# Volatiles in Basaltic Melt Inclusions

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# Outline

- Inferring trapping pressures from H<sub>2</sub>O-CO<sub>2</sub> data
- Post-entrapment modification of melt inclusion volatile contents
- Degassing of volatiles recorded in melt inclusions
- Melt inclusion evidence for gas fluxing in upper crustal magma bodies and conduits
- Initial (pre-degassing) volatile contents of mafic magmas from different tectonic environments

# H<sub>2</sub>O and CO<sub>2</sub> in variations basaltic melt inclusions



- Melt inclusion data from a single volcano or even a single eruptive unit often show a range of H<sub>2</sub>O and CO<sub>2</sub> values.
- Must consider possible post-entrapment modification processes before interpreting in terms of original trapping pressure

#### Post-Entrapment Modification of Melt Inclusions



 Melt inclusions in tephra deposits are often naturally quenched to glass, making them preferably to inclusions from lava flows

# Formation of shrinkage bubble



- Heating stage experiment on quartz-hosted melt inclusion from Pantelleria
- Vapor bubble nucleates during cooling (E)

### Pressure vs. temperature for a melt inclusion in quartz



- Silicate melt has much greater thermal expansion than crystals
- On cooling, if no vapor bubble is present, pressure in an inclusion decreases rapidly
- Once a vapor bubble nucleates, pressure decreases more slowly
- Low solubility CO<sub>2</sub> partitions strongly into the vapor bubble

# CO<sub>2</sub> loss to shrinkage bubbles in basaltic melt inclusions

- Shrinkage bubble size in basaltic melt inclusions is commonly ~2 to 4 vol% of inclusion, indicating a post-trapping temperature interval of ≤ 100° C.
- Larger vapor bubbles may be primary bubbles that were co-entrapped together with silicate melt at the time of formation.
- CO<sub>2</sub> loss been demonstrated in heating experiments on olivine (Fo<sub>88</sub>) from a Mauna Loa picrite (Wallace & Kamenetsky, unpublished).
- Naturally glassy melt inclusions were re-homogenized at 1400° C for <10 min.</li>
- Results showed that as much as 80% of the initial  $CO_2$  can be transferred to a shrinkage bubble over a cooling interval of ~ 100° C.

# Post-entrapment diffusive loss of H<sub>2</sub>O from melt inclusions

- It is well established that hydrogen can diffuse rapidly through olivine by coupled diffusion of protons & metal vacancies (Demouchy & Mackwell, 2006).
- Diffusion of molecular H<sub>2</sub>O in olivine has been reported (Portnyagin et al., 2008)
- Heating stage experiments (1 atm) show that substantial H<sub>2</sub>O is lost from olivinehosted melt inclusions on timescales of hours
- Must use short heating times when rehomogenizing inclusions. Best to always use naturally glassy inclusions from tephra



MI from Piton de la Fournaise Heating at 1190°C & 1 atm. Multiple heating & quenching cycles

### H<sub>2</sub>O variations in melt inclusions

Diffusive loss or variable melt degassing before inclusion entrapment?

QuickTime™ and a decompressor are needed to see this picture.

### Degassing & variable trapping pressure during magma ascent



• In many cases, variations in H<sub>2</sub>O & CO<sub>2</sub> reflect variable degassing during ascent <u>before</u> the melts were trapped in growing olivine crystals (polybaric crystallization)

### Degassing of H<sub>2</sub>O-rich basaltic magma from an arc volcano

Cerro Negro, Nicaragua, 1867 eruption

QuickTime™ and a decompressor are needed to see this picture.

Roggensack (2001)

#### Why do many MI data sets not follow equilibrium degassing paths?



Melt inclusions from Mount Etna

QuickTime™ and a decompressor are needed to see this picture.

Spilliaert et al. (2006)

QuickTime™ and a decompressor are needed to see this picture.

Deviations from equilibrium degassing paths are observed for many melt inclusions

But a subset of the data (with low  $CO_2$ ) follow the equilibrium paths



Johnson et al. (in review)

QuickTime™ and a decompressor are needed to see this picture. Gas fluxing of magma in upper crustal magma bodies & conduits

- Combined effect of open-system addition of CO<sub>2</sub>-rich gas to ascending or stored magma (Anderson et al., 1989; Wallace, 2003; Rust et al., 2004; Spilliaert et al., 2006; Johnson et al., 2008)
- This process is consistent with:
  - high CO<sub>2</sub> in primary magmas (e.g. Kilauea, Gerlach et al., 2002; Etna, Allard et al., 1999)
  - high CO<sub>2</sub> flux at basaltic volcanoes (Fisher & Marty, 2005; Wallace, 2005, for reviews)
  - high CO<sub>2</sub>/SO<sub>2</sub> ratios in gas emissions with increasing explosivity of eruption (e.g. Burton et al., 2007; Aiuppa et al. 2007)
- If this interpretation is correct, such a process should be common at open-conduit basaltic volcanoes

#### Effects of Gas Fluxing

Melt inclusions from Mount Etna

CO<sub>2</sub>-flushed magma ponding zone. Causes dehydration of magma

Spilliaert et al. (2006)

# Gas fluxing, H<sub>2</sub>O loss and crystallization

Jorullo (Mexico), a monogenetic mafic cinder cone (Johnson et al., 2008)



Jorullo melt inclusions

Phase diagram for early Jorullo melt composition (10.5 wt.% MgO) constructed using MELTS and pMELTS.

• CO<sub>2</sub>-rich gas fluxing depletes melt in H<sub>2</sub>O and thereby causes olivine crystallization

# Sulfur Degassing

Wade et al. (2006)

Arenal

Fuego Cerro Negro

QuickTime™ and a decompressor are needed to see this picture.

- Sulfur solubility in arc basaltic magmas is equal to or higher than H<sub>2</sub>O
- This causes S to correlate with H<sub>2</sub>O in some cases & to remain dissolved as H<sub>2</sub>O is lost in others

### Sulfur degassing recorded in 2002 Mount Etna melt inclusions

QuickTime™ and a decompressor are needed to see this picture.

• Loss of S is shown only by melt inclusions with lower H<sub>2</sub>O contents

Spilliaert et al. (2006)

# Effects of pressure & oxygen fugacity on sulfur degassing

Johnson et al. (in review)

QuickTime™ and a decompressor are needed to see this picture.

- S solubility model of Scaillet & Pichavant (2005) can be used to calculate the vapor-melt partition coefficient for S (curves)
- D<sub>s</sub> values estimated from melt inclusion data are shown by symbols

H<sub>2</sub>O loss, crystallization, and incompatible behavior of S & CI

- H<sub>2</sub>O loss from degassing magma causes crystallization
- The resulting crystallization causes an increase in incompatible S & CI that partially or totally offsets any loss by degassing

Etna 2002 eruption

QuickTime™ and a decompressor are needed to see this picture.

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> > Spilliaert et al. (2006)

# Evidence for CI loss by degassing

• Effects of crystallization crystallization & degassing can be distinguished by using ratios of S & CI to another incompatible element

Melt inclusions from Central Mexico cinder cones

QuickTime™ and a decompressor are needed to see this picture.

Johnson et al. (in review)

# Primary (or Initial) Volatile Contents of Mafic Magmas



Blue Lake Maar, Oregon Cascades



Jorullo volcano, Mexico

- How do we see through the "haze" of degassing & other post-entrapment effects?
- The general approach is to analyze a large number of MI from a given eruptive unit & use the highest measured concentrations as a <u>minimum</u> indication of the undegassed volatile content of the magma

#### H<sub>2</sub>O and CO<sub>2</sub> in Basaltic Magmas



- MORB & OIB have relatively low H<sub>2</sub>O contents
- H<sub>2</sub>O contents of arc basaltic magmas are high & quite variable
- CO<sub>2</sub> contents of arc magmas are lower than estimates based on global arc CO<sub>2</sub> flux

# **Chlorine in Basaltic Magmas**



- CI contents in arc and back-arc magmas are much higher than in MORB
- Indicates substantial recycling of seawater-derived CI into the mantle wedge

Sulfur concentrations in melt inclusions & submarine basaltic glasses



• S contents of arc magmas are typically higher than for MORB

Data sources: Anderson (1974); Wallace & Carmichael (1992); Métrich et al. (1996; 1999); Cervantes & Wallace (2002)



# Key points to remember:

- Post-entrapment shrinkage bubble formation mainly affects CO<sub>2</sub> because of its low solubility
- Post-entrapment diffusive loss of H can occur from melt inclusions, though timescales and mechanisms affecting natural melt inclusions are still uncertain
- Large variations in H<sub>2</sub>O and CO<sub>2</sub> for inclusions from a single volcano or even a single eruptive unit are common. In most cases, appear to reflect trapping of inclusions at variable pressures in the upper crust during magma ascent & degassing
- Data commonly do <u>not</u> follow equilibrium degassing paths for H<sub>2</sub>O and CO<sub>2</sub>. This may be related to strong fluxing of CO<sub>2</sub>-rich gases from deeper in the magma system.
- S and CI tend to be relatively soluble during degassing. S commonly degasses with H<sub>2</sub>O, but CI is even more soluble & is less affected by degassing.
- Subduction zone basaltic magmas have much higher H<sub>2</sub>O and CI than MORB & OIB.
  S is also higher. Less is known about primary CO<sub>2</sub> contents of magmas because low solubility causes it to degas early.