



## **Filtering volcanic gases: Non-random, heterogeneous nucleation on single fibers, chemical composition of adsorber fluids and a link to the hydrogen economy**

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Filter experiments by clogging were conducted using a fumarole vent (crater rim) of La Fossa v., Vulcano Island, Italy to document nucleation of crystals and amorphous matter on glass and tremolite asbestos fibers (in-line experiment). At ca. 300°C and pH =1-2 single particles (sulfides) nucleate throughout the filter body. FESEM/EDS studies document single fibers, which are occupied by only one metal chloride whereas glass fibers in the vicinity are unaffected. Non-randomly nucleated crystals can be single crystals or single crystals in an aggregate, which grow around the fiber. On single asbestos fibers (O, Ca, Mg, Si) a continuous, slightly structured coating exists (Al, S, Cl, Ti, Ni). The classical theory of heterogeneous nucleation does not consider a single fiber anomaly (Smorodin et al., 2004). Most of the fibers do not show alteration features at the FESEM resolution.

The non-random, heterogeneous nucleation had been detected on glass and crystalline fibers of experiments in Aug. 2004, Jan. 2005 and May 2005 at similar T and pH conditions. It had not been detected yet on fibers exposed to ca. 400°C. This high T vent had a blue flame (ca. 10 min) and corona borealis-like light phenomena (ca. 0.5 h) in May 2005. In addition to crystals previously reported (Obenholzner et al., 2005), this work found nucleated crystals: Al-Sc-C- (300°C) and V-bearing particles (400°C). La, Ce carbonate particles deposited on filters could be detected (Jan. 2005, 30°C). The single fiber anomaly also occurred on glass fibers (barberite) at ca. 25°C.

Assuming a continuous flow of a homogeneous gas/vapor during 4 h sampling time

through a homogeneous filter material, the occurrence of single fiber anomalies resembles unpredictable heterogeneities at the micrometer scale. A different experiment utilized 47 mm aerosol particle filters and adsorber solution at Solfatara, Stromboli and Vulcano Island in Italy (vent, ambient air and soil gases). ICP-MS analyses of the liquid in the bubbled solution suggest that 2 processes are probably responsible for distribution of trapped materials. 1. Particles are scavenged from the gas in bubbler 1 and a dispersion less in particles is scavenged in bubbler 2. The result is a higher element content in bubbler 1 (“normal”). 2. After bubble burst in bubbler 1 aggregates of micro-droplets and particles are formed which are scavenged at high efficiency in bubbler 2, producing a higher element content there (“reverse”). Si, P and Ca are distributed “normal”, Fe, Cr and Cu “reverse”. Cr and Fe are always bdl in the first bubbler. Cu-bearing NaCl and KCl nanoparticles (Ammann et al., 1993; plume of Mt. Etna) can be excluded, as Cu at Bocca Nuova is bdl (1h). 12 h sampling in the vicinity of the Solfatara crater revealed 0.4-2 ppb Cu. The existing data suggest a partial overlap of these 2 hypothetical transport mechanisms (Mg, Al, K, Mn, Ni, Zn, As). If Si, P, Ca, Fe, Cr and Cu represent a non-random distribution remains speculative. Nanometer-sized volcanic particles (HRTEM/AFM study by Pfeffer et al., 2006) and semi-volatile metals pass through HEPA type and higher efficiency filters, which is an alarming fact concerning i.e. air conditioning systems and gas masks. Some experiments utilized 2 high efficiency filters on top of each other. Fibrous filters more than membrane filters (pore diam. 0.2  $\mu\text{m}$ ) let cigarette smoke particles (0.01-1  $\mu\text{m}$ ) pass at a flow rate of ca. 1l/min. Condensing water on the filters in the fumarole environment should increase the efficiency (Agranovsky et al., 1999). Mather et al. (2006) assume, based on Allen et al. (2000), that a 1  $\mu\text{m}$  pore size membrane filter in a filter pack lets only gases pass. Hidy (1984) mentions that all filters and cascade impactors let nanometer-sized particles pass.

The corrosion of parts of the equipment (Al, Si) by the volcanic gas, the possible existence of semi-volatile metals and metal transport by the gas have to be understood in detail. Hydrides react with water, so metal hydrides are supposed to not exist in nature. Gaseous  $\text{AsH}_3$  (solubility in water: 0.07 g/100 mL at 20°C) would explain the As contents of bubbler liquids after filtering. Gas sampling in 2005 (Jan. and May) documented  $\text{PH}_3$  at the rim fumaroles of La Fossa v. (0-201  $\text{ng/m}^3$ ; 3-10  $\text{ng/m}^3$  at base of crater and geothermal area).  $\text{PH}_3$  might be responsible for P data in bubbler liquids. Water samples taken close to subaqueous vents of the pools at Vulcano Island (May 2005) revealed an average of 1.2-1.3  $\text{ng/m}^3$   $\text{PH}_3$ . At La Fossa v.  $\text{H}_2\text{S}$  correlates positively with  $\text{PH}_3$ . As the fumaroles of Solfatara crater release only  $\text{H}_2\text{S}$ , no  $\text{SO}_2$  (Chiodini et al., 2001), ICP-MS detectable P in bubbler liquids might relate to  $\text{PH}_3$ .

Holub et al. (2001) explain their hypothesis of a macroscopic quantum effect concern-

ing unfilterable geoaerosols based on the documented 100% efficiency of 0.8  $\mu\text{m}$ , tortuous pores of filters (CNC values after this filter had been zero, Holub, pers. comm., 2005). The preliminary experimental set-up, low amount of data and operating conditions of this study did not find positive or negative evidence for the proposed existence of the geoaerosol in volcanic areas.

All bubbler liquids contain Zn, even the samples from soil gases (and diffuse degassing) of the base of La Fossa v. and close to the shore at Stromboli v.. Allard et al. 2000 calculated an average flux of Zn from Stromboli v. as  $1.3\text{E}+02$  Mg/yr from craters-based aerosol collection on a filter which equals 2% of the global volcanic Zn emissions. Zn is known from many fumaroles. A study in 2001 documented Zn-S nucleating on borosilicate fibers (5 min) and Zn-S on coarse particles at a vent inside Solfatara crater. Metallic Zn starts vaporizing at ca. 500°C. Experiments by Morey et al. (1951) document alteration of sphalerite in superheated steam at 500°C and 1000 bars. Zn halos around hydrocarbon and sulfide deposits are documented in rare soil gas studies, coinciding with CO<sub>2</sub> fluxes at ambient T (Pauwels et al., 1999; Sikka et al., 2002).

Nucleating Ba-S-O had been detected on borosilicate fibers (Milos, La Fossa v., Solfatara), nucleating Tl-Cl only at la Fossa v.. Further at Solfatara nucleating Cu-S, Hg-S (both also as single fiber anomalies) and As-S are common. In the presence of SO<sub>2</sub> sulfate artifacts are known on glass fibers (Hinds, 1999) from non-volcanic environments. Barite is known as aerosol particle (Jan. 2005) and around fumarole vents (Fulginiti et al. 1998) at La Fossa v..

Within the complex system of an active volcano an overinterpretation of the occurrence of a single element known from soil gases, fumaroles or plumes should be avoided. However, the economic importance of Zn led to a long lasting record of geoscientific research. "Megaw et al. (1988) make the important point that many zinc skarn districts "grade outward from intrusion-associated mineralization to intrusion-free ores, which suggests that those districts lacking known intrusive relationships may not have been traced to their ends". Besides their Zn-Pb-Ag metal content, zinc skarns can be distinguished from other skarn types by their distinctive manganese- and iron-rich mineralogy, by their occurrence along structural and lithologic contacts, and by the absence of significant metamorphic aureoles centered on the skarn. A typical zonation sequence from proximal to distal is: altered/endoskarned pluton, garnet, pyroxene, pyroxenoid, and sulfide/oxide replacement bodies, sometimes called mantos and chimneys based upon geometry and local custom" (Meinert, 1992). Zn contents in bubbler 1 and 2 at Solfatara crater are 36.1 – 340 ppb, Mn contents are bdl - 4.5 ppb, Fe contents are bdl – 28.6 ppb, Pb contents are bdl – 0.4 ppb, Ag not detected yet.

MnCl<sub>2</sub> (scacchite) triggers sporulation of Carboxydotherrnus hydrogenoformans (Wu et al., 2006), isolated from hot springs of Kunashir Island, Russia . Does this hydrogen-producing bacteria know something about a precursor value of Mn, which we missed until now? A review of known indicators of Mn fluxes of active volcanoes is missing.

Can the observed Zn fluxes at La Fossa v., Stromboli v. and Solfatara crater be interpreted geologically and volcanologically? Several models could be sketched:

1. The open-conduit system at Stromboli v. including high-level magma storage releases Zn according to high-level magma storage processes and/or periodic eruptions with diffuse degassing. It remains unknown if plume-derived Zn is available in soils.
2. At La Fossa v. Zn fluxes are governed by a more or less continuous emanation from a magma chamber and diffuse degassing. It remains unknown if fumarole-derived Zn is available in soils.
3. It remains unknown if sulfide deposits formed earlier in the history of these 2 edifices are mobilized by gases or interaction with magma. The massive sulfide samples dredged from Palinuro seamount (N of the Eolian Islands) might be such an example (Tufar 1992). Tufar mentions that these ores are rich in pyrite, barite and Tl. Sphalerite is common.
4. Within the concepts of Zn skarns (Meinert, 1992) and low-sulfidation epithermal ore deposits (Hedenquist et al., 1994), the question appears, if the fumaroles inside the Solfatara crater are the distal product of a shallow (?) intrusion off-axis of the Solfatara vent?

Is the Zn signal in volcanic soil gases related to nanometer-sized particles? A photo-electrical charging experiment might be forewarding (Burtscher et al., 1987). If the permeable volcanic edifice works like a mega-filter, it remains barely understandable how Zn-rich nanometer-sized particles can pass 100s of meters without being adsorbed to walls of pores. This study documents that even after 0.02 μm pore size filters Mg, Al, K, Mn, Ni, Zn, As, Si, P, Ca, Cr and Cu are detectable in bubbler liquids by ICP-MS. This might be related to high vapor pressures of supercooled, metastable particles. Developments in electron microscopy, AFM, chemistry and aerosol sciences would permit to reevaluate the simple and cheap filter bubbler system, known since decades, as an additional monitoring tool for active volcanoes. At the moment discrepancies seem to exist between hypotheses of different researchers concerning which particles can pass a filter and what are the consequences in interpretation and modeling. Observed nucleation of crystals and amorphous (?) substances on fibers, unexpected penetration of particles (?) through filters, as documented by ICP-MS data of bubbler liquids, are suggesting to design new experiments.

If Solfatara crater and its fumarole field - as a type locality of solfatara fields (UNESCO Catalogue of Active Volcanoes and Solfatara Fields, 1967), known from all over the world - dominated by continuous H<sub>2</sub>S degassing - a potential H<sub>2</sub> source is available by leading H<sub>2</sub>S through Fe-pipes (producing Fe sulfides and H<sub>2</sub>). If volcanological arguments and data can be gathered that such sites are actually distal from existing magma chambers and in a way safe - a new energy production could start at many places to supply at least locals as hydrogen fuel cell technology increases (Obenholzner, 2005). New filter technology can provide a safer and un toxic environment for people to work there.

The authors are grateful to ZFE/TU-Graz and P. Hopke (Clarkson Univ.) for EM data. C. Cigolini (Univ. Torino) suggested a Rn sampling site at Stromboli v. of the soil gas experiment. Presented data are preliminary. S and halogen data are not available yet.

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