VESUVIUS 2000 – forum 2004, September 2-3, 2004, Ercolano (Napoli), Italy

SI-RICH FIBERS AND PARTICLES EMITTED FROM VOLCANOES

J.H. Obenholzner[1], P. Poelt[2], H. Schroettner[2], S. Simic[2], S. Mitsche[2], T. Caltabiano[3], G. Steinhauser[4], A. Musilek[4], P. Kregsamer[4], T.A. Mather[5], H. Delgado[6]

[1]Naturhistorisches Museum/Mineralogie, Postfach 417, A-1014 Vienna, Austria
[2]Zentrum für Elektronenmikroskopie/Univ. of Technology Steyrergasse 17, A-8010 Graz, Austria
[3]Istituto Nazionale di Geofisica e Vulcanologia - Sezione di Catania, Piazza Roma 2, I-95123 Catania, Italy
[4]Atominstitut der Österreichischen Universitäten, Department of Radiochemistry, Univ. of Technology Stadionallee 2, A-1020Vienna, Austria
[5]Dept. of Earth Sciences, Univiversity of Cambridge CB2 3EQ, Cambridge, UK
[6]Instituto de Geofisica, UNAM, Coyoacan 04510, Mexico D.F., Mexico

Preliminary volcanic aerosol particle collection at the F0 fumarole at Vulcano, Italy utilizing several different types of filter material and subsequent field emission gun scanning electron microscopy/energy-dispersive X-ray spectrometry (FESEM/EDS) studies suggest that the particles collected on filters may not be representative for naturally occurring particles in the volcano-atmosphere environment. I.e. Ba-S-O particles collected on Ba-containing borosilicate (BS) glass fiber filters do not occur on Ba-free Si-(Al)-O glass wool (GW). FESEM could not detect corrosion of the BS fibers. GW collected abundant Zn-Cl and to a lesser degree Tl-Cl (cubic?, diam. ca.400 nm), Tl-Pb-(Cd)-(F)-Cl-Br (<1-5 μm, mostly anhedral), As-S, and rare Ag-bearing particles (March 2004). Loosely mounted GW on a filter holder collected additionally F>>N particles which might be NH_4BF_4 ["barberiite"?, B not detected!]. The latter can be: (a.) anhedral, elongated (l=ca. 10μm), oriented along fibers, (b.) partial euhedral (diam. ca. 10 μm), oriented perpendicular to fibers, or (c.) spindle-shaped (l= 40 μm), oriented along fibers. On top of F>>N particles (a) and (c) Tl-Pb-Cl-Br particles are present as well. The NH3 component of F>>N particles probabely indicates the influence of ambient air. On GW inside a silicon hose these particles did not form. GW had been applied at ca. 25-38°C (ambient temperature: ca. 10°C) showing collection of major toxic elements: Tl, Pb and F from volcanic gases/vapors. According to total reflexion X-ray fluorescence (TXRF) GW contains 0.29+/- 0.03 ppm Tl. These low contents of Tl and missing features of corrosion exclude Tl leaching from GW.

I contradiction to these results amorphous Si-rich material is generally assumed to be a poor nucleator. It needs further studies (FESEM, AFM) if homogeneous (?) and smooth fiber surfaces are clean, or if nanometer-sized dust triggers crystallization. Summarizing preliminary results the question arises if designed fibers could cause crystallization of particles containing elements which can be attributed to i.e. magmatic processes?

Tl data of volatiles are documented from only a few volcanoes [1-4]. BS and GW had been applied in a ca. 24 h interval (2004). In Sept. 2003 (night) BS had been applied at F0 but no Ba-S-O particle formation could be detected. Zn-, Hg-, As- and Cu-S particles could be detected on BS (Solfatara, 2001). Airborne collection of particles at the passively degassing plume of Popocatepetl (Mexico) demonstrated the presence of Ba-S-O grains on Teflon filters and Ba-S-O particles growing on BS [5]. When Al-P-O, disc ceramic filters were applied for a short time (ca. 10 min, F0, 2001), silicates and glass with Hg-, Cu-, As-S particles adhering were collected. After ca. 1h exposure (Sept. 2003) the Al-P-O filter had been destroyed. The incompatibility of results obtained from chemically and physically different filter media indicate different micro--

chemical environments and micro-physical yields during sampling. Tl is known to be a health hazard, Br had been a component of remedies aginst sleeping disorders. A geological consequence of the obtained results on filters might be that quartz sands deposited on i.e. intra-rift volcanoes might become a trap for selected metals as volcanic volatiles pass through such sediments. Can quartz-rich desert dust collect Tl from volcanically polluted troposphere and transport Tl into regions far away from volcanic activity? Si-rich ash and pumice might become a similar substratum for the post-eruptive deposition of metal-bearing minerals. Metamorphosed ancient volcanic--non-volcanic sedimentary successions need further investigations. However, it remains unknown if naturally occurring quartz grains provide similar nucleation sites as Si-rich fibers. Time-resolved sampling utilizing this technique might be able to detect changes of element fluxes of fumaroles.

Organic, fibrous coalescers used for air filtration in aeroplanes had also be tested in the fumarole environment (Sept. 2003 and March 2004). Commonly aggregates of Na/K-Cl, Na-(K)-F-Cl, Al-F-Cl-(S), rare (As)-Pb-S-(Cl) and chemical alteration of fibers (enrichment of Al-F-Cl-S-Ti-Na-Mg) are present. An airborne test in the non-eruptive plume and in the plume-surrounding air of Stromboli (ca. 10 min; Sept. 2003) showed similar results. According to these preliminary FESEM/EDS studies Tl is not present in particles on this coalescer. The saame coalescer used by NASA DC-8 during the potential encounter with the Hekla plume (2000) had been investigated by FESEM. S- and Cl-rich particles are common, As, Tl, Pb, Hg could not be detected yet. Aeroplanes crossing volcanically, or industrially, polluted airmasses containing Tl, Hg etc. might be equipped with insufficient air filtering systems.

FESEM/EDS and a set of filters could help monitoring the air quality down-wind of active volcanoes. Gas masks utilized by volcanologists should be tested for their filtering capacities of toxic elements. Dust protection material tested in the F0 environment is currently analyzed by FESEM/EDS and chemical techniques. Aerosol particle collections for subsequent electron microscopic analysis mostly utilize filters and/or TEM grids. Systematic research on the collection behavior of different filter media is missing. Recent studies indicate the influence of acoustic fields on particle loading of fibrous filters [6]. This parameter can be important for volcanological and i.e in-plane studies.

Tl is also released into the atmosphere during combustion of coal (i.e. W-Germany released in the 1980ies ca. 4t of Tl/year). Analyzing Tl in volcanic environments shoud consider the combustion of coal as a potential source if near-by civilizational structures exist or if prevailing winds could transport airmasses from i.e. coal-fired power plants. Magma and/or high heat flow in contact metamorphosed, coal-bearing strata underneath volcanic edifices might also contribute to high Tl fluxes of fumaroles. 1 g of Tl_2SO_4 can be lethal to human adults.

Rehkämper and Nielson [4] used an average (Tl/Pb)wt ratio in volcanic particles of ~0.65 (based in measurements from White Island, New Zealand, Kilauea, USA and Etna, Italy). The Pb flux from Masaya volcano, Nicaragua has been estimated to be ~3.2 x 10^-5 kg/s ((7)Vallelonga and Mather, 2003). Combining these measurements with the approach outlined above yields a Tl/S(g) ratio of 8 x 10^-6 and a Tl flux of ~2 x 10^-5 kg/s or ~0.7 ton/yr.

Note: Elements in brackets indicate low values relative to co-occurring elements. Sampling time had been ca. 1 h, if not indicated otherwise. The corrosion of the filter holder could cause contamination of the filter by Al. All samples had been transported and stored at ambient temperatures in dry boxes.

[1] Hinkley, **Bull. Volcanol. 53**, 395-400, 1991.

[2] Toutain et al., **JVGR 123**, 95-103, 2003.

[3] Wahrenberger, Diss. ETH, No. 12252, 1997.

[4] Rehkämper et al., **Mar. Chem 83**, 125-139, 2004.

[5] Obenholzner et al., in: **Volcanic Degasing** (eds. Oppenheimer, Pyle, Barclay), Geol. Soc., SP 213, 123-148, 2003.

[6] Gutfinger et al., in: **Particle Loading and Kinetics of Filtration in Fibrous Filters** (eds.: Lehmann & Kasper), 2002.

[7] Vallelonga, P. and T.A. Mather, Lead (Pb) fluxes and Pb isotopic compositions from Masaya Volcano, Nicaragua, **Atmospheric Environment 37**, 4453-4460, 2003.