The Fate of Sulfur and Halogen Gases in a Plinian Volcanic Plume

PETER M. SACHS, GEOMAR, VOLCANOLOGY AND PETROLOGY, KIEL
CHRISTIANE TEXTOR, HANS-F. GRAF, MAX-PLANCK-INSTITUTE FOR METEOROLOGY, HAMBURG

psachs@geomar.de, textor@dkrz.de

MOTIVATION

Plinian volcanic eruptions inject large amounts of sulfur, water, and possibly halogens into the stratosphere.

THE MASS OF VOLCANIC HALOGENS INJECTED INTO THE STRATOSPHERE IS UNKNOWN AT PRESENT!

Volcanic emissions in the stratosphere:
- effect the climate for up to three years,
- destroy stratospheric ozone
  Pinatubo (1991) over Europe, North America and Central Africa: 10-20%.

Halogen species (Cl, Br, I)
- destroy ozone, Br about 400 times more effective than Cl (McKinney 1997)

Sulfur gases (SO_2, H_2S)
- increase the stratospheric sulfate aerosol layer
- aerosols strongly increase ozone-depleting potential of halogen species
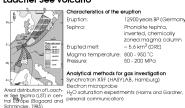
OBJECTIVES

- To what extent do volcanic gases from a typical plinian eruption reach the stratosphere?
- Which processes in the eruption column determine the scavenging efficiency?

METHOD

Numerical simulation of the Plinian eruption of the Laacher See volcano, Germany, 12900 BP, with the plume model ATHAM.

Laacher See volcano

Characteristics of the eruption

Eruption:	12900 years BP (Germany)
Tephra:	Phonolite tephra, inverted, chemically zoned magma column
Erupted melt:	~ 5.6 km³ (DRE)
Magma temperature:	800 - 950 °C
Pressure:	50 - 200 MPa

Areal distribution of Laacher See Tephra (LST) in central Europe (Bogaard and Schmincke, 1985).

Analytical methods for gas investigation
Synchrotron XRF (HASYLAB, Hamburg)
Electron microprobe
H_2O saturation experiments (Harms and Gardner, personal communication)

Estimate of volatile release of F, Cl, Br, I, SO_2, and H_2O

- Chlorine, fluorine, sulfur
  The eruptive release of Cl, F and SO_2 can not be calculated by application of the petrologic method (Devine et al., 1994), due to a late magmatic contamination (prograde fenitization and amphibole and probably sulfide break-down) (Sachs and Harms, 2000).
- Bromine
  The clearest evidence for the syneruptive atmospheric emission is provided by bromine. The mass of Br is determined by the petrologic method.

Mass of released F, Cl, SO_2 and H_2O: $M = M_{Br}(D_x/D_{Br})(C_x/C_{Br})$.

C_{Cl}/C_{Br}	= 64...85	
C_F/C_{Br}	= 41...55	
C_I/C_{Br}	< 0.003	(I: below detection limit of SYXRF)
C_{SO_2}/C_{Br}	= 18...25	
C_{H_2O}/C_{Br}	= 65500/35 = 1871	

M:Erupted mass of Br or components x which can be F, Cl, I, SO_2 or H_2O
C: Preeruptive equilibrium concentrations in the melt, represented at best through glass inclusions which have the highest concentrations of Br ($C_{Br} = 30...40 \mu g/g$).
D: Partition coefficients between fluid and melt (Webster 1990, Keppler 1999, Bureau et al., 2000, D_{H_2O} = 100/6.55 = 15.27: Harms and Gardner, pers. comm.)

Release into the atmosphere (Tg)

component	new method	petrologic method
Br	0.38...0.39	0.38...0.39
Cl	11.5...15.1	6.6
I	<0.007	-
F	0.16...0.22	<0
SO_2	18.9...26.2	3.8
H_2O	743...558	403

The ratio of the mass of SO_2 relative to the volume of the erupted magma (19.9-27.6 Tg SO_2, 5.6 km³ DRE magma) is similar to the emissions of the Pinatubo eruption (>=17 Tg SO_2 in the stratosphere (TOMS), 3.7-5.3 km³ DRE magma, as cited in Kress (1997)).

GAS SCAVENGING

Solution of gases in water drops

Kinetics of the phase transfer+ dissociation of acidic gases in water (Schwartz 1986)

$$\frac{\Delta c_{aq,i}}{\Delta t} = k_t L(c_{g,i} - c_{g,i,eq})$$

$c_{aq,i}$	conc. of species i in water
$c_{g,i}$	conc. of species i in gas
$c_{g,i,eq}$	equilibrium gas conc.
k_t	phase transfer coefficient
L	liquid water content

Incorporation of volcanic gases into ice particles

Transfer of volcanic gases proportional to water vapour transfer (Dominé et al. 1995, Dominé and Thibert 1996)
Concentration of gases in ice is determined by the kinetics of condensation.

$$\frac{\Delta c_{g,i,1}}{\Delta t} = \frac{1}{c_j}\alpha_i \bar{v}_i = \frac{\Delta q_v}{\Delta t}\frac{1}{q_v}\alpha_v \bar{v}_v$$

$\bar{v}$	mean speed of gas
$c_{g,i}$	Conc. of species i in gas
q_v	Conc. of water vapour
Δt	time step
α	Sticking coefficient

Transfer of solutes during microphysical processes

Time dependent change of chemical species in hydrometeors: proportional to the change of hydrometeors caused by different processes:

$$\frac{\Delta c_x}{\Delta t} = \sum_{proc}\frac{\Delta q_x}{\Delta t}\frac{c_x}{q_x}$$

q_x	hydrometeor category x
c_x	chemical species
proc	processes changing q_x

Sensitivity studies in a box model showed that photochemistry is suppressed in the eruption column due to the lack of light!
$HBr \rightarrow Br_2$,like suggested by Bureau et al. 2000, is negligible.
(R. Sander, pers. comm)

ATHAM

Active Tracer High Resolution Atmospheric Model

Non-hydrostatic model, implicit time stepping scheme

Modules

• Dynamics	Advection and thermodynamics Solution of the Navier-Stokes equation (Oberhuber et al. 1998, Herzog 1998)
• Turbulence	Entrainment of ambient air (Herzog 1998, Oberhuber et al. 1998)
• Microphysics	Complete cloud microphysics Liquid water and ice Feedback on the dynamics included (Graf et al. 1999, Herzog et al. 1998, Textor 2000)
• Aerosol	Scavenging of Particles by hydrometeors Particle growth due to interaction with hydrometeors (Textor et al. 2000)

Simulation Conditions

The eruption conditions correspond to the Laacher See volcano.

Model version
2d version, cylindrical coordinates
126 x 125 grid points
150 x 50 km², focusing grid (Δx_{min}=50m)

Simulation time	60	min.
duration of the eruption	30	min.

Geometry of the volcano

mountain height (asl)	400	m
diameter of the crater	600	m
depth of the crater	200	m

Volcanic forcing

eruption temperature	1000	K
eruption velocity	350	m/s
mass eruption rate	$4 \cdot 10^8$	kg/s

Composition of the magma

ash	95	wt.%
normalised gamma distribution		
2 classes	40 % radius=25 μm	
	60 % radius=50 μm	
gases	5	wt.%
H_2O	4.35E-4 wt. %	
SO_2	1.54E-5 wt. %	
HCl	8.42E-6 wt. %	
HBr	2.59E-7 wt. %	

Atmospheric profiles
for temperature and relative humidity
Midlatitudes winter conditions (McClatchey 1972)

Simulation Results for Hydrometeors

30 min. of eruption

Total condensed water and ice mass mixing ratio (g/kg)

Vertical profiles mass per height level

- Frozen hydrometeors are highly dominant in the plume.
- Liquid water exists only in the central rising zone (<1%).

Conclusions

For the Plinian Laacher See volcano, which happened in a dry environment, all gases reach the neutral buoyancy height in the stratosphere. The injection into the stratosphere is > 99 % of the total eruption. The species are partly scavenged by hydrometeors.

The **scavenging efficiency** depends on:
- the individual solubility of the species,
  HCl / HBr: up to 40% contained in ice
  high solubility in liquid water
  incorporation in ice
  SO_2 / H_2S: up to 10% contained in ice
  low solubility in liquid water
  incorporation in ice
- the amount of hydrometeors in the plume
  In a wet environment the entrainment of humid ambient air increases the hydrometeor content. This might strongly enhance the scavenging of volcanic gases.
- the amount of liquid water
  A coignimbrite eruption with a slower vertical velocity might show a much higher content of liquid water, which could efficiently remove HCl from the atmosphere.

The **final amount of volcanic gases in the stratosphere** depends on the fate of the contaminated hydrometeors:
- Precipitation would remove species from the stratosphere.
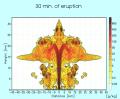- Sublimation releases species into the gas phase.

In our study, sublimation of ice releases the species back to the gas phase in the stratosphere at the end of the simulation time.
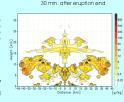
> The stratospheric injection of volcanic gases is determined by the volcanic and the atmospheric conditions!

References

Bureau H, Keppler, H, Métrich N: Earth Planet Sci Lett 183: 51-6, 2000.
Bogaard and Schmincke, 1985.
Devine JD, Sigurdsson H, Davies AN: J Geophys Res89 (B7): 6309-6325, 1994.
Dominé, F., and E. Thibert: Geophysical Research Letters, 98, 4223-4239, 1996.
Dominé, F., E. Thibert, E. Silvente, M. Legrand, and Jaffrezo: J. Atmos. Chem, 21, 1653 - 1686, 1995.
Graf, H.-F., M. Herzog, J.M Oberhuber, and Textor, C.: J. Geophys. Res., 104, 24309-24320, 1999.
Harms E, Schmincke H-U: Contrib Mineral Petrol 138, 84-98, 2000.
Herzog, M., H-F Graf, C. Textor, and J.M Oberhuber: J. Volcanol. Geotherm. Res., 87, 55-74, 1998.
Herzog, M.: Ph.D. thesis, University of Hamburg, 1998.
Keppler H: Science 284: 1652-1654, 1999.
Kress V: Nature 389:591-593, 1997.
McKinney et al, Geophys. Res. Lett. 24 (8), 883-886, 1997.
Oberhuber, J.M., M. Herzog, H.-F. Graf, and K. Schwanke: J. Volcanol. Geotherm. Res., 87, 29-53, 1998.
Sachs P.M, Harms E: Bei Deutsche Mineral Ges, Beih.: Eur J Mineral 12: 174, 2000.
Schwartz, S.E: in Chemistry of Multiphase Atmospheric Systems, ed. W.Jaeschke, Springer Verlag, N.Y., 1986.
Textor, C., H.-F. Graf, M. Herzog, J.M.O. Oberhuber: to be submitted to J. Geophys. Res 1999.
Textor, C.,H.-F. Graf, M. Herzog, J.M.O. Oberhuber: accepted at J. Volc. Geotherm. Res. 2000.
Webster JD: Contrib Mineral Petrol 104:424-438, 1990.

Volcanic Particles
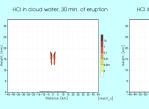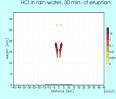

30 min. of eruption

30 min. after eruption end

- The neutral buoyancy height around 15 km, well in the stratosphere.
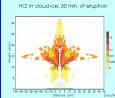- Sedimentation removes particles from the stratosphere.
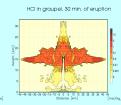- ~30 % or the particles are deposited 30 min. after the eruption end.

HCl

total HCl, 30 min. of eruption

total HCl, 30 min. after eruption end

- The neutral buoyancy height around 15 km in the stratosphere.
- Most of the HCL stays at the neutral buoyancy height after the eruption end.
- Gas particle separation is very efficient.

HCl in cloud water, 30 min. of eruption

HCl in rain water, 30 min. of eruption

HCl in cloud ice, 30 min. of eruption
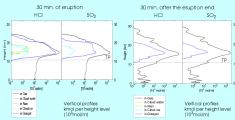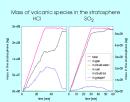
HCl in graupel, 30 min. of eruption

- HCl is contained in all phases of hydrometeors.
- Despite its high water solubility the scavenging by liquid water is not very significant.

Distribution of volcanic species in different phases

30 min. of eruption
HCl SO_2

30 min. after the eruption end
HCl SO_2

Vertical profiles kmol per height level (10^3mol/m)

- More than 99 % of the total erupted HCl and SO_2 reach the stratosphere.
- The species are partly contained in ice (HCl up to 40 %, SO_2 up to 10 %).
- Precipitation of graupel from the stratosphere is insignificant (particle size ~ 1μm).

HCl
- is partly scavenged by liquid water drops in the central rising zone or the plume,
- freezing of these drops transfers dissolved HCl to ice particles,
- HCl is incorporated in growing ice,
- sublimation of graupel releases HCl to the gas phase, only ~ 4% stays in graupel.

SO_2
- is not dissolved in liquid drops,
- is incorporated in growing ice,
- the sublimation totally releases SO_2 back to the gas phase.

Mass of volcanic species in the stratosphere
HCl SO_2