Volatile solubility models and their application to magma storage and transport in the mantle and he crust

Julie Roberge
ESIA-Ticoman, IPN
Mexico
Melt Inclusions

What are they?

How to use them → volatiles

What information can we get from...

What information can we NOT...

Examples

Popocatepetl
Melt Inclusions – What are they?

Melt inclusions (MI) are small (usually < 100 µm) blebs of silicate melt that are trapped within igneous crystals.

Quartz – Bishop Tuff
Roberge et al. (2013)

Olivine - Popocatepetl
Roberge et al. (2009)

Plagioclase – Montserrat
Mann et al. (2013)
Melt Inclusions – What are they?

They can be glassy or partly crystallized.

Quartz – Bishop Tuff
Roberge et al. (2013)

Olivine - Irazu
Roberge and Moune (in prep)
Melt Inclusions – What are they?

or fully crystallized

Crystallized = Crystals grew from melt

Devitrified = Crystals grew from glass

 Depending on cooling rate

Qz – Pantelleria
Lowenstern (1994)
A bubble may nucleate during less-rapid cooling. Very slow cooling permits nearly full crystallization of the inclusion and growth of a layer of host mineral on the MI wall. Rapid cooling, no crystals nor bubble form. Diffusion during slow cooling allows the bubble to grow and the melt to partly crystallize.
Quartz and most other magmatic crystals are incompressible after entrapment: inclusion volume ~ constant

1- Melt inclusion is trapped
2- Decompression
3- Reach the melt/vapor saturation curve
4- Follow the melt/vapor saturation curve until reaches the glass transition
Because they can form at high pressures and are contained within relatively incompressible crystal hosts, they may retain high concentrations of volatile elements that normally escape from magmas during degassing.
Solubility is the concentration of a volatile species that can be dissolved in a melt at a certain P-T-X. Most important are composition (X) and pressure (P).
What happens with increasing $P$?

This means that solubility increases with pressure.

Soda analogy.
Solubility Vs Composition

Water speciation in Silicate Melts

From Silver et al., 1990
Depolymerization of Silicate Melts

Si–O polymer in anhydrous melt

Water molecule

Broken Si–O polymer in hydrous melt

(OH)−
Solubility

Water and CO₂ solubility in Silicate melts

Rhyolite (850°C)

Basalt (1200°C)

H₂O (wt%)

CO₂ (ppm)

Pressure (kb)

Saturated
Solubility

Undersaturated
Oversaturated
Chlorine Solubility

From Webster et al., (1995)

Continuous transition from vapor to hydrosaline melt as Cl concentration in vapor (% values) rapidly increases.
Some rhyolitic melts (e.g., Augustine volcano) have high enough dissolved Cl for the melt to be saturated with hydrosaline melt before eruption.
Sulfur Solubility

- S solubility is more complicated because of multiple oxidation states
  - Dissolved S occurs as either $S^{2-}$ or $S^{6+}$
  - Solubility is limited by saturation with pyrrhotite, Fe-S melt, anhydrite, or CaSO$_4$ melt
- S in vapor phase occurs primarily as H$_2$S and SO$_2$

Measure the oxidation state of S in minerals & glasses by measuring the wavelength of S Kα radiation by electron microprobe

From Jugo et al. (2005)
Changes in oxygen fugacity have a strong effect on solubility because $S^{6+}$ is much more soluble than $S^{2-}$.
Sulfur solubility effects of T, P & composition

S solubility at low oxygen fugacity: $S^{2-}$ is the dominant species

Solubility of both $S^{2-}$ and $S^{6+}$ are temperature dependent.
This led earlier workers to erroneously conclude that eruptions of such magma would release little SO$_2$ to Earth’s atmosphere.
Solubilities with more than 1 volatile component present

In natural systems, melts are saturated with a multicomponent vapor phase

From Dixon & Stolper (1995)

• $\text{H}_2\text{O}$ and $\text{CO}_2$ contribute the largest partial pressures, so people often focus on these when comparing pressure & volatile solubility.
Solubility

$\text{CO}_2 \iff \text{H}_2\text{O} \iff \text{S} \iff \text{Cl}$
Data obtainable from M.I.

- Dissolved volatile concentrations in magmas
- Minimum pressure of crystallization (solubility)
- Approximate temperature during crystallization
- Evidence of magma mixing
Data obtainable from M.I.

✓ When M.I. are trapped in zonal arrays, it allows studies on the sequence of inclusion formation.

![Graph showing data points with labels Bt96-24A and H, indicating a trend with a 2σ error bar.](image)
Data NOT obtainable from M.I.

- The composition of the bulk magma (i.e., melt + phenocrysts + exsolved fluid)
- Maximum pressure (depth) of entrapment
- Fate of fluids exsolved from the magma
How to obtain data from MI?

H₂O, CO₂ $\rightarrow$ FTIR

Cl, S, F $\rightarrow$ Microprobe

H₂O, CO₂ Cl, S, F $\rightarrow$ SIMS
Sample Preparation
Sample Preparation
Sample Preparation

Mount selected crystals in dissolvable crystal bond
Grind until inclusion is intersected

Sample Preparation

Final Polish

Flip the crystal
Grind until inclusion is intersected (second side)

Flip the crystal

Final Polish

Remember

... Melt inclusions (MI) are small < 100 µm) ...
Grind until incl intersected

Flip the crystal

Handle with care!!

Quartz crystal
Melt inclusion
FTIR analysis

The transmitted light reveals how much energy was absorbed at each wavelength
### Infrared Vibrational Modes

<table>
<thead>
<tr>
<th>Symmetrical stretching</th>
<th>Antisymmetrical stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Symmetrical Stretching" /></td>
<td><img src="image2.png" alt="Antisymmetrical Stretching" /></td>
</tr>
<tr>
<td>Scissoring</td>
<td>Rocking</td>
</tr>
<tr>
<td><img src="image3.png" alt="Scissoring" /></td>
<td><img src="image4.png" alt="Rocking" /></td>
</tr>
<tr>
<td>Wagging</td>
<td>Twisting</td>
</tr>
<tr>
<td><img src="image5.png" alt="Wagging" /></td>
<td><img src="image6.png" alt="Twisting" /></td>
</tr>
</tbody>
</table>
FTIR analysis

Fourier transform allow to measure all wavelengths at once, and produced the absorbance spectrum showing at which IR wavelengths the sample absorbs.
Acquiring Data

Symmetrical stretching

Water

Asymmetrical stretching

Carbon dioxide

3550 cm\(^{-1}\) = fundamental O-H molecule

1430 and 1515 cm\(^{-1}\) = CO\(_3^{2-}\) doublet
3550 cm$^{-1}$ = Fundamental O-H
Beer’s Law

\[ c = \frac{M \cdot A}{\rho \cdot d \cdot \varepsilon} \]

M = Molecular weight
A = Absorbance
\( \rho \) = density of the glass at 25°C
d = Thickness of the waffer
\( \varepsilon \) = Molar absorption coefficient
The reflection method

\[ \partial = \frac{m}{2n (v_1 - v_2)} \]

Thickness of the wafer

Wysoczanski & Tani (2006)
Data reduction - Carbon Dioxide

Shape of the background is complex

Necessary to subtract a carbonate-free reference spectrum (Dixon et al., 1995)

- 1430 and 1515 cm$^{-1}$
- $\text{CO}_3^{2-}$ doublet
- Distorted asymmetric stretching

Absorbance vs. Wavenumber graph
Data reduction - Carbon Dioxide

Measure absorbance intensity using a peak fitting program* that fits the sample spectrum:

- Subtract a devolatilized spectrum
- Fit to a pure 1630 cm\(^{-1}\) band for molecular H\(_2\)O
- Fit to a pure carbonate doublet

* Unpublished program by Sally Newman
<table>
<thead>
<tr>
<th>Inclusions</th>
<th>FTIR</th>
<th>Microprobe</th>
<th>LA-ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>#2</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>#3</td>
<td>✗</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>
Popocatépetl is the site of open vent degassing since the beginning of its new eruption phase in 1994.

Open vent degassing:
- Release of large masses of gas (CO₂, SO₂)
- Short explosive activity
Need a large masses of degassing magma below the volcano.

New data on Popocatépetl

+ Thermodynamic model of the gas composition

We suggest deep degassing of CO$_2$-S-rich magma
M.I. in Px show that resident melt at Popo is highly evolved (dacite to rhyolite)

From Roberge et al. (2009)
The olivine host are $\text{Fo}_{87-90}$

More Mg-rich than Witter et al. (2005)

Similar to Straub and Del Pozzo (2001)
The olivine host are Fo$_{87-90}$

More Mg-rich than Witter et al. (2005)

Similar to Straub and Del Pozzo (2001)

**New Ol-hosted M.I.**

Basalt–basaltic andesite mafic melt that resupply and thermally sustain Popo’s system

Parent to more evolved components
MI trapped variably degassed melts over a wide range of pressures +100-200MPa

Depth, beneath the summit down to 17 km

Not equilibrium degassing
Degassing induces crystallization of olivine.

Sat. Pressure ↓
As
Crystallization ↑

From Roberge et al. (2009)

Graph showing the relationship between pressure (MPa) and K₂O (wt%) with points indicating decompression crystallization.
**Degassing Model**

### Emission rates:

(For Delgado Granados, unpublished data)

<table>
<thead>
<tr>
<th></th>
<th>April 23</th>
<th>June 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2$</td>
<td>7200 t/d</td>
<td>6150 t/d</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>33280 t/d</td>
<td>37240 t/d</td>
</tr>
</tbody>
</table>

- CO$_2$/SO$_2$ ratio: 4.6 (April 23) vs. 6 (June 19) higher than Gerlach et al. (1997) and similar to Goff et al. (2001).

We used CO$_2$/SO$_2$ ratio of 1-8.
Degassing Model

We model degassing as a function of depth (pressure) at Popocatépetl

By

Calculating the CO$_2$/SO$_2$ mass ratio of gas at equilibrium with the basaltic melt (M.I.) as a function of Pressure

Using

Vapor-melt partitioning model of Scaillet and Pichavant (2005)
Degassing Model

Model Inputs:

Melt composition - average of all M.I.

$T^\circ$ - average of 1140°C from Sagawara, 2000

$H_2O$ content

$S \geq 150$ MPa = 2000ppm, $< 150$ linear variation with $P$

$f_{O_2}$ - Used range between NNO+0.5 to NNO+1.5 because $f_{O_2}$ directly related to the mole fraction of $SO_2$ in gas

BIGGEST UNCERTAINTY OF THE METHOD
Degassing Model

Varied Pressure and used the method of Pichavant (2005) to get $f_{SO_2}$

Converted $f_{SO_2}$ in mole fractions using the Redlich-Kwong equation of state
Degassing Model

Degassing of mafic magma between ~150 and 350 MPa beneath Popocatépetl releases gas with CO$_2$/SO$_2$ values comparable to the measured values (1-8) similar to Stromboli + Etna (Scaillet and Pichavant, 2005)

No need of conduit convection

From Roberge et al. (2009)
Summary

The shallow Dacite-Rhyolite magmas do not have (cannot have) sufficient CO$_2$ and S content to produce the high gas emissions at Popocatépetl.

Degassing of mafic magma at depth is the culprit for the high gas emission at Popocatépetl.

Decompression drives the degassing during intrusion in mid-crustal depth,

Followed by gas exsolution due to crystallization.

The encounter of this mafic magma with smaller batch of the more evolved end-member produced the small eruptions seen at Popocatépetl.
Summary

The shallow Dacite-Rhyolite magmas do not have (cannot have) sufficient CO$_2$ and S content to produce the high gas emissions at Popocatépetl.

Degassing of mafic magma at depth is the culprit for the high gas emission at Popocatépetl.

Decompression drives the degassing during intrusion in mid-crustal depth.

Followed by gas exsolution due to crystallization.

The encounter of this mafic magma with smaller batch of the more evolved end-member produced the small eruptions seen at Popocatépetl.
Summary

The shallow Dacite-Rhyolite magmas do not have (cannot have) sufficient CO$_2$ and S content to produce the high gas emissions at Popocatépetl.

Degassing of mafic magma at depth is the culprit for the high gas emission at Popocatépetl.

Decompression drives the degassing during intrusion in mid-crustal depth.

Followed by gas exsolution due to crystallization.

The encounter of this mafic magma with smaller batch of the more evolved end-member produced the small eruptions seen at Popocatépetl.
Summary

The shallow Dacite-Rhyolite magmas do not have (cannot have) sufficient CO$_2$ and S content to produce the high gas emissions at Popocatépetl.

Degassing of mafic magma at depth is the culprit for the high gas emission at Popocatépetl.

Decompression drives the degassing during intrusion in mid-crustal depth.

Followed by gas exsolution due to crystallization.

The encounter of this mafic magma with smaller batch of the more evolved end-member produced the small eruptions seen at Popocatépetl.
Need 0.8 km$^3$
of the mafic magma to produce the 9 Mt measured by Delgado-Granados (2001)

< 1% erupted

The ongoing eruption of Popocatépetl is essentially an intrusive event
Degassing at Popocatepetl

What about the hypothesis of limestone assimilation proposed to explain the short-lived (0.5-3 hr), very high (≤140) CO$_2$/SO$_2$ ratios during 1998 (Goff et al., 2001)?

Even deeper degassing of mafic magma (~650 MPa) could cause CO$_2$/SO$_2$ ratios as high as ~140
April - May, 2012
April 13, 2013

April 16, 2013

Almost no ash
10 pm, May 7, 2013

Lots of ashes!!!

7:30 am, May 8, 2013
Muchas Gracias
Data obtainable from M.I.