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: \( \text{H}_2\text{S} \)-rich LT fumarolic emissions
  - Mutnovsky 2011, Kamchaka
  - While Island 2002, NZ
  - Yellowstone, USA

- Open-conduit volcanoes: persistent \( \text{SO}_2 \)-prevalent HT degassing (plumes)
  - Stromboli 1997, Italy
  - Nyiragongo 2007, RDC
  - Nyiragongo 2017

- Erupting volcanoes: discrete \( \text{SO}_2 \)-rich gas emissions
  - Etna 2000, Italy
  - Etna 04/12/2015
  - Una-Una 1983, Indonesia
A number of good motivations to study and monitor volcanic gas emissions.

Motivation:
- SO₂, HF, CO₂,
- CO, H₂S, HCl,
- BrO, acid aerosol,
- trace metals...

Global geochemical budgets:
- Origins and fate (cycles) of volatiles on Earth

Forecasting:
- Eruption precursors
- Mitigating hazards

Impacts on the climate

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
   \[\textit{delicate access to degassing sites, risks}\]

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.

\[\text{– Frank Perret (1913), Lava Fountains of Kilauea, Am. J. Sci.}\]

\[\text{“Gas is the active agent, and the magma is its vehicle”}\]

\[\text{(F.A. Perret, 1924: The 1906 Vesuvius eruption)}\]
Field studies of volcanic gases started to gradually develop in 20th century thanks to some obstinated pioneers.

Discovery of water predominance in volcanic gas (!)

The first measurements of \( \text{SO}_2 \) and \( \text{H}_2\text{S} \) ratio in fumarolic discharges (\( \text{NH}_4\text{OH}-\text{AgNO}_3 \) filled bottles; Sicardi, 1955)

“.gas chemistry is the heart of the volcano magma problem.” (Jaggar, “Magmatic Gases”, 1940)
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)
  - \( \text{H}_2\text{O}, \text{H}_2 \)
  - \( \text{CO}_2, \text{CO} \)
  - \( \text{SO}_2, \text{H}_2\text{S} \)
  - \( \text{HCl}, \text{HF}, \text{HBr}.. \)
  - \( \text{N}_2, \text{He}, \text{Ar}.. \)
  - Volatile trace metals
    - (Po, Bi, Se, Hg, Cd, As, Ag, Pb, Au, Tl, Cu, Zn...)

- **Volatile content & solubility in magmas**
  - 100 µm
  - Olivine crystal
  - Inclusion
  - Crystal melt inclusions

- **Merapi**
  - Erta Ale 1974, 1130°C
  - 870°C

- **Mt. St. Helens, 1982**

+ Analog experiments and numerical modelling
VOLCANIC GASES AND GEODYNAMICS
chemical variations and sources (isotopes)

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 CO₂ 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$_2$O, C, S, N) derived from the subducting plates (± crustal additions).

**ARC VOLC GASES**
- $\delta^D$: -40 to -10 ‰
- $\delta^{13}C$: -4 to 0 ‰
- $\delta^{34}S$: +2 to +12 ‰

**SEA WATER**
- $\delta^D$: 0 ‰
- $\delta^{34}S$: +20 ‰

**MANTLE**
- $\delta^D$: -80 to -60 ‰
- $\delta^{13}C$: -8 to -4 ‰
- $\delta^{34}S$: -0.5 to +1 ‰

**Subduction Zone Processes**

- **Stage 2:** Island Arc Magmatism
  - a. Slab devolatilisation & partial melting
  - H$_2$O, CO$_2$, S, Cl, N, Ar
  - $^{10}$Be
  - Sediments (Corg: -20 to -40 ‰)
  - Carbonates $\delta^{13}C$: 0 ‰

- **Stage 3:** Back-Arc Spreading and Magmatism
  - c. Crustal additions? $\delta^{13}C$: 0 ‰

- **b. Mantle melting & degassing**
  - H$_2$O, CH$_4$, H$_2$
  - dehydration and decarbonation reactions

(modified from SubFac)
VOLCANIC GASES AND ERUPTION PROCESSES

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

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)
$\text{CO}_2 \ll \text{H}_2\text{O} < \text{S} < \text{Cl} < \text{F}$

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 ($\text{H}_2\text{O}$, $\text{CO}_2$, S, Cl) solubility evolutions during magma decompression (HT-HP lab experiments and crystal melt inclusions)

General exsolution order and bulk loss rate: $\text{CO}_2 >> \text{H}_2\text{O} \geq S > \text{Cl} > \text{F}$

**Experimental measurements**

At volatile saturation

$P_{\text{CO}_2} + P_{\text{H}_2\text{O}} \approx P_{\text{tot. fluid}} \approx P_{\text{lithostatic}}$

$\text{CO}_2$: 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

<table>
<thead>
<tr>
<th>2010 Fumarole gas analyses (mol%)</th>
</tr>
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<tbody>
<tr>
<td>26 May</td>
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<tr>
<td>T (°C)</td>
</tr>
<tr>
<td>H$_2$+O$_2$</td>
</tr>
<tr>
<td>N$_2$</td>
</tr>
<tr>
<td>CH$_4$</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO$_2$</td>
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<tr>
<td>SO$_2$</td>
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<tr>
<td>H$_2$S</td>
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<tr>
<td>HCl</td>
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<tr>
<td>HF</td>
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<tr>
<td>NH$_3$</td>
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<td>H$_2$O</td>
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</thead>
<tbody>
<tr>
<td>CO$_2$/S</td>
<td>5.6</td>
<td>6.3</td>
<td>12</td>
</tr>
<tr>
<td>CO$_2$/HCl</td>
<td>28</td>
<td>28</td>
<td>58</td>
</tr>
<tr>
<td>CO$_2$/H$_2$O</td>
<td>0.06</td>
<td>0.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

0.44 Mt SO$_2$
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!

**In situ MultiGAS plume analysis**

1. Gas pumped in
2. GAS sensing: 30 minute cycle at 0.1-0.5 Hz (4-10 cycles per day)
3. Automatic data-logging in memory board
4. Radio transfer back to observatory after each acquisition cycle

**Remote OP-FTIR spectroscopy**

H$_2$O, CO$_2$, SO$_2$
HCl, HF, CO, COS, CH$_4$,

Etna - Italy
Miyakejima (Japan)


Bulk gas composition scaled to SO$_2$ flux $\rightarrow$ 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*

**Mini-DOAS**
(Differential Optical Absorption Spectroscopy)

*Galle et al. 2000*
*Arellano et al. 2012*

**Dual UV-cameras**
(high-resolution SO$_2$ imaging, up to 25 Hz)

*Mori & Burton 2005*
*Kern et al. 2008*
*Tamburello et al. 2013*
**CO₂ precursors of paroxysmal explosions**

**Stromboli: Aiuppa et al. 2009**

- **CO₂ fluxes**
- **Lava effusion**
- **March 15 paroxysm**
- **December 15 major explosion**

**Multi-GAS**

- CO₂, H₂O: IR spectrometry
- SO₂, H₂S: electrochemical sensors

**CO₂/SO₂**

**CO₂ flux**

**CO₂ flux** = SO₂ flux \( \times (\frac{\text{CO₂}}{\text{SO₂}}) \)

**Graphs and diagrams**

- Summit plume
- Time-averaged quiescent plume
- Time series of CO₂ and SO₂ fluxes
- March 15 paroxysm
- December 15 major explosion
- Lava effusion
- Pulsating ash explosions
- Stromboli activity

**Map**

- Stromboli island
- Tyrrhenian Sea
- SDF Craters
- UV Scanner
- MultiGAS

**Images**

- Photographs of Multi-GAS equipment
- Photographs of Stromboli volcano activity
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 (Mís) (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)**

**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.
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 CO₂ 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!**

Molar gas ratios in explosive emissions from Etna 2750 m vent measured with FTIR spectrometry (14/12/02; d = 400 m; one spectra every 4 sec)

P. Allard and M. Burton, 2004
High frequency SO$_2$ flux measurements correlate well with shallow-sourced geophysical signals (tremor, LP-VLP)

- **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)

Dual UV-Camera imaging: 1-5 Hz SO$_2$ flux time-series

2 band-pass optical filters:
- 310 nm (SO$_2$)
- 330 nm (aerosols & particles)
Volcanic $\text{SO}_2$ fluxes and magma degassing rates (by scaling to the magma sulfur content)

Volume of degassed magma

$$V_d = \frac{1}{2} F_{\text{SO}_2} / [\Delta S \ast \rho_m \ast (1-x_c)]$$

$\Delta S \equiv$ initial magma S content
$\rho_m =$ 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 (solidified) magma beneath many volcanoes (e.g. at Etna, Asama, etc....)

Top ten volcanic CO$_2$ emitters

Shinohara, 2008
Burton et al., 2013

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

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Country</th>
<th>CO$_2$ Flux (t/d)</th>
<th>CO$_2$ Flux (Mt/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nyiragongo</td>
<td>DR Congo</td>
<td>52,410</td>
<td>19.13</td>
</tr>
<tr>
<td>Popocatépetl</td>
<td>Mexico</td>
<td>29,000</td>
<td>10.59</td>
</tr>
<tr>
<td>Ambrym</td>
<td>Vanuatu</td>
<td>20,000</td>
<td>7.30</td>
</tr>
<tr>
<td>Etna</td>
<td>Italy</td>
<td>16,363</td>
<td>5.97</td>
</tr>
<tr>
<td>Miyakejima</td>
<td>Japan</td>
<td>14,500</td>
<td>5.29</td>
</tr>
<tr>
<td>Oldoinyo Lengai</td>
<td>Tanzania</td>
<td>6,630</td>
<td>2.42</td>
</tr>
<tr>
<td>Kilauea</td>
<td>USA</td>
<td>6,549</td>
<td>2.39</td>
</tr>
<tr>
<td>Stromboli</td>
<td>Italy</td>
<td>1,991</td>
<td>0.73</td>
</tr>
<tr>
<td>Masaya</td>
<td>Nicaragua</td>
<td>1,935</td>
<td>0.71</td>
</tr>
<tr>
<td>White Island</td>
<td>New Zealand</td>
<td>1,780</td>
<td>0.65</td>
</tr>
<tr>
<td>Augustine</td>
<td>USA</td>
<td>1,760</td>
<td>0.64</td>
</tr>
<tr>
<td>Erebus</td>
<td>Antarctica</td>
<td>1,630</td>
<td>0.59</td>
</tr>
<tr>
<td>Soufrière Hills</td>
<td>Montserrat</td>
<td>1,468</td>
<td>0.54</td>
</tr>
<tr>
<td>Galeras</td>
<td>Colombia</td>
<td>1,020</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Excess degassing also verified during discrete eruptions of various magma types!

Wallace 2005

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

non-thermal (invisible) emanations of carbon dioxide (± minor H$_2$S, H$_2$, He, $^{222}$Rn)

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

Campi Flegre caldera
*Cardellini et al., 2017*

East African Rift
*Hunt et al., 2017*

Mammoth Mountains
*Hill et al., 1998*
Gaseous carbon dioxide is 1.6 times denser than air at ambient temperature!

**THE HAZARD FROM COLD EMISSIONS OF NOXIOUS VOLCANIC CO₂**

- **Vesuvius 1944**: 8 deaths at the base six months before the eruption
- **Dieng 1979**, Java: 149 persons died while crossing a thick CO₂ stream released during phreatic eruptions (Le Guern et al 1981; Allard et al 1989)
- **Lake Nyos 1986**, Cameroon: dense CO₂ flows kills 1700 people up to 16 km distance (Barberi et al 1987)
UV satellite remote sensing of volcanic SO\textsubscript{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\textsubscript{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)
Volcanic SO$_2$ emissions from 91 volcanoes in 2005–2015 derived from global satellite (OMI) measurements

Carn et al. 2017

Satellite-based SO$_2$ flux inventories in 2005-2015

Eruptive SO$_2$  
Passive SO$_2$

$\sim 23 \pm 2$ Tg/yr
Strategy: a top few CO$_2$ and SO$_2$ volcanic outgassers dominate flux

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

Carn et al., 2017
Global Volcanic Carbon Budget

- Subaerial eruptive degassing
  - %Arc
  - Ocean islands

- Subaerial diffuse degassing
  - Central Italy
  - East African Rift
  - Other Rift
  - **Restless dormant calderas
  - Geothermal areas

- Submarine volcanism
  - %MORB
  - %Other

* Those also emitting SO₂ and including ‘passive’ degassing

# Including Yellowstone, Solfatara

Large uncertainties

- Total:
  - 250-400 Tg CO₂/year

Werner et al., 2019, in press
The future: Direct detection/survey of volcanic CO$_2$ from space?

- **Challenge:** “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 **space-borne (OCO-2)** detection of volcanic CO$_2$ in 2015 at Yasur, Ambrym, Aoba (Vanuatu) (Schwandner et al., Science 2017)

Limitations: 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.

Problem with direct detections from space: Satellites can’t *directly* detect ‘mild’ long-term precursory signals due to the dilution problem of $X_{CO2}$ measurements.

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

- 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*).
Thank you for your attention

Ambrym volcano, Vanuatu arc
Photo: P. Allard