REE minerals in roadside dusts of the Barcelona area: anthropogenic origin?

Robert Morera-Valverde (1*), Dídac Navarro-Ciurana (1, 2), Joaquín A. Proenza (2), Júlia Farré-de-Pablo (2), Núria Pujol-Solà (2), Mercè Corbella (1)

(1) Dpt. Geologia. Universitat Autònoma de Barcelona. Campus UAB, Edifici C, 08193, Bellaterra, España.
(2) Dpt. de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona, c/Marti i Franquès, s/n, 08028, Barcelona, España.
*corresponding author: robertmoreravalverde@gmail.com

Palabras Clave: Mineralogía, tierras raras, polvo de carretera. | **Key Words:** Mineralogy, Rare Earth Elements, road dust.

INTRODUCTION

The growth of the population, industrial and commercial activities and vehicle traffic flow are the major causes of pollution in urban environments. Road dust is known to contain several pollutant heavy metals, as Rare Earth Elements (REE) and polycyclic aromatic hydrocarbons (e.g., Aryal et al., 2010), which are the most harmful to human's health and to the environment in urban systems (Saeedi et al., 2012).

Technological developments have dramatically increased the use of REEs in defence, aerospace, medical and automotive industries. Furthermore, REEs are classified as critical metals due to their high industrial applications and economic importance coupled to possible supply shortfalls (Goodenough et al., 2018). Among others, they are essential components of vehicle catalysts, high-strength magnets, super-alloys, display technology and lasers (Wall, 2013). The presence of these critical metals in the environment, as road dusts, has increased in the lasts decades. This has encouraged researchers to carry out geochemical studies to identify the anthropogenic sources of REEs in dust deposited on roads and tree leaves, as well as their potential use as fingerprints to evaluate the environmental impact (e.g., Amato et al., 2011; Shaltout et al., 2013). The main anthropogenic activities that contribute to the presence of REEs in roadside dust are vehicle exhaust emissions; degradation of catalysts and batteries, and vehicle tyres, brakes and bodywork wears (e.g., Shaltout et al., 2013 and references therein).
Accurate data on the mineralogy of the anthropogenic REE phases in road dusts from Spain, and also across de globe, are scarce so far (e.g., Varrica et al., 2002). Therefore, we aim to provide preliminary data on the REE mineralogy of roadside dusts from Barcelona and surrounding roads, by means of a petrographic and geochemical characterization, including the investigation of other heavy mineral concentrates.

SAMPLES AND METHODOLOGY

Four composite roadway dust samples were collected in the area of Barcelona (Fig. 1) in January 2019, after a dry period of 15 days. One sample, obtained in Barcelona city (Colon square; sample S3), was chosen as representative of one of the areas in town with densest traffic. On the other hand, three samples were taken in nearby areas (Fig. 1): i) entrance of Sabadell (sample S1); ii) road to Badalona (sample S2); and ii) Sitges (sample S4). At each sampling sites, about 6 kg of road dust composite were collected by sweeping with a soft touch brush and a plastic dust pan.
The sample was initially sieved through a 500 μm sieve to remove extraneous stones, pebbles and grass and then sieved to <125 μm, obtaining around 150 g of sieved road dust. The resulting material was prepared as closely-packed monolayer polished sections, which were investigated using a Zeiss EVO MA 10 Scanning Electron Microscope (SEM) with accelerating voltage of 20 kV at the Servei de Microscopia of the UAB. Different mineral phases were identified by means of qualitative analyses using an Energy-Dispersive Spectrometer (EDS) with an average count time of 30 s per analysis.

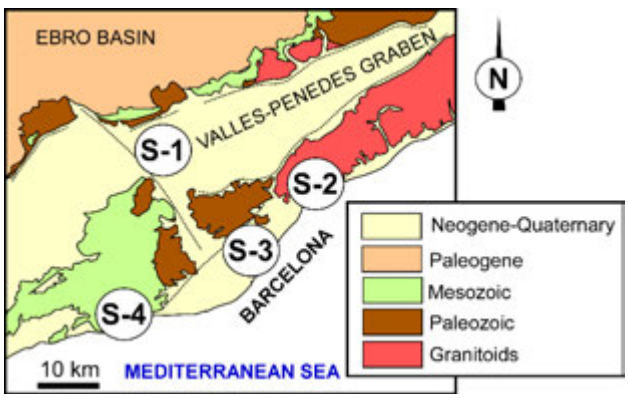

Fig 1. *Simplified geological map of the Vallès-Penedès Basin. The area enclosed by circles shows the sample points: S-1 Sabadell; S-2 Badalona; S-3 Barcelona; and S-4 Sitges.*

MINERALOGY OF ROAD DUSTS

Abundant heavy mineral phases were found within the investigated road dusts and these include: barite ($BaSO_4$); Sn, Cu, Zn, Fe, Fe-Cu, Sb and Pb sulphides; Fe, Pb, Sn, Cu and Sb native elements; Fe-Zn, Fe-Mn, Fe-Cu, Fe-Sn, Fe-Cr-Ni, Fe-Ti, Bi-Fe and Cu-Zn alloys; and in a lesser extent Ce-La-Nd-Th-phosphates and Ce-La-(Fe)-silicates (Fig. 2). It is known that barite is used as a component of brake pad composites, but also covellite, sphalerite, pyrite, chalcopyrite, stibnite and metallic Cu (e.g., Amato et al., 2012). Consequently, the presence of these mineral phases in the studied road dusts can be related to erosion of vehicle brake linings. Moreover, Ce is widely used in automotive catalytic converters, where it is introduced as CeO_2 to promote the water–gas shift reaction and to store oxygen (e.g., Varrica et al., 2002). The presence of REE minerals in all the studied dust samples suggests that they derive from anthropogenic sources, probably related to automobile exhausts. In addition, similar REE minerals are identified in road dusts from Palermo (Italy) by Varrica et al. (2002).

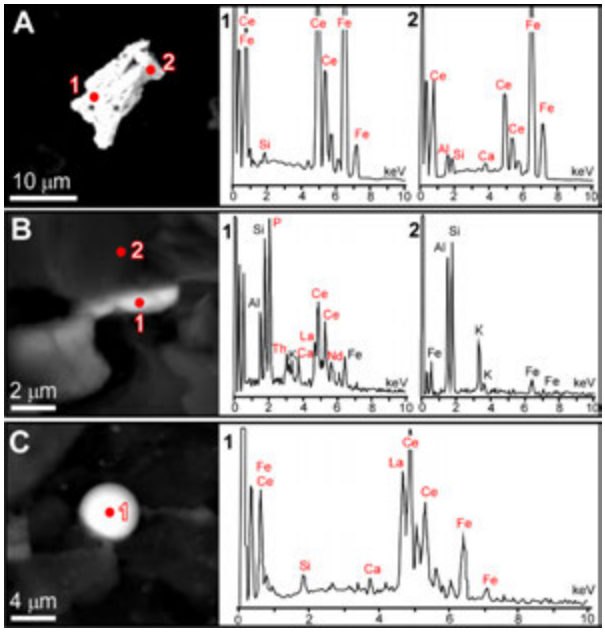

Fig 2. *SEM images and EDS spectra of dust particles containing Ce-Fe-Si-(Ca-Al) (**A**), Ce-La-Nd-Th-P (**B**) and Ce-La-Fe-Si (**C**).*

REE minerals within the studied road dusts can be divided into two groups according to their appearance: i) isolated euhedral crystals, with sizes around 20 µm (Fig. 2A); and ii) irregular particles, which are less than 5 µm in size, and display elongated (Fig. 2B) and spherical (Fig. 2C) morphologies. The isolated euhedral crystals are Ce-Fe-(Ca-Al)-silicates with porous (spongy) surfaces and irregular zonation, showing a decrease of Ce content towards the outer parts (Fig. 2A). According to these textures, euhedral phases seem to have been affected by alteration with significant Ce mobilization. These particles were mechanically extracted probably from catalytic converters. On the other hand, the irregular particles are more chemically homogeneous (Fig. 2B). The elongated particles are Ce-La-Nd-Th-phosphates and Ce-Fe-silicates, which might correspond to monazite-(Ce) and biraite-(Ce) respectively. The spherical particles are Ce-La-Fe-Ca-silicates, which agrees with cerite-(La). These irregular particles generally occur as aggregates or overgrowths of other dust particles, suggesting they might be neo-formed mineral.

CONCLUDING REMARKS

The petrography of the studied roadside dusts from Barcelona area reveals the presence of REE-bearing minerals, which consist of mechanically extracted euhedral crystals probably from catalytic converters of vehicles, and neo-formed crystals added and/or precipitated into other dust particles. The fact that REE minerals are found in road dusts certainly opens the door for further investigations in order to respond to questions such as: What is the cause for the alteration of euhedral REE phases? Under what physicochemical conditions are REE mobilized from dust particles enriched in these critical metals? Are neo-formed REE minerals precipitated in high or low temperatures?

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