Rapid ozone loss following humidification of the stratosphere by the Hunga Tonga Eruption

Stephanie Evan, Jerome Brioude, Karen Rosenlof, Ru-Shan Gao, Robert Portmann,
Rainer Volkämer, Christopher Lee, Jean-Marc Metzger, Kevin Lamy, Paul Walter, Sergio Alvarez,
James Flynn, Elizabeth Asher, Michael Todt, Sean Davis, Troy Thornberry,
Holger Vömel, Frank Wienhold, Ryan M. Stauffer,
Luis Millán, Michelle L. Santee, Lucien Froidevaux, William Read





Balloon Soundings

- Maïdo Observatory, La Reunion 21°S
- ECC ozonesonde, CFH water vapor, SO₂ sonde, POPS, COBALD backscatter sonde
- Concurrent LIDAR
- 2-4 launches per night with different payloads,
- 6 consecutive nights (a week after the eruption)



H₂O/O₃ Measurements

- ECC ozonesonde is part of all payloads
- 4 out 5 successful CFH water vapor profiles
- 8 out 11 successful ECC O₃ profiles
- COBALD backscatter sondes present with CFH&ECC O3 payload on 20/01 (pre-plume flight) and 22/01(max of H₂O), measures backscatters @455 and 940 nm



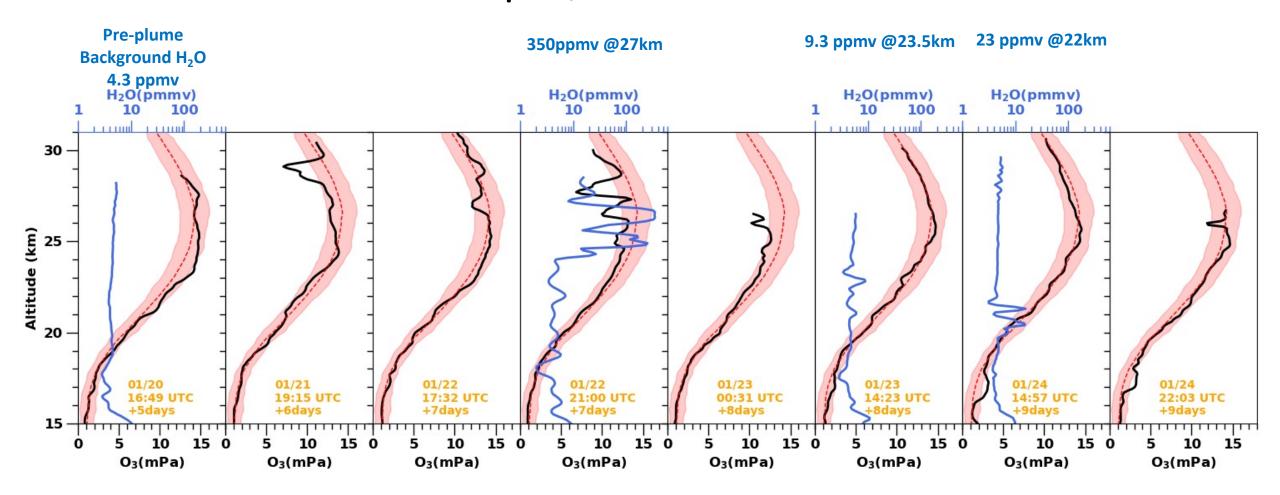


Ozone Data processing

- Follows the guidelines of SHADOZ: Witte et al., 2017
- ➤ Absorption Efficiency Correction
- ➤ Pump Temperature Correction, pump efficiency factors from Komhyr et al., 1986
- ➤ Correction for evaporative effects using RH, Pressure and Temperature conditions during the ozonesonde preparation Smit et al., 2014

The same corrections are used for all ozonesondes profiles at Maïdo Observatory and to compute an ozone climatology for La Réunion for Jan/Feb.

Evolution of water vapor/ozone over La Réunion



An inverse modeling (FLEXPART lagrangian model + in situ H2O measurements) model calculation shows that the Hunga Tonga volcano Injected 120 Tg of water vapor in the stratosphere.

SO₂ interference: example of 2022/01/21 19UTC

The presence of SO_2 interferes with ECC ozonesonde measurement, resulting in – 1 molecule of O_3 reported for each molecule of SO_2 present (if [O3]>[SO2]), causing the O_3 reported to be too low.

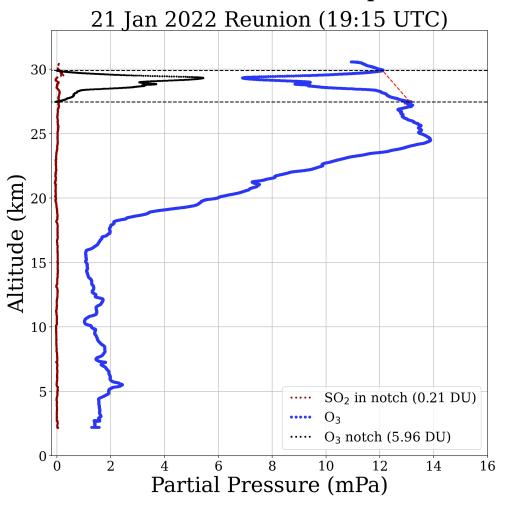
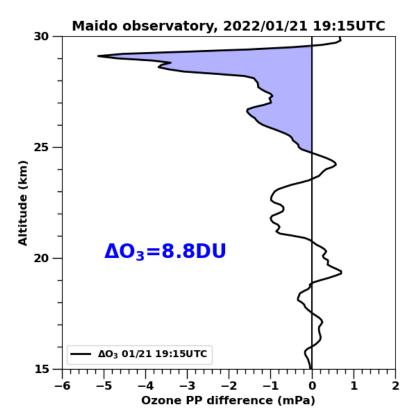


Figure courtesy of Paul Walter

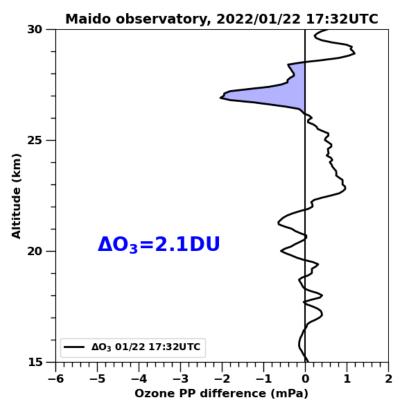
Actual O_3 loss (28.5-31km) = 5.96-0.21 = 5.75DU

An estimated 3-5% and an upper limit of 9% of ozone decrease can be explained by SO₂ interference

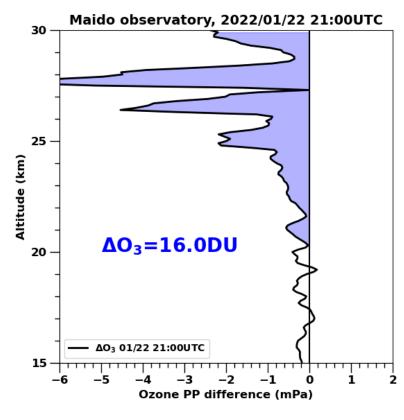
Fast ozone loss following the eruption



Coincident SO₂ measurement, peak of 1.1mPa at 29.5km



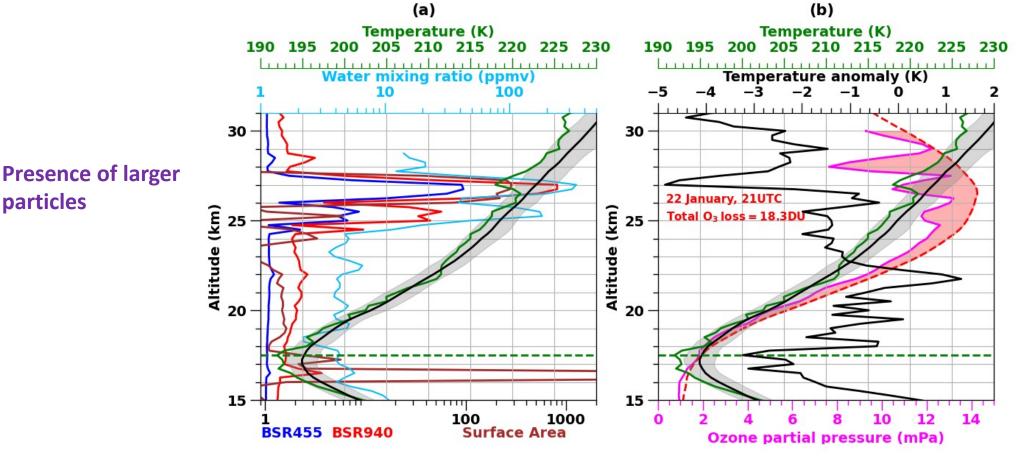
Coincident SO₂ measurement, max SO2 of 0.1 mPa at 27.5km



Presence of high water vapor

O₃ column loss observed a week after the Hunga Tunga eruption is around 2 to 16DU

Ozone loss under enhanced water vapor conditions on 22/01 21UTC



Stronger O_3 decrease observed on 22 Jan, 21UTC is correlated to the presence of aerosols , high water vapor layers and negative temperature anomalies.

The amplitude of the O3 loss is agreement with post-Pinatubo observations

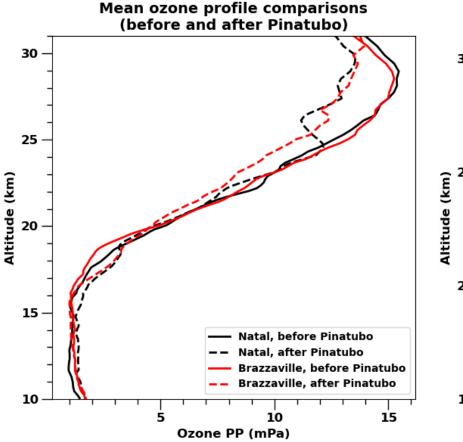
Tropical ozone loss following the eruption of Mount Pinatubo

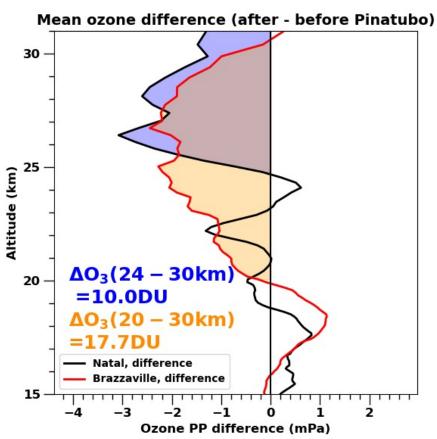
 Schoeberl et al., 1993: decrease of 6% of equatorial total ozone a month after the eruption of Mt. Pinatubo.

Ozone loss is estimated using ozonesonde data from Natal, Brazil taken before and 2 months after the eruption.

 Grant et al., 1992 used ozone profiles at Brazzaville, Congo obtained months before and after the eruption of Mt. Pinatubo.

A decrease in O₃ is observed between 20 and 29km after the eruption of Mt. Pinatubo, with a maximum difference of 20% at ~25km.





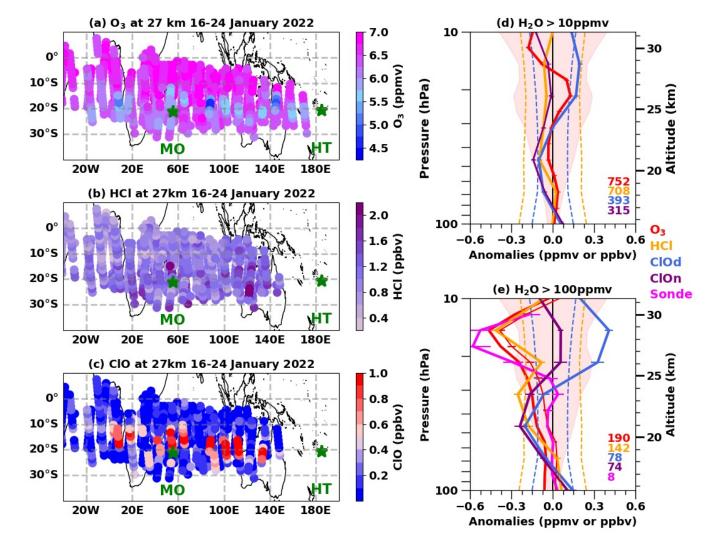
Decrease in O₃ can be due to heterogeneous chemistry, radiative effects or uplift of tropospheric air with lower O₃ to the stratosphere.

MLS HCI/CIO/O₃ observations inside the volcanic plume

MLS HCl, ClO and O₃ v4 data going through standard quality screening.

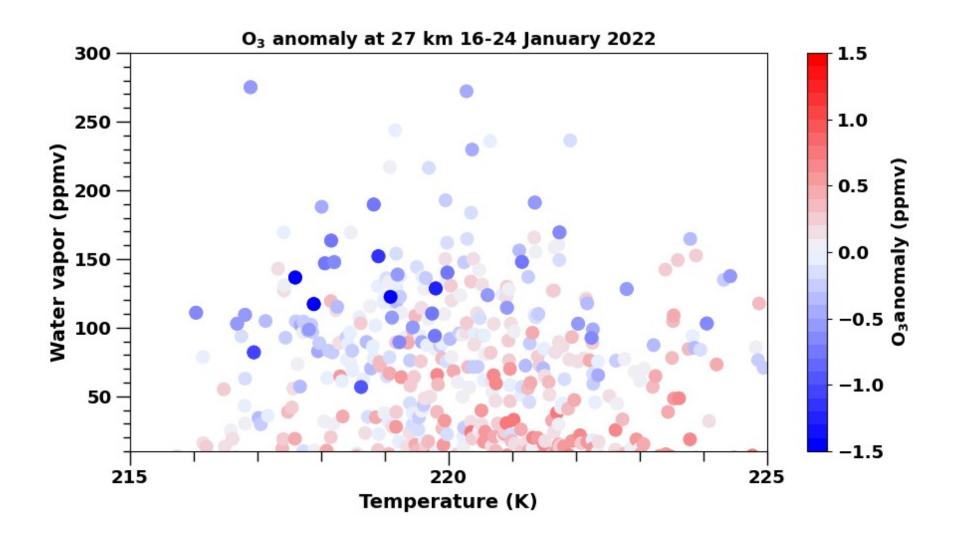
MLS measurements inside the volcanic plume are identified by using a H₂O threshold of 10 ppmv at 21 hPa.

Average O₃/HCl anomaly profiles inside the plume for the period 16-23 January for different H₂O thresholds from 10 to 150 ppmv to assess the sensitivity of stratospheric ozone decrease to H₂O conditions

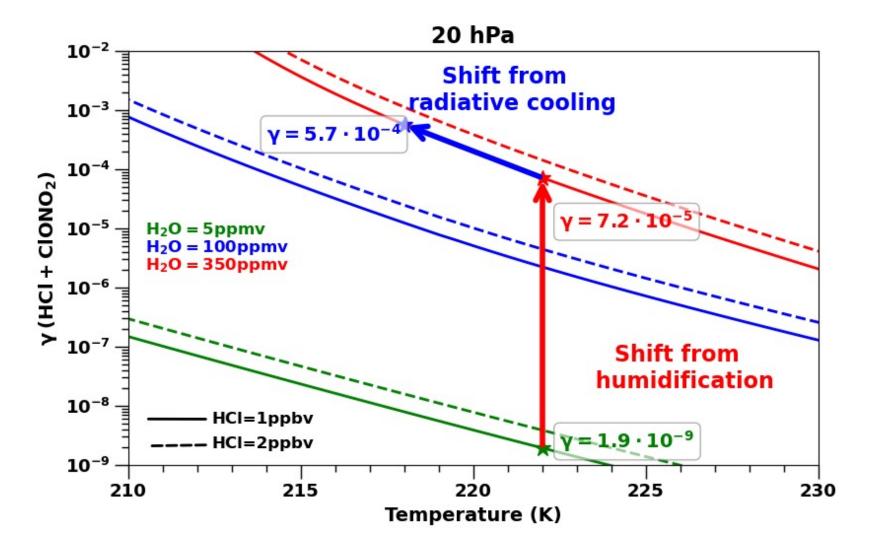


Ozonesonde and MLS data agree on the altitude and amplitude of the negative O_3 anomaly ~ 0.5 ppmv when water vapor mixing ratios > 100ppmv

Heterogeneous chemistry under enhanced water vapor conditions.



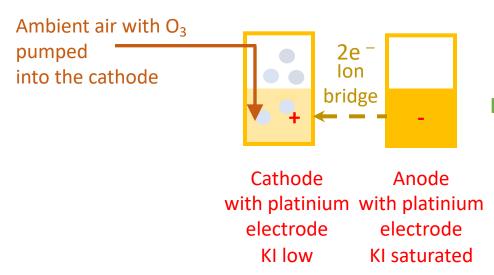
Heterogeneous chemistry under enhanced water vapor conditions.



Conclusions

- High water vapor (up to 350ppmv) was observed above Reunion island a week after the eruption, total of 120Tg of water vapor injected in the stratosphere
- Varying ozone loss of 2 to 16DU was observed one week after the eruption, previously ozone loss reported after Mt Pinatubo was 10 to 17DU 2 months after the eruption
- The vast majority of the decreases in the ozone profiles are NOT explained by SO₂ interference
- Rapid Ozone loss can not be explained by dynamics
- Ozone loss (-0.5 ppmv between 25-30 km) confirmed by MLS observations
- The rapid strong O₃ loss was chemical and most likely facilitated by halogen chemistry on humidified surfaces of sulfate or ash aerosols.

Interference of SO₂ with O₃ by the KI method



Cathode reaction:

$$2KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2KOH$$

Iodide Potassium Free iodine

$$I_2 + 2e^- Pt \rightarrow 2I^-$$

The iodine makes contact with a platinum cathode and is reduced back to iodide ions by the uptake of 2 electrons per molecule of iodine

$$3 \stackrel{-}{\rightarrow} I_3^- + 2e^-$$
 (anode)
 $I_2 + 2e^-$ Pt $\rightarrow 2 \stackrel{-}{\rightarrow} 2 \stackrel{-}{\downarrow}$ (cathode)

An electrical current I_M is generated in the external circuit of the electrochemical cell

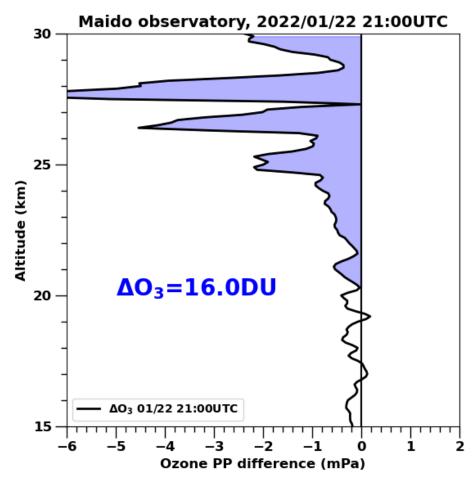
Partial Pressure $O_3 \propto I_M$ cell current

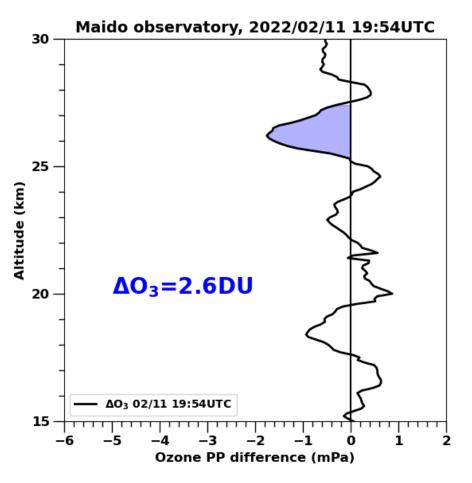
If SO₂ is present, the cathode chamber chemistry is altered: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

The SO2 reaction in the cathode chamber supplies the electrons needed to rebalance the ECC

The ozonesonde actually reports [O3] – [SO2], causing the O_3 recorded to be too low.

Ozone loss a week and a month after the eruption





15

Summary of flights/Data

	Burst altitude (km)	ECC O3	CFH	COBALD	POPS	SO2	LOAC
20/01 17UTC	28.8	X	X	X			
21/01 19UTC	30.3	X			X	X	
21/01 21UTC	19.9	X	X	X			
22/01 18UTC	31.6	X			X	X	
22/01 21UTC	31.5	X	X	X			
23/01 00UTC	26.4	X			X	X	
23/01 14UTC	30.0	X			X	X	
23/01 18UTC	30.6	X	X	X			
23/01 21UTC	33						X
24/01 15UTC	31.2	X			X	X	
24/01 17UTC	31.05	X	X	X			
24/01 22UTC	27.8	X					
25/01 17UTC	30				X	X	
25/01 20UTC	33						X
26/01 15UTC	36						X

MLS SO₂ near Réunion Island

