Volcanic signature of volatile trace elements on atmospheric deposition at Mt. Etna, Italy

S. CALABRESE[1], G.H. FLOOR[2], W. D'ALESSANDRO[3], F. PARELLO[1], A. AIUPPA[1-3] AND G. ROMAN-ROSS[2]

[1]University of Palermo, Dip. CFTA, Via Archirafi 36, Palermo, Italy (sergio.calabrese@unipa.it)
[2]University of Girona, Campus de Montilivi, Girona, Spain.
[3]Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy

Volcanic volatiles and aerosol emitted into the atmosphere ultimately fall on the Earth's surface as wet or dry deposition, and they can influence the environment and the ecosystems at local and regional scales. Therefore, atmospheric deposition plays a key-role in the geochemical cycles, redistributing volcanogenic elements to the ground. For this reason, estimating the volcanogenic trace element fluxes from the atmosphere to the surface is necessary for a better knowledge of the environmental impact of the volcanic emissions. Nevertheless, from a literature review, we have recognized the scarcity of investigation on trace element deposition in the surroundings of active volcanoes. Here, we present a chemical characterization of bulk deposition around Mt. Etna, Italy, including both major and many trace elements.

Bulk depositions were collected approximately fortnightly, from April 2006 to December 2007, using a network of five rain gauges, located at various altitudes on the upper flanks around the summit craters of the volcano. For most elements highest concentrations have been found close to the emission vent, confirming the prevailing volcanic contribution to rainwater composition close to the summit craters. Comparison with contemporaneously collected plume emissions shows that deposition processes produce no evident element-to-element fractionation. By contrast, comparison with whole rock composition indicates a contrasting behaviour between volatile elements, which are highly-enriched in rainwater, and refractory elements, which have low rainwater/whole rock concentration ratios.

Chemical concentrations in bulk deposition were used to estimate the deposition rates of a large suite of elements. Deposition rates for volatile trace elements like Se, As, and Cd range from 1.7, 1.2 and 0.9 μg m^{-2} day^{-1} nearby to the summit vents, to 0.5, 0.3, and 0.1 μg m^{-2} day^{-1} at the local background site on the upwind western sector.

Uranium trapping on opals from the Nopal natural analogue : Evidence for complexation on internal surface of opal

G. CALAS*, L. GALOIS AND T. ALLARD

IMPMC, UMR7590, CNRS, Universités de Paris 6§7 and Institut de Physique du Globe de Paris, 75015 Paris, France (calas@impmc.jussieu.fr, galoisy@impmc.jussieu.fr, allard@impmc.jussieu.fr)

Uranium is an important environmental contaminant. The modeling of uranium mobility, controlled by its chemical behavior, helps understand the migration of transuranic elements, a major concern in nuclear waste management. In the volcanic-hosted uranium deposit of Nopal I (Chihuahua, Mexico), considered to be a natural analogue for the proposed high-level nuclear waste repository at Yucca Mountain (Nevada, USA), uranium occurs under both reduced and oxidized forms [1]. Late opal deposition accompanied the last alteration event, the $\delta^{18}O$ values indicating that opal formed at around 30°C. This opal contains low amounts of uranium, typically in the 500-2000 ppm range, and corresponds to a late mobilization of uranium. It is then important to determine the form under which uranium occurs in this opal to understand the trapping processes, which may be at the origin of a potential retardation of radionuclide migration.

In order to investigate uranium speciation, we have used fluorescence spectroscopy, a tool well-suited at low-level concentrations. The spectra, recorded at room temperature and 77K, are different of those found in secondary uranium minerals, showing that fluorescent properties of opal do not arise from (nano-)mineral inclusions, despite opal usually covers secondary uranium silicate minerals at Nopal I. In addition, fluorescence is observed at room temperature, as uranyl silicates show short fluorescence lifetimes at room temperature. The position and relative intensity of the vibronic components of the fluorescence spectrum are also different from those found on the spectra of uranyl complexes sorbed on silica. The O=U=O symmetrical stretch frequency, measured from the spacing of the vibronic bands of the fluorescence spectra data, is consistent with aqueous uranyl-phosphate complexes adsorbed as ternary surface complexes on the internal surface area of the colloidal array. They indicate uranium trapping under oxidized conditions and shed light on potential retardation mechanisms.

[1] Calas *et al*. (2008) *Terra Nova* **20**, 206-21.