Chemistry of SO_2 in tropospheric volcanic plumes

by

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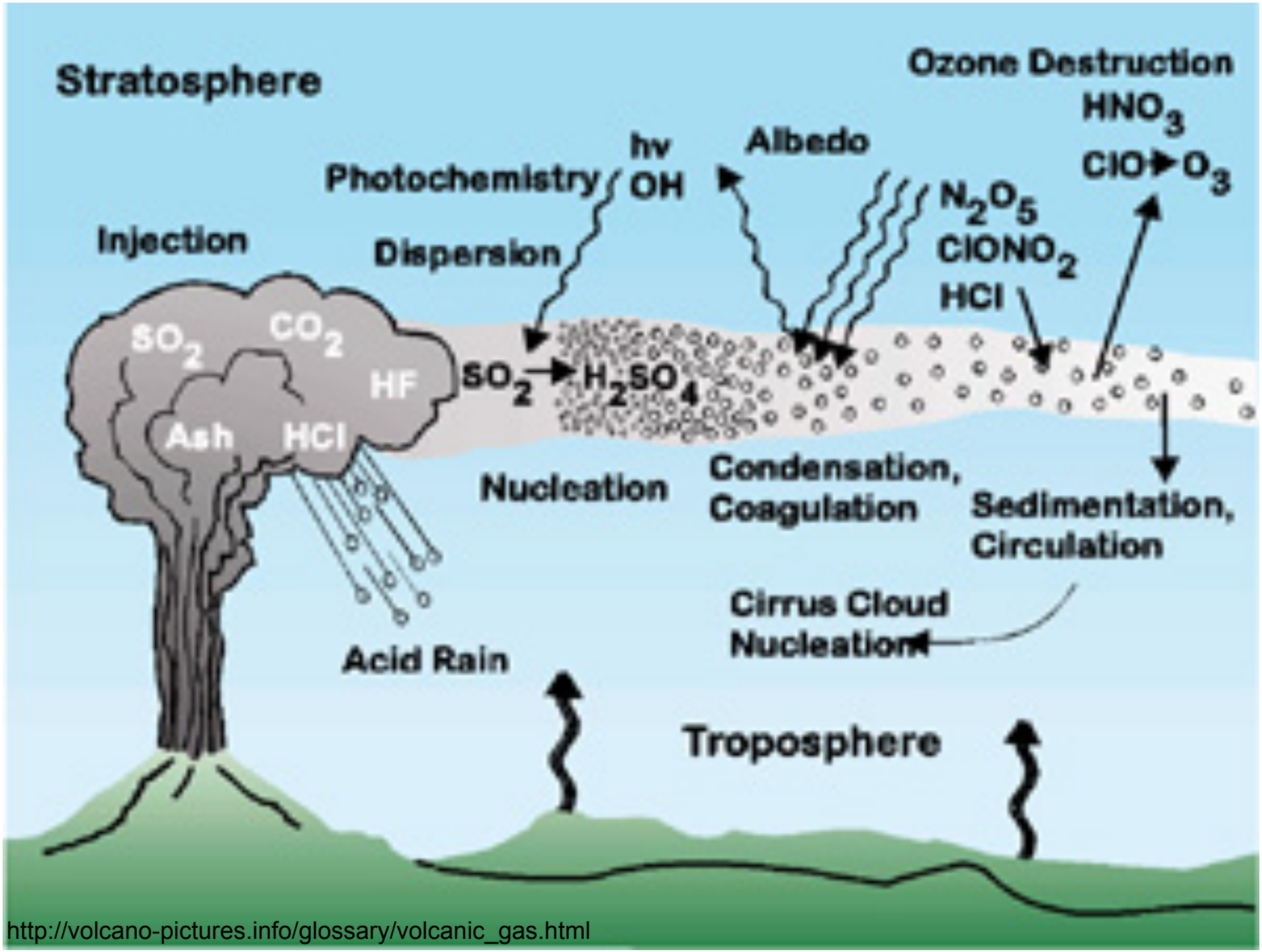
Photo: L. Rodriguez



http://volcano-pictures.info/glossary/volcanic_gas.html

Introduction

- SO_2 emission rates are commonly measured using ground-based spectroscopic techniques, a few km downwind from the vent and km from the plume
  - This allows time for SO_2 to interact with other volcanogenic gases, particles and droplets of volcanogenic and/or meteoric origin, as well as atmospheric gases and aerosols, and for the possibility of attenuation of the SO_2 signal by airlight or scattering.
  - Measured SO_2 flux will not usually represent the at-source SO_2 emission rate

Cont. Introduction

- An important SO_2 depletion process is the conversion of SO_2 to SO_4^{-2} (sulfate aerosols)
  - SO_2 loss rates ranging from 10^{-7} to 10^{-3} s^{-1} have been estimated for tropospheric volcanic plumes at various altitudes.
- Reactions SO_2 can undergo, leading to formation of particulate sulfate: gas-phase homogeneous (slower: days to weeks), aqueous-phase (hours), heterogeneous reactions on the surface of solids.

Cont. Introduction

- **Local meteorology** affects the fate of tropospheric plumes both directly, through dispersion and transport downwind, and indirectly, through factors such as humidity, T, amount of sunlight reaching the plume, cloud cover, fog, and precipitation.
- Other factors affecting reactions: **aerosol concentration and pH, availability of oxidants (e.g. OH, O_3, H_2O_2)**

Methodology

- SO_2 fluxes are used to obtain loss rates

  k, $\phi_{t1}=\phi_{t2}e^{k1(t2-t1)}$

  where ϕ_t represents an SO_2 flux at a given time t

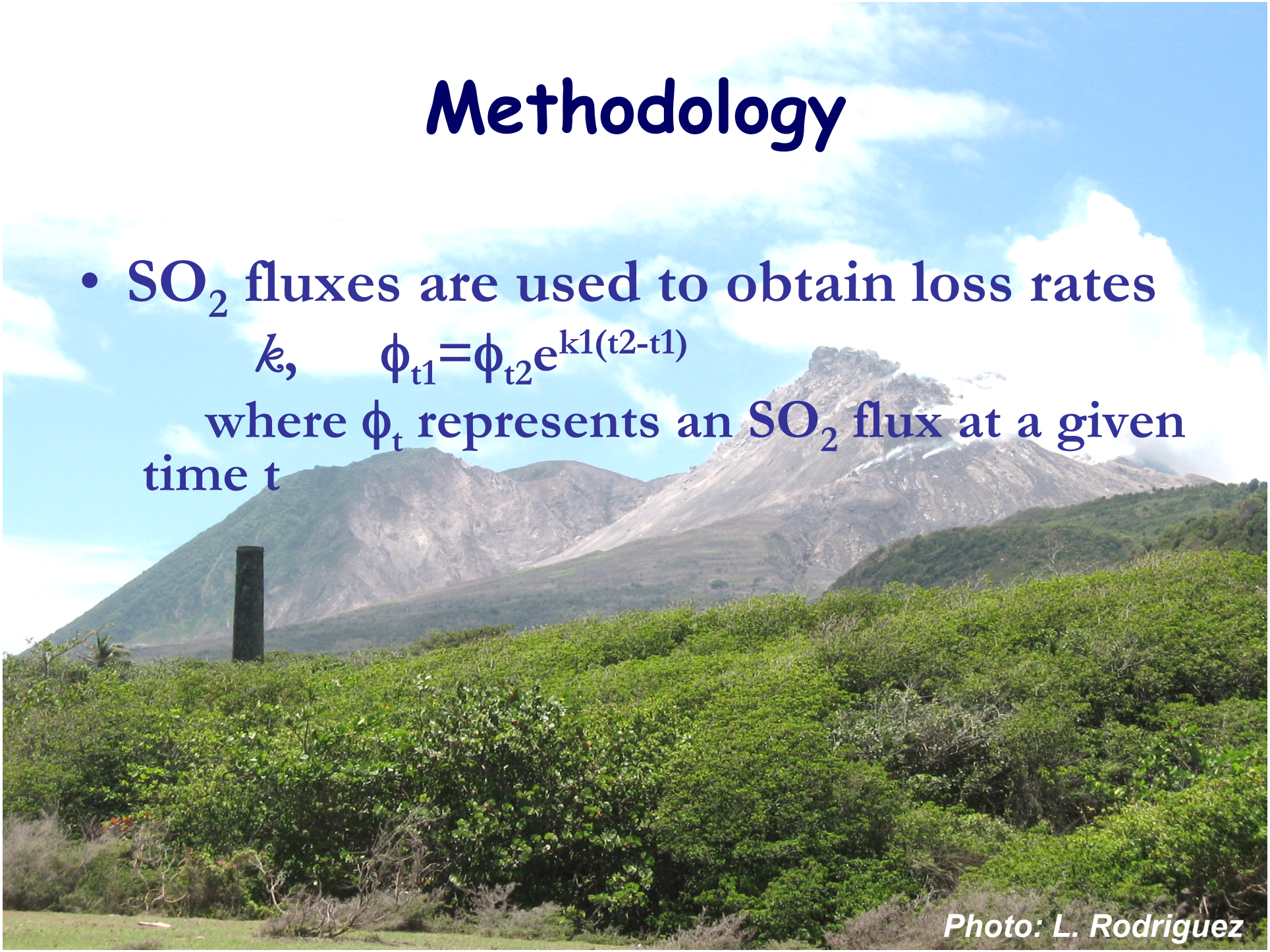


Photo: L. Rodriguez

Why?

- Uncertainties in near-source plume chemistry can complicate interpretations of volcanic activity and hazards, petrology, global emission rates* and climatic effects of emissions.

- Consideration of variable SO_2 depletion rates in volcanic plumes could contribute to future modeling of global S sources and distributions, as well as relative contributions.

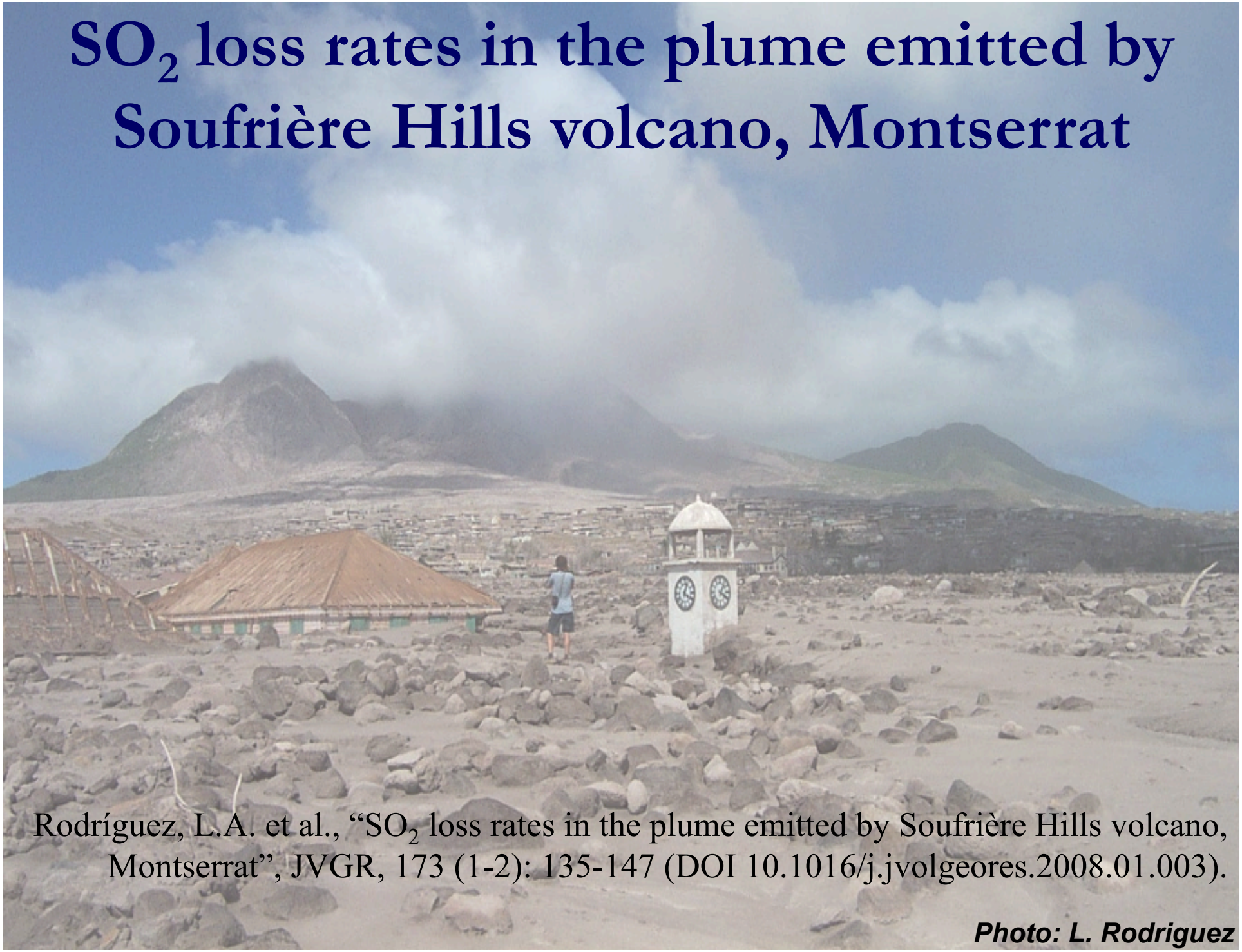
Why?

- Volcanic sulfate aerosols:
  - injected into the free troposphere, where removal processes are slow
  - uncertainties in their contribution are important for climate change studies
  - cool the climate due to backscattering of sunlight and through an increase in cloud reflectivity and residence time
  - can absorb outgoing LW terrestrial radiation
- 18-40% of the global tropospheric sulfate burden is volcanogenic

Previous Work

- Eatough et al., 1994
  - Anthropogenic emissions of SO_2 and chemistry of the conversion
- Thornton et al., 1996
  - Measurements in remote marine areas
- Oppenheimer et al., 1998
  - SHV measurements (1996)
- Horrocks et al., 2003
  - FTIR Masaya – negligible loss
- McGonigle et al., 2004
  - Depletion rates at Masaya – negligible loss
- Nadeau and Williams-Jones, 2009
  - Depletion rates at Masaya – 33-50% less @15 km away: conversion negligible, probably caused by dilution of plume by greater wind speeds at different altitudes. Apparent loss.

SO_2 loss rates in the plume emitted by Soufrière Hills volcano, Montserrat



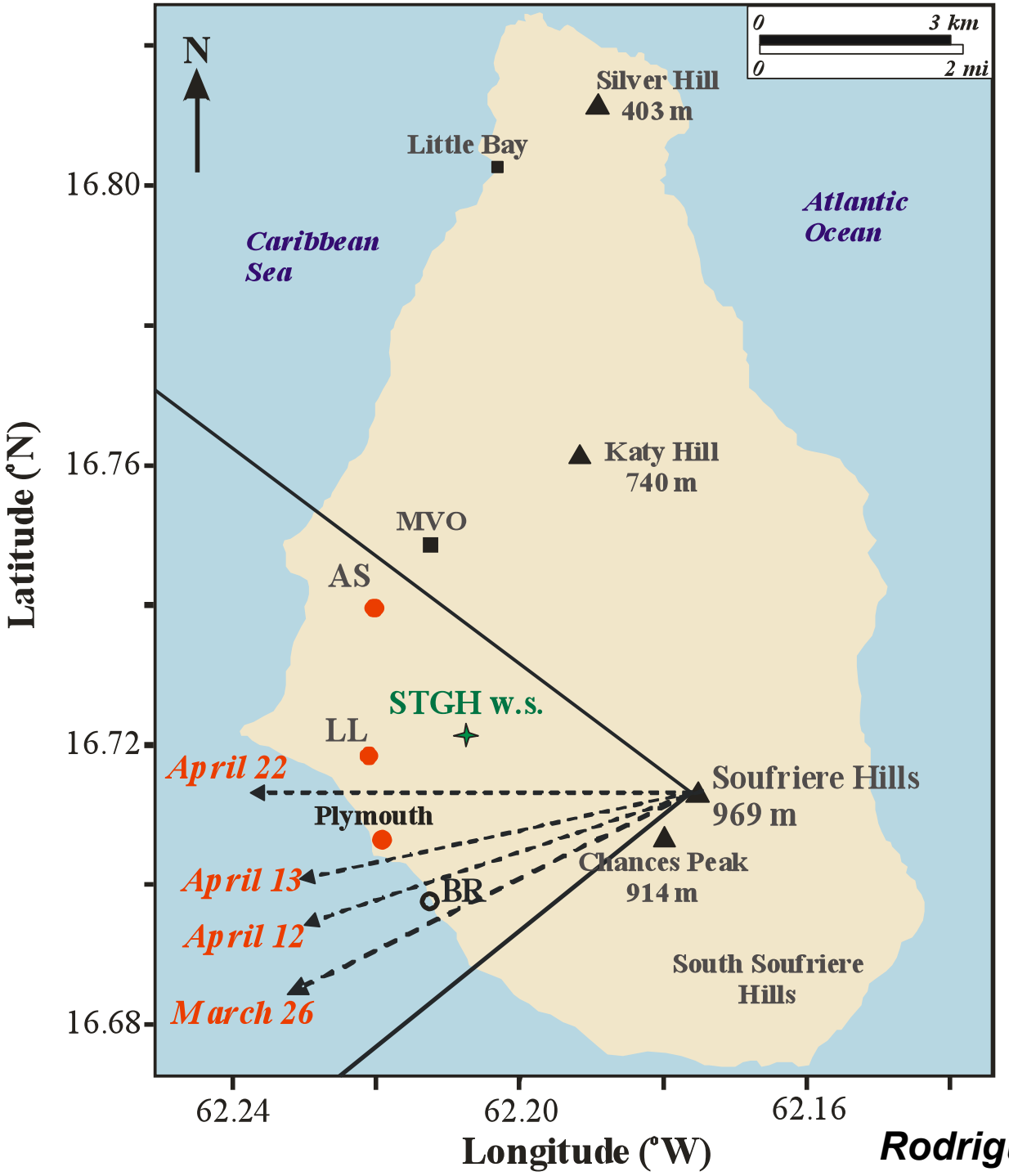
Rodríguez, L.A. et al., "SO_2 loss rates in the plume emitted by Soufrière Hills volcano, Montserrat", JVGR, 173 (1-2): 135-147 (DOI 10.1016/j.jvolgeores.2008.01.003).

Photo: L. Rodriguez

Objectives

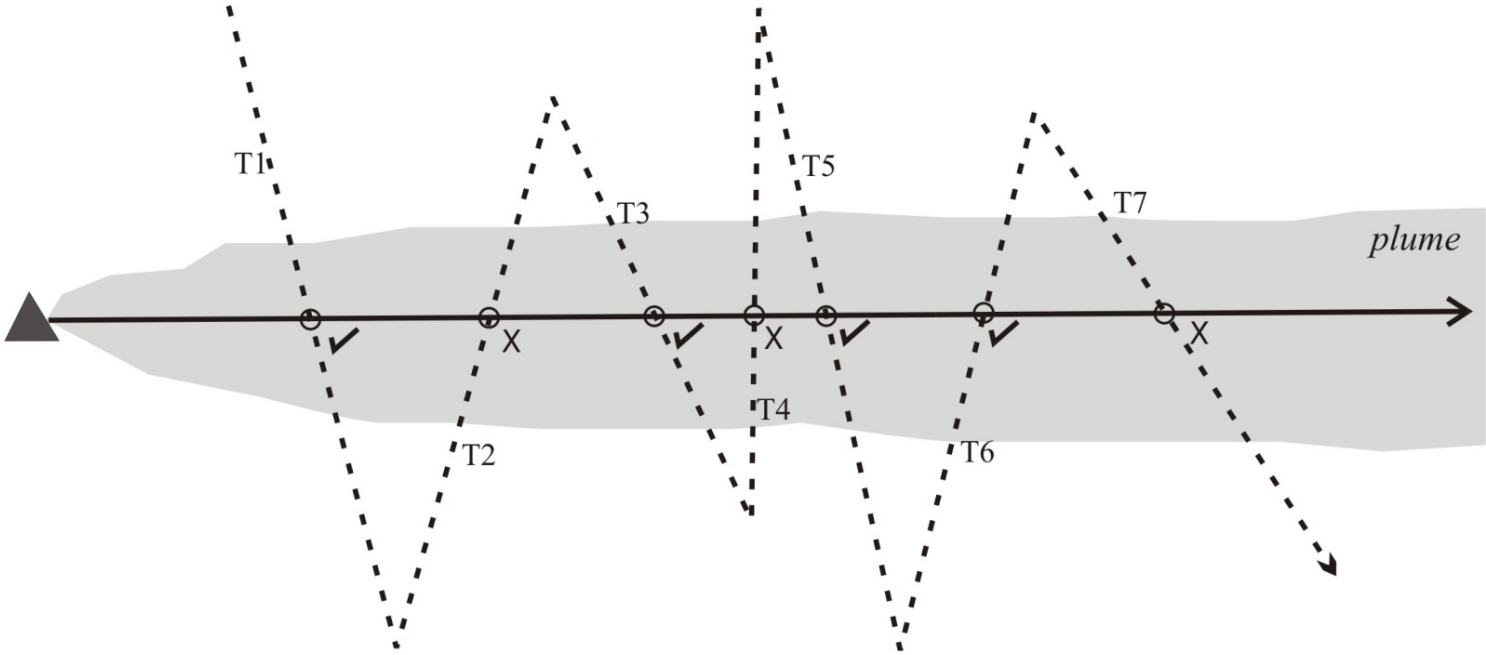
- Quantify SO_2 depletion rates in volcanic plumes injected into the boundary layer, from tropical low altitude volcanoes in a humid environment (typical of ~20% of active volcanoes worldwide), using ground-based remote sensing techniques

- SO_2 fluxes were measured near to the eruptive vent and at various distances downwind of the Soufrière Hills volcano (SHV)



Rodriguez et al., 2008

Plume tracking to follow a plume portion downwind



▲ Vent

→ Plume azimuth

- - → Helicopter track

○ Intersections between helicopter track and plume azimuth

Tx Traverse number

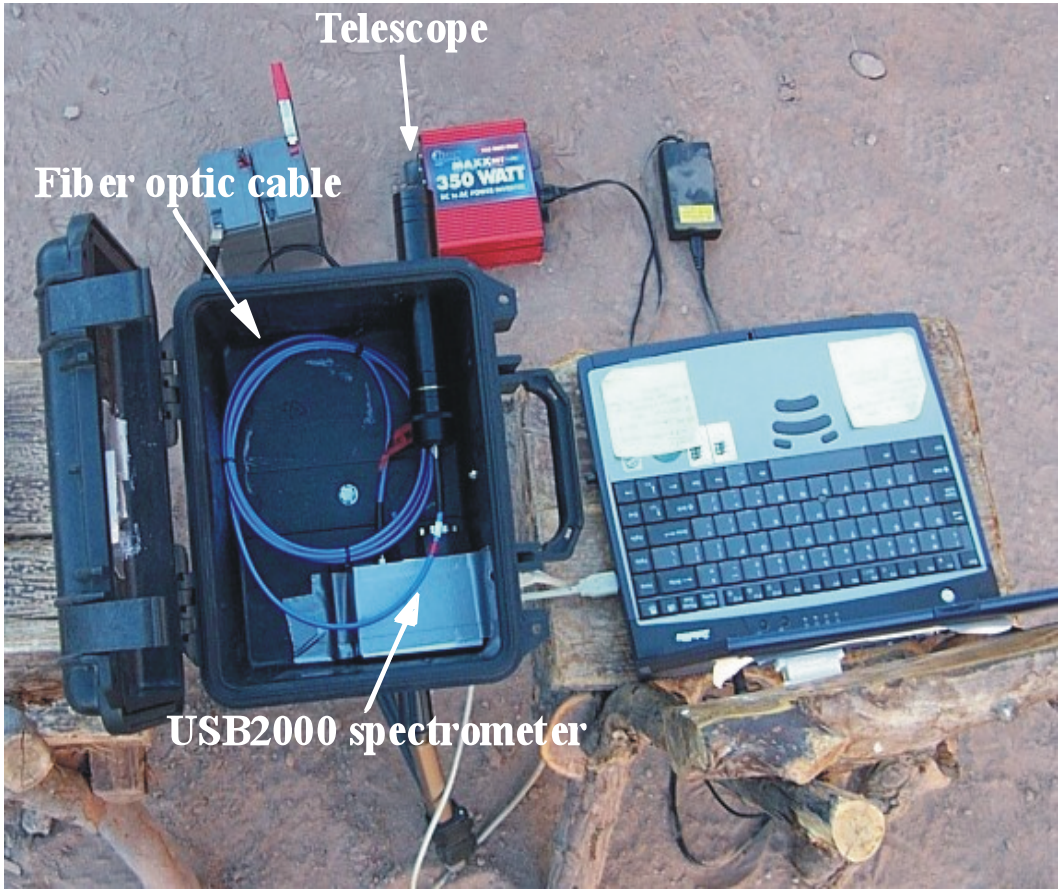
✔ SO_2 fluxes used to calculate loss rates for a plume portion traveling from t1

X SO_2 fluxes that did not follow criteria and were not used for loss rate calculation

Rodriguez et al., 2008

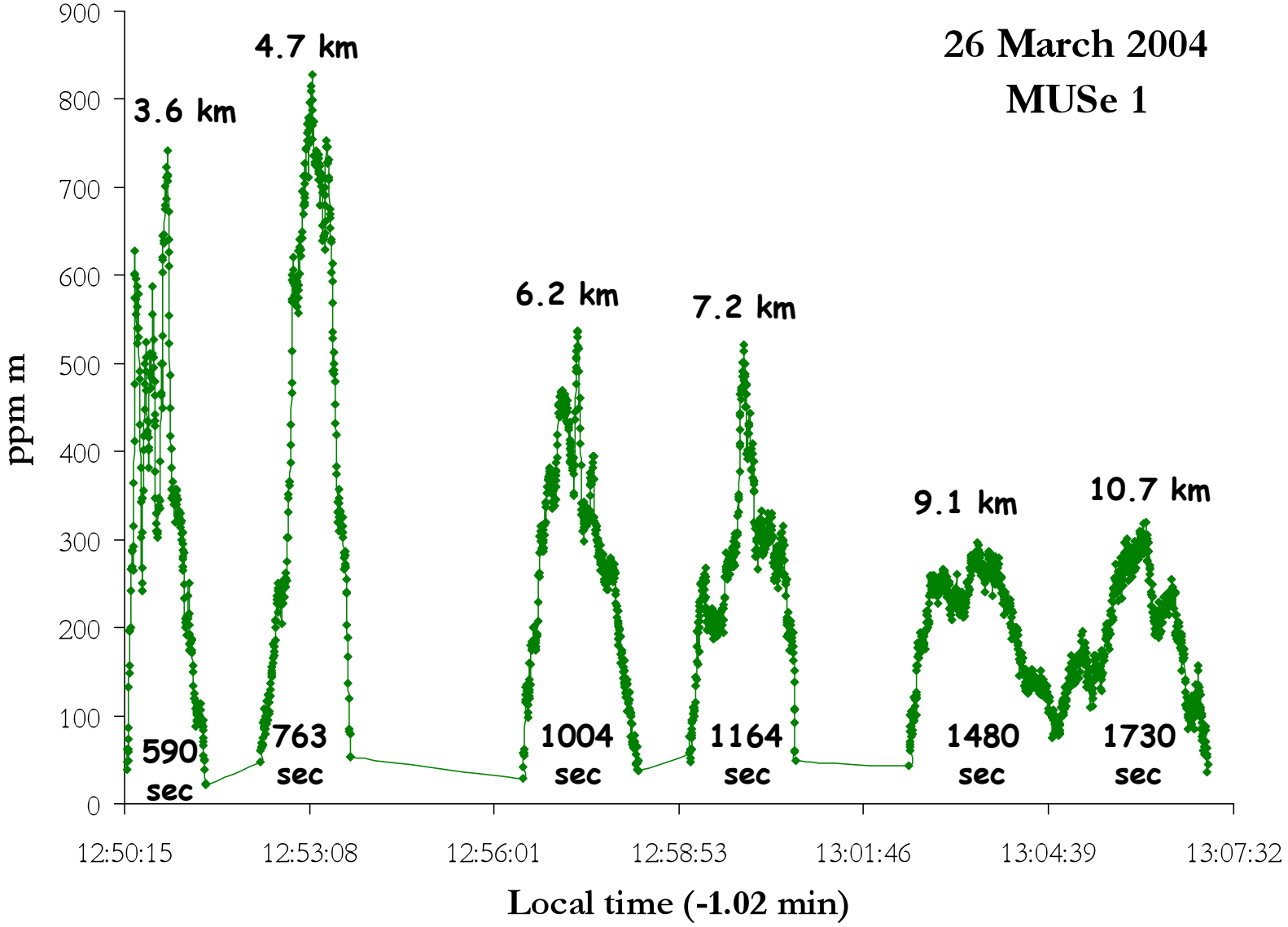
Equipment: (a) Mini-UV spectrometer (MUSe), optical assembly and laptop computer used for measurements. (b) Telescope setup

(a)



(b)

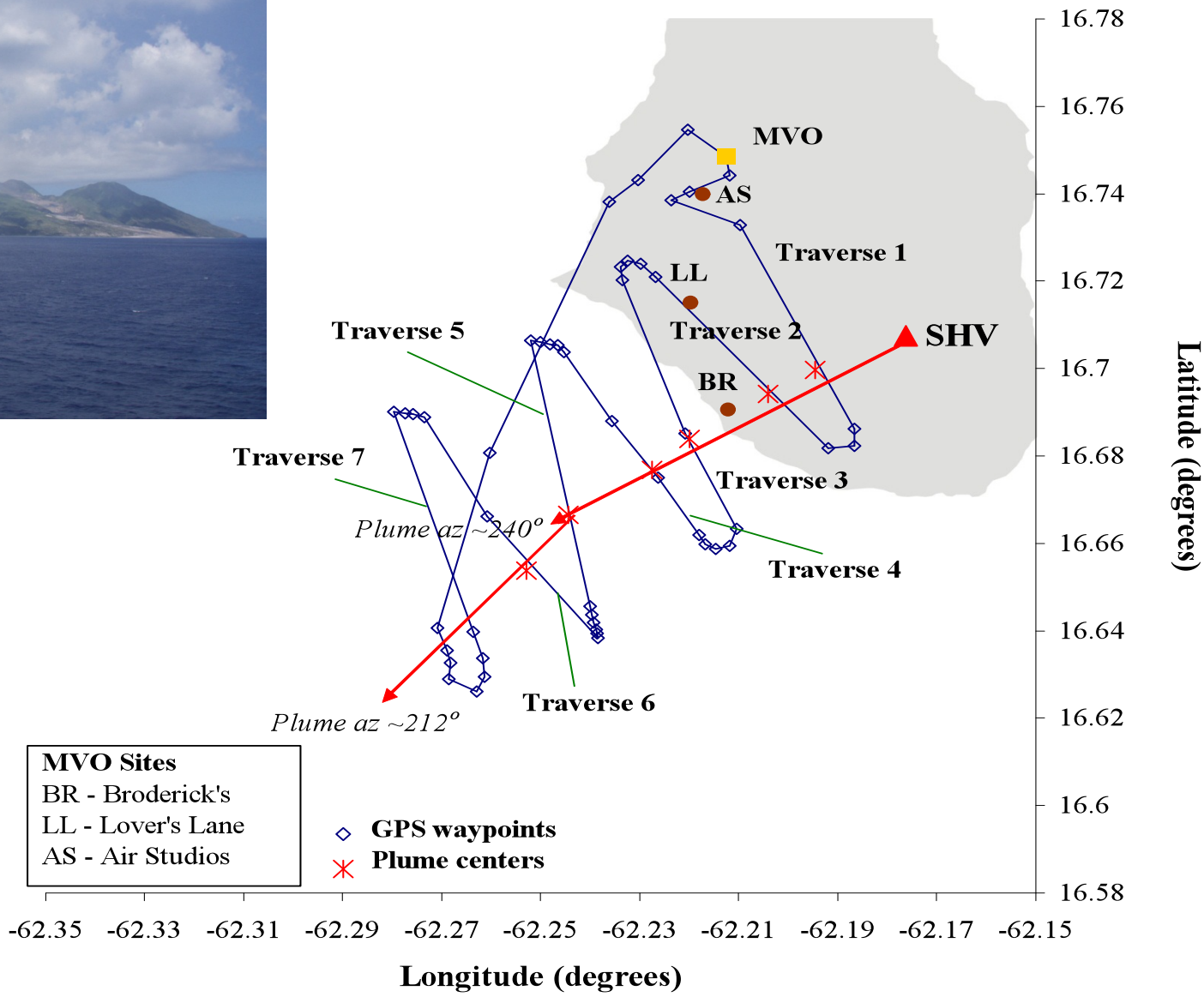
Rodriguez et al., 2008



By: L. Rodriguez

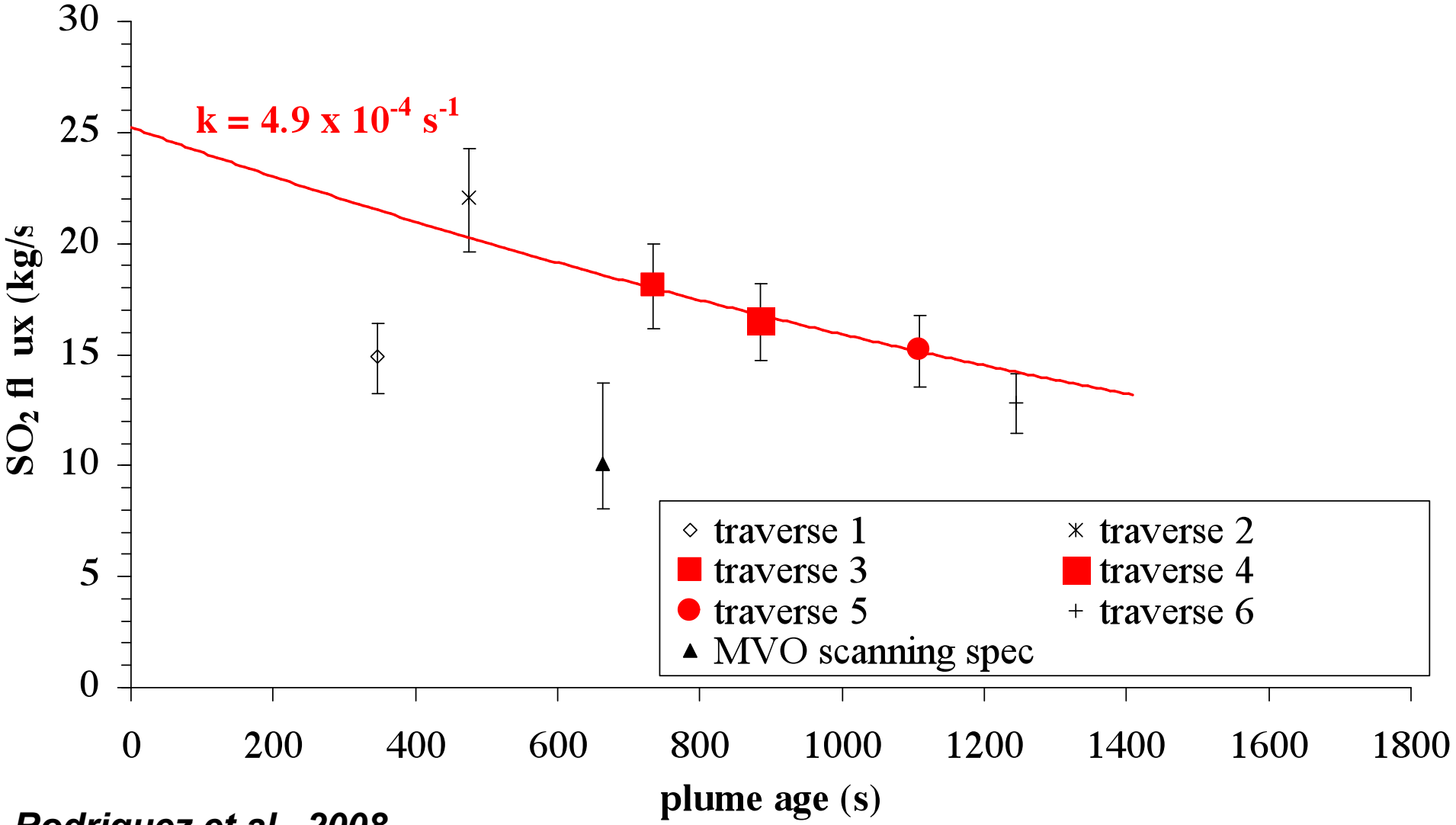
26 March 2004

*Plume centers are 2.1 to 11.9 km from the vent (coastline at plume az is ~4.2 km from vent).



Rodriguez et al., 2008

SO_2 flux vs. plume age (a best-fit exponential curve yields the flux at time=0 s: *25 kg/s (2160 t/d)*)



Rodriguez et al., 2008

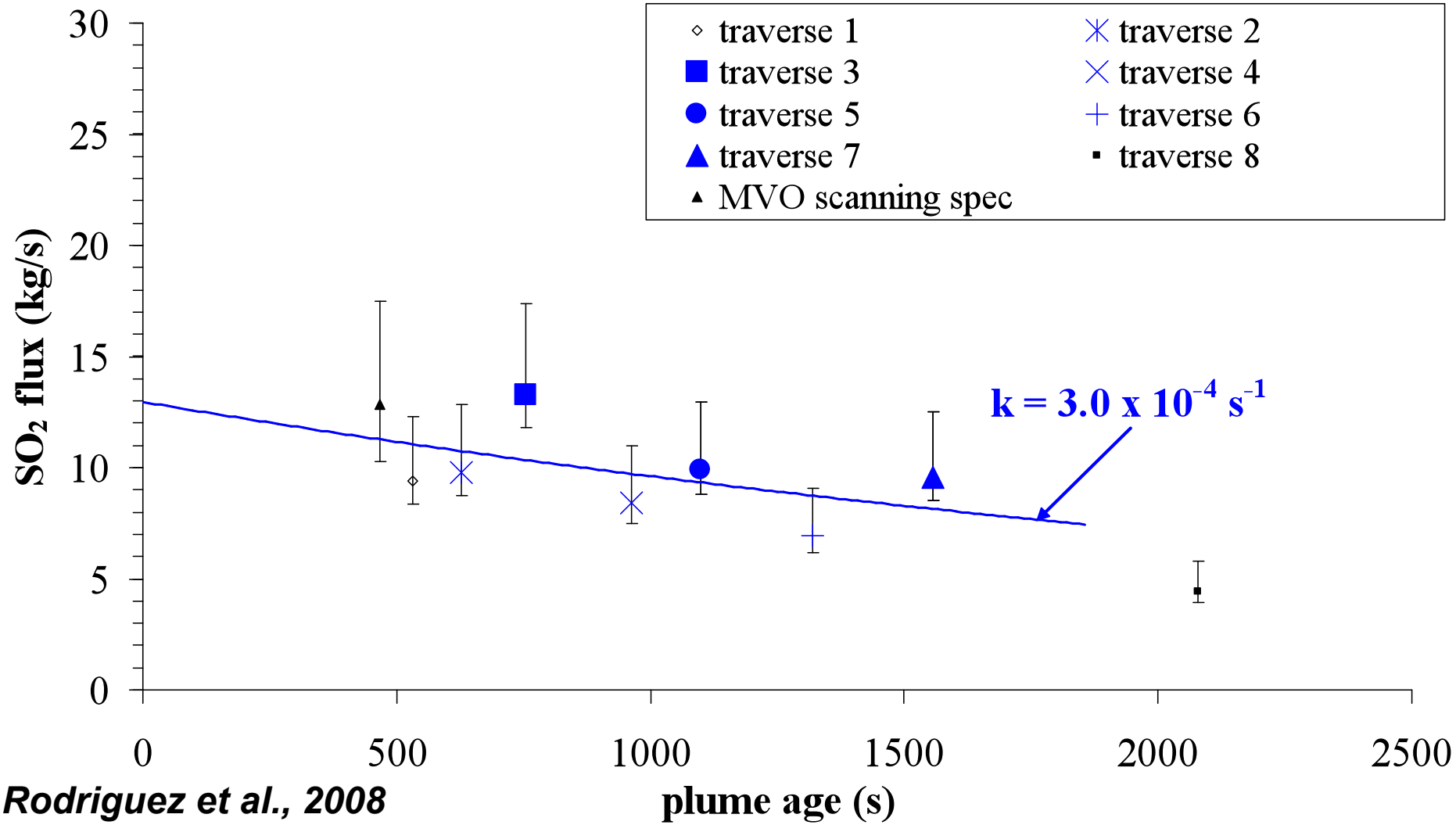
Error bars are -11% +10%. BR's ave emission rate - error bar is -20% +36%.

13 April 2004

* Plume centers are 4.3 to 16.2 km from the vent (coastline at plume az is ~4.4 km from vent).

Rodriguez et al., 2008

SO_2 flux vs. plume age (a best-fit exponential curve yields the flux at time=0 s: *13 kg/s (1120 t/d)*)



Rodriguez et al., 2008

Error bars are -11% +31%. BR's ave emission rate - error bar is -20% +36%.

Discussion

- SO_2 fluxes measured at progressively larger distances (and hence plume ages) downwind decrease at a predictable rate.
  - Calculated loss rates ranged from 3.0×10^{-4} s^{-1} to 1.4×10^{-3} s^{-1} (e-folding times: 0.9-0.2 hrs): ascribed mainly to heterogeneous removal of SO_2.
- Extrapolation of data back to t = 0 s gives an average of the at-source emission rate, based on an exponential decay of SO_2.
  - Results reported by MVO were significantly lower than ours, which take into account SO_2 loss. Further validation and comparison of the techniques would be of value.

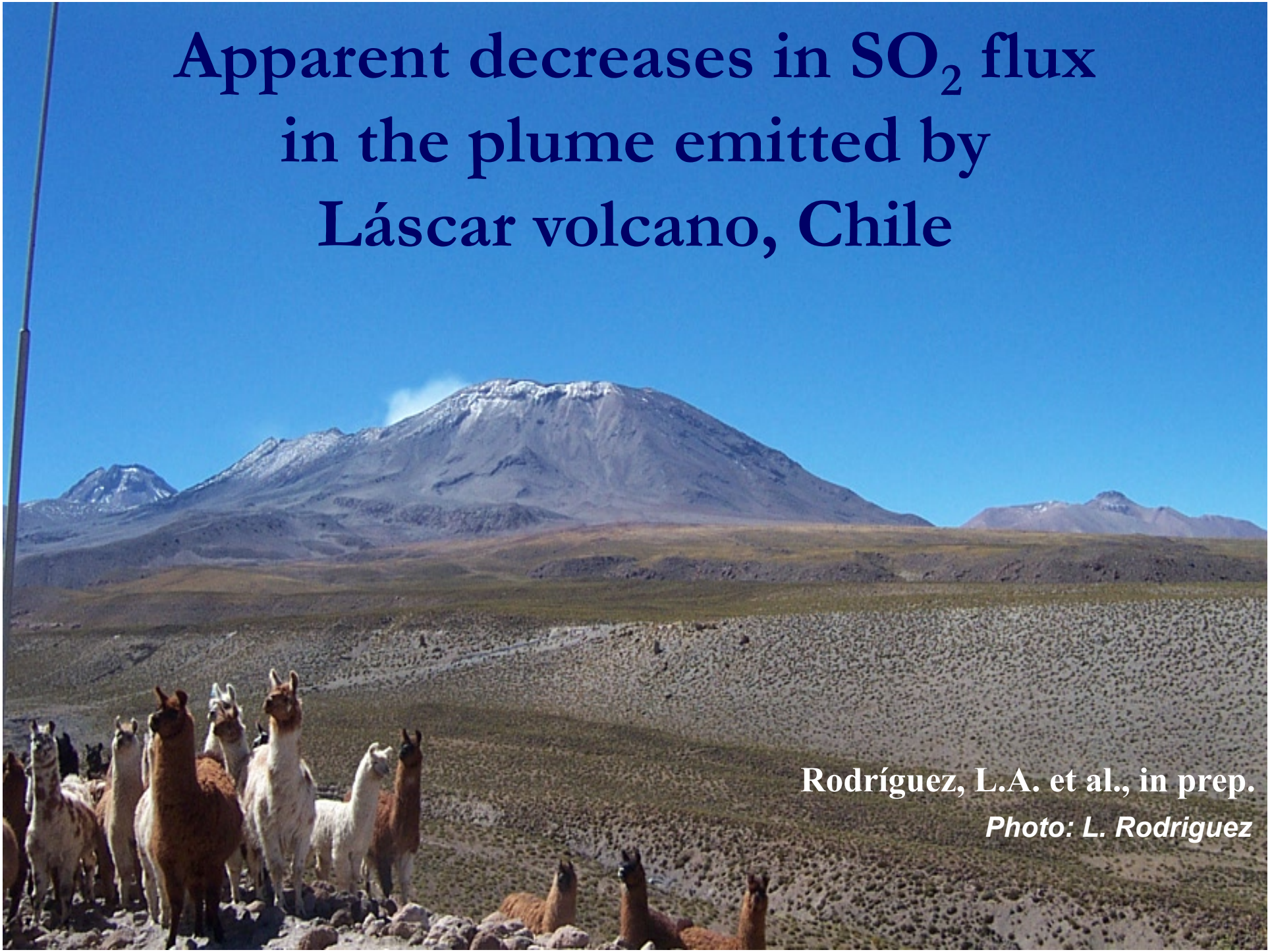
Cont. Discussion

- Similar study in 1996 (Oppenheimer et al., 1998): loss rates ~10^{-3} s^{-1}, an order of magnitude faster than ours, which included more traverses over a longer period.
  - Conditions differed in that we measured ash-free plumes during the dry season, while Oppenheimer et al. (1998) measured ash plumes during the peak of the rainy season (greater concentration of available condensed atmospheric water).
  - Criteria used to choose the traverses is different

Conclusions

- These differences are carried forward to models, and introduce an error.
- Contributions of volcanoes to the global SO_2 budget are underestimated.

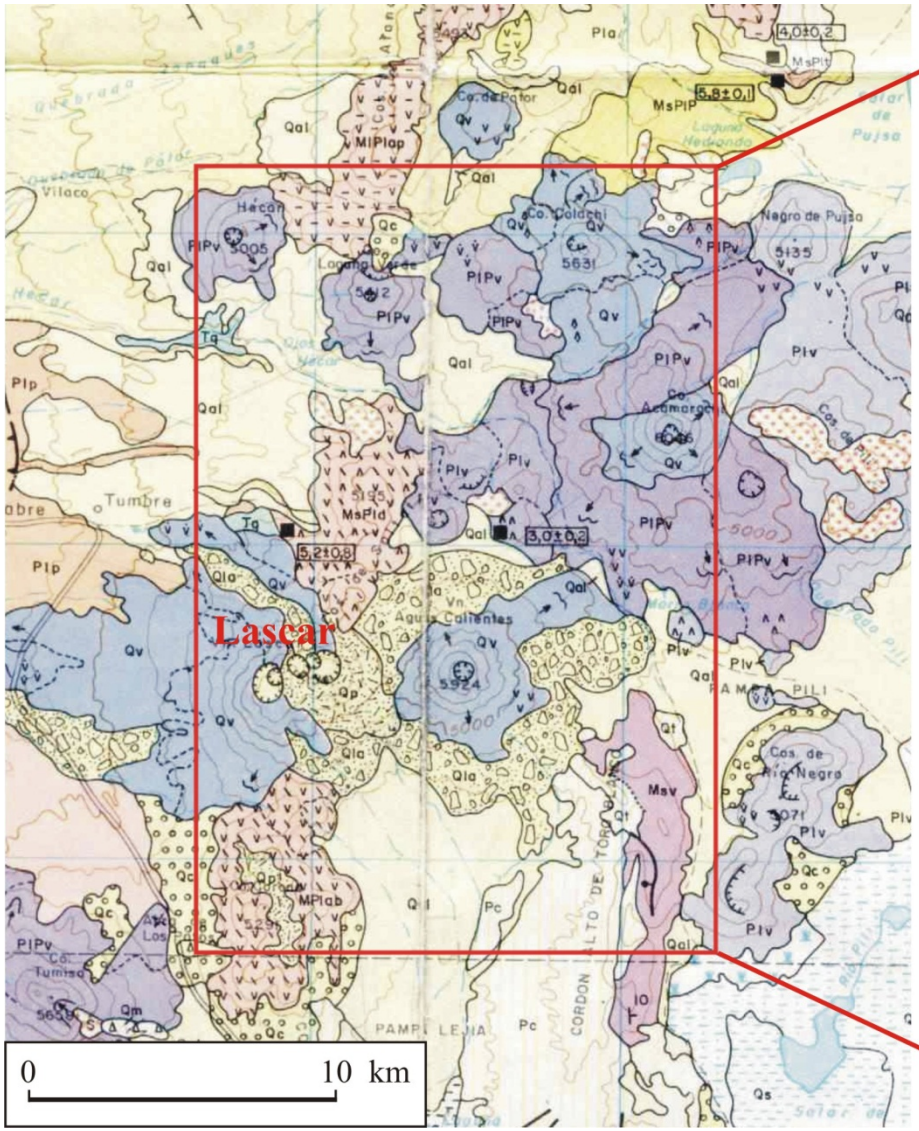
Apparent decreases in SO_2 flux in the plume emitted by Láscar volcano, Chile



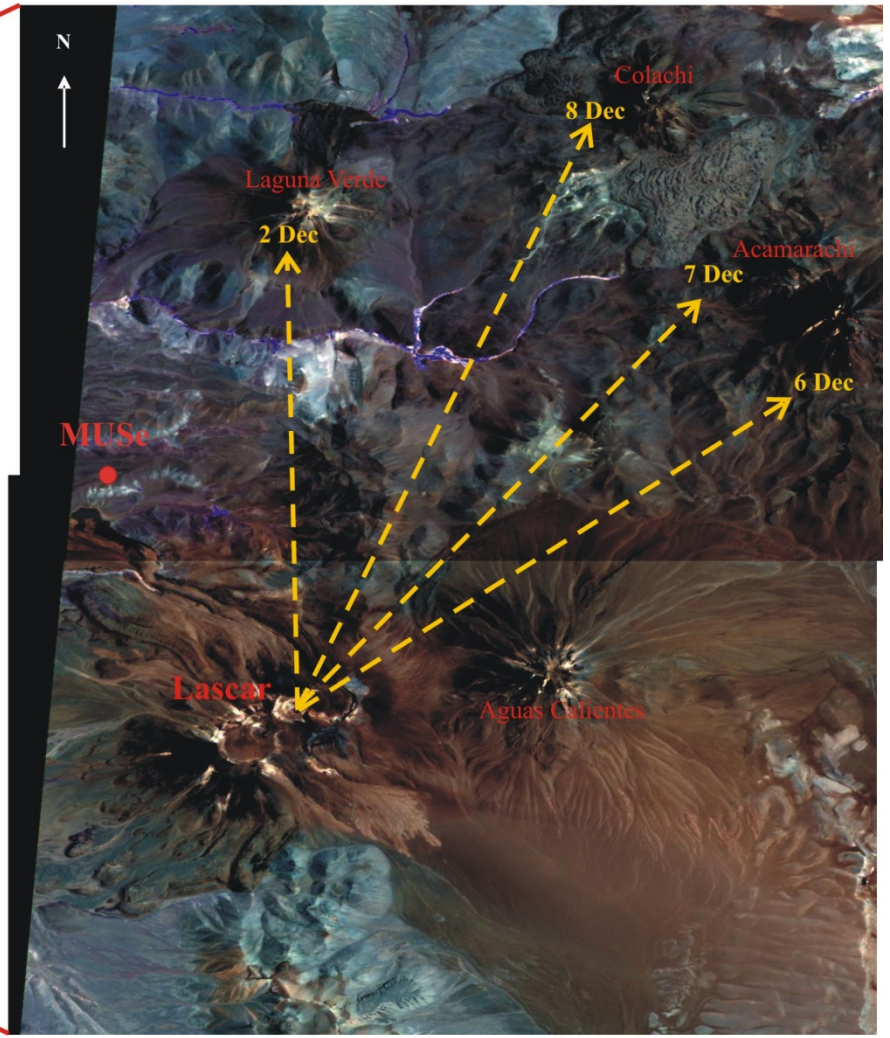
Rodríguez, L.A. et al., in prep.

Photo: L. Rodriguez

Location of Láscar, approximate position of MUSe during measurements, and plume azimuths



Toconao quadrangle (1:250,000)



ASTER image (1-2-3 visible composite)

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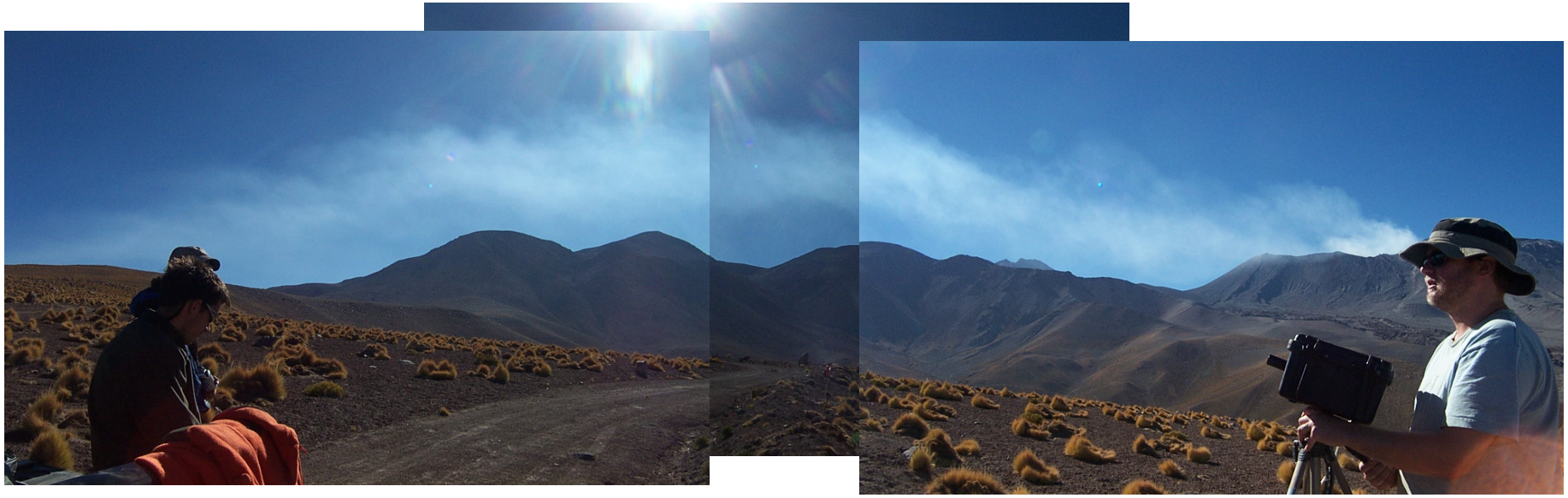
MUSe measurements

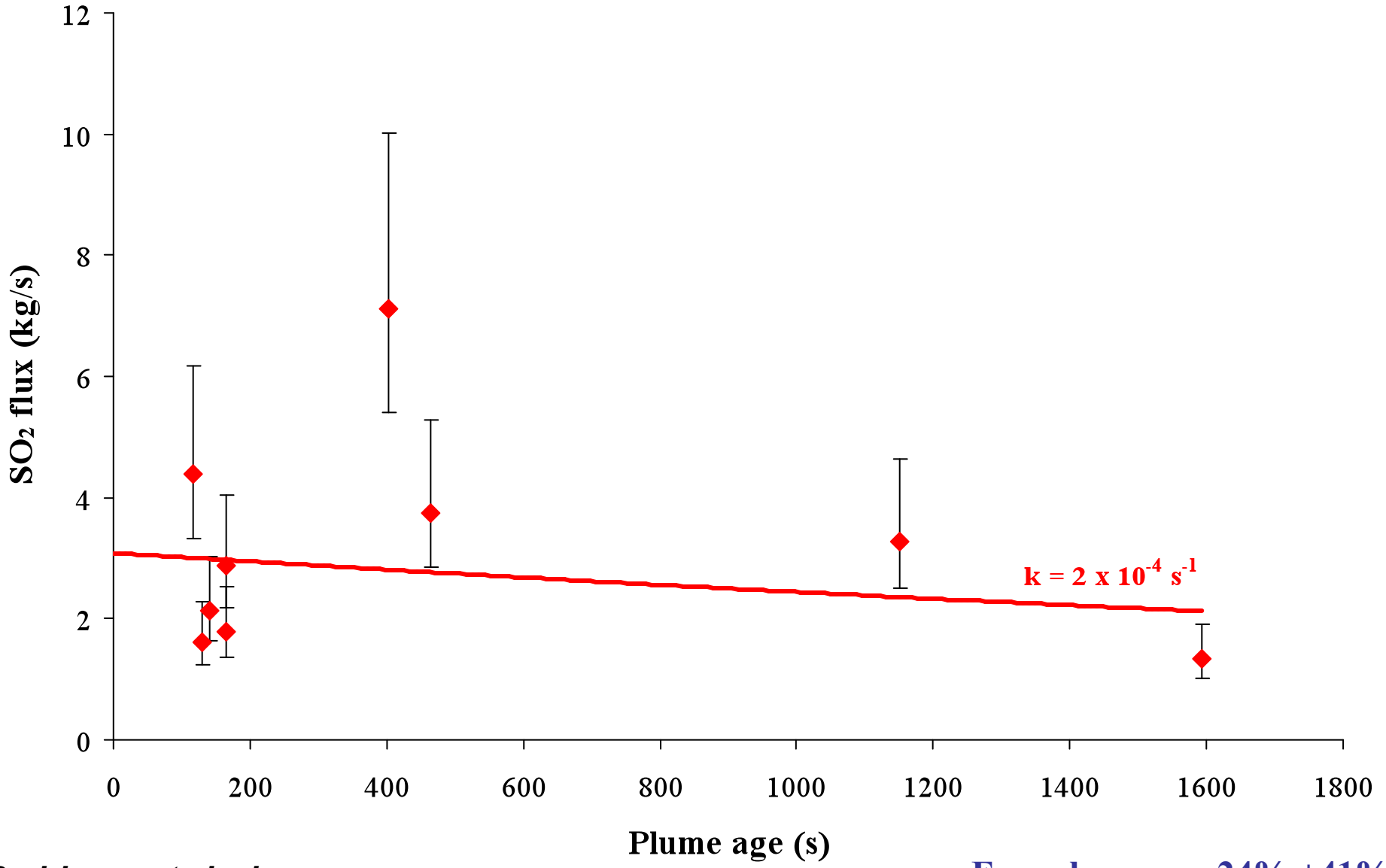


December 7, 2004. Plume traveling to the NE.

2 MUSe's, one measuring upwind (close to vent) and the other measuring downwind

Photos: L. Rodriguez

SO_2 flux vs. plume age (7 Dec) (best-fit exponential curve yields flux at time=0 s: *3 kg/s (260 t/d)*)



Rodriguez et al.,, in prep

Error bars are -24% +41%

Discussion

- SO_2 fluxes averaged ~200 t d^{-1}, an order of magnitude lower than previous measurements of 2300 t d^{-1} on Jan 2003 (Mather et al., 2004)

- Calculated loss rates ranged from 2.0 x 10^{-4} s^{-1} to 7 x 10^{-4} s^{-1} (e-folding times: 1.4-0.4 hrs), which are subject to large errors.
  - Most accurate estimate: 2.0 x 10^{-4} s^{-1} (Dec 7).

Rodriguez et al.,, in prep

Cont. Discussion

- Apparent loss of SO_2 because of the errors in the calculation of fluxes:
  - UV scattering causing attenuation as distance between instrument and plume increases – causes underestimates in the flux measurements
  - Errors in the plume azimuth

- These will produce an apparent faster loss of SO_2 in the plume

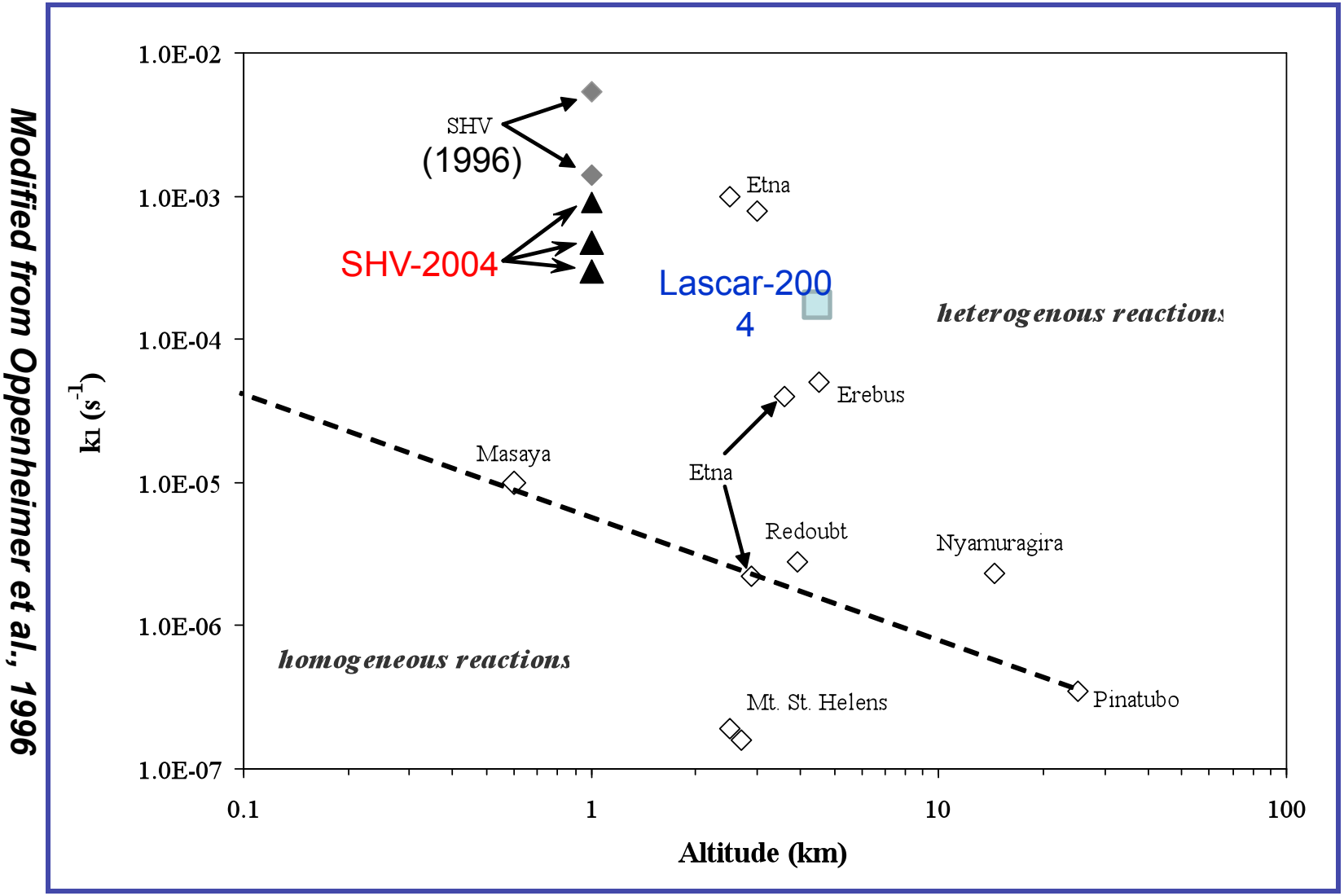
Rodriguez et al.,, in prep

Conclusions

- SO_2 loss rates obtained are a combination of depletion of SO_2 by heterogeneous reactions, of the effects of errors in the plume azimuth calculation, and of the long distances between the instruments and the plume
  - Latter effect due to UV scattering, which can produce decreases in the flux and consequently make the loss rates appear faster, without any removal mechanism acting on the plume.
  - Residence times are longer than calculated

Rodriguez et al.,, in prep

SO_2 depletion rates as a function of altitude of the plume



Dashed line indicates the approximate transition between homogeneous and heterogeneous reactions (based on Eatough et al., 1994 and Thornton et al., 1996).