Hundred-year advances in understanding and surveying volcanic degassing

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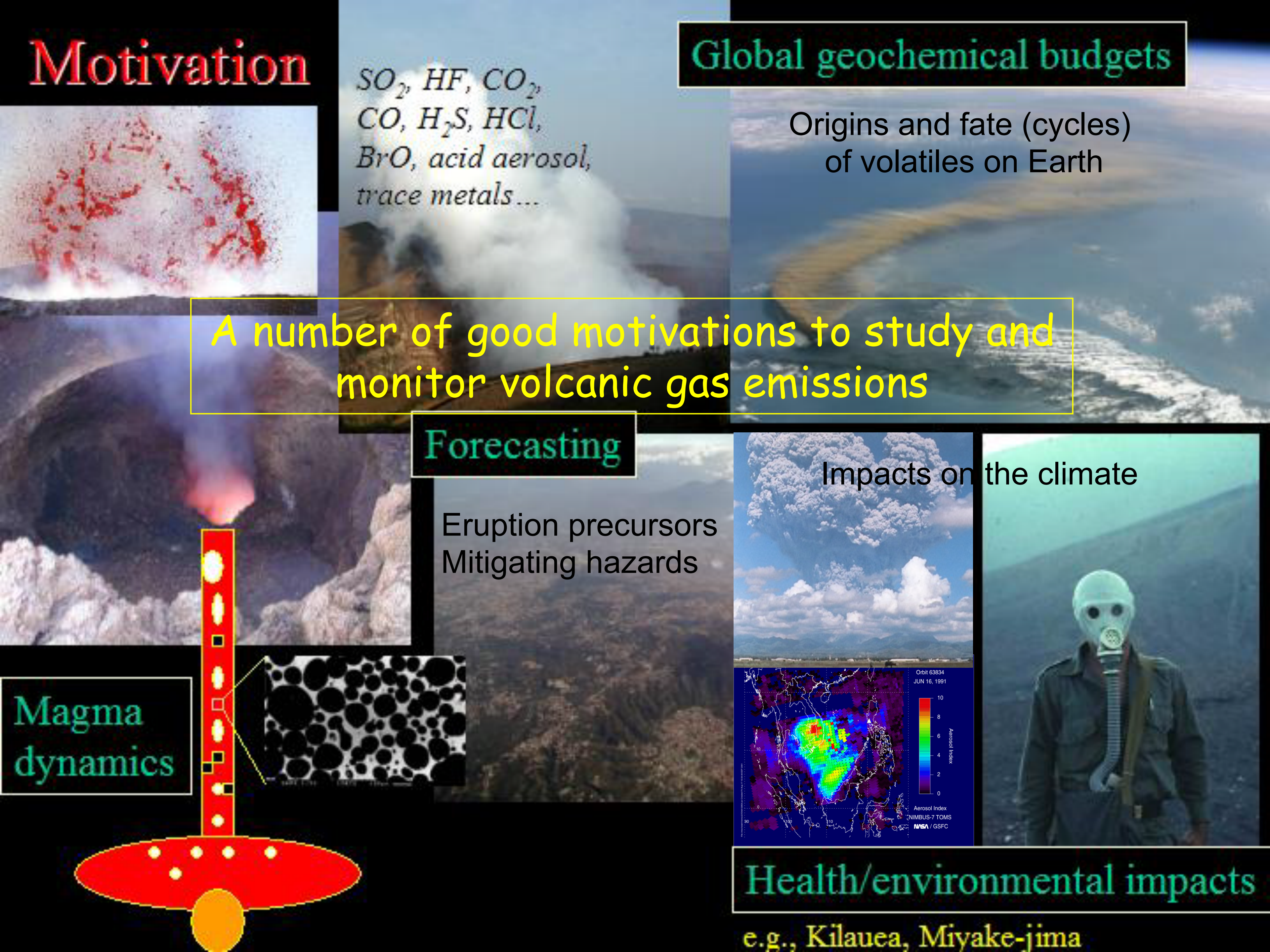
Gas release: a systematic manifestation of active volcanoes ! (erupting AND dormant ones)

- Dormant (closed-conduit) volcanoes: **H_2S**-rich LT fumarolic emissions

- Open-conduit volcanoes: persistent **SO_2**-prevalent HT degassing (plumes)

- Erupting volcanoes: discrete **SO_2**-rich gas emissions


Motivation
SO_2, HF, CO_2,
CO, H_2S, HCl,
BrO, acid aerosol,
trace metals…
Global geochemical budgets
Origins and fate (cycles)
of volatiles on Earth
A number of good motivations to study and
monitor volcanic gas emissions
Forecasting
Eruption precursors
Mitigating hazards
Impacts on the climate
Orbit 63834
JUN 16, 1991
10
8
6
4
2
0
Aerosol Index
Aerosol Index
NIMBUS-7 TOMS
NASA / GSFC
Magma
dynamics
Health/environmental impacts
e.g., Kilauea, Miyake-jima

However, studying volcanic degassing has long received poor attention in early developing volcanology

Two main reasons:

a) Field and technical challenges
(*delicate access to degassing sites, risks*)

b) Information relevance ?

Magmatic volatiles considered negligible components by most igneous petrologists since making only a few weight % of magmas

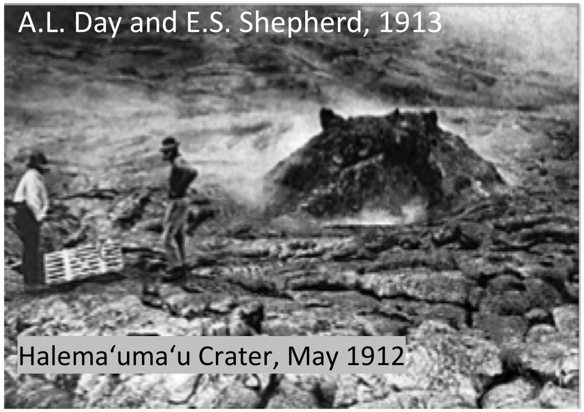
Magmatic volatiles: « the Maxwell's devils » *(N.L. Bowen, 1928)*

Only a few rare scientists early intuited a key role of magmatic volatiles in volcanic processes
(*Albert Brun, Reginald Daly, Frank Perret, Alfred Lacroix*)

Now, that a heavy liquid should be mobile need not cause surprise…this is to be found, I believe, in its high gas content.
– *Frank Perret (1913), Lava Fountains of Kilauea, Am. J. Sci.*

"Gas is the active agent, and the magma is its vehicle"
(F.A. Perret, 1924: The 1906 Vesuvius eruption)

Field studies of volcanic gases started to gradually develop in 20th century thanks to some obstinated pioneers



Discovery of water predominance in volcanic gas (!)

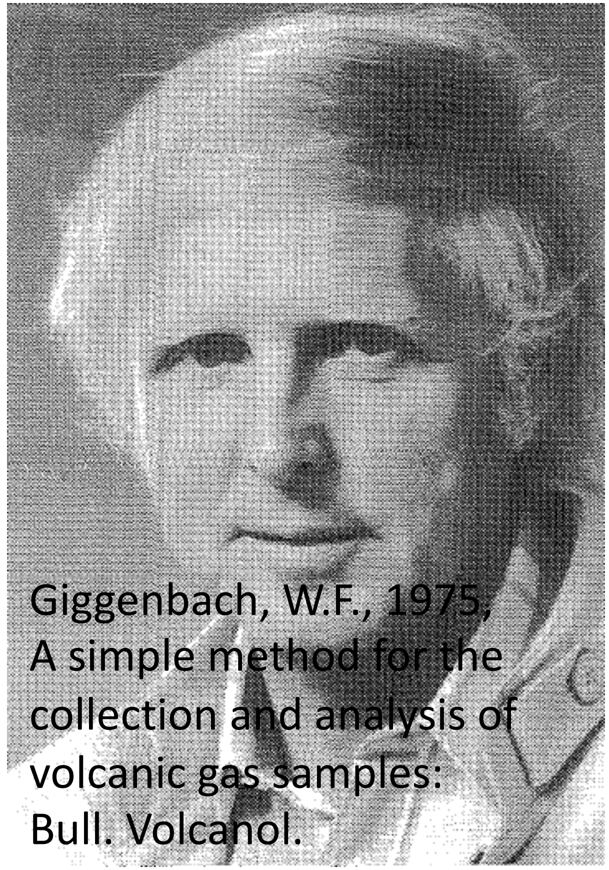
Ludovico SICARDI, Italy

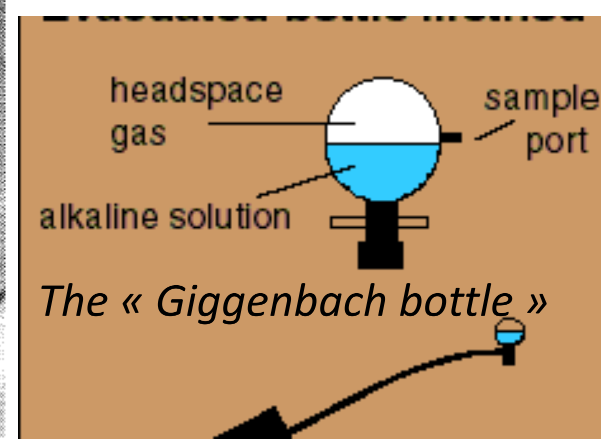
Sadao MATSUO
Japan

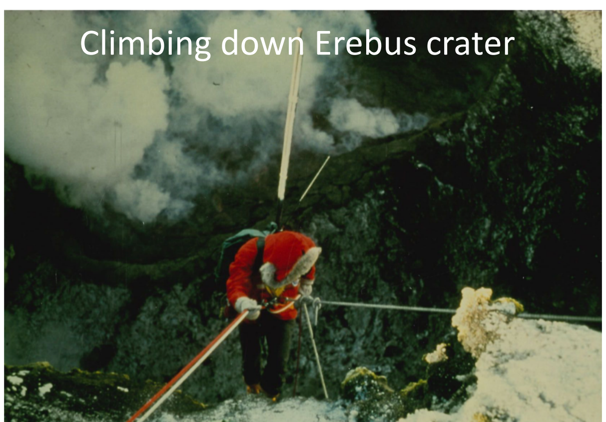
Gudmundur SIGVALDASON, Iceland

"..gas chemistry is the heart of the volcano magma problem." (*Jaggar, "Magmatic Gases", 1940*)

The first measurements of SO_2 and H_2S ratio in fumarolic discharges (NH_4OH-$AgNO_3$ filled bottles; Sicardi, 1955)







A very special tribute to **Werner F Giggenbach**

New Zealand (1937-1997)

Giggenbach 1996, Chemical composition of volcanic gases

Progress from combined studies of volcanic gases (chemistry, thermodynamics, isotopes) and laboratory analysis of volatiles dissolved in magmas

Gas sampling (chemistry, isotopes)

H_2O, H_2

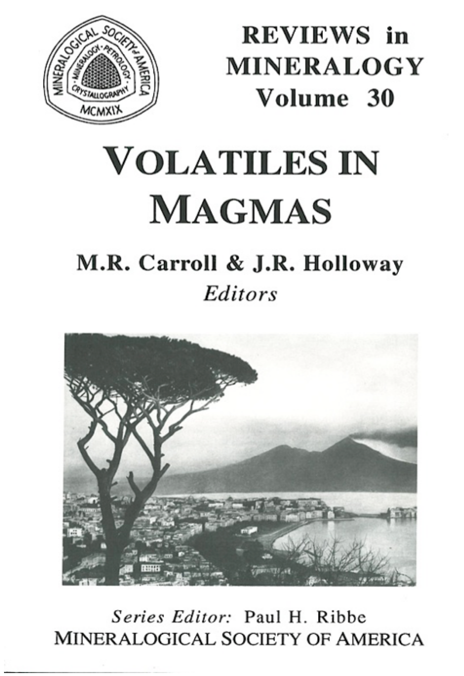
CO_2, CO

SO_2, H_2S

HCl, HF, HBr..

N_2, He, Ar…

Volatile trace metals (Po, Bi, Se, Hg, Cd, As, Ag, Pb, Au, Tl, Cu, Zn…)


REVIEWS in MINERALOGY Volume 30

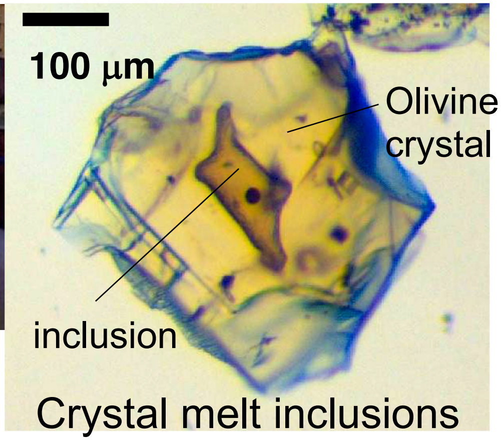
VOLATILES IN MAGMAS

M.R. Carroll & J.R. Holloway
Editors

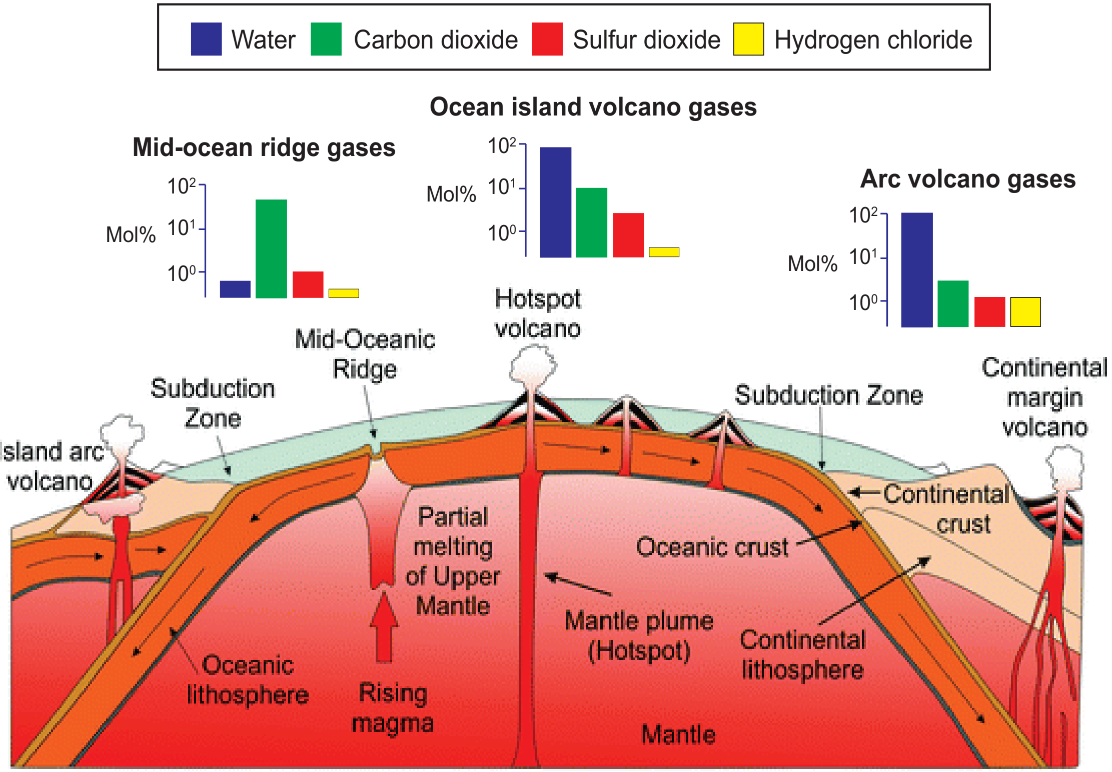
Series Editor: Paul H. Ribbe
MINERALOGICAL SOCIETY OF AMERICA

+ Analog experiments and numerical modelling

Volatiles content & solubility in magmas



VOLCANIC GASES AND GEODYNAMICS
chemical variations and sources (isotopes)

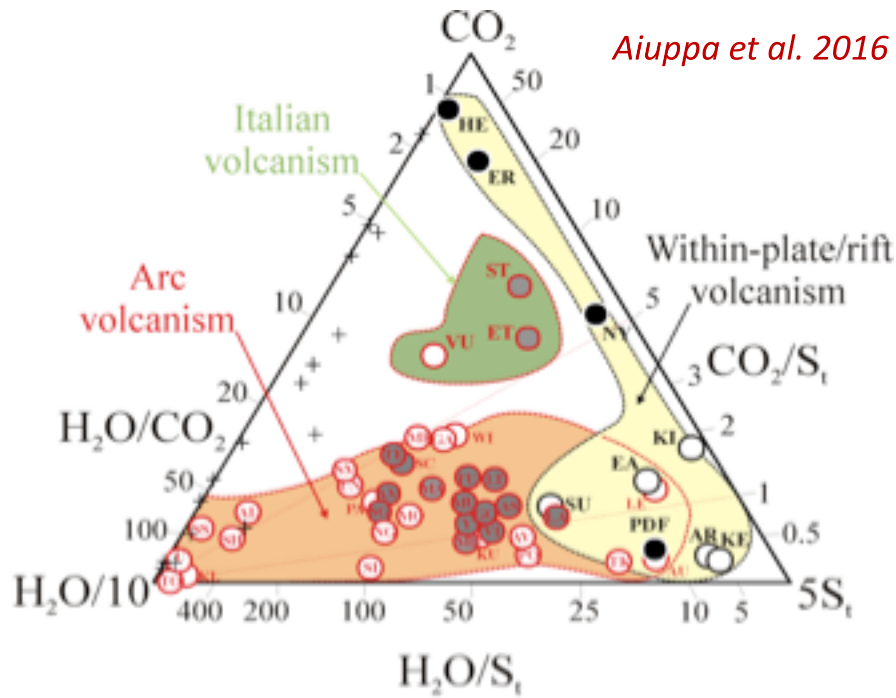


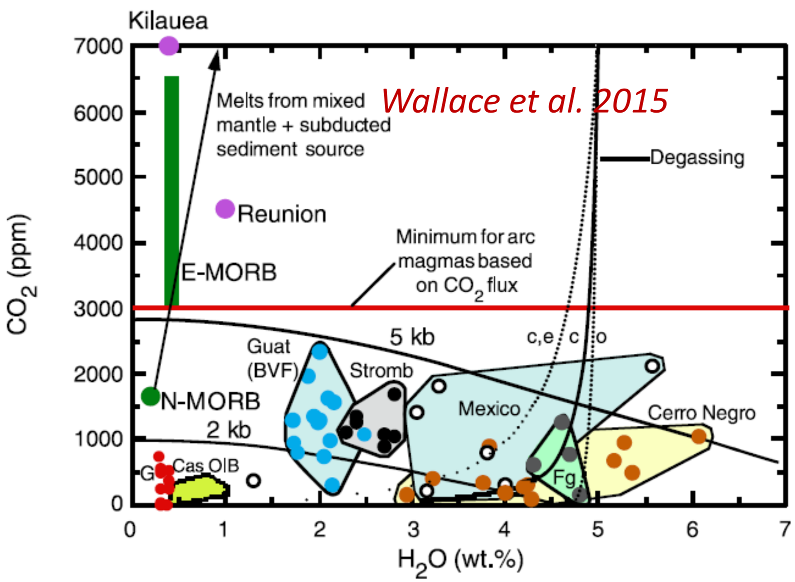
(e.g. Anderson 1975; Gerlach, 1980, 1981; Allard 1983, 1986; Taylor 1986; Gerlach and Graeber, 1985; Symonds et al., 1994; Giggenbach 1996; Hilton et al 2002; Fisher 2008; Métrich and Wallace, 2008; Edmonds et al 2015; Aiuppa et al., 2016; Shinohara 2018)

Volcanic gases in different tectonic settings have different compositions, in good agreement with the dissolved volatile record in magmas

Arc volcanic gases
- rich in water
- C/S <10 (but mostly between 1 and 5)

Non-arc
- poorer in water
- wider spread in C/S



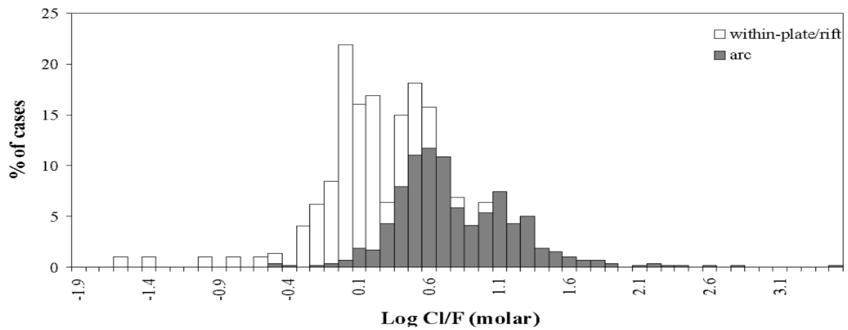


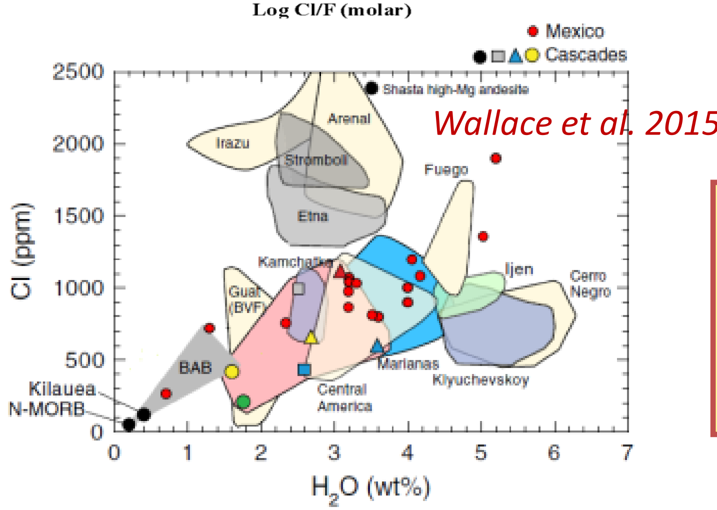
Consistent with the volatile record in melt inclusions trapped in crystals and, hence, with **volatile abundances in magma sources !**

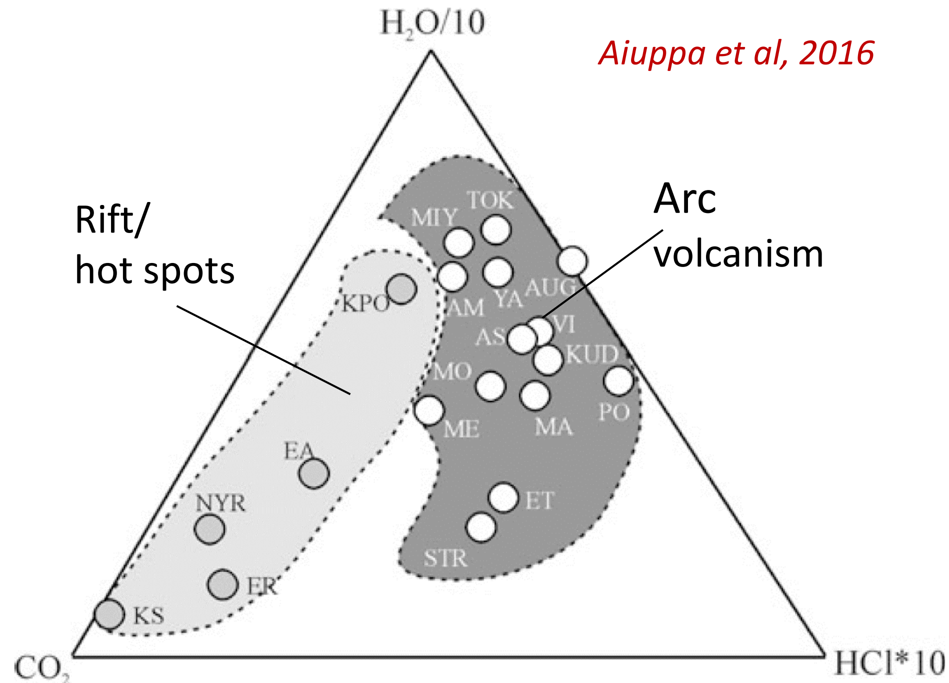
Volcanic gases in different tectonic settings have different compositions, in good agreement with the dissolved volatile record in magmas

Arc volcanic gases
- richer in both water and chlorine
- Cl/F ratio systematically higher

Non-arc
- richer in both CO_2 and fluorine

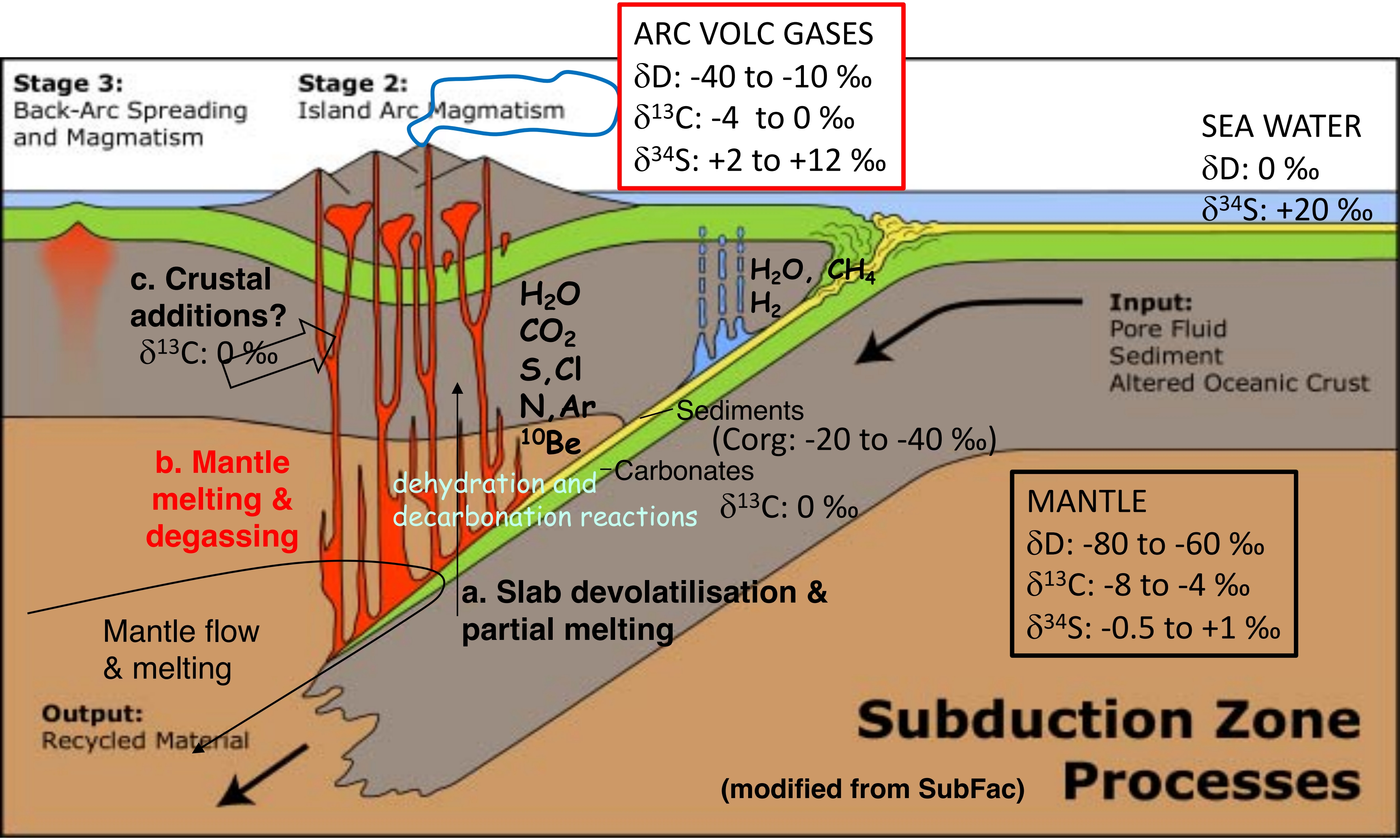






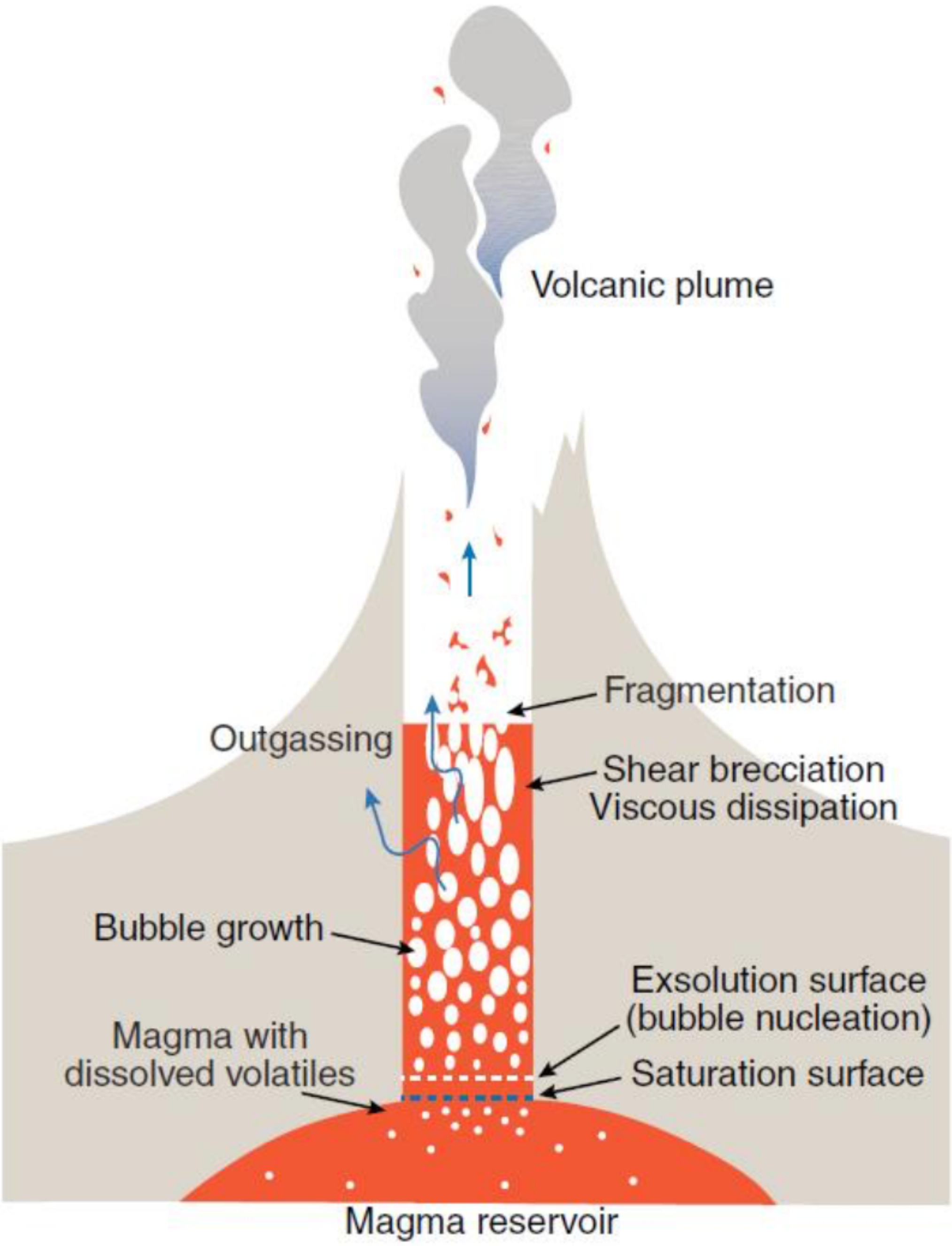
Again, consistent with the volatile record in melt inclusions trapped in crystals and, hence, with volatile abundances in magma source regions !

Isotopic tracers confirm that arc volcanic gases are enriched in volatiles (H_2O, C, S, N) derived from the subducting plates (± crustal additions)



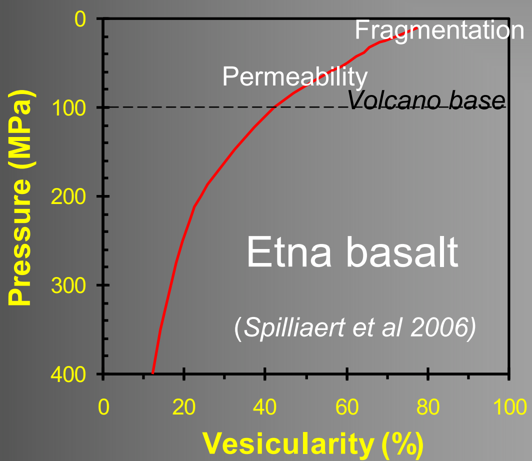
VOLCANIC GASES AND ERUPTION PROCESSES

Gas survey and precursors



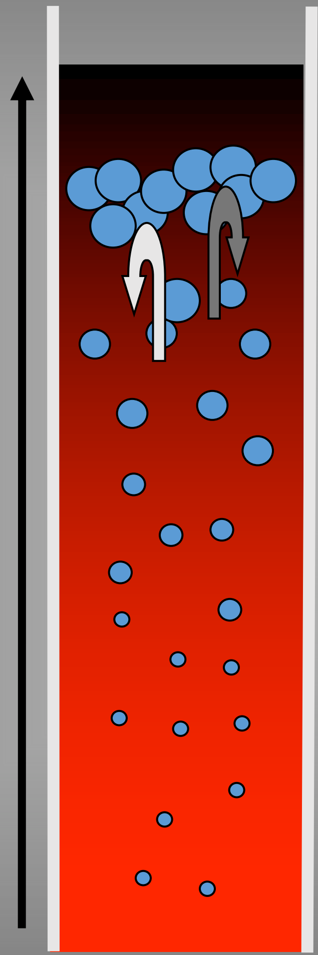
Key properties and roles of the magmatic gas phase in magma dynamics

Magma



Crystallisation paths

Rheological properties (T_L, ρ, μ, β_m)



Gas phase

The driving force of eruptions!
(control of eruption style & intensity)

Highly mobile (fast vector of info on underground processes)
(bubble expansion & coalescence, foams, separate upflow, gas precursors

Composition evolves as pressure decreases (diff. volatile solubilities)
CO_2 << H_2O < S < Cl < F

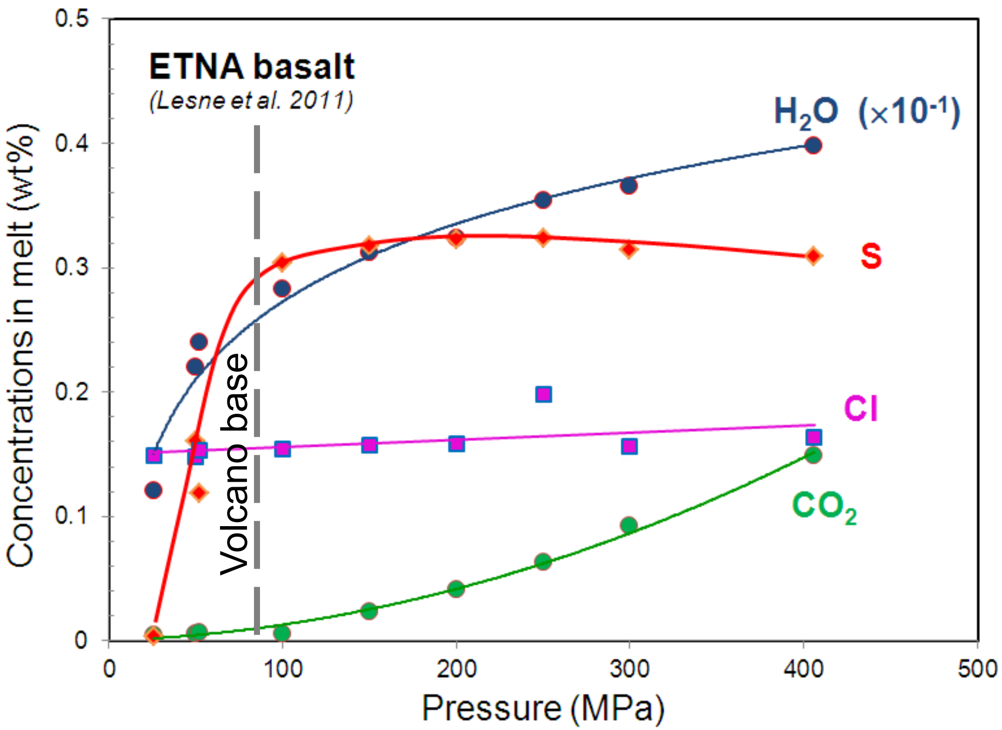
Bubble nucleation & growth
(volatile exsolution, diffusion/expansion)

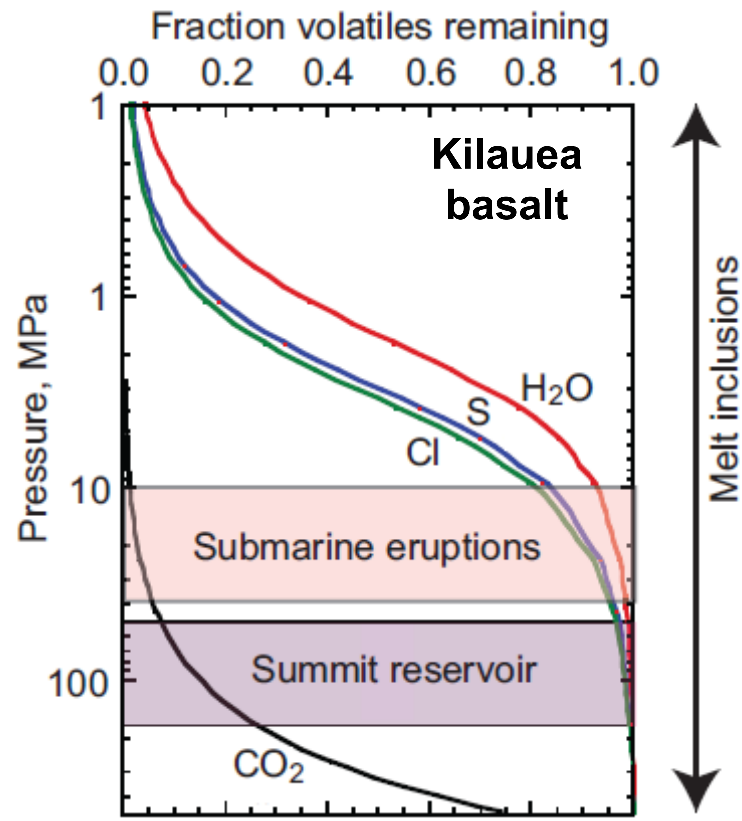
Decompression of 1 m^3 of melt containing 1 wt% dissolved water at 1 kbar (3 km) generates about 100 m^3 of gas at 1 bar and 1000°C

Multi-component (H_2O, CO_2, S, Cl) solubility evolutions during magma decompression (HT-HP lab experiments and crystal melt inclusions)

General exsolution order and bulk loss rate: **$CO_2 >> H_2O \geq S > Cl > F$**

Experimental measurements





Edmonds et al. 2014, and ref. therein

At volatile saturation

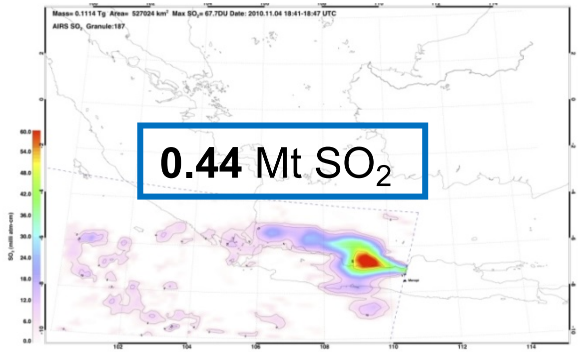
$P_{CO2} + P_{H2O} \cong P_{tot.\ fluid} \cong P_{lithostatic}$

CO_2: the first volatile species to form gas bubbles in melts at depth and, therefore, a key tracer of deep gas supply

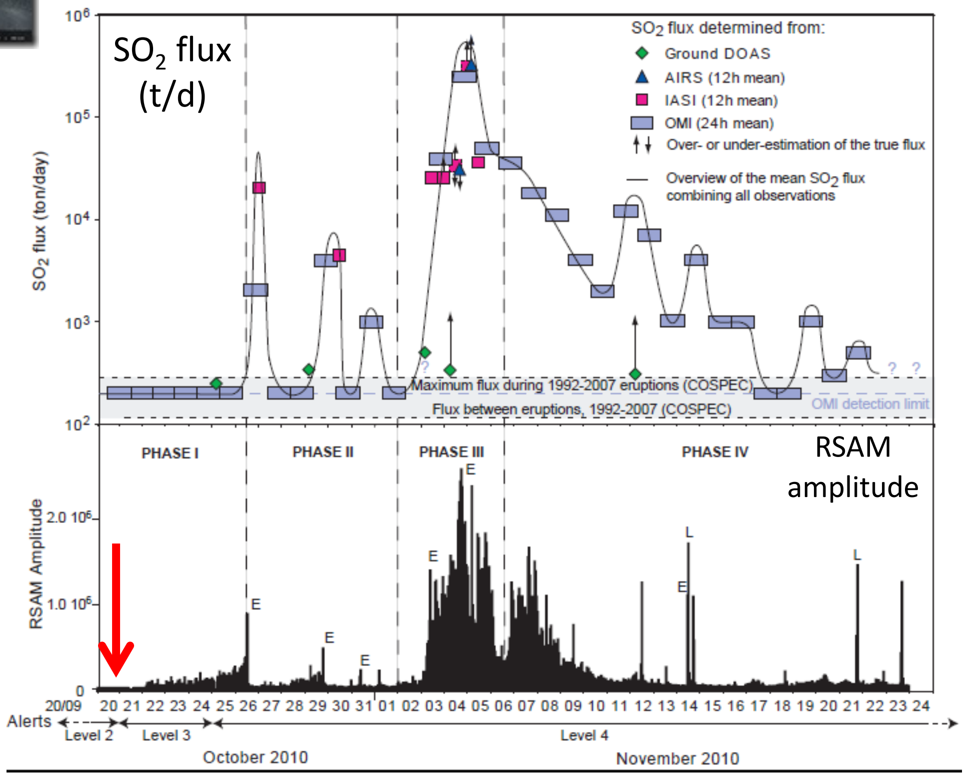
MERAPI: CO_2 precursor of the November 2010 sub-Plinian eruption

(~ 1.5 million evacuees, ~400 casualties)

Intermittent gas sampling



Surono et al. JVGR 2012

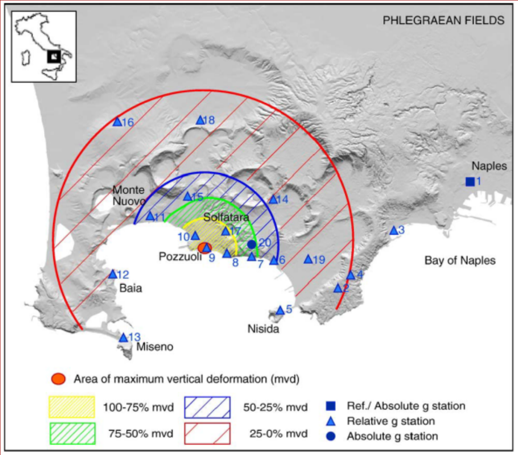


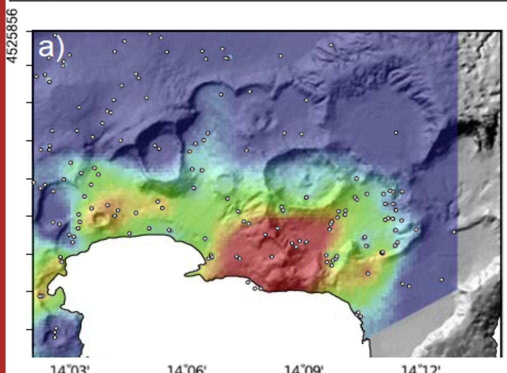
2010 Fumarole gas analyses (mol%)

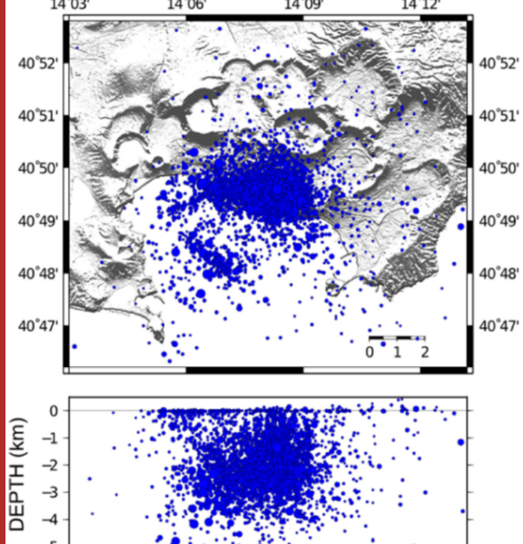
	26 May	Sept. avg	20-Oct.
T (°C)	460	575	575
H_2+O_2	0.07	0.0013[c]	0.02[c]
N_2	1.1	0.1	0.02
CH_4	0.01	n.d.	0.01
CO	n.d.	0.01	0.03
CO_2	5.6	10	34.6
SO_2	0.8	1.0	0.3
H_2S	0.2	0.45	2.5
HCl	0.2	0.36	0.6
HF	n.d.	n.d.	n.d.
NH_3	0.01	0.5	2.8
H_2O	92	87	58.8

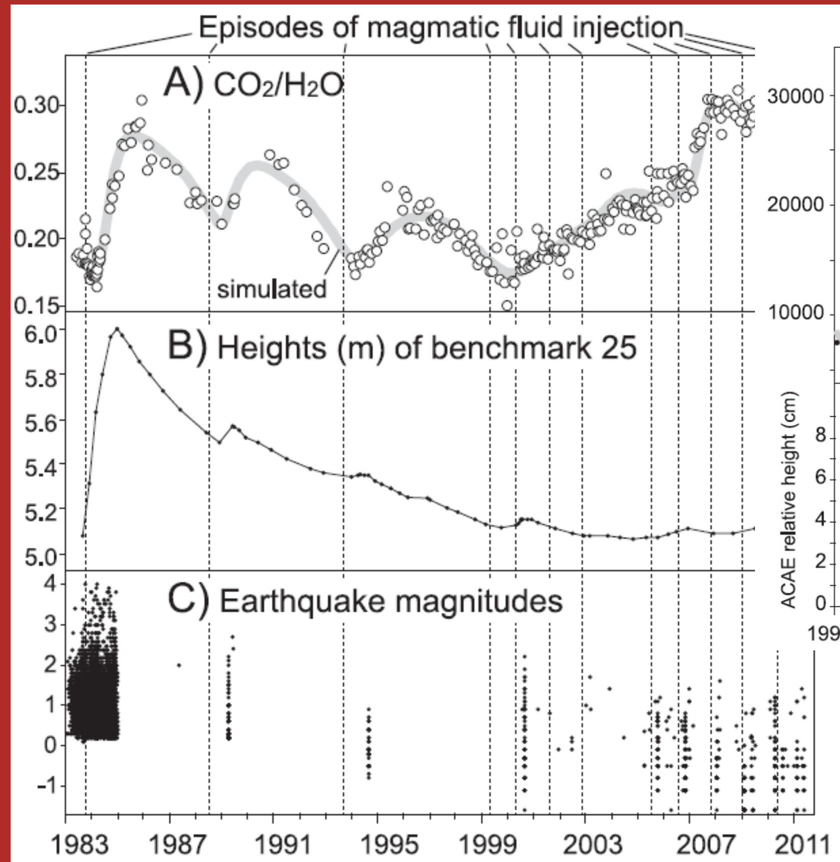
CO_2/S	**5.6**	**6.3**	**12**
CO_2/HCl	28	28	**58**
CO_2/H_2O	0.06	0.1	**0.6**

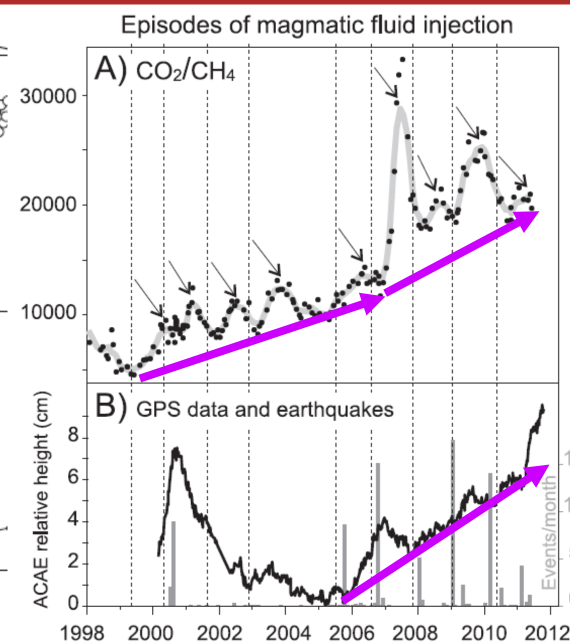
Fumarolic gas survey - Long-term signals
Ex.: stepwise inputs of magma-derived CO_2 and caldera unrest at Campi Flegrei, Italy







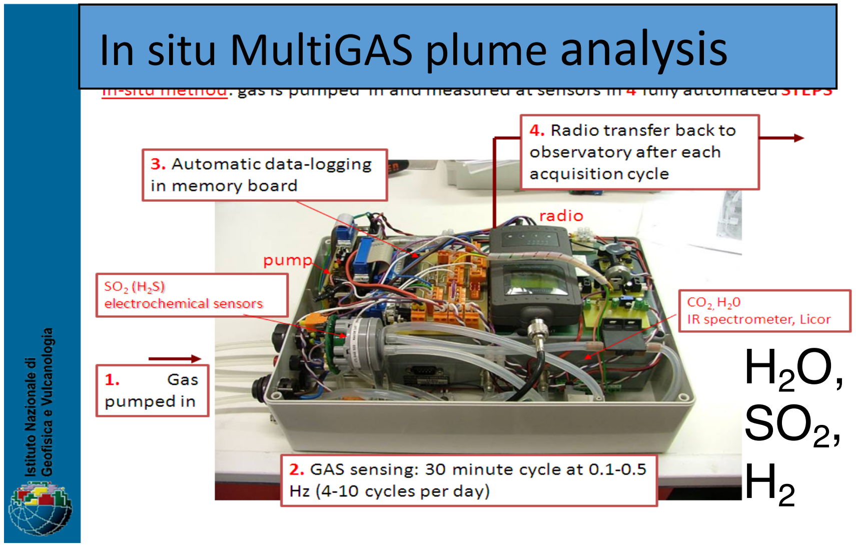




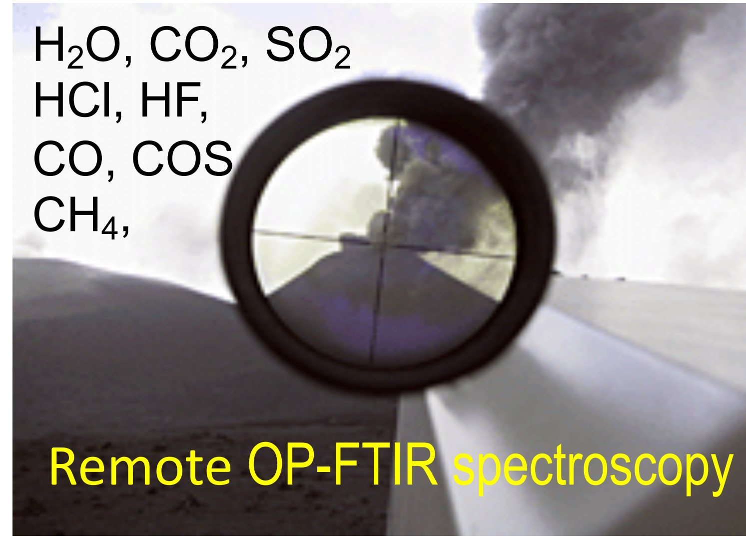
Chiodini et al. 2012

Routine gas sampling

A revolution in last two decades: new tools allowing high-frequency (≥1 Hz) in situ or remote sensing of volcanic gas composition, even during eruptions!



H_2O, CO_2, SO_2, H_2S, H_2



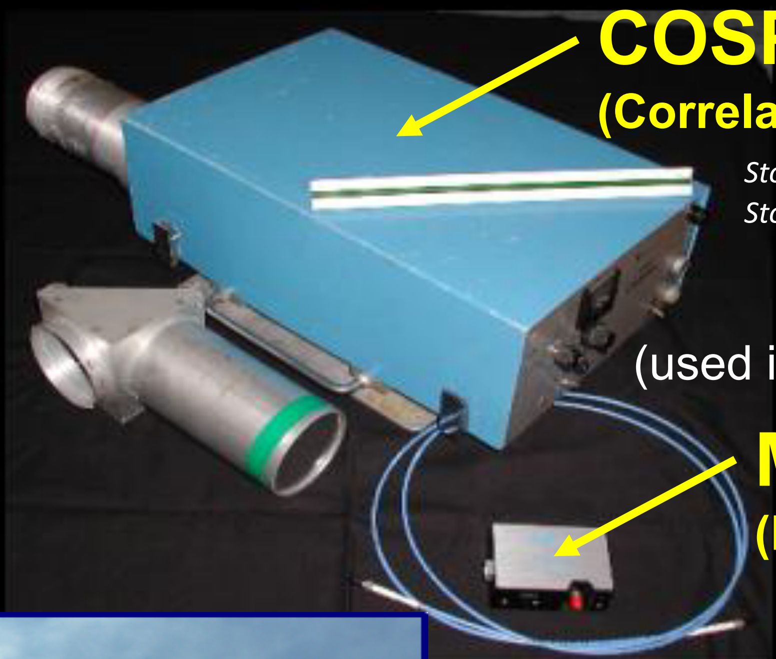
Shinohara et al. 2005; Aiuppa et al. 2005, 2011, 2016; De Moor et al. 2017, Moussallam et al. 2018…

Mori et al. 1993, 1995; Francis et al. 1998; Burton et al. 2000, 2007; Oppenheimer et al 2008; Sawyer et al., 2008a-b; Edmonds & Gerlach 2009; Allard et al. 2002, 2005, 2012, 2016

Bulk gas composition scaled to SO_2 flux ⇨ total gas flux

Coupled with UV remote quantification of volcanic SO_2 fluxes

(absorption of scattered sunlight by SO_2 in the 300-325 nm UV band)



COSPEC

(Correlation Spectrometry)

Stoiber & Malone 1973
Stoiber et al. 1983

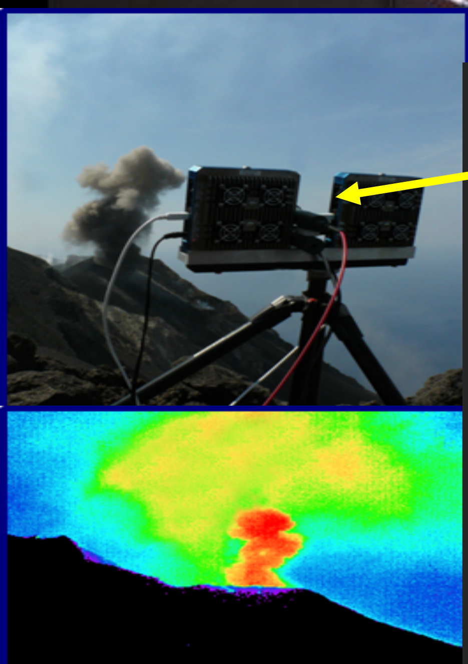
UV

(used in mobile or fixed scanning modes)

Mini-DOAS

Galle et al. 2000
Arellano et al. 2012

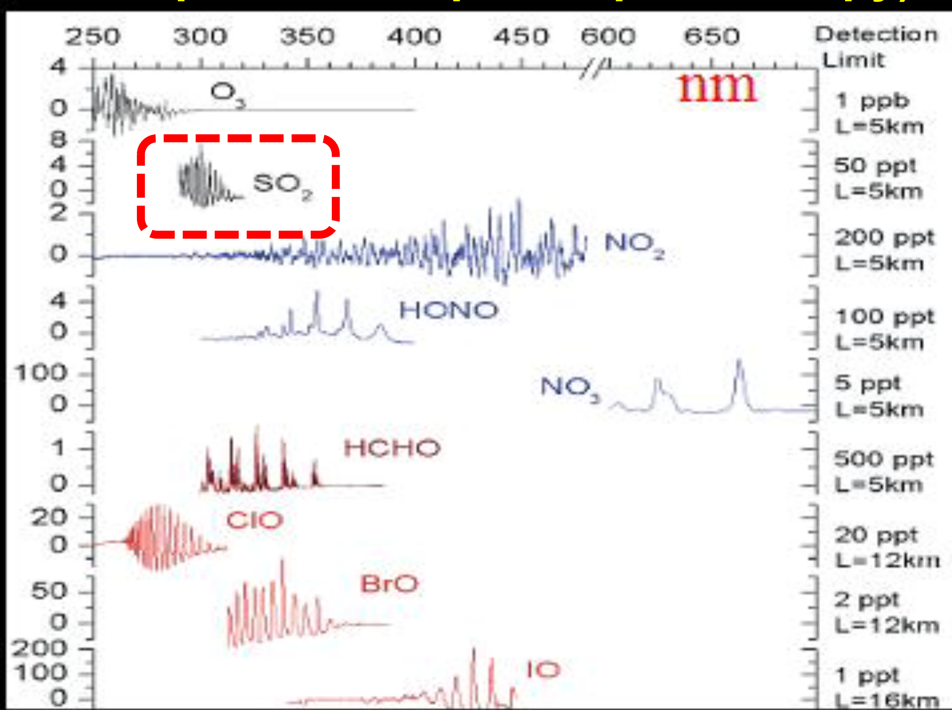
(Differential Optical Absorption Spectroscopy)



Dual UV-cameras

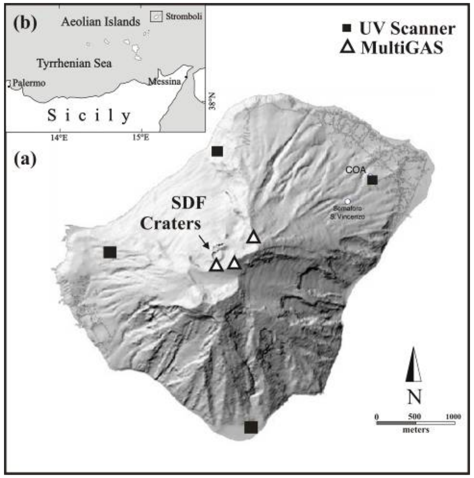
(high-resolution SO_2 imaging, up to 25 Hz))

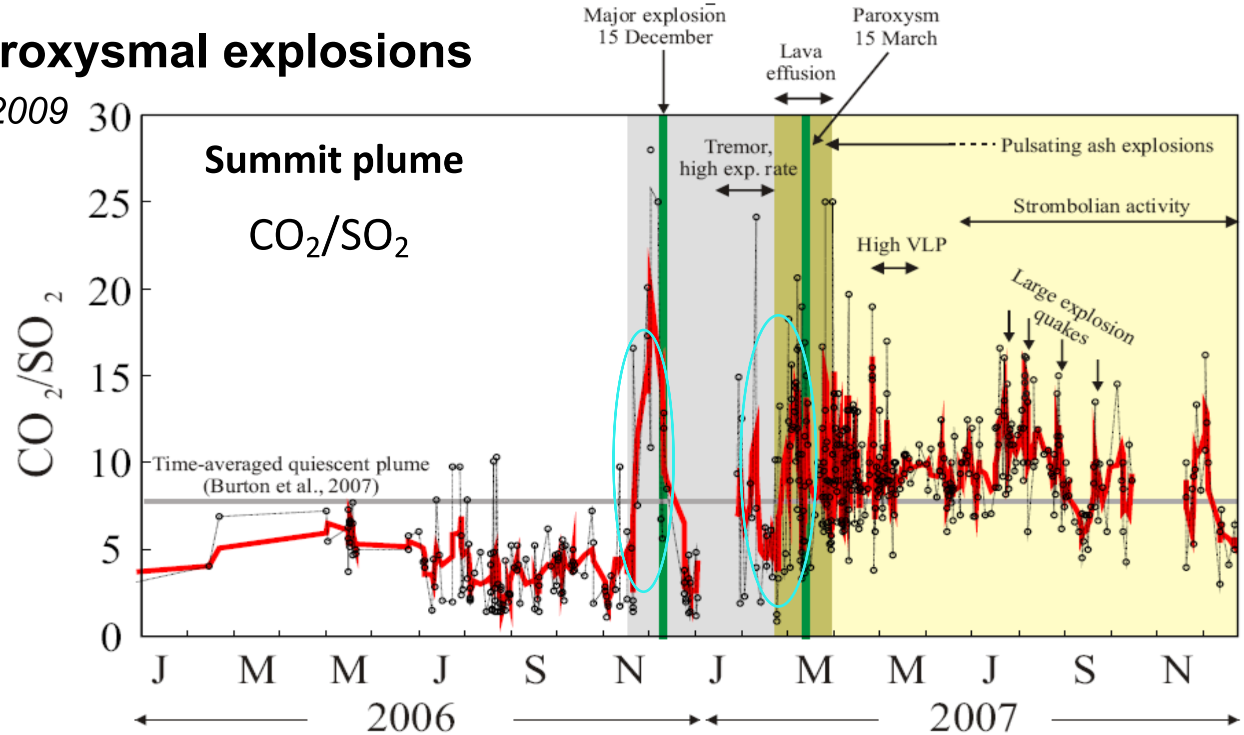
Mori & Burton 2005
Kern et al. 2008
Tamburello et al. 2013



CO_2 precursors of paroxysmal explosions

Stromboli: *Aiuppa et al. 2009*

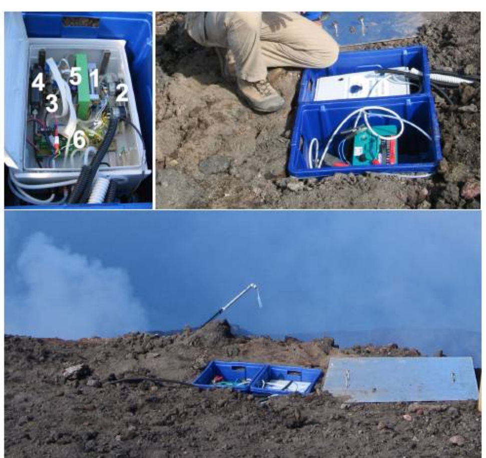


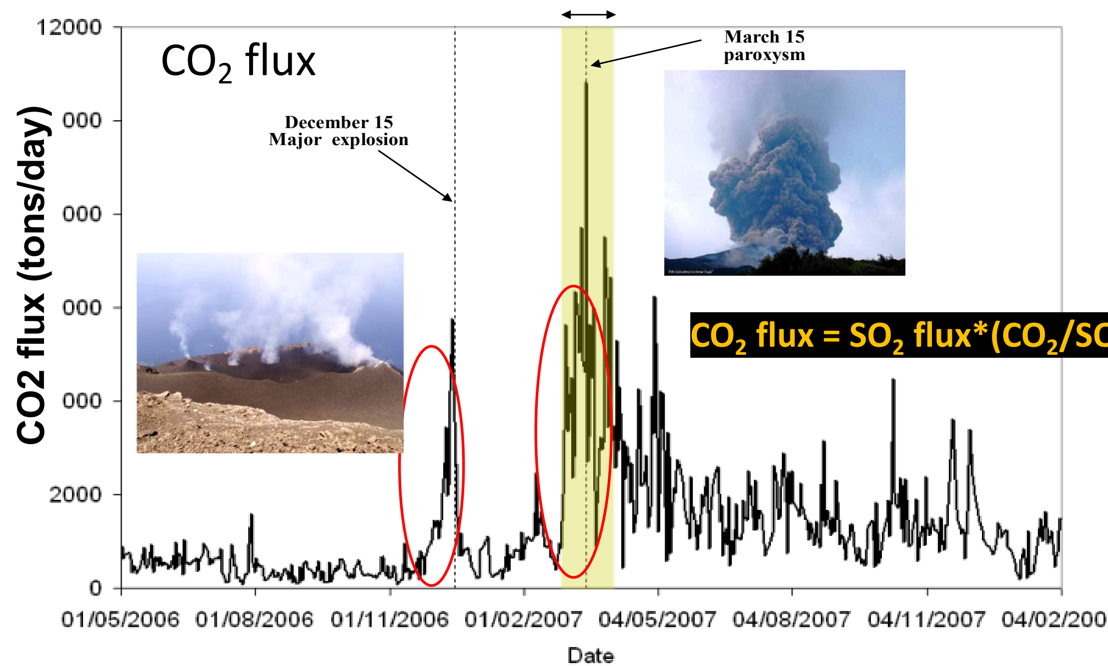


Multi-GAS

CO_2, H_2O: IR spectrometry

SO_2, H_2S: electrochemical sensors

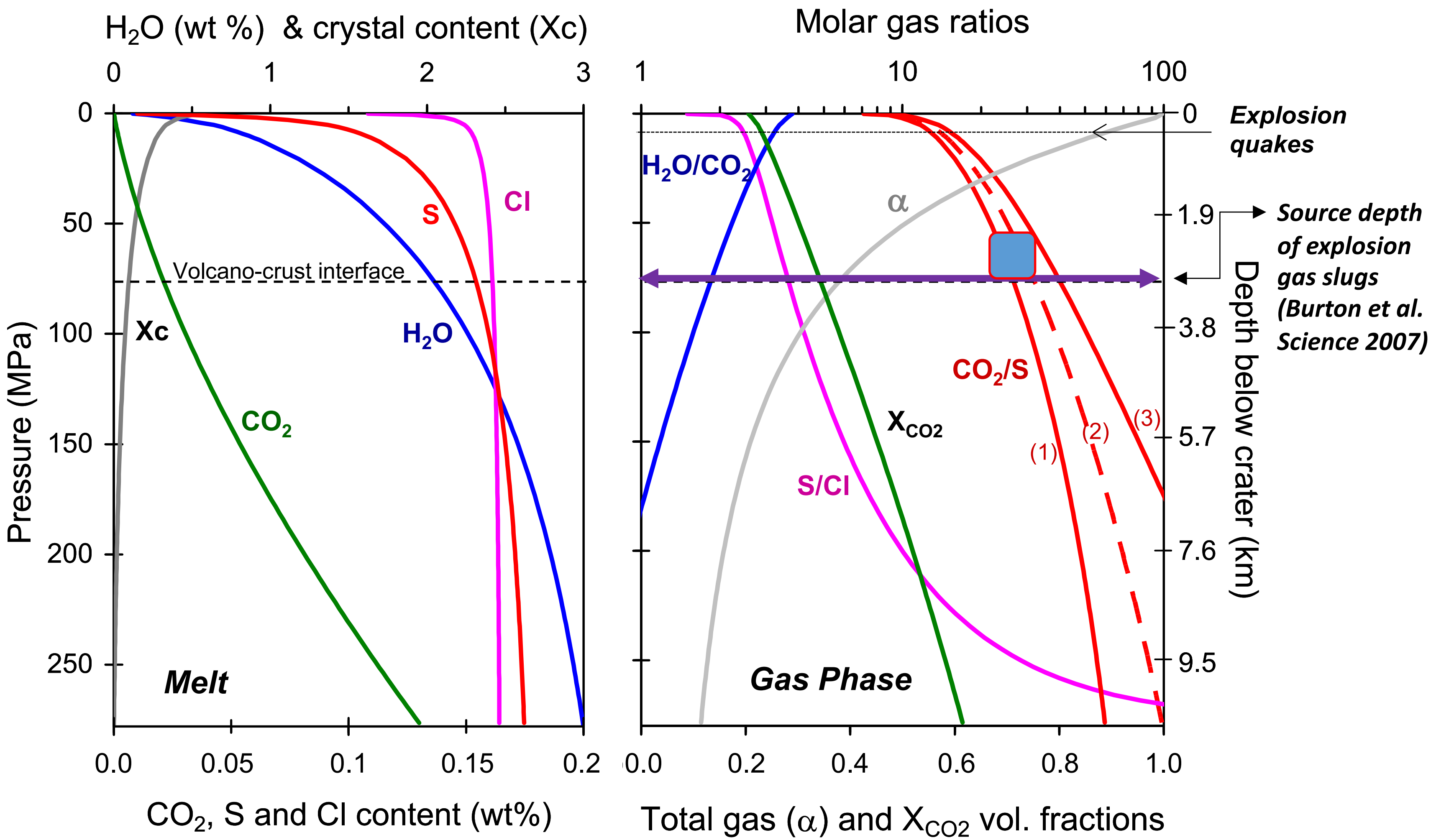




CO_2 flux = SO_2 flux*(CO_2/SO_2)

Volcanic gas ratios as 'geobarometers'

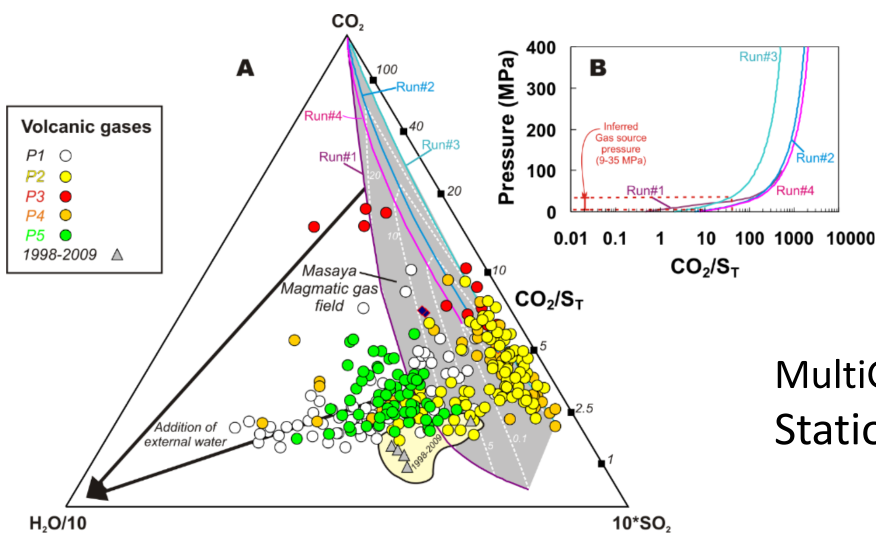
Ex.: *P-related evolution of molar ratios in the magmatic gas phase during CSD decompression of Stromboli basalt from 280 MPa (~10.5 km depth) to the surface, computed from the measured amounts of dissolved volatiles in the melt (Mis)* *(Allard, 2010)*

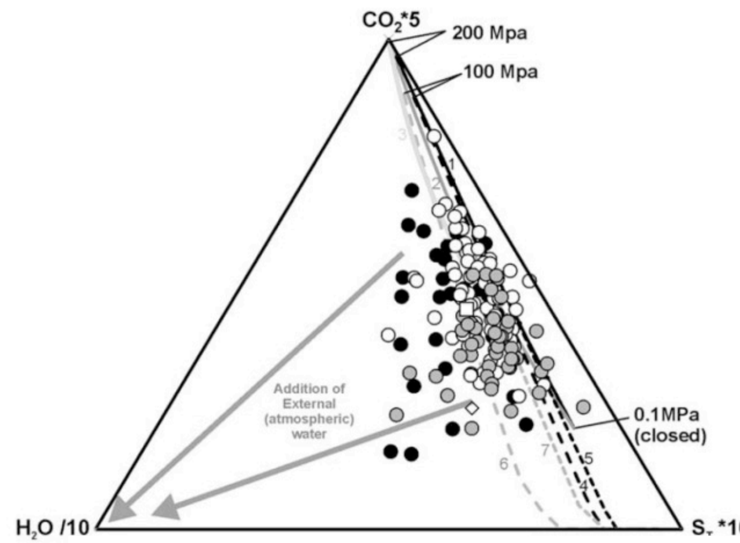


Also, solubility and thermodynamic models (Newman & Lowenstern 2002; Papale et al., 2006; Burgisser and Scaillet 2008; Moretti et al., 2013....)

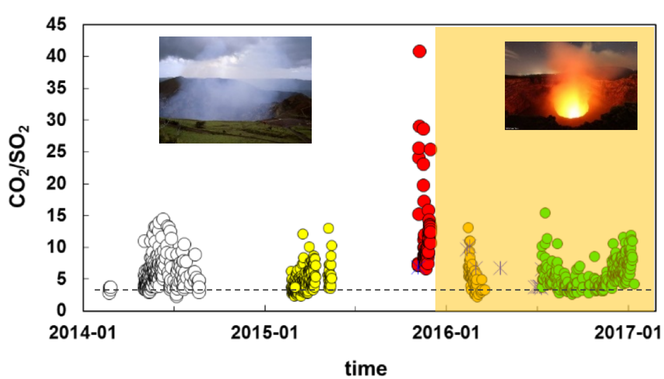
Masaya, Nicaragua (2014-2017)

Villarrica, Chile (2014-2015)

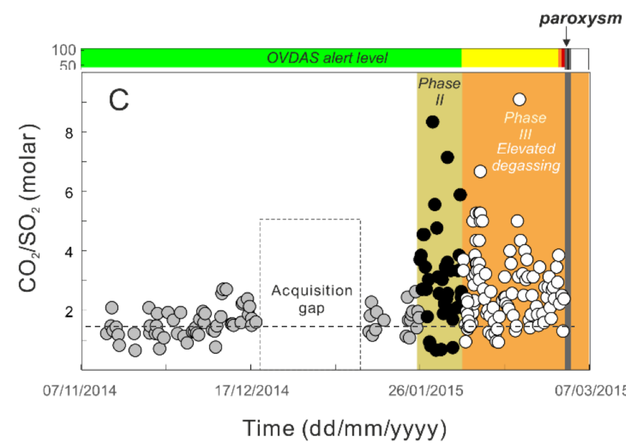




MultiGAS Stations



Aiuppa et al. 2016
Aiuppa et al. 2018



CO_2/SO_2 ratio variations weeks/months prior to unrest or eruption due to supply of CO_2-rich, deeply sourced (10-40 MPa) bubbles during magma decompression

DEEP CARBON OBSERVATORY
RESERVOIRS AND FLUXES

DECADE

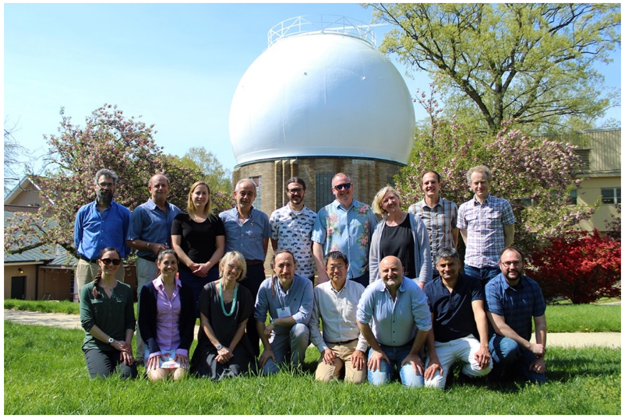
The DCO-DECADE (DEep CArbon DEgassing) Initiative, 2012-2019

3 main goals

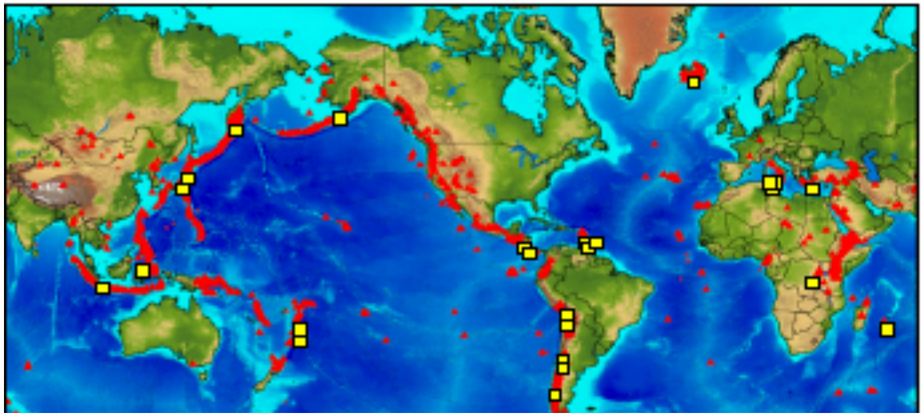
A. Improve **current estimates of deep carbon emission budget from global subaerial volcanism and active lithospheric regions**, in particular from subduction zones.

B. Develop **a network for continuous CO_2 survey on about 25-30 of the most actively degassing volcanoes on Earth**, in connection with volcano Observatories & Agencies.

C. Build up a **database** for global deep carbon emissions from volcanic and lithospheric regions (plumes, hydrothermal fluids, soil emanations, groundwater flows, etc.)

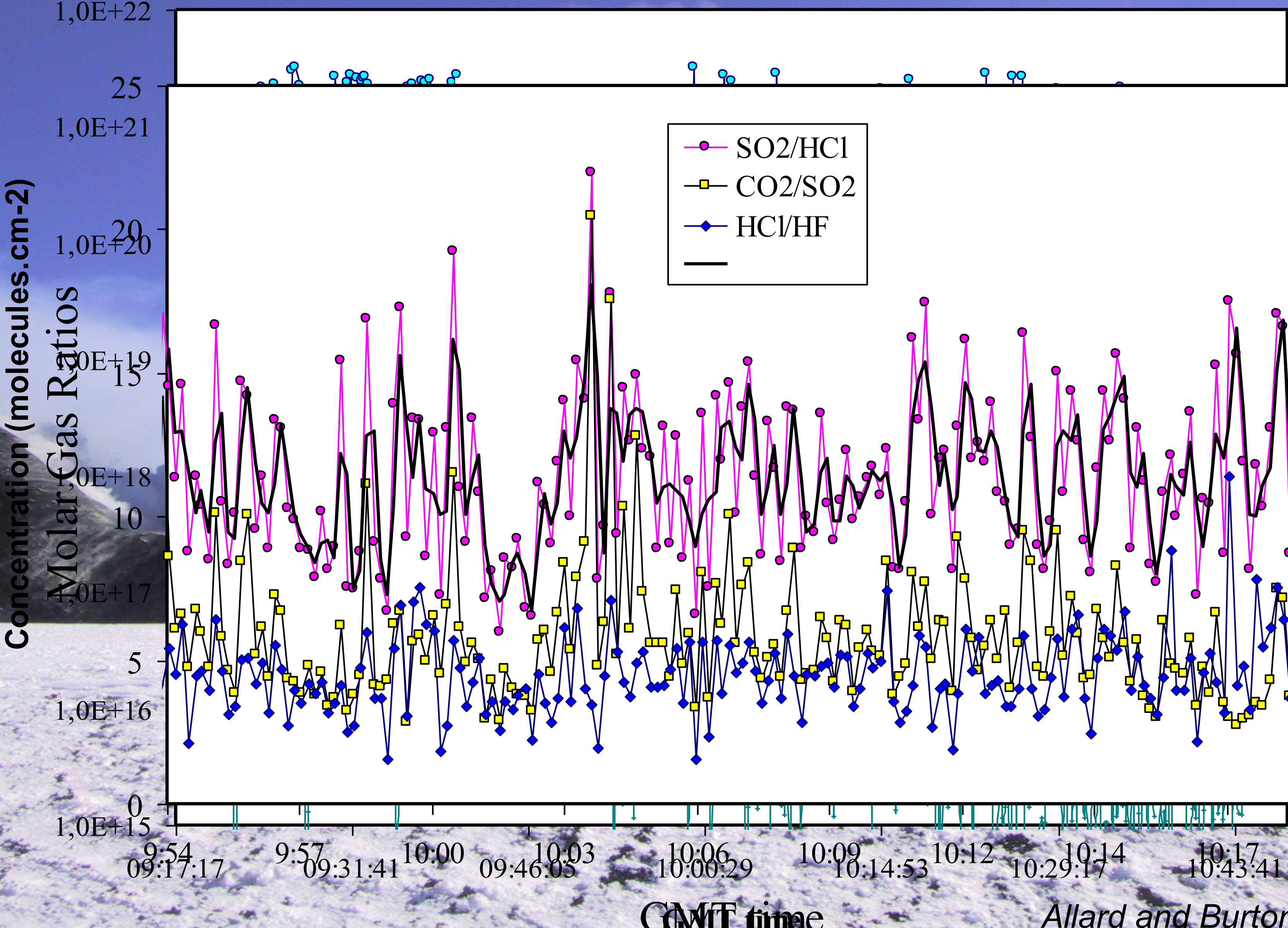


Board Synthesis Meeting, Carnegie Washington, April 2018



28 main volcanoes worldwide now permanently monitored with **MultiGAS stations**

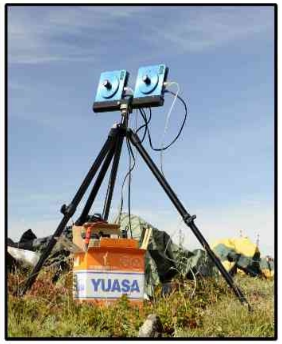
HF OP-FTIR sensing: example of explosive degassing at Etna 14/12/2002
d = 400 m, 1 FTIR spectrum every 4 sec. = 900 gas samples in one hour!



Allard and Burton 2004

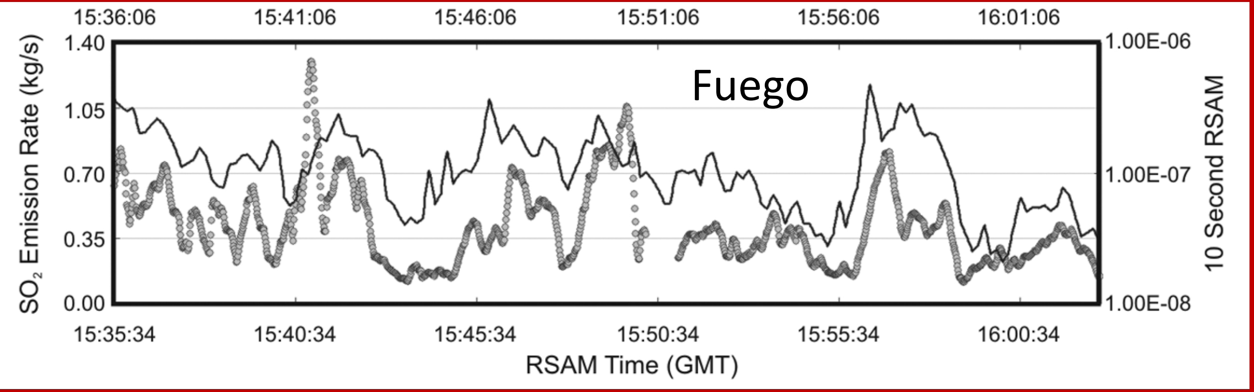
High frequency SO_2 flux measurements

Correlate well with shallow-sourced geophysical signals (tremor, LP-VLP)

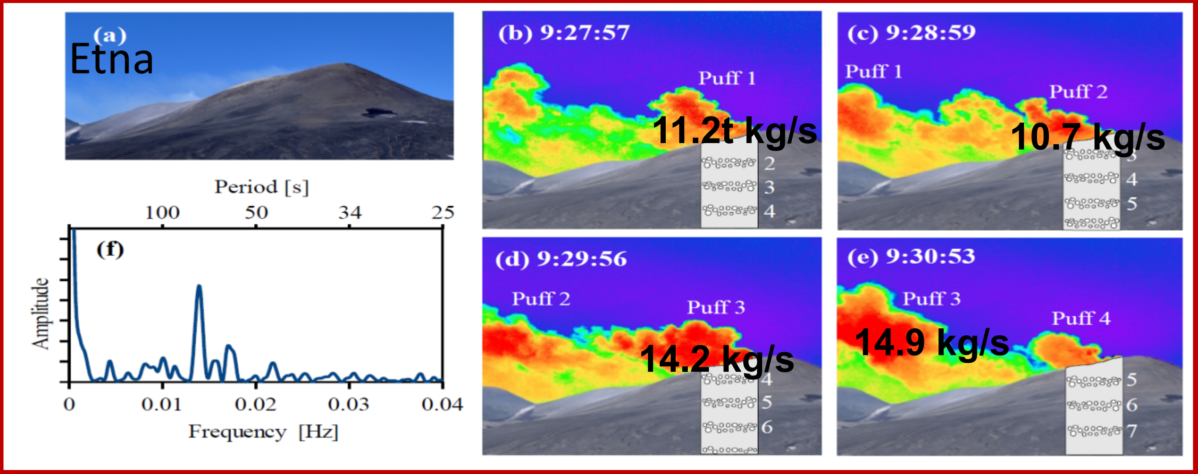


Dual UV-Camera imaging: 1-5 Hz SO_2 flux time-series

- *FUEGO (Guatemala): co-variations of SO_2 flux and RSAM (Nadeau et al. 2011)*



- *ETNA: Distinct periodic structure in conduit bubble layering (Tamburello et al. GRL 2013)*

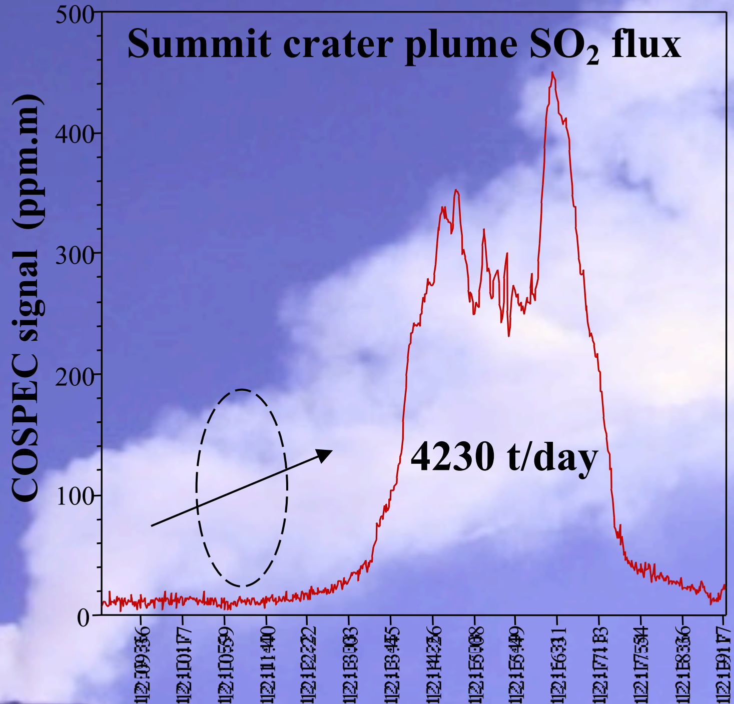


2 band-pass optical filters:
- 310 nm (SO_2)
- 330 nm (aerosols & particles)

Volcanic SO_2 fluxes and magma degassing rates
(by scaling to the magma sulfur content)

Volume of degassed magma

$V_d = ½ F_{SO2} / [\Delta S * \rho_m *(1-x_c)]$



$\Delta S \cong$ initial magma S content

ρ_m = magma density

X_c = crystal vol. fraction

$(1 – X_c)$ = melt vol. fraction

V_d/V_e ratio:

total degassed vs erupted magma

Mount Etna

EXCESS DEGASSING: most volcanoes actually emit more to much more gas than allowed by co-erupted magma volumes !

❖ Persistently degassing open-conduit volcanoes

Examples (time-averaged V_d/V_e)

- Etna: 4 (Allard 1997; Allard et al. 2006)
- Merapi: 7 (Allard et al. 2011)
- Villarica: 9 (Witter et al. 2005)
- Stromboli: 10 (Allard et al. 2008)
- Ambrym: 16 (Allard et al. 2016)
- Yasur: 18 (Métrich et al. 2011)
- Lava lakes: >10^2-10^4

Probable mechanisms (single or combined):

- *Differential bubble transfer across volcanic systems and conduits*
- *Gas percolation through permeable magma or/and sheared stress conduit walls*
- *Convective magma overturn in conduit-reservoir systems*

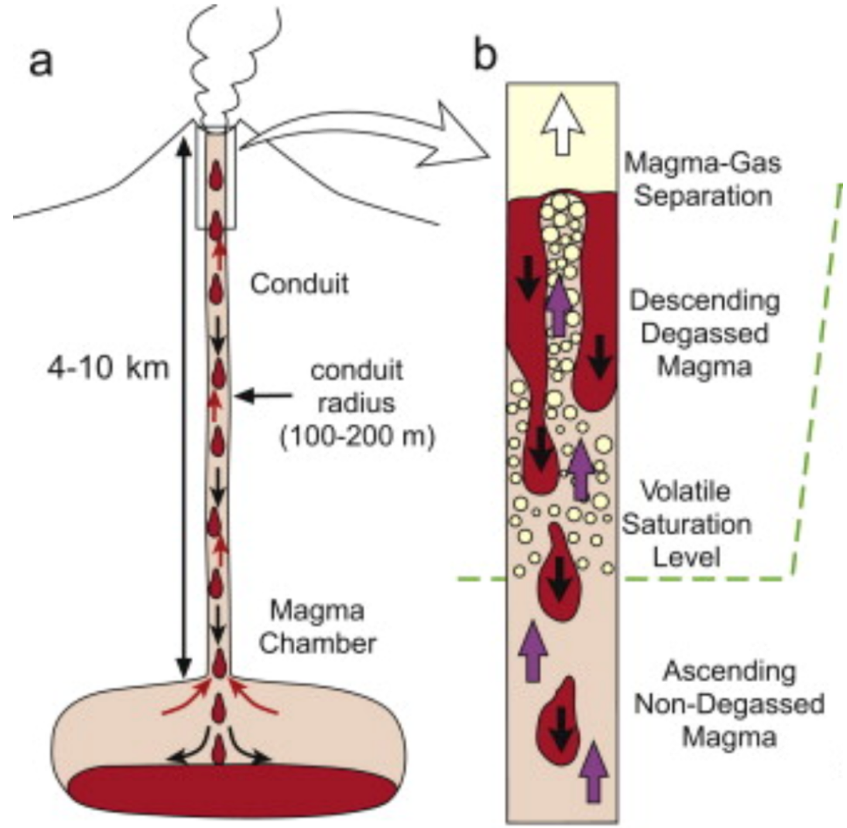
➢ Major IMPLICATION: growth of large bodies of degassed (solidifed) magma beneath many volcanoes (e.g. at Etna, Asama, etc.…)

DEEP CARBON OBSERVATORY RESERVOIRS AND FLUXES

DCO-DECADE

Top ten volcanic CO_2 emitters

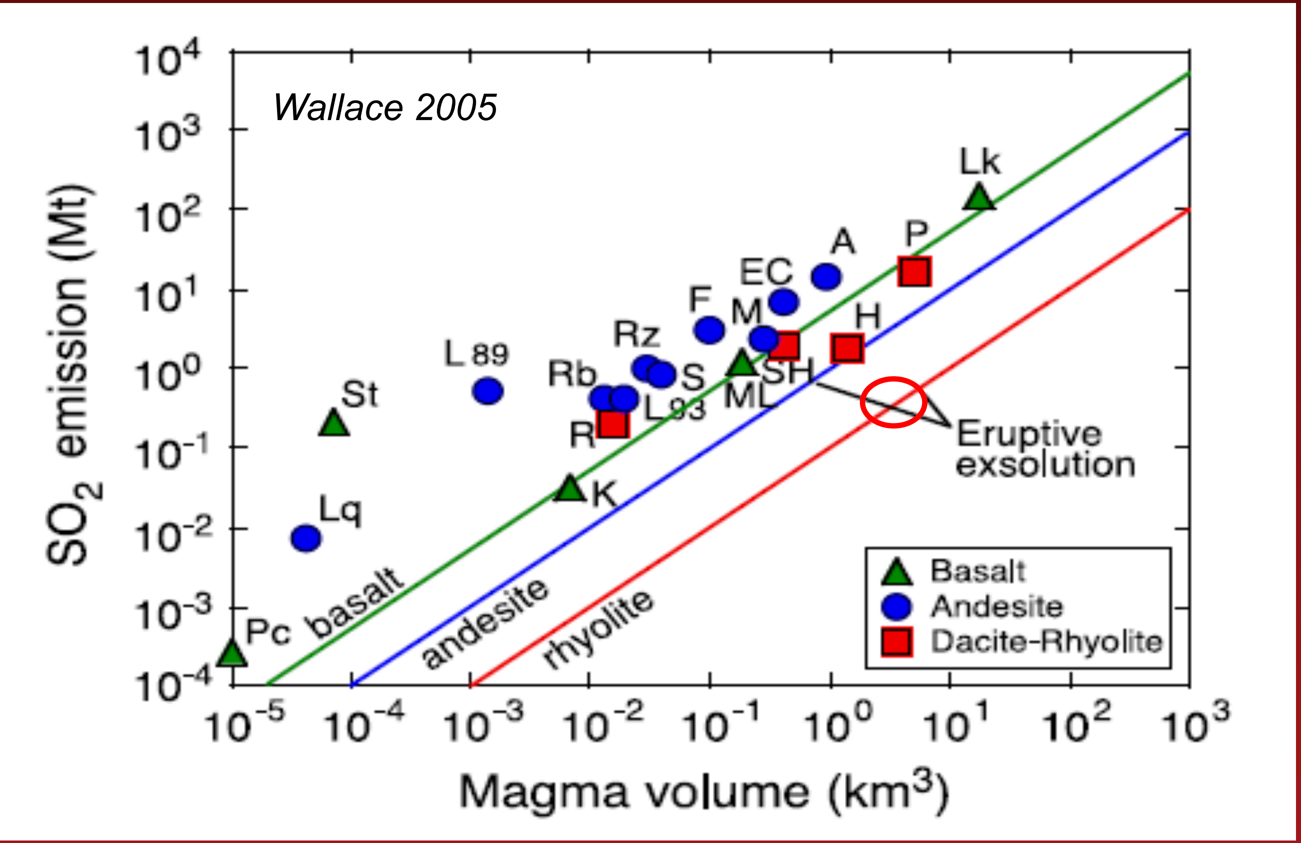
Volcano	Country	CO_2 Flux (t/d)	CO_2 Flux (Mt/yr)
Nyiragongo	DR Congo	52,410	19.13
Popocatépetl	Mexico	29,000	10.59
Ambrym	Vanuatu	20,000	7.30
Etna	Italy	16,363	5.97
Miyakejima	Japan	14,500	5.29
Oldoinyo Lengai	Tanzania	6,630	2.42
Kīlauea	USA	6,549	2.39
Stromboli	Italy	1,991	0.73
Masaya	Nicaragua	1,935	0.71
White Island	New Zealand	1,780	0.65
Augustine	USA	1,760	0.64
Erebus	Antarctica	1,630	0.59
Soufrière Hills	Montserrat	1,468	0.54
Galeras	Colombia	1,020	0.37



Shinohara, 2008
Burton et al., 2013

Convective magma overturn likely a key process at top ten degassing volcanoes !

❖ Excess degassing also verified during discrete eruptions of various magma types !

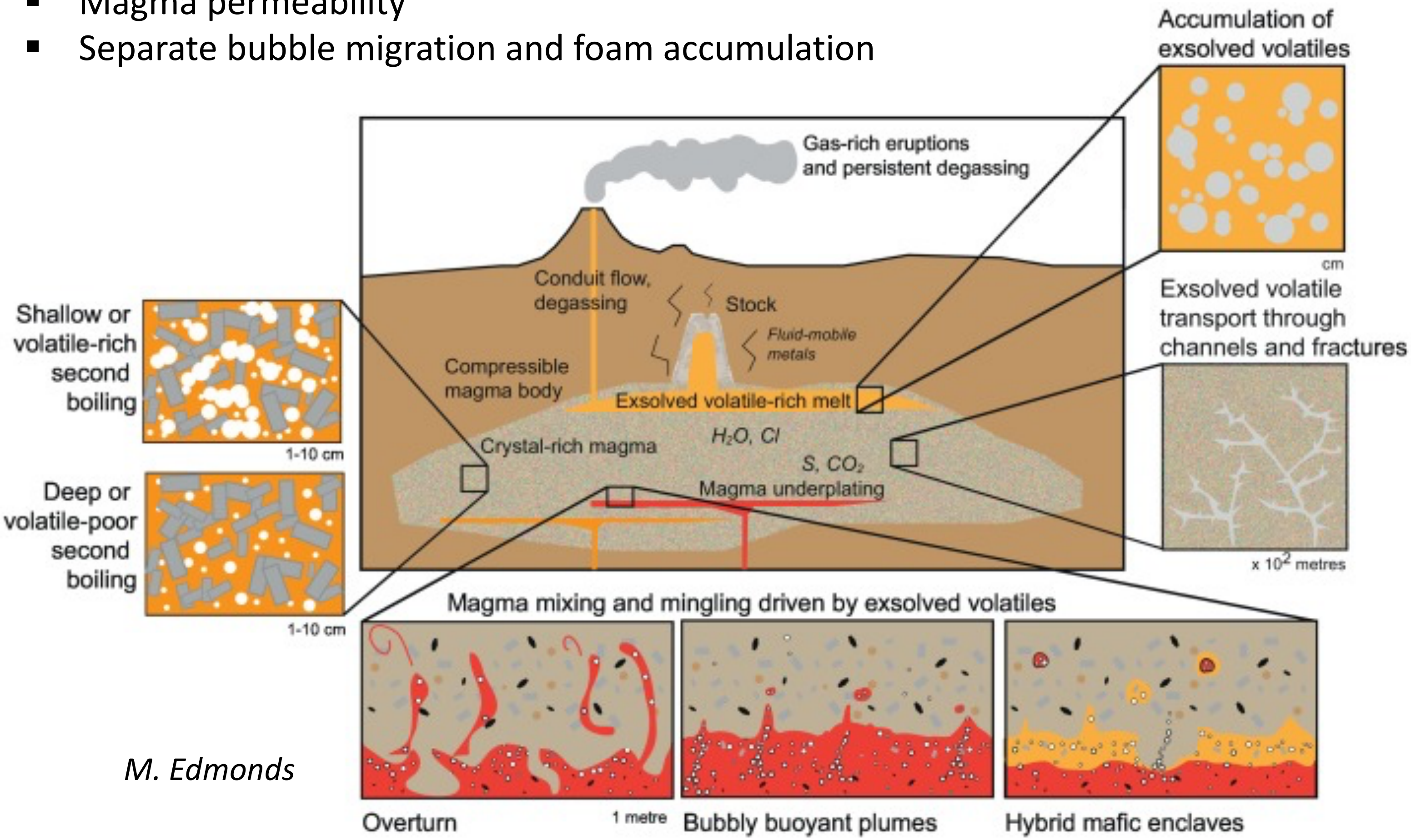


➢ *Likely: pre-eruptive accumulation of an exsolved gas phase*

e.g. Pinatubo (Westrich and Gerlach 1992)

Hence, multiple complex degassing processes affect volcano feeding systems, deserving further investigations

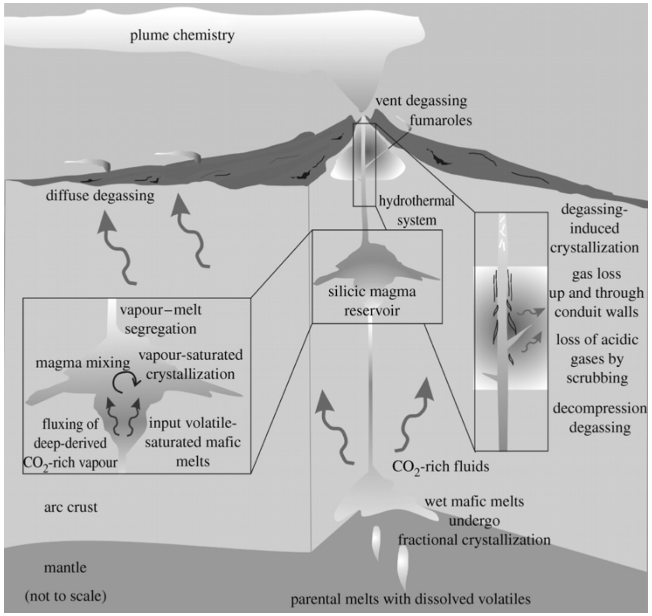
- Gas percolation in crustal magma reservoir (*Bachmann-Bergantz 2006*)
- Magma permeability
- Separate bubble migration and foam accumulation

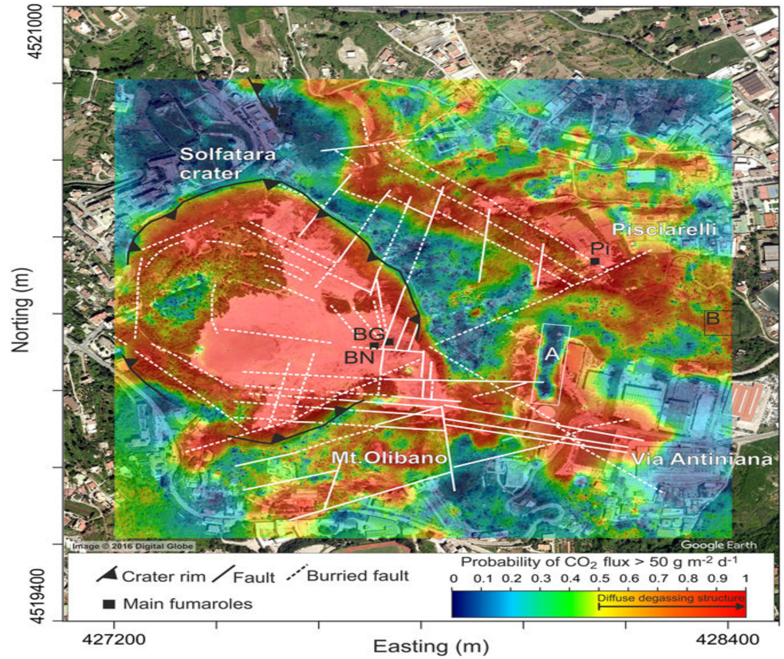


M. Edmonds

Another main discovery: **diffuse soil degassing through volcanic systems**

non-thermal (invisible) emanations of carbon dioxide (± minor H_2S, H_2, He, ^{222}Rn)





Campi Flegre caldera
Cardellini et al., 2017

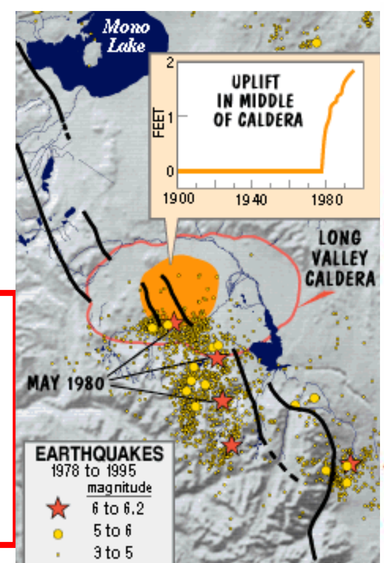
East African Rift
Hunt et al., 2017

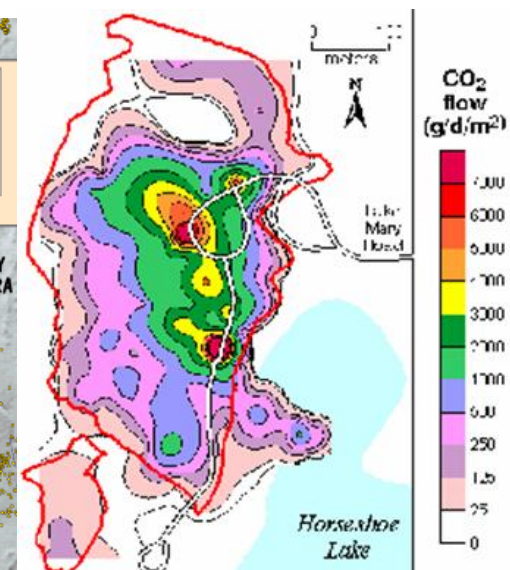
Mamouth Mountains
Hill et al., 1998

NATURE · VOL 351 · 30 MAY 1991

Eruptive and diffuse emissions of CO_2 from Mount Etna

P. Allard*, J. Carbonnelle†, D. Dajlevic†, J. Le Bronec†, P. Morel†, M. C. Robe†, J. M. Maurenas‡, R. Faivre-Pierret‡, D. Martin§, J. C. Sabroux* & P. Zettwoog†



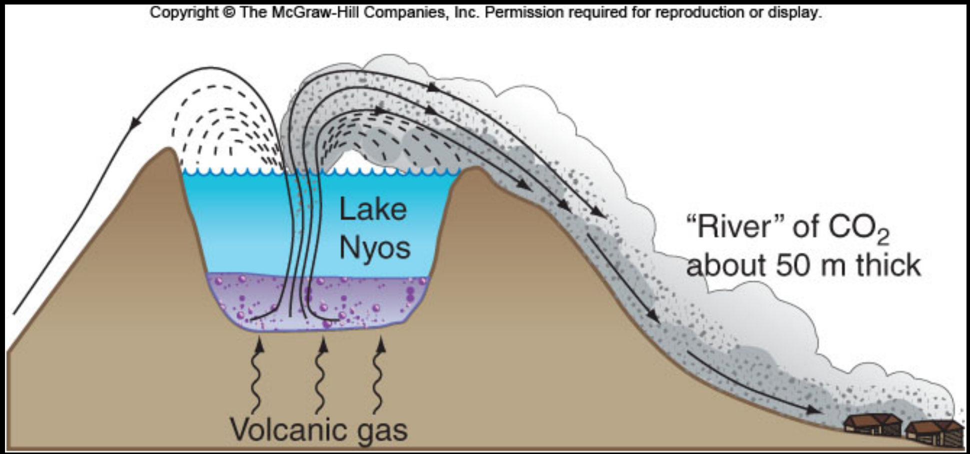


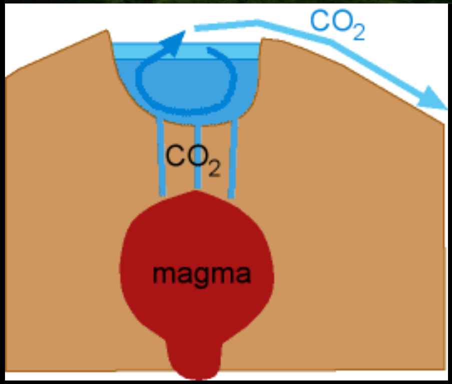
Studying/surveying diffuse volcanic degassing has become a new research field in volcanology over the past 25 years !

- **Vesuvius 1944**: 8 deaths at the base six months before the eruption
- **Dieng 1979**, Java: 149 persons died while crossing a thick CO_2 stream released during phreatic eruptions *(Le Guern et al 1981; Allard et al 1989)*
- **Lake Nyos 1986**, Cameroon: dense CO_2 flows kills 1700 people up to 16 km distance *(Barberi et al 1987)*

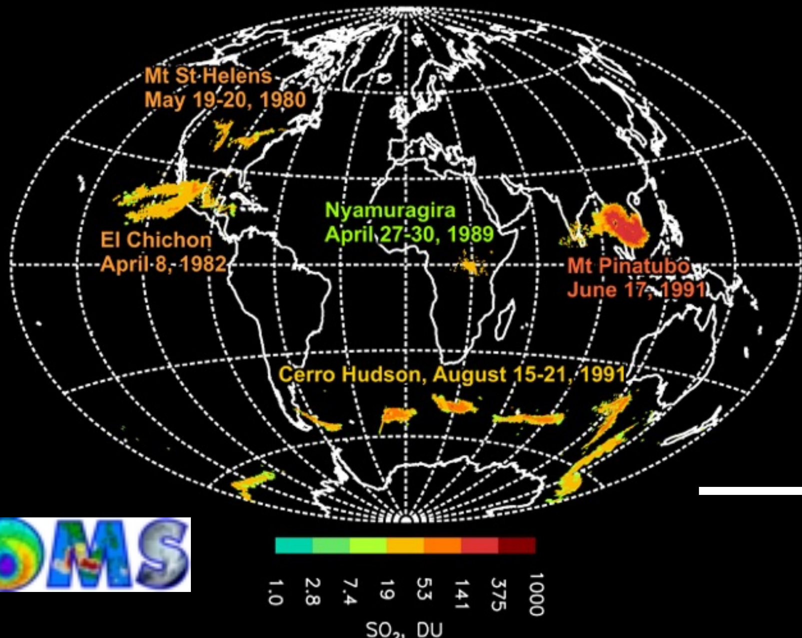
❖ THE HAZARD FROM COLD EMISSIONS OF NOXIOUS VOLCANIC CO_2

Gaseous carbon dioxide is 1.6 times denser than air at ambient temperature!

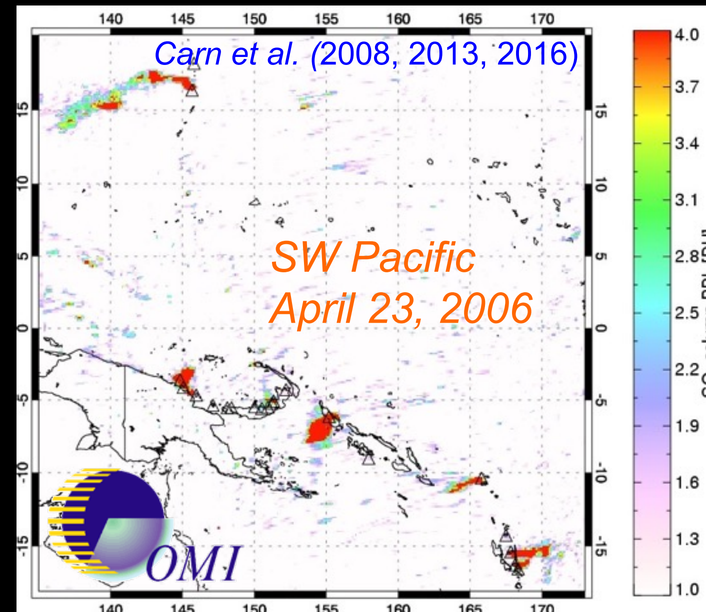




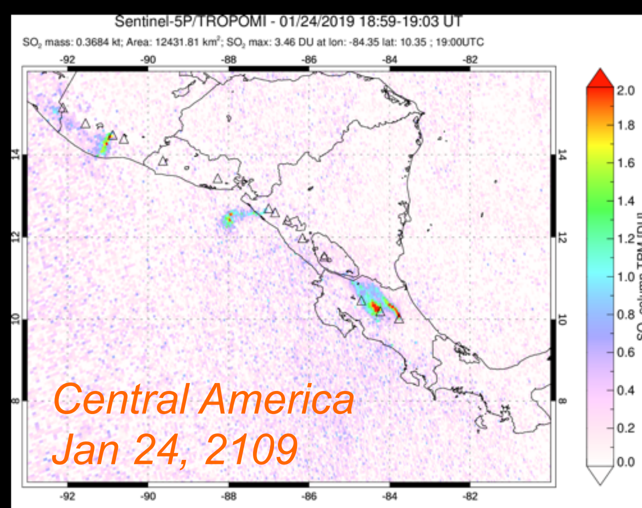
UV satellite remote sensing of volcanic SO_2



1978-2005: Total Ozone Mapping Spectrometer (TOMS) -> Eruptive degassing



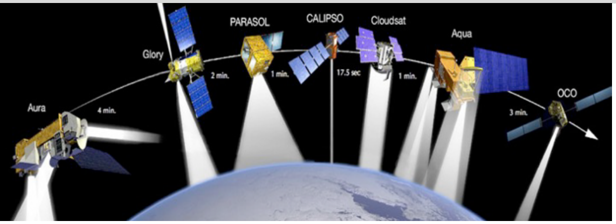
2004- : Ozone Monitoring Instrument (OMI) -> Eruptive and passive degassing

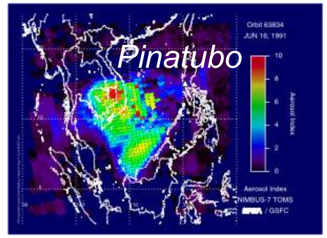


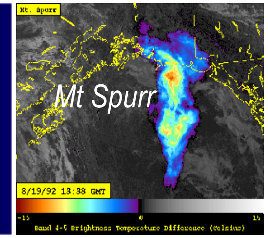
2017- : Sentinel 5P TROPOMI -> Higher spatial resolution of volcanic SO_2 plumes

Theys et al. (2019)

Space-borne quantification of eruptions' SO_2 mass output

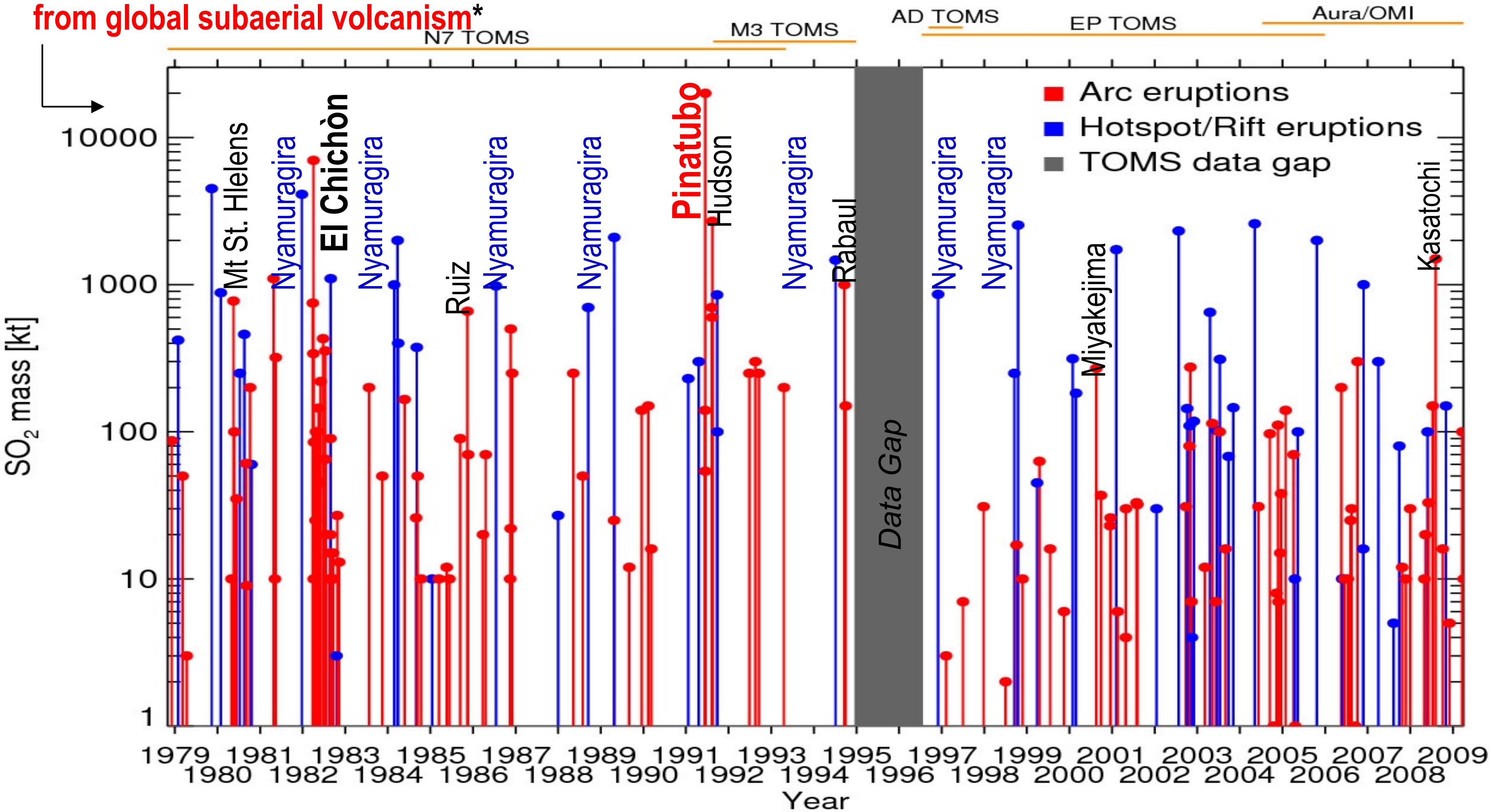






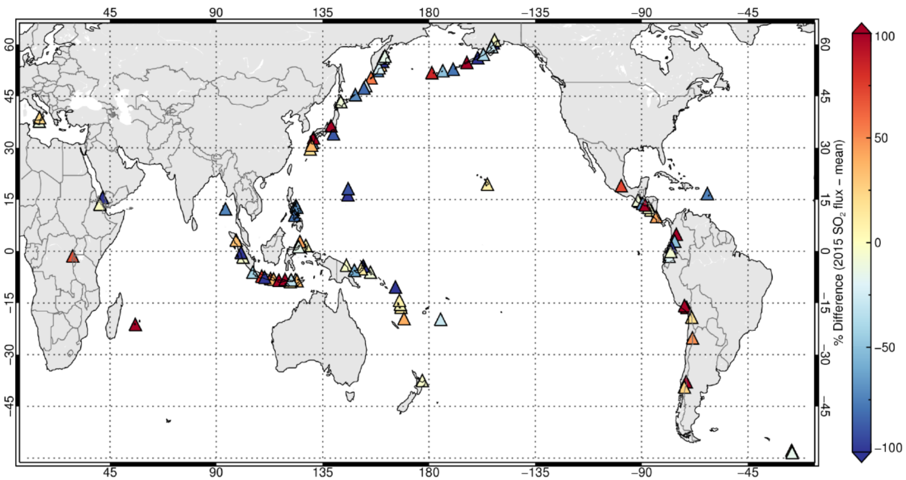
(1979 – 2009, TOMS then OMI)£

Average SO_2 discharge of ~20 Mt/yr from global subaerial volcanism*

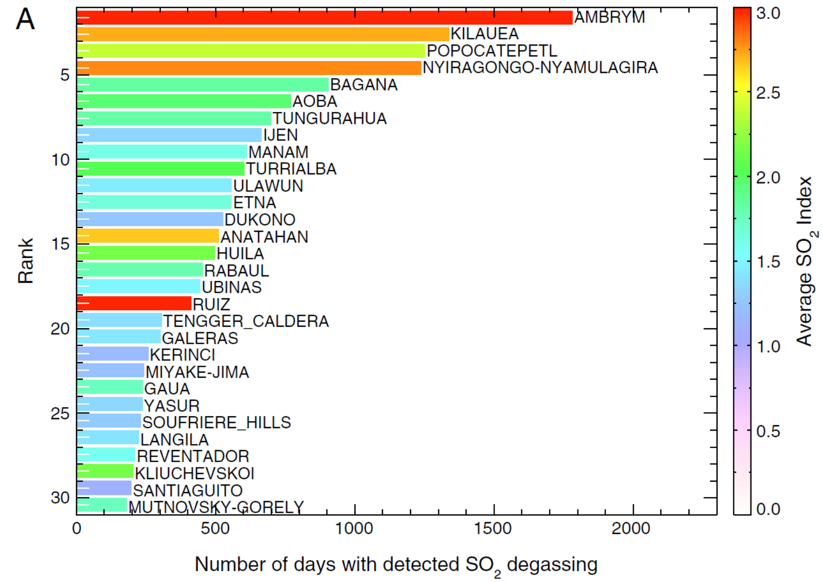


*£ NASA's SO_2 Emissions Group; *Halmer et al. (2002), Bluth et al. (1993); Carn et al. (2016)*

Satellite-based SO_2 flux inventories in 2005-2015



Carn et al. 2017



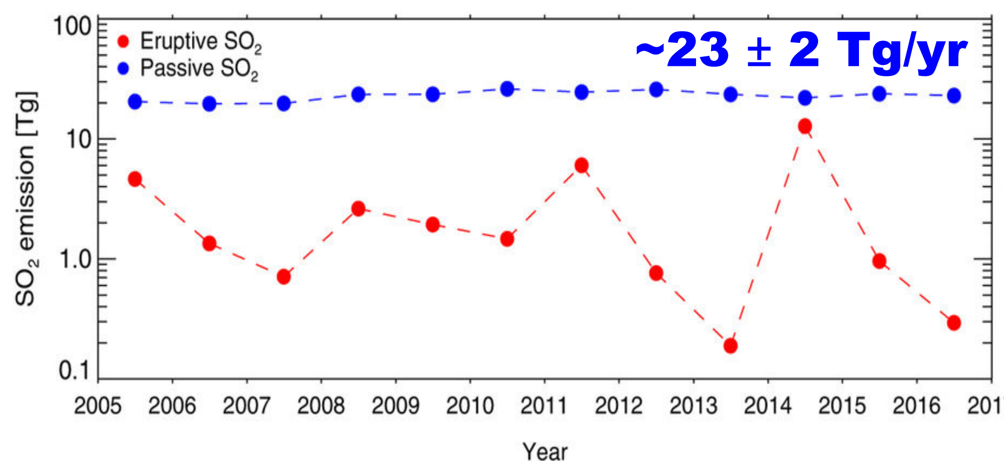
Volcanic SO_2 emissions from 91 volcanoes in 2005–2015 derived from global satellite (OMI) measurements

SCIENTIFIC REPORTS

OPEN

A decade of global volcanic SO_2 emissions measured from space

S. A. Carn[1], V. E. Fioletov[2], C. A. McLinden[2], C. Li[3,4] & N. A. Krotkov[4]



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Review

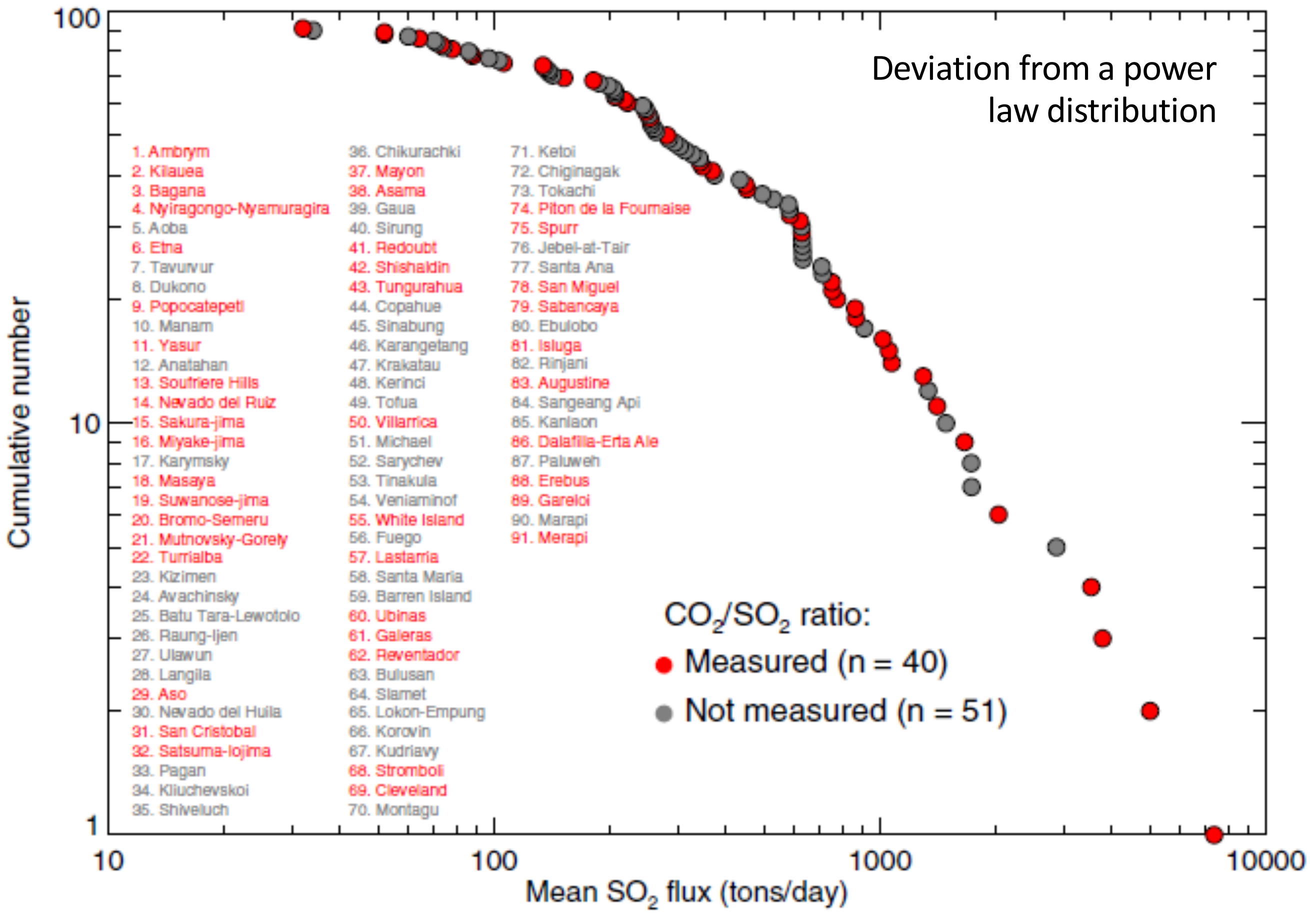
Multi-decadal satellite measurements of global volcanic degassing

S.A. Carn [a,b,*], L. Clarisse [c], A.J. Prata [d]

DEEP CARBON OBSERVATORY
RESERVOIRS AND FLUXES

DCO-DECADE

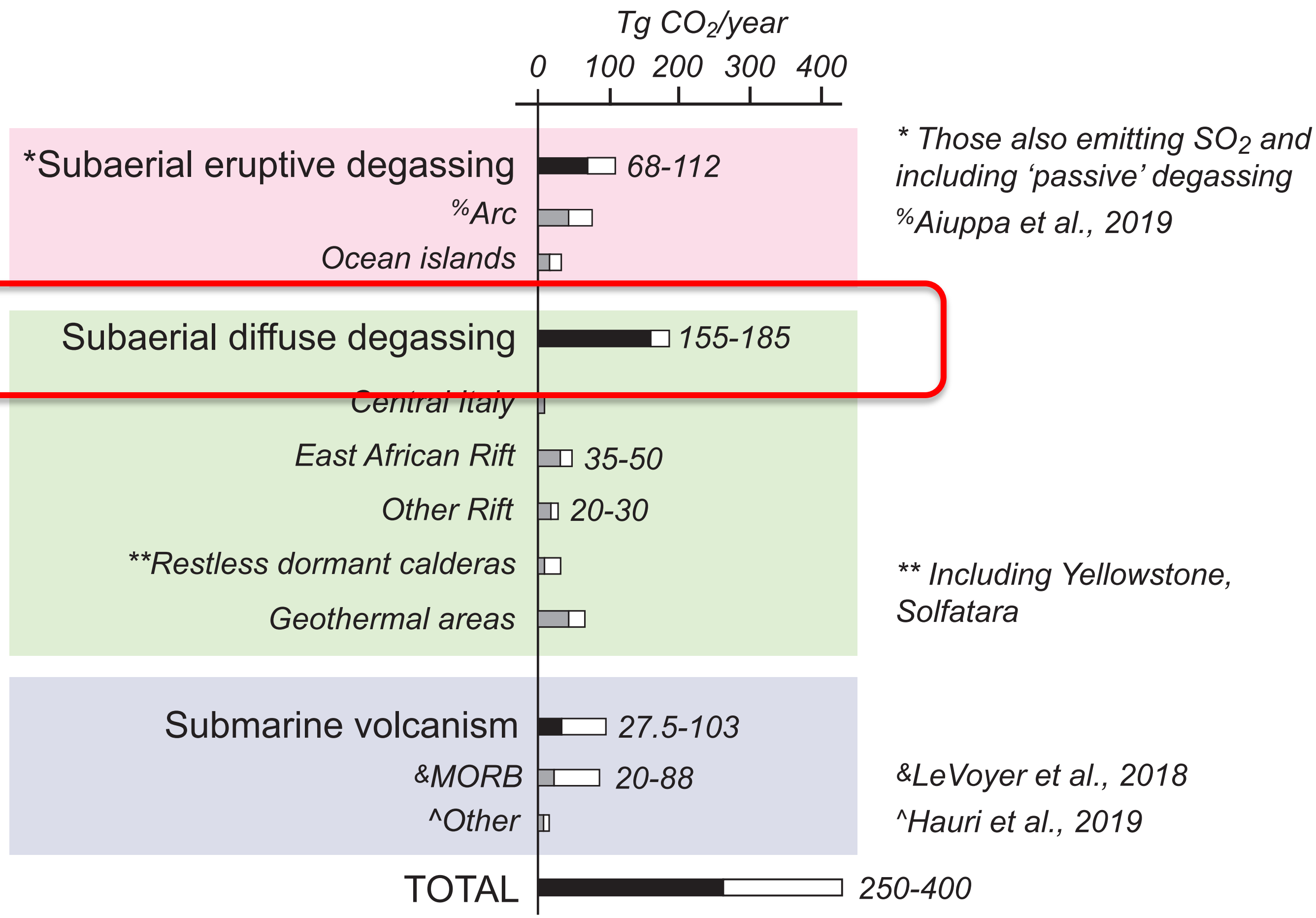
Strategy: a top few CO_2 and SO_2 volcanic outgassers dominate flux



Carn et al., 2017

10-12 volcanoes produce 95% of the sulfur flux to the atmosphere.

Global Volcanic Carbon Budget

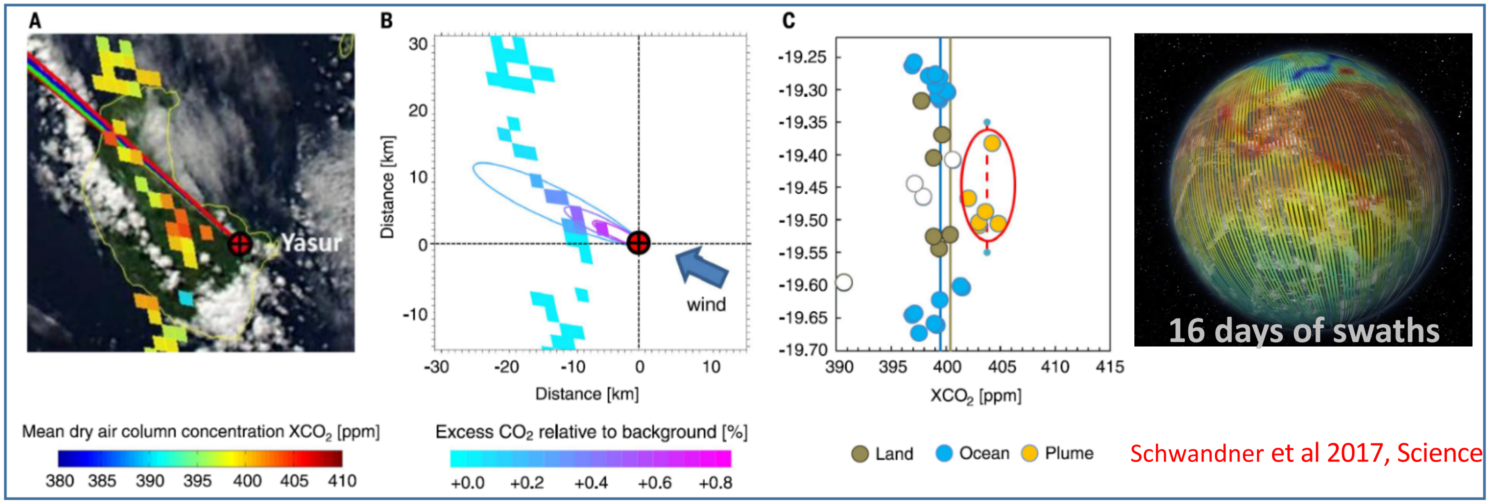


Large uncertainties

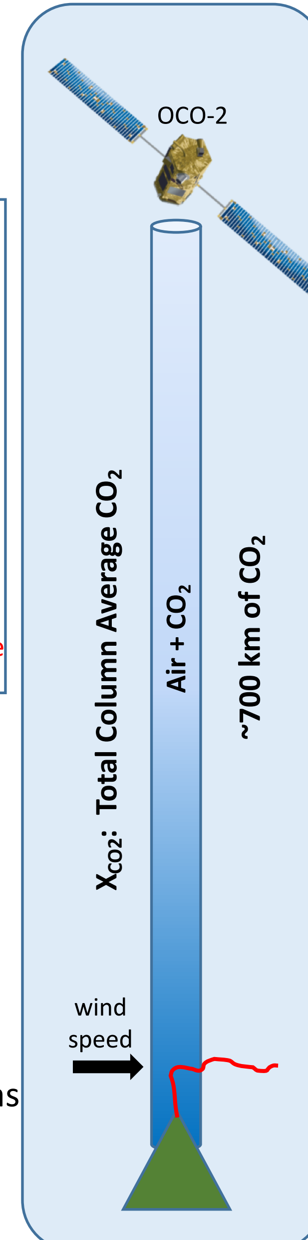
Werner et al., 2019, in press

The future: Direct detection/survey of volcanic CO_2 from space ?

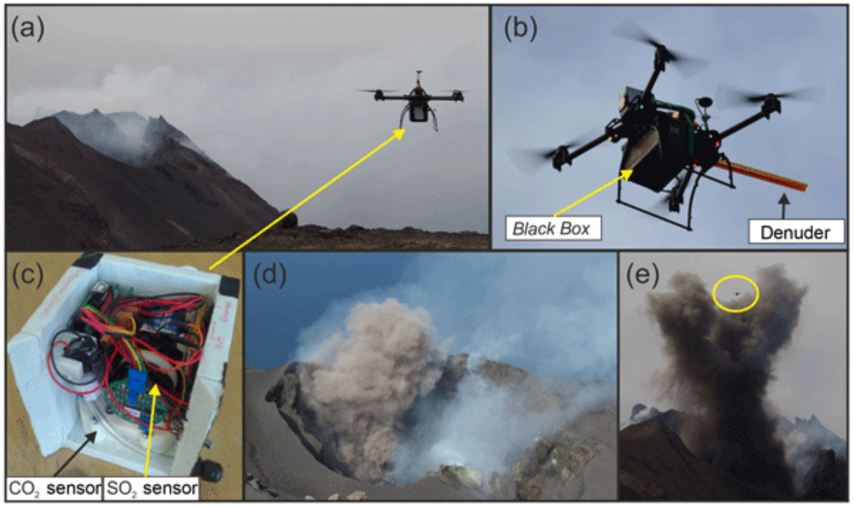
- <u>**Challenge:**</u> "total column" average CO_2 (X_{CO2}) signal requires >99.75% precision (**1/410 ppm**)
- NASA and JAXA satellites (**OCO-2, GOSAT**) observed CO_2 over >**45 volcanoes since 2010**
- First <u>space-borne (OCO-2) detection of volcanic CO_2 in 2015 at **Yasur**</u>, Ambrym, Aoba (Vanuatu) (*Schwandner et al., Science 2017*)

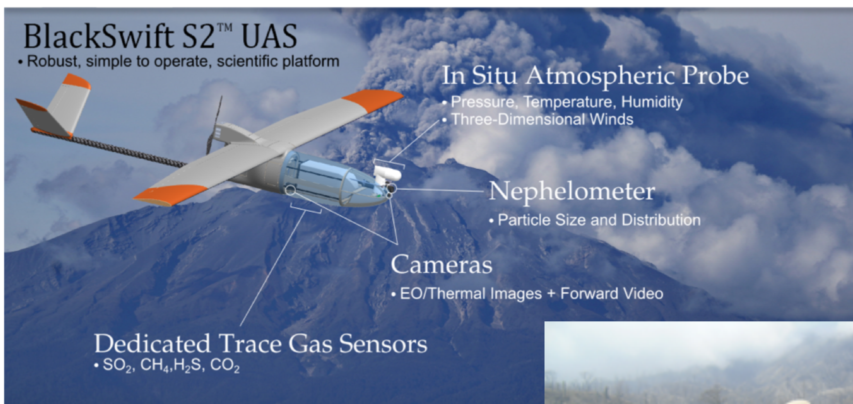


- <u>**Limitations**</u>: OCO-2 detections are limited by sparse narrow-swath sampling pattern.
- New: **OCO-3** (launched to ISS May 4th 2019) will **cover several tens of volcanoes in dedicated mapping and target modes**, a significant improvement over OCO-2's capabilities.
- <u>Problem with direct detections from space:</u> Satellites can't *directly* detect 'mild' long-term precursory signals due to the dilution problem of X_{CO2} measurements.
- <u>**Solution**</u>: Plants *glow and grow* with volcanic CO_2: The "**Trees as sensors**" concept (*Bogue, Schwandner, et al 2019, Biogeosciences*).
  Plants grow and fluoresce more under mild CO_2 enhancements; measurable by remote sensing as increases in biomass (long-term response) and photosynthesis (short-term response).



The future: using unmaned airborne platforms or drones for locally measuring volcanic degassing, even during eruptions (already ongoing)





ABOVE
Aerial-based Observations of Volcanic Emissions

Today, a large (and young) international scientific community studying volcanic degassing. Gas monitoring now operated in many volcano Observatories!

Commission on the Chemistry of Volcanic Gases (CCVG) - IAVCEI

CCVG
COMMISSION ON THE CHEMISTRY OF VOLCANIC GASES

- Inter-comparison of techniques and results in direct sampling of volcanic gases, widened to studies with ground and satellite remote sensing, in-situ automated devices, diffuse gas probes, airborne measurements, petro-chemical modelling, etc.
- A **Field Workshop every 3 years**, in different volcanic places, since 1982!
- Joint publications, a Newsletter (*Telegram from the Earth's Interior*)..

Ambrym volcano, Vanuatu arc
Photo: P. Allard