MICROSTRUCTURAL CHARACTERISTICS OF MAGNETIC PARTICLES IN URBAN AND INDUSTRIAL DUSTS FROM THESSALONIKI AREA, GREECE: PRELIMINARY RESULTS

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ABSTRACT

Road dust, an accumulation of solid particles in the form of organic and inorganic pollutants on outdoor ground surfaces, is a valuable medium for characterizing environmental quality. Several recent studies have reported that road dusts contain a significant amount of ferromagnetic particles being the cause of enhanced magnetization, especially those in urban areas and sites downwind of industrial centers. Eventhough the morphological characteristics of the magnetic particles contained in urban road dusts have been extensively studied, up to now, there is no detailed study on the internal structure and phase composition of these particles. The aim of the present study was to obtain detailed microstructural characteristics and microchemical data on single magnetic particles from road dust magnetic phases. For this reason road dust samples were collected from selected sites in Thessaloniki's city core and roads near big industrial units. Magnetic extracts were separated using a hand magnet sealed in a polyethylene bag. These extracts were analyzed using a scanning electron microscope (JEOL JSM-840) connected to an X-ray Energy Dispersion Spectrometer- EDS (INCA 300). SEM observations revealed the dominance of two different types of magnetic particles: a) spherules originating probably from industrial and domestic heating systems and b) angular particles possibly deriving from vehicle emissions. The magnetic spherules identified exhibited various grain sizes (diameters ranging from a few to hundred micrometers), while spherules with different surface morphology and structure were found simultaneously. Generally smooth, orange-peel, polygonic and dendritic spherules were observed. Melt-like and fibre-like particles containing heavy metals were also identified. Furthermore polished thin sections of the magnetic extracts were prepared, while an initial examination using optical microscopy revealed the presence of spherical shape particles with either dense or hollow internal structure and non-homogeneous angular particles. SEM observations of magnetic spherules cross sections revealed either a dense homogeneous internal or a dendritic structure. On the other hand the angular magnetic particles presented a very complex internal structure with non-homogeneous layers resulting from the presence of combined mixed phases within the particle. Microprobe analyses suggest that there are different components with elevated heavy metal contents characteristic of alloys used in the automotive industry.

Keywords: environmental dusts, magnetic particles, spherules, heavy metals

1. Introduction

Magnetic particles are considered an important pollutant in urban environments and seem to be one of the main objectives for present and future environmental research. Magnetic particles in urban environments are mainly derived from combustion of fossil fuels (Muxworthy *et al*., 2001), abrasion/corrosion of brake lining (Osterle *et al*., 2001) and the erosion of asphalted roads (Hoffmann *et al*., 1999), and are generally accompanied by hazardous heavy metals (Maher *et al*. 2008; Wang and Yong 2007). Vehicle emissions are suggested to be another significant source of magnetic pollutants (Hoffmann *et al*. 1999), while subsequent studies (Muxworthy *et*

al. 2001) have confirmed that, in the absence of heavy industry, circulation of motor vehicles is the main source of magnetic particles.

Road dust, which is generally formed by several components including both natural materials and anthropogenic matters, contain a significant amount of strongly magnetic, iron-rich particles (Goddu *et al*. 2004; Jordanova *et al*. 2006; Yang *et al*. 2007) being the cause of its enhanced magnetization especially in urban areas and sites downwind of industrial centers. In particular, in the city of Thessaloniki which is densely populated (over 1,000,000 inhabitants) and is characterized by aggravated air quality, road dusts exhibit elevated values of mass-specific magnetic susceptibility indicating the presence of a considerable amount of ferrimagnetic particles (Bourliva *et al*. 2011). Though mineralogy, morphology and composition of magnetic dust particles were extensively investigated during earlier studies (Bourliva *et al*. 2011; Bucko *et al*., 2010), there is still a lack of detailed information concerning their microstructural characteristics. The aim of the present study was to investigate and obtain detailed information on the internal structure and phase composition of single magnetic particles from road dust magnetic phases.

2. Materials and methods

2.1. Sample collection and preparation

Road dust samples (each weighting almost 100 g) were collected from the accumulated matter at the edges of selected roads in Thessaloniki's city core and roads near big industrial units. The dust samples were mainly collected by gently sweeping an area of about 1 m^2 from road surface using clean plastic dustpan and brushes for each sampling site. The samples were dried in an oven at 35^{o}C for 3 days and mechanically sieved (<250 μm). The magnetic extracts (magnetic fractions, MFs) studied in the present work were obtained by using a hand magnet sealed with a propylene bag. The extraction procedure was run continuously until no magnetic particles were attached to the magnet.

2.2. Analytical procedures

A scanning electron microscope (JEOL JSM-840) was used to analyze the overall size distribution and morphology of road dust magnetic particles. A representative portion of selected magnetic fraction samples was sprinkled onto double-sided aluminum tape mounted on a SEM stub, carbon-coated and observed by randomly selected fields of view. Elemental composition of the magnetic particles was determined using an X-ray energy dispersive spectrometer-EDS (INCA 300). The elemental analysis was performed in a "spot mode" in which the beam is localized on a single area manually chosen within the field of view. Furthermore, in order to study the internal morphology and structure of the magnetic particles, thin polished sections of representative magnetic fraction samples were prepared and studied.

3. Results and discussion

3.1. Morphological characteristics of magnetic dust particles

SEM observations were conducted on magnetic particles separated from selected road dust samples. Based on the morphology, the magnetic particles observed can be grouped into two types: spherules and angular/aggregate particles.

Iron-rich spherules known as "ferrospheres" with diameters of 30-250μm were commonly identified in all samples, while spherules with different surface morphology and structure were found simultaneously. Most of the spherules have rough surfaces and their shapes are close to an ideal sphere, while according to their microstructural characteristics can be divided into several types, namely smooth spherules, dendritic or orange peel spherules (Fig.1a), polygonic spherules (Fig.1b) and molten drop spherules (Fig.1c). In some cases spherules with noticeable holes (cenospheres) were detected. The presence of these surface textures reveal the high-temperature origin of these particles and therefore iron-rich spherules are doubtless of anthropogenic origin and are considered characteristic particles deriving from combustion processes (Lu *et al*. 2008). Among analyzed spherules, about 70% of them were of pure iron,

while the other 30% were iron-oxide spherules with significant abundance of Fe (>80%) and subordinate amounts of Si, Al, and Ca.

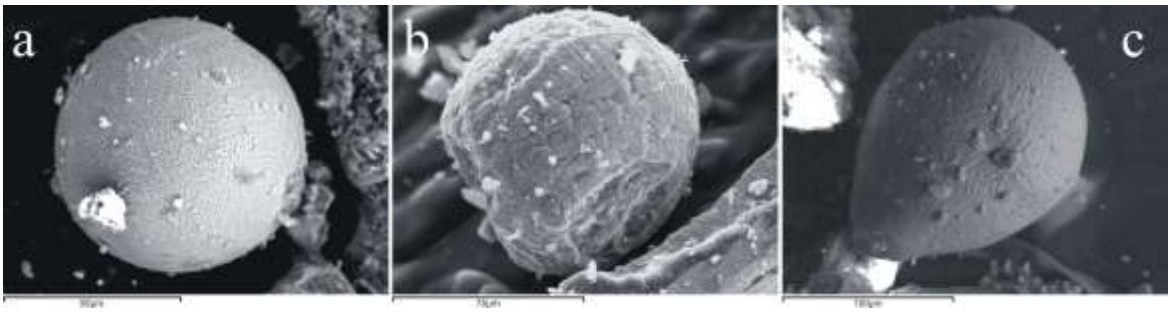

Figure 1: Backscattered SEM images of iron-rich spherules. a) Dendritic or orange peel spherule, b) Polygonic spherule and c)Molten drop spherule.

On the other hand the most frequently observed magnetic particles were angular/aggregate magnetic particles (Fig.2) generally produced from vehicles via exhaust emissions, braking systems and the abrasion or corrosion of vehicle engine and body work (Hoffmann *et al*. 1999). Elemental analysis of irregular and angular particles showed that Fe was the most abundant element (>70%) associated with heavy metals like Cr, Ni, Cu, Pb, Zn and Sb. For example, magnetic particles with Cr and Cu contents up to 13% and 22%, respectively, were observed in the magnetic extracts both from the city core and the industrial area road dust samples (Fig.2c).

Figure 2: Backscattered SEM images of angular magnetic particles.

3.2. Internal structure of magnetic dust particles

Thin polished sections were prepared from the magnetic extracts of the road dusts in order to study the internal structure of the magnetic particles. An initial examination using optical microscopy confirmed the presence of particles of clearly anthropogenic origin as shown in Figure 3. Spherical magnetic dust particles with dense (Fig.3a) and hollow (Fig.3b,c) interior were observed, while non-homogeneous layers were typical of most angular magnetic dust particles (Fig.3).

Figure 3: Optical microscopy images of magnetic particles from thin polished sections of magnetic extracts from road dusts.

More detailed SEM observations on polished sections indicated the presence of spherical magnetic particles with non-homogeneous composition as shown in Figure 4. The polished sections revealed spherical particles with big holes inside (Fig.4a) suggesting that a gas bubble was encapsulated during the formation of the particle (Jordanova *et al*. 2004). Others exhibit complex internal structure consisting of dendritic bright veins spreading over the whole particle (Fig.4b). Spherical particles with dense internal structure were also observed. Microprobe analyses of these particles revealed that they are composed of iron or iron oxides, while particles with hollow interior appear were presented more oxidized on the external surface. Angular particles present a complex structure with non-homogeneous distribution of the magnetic phases inside the grains (Fig.4c).

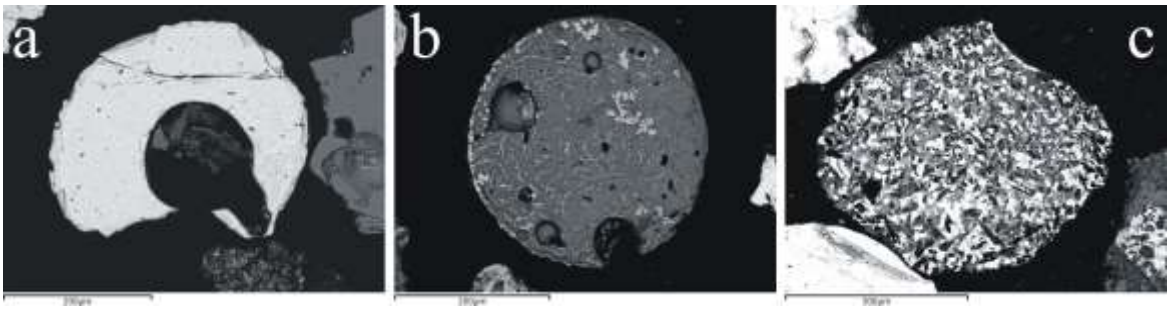

Figure 4: Backscattered SEM images of magnetic particles from thin polished sections of magnetic extracts from road dusts.

4. Conclusions

Different amounts of magnetic particles were extracted from road dust samples from the city of Thessaloniki and were studied by scanning electron microscopy. The detailed SEM observations exhibited the dominance of spherules and angular/aggregate dust particles. The spherules presented different surface microstructure characteristics, while the angular magnetic particles observed were highly associated with elevated heavy metal contents. Detailed study revealed that in some cases the spherules possess a complex internal structure in which the magnetic phase is presented as dendrites or in other cases big voids were observed. On the other hand, angular magnetic particles with complex internal structure consisting of non-homogeneous layers were the most commonly observed particles.

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REFERENCES

1. Bourliva A., Kantiranis N., Papadopoulou L., Aidona E., Christoforidis C. and Kollias P. (2011), On the morphology, geochemical characteristics and magnetic properties of urban road dust particles from the historic center of the city of Thessaloniki, Greece. Proceedings of the 12th International Conference of Environmental Science and Technology, A238-245.
2. Bucko M.S., Magiera T., Pesonen L.J. and Janus B. (2010), Magnetic, geochemical, and microstructural characteristics of road dust on roadsides with different traffic volumes dcase study from Finland. Water Air and Soil Pollution, **209**, 295-306.
3. Goddu S.R., Appel E., Jordanova D. and Wehland F. (2004), Magnetic properties of road dust from Visakhapatnam (India): relationship to industrial pollution and road traffic. Physics and Chemistry of the Earth, **29**, 985-995.
4. Hoffmann V., Knab M. and Appel E. (1999), Magnetic susceptibility mapping of roadside pollution. J. Geochem. Exp., **66**, 313-326.

5. Jordanova D., Jordanova N. and Hoffmann V. (2006), Magnetic mineralogy and grain-size dependence of hysteresis parameters of single spherules from industrial waste products. Physics of the Earth and Planetary Interiors, **154**, 255-265.
6. Lu S.G., Zheng Y.W. and Bai S.Q. (2008), A HRTEM/EDX approach to identification of the source of dust particles on urban tree leaves. Atm. Environ., **42**, 6431-6441.
7. Maher B. A., Moore C. and Matzka J. (2008), Spatial variation in vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves. Atm. Environ., **42**, 364-373.
8. Muxworthy A.R., Matzka J. and Petersen N. (2001), Comparison of magnetic parameters of urban atmospheric particulate matter with pollution and meteorological data. Atm. Environ., **35**, 4379-4386.
9. Osterle W., Griepentrog M., Gross Th. and Urban I. (2001), Chemical and microstructural changes induced by friction and wear of brakes. Wear, **251**, 1469-1476.
10. Wang X. and Yong Q. (2007), Relationships between heavy metals and iron oxides, fulvic acids, particle size fractions in urban roadside soils. Environ. Geol., **52**, 63-69.
11. Yang T., Liu Q.S., Chan L.S. and Cao G.D. (2007), Magnetic investigation of heavy metals contamination in urban topsoils around the East Lake, Wuhan city, China. Geophysical Journal International, **171**, 603-612.