce airborne lead particles around the world. The use of leaded gasoline has been banned in the United States and Europe since 1975 and mid-1980s, respectively, to control airborne lead particles from vehicle emission, which is one of the major sources of airborne lead particles (Zhang *et al.*, 2009). China, the top producer and exporter of refined lead products in the world since 2000 (<http://www.ila-lead.org>), has also banned the use of leaded gasoline in big cities, such as Beijing, Shanghai, and Guangzhou, since 1997. In Guangzhou, Wuhan, Lanzhou, and Chongqing, the lead concentrations in PM_{2.5} were reported to range from 476.4 to 635.9 ng/m³ in

1995 and 1996, which was before the phase-out of leaded gasoline (Hu and Wu, 1999). High levels of airborne lead, however, have still been reported in China. In 1999 and 2000, after the phase-out of leaded gasoline, the lead level was still high, more than 300 ng/m^3 in Beijing (He *et al.*, 2001). The mean Pb concentrations were also reported to be $100\text{--}300 \text{ ng/m}^3$ during 2000 and 2004 in Beijing (Sun *et al.*, 2006). These studies suggest that the lead level still remained high due to the presence of other sources, even though lead emission from vehicles has been reduced, which was pointed out in other studies (Widory *et al.*, 2010; Xiao *et al.*, 2008; Wang *et al.*, 2006).

Currently, the highest levels of lead in particulate matter (PM) is normally found near lead smelters (<http://www.epa.gov/oar/lead>), and lead refining smelters have been identified as one of the three major sources for airborne lead particles, along with aviation gasoline use and coal combustion in United States (Murphy *et al.*, 2007). In Jiyuan, Henan province, China, there are more than 30 lead refining smelters, one of which is the largest lead producer in Asia. These companies have produced lead for more than 50 years. Lead particles from these smelters might be responsible for the high level of airborne lead, resulting in an adverse health effect. For example, it was reported that the blood lead concentrations in approximately one third of children examined in 2009, who lived near lead smelters at Henan province, exceeded the lead poisoning standard ($100 \mu\text{g/L}$) according to the World Health Organization, with symptoms of lead poisoning (<http://news.sina.com.cn/c/2009-10-16/022518838893.shtml>). Airborne lead from lead smelters can be transported to other regions by the wind, possibly affecting people in wide range of areas. So it is imperative to elucidate the characteristics of aerosol particles near the smelter to determine the characteristics of aerosols emitted from a lead smelter. Bulk analysis, which provides only average composition of the particulate samples, may not be proper for the analysis of this type of samples because lead-containing particles are usually on trace level in the atmosphere. In this study, an airborne sample collected near the lead smelter was analyzed using a single particle analysis technique, named low-Z particle electron probe X-ray microanalysis (low-Z particle EPMA). Low-Z particle EPMA was also performed for individual standard particles, such as PbO, PbS, PbSO₄, PbCl₂, and PbCO₃, to help identify the lead-containing aerosol particles.

2. EXPERIMENTAL

2.1 Samples

The aerosol sample was collected near a lead smelter

located in Jiyuan, Henan province, China, which is one of the largest lead producers in Asia, over a 24-hour period starting from 8 pm on May 31, 2002, using a high volume TSP sampler. The population of Jiyuan is approximately 682,500 over $1,931 \text{ km}^2$ area, and there are more than 30 lead smelters. Sampling was carried out on the roof of a building, which was approximately 500 meters away from the smelter. During the sampling, the wind direction was from the smelter to the sampling place although the wind was not strong ($\sim 3\text{--}4 \text{ m/s}$). The sample is an ambient TSP sample in nature but appeared to have a high lead content. Therefore, it can be used as a near source sample. Hereafter, the particle sample collected near the lead smelter was designated a "near source sample". For single particle investigation using low-Z particle EPMA, aerosol particles were transferred on Ag foil (0.025 mm thickness, 99.95%, Goodfellow). Ag foil was simply rubbed over the surface of the sample collected by TSP sampler. Some particles adhering to the Ag foil by the electrostatic nature of the adhesive forces were analyzed.

Low-Z particle EPMA analysis was also carried out for individual standard particles, such as PbO (Aldrich, PN 211907, $\geq 99.9\%$), PbS (Aldrich, PN 372595, 99.9%), PbSO₄ (Aldrich, PN 307734, 98%), PbCl₂ (Aldrich, PN 268690, 98%), and PbCO₃ (Aldrich, PN 336378, $\geq 99.98\%$), to help identify the lead-containing aerosol particles. For single-particle investigation, micrometer sized standard particles were collected on Ag foil. Sampling was done in the same way as for the near source sample particles.

2.2 Low-Z Particle EPMA Single Particle Analysis

The elemental analyses were carried out using the JEOL JSM-6390 scanning electron microscope equipped with an Oxford Link SATW ultrathin window EDX detector with a resolution of 133 eV for Mn-K α X-rays. The X-ray spectra were recorded under the control of INCA Oxford software (Oxford Instruments Analytical Ltd, INCA suite version 4.09). A 20 kV accelerating voltage and a beam current of 0.5 nA were used for all measurements. A typical measuring time of 15 s was used to obtain sufficient counts in the X-ray spectra while limiting the beam damage effects on sensitive particles. A more detailed discussion on the measurement conditions was reported elsewhere (Ro *et al.*, 1999). X-ray data acquisition for individual particles was carried out manually in point analysis mode, where the electron beam was focused at the center of each particle. The X-rays were acquired while the beam remained fixed on this single spot. Overall, 377 particles for the near source sample were analyzed.

The net X-ray intensities for the elements were

obtained using a non-linear least-squares fitting of the collected spectra using the AXIL program (Vekemans *et al.*, 1994). The elemental concentrations of the individual particles were determined from their X-ray intensities using a Monte Carlo calculation combined with reverse successive approximations (Ro *et al.*, 2003, 2001). The quantification procedure provided accurate results within the 12% relative deviations between the calculated and nominal elemental concentrations when the method was applied to a range of standard particles, such as NaCl, Al₂O₃, CaSO₄ · 2H₂O, Fe₂O₃, CaCO₃, and KNO₃ (Ro *et al.*, 2004, 2003, 2000). Low-Z particle EPMA can provide quantitative information on the chemical composition, and particles can be classified based on their chemical species.

3. RESULTS AND DISCUSSION

3.1 Lead-containing Standard Particles

Individual standard particles of PbO, PbS, PbSO₄, PbCl₂, and PbCO₃ were investigated by low-Z particle EPMA to assist in the clear identification of lead-containing particles. In particular, differentiation of the Pb M X-ray and S K X-ray lines was a major concern because their respective energies (2.342 and 2.307 keV, respectively) were too close to distinguish using an EDX detector. In addition, airborne lead particles can exist as a variety of sulfur-containing species, such as PbSO₄, PbS, PbSO₄ · PbO, etc (Choël *et al.*, 2006; Tan *et al.*, 2006; Batonneau *et al.*, 2004; Sobanska *et al.*, 1999). On the other hand, the accurate curve fitting of the AXIL program for the Pb M-line and S K-line X-ray peaks could be performed based on the different peak shapes of Pb M and S K X-rays.

For each standard powder sample, 20-25 particles were analyzed. Table 1 lists the mean diameter and

elemental concentrations of the standard particles. The sizes of analyzed particles ranged from 0.97 to 11.97 μm, where particles are mostly in the 2-6 μm size range. As shown in Table 1, the atomic concentrations of the standard particles are close to their stoichiometries, i.e. [Pb] : [O]=1 : 1.34 for PbO, [Pb] : [C] : [O]=1 : 1.29 : 3.40 for PbCO₃, [Pb] : [S]=1 : 1.07 for PbS, [Pb] : [S] : [O]=1 : 0.93 : 3.92 for PbSO₄, and [Pb] : [Cl]=1 : 2.30 for PbCl₂. For the PbCl₂ standard particles, the atomic concentration of chlorine was higher than their stoichiometry because overlap of the Ag L X-ray line of the collecting substrate with Cl K X-ray line resulted in an inaccurate estimation of the Cl K-line intensity. Good results for PbS and PbSO₄ standard particles clearly demonstrate that an accurate resolution of the Pb M-line and S K-line X-ray peaks had been achieved. On the other hand, all Pb-containing standard particles contained significant amounts of carbon, particularly PbO and PbCl₂, which had carbon contents of 16.6 and 20.1 at.%, respectively. This appears to result from the carbonation at the particle surface by CO₂ in the air and/or the absorption of carbonaceous species. Surface oxidation also appears to be significant for PbO and PbS, which had oxygen contents of 49.7 and 47.3%, respectively. Those carbon and oxygen species were probably entrained on the active surface of the particles when they were exposed to air and/or were ground using a mortar and pestle. Based on an analysis of standard Pb-containing particles, it is clear that the Pb M-line and S K-line X-ray peaks can be resolved by applying a non-linear least-squares fitting using the AXIL program, and significant levels of surface carbonation and oxidation will make the speciation of Pb-containing aerosol particles somewhat difficult.

3.2 Near Source Sample

Fig. 1 shows typical secondary electron images (SEIs)

Table 1. Elemental atomic concentrations and average diameters of standard lead-containing particles.

Particle type	Number of particles analyzed	Average elemental concentration (at. %)			Average diameter (μm)	
		Pb	O	C		
PbO (Aldrich, PN 211907, ≥99.9%)	20	Pb	O	C	4.05	
		37.0±6.0	49.7±5.3	16.6±4.8		
PbCO ₃ (Aldrich, PN 336378, 99.98%)	20	Pb	O	C	2.62	
		17.6±3.6	59.8±4.5	22.6±2.7		
PbS (Aldrich, PN 372595, 99.9%)	25	Pb	S	O	C	3.75
		23.4±5.3	25.1±7.0	47.3±14.6	5.9±4.5	
PbSO ₄ (Aldrich, PN 307734, 98%)	25	Pb	S	O	C	2.06
		16.5±2.3	15.4±3.3	64.6±4.8	4.6±3.3	
PbCl ₂ (Aldrich, PN 268690, 98%)	20	Pb	Cl	C	6.24	
		25.1±3.7	57.8±6.3	20.1±5.2		

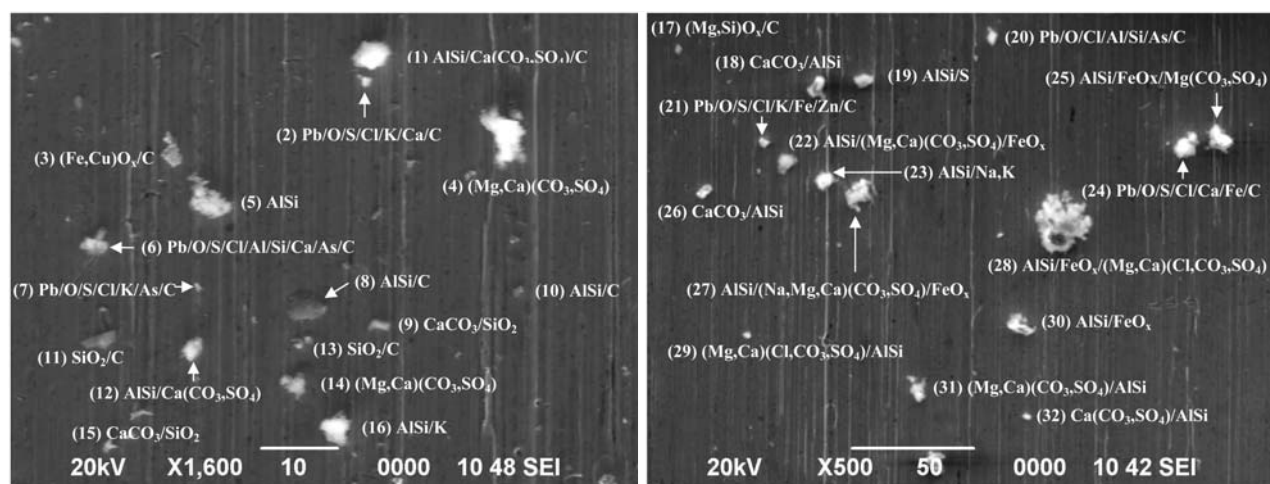


Fig. 1. Exemplar secondary electron images of aerosol sample collected near a lead smelter.

of the near source sample, where the chemical species of each particle is noted together with its particle number. Low-Z particle EPMA can provide quantitative information on the chemical composition, and particles can be classified based on their chemical species. First, a particle was regarded as being composed of a single chemical species when this species constituted at least 90 at.%. Second, the chemical species were specified even for particles mixed internally with two or more chemical species. Third, as energy dispersive EPMA has high detection limits of 0.1-1.0% in weight, due mainly to its high Bremsstrahlung background level, the elements at trace levels could not be investigated reliably. Accordingly, elements with concentrations < 1.0 at.% were not included in the procedure for chemical speciation (Ro *et al.*, 2000). A unique denotation method was devised to represent the chemical species of internal mixture particles. For example, particle #4 in Fig. 1, which is an internal mixture of the cations, Mg^{2+} and Ca^{2+} , and anions, CO_3^{2-} and SO_4^{2-} , is denoted as “(Mg,Ca)(CO₃,SO₄)”. For particle #1 in Fig. 1, its chemical species was determined to be an internal mixture of aluminosilicate (“AlSi”), Ca(CO₃,SO₄), and carbonaceous species, and the particle is denoted as “AlSi/Ca(CO₃,SO₄)/C”.

As shown in the SEIs, particles commonly encountered in the near source sample are mineral dust particles, aged aerosols reacted with NO_x and SO_x, and metal-containing particles, such as Pb, As, Fe, and Cu. Among the metal-containing particles, Pb- and As-containing particles were assigned when their metal concentrations were > 1 at.% because the ambient levels of those Pb and As metals are quite low. Most particles in the near source sample were mixed with two or more species. Table 2 lists the particle types determined

based on their chemical species and morphology, and their encountering frequencies at different particle size bins. For a total of 377 particles analyzed, 15 particle types were classified as carbonaceous particles, such as carbon-rich and organic; mineral dust particles such as aluminosilicates, AlSi/misc, SiO₂, CaCO₃, CaCO₃/misc, and (Mg,Ca)CO₃; aged aerosol particles, such as reacted CaCO₃ and (Mg,Ca)SO₄/C; Fe-, Cu-, As-, and Pb-containing particles; and fly ash. Pb-containing particles were most abundant in the near source sample. AlSi/misc, SiO₂, reacted CaCO₃, (Mg,Ca)SO₄/C, and AlSi+(N,S) were also encountered frequently.

The smallest equivalent diameter of the analyzed particles was 0.32 μm with the largest being 19.61 μm, where the equivalent diameter was calculated by assuming that a particle with the same area for a particle on the SEI was circular. All particles were < 20 μm in size with most being within 1-4 μm. Particles, 1-2 μm in size, were the most abundant with a 30.0% encountering frequency. Particles, 2-3 μm and 3-4 μm in size, had encountering frequencies of 23.6% and 21.2%, respectively. A similar observation on the size distribution of particles collected in the vicinity of a lead smelter in France was also reported (Choël *et al.*, 2006). Metal-containing particles, such as Fe, Cu, As, and Pb, were also encountered frequently in the size range of < 4 μm, most of the aged aerosol particles were 2-4 μm in size, and mineral dust particles were somewhat evenly distributed.

3.2.1 Lead-containing Particles

In our previous single-particle characterization of various ambient aerosol particle samples, it is quite rare to encounter lead-containing particles because the ambient level of lead-containing particles was quite low

Table 2. Particle types based on their chemical species and morphology and their encountering frequencies in the near source sample.

Particle types	Particle size bins										Sum
	$\leq 1 \mu\text{m}$	1-2 μm	2-3 μm	3-4 μm	4-5 μm	5-6 μm	6-7 μm	7-8 μm	8-10 μm	$> 10 \mu\text{m}$	
Carbonaceous		6	2	4		1					13
AlSi	1	3	3	3	6	1		1			18
AlSi/misc.	1	7	8	7	1	1	2	1	3		31
SiO ₂	1	11	6	5	3	2	1				29
CaCO ₃	1	11	6	5		1					24
CaCO ₃ /misc.		8	3	7	4	2	1	1	1	1	28
(Mg,Ca)CO ₃		1	2		1	2	1				7
Reacted CaCO ₃		6	6	8	2	3	2	1			29
(Mg,Ca)SO ₄ /C		9	9	12	4	2	2		1	1	40
AlSi+(N,S)		9	16	8	1	1	1		3		39
Fe species		4	8	4	1		1	1		1	20
Cu species		5	2	1							8
As species	3	2	1	1	1	1		1			10
Pb species	4	27	16	14	5	1	1	2	1	2	73
Fly ash		3	1	1							5
Others	2	1									3
Sum	13	113	89	80	29	18	12	8	9	6	377

compared to those of other types of particles, such as mineral dust, sea-salt, carbonaceous particles, bioaerosols, inorganic salts, etc (Geng *et al.*, 2011, 2010, 2009; Maskey *et al.*, 2011; Kim and Ro, 2010; Kim *et al.*, 2010). On the other hand, lead-containing particles were encountered most frequently with relative abundances of 19.4% (73 among 377 particles) in the near source sample as the sample was collected near the lead smelter. Other studies on particle samples collected nearby and/or at lead smelters also reported high levels of lead-containing particles (Zhang *et al.*, 2009; Murphy *et al.*, 2007; Choël *et al.*, 2006). As mentioned above, lead-containing particles originating from anthropogenic sources appeared mainly in the fine fraction (Zhang *et al.*, 2009; Murphy *et al.*, 2007; Sun *et al.*, 2006; Tan *et al.*, 2006; Wang *et al.*, 2006). Lead-containing particles, less than 2 μm in size, in the near source sample were encountered most frequently with relative abundances of 42%. Particles, 2-3 μm and 3-4 μm in sizes, had relative abundances of 22% and 19%, respectively, indicating that lead-containing particles collected near the lead smelter were distributed mostly in the fine fraction (see Table 2).

Figs. 2-7 show secondary electron images (SEIs), X-ray spectra, and elemental atomic concentration data of some typical Pb-containing particles encountered in the near smelter sample. Fig. 2(a) shows a SEI of a coagulated particle where the left-part and right-part of the particle composed of Pb, Zn, S, Cl, K, C, and O (Fig. 2(b)) and Al, Si, S, Cl, C, and O (Fig. 2(c)), respectively. As shown in Fig. 2(a), the atomic concentrations of Pb and Zn of the left-part

were high (10.7% and 6.6%, respectively), confirming that the major species are Pb and Zn species. On the other hand, significant amounts of C, S, Cl, and K were also observed in the left-part. An analysis of Pb-containing standard particles showed that Pb species can be carbonated and/or oxidized easily. Moreover, it is somewhat difficult to identify Pb-species based on the elemental concentrations, even though this particle might contain PbS, PbSO₄, PbCl₂, and/or PbO. The right-part particle is mainly aluminosilicate mixed with minor component of S and Cl. The main source of aluminosilicates is the soil, but sometimes aluminosilicates can be generated as fly-ash during the high temperature combustion process (note its somewhat spherical morphology, which is characteristic of fly-ash particles.). In addition, it is quite rare for airborne aluminosilicate particles of a soil origin to contain minor S and Cl species together. Therefore, this right-part particle appears to have been emitted from the same source as the left-part particle, i.e. the lead smelter, and coagulated with the left-part particle during the emission process.

Fig. 3(a) shows a SEI of a Pb-containing particle, whose size is quite large (its equivalent diameter is $\sim 5 \mu\text{m}$) and irregular, and which appears to be agglomerated with nano-size particles and chemically heterogeneous. The particle is composed mainly of major C and O with minor Si, S, and Cl (see Fig. 3(b)). In Fig. 3(c), a fraction of the particle, which appears to contain embedded nano-size particles, contained Pb, S, Cl, K, C, O, Al, and Si elements with major C and O. Fig. 4(a) shows another type of mixture particles, which is

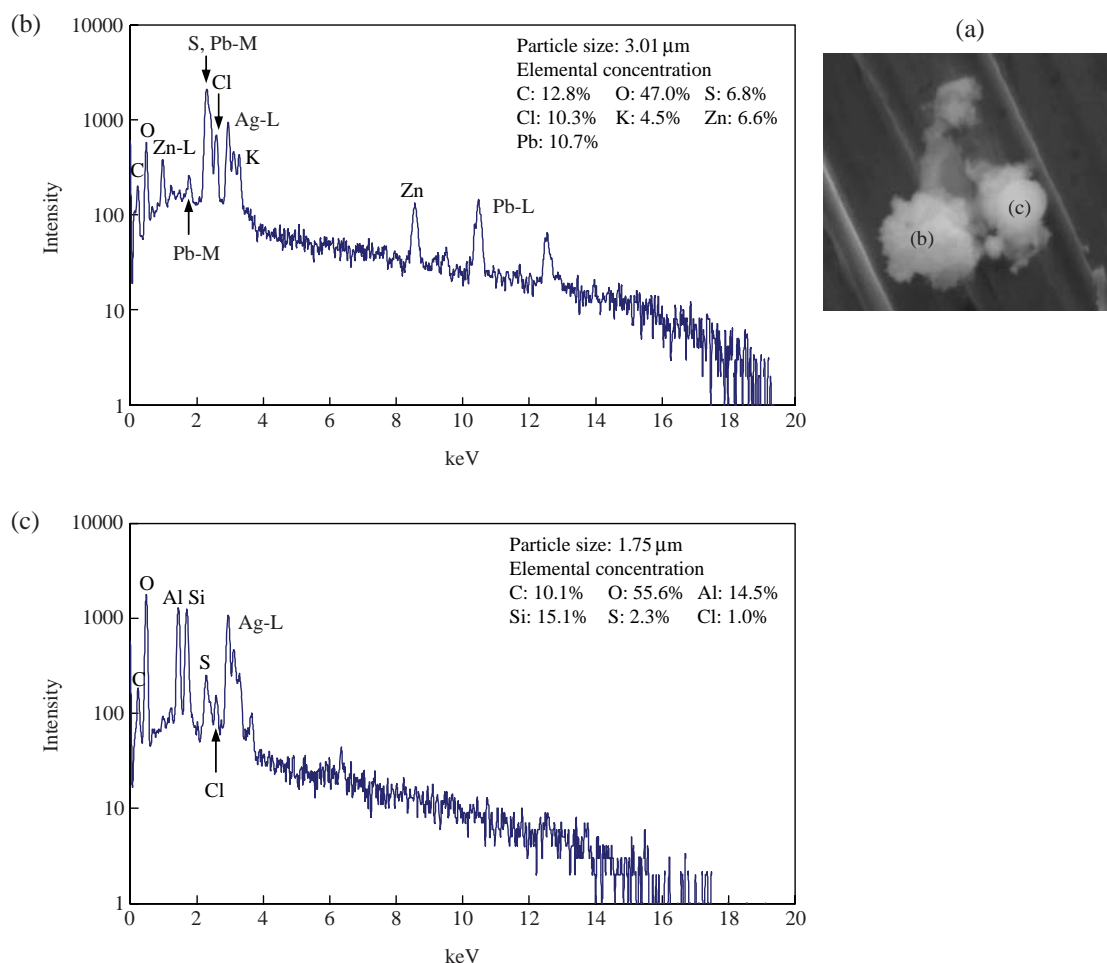


Fig. 2. Secondary electron image, X-ray spectra, and elemental atomic concentrations of a Pb-containing particle.

a micrometer-size particle ((b) in Fig. 4(a)) containing embedded nano-size particles appearing brighter in their SEI (see a nano-size particle notated as (c) in Fig. 4(a)). This particle was also composed of major C and O with minor S and Cl (Fig. 4(b)), and nano-size particles were composed of major C and O with minor Pb, S, and Cl, indicating that Pb-containing particles were embedded in other types of particles during the emission process. The particles shown in Figs. 2-4 appear irregular, and are composed mainly of C and O with minor Pb, S, Cl, K, Al and/or Si in atomic fraction. Most Pb-containing particles were mixed internally with other chemical species, either by coagulation or embedding. Although the particles were collected near the lead smelter, the Pb atomic concentrations of the Pb-containing particles were not that high (mostly less than 5%). On the other hand, the mass concentrations would be much higher for Pb because the atomic weight of Pb is much larger than those of the other elements.

The SEIs shown in Figs. 5 and 6 indicate that the Pb-containing particles were generated by a high temperature combustion process, as recognized by their spherical morphology. They are composed of Pb/Zn/K/Cl/Si/Al/O/C and Pb/Cl/S/O/C, respectively, with a Pb content of > 10 atomic %. The particle shown in Fig. 7 is lead-rich containing a high lead content throughout the entire particle despite its large size of approximately 12 μm . Particles were considered “lead-rich” particles when the lead content was > 10 at.%. Other studies reported that those lead-rich particles tend to be smaller than the other Pb-containing particles, suggesting that Pb-containing particles could be aged from lead-rich particles after being mixed with other species (Zhang *et al.*, 2009; Murphy *et al.*, 2007; Choël *et al.*, 2006). On the other hand, many of the lead-rich particles were large in the present study, suggesting that this near smelter sample contains many fresh lead-rich particles due to the short distance of the sampling site from the lead smelter.

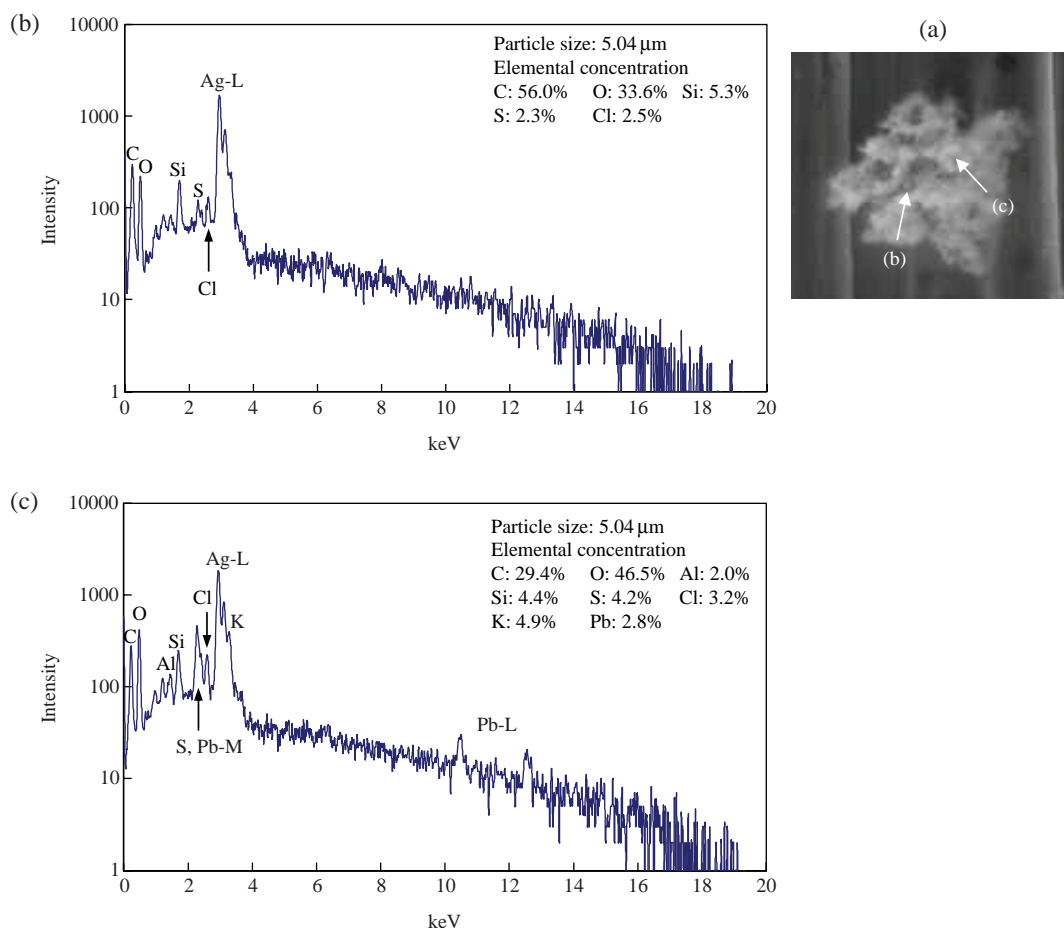


Fig. 3. Secondary electron image, X-ray spectra, and elemental atomic concentrations of a Pb-containing particle.

As shown for the above exemplar Pb-containing particles, the elemental lead concentration data obtained by low-Z particle EPMA were not sufficient to clearly identify the Pb chemical species because there are many other chemical species in the Pb-containing particles. Therefore, Pb-containing particles were classified according to the chemical elements detected, which are listed in Table 3. Among the various lead-containing particle types, Pb/O/S/Cl/K/Ca/C/misc and Pb/O/S/Cl/K/C/misc types were encountered often. Sulfur was detected in 88% of the Pb-containing particles, which can be from natural soil minerals, such as anglesite (PbSO_4) and galena (PbS) (Zhang *et al.*, 2009; Tan *et al.*, 2006; Greenwood and Earnshaw, 1984). On the other hand, sulfur can be entrained in Pb-containing particles as sulfates, which were formed by the oxidation of SO_2 generated in the refining process of lead smelters, which is more probable for this sample collected near the lead smelter (Li *et al.*, 2003; Sobanska *et al.*, 1999). In addition, Pb-particles containing chlorine were encountered with an encountering frequency

of 85%. This suggests that the chlorine species can exist as PbCl_2 , which has been reported to be generated by a reaction of HCl and Pb during the combustion process (Zhang *et al.*, 2009; Green berg *et al.*, 1978). C, K, Ca, As, Fe, and Zn were observed frequently in Pb-containing particles, which might be entrained during the lead refining process of Pb ore, even though their entrainment processes were unclear.

Several studies on the chemical species of airborne lead-containing particles have been carried out at various sites around the world. Lead species observed in samples collected at lead smelters in France were reported to be mainly PbSO_4 , with other PbS , $\text{PbSO}_4 \cdot \text{PbO}$, and Pb metal species, as determined by micro-Raman spectrometry (Choël *et al.*, 2006; Batonneau *et al.*, 2004; Sobanska *et al.*, 1999). The airborne lead-containing particles collected in Shanghai (China) were mainly PbCl_2 , PbSO_4 , and PbO (Tan *et al.*, 2006). In Manchester, the major lead species collected in road dust sediments were reported to be PbCrO_4 , Pb-sorbed goethite, PbO, PbCl_2 , and Pb carbonates (Barrett *et al.*,

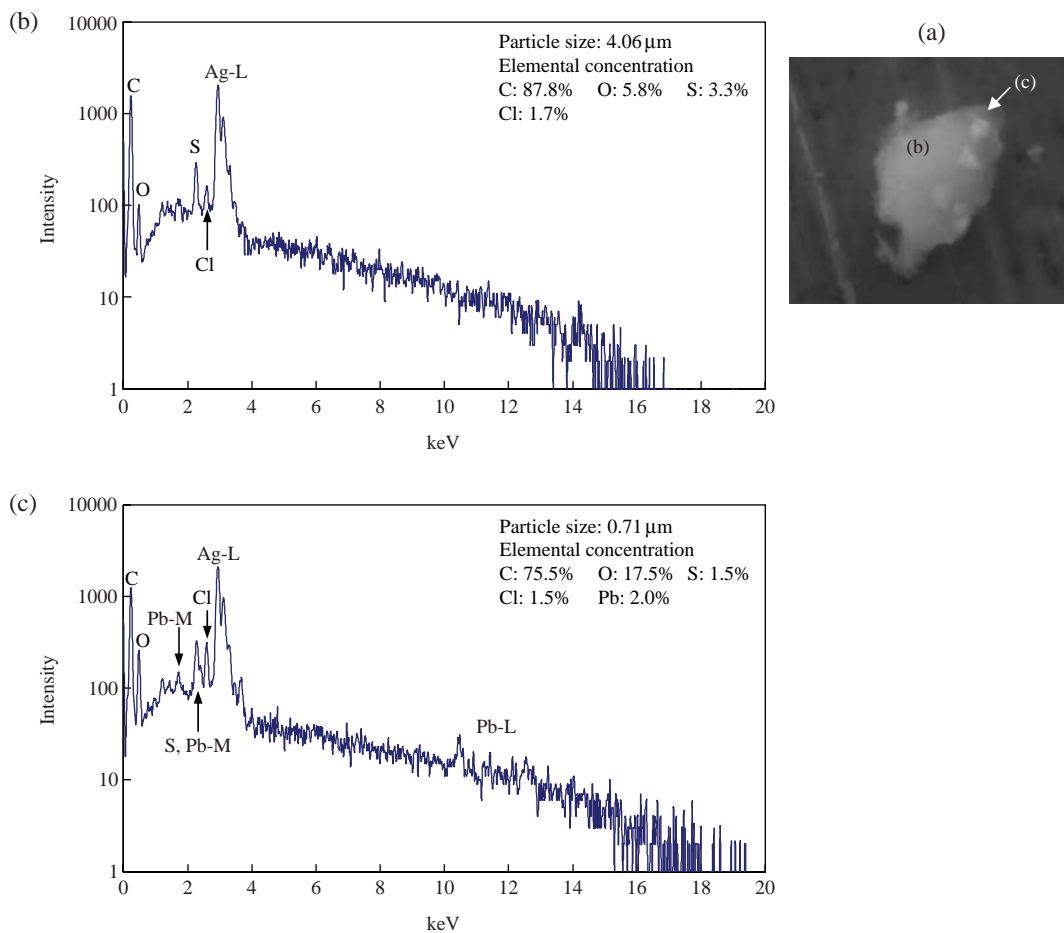


Fig. 4. Secondary electron image, X-ray spectra, and elemental atomic concentrations of a Pb-containing particle.

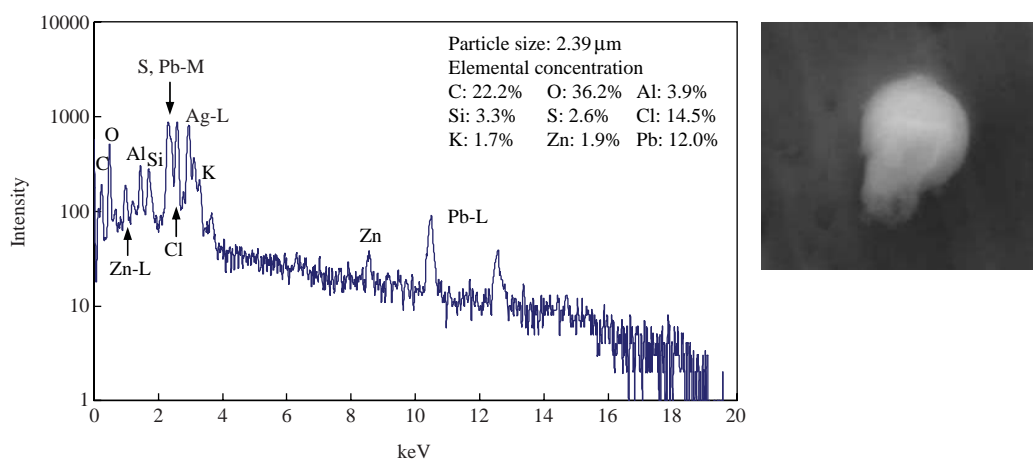


Fig. 5. Secondary electron image, X-ray spectrum, and elemental atomic concentrations of a Pb-containing particle.

2010). Ishizaka *et al.* (2009) reported that PbO , PbSO_4 , PbCl_2 , and PbCO_3 particles were observed in the samples collected in Korea and Japan during Asian dust

storm events and PbCO_3 particles can be generated by a reaction of CaCO_3 and PbSO_4 in the aqueous phase. Although previous studies reported that airborne Pb-

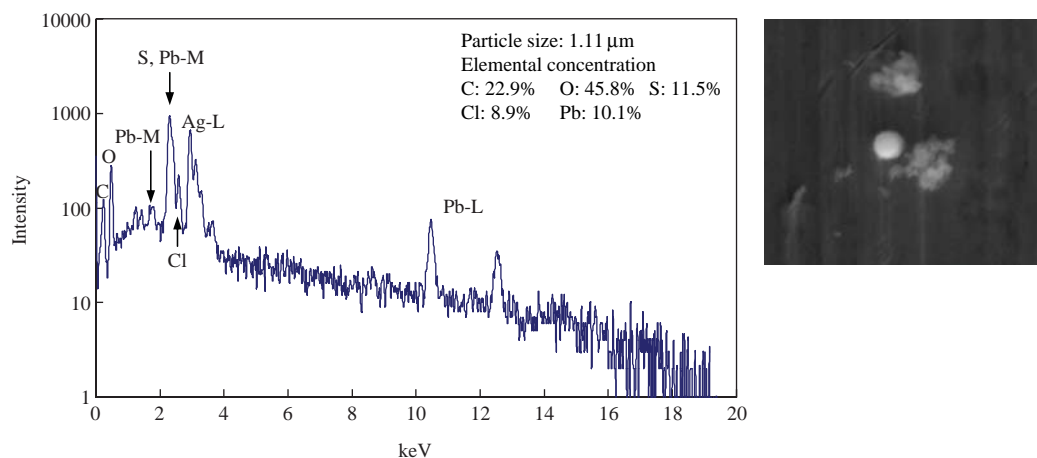


Fig. 6. Secondary electron image, X-ray spectrum, and elemental atomic concentrations of a Pb-containing particle.

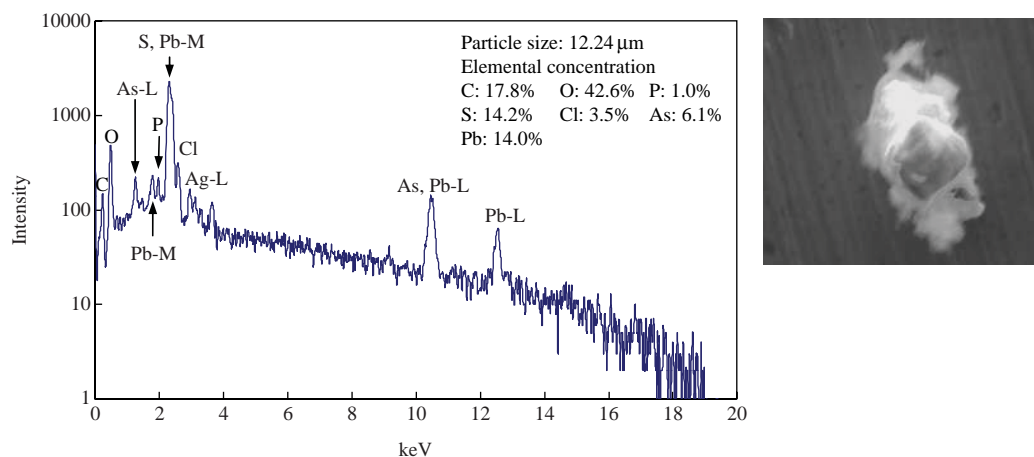


Fig. 7. Secondary electron image, X-ray spectrum, and elemental atomic concentrations of a Pb-containing particle.

containing particles were mainly PbSO_4 , PbS , PbO , PbCl_2 , and PbCO_3 , the chemical speciation of the Pb-containing particles is somewhat difficult, according to low-Z particle EPMA. On the other hand, it is clear that the Pb-containing particles are complicated mixtures containing a range of chemical species including C, S, Cl, Ca, K, Zn, As, and/or Fe.

3.2.2 Mineral Dust Particles

A range of mineral dust particles were encountered in the near source sample. The number of CaCO_3 -containing particles, such as CaCO_3 , $\text{CaCO}_3/\text{misc}$, and $(\text{Mg,Ca})\text{CO}_3$, was 59 among a total of 377 particles analyzed, which are the most abundant minerals with a relative abundance of 15.6%. This was followed by AlSi-containing and SiO_2 particles with relative abundances of 13.0% and 7.7%, respectively (Table 2). Aluminosilicate particles can exist as a variety of min-

erals, such as feldspar, montmorillonite, muscovite, kaolinite, etc (Jung *et al.*, 2010). On the other hand, the specific mineralogy of aluminosilicate particles cannot be performed unambiguously based only on their X-ray spectral data. Accordingly, aluminosilicate particles are just classified as "AlSi" particles. When aluminosilicate particles are mixed with other chemical components, they are classified as AlSi/misc.

These CaCO_3 -containing and AlSi-containing particles are generally considered to be of a soil origin and particles of soil origin are generally large. On the other hand, CaCO_3 -containing and SiO_2 particles in a size of 1-2 μm were the most abundant (Table 2), which are relatively small for them to be sourced only from the soil. In addition, the more abundant observation of CaCO_3 -containing particles than aluminosilicates suggests that CaCO_3 -containing particles are from sources other than soil because the content of alumin-

Table 3. Different types of Pb-containing particles and their encountering frequencies.

Chemical species	Number of particles	Chemical species	Number of particles
Pb/S/Cl	1	Pb/O/S/Cl/Ca/As/C	3
Pb/O/S	2	Pb/O/S/Cl/Ca/As/C/misc	1
Pb/O/S/C	4	Pb/O/S/Cl/As/C	2
Pb/O/S/Cl	1	Pb/O/S/Cl/As/Zn/C	2
Pb/O/S/Cl/C	5	Pb/O/S/K/Ca/C/misc	1
Pb/O/S/Cl/K/C/misc	7	Pb/O/C/misc	1
Pb/O/S/Cl/K/Ca/C/misc	8	Pb/O/Fe	1
Pb/O/S/Cl/K/Ca/Fe/C/misc	5	Pb/O/Ca/Fe	1
Pb/O/S/Cl/K/Ca/As/C	6	Pb/O/Cl/Fe/C	1
Pb/O/S/Cl/K/Ca/As/C/misc	6	Pb/O/Cl/K/Zn/C/misc	1
Pb/O/S/Cl/K/Ca/As/Fe/C/misc	1	Pb/O/As/C/misc	1
Pb/O/S/Cl/K/As/C/misc	3	Pb/O/Cl/As	1
Pb/O/S/Cl/K/Zn/C	2	Pb/O/Cl/Ca/As/C	1
Pb/O/S/Cl/K/Zn/Fe/C	1	Pb/O/Cl/K/Ca/As/C/misc	1
Pb/O/S/Cl/Ca/C/misc	3	Total	73

silicate minerals is much higher than that of CaCO_3 minerals. SiO_2 , CaCO_3 , and Fe_2O_3 are added during an ore grilling process, which is one of the pyro-metallurgical processes performed in lead smelters, to obtain a high yield (Sobanske *et al.*, 1999). This can be related to the present observations, such that some Pb-containing particles contain Ca and/or Fe (Table 3). Several studies also reported that the relatively small size CaCO_3 particles can be generated from incineration (Hwang and Ro, 2006; Fermo *et al.*, 2000; Speiser *et al.*, 2000).

3.2.3 Nitrate and/or Sulfate Particles

Sulfate and/or nitrate particles (mostly sulfates) were also encountered in the near source samples. The overall relative abundance of these sulfate and/or nitrate particles was 28.6%, and were mainly mineral dust particles that reacted with nitrate and sulfate, such as reacted CaCO_3 , $(\text{Mg,Ca})\text{SO}_4/\text{C}$, and $\text{AlSi}+(\text{N,S})$ (Table 2). Nitrate and/or sulfate particles are the most abundant in the 2-4 μm size range. As mentioned above, these sulfate particles are most likely the result of SO_2 oxidation in the refining process of a lead smelter (Li *et al.*, 2003; Sobanska *et al.*, 1999).

3.2.4 Metal-containing Particles

In the near source sample, metal-containing particles were encountered frequently. As stated above, the most common species were lead-containing particles with a relative abundance of 19.3%. Iron, arsenic and copper-containing particles were also encountered with relative abundances of 5.3%, 2.7%, and 2.1%, respectively. These metal-containing particles normally appeared irregular. Their size was mostly smaller than 4 μm with particles < 2 μm in size comprising a considerable proportion. Although Zn species are not listed in Table 2 as a chemical type, the Zn component was also observed in some of lead-containing particles (Table 3). Iron-containing particles, which are generated

by soil dust, industrial operations, exhaust from combustion engines, etc (Zhang *et al.*, 2009; Flament *et al.*, 2008; Seinfeld, 1986), were next in abundance to lead-containing particles. On the other hand, Fe-containing particles may be from the Fe_2O_3 added for a higher yield during the ore grilling process. The relative abundance of arsenic and copper containing particles was quite low (< 5%), but much higher than those in ambient aerosol samples (Geng *et al.*, 2010, 2009; Kim and Ro, 2010; Kim *et al.*, 2010), which were reported to be detected normally in non-ferrous metallurgical emission (Mattielli *et al.*, 2009; Choël *et al.*, 2006; Batonneau *et al.*, 2004; Sobanska *et al.*, 1999). These various metal components appear to be unique signatures of the particles collected near a lead smelter that are generated during the smelting process of lead. On average, refined ores were reported to contain 60-75% lead (PbS), 3-10% zinc (ZnS), and 0.5-1% copper (CuS) with Bi, Cd, Sb, As and Sn at trace levels (< 0.3%) (Sobanska *et al.*, 1999).

3.2.5 Fly-ash Particles

As the smelting process is a typical industrial combustion process, spherical fly-ash particles generated in a high-temperature process were observed in the near source sample with a distribution of approximately 5%. Fly-ash particles are easily distinguishable on their SEIs due to their spherical morphology. As they were generated during combustion, their size was relatively small, mostly < 4 μm , and the major chemical components were aluminosilicates mixed with a small amount of Ca, Fe, and C. Some of the fly ash particles contained lead.

3.2.6 Carbonaceous Particles

The speciation of carbonaceous particles based on their X-ray spectral data is difficult because EPMA cannot detect hydrogen. On the other hand, the parti-

cles are identified as carbonaceous particles when the sum of the C and O contents of particles in the atomic fraction is $>90\%$. Among the carbonaceous particles, carbon-rich particles are differentiated from organic particles when their carbon content is 3-times higher than the oxygen content (Ro *et al.*, 2000). Among the carbonaceous particles, carbon-rich particles, which are mostly $<4\ \mu\text{m}$ in size, are encountered more frequently than organic particles. These carbon-rich particles were reported to be generated by a range of combustion processes (Geng *et al.*, 2010; Zhang *et al.*, 2009; Wang *et al.*, 2006). Although their distribution is approximately 3% in the near source sample, most particles, regardless of their major chemical species, were mixed with a considerable amount of C and O, which also suggests that carbonaceous species were generated during the combustion process.

4. CONCLUSIONS

The chemical compositions and size distributions of airborne aerosol particles collected near a lead smelter were analyzed by low-Z particle EPMA. Individual standard particles, such as PbO, PbS, PbSO₄, PbCl₂, and PbCO₃, were examined to help identify the lead-containing aerosol particles. An examination of PbS and PbSO₄ standard particles confirmed that low-Z particle EPMA can separate the Pb M-line and S K-line, resulting in a good estimation of the elemental concentrations of S and Pb. For the near smelter sample, lead-containing particles were observed most abundantly with a relative abundance of 19.4%. This means that airborne particles around lead smelters were affected by the emissions from the lead smelter. Lead-containing particles were mixed frequently with other species (S, Cl, K, Ca, and/or C) as well as As, Fe, and Zn. CaCO₃-containing, carbonaceous, metal-containing, nitrates, sulfates and fly-ash particles are also believed to have been influenced by lead smelters, where these particles were abundant in the fine fraction. Although airborne particles collected near the lead smelter contain elevated lead levels, the other type of particles, such as CaCO₃-containing, carbonaceous, metal-containing, nitrates, sulfates, and fly-ash particles, were found to be unique signatures for a sample influenced by the emissions from lead smelters.

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