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Characterisation of aerosol from Santiago, Chile: an integrated PIXE–SEM–EDX study

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Abstract Santiago de Chile is a big city with huge air quality problems, being one of the most polluted cities in the world. This is aggravated during winter by the topography and meteorological conditions of the city. Although public policies have been developed to minimise the atmospheric aerosol pollution, there is a lack of adequate knowledge and poor characterisation of these aerosols (in its $PM_{2.5}$ and PM_{10} fractions). In this study we sampled atmospheric particles during winter in two distinct areas of Santiago: downtown (Teatinos Street) and in a more residential area (Macul). Major (Si, Al, Fe, Ca and K) and some trace element (S, Cl, Ti, P, Cr, Cu and Zn) compositions were obtained by proton-induced X-ray emission (PIXE). Morphological, type and chemical characterisation was also performed using scanning electron microscopy (SEM) coupled with an energy dispersive X-ray microanalysis system (SEM–EDX). Besides the carbon particles, the contribution of which can be quite important in the atmospheric aerosol, especially in downtown, unambiguously lithogenic (i.e. of geological origin) particles and elements are the second highest contributors. Enrichment factor calculation, together with particle identification and element correlation allow the origin of some elements and particles to be traced, revealing anthropogenic origins for some of them that are specific to the Santiago area.

Keywords Atmospheric aerosol · Particle analysis · Mineralogy · Geochemistry · Environmental pollution

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Introduction

All mega and big cities in the world suffer from heavy atmospheric pollution, both from more or less toxical gases (NO, CO, O_3, etc.) and from very small solid particles inhaled by humans. This has become a major health issue and most megacities are now developing survey programs in order to identify these pollutants with the aim, of first, being able to forecast pollution peaks and ultimately, to attempt to reduce their amount. Recent research has shown a clear connection between high levels of atmospheric particles and adverse effects on human health (see references in Moreno et al. 2003, 2004b, Yadav and Rajamani 2004, among others). Therefore it becomes very important to characterise solid aerosols as best as possible, both mineralogically and chemically and to determine their sources.

The inhalable particulate matter suspended in the atmosphere is heterogeneous in size, composition and origin. Typically, any sample collected in a city with a

problem of particulate matter pollution would contain different types of salts (mostly ammonium and calcium sulphates, ammonium nitrates, sodium chlorides) organic and elemental carbon (mainly derived from road traffic), biological components (pollen and micro-organisms), iron and other metal compounds derived from industrial processes, and minerals and rocks fragments derived from the surrounding geological formations. They can be defined as: organic and/or inorganic, natural (biological/geological) and/or anthropogenic, and primary and/or secondary. This diversity makes it difficult to identify pollutant sources as well as to model the particulate matter distribution in relation to meteorological parameters. Because of this diversity, estimation of the mass alone of the particle matter and its carbon content provides insufficient information about its origins and its potential health effects (Moreno et al. 2004a).

Typical geological analytical techniques for the identification of mineral phases and their chemical characterisation (e.g. scanning electron microscopy (SEM) coupled with microanalysis, X-ray diffraction and chemical analyses) have been recently applied in order to trace the origin of particulate matter in the atmosphere (e.g. Kasparian et al. 1998; Boix et al. 2001; Moreno et al. 2003, 2004a, b, c, 2005; Celis et al. 2004; Kruger et al. 2004; Yadav and Rajamani 2004; Suzuki 2006, etc) and provide valuable information both for scientists tracing the sources of these aerosols and for civil servants in charge of pollution reduction.

Santiago is one of the most polluted cities in the world, which is aggravated during winter by the topography and meteorological conditions of the city. Previous studies of particulate matter in the air of Santiago have been focussed on the application of optical techniques (e.g. Trier 1997; Gramsch et al. 2004; Koutrakis et al. 2005) or gravimetric methods for determination of the particle mass (Jorquera 2002) followed by the elaboration of statistical models to define its distribution and the establishment of atmospheric monitoring networks (Morel et al. 1999; Pérez and Reyes 2003; Silva and Quiroz 2003). However, no information has been available concerning the types of particles present in the air, and their origins. As previously shown by the other geologists (e.g. Moreno et al. 2004a, b, c, 2005), SEM, together with proton-induced X-ray emission (PIXE) are useful tools for the identification of the different particle types (e.g. Miranda and Andrade 2005; Cong et al. 2007) and the quantification of their relative proportions in particulate atmospheric matter. Here we applied these techniques to the particulate matter of Santiago, which allowed us to characterize and list all the different types of particles present, together with their variation between the two sites in relation to meteorological conditions. This preliminary study is part of a larger program, including chemical and isotopic analysis and magnetic characterization of the particles in a set of atmospheric samples collected in Santiago, Chile.

Geographical, meteorological and geological context

Santiago (33.5°S, 70.8°W), the capital of Chile, a city with almost 6,000.000 inhabitants (37.5% of the national population, http://www.ine.cl), is located on a gentle slope (from 450 m above sea level in the west to more than 750 m in the east) in a geographically confined basin (the Central Valley) between the Andean Cordillera (altitude >4,500 m) to the east and the coastal range (altitude up to 2,000 m), to the west (Fig. 1a, b). Due to its subtropical latitude, the vertical exchange of air during most of the year is controlled by permanent subsidence and the formation of a thermal inversion layer, caused by the South Pacific sub-tropical anticyclone. This results in a semiarid climate with temperatures ranging between −2 and 35°C (average values around 14°C) and an average rainfall of 350 mm per year but large interannual variability (Rutland and Garreaud 1995). The prevailing wind direction over the city is southwesterly throughout the year. The thermal inversion subsidence layer lies at about 400 m above the ground during winter and autumn and at 1,000 m during spring and summer. During these thermal inversion periods, the vertical ventilation is highly restricted and air pollution increases dramatically as a mass of cold air is trapped below warmer air. Consequently, the geography and climate of the Santiago basin are, in general, unfavourable for the diffusion of air pollutants. Extreme events of air pollution occur frequently during the high pollution season, extending from April to August (Rutland and Garreaud 1995). Moreover, the urban area is showing rapid growth, concentrating most of the new services, housing and industries as compared to the rest of the country (Romero et al. 1999), thus reinforcing the magnitude of this pollution problem.

Geologically, Santiago is located in a basin filled by quaternary alluvial sediments mostly derived from the chemical and mechanical erosion of the Cenozoic intermediate and basic volcano-sedimentary formations of the Andes (Fig. 1c). Three steep hills inside the city are composed of dacitic domes or necks covered by the same Quaternary alluvial material. The 450 ± 60 ka old Pudahuel rhyolitic tuff (e.g. Stern 2004) crops out along the western side of the town. Both the alluvium and rhyolitic tuff are unconsolidated and covered by scarce vegetation, which becomes dry in summer, leaving unprotected soils during a large part of the year.

Some active copper mines are present in the proximity of Santiago, including the world class El Teniente Mine.

Fig. 1 Location, topography and geology of the Santiago de Chile area (based on the geological map of SERNAGEOMIN 2003) indicating the sampling sites. Symbols in **c**: *1*: pre-Mesozoic rocks, *2*: Mesozoic volcano-sedimentary rocks; *3*: Cenozoic volcano-sedimentary rocks; *4*: Cretaceous granitoids; Holocene-Quaternary in white. Legend in **d**: *T*: Teatinos Street; *M*: Macul site
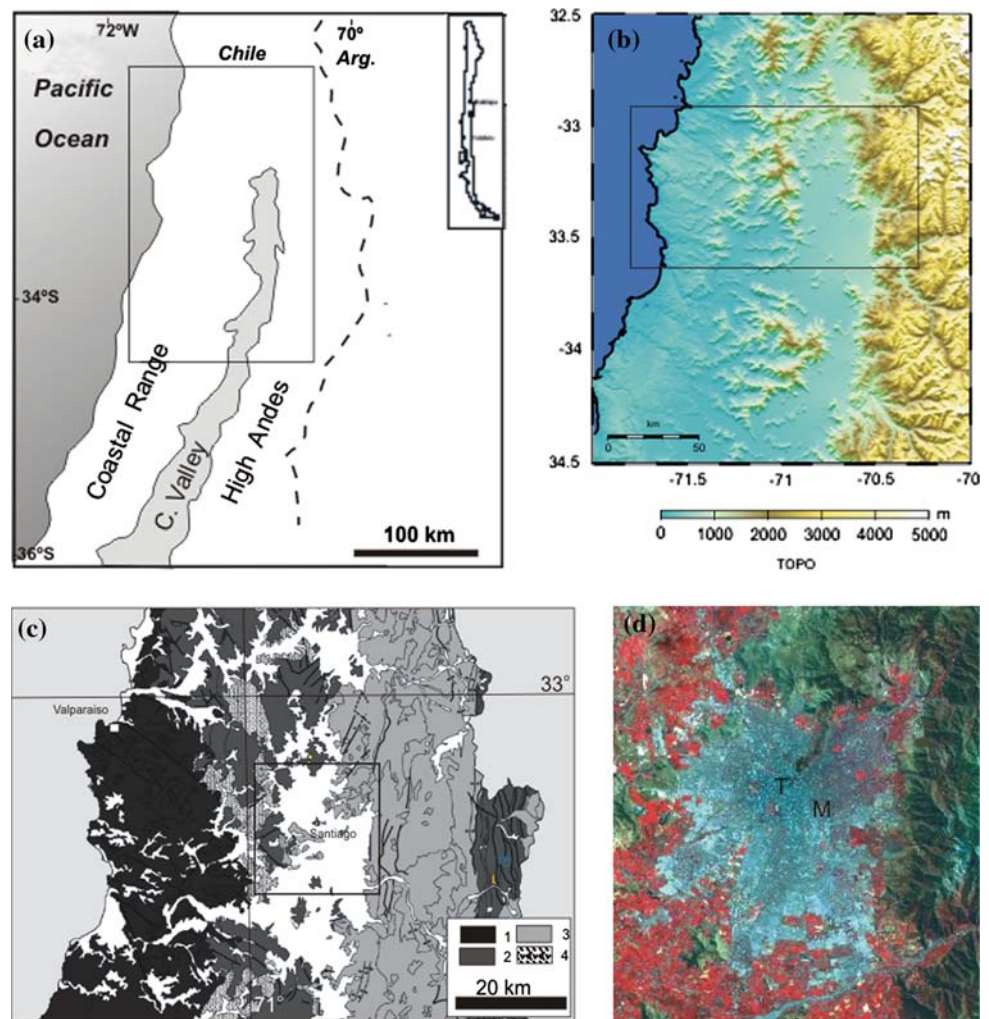
Cu smelting industries are also located a few kilometres from the town.

Sampling and analytical techniques

Aerosol samples were collected at two different sites in Santiago (Fig. 1d), about 7 km apart: (1) downtown Teatinos Street, a canyon street used by many buses and lined by crowded sidewalks. Moreover, it is located 150 m from Alameda Street, a five-lane avenue (three of which are dedicated to buses), one of the most heavily used roads of Santiago; and (2) on the campus of the Faculty of Sciences at the University of Chile, located on the east side of the city in a residential area, 300 m away from two major roads.

Sampling in Teatinos Street (only PM_{10} fraction) was done using a stacked filter unit (SFU) sampler placed on the top of an eight-floor building (ca. 30 m above ground level). Samples were taken from 24 h, three times per week, for a total period of 12 weeks during the winter of 2004 (Table 1). One day classified as critical by the air quality national agency (ICAP value of 244, http://www.conama.cl, Table 1) was also sampled. On the campus (sampling referred to as "Macul"), the double PM_{10}–$PM_{2.5}$ collector was placed 2 m above ground level. Typical collection rates were around 18 L/min. Samples from Macul were collected during one week in June (10 samples), and those from Teatinos during 1 month in July–August 2004 (7 samples).

All filters, whatever their type (Teflon, quartz or polycarbonate), were gravimetrically analysed before and after sampling with a ±0.001 mg microbalance in order to determine the amount of collected particulate matter (Table 1). Sampling conditions and mass concentrations are shown in Table 1. The filters were stored under sterile Petri dishes and in constant humidity- and temperature-regulated chambers. Following an integrated procedure of characterization and identification of the particulate matter using destructive and non-destructive analytical techniques, each filter (47 mm diameter) was cut into four quarters with ceramic scissors in a clean room. One quarter

Table 1 Meteorological (internal data from the Department of Geophysics, University of Chile) and gravimetric (or PM$_{10-2.5}$ mass concentration) data

Sample	Sampling date	Timing sampling	$T_{max} - T_{min}$ (°C)			Relative humidity (%)	PM$_{10}$ weight (mg)	PM$_{2.5}$ weight (mg)	ICAP
Macul									
1-1147	03/06/04	12:00–18:00	23.8	–	17.4	30.9	–	0.479	91
2-1148							0.232	–	
1-1149	04/06/04	5:00–11:00	13.4	–	8.1	61.2	–	0.114	127
2-1150							0.349	–	
1-1151	05/06/04	5:00–11:00	11.0	–	8.8	87.5	–	0.171	70
2-1152							0.130	–	
1-1153	06/06/04	5:00–11:00	10.2	–	4.0	83.0	–	0.153	55
2-1154							0.120	–	
1-1155	07/06/04	5:00–11:00	11.8	–	3.7	73.0	–	0.106	71
2-1156							0.106	–	
1-1157	08/06/04	5:00–11:00	12.5	–	9.6	61.7	–	0.153	77
2-1158							0.446	–	
1-1159	09/06/04	5:00–11:00	11.5	–	9.8	71.3	–	0.180	98
2-1160							0.239	–	
1-1161	10/06/04	5:00–11:00	6.7	–	1.3	86.7	–	0.114	45
2-1162							0.164	–	
1-1163	10/06/04	12:00–22:00	11.4	–	6.0	65.2	–	0.226	45
2-1164							0.440	–	
1-1165	11/06/04	13:00–17:00	15.6	–	11.5	32.0	–	0.117	70
2-1166							0.113	–	
Teatinos street									
S14F1	10/08/04	24 h	17.2	–	7.3	75.9	2.766	–	60
S12F1	05/08/04	24 h	14.1	–	3.5	70.6	1.604	–	38
S10F1	30/07/04	24 h	24.3	–	4.7	54.4	1.677	–	89
S8F1	28/07/04	24 h	13.3	–	5.6	77.9	1.892	–	11
S6F1	23/07/04	24 h	16.8	–	6.6	59.0	2.601	–	62
S4F1	20/07/04	24 h	14.0	–	9.6	68.5	0.717	–	74
S2F1	17/07/04	24 h	18.0	–	6.9	64.3	2.620	–	244

ICAP: particle air quality index (SEREMI-Salud Región Metropolitana, Chile)

was used for PIXE and then SEM analysis and the remainder was kept for other analytical measurements (magnetic characterization, chemical and isotopic analysis) currently in progress.

Mean major element (Si, Al, Fe, Ca and K) and some trace element (S, Cl, Ti, P, Cr, Cu and Zn) compositions of particulate matter were obtained by proton-induced X-ray emission (PIXE) using a 2.2 MeV protons flux produced by a KN3750 Van de Graaff electrostatic accelerator at the Physics Department of the University of Chile. Detection limits (0.03–0.3 mg/cm^2) and detailed experimental conditions and technical specifications are given in Morales et al. (1995) and Miranda et al. (2006). Data are reported in Table 2.

Characterization of the particles (morphology, type and chemistry) was performed using SEM coupled with an energy-dispersive X-ray microanalysis system (SEM–EDX). Some filters were examined at the Department of Geology of the Catholic University of the North (Antofagasta, Chile) with a JEOL JSM 5900 LV-SEM. Others were studied at the LMTG in Toulouse (France) with a JEOL JSM 6360 LV-SEM. As most filters, especially in Teatinos, were covered by very small aerosol carbon particles, they did not need to be coated for conductivity. However, we found, that a gold coating made the filters more resistant to the effects of the flux. As the SEM in Toulouse is adapted to environmental observation (biological samples) no filters studied in Toulouse required any preparation. In each studied sample, a square was randomly selected in which all particles exceeding 2 μ were analysed. Secondary electron images (SEI) were obtained together with their EDS spectra of the major chemical components

Table 2 PIXE elemental concentrations ($\mu g/m^3$) measured in aerosols from Santiago

Sample	Si	Al	Fe	Ca	K	Ti	Cr	Mn	Cu	Zn	P	S	Cl
Macul													
1-1147	1.471	0.219	0.809	0.420	0.151	–	–	–	–	–	–	0.555	0.054
2-1148	4.223	0.690	1.817	1.594	0.305	0.108	–	–	–	0.125	–	0.389	0.113
1-1149	1.641	0.360	0.307	0.118	0.148	–	–	–	–	–	0.022	0.573	
2-1150	7.242	1.352	–	1.413	0.328	–	–	1.358	–	–	0.071	0.683	
1-1151	1.168	–	0.802	0.193	0.417	–	–	–	–	–	–	1.754	
2-1152	6.574	1.279	0.994	1.184	0.197	–	–	–	–	–	0.071	0.856	–
1-1153	0.423	–	0.359	0.134	0.170	–	–	–	–	–	–	0.725	–
2-1154	3.601	0.803	0.525	0.416	0.136	–	–	–	–	–	0.031	0.403	–
1-1155	1.031	–	0.526	0.290	0.229	–	–	–	–	–	–	0.591	–
2-1156	4.824	0.794	0.965	0.801	0.188	–	–	–	–	–	0.036	0.360	–
1-1157	1.282	0.200	0.637	0.295	0.326	–	–	–	–	0.139	–	0.562	–
2-1158	11.126	2.027	3.876	2.355	0.750	0.090	0.158	0.235	–	–	0.049	1.362	0.149
1-1159	0.496	–	0.384	0.189	0.258	–	–	–	–	0.205	–	0.550	–
2-1160	8.298	1.674	1.892	1.373	0.422	–	–	–	–	–	0.095	0.915	–
1-1161	0.811	–	0.467	0.225	0.146	–	–	–	–	–	–	0.258	–
2-1162	8.773	1.529	1.784	1.383	0.294	0.118	–	–	–	–	0.038	0.520	0.098
1-1163	0.881	–	0.601	0.280	0.172	–	–	–	–	0.132	–	0.416	0.050
2-1164	6.727	0.961	2.828	2.140	0.413	0.127	–	0.089	–	–	–	0.424	0.155
1-1165	1.685	–	1.081	0.537	0.216	–	–	–	–	–	–	0.675	–
2-1166	5.431	0.914	2.439	1.760	0.343	0.138	–	–	–	–	–	0.393	0.107
Teatinos street													
S14F1	18.232	7.379	20.547	14.911	7.733	1.894	1.370	0.888	0.925	1.502	–	9.116	3.551
S12F1	25.547	10.426	27.251	19.479	9.069	2.048	1.348	1.198	0.760	1.901	–	8.127	4.192
S10F1	4.133	1.384	5.420	3.669	1.662	0.369	0.303	0.197	0.094	0.200	–	0.967	0.441
S8F1	2.326	0.902	2.340	1.618	0.834	0.193	0.199	0.100	0.071	0.197	–	0.753	0.494
S6F1	1.441	0.504	1.541	1.007	0.599	0.104	0.106	0.069	0.067	0.072	–	0.546	0.787
S4F1	1.129	0.651	1.186	0.887	0.408	0.087	0.076	0.051	–	0.101	–	0.282	0.418
S2F1	2.067	1.234	2.264	1.288	0.996	0.130	0.090	0.072	0.120	0.229	–	0.622	0.483

(–) Below detection limit

present in each individual grain. This information allowed, in most cases, the identification of the grain and its origin (geological, biogenic, anthropogenic or atmospheric).

Statistical data were obtained on two types of filter: polycarbonate and Teflon. Both contain chemical components that could interfere and bias the interpretation. Therefore clean filters were first analysed in order to obtain their chemical spectrum. Polycarbonate filters have a very smooth surface in which particles appear clearly, whereas on the Teflon filters the fibrous surface can sometimes cause confusion between very small particles and Teflon glomerules on the lattice. Moreover, Teflon filters always provide C and F peaks that can disturb the EDS spectrum of very small grains ($\approx 1\ \mu$) whereas polycarbonate filters only contribute to the C peak.

With the optical resolution of both SEM, particles smaller than $1\ \mu$ could not be analysed correctly. Unfortunately, in many cases important geological information was thus lost, so that all the observations and conclusions are valid only for particles larger than $1\ \mu$. Further work with HR-TEM will be needed to get information on these smaller particles. This is of crucial importance because, as we will see later, it seems that the type and origin of the particles vary in relation to their size.

Here we present a preliminary classification of the particle types we found, based on more than 300 grain identifications collected in five samples—three from downtown (Teatinos) and two from the campus (Macul).

Results

Gravimetric data

Particulate matter daily weights range from 0.1 to 0.45 mg in Macul where sampling lasted an average of 6 h, and

from 0.7 to 2.8 mg in Teatinos, where it lasted 24 h (Table 1). In Macul, where two sizes were sampled, the PM_{10} weights were heavier than those of the $PM_{2.5}$, with the 03/06/04 sample being the exception. If calculated back to the same sampling time (24 h), recalculated sample weights in Macul vary from 0.424 mg (07/06/04) to 1.784 mg (08/06/04). In Teatinos they vary from 0.717 mg (20/07/04) up to 2.766 mg (10/08/04). Clearly, the particulate matter content is higher in Teatinos than in Macul. Due to the small number of samples studied, however, we did not detect statistically significant relations between sample weight and atmospheric and meteorological conditions.

PIXE data

PIXE analyses were performed on 27 samples, 20 from Macul (10 for the PM_{10} and 10 for the $PM_{2.5}$ fractions) and 7 from Teatinos. Elemental concentrations (expressed as $\mu g/m^3$) are given in Table 2. We expressed the data in $\mu g/m^3$, because this is the unit traditionally used in atmospheric chemistry and because it is representative of what is inhaled by the inhabitants, even if this concentration unit is geologically non-significant. We consider the filter deposit to be homogeneous and the data to be representative of the whole filter concentration. The total of these concentrations compared to the sample mass showed that the measured elements contribute up to roughly 50% of the sample mass in Macul but less than 10% of the sample mass in Teatinos. This means that most of the constituents in Teatinos were not analysed; they are probably elemental carbon and organic carbon compounds, as indicated by the black colour of the filters.

In general, of the 13 analysed elements, Si, Al, Fe and Ca (typical lithogenic elements) dominate. Si (Al), P, S and Cl are present as anionic groups (silicate or Al–silicate, phosphate, sulphide and/or sulphate and chloride, respectively), whereas Fe, (Al), Ca, K, Ti, Cr, Mn, Cu and Zn are mostly present as cations in combination with the former anion groups.

Element concentrations in filters from Teatinos were always one order of magnitude higher than those from Macul. This could simply reflect the heavier weight of the Teatinos samples when compared to Macul due to the longer sampling time together with higher particle concentration in the air in Teatinos. At the same time, the measured element fraction from Teatinos is a small part of the total matter. Thus no sound conclusions can be drawn from these raw concentrations in $\mu g/m^3$. As a consequence, correlation matrix coefficients have been calculated (Table 3) with the aim of understanding the chemical composition of the particulate matter. Diagrams based on

elements ratios have also been used as they allow sources with different element ratios to be identified.

In the Macul samples, some important differences were observed between the two size fractions analysed. In the $PM_{2.5}$ significant positive correlations were observed only between Ca and Fe (Table 3a). Nevertheless, if elements with only three analyses are considered in the statistics (samples in italic in Table 3a), a positive correlation ($r > 0.8$) was found between Si and Al, as well as Al and S, and a negative correlation between Al and Ca, Al and Fe, Si and Zn, Ca and Zn, and Fe and Zn. A positive correlation between Si and Al would be indicative of the presence of Al–silicates, whereas a negative Fe–Zn correlation could indicate the presence of Fe-oxide minerals. The positive Ca–Fe correlation suggests ferromagnesian silicates, where Ca is always present (pyroxene and/or amphiboles).

In the PM_{10} fractions of the Macul samples, positive correlation was found between Si–Al, Si–S, Al–S, Si–K, Cl–Ca, Cl–Fe, Ca–K, K–Fe and Ca–Fe, and a negative correlation between S and Ti (Table 3b). Moreover, if samples with only three data (values in italic in Table 3b) are also considered, a negative Ca–Mn correlation is also observed. The fact that a better correlation exits in the PM_{10} fraction than in the $PM_{2.5}$ fraction could be due to either: (1) higher absolute element concentrations in PM_{10}, which allow higher measurements and, consequently, improve the r factor; and (2) a higher quantity of discrete minerals controlling the whole chemistry. Indeed, silicate minerals are presumed to be present in this fraction as evidenced by the high Al–Si-element ratios.

In the Teatinos samples, from which samples S14F1 and S12F1 were excluded due to their very high elemental concentrations, a very good correlation coefficient was found between almost all elements except Cl, Cu and Zn (Table 3c). This might indicate a better-defined mineralogy for the particulate matter but could also reflect the higher quality of the measurements due to higher concentrations. The chemistry of these samples could be explained by the presence of both felsic and mafic Al–silicates (as evidenced by the good Al–Si and Si–lithophile and transitional element correlations). Sulphate, and/or sulphide minerals are probably present too, as evidenced by the good correlation between S–K/Ca and S–transitional elements (Fe, Mn, Cr, Ti).

The diagram Si/S versus Si/Al (Fig. 2a) shows that the Si/Al ratios in Macul samples (whatever the size fraction considered) are always greater than those from Teatinos. This implies the occurrence of a higher amount of polymerized silicates in Macul (probably tectosilicates) with respect to Teatinos (which might have higher amounts of inosilicates and/or phyllosilicates). Moreover, the Si/S ratio in the PM_{10} fraction from Macul is 12 times the value found in the $PM_{2.5}$ from Macul or the Teatinos

Table 3 Correlation matrix (Pearson's coefficient) of elements measured by PIXE in the particulate matter from Santiago

(a) Macul Fraccion F1 (PM$_{2.5}$)

	Al	Si	S	Cl	K	Ca	Fe	Zn
Al	1.000							
Si	*0.902*	1.000						
S	*0.854*	0.110	1.000					
Cl		–	–	1.000				
K	−0.602	0.022	0.776	–	1.000			
Ca	*−0.862*	0.540	−0.149	–	−0.058	1.000		
Fe		0.575	0.333	–	0.314	0.864	1.000	
Zn	*−0.900*	*−0.810*	0.515		0.160	*−0.975*	*−0.975*	1.000

(b) Macul Fraccion F2 (PM$_{10}$)

	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe
Al	1.000									
Si	0.958	1.000								
P	0.442	0.321	1.000							
S	0.896	0.822	0.461	1.000						
Cl	0.267	0.371	–	0.490	1.000					
K	0.714	0.800	0.231	0.738	0.703	1.000				
Ca	0.440	0.624	0.301	0.439	0.926	0.851	1.000			
Ti	−0.645	−0.595	–	−0.808	−0.341	−0.701	−0.377	1.000		
Mn	−0.047	−0.306	–	−0.147	–	*−0.572*	*−0.948*	–	1.000	
Fe	0.544	0.700	0.156	0.526	0.800	0.943	0.956	−0.473	–	1.000

(c) Teatinos (without the two first samples with very high concentrations)

	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
Al	1.000											
Si	0.831	1.000										
S	0.739	0.930	1.000									
Cl	−0.587	−0.348	−0.108	1.000								
K	0.893	0.978	0.911	−0.318	1.000							
Ca	0.760	0.983	0.864	−0.351	0.945	1.000						
Ti	0.751	0.987	0.898	−0.352	0.936	0.993	1.000					
Cr	0.624	0.940	0.900	−0.270	0.853	0.945	0.974	1.000				
Mn	0.717	0.981	0.891	−0.283	0.933	0.995	0.996	0.968	1.000			
Fe	0.811	0.991	0.884	−0.338	0.975	0.994	0.984	0.921	0.986	1.000		
Cu	0.768	0.256	0.113	−0.591	0.457	0.171	0.113	−0.118	0.081	0.266	1.000	
Zn	0.895	0.627	0.650	−0.585	0.680	0.497	0.530	0.456	0.469	0.555	0.721	1.000

(a) Macul samples, PM$_{2.5}$ fraction. (b) Macul samples, PM$_{10}$ fraction. (c) Teatinos samples, excluding S14F1 and S12F1. In all cases, only variables with $n > 3$ have been considered. Variables with $n = 3$ are in italic

PM$_{10}$ samples. The very high S content in the latter two samples could be related to a high sulphide, sulphate or sulphur content. Indeed, a highly positive correlation value ($r = 0.884$) between S and Fe in the Teatinos samples indicates the occurrence of pyrite (or any other Fe-bearing sulphide). High correlation values between S and K ($r = 0.776$ in the Macul PM$_{2.5}$ fraction; $r = 0.738$ in the Macul PM$_{10}$ fraction and 0.911 in Teatinos PM$_{10}$

fraction) could be related to potassium sulphate, the origin of which will be discussed later. The PM$_{10}$ fractions of Macul display high S/Cl ratios (from 3 to 6), as compared to those of the Teatinos PM$_{10}$ fraction (<2.5, Fig. 2b). This could be explained by the relatively low chlorine content in the first fractions. Nevertheless, the high Cl content in the Teatinos samples, associated with the lack of correlation between Cl and any other analysed element
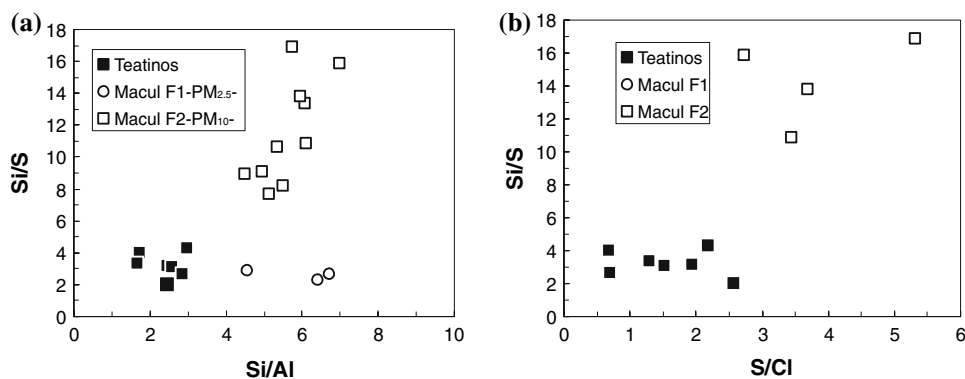
(Table 3), probably reflects its association with non-ana-
lysed elements (most probably Na).

SEM data

This preliminary result is based on statistical data obtained
from a couple of $PM_{10}/PM_{2.5}$ filters from Macul, comple-
mented with data from another PM_{10} filter (samples 2-
1150). For Teatinos Street, statistical data were obtained
from two PM_{10} filters (S4F1 and S8F1), complemented
with observations on a third (S7F1, not listed in Table 1).
Meteorological conditions during sampling are summarised
in Table 1.

Even before any microscopic work, it is evident that all
filters from Teatinos (downtown area) are black, all cov-
ered with elemental (EC) or organic (OC) carbon
nanoparticles, whereas filters from Macul (a more resi-
dential area) are beige. Moreover, in Teatinos, OC/EC
ratios have been measured on eight size fractions of two
samples (Leiva et al. 2005). Within each sample, variations
of the OC/EC are bimodal, with one peak at the 0.18 μm
fraction and the other peak between the 3.2 and 18 μm
fractions. The 0.18 μm OC/EC peaks of the two samples
reach 6.9 and 8.2, respectively, and those of the 3–18 μm
fractions have values of 5.5 and 2.5, respectively. These
figures are interpreted as typical of a secondary origin for
these very small (0.1–1 μm) carbon compounds (Castro
et al. 1999), which could originate from the intensive
traffic. To summarize, Teatinos samples are loaded with
more particles (for the same sampling time) than Macul
samples, among which many complex carbon particles
from exhaust pipes.

Most grains have irregular shapes where it is difficult to
recognize any mineral feature. They sometimes form
aggregates and very seldom show specific shapes, gener-
ally spheres, but also ovaloids, smooth tiles, etc. (Fig. 3).
Grain abundance is higher in the Teatinos filters than in

Macul, where the free filter surface can be observed
between grains.

SEM interpretations are mostly based on the EDS
chemical spectrum of the particles, which allows the dif-
ferent Al silicates, the ferro-magnesian minerals, and other
inorganic and organic phases to be characterised. However,
these spectra are disturbed by the fact that these minerals
do not expose their flat surfaces to the RX gun, as they are
grains randomly scattered on the filters. Therefore relative
peak heights are meaningless, sometimes leading to
ambiguous determinations noted as "non-characterised Al
silicates", for example. Beside its chemical spectrum, the
shape of the particle is always considered as being very
regular, spherical for example, and even if associated with
a typical Fe oxide or an Al oxide formula, it would not be
interpreted as a geological feature. Moreover, $CaSO_4$,
which corresponds to both natural gypsum and industrial
plaster, would be interpreted to reflect the regional geol-
ogy, but also of the occurrence of quarries or building
construction. Finally, there are cases where the ambiguity
in the interpretation cannot be solved; for example it is
difficult to decide if the many Fe oxides are natural or
anthropogenic, when corresponding grains have no specific
shape. All in all, errors in the interpretation might exist, but
this changes none of our general observations and
conclusions.

1. Nature of the particles and their distribution in both
   sites: site effect.

The most striking observation is that, beside the C cover,
whatever the filter size and the site considered, geological
particles are the most numerous. Indeed, Fig. 4 shows that
on the two PM_{10} filters from Macul (sample 2-1164) and
Teatinos (sample S8F1) unambiguous minerals such as
plagioclase, pyroxene, phyllosilicates, clays and quartz
contribute 66–73% of the total of the identified particles.
Other inorganic compounds (Fe oxides, Ca and Ba
sulphates) corresponding to grains devoid of typical forms

Fig. 3 SEM image of particulate matter with characteristic EDX spectra. Particles 20 and 21 correspond to titanite and barite, respectively (EDX spectra not shown)
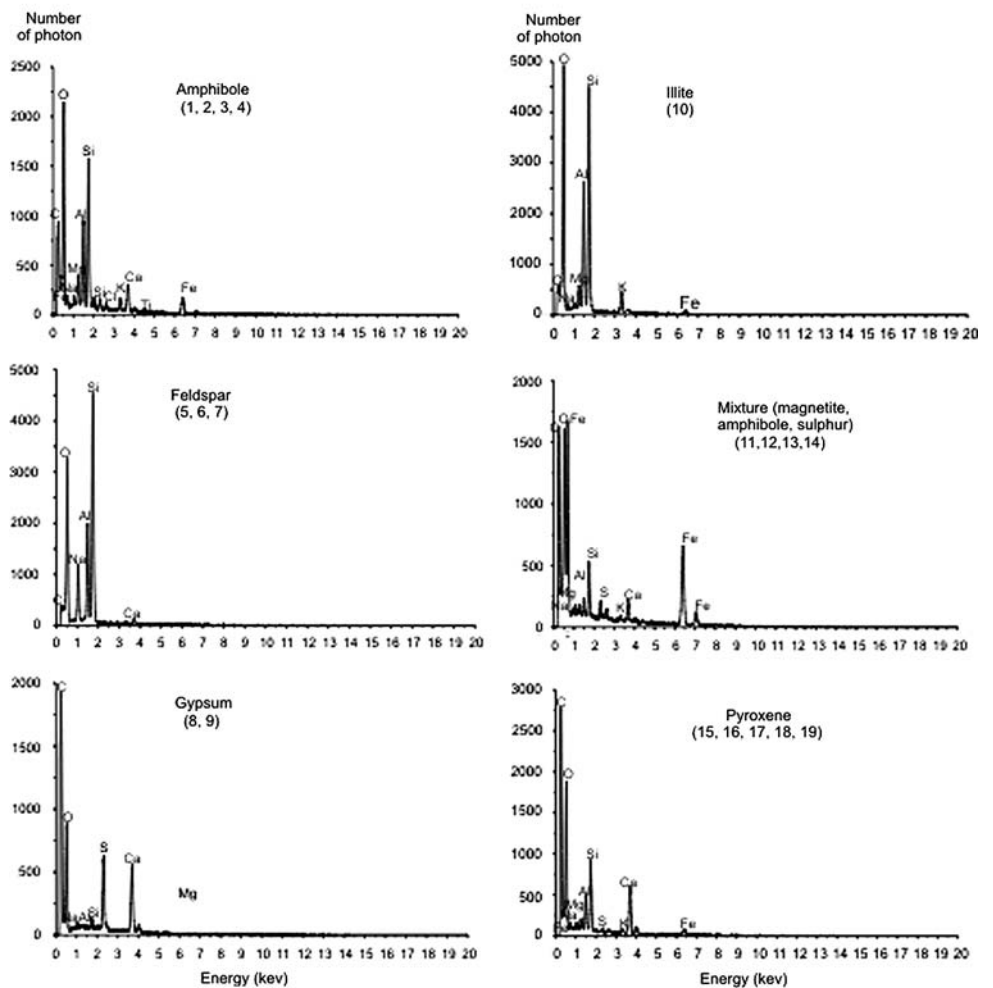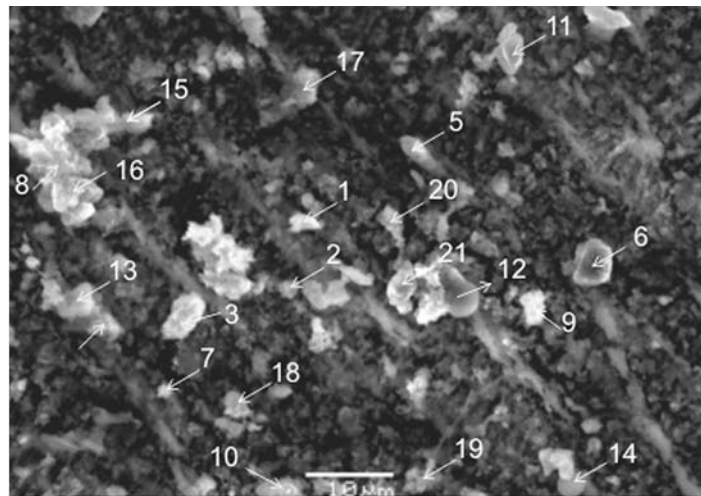
and which could be either of geological or atmospheric/anthropogenic origin will be discussed later. Finally, presumably anthropogenic grains with striking features (spheres) and various compositions and biogenic remains account for the rest of the particles.

(a) Geological particles

In the two PM$_{10}$ samples from the two sites, the frequency of minerals decreases in the order pyroxene, plagioclase, amphibole, clay, silica, and iron oxides. Some discrepancies
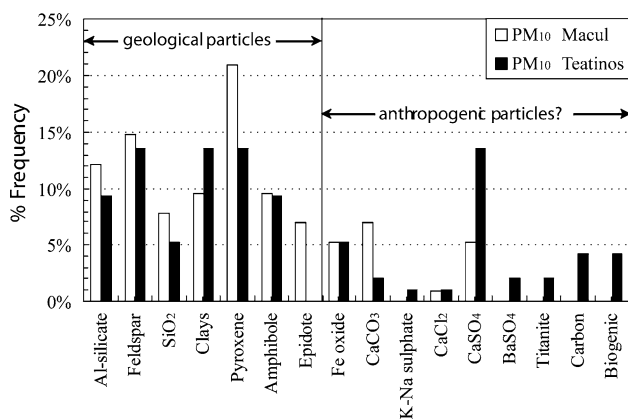
Fig. 4 Histogram frequency of air particles identified by SEM–EDX on PM$_{10}$ filters from Macul (sample 2-1164, 115 analysed particles) and Teatinos (sample S8F1, 97 analysed particles)

also occur between the sites. Epidote-group minerals exist in Macul but not in Teatinos. CaCO$_3$ occurs with a greater percentage in Macul than in Teatinos, while CaSO$_4$ shows an inverse pattern. CaCO$_3$ and CaSO$_4$ spectra could correspond to limestone and gypsum, respectively, but their presence and concentration could also be related to human activity (CaCO$_3$ quarries and plaster used in construction). This also applies to iron oxides which are observed here but could be either natural, from surrounding soils, or anthropogenic. Only iron oxides, which appear as spheres are clearly anthropogenic.

Pyroxenes and amphiboles generally display EDX spectra (Fig. 3) showing no clear difference in composition between the two sites. In Macul, 10 of 15 plagioclase grains are albites, the rest being intermediate plagioclases, and only 1 K-feldspar was identified. In Teatinos, half of the grains are albites and half intermediate plagioclases. All grains have weathered irregular surfaces and shapes, which could suggest a secondary origin. Clays at both sites are generally illites, but some grains have spectra closer to that of montmorillonite.

(b) Other particles

Other particles include sulphates (KSO$_4$, NaSO$_4$, BaSO$_4$), chlorides (CaCl$_2$), exotic particles such as titanite (two grains), carbon (EC or OC) grains with specific shapes (spheres, tiles) and biogenic remains. They are nearly inexistent in Macul but reach 14.6% of the total in Teatinos. Sulphates have either an anthropogenic or atmospheric origin, while carbon is clearly anthropogenic. In addition to the C spheres, we also found spheres of Fe oxide, alumina, Cu alloy and Ti oxide. All exist as unique grains, but confirm the great heterogeneity of these anthropogenic particles. The combination of their low frequency and

diversity will make the identification of each source difficult, but is worth noting.

Biogenic grains have been found in very small quantities and only in Teatinos. They are not pollen, but insect more probably remains. This agrees with the fact that our sampling was done in winter when biogenic activity is at a minimum.

2. The nature and distribution of the particles between PM$_{10}$ and PM$_{2.5}$ fractions (Macul): size effect

A comparison between the nature of grains nature and their frequency in the two fractions of a sample collected in Macul is given in Fig. 5.

The nature and percentage of clearly geological particles are different in the two fractions. Micas are not present in the PM$_{10}$ fraction while epidote-group minerals are absent from the PM$_{2.5}$ fraction. Pyroxenes and amphiboles are notably less numerous in the PM$_{2.5}$ fraction than in that of the PM$_{10}$. This can be attributed to the mechanical resistance of these minerals, which therefore survive as larger grains throughout all transport processes, as opposed to plagioclase and feldspar, which break more easily and occur in roughly the same proportions in both fractions. Silica behaves similar to plagioclase, which is an argument for assuming that they are not quartz grains which have a
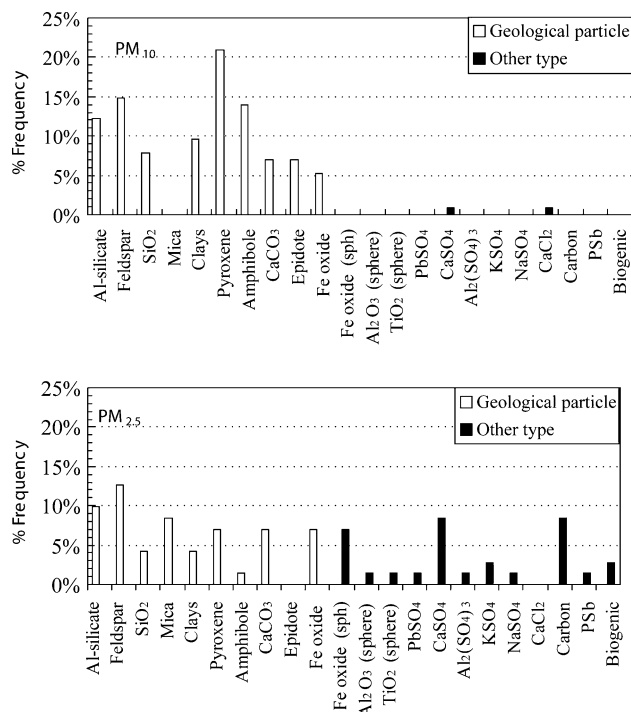

Fig. 5 Histogram frequency of air particles identified by SEM–EDX on PM$_{10}$ and PM$_{2.5}$ filters collected from Macul (sample 2-1164, 115 PM$_{10}$ analysed particles, SAMPLE 1163, 71 PM$_{2.5}$ analysed particles)

high mechanical resistance but more probably amorphous silica. CaCO$_3$ also exists in the same proportions in the two fractions, for the same reason or because of the same anthropogenic influence on both fractions.

Strong differences exist in the respective proportions of the non-geological particles between PM$_{10}$ and PM$_{2.5}$. The latter has a higher global content in these particles together with a greater diversity in their composition. This might have strong implications for the health impact of PM$_{2.5}$ as compared to PM$_{10}$ because both the sulphates, sulphides and metal compounds can release chemicals more easily than silicates.

3. The nature and distribution of the particles in relation to the date (meteorological conditions)

Statistical data on two PM$_{10}$ filters from Teatinos, taken at an interval of 1 week during the most polluted season are plotted in Fig. 6. The most important feature concerns the non-geological particles, where sample S4F1 contains spheres of various compositions and NaCl grains of atmospheric origin, while S8F1 contains more CaSO$_4$ grains. Sample S4F1 also contains more Fe oxides, less pyroxene and amphiboles and no clay compared to sample S8F1.

Discussion

The PIXE and SEM analyses give convergent information concerning both the general mineralogy of the particles and their origins. Thus is important as the PIXE gives

Fig. 6 Histogram frequency of air particles identified by SEM–EDX on PM$_{10}$ filters collected at the same site (Teatinos Street) during two different sampling days. Sample S8F1, 96 PM$_{10}$ analysed particles; sample S4F1, 54 PM$_{10}$ analysed particles)

information derived from all particle sizes in samples while the SEM deals only with particles greater than 1–2 μm. Both techniques confirm that besides C-bearing nanoparticles, lithogenic minerals constitute an important to major part of all particles.

Both the PIXE and SEM confirm that felsic Al–silicates dominate in the Teatinos samples and are also present in the Macul samples, associated with a more complex mineralogy. Sulphates and chlorines are also present at both sites, with a higher content in S-bearing components in Teatinos with respect to Macul as shown by both the S content and SEM observations. Highly positive correlations between S-transitional elements and S-lithophile in Teatinos samples can be explained by a higher sulphide and sulphate content.

The combined SEM–EDX study allows the identification of both lithogenic and anthropogenic particles and their potential origin, but it does not give many clues concerning the origin of the chemicals. This problem also arises when studying soils and potentially polluted water. Calculating enrichments factors (EF) is a powerful tool commonly used for tracing the anthropogenic contribution in chemical budgets. Following the methodology described in Cong et al. (2007), the EF of elements in aerosols relative to the upper crust composition is defined by the expression:

$$EF_X = \frac{(C_X/C_R)_{aerosol}}{(C_X/C_R)_{crust}}$$

where X represents the element to be considered, EF$_X$ is the enrichment factor of X, C_X the concentration of X, and C_R the concentration of a reference element. According to this expression, elements with EF values close to unity would indicate a strong crustal origin, while high EF values could indicate a non-crustal (including anthropogenic) origin. In our study, because Al is abundant in crustal materials and is not involved in anthropogenic particles, it was used as the reference element and, consequently, EF$_{Al}$ will be 1.

Because the chemical composition of the different lithologies present in the geological environment of Santiago does not necessarily have the same chemical composition as the average Upper Continental Crust as estimated by Taylor and McLennan (1995) and used for the EF calculations, only elements with EF higher than ten could be considered to have a high non-crustal (anthropogenic?) origin. Calculations of EF are represented in Fig. 7, in which Si, P, K, Ti, Ca and Fe present EF values <10, suggesting an origin dominated by geological sources (soil and dust). On the contrary, S, Cl, Cr, Cu and Zn (and to a lesser extent Mn) display EF >> 10 and, consequently, a variable and high contribution (100–1,000 times) of non-crustal (anthropogenic?) origin would be proposed. It is
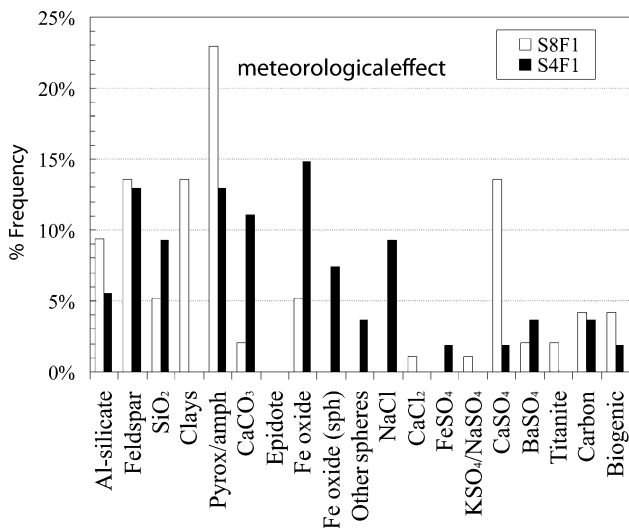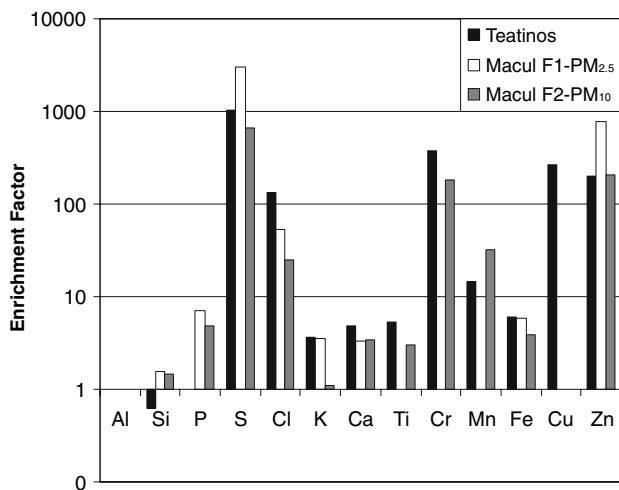
Fig. 7 Average enrichment factors of elements (PIXE determinations) derived from the average Upper Continental Crust (Taylor and McLennan 1995; S and Cl data from Rudnick and Gao, 2003) of the aerosol particulate matter in Santiago, with Al as the reference element

worth noting that the difference in EF in the Macul site for Zn and S between the $PM_{2.5}$ and PM_{10} fraction, being higher in the first one, indicates an element partition based on the particle size and origin, thus confirming the SEM observations.

Sources of the particles

The air particles in Santiago are a mixture of lithologic, biogenic and anthropogenic particles with proportions varying with the location, the date and the particle size. If lithogenic particles are clearly primary, some salts can have a secondary origin, being synthesized in the atmosphere from chemicals whose origin is generally related to human activity. The relative contribution of each source could be a function of dominant winds and location compared to major pollution centres. Based on our PIXE + SEM–EDX study, we have identified the particle nature and estimated their relative percentages in the two sampling sites. Some hypotheses can be proposed with respect to the source of these different particles. Moreover, specific chemicals have been found, through their high EF, to be enriched in the particles mainly due to anthropogenic activity.

Sources for the geological particles

The high percentage of geological particles in the air is typical of semi-arid climates where soils and rocks are not protected by a dense vegetation cover and can be

transported by the wind (e.g. Yadav and Rajamani 2004). In fact, most of the geological particles identified on the filters are typical of the surrounding volcanic rocks (pyroxene, amphibole, plagioclase, feldspar) or their alteration/weathering products (clay minerals, epidote-group minerals, etc.). Parameters such as mineral resistance and density would control the relative proportion of these minerals at the different sampling sites. The high erosion rate of the mountains around Santiago is favoured by the low vegetation cover. These fine materials are also present on the streets, the parks and sidewalks. They are permanently remobilised by the intense traffic and, consequently, the finer particles stay suspended in the air during low wind circulation and fair weather conditions. Moreover, intense daily sweeping of all dirt footpaths and alleys together with the existence of dirt streets within the greater city exacerbate the problem. During winter, the inversion layer is at a fairly low altitude over the city and acts as a lid, keeping all these constantly remobilised particles in the air as long as it does not rain. Only rain events will clean the air of all these lithogenic particles.

Origin of Fe oxides

Fe oxides are ubiquitous, existing at both sites and in both size fractions. Fe oxides could be primary magnetites from the magmatic rocks, secondary goethite in the soils formed during weathering of the rocks, or they could be anthropogenic particles from the weathering of all Fe bars, tiles, exhaust grating equipments or from vehicles, exhaust pipes. None of the observed Fe oxide particles have crystal shapes compatible with them being primary lithogenic magnetite. On the contrary, they appear to be poorly to non-crystallised, shapeless grains. The magnetic properties of the same filters support the hypothesis of Fe oxides being magnetites (Silva-Padilla 2005). Moreover, Matzka and Maher (1999) and Muxworthy et al. (2001) also demonstrated the occurrence of magnetite in air particles, their sizes ranging between 0.3 and 5 μm, whose assumed origin was from vehicles exhaust pipes. Their observed sizes are compatible with the present observations. Therefore most observed Fe oxides are assumed to be poorly crystallised magnetites with an anthropogenic (traffic-related) origin. However, we cannot exclude the presence of some lithogenic alteration-related Fe-bearing minerals.

Origin of $CaCO_3$ and $CaSO_4$ particles

$CaCO_3$ and $CaSO_4$ particles could have both lithogenic and anthropogenic sources. Due the geological nature of the studied area, which is dominated by basic to intermediate

volcanic and/or volcaniclastic rocks with very few sedimentary intercalations (which could be natural sources for these particles), it is assumed that they are disseminated in the same way as the silicates. However, cement industries exist a few kilometres north of Santiago in the proximity of a limestone quarry. As for $CaSO_4$, small gypsum quarries are exploited in the Cordillera roughly 70 km northeast of Santiago. Thus $CaCO_3$ and $CaSO_4$ particles could have a lithogenic origin, with their contribution to the general budget being amplified by human activity. Another probable origin for $CaSO_4$ could be related to the neo-formation of salts in the atmosphere as a result of reactions between sulphate (and carbonate?) anions, themselves formed by atmospheric SO_2 oxidation (Morales and Leiva 2006), and Ca^{2+} (Ba^+) cations.

Sources of the different anthropogenic particles

High to extremely high EF values have been found for S, Cl, Cr, Mn, Cu and Zn as shown in Fig. 7. Thus the potential anthropogenic control on their origin and recycling should be checked. Previous studies have shown that Cr, Mn, Cu and Zn could be anomalously enriched in aerosol particulate matter from a variety of anthropogenic sources: emission from fossil fuel combustion, motor vehicle emission, traffic-related sources, the steel industry, solid waste dumping, industrial metallurgical processes and waste incineration (Isakson et al. 1997; Toscano et al. 2005; Chucinta et al. 2000; Rogge et al. 1993). Moreover, Batonneau et al. (2004) identified $PbSO_4$, ZnS and CdS as the major phases generated by non-ferrous smelting operations. In addition, Cong et al. (2007) have shown that these metals might be long-range transported by atmospheric circulation. Consequently, their precise source might not be traced using only plain trace element geochemistry, so that isotopic research programs seem to be necessary to determine the origin of the metals (e.g. Grousset and Biscaye 2005; Dolgopolova et al. 2006).

In Santiago, S has a high EF_S at both sites. A lack of a good correlation between S and Cu or Zn (Table 3) precludes S being a primary sulphide phase. S appears more likely in sulphate phases, as demonstrated by the SEM–EDX study. Its probable origin could be related to the copper mining industry, which constitutes the most significant source of ambient SO_2 in central Chile (Gallardo et al. 2000). Indeed, in central Chile, three industrial copper smelters emit >3 tonnes of sulphur per day (García-Huidobro et al. 2001). However, two mathematical models by Gallardo et al. (2000) and García-Huidobro et al. (2001), respectively, reached contradictory conclusions concerning the impact of these smelters on the S budget of Santiago. According to García-Huidobro et al. (2001) SO_2

concentrations in Santiago area are mostly controlled by local urban and industrial emissions, with sporadic contributions from the copper smelters. On the other hand, Gallardo et al. (2002) and Olivares et al. (2002) argued that a high contribution from one of these three Cu-smelters (namely Caletones) is present in the Santiago basin. We support an origin related to the copper smelters for S, because of the very high EF for Cu and Zn in Teatinos, and for Zn in Macul. However, due to our limited sampling, we cannot prove one or the other model.

Finally, the anomalously high Cl content is probably not due to NaCl from marine salts, because very few NaCl grains were observed during the SEM study. Unfortunately this direct observation cannot be confirmed as the Na content of the samples is unknown. Nevertheless, the origin of Cl is probably anthropogenic and related to industrial emissions. This aspect will have to be confirmed by further studies.

Conclusions

This preliminary study focussed on some major element chemistry and particle identification showed that these two tools, even if imperfect, yield valuable information on the solid particles and chemical elements present in the air of Santiago. Besides the contribution of carbon particles, which can be quite important, especially downtown, unambiguously lithogenic particles and elements are the second highest contributors. Major element and particle identification together with magnetic properties show that the origin of disputable particles, such as iron oxides, is mostly anthropogenic magnetites. Enrichment Factors together with particle identification and element correlation indicate anthropogenic origins that are specific to the Santiago area.

However, accurate data on metal concentrations are needed to obtain a clearer insight into the cause of medical diseases in relation to chemical components. Indeed, it should be kept in mind that even lithogenic particles can transport (through adsorption or reaction processes) chemicals, including toxic metals. Therefore the toxic metal content of these particles, in relation to their size, type, sample date, location, etc. will have to be measured. Moreover, as small particles are richer in anthropogenic compounds, high-resolution techniques (TEM and FEG–SEM) are necessary to understand the mineralogy and chemistry of the $<PM_{2.5}$ fractions.

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