

Photoelectric Charging of Ultrafine Volcanic Aerosols: Detection of Cu(I) as a Tracer of Chlorides in Magmatic Gases

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Volcanic gases contain ultrafine aerosol particles in the nanometer size range; typical concentrations are 10^5 to 10^6 cm⁻³. Photoelectric charging of particles (PCP) is an in situ method for the material specific detection of very small particles in a gas. Field studies at degassing lava flows of Mount Etna, Sicily, and Kilauea, Hawaii, show that the chemistry of the ultrafine aerosols depends strongly on the degassing state of the lava. Heating of a relatively undegassed lava sample in the laboratory reveals the chemical nature of the particles that form by nucleation and condensation in the cooling gas. In the initial stages of degassing, the particles are mainly NaCl and KCl nanocrystals that contain iron oxide and copper chloride. Cu is in the monovalent state, which is stable even in an oxidizing environment due to a redox mechanism with the Fe ions. The fraction of Cu(I) in the aerosols is determined by PCP. The evolution of the Cu(I) fraction is considered an effective tracer of chlorides in the magmatic gases and thereby of magma degassing. The PCP technique allows a fingerprint to be obtained of the magmatic gas by an aerosol measurement in the diluted plume.

INTRODUCTION

It is well known that a variety of metals are strongly enriched in volcanic aerosols compared to the magma [Buat-Menard and Arnold, 1978]. Most of these metals are released from the magma as volatile chlorides or sulfides which condense to fine particles as the gas cools down [Naughton et al., 1974; LeGuern and Bernard, 1982; Quisefit et al., 1989; Pennisi et al., 1988]. The composition of the condensed phases corresponds to the intensive parameters of the magmatic gas [Symonds et al., 1987, 1992]. In previous aerosol field studies, samples were taken using cascade impactors or filters and analyzed later by a variety of methods [Rose et al., 1986; Vié Le Sage, 1983; Chuan et al., 1986]. The very fine particles with sizes well below 100 nm are not sampled with adequate efficiency by these techniques [Hidy, 1984].

However, Ammann and Burtscher [1990] show that volcanic plumes contain concentrations of the order of 10^5 to 10^6 cm⁻³ of ultrafine aerosol particles with radii from 2 to 20 nm. They used a technique, called photoelectric charging of particles (PCP), also known as aerosol photoemission, which is selectively sensitive to aerosol particles and their chemical composition in the submicron size range only. Using this technique, they obtained a fingerprint of volcanic activity and degassing processes of the magma from measurements in the volcanic plume. Due to the low mass of these particles, it was not possible for them to establish the relationship between the observed volcanic activity and the

chemical composition of the particles. But their data suggest that these ultrafine particles constitute the primary product of gas to particle conversion in the early stages of plume formation. Secondary reactions such as coagulation with each other, with the larger rock particles (from wall rock erosion or magma spray) or with acid droplets could account for the structure of the larger particles observed in the other studies. However, considerable amounts of ultrafine particles seem to survive such aerosol aging effects; they may thus be regarded as information carriers from the magmatic gas.

Therefore it is the aim of the present study to understand the magma degassing processes involved in the formation of the nanometer aerosol in the volcanic gas. This is achieved by improving the PCP method but also by concomitant magma degassing experiments in the laboratory. Aerosol analysis by PCP and X ray photoelectron spectroscopy is used to investigate the relationship between PCP and volcanic activity. Furthermore, we will propose a model of the crystalline structure of ultrafine particles in the plume of an active volcano.

AEROSOL SAMPLING AND ANALYSIS

Photoelectric Charging of Particles (PCP)

In PCP the gas containing the submicron aerosol particles is irradiated with UV light. If the photon energy is higher than the surface barrier potential of the particle (photoelectric threshold), excited electrons may leave the particles. In this case, the particles hold a positive charge which establishes the photoelectric signal [Burtscher et al., 1982]. This charging mechanism is restricted to particles smaller than 1

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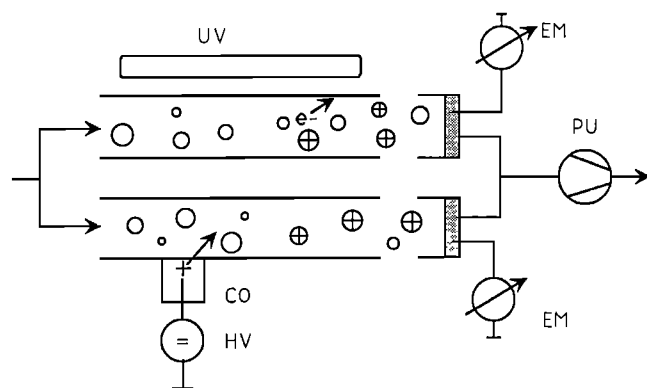


Fig. 1. Diagram of the PCP measurement. UV, low-pressure Hg lamp (185 nm); CO, electrical corona discharge supplied by high voltage (HV), producing positive ions; EM, electrometer; PU, pump, provides flow rates of 5 L/min in each channel. The photoelectric activity ϵ is the quotient of the electrometer signals.

μm . The probability of charging depends on the electronic structure and the cross sectional area of the particles. On the other hand, for particles smaller than 100 nm, the process of unipolar diffusion charging by positive ions is only dependent on the surface area [Hidy, 1984]. Therefore the photoelectric activity ϵ is defined as the ratio of the photoelectric charge and the diffusion charge [Ammann and Burtscher, 1990; Ammann et al., 1992a]. ϵ is a normalized quantity that depends on the intrinsic material properties of the individual particles but not on the aerosol parameters size and concentration.

A schematic diagram of the PCP principle is given in Figure 1. It is a compact probe as described by Ammann and Burtscher [1990]. By electrostatic and inertial precipitation, all particles in the size ranges above 100 nm are removed from the gas flow at the aerosol inlet. This makes it possible to detect the ultrafine size fraction only.

Additionally, a sampling device is incorporated in the PCP probe, where the charged particles are precipitated onto a highly oriented pyrolytic graphite (HOPG) substrate for surface chemical analysis. In blank samples from the field and the laboratory, the graphite surface proved to be extremely inert to any contamination. The sampling efficiency varies from 10 to 50% depending on the particle size. Typical sampling times are about an hour with particle concentrations of 10^6 cm^{-3} .

Photoelectric activity ϵ is measured in situ and has a response time of a few seconds. The detection limit for species with high ϵ is below 0.1 ng/min. Although ϵ is by no means uniquely defined by the chemical composition of the aerosol, it provides an extremely sensitive tool to detect delicate changes of chemical species and oxidation states in small particles [Burtscher et al., 1982; Ammann et al., 1992a].

Table 1 gives photoelectric activities of various artificial aerosols measured in the laboratory with the PCP probe. The materials chosen may be present in the magmatic gas or in the volcanic plume. The respective aerosols are produced either by a solution nebulizer or by a gas evaporation technique in a tube furnace, both being common methods for aerosol production [Hidy, 1984]. As a carrier gas for the condensing particles, we use air, N_2 or Ar. The particle radii obtained with the present furnace and the solution nebulizer

TABLE 1. Photoelectric Activity ϵ for Various Inorganic Salts

Compound	ϵ	Experiment
NaCl	0	f, s
KCl	0	f, s
CuCl	0.9	f
CuCl ₂	0.02	s
ZnCl ₂	0	f, s
FeCl ₂	0.05	f, s
SnCl ₂	0.04	s
PbBr ₂	0.02	f
MgCl ₂	0	s
CaCl ₂	0	s
Na ₂ SO ₄	0	s
K ₂ SO ₄	0	s
CuSO ₄	0.02	s
ZnSO ₄	0	s
FeSO ₄	0.02	s
(NH ₄) ₂ SO ₄	0	s

The f and s denote particle generation with tube furnace and solution nebulizer, respectively.

are 2–10 nm and 5–20 nm, respectively. Particle sizes are distributed lognormally. The photoelectric activities of alkali and alkaline earth compounds are zero because of their high ionization energies. Distinct ϵ values are obtained for the transition metal compounds. In the case of copper, ϵ is more than an order of magnitude higher for the monovalent chloride than for the divalent chloride or sulfate. Among the selected materials, PCP responds mainly to monovalent copper ions. The detection limit for pure CuCl nanoparticles is of the order of 10 ng/m³ for an in situ measurement corresponding to a mass flux of 0.04 ng/min; in mixed aerosols it may be higher due to absorption of photoelectrons in the surrounding matrix.

X Ray Photoelectron Spectroscopy (XPS)

For chemical information on deposited aerosol particles, samples are analyzed by X ray photoelectron spectroscopy (XPS). In XPS the surface under investigation is irradiated with Mg-K α radiation at $h\nu = 1253.6 \text{ eV}$. The energy spectrum of the emitted electrons provides information on core electrons of the elements present at the surface. Small deviations in the peak position of an element, namely the chemical shift, reveals the valence state or the coordination of the different elements involved. The depth of the chemical analysis is determined by the inelastic mean free path of the electrons in the range of 1–3 nm [Briggs and Seah, 1990], so that XPS provides information from the outermost surface layer of the sample.

XPS measurements were carried out on a PHI 5400 ESCA system. The electron energy analyzer was operated at a constant pass energy of 35.36 eV, the total energy resolution being 0.89 eV (Ag 3d_{5/2}), for an analyzed area that is 1.1 mm in diameter. The binding energy scale was calibrated for the Au 4f_{7/2} signal at $83.8 \pm 0.1 \text{ eV}$.

MEASUREMENTS AND RESULTS

Field Experiments

Field sampling at Mount Etna, Sicily, between 1988 and 1990 has revealed a relationship between PCP and volcanic activity [Ammann and Burtscher, 1990]. When fresh magma

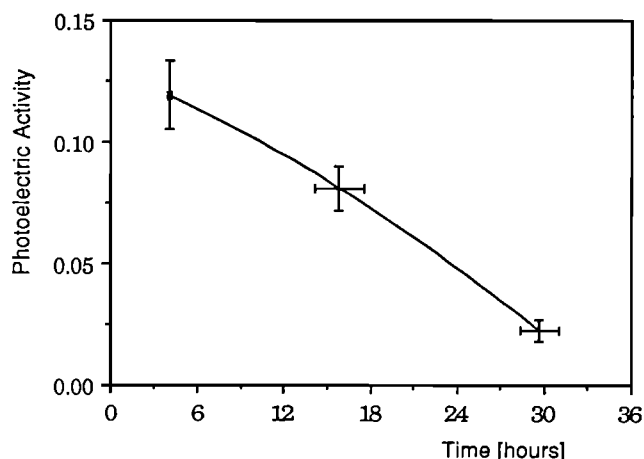


Fig. 2. Photoelectric activity ϵ of the aerosol at an aa lava flow, Mount Etna, September 1989 [from Ammann and Burscher, 1990]. Time is given in hours after onset of eruption. The distance to the conduit is about 1 km.

risks from a deeper source to the conduit, the emitted particles contain one or more volatile species with high photoelectric activity ϵ . Further evidence for this phenomenon has been found in outgassing measurements of an aa lava flow during the 1989 eruption of Mount Etna (Figure 2, a detailed description of the eruption is given by Barberi [1990]): particles emitted through fractures of near constant temperature undergo a clear decrease in ϵ with aging of the lava, suggesting control by a degassing process [Ammann and Burscher, 1990]. Some preliminary tentative energy dispersive spectroscopy (EDS) analysis of single particles in the electron microscope showed Na, K, Fe, and Cu as major cations and Cl as the anion.

A similar experiment was conducted at Kilauea, Hawaii. During 1990 the lava flow from Pu'u O'o entered a tube system below the Kupaianaha lava pond and followed it for over 12 km. Measurements with the PCP probe were performed along the tube at all visible major fractures or holes in the ceiling of the tube. The PCP probe was always placed in the plume after mixing of the emitted gases with the atmosphere. Care was taken not to measure downwind of burning woods to avoid the wood smoke aerosol. Particle concentrations upwind of the tube system were always below the detection limit of the instrument. Figure 3 shows the decrease in photoelectric activity along the lava tube. It is obvious that the decrease begins close to the end of the tube system after considerable amounts of gases have been released. Approaching the Kalapana Garden area part of the lava left the tube and poured out to the ground. As the pahoehoe lava is exposed to ambient air, the rapidly cooling superficial skin prevents aerosol formation over large areas already after very short time, in contrary to aa lava flows, where volatiles can escape through a lot of fractures in the broken surface.

Laboratory Measurements

The field measurements show that very fine aerosol particles are present in the plume when magma or lava is degassing. The chemical composition of the particles depends significantly on the temporal evolution of the lava. In order to study the exsolution of volatiles and the subsequent

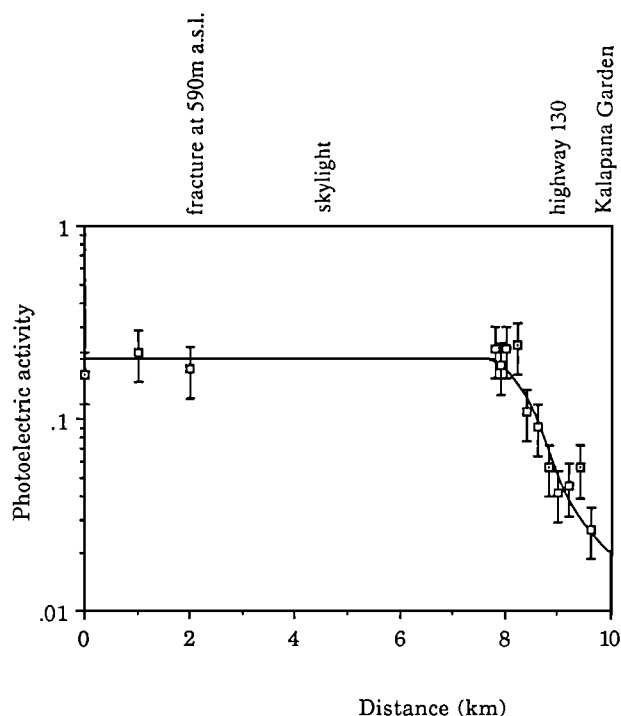


Fig. 3. Photoelectric activity ϵ along the lava tube of Pu'u O'o, Kilauea, Hawaii, June 1990. Points of interest along the tube are labeled. The skylight denotes a hole in the tube ceiling of 1 m in diameter; due to the unstable emissions from the hole, no appropriate measurement could be carried out.

particle formation by nucleation, lava samples were heated in the laboratory in a tube furnace. The sample is from the core of a lava bomb emitted in a strong strombolian explosion from Bocca Nuova, Mount Etna, 1989. Such material is expected to represent the volatile content of the partly degassed magma below the vent just before emission [Swanson and Fabbri, 1973]. During the experiment the inner part of the furnace is heated continuously from 20° to 1100°C in about 2 hours. The nature of the carrier gas (air or Ar(99.999%)) had no noticeable effect on the result of the experiment.

Figure 4 shows ϵ of the generated aerosol and the furnace temperature as function of time. Aerosols with high ϵ values

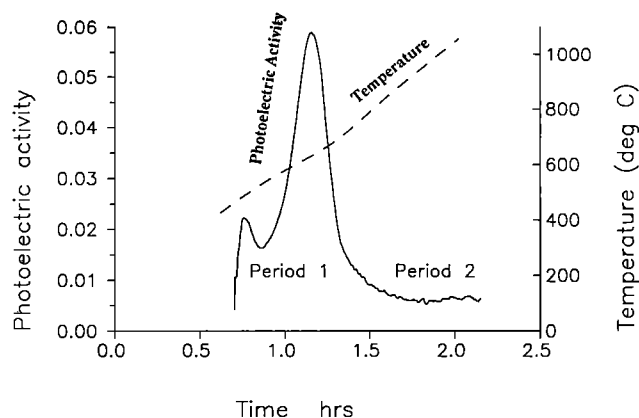


Fig. 4. Photoelectric activity ϵ and temperature during heating of lava in the tube furnace. The carrier gas is air.

TABLE 2. XPS Analysis of Aerosol Samples in Two Stages of the Lava Outgassing Experiment in the Tube Furnace

Element	Period 1, at %	Period 2, at %
Na	10	5
K	32	18
Cu	1	0
Fe	>0.5 ^a	^a
Zn	<0.1 ^a	0
Pb	<0.1 ^a	<0.1 ^a
Sn	0	0.4
S	2	2
Si	4	8
As	0	<0.1 ^a
P	0	7
Cl	26	2
F	13	25

^aElement identified in the XPS spectrum, a quantitative intensity analysis was impossible due to line interference. The given values are estimations.

are emitted already at relatively low temperatures, indicating a high volatility of the involved materials; at higher temperatures ϵ decreases strongly, but the particle concentration remains high (not shown on the plot). Aerosol samples have been taken during the first (high ϵ) and the second (low ϵ) periods of degassing. Table 2 gives the results of the XPS analysis. The first period of degassing is clearly dominated by sodium and potassium as cations and chlorine as anion with smaller amounts of Fe, Cu, Pb, and Zn. In the second period, F is present as main anion together with K, Si, Sn, P, As. The oxygen peaks were not analyzed, because oxygen represents to a big part the usual contamination layer on the sample surface from exposure to ambient air. The line shapes and the chemical shifts associated with the different lines in the XPS spectrum give some additional information. In the first period KCl, NaCl, CuCl can be clearly identified, and iron is either present as an oxide or as a chloride. In the second period the F is bound mainly as KF and together with Si as K_2SiF_6 . The fluorine in the period 1 sample is due to mixing with period 2, as the F peak disappeared in experiments with shorter sampling times. The high ϵ of the aerosol emitted during period 1 is probably from CuCl, which has a high ϵ value (Table 1) [Ammann *et al.*, 1992a]. Figure 5, curve a, presents the relevant part of the XPS spectrum of the period 1 sample with the Cu_{2p} lines which serve to distinguish between the monovalent (twofold splitting) and the divalent state (fourfold splitting). Since the experiment was performed in air it is surprising that no oxidation of copper was found on the surface of the particles. However, the spectrum of pure CuCl particles which were exposed to air after condensation reveals the surface oxidation of the monovalent Cu, as shown by Figure 5, curve c. Additional experiments with different composite aerosol systems (Na, K, Fe, Cu as cations and Cl, SO_4 as anions) showed that in chlorides and sulfates a solid state reaction occurs between Fe(II) and Cu(II) yielding Cu(I) and Fe(III) [Ammann *et al.*, 1992a]. An example of the copper line of the XPS spectrum of an iron-copper chloride is given in Figure 5, curve b. It is evident that Cu(I) is stabilized by the presence of Fe ions, even if the particles are exposed to atmospheric oxygen.

DISCUSSION

The laboratory experiments reveal the major elements present in the ultrafine aerosol particles produced from

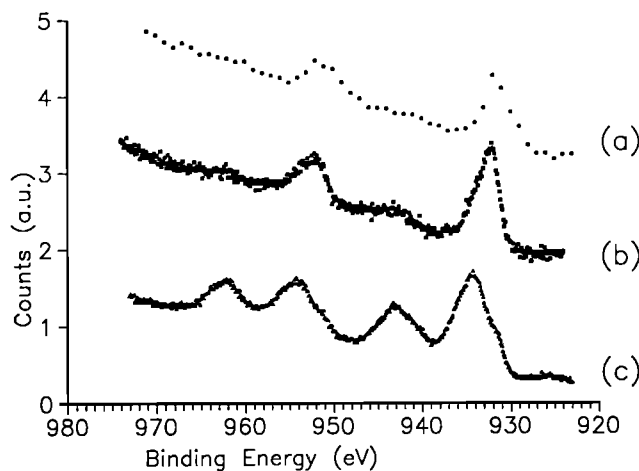


Fig. 5. XPS spectrum of aerosol samples (as deposited) around the Cu 2p lines. Curve a, sample of period 1 in the tube furnace experiment (Figure 4): Cu(I); curve b, mixed iron copper chloride particles (artificial): Cu(I) in $CuFeCl_4$; and curve c, pure CuCl particles (artificial) after exposure to air: Cu(II) on the surface.

different stages of degassing of lava. These particles are generated by gas to particle conversion of magmatic volatiles. Gaseous CuCl has been detected in magmatic gases by Tazieff [1960] and Murata [1960]. Several field studies on fumarolic incrustations, experiments with sublimation tubes and associated thermochemical modeling show that Na, K, Cu, Pb, and Zn are transported as chlorides in magmatic gases [Naughton *et al.*, 1974; Le Guern and Bernard, 1982; Symonds *et al.*, 1987; Quisefit *et al.*, 1988, 1989; Symonds *et al.*, 1992]. Thomas *et al.* [1982] suggest that zinc chloride was released in the first stages of activity at Mount St. Helens. Our laboratory experiment confirms the high volatility of K, Na, Cu, and Fe as chlorides. Pennisi *et al.* [1988] calculated emanation coefficients from aerosol filter measurements for various metals. For Na, K, and Cu the product of their emanation coefficients with the corresponding elemental concentration of typical Etna lava gives about the same order of magnitude for the relative concentration of these elements in the aerosol as in our laboratory samples (Table 3), except for Pb and Zn, which could not be detected quantitatively by XPS.

The most stable molecular form of gaseous copper chloride at magmatic temperatures is CuCl [Murata, 1960; Symonds *et al.*, 1987; Quisefit *et al.*, 1989], whereas the formation of a trimer $(CuCl)_3$ should be considered at lower temperatures [Rosenstock *et al.*, 1955; Symonds *et al.*, 1987]. Since the vapor pressure of CuCl is by orders of magnitude higher than that of Cu_2S [Wedepohl, 1969], the vapor transport of Cu as a sulfide is assumed unimportant. Divalent copper compounds are not stable at high temperatures [Allen and Clark, 1966].

A qualitative model of aerosol formation may be developed as follows. The first period of degassing produces NaCl and KCl as major components and copper and iron chlorides as most abundant traces. Referring to thermochemical considerations [Symonds *et al.*, 1987] or other field studies [LeGuern and Bernard, 1982], we suggest that aerosol formation begins with nucleation of Fe_3O_4 particles at high temperatures. At lower temperatures, NaCl and KCl may condense before CuCl onto the Fe_3O_4 nuclei, according to

TABLE 3. Expected Relative Amounts of Na, K, Cu, Pb, and Zn in Aerosols, Using Emanation Coefficients ϵ Reported by Pennisi *et al.* [1988] Compared to Concentrations Obtained in This Study

Element	$c = (c_i - c_f)/c_i$	$c_i, \mu\text{g/g}$	$\epsilon c_i, \mu\text{g/g}$	$c_{ae}, \text{w } \%$
Na	2×10^{-4}	30,000	6	8
K	6×10^{-4}	16,000	10	43
Cu	3×10^{-3}	150	0.5	2
Pb	1×10^{-2}	10	0.1	<0.7
Zn	1×10^{-3}	100	0.1	<0.2

c_i is initial concentration of an element in the magma represented by values of typical Etna lava; c_f is concentration of an element after degassing; ϵ is emanation coefficient defined by $\epsilon = (c_i - c_f)/c_i$, experimental values from Pennisi *et al.* [1988]; ϵc_i is expected relative amounts in the aerosol; c_{ae} concentration of an element in the aerosol from the outgassing experiment in the tube furnace period 1, Table 2.

the different vapour pressures [Wichterle and Linek, 1971]. The idea of this heterogeneous condensation process is supported by the monomodal size distributions reported in our former field studies [Ammann and Burtcher, 1990]. Homogeneous nucleation of the individual condensed phases is rather improbable and would yield different modes in the resulting particle size distributions. Unfortunately, the high volatility and the low contrast of these materials do not allow high-resolution analysis of the ultrafine particles in the transmission electron microscope. Nevertheless, the proposed condensation process leads to a tentative model of the structure of these particles. According to experiments with heavily Cu(I) doped NaCl crystals by Itoh *et al.* [1988], small islands of CuCl may form within the alkali chloride matrix by a diffusion process. Thus the volcanic particles may consist of trace amounts of iron and copper chlorides embedded in alkali chloride crystallites in the nanometer size range. Due to the redox equilibrium between the Fe and Cu cations, the Cu remains in a stable monovalent state without being oxidized by atmospheric oxygen.

The laboratory experiments show that ϵ is a measure of the Cu(I) fraction in particles which are formed from volatiles exsolving from degassing lava. Because Cu and the other main cations, Na, K, and Fe, are volatilized as chlorides, we suggest that ϵ may be considered a tracer of the chlorine degassing process of the lava. The PCP measurements at the lava tube of Pu'u O'o show that an equilibrium between the lava and the gas in the headspace of the almost closed tube is established. Volatiles that escape through the ceiling of the tube and produce the measured aerosol are supplied from the lava as long as enough chlorine is available (constant ϵ values along part of the tube). Thus the lava conserves its chlorine content in a closed tube. The same result was obtained by Swanson and Fabbi [1973], who analyzed the loss of chlorine in the lava during flowage in a similar tube.

The SO₂ content of gases exsolving from juvenile magma is high. Depending on the humidity of the ambient air and the characteristics of dilution of the volcanic gas, part of the chloride particles may be converted to sulfates. Bergametti *et al.* [1986] showed that this secondary reaction does not change the cation distribution in the aerosol. Laboratory experiments with mixed sulfate aerosols have revealed that ϵ is a function of the Cu(I) fraction in chlorides and in sulfates

[Ammann *et al.*, 1992a]. Therefore information about the degassing of CuCl from the magma may still be derived from ϵ measurements in an altered plume.

CONCLUSIONS

PCP is an extremely sensitive tool to detect monovalent copper ions in situ in very fine aerosol particles. It has been used to study the degassing behavior of lava flows in the field and lava samples in the laboratory.

The degassing, vapor phase transport and subsequent condensation of potassium and sodium chlorides constitutes the dominant process in the formation of ultrafine aerosol particles from magmatic volatiles. The most abundant trace gas species involved in particle formation are CuCl and FeCl₂. The resulting particles consist of iron oxide and copper chloride embedded within alkali chloride nanocrystals. Cu is kept in the monovalent state by the Fe ions by a redox mechanism. The Cu(I) fraction in the particles relates the measurement of photoelectric activity ϵ of the aerosol to the presence of chloride species in the magmatic gas. Under the assumption that the degassing of the involved alkalis and metals is controlled by chlorine, information about the degassing process in shallow magma may be obtained by the PCP measurement.

The PCP technique allows one to obtain a fingerprint of the magmatic gas by an aerosol measurement in the diluted volcanic plume, which is generally safer than traveling close to active vents. It can be used for volcano monitoring purposes by recording the temporal evolution of the Cu(I) fraction in the volcanic plume aerosol with a permanent measurement station [Ammann *et al.*, 1992b].

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