



Ions, vapors and/or nanoparticles penetrating volcanic edifices?

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A top-sealed plastic tube with a diameter of ca. 15 cm had been buried ca. 70 cm deep vertically at the base of La Fossa volcano, Vulcano island, Italy, next to the front of the obsidian flow. The tube had been filled with layered rock and quartz wool to condense vapors emanating from the soil. At ca. 75 cm below the surface the sample had been exposed to vapors from Sept. 2005 to April 2006. The leached sample had not been in touch with the ground. 2 other glass wool cushions (ca. 10 cm thick, uncompacted) had been underneath to minimize capillary effects. A rock wool layer not touching ground revealed nucleated sylvite ($\text{KCl} \sim 10 \mu\text{m}$ in size) and barite ($\text{BaSO}_4 \sim 5\text{-}10 \mu\text{m}$ in size) crystals by SEM/EDS in its basal portion. Other very small ($< 2 \mu\text{m}$) particles were observed on the rock wool fibers but we could not identify them because they were suddenly volatilized by the electron beam during the analysis. The bright appearance of these particles in backscattered images suggests that these particles may be metal compounds. The nucleation of sylvite and barite documents the presence of ions. Leaching of the quartz wool at room temperature with deionized H_2O and ICP-MS analysis documented positive values for: Mg, Al, Si, P, K, Ca, Cr, Mn, Ni, Cu, Zn, Cd, Sn, Pb and partially W. Leaching with nitric acid documented also V and Fe. Acid leaching produced higher values for all elements, except K and Sn. Negative values had been obtained for As, Se, Mo. Influence from soil breathing can be excluded as the active fumaroles contain As and Se. This experiment documents for the first time an unknown element transport by vapors/gases through a volcanic edifice interacting with hydrothermal and magmatic gases. In comparison with blank data, 4 groups of elements can be distinguished: 1. positive signal: Mg, K, Ca, Cr, Mn, Ni, (Ba); low to moderate volatility at magmatic conditions. 2. unclear signal: Al, Si, P, Fe; low volatility at magmatic conditions. 3. no signal: V, As, Se, Mo, Co. As, Se, Mo, V are considered to be highly volatile, Co got a low volatility. 4. positive signal: Cu, Zn, Cd, Sn, Pb, W; high volatility at magmatic conditions.

Charging, and to a lesser degree ions, in volcanic environments had been documented after fracture-charging in eruptive plumes and in phreatomagmatic and steam plumes (James et al., 2000). The sampling site is not within well defined CO_2 anomalies around La Fossa v.. The heating events 2005/2006 (Granieri et al., 2006) might have shifted anomalous CO_2 degassing in the vicinity. Ba ions exist at very low pH values (0-1). No acidic alteration at the site is detectable at macro-scale. The bottom of the site had been dry even after heavy rainfalls (Sept. 2006). Bottom temperatures at Sept. 2005, April 06 and Sept. 2006 had been 19-21°C (3 measurements).

Are ions documented as nucleated particles penetrating the volcanic edifice or are other sources of these ions possible? However, all ions, vapors or nanoparticles have to go through porous systems to nucleate or getting deposited at the experimental site. Why are they not nucleating somewhere at depth? Sea water encountering hot lava is known to produce charged particles. Is seawater reaching magma storage at depth of the edifice? Sylvite and K data of leaching seem to be in correspondence. The leaching technique would not permit dissolution of barite. P data might indicate condensed products of PH_3 . PH_3 had been already detected by Obenholzner et al. (2006). All other elements detected by ICP-MS could be related to sulfates, sulfides and halogenides or to unspecified nanoparticles. Halocarbons and chlorinated benzenes are reported from the base of La Fossa v. (Schwandner et al., 2004). A GeoRef search (geogas) documents element and nanoparticles transport by an even non-volcanic geogas. The origin of ions, the question if ions or nanoparticles are responsible for ICP-MS detected elements, are crucial if there will be future approaches to develop a new generation of chemical or physical sensors to monitor active volcanoes. At the moment glass wool-filled tubes are installed at Vesuvius, Solfatara, La Fossa v. and Vulcanello. A blank experiment is installed at Monte Lattari, Sorrento Peninsula, Italy. However, the geogas makes it difficult to locate a blank volcano or any kind of a blank site on Earth. It remains unknown if elements detected are entering the atmosphere or are getting adsorbed onto the volcanic ash/soil particles derived from reworked surge beds

and alteration at La Fossa v.. Theoretical and empirical studies exist if particles from the lithosphere can reach the ionosphere and cause disturbances (Liperovsky et al., 2005; Dautermann et al. 2007). Refined experiments at the base of several volcanoes at different stages of activity are needed. Better EM studies of exposed glass wool are necessary. Geochemical data on recent Vulcano rock coatings suggest that metals and trace elements are at least partially fixed on the surface of the ground (Fulignati et al., 2002). It remains unknown if old, buried rock coatings exist at depth. Soil air sampling through filter-bubbler equipment and subsequent ICP-MS analyses of liquids at the experimental site at the base of La Fossa v. and on Stromboli revealed various trace elements in bubbler liquids. Ref: Dautermann et al., 2007. J. Geophys. Res., Vol. 112, B02106, doi: 10.1029/2006JB004447. Fulignati et al., 2002. JVGR, 115, 397-410. James et al., 2000. J. Geophys. Res., 105, B7, 16641-16649. Granieri et al., 2006. GRL, 33, L13316, doi:10.1029/2006GL026460. Liperovsky et al., 2005. Natural Hazards and Earth System Sciences, 5, 783-789. Obenholzner J.H. et al. (2006). Geophysical Research Abstract, vol. 8, 05721. Schwandner et al., 2004. J. Geophys. Res., 109, D04301, doi:10.1029/2003JD003890.