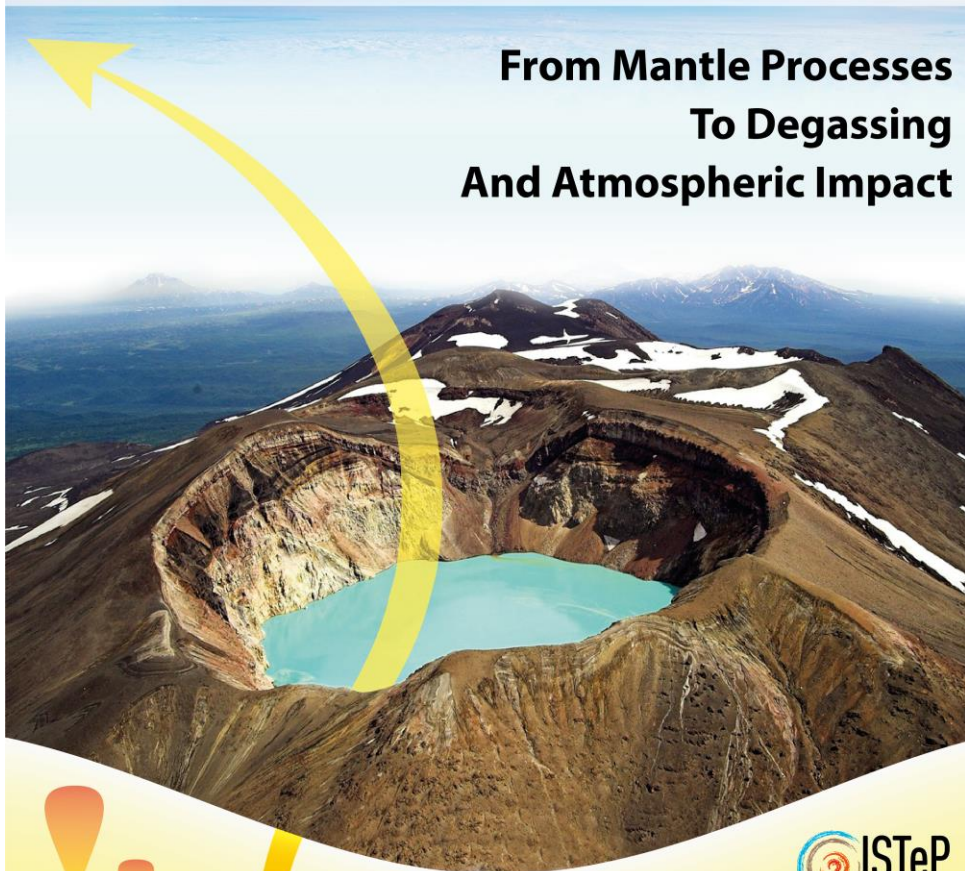


5 & 6 November 2019

Cycl'Hal : Volcanic Halogen Workshop

**From Mantle Processes
To Degassing
And Atmospheric Impact**



Sorbonne Université
Amphi Charpak
Room 417

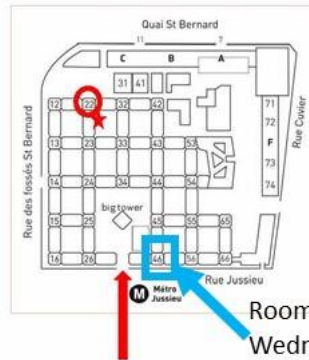
Contact : helene.balcone_boissard@sorbonne-universite.fr
Website : <https://cycl-hal.sciencesconf.org/>



How to get to Amphitheatre Charpak

From the entrance:

- Go to Tower 22.
- Enter it by the door to the down-stairs or by the lift.
- Go down one level.
- Exit Tower 22 (outside!), by following the signs to Amphi Charpak.



Main entrance
Jussieu Campus

Room 417 (lunch on
Wednesday)
Tower 46, 4th floor
Corridor 46-00

Jussieu Campus (4 Place Jussieu) is located in central Paris, just south of the river. The metro station "Jussieu" is right at the entrance, and can be reached by lines 7 and 10. Also, Jussieu Campus is walking distance from tourist sites in Paris centre, and e.g. is about 15 min walk from Saint-Michel Notre Dame metro/RER station.

Jussieu campus has many concrete towers: one big one in the middle and many small ones, which are linked by corridors above ground-level. The campus is also on a slope.

Therefore it is easy to get lost both horizontally and vertically!

The small towers are numbered. The Cycl'hal workshop sessions are in Amphitheatre Charpak, which is near to Tower 22 and one level downstairs.

Tuesday 5th November

1.30 pm Welcoming of participants (*Room Charpak*)

2 – 4.30 pm

« Magma reservoir and crust »

Room Charpak

4.30 pm **Posters** (*Charpak hall*)

Free evening

Wednesday 6th November

9 – 12 pm

« Plume and Atmosphere »

Room Charpak

12 pm Lunch time (*Room 417*)

2 – 4.30 pm

« Deep in the Mantle »

Room Charpak

4.30 pm **Final discussion**

Tuesday 5th November

« Magma reservoir and crust »

Room Charpak

Conveners: H     Balcone-Boissard and Erwan Martin

14h00 Tamsin Mather (Invited)

Halogens in igneous processes and their fluxes to the surface environment

14h30 Beno  t Dubacq

Distribution and partitioning of halogens in silicates

15h00 Ga  lle Prouteau (invited)

Halogens behavior in magmas, from storage to emission

15h30 Magali Bonifacie

Brief review of the use of Cl and Br stable isotopes as geochemical tracers and on-going projects in the Lesser Antilles arc

16h00 Guillaume Carazzo

PPM - a 1D model of volcanic eruption columns

16h30 Discussion around posters – Charpak hall

Free evening

Posters list

1. **Aroskay** et al.,
2. **Baudouin** et al., Role of volatiles on the crystallization of sodalite group minerals in phonolitic magmas (Case studies from Eifel (Germany) and Saghro (Morocco))
3. Bureau et al., Fluorine and Chlorine in the Transition Zone
4. **Dalou** et al., In-situ measurements of fluorine and chlorine speciation and partitioning between melts and aqueous fluids in the Na₂O-Al₂O₃-SiO₂-H₂O system
5. **Debré** et al.,
6. **Dinger** et al., Comparison of the BrO/SO₂ series in the gas plumes of six NOVAC volcanoes
7. **D'Augustin** et al., Halogen degassing budget
8. **Figowy** et al.,
9. **Foucart** et al., Temporal and spatial location of sulfuric acid-water particles formation in the Piton de La Fournaise volcanic plume revealed by three-dimensional simulations
10. **Lurton** et al., Model Simulations of the Chemical and Aerosol Microphysical Evolution of Sarychev Peak 2009 Eruption Cloud (SO₂, HCl, particles) compared to In Situ and Satellite Observations.
11. **Mason** et al., Aerosol chemistry of the 2018 Kīlauea Lower East Rift Zone eruption – from source to exposed communities
12. **MIST** (Modeling Imaging Sensing and Tracing of emissions and volcanic plumes)
13. **Roberts** et al., High-Temperature Chemistry of Volcanic Gases in Air
14. **Schmitt** et al., An atmospheric smog chamber setup for the investigation of volcanic plume chemistry
15. **Schmitt** et al., Variation of the BrO/SO₂ molar ratio in the plume of Tungurahua volcano between 2007 and 2017 and its relationship to volcanic activity
16. **Warnach** et al., Bromine measurements in volcanic plumes from Sentinel 5 Precursor/TROPOMI

Wednesday 6th November

Room Charpak

« Plume and Atmosphere »

Conveners: Tjarda Roberts, Luke Surl, Slimane Bekki

9h00 Mike Burton (Invited)

Insights into magma dynamics at Mt Etna (Sicily) from SO₂, HCl and HF flux measurements 2008-2011

9h30 Kirstin Krüger (Brenna et al.)

The Los Chocoyos super volcanic eruption disrupts the Quasi-Biennial Oscillation

9h45 Nicole Bobrowski (Invited)

An update on bromine in volcanic plumes

10h15 Stefan Schmitt

HALVIRE - HALogen activation in Volcanic plumes In Reaction chamber Experiments

10h30 – 10h45 - Pause

10h45 Florian Dinger

Six years of BrO/SO₂ molar ratios in the volcanic gas plume of Masaya

11h00 Christopher Fuchs

Measurement of high resolution BrO distributions in early volcanic plumes by ground based imaging

11h15 Luke Surl

Using WRF-Chem Volcano to model in-plume halogen and mercury chemistry on a regional scale

11h30 Simon Warnach

Bromine measurements in volcanic plumes from Sentinel 5 Precursor/TROPOMI

11h45 – 12h00 Summary Discussion & Poster highlights

12 pm Lunch time (Room 417)

« Deep in the Mantle »

Room Charpak

Conveners: H  l  ne Bureau and C  lia Dalou

14h00 Ray Burgess (Invited)

Influence of seawater subduction processes on the global halogen cycle - Implications for environmental changes

14h30 Daniele Pinti

A newly proposed bromine and chlorine composition of the mantle based on geothermal data

15h00 Etienne Balan

Atomic-scale perspective on volatile elements incorporation in olivine

15h30 Tobias Grützner

Experimental studies on fluorine defects in forsterite and wadsleyite

16h00 Ken Koga (invited)

Bulk fluorine partition coefficient during mantle partial melting:
do we know the value now?

4.30 pm

Final discussion

Abstracts

« Magma reservoir and crust »

Halogens in igneous processes and their fluxes to the surface environment

Tamsin Mather¹

¹ Oxford University

In order to understand the halogen behaviour in igneous systems and emission to the surface environment we need to know about the distribution of halogens in Earth's interior reservoirs, and the principal controls on their behaviour during partial melting, crystallisation and degassing. Recent advances in measurement techniques have opened new opportunities to improve the inventories of halogen emissions from the open-vent, continuously-degassing systems that dominate the background contribution of volcanoes to the atmosphere. As different approaches to estimating the fluxes of HCl and HF to the atmosphere from arc and global volcanism converge, they can now be used to place important constraints on the global cycling of halogens through subduction-zone systems and the balance between arc-related volcanic emissions of halogens compared to other tectonic settings within the global volcanic halogen degassing budgets.

Distribution and partitioning of halogens in silicates

Benoît Dubacq¹

¹ IStEP, Sorbonne Université - Paris

Halogens are widespread in metamorphic fluids and are found in salt and fluid inclusions as well as in minerals of all metamorphic grades. Silicates may incorporate halogens in their crystal structures via several exchange mechanisms, involving departure of oxygen from the mineral structure for anhydrous silicates (e.g. in sphene: $\text{Ti}^{4+} + \text{O}^{2-} = \text{Al}^{3+} + \text{F}^-$) and exchange with hydroxyl groups in hydrous silicates (e.g. in mica, chlorite, amphibole: $\text{OH}^- = \text{F}^-$). The energetic cost of these exchange mechanisms may be rationalized and modelled with various approaches, it controls the partitioning of halogens between phases. This presentation will focus on the thermodynamic modelling of defects in minerals and more specifically on incorporation of halogens in metamorphic silicates

Halogens behavior in magmas, from storage to emission

Gaëlle Prouteau¹, Bruno Scaillet¹, Morgane Rondet¹, Federica Carmela Faranda¹, Zara Franceschini^{1,2}, Giada Iacono¹, Juan Andujar¹, Stéphane Scaillet¹, Raffaello Cioni², Aneta Slodczyk¹ & Manuel Moreira¹

1 : ISTO - Institut des Sciences de la Terre d'Orléans – UMR 7327

2 : Dip.to Scienze della Terra, Università degli Studi di Firenze

Volcanic eruptions are capable of injecting enormous amounts of climate sensitive species into the atmosphere, among which CO₂ and SO₂ figure prominently as illustrated by the Pinatubo 1991 eruption. Minor species, such as the halogens, also play a key role, in particular as destructive agents of the ozone layer, but large uncertainties persist as to their abundances on the global scale, past or present. While global and spatially constrained estimates exist for both C- and S-bearing fluxes, there is no such a knowledge for volcanic halogens. The main reason is several fold : (1) halogen behavior in magmas is not well constrained, in particular their partitioning between fluid and silicate melt, (2) their fate during volcanic gas-atmosphere mixing is not well understood either, and, as a result, (3) geographically constrained fluxes of halogens are not available for present-day volcanic eruptions or past events. This presents a serious limitation to any attempt at deconvoluting the role of volcanic halogens as a forcing agent of the climate system.

In the frame of the ANR VOLC-HAL-CLIM and Labex Voltaire (Orléans), our project set up to address long standing gaps regarding halogens (Cl, F, Br, I) behavior in magmas during magma crustal storage in shallow reservoir and its final transfer toward the surface. Despite the wealth of fluid/melt experimental partitioning data, especially for Cl, there is no comprehensive thermodynamic model of Cl-F behavior in silicate melts that allows to relate the concentration of Cl-F to their fugacity. This issue is currently addressed within the framework of M. Rondet PhD thesis. The behavior of Cl and F in coexisting apatite, fluids and a variety of silicate melts (rhyodacite, basalt, phonolite) is investigated experimentally as a function of pressure, temperature, fO₂, and fluid composition. We will expand this effort toward including Br and I elements (F.C. Faranda PhD thesis). As a complement to conventional experiments, we will also perform sampling experiments, using a transparent IHPV equipped with sapphire windows connected to a Raman spectrometer. These *in situ* experiments allow to extract and measure directly “on line” the HP-HT degassed fluids (HF, HCl, HBr, HI contents, alongside other species (H₂O, CO₂, SO₂ ...)). Halogens content are determined with EPMA, ion microprobe, FTIR/Raman or micro-XRF. During the course of the project, we will also use the neutron irradiation noble gas mass spectrometric technique as a complementary analytical tool for heavy halogens determination. Experimental data will be used to produce halogens solubility laws for the pressure range investigated. A general degassing code will be developed, to calculate melt-fluid equilibrium at various pressures.

Melt inclusions will be analysed as input to the CHOS-halogens degassing model that will be used to predict volcanic emissions for the field case studies. Our current targets include large-scale explosive events in the Main Ethiopian Rift (Z. Franceschini PhD thesis).

Brief review of the use of Cl and Br stable isotopes as geochemical tracers and on-going projects in the Lesser Antilles arc

M. BONIFACIE

Institut de Physique du Globe de Paris, France, Sorbonne Paris Cité, Univ Diderot, UMR 7154 CNRS, F-75005 Paris, France (bonifaci@ipgp.fr) and Observatoire Volcanologique et Sismologique de Guadeloupe, FWI, France

Among the main volatile precursors, halogens show a unique combination of geochemical features that can be used to inimitably trace the history of magmas from their origin through their differentiation, degassing and interactions with meteoric or hydrothermal fluids. Indeed, chlorine and bromine are: the latest (i.e. shallowest) degassed from magmas, and mainly as halogenated acids (HCl, HBr); highly hydrophilic and can thus be completely trapped as chloride and bromide forms in shallow groundwaters or lakes overlying magma bodies; and unlike most other main volatiles, they are considered as conservative (i.e., chemically non-reactive). We will present a brief review of the knowledge on halogen stable isotopes systematics ($\square^{37}\text{Cl}$ and $\square^{81}\text{Br}$ that are respectively referring to deviations of $^{37}\text{Cl}/^{35}\text{Cl}$ and $^{81}\text{Br}/^{79}\text{Br}$ ratios in measured sample relative to seawater, in per mil units) and their potential as tracers of magmatic processes and interactions with hydrothermal systems. Chlorine stable isotope compositions ($\square^{37}\text{Cl}$) of Earth's reservoirs have been used for 10 years to constrain the origin of Cl in arc magmas [e.g., 1-4], and only recently used in volcanology, as tracers of magmatic degassing and/or subsurface gas/liquid interactions [5-6]. We also anticipate that $\square^{81}\text{Br}$ compositions (recently developed on micro-quantities at IPGP [7]) should significantly improve our understanding of volcanic systems. In order to constrain the sources and fate of Cl associated with arc volcanism, we report $\square^{37}\text{Cl}$ signatures of thermal springs from several locations along the Lesser Antilles arc (West Indies): la Soufrière de Guadeloupe (French West Indies); Boiling Lake, Valley of Desolation and other locations (Dominica); and LiaMuiga (St-Kitts). The studied samples show wide ranges of temperature (22-92°C), pH (3-8), Cl content (10-2000 ppm), Cl/Br ratio (100-1000) and $\square^{37}\text{Cl}$ value (-1‰ to 0‰). These results unravel that magmatic Cl displays negative $\square^{37}\text{Cl}$ values, close to -0.7‰, all along the arc, that is consistent with a slab-derived origin. The consistency with the melt inclusion data from Saint Vincent, located at the South of the arc ($\square^{37}\text{Cl}$ averaging -0.64‰ [4]), further confirms our starting hypotheses, made in [3], that Cl isotopes do not fractionate (ie. no loss of magmatic Cl) over their high-temperature path from magma to thermal springs. For further constraining local magmatic and hydrothermal processes at la Soufrière de Guadeloupe, we are also currently studying $\square^{37}\text{Cl}$ data on fumarolic gases (mean temperature of 96°C, ranging from 96 to 115°C, with $\square^{37}\text{Cl}$ up to +8‰). We quantify that more than 90% of the HCl escaping the large hydrothermal system of La Soufrière is likely lost (ie. not sampled) via scrubbing over subsurface water condensation on its way up to the surface, at least at site CSC. More broadly, we suggest that for locations where the magma $\square^{37}\text{Cl}$ is known, the $\square^{37}\text{Cl}$ value of the emitted gas is a quantitative tracer for scrubbing of chlorine and other water-soluble gas species. [1] Bonifacie, *Encyclopedia of Geochemistry* (2017). [2] Bonifacie et al., (2008), *Science* 319, 1518-1521. [3] Li et al. (2015), *EPSL* 413, 101-110. [4] Manzini et al. (2017), *Chem. Geol.* 449, 112-122. [5] Liotta et al. (2017) *JVGR* 336, 168-178. [6] Rodriguez et al. (2016) *JVGR* 325, 70-85. [7] Louvat et al. (2016), *Analytical Chemistry*, 88, 3891-3898.

PPM - a 1D model of volcanic eruption columns

G. Carazzo¹, A. Michaud-Dubuy¹, F. Girault¹, E. Kaminski¹, S. Tait¹

¹ Université de Paris, Institut de physique du globe de Paris, CNRS, F-75005 Paris

The impact of explosive volcanic plumes on climate and on air traffic strongly depends on the concentration and grain-size distribution (GSD) of pyroclastic fragments injected into the atmosphere. Accurate and robust modeling of the evolution of GSD during pyroclast transport from the volcano's vent to the ash cloud is therefore crucial for the assessment of major volcanic hazards. Here, we present a steady-state 1D model of explosive volcanic eruption columns (PPM) that tracks the evolution of GSD in the column and calculates the dynamical variables at any distance from the vent. The model solves the conservation laws of mass, axial and radial momentum, and energy fluxes for a particle-laden turbulent jet rising in a windy atmosphere. The effects of particle fallout, gas entrapment in large pumice fragments, which lowers the effective gas content, depending on the total grain-size distribution of pyroclastic fragments, and the development of an open porosity are taken into account in the model, as well as the reduction of turbulent entrainment at the base of the volcanic column due to its negative buoyancy. We further test the model using several well-documented historical events. The good agreement obtained between the theoretical predictions and the geological records suggests that the model can be used to robustly calculate the atmospheric input of an explosive eruption from its source magmatic conditions. Our results thus contribute to the improvement of volcanic source term characterization that is a required input for meteorological dispersion models.

« Plume and Atmosphere »

Insights into magma dynamics at Mt Etna (Sicily) from SO₂, HCl and HF flux measurements 2008-2011

Mike Burton¹, Alessandro La Spina², Giuseppe Salerno³, Tommaso Caltabiano⁴

¹University of Manchester, UK; ²Istituto Nazionale di Geofisica e Vulcanologia – Osservatorio Etneo, Italy

Magma convection occurs when low viscosity gas-rich magma ascends, degasses and crystallises before sinking down the same conduit in either annular or side-by-side flow, producing persistently active basaltic volcanoes which exhibit excess gas fluxes relative to erupted lava volumes. Experimental studies show that convection is produced by the density contrast between ascending gas-rich magma and descending degassed magmas, while geophysical studies point to the endogenous growth of active volcanoes through magma accumulation in plutons. However, the depth to which magma ascends before overturning is unclear. Models where overturn occurs at the near-surface and to depths >2 km within the magma column have been proposed. The long-term monitoring of volcanic gas compositions and fluxes may reveal new insights into the convection process, as each gas has a unique solubility-pressure profile. Here, we report measurements of SO₂, HCl and HF gas fluxes from Mt. Etna between January 2008 and May 2011, in which a 90% collapse in halogen flux was observed together with a lava flow, supplied by the shallow plumbing system, while SO₂ fluxes remained largely unperturbed. Our observations indicate that high halogen fluxes observed during quiescent periods on Etna require both magma supply to and a period of storage in the shallow plumbing system. We observe a lag between the onset of the effusive eruption and decline in halogen fluxes (~6 months) which, together with observations of lava effusion rate (2 m³s⁻¹), provides a first-order constraint on minimum volume of ~34 million m³ for the shallow magma reservoir. We further highlight that the bulk of this halogen flux is emitted from just one of the main degassing craters on Etna, the Northeast crater, suggesting that there is typically a shallow accumulation of magma under this crater. These results provide new insights into magma convection processes, and demonstrate the strength measurements of SO₂, HCl and HF have when interpreting magma dynamics, due to their sensitivity to magma supply and geometry.

The Los Chocoyos super volcanic eruption disrupts the Quasi-Biennial Oscillation

Hans Brenna¹, Steffen Kutterolf², Mike Mills³, Ulrike Niemeier⁴, Claudia Timmreck⁴, and **Kirstin Krüger**¹

¹University Oslo, Norway,

²GEOMAR, Kiel, Germany

³NCAR, Boulder, USA

⁴MPI, Hamburg, Germany

The Los Chocoyos super eruption happened ~81 kyrs ago in Guatemala, and was one of the largest eruptions of the past 100,000 years. The eruption emitted enormous amounts of sulfur, chlorine and bromine, with multi-decadal consequences for the global climate and environment (Brenna et al 2019 ACPD). In this paper, we simulate the impact of this sulfur- and halogen-rich super-eruption on the quasi-biennial oscillation (QBO), an oscillation of the zonal winds in the tropical stratosphere, with the comprehensive aerosol chemistry Earth System Model CESM2(WACCM6). We find a ~10 year disruption of the QBO before returning to QBO conditions with a slightly prolonged periodicity. Volcanic induced aerosol heating and ozone depletion cooling leads through radiative changes and wave-mean flow interactions to the QBO disruption and anomalous wind regimes. Different model ensembles, volcanic forcing scenarios and one other model backs up the robustness of our results.

References

Brenna, H., Kutterolf, S., Mills, M. J., and Krüger, K.: The sulfur- and halogen-rich super eruption Los Chocoyos and its impacts on climate and environment, Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-827>, in review, 2019.

An update on bromine in volcanic plumes

Nicole Bobrowski & Team Atmospheric Chemistry

IUP University of Heidelberg & Analytical Chemistry, University of Mainz

Water, carbon dioxide and sulfur compounds are the most abundant volcanic gases. However, significant amounts of halogens are emitted as well into the atmosphere from volcanic sources. Often less attention is given to the heavy halogens bromine and iodine. The discovery of bromine monoxide (BrO) in volcanic plumes 16 years ago, led to new interest especially in volcanic bromine chemistry and its impact on atmospheric processes. The BrO detection came along with advances in volcanic remote sensing techniques, in particular, robust DOAS applications and the possibility of continuous measurements by automated instruments located at safe distances from the volcano.

As one of the consequences, beside atmospheric scientist also the volcanic community developed an interest to use BrO/SO₂ ratios as a potential tracer of volcanic activity. BrO is a secondary volcanic gas, but the only bromine species in volcanic plumes, which has been measured by remote sensing techniques today.

For a better understanding on bromine chemistry in volcanic plumes and to gain information on the original amount of emitted bromine by only measuring BrO, additional techniques were developed and are under development (alkaline traps, diffusion denuders) and adapted for drone-based sampling to determine further gaseous bromine species (i.e. Br₂, HBr, HOBr, interhalogens) at various plume ages.

Today model studies simulating plume conditions indicate that a complex atmospheric chemistry mechanism transforms emitted HBr into BrO and other reactive bromine species such as BrOH, Br₂, BrCl, BrONO₂ or BrNO₂. To reproduce the very rapid formation of BrO observed in volcanic plumes, amount of bromine (as well as the entire composition of the volcanic gases) emitted but also plume mixing processes, relative humidity, and aerosol particle acidity, the high-temperature near-vent plume conditions, as represented by thermodynamic models etc. needs to be considered. However, uncertainties remain in the validation of the plume chemistry models by a lack of field-measurements.

This overview provides attempts to give a summary on volcanic bromine data of the last 16 years achieved from established and cutting edge measurement techniques as well as their treatment and interpretation in recent model experiments. It points out controversially discussed relation of bromine degassing to volcanic activity and puts a light on remaining uncertainties.

HALVIRE - HALogen activation in Volcanic plumes In Reaction chamber Experiments

Stefan Schmitt (1), Julian Rüdiger (2,3), Dominik Pitton (4), Nicole Bobrowski (1), Jan-Lukas Tirpitz (1), Andreas Held (2,3), Rolf Sander (5), Cornelius Zetzsch (5), Ulrich Platt (1,5)

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(2) *Institute of Environmental Science and Technology, Berlin, Germany*

(3) *Bayreuth Center of Ecology and Environmental Research, Bayreuth, Germany*

(4) *Institute of Inorganic and Analytical Chemistry, Mainz, Germany*

(5) *Max-Planck Institute for Chemistry, Mainz, Germany*

The investigation of reactive halogen species (RHS, e.g. BrO, OCIO, IO, I₂) made great progress in recent years, but also revealed uncertainties concerning the formation mechanisms and the impact of environmental parameters (e.g. plume gas and aerosol composition, relative humidity). Understanding the influence of these parameters on the halogen activation (i.e. conversion from hydrogen halides to RHS) in volcanic plumes is essential for an interpretation of field observations e.g., relating them to magmatic processes and investigating the atmospheric impact of volcanic halogen emissions.

The influence of multiple parameters (initial HBr/SO₂ ratio, relative humidity, O₃ intrusion, particle abundance and composition) on the strength and rate of BrO formation were investigated in an atmospheric simulation chamber in Bayreuth. BrO formation with peak values between 100 and 900 ppt was observed with BrO/SO₂ ratios ranging from $0.3 \cdot 10^{-4}$ to $1.8 \cdot 10^{-4}$ for different initial experiment conditions. The temporal progression of the BrO signal showed three distinct phases for each of the 20 chamber experiments performed. (1) Initiation phase (HBr, Aerosol, SO₂, O₃ but no significant BrO), (2) Ignition (strong increase in BrO at expected O₃ depletion rate) and (3) Steady state (BrO decreases again to constant level between 100 and 250 pptv). The duration and BrO peak levels of phases 1 and 2 were highly sensitive to the choice of initial experiment parameters such as RH, O₃ and presence of aerosols and, surprisingly, also SO₂. However, the BrO abundance during the steady state phase seems mainly limited by the amount of O₃ being mixed into the chamber (i.e. the plume).

Six years of BrO/SO₂ molar ratios in the volcanic gas plume of Masaya

Florian Dinger (1,2), Nicole Bobrowski (2), Ulrich Platt (1,2), Thomas Wagner (1,2)

(1) Max Planck Institute for Chemistry, Mainz, Germany

(2) Institute of Environmental Physics, University of Heidelberg, Germany

The Network for Observation of Volcanic and Atmospheric Change (NOVAC) monitors the SO₂ and BrO emissions of more than 40 volcanoes using scanning UV-spectrometers. The volcanic gas emissions are retrieved from the recorded spectra by applying Differential Optical Absorption Spectroscopy (DOAS). We present semi-continuous (only during daytime) time series of the slant column densities (SCDs) of SO₂ and BrO as well as of the calculated BrO/SO₂ molar ratios in the volcanic gas plume of Masaya (Nicaragua, 12°N, 86°W, 635m a.s.l.) from March 2014 until May 2019. The volcanic gas emissions have been significant throughout the overall period, with most of the time SO₂-SCDs of at least 3×10^{18} molec/cm² and daily maximum BrO-SCDs of at least 2×10^{14} molec/cm². The BrO/SO₂ molar ratios varied between $1\text{--}10 \times 10^{-5}$. Two major patterns have been observed in the BrO/SO₂ time series: (1) An annual periodicity with an amplitude of about 2×10^{-5} and (2) a step increase in the periodicity-corrected data in late 2015 from an annual mean of 2.7×10^{-5} until mid 2016 to 4.1×10^{-5} from late 2015 on (the actual increase is not observed due to a data gap). The step increase coincides with the formation of a shallow lava lake and is thus most likely caused by a change in the magmatic system. A comparison of the BrO/SO₂ data with meteorological data from the ECMWF forecast model indicates an anti-correlation between BrO/SO₂ molar ratios and the specific humidity (correlation coefficient of -39%). The annual periodicity in the BrO/SO₂ time series may thus be caused by atmospheric effects. Furthermore, no systematic dependency between the BrO/SO₂ molar ratios and the atmospheric plume age has been observed for an age range of 1–12min after the release from the volcanic edifice – indicating an early stop of the autocatalytic, partial transformation of bromide solved in aerosols to atmospheric BrO (the so-called “bromine explosion”). As a possible direct causality, high humidity levels may have diluted the bromide concentration in the aerosols and thus the bromine explosion would have been humidity-limited in these cases. Alternatively, the humidity variations may be just a proxy for coinciding variations in other meteorological parameters such as the position of the ITCZ which affects e.g. the ozone background and the irradiation conditions.

Measurement of high resolution BrO distributions in early volcanic plumes by ground based imaging

Christopher Fuchs (1), Jonas Kuhn (1,2), Nicole Bobrowski (1,2), and Ulrich Platt (1,2)

(1) Institute for Environmental Physics, Heidelberg University, Germany

(2) Max Planck Institute for Chemistry, Mainz, Germany

Recent advances in satellite imaging of sulphur dioxide (SO₂) and bromine monoxide (BrO) allow for studying spatial trace gas distributions and thereby halogen chemistry in volcanic plumes. The spatio-temporal resolution is on the order of some km and one day (for a daily overpass at around noon time) and global coverage. Therefore, the observations are mostly limited to eruptive and widely dispersed volcanic plumes.

In this study we focus on imaging volcanic reactive halogen distributions on scales of metres and seconds, respectively, using ground based imaging spectroscopy. Several measurements and model studies conclude that due to mixing with ambient trace gases and photochemistry, the first few minutes of (quiescent) plume evolution are particularly interesting when observing the formation and transformation of reactive halogen. Spatially resolved measurements – in particular for species other than SO₂ - are, however, difficult to perform with standard plume sampling methods (e.g. DOAS).

We develop an imaging technique based on Fabry P  rot Interferometer Correlation Spectroscopy that allows to extend the widely used SO₂ camera technique to other trace gases, like e.g. BrO. Thereby, the evolution of spatial trace gas gradients within the early plume can be measured and evaluated using current understanding of the chemistry.

Current prototype cameras implementing the novel technique already allow for volcanic SO₂ imaging and sensitivity studies of further trace gases have been performed in our laboratory, resulting in prospected BrO detection limits < 10¹⁴ molec cm⁻² corresponding to 10 to 100 ppt.

Using WRF-Chem Volcano to model in-plume halogen and mercury chemistry on a regional scale

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² Laboratoire Atmosphères, Milieux, Observations Spatiales, Service d'Aéronomie (LATMOS), CNRS, Institut Pierre Simon Laplace, Pierre et Marie Curie University, Paris, France

After emission, the mixture of gases emitted by a volcano mix with the background atmosphere as the plume travels downwind. As well as a physical dispersion of the plume, several chemical processes are known to occur over regional spatial scales (from a few km to hundreds of km). One system of particular interest is the “bromine explosion”: an autocatalytic cycle of bromine reactions, including photolysis and heterogenous reaction steps, which converts volcanically-emitted HBr into other more reactive forms. Bromine monoxide (BrO) created by this process can be seen from both ground-based and satellite-based spectroscopic monitoring. Quantitative analyses of the processes generating BrO has the potential to substantially increase the utility of these measurements for volcanic plume monitoring.

We present WRF-Chem Volcano (WCV), a modified version of the regional atmospheric chemistry and transport model WRF-Chem and associated utilities. WCV is able to model various aspects of the chemistry of a volcanic plume. WCV simulates sulphur dioxide oxidation and associated aerosol formation, and a removal of oxidants from the atmosphere, as well as the cycling of oxidized chlorine and bromine species.

We focus on the halogen chemistry and associated results regarding mercury in case studies of Etna and Piton de la Fournaise volcanoes. WCV is able to reproduce the bromine explosion, and shows reasonable skill in reproducing results from satellite observations. These results also allow for an initial assessment of the fraction of volcanic bromine that exists as observable BrO in different parts of the plume, a fraction required for estimating total volcanic bromine flux from remote BrO observations.

We find that reactive bromine oxidises a small fraction of elemental mercury within the plume, either volcanogenic or mixed in from the background.

Bromine measurements in volcanic plumes from Sentinel 5 Precursor/TROPOMI

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In this presentation, the potential of the recently launched S5-P Tropomi instrument to detect bromine monoxide (BrO) in volcanic plumes is investigated. So far BrO in volcanic plumes has been successfully retrieved from satellite only during major eruptions. The higher spatial resolution of S5-P/Tropomi (3.5x7km², and most recently 3.5x5.5km²) and the daily coverage allows for an investigation of volcanic BrO during smaller eruptions and even during continuous passive degassing. The continuous observation of passive degassing volcanoes yields the potential for long-term monitoring of volcanoes from satellite. Also, the volcanic plumes can be tracked over larger distances and, thus, advanced plume ages.

We present column densities of BrO as well as SO₂ column densities retrieved using Differential Optical Absorption Spectroscopy (DOAS) and BrO/SO₂ molar ratios in volcanic plumes with varying emission strength from S5-P/Tropomi data. By deriving time series', we investigate the variation of the BrO/SO₂ molar ratio of various volcanoes, in order to investigate plume chemistry and emission composition

« Deep in the Mantle »

Influence of seawater subduction processes on the global halogen cycle - Implications for environmental changes

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Halogens play a critical role in establishing habitable conditions on Earth. These elements control the salinity of the oceans and, during volcanic emissions, can cause ozone destruction in the upper atmosphere. Short and long-term changes in the global halogen cycles may therefore exert a strong influence on the oceans ability to support life and the levels of UV radiation at the surface of the Earth. In my talk, I will consider the influence of seawater subduction processes on the global halogen cycle, with implications for environmental changes. The direction, magnitude and timescale of halogen fluxes in or out of the Earth's mantle are largely unknown. The sub-continental lithospheric mantle may act be a repository of halogens and other volatiles that may periodically be mobilised and released during large volcanic eruptions associated with flood basalt provinces. In contrast, deeper subduction to the mantle regions supplying magma to the mid oceanic ridges, may provide a means to reduce the salinity of the oceans overs billion year timescales.

A newly proposed bromine and chlorine composition of the mantle based on geothermal data

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Chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$) isotopic composition were measured together with helium isotopic ratios ($^3\text{He}/^4\text{He}$) in high-enthalpy geothermal fluids sampled from Mexican fields. Selected samples were collected from deep production wells and not fumaroles or springs, where chlorine is known to highly fractionate in the vapor phase. A direct relationship between $^3\text{He}/^4\text{He}$ and $^{37}\text{Cl}/^{35}\text{Cl}$ and $^{81}\text{Br}/^{79}\text{Br}$ have been observed and it excludes any physical process of fractionation in the reservoir, which should favor either the lighter or heavier masses. The data plot on a triangle mixing space between three endmembers: a component with a $^3\text{He}/^4\text{He}$ ratio, R , normalized to that of the atmosphere ($R_a = 1.384 \times 10^{-6}$) of 8 and $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Kr}$ of ca. +0.8‰, which may represent the convective mantle; a second component with R/R_a of ca. 6 and a $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Kr}$ of -0.4 and -0.6‰, respectively, which could correspond to fluids related to subducting serpentines at the mantle wedge; and finally a third crustal component with R/R_a lower than 2 and $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Kr}$ of 0‰ which may represent local crustal sources as poral seawater. This study suggests that the halogen isotopic composition of the mantle is ca. 1‰ higher than that of seawater, a different result than that obtained by measuring e.g., Cl isotopes in MORBs and OIBs, which show variable results from -3 to +3‰ in composition.

Atomic-scale perspective on volatile elements incorporation in olivine

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Our knowledge of Earth dynamic increasingly requires a detailed understanding of the incorporation mechanisms of trace elements in minerals, sustaining thermodynamical modeling of large scale processes and offering clues about the geological history of natural samples. Among the elements of interest, volatiles play a key role in the coupling between deep Earth reservoirs and external envelopes. However, the diversity of atomic-scale environments and the low concentration levels hamper a straightforward determination of their incorporation mechanisms from bulk chemical analyses, macroscopic properties, or spectroscopic observations. In this context, quantum-chemical modeling can help to specify the relations between experimental observations and peculiar atomic-scale environments (1). Selected examples of this approach applied to the interpretation of the vibrational spectra of hydrous defects in forsterite will be discussed, unraveling peculiar interactions of hydroxylated defects with other volatile elements, such as boron (2), fluorine (3) and potentially chlorine (4).

(1) Balan E., Blanchard M., Lazzeri M., Ingrin J. (2017) Theoretical Raman spectrum and anharmonicity of tetrahedral OH defects in hydrous forsterite. *European Journal of Mineralogy* 29, 201-212

(2) Ingrin J., Kovacs I., Deloule E., Balan E., Blanchard M., Kohn S.C., Hermann J. (2014) Identification of hydrogen defects linked to boron substitution in forsterite and olivine. *American Mineralogist* (Letter), 99, 2138-2141.

(3) Crépisson C., Blanchard M., Bureau H., Sanloup C., Withers A.C., Khodja H., Surblé K., Béneut K., Leroy C., Giura P., Balan E. (2014) Clumped fluoride-hydroxyl defects in forsterite: Implications for the upper mantle. *Earth and Planetary Science Letters*, 390, 287-295.

(4) Balan E., Créon L., Sanloup C., Aléon J., Blanchard M., Paulatto L., Bureau H. (2019) First-principles modeling of chlorine isotope fractionation between chloride-bearing molecules and minerals. *Chemical Geology*, 525, 424-434.

Experimental studies on fluorine defects in forsterite and wadsleyite

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The halogen elements, F, Cl, Br and I, are important volatile components of the upper mantle rocks. Over the last few years, several studies focused on the influence of fluorine on upper mantle phase relations and element partitioning. These studies show that F is less incompatible than water in forsterite and enstatite [1], but it tends to be more incompatible than water in wadsleyite [2]. This implies that F may be fractionated from water in the upper mantle and its transition zone.

To further our understanding of how F is incorporated into olivine, we synthesized F-saturated Forsterite at pressures between 1 to 8 GPa and 1500-1700 °C in piston cylinder and multi anvil presses at Münster. We also synthesized F-saturated wadsleyite at 21 GPa and 1700-1900 °C using the 5000 ton multi anvil press in Bayreuth. Further experiments were conducted in a F- and water-saturated system to study the influence of water on F incorporation. The experiments were characterized with EPMA and Raman Spectroscopy in Münster and ¹⁹F NMR spectroscopy was performed in Bochum.

Preliminary results show that the formation of F-clinohumite lamellae is the most important mechanism by which F is stored in forsterite and even to relevant amounts in wadsleyite at these experimental conditions. The mechanism is independent from the water content and seems to change only slightly with increasing P-T. Therefore, F incorporation is quite different from the favoured mechanism for OH incorporation in high-pressure forsterite, i.e. Si vacancies [3].

Understanding the incorporation mechanisms for F and OH in forsterite and wadsleyite, as well as the shift of this mechanism at varying P-T-X conditions may help to better constrain storage of both volatiles in the mantle.

[1] Grützner et al., 2017, *GCA* **208**, 160-170. [2] Grützner et al., 2018, *EPSL* **482**, 236-244. [3] Xue et al., 2017, *Am. Min.* **102**, 529-536.

Bulk fluorine partition coefficient during mantle partial melting: do we know the value now?

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Over the last 15 years or so, the community of mantle geochemistry has significantly advanced the knowledge concerning the fractionation of halogens during mantle partial melting. Today, there are about ten studies reporting fluorine partition coefficients between mantle minerals and melt. In the meantime, it has become nearly a routine to measure fluorine along with other volatile elements (i.e. H, C, S, Cl) in pristine undegassed magmas found in nature. The number of reported halogen (especially fluorine) concentrations has easily doubled compared to 2005. It has been known to geochemistry community that the abundance of fluorine in various basaltic samples correlate well with other trace elements, such as phosphor, neodymium, and strontium. For example, an average F/Nd ratio of global MORB samples is 21 ± 5 , over 500 data points. Such coherence is observed despite taking an average with basaltic samples with various degrees of melting (various trace element abundance), and crystal fractionation (various MgO content). This robust geochemical observation is often called ‘canonical ratio’ and it is considered representing a ratio of elements which fractionate similarly during mantle melting and crystal fractionation. Therefore, natural basalt data implies $D(F, \text{peridotite/melt}) \sim D(Nd, \text{peridotite/melt})$.

Many experimental data, however, report the value $D(F, \text{cpx/melt}) \sim D(La, \text{cpx/melt})$. As cpx is the mineral which can host the majority of trace element budget in mantle, it is usually considered that D values of cpx approximately represent the D values of peridotite. The results of melting calculations with the new $D(F, \text{cpx/melt})$ produce significant changes of F/Nd during mantle partial melting. Such experimentally determined partitioning data fails to reproduce well-constrained natural observations.

For a contribution for the discussion for CYCL’HAL workshop, we will outline the detailed comparisons of currently available experimental data and identify key parameters to be considered. As a first order, $D(F)$ depends strongly on the melt composition, most likely due to the changes of melt structure, in addition to activity of Al in pyroxene which is the main charge compensating element. Change of melt composition and Al activity during the mantle partial melting must be considered for the models of mantle partial melting.

POSTERS

Comparison of the BrO/SO₂ series in the gas plumes of six NOVAC volcanoes

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The Network for Observation of Volcanic and Atmospheric Change (NOVAC) monitors the SO₂ and BrO emissions of more than 40 volcanoes using scanning UV-spectrometers. The volcanic gas emissions are retrieved from the recorded spectra by applying Differential Optical Absorption Spectroscopy (DOAS). We present and compare the semi-continuous (only during daytime) time series since 2007 of the slant column densities (SCDs) of SO₂ and BrO as well as of the calculated BrO/SO₂ molar ratios in the volcanic gas plume of the six NOVAC volcanoes Masaya (Nicaragua), Nevado del Ruiz, Galeras (both Colombia), Cotopaxi, Tungurahua (both Ecuador), and Villarrica (Chile).

Temporal and spatial location of sulfuric acid-water particles formation in the Piton de La Fournaise volcanic plume revealed by three-dimensional simulations

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Volcanic activity can be a natural source of atmospheric gases and aerosols both during and between eruptions (Mather et al., 2003). These emissions can impact the environment, climate and human health (Schmidt et al., 2011; Baxter and Horwell, 2015; and Ilyinskaya et al., 2017). The Piton de la Fournaise located on La Réunion island is one of the most active basaltic volcanoes in the world. Its sporadic eruptions generate volcanic plumes consisting mainly of gases (H_2O and SO_2 predominantly) and nanoparticles that travel through the atmosphere and can cause significant exceedances of air quality alert thresholds (Durand et al., 2014). During the day, atmospheric SO_2 oxidation forms sulphuric acid (H_2SO_4). Acid molecules can react with water molecules to form clusters via the homogeneous binary nucleation process (Petäjä et al., 2009). These freshly formed nanoparticles can grow by condensation and/or coagulation processes leading to the formation of a submicron volcanic aerosol (Boy et al. 2005). The occurrence of New Particle Formation (NPF) in volcanic plumes was suspected in several earlier studies (Deshler et al., 1992, Robock, 2000 and Mauldin et al., 2003) then observed by Boulon et al., 2011 during the Eyjafjallajökull 2010 eruption and recently analysed by Shayoun et al., 2019 and Rose et al., 2019 within the Etna and Piton de la Fournaise volcanic plumes respectively. As other studies (Allen et al., 2002 at Massaya volcano in Nicaragua and Mather et al., 2004 at the

Chilean Lascar and Villarica volcanoes), Rose et al., 2019 highlighted the existence of “primary particle” emissions (sulphates) at the vent. These nanoparticles can act as pre-existing particles and constitute both a barrier to the nucleation process and a source to the condensation one. This competition has a strong impact on the variation in the number of aerosols in a volcanic plume. Unfortunately, nowadays it is very difficult to obtain the flux of “primary particles” by means of measuring instruments, which constitutes a scientific lock. Thanks to modelling tools, it is possible to estimate this flux using appropriate NPF processes parameterizations and doing obs/model comparisons of the aerosol number. The aims of our study are to (i) reveal the NPF processes occurrence privileged zones and periods within the Piton de la Fournaise volcanic plume (ii) quantify (number) the “primary particles” emissions observed by Rose et al., 2019 and (iii) understand their impact on aerosol formation and number variation. In order to simulate the Piton de la Fournaise volcanic plume and the atmospheric processes involved we use mesoscale Meso-NH model. We activate the ORILAM aerosol scheme (Tulet et al., 2005) in which we included the most recent neutral Sulfuric Acid- Water Particle Formation (Määttänen et al., 2017). We compare the results of our simulations to those from the STRAP campaign that occurred in 2015 (Tulet et al., 2017) and those provided by Rose et al., 2019.

Model Simulations of the Chemical and Aerosol Microphysical Evolution of Sarychev Peak 2009 Eruption Cloud (SO₂, HCl, particles) compared to In Situ and Satellite Observations.

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Numerical model assessments of the impact of volcanic eruptions on past climate requires that the modelling tools have been well-evaluated against observations in the present-day, and that they accurately reproduce the atmospheric processes following an eruption. Volcanic eruptions impact climate through the injection of sulfur dioxide (SO₂), which is oxidized to form sulfuric acid particles that enhance the stratospheric aerosol optical depth (SAOD). Previous studies have been hampered by limitations in model representations of particle microphysics and size and by biases in satellite estimates of post-eruption SAOD. Furthermore, the potential impacts of co-injected volcanic halogens had not been considered for modern-day eruptions.

Lurton et al. (2018) addresses these limitations in a model-observation study of the 2009 Sarychev Peak eruption that injected both sulfur and volcanic halogens into the stratosphere.

Simulations are performed using the CESM1-WACCM-CARMA sectional aerosol microphysics model (with no a priori assumption on particle size). The eruption injected 0.9 Tg of SO₂ into the UTLS, enhancing the aerosol load in the Northern Hemisphere. The post-eruption volcanic SO₂ is well reproduced by the model compared to IASI satellite data. Co-injection of 27 Gg HCl causes a lengthening of the SO₂ lifetime and a slight delay in the formation of aerosols, and acts to enhance the destruction of stratospheric ozone and mono-nitrogen oxides (NO_x) compared to the simulation with volcanic SO₂ only. We highlight the need to account for

volcanic halogens alongside sulfur when simulating the chemistry-climate impacts of volcanic eruptions.

The model-simulated evolution of effective radius reflects new particle formation followed by particle growth to reach up to 0.2 μm on zonal average. Comparison of the model-simulated particle number and size distributions to balloon-borne in situ stratospheric observations over Kiruna, Sweden (Aug-Sept 2009), and Laramie, USA, (June, Nov, 2009) show good agreement and quantitatively confirm the post-eruption particle enhancement. We show that the model-simulated SAOD is consistent with that derived from OSIRIS when both the saturation bias of OSIRIS and the fact that extinction profiles may terminate well above the tropopause are taken into account. Previous model studies (involving assumptions on particle size) that reported agreement with (biased) post-eruption estimates of SAOD derived from OSIRIS likely underestimated the climate impact of the 2009 Sarychev Peak eruption.

Lurton, T., et al. Model simulations of the chemical and aerosol microphysical evolution of the Sarychev Peak 2009 eruption cloud compared to in situ and satellite observations, *Atmospheric Chemistry and Physics*, 18, 3223–3247, 2018.

Aerosol chemistry of the 2018 Kīlauea Lower East Rift Zone eruption – from source to exposed communities

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Team: University of Cambridge, University of Oxford, University of Leeds, USGS

In 2018, an opportunity arose to characterise the size-resolved chemistry and air quality impacts of a significant ash-poor volcanic plume when a sequence of fissures opened in a populated area on the Lower East Rift Zone (LERZ) of Kīlauea Volcano, Hawai‘i. During a 3-week campaign in July-August 2018, we sampled the plumes associated with the active Fissure 8 (F8) vent and the lava ocean entry. Fluxes of metal and metalloid elements were approximately two orders of magnitude greater than when measured in 2009 for emissions from Halema`uma`u lava lake at Kīlauea’s summit (e.g., for Cu, 211 ± 80 kg/day in 2018 vs. ≤ 8.6 kg/day in 2009 [1]). However, element/SO₂ ratios are similar between the two eruptive periods. A monitoring network was established in populated areas around the Island of Hawai‘i during the field campaign and we sampled the aerosol every 2–3 days (at Kona, Ocean View, Pahala, Volcano Village and the NOAA Mauna Loa Atmospheric Observatory). At up to 60 km distant from the eruption site, relatively low aerosol concentrations were recorded (maximum 24 hr average = $25 \mu\text{g}/\text{m}^3$). Higher concentrations of up to $58 \mu\text{g}/\text{m}^3$ (comparable with the $35 \mu\text{g}/\text{m}^3$ EPA National Ambient Air Quality Standards level for PM_{2.5}) were recorded ~100 km from F8. We also clearly demonstrate the conversion of sulfur in the plume from ~100% SO₂ gas at source to up to ~25% particulate sulfate (SO₄²⁻) at downwind stations. We find evidence of metal depletion in the volcanic plume downwind, with variability in the metal/SO₂ ratios between near- and far-field sites beyond that which can be attributed to plume dilution, addition of ash and SO₂ dissolution or oxidation.

[1] Mather et al. (2012) GCA 83:292-323

High-Temperature Chemistry of Volcanic Gases in Air

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When volcanic gases enter the atmosphere, they encounter a drastically different chemical and physical environment, triggering a range of rapid processes including photochemistry, oxidation, and aerosol formation. These processes are critical to understanding the reactivity and evolution of volcanic emissions in the atmosphere yet are typically challenging to observe directly due to the nature of volcanic activity. Inferences are instead drawn largely from observations of volcanic plumes as they drift across a crater's edge and further downwind, and the application of thermodynamic models that neglect reaction kinetics as gas and air mix and thermally equilibrate. Here, we foreground chemical kinetics in simulating this critical zone. Volcanic gases are injected into a chain-of-reactors model that simulates time-resolved high-temperature chemistry in the dispersing plume. Boundary conditions of decreasing temperature and increasing proportion of air interacting with volcanic gases are specified with time according to an offline plume dynamics model. In contrast to equilibrium calculations, our chemical kinetics model predicts that CO is only partially oxidized, consistent with observed CO in volcanic plumes downwind from source. Formation of sulfate precursor SO_3 at $\text{SO}_3/\text{SO}_2 = 10^{-3}$ mol/mol is consistent with the range of reported sulfate aerosol to SO_2 ratios observed close to crater rims. High temperature chemistry also forms oxidants OH, HO_2 , and H_2O_2 . The H_2O_2 will likely augment volcanic sulfate yields by reacting with $\text{SO}_{2(\text{aq})}$ in the cooled-condensed plume. Calculations show that high-temperature OH will react with volcanic halogen halides (HBr and HCl) to yield reactive halogens (Br and Cl) in the young plume. Strikingly, high-temperature production of radical oxidants (including HO_x) is enhanced by volcanic

emissions of reduced gases (CO, H₂, and H₂S) due to chemical feedback mechanisms, although the kinetics of some reactions are uncertain, especially regarding sulfur. Our findings argue strongly that the chemistry of the hot near-source plume cannot be captured by equilibrium model assumptions, and highlight the need for development of more sophisticated, kinetics-based, high-temperature CHONS-halogen reaction models.

Roberts T.J., Dayma G., Oppenheimer C., (2019), Reaction rates control high-temperature chemistry of volcanic gases in air, *Frontiers in Earth Science*, 7, 154, <https://doi.org/10.3389/feart.2019.00154>

An atmospheric smog chamber setup for the investigation of volcanic plume chemistry

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To overcome the limits of remote sensing (quantification of trace gas abundances) and in situ measurements in the field (plume representativeness, accessibility), atmospheric simulation chamber (4 m³ made of Teflon) experiments were carried out at Bayreuth to investigate halogen chemistry in a simplified volcanic plume under controlled conditions. To simulate the dilution of volcanic gases by the atmosphere after emission, the reaction volume was diluted with a constant admix of ozone and zero air. Solar like radiation was provided by a solar simulator. A White multi-reflection cell as well as a multichannel cavity enhanced DOAS (Differential Optical Absorption Spectroscopy) instrument enabled online observation of BrO formation (detection limit of several 10 pptv) and other trace gases. Additional instruments and sampling techniques were employed such as alkaline trap sampling for total bromine and sulfur measurements and gas diffusion denuders for bulk reactive bromine species measurements. Particle size distributions were determined by SMPS (Scanning Mobility Particle Sizer Spectrometer) and SO₂, NO_x and O₃ were monitored by in-situ gas analyzers. The experimental setup will be presented.

An overview of bromine monoxide observations in volcanic plumes from ground, space and in the laboratory

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BrO levels in volcanic gas plumes can reach extraordinarily high levels compared to the atmospheric background. The spectral absorption features of BrO enable its detection by multiple remote sensing techniques from ground, from space, and in the laboratory using scattered or reflected sun light or artificial light sources. Here we report on our studies.

1) Within the Network for Observations of Volcanic and Atmospheric Change (NOVAC), multiple ground-based remote sensing instruments acquired BrO/SO₂ data over more than 10 years. Both, the ground-based measurements and volcanic plume modelling, indicate that BrO is not directly emitted by volcanoes but is formed after the emission plume is mixed with the atmosphere.

2) In addition, satellite-based BrO/SO₂ data from TROPOMI shows that BrO can still be observed in plumes with ages of several hours up to days.

3) Recent atmospheric chamber experiments of artificial plumes being diluted within ozone enriched air show BrO dynamics, which are qualitatively comparable to the observations from NOVAC and TROPOMI, but are quantitatively affected by initial experimental parameters such as HBr, SO₂, aerosol abundance and relative humidity.

4) Based on the results of our observations, we will further present future needs and prospects in field-studies and instrument design such as novel imaging techniques and high-resolution spectroscopy.

Variation of the BrO/SO₂ molar ratio in the plume of Tungurahua volcano between 2007 and 2017 and its relationship to volcanic activity

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In this study, we present long-term bromine monoxide (BrO) to sulphur dioxide (SO₂) molar ratios inside the plume of Tungurahua volcano derived from spectroscopic measurements with UV scanning-DOAS instruments for the period 2007-2017 and study their relation to eruptive style.

After continuous eruptive activity in 2007 and 2008, Tungurahua showed alternating phases of quiescence and explosive behavior between late 2008 and March 2016, after which degassing intensity decreased below detection limits of the monitoring instruments. While the link between volcanic activity and the amount of volcanic gas emissions is well established, links to the plume composition of volcanic gas emissions, in particular the molar ratio of BrO and SO₂, have been suggested only recently. While BrO and the BrO/SO₂ molar ratio have been observed on multiple occasions, the knowledge about the mechanisms linking the BrO/SO₂ ratio to the volcanic activity is still limited due to the lack of studies of volcanic bromine release mechanisms from the melt into the atmosphere.

This study aims at broadening our observational data base by looking at 13 eruptive phases of Tungurahua volcano during the study period, where we successfully retrieved BrO as well as the BrO/SO₂ ratio.

We identify a recurring eruptive cycle of the molar BrO/SO₂ ratio, which is clearly observed in 8 of the 13 eruptive phases. The first observed feature, which is governed by enhanced volcanic activity, shows low BrO/SO₂ molar ratios of $2 - 5 \times 10^{-5}$. When the volcanic activity subsides bromine emission increases rapidly and the molar BrO/SO₂ ratio increases to $5 - 17 \times 10^{-5}$. After roughly one week the BrO/SO₂ molar ratio decreases again to the initial value and the cycle ends. This clear pattern indicates a magma driven eruption cycle which can be correlated to the BrO/SO₂ ratio and we propose two ways of interpreting this correlation with respect to bromine partitioning from the melt, one if bromine partitions earlier than sulphur and the other if bromine partitions later.

The case of Tungurahua shows us that combining long-term geochemical and geophysical