

# Tropospheric Volcanic Aerosol

T. A. Mather and D. M. Pyle

*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, United Kingdom*

C. Oppenheimer

*Department of Geography, University of Cambridge, Downing Place, Cambridge, United Kingdom*

Volcanic emissions represent an important source of aerosol to the global troposphere, and have important implications for the Earth's radiation budget at various temporal and spatial scales. Volcanogenic aerosol can also transport trace metals and other pollutants, with impacts on terrestrial ecosystems and human health. We provide here a primer on the current understanding of the origins and transformations of volcanogenic particles in the troposphere, covering their fluxes, size distribution, composition and morphology, and focusing on sulfur, halogen, and trace metal compounds. Such an understanding is essential to investigations of the atmospheric, environmental and human health impacts of volcanic volatile emissions.

## 1. INTRODUCTION

Volcanoes represent one of the most important natural sources of pollutants to the atmosphere, both during and between eruptions (Tables 1a and 1b; *Oppenheimer et al.* [2003]). A good understanding of volcanic volatile emissions in space and time, and of their atmospheric chemistry, and physical and radiative effects, is essential for various branches of atmospheric science. Eruptions of El Chichón (Mexico) in 1982 [e.g. *Pollack et al.*, 1983; *Hofmann*, 1987] and Mt Pinatubo in 1991 [e.g. *McCormick et al.*, 1995; *Fiocco et al.*, 1996; *Robock*, 2002] highlighted the radiative and chemical significance of *stratospheric* aerosol veils associated with large explosive volcanic eruptions, and contributed to understanding of the composition and evolution of volcanic clouds, and their wider impacts [see recent reviews by *Solomon*, 1999; *Robock*, 2000, 2002]. In con-

trast, the atmospheric and environmental impacts of volatile emissions into the *troposphere* by smaller eruptions and sustained magmatic and hydrothermal degassing are poorly understood, even though the time-averaged magnitude of such emissions exceeds that due to the rare, large events (Table 1b).

Tropospheric volcanic aerosol plays an important role in atmospheric radiation, both directly by backscattering and absorbing short-wave radiation, and modifying cloud cover and cloud radiative properties [e.g. *Hobbs et al.*, 1982; *Albrecht*, 1989, and references therein and *Kaufman et al.*, 2002]. Despite the lower source strength of volcanic emissions compared with anthropogenic sources (e.g. SO<sub>2</sub> in Table 1a), volcanogenic sulfur species may have at least as large an effect on the Earth's radiative budget as anthropogenic sulfur [*Graf et al.*, 1998]. This is due primarily to the comparative altitude of these sources: many volcanoes degas into the free troposphere, whereas anthropogenic emissions are generally entrained in the planetary boundary layer where species lifetimes are reduced [*Graf et al.*, 1998; *Stevenson et al.*, 2003].

Tropospheric volcanic aerosol can also affect terrestrial ecosystems and human health on local to regional scales

**Table 1a.** Estimates of some tropospheric aerosol and gas emission rates from volcanoes and other sources.

Material	Mean annual emission rate (Tg/yr)	Range	Reference
<b>Primary Particle Emissions</b>			
Sea salt	3340	1000–6000	a, b
Soil dust	2150	1000–5000	a, b
Carbonaceous aerosols	150	66–220	b
Fine ash production from small volcanic eruptions	20		c
Time-averaged volcanic sulfate return flux to the upper troposphere from the stratosphere	0.5–2	0–25	d, e
<b>Emissions available for gas-particle conversion (Tg S/yr)</b>			
Biogenic sulfides	25	12–42	b
Anthropogenic SO <sub>2</sub>	79	60–110	b
Volcanoes (SO <sub>2</sub> ), troposphere only.	5–10	3–25	e, f

a – Raes *et al.* [2000]; b – Penner *et al.* [2001]; c – this work; d – Pyle *et al.* [1996]; e – Halmer *et al.* [2002]; f – see also Table 1b.

**Table 1b.** Recent estimates of volcanic SO<sub>2</sub> release to the atmosphere.

Source of estimate	Total volcanic emission (Tg S/yr)	Sporadic <sup>#</sup> volcanic emissions (Tg S/yr)	All continuous volcanic emissions (Tg S/yr)		
			Total	Continuously erupting	Non-erupting
Stoiber <i>et al.</i> [1987]	9.4	4.8	4.6	1.2	3.4
Andres and Kasgnoc [1998]	6.7	2.0	4.7		
Halmer <i>et al.</i> [2002]	7.5–10.5	4.5–6.3	3.0–4.2		

<sup>#</sup>– includes both ‘small’ eruptions that release SO<sub>2</sub> only to the troposphere, and ‘large’ eruptions that release SO<sub>2</sub> to the stratosphere. The time-averaged sulfur flux to the stratosphere from large eruptions is ~ 0.5–2 Tg S/yr [Pyle *et al.*, 1996; Halmer *et al.*, 2002].

[e.g. Baxter *et al.*, 1982; Mannino *et al.*, 1996; Allen *et al.*, 2000; Delmelle *et al.*, 2001; Grattan *et al.*, 2003]. Coarse particles (2.5–10 µm) are primarily associated with the aggravation of respiratory conditions, such as asthma, in humans. Fine particles (<2.5 µm) are implicated in increased heart, lung and respiratory disease, and symptoms such as asthma, decreased lung function, and premature death.

While volcanic emissions have contributed to atmospheric evolution throughout the history of the Earth [e.g. Holland, 1984; Oppenheimer, 2003], the increases in anthropogenic emissions since the Industrial Revolution mean that the environmental impacts of natural emissions may now be modified. It is important to understand the character and chemistry of natural tropospheric emissions in order to identify and interpret the possible effects of their interactions with anthropogenic pollutants. Air pollution studies in Mexico City, for example, have demonstrated

how anthropogenic SO<sub>2</sub> emission mitigation strategies may be compromised by the adsorption of volcanic SO<sub>2</sub> from Popocatepetl on to existing anthropogenic particulates, leading to increased sulfate production [Raga *et al.*, 1999].

In addition to their impacts on the Earth’s climate and global chemical cycles [Phelan *et al.*, 1982], there are more directly volcanological motives for studying volcanic particle emissions. Studies of volcanic gas, aerosol and condensates may provide valuable information about sub-surface magmatic conditions [e.g. Symonds *et al.*, 1992, 1994]. Monitoring of particle emissions can support volcano monitoring efforts [Rose *et al.*, 1982, Woods *et al.*, 1983, Ammann *et al.*, 1992], tracking of volcanic plumes [e.g. Chuan *et al.*, 1981], and evaluation of their potential health impacts [e.g. Moore *et al.*, 2002].

The aim of this review is to report on the state of the art of the characterization of ‘near-source’ non-silicate volcanic particles, our understanding of their possible origins, emission

rates and impacts, and the limitations of our current knowledge. The generation and dispersal of volcanic ash in violent eruptions has been comprehensively reviewed elsewhere [e.g. *Sparks et al.*, 1997] and is referred to only in passing here.

## 2. CHARACTERIZING PARTICLE EMISSIONS

Aerosol is defined as a suspension of fine solid or liquid particles in a gas. Particles are collections of atoms or molecules large enough to display a structure similar to that of the equivalent bulk material; smaller entities are referred to as ‘clusters’ and can be up to  $10^5$  atoms in size, depending on composition [*Waychunas*, 2001]. Individual atmospheric aerosols typically range from a few nanometers (nm) to tens of microns ( $\mu\text{m}$ ) in diameter, and comprise ‘primary’ components, emitted directly as particles (e.g. sea spray) and ‘secondary aerosol’, formed in the atmosphere by gas-to-particle conversion processes. (Sometimes care must be taken with this distinction. In the case of particles formed at high temperatures in volcanic vents, or during combustion, there is confusion over whether to classify them as primary or secondary. The term ‘primary sulfate’ has been used to describe particles formed from  $\text{SO}_2$  by combustion sources in power plants and smelters and then emitted to the atmosphere [*Holt et al.*, 1982]. These particles are however not emitted directly as particles from the fuel source.)

Four key parameters influence the nature and impact of volcanic particulate emissions:

1. Particle emission rates, and their distribution in space and time
2. Particle size distributions
3. Size-resolved chemical compositions
4. Particle morphologies

### 2.1. Particle Emission Rates, and Their Distribution in Space and Time

Volcanic volatile emissions into the troposphere vary in space and time, and are strongly influenced by the style of volcanic activity. There are significant differences between the large, short-lived perturbations that accompany major explosive eruptions, and the sustained outputs from persistently active volcanoes that contribute to the tropospheric ‘background’, and it is essential to distinguish between these. We can broadly divide primary sources of volcanic particulate emissions into three types:

- (i) *Emissions from ephemeral, major eruptions.* Large explosive (tephra-producing) and effusive (lava-produc-

ing) eruptions release considerable quantities of volatiles in a relatively short time period (hours–days). While the largest explosive events inject a substantial proportion of their volatiles into the stratosphere, some will remain within the troposphere [*Textor et al.*, 2003b].

- (ii) *Emissions sustained over years and decades from persistently active, or erupting, volcanoes.* Mount Etna and Stromboli (Italy) and Masaya (Nicaragua) provide examples of long-lived ‘passive’ or ‘quiescent’ degassing directly from a lava pond or lake. Such ‘open vent’ volcanoes discharge considerable quantities of volatiles into the troposphere. This background degassing may be punctuated by explosive eruptions that recur on timescales ranging from tens of minutes (Stromboli) to weeks and months (Etna). Long-term lava dome eruptions of Merapi (Indonesia; 18th Century–present), and Soufrière Hills (Montserrat; 1995–present); and the lava-flow eruptions of Kilauea (Hawaii; 1983–present) can also be included in this class of activity.
- (iii) *Non-eruptive ‘fumarolic’ discharges, usually dominated by steam, from inactive volcanoes, or between periods of magmatic activity.* Examples include White Island (New Zealand), Solfatara and Vulcano (Italy).

In addition to these primary emission sources, a fourth can also be identified: the return of particulates (fine volcanic ash, sulfate particles) and gases from the stratosphere into the upper troposphere, following large explosive eruptions. Note that this source re-enters the troposphere by crossing the tropopause, while the others are entrained at varying heights within the troposphere.

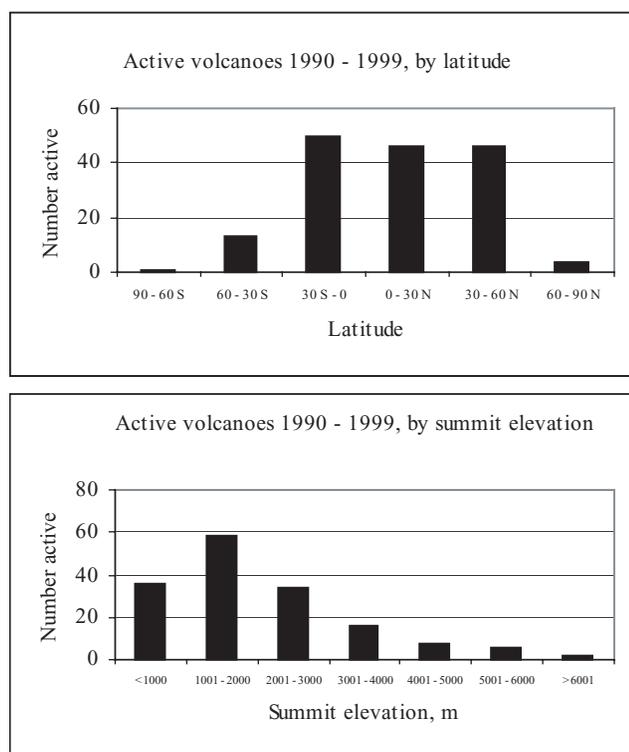
While the division between classes (i) and (ii) is arbitrary, it is important to distinguish the individual volcanoes that perturb the atmospheric aerosol budget to such an extent that they constitute a radiative forcing, from those that collectively contribute to background aerosol levels over long timescales.

As well as the temporal variability of emissions from individual volcanoes, there are also significant spatial variations in emissions, both in terms of source elevation and latitude. Uncertainties in these parameters contribute substantially to the differences between global models of the fate and impacts of volcanic sulfur emission [*Graf et al.*, 1998; *Stevenson et al.*, 2003]. In the troposphere, modeled lifetimes of volcanic sulfate aerosol vary from 2–5 days at low altitudes (< 2 km) to > 10 days (at 4 km and outside the tropics) [*Stevenson et al.*, 2003].

Due to their very nature, volcanoes tend to be located at high elevations, thereby contributing to the extended life-

times of their emissions. Seventy-five percent of volcanoes active between 1990 and 1999 have a summit elevation > 1 km and 20% exceed 3 km (Figure 1). The latitude of emission also influences aerosol lifetime. Sixty percent of recently active volcanoes lie between 30°S and 30°N (Figure 1). In this region, gas and aerosol lifetimes remain short (< 5–10 days) to considerable elevation, due to the strong convective activity in the equatorial troposphere [Graf *et al.*, 1998].

The structure and circulation of the atmosphere varies temporally and spatially on a range of scales, and influences interactions between volcanic particles and the atmosphere. On a seasonal timescale, the tropical tropopause is higher (~ 100 hPa, ~ 16 km) and colder (~ -76°C) in the Northern Hemisphere (NH) winter, and lower (~ 115 hPa) and warmer (-70°C) during the NH summer [e.g. Highwood and Hoskins, 1998]. The extra-tropical winter tropopause tends to be lower than the summer tropopause, with the



**Figure 1.** Latitude and summit elevation of the 160 volcanoes active between 1990 and 1999, as recorded by the Smithsonian Institution Global Volcanism Project [Simkin and Siebert, 1994] (including 18 submarine volcanoes). 60% of these volcanoes lie in the Northern Hemisphere; more than 75% have summit elevations of over 1 km. 1 km is the approximate height of the boundary between the planetary boundary layer and the free troposphere.

minimum pressure (peak altitude) in September (NH), or January–March in the Southern Hemisphere (SH) [e.g. Wong and Wang, 2000]. Thus, one might expect a higher proportion of volcanic eruptions during (local) winter months to reach the stratosphere. The transport of material from the stratosphere into the troposphere is asymmetric (stronger in the NH), and varies seasonally [e.g. Holton *et al.*, 1995]. Over the period 1979–1998, the peak downward flux of volcanic aerosol from the stratosphere into the upper troposphere was in local spring in each hemisphere, and concentrated at latitudes of >70°S, and >50°N [Kent *et al.*, 1998]. The tropopause also shows short timescale variability associated, for example, with atmospheric waves [e.g. Holton *et al.*, 1995], and interannual variability associated with features such as the El Niño-Southern Oscillation [e.g. Kiladis *et al.*, 2001].

More specific geographical considerations, such as local topography, surface properties and meteorology, have important implications for particle emissions, especially in terms of plume transport, dilution and atmospheric lifetime. The background atmospheric chemical composition of the atmosphere will further determine what reactions the volcanic emissions may undergo during transport. Neither aspect has been evaluated in detail, other than at a handful of volcanoes [Delmelle, 2003].

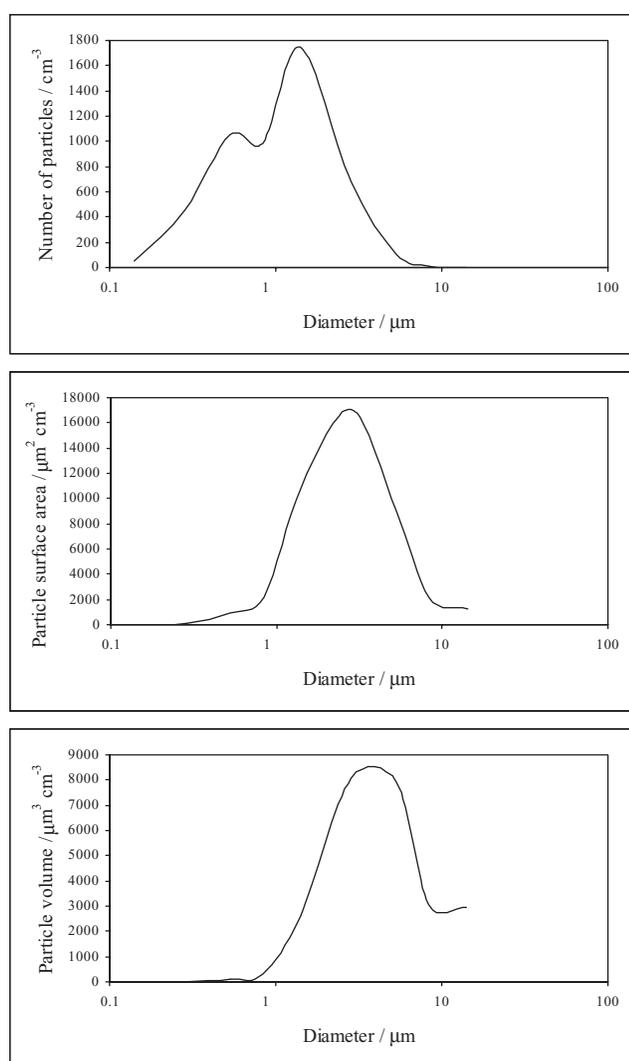
## 2.2. Particle Size Distributions

The size characteristics of a particle population may be described by a particle number distribution. Assuming spherical particles, the number distribution can be used to calculate particle surface area, volume and mass (assuming a density) distributions with respect to particle size. Because of the  $r^2$  and  $r^3$  dependences, the larger particles in the distribution become more important in the surface area distribution, and even more so in the volume distribution (Figure 2).

The particle size spectrum is fundamental to many of an aerosol's properties and to the fate of particles in the atmosphere, not least because of its control on atmospheric lifetimes. Considering sedimentation alone, 1  $\mu\text{m}$  diameter spheres at 5 km elevation with a density of 2000  $\text{kg m}^{-3}$  have an atmospheric residence time of 220 days, compared to just 4 days for 20  $\mu\text{m}$  particles [Junge, 1963]. However, sedimentation velocities do not present the complete picture. Particle deposition occurs both in the absence of precipitation (dry deposition) and through scavenging by atmospheric hydrometeors (wet deposition). Both pathways require the collection of particles by a surface (e.g. a plant, the sea, or soil for dry deposition; a hydrometeor surface for wet deposition). Small particles

(< 0.05  $\mu\text{m}$ ) act much like gases, and are efficiently transported to surfaces by Brownian diffusion. Larger particles (2–20  $\mu\text{m}$ ) tend to impact on surfaces due to their inertia, while the very largest particles (> 20  $\mu\text{m}$ ) settle out under gravity.

Collection mechanisms for particles in the 0.1–2  $\mu\text{m}$  diameter range (known as the accumulation mode) are inefficient. These particles experience extended atmospheric lifetimes, unless they act as nucleation sites for cloud particles, or undergo a change in size that takes them out of the accumulation mode. Particles in this size range can have prolonged and wide reaching atmospheric effects [e.g. Seinfeld and Pandis, 1998; Hobbs, 2000].



**Figure 2.** Alternative descriptions of particle size distributions according to particle concentration (upper plot), surface area (center plot) and volume (lower plot), shown here for the same dataset.

Whitby [1978] summarized the different particle sizes observed in the atmosphere as follows:

- (i) < 0.1  $\mu\text{m}$ : the “nucleation” mode, generated primarily by gas-particle conversion processes associated with high temperature processes (e.g. combustion),
- (ii) 0.1  $\mu\text{m}$  - 2  $\mu\text{m}$ : the “accumulation” mode, resulting from the condensation of low volatility vapors and agglomeration and growth of particles in the nucleation mode,
- (iii) > 2  $\mu\text{m}$ : the “coarse particle” mode, largely consisting of mechanically generated particles (e.g. wind-blown dusts).

Since particles < 2.5  $\mu\text{m}$  diameter can penetrate deep into human lungs, monitoring of the accumulation mode is particularly important in terms of health impacts. The radiative effects of particles depend strongly on size, with smaller particles tending to backscatter incoming short-wave solar radiation, and larger particles tending to absorb outgoing terrestrial radiation. In the stratosphere, the transition radius between these two regimes is around 2  $\mu\text{m}$  [Lacis *et al.*, 1992]. The particle size distribution as well as particle composition, determines the potential for particles to act as cloud condensation nuclei (CCN). For a given atmospheric supersaturation and composition, there will be a minimum particle diameter above which it can act as a CCN, thereby influencing the particle’s atmospheric lifetime and indirect radiative effects.

The particle surface area distribution yields information concerning the area available for surface reactions. Particle growth by coagulation can increase as the particle surface area increases [Pruppacher and Klett, 1980].

*2.2.1. Volcanic particle size distributions.* Particle size distributions of volcanic aerosol have been characterized for several volcanoes (Table 2). Volcanic particle emissions tend to be multimodal, suggesting multiple processes of formation. Following Whitby, we expect fragmented magma and erosion of particles from the vent walls to be in the coarse fraction (> 2  $\mu\text{m}$ ), and the finer particles resulting from the condensation of volatiles and gas phase reaction products to be in the accumulation mode.

Size distributions evolve as the aerosol is advected from the vent (the larger fractions tend to settle out more rapidly) and during different stages of volcanic activity. Large explosive eruptions tend to have elevated particle concentrations, especially in the larger modes due to silicate fragments, while plumes from the waning stages of explosive activity

**Table 2.** Techniques used for the determination of particle size distributions in volcanic emissions. Adapted from *Watson and Oppenheimer [2001]*.

Volcano	Basis of Data <sup>a</sup>	Plume height (km)	Method <sup>b</sup>	Particle diameter modes (μm)	Reference	
Mt St. Helens, USA	A, D	15–20	QCM	0.2 – 1, > 10	<i>Chuan et al.</i> [1981]	
	A, D	12–19	APS	1 – 2	<i>Farlow et al.</i> [1981]	
	A, D	2.4–3.8	EAA, AC, CI	< 0.2, 1, >10	<i>Hobbs et al.</i> [1982]	
	A, D	< 6	QCM	< 0.2, 3, 10	<i>Rose et al.</i> [1982]	
Erebus, Antarctica	A, D	4–5	OPC	< 0.2, 0.2–1	<i>Radke</i> [1982]	
	A, D	4.5–6	QCM	0.2, 2–6, > 20	<i>Chuan et al.</i> [1986]	
Various (Central America)	A, D	2.5–5	QCM	0.2–0.8, 2–10	<i>Rose et al.</i> [1980]	
	A, D	2–5	QCM	0.1–0.2	<i>Casadevall et al.</i> [1984]	
El Chichon, Mexico	A, D	16.8–19.2	LSS/LII	4–10, > 20	<i>Gooding et al.</i> [1983]	
	A, D	12.5–21.4	AC	0.8, 2.4	<i>Knollenberg and Huffman</i> [1983]	
	A, D	18–21	PWI	0.2, ~ 2.0	<i>Oberbeck et al.</i> [1983]	
	G, R	> 10	SP	0.6	<i>Asano et al.</i> [1985]	
Etna, Italy	G, D	3–3.3	PCP	0.2–2.0	<i>Burtscher et al.</i> [1987]	
	G, D	3–3.3	PCP / TEM	< 0.004	<i>Ammann and Burtscher</i> [1990]	
	G, D	3–3.3	PCP / XPS	< 0.1	<i>Ammann et al.</i> [1992]	
	G, D	3–3.3	PCP	< 0.1	<i>Ammann and Burtscher</i> [1993]	
	G, R	3.5	SP	0.2–2.0, > 10	<i>Watson and Oppenheimer</i> [2000, 2001]	
Etna + Kilauea	G, D	3–3.3	PCP / TEM	< 0.004	<i>Ammann et al.</i> [1990]	
	G, D	3–3.3	PCP / TEM	0.02	<i>Ammann et al.</i> [1993]	
Kilauea	A, D	3–4	OPC, DMA	0.4	<i>Porter and Clarke</i> [1997]	
White Island, New Zealand	A/G, D	0.2–2	QCM	0.2, > 20	<i>Rose et al.</i> [1986]	
Redoubt, Alaska	A, D	2.6–3.8	EAA, AC, CI	< 0.2, 1, > 10	<i>Hobbs et al.</i> [1991]	
	Pinatubo, Philippines	B, D	0–40	OPC	~ 0.2	<i>Deschler et al.</i> [1992]
		G, R	> 10	SP	1.2	<i>Asano et al.</i> [1993]
	G, R	> 10	SP	0.5	<i>Schmid et al.</i> [1997]	

<sup>a</sup> Instrument Platform: A = Airborne, B = Balloon-borne, G = Ground based. Sampling method: D = Direct, R = Remote sensing.

<sup>b</sup> AC = Aerosol Counter, APS = Airborne Particle Sampler, CI = Cascade Impactor, DMA = Differential Mobility Analyser EAA = Electrical Aerosol Analyser, LII = Lucite Inertial Impactor, LSS = Laser-based Size Spectrometer, OPC = Optical Particle Counter, PCP = Photoelectron Charging (also called Aerosol Photoemission, APE), PWI = Palladium Wire Impactor, QCM = quartz crystal microbalance cascade impactor, SP = Sun-Photometer, TEM = Transmission Electron Microscopy, XPS = X-ray Photoelectron Spectroscopy.

are dominated by smaller particle modes [e.g. *Hobbs et al.*, 1982; *Rose et al.*, 1982]. Particle size distributions also change significantly with distance from the vent, as the coarser mode is deposited [e.g. *Hobbs et al.*, 1982].

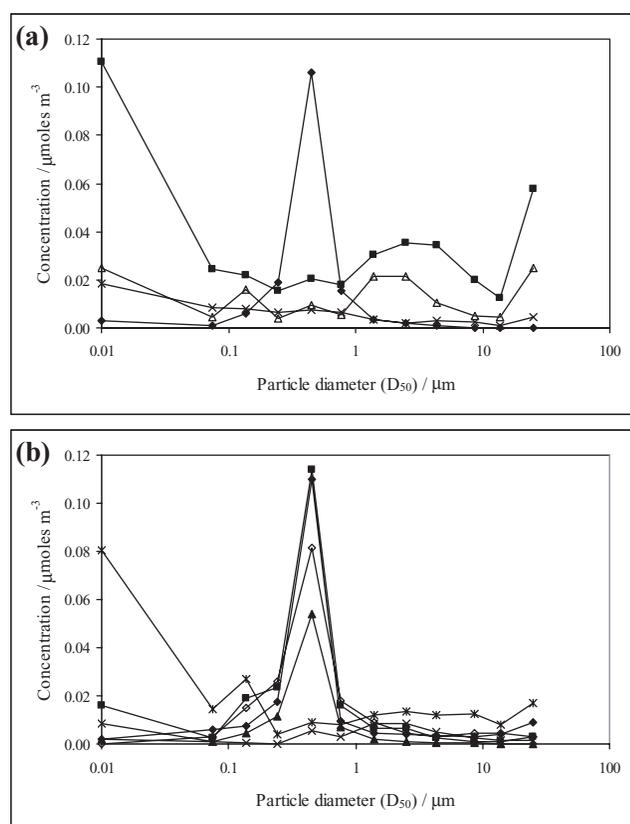
### 2.3. Size-Resolved Chemical Compositions

The size-resolved chemical distribution can convey valuable information about the sources and evolution of particles. For example, a chemical component that corre-

lates with the area distribution of particles may have been incorporated by surface adsorption; whereas a component following the volume distribution may comprise part of the bulk of the particulate matter. Given limitations in measurement techniques, it may, in practice, be difficult to differentiate between the two possibilities [*Hobbs et al.*, 1982].

The size-resolved chemical composition is important in terms of a range of aerosol properties. Particle composition influences density, and thus settling velocity, inertia,

and particle lifetime. Knowledge of the composition of fine particles is also important when evaluating potential health effects. For example, acidic particles  $< 2.5 \mu\text{m}$  can be particularly damaging to lung tissue. Information on the soluble and insoluble mass components of particles of various sizes can be used to estimate CCN emissions. Figure 3 shows an example of the size-resolved chemical composition of particles from the plume of Masaya volcano in Nicaragua. The species  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  are all concentrated in the accumulation modes in particles of about  $0.5 \mu\text{m}$  in diameter, thus these species will experience extended atmospheric lifetimes. These fine acidic aerosols may also pose a health risk to people in the local area.



**Figure 3.** An example of the size resolved particle composition (of soluble ions) from the plume of Masaya volcano, Nicaragua. Measurements were made using a 10-stage micro-orifice uniform deposit impactor and species concentrations were determined using ion-chromatography. (a) Anions: diamonds =  $\text{SO}_4^{2-}/10$ ; squares =  $\text{Cl}^-$ ; triangles =  $\text{F}^-$ ; crosses =  $\text{NO}_3^-$ ; and (b) cations: diamonds =  $\text{H}^+/10$ ; squares =  $\text{Na}^+/10$ ; triangles =  $\text{K}^+/10$ ; open diamonds =  $\text{NH}_4^+$ ; crosses =  $\text{Mg}^{2+}$ ; stars =  $\text{Ca}^{2+}$ . Data taken from Mather et al., 2003.

#### 2.4. Particle Morphologies

Particle morphology offers further valuable information on the formation and history of a particle, and, when coupled with chemical information, may indicate whether a particle is the product of a single nucleation event, or whether coagulation, overgrowth (growth of another substance over the surface of a particle) or surface deposition have played a role in its formation [e.g. Obenholzner et al., 2003]. Particle shape and the formation of aggregates affect particle lifetimes [e.g. Gooding et al. 1983; Oberbeck et al., 1983]. Fine ash from the Mt. St. Helen's plume was removed rapidly by aggregation, a process that was particularly successful at removing glass shards with high surface area-to-mass ratios [Rose et al., 1983]. The influence of size, shape, and other factors, on the fall velocities of small ash particles has been extensively considered elsewhere [Sparks et al., 1997; Bonadonna et al., 1998].

#### 2.5. Measurement Techniques

A variety of remote-sensing and direct sampling techniques has been employed in the measurement of volcanic aerosol and the characterization of volcanic plumes (Table 3). Lidar techniques can be used to give more detailed information on plume structure and location [Hobbs et al., 1991]. Weather radar is useful for studies of more ash-rich clouds [Harris et al., 1983].

While remote sensing techniques are widely applicable, and safe, there are as yet no satisfactory techniques for inferring the composition or shape of volcanic particles from such data. Direct sampling of volcanic plumes, either from the ground or from aircraft or other airborne platforms, remains a necessity. Currently available techniques for particle characterisation are limited to particles and clusters larger than  $\sim 100 \text{ nm}$  (Figure 4). With the development of suitable substrates [e.g. Cu grids, Pfeffer et al., 2001], transmission electron microscopy (TEM) techniques could be more widely used. For further discussion of the study of nanoparticles in the environment see Banfield and Navrotsky [2001].

### 3. ORIGINS AND CHARACTERISTICS

The aerosol measured in volcanic plumes may originate in any of four ways:

- (i) *Pyroclastic material (tephra)*
  - juvenile fragments from the magma, including glass and crystals
  - lithic fragments eroded from the vent walls

**Table 3.** Techniques previously used for volcanic particle measurements. For a general review of atmospheric aerosol measurements see *McMurry [2000]*.

Technique	Information given on: Size distribution	Chemical composition	Particle shapes	Example reference
<b>Ground based</b>				
<b>Remote Sensing</b>				
Sun Photometry (SP)	Aerosol optical depth, size, surface area and volume spectra	–	–	<i>Watson and Oppenheimer [2000]</i>
Passive infra-red (IR) Spectroscopy	Some information of aerosol sizes by comparison with models. Particle size distribution is poorly constrained.	Can distinguish for example silicates and carbonates from water / ice	Some information on shape by comparison with models.	<i>Lynch [1996]</i>
<b>Direct sampling</b>				
Single filters (e.g. Teflon, polycarbonate, cellulose, Lucite inertial impactor, LIH)	Total mass can be used in size distribution models. Sizes of individual particles from imaging.	Total chemical compositions can be determined by techniques such as ion chromatography, for soluble ions, and ICP-MS*. SEM*/FESEM*/TEM* in conjunction with, for example XPS* can also give compositional data for individual particles.	If suitable substrates are used SEM/FESEM/TEM imaging techniques can be used. Short exposure times may also be necessary to ensure the integrity of individual particles.	<i>Hobbs et al. [1991]; Gooding et al. [1983]</i>
Filters in series	Can separate particles into 2 size fractions	As for single filters	As for single filters	<i>Allen et al. [2000]</i>
Cascade impactor (CI)	Separates particles into different size fractions by impacting them onto a series of plates.	As for single filters	As for single filters	<i>Hobbs et al. [1991]</i>
Quartz crystal microbalance impactor (QCM)	Can give real-time mass by size readings.	Can be used in SEM/FESEM/TEM	SEM/FESEM/TEM	<i>Chuan et al. [1981]</i>
Laser-based size spectrometer (LSS)	Size spectrum for particles $> 2 \mu\text{m}$ - by re-suspension of particles after collection.	–	–	<i>Gooding et al. [1983]</i>
Electrical aerosol analyzer (EAA) and aerosol counter (AC)	Size spectra ( $0.01 \mu\text{m} - 4.9 \mu\text{m}$ by electrical mobility forward and $90^\circ$ light scattering particle imaging by lasers.	–	–	<i>Hobbs et al. [1982]</i>
Differential mobility analyzer (DMA)	Real-time size spectrum of particles	Hygroscopic Tandem Differential Mobility Analyser can give information on hygroscopicity.	–	<i>Porter and Clarke [1997]</i>
Optical Particle Counters (OPC)	Real-time size spectrum of particles although there can be limitations on the size range.	–	Some new models can distinguish particle non-sphericity.	<i>Hobbs et al. [1991]</i>

Table 3. (continued)

Technique	Information given on: Size distribution	Chemical composition	Particle shapes	Example reference
Photoelectric Charging of Particles (PCP)	The diffusion charge is proportional to the total surface area and may be used as an estimate for the particle concentration for a given size distribution. This can study particles below 100 nm missed by impactors.	Allows extremely sensitive and selective detection of monovalent copper in alkali chloride and sulfate aerosols containing different metal traces.	-	<i>Ammann et al.</i> [1992]
Airborne Particle sampler (APS)	Particles collected on wires and size distribution recovered using SEM and statistical methods.	SEM and XPS	SEM	<i>Farlow et al.</i> [1981]
Palladium wire impactor (PWI)	Size distribution recovered using SEM and statistical methods.	SEM and XPS	SEM	<i>Oberbeck et al.</i> [1983]

\* ICP-MS = Inductively Coupled Plasma Mass Spectroscopy, SEM = Scanning Electron Microscope, FESEM = Field Emission Gun SEM, TEM = Transmission Electron Microscope, XPS = X-ray Photoelectron Spectroscopy.

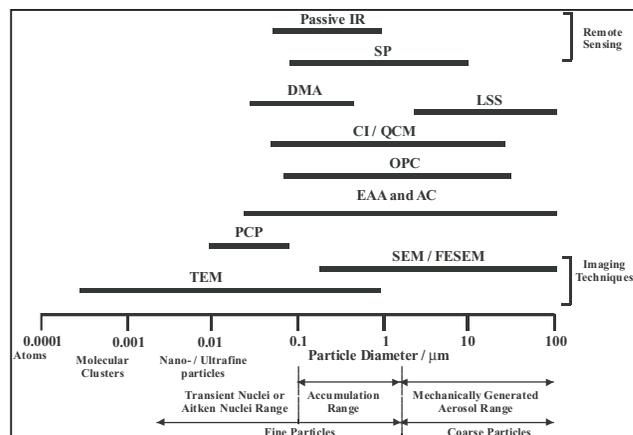
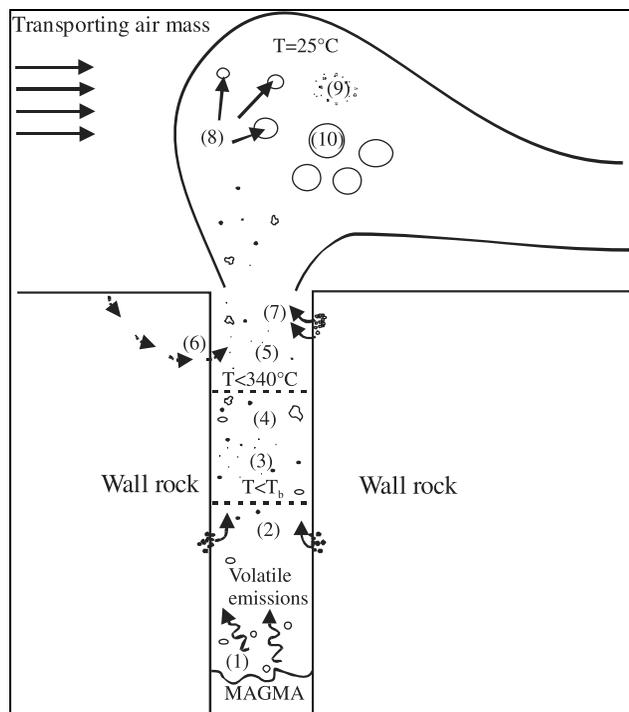


Figure 4. Size ranges covered by different particle measurement techniques. Refer to Tables 2 and 3 for explanation of abbreviations.

- (ii) *Condensation of volcanic gases (originating from the following possible sources) as they cool*
- volatile species (including trace metals) released directly from the magma
  - high-temperature gas-phase reaction products (involving volcanic and perhaps atmospheric components)
  - boiling of hydrothermal fluids
  - wall rock interactions (by condensed acid liquids and other plume components)
- (iii) *Transformations of existing particles*
- adsorption of species on to the surfaces of other particles (with possible subsequent reaction or leaching of material from the host particle)
  - dissolution of species into the aqueous phase
- (iv) *Low temperature reactions (gas-to-particle reactions at ambient temperature and aqueous phase reactions)*

The different processes of particle formation are shown schematically in Figure 5. Many of these processes are complex, and temperature-dependent. The upper limit for condensation of magmatic volatiles is determined by the thermodynamic properties of the salt, or compound, and the temperature at which the vapors reach supersaturation. These processes have been explored by equilibrium thermodynamic modeling of gas mixtures [e.g. *Symonds et al.*, 1992, 2001; *Symonds and Reed*, 1993]. One of the key species in plumes is sulfuric acid, which has a boiling point of 330 °C. However thermodynamic modeling of the temperature of formation of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_{(\text{aq})}$  suggests that, amongst other things, it is strongly dependent on the S content of the gas. At 10% S,  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  forms below 261 °C; while at 0.1% S, the satu-



**Figure 5.** Cartoon illustrating processes that contribute to particle formation in volcanic plumes. The relative importance of different processes will vary between different volcanic systems (e.g., in fumarolic systems there will be few if any particles from magma fragmentation): (1) fragmented magma; (2) erosion of rock particles from the vent walls; (3) condensation of volatile species (including trace metals) released directly from the magma; (4) adsorption of species onto the surfaces of other particles and possible subsequent leaching of material from the host particle; (5) condensation of high temperature gas phase products; (6) boiling of meteoric water or water from another source that has leached the surrounding country rock into the gas; (7) interactions with the wall rock by condensed acid liquids and other plume components; (8) dissolution of species into the aqueous phase; (9) gas to particle reactions at ambient temperature; (10) aqueous phase reactions.  $T_b$  represents the boiling temperature of the different volatiles in the plume. Adapted from Symonds *et al.* [1992] and Smith *et al.* [1982].

ration temperature drops to 202 °C [Symonds *et al.*, 1992]. If such low temperatures are not achieved before the gas exits the vent, then trace element scavenging from wall rock by condensed acid droplets will not contribute significantly to the particles formed. At temperatures between those for salt crystallization and  $H_2SO_4$  formation, adsorption of HCl and HF gas on to the surface of solidified silicates may become important [Óskarsson, 1980].

The presence of an aqueous phase is important for the dissolution of soluble species, and for chemical reaction path-

ways. Since  $H_2SO_4$  is hygroscopic, condensation will take water into the particulate phase at  $T < 202$  °C. The initial high acidity of these small droplets will dictate what else they can dissolve, and which reactions can take place within them. Later in the development of a plume, aqueous droplets may form independently of  $H_2SO_4$ , a process that will be greatly influenced by the meteorological conditions of the transporting air mass.

### 3.1. Pyroclastic Material

Volcanic ash particles have characteristic morphologies and compositions [e.g. Heiken and Wohletz, 1985] and usually remain recognizable even when alteration by acid leaching, surface adsorption, or the formation of overgrowths occurs in the plume during transport. When present, rock fragments usually account for most of the larger mode in the size distribution ( $> 2$   $\mu m$ ). The coarse fraction of ash-poor emissions may contain materials ranging from amorphous and crystalline elemental sulfur particles [e.g. Mt. Erebus, Antarctica; Chuan *et al.*, 1986; Popocatepetl, Mexico, Obenholzner *et al.*, 2003] to water droplets [e.g. fumarolic emissions at White Island, New Zealand; Rose *et al.*, 1986].

Rock fragments are not always limited to the larger size fractions. The 1986 plume of Mt. St. Augustine (Alaska) contained silicates in all fractions down to 0.1 mm [Rose *et al.*, 1988]. Crystals and crystal fragments often comprise a significant proportion of the silicate fraction of the smaller size fractions [e.g. Rose *et al.*, 1980; Cadle *et al.*, 1979]. Since the scale of inhomogeneities in the melt influences tephra particle size, more-crystalline magmas are likely to be a source of larger amounts of finer particles. Dome-forming eruptions of highly crystalline magma, such as that at the Soufrière Hills Volcano (Montserrat), release considerable quantities of fine ash. Typical ash emissions on Montserrat contain 10–30 wt% of  $< 10$   $\mu m$  particles [Baxter *et al.*, 1999; Bonadonna *et al.*, 2002; Moore *et al.*, 2002].

The flux of volcanic ash into the troposphere is very poorly constrained. Previous estimates dating from the 1970s [compiled in Warneck, 2000] range from 4–150 Tg yr, with a ‘best estimate’ of 33 Tg yr [Andreae, 1995] based on such disparate arguments as the rate of accumulation of clays in the ocean, and the abundance of volcanogenic particles in the stratosphere. The largest mass fluxes tend to be from explosive eruptive events, which will be dominated by larger particle sizes ( $> 50$   $\mu m$ ) with short atmospheric lifetimes. Large explosive ‘magmatic’ eruptions also have proportionally lower small particle emissions than the typical ‘smaller’ events [Hobbs *et al.*, 1982; Baxter *et al.*, 1999]. Since quiescent plumes account for most of the global volcanic flux of sulfur and other gases to the atmosphere [e.g.

*Berresheim and Jaeschke* 1983; *Stoiber et al.* 1987 and see Table 1b], the same is likely to be true for particles. There are so few data on volcanic ash emission rates from quiescently degassing and weakly active volcanoes that it is not possible to make any meaningful estimate of the ash flux from these sources. However, the emission rate of ash to the troposphere from small explosive volcanic eruptions may be constrained from the records of historical eruptions. Small explosive eruptions (involving  $< 10^{11}$  kg of erupted magma) occur at a rate of about 24 per yr, and release  $6500 \text{ kg s}^{-1}$  of tephra to the troposphere [*Pyle*, 1995, 2000]. Of this mass, typically  $< 10\%$  comprises particles smaller than  $10 \mu\text{m}$  [e.g. *Carey and Sigurdsson*, 1982; *Wilson and Walker*, 1985], giving a ‘typical’ flux of fine ash from small explosive eruptions of  $< 20 \text{ Tg yr}$  (Table 1a). Perturbations following the very largest explosive events ( $> 10^{15}$  kg of erupted magma), may briefly increase the tropospheric fine ash load to  $\sim 10^5 - 10^6 \text{ Tg}$ .

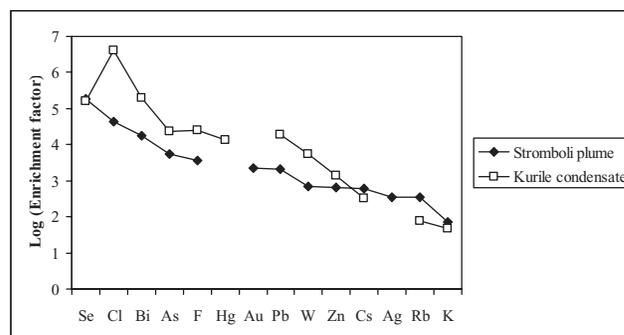
Large explosive eruptions transport particles higher into the atmosphere, leading to an extended lifetime compared to equivalent lower level emissions. For reasons discussed earlier, a bulk global value for particle emission may not be the most useful value for the purposes of modeling the radiative effects of volcanic aerosol. An appreciation of the particle size distribution and altitude and latitude of emission will be essential to a proper assessment of volcanic dust source strengths and impacts; at the present time, however, such data are almost non-existent.

### 3.2. Condensation of Volcanic Gases as They Cool

#### 3.2.1 Volatile species released directly from the magma.

Many elements have been identified in volcanic emissions (e.g. Figure 6). *Vie le Sage* [1983] documented forty. By the time of sampling, however, many of these elements are combined into distinct phases, whose formation is not well understood. Furthermore, analyses often yield information only on individual elements or ions, such that the actual compounds present must be inferred (e.g. the data presented in Figure 3). Many of these elements are trace metals. Some may have been incorporated via acid leaching of wall rock and rock fragments but they also occur independently of acid, and are thus supposed to have been directly emitted from the magma. General trends can be observed between different volcanoes. In the non-eruptive plume of Mount St. Helens, Cu-Zn oxide and Al-salts (mostly sulfate) were the dominant solid, non-silicate particles [*Rose et al.*, 1982]. At Fuego (Guatemala) and Cerro Negro (Nicaragua),  $\text{CaSO}_4$  and NaCl were more prevalent [*Rose et al.*, 1973], while in emissions from Mt. Erebus, Al-salts are common [*Keys and Williams*, 1981; *Rosenberg*, 1988].

Volatile solubility is controlled by the temperature, pressure, oxidation state and composition of the melt [e.g., *Carroll and Holloway*, 1994; *Wallace and Anderson*, 2000; *Scaillet et al.*, *this volume*]. As the major volatile constituents ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) exsolve from the magma forming bubbles, trace species also partition into the gas phase. *Vie le Sage* [1983] invoked the degree of covalency to explain differing trace metal volatilities and abundance in volcanic emissions. However, the prevalence of metals, such as K, Ca and Al, that tend to form predominantly ionic compounds in volcanic aerosol suggests limitations to this approach. Most information concerning the speciation of volatile constituents comes from inference, or thermodynamic calculations. Modeling approaches that assume equilibrium between gas and magma have emphasized the importance of halogens, in particular, in influencing the transport of trace species in magmatic gases [e.g. *Symonds et al.*, 1987]. This is supported by limited direct observations using spectroscopic methods [*Murata*, 1960] and the correlation of trace constituent concentrations with halogen levels [*Zoller et al.*, 1983]. Oxidation state is also an important control on speciation and solubility of species such as S [e.g. *Carroll and Webster*, 1994; *Scaillet and Pichavant*, 2003], and other trace constituents [e.g. *Mizutani* 1970; *Rose et al.*, 1982].



**Figure 6.** Abundances (relative to Mg) of selected volatile species in magmatic gas emissions from Stromboli [*Allard et al.*, 2000], and high-temperature fumarolic condensates at Kudryavy volcano, Kurile islands [*Taran et al.*, 1995]). The ‘enrichment factor’ [E.F.] for each element  $X$  compares the relative concentration of element  $X$  in the aerosol over that in the reference material, normalized to a reference element,  $R$ :

$$\text{E.F.}(X) = (X/R)_{\text{aerosol}} / (X/R)_{\text{initial material}}$$

In this case,  $R$  is Mg, and the reference material is magma. For volcanic particles, the magma composition is usually taken as the reference material, and Al, Mg, Br and Sc have all been used as reference elements [*Vie le Sage*, 1983; *Varekamp et al.*, 1986; *Allard et al.*, 2000]. The most volatile species (Se, Cl, Br) may be enriched in the plume by five or six orders of magnitude compared to non-volatile Mg; alkali metals show 100-fold enrichment relative to Mg.

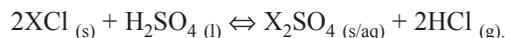
As volcanic gases cool in the atmosphere, they condense to form particles whose sizes will depend on the temperature gradient and the quantity of condensable volatiles available. Condensation products display a variety of morphologies, from the droplets and spheroids suggestive of liquid phase products, to regular, faceted structures suggestive of solid particles [e.g. *Varekamp et al.*, 1986; *Obenholzner et al.*, 2003]. Information about particle formation can be gleaned from chemical and textural particle analysis. Plumes often contain not only particles inferred to have precipitated as a single homogeneous phase at high temperatures, but also particles with multiphase histories, showing chemical zoning, concentric overgrowths, or intergrowths [e.g. *Stoiber and Rose*, 1974; *Meeker et al.*, 1993; *Obenholzner et al.*, 2003]. Thus far, most published investigations are of particles of  $\geq 1 \mu\text{m}$  size. Refinements in sampling techniques [e.g. *Pfeffer et al.*, 2001] and high-resolution imaging hold much promise for extending analysis to smaller particles.

An important issue regarding trace metals is the role of gas phase transport after the magmatic vapors have left the vent. *Hinkley et al.*, [1991] showed that, within metres of an open vent on Kilauea, negligible Cd, In, Pb, Ti or Bi remained in the gaseous phase. This observation, and the high boiling points of many trace metal species, suggests that the atmospheric transport of many trace metals is predominantly in the solid phase. There are however, exceptions: appreciable quantities of Hg, Se and As are thought to be transported as gases [e.g. *Lambert et al.*, 1988; *Le Cloarec and Marty*, 1991].

*3.2.2. High-temperature gas phase reaction products.* Although halogens may be a key species in trace metal transport, trace metals may not be preserved as halogen compounds if they undergo reaction during transport. For example, hydrolysis of  $\text{AlCl}_3$  by atmospheric water may be responsible for the formation of  $\text{Al}_2\text{O}_3$  near Vulcano's fumaroles [*Vie le Sage*, 1983].

Other than trace metals, the major gas phase reaction product of interest is sulfuric acid, which is generally considered an oxidation product of  $\text{SO}_2$  or  $\text{H}_2\text{S}$ . The atmospheric sulfate production routes (discussed later) require oxidizing agents to mix from the ambient air. The existence of sulfate particles in the near-vent, and undiluted, emissions of some volcanoes systems may suggest a different oxidation pathway occurring in volcanic vents [e.g. *Allen et al.*, 2002]. The potential mechanism is as yet unclear, but it has been suggested that nucleation on ultrafine metal chlorides may play a role, with the metallic cations enhancing the reaction rate [*Berresheim and Jaeschke*, 1986]. Once formed, this sulfuric acid may modify

trace metal speciation by revolatilisation of HCl and the formation of metal sulfates:



Etna volcano frequently shows distinctive differences between the emissions from lava flows, degassed at low pressures, and the summit plumes [e.g. *Gauthier and Le Cloarec*, 1998; *Burton et al.*, 2003]. The former tend to be halogen-rich, with very small particles ( $< 1 \mu\text{m}$ ) dominated by Na and K sulfates and chlorides [e.g. *Toutain et al.*, 1995], in contrast to the 'stacked-platelet' morphology of S-Na-K bearing particles in the Cl-poor summit plumes. This may reflect reduced formation of ultrafine chloride particles in the summit plume leading to reduced S oxidation.

Other suggestions have been put forward for the absence of  $\text{SO}_4^{2-}$  in volcanic emissions. *Ammann et al.* [1992] suggested that where magmatic gases cool completely before emission, such as above lava flows and at fumaroles, no acid droplets are observed. They conclude that when gases cool under S-depleted or completely reduced conditions, initial acid formation may be suppressed because, at near ambient temperatures,  $\text{SO}_2$  conversion rates are low. No elevated sulfate levels were observed in the Mount St. Helens eruption cloud, perhaps because opaque plumes limit photolysis, and/or because the kinetics were too slow compared with the risetime of the plume [*Hobbs et al.*, 1982]. Similar conclusions were drawn from airborne measurements of fumarole emissions from White Island [*Rose et al.*, 1986]. Since the mechanisms of sulfate production in plumes remain unclear, it is hard to say what conditions will lead to the observation of near-source sulfuric acid.

*3.2.3. Wall rock interactions.* Interactions of wall rock materials with acidic and reactive gases in volcanic plumes are likely to be important, but have been little studied. Extraction of fluorine from volcanic gases by reaction with the wall rock has been invoked to explain variations of F with time and temperature in fumaroles [e.g. *Stoiber and Rose*, 1970], and suggested as the basis of a geothermometer [e.g., *Francis et al.*, 1996]. Studies of HCl-rich fumaroles at Augustine, Alaska, showed that wall rock leaching is important in the case of cooler emissions, where acids are likely to be more stable, and may also mobilize less volatile species such as Al, Ba, Sr and Mg [e.g. *Symonds et al.*, 1990].

*Obenholzner et al.* [2003] used high resolution scanning electron microscopy (FESEM) techniques to show the signature of a variety of contact metamorphic and related minerals in the particulate emissions from Popocatepetl. This

indicates the interaction of magma and magmatic fluids with carbonate-bearing rocks and other sediments beneath the volcano, as well as interactions at higher levels such as wall rock-magma interactions during ascent.

### 3.3. Transformations of Existing Particles

*3.3.1. Adsorption of species on to the surfaces of other particles.* The nucleation of acids on to ultrafine chloride particles can cause modification of particle morphology, resulting in acid-etched particle surfaces and overgrowths. Processes operating on larger scales are similar. Scavenging of volatiles by silicates can occur directly on to the surface, or be water-mediated. In some cases, all silicate particles are coated with a thin acidic film [e.g. *Casadevall et al.*, 1984]; in others, acidic coatings are absent [e.g. *Hobbs et al.*, 1991]. These observations are ascribed to differences in SO<sub>2</sub> oxidation rate under different conditions. Scavenging by ash can be an important sink for volcanic volatiles during eruptions [e.g. *Rose*, 1977; *Stith et al.*, 1978]. During explosive eruptions of Fuego, up to 33% of S and 17% of Cl were rapidly deposited to the ground by adsorption on ash [*Rose*, 1977]. For this process to occur, acidic particles must have formed, and the ash and acid particle densities must be sufficient to promote particle collisions. *Rose* [1977] observed a maximum in the soluble material on ash particles at intermediate distances from the vent, where acid droplets had had time to form but the plume was not yet dilute enough to impede particle interactions. As with smaller particles, the acids scavenged on to the ash can leach out soluble elements from the ash. Estimates can be made of the origin of any element found on the surface of an ash particle by comparing its surface enrichment with its relative concentration within the particle.

*3.3.2. Dissolution of species into the aqueous phase.* Once the plume exits the vent it will mix with ambient air. This background air may already contain an aqueous droplet phase, or else the cooling might cause more of the water vapor in the volcanic plume itself to condense, with the potential for small particles in the plume to seed aqueous droplets. Once formed, these aqueous droplets may be modified as they scavenge soluble species from the gas phase. The physical solubility of an arbitrary gas HA is described by the Henry coefficient H<sub>e</sub>:

$$H_e = [\text{HA}]_{\text{aq}} / [\text{HA}]_{\text{g}}$$

where [HA]<sub>aq</sub> and [HA]<sub>g</sub> are the concentrations in the aqueous and gaseous phase, respectively. Acidic gases undergo acid-base reactions, such as:



and these reactions enhance gas uptake. To take this into account, acid gas solubility is described by an effective Henry coefficient, H<sub>e</sub><sup>\*</sup>. This is also a function of pH and temperature. At room temperature and a pH of 2, H<sub>e</sub><sup>\*</sup> for HCl and SO<sub>2</sub> are 1.9 x 10<sup>4</sup> and 3.0 mol l<sup>-1</sup> atm<sup>-1</sup>, respectively [taken from *Sander*, 1994 cited in *Textor et al.*, 2003b], hence HCl is preferentially scavenged into the aqueous phase. Enhancement of Cl over S in the particulate phase has been recognized, for example, in the plume of Augustine volcano [*Rose et al.*, 1988] and in studies of wet deposition rates for the two gases, and plume-affected rainwater analysis [e.g. *Johnson and Parnell*, 1986; *Kawaratani and Fujita*, 1990; *Aiuppa et al.*, 2001; *Edmonds et al.*, 2003].

Once SO<sub>2</sub> is oxidized to sulfate, the product is extremely hygroscopic, and the resulting increased acidity can decrease the H<sub>e</sub><sup>\*</sup> of HCl and effectively re-volatilise it. *Allen et al.* [2000] observed such an effect in the plume from Soufrière Hills, Montserrat where NaCl reacted with acid in the fine particle mode, resulting in the volatilisation of HCl from fine particles (showing high [Na<sup>+</sup>]:[Cl<sup>-</sup>] ratios), and followed by scavenging by coarser particles (showing low [Na<sup>+</sup>]:[Cl<sup>-</sup>] ratios).

### 3.4. Low Temperature Reactions

During atmospheric transport in the plume, the most important reactions are likely to be SO<sub>2</sub> oxidation and acid neutralization by background ammonia. SO<sub>2</sub> oxidation is thought to account for a number of observations in volcanic plumes. For example, *Farlow et al.* [1981] observed that ash collected only a day after a 1981 eruption of Mount St Helens was completely dry, whereas after that it was acid coated. SO<sub>2</sub> can undergo three classes of reactions in the atmosphere that may lead to the formation of particulate sulfate: gas-phase homogeneous reactions, aqueous-phase reactions, and heterogeneous reactions on the surface of solids [*Eatough et al.*, 1994].

The hydroxyl radical (OH) is considered the main agent for gas phase oxidation. OH forms in the troposphere by the reaction of photochemically generated oxygen radicals with water, and has a short lifetime. In the absence of clouds or fog, SO<sub>2</sub> conversion to particulate sulfate proceeds more rapidly during the day than at night, and more rapidly in summer than in winter. Studies of industrial plumes suggest that the OH reaction with SO<sub>2</sub> does not become important until the plume is dispersed and mixed with ambient air.

An increased conversion rate of SO<sub>2</sub> to sulfate is observed when water droplets are present, due to aqueous phase sul-

fur chemistry. The main oxidants are hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ozone ( $\text{O}_3$ ) entrained from the surrounding atmosphere. Dissolved molecular oxygen is only a strong enough oxidizing agent in the presence of iron, manganese or other transition metal catalysts. The effectiveness of  $\text{O}_3$  as an oxidant decreases with decreasing pH, whereas that of  $\text{H}_2\text{O}_2$  shows little pH dependence. At the low pH associated with volcanic water droplets,  $\text{H}_2\text{O}_2$  is the dominant oxidant. Although both  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are photochemically produced, their longer lifetimes in the atmosphere mean that the aqueous phase oxidation of  $\text{SO}_2$  is much less photo-dependent than its gaseous phase equivalent. Couple this with expected lower nocturnal temperatures leading to a higher proportion of the water being in the liquid phase, and it seems likely that this oxidation pathway will be dominant at nighttime.

$\text{SO}_2$  can be oxidized on a variety of particle surfaces such as soot or dust. The rate of conversion depends on the nature of the surface, the presence of co-pollutants and the relative humidity. The oxidation rate can be enhanced when a film of water covers the particles, although this suggests that aqueous phase oxidation is in fact occurring. These types of reactions are thought to be important only in plumes of high particle density ( $> 100 \mu\text{gm}^{-3}$ ).

In summary, slower gas phase reactions dominate in conditions of low humidity and daylight, with 5–10%  $\text{h}^{-1}$  of  $\text{SO}_2$  reacted in summer and 0.3–1%  $\text{h}^{-1}$  of  $\text{SO}_2$  reacted in winter; faster aqueous phase reactions dominate at higher humidity and at night (20–100%  $\text{h}^{-1}$  of  $\text{SO}_2$  reacted). If the plume has a high dust/ash density then heterogeneous surface reactions may play a part too.

$\text{SO}_2$  loss rates, assumed to be primarily due to sulfate formation, have been calculated for several volcanic plumes. As might be expected, background atmospheric conditions strongly influence these rates. Studies of plumes in the cold Antarctic and Arctic atmospheres have shown little or no oxidation of  $\text{SO}_2$  [e.g. Erebus, Chuan *et al.*, 1986; Mt. Redoubt, Hobbs *et al.*, 1991]. Elsewhere, Hobbs *et al.* [1982] observed oxidation rates in the Mt. St. Helens plume that were comparable to those observed in power-plant plumes (0.1%  $\text{h}^{-1}$ ). If the loss rate is modeled in terms of first order kinetics, apparent rate constants range from  $1.9 \times 10^{-7}$  to  $5.4 \times 10^{-3} \text{ s}^{-1}$  [Oppenheimer *et al.*, 1998].

The other major process that may occur as the plume ages is neutralization of aqueous acidic species by background ammonia. Variation is again observed in the degree of neutralization of acidic volcanic species by ammonia: Allen *et al.* [2000] documented unambiguous ammonia neutralization in the Soufrière Hills plume, but Clarke [cited in Porter *et al.*, 2002] observed very little in Kilauea's plume. Enhanced neutralization may help to mitigate the potential-

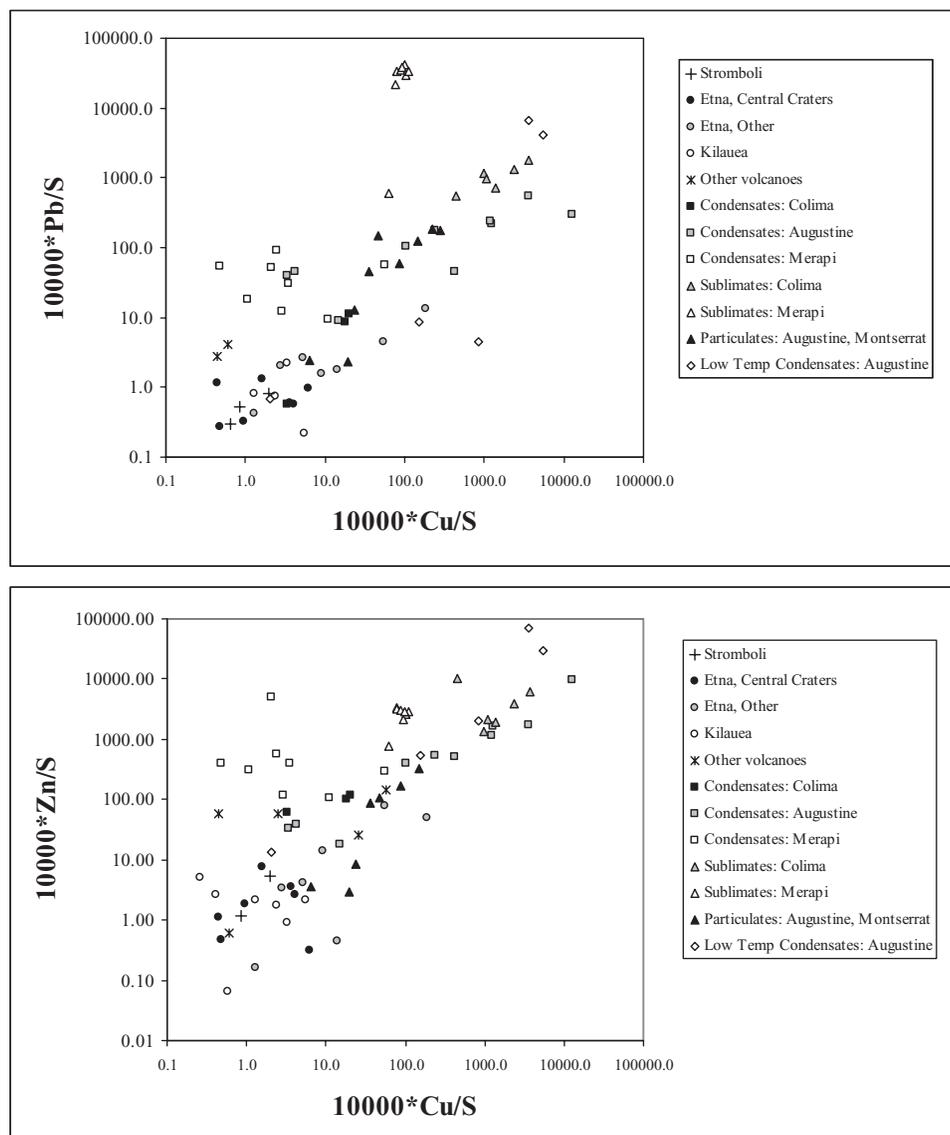
ly detrimental environmental and health impacts of volcanic acid particles.

#### 4. EMISSION RATES OF TRACE METAL AEROSOLS TO THE TROPOSPHERE FROM VOLCANOES

Degassing and erupting volcanoes release prodigious quantities of volatile heavy metals to the troposphere, predominantly in the particle phase (see section 3.2.1). This particle flux is not well constrained but is thought to constitute an important natural source of pollution, whose effects may be detected globally, for example in polar ice cores [e.g. Ferrari *et al.*, 2000; Matsumoto and Hinkley, 2001]. For some species (e.g. As, Bi, Cd, Cu, Pb, Se) volcanoes may be the largest natural emission source [e.g. Nriagu, 1989].

Two methods have been adopted to estimate volcanic metal fluxes. The first approach is to estimate the metal/sulfur ratio of volcanic emissions, and then use the known emission rates of sulfur to estimate the metal flux. This has been used to constrain individual metal fluxes from a few volcanoes [e.g. Erebus, Zreda-Gostynska *et al.*, 1997; Etna, Gauthier and Le Cloarec, 1998 and Stromboli, Allard *et al.*, 2000], as well as to estimate global emission rates [e.g. Nriagu, 1989; Hinkley *et al.*, 1999]. The difficulties with this approach are obvious: metal:sulfur ratios vary not only from volcano to volcano, but also temporally and spatially at any site. In part this reflects decoupling of the metal-rich particulate phase from the S-rich gas phase, but also, as is clear from Figure 7, this will also be influenced by the nature of degassing. For example, fumarolic emissions are considerably enriched in heavy metals, compared to sulfur, in contrast to the emissions from high-temperature magma degassing (Figure 7). At Etna, post-eruptive emissions from flank lava flows are also significantly enriched in heavy metals, compared to the emissions from the central craters [e.g. Gauthier and Le Cloarec, 1998].

In addition to uncertainties in the metal:sulfur ratio, there is significant uncertainty in the global tropospheric source strength of volcanic sulfur, which receives contributions from fumarolic activity and quiescent degassing as well as eruptions (Table 1b). While flux estimates for 'continuous' volcanic emissions of  $\text{SO}_2$  to the troposphere agree fairly closely (3.0–4.7 Tg yr, Table 1b), there is more uncertainty (as well as spatial and temporal variability) over the proportion of sulfur (as  $\text{SO}_2$ ) from small explosive eruptions emitted to the troposphere alone (2.0–6.3 Tg yr, see Table 1b). The flux of other sulfur species, such as  $\text{H}_2\text{S}$ , is so poorly known as to be unconstrained (ranging, for example, from  $< 0.2$  Tg yr, Stoiber *et al.* [1987] to 1.5–37 Tg yr, Halmer *et al.* [2002]).



**Figure 7.** Covariation plots to show the metal/sulfur mass ratios in a variety of volcanic emissions and for three moderately volatile metals, Cu, Zn and Pb. Data represent determinations of: ‘bulk plume’ compositions (metals and sulfate collected on filters, SO<sub>2</sub> on base-treated filters; Stromboli, Etna, Kilauea and ‘Other Volcanoes’); condensates (direct samples of condensed gas from high-temperature fumaroles); sublimates (precipitates collected in sampling tubes from high-temperature fumaroles); and particulates (filter samples of the volcanic plume). Both plots show strong correlation between metal/sulphur ratios, suggesting that the variability in metal: metal ratios in volcanic emissions is considerably less than the variability in metal/sulfur ratios. Data sources: *Allen et al.* [2000]; *Allard et al.* [2000]; *Crowe et al.* [1987]; *Hinkley et al.* [1999]; *Gauthier and Le Cloarec* [1998]; *Lepel et al.* [1978]; *Symonds et al.* [1990, 1992]; *Taran et al.* [2001]; *Zreda-Gostynska et al.* [1997].

Despite these difficulties, estimates of the *total* metal flux from degassing volcanoes agree fairly well, even if there are wide disparities for certain metals (e.g., Cu, Table 4). After correcting for a systematic error of a factor of 2 in *Nriagu’s*

[1989] quoted volcanic S flux, there is a close correspondence between his estimate of 14 Gg yr<sup>-1</sup> of Cu, Pb, Cd, Zn, As, Se released, and the estimate of *Hinkley et al.* [1999] of 10 Gg yr. This reflects the relatively similar ‘global’

**Table 4.** Comparison of volcanic, natural and anthropogenic fluxes to the atmosphere of selected species.

Element	Volcanic (Gg/yr)	Natural (Gg/yr)	Anthropogenic (Gg/yr)
S	6700–10500 <sup>a</sup>	27200 <sup>b</sup>	77 000 <sup>b</sup>
Al	13 280 <sup>c</sup>	48 900 <sup>d</sup>	7 200 <sup>d</sup>
Co	0.96 <sup>e</sup>	6.1 <sup>e</sup>	4.4 <sup>d</sup>
Cu	1.0 <sup>f</sup> , 4.7 <sup>e</sup> , 15 <sup>g</sup> , 22 <sup>h</sup>	28 <sup>e</sup>	35 <sup>e</sup>
Zn	4.8 <sup>e</sup> , 7.2 <sup>f</sup> , 8.5 <sup>h</sup>	45 <sup>e</sup>	132 <sup>e</sup>
Pb	0.9 <sup>f</sup> , 1.7 <sup>e</sup> , 2.5 <sup>g</sup> , 4.1 <sup>h</sup>	12 <sup>e</sup>	332 <sup>e</sup>
As	1.9 <sup>e</sup>	12 <sup>e</sup>	19 <sup>e</sup>
Se	0.3 <sup>h</sup> , 0.5 <sup>e</sup>	9.3 <sup>e</sup>	6.3 <sup>e</sup>
Mo	0.2 <sup>e</sup>	3.0 <sup>e</sup>	3.3 <sup>e</sup>
Cd	0.4 <sup>e</sup>	1.3 <sup>e</sup>	7.6 <sup>e</sup>

Data sources: <sup>a</sup> See Table 1b; <sup>b</sup> *Bates et al.* [1992]; <sup>c</sup> *Symonds et al.* [1988]; <sup>d</sup> *Lantzy and Mackenzie* [1979]; <sup>e</sup> *Nriagu* [1989]; <sup>f</sup> *Hinkley et al.* [1999]; <sup>g</sup> *Lambert et al.* 1988; <sup>h</sup> *Le Cloarec and Marty* [1991];

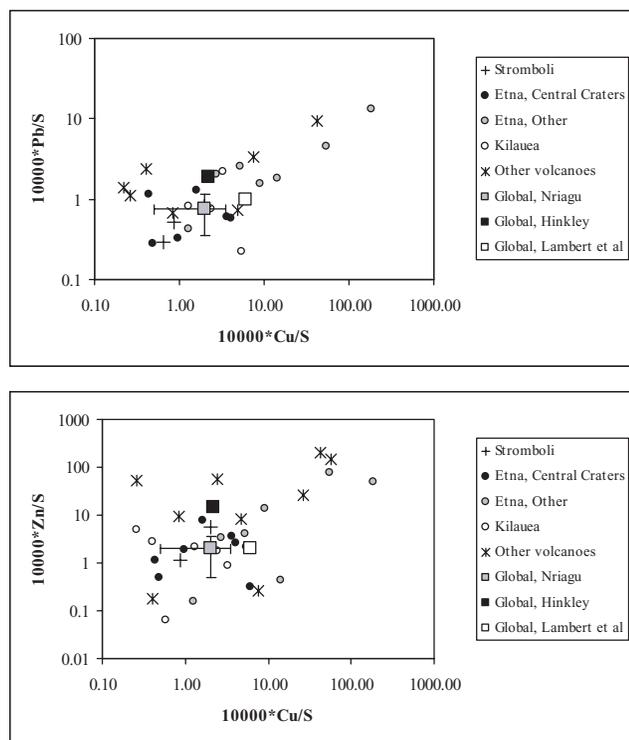
Note: *Nriagu's* [1989] published volcanic metal emission rates were based on a range of S fluxes that were 50% too high (he quoted 15–50 Tg yr of S, when this value was actually 15–50 Tg yr of SO<sub>2</sub>). The values quoted here have been corrected for this factor alone.

metal/sulfur ratios these authors adopt for degassing from purely 'magmatic' sources (for which there are relatively few data, e.g. Figure 8). Such 'global' estimates take no account of heavy metal emissions during explosive eruptions, which account for a significant but sporadic component of the annual global volcanic sulfur flux (30–70%, Table 1b), and for which the metal/sulfur ratios are essentially completely unconstrained. The estimates also neglect the fumarolic emis-

sions (both bulk fluid condensates, and the sublimates that precipitate from them) that may be considerably enriched in metals over sulfur (compare Figures 7, 8).

The second approach is to use the flux of a radioactive volatile metal (<sup>210</sup>Po) as the normalizing factor [e.g. *Lambert et al.*, 1988]. While there are still relatively few <sup>210</sup>Po/S ratios measured on volcanic emanations, the metal/sulfur ratios estimated using this technique [e.g. *Lambert et al.*, 1988; *Le Cloarec and Marty*, 1991] are nonetheless consistent with the estimates derived by *Nriagu* [1989] and *Hinkley et al.* [1999] using the previous method (see Figure 8). Early estimates of the global volcanic S flux derived from this method (25 Tg yr<sup>-1</sup>) are however somewhat higher than other estimates (see Table 1b) leading to higher metal flux estimates.

Both approaches have obvious limitations when attempting to assess the global fluxes of material to the troposphere from volcanic eruptions. First of all, many of the metals are thought to be transported as particulate halides; yet the flux measurements depend on establishing a 'typical' particulate metal to gas-phase sulfur ratio. Clearly the point of meas-



**Figure 8.** Estimates of metal/sulfur mass ratios (for Cu, Zn and Pb) in the 'magmatic' plumes emitted from erupting and degassing volcanoes, with three estimates for the 'Global' mean volcanic metal/sulfur value [*Nriagu*, 1989; *Hinkley et al.*, 1999; *Lambert et al.*, 1988]. Data sources as in Figure 7. 'Other volcanoes' includes data from Erebus (Cu, Zn; *Zreda-Gostynska et al.* [1997]), the Merapi Dome and Papandayan, Indonesia [*Nho et al.*, 1996]. *Nriagu's* global estimate includes error bars based on his published range of values. Note that metal/sulfur ratios from different vents at a single volcano [e.g. Etna, *Gauthier and Le Cloarec*, 1998] may vary by three orders of magnitude.

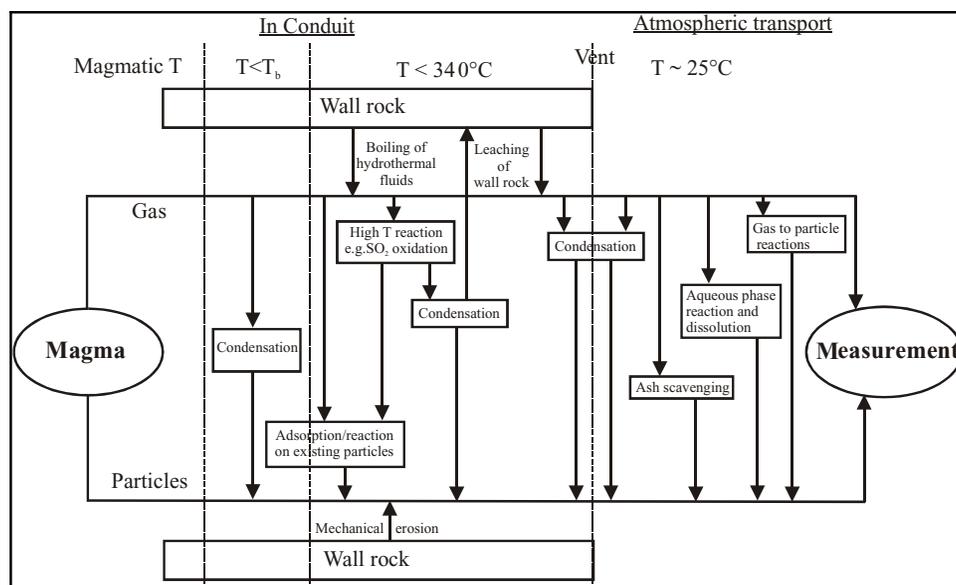
urement, and the amount of gas—particle separation that may have occurred by that point, will strongly influence the measurement [c.f. *Hinkley*, 1991]. Attempts to normalize to halogen flux might prove useful, but would be hindered by the currently poorly constrained volcanic emission rates of halogen species [e.g. *Symonds et al.*, 1988]. Finally, it is clear that even small variations in the contribution of fumarolic gases to volcanic plumes could give rise to considerable variations in the metal/sulfur ratios, and consequently flux estimates.

## 5. CONCLUDING REMARKS

Volcanic plume geochemical studies in the past have tended to focus on the measurement of composition and emission rates of gases. The benchmark work on *particle* composition of tropospheric volcanic plumes dates back to a number of pioneering (and courageous!) airborne campaigns carried out in the 1970s and 1980s [e.g., *Hobbs et al.*, 1982; *Rose et al.*, 1986]. Although there are exceptions [e.g., *Casadevall et al.*, 1984], most of these investigations concerned measurements of dilute eruption clouds rather than passive plumes (which typify many sustained volcanic emissions worldwide), and provided information on total particle fluxes (i.e., sulphate, ash) rather than detailed analyses of particle:gas phase ratios for individual species, and as a function of aerosol size.

There remains considerable scope, therefore, to design future field experiments on tropospheric volcanic plumes aimed at characterizing the size-resolved chemistry of aerosol, gas-particle interactions between plume constituents and the ambient atmosphere (including rural and urban atmospheres), and transport and deposition of both gaseous and particulate volcanogenic components. *Delmelle et al.* [2001] have begun work on dry deposition rates of  $\text{SO}_2$  and HCl for the plume from Masaya volcano but indicate that considerable efforts are required to make meaningful characterizations. Physical and chemical characterization of both the gases and particles emitted by volcanoes will also feed directly into the adaptation of numerical models describing the transport and chemical evolution of plumes. Such efforts would support assessments of volcanogenic pollution scenarios, as well as contributing to understanding of the scavenging of volatiles from explosive eruption plumes bound for the stratosphere [*Textor et al.*, 2003a].

The observed variations in volcanic particle type and composition can reflect magmatic conditions, magmatic-hydrothermal processes [*Oppenheimer*, 1996], and wall rock contributions and reactions prior to emission. Once in the atmosphere, plume components undergo further modification during transport and dilution, with background meteorological conditions playing an important role. The result of all these interactions (Figure 9) is that particles may convey only limited information on mag-



**Figure 9.** Flow chart to show the different processes that may contribute to particle development, between the point of emission from the magma and measurement. The pathways that are dominant will depend upon the nature of the volcanic system and the type of eruption. ( $T_b$  represents the boiling temperature of the different species in the plume).

matic processes. As *Ammann et al.* [1992] indicated, new tools and programmes for continuous, real-time volcanic particle monitoring are needed to identify potential indicators for magmagenesis and volcanic activity that could aid hazard assessment. Figure 9 also indicates that the point of measurement, i.e., the age and environment of the sample, influences the observed composition and size spectrum of any aerosol.

Table 5 summarizes particle flux estimates for individual volcanoes. This reveals orders of magnitude of variation, even for the same volcano in the same phase of activity, implying that large datasets are required to obtain meaningful averages. Due to transformation processes within the

plume and deposition, particle fluxes will also vary with plume age, further complicating these measurements. Again, future field experiments will certainly improve the emission estimates. In particular, more detailed studies of fumarolic and open-vent plumes, which are inherently more accessible and commonplace, should lead to a better understanding of emission characteristics under different conditions. Lessons from such studies could be generally applicable to larger-scale, rarer, explosive plumes, though nonlinearities in scaling up are likely, especially where ash particle densities are high. Further measurements will also help to improve the global source strength estimates (Tables 1a and 4).

**Table 5.** Summary of published estimates of volcanic particle fluxes.

Volcano	Activity	Total Particle Mass Flux (kg s <sup>-1</sup> )	Sulfate Flux (kg s <sup>-1</sup> )	SO <sub>2</sub> Flux (kg s <sup>-1</sup> )	Reference
Erebus, Antarctica	Lava lake degassing	–	6.0 x 10 <sup>-2</sup>	0.4	a
	Lava lake degassing	0.24	–	3.36	b
Kilauea, Hawaii	Lava effusion	0.6*	0.6*	16.8	c
Etna, Italy	Strombolian explosions	4.6–8	0.5–0.8	~ 10	d
Redoubt, Alaska	Intraeruptive	1–6	0.1–2	1–140	e
	Post-eruptive	0.06–0.08	–	> 2–5	e
Mt St Helens, USA	Paroxysmal	1 x 10 <sup>-2</sup> –6 x 10 <sup>4</sup>	2 x 10 <sup>-3</sup> –8	0.03–90	f
	Post-eruptive	0.1–0.02	0.05	0.3–0.05	f
Augustine, Alaska	Paroxysmal	3–6 x 10 <sup>5</sup>	–	100	g
	Intra-eruptive	1–2 x 10 <sup>3</sup>	–	2–300	g
	Post-eruptive	0.03–0.9	–	2–100	g
Ukinrek Maars, Alaska	Post-eruptive	0.01–5 x 10 <sup>-4</sup>	–	0.05–2 x 10 <sup>-5</sup>	g
White Island, New Zealand	Fumarolic	0.15	–	142	h
Mount Martin, Alaska	Fumarolic	0.03	–	0.01	g

a - *Radke* [1982]; b - *Chuan et al.* [1986]; c - *Porter et al.* [2002]; d - *Watson and Oppenheimer* [2000]; e - *Hobbs et al.* [1991]; f - *Hobbs et al.* [1982]; g - *Stith et al.* [1978]; h - *Rose et al.* [1986]

\* Dry mass flux rate

Descriptions of activity follow *Stith et al.*, [1978]: *paroxysmal*—eruptive event occurring on a timescale of minutes; *intraeruptive*: Between paroxysmal events on a timescale of days; *post-eruptive*: After an eruptive period on a timescale of days to years.

Particle fluxes (refs. a, b, e–h) based on airborne plume traverses and direct determination of mass concentrations and plume cross-sectional area. Kilauea estimate (ref. c) based on below-plume traverses with a sunphotometer, with an aerosol mass scattering coefficient based on assumed particle composition. Etna estimate (ref. d) based on sunphotometry, with an assumed plume geometry, and particle densities based on assumed particle compositions. All methods required wind speed to be included in the calculation. Poorly constrained plume transport speeds are a major source of error for ground-based measurements.

**Table 6.** Comparison of CCN fluxes from volcanic and anthropogenic sources, adapted from *Hobbs et al.* [1982]

Source	Strength (CCN s <sup>-1</sup> at 1% Supersaturation)	Reference
Mt. St. Helens, 1980 eruption	5 x 10 <sup>15</sup> – 2 x 10 <sup>17</sup>	<i>Hobbs et al.</i> [1982]
Augustine, 1976 eruption	10 <sup>16</sup> –5 x 10 <sup>17</sup>	<i>Stiith et al.</i> [1978]
Large coal-fired power plant	10 <sup>16</sup> –10 <sup>17</sup>	<i>Hobbs et al.</i> [1980]
Aluminium smelters	10 <sup>14</sup> –5 x 10 <sup>15</sup>	<i>Hobbs et al.</i> [1970]
City (Denver)	1.7 x 10 <sup>17</sup>	<i>Frisbie and Hudson</i> [1993]
Urban Industrial area (E seaboard, USA)	6 x 10 <sup>19</sup>	<i>Radke and Hobbs</i> [1976]
Global Anthropogenic	6 x 10 <sup>21</sup>	<i>Radke and Hobbs</i> [1976]
Global Natural	~ 1 x 10 <sup>21</sup>	<i>Radke and Hobbs</i> [1976]

In terms of indirect climate forcing by cloud formation, particle composition is also important. *Hobbs et al.* [1982] used *Fitzgerald's* [1973] theory and their measurements of the composition of the particles from the Mt. St. Helens plume to estimate the number of CCN. Table 6 compares their results to those for the 1976 Augustine eruption and anthropogenic sources. Even relatively small volcanic plumes can represent significant CCN sources. Further evaluations of volcanogenic CCN would contribute to evaluation of natural background levels, which are essential when calculating the regional and global levels of anthropogenic pollution.

Finally, we recognize that environmental and human health impact assessments in areas affected by volcanic pollution will need to take account of both gaseous and particulate emissions, and the size distribution and composition of particles. For example, the potential significance of emissions of fine, very acidic aerosol from volcanoes for human health has only recently come into focus [e.g., *Allen et al.*, 2002] but may well have important implications for public health in many populated areas located downwind of degassing volcanoes. Future field-based studies to define the key parameters that determine the effects of volcanic emissions in terms of pollution and human health are to be encouraged.

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T. A. Mather and D. M. Pyle, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK. (tam21@cam.ac.uk)

C. Oppenheimer, Department of Geography, University of Cambridge, Downing Place, Cambridge, CB2 3EN, UK.