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The use of moss-bags technique for volcanic aerosols investigation on Mt. Etna (Italy)

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Abstract

Explosive eruptions and volcanic passive degassing inject large quantities of gas and particles into the atmosphere that are ultimately deposited at the Earth's surface through wet or dry deposition processes, affecting the atmosphere, the hydrosphere and the biosphere. Mount Etna (Italy) is one of the most prodigious and persistent sources of gases and particles to the troposphere. Volcanic emissions were studied at Etna volcano by using moss-bags technique. Mosses (*Sphagnum* species) were exposed around the volcano at different distances from the active vents to evaluate the impact of its emissions into the atmosphere and in the local surrounding. The results confirmed the huge amount of silicates, sulfates and halides compounds emitted into the atmosphere from Mount Etna. X-ray microanalysis showed that chemical composition of the particles is mostly defined by silicate (from pure silica to metal-rich silicate composition) and sulfate/halide compounds. The contents of major and trace elements in the *Sphagnum* moss-bags significantly increased after their exposure to volcanic emissions, confirming mosses as efficient accumulators. Metals uptake rate rapidly decreases with the distance from the volcanic emission vents. The elements that showed the greatest accumulation after exposition were S, Na, Fe, Al, Cu, V, As, Cd, Li, Se, Sc, Th, Bi and Tl. This study confirmed the marked environmental impact of volcanic emissions in the eastern sector of Etna, leading to an intense “geochemical anomaly” of volatile major and trace elements due to the fumigation by the volcanic plume, in agreement with passive biomonitoring studies reported by previous authors. Finally, moss-bags techniques provide a cheap and efficient method to investigate quantitatively in space and time the environmental impact of volcanogenic atmospheric deposition.

Keywords: Trace elements; volcanic emissions; atmospheric deposition; biomonitoring; geochemistry.

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1. Introduction

Tropospheric volcanic aerosols affect terrestrial ecosystems and human health on local to regional scales (Mather et al., 2003) and are the main “carriers” of trace elements, including a number of potentially toxic chemicals (e.g., As, Cd, Cu, Pb, Se, Tl, Te, U, Th, Zn). Volcanogenic gases and aerosols emitted into the troposphere ultimately falling back on the earth’s surface, as wet or dry deposition, can be taken up by plants and soils inducing both harmful and beneficial effects (Delmelle, 2003). Mount Etna is an open conduit stratovolcano located in north eastern sector of Sicily, and is considered the largest volcano in Europe, covering an area of about 1250 km² and reaching an altitude of about 3340 m. It is one of the most active volcano in the world and its persistent passive degassing from the summit craters produces a majestic plume that continuously escapes from the volcano, resulting in the major Mediterranean point-source of reactive gases (e.g. SO₂, HCl, HF) and trace metals to the local and regional troposphere (Caltabiano et al., 2004; Gauthier & Le Cloarec 1998; Calabrese et al., 2011a). Many biomonitoring studies were successfully carried out on Mount Etna, due to the favourable conditions for sampling and monitoring the dispersion of volcanogenic species (Notcutt & Davies, 1989; Martin et al., 2009, 2012; Quayle et al., 2010). However, above the treeline limit (about 2000 m a.s.l.) begins the desert zone where the ground is usually characterized by bare volcanic ash and lava flows. In this zone only few pioneer plants resist to the extreme environmental conditions (Calabrese et al., 2011b) and passive biomonitoring techniques are not easily applicable. Therefore, in this work we tested the efficacy and the robustness of the moss-bags active biomonitoring technique on Mt. Etna. The *moss-bag* technique was introduced about 40 years ago (Goodman & Roberts, 1971), becoming an efficient and inexpensive tool for environmental studies concerning anthropogenic pollution. It is an active biomonitoring technique very useful in highly-polluted areas and has been widely used in anthropogenically modified environments (industrial and/or urban areas) to study local deposition, to identify sources of pollution and to map the dispersion of pollutants (Ares et al., 2012; and references therein).

2. Material and methods

The biomonitoring survey was carried out during the summer 2007. A network of 24 sites was set-up on the upper part of the volcano, from about 800 to up 3,300 m a.s.l., mainly on the downwind flank with respect to the active summit craters (Fig. 1a). A mixture of *Sphagnum* mosses collected in a rural area were rinsed several times with deionized water to remove extraneous material. After the excess water had been squeezed out, the cleaned moist moss was dried at room temperature under a laminar hood. Approximately 2 g (dry weight) of moss was packed in nylon mosquito net with 2 mm mesh size, forming a spherical bag. At each sampling site a pole was fixed to the soil, and the moss-bags were attached by means of nylon strings to wooden rods mounted on the top of the pole, about 2 m above the ground (Fig. 1b): moss-bags were exposed at each site for about one month, except for the most exposed site close to the craters. At the end of the exposition period, the samples were carried to the laboratory and dried at 40 °C for 48 hours. Some shoot of the exposed moss was preserved and graphite-metallised for microscopy investigation. Chemistry, micromorphology and mineralogy of volcanic particulate intercepted by mosses were investigated using scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS). The rest of the moss was powdered by planetary ball mills. About 250 mg (dry weight) of the sample were digested

through a microwave oven using Teflon vessels with a mixture of ultrapure grade nitric acid and hydrogen peroxide. Analytical methodology was tested analysing *certificate reference materials* (CRM), *replicates*, *method blanks*, and *moss blanks* (the washed unexposed moss). After dilution, the solutions were analysed by Inductively Coupled Plasma Mass (ICP-MS, Agilent 7500-ce) and Optical Emission (ICP-OES, Jobin Yvon Ultima2) spectrometers. The reproducibility was verified by using repetition of several random samples. The reliability of results was checked analysing four certified references materials (CRM) and quality control was assessed by comparing our results with the certified values. For most of the elements the reproducibility was within $\pm 10\%$.

3. Results and discussion

In general, the chemical concentrations of all analyzed elements showed a significant increase after about one month of exposition respect to the moss blank (black lines in Fig. 1a). As showed in Fig. 1a, the elements that show the highest concentrations are S, K, Ca Na, Fe, Mg, Al, Si, ranging from 10^2 to 10^4 $\mu\text{g/g}$. These elements reflect the composition of local geological substrate (mainly basaltic rocks) except for sulphur (related to the volcanic source).

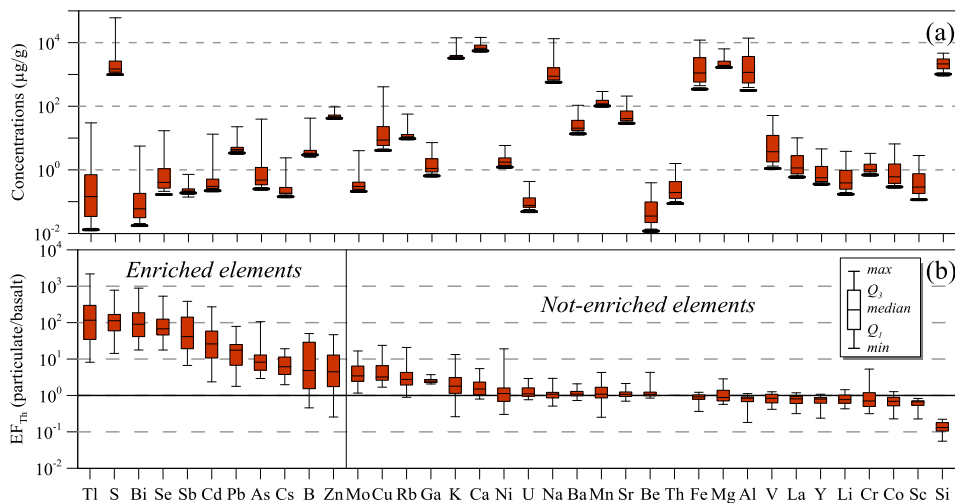


Fig. 1. (a) Box and whiskers plots of the chemical concentration in the moss-bags; the black line represents the concentration in the unexposed moss-bags. (b) Box and whiskers plots of enrichment factors (EF) of elements accumulated in moss-bags (see text). EFs were calculated with respect to the average composition of Etnean lavas using Thorium as normalizing element.

In order to evaluate their different geochemical behaviour, Enrichment Factors (EFs) were calculated for each element and for all sites. The enrichment factor compares the concentration of an analyte of interest (C_x) to a conservative element, in moss versus local parent material. Thorium has been selected as reference element (C_{Th}) and typical concentrations of Etnean basalt, as parent material (data for basalt were taken from Calabrese et al., 2011a; and references therein) and EFs were calculated according to the following formula:

$$EF_x = (C_x / C_{Th}) \text{ exposed moss} / (C_x / C_{Th}) \text{ basalt} \quad (1)$$

Concentrations of the moss blank were subtracted from exposed moss-bags before calculation, in order to evaluate EFs only for the accumulation. Results are plotted using histograms and elements are ordered by decreasing median values of the EFs with respect to the basalt (Fig. 1b). Considering the EFs of mosses related to the basalt composition, volatile elements with high geochemical mobility like Tl, S, Bi, Se, Sb, Cd, Pb, As and B showed a considerable enrichment (median values comprised between 10 and 300), reflecting an excess of these elements with respect to what would normally be supplied by the local geological substrate (mainly basaltic parent material). Some of these elements reach maximum EF values close to 1000 (S, Bi and Se) or higher (Tl up to 2177 at the summit crater site). In contrast, the remaining elements (e.g., Si, Al, Fe, Cr, Th, U, REE and others) do not show significant enrichments, with median values comprised between 0.4 and 1.5 (*refractory elements* with low geochemical mobility). The elements with high EFs are those that are emitted through volatile degassing and then condense into particles as the plume cools. Clear evidences of sulphate and halide (mainly fluorides but also chlorides) compounds were found by using electron microscopy techniques (Calabrese & D'Alessandro, 2014).

Morphology and mineralogy of particulates adhering on moss tissue were investigated by SEM-EDS. Moss leaves of non-exposed samples showed externally well preserved tissues and a particle-free surface (Fig. 2a), in contrasts with that of exposed samples (Fig. 2b, 2c, 2d) that were covered with particles of different size and shape. Scanning electron micrographs in Fig. 2a show the peculiar structure of moss leaves: the tissue is typically composed of a regular mosaic of chlorocysts and hyalocysts, with large pores that can act as a trapping system for airborne particulate (as passive samplers). The pores are irregular or oval-shaped with variable size from 5 to 15 μm . After 30-days exposure, abundant heterogeneous particles and minerals of nano- to micro-meter size were found on the surface and inside the hyalocyst pores, and damage was visible in some of the external cell walls of the exposed mosses. Total collapse of the structure was found in the mosses exposed closest to the craters, due to the corrosive acid droplets directly derived from volcanic acid gases (SO_2 , HCl, HF).

At the site most exposed to volcanic emissions (VOR) a large amount of elongated tabular crystals can be evidenced on the moss tissues, with sizes ranging from a few up to 15 micrometres. The largest crystals have a well-defined monocline/prismatic habitus and the EDS spectra of the crystals show peaks corresponding to sulphur (S), calcium (Ca) and oxygen (O) confirming the identification as gypsum crystals (Fig. 2c).

Chloride compounds were rarely observed at the summit sites, mainly as incrustations and as clusters of micrometric and sub-micrometric crystals inside the hyalocyst pores (Fig. 2b).

Other common particles in down-wind sites exposed to volcanic deposition include shard of silicate glass with agglomerates and incrustations of soluble salts (mainly sulphate and halides) overgrown onto their surface. These polygenic particles testify overgrowing processes that occur inside the plume when decreasing temperature induce gas-liquid-solid reactions leading to the formation and deposition of salts on the surface of pre-existent particles (fresh volcanic glass or erosive fragments of the conduit walls). These particles originating from primary volcanic sources are characterized mainly by large angular fragments with a silicate chemical composition, have variable size from few up to 15 μm , and were frequently found in mosses exposed close to the craters and, sporadically, also some kilometres away from the active vents Fig. 2d).

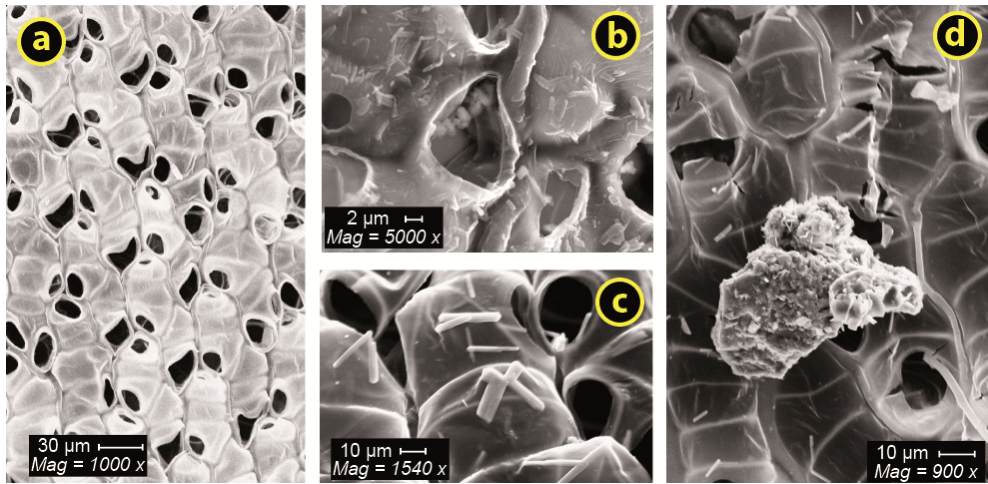


Fig. 2. Scanning electron microscopy (SEM) images of: (a) the unexposed *Sphagnum* (moss blank) shoot, (b) chlorides inside the pores of moss tissue, (c) sulphate crystals and (d) typical polygenic particle emitted from Etna (shard of silicate glass with overgrown soluble salts onto the surface) at the site closest to the summit craters.

4. Conclusions

The contents of major and trace elements in the *Sphagnum* moss-bags significantly increased after their exposure to volcanic emissions, confirming mosses as efficient accumulators. Moreover this study confirms the suitability of active biomonitoring as a low-cost and robust technique to investigate chemistry, morphology and mineralogy of particulates in active volcanic/hydrothermal environments. Metals uptake rate rapidly decreases with the distance from the volcanic emission vents (summit craters). This study confirmed the marked environmental impact of volcanic emissions at Mount Etna, leading to an intense local “geochemical anomaly” of volatile major and trace elements due to the fumigation by the volcanic plume, in agreement with passive biomonitoring studies reported by previous authors. The accumulation rate of the elements in moss-bags showed a linear increase in concentrations for As, Bi, Cd, Cu, S, Se and Tl, suggesting a constant accumulation in time and highlighting that there are no saturation problems of the moss-bags at least for an exposure period of one month. Enrichment factors allowed to distinguish plume-carried volatile elements (volcanic source) from soil-derived elements (geogenic source). Our results confirmed the huge amount of silicates, sulphates and halides compounds emitted into the atmosphere from Mount Etna, greatly influencing the deposition in the surrounding area. Moreover, the study of the particles trapped in the moss, allowed us to interpret their complex history and formation mechanism. Finally, moss-bags techniques provide a cheap and efficient method to investigate quantitatively in space and time the environmental impact of volcanogenic atmospheric deposition. The use of moss-bags can be particularly useful in all those extreme volcanic environments, like degassing summit craters or fumarolic fields, where commercial monitoring stations for atmospheric pollutants cannot be used (due to the corrosive environment and the absence of power

supply) and traditional passive biomonitoring techniques are not applicable due to the absence of vegetation.

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