Measurements of HCl in the volcanic plumes of Calbuco (2015) and Raikoke (2019)

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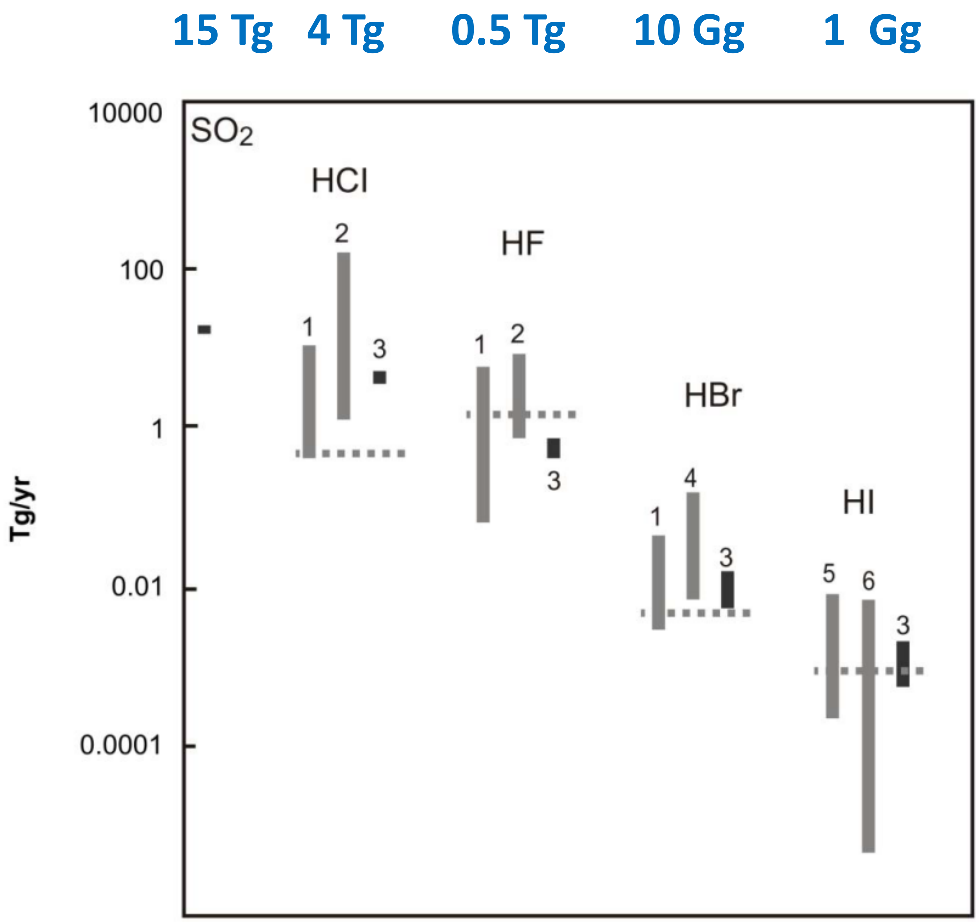
EGU General Assembly, May 2020

Volcanic emissions of HCl

- After H_2O, CO_2 and SO_2, **Hydrogen chloride (HCl)** is the main volcanic gas species, and most important halogen halide (Symonds, Rose and Reed; 1988).
- Important effects on environment/ecosystems/soils/air quality (acidification)
- Chemical tracer of magma degassing and other subsurface processes in both syn-eruptive and quiescent degassing
- Estimated yearly emissions between 1 and 10 Tg. But very little is known on the halogen budget of large-size eruptions



Arc related volcanic emissions of halogens
Pyle, D. M., and T. A. Mather. "Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: a review." *Chemical Geology* 263.1-4 (2009): 110-121.

HCl/SO_2 ratios

- Average HCl/SO_2: $\sim$ **0.3** – but 4 orders of magnitude variation: from 0.001 (Erta Ale) to 10 (Montserrat) (Pyle and Mather, 2009)

- Relative ratios vary in time, with applications to volcano monitoring

- Cl is highly soluble, and generally the more volatile gases are exsolved first (CO_2 before SO_2 before HCl) (Aiuppa et al, 2009):
  → High ratios are associated with the *concluding* stages of basaltic eruptions
  → During periods of reduced magma supply
  → HCl from silicic systems harder to interpret

- Deposition and plume chemistry adds to the complexity
  - Wet deposition of HCl can be very significant (uptake in clouds, dissolution in condensated water vapour when RH is large; see Aiuppa et al. 2007, Burton et al. 2001)
  - Dry deposition
  - Uptake by (volcanic) ice and ash (see next slide)
  - Heterogeneous (gas-aerosol) reactions (see next slide)

Stratospheric emissions and role

- HCl is the most important Cl reservoir species. In the stratosphere can be transformed to reactive forms, leading to the destruction of ozone.

- Presence of bromide in volcanic plumes leads to “explosion” of reactive halogens (BrO and OClO) via heterogeneous reactions

- Documented stratospheric injections are modest, e.g.
  Augustine 1976: 0.08-0.18 Tg (Johnston, 1980); El Chicon 1982: 0.04 Tg (Mankin et al., 1983); Hekla 2001 (Rose, 2006); MLS ratios ~0.03, a factor 10 lower than what is measured in degassing/smaller tropospheric eruptions

- Direct stratospheric effect of HCl difficult to disentangle from the contribution of volcanic induced heterogeneous reactions that activate Cl reservoir species (ClONO2, HCl).

- Uptake and removal processes
  - Scavenging by ***liquid supercooled water*** unimportant (<1%, Textor et al, 2003)
  - Scavenging by ***ice particles*** important. Textor et al. (2003) : removes 75% of all initial HCl within the hour. Leaves 25% that reaches the stratosphere but in majority incorporated in those particles.
  - Scavenging of HCl on ***volcanic ash*** may or may not important (Gutiérrez et al, 2016; Delmelle et al., 2018)
  - Large uncertainty on stratospheric injections!

Satellite measurements of gases in volcanic plumes

Sensor[a]	Volatile species: H_2O	CO_2	CO	SO_2	H_2S	HCl	BrO	OClO	CH_3Cl	Timespan	Reference(s)[b]
TOMS*				■						1978–2005	1, 2
SBUV* (P)				■						1978–present	3, 4
HIRS*				■						1978–present	5
GOME	□			■			□	□		1995–2003	6, 7, 8
MODIS*	□			■						1999–present	9, 10
ASTER				■						1999–present	11, 12, 13
MOPITT			■							1999–present	14
SCIAMACHY (L)	□	□	□	■			■	■		2002–2012	8, 15, 16
MIPAS (L)				■						2002–2012	17
AIRS	□	□	□	■						2002–present	18, 19
ACE (L)	□	□	□	■		□			□	2003–present	20
SEVIRI				■						2004–present	21
OMI				■			■	■		2004–present	16, 22, 23,24
MLS* (L)	□		□	■		■	□	□	■	1991–2001; 2004–present	25, 26, 27, 28
TES (P)				■						2004–present	29
GOME-2*	□			■			■	■		2006–present	16, 30, 31
IASI*	□	□	■	■	■					2006–present	14, 32, 33
OMPS*				■			□	□		2011–present	34
VIIRS				■						2011–present	35
CrIS				□						2011–present	36
AHI				□						2015–present	37
GOSAT (P)		□		□						2009–present	38
OCO-2		□								2014–present	39

HCl only observed from Limb measurements (UTLS)

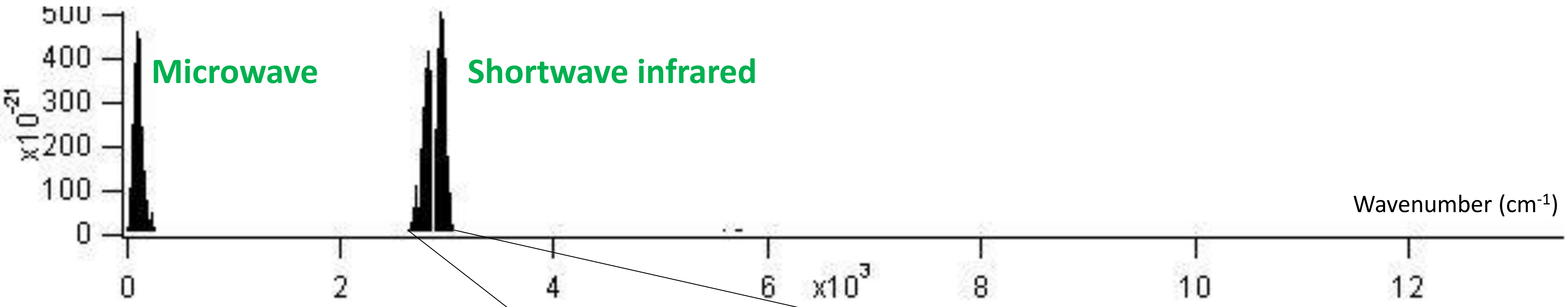
Table 7
HCl and SO_2 mixing ratios measured by Aura/MLS in volcanic clouds.

Volcano	Eruption Date	HCl (ppbv)	SO_2 (ppbv)	Pressure (hPa)	HCl/SO_2
Manam	Jan 27, 2005	4–6	279	68–100	0.01
Anatahan	Apr 6, 2005	3.5	133	100	0.02
Soufriere Hills	May 20, 2006	3	200	68	0.01
Chaitén	May 6, 2008	1.6	28	147	0.03
Okmok	Jul 12, 2008	5	212	147	0.01–0.02
Kasatochi	Aug 7, 2008	5–6	392	68–215	0.01–0.014
Redoubt	Mar 26, 2009	4–5	175	100–215	0.02
Sarychev Peak	Jun 15, 2009	7–9	529	32–215	0.03
Merapi	Nov 5, 2010	6–7	172	100–215	0.03
Cordón Caulle[1]	Jun 4, 2011	2–3	77	147–215	0.03
Nabro	Jun 15, 2011	9	306	46–215	0.03
Paluweh	Feb 2, 2013	2.2	129	100–215	0.01
Kelut	Feb 14, 2014	7	398	32–147	0.01
Sangeang Api	May 31, 2014	2–3	53	146	0.03

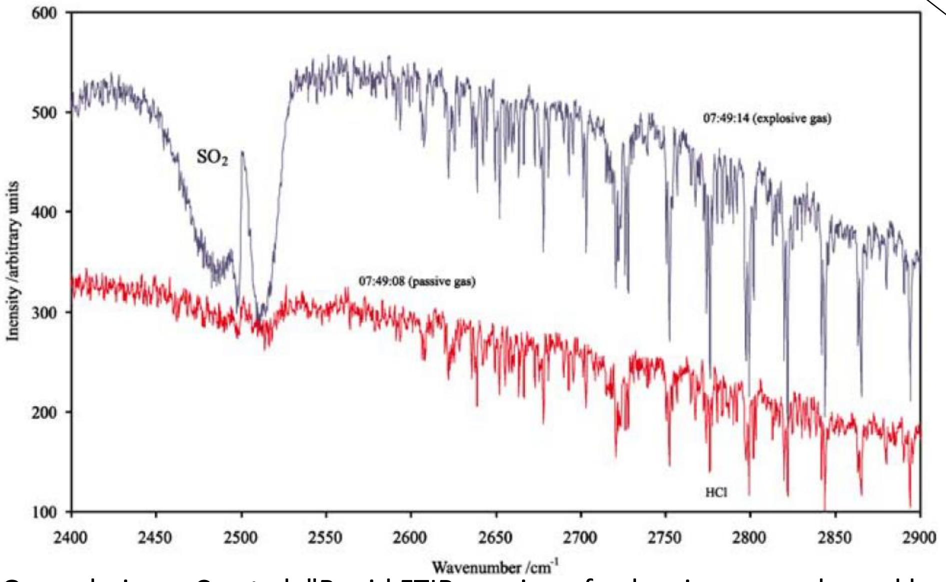
Ratios a factor 10 lower than what is measured in-situ – in degassing/smaller tropospheric eruptions

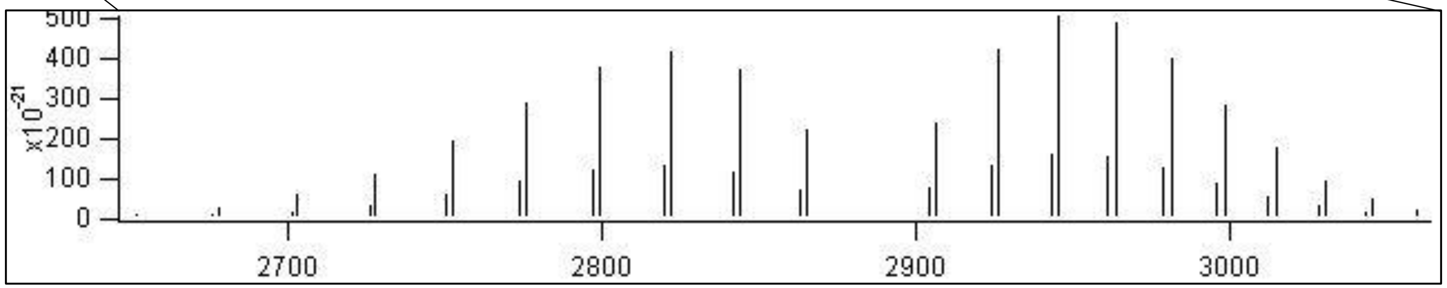
Carn, S. A., Clarisse, L., & Prata, A. J. (2016). Multi-decadal satellite measurements of global volcanic degassing. *Journal of Volcanology and Geothermal Research*, *311*, 99-134.

Hydrogen chloride spectrum



Measured with ground-based FTIR



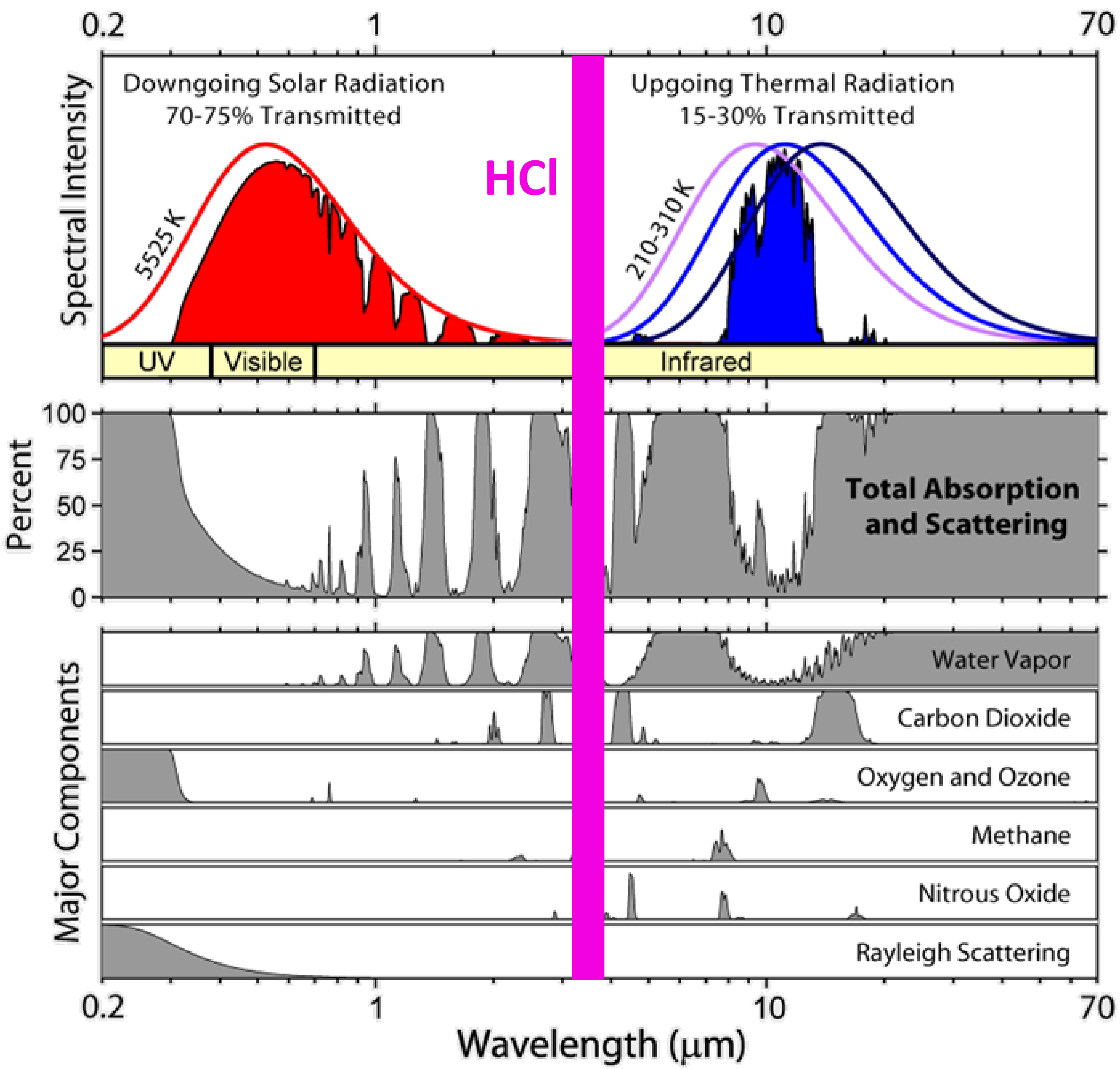


Wavenumber (cm-1)

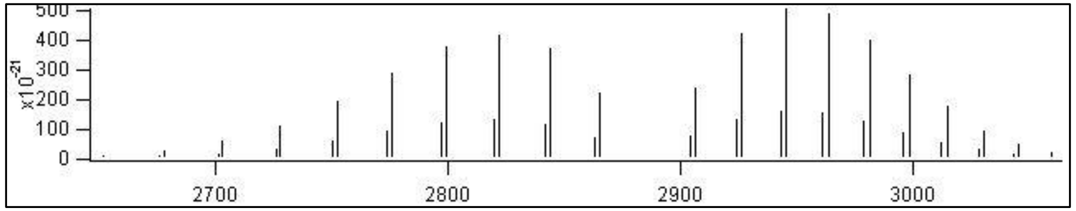
Oppenheimer, C., et al. "Rapid FTIR sensing of volcanic gases released by Strombolian explosions at Yasur volcano, Vanuatu." *Applied Physics B* 85.2-3 (2006): 453-460.

http://vpl.astro.washington.edu/spectra/hcl.htm

Location of the HCl SWIR band



https://commons.wikimedia.org/wiki/File:Atmospheric_Transmission.png



http://vpl.astro.washington.edu/spectra/hcl.htm

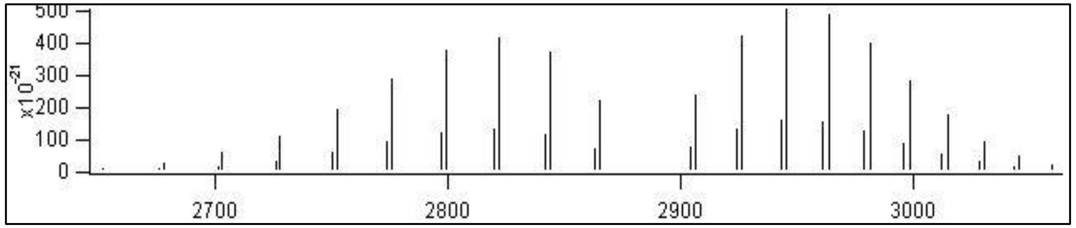
- Its spectral band is located **unfavourably in terms of source radiation**:
  - Thermal emission too low to be useful
  - Solar reflected radiation weak -> measurement possible in daytime
- Its spectral band is located **favourable in terms of competing absorbers:**
  - A few water and methane interferences

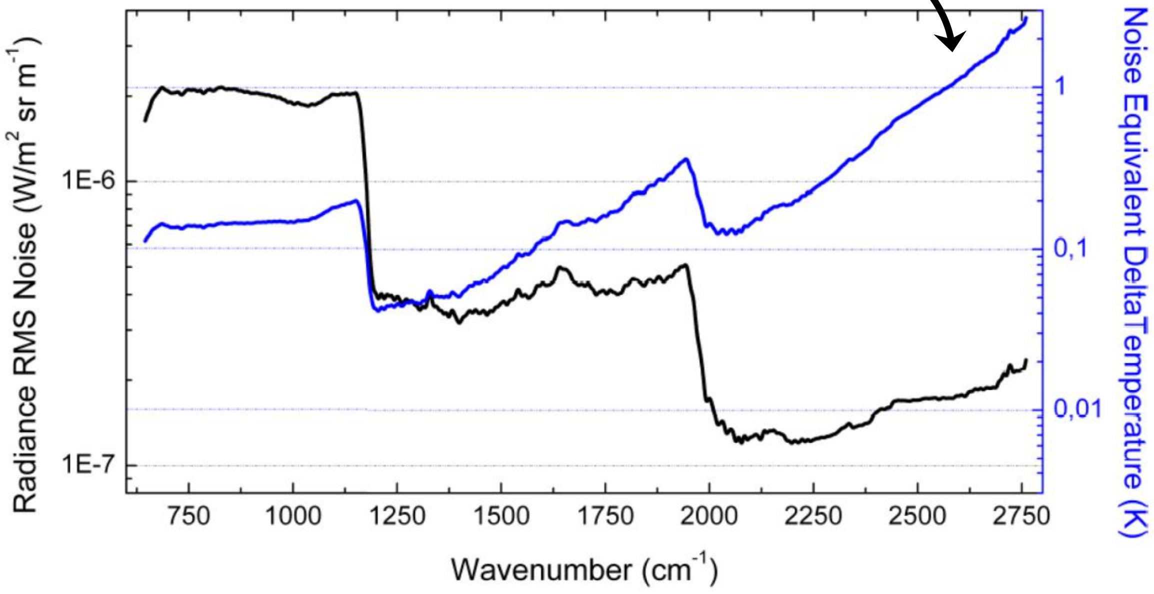
Satellite measurements of HCl using its SWIR band

Currently only IASI covers this band, but only partially (645-2760 cm^{-1})

But retrieval will be challenging:

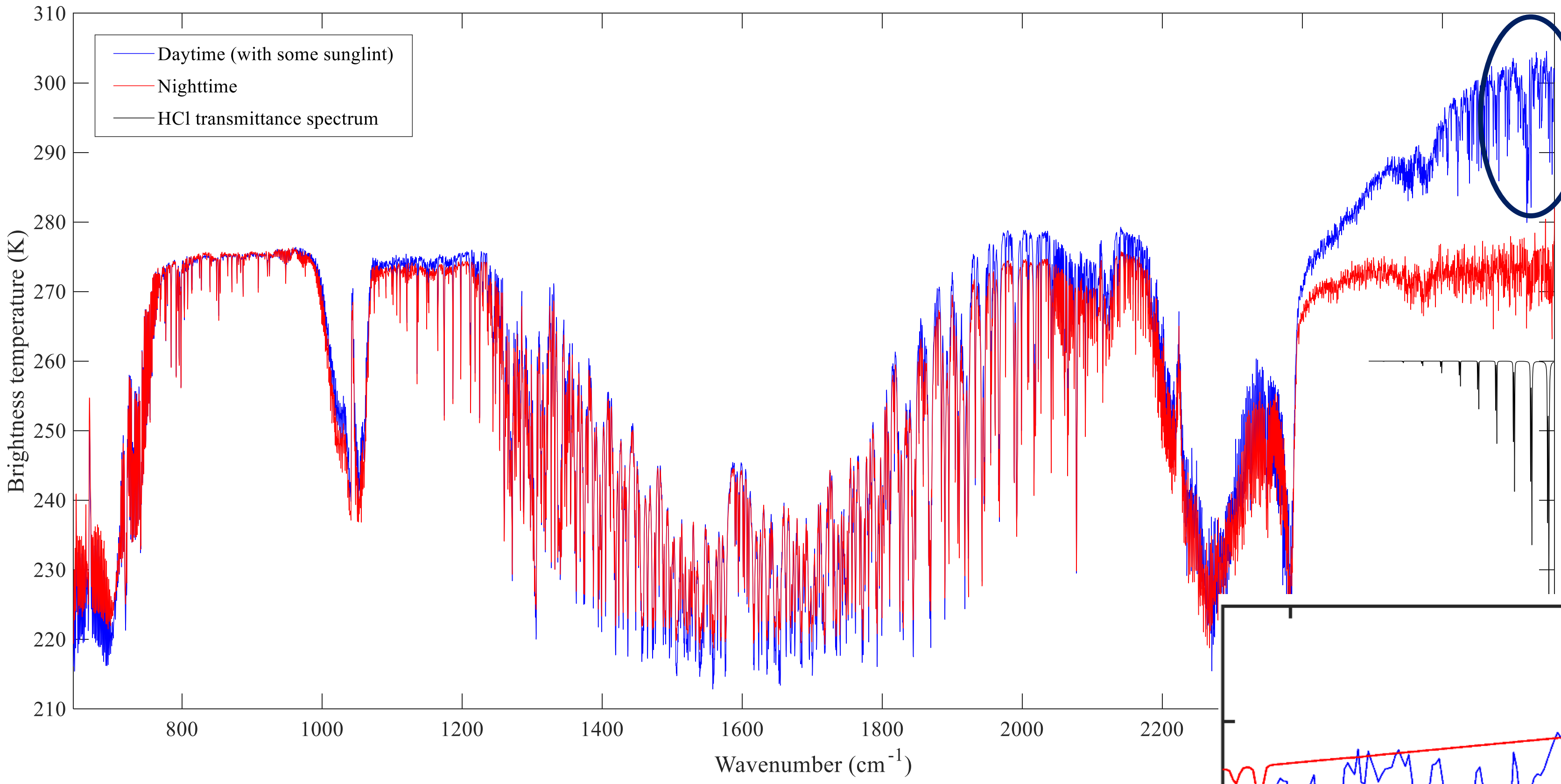
- weak background signal (daytime only)
- doesn't cover the strongest lines
- low signal to noise

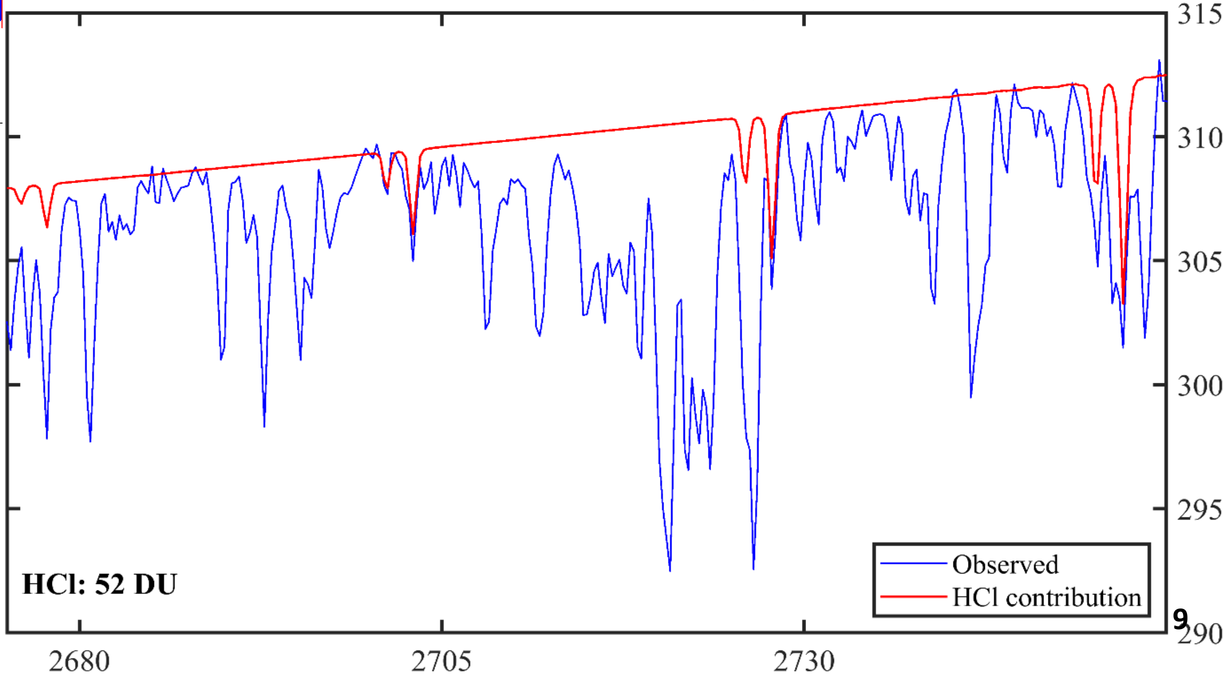




Clerbaux, C. et al. Monitoring of atmospheric composition using the thermal infrared IASI/MetOp sounder, Atmos. Chem. Phys., 9, 6041–6054, 2009.

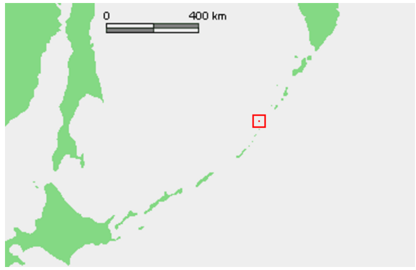
First IASI observations of HCl





Unambiguous identification of HCL in the volcanic plumes of Raikoke and Calbuco

Raikoke



Source: wikipedia

Where: Kuril Islands
Type: (basaltic) arc volcano
Elevation: 551 m
Eruptions: VEI ≥4 eruptions in 765, 1778, 1924 and 2019

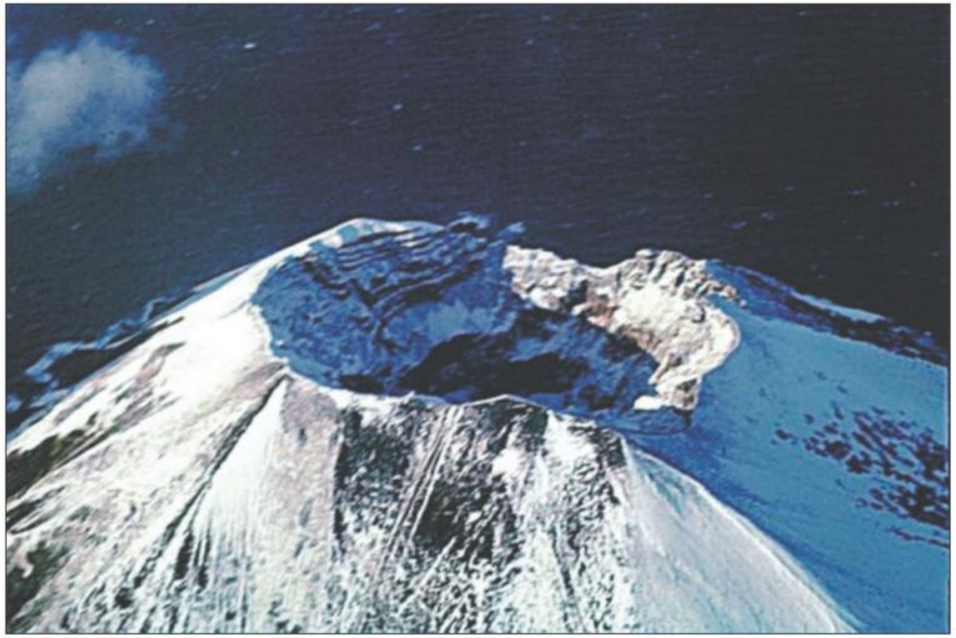


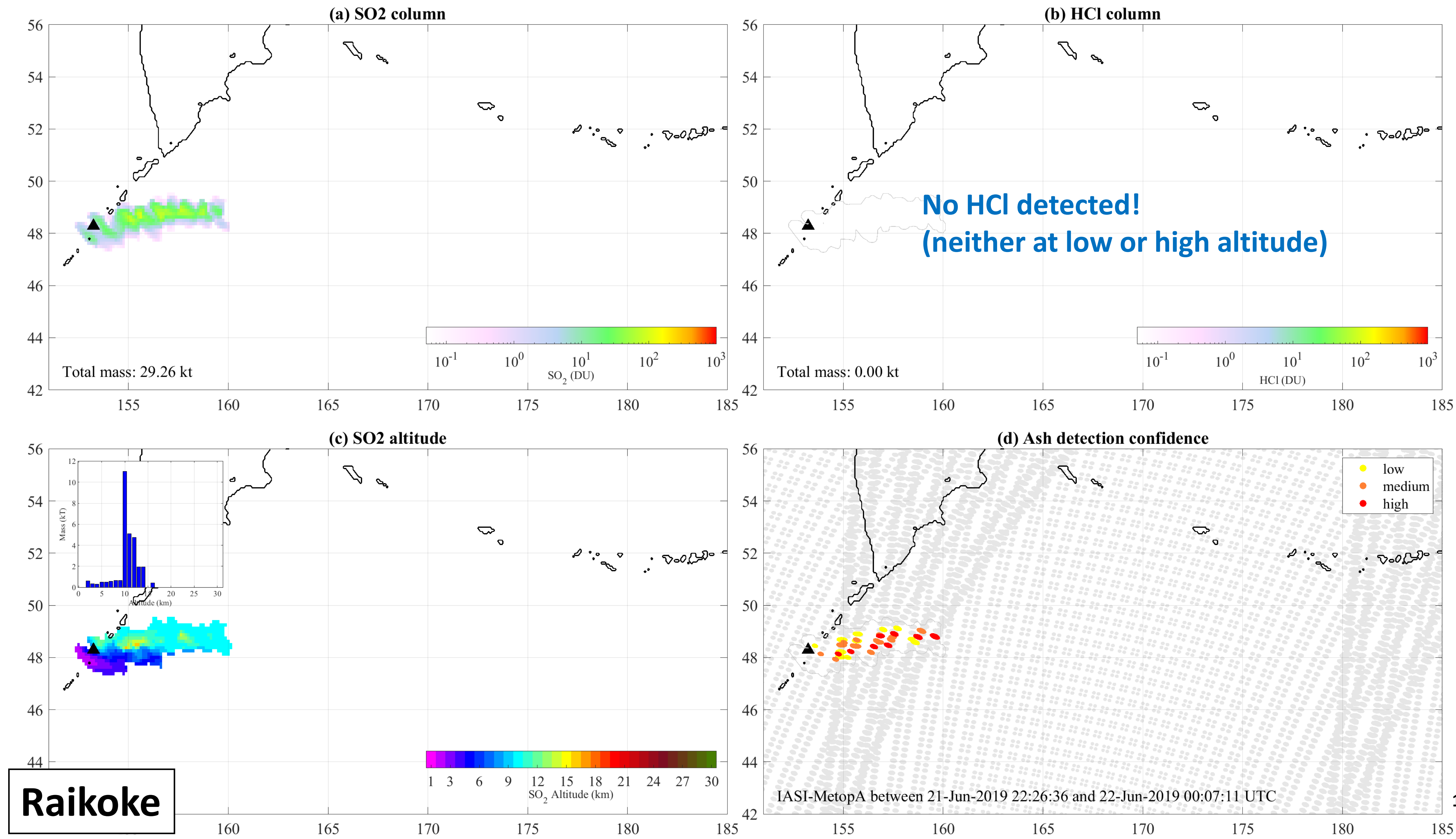
Figure 100. Raikoke Volcano. Photograph by R. Bulgakov.

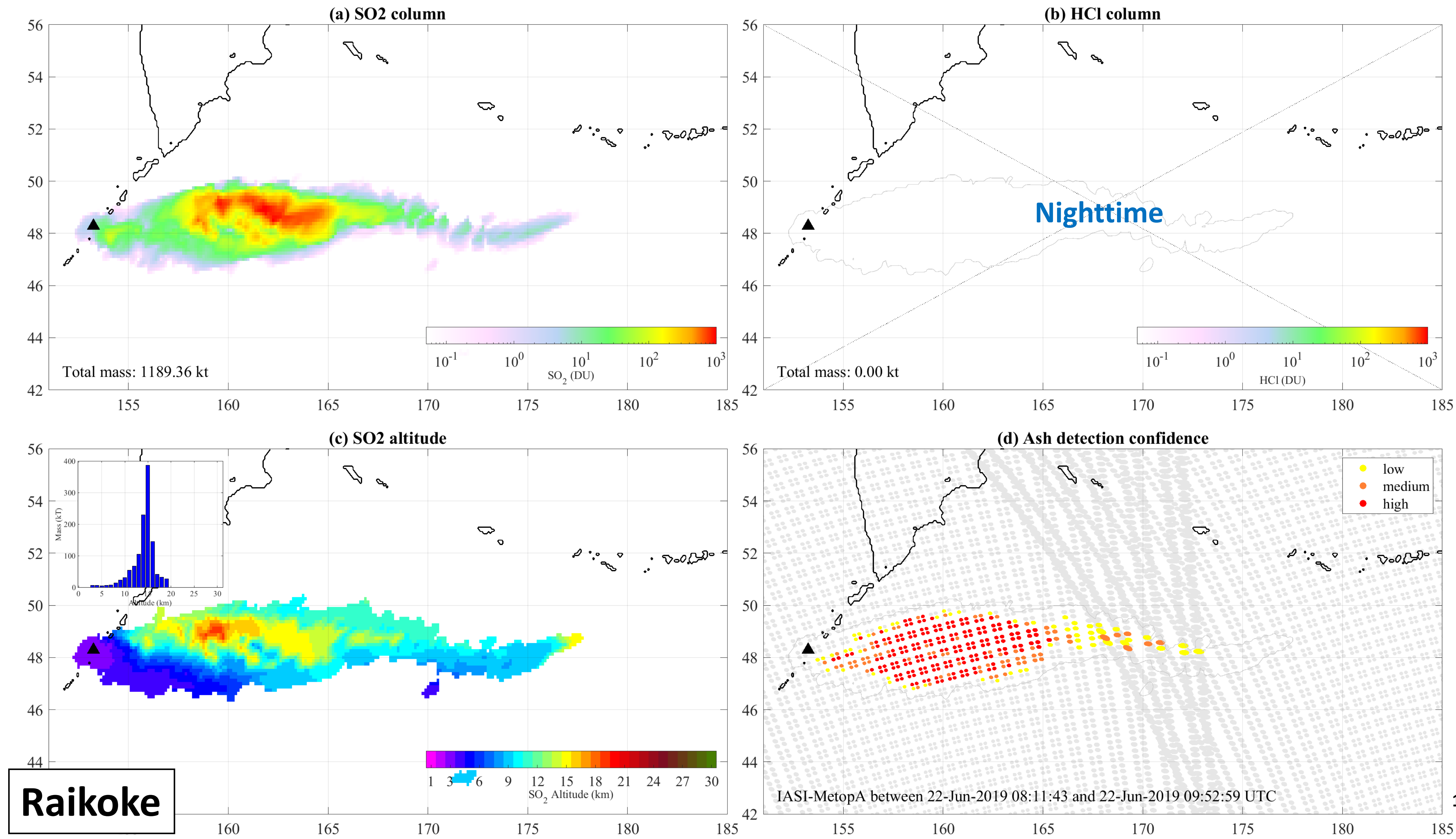
10.3133/sir20135213

21 June 2019 eruption

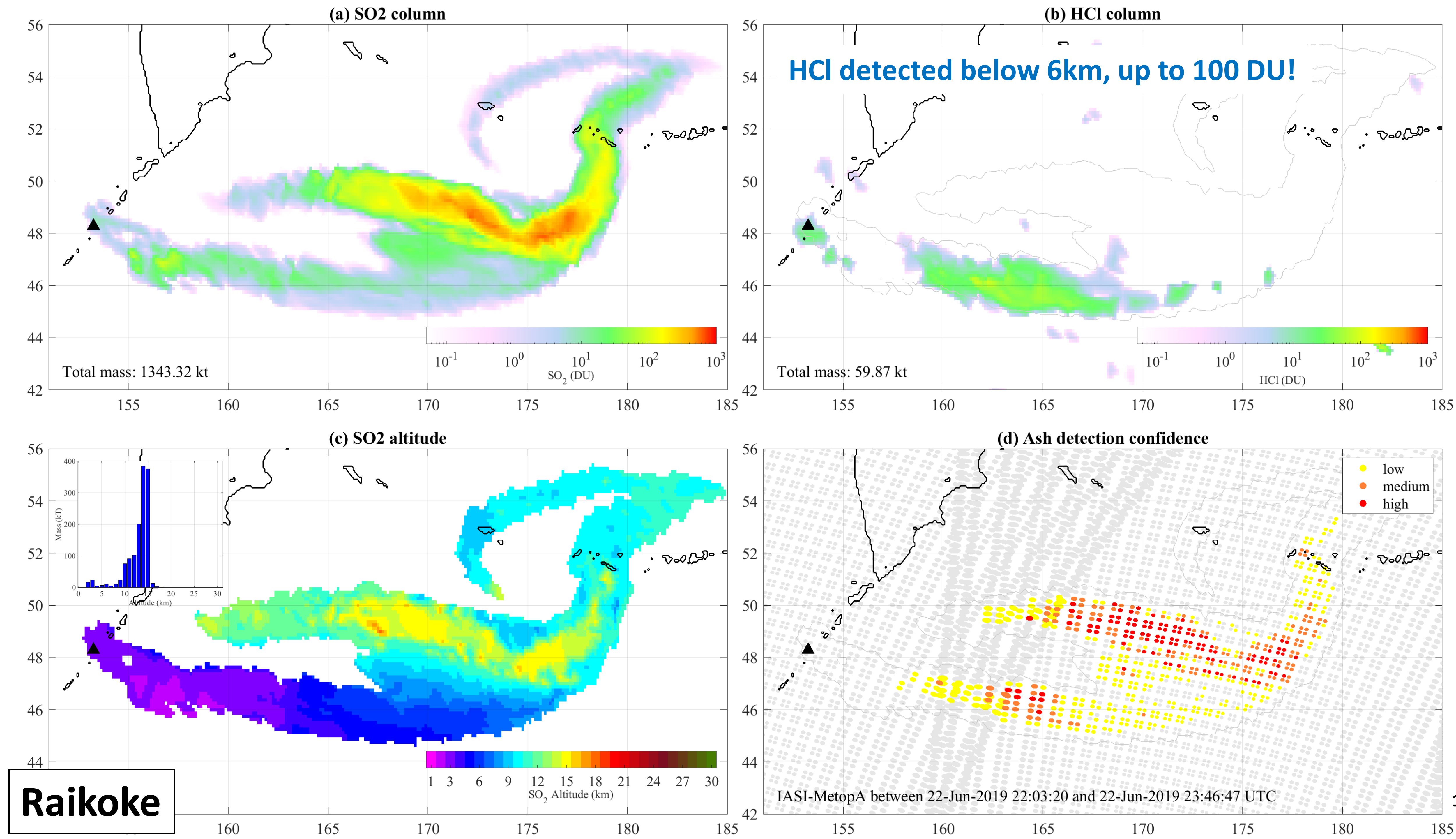
- Start of eruption around 1750 UTC (Himawari-8 +infrasound)
- Duration ~15h
- 1-2 Tg SO_2
- Injection altitudes >15 km

https://earthobservatory.nasa.gov/images/145226/raikoke-erupts

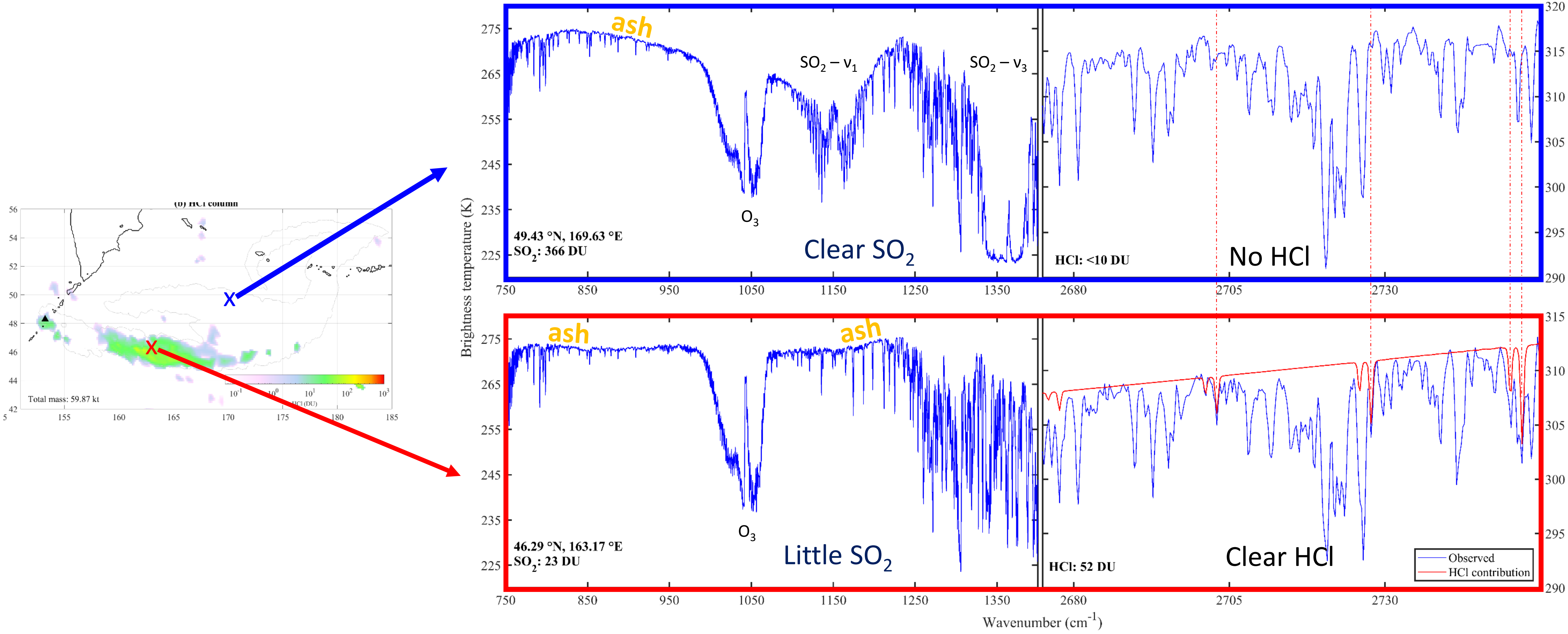

(a) SO2 column
Total mass: 29.26 kt
SO_2 (DU)
(b) HCl column
No HCl detected!
(neither at low or high altitude)
Total mass: 0.00 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO_2 Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 21-Jun-2019 22:26:36 and 22-Jun-2019 00:07:11 UTC
Raikoke



(a) SO2 column
Total mass: 1189.36 kt
SO_2 (DU)
(b) HCl column
Nighttime
Total mass: 0.00 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO_2 Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 22-Jun-2019 08:11:43 and 22-Jun-2019 09:52:59 UTC
Raikoke


(a) SO2 column
Total mass: 1343.32 kt
SO$_2$ (DU)
(b) HCl column
HCl detected below 6km, up to 100 DU!
Total mass: 59.87 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO$_2$ Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 22-Jun-2019 22:03:20 and 22-Jun-2019 23:46:47 UTC
Raikoke

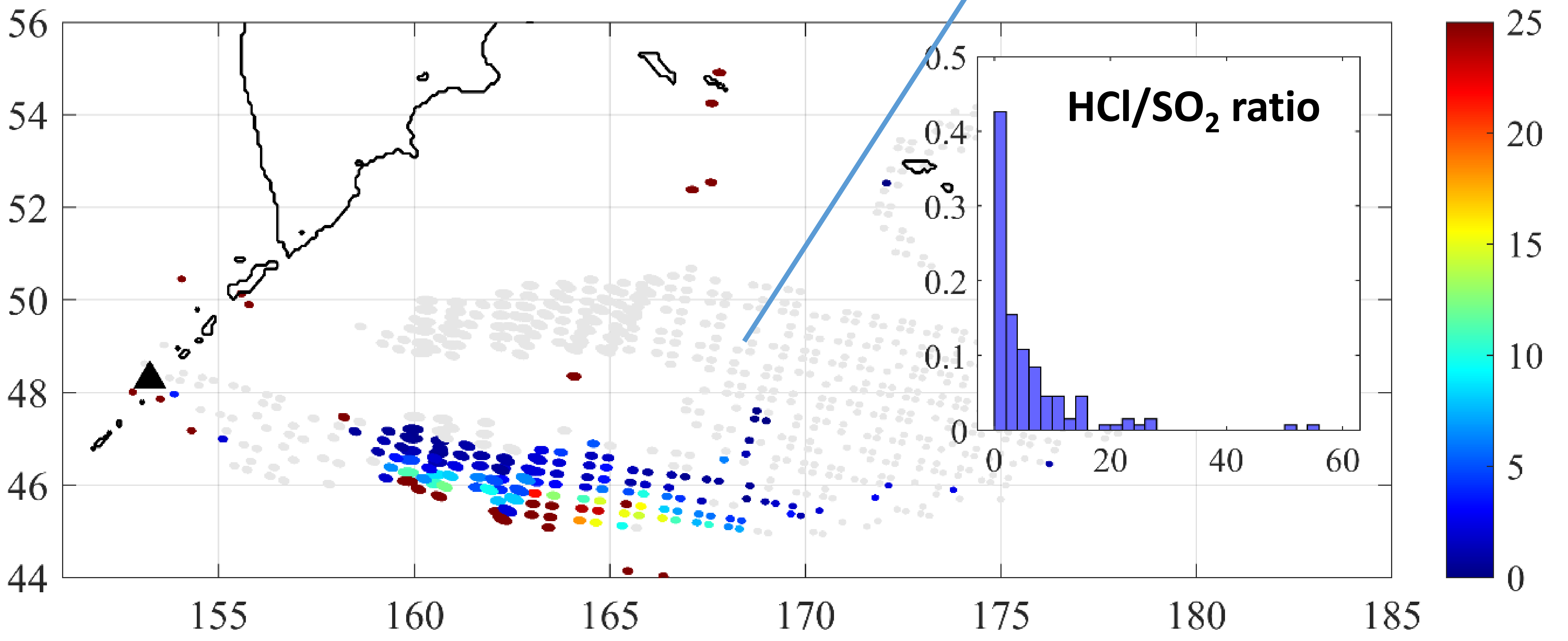
Two example spectra, in either part of the plume



Raikoke

HCl/SO_2 ratios

HCl below detection limit



Large variability in ratios, from <0.05 (estimate) to > 50

Raikoke

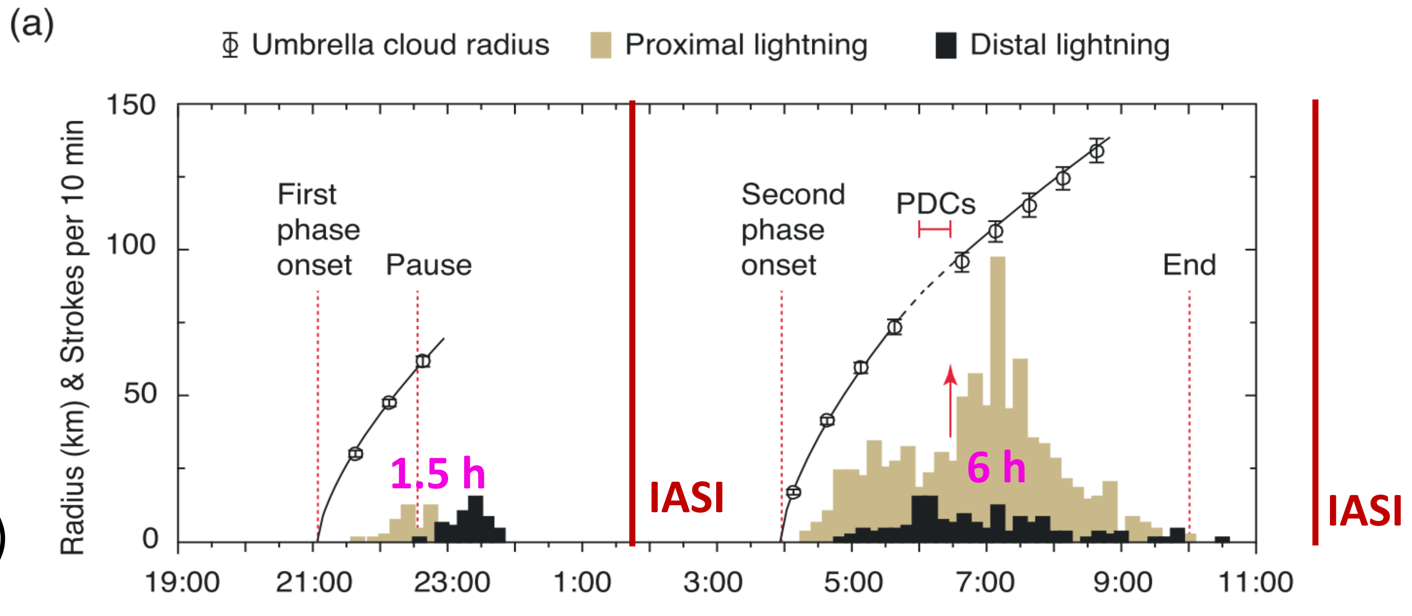
Calbuco

Where: southern Chile
Type: (basaltic) andesitic arc volcano
Elevation: 2,015 m
Eruptions: History of moderately explosive to sub-plinian eruptions throughout the Holocene. 13 eruptions in 20th century, last one in 1972

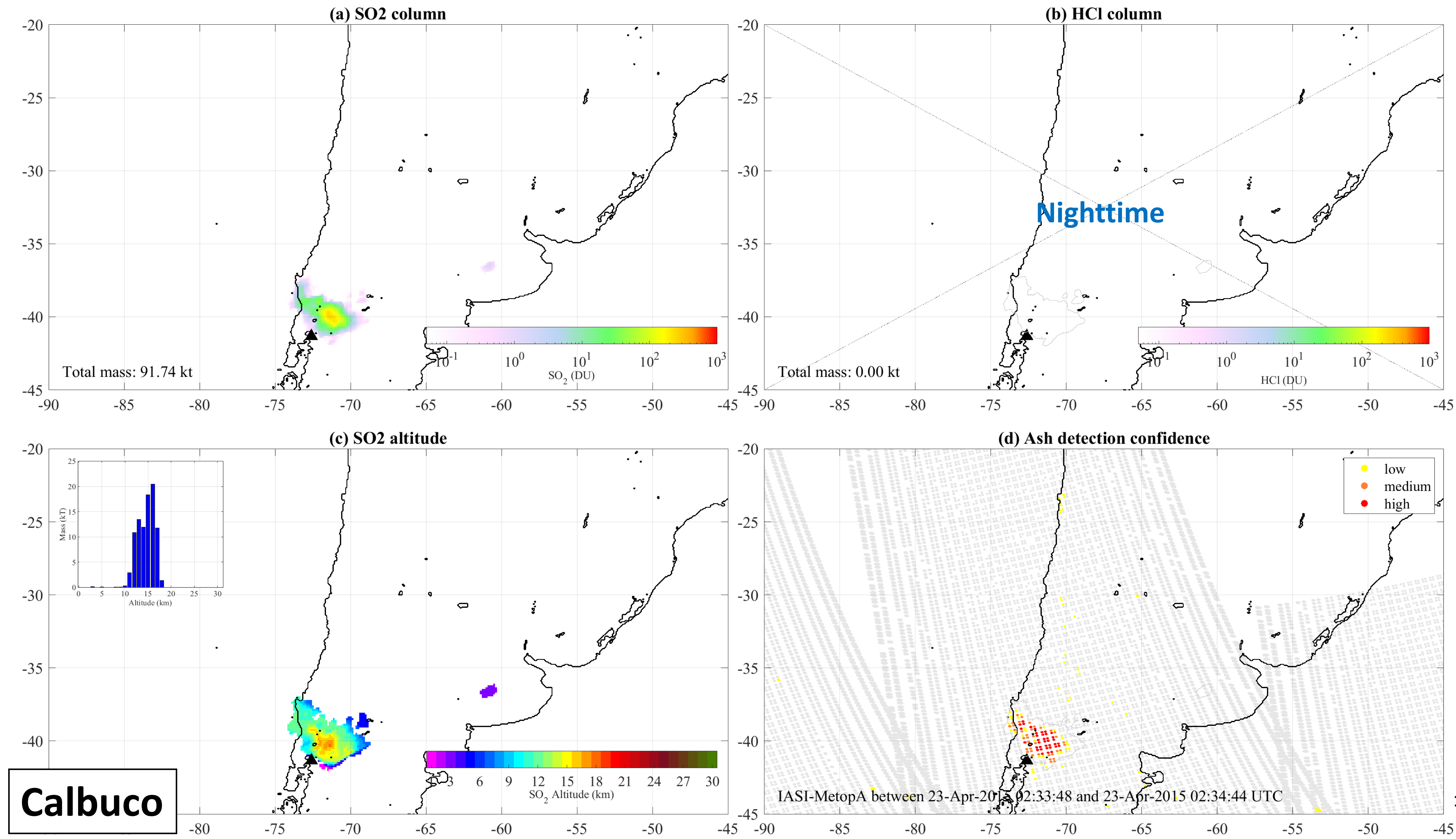
Wikipedia/Marcelo Utreras

22-23 April 2015 eruption

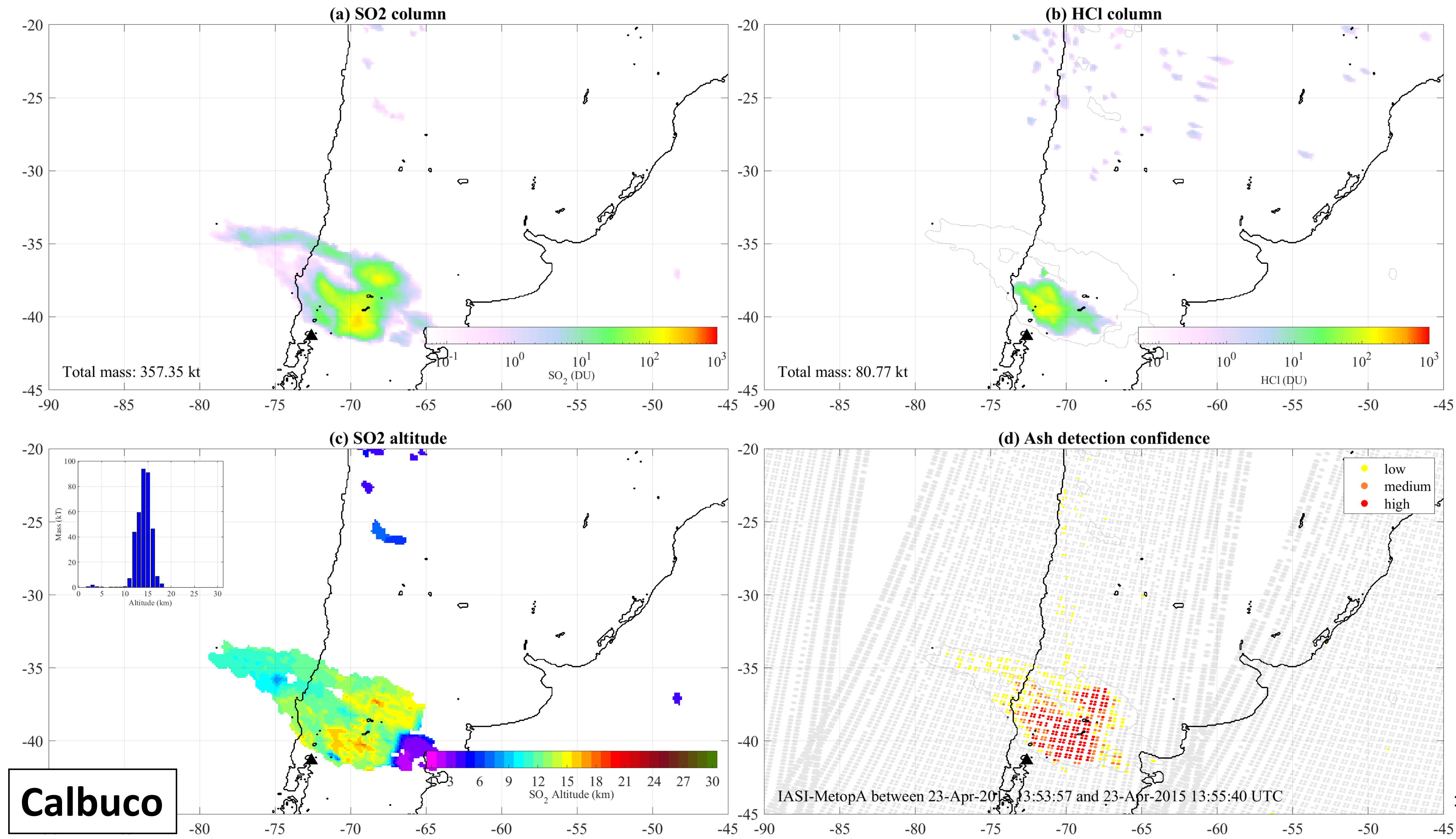
- <3h precursory seismic activity
- Triggered by continued crystallisation of a cooling magma, which led to second boiling and (over)pressurisation of the system, and rapid onset of the eruption (Arzilli et al 2019).
- Two eruption pulses (of 1.5 and 6 h duration)
- 300 – 400 kt SO_2
- 0.3 – 0.9 km^3 erupted tephra (sub-plinian, VEI 4)
- Injection altitudes >15 km (twice)
- Caused measurable destruction of ozone (Solomon et al., 2015)



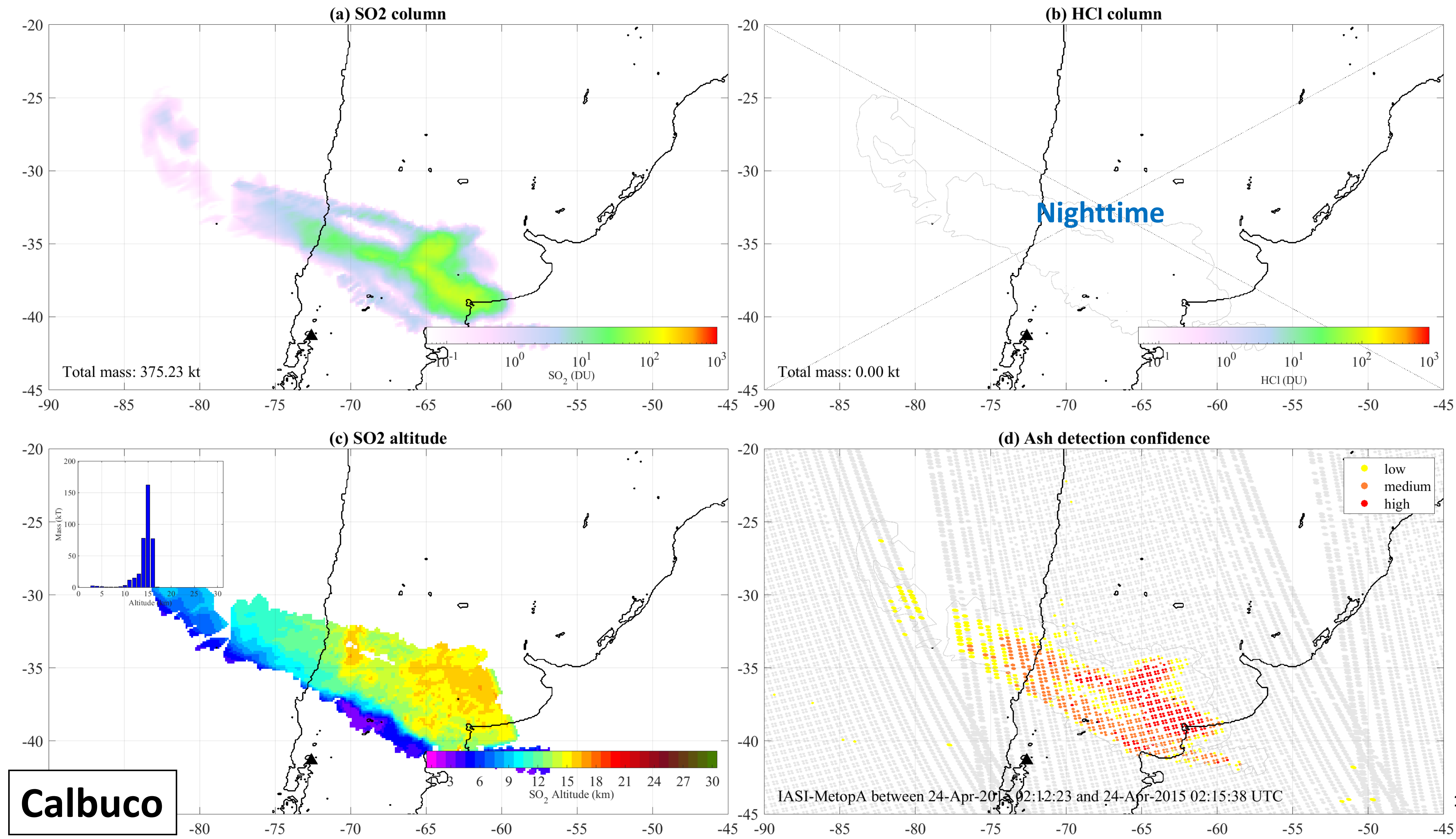
Van Eaton, Alexa R., et al. "Volcanic lightning and plume behavior reveal evolving hazards during the April 2015 eruption of Calbuco volcano, Chile." *Geophysical Research Letters* 43.7 (2016): 3563-3571.



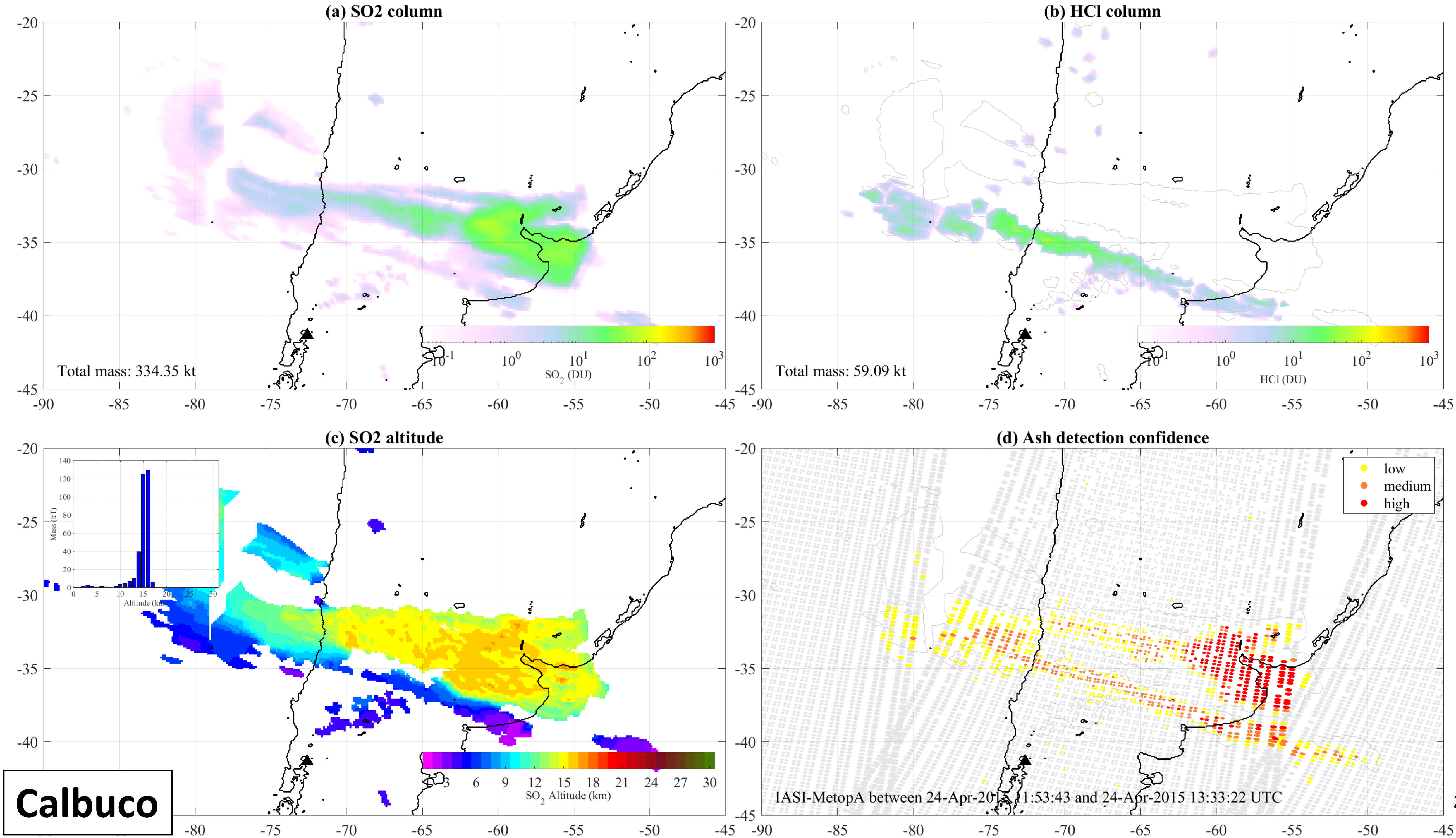
(a) SO2 column
Total mass: 91.74 kt
SO$_2$ (DU)
(b) HCl column
Nighttime
Total mass: 0.00 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO$_2$ Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 23-Apr-2015 02:33:48 and 23-Apr-2015 02:34:44 UTC
Calbuco


(a) SO2 column
Total mass: 357.35 kt
SO$_2$ (DU)
(b) HCl column
Total mass: 80.77 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO$_2$ Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 23-Apr-2015 13:53:57 and 23-Apr-2015 13:55:40 UTC

Calbuco



(a) SO2 column
Total mass: 375.23 kt
SO$_2$ (DU)
(b) HCl column
Nighttime
Total mass: 0.00 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO$_2$ Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 24-Apr-2015 02:12:23 and 24-Apr-2015 02:15:38 UTC
Calbuco

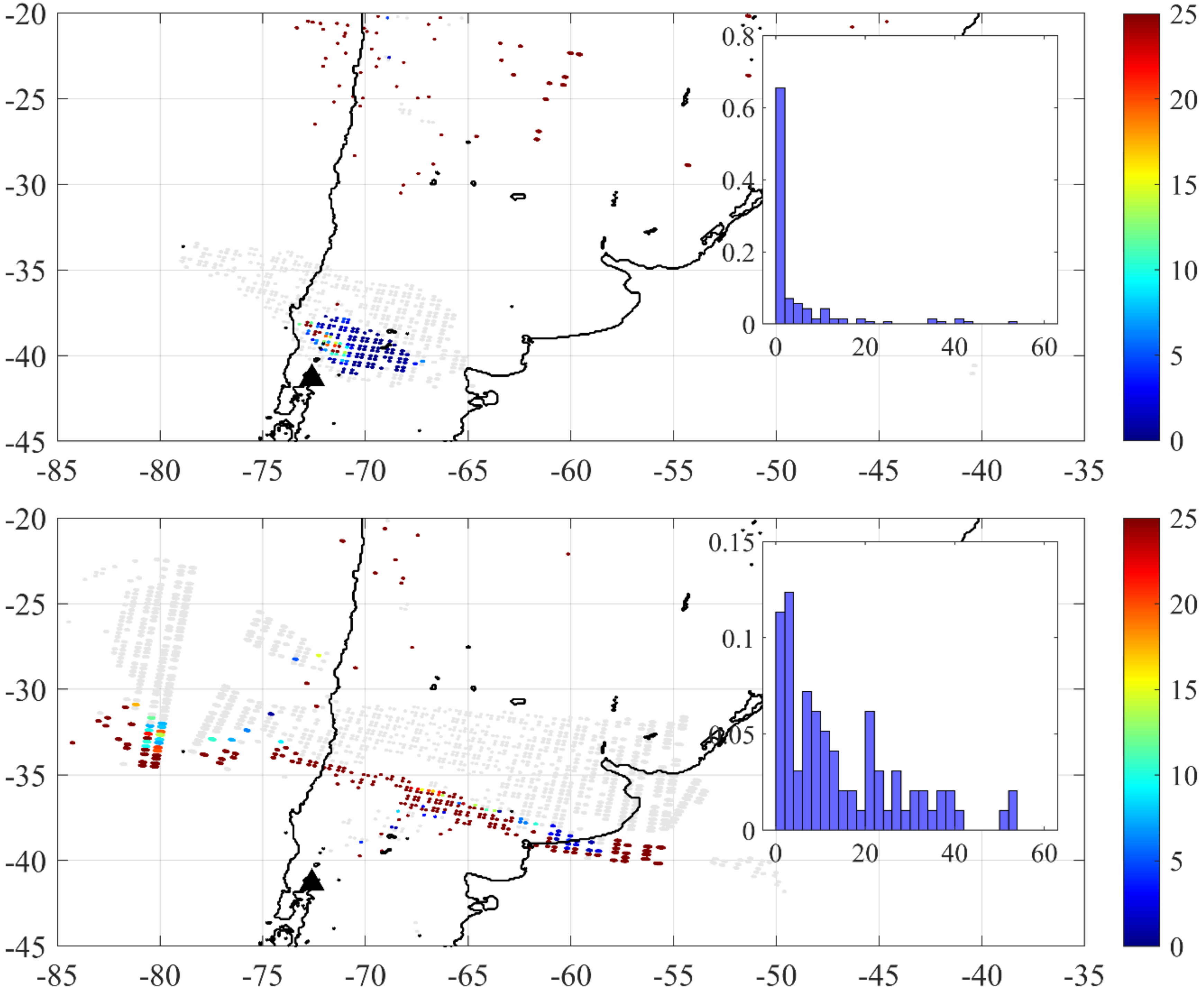


(a) SO2 column
Total mass: 334.35 kt
SO_2 (DU)
(b) HCl column
Total mass: 59.09 kt
HCl (DU)
(c) SO2 altitude
Mass (kT)
Altitude (km)
SO_2 Altitude (km)
(d) Ash detection confidence
low
medium
high
IASI-MetopA between 24-Apr-2015 11:53:43 and 24-Apr-2015 13:33:22 UTC
Calbuco

HCl/SO_2 ratios

In large part of the plume, no SO2 is detected!

Possible explanation: Gas that was scavenged (e.g., by ice or ice-ash mixtures) at higher altitudes in the eruption column fell out to lower altitudes where it was released upon sublimation. The high ratio would reflect the 'scavenging efficiency' which is higher for HCl than for SO_2.



Calbuco

Conclusions

- Large HCl plumes observed in both eruptions at low altitude near the final stages of the eruptions

- Some very high HCl/SO_2 ratios measured, 10 and above

- No HCl is observed in the high altitude parts, leading to a low upper bound on the (gaseous) HCl/SO_2 ratio (<0.05).

- Relative low stratospheric ratios as measured by MLS confirmed

- A combination of scavenging, plume chemistry, uptake by ice particles and variable emission ratios likely explain the observed variations.

- The large Calbuco HCl plume is likely the result of sublimation from ice fall