



Isolation of technogenic magnetic particles



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HIGHLIGHTS

- The developed method offers a low-cost approach of large-scale dry deposition.
- Tombstones are excellent supports for sampling these atmospheric deposits.
- Smelted elements crystallise after cooling, giving typical technogenic magnetic particles (TMPs).
- Coupling microscopic and bulk analyses allows identifying TMP origin.
- Magnetic TMPs issued from steel industry were separated by a new technique.

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ABSTRACT

Technogenic magnetic particles (TMPs) emitted by various industrial sources, such as smelting plants, end up after atmospheric transfer on the soil surface. In the present study, we characterised the origin and composition of such particles emitted by a large iron smelting plant and deposited on particular substrates, namely tombstones, which act as a very interesting and appropriate matrix when compared to soil, tree bark, lichens or attic dust. The isolation and subsequent description of TMPs require a critical step of separation between different components of the sample and the magnetic particles; here, we described an efficient protocol that fulfils such a requirement: it resorts to water suspension, sonication, repeated magnetic extraction, sedimentation, sieving and organic matter destruction at 550 °C in some instances. The isolated TMPs displayed a noticeable crystalline shape with variable compositions: a) pure iron oxides, b) iron + Cr, Ni or Zn, and c) a complex structure containing Ca, Si, Mg, and Mn. Using Scanning Electron Microscope Energy Dispersive X-ray (SEM–EDX), we obtained profiles of various and distinct magnetic particles, which allowed us to identify the source of the TMPs.

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1. Introduction

A consequence of several types of activities specific to industrial societies is the atmospheric emission of inorganic and organic compounds (Murphy and Allen, 2005; Sims et al., 2009). A majority of these substances do not remain in a dispersed volatile state, in contrast to oxygen or nitrogen for instance, but are deposited on the surface of the Earth after a complex transfer (Gunindi and Tasdemir, 2011; Skarzynska et al., 2006). The duration and distance of such a transfer are linked to several factors, such as the size and density of the particles,

the strength of the wind, the thermal atmospheric movements and the landscape topography (Ewing et al., 2010; Uematsu et al., 2010).

An essential part of the substances present in the air contributes to the constitution of solid particles (Zhu et al., 2011). They may also be adsorbed especially on clay or on organic constituents (Callen et al., 2011; Lu et al., 2007) or be involved in more complex structures, named “aerosols” (Korzhova et al., 2011; Prather et al., 2008; Seinfeld and Pandis, 1998). All these structures are subjected to a deposition process (Chabas et al., 2010; Garnaud et al., 1999).

Since atmospheric contaminants can be responsible for dysfunctions in the ecosystem and even lead to detrimental impacts on human health the need for identifying such contaminants in air samples arose by the end of the 20th century, and dedicated methods were rapidly developed for this purpose (Kampa and Castanas, 2008; Lovett et al., 2009; Taylor et al., 1994). Concomitantly, it was also critical to study the deposition of these contaminants for three main reasons: (1) the deposition is uneven and leads to an unequal contaminant distribution on the surface of the

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Earth; (2) particle concentrations reached in heavily contaminated locations are directly responsible for ecological perturbations and health disorders (Meyer et al., 2010; Tagaris et al., 2009) and (3) contaminants may accumulate over a long period of time (Catinon et al., 2008). Previous studies focused on various types of matrices (e.g., bark pockets (Bellis et al., 2002); ash tree bark (Catinon et al., 2008); glue plates (Sabin et al., 2006); attic dust (Tye et al., 2006)) through decades of particle deposits, and all showed how complex the deposition phenomenon was. The anthropogenic deposits were systematically mixed with geogenic or biologic materials. Relatively complex calculations were then required to evaluate the anthropogenic part (Catinon et al., 2009a,b; Reimann and de Caritat, 2005). Another factor increasing the complexity of deposition studies was the relatively steady rate of deposition arising from the average atmospheric contamination, which can be superimposed to fortuitous events of short duration (for instance, accidental industrial fires, dysfunctioning fume filters or field burning), able to provide large amounts of specific substances.

In such a context, it was of great interest to generate protocols as to appropriately study transfer and deposition of a single class of anthropogenic contaminants. We initially chose a class of contaminants, which can be unambiguously separated from other constituents of complex mixtures submitted to an atmospheric transfer. We therefore focused our study on technogenic magnetic particles (TMPs), since the presence of typical ferromagnetic spherules has previously been well described (Magiera et al., 2011, 2013; Bucko et al., 2011). Although TMP isolation is mainly based on the high magnetic susceptibility of magnetite, maghemite and iron, but does not take into account other iron derivatives, such as hematite or goethite, TMPs could still represent a distinctive signature within several technogenic pollutant mixtures (Hoffmann et al., 1999; Matzka and Maher, 1999; Sagnotti et al., 2006; Bucko et al., 2010).

To test our experimental TMP isolation procedure, we assessed the deposition of TMPs in an industrial valley with a long history of intense steel industry. In order to gather valuable information on the studied particles with a good statistical significance, it was necessary (1) to sample large amounts of particles having a high magnetic susceptibility and (2) to extract these in order to establish their structure, shape, size distribution and chemical composition, as explained in the following report.

2. Material and methods

2.1. Sampling method and sites

An intense steel industry has been developed in the Gier valley between St Chamond and Givors (S.E of France) since the middle of the 19th century (see location map Fig. S1 in Supplementary material). The main sampling area for atmospheric deposits is located on the top of a hill (alt. 280 masl), which looks down onto the Chateauneuf village (alt. 221 masl) and onto an important iron smelting estate.

Sampling the deposit on tombstones was carried out by spraying the stone with distilled water (300 ml m^{-2}) and scraping out the suspension with an abrasive sponge (Carrefour products TSA 50010, Levallois, France), which was previously rinsed with distilled water. Immediately after careful sampling on a 1 to 2 m^2 area, a second washing and sponging steps were carried out. The dry weight, mineral content and TMP content measured from the second sample were always negligible. Tombstones chosen in the village graveyard located on the top of the studied hill were polished, strictly horizontal and generally constituted of syenite (coarse grained plutonic rock). The tombstones made of concrete were inappropriate for sampling. The main criterion for a good matrix was that it was made of a very tough rock and submitted to a careful polishing, by diamond buffing wheels, resulting in a perfectly smooth surface. The sampling of deposits on tree barks was previously described in Catinon et al. (2008).

2.2. Total mineral content and organic matter content determination (loss on ignition)

An aliquot of each sample (from 100 to 500 mg) was heated at 550 °C overnight under controlled conditions to minimise mineral volatilisation (Reimann et al., 2008; Saarela et al., 2005). The ashes were weighed and ash-to-dry weight (DW) ratios calculated. The organic matter content was calculated as DW minus ashes weight/DW expressed as %.

2.3. Measurement of TMP concentration

The extraction of magnetic particles was carried out using a hand ferrite magnet $150 \times 100 \times 25.4 \text{ mm}$ (Walker Brailon Magnetics, Montmélian, France) wrapped in a double polyethylene bag. The sonication was carried out in an ultrasonic bath ($2 \times 1 \text{ min}$) with an Ultraschall Generator T 460, 35 kHz no. 88155 (Fisher Scientific).

The magnetic particles were air dried at 60 °C, weighed and the ratio of magnetic particles to total dry weight was calculated. The ratio of the mass of purified magnetic particles per matrix area unit was also calculated.

2.4. SEM–EDX studies

Sample characterisation was performed using a ZEISS SUPRA 55VP Scanning Electron Microscope (SEM) (3rd generation of GEMINI field emission column), allowing a spatial resolution down to 1.0 nm, coupled to an Energy Dispersive X-ray (EDX) microanalysis system (SAHARA Silicon Drift Detector with Spirit Software of PGT) allowing high counting rates.

Samples were studied using electronic imaging (secondary electrons [SE] and back scattered electrons [BSE]), X-ray qualitative analysis and X-ray elemental mapping.

Analytical conditions were as below:

- accelerating voltage: 15 kV
- working distance was about 7 mm (optimal distance for EDX analysis)
- samples were carbon-coated to reduce charging effects.

2.5. ICP–MS: determination of elemental content

The solids were totally digested using a previously described three-step acidic method (Priadi et al., 2011). All solutions were ultrapure reagents to ensure minimum contamination (HNO_3 and HCl Normatom grade, VWR France, and HF and HClO_4 “for trace metal analyses”, Baker, from Sodipro France). Major and trace metal concentrations (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Ni, Pb, Sb, Ti, V, and Zn) were determined using Inductively Coupled Plasma Quadrupolar Mass Spectrometry (ICP–QMS) (XICCT-Series, ThermoElectron, France). ICP–QMS spectrometer was calibrated using standard solutions and routinely checked with certified river water (SRM 1640, National Institute for Science and Technology, Gaithersburg, USA). Instrumental drifts and plasma fluctuations were corrected using internal standards (Re, Rh, and In (SPEX, SCP Science, France)) for all studied metals, and Ge for major elements including Ca, Al, and Mg. To minimise isobaric interferences, an analysis with the Collision Cell Technology (CCT) introducing a supplementary gas mixture of H_2 (7%) and He (93%) was applied to determine the concentrations in Fe, Mn, and Cd, Cr, Co, Cu, Mn, Ni, Pb, and Zn. Values obtained for the reference sediment SL1 (3 replicates) were compared to certified values, and recovery was 90–99% for all elements analysed except 115% for Cd, with a standard deviation of 10% or less for all elements, except Ag, Ba, Cd, Mn and Ti with a SD of 18%, and Ca and Fe with a SD of 24%.

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