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Volcanogenic particulates and gases from Etna volcano (Italy)

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Abstract

Volcanic emissions represent one of the most relevant natural sources of trace elements to the troposphere. Due to their potential toxicity they may have important environmental impacts from the local to the global scale and they can severely affect the atmospheric and terrestrial environment also at timescales ranging from a few to million years. Etna volcano is known as one of the largest global contributors of magmatic gases (CO_2, SO_2, and halogens) and particulate matter, including some toxic trace elements. The aim of this study was to characterize the chemical composition and the mineralogical features of the volcanogenic aerosol passively emitted from Mt. Etna. Nine samples were collected by using the filtration technique at different sites on summer 2010 and 2011. Chemical and mineralogical analyses allowed to discriminate two main constituents: the first is mainly referable to the silicate component in the volcanic plume, like lithic and juvenile fragments, crystals (e.g., plagioclases, pyroxenes, oxides) and shards of volcanic glass; the second one is linked to the soluble components like sulfosalts or halide minerals (sulfates, chlorides and fluorides). These investigations are especially important in the study area because the summit of Mt. Etna is yearly visited by nearly one hundred thousand tourists that are exposed to potentially harmful compounds.

Keywords: Volcanic emissions; volcanic aerosol; trace elements; environmental impact.

1. Introduction

Volcanic emissions represent one of the most important natural sources of trace elements into the atmosphere (e.g., As, Cd, Cu, Hg, Pb, Sb, Tl and Zn), sequentially influencing the other geochemical spheres (hydrosphere, lithosphere and biosphere). Mount

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Etna, located in eastern Sicily, is the largest alkali basaltic stratovolcano in Europe and one of the most active in the world. Its volcanic activity is dominated by persistent open conduit passive degassing at the summit craters (Voragine, Bocca Nuova, Southeast and Northeast), interrupted by sporadic effusive and/or paroxysmal explosive events. A huge summit plume continuously escapes from the volcano, resulting in a strong source of reactive gases and trace metals to the regional troposphere. Exposition to high atmospheric concentrations of potentially harmful elements in volcanic areas is a problem that should not be neglected because many millions of people visit volcanic areas each year (Erfurt-Cooper & Cooper, 2010) and many of them get close to the volcanic vents. Mount Etna is one of the major destinations of the worldwide volcano tourism and the tourist facilities provide access to areas very close to the summit craters which are the source of huge quantities of harmful elements and compounds (Aiuppa et al., 2003; Calabrese et al., 2011; Tassi et al., 2012). Besides the most recent ash emissions of the Etna volcano blanketed the city of Catania, leading to severe risks to people's health as well as to monuments, infrastructures, agriculture and so on (Montana et al., 2012; and references therein). The present contribution is aimed to estimate and characterize from a chemical and mineralogical point of view volcanogenic particulates and gases emitted from the Etna Volcano in order to evaluate volcanic emissions in term of harmfulness for people and cultural heritage as well.

2. Material and methods

Gases and particulate samples (TSP – total suspended particulate, i.e. particle-size fractions with diameter lower than 100 μm, which reach the upper part of the respiratory tract) were collected at Etna volcano (Italy) on summer 2010 and 2011. Nine filters were sampled in different location and at various distances from the active vents (Fig. 1A): one filter was sampled on the rim of Bocca Nuova crater (BNC); three samples were from Torre del Filosofo site (TDF), 1.5 km far the summit craters in downwind direction; three filters from Catania (CT), the main town at the base of the volcano; two background samples were taken from the upwind site Pizzi Deneri (PDN) in the summit area, and Bosco Ragabo (BR) in a rural area far from volcanic and anthropogenic sources.

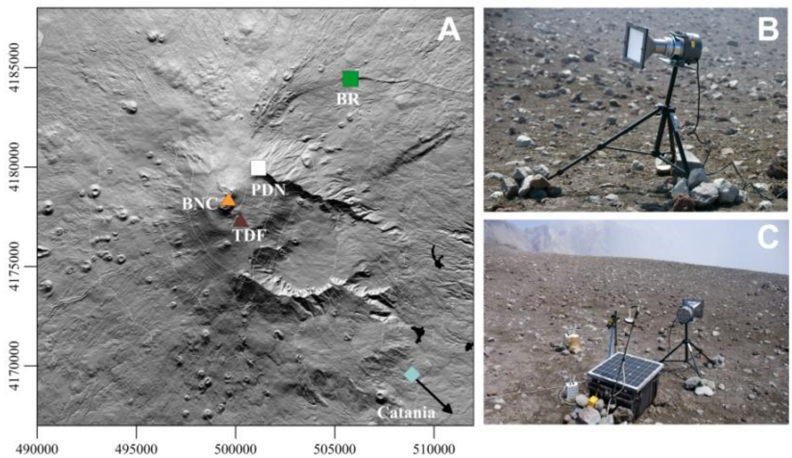

Fig. 1. Map of Mt. Etna with sampling sites (A), and pictures of the high volume sampler (B and C).

Sampling was performed by a high volume air sampler (Staplex Model TF-1A) using PTFE filters (Fig. 1B and 1C). Particle size and micromorphology of Etna particulates were investigated by means of a scanning electron microscope (SEM, Leica Stereoscan Leo 440) by secondary electron imaging (SEI). Qualitative EDS analyses (Oxford Instruments Link Isis) were carried out to acquire elemental compositions. In addition, the bulk chemical composition of aerosols was determined by using ICP-MS (Agilent 7500ce) after total acid digestion (HNO_3-HF-$HClO_4$) of the filters and 46 elements were determined.

3. Results and discussion

The total particulate concentrations ranged from about 50 $\mu g/m^3$ (local background) to more than 1000 $\mu g/m^3$ close to the crater rim. PM_{10} and $PM_{2.5}$ are the most represented size fractions observed on filters and their concentrations exceed often the limit values established by the Italian normative regarding air quality control (D. Lgs. 155/2010). Thus, at local and regional scales, several gas species and aerosols (including sulfate and fine ash) emitted into the atmosphere by Etna volcano can affect the health of humans and animals and they have also an effect of blackening on art monuments.

As a result of microscope observation and EDS analyses, different clusters of particles can be discriminated on the basis of morphology and/or composition allowing to classify the aerosol particles into four groups: silicates, Fe/Ti oxide, sulfates, halides (chlorides and fluorides) and polygenic particles. Particles resulted mainly composed of euhedral and/or subhedral crystals of gypsum ($CaSO_4.2H_2O$) (Fig. 2A), sometimes associated with Ca, K and Na sulfates (syngenite and thenardite). Comparable quantities of volcanic minerals and glass shards having size for the most part ranging between 40-60 µm have been also observed (Fig. 2B), together with agglomerates and incrustations made of sulfates and fluorides (Fig. 2C).

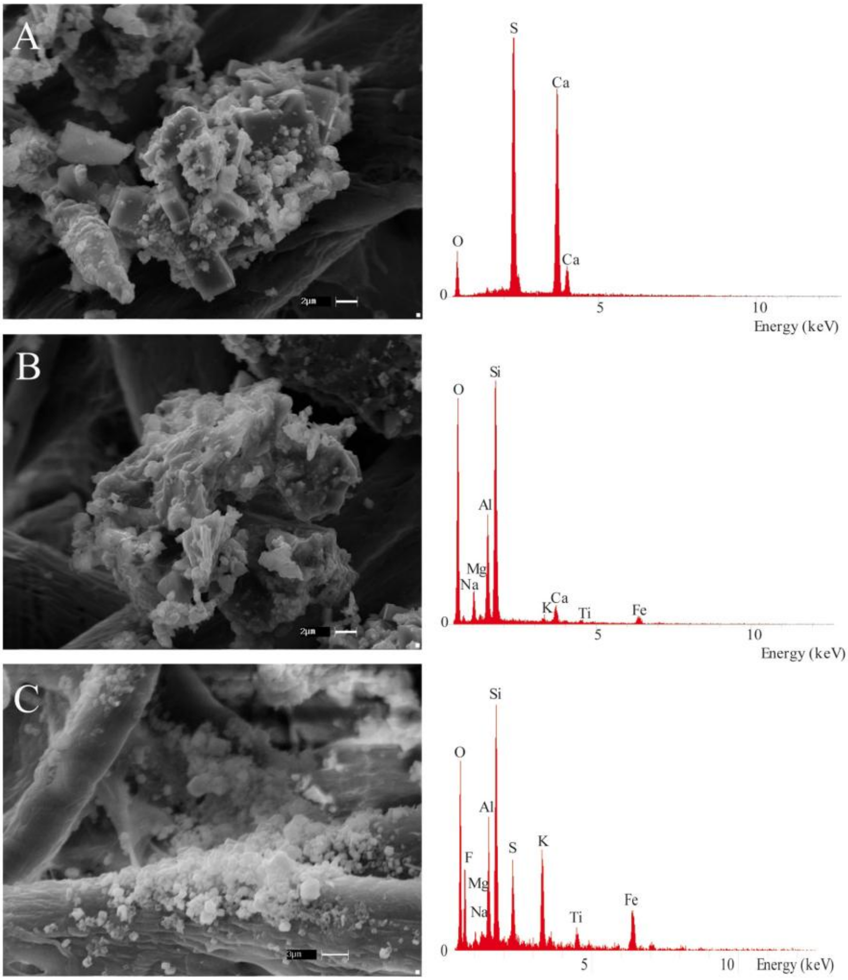

Fig. 2. SE images and relative EDS spectra of various TSP filters collected at Etna volcano: (A) sulphate crystals with prismatic habit, (B) volcanic glass shards, (C) agglomerates and incrustations of sulfates, fluorides and oxides.

The chemical results show a significant enrichment in the filters collected in the summit area in contrast with the local background. In particular, the most abundant elements were Si, Al and Fe (up to 100-200 μg/m^3), followed by Ca, Na, Mg, K, Ti (ranging from 10 to 50 μg/m^3). Among with major constituents of aerosols, high concentrations of potentially toxic elements were also found (As, B, Cu, Pb, Se and Tl, ranging from 0.2 to 2 μg/m^3).

Depending on their geochemical behaviour and origin, elements show different enrichments at the various sampling stations (Fig. 3). Highly volatile elements (Cd, As, Pb) show their highest values at the crater rim (BNC) and the lowest value in both background sites (BR and PDN). Refractory elements like Al and La, mainly related to silicate particles, are most enriched at the TDF site (Fig. 3). This is probably due to the fact that silicate particle do not derive exclusively from the plume emission but also from the resuspension of volcanic ash deposited along the flank of the volcano. A similar process could likely explain the strong enrichment of these elements in the local background (PDN) with respect to the far background (BR). The former site is, in fact, devoid of vegetation, similarly to the TDF site while the latter is in a woody area. Finally, the urban sites are highly enriched in Zn and show also moderate enrichments in Pb. Both elements are generally related to anthropogenic activities but the latter is also strongly enriched in the Etnean plume as evidenced by the high contents in the filter collected at BNC.

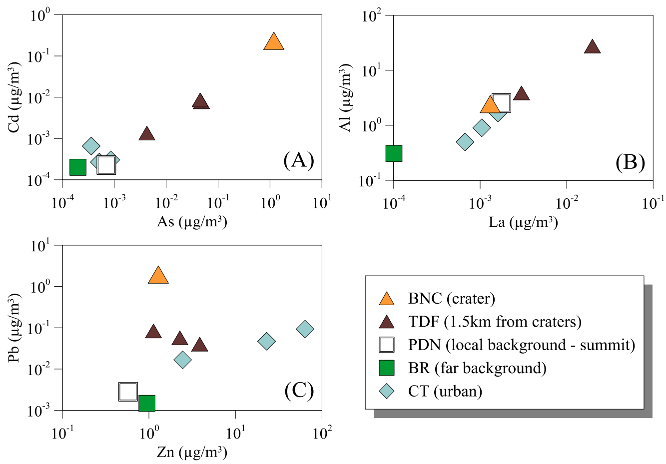

Fig. 3. Binary diagram of trace element concentrations.

Chemical concentrations were normalized with respect to the local background values (PDN) and to the total particulate concentrations. The obtained patterns (Fig. 4) show enrichment of volatile elements (K, As, Se, Rb, Cd, Te, Cs, Tl, Pb and Bi) in the sample collected at the rim of the crater (BNC). By contrast, the sample collected in urban environment (CT) shows enrichment in Zn, Mo, Cd and Pb.

Chemical and mineralogical results clearly allow to discriminate two main constituents of the particles in the summit area of the volcano: the former is mainly referable to the silicate component in the volcanic plume, like lithic and juvenile fragments, crystals (e.g. plagioclases, pyroxenes, oxides) and shards of volcanic glass; the second one is linked to the soluble component like sulfosalts or halide minerals (sulfates, chlorides and fluorides).

A significant anthropogenic contribution could be highlighted only at the sampled urban sites.

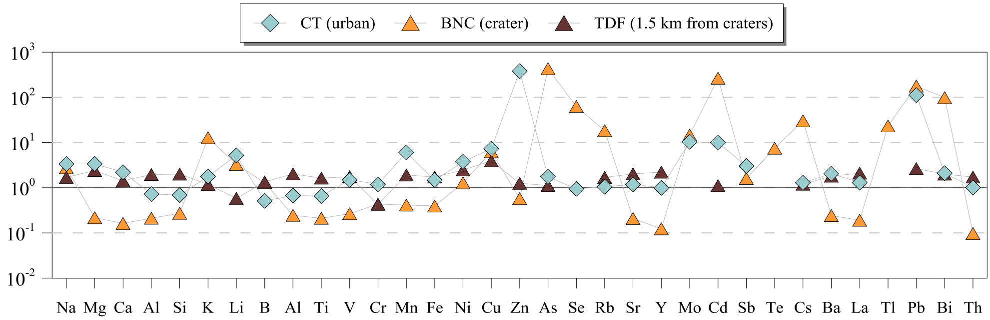

Fig. 4. Normalized concentrations of major and trace elements from particulates collected at BNC, TDF and CT.

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