

Reactive halogen chemistry in volcanic plumes – an overview on our current understanding

Nicole Bobrowski^{1,2} and Ulrich Platt¹

, Peter Lübcke¹ Jonas Gliss³, Santiago Arellano⁴, Leif Vogel^{1,8}, Florian Dinger¹, Bo Galle², Gustavo Garzón⁵, Julian Peña⁷, Zoraida Chacon⁷, Mathiew Yalire⁶, Abel Minani⁶, Simon Warnach¹

¹ Institute of Environmental Physics (IUP), Heidelberg University, INF 229, D-69120 Heidelberg, Germany

² Institut fuer Geowissenschaften, Universitaet Mainz, Germany

³ Norwegian Institute for Air Research (NILU), Kjeller, Norway

⁴ Department of Earth and Space Sciences, Chalmers University of Technology, Gothenburg, Sweden

⁵ FISQUIM Research Group, Laboratory Division, Colombian Geological Survey, Cali, Colombia

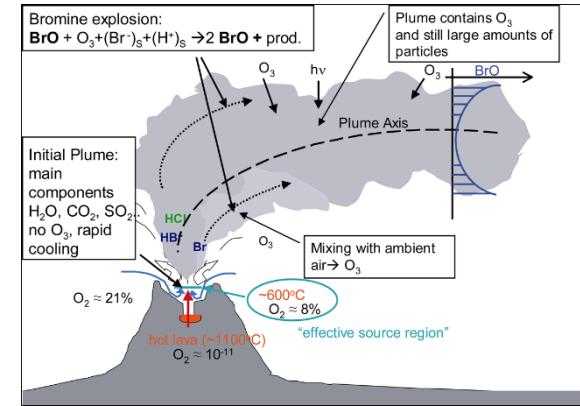
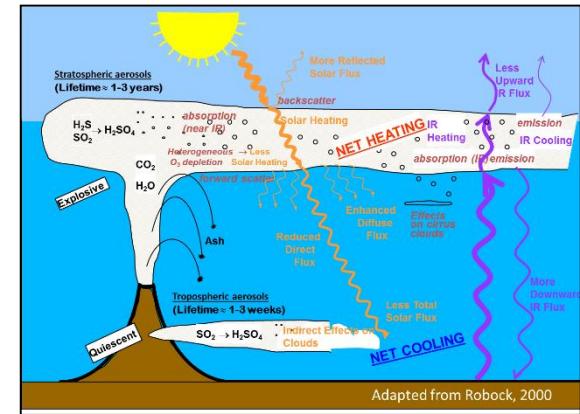
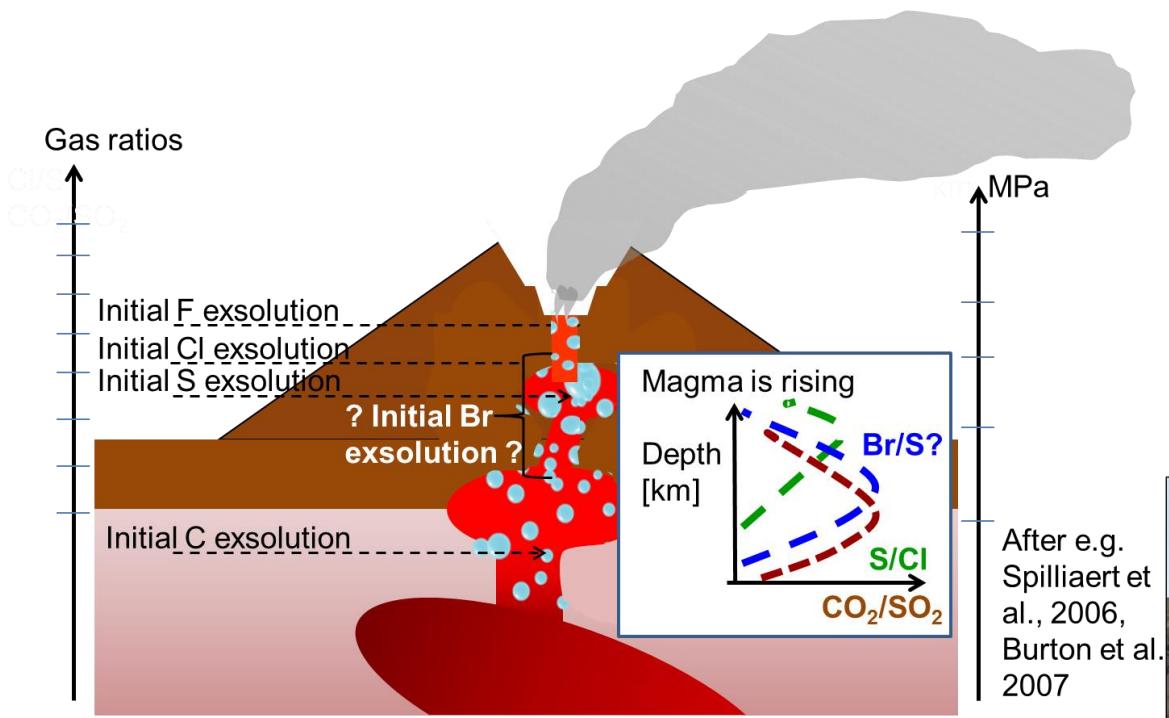
⁶ Observatoire Volcanologique de Goma , Goma, DR Congo

⁷ Colombian Geological Survey, Manizales, Colombia

⁸ now at Earth Observation Science Group, Space Research Centre, Department of Physics and Astronomy, University of Leicester, Leicester, UK

Motivation for volcanic halogen studies

- Volcanic Activity Changes
- Plume Chemistry, Atmospheric Chemistry, Radiation Budget,..
- Environmental and Health Impact



Bobrowski et al., 2007

Robock, 2000

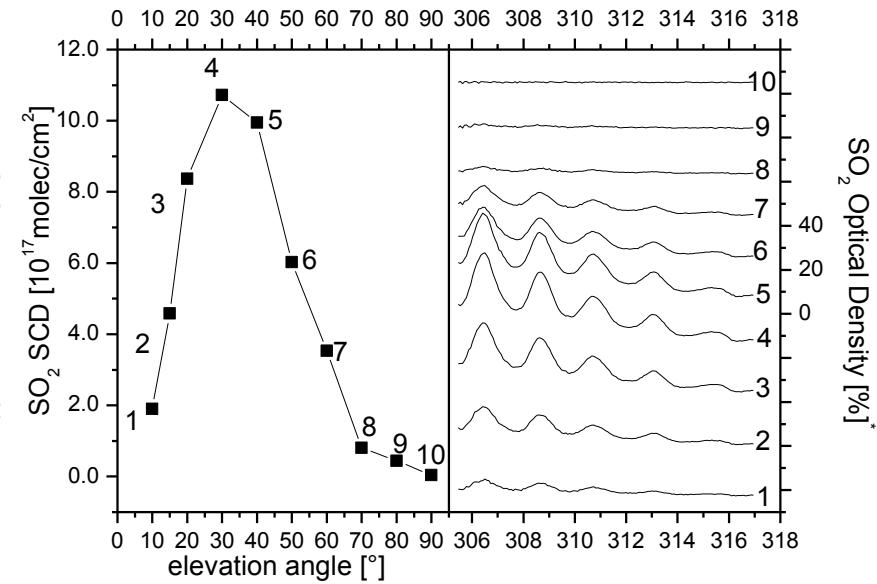
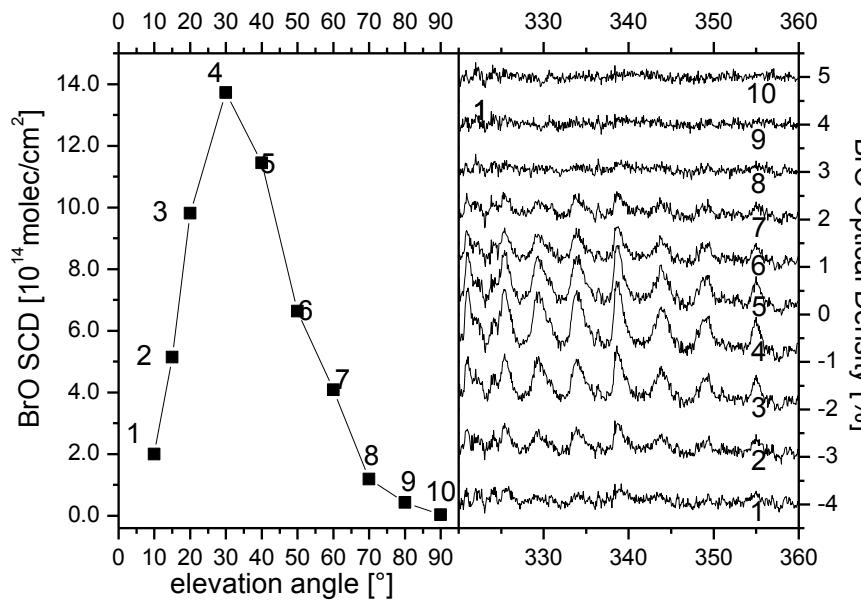
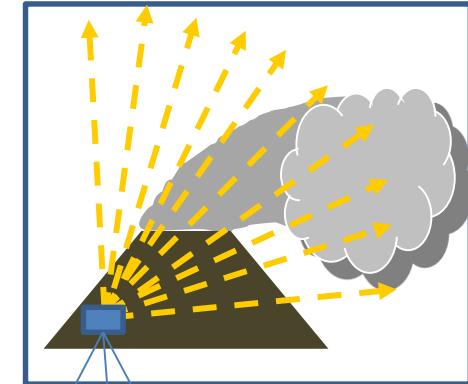
Tropospheric chemistry could be influenced by volcanic halogen emission in various ways

(Platt and Bobrowski 2015):

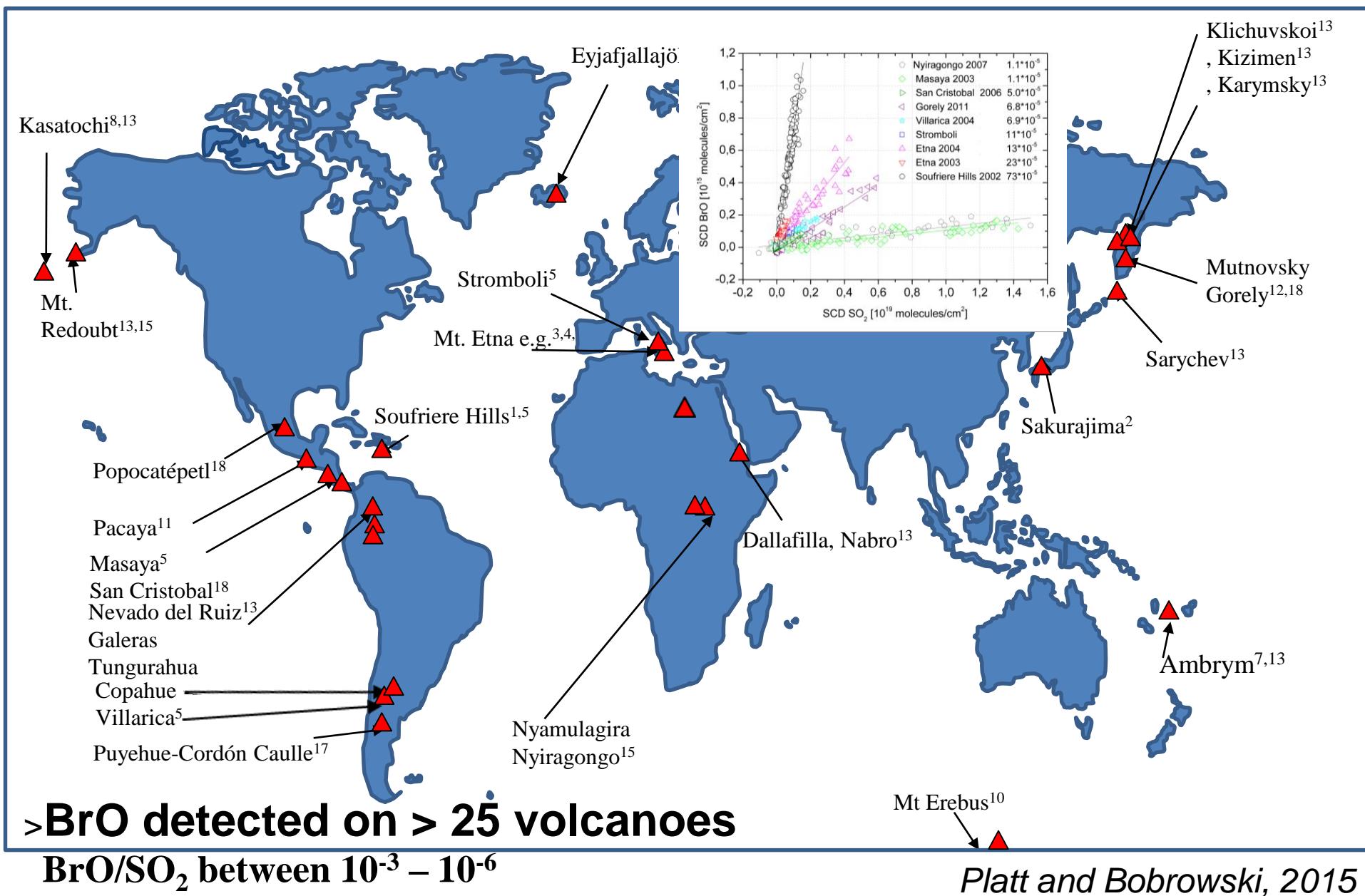
- 1) Bromine catalyses O_3 destruction
 - 2) Bromine inhibits the O_3 production in the troposphere
 - 3) RHS reactions interfere with the NO_x reaction cycle.
 - 4) RHS reactions enhance the OH/ HO_2 ratio
 - 5) Hypohalous acids (HOBr, HOCl) contribute to the formation of sulphate in aqueous particles
 - 6) RHS can induce secondary organic aerosol formation
(shown in lab studies by Cai et al. 2008 for Cl atoms and Ofner et al. 2013 for Cl and Br)
 - 7) Bromine can oxidize mercury, and therefore reduce its atmospheric lifetime
-

There is reactive halogen chemistry in the volcanic plume: MAX-DOAS BrO and SO₂ from Soufriere Hills Volcano on Montserrat, May 2002

N. Bobrowski, G. Hönniger,
B. Galle, and U. Platt, (2003),
Detection of bromine
monoxide in a volcanic
plume, Nature, 423, doi:
10.1038/nature01625

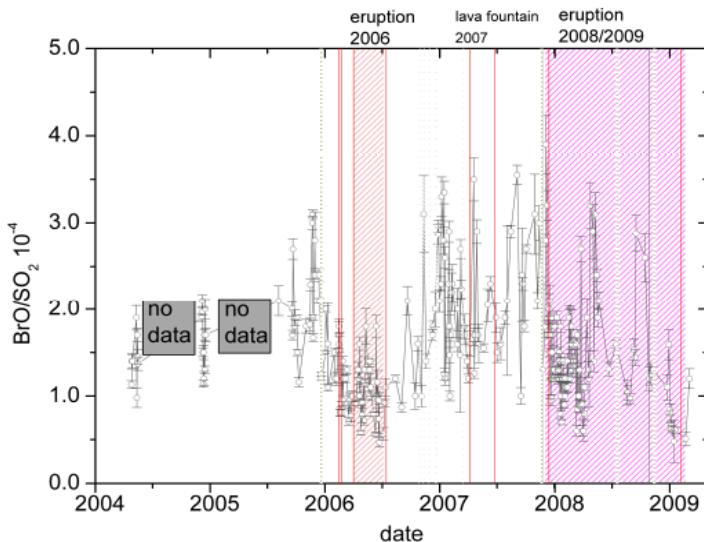


BrO is nothing exceptional in a volcanic plume

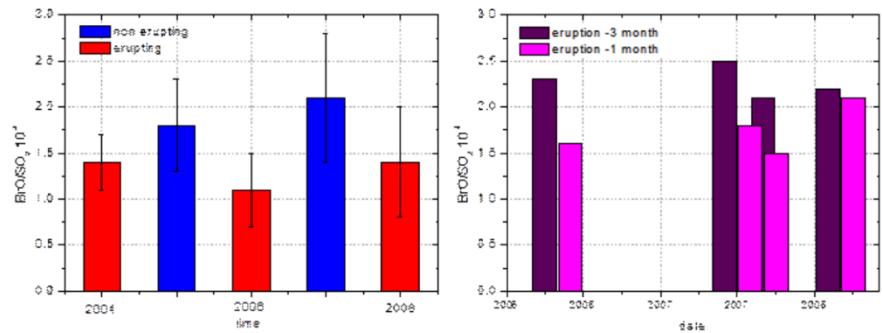


BrO/SO₂ time series

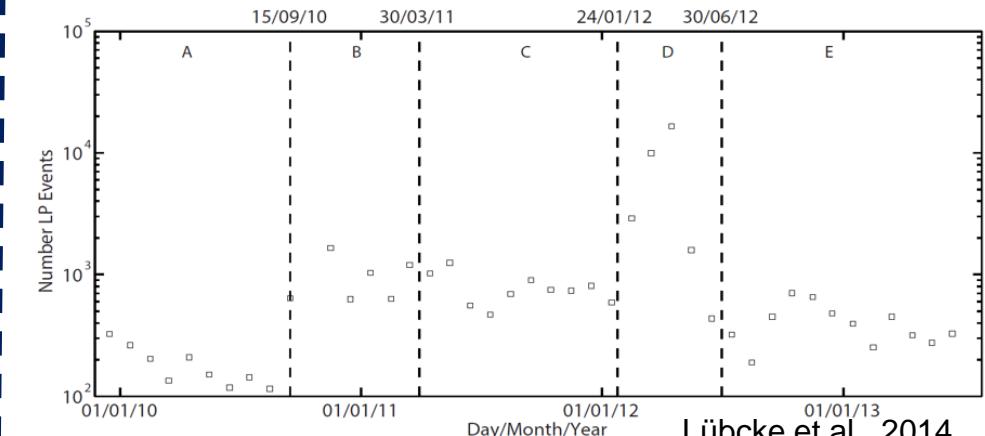
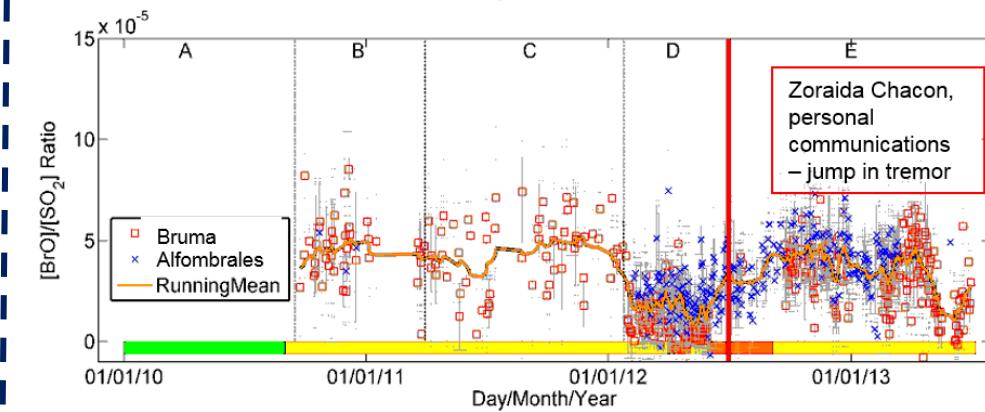
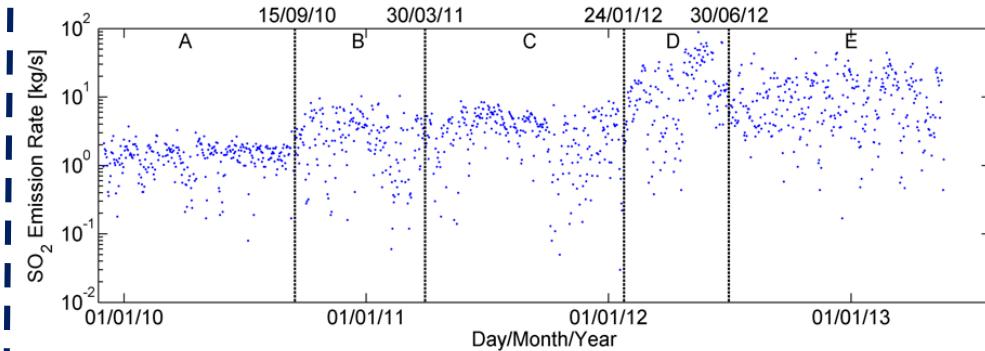
Etna, Italy



Bobrowski and Giuffrida, 2012

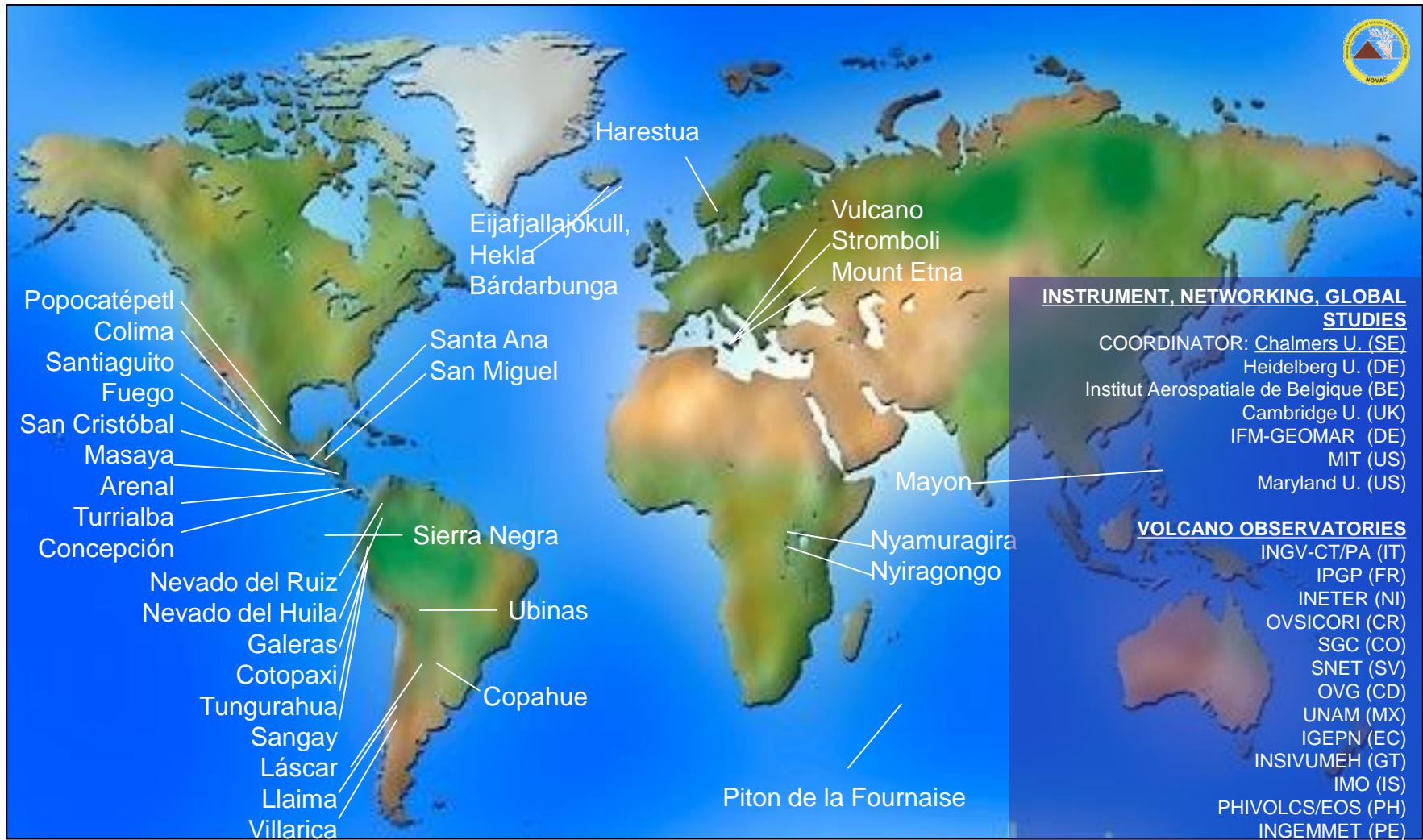


Nevado del Ruiz, Colombia



Lübcke et al., 2014

Global volcanic gas studies: NOVAC – the great opportunity



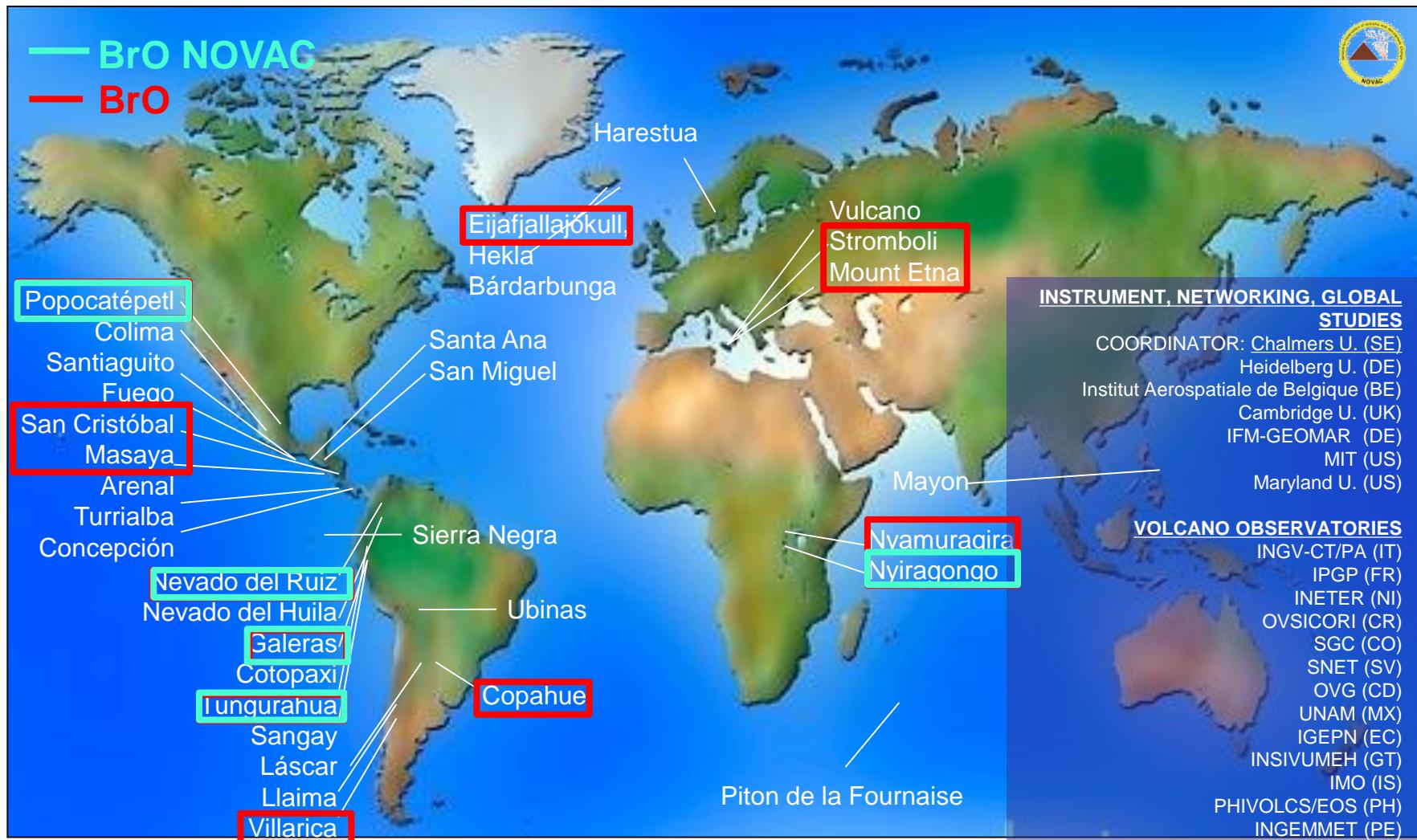
33 volcanoes, ~80 instruments, 21 volcanoes actively monitored today

Global volcanic gas studies: NOVAC – the great opportunity



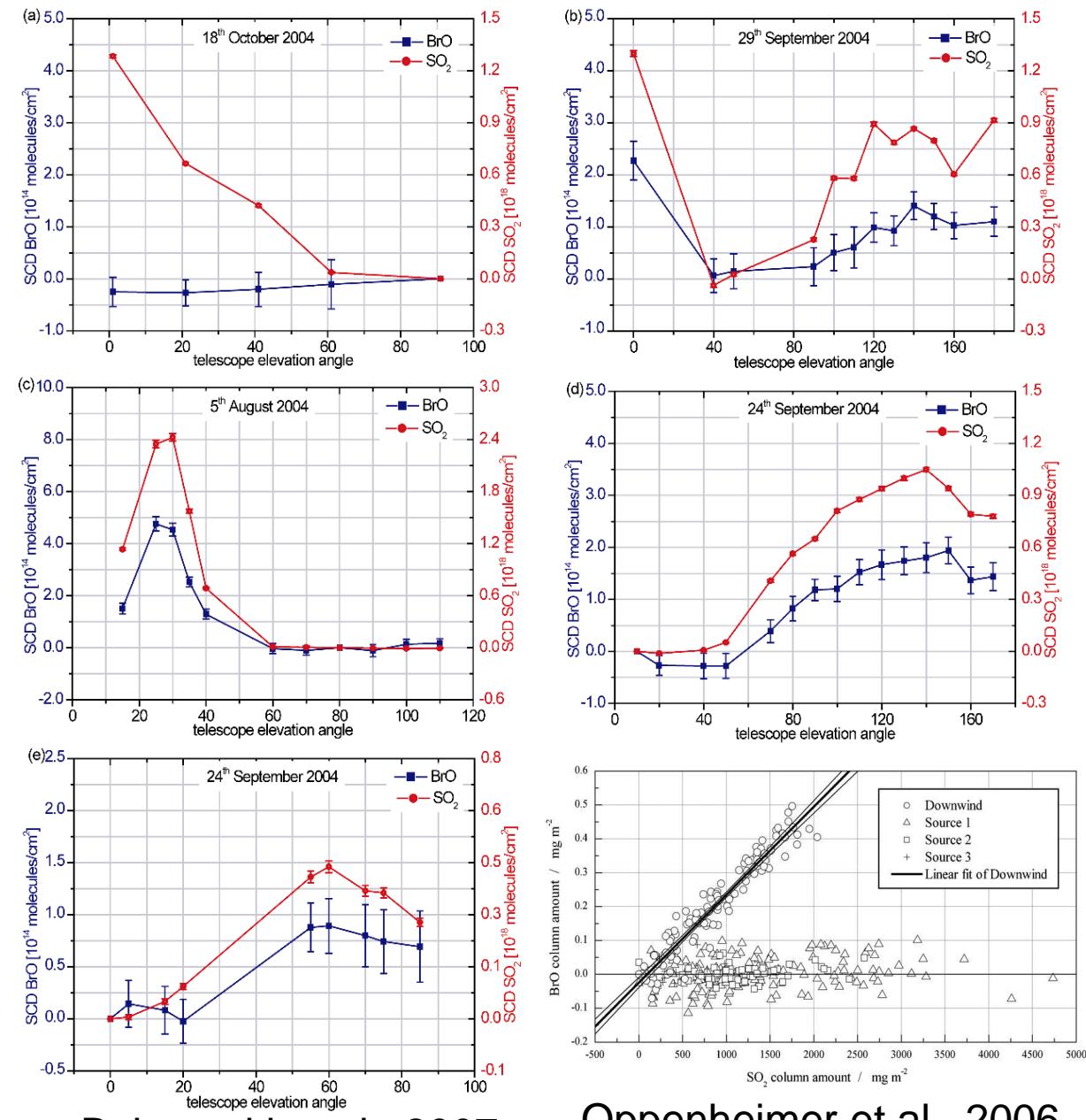
33 volcanoes, ~80 instruments, 21 volcanoes actively monitored today

Global volcanic gas studies: NOVAC – the great opportunity



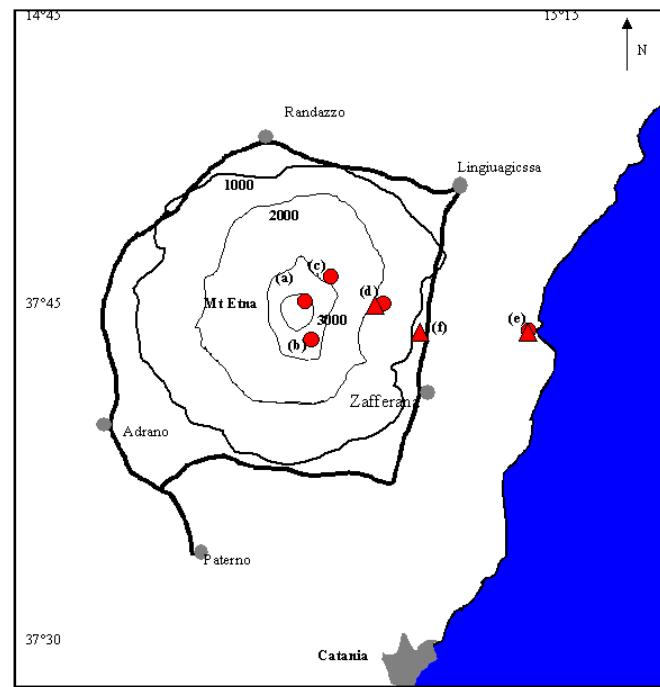
33 volcanoes, ~80 instruments, 21 volcanoes actively monitored today

BrO and SO₂ at different distances downwind from the crater of Etna

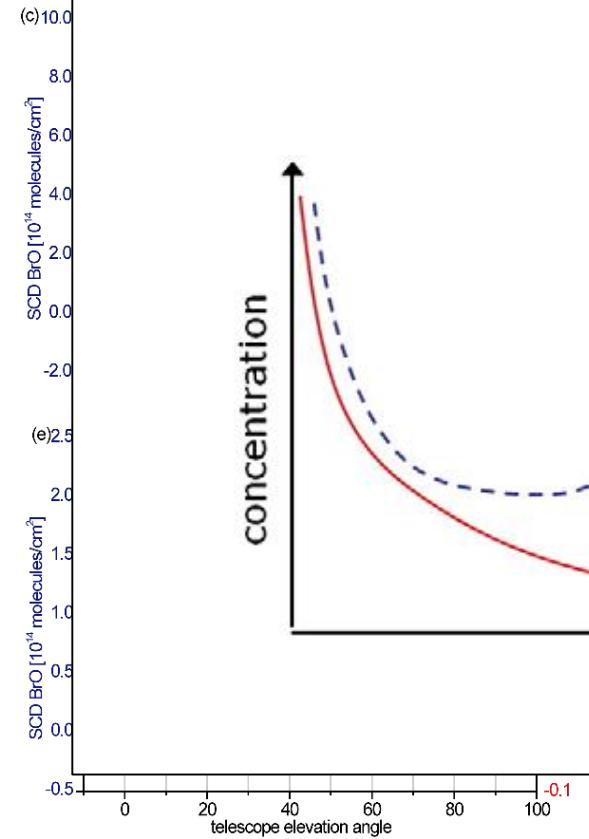
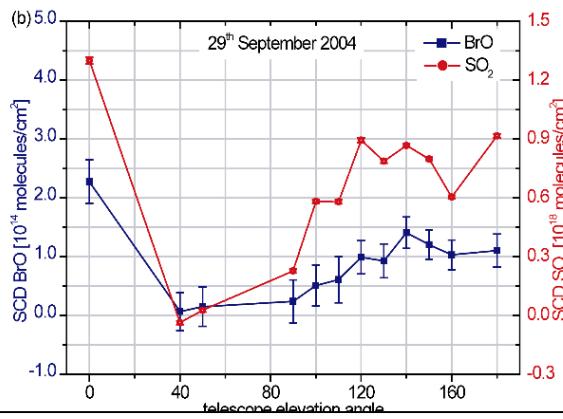
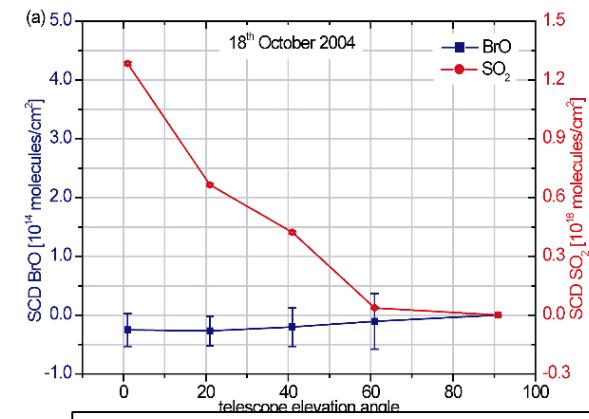


Bobrowski et al., 2007

Oppenheimer et al., 2006



BrO and SO₂ at different distances down-wind from the



- Evolution of a passive tracer (red) and a fictitious reactive component (blue) with time in the volcanic plume.
- By taking a ratio, atmosphereric dilution effects and temporal variations of emitted amounts are eliminated

Oppenheimer et al., 2006

Bobrowski et al., 2007

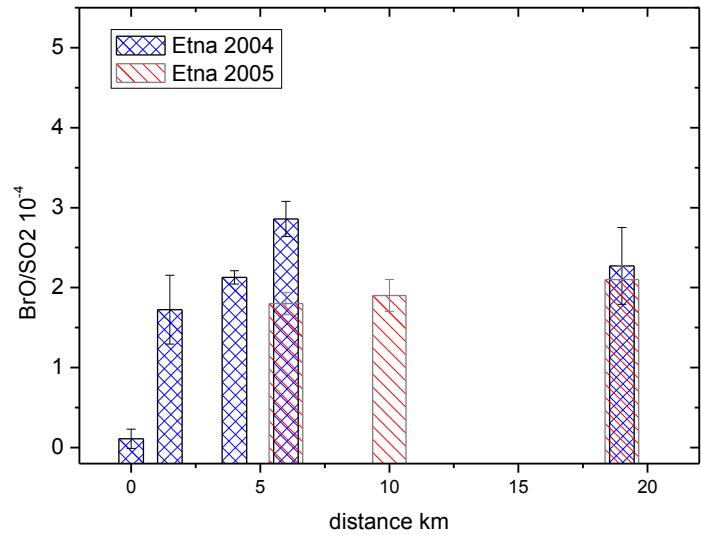
SO₂ column amount / mg m⁻²

37°30'

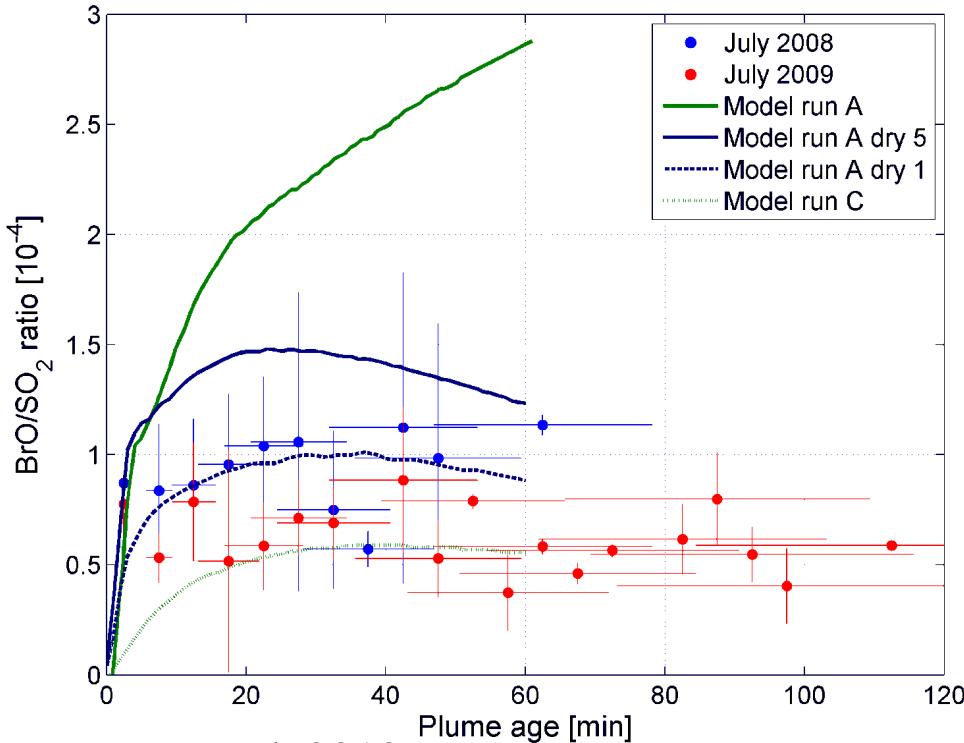
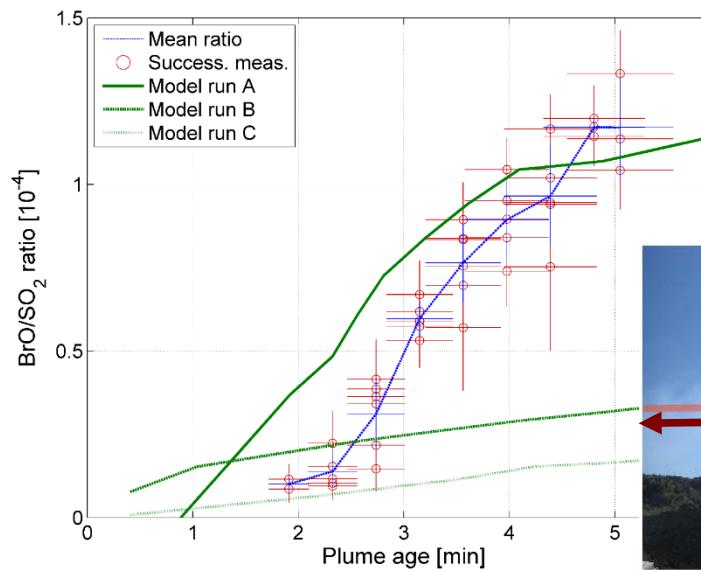
Catania



BrO/SO₂ ratio dependence of the distance from the source



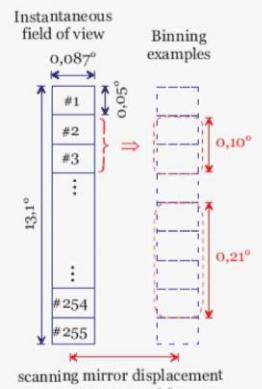
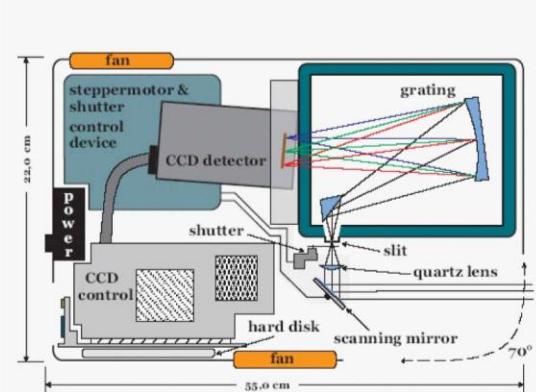
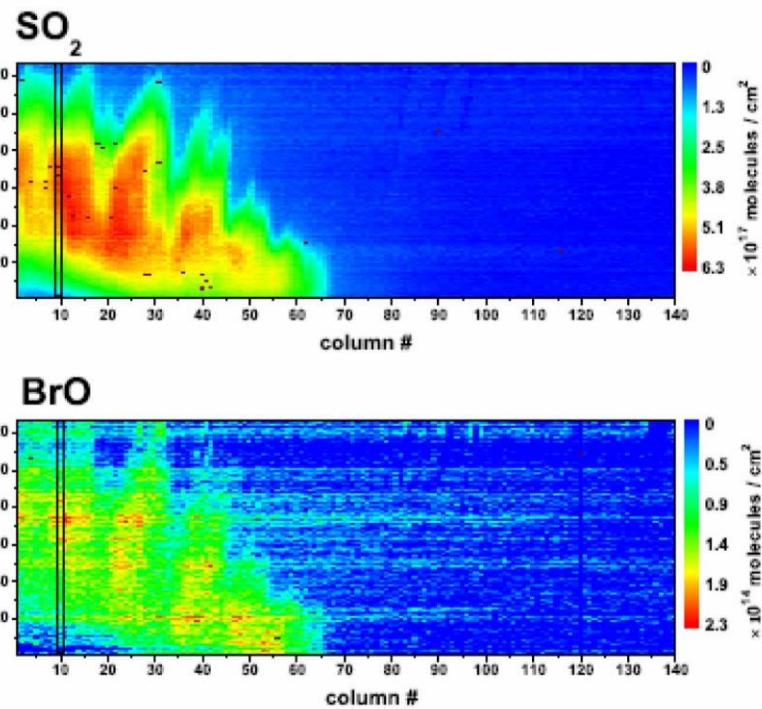
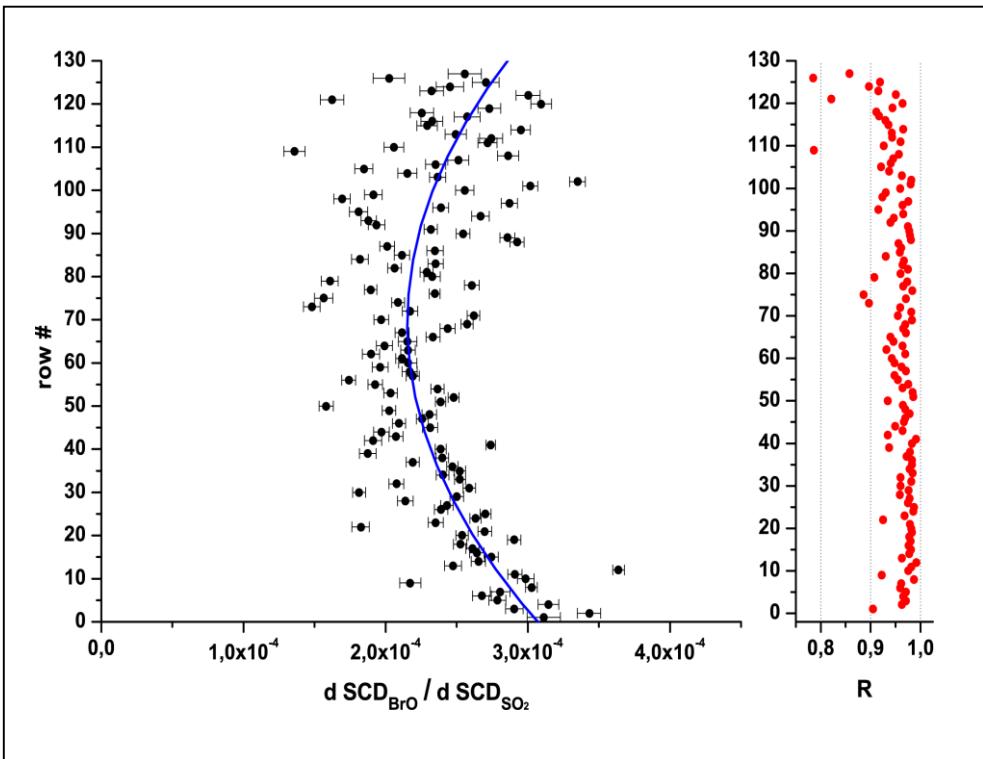
Adapted from
Bobrowski et al., 2005



Vogel, 2010

General agreement with
model data possible

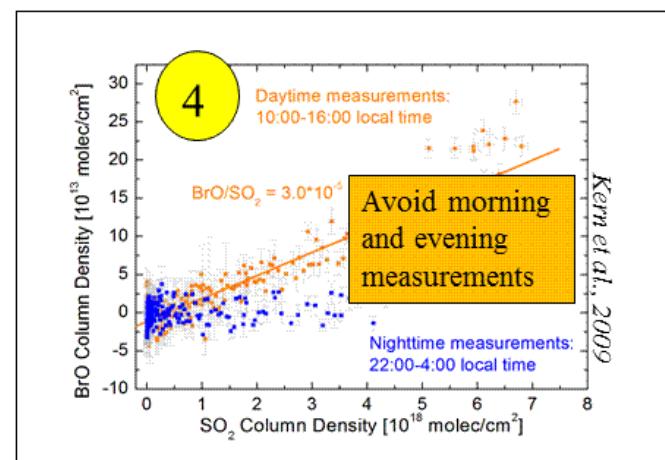
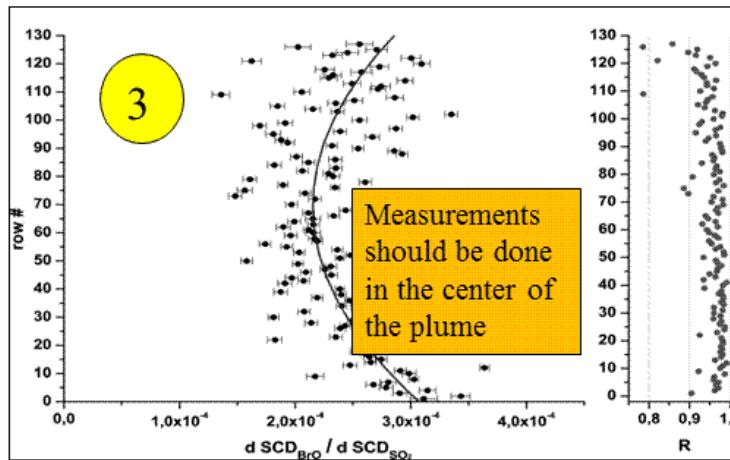
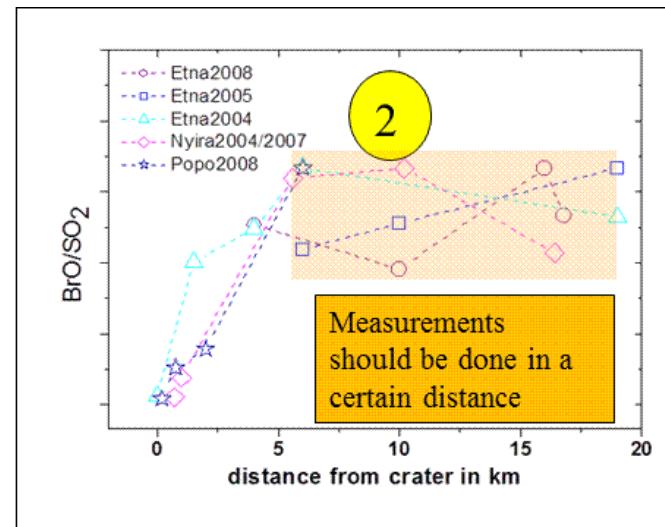
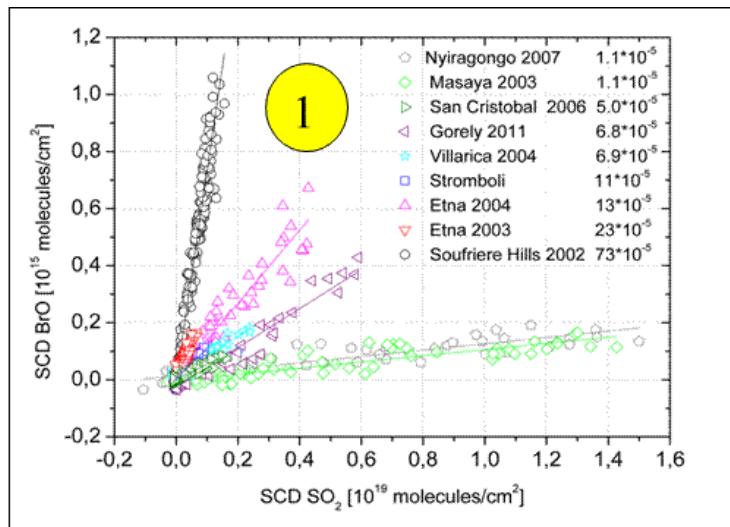
SO₂ and BrO- spatial distribution in a volcanic plume



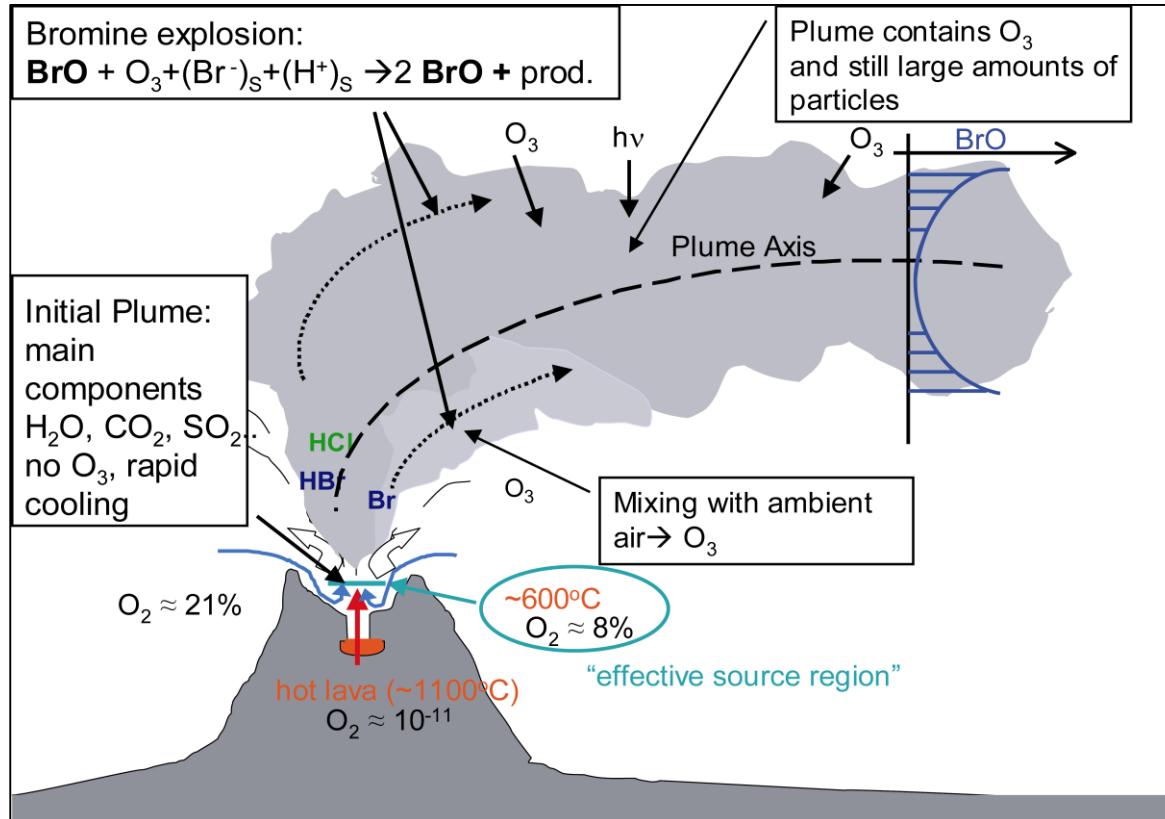
Louban et al., 2009

What do we know about BrO in volcanic plumes?

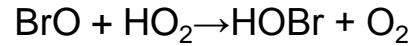
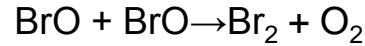
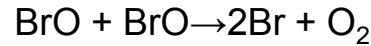
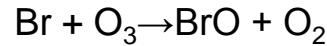
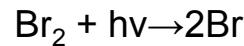
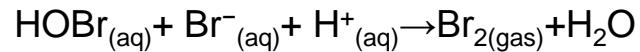
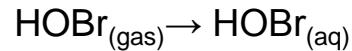
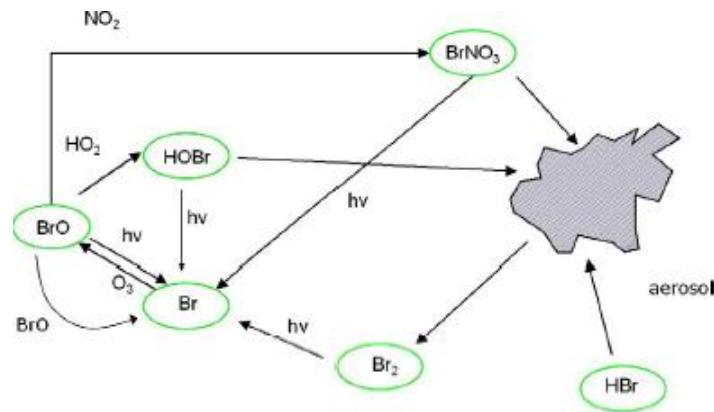
BrO is a secondary gas a bit of attention is needed when using it as volcanic activity tracer



Bromine explosion



e.g. Bobrowski et al. 2007 Glasow et al. 2009



Is this everything ?

Ozone depletion Etna 2012

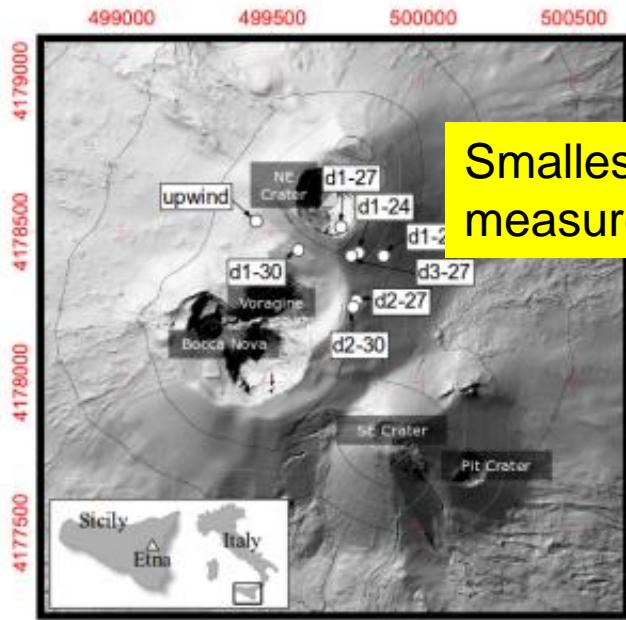


Fig. 1. Map of the sampling sites and summit craters. Terrain from Neri et al. (2009). Coordinates are UTM Easting/Northing.

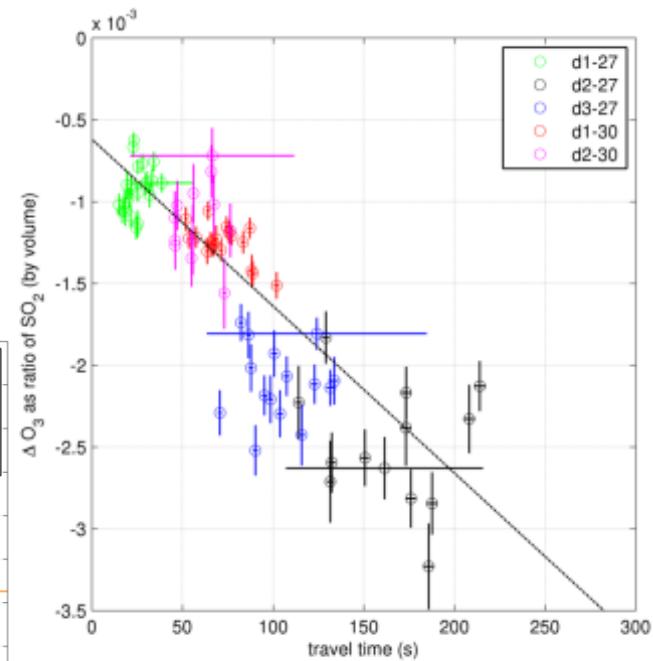
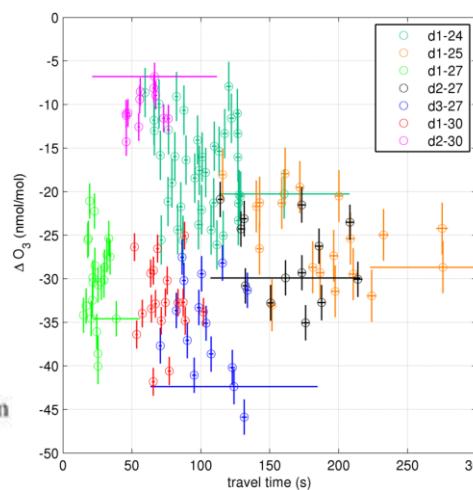
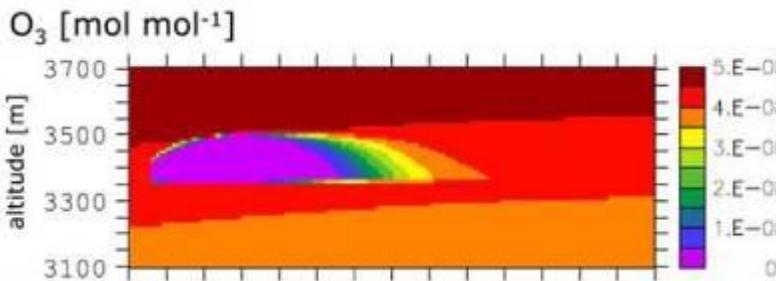


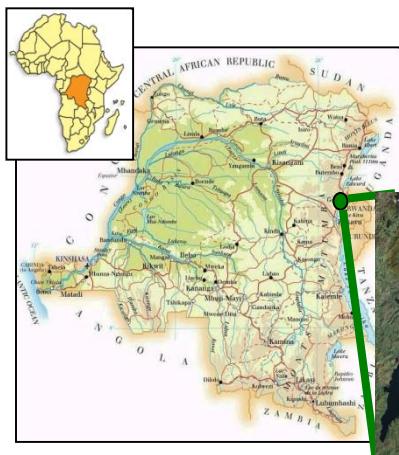
Fig. 5. $\Delta O_3/\text{SO}_2$ against calculated processing time at the in-plume measurement sites. The gradient of the linear line of best fit is $(1.02 \pm 0.07) \times 10^{-5} \text{ s}^{-1}$ and the y-intercept is $(-6.2 \pm 0.5) \times 10^{-4}$

Surl, et al., 2014

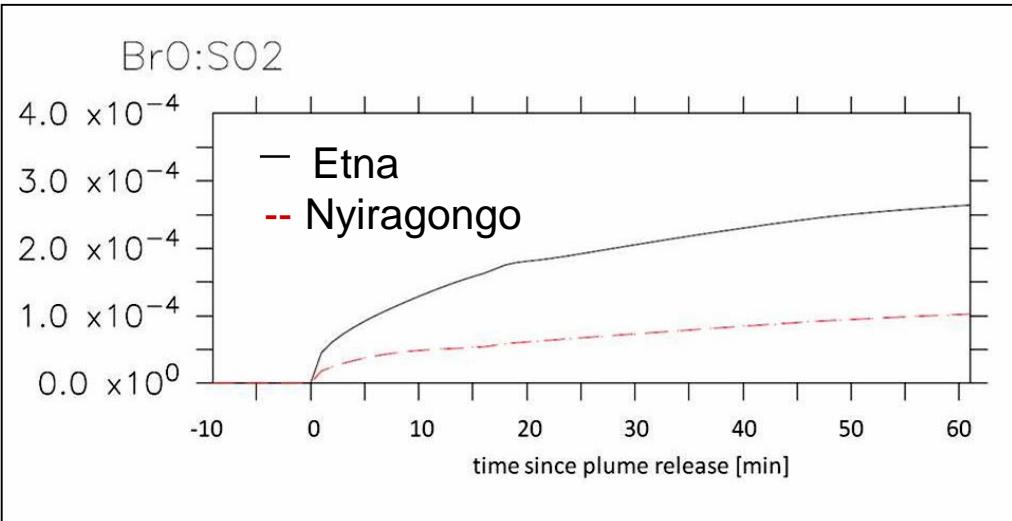
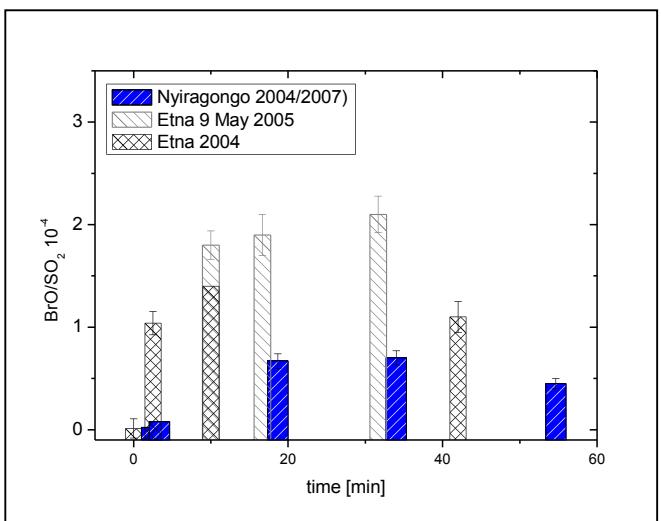
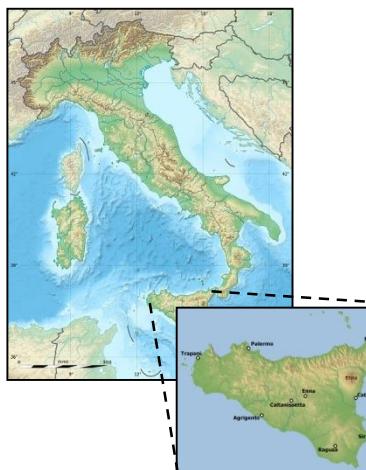
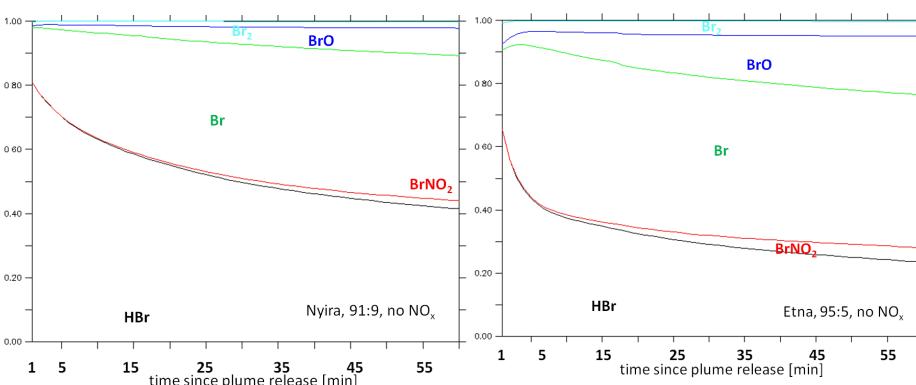


Models predict complete ozone depletion in plume

Von Glasow



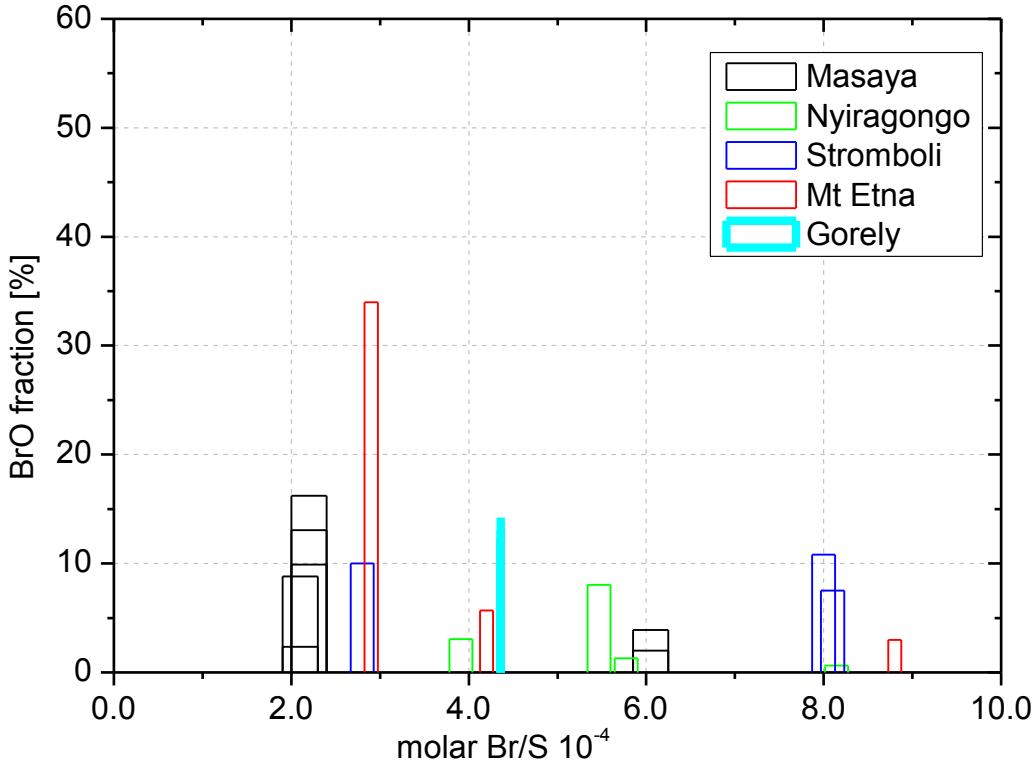
Nyiragongo and Etna



Bobrowski et al., 2015

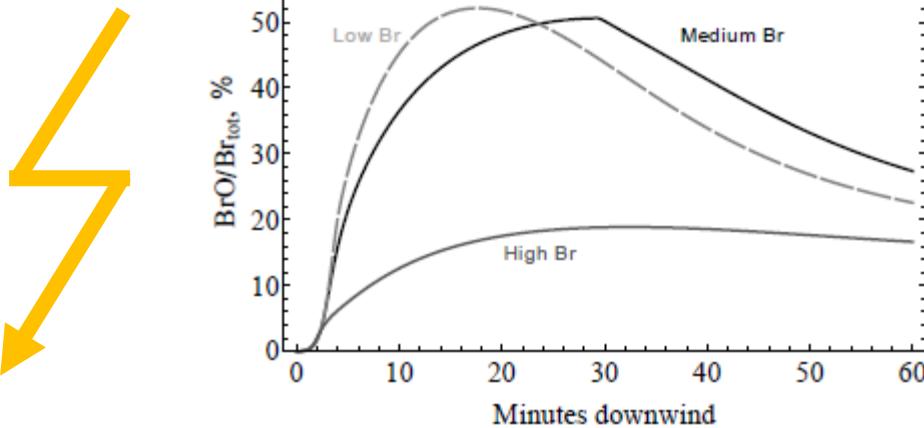
Variation in initial plume composition lead to significant difference in BrO formation in an ageing plume, shown in measurements and model

Simultaneous Br/S and BrO/SO₂ data:



Measurements

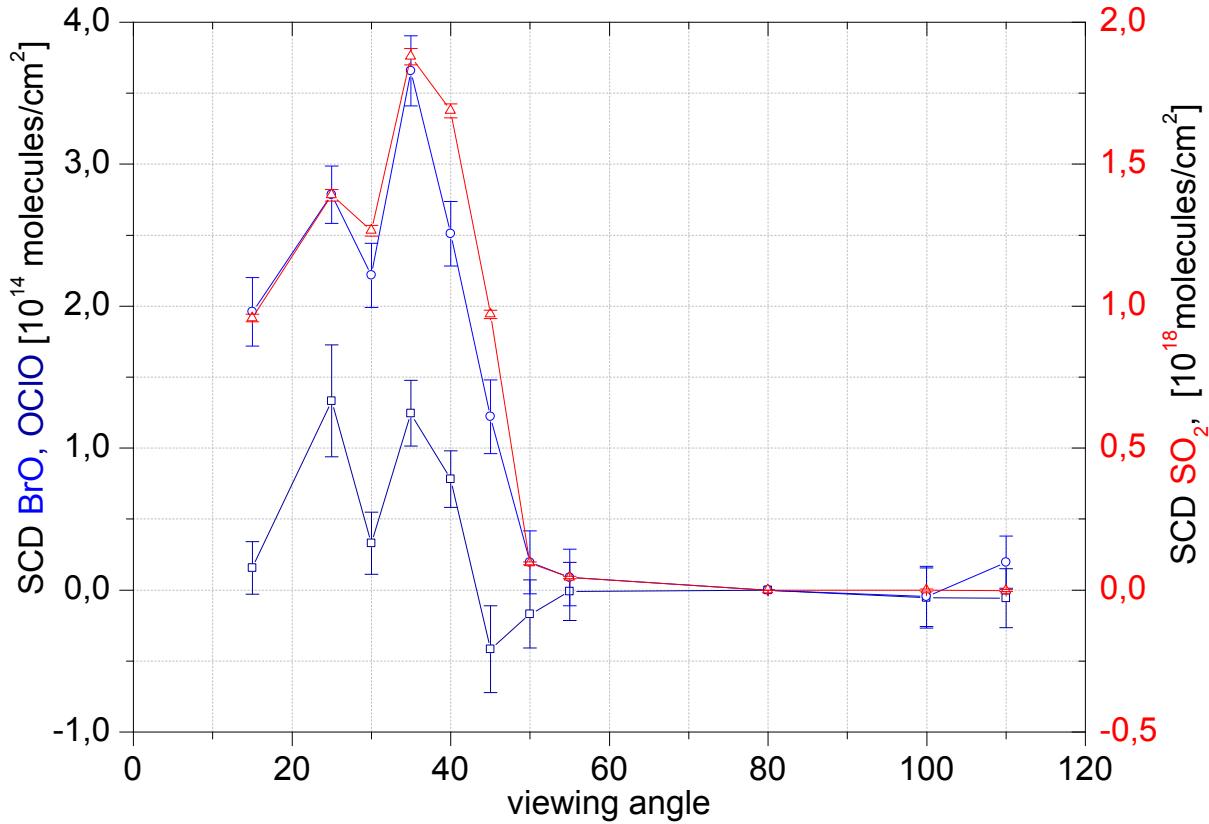
Simultaneous measurements of Br/S and BrO/SO₂ ratios at 5 different volcanoes



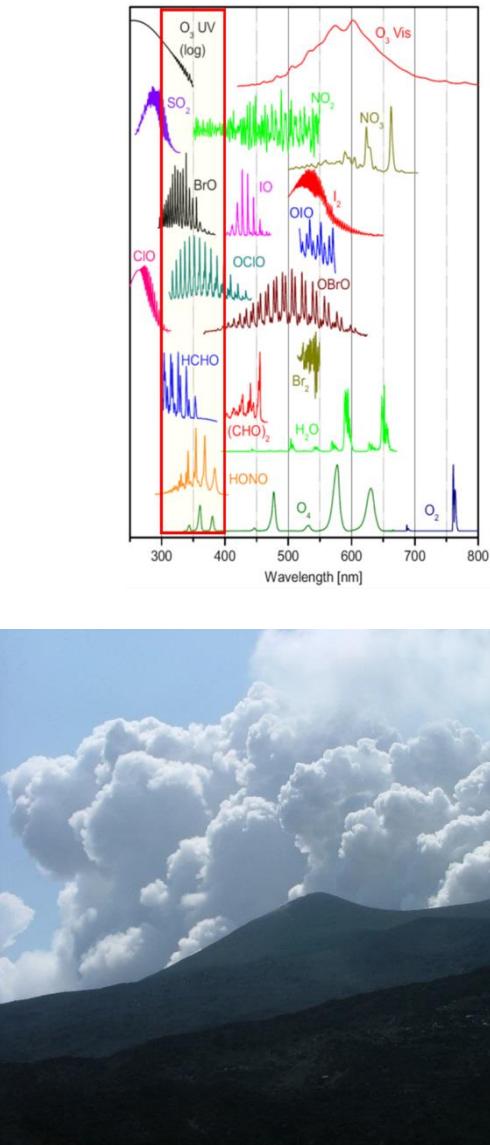
Model

Recent Model studies of T. Roberts et al., 2014

Further Gases: Etna 5th August 2004 – OCIO detection

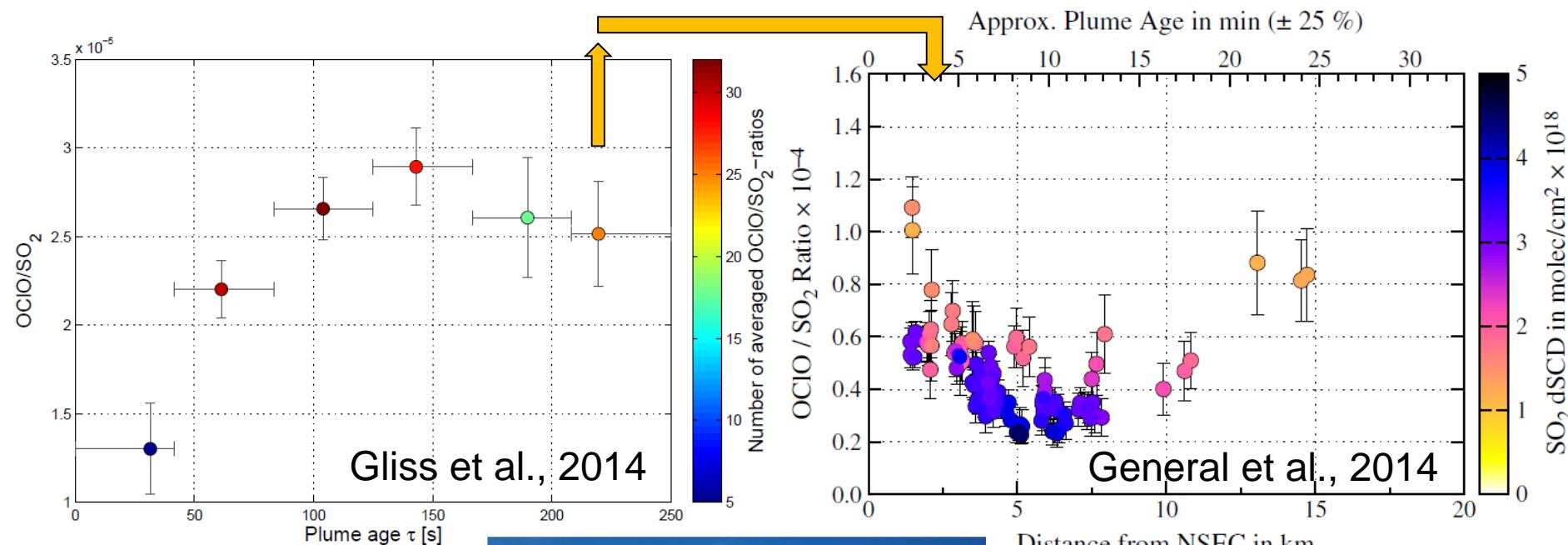


Bobrowski et al., 2007



Chlorine chemistry

OCIO formation in the plume of Mt Etna



scanning
DOAS

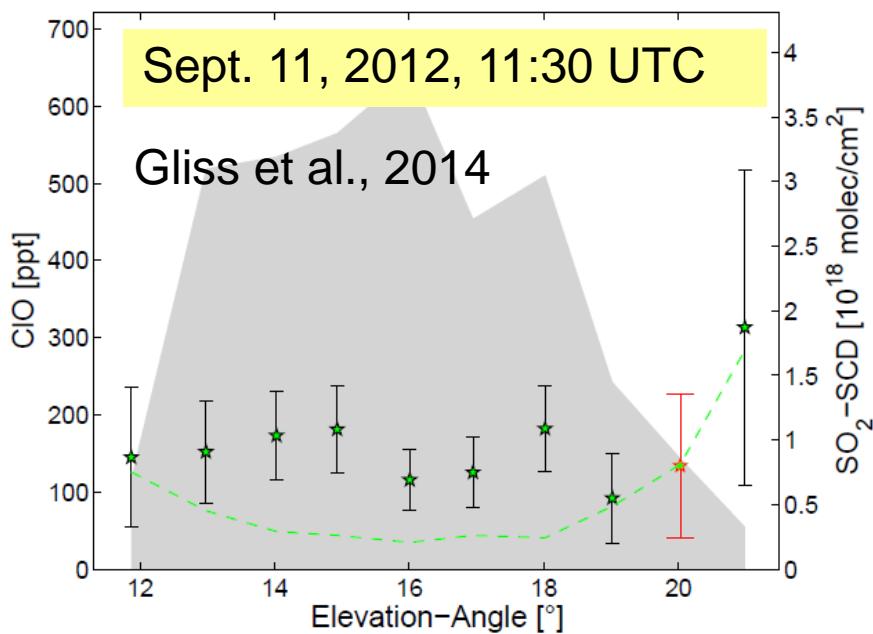


Airplane measurements

Chlorine Chemistry

Formation of OCIO: $\text{BrO} + \text{ClO} \rightarrow \text{OCIO} + \text{Br}$, $k = 6 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 \rightarrow other products

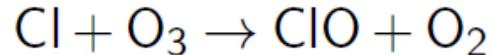
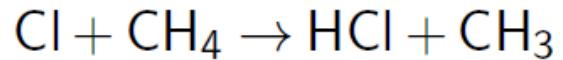
OCIO Destruction: $\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}$



Assuming a photo-stationary state:

$$\frac{d}{dt} [\text{OCIO}] = [\text{BrO}] \cdot [\text{ClO}] \cdot k_1 - [\text{OCIO}] \cdot J_1 = 0$$
$$\Rightarrow$$
$$[\text{ClO}] = \frac{[\text{OCIO}] \cdot J_1}{[\text{BrO}] \cdot k_1} = \frac{S(\text{OCIO}) \cdot J_1}{S(\text{BrO}) \cdot k_1}$$

From ClO we can calculate also the amount of Cl atoms \rightarrow



Reduction of CH_4 lifetime 2 orders of magnitude – however even assuming only 1 pbb O_3 would lead to a CH_4 lifetime of the order of half a day (CH_4 mean lifetime in the atmosphere 10 years)

Summary

- Reactive halogens (e.g. BrO, OClO) abundant in volcanic plumes
- Measured mixing ratios can be roughly explained by known chemistry, however in detail model and measurements are in disagreement
- Influence on tropospheric chemistry poorly studied
- How much of emitted bromine is transformed into BrO
- Is the transformation factor constant ? (how to measure total bromine?)
- Sensitivity to environmental and volcanic factors ?
- What about iodine?
- ...



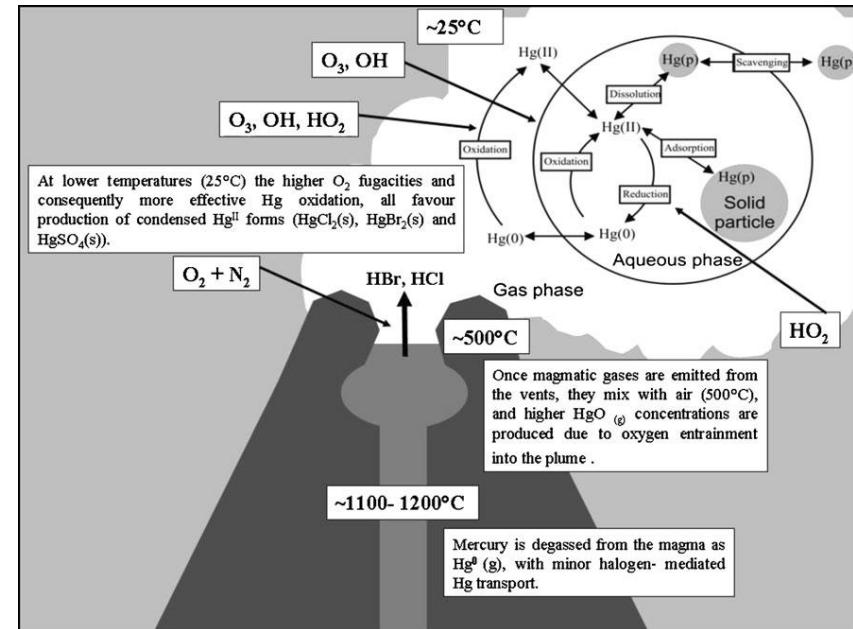
Merci !
Danke – Grazie - Gracias -
Aksanti – Thanks

Questions???

Mercury in volcanic plumes

Major emitted species GEM
 (Hg^0) – chemical inert, low water solubility

Bagnato, et al., 2011

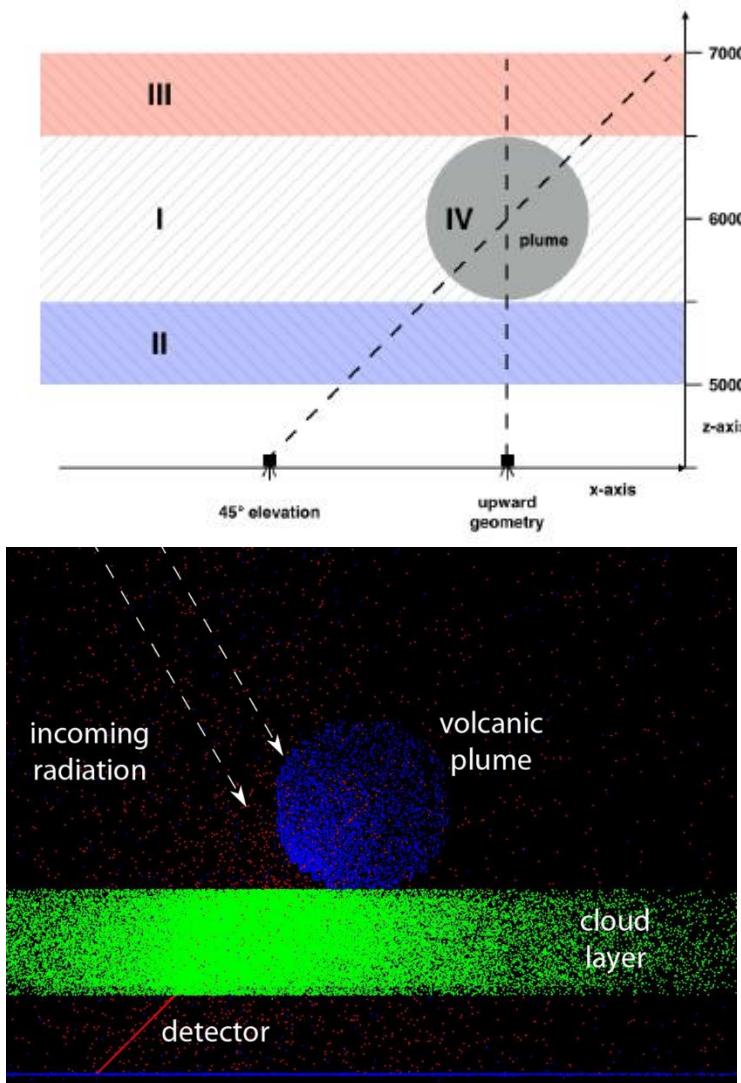


Natural Emission Estimates		Tonnes emitted globally in 2000	
Ocean volatilisation	600-2800	Coal and oil combustion	1422
Volcanic processes	700*	Pyrometalluric	452
Soil emissions	500-1000	Caustic soda production	65
Vegetation emissions	1650-4300	Waste incineration	66
		Cement production	140
		Other	45
Total natural	3450-8800	Total anthropogenic	2190

Adapted from Pacyna et al., 2006



An advantage of ratios: radiative transfer can be a smaller issue

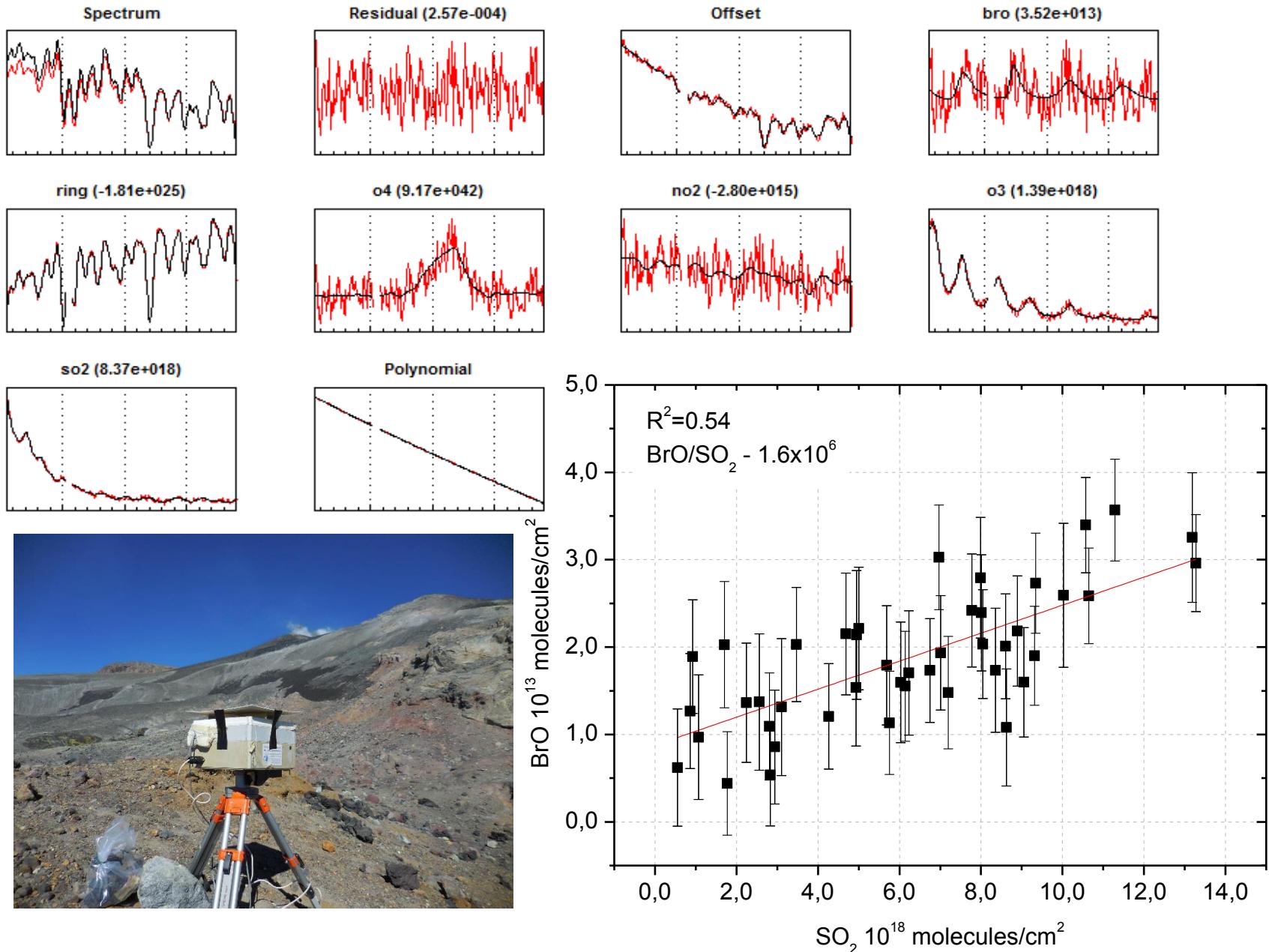


	$\lambda(SO_2)$: 315.39 nm	$\lambda(BrO)$: 340.00 nm	AOD: 12.75 / 12	SO_2 [molec/cm ²] $\times 10^{18}$	BrO [molec/cm ²] $\times 10^{14}$	BrO/SO_2 Ratio $\times 10^{-4}$	Deviation [%]
I	0	90°		0.96	0.98	1.017	1.7
		45°		0.90	0.93	1.032	3.2
II	I	90°		1.32	1.36	1.030	3.0
		45°		1.11	1.20	1.080	8.0
III	II	90°		0.78	0.83	1.067	6.7
		45°		0.20	0.22	1.071	7.1
IV	III	90°		0.98	0.99	1.006	0.6
		45°		1.02	1.04	1.006	1.5
	IV	90°		1.23	1.26	0.999	2.0
		45°		1.16	1.22	1.024	5.8

=> The ratio of two gases is less influenced by radiative transfer than the absolute column density

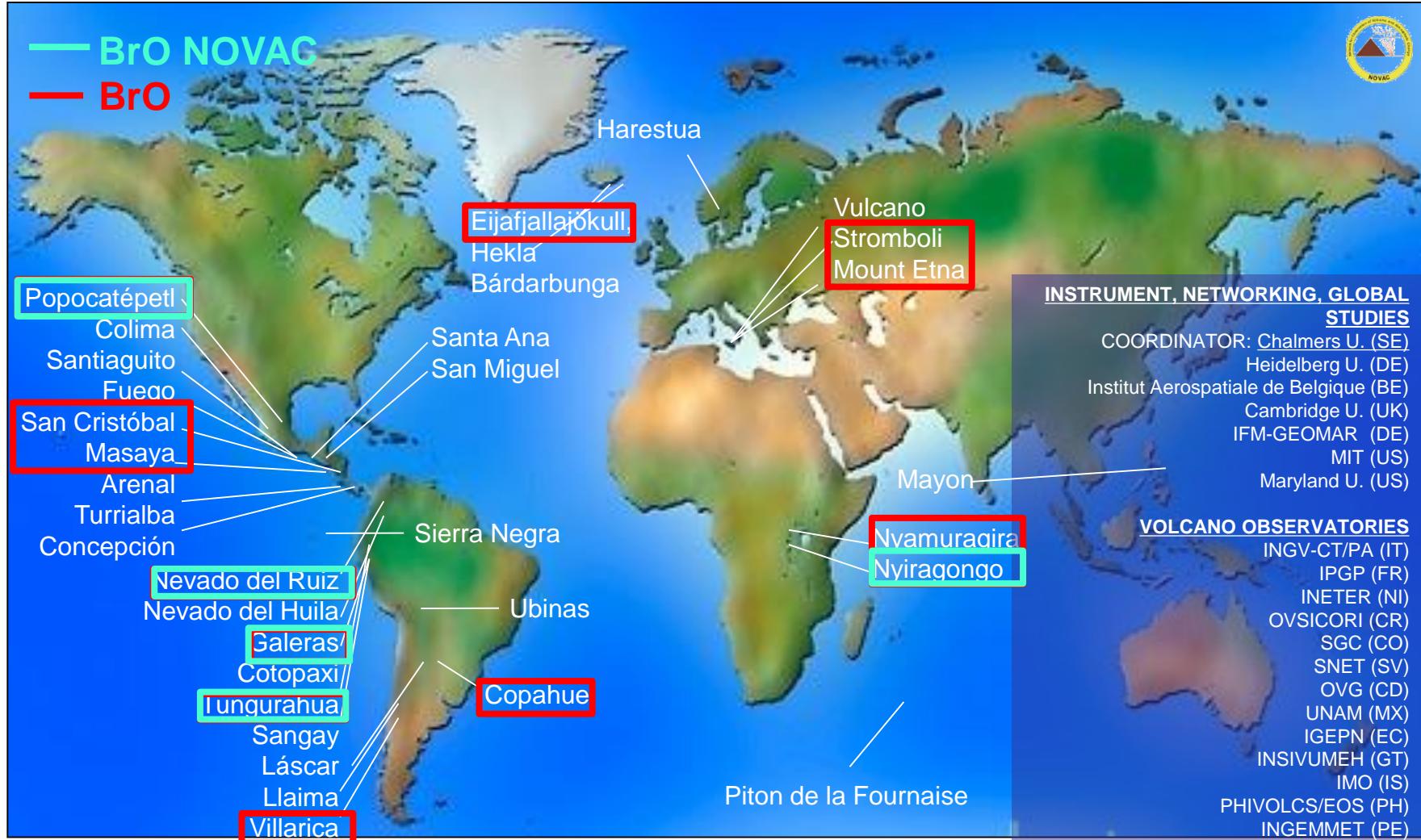
Lübcke, 2014

Preliminary results – Copahue, Argentina



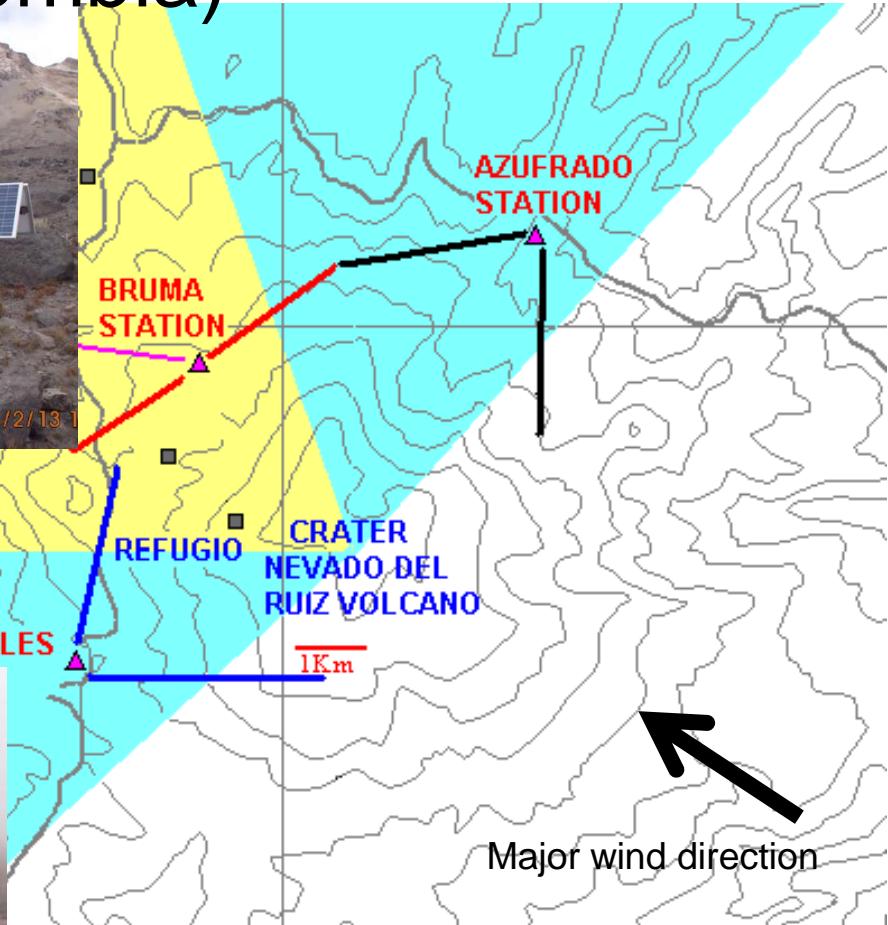
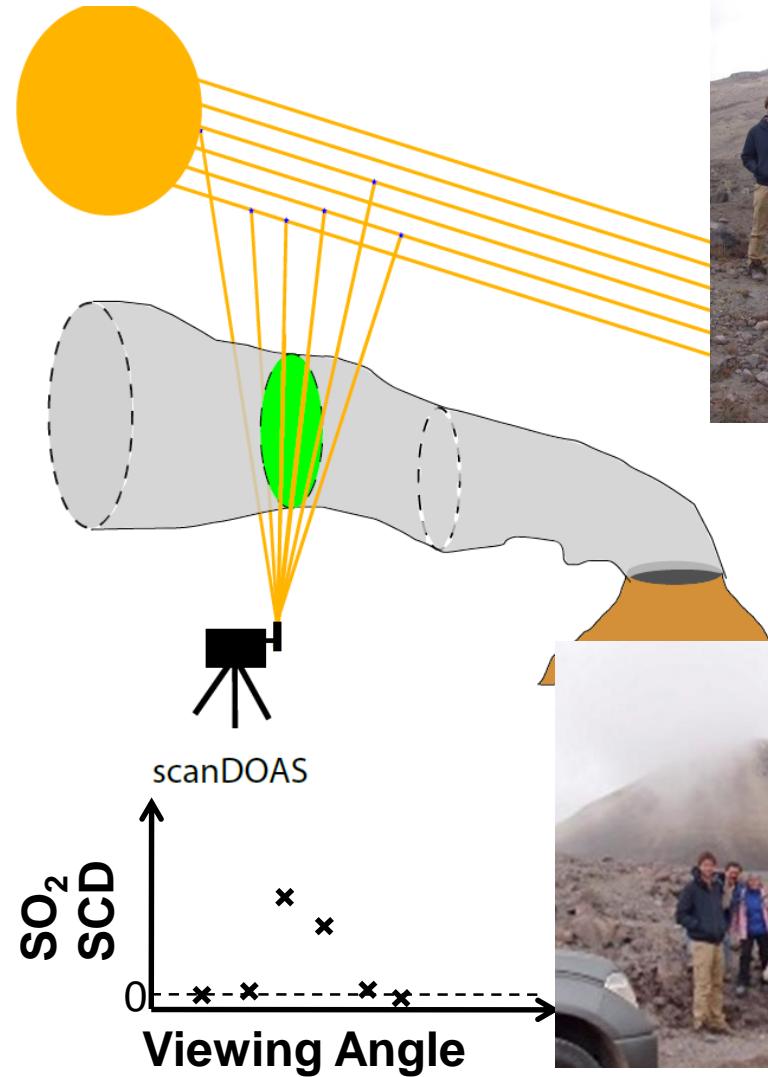


Global volcanic gas studies: NOVAC – the great opportunity





Example 1: The NOVAC instruments at Nevado del Ruiz (Colombia)



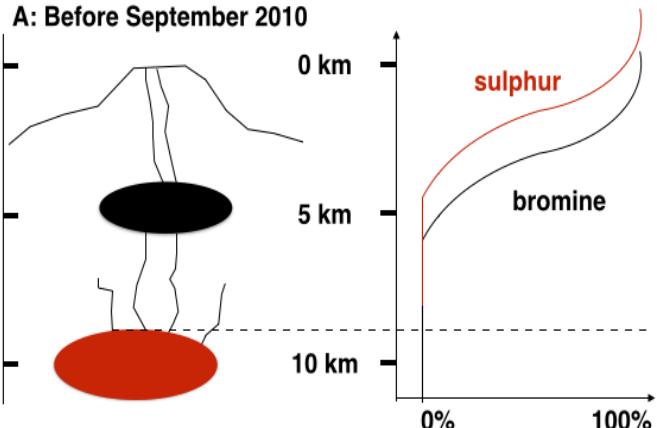
Robust, simple instruments
Measurements since Nov. 2009



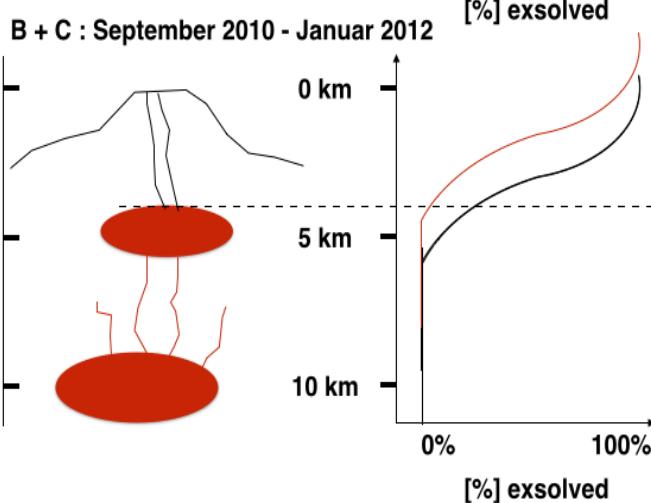
Possible interpretation of the BrO/SO₂ ratio



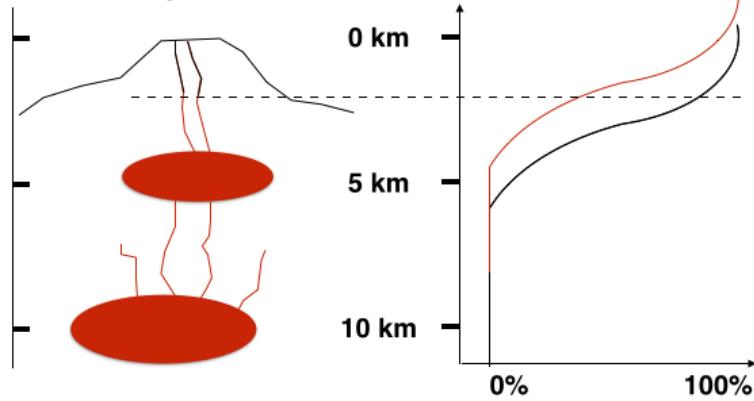
A: Before September 2010



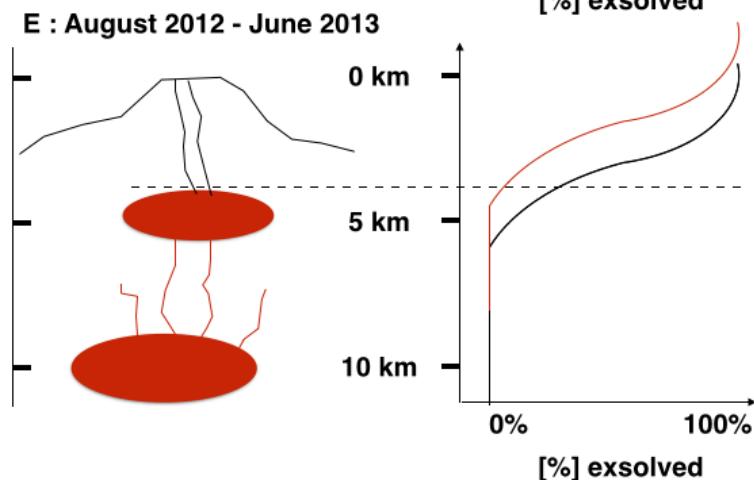
B + C : September 2010 - Januar 2012



D : February 2012 - June 2012



E : August 2012 - June 2013

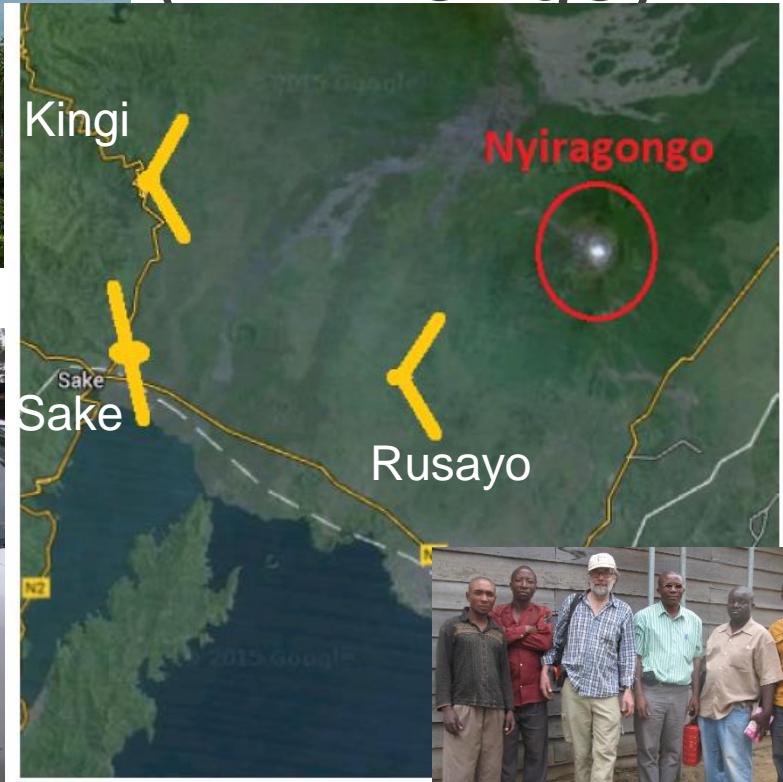
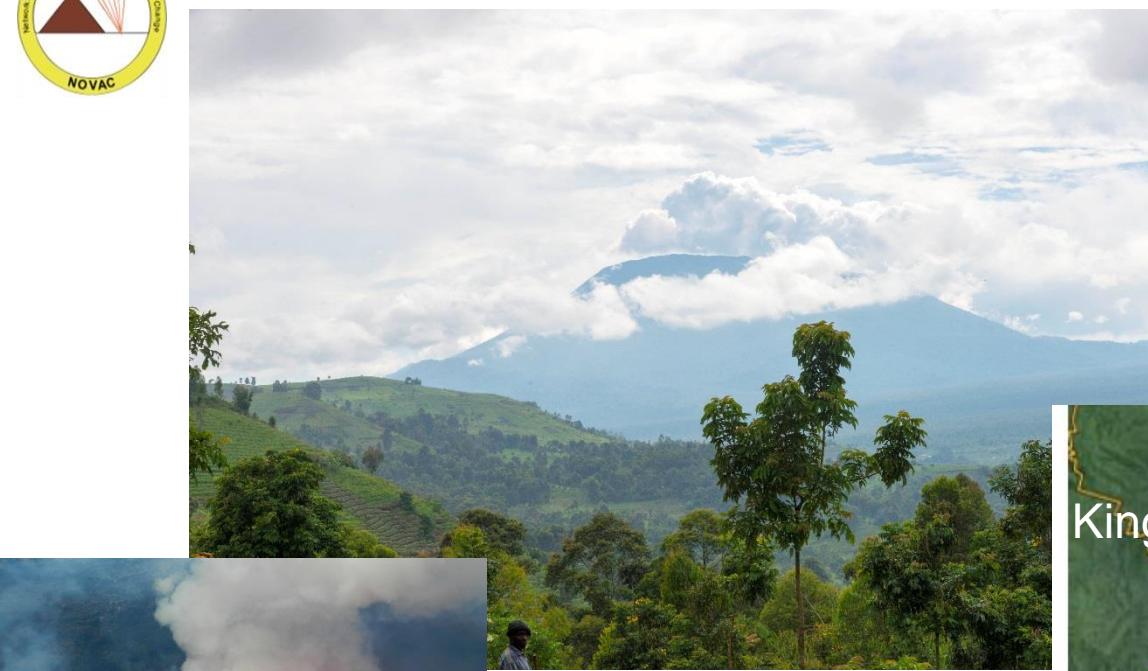


Lübcke et al., 2014

Questions and Problems:

- How much of bromine is transformed into BrO (atmospheric interest)
- Is the transformation factor constant ?
(how to measure total bromine?)
- Sensitivity to environmental and volcanic factors ?
- ...





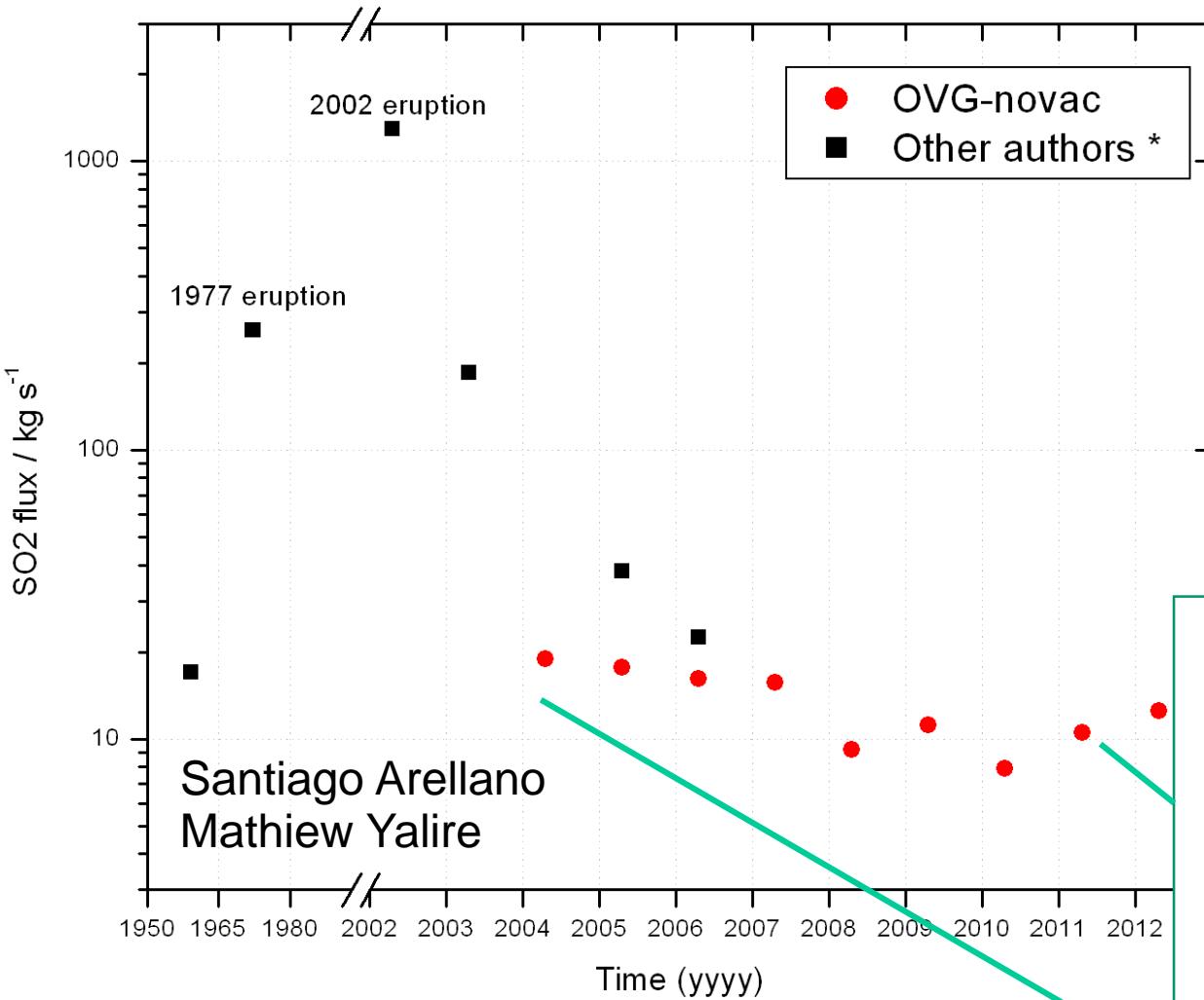
[Figure from Google Maps]

Example 2: Nyiragongo – Nyamulagira (DR Congo)

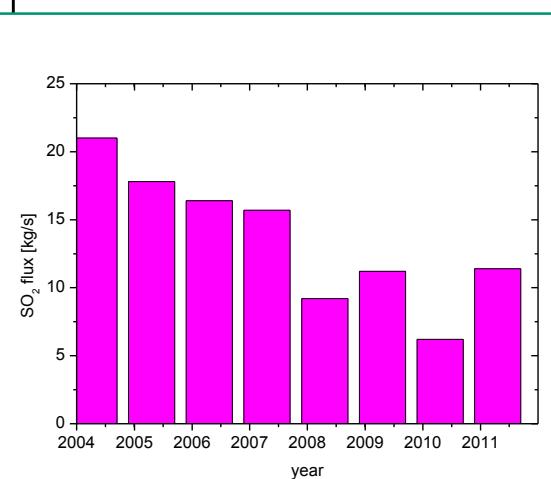




Recent and earlier SO₂ flux studies

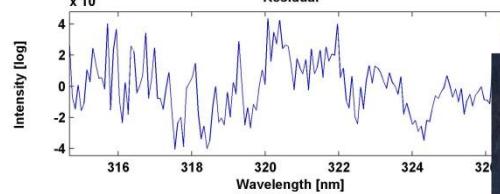
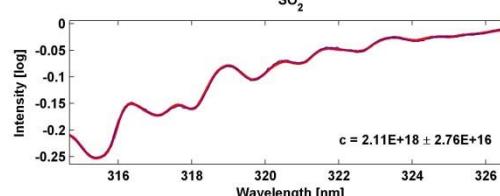
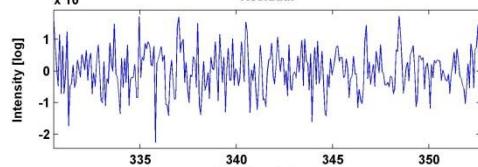
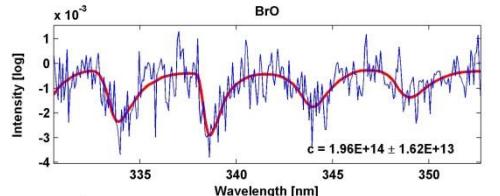


* Previous studies compiled by Sawyer et al. [2008]:
Delsemme [1960]; Le Guern [1987]; Carn [2004]; Galle et al. [2005]

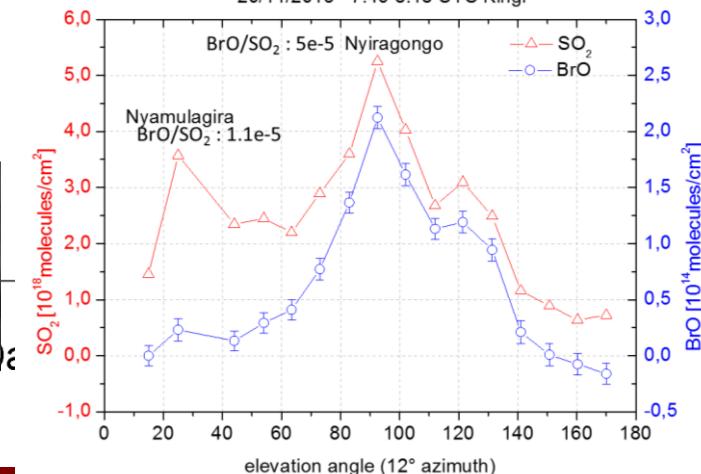
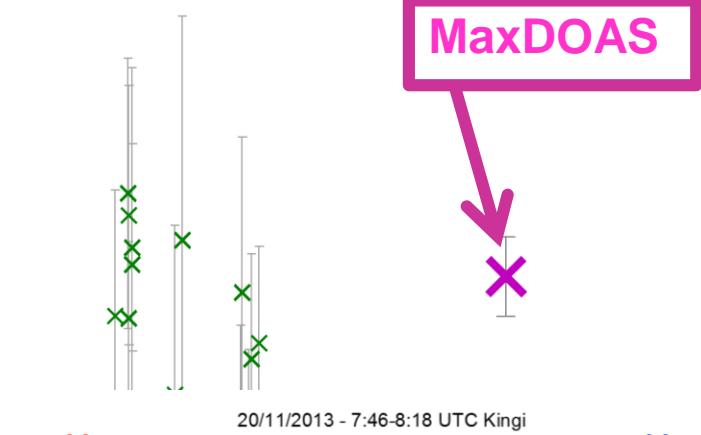
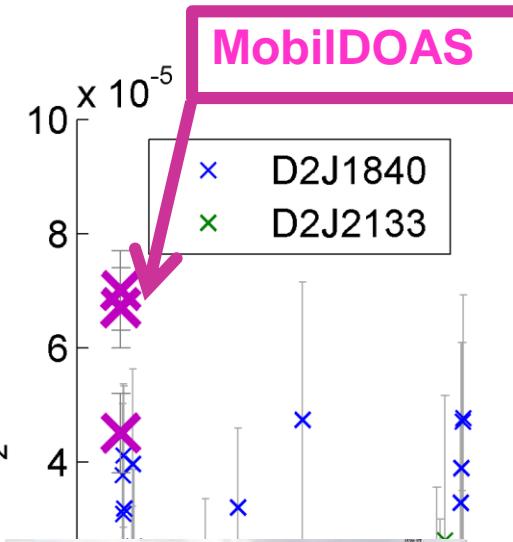




BrO/SO₂ ratios NOVAC Network - Nyiragongo

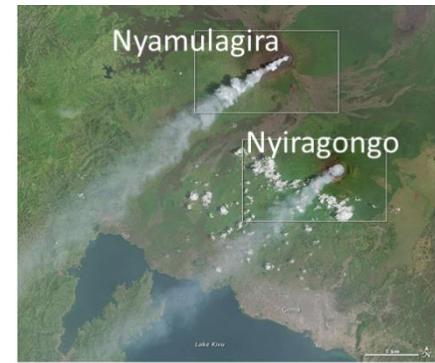
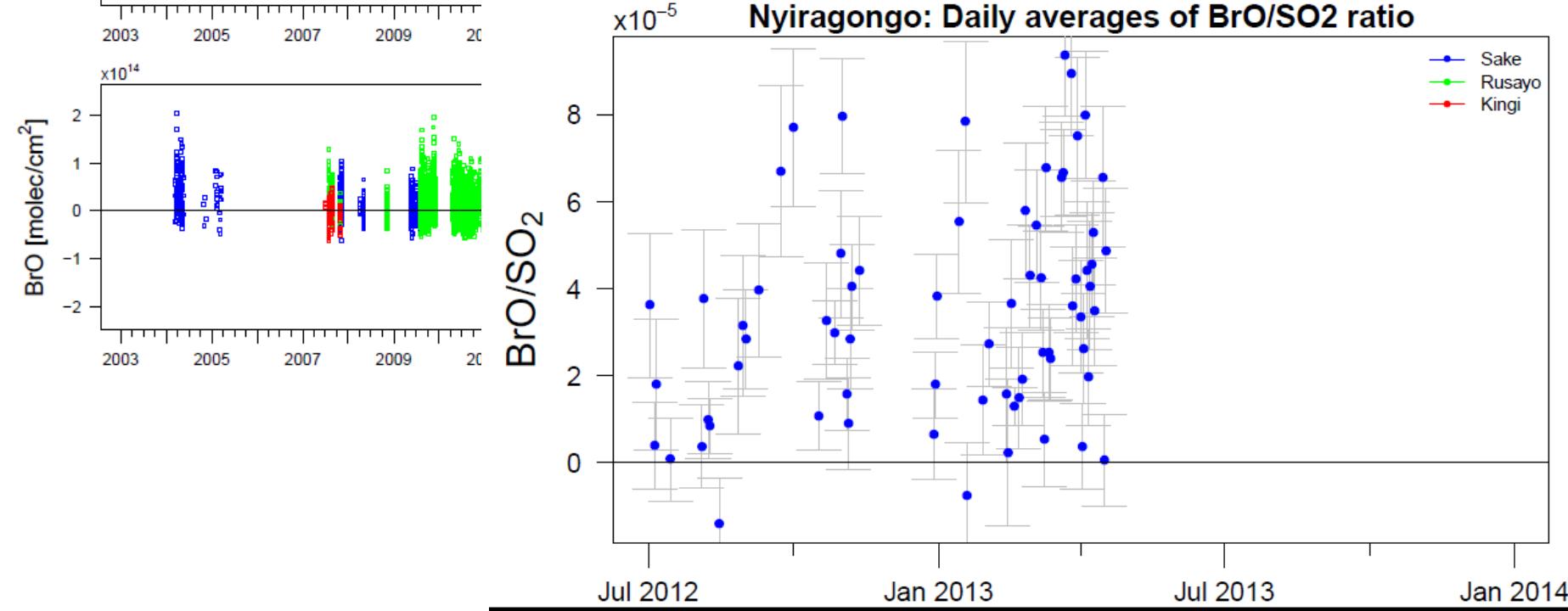
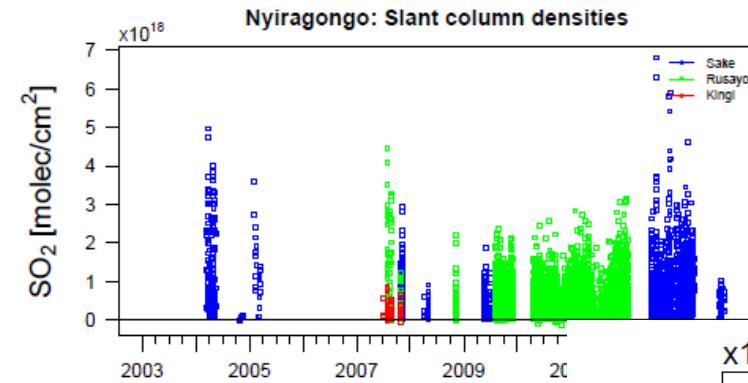


BrO/SO₂ ratio





BrO/SO₂ ratios - NOVAC Network Nyiragongo/Nyamulagira



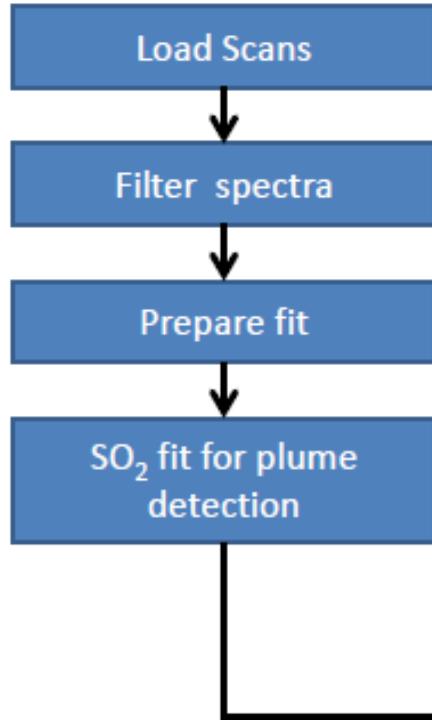


The BrO retrieval

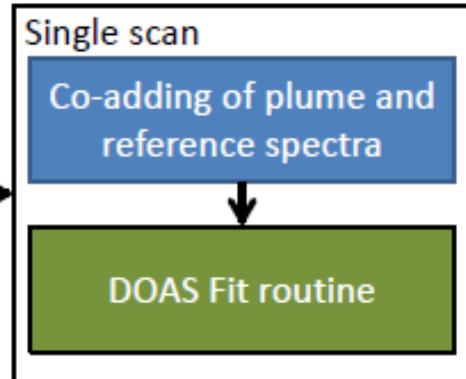
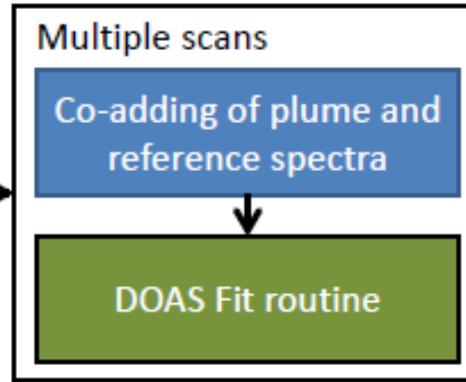
How to evaluate NOVAC data for BrO



Preparation of spectra

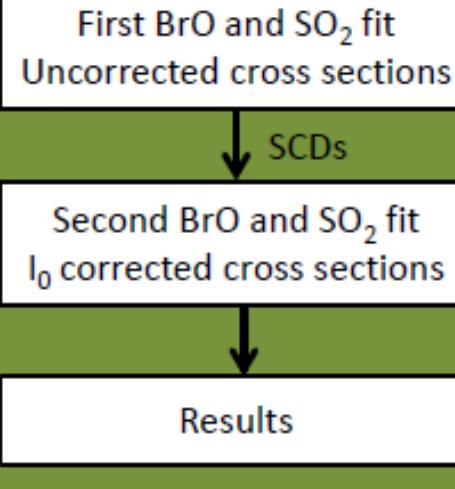


Collective plume and reference spectra



Results

DOAS Fit routine



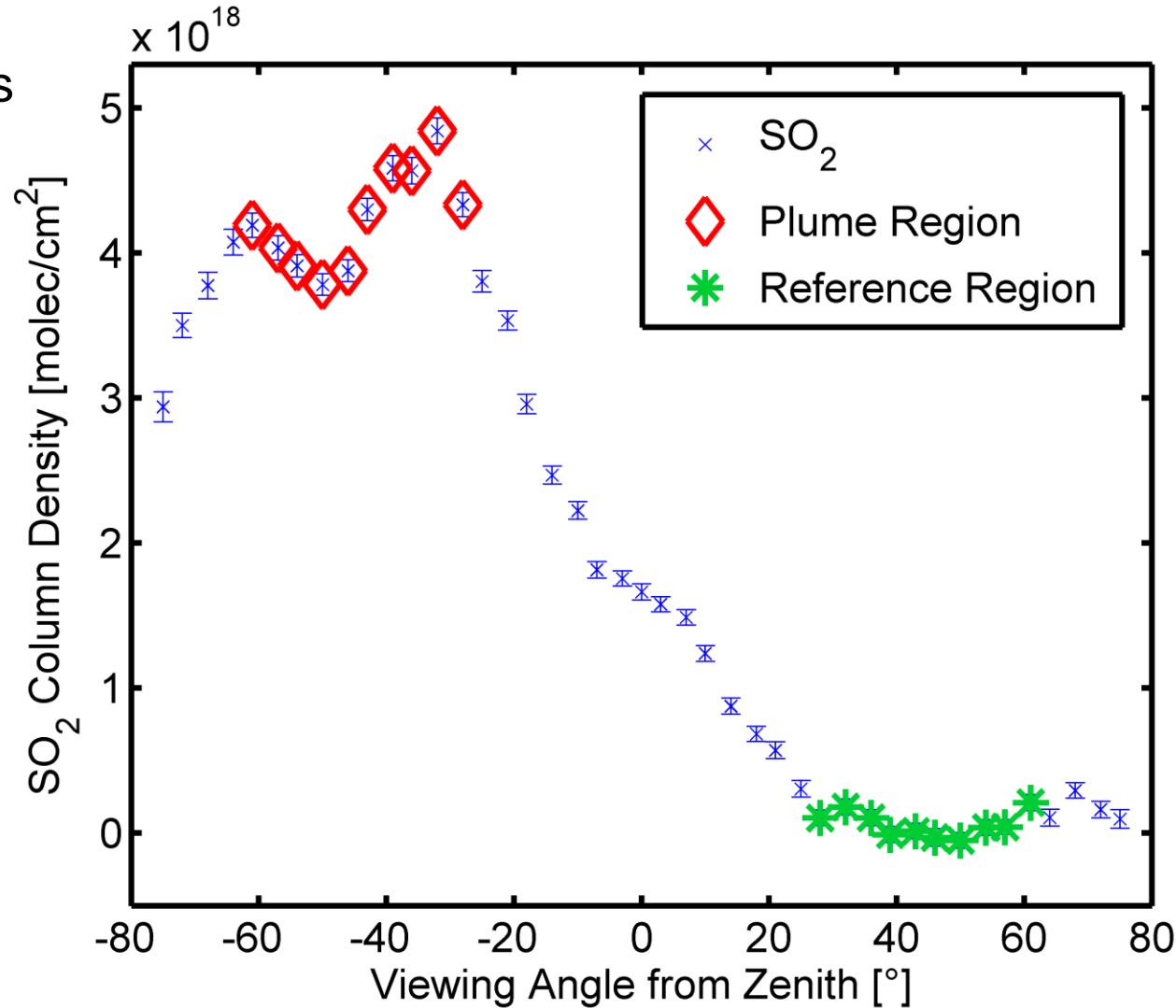
Co-addig necessary due to the lower optical density of BrO in volcanic plumes



Choosing the spectra

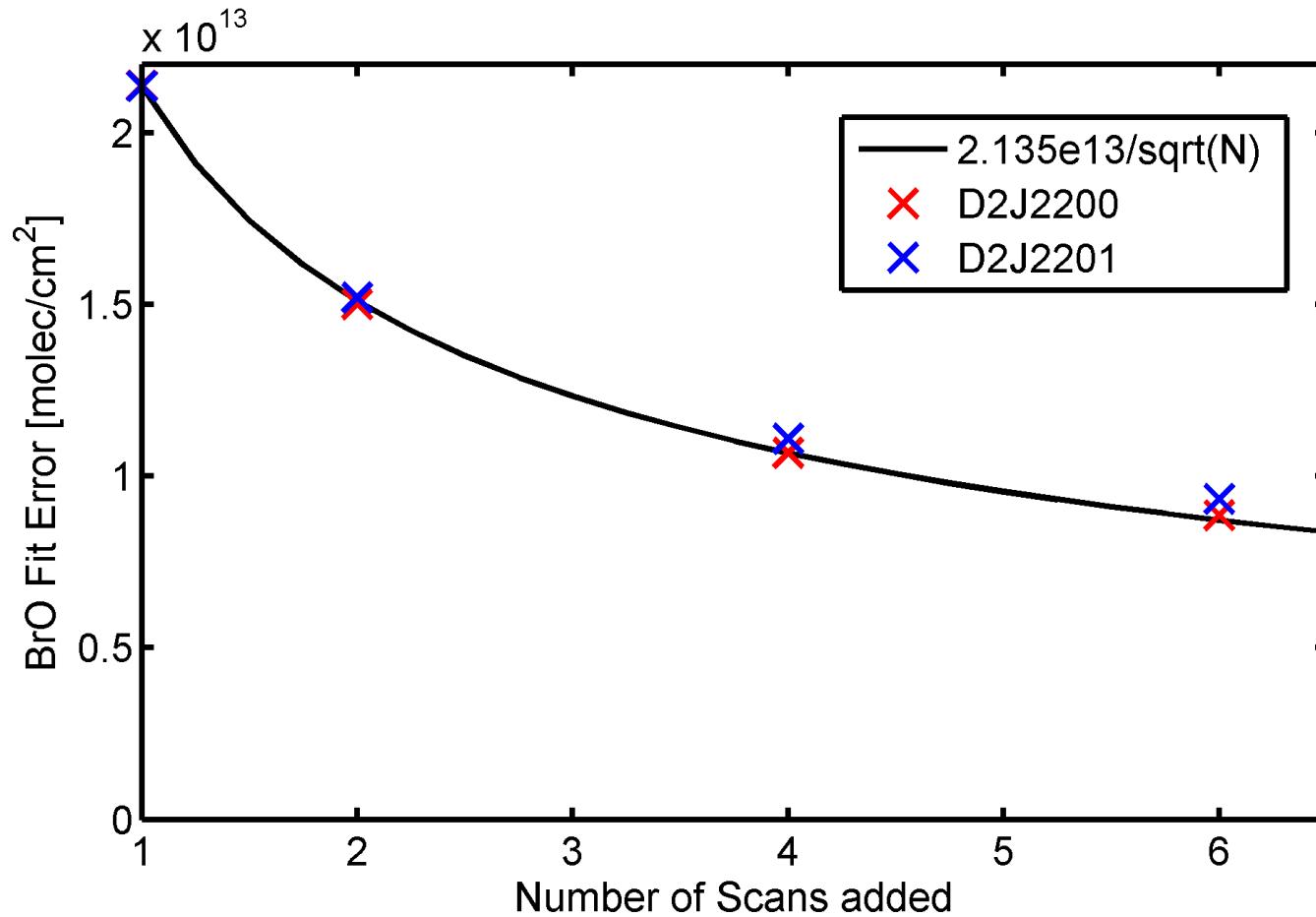


- DOAS evaluation needs a plume-free reference spectrum
- First step: zenith spectrum used as reference
- Second step: Ten consecutive spectra at different viewing angles were defined as reference and plume region to improve the signal to noise ratio





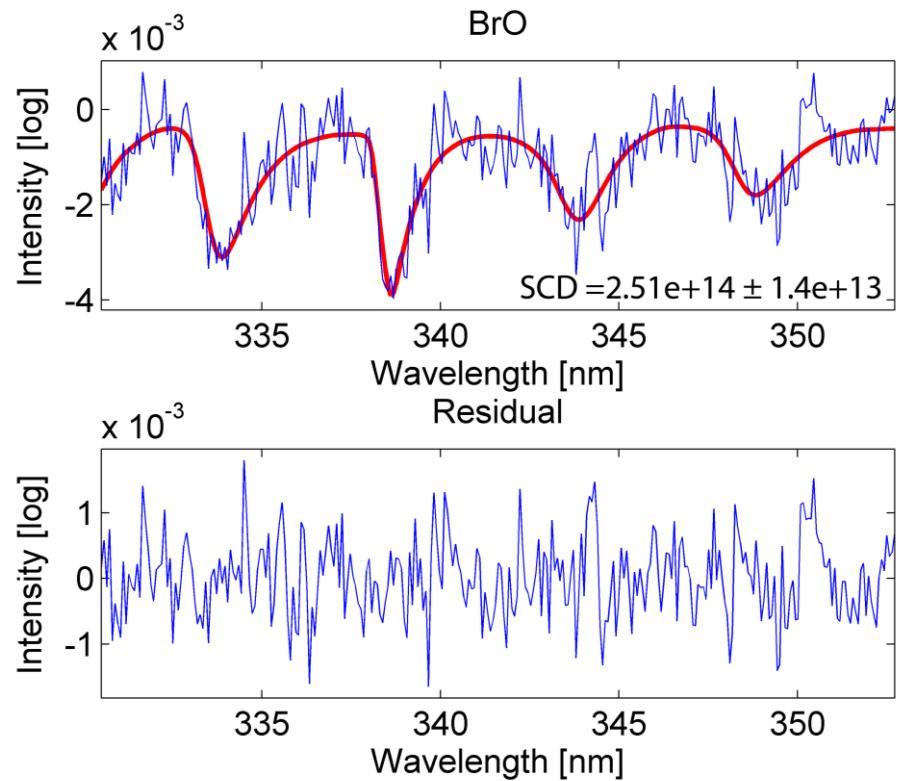
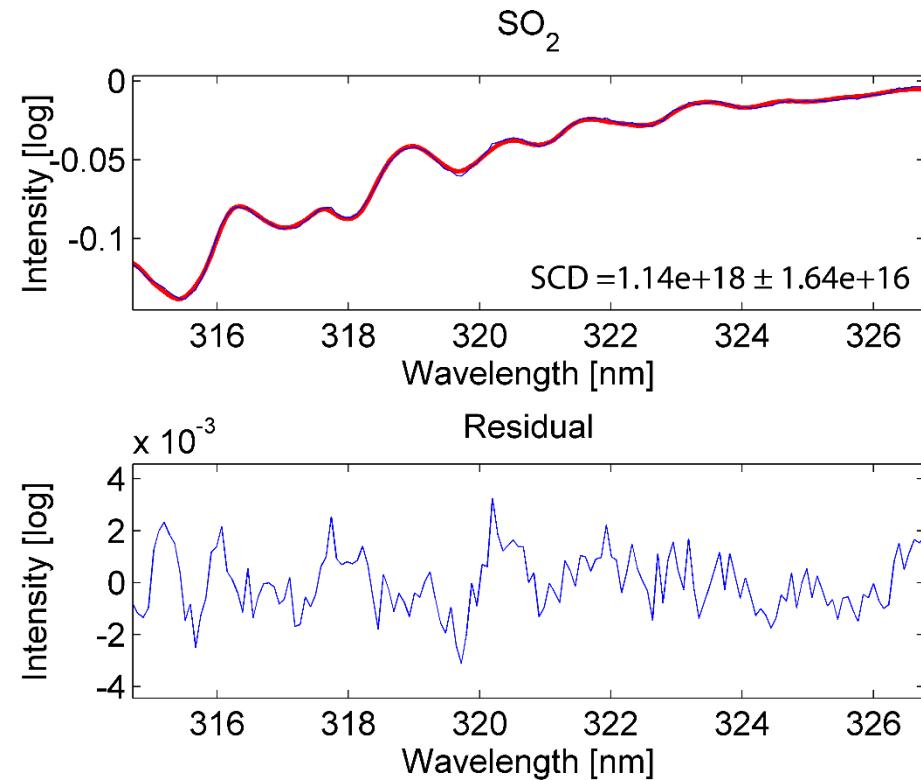
Improving signal to noise by averaging



- Adding spectra from several consecutive plume scans greatly improves the S/N ratio
- Fit error probably photon shot noise dominated
- Trade off between S/N and absolute signal & time resolution

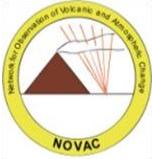


DOAS evaluation



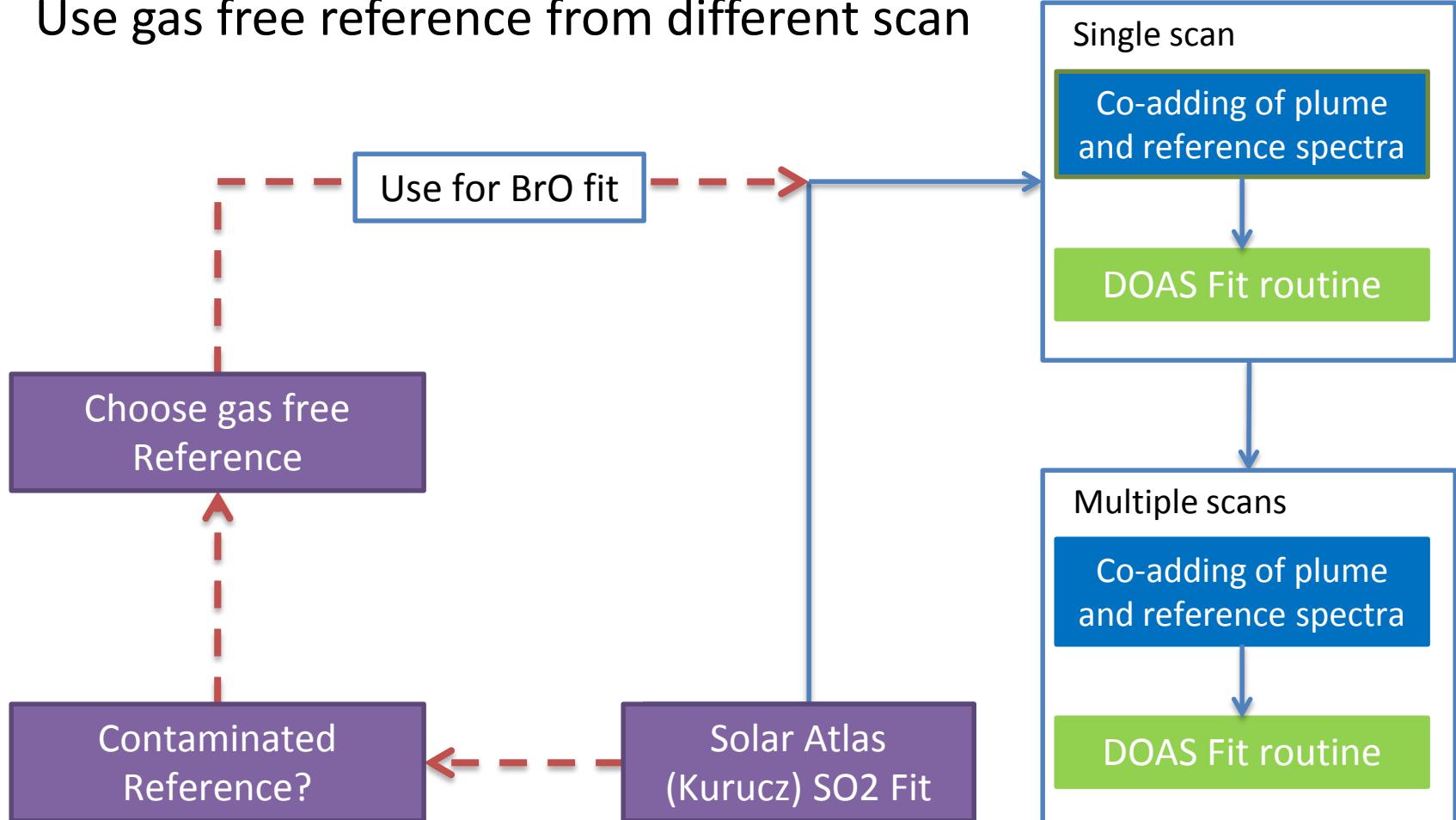
Evaluation range: 314.6 – 326.8 nm
Other spectra in the evaluation: O_3 ,
Ring spectrum

Evaluation range: 330.6 – 352.8 nm
Other spectra in the evaluation:
 SO_2 , O_3 , O_4 , NO_2 , CH_2O ,
Ring spectrum



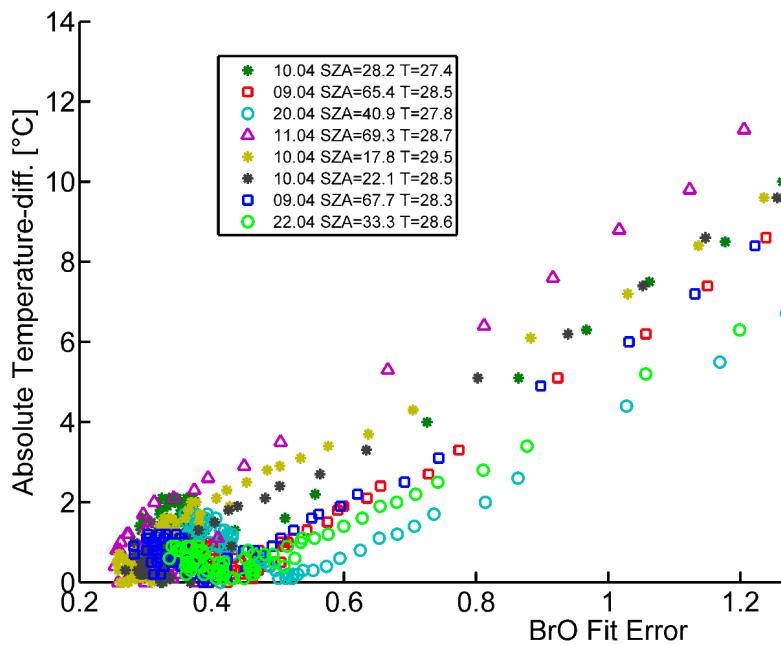
Improved Evaluation

- Use gas free reference from different scan





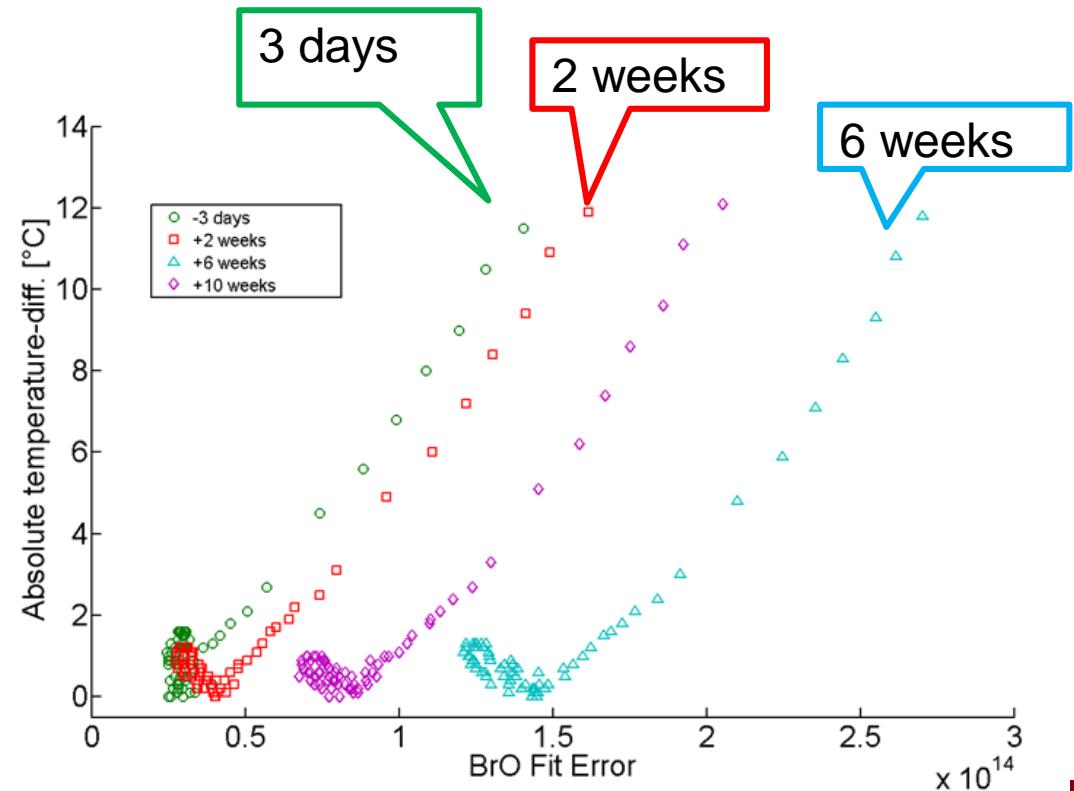
Temperature effects



Mean NOVAC fit error :
 $(2.086 \pm 0.313) \times 10^{13}$

Simon Wahrnach 2015

Changes over Time





Conclusions

- NOVAC can do more than SO₂ fluxes
- Spectra from NOVAC do have a sufficient quality for BrO evaluation
- And there is still more inside the spectra..... e.g. OCIO + ClO, H₂O

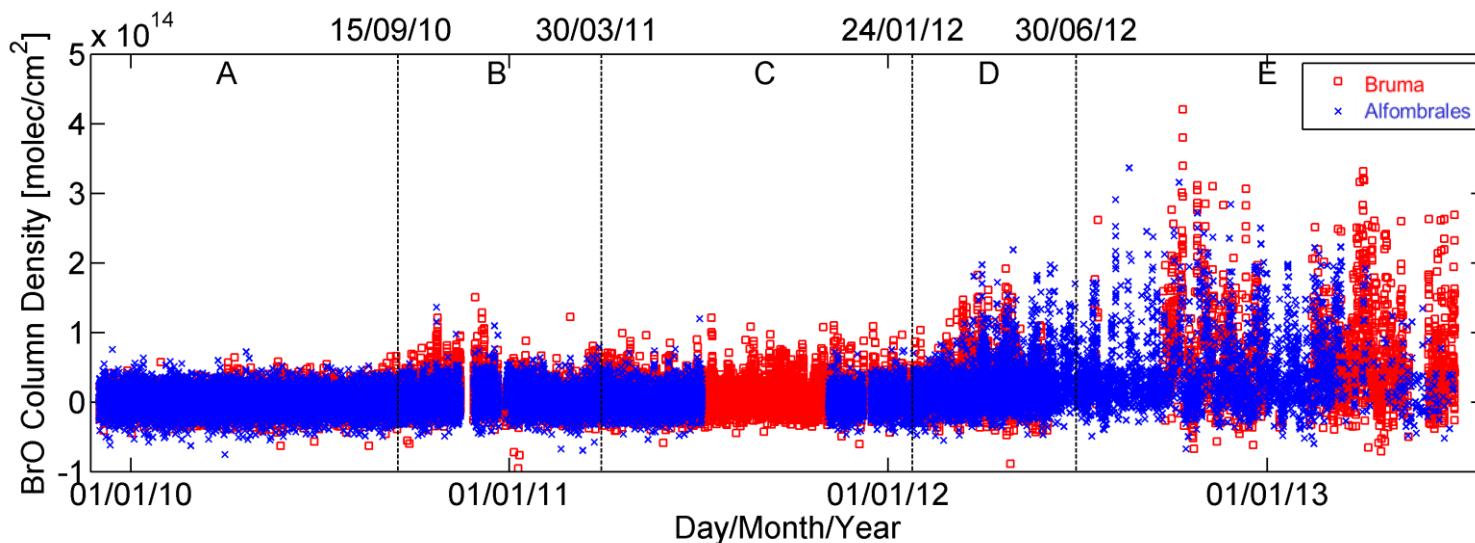
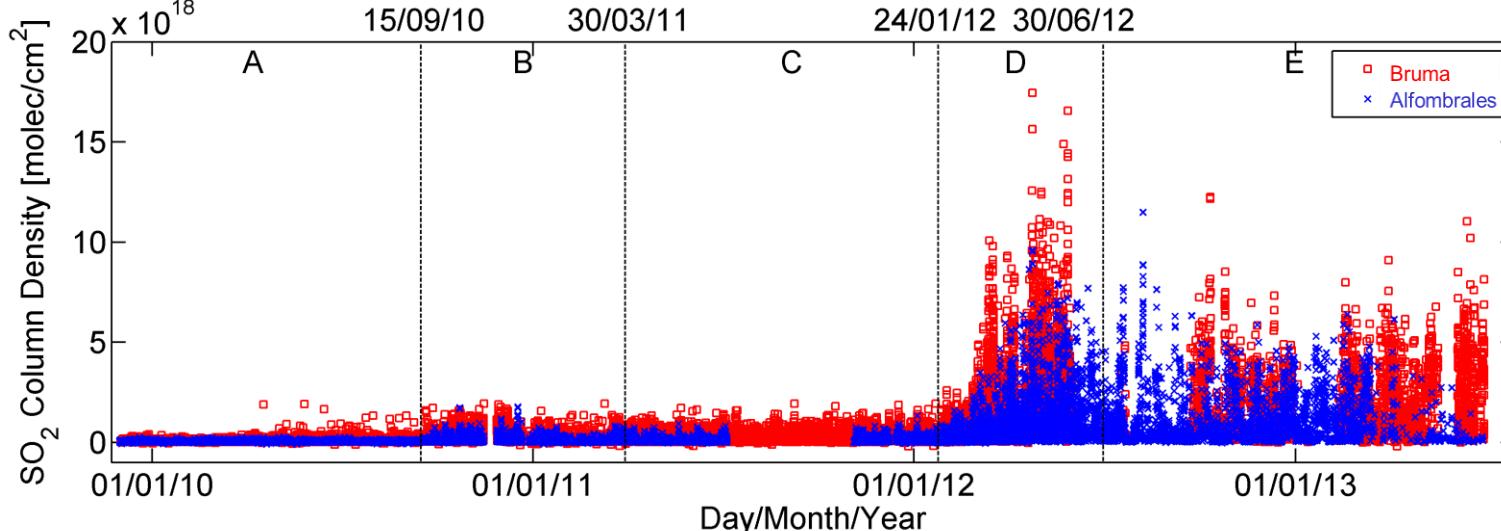


Outlook

- We work on improvements and automation of BrO/SO₂ evaluation
- Long term time-series of the BrO/SO₂ ratio for **all** volcanoes in the NOVAC network
- Studies on other parameters possible e.g OCIO, in particular useful to study atmospheric chemistry and impacts
- Further instrumental developments e.g CO₂ remote sensing



SO₂ and BrO SCD time series from Nevado del Ruiz



Lübcke
et al.,
2014