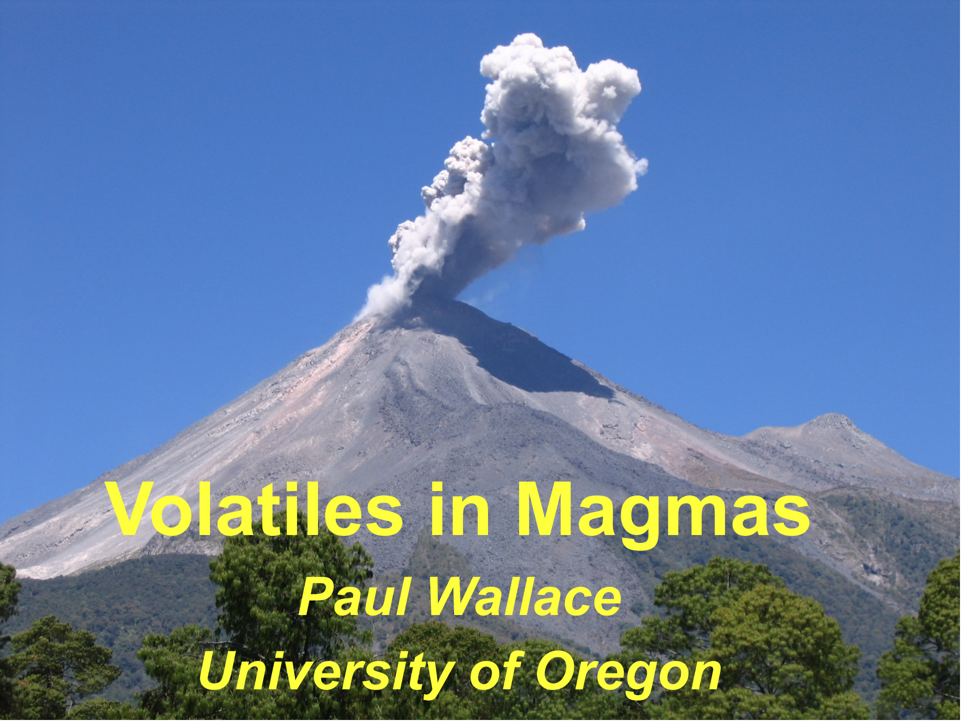
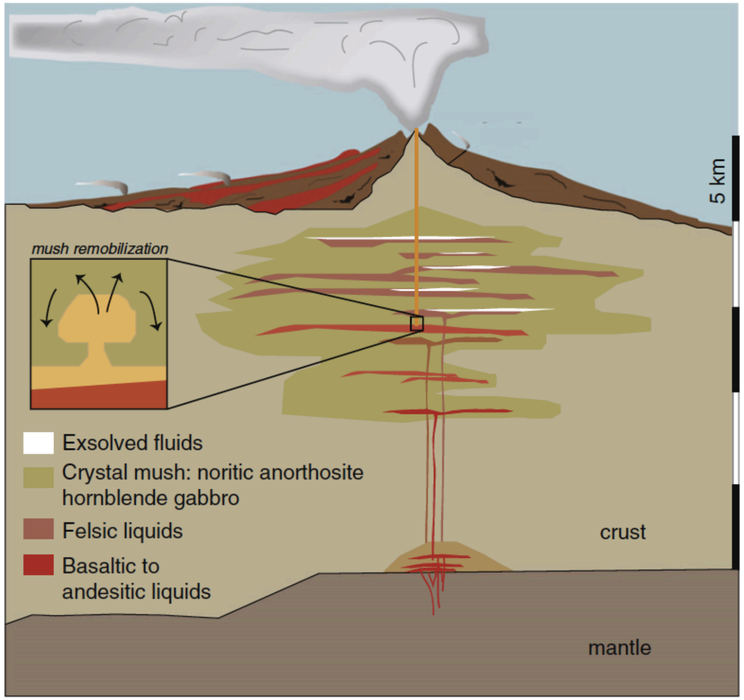
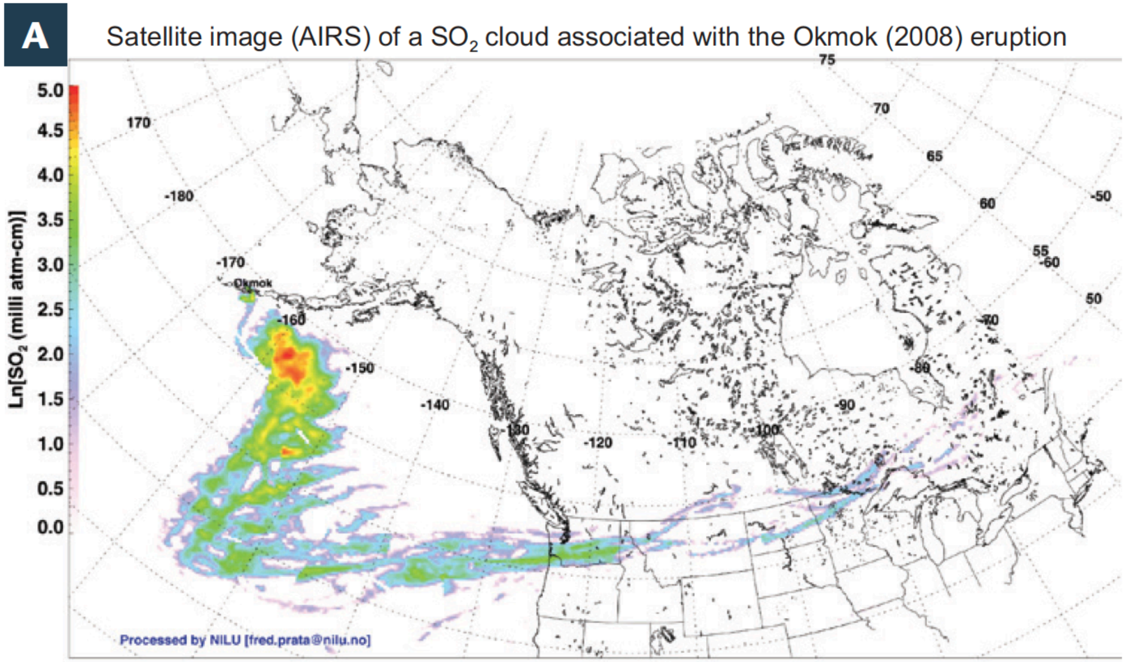


Volatiles in Magmas

Paul Wallace

University of Oregon



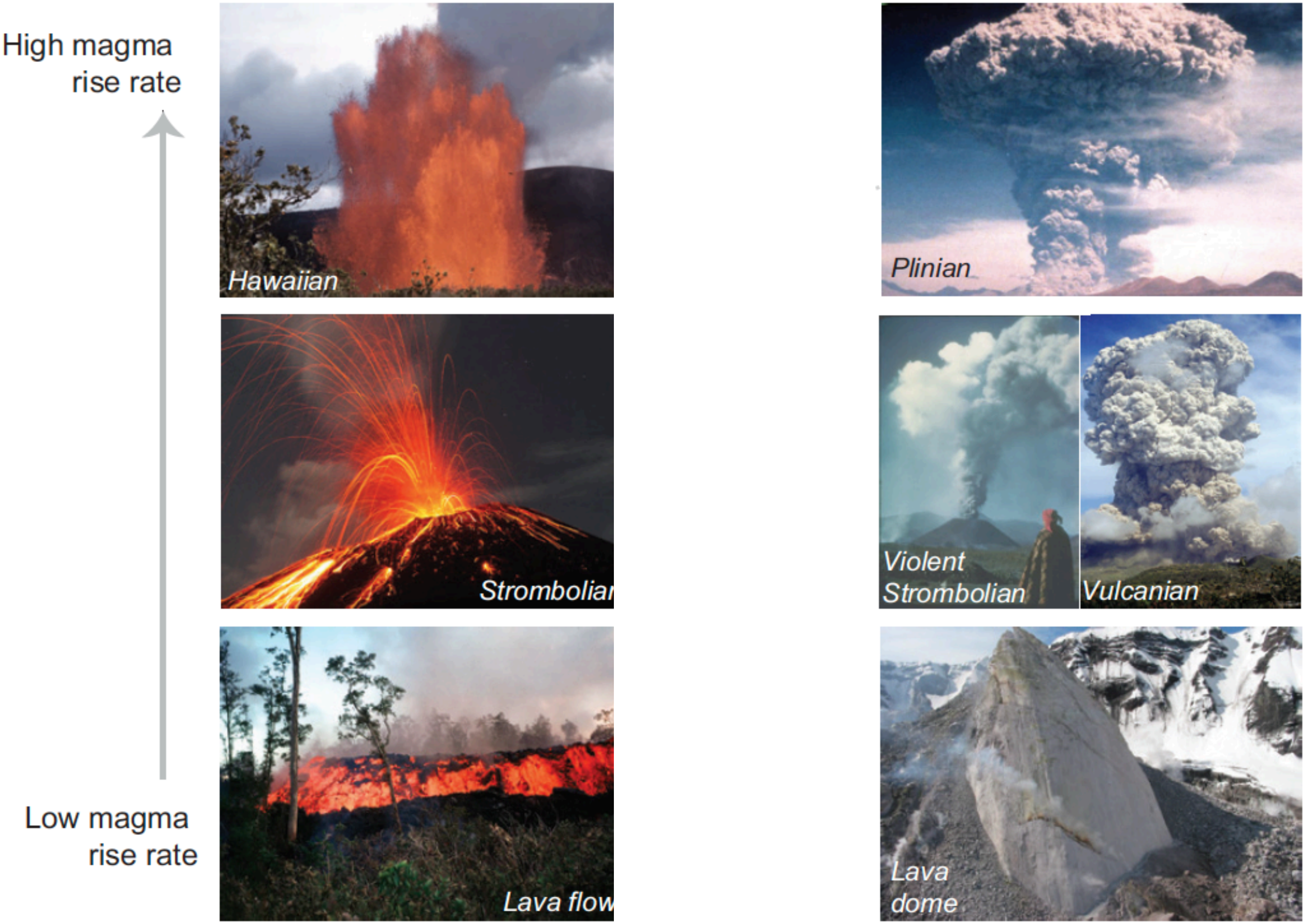


A Satellite image (AIRS) of a SO_2 cloud associated with the Okmok (2008) eruption

Volatiles & Eruption Styles

Low viscosity magmas

Higher viscosity
Higher H_2O contents



Edmonds & Wallace (2017)

Role of Volatiles

- Phase equilibrium; mantle and crustal melting; degassing induced crystallization
- Magma buoyancy, compressibility & viscosity
- Overpressure & eruption triggering
- Subduction zones
- Long term C, S, H, Cl cycles on Earth
- Effects on Earth’s atmosphere & climate
- Ore deposits & hydrothermal systems

Outline

- How do we measure volatile contents? – the problem of magma degassing
- Solubility experiments (H_2O, CO_2, Cl, S) & comparisons with natural systems
- Using melt inclusions to infer crustal storage depths
- Degassing paths & diffusive H loss from melt inclusions
- Excess sulfur & exsolved volatiles in crustal magma reservoirs
- Challenges in determining magma CO_2 concentrations
- Volatiles & eruption triggering
- Using H diffusion out of melt inclusions to infer magma ascent rates

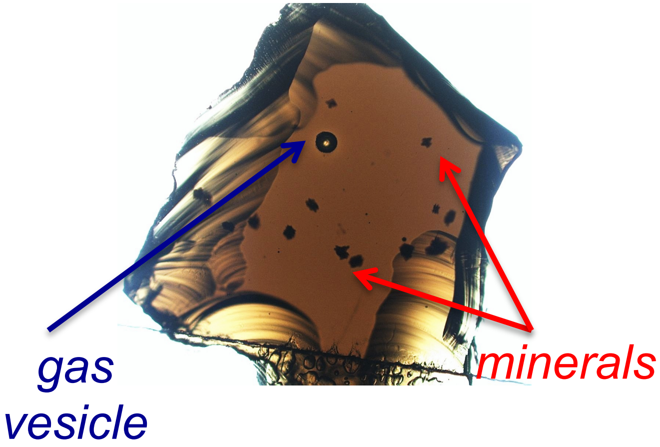
Problem of Magma Degassing

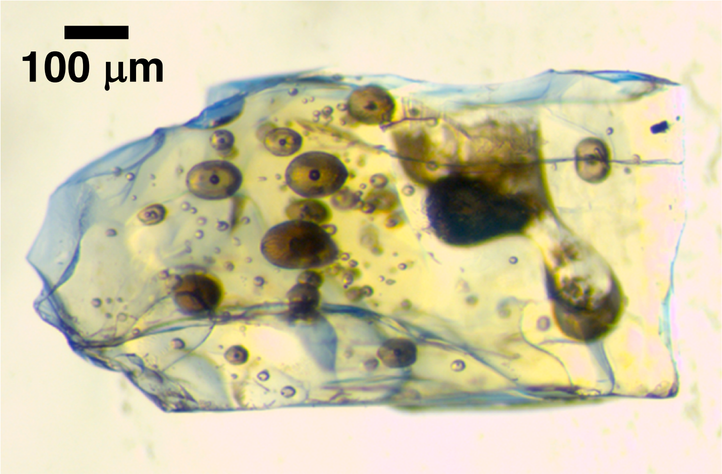
- Solubility of volatiles is strongly pressure dependent
- Volatiles are degassed both during eruption & at depth before eruption
- Bulk analysis of rock & tephra is not very useful


USGS

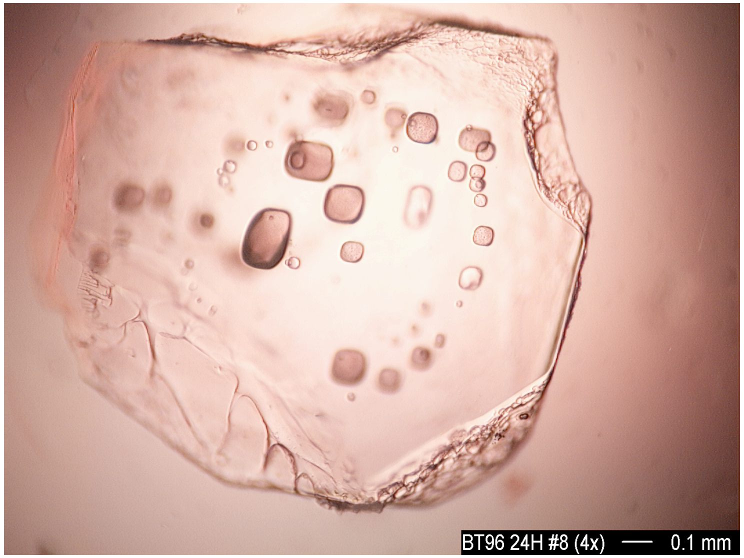
How do we measure volatile concentrations in magmas?

Submarine pillow rim glasses



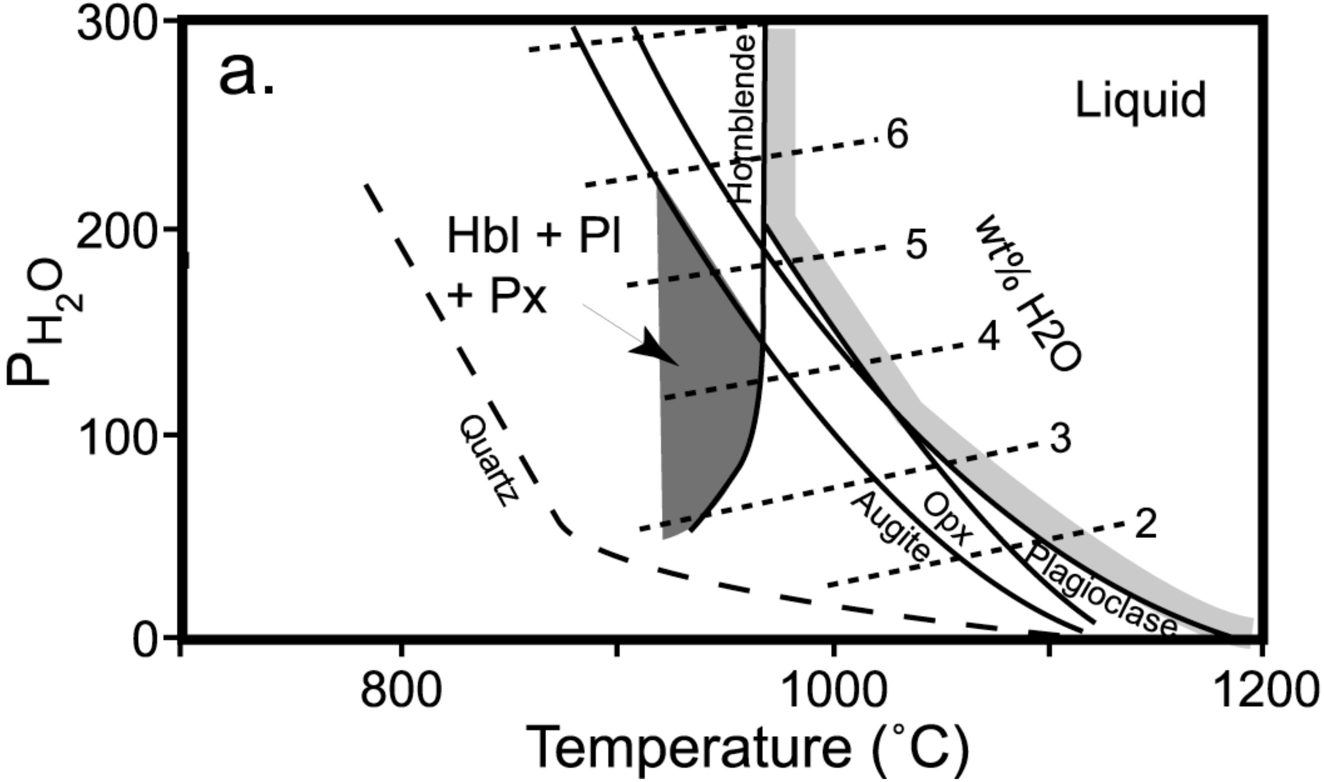


Melt inclusions



How do we measure volatile concentrations in magmas?

Experimental petrology



Phase equilibria for andesite (Moore & Carmichael, 1998)

How do we measure volatile concentrations in magmas?

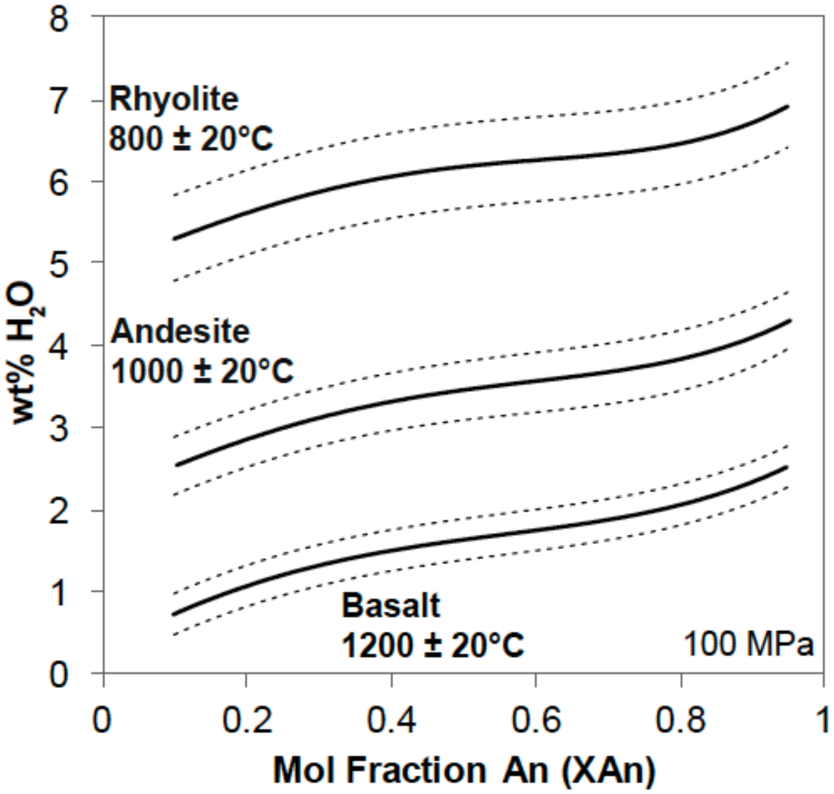
Thermodynamic calculations

Plagioclase – melt hygrometer

$$\mathrm{CaAl_2Si_2O_8^{crystal} + NaAlSi_3O_8^{liquid} = CaAl_2Si_2O_8^{liquid} + NaAlSi_3O_8^{crystal}}$$

$$\ln(K) = \ln\left(\frac{a^{\mathrm{liquid}}_{\mathrm{CaAl_2Si_2O_8}}}{a^{\mathrm{liquid}}_{\mathrm{NaAlSi_3O_8}}}\right) + \ln\left(\frac{a^{\mathrm{crystal}}_{\mathrm{NaAlSi_3O_8}}}{a^{\mathrm{crystal}}_{\mathrm{CaAl_2Si_2O_8}}}\right).$$

$$\ln\left(\frac{\gamma^{\mathrm{liquid}}_{\mathrm{CaAl_2Si_2O_8}}}{\gamma^{\mathrm{liquid}}_{\mathrm{NaAlSi_3O_8}}}\right) = a + \frac{b}{T} + \sum d_i X_i + d_{\mathrm{H_2O}} X_{\mathrm{H_2O}}$$



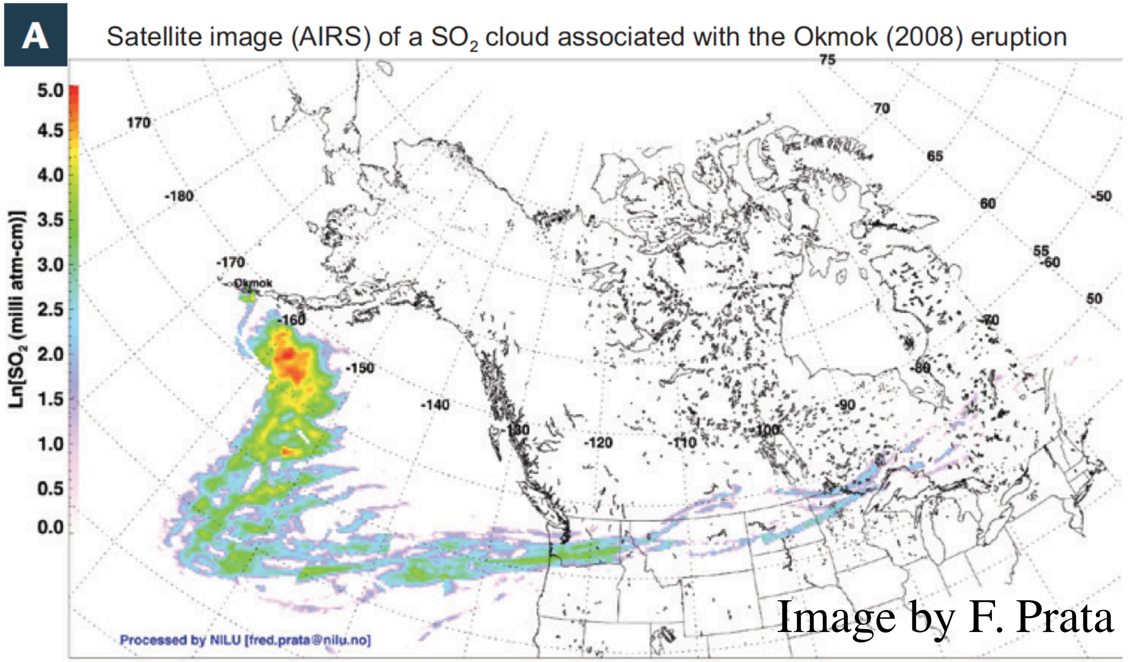
Waters & Lange (2015)

Volcanic gases

- Ground & airborne remote sensing
- Satellite-based remote sensing
- Direct sampling & analysis

FLYSPEC (DOAS)

Sampling gases at Cerro Negro



A Satellite image (AIRS) of a SO_2 cloud associated with the Okmok (2008) eruption

Image by F. Prata

Solubility Experiments & Application to Natural Systems

Some key things to remember:

- Volatiles occur as dissolved species in silicate melts & also in a separate vapor phase if a melt is vapor saturated.

- At pressures of a few kbar and higher, the vapor phase is dense, more like a liquid than a gas. The words vapor, fluid, or gas are used to describe this phase.

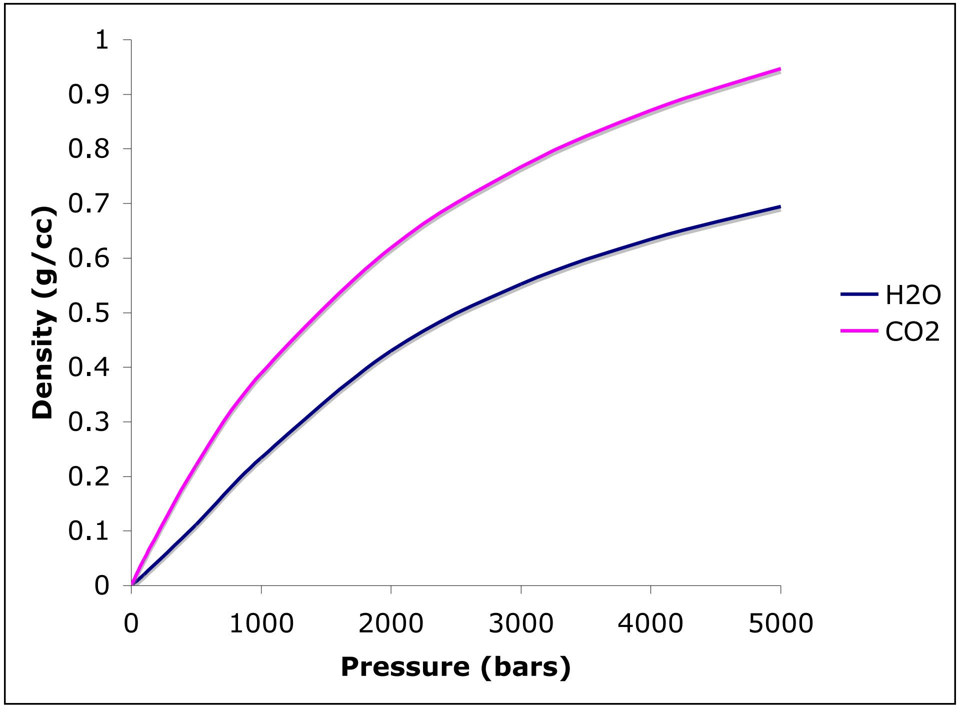
- In laboratory experiments, melts can be saturated with a nearly pure vapor phase (e.g., H_2O saturated or CO_2 saturated).

- In natural systems, however, multiple volatile components are always present, forming a gas mixture (H_2O, CO_2, S, Cl, F, noble gases, volatile metals, alkalies)

- Referring to natural magmas as being H_2O saturated or CO_2 saturated is, strictly speaking, incorrect because the vapor phase always contains other volatiles.

- Sulfur solubility is complex because of multiple valence states. The maximum solubility of S is limited by sulfide or sulfate phases, not by vapor saturation.

Gas (Fluid) Densities



Densities at 800° C

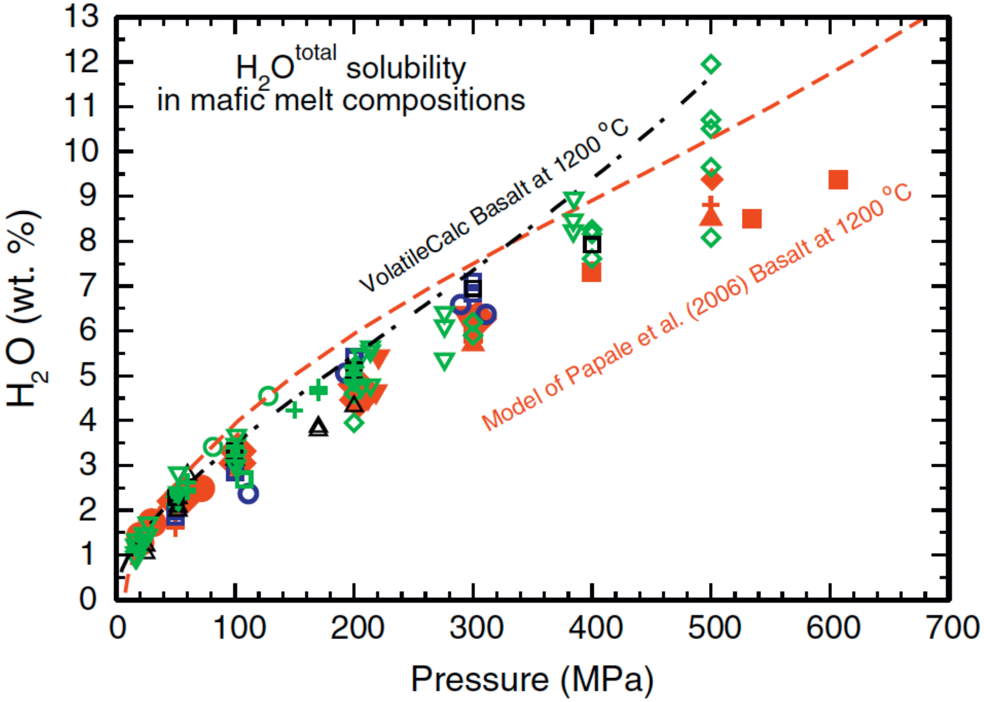
Calculated using the Redlich-Kwong (1949) equation of state:

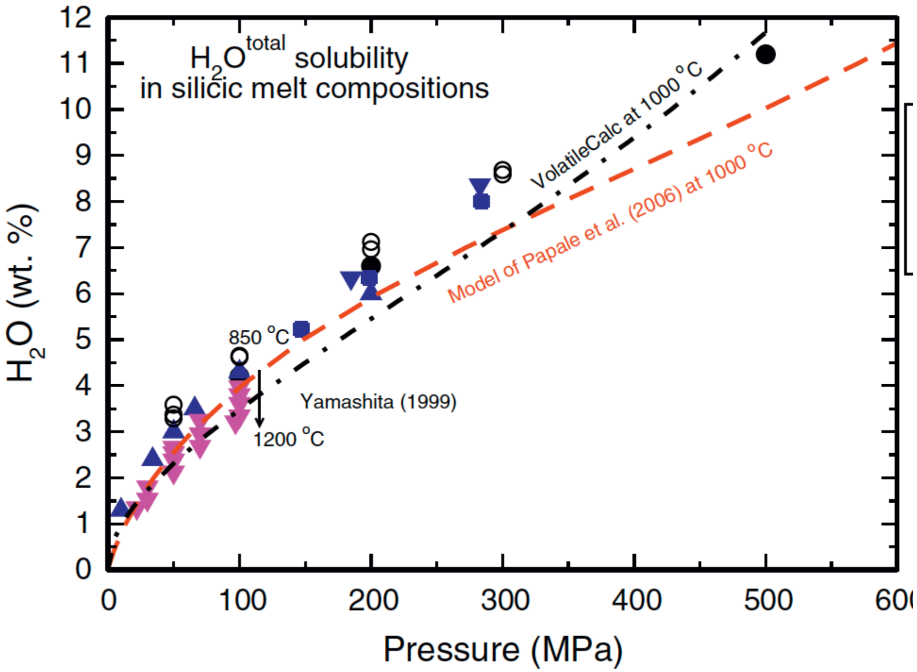
$$p = \frac{RT}{V - b} - \frac{a}{V(V + b)T^{0.5}}$$

where a is a measure of attractive forces between molecules & b is related to the size of the molecules.

Experimentally Determined H_2O Solubility in Silicate Melts

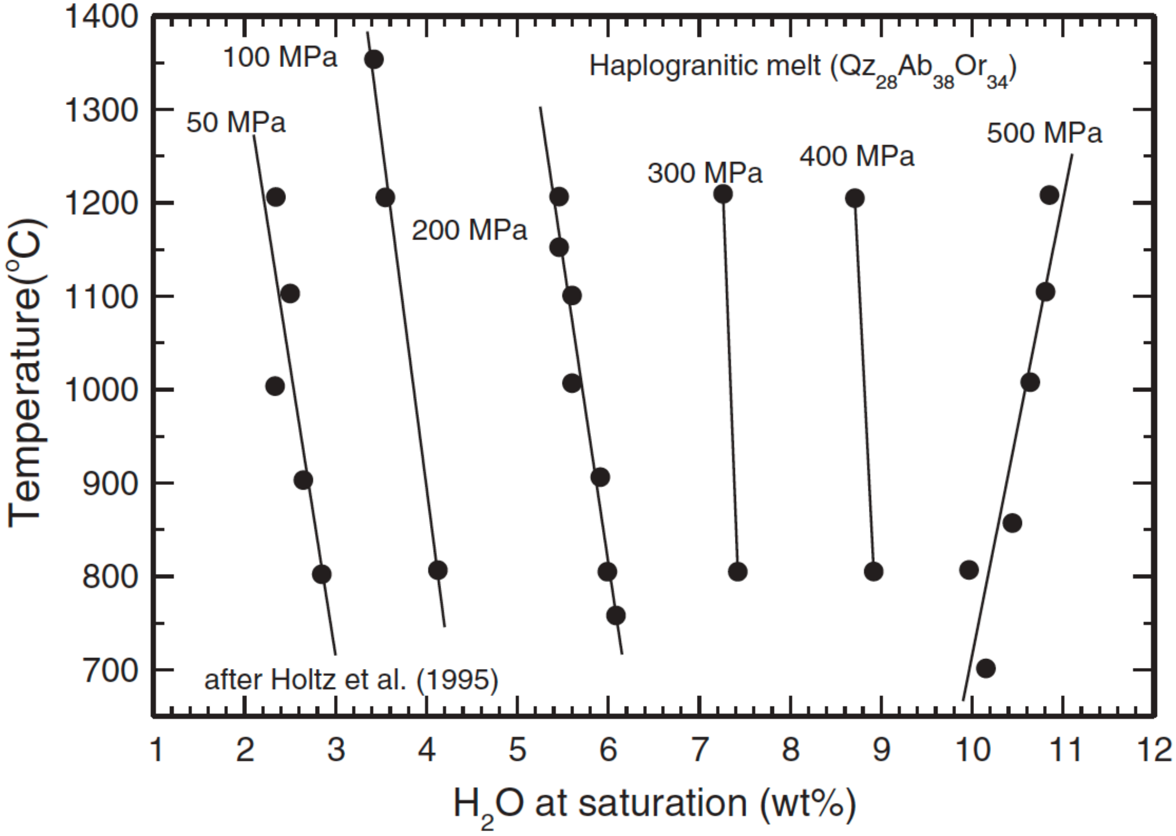
Baker & Alleti (2012)





- Solubility is strongly pressure dependent
- Solubility does not vary strongly with composition – differences seen in these plots are mainly caused by temperature differences

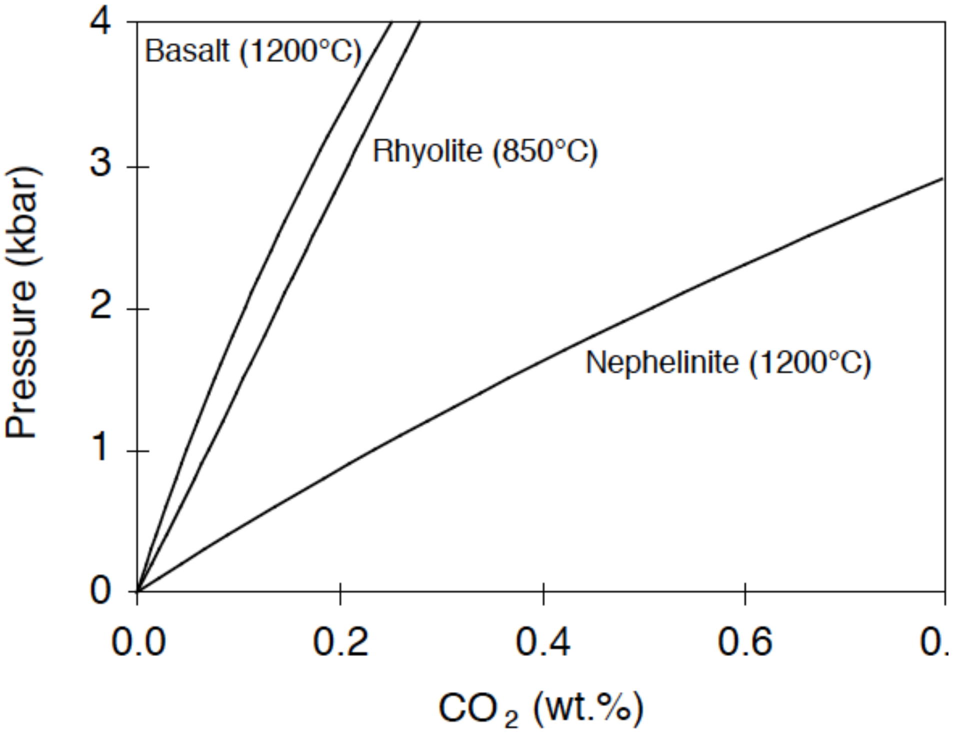
Temperature Dependence of H_2O Solubility

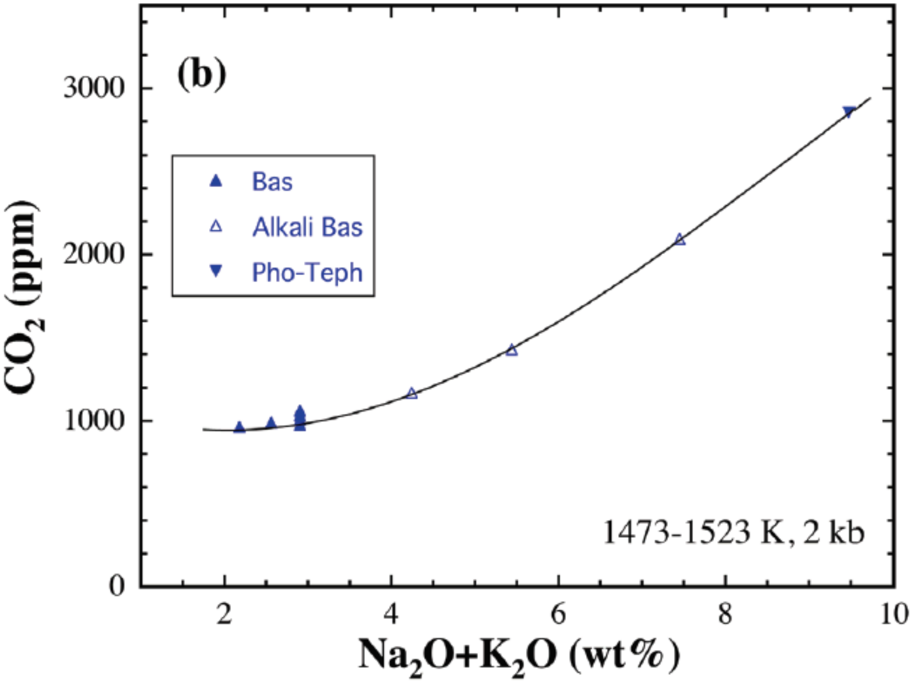


Baker & Alleti (2012)

- Negative dependence of solubility on temperature at lower pressures
- Also for glasses – cooling shards/pyroclasts can hold more H_2O

CO_2 Solubility in Silicate Melts

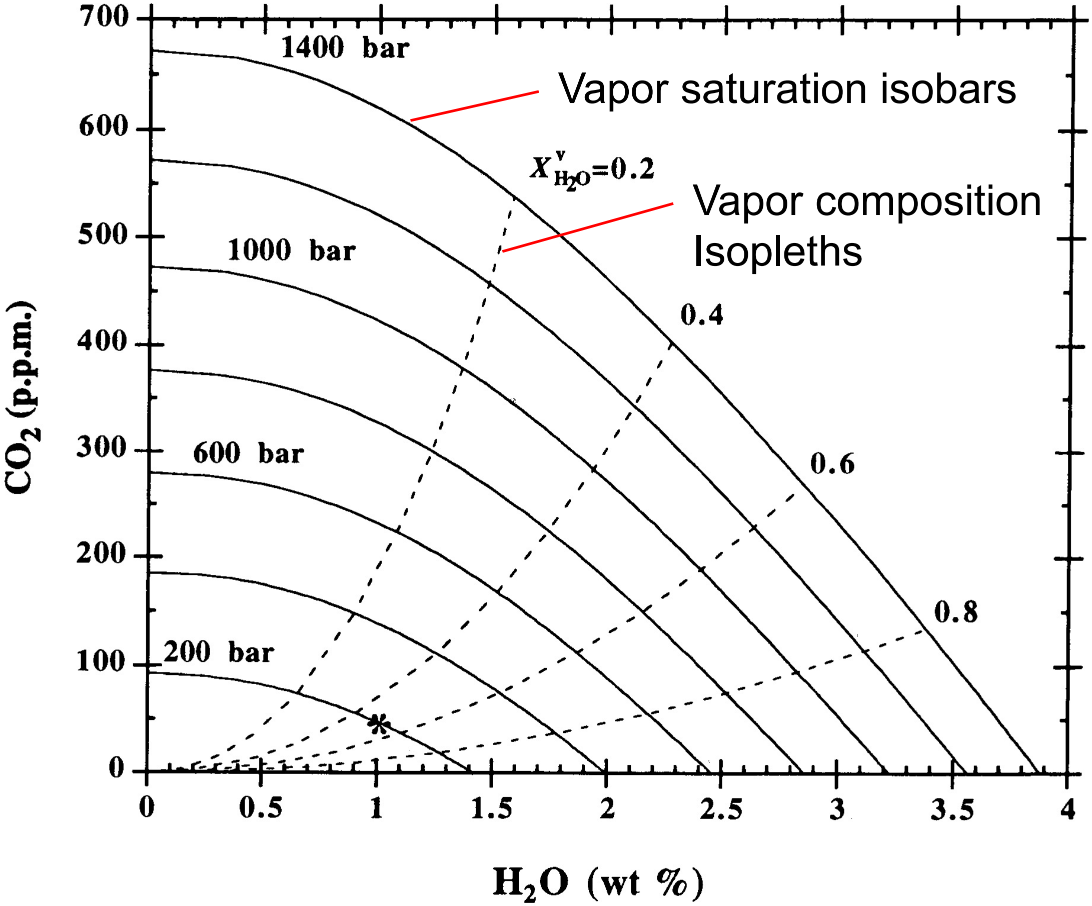




Ni & Keppler (2013)

- Silica-undersaturated melts (e.g., basanite, nephelinite) have much higher CO_2 solubility than basalt because they are more depolymerized (fewer bridging oxygen)

Solubilities with more than one volatile component present



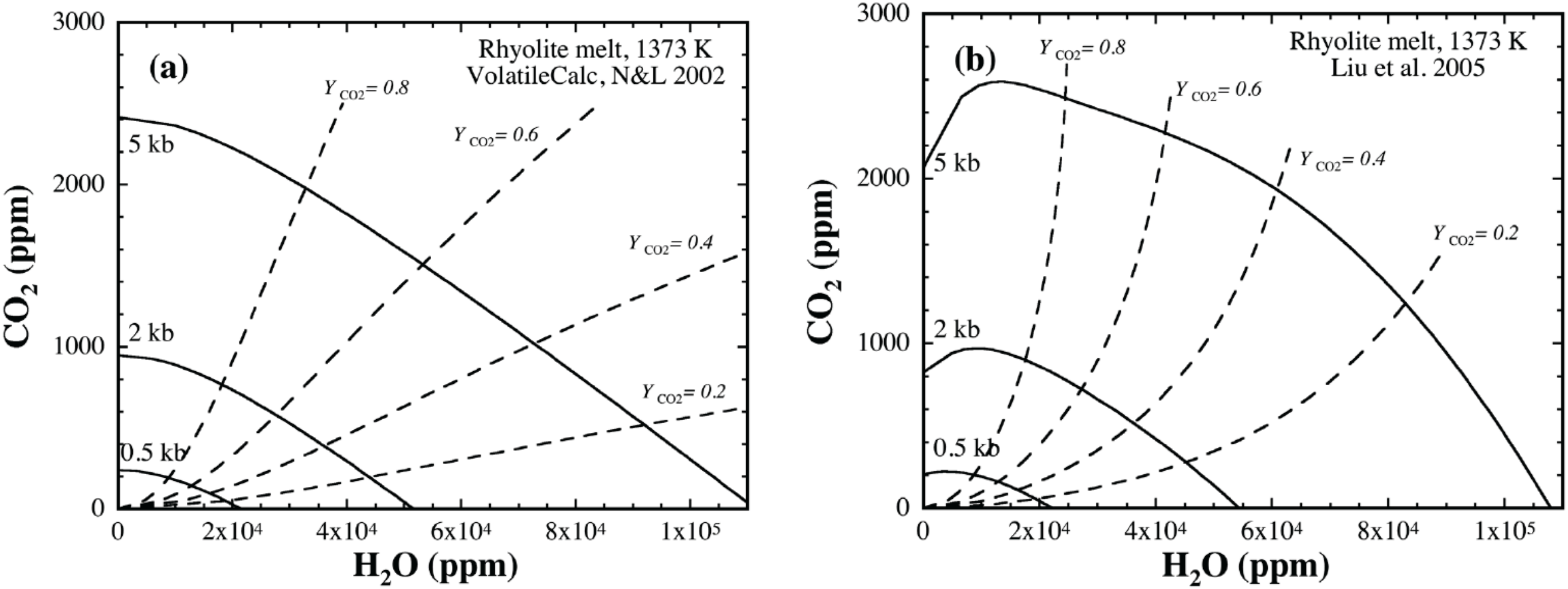
Vapor saturation isobars

Vapor composition Isopleths

Dixon & Stolper (1995)

- In natural systems, melts are saturated with a multicomponent vapor phase
- H_2O and CO_2 contribute the largest partial pressures, so people often focus on these when comparing pressure & volatile solubility

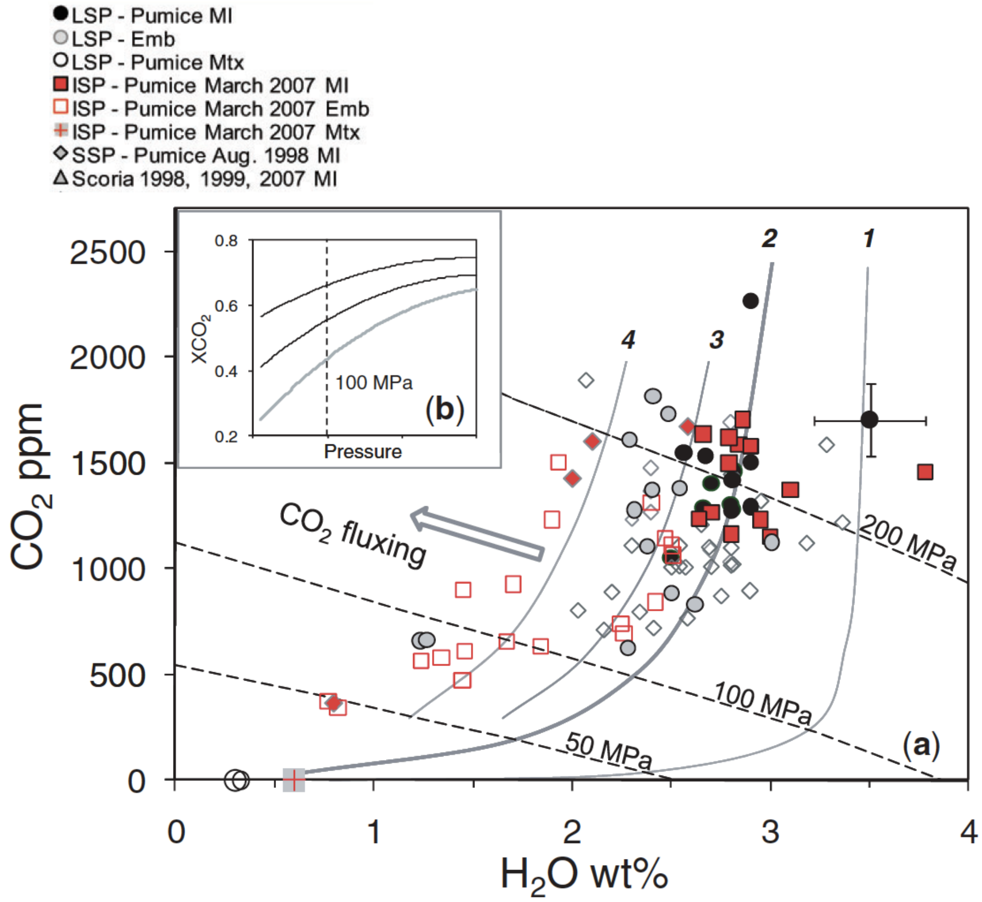
Rhyolitic melts saturated with H_2O-CO_2 vapor

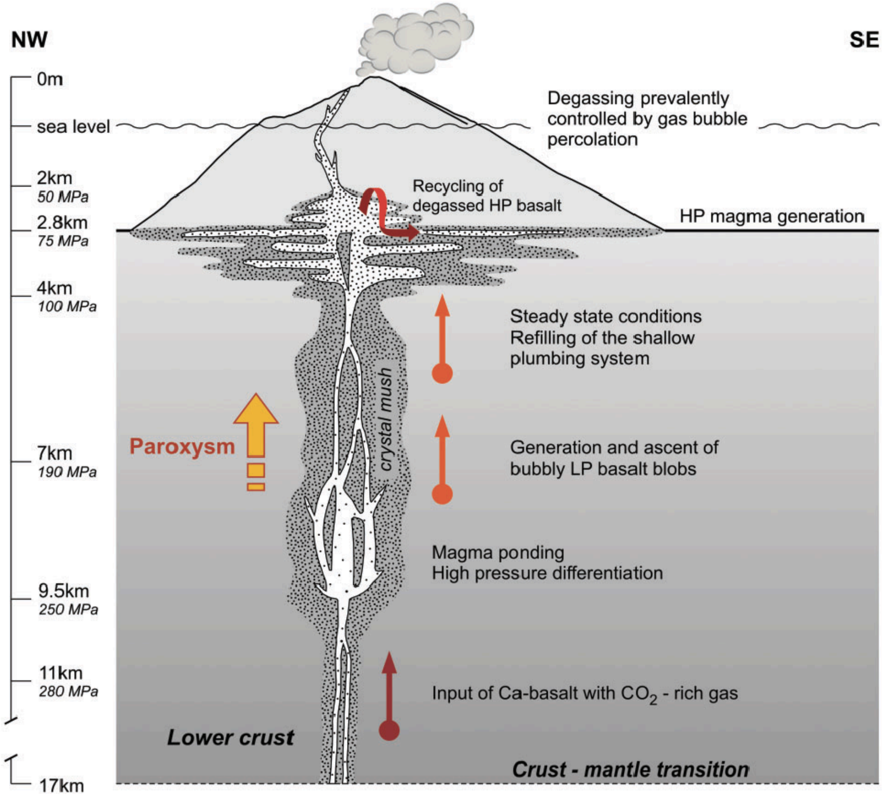


- At higher pressures, dissolved H_2O enhances CO_2 solubility

Ni & Keppler (2013)

Melt inclusions & magma plumbing system at Stromboli

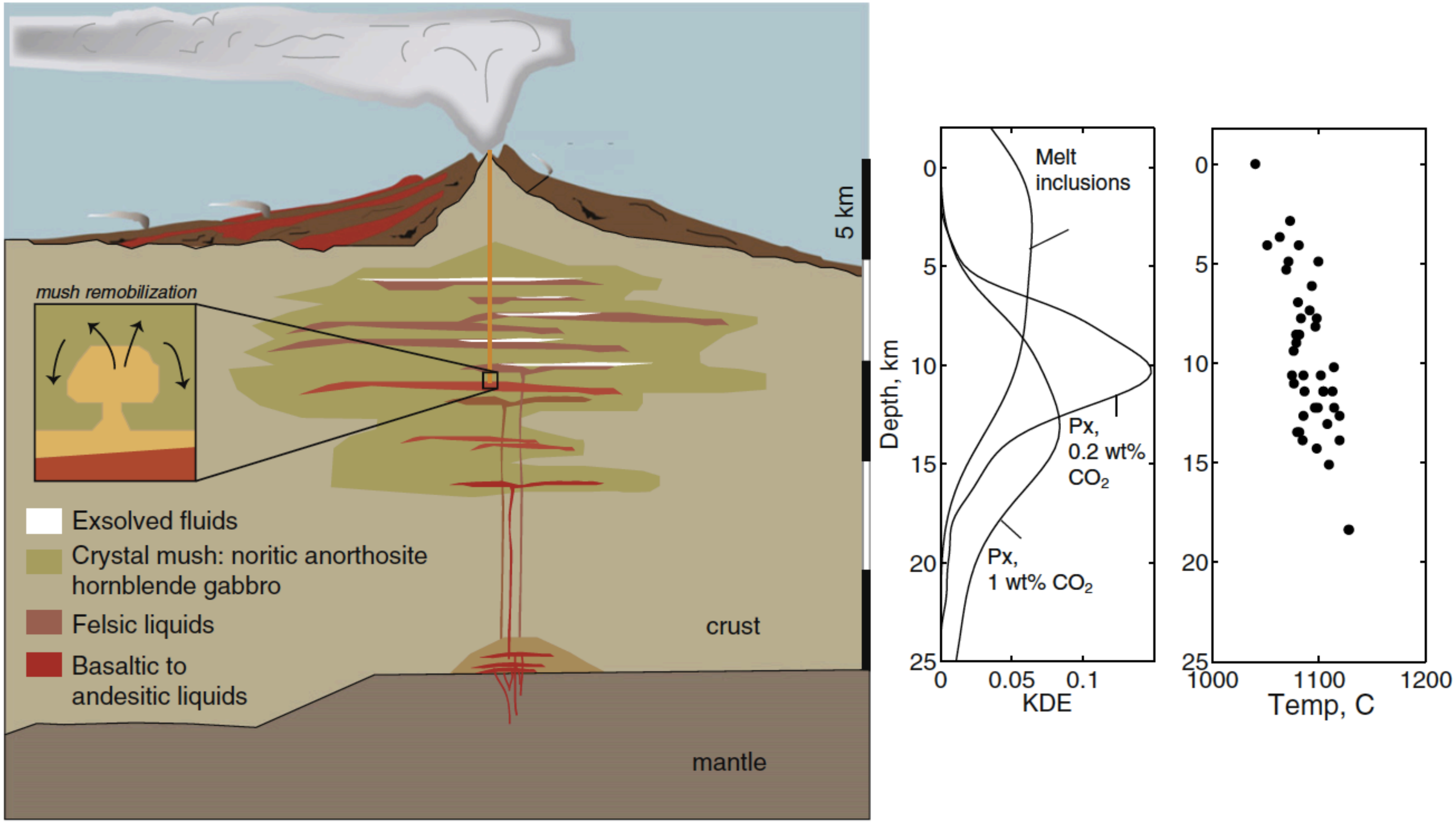




- Melt inclusions can be used to infer depths of crystallization & magma storage
- Very powerful when combined with other crystal-scale data e.g., compositional zoning, cathodoluminescence imaging.

Metrich et al. (2010)

Magmatic architecture beneath Soufriere Hills Volcano

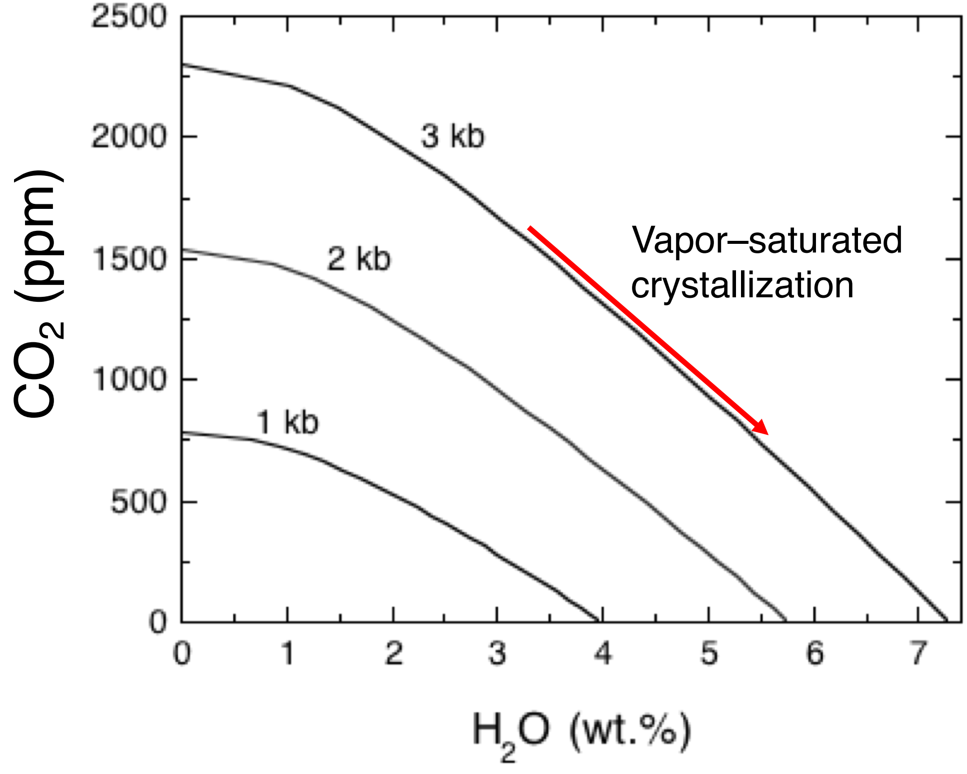


- Evidence for vertically protracted, crystal-rich mush with heterogeneous bodies of eruptible magma in the upper crust.

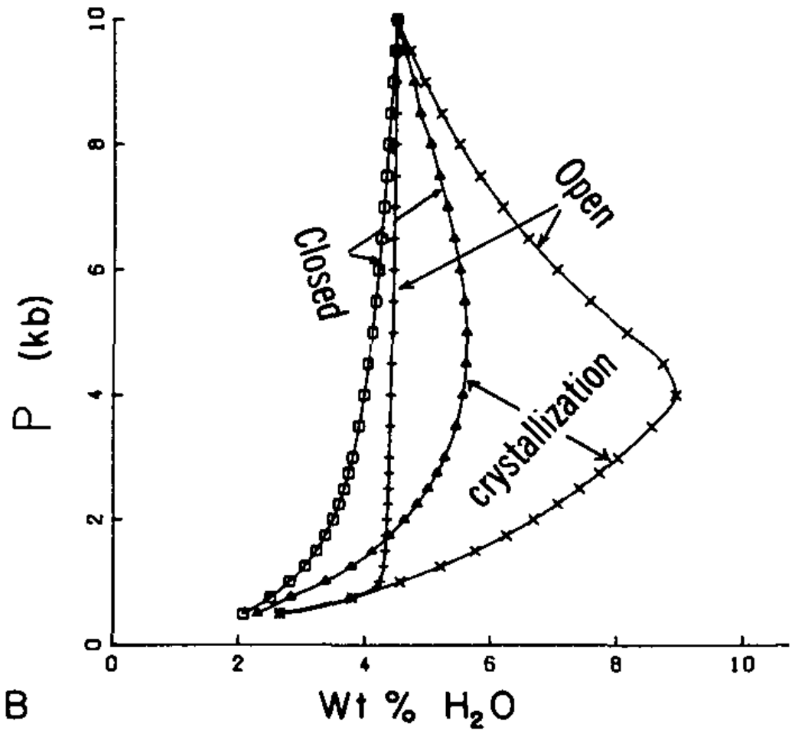
Edmonds et al. (2016)

Vapor–Saturated Crystallization

Isobaric crystallization



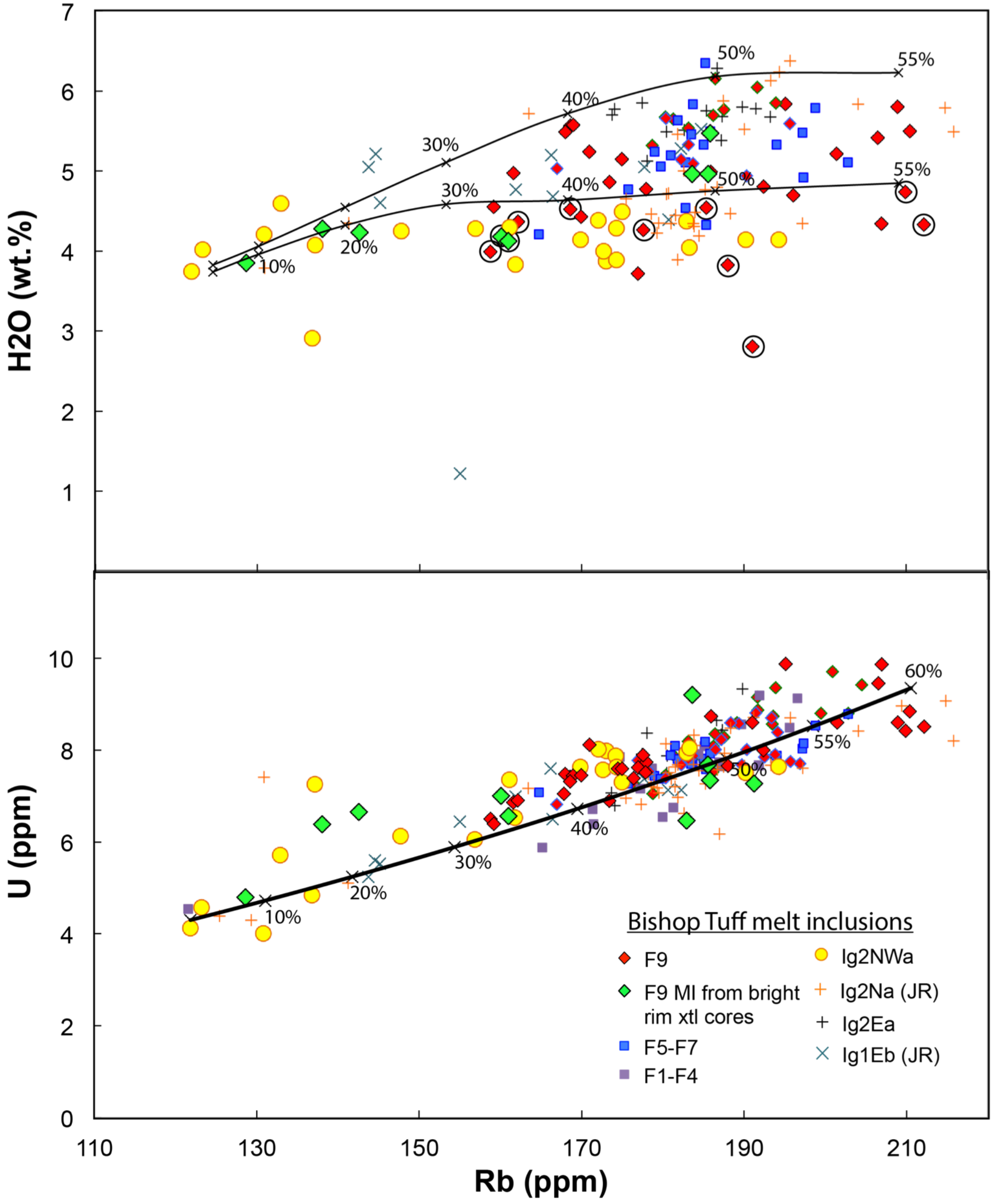
Crystallization during ascent



Holloway (1976)

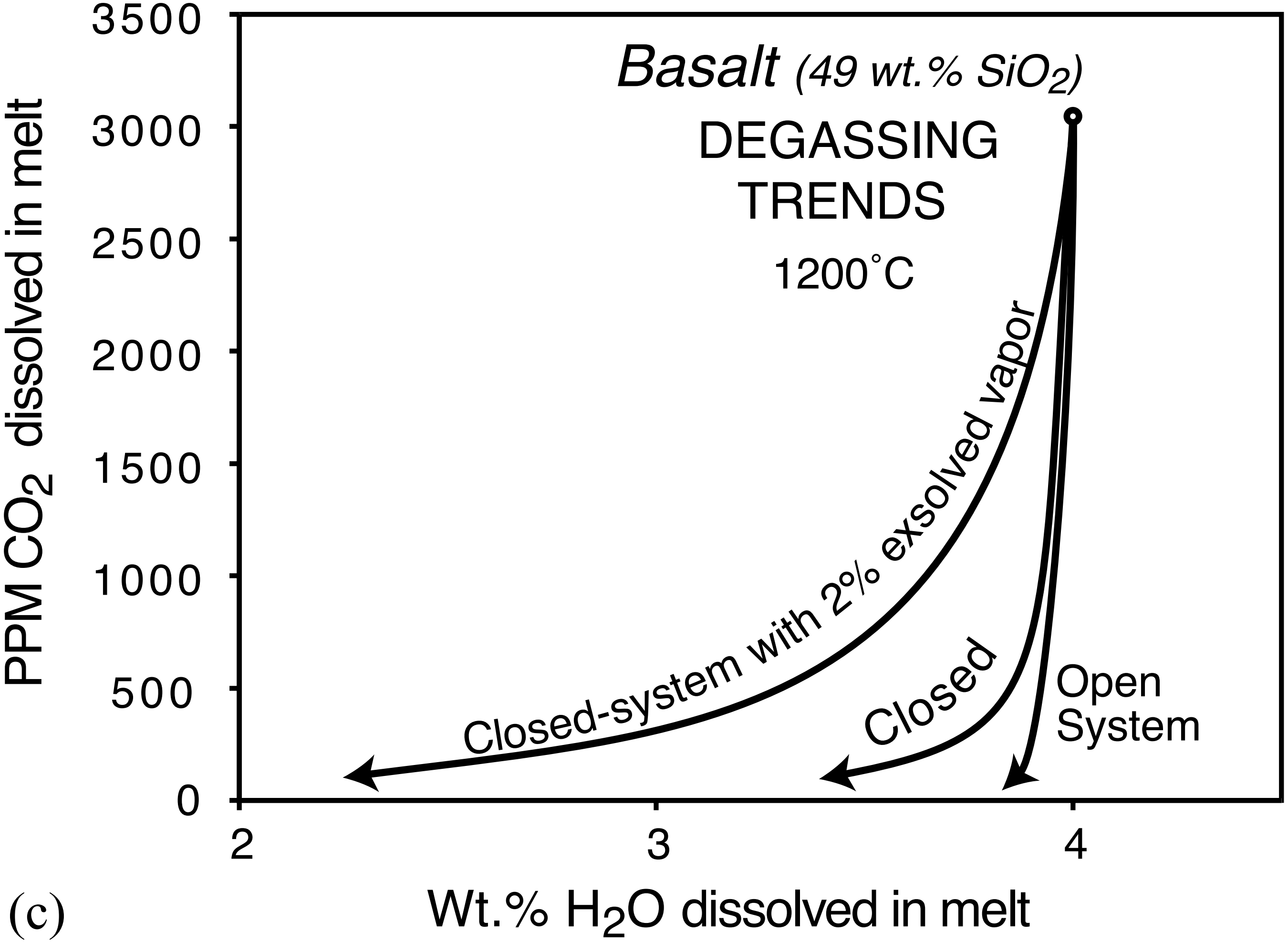
- Magmatic H_2O contents increase during vapor-saturated crystallization if CO_2 is present

H_2O variations during differentiation in rhyolitic melts



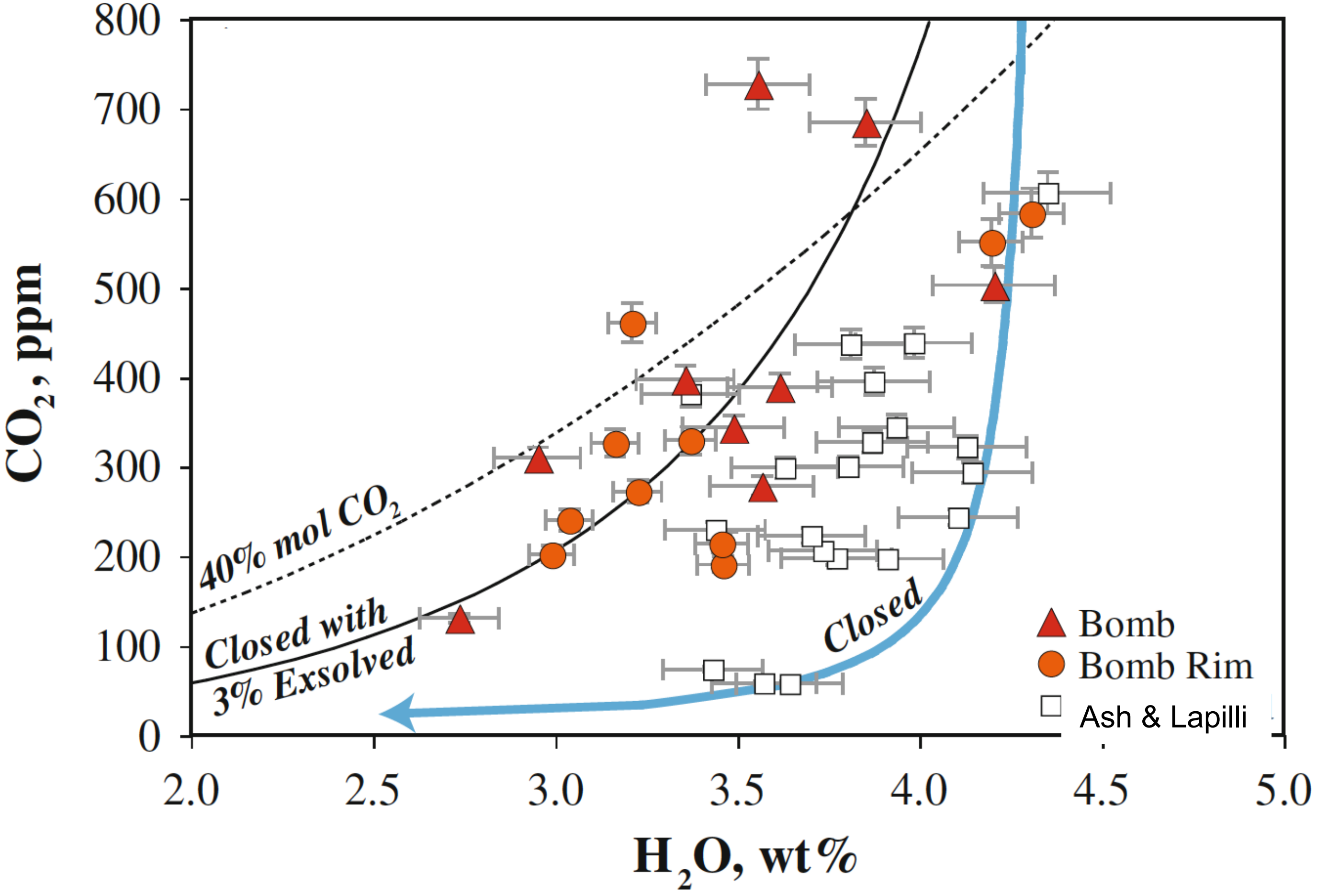
Fulton et al., in prep.

Effect of low CO_2 solubility on degassing during ascent



Newman & Lowenstern (2002)

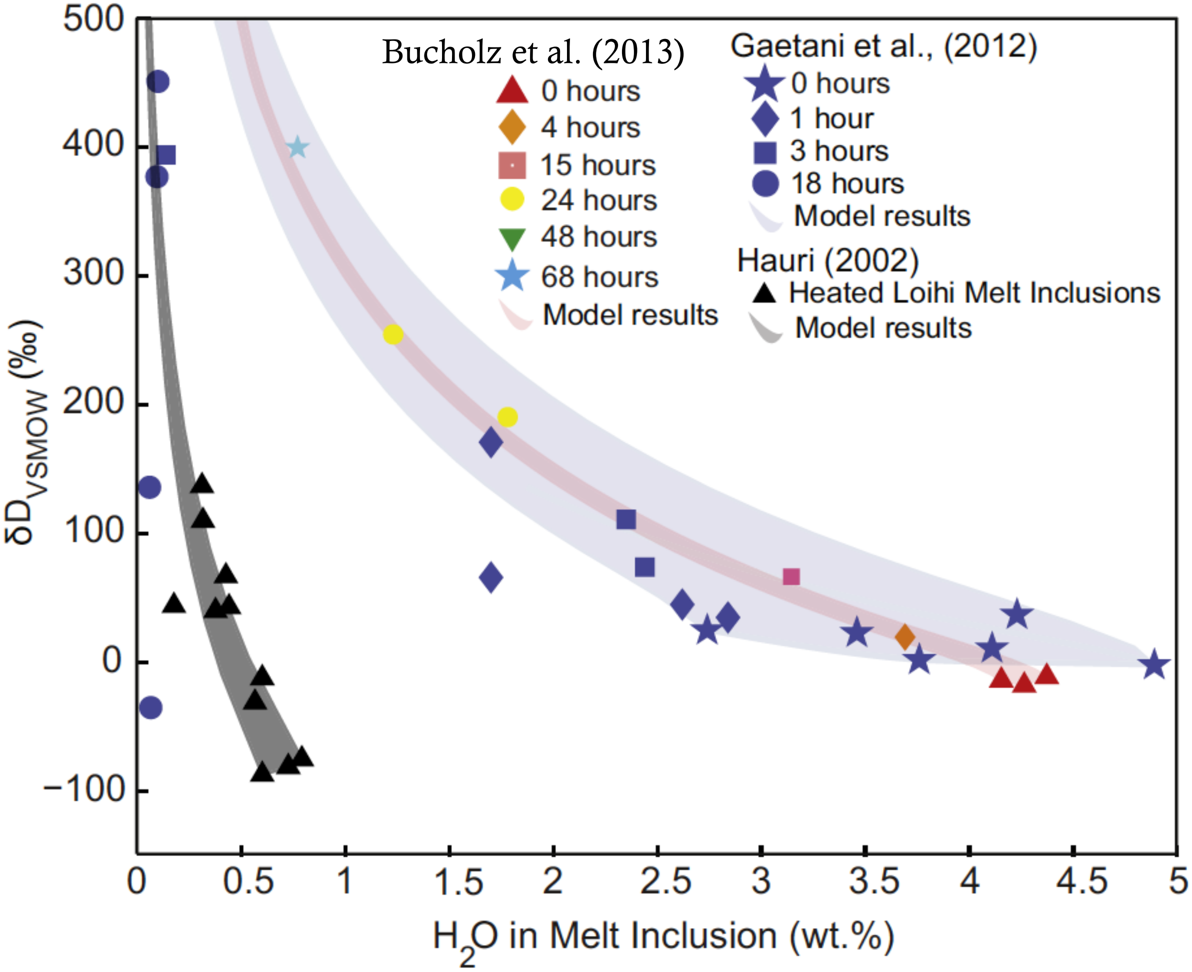
Melt Inclusions from Volcán de Fuego, Guatemala



- How much H_2O was in melts at time of trapping?
- Why so much variation in H_2O from one eruption?

Lloyd et al. (2013)

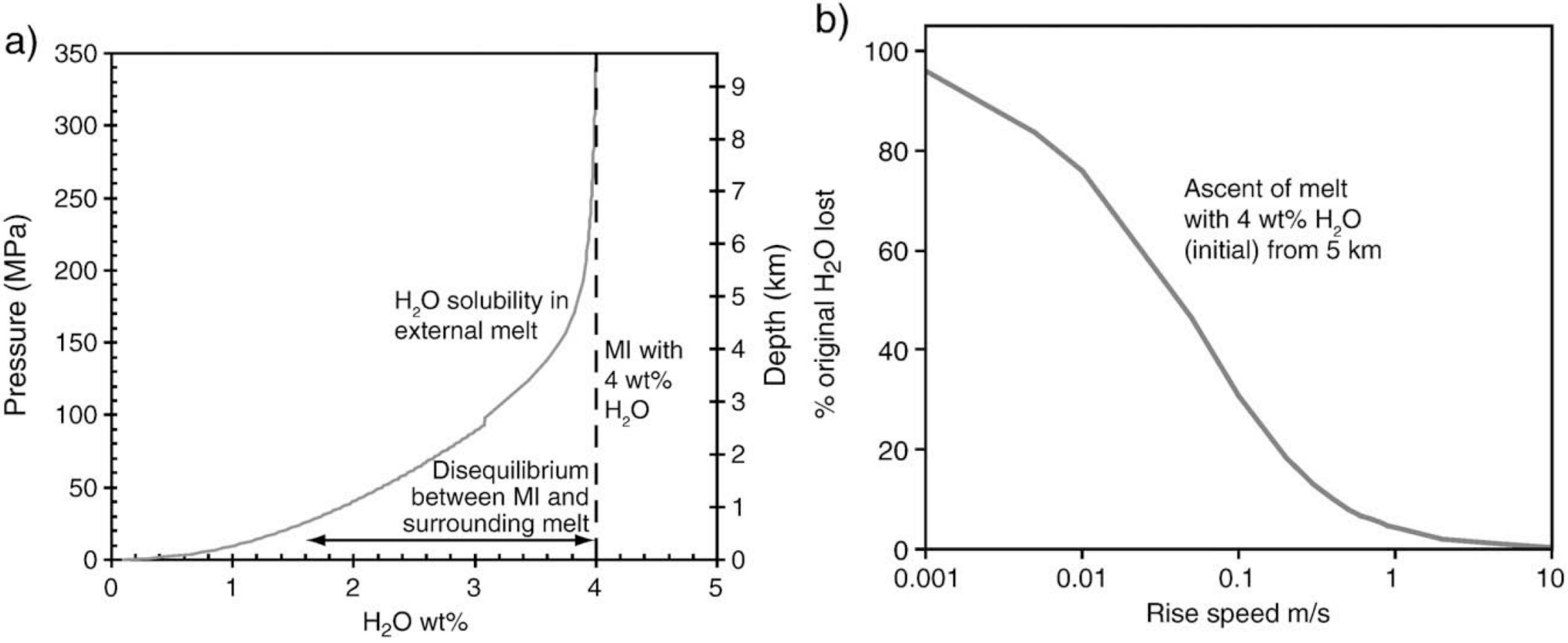
Diffusive loss of H from melt inclusions



- Diffusive H loss occurs over timescales of hours at magmatic temperatures and results in increased D/H ratio (δD) in melt inclusions

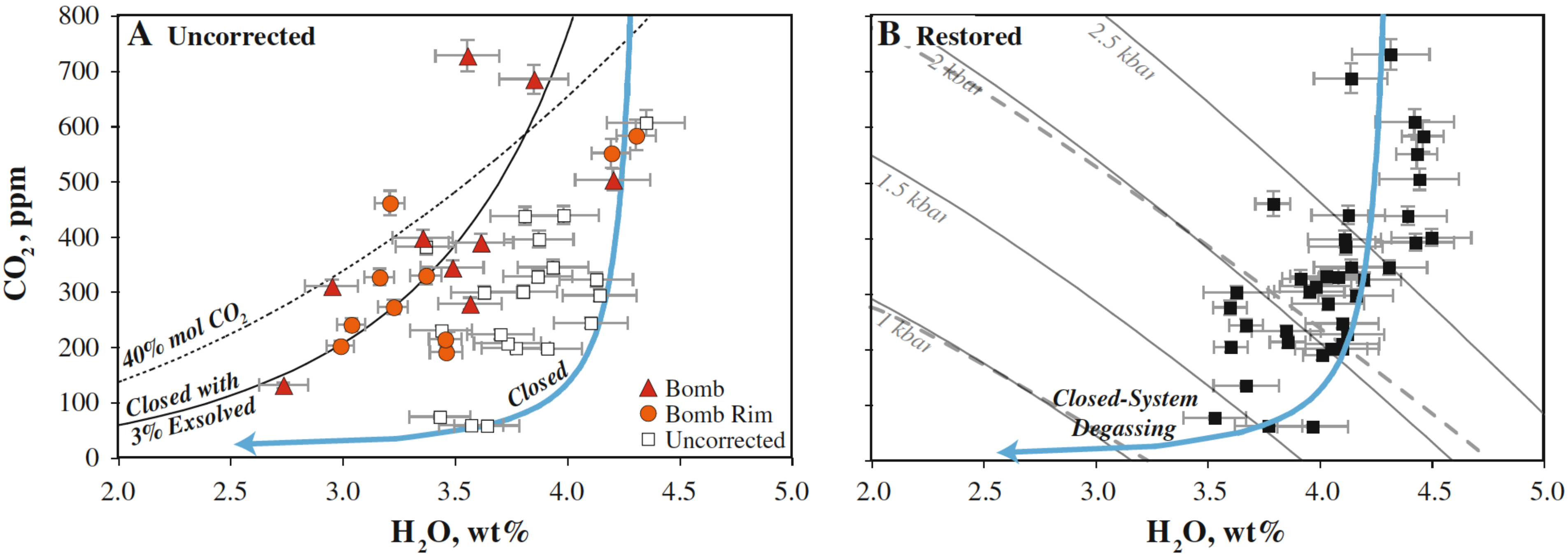
Bucholz et al. (2013)

Diffusive loss of H from melt inclusions during magma ascent



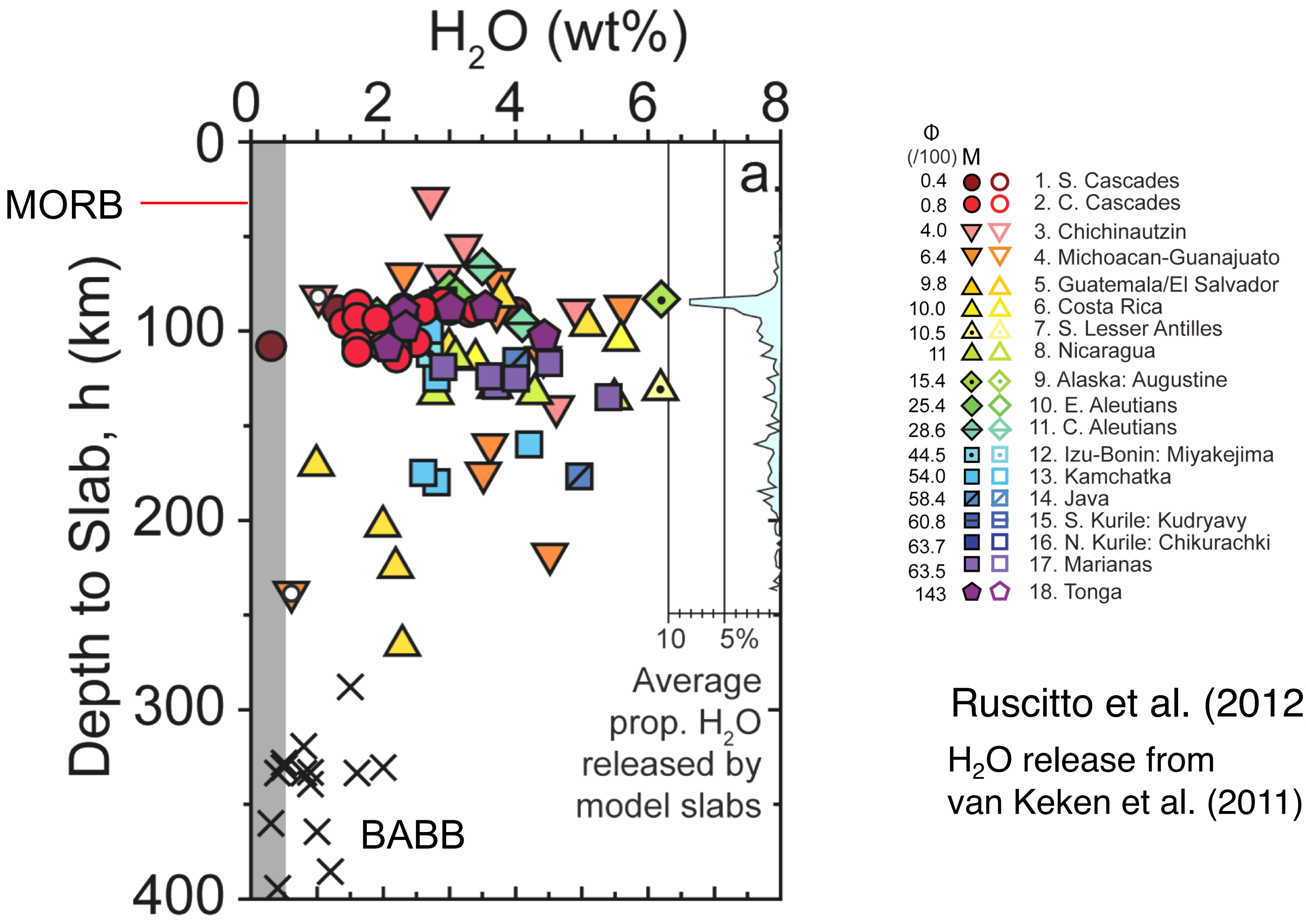
Johnson et al. (2010)

Melt inclusions corrected for H loss using K_2O & crystallization modeling



Lloyd et al. (2013)

H_2O Contents of Primitive Arc Magmas

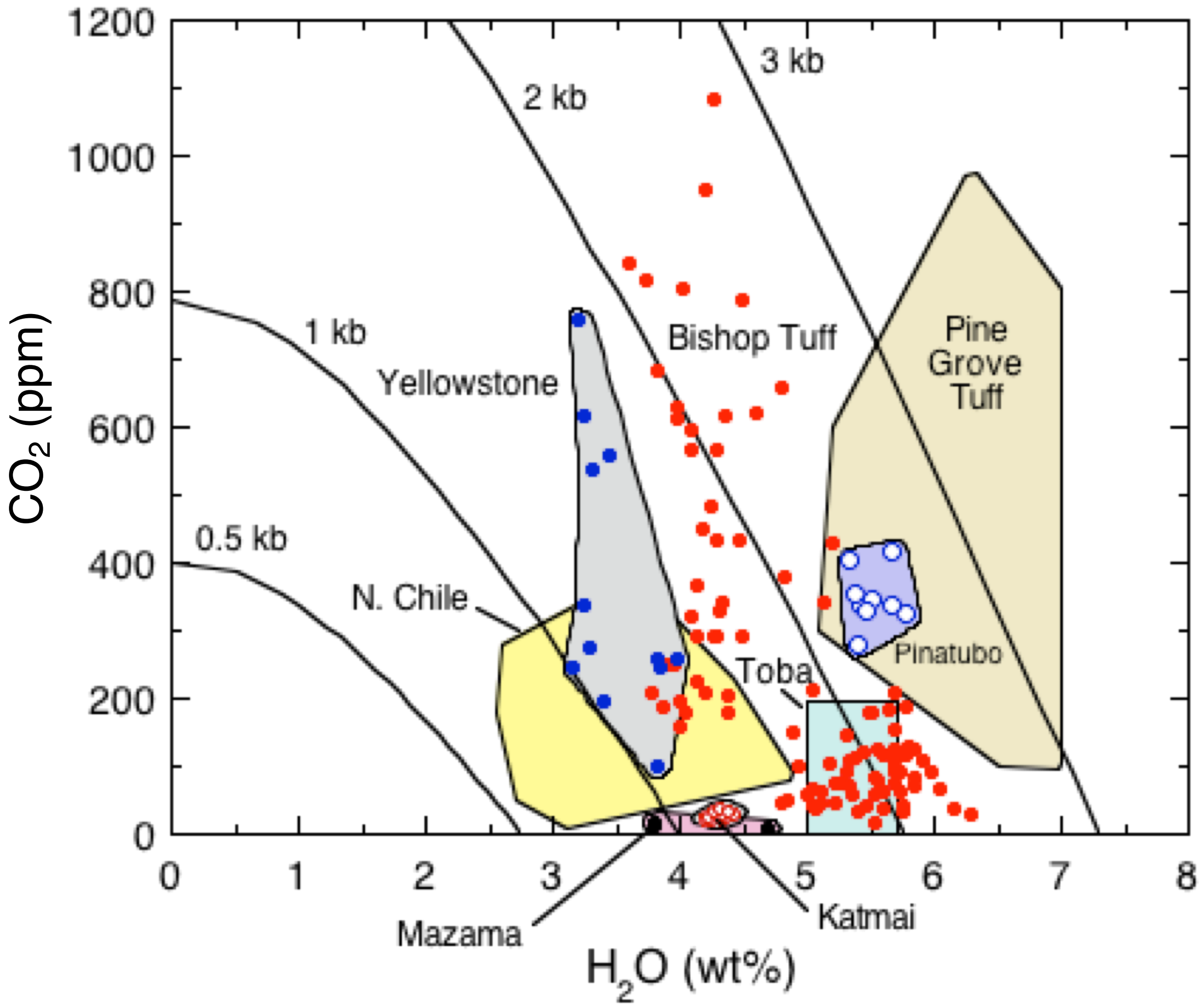


Ruscitto et al. (2012)

H_2O release from
van Keken et al. (2011)

- Based on published data for 100 volcanoes from 18 subduction zone segments
- Each data point represents a single volcano based on melt inclusion data
- All compositions have been corrected to equilibrium with Fo_{90} olivine

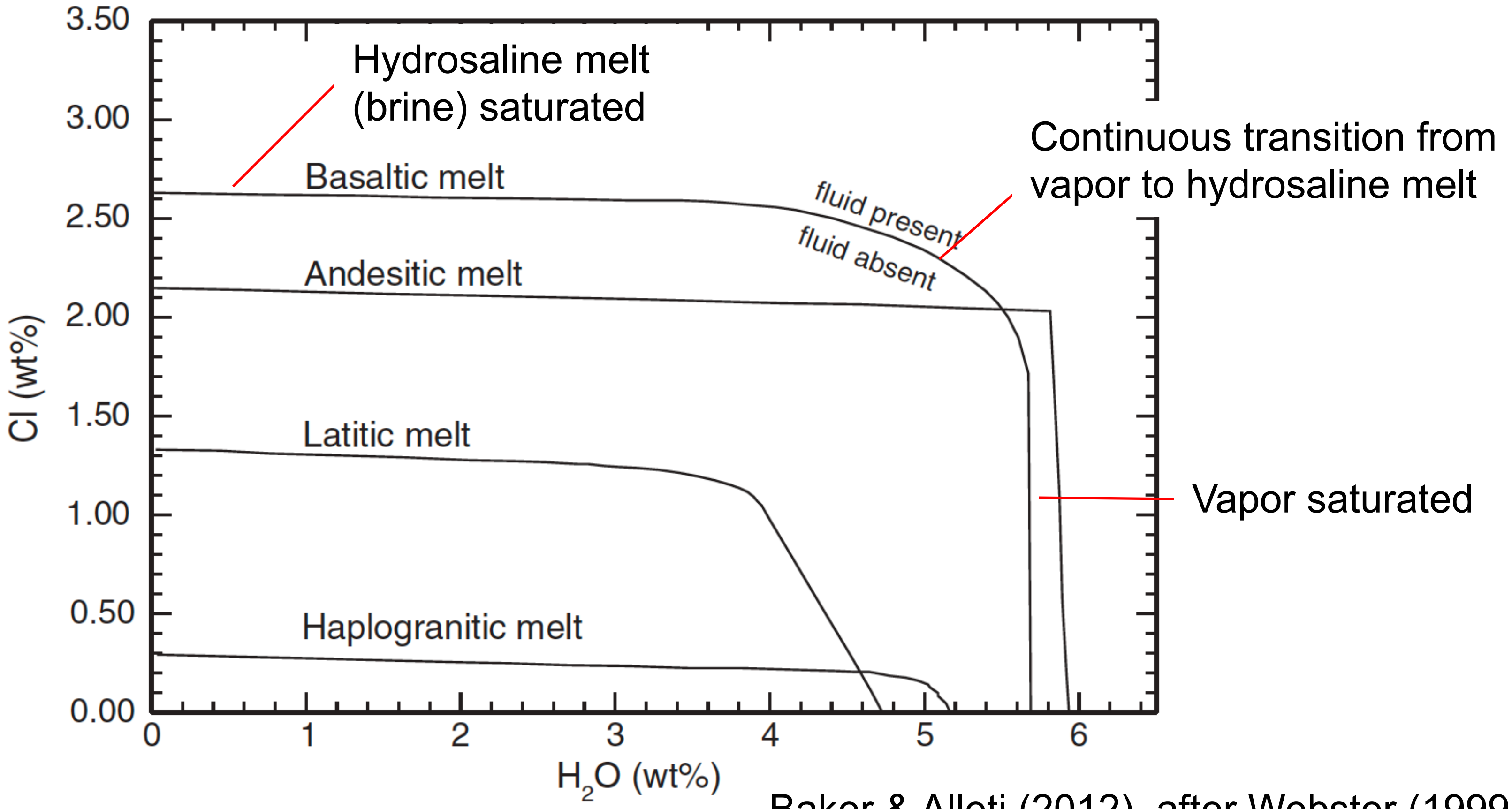
H_2O and CO_2 in rhyolitic melt inclusions



Wallace (2005)

Chlorine Solubility in Silicate Melts

200 MPa)



Hydrosaline melt (brine) saturated

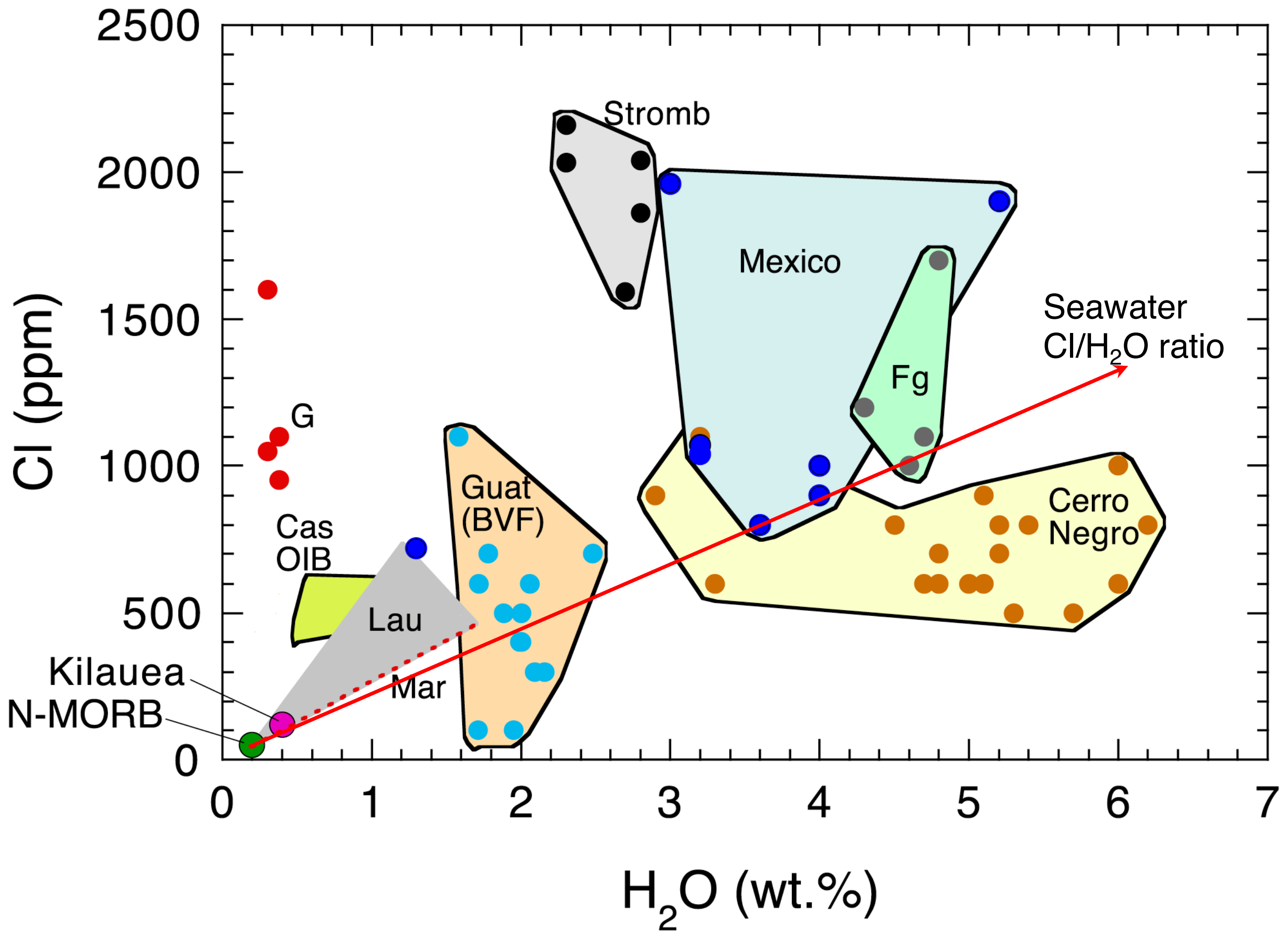
Continuous transition from vapor to hydrosaline melt

Vapor saturated

Baker & Alleti (2012), after Webster (1999)

- Melts can be saturated with either H_2O-Cl vapor or molten NaCl with dissolved H_2O (hydrosaline melt)
- Natural basaltic melts typically have <0.25 wt% Cl and thus are not saturated with hydrosaline melt

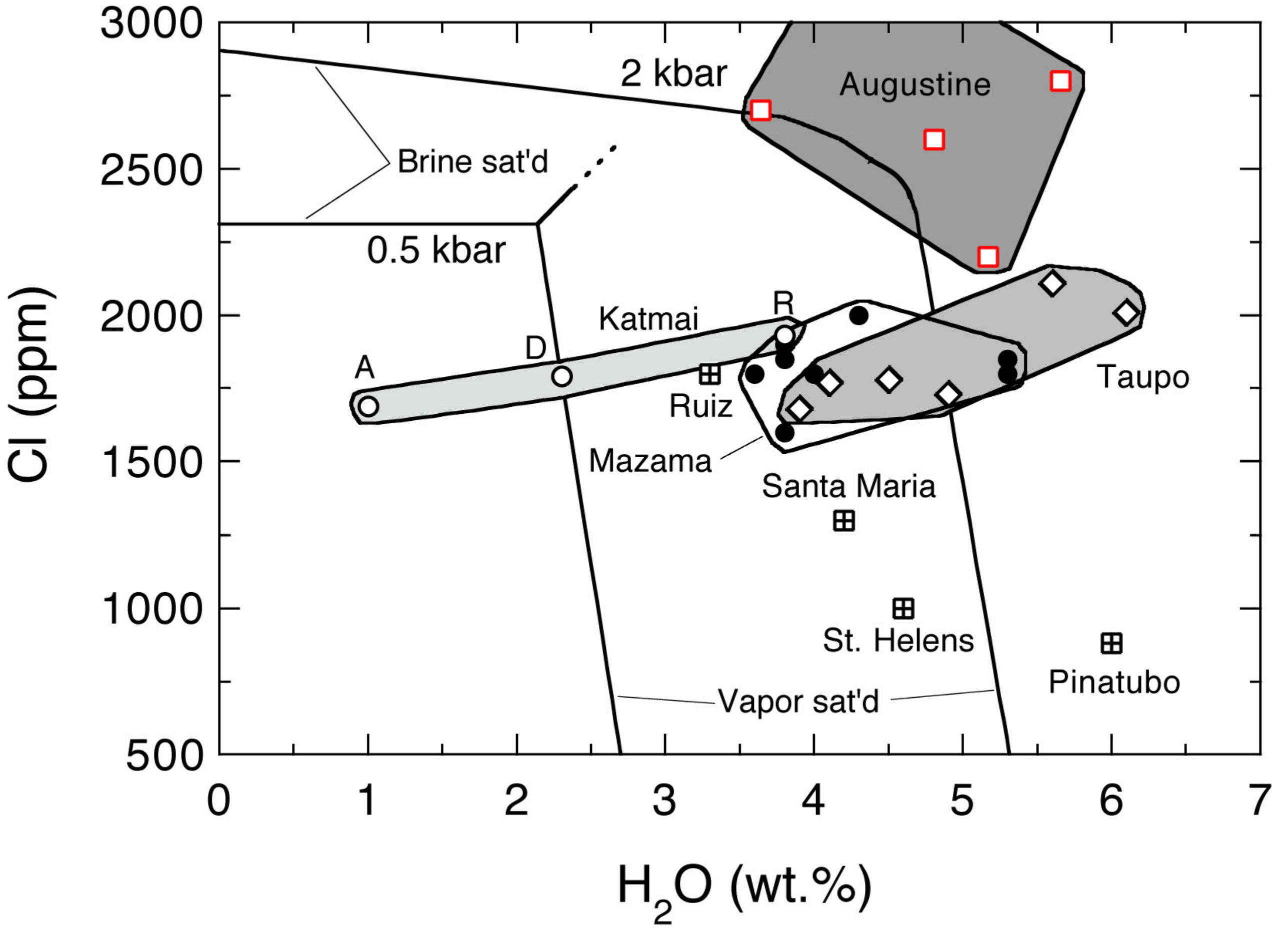
Chlorine in basaltic magmas



Wallace (2005)

- Cl in arc & back-arc magmas is much higher than in MORB & OIB
- Indicates substantial recycling of seawater-derived Cl into the mantle wedge

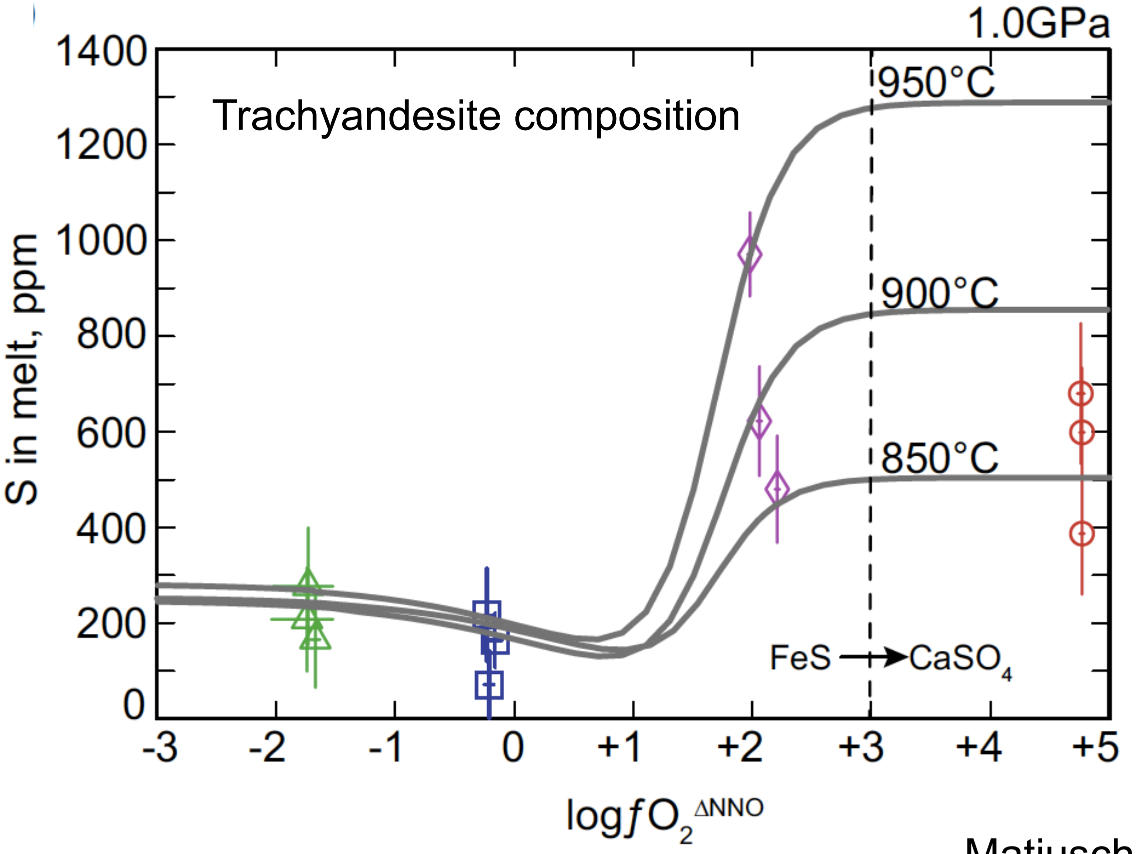
Chlorine in rhyolitic melts



- Cl solubility is much lower in rhyolitic melts compared to basaltic melts
- 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

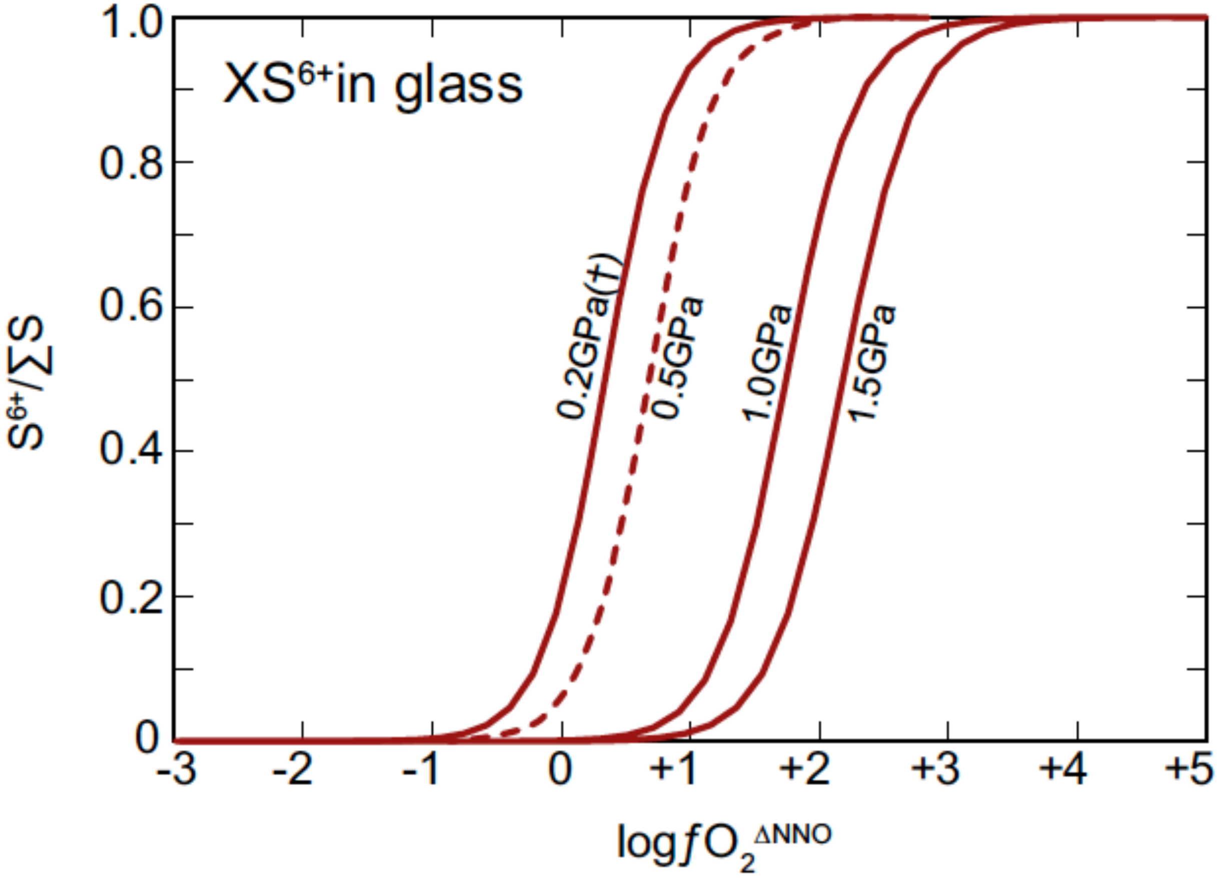
- Sulfur solubility depends on temp., pressure, melt composition & oxygen fugacity.



Matjuschkin et al. (2016)

- Changes in f_{O_2} have a strong effect on solubility because S^{6+} is more soluble than S^{2-}.

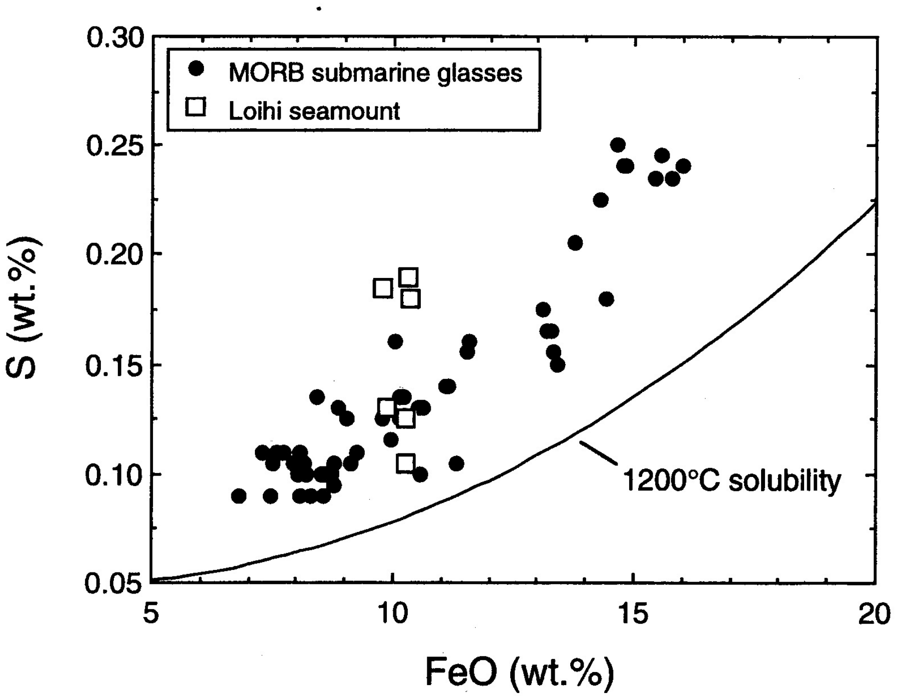
Sulfur redox state in silicate melts



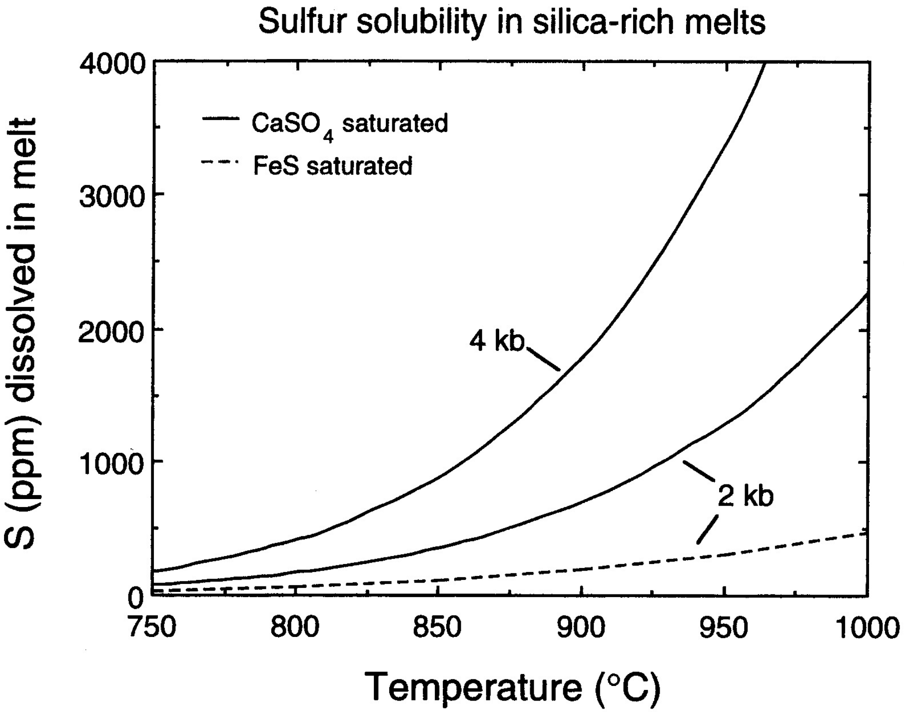
Matjuschkin et al. (2016)

- A rapid change from mostly S^{2-} to mostly S^{6+} occurs over the oxygen fugacity range that is common for arc magmas (NNO to NNO+1)

Sulfur solubility – effects of temperature, pressure & composition

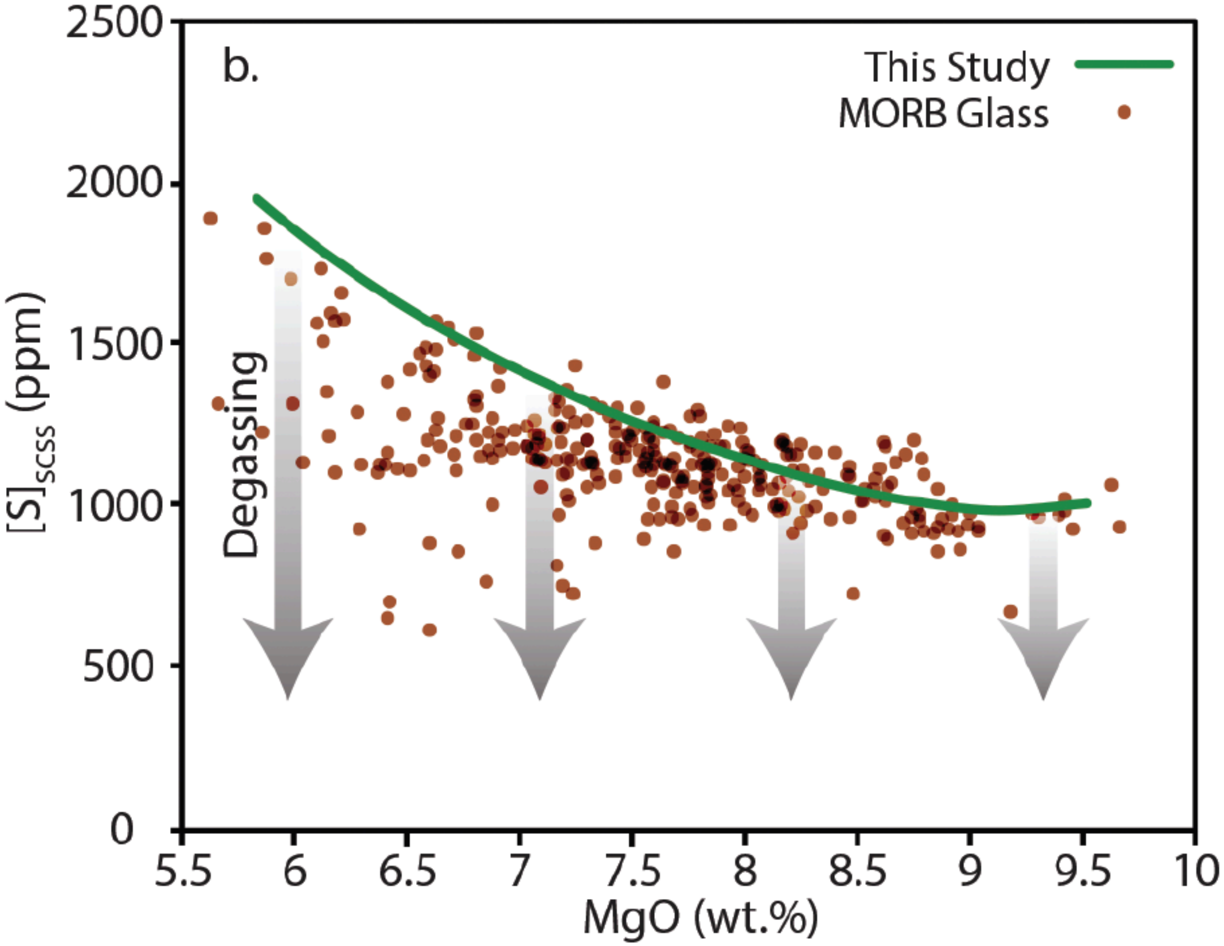


Melt FeO content has a strong effect on solubility when S^{2-} is the dominant species



Solubility of both S^{2-} and S^{6+} are temperature & pressure dependent

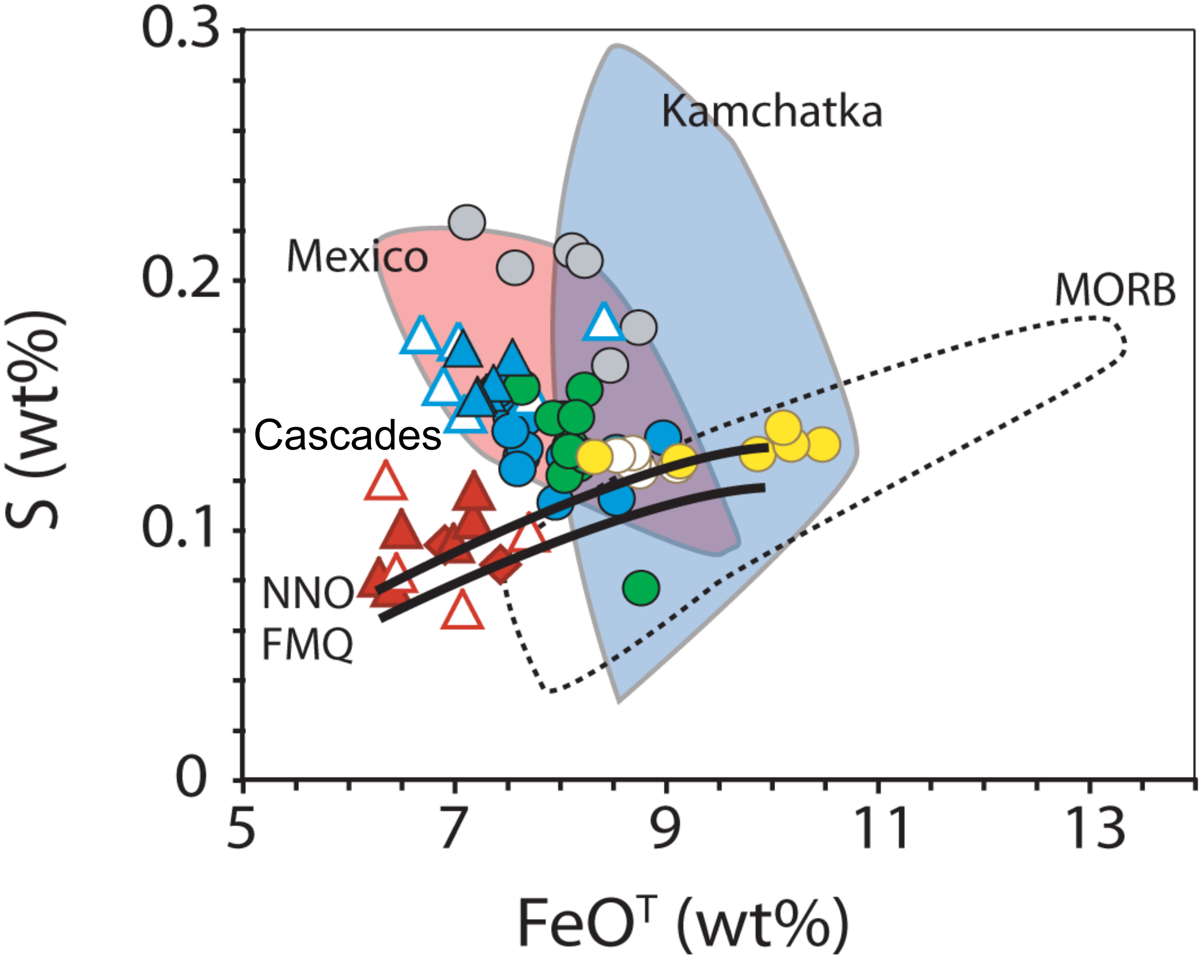
Sulfur & sulfide saturation in MORB glasses



$$\ln[\mathrm{S}]_{\mathrm{SCSS}} = \frac{A}{T} + B' + \frac{CP}{T} + \sum_{\mathrm{M}} \frac{X_{\mathrm{M}} A_{\mathrm{M}}}{T} + \ln a_{\mathrm{FeS}}^{\mathrm{sulfide}} - \ln a_{\mathrm{FeO}}^{\mathrm{silicate}}$$

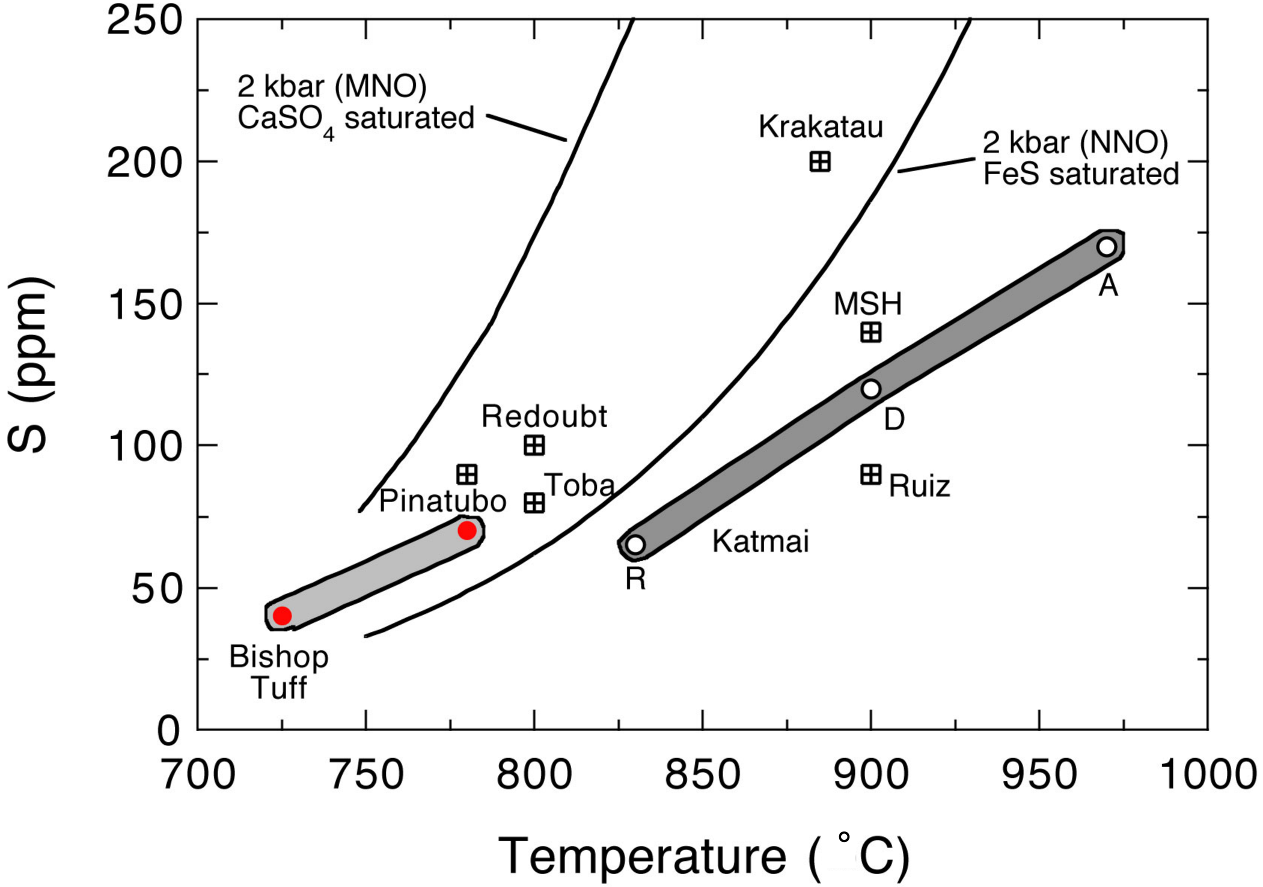
Smythe et al. (2017)

Comparison of sulfur in MORB and arc magmas



Ruscitto et al. (2010)

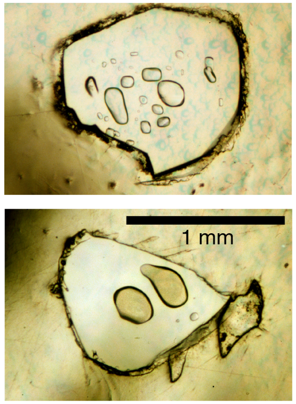
S solubility in intermediate to silicic melts

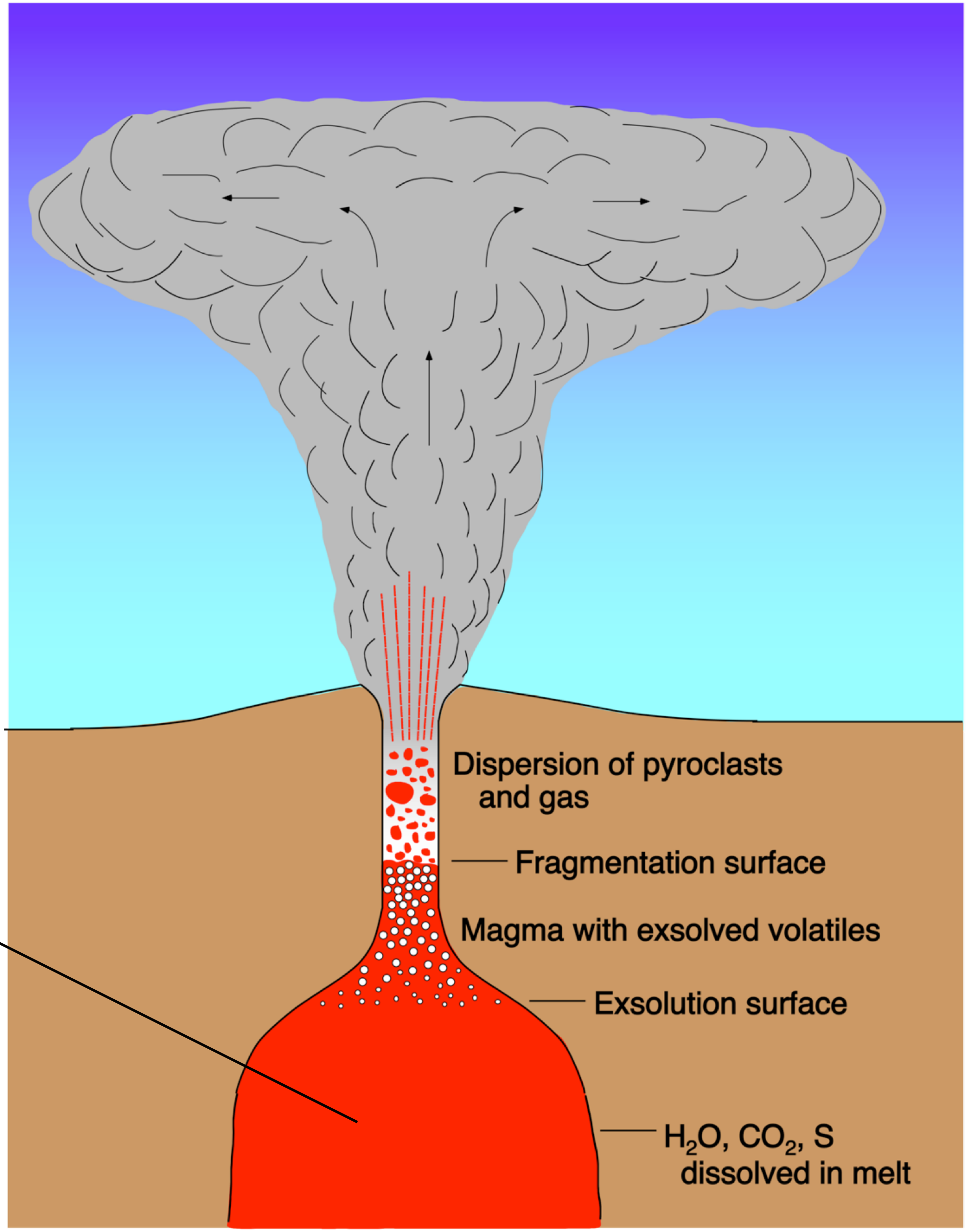


- Because of strong temperature dependence of S solubility, low temperature magmas like dacite and rhyolite have very low dissolved S.
- This led earlier workers to erroneously conclude that eruptions of such magma would release little SO_2 to Earth's atmosphere

Gas Fluxes and the Excess Sulfur Problem

Melt Inclusions





Dispersion of pyroclasts and gas

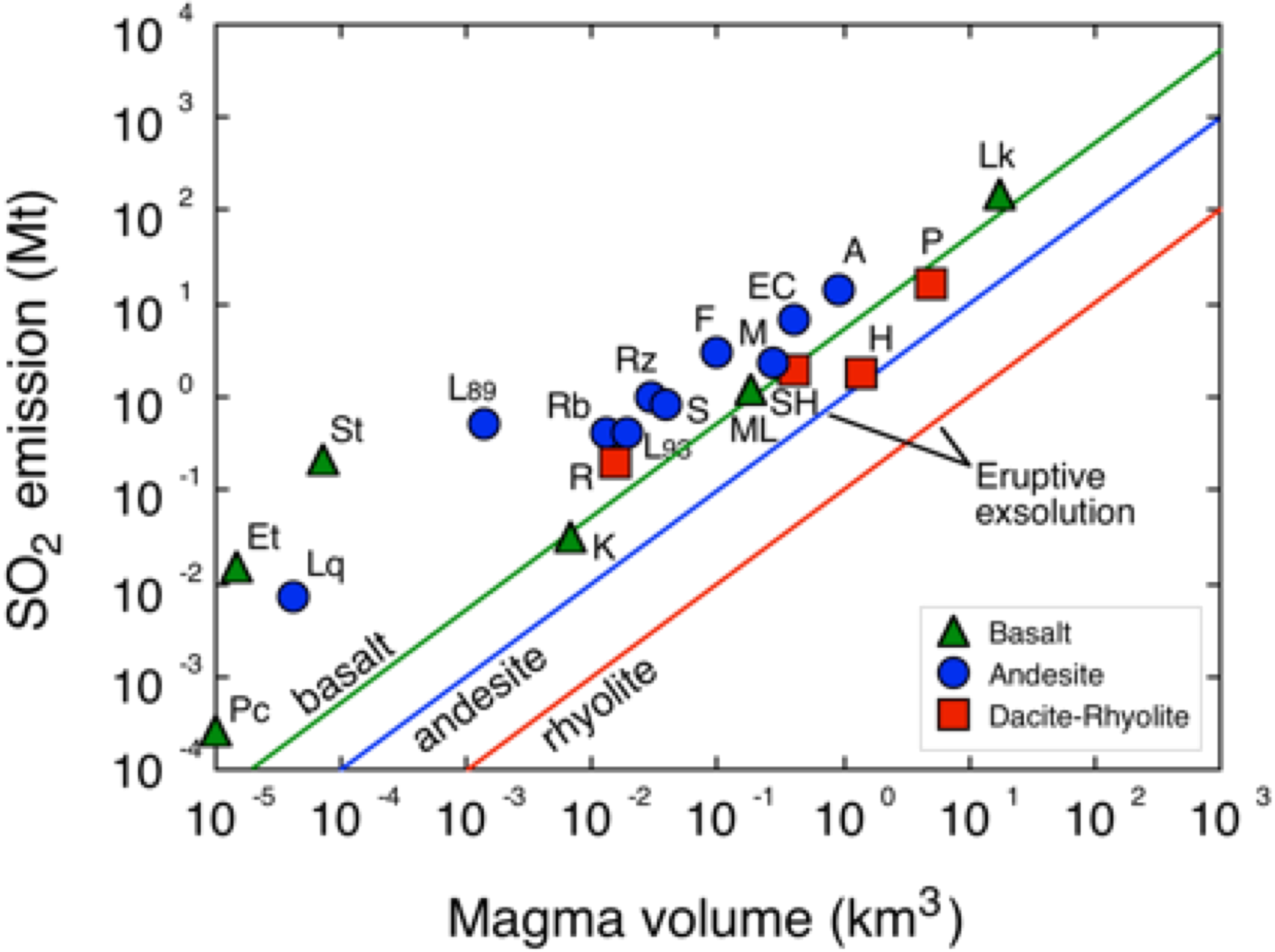
Fragmentation surface

Magma with exsolved volatiles

Exsolution surface

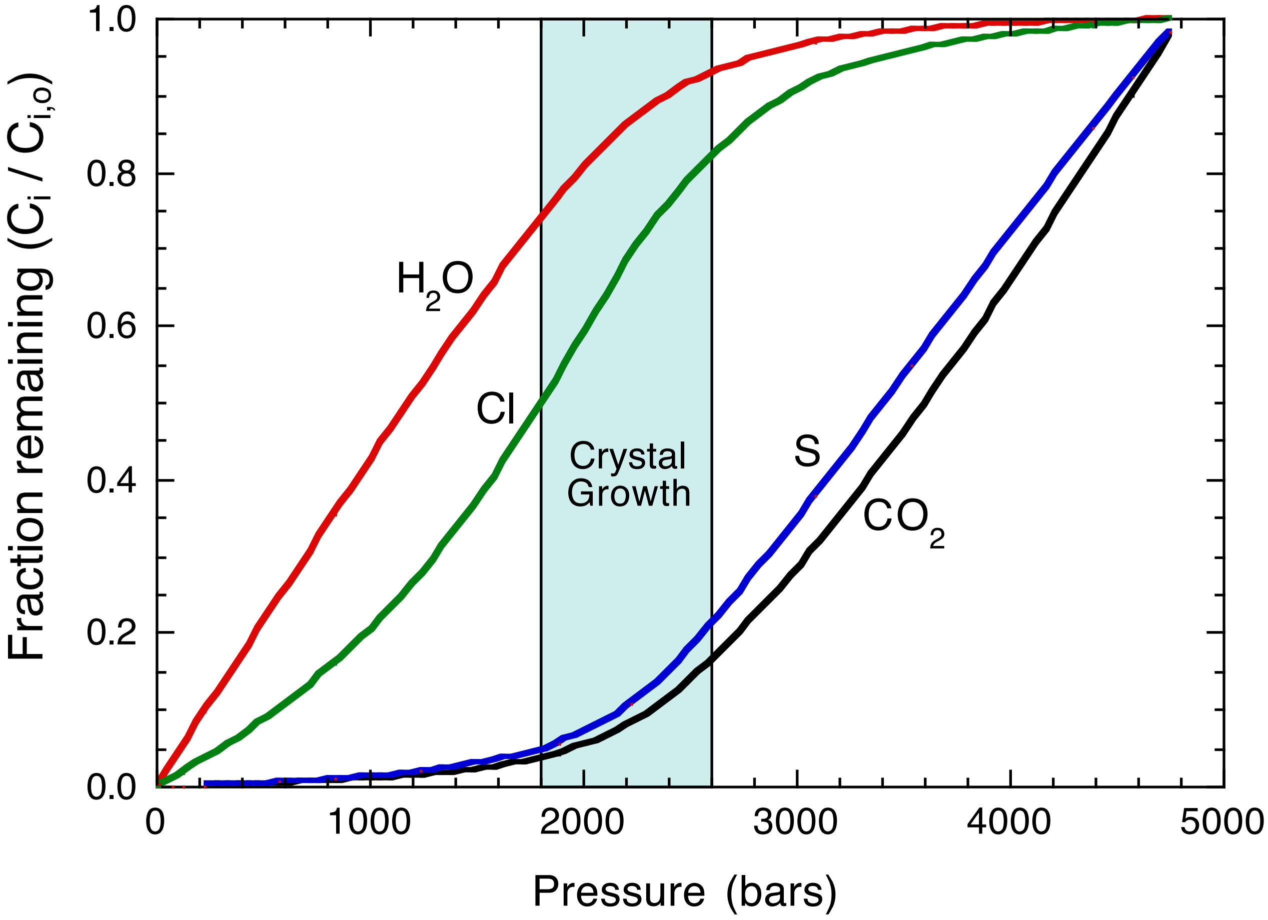
H_2O, CO_2, S dissolved in melt

Comparison of Remote Sensing & Petrologic Methods



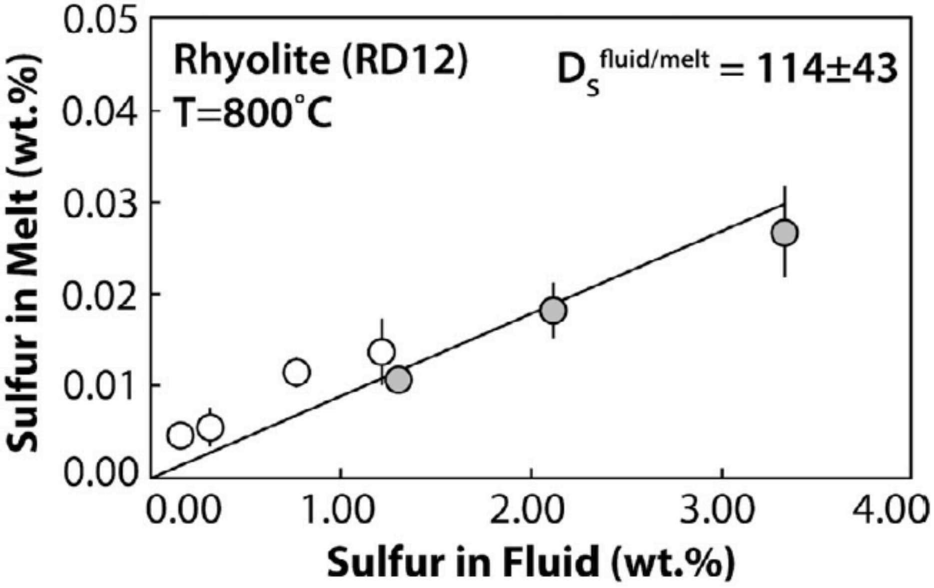
Wallace (2001)

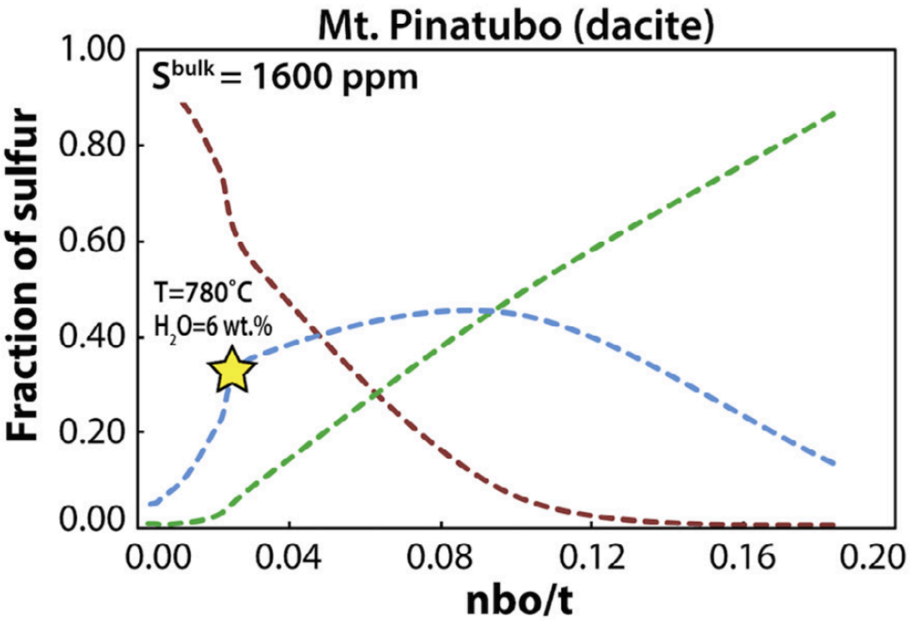
Degassing of H_2O-rich rhyolitic magma



- When rhyolitic melt inclusions are trapped in quartz or feldspar at typical magma chamber depths, most of the original CO_2 and S has been degassed

Vapor – melt partitioning of sulfur





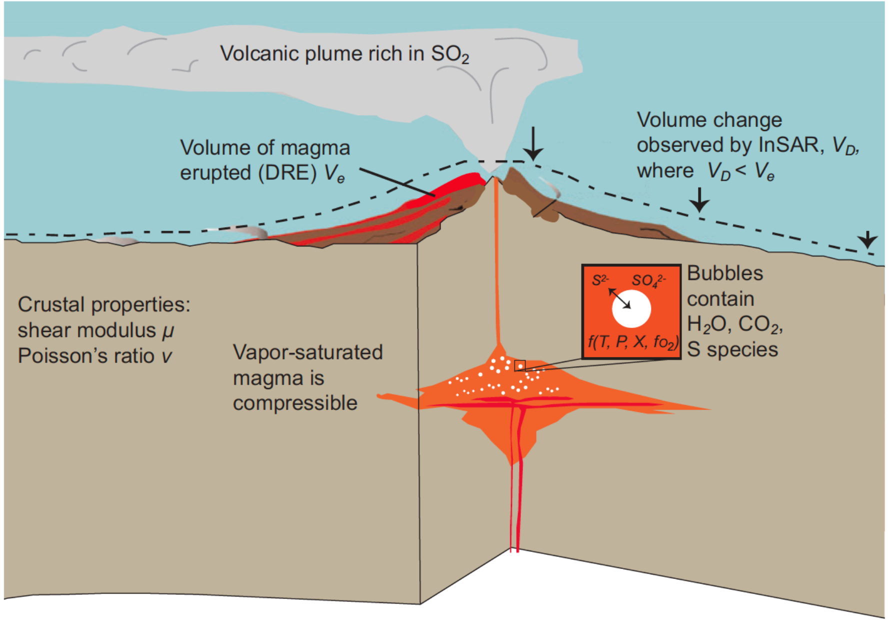
←

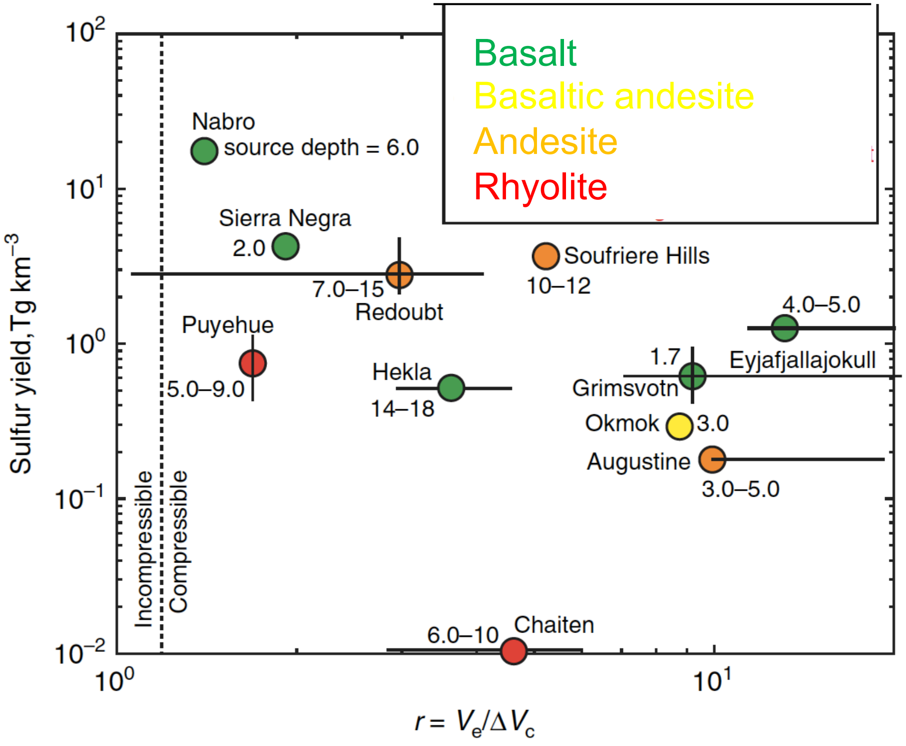
Increasing melt SiO_2
Decreasing temperature

Masotta et al. (2016)

Sulfur emissions & volcano deformation measured by InSAR

B An exsolved gas phase in the magma reservoir causes **large sulfur-rich gas clouds** and **muted syn-eruptive ground deformation**



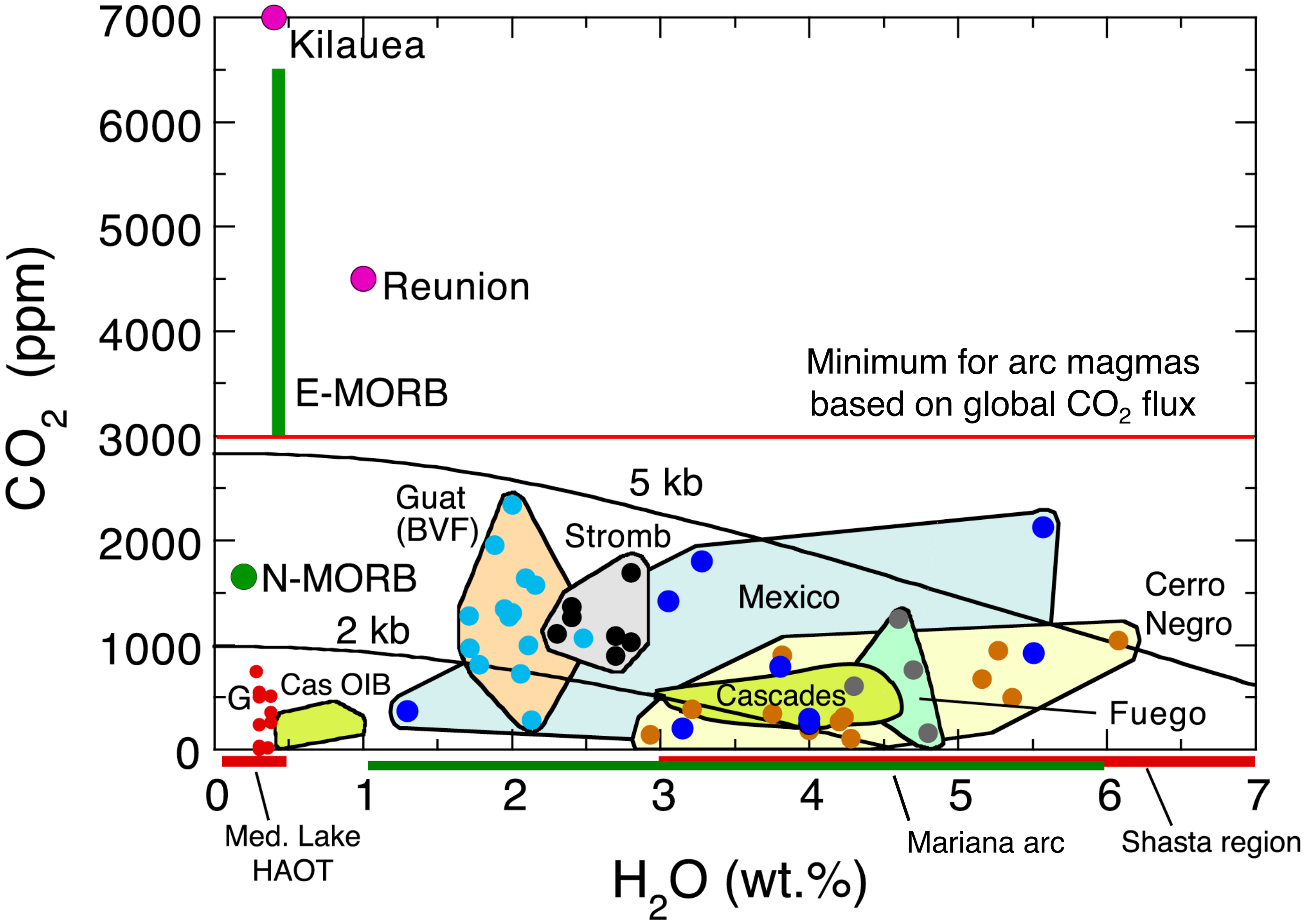


Erupted volume
Observed volume change of a modeled source, from ground deformation

- Vapor bubbles make magma compressible

McCormick Kilbride et al. (2016)

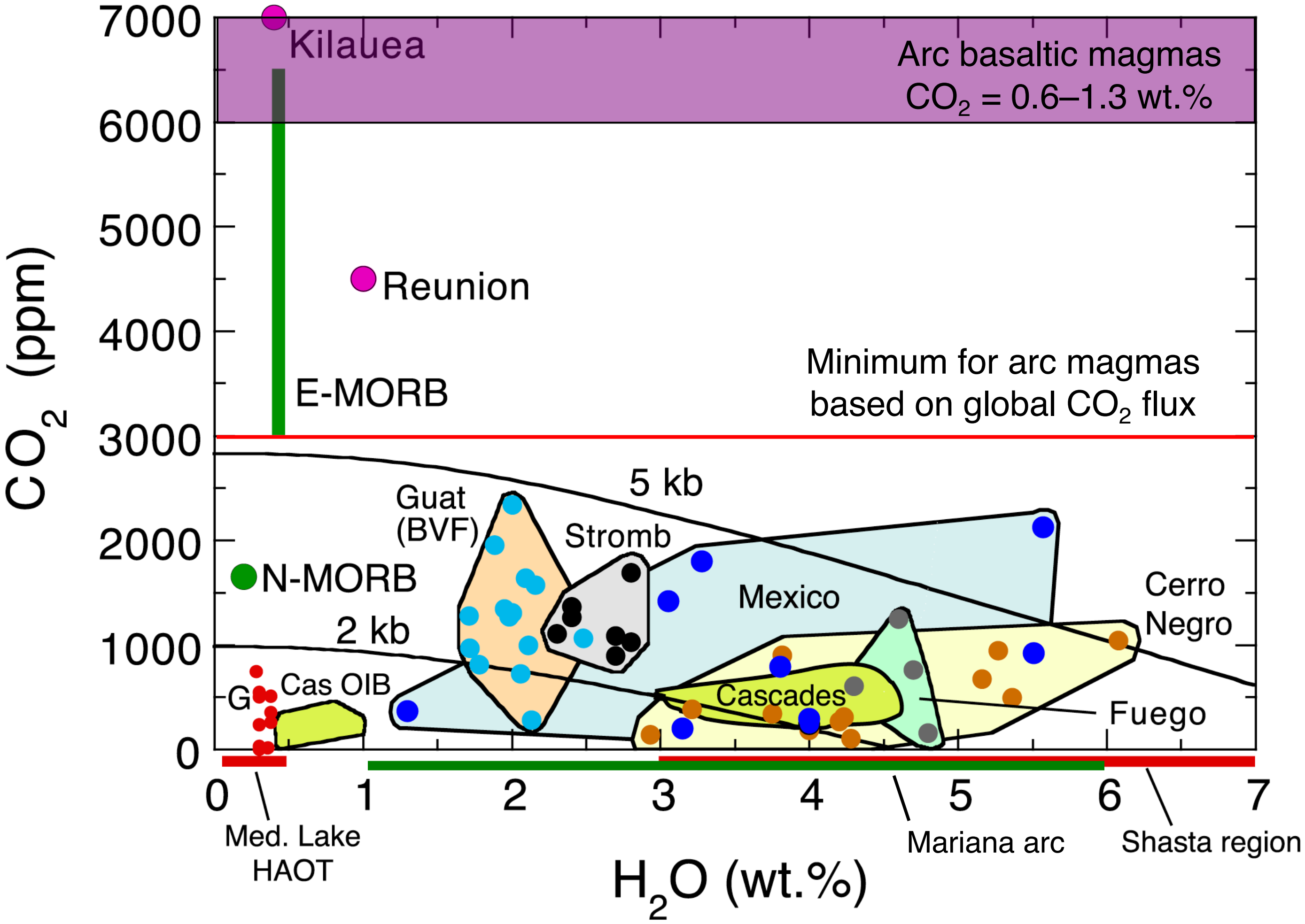
H_2O and CO_2 in Basaltic Magmas



Magma flux
= 8 km^3/yr

Wallace (2005)

H_2O and CO_2 in Basaltic Magmas

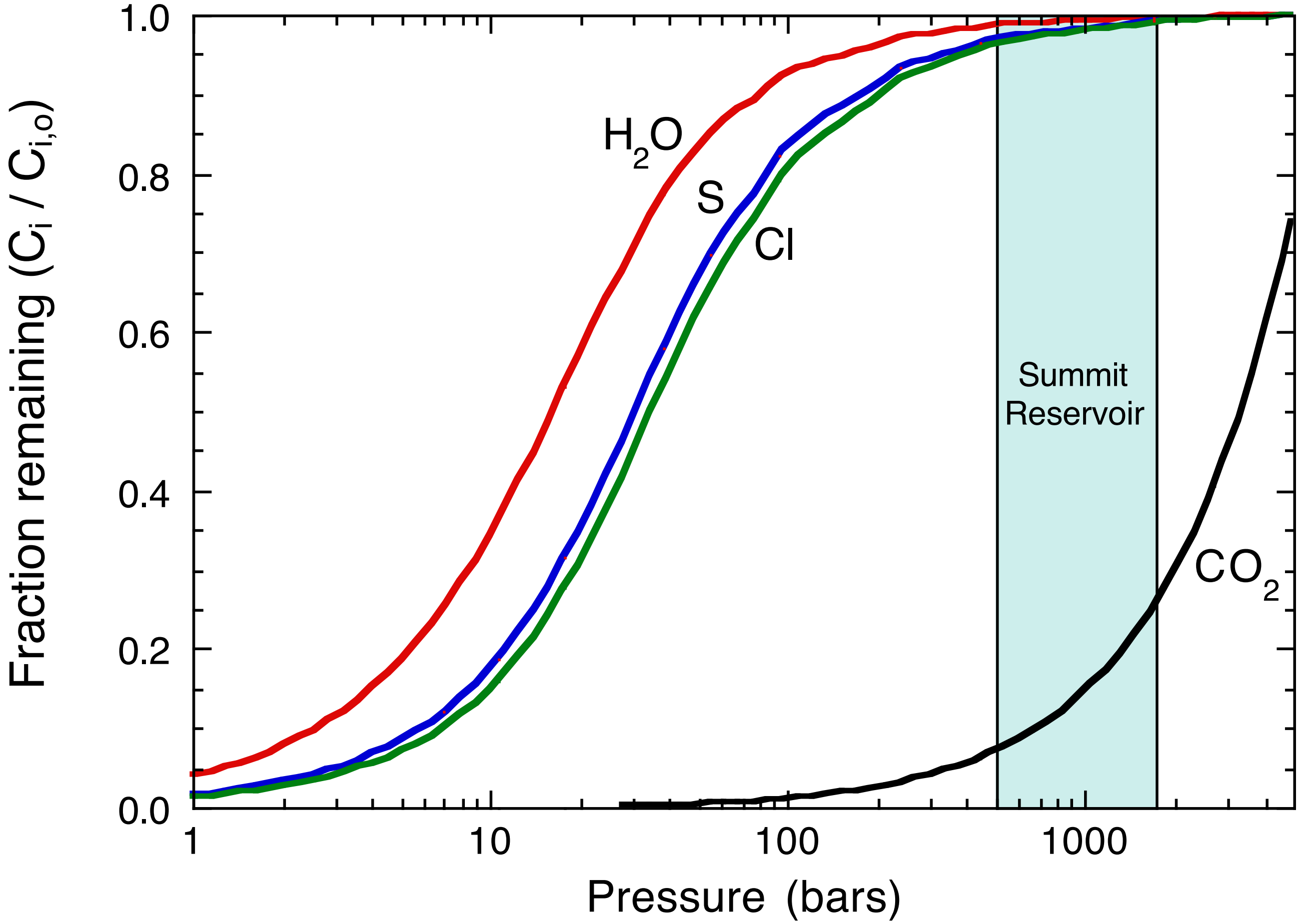


Magma flux
= 2–4 km^3/yr

Wallace (2005)

Melt Inclusions & CO_2

Problem 1: Low CO_2 solubility at crustal depths where inclusions are trapped

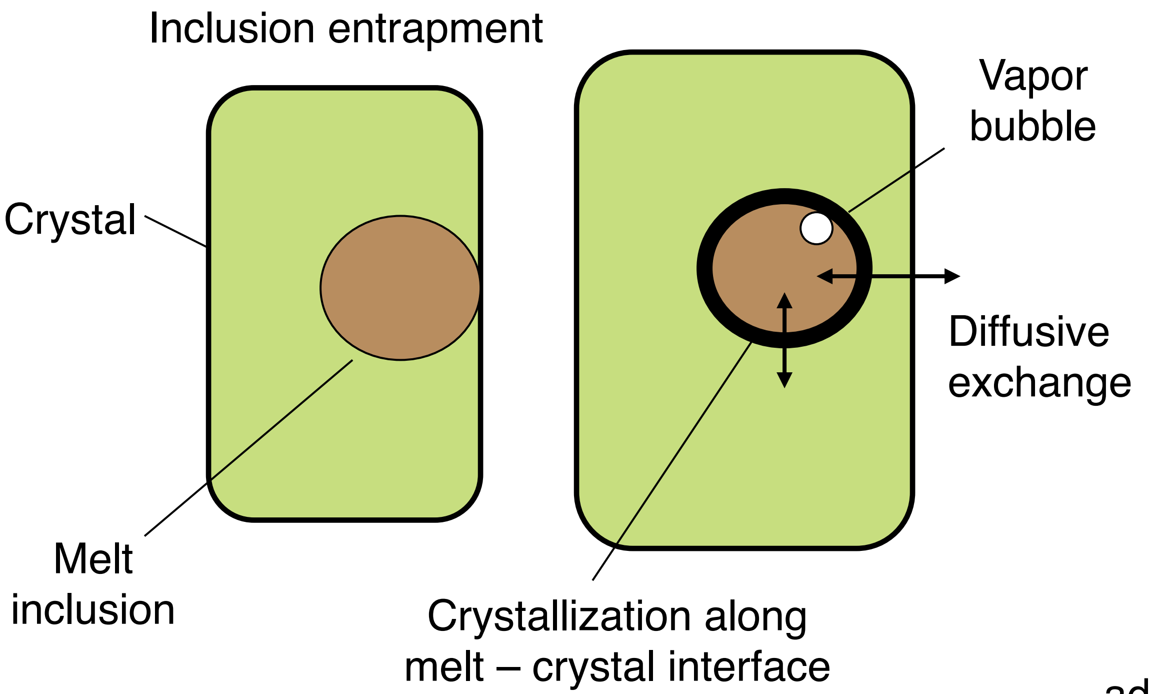


- When basaltic magma reaches a shallow crustal magma chamber, much of the original dissolved CO_2 has already been degassed.

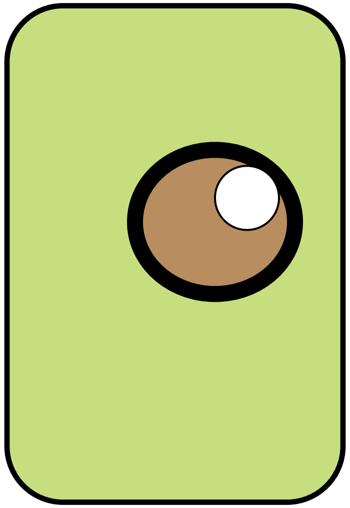
Melt Inclusions & CO_2

Problem 2: Post-Entrapment Bubble Formation

Pre-eruption cooling

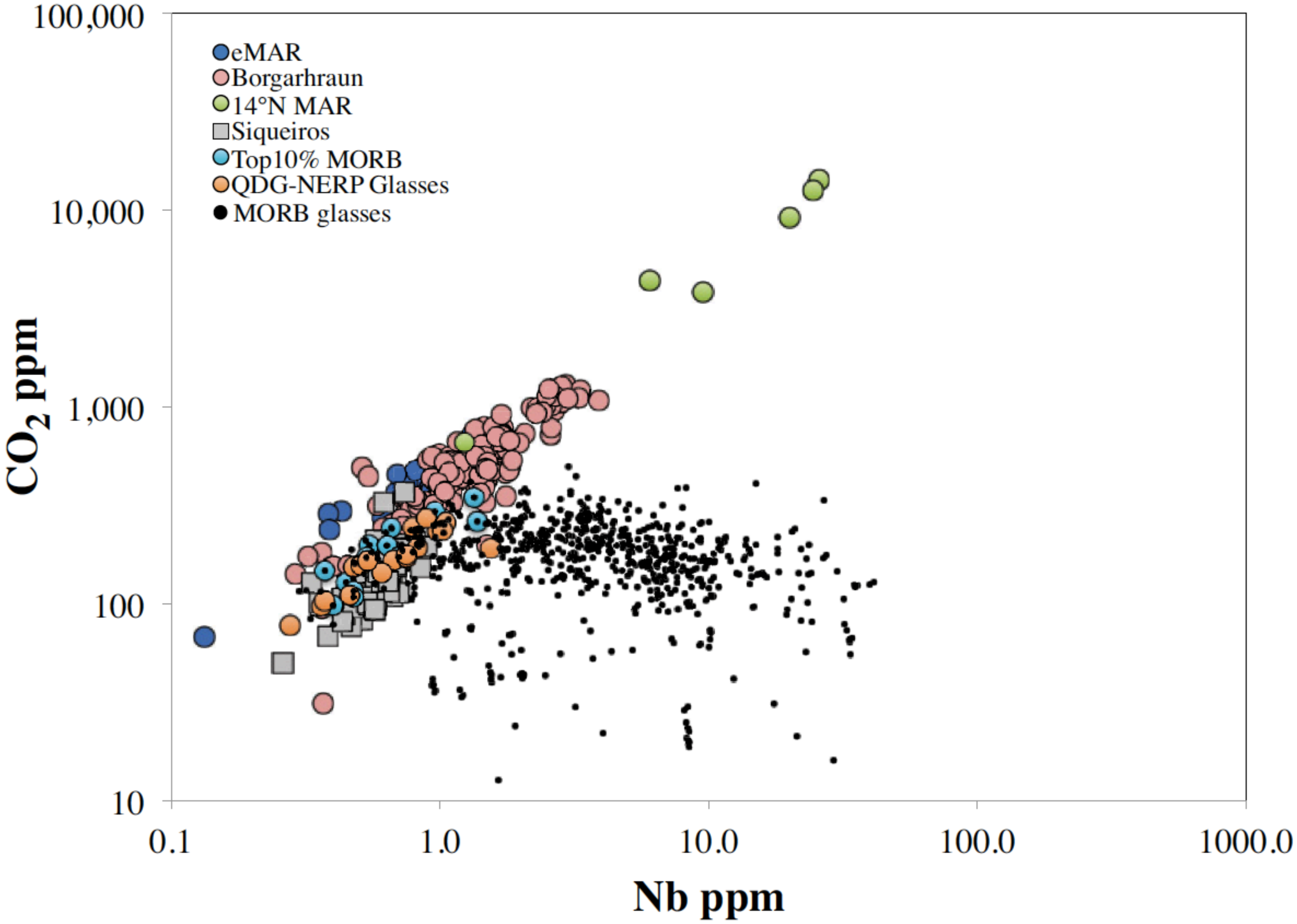


Eruptive cooling



Bubble expansion but little additional olivine crystallization or diffusion of CO_2 into the bubble

One approach is to use rare, undegassed MORB glasses & melt inclusions



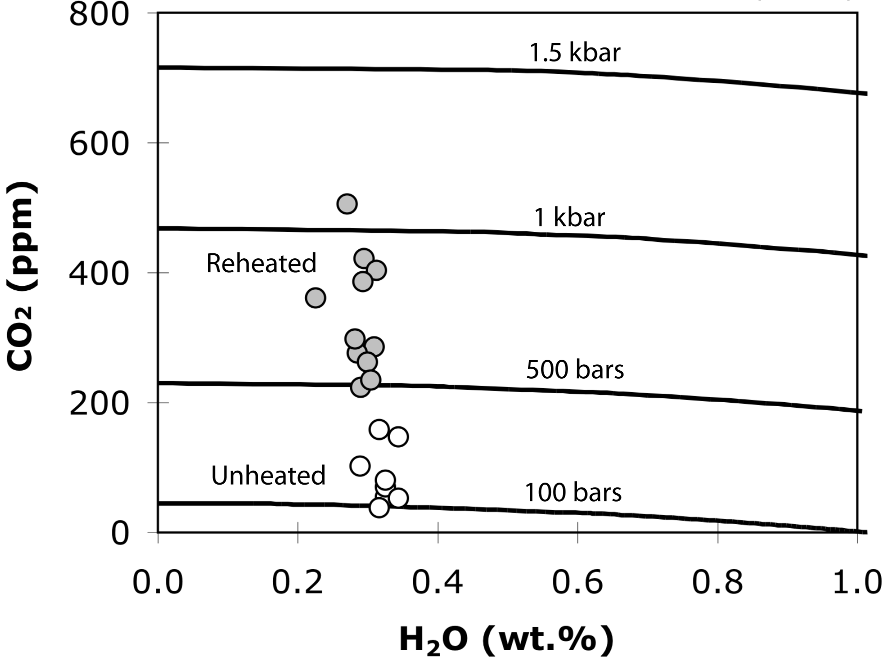
- CO_2 / Nb for Atlantic MORB & Iceland = 410
- For Pacific MORB = 240

Hauri et al. (2018)

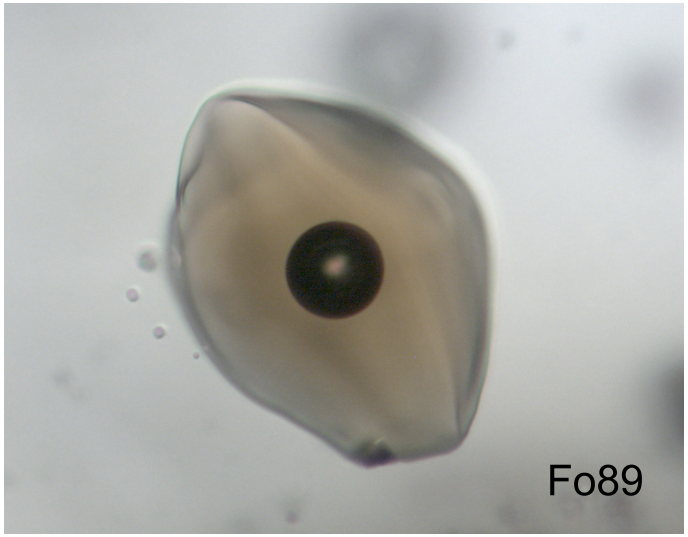
Another approach is to determine how much CO_2 is in bubbles in melt inclusions

Experimentally heated vs. naturally quenched MI

Wallace et al. (2015)



Mauna Loa melt inclusion



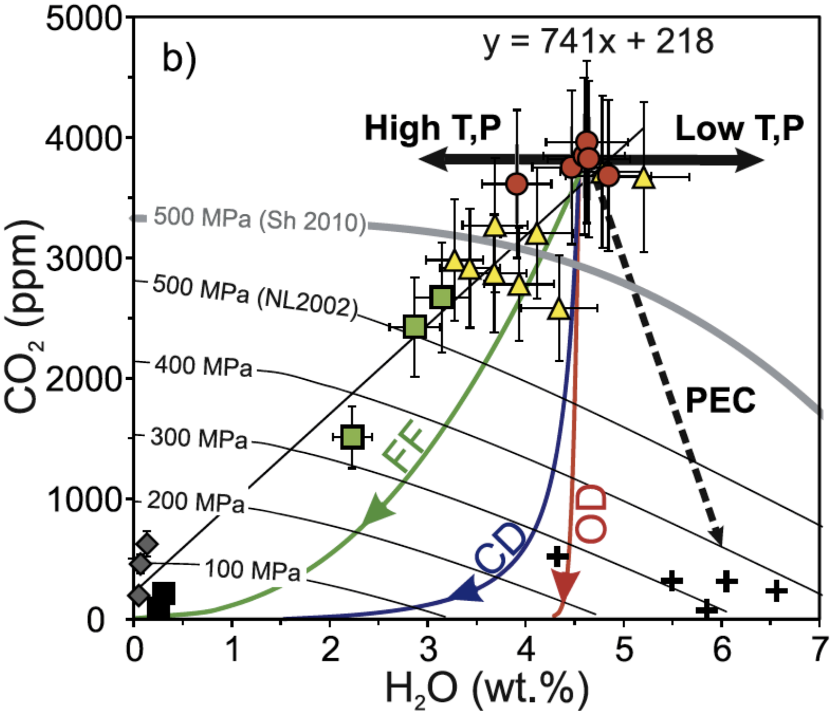
Methods for ‘restoring’ CO_2

1. Experimental rehomogenization
2. Raman determination of bubble CO_2 density
3. Modeling of cooling, crystallization & bubble exsolution

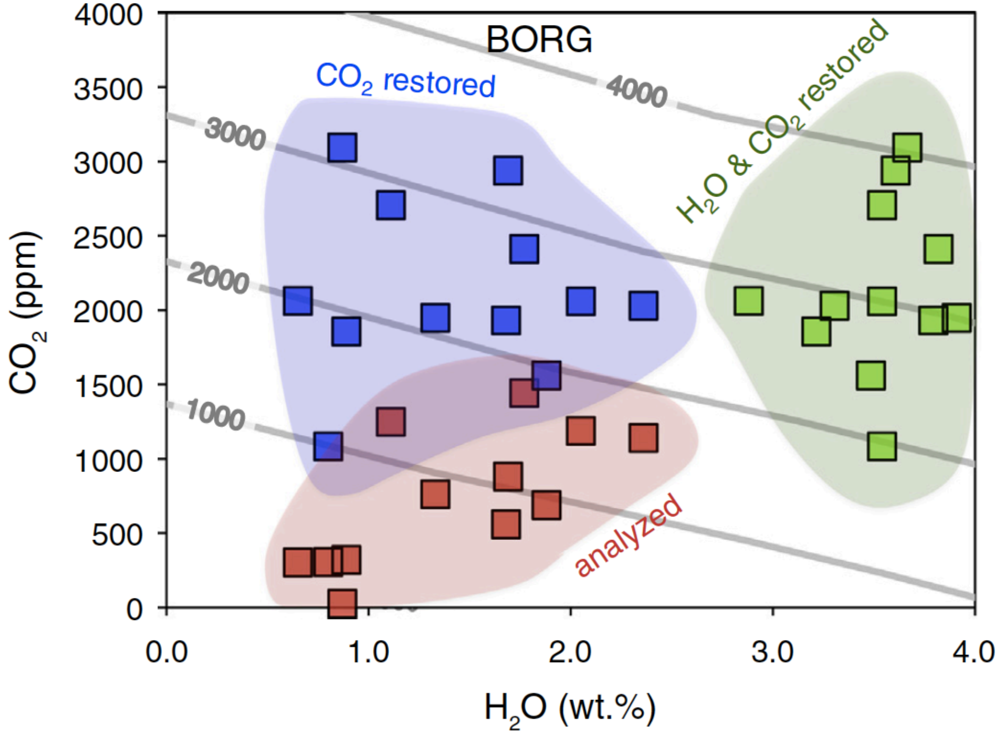
As much as 90% of initial CO_2 can be lost to a bubble (Moore et al., 2015)

Examples of restored CO_2

Experimental rehomogenization



Crystallization modeling & correction for diffusive H loss



Klyuchevskoy

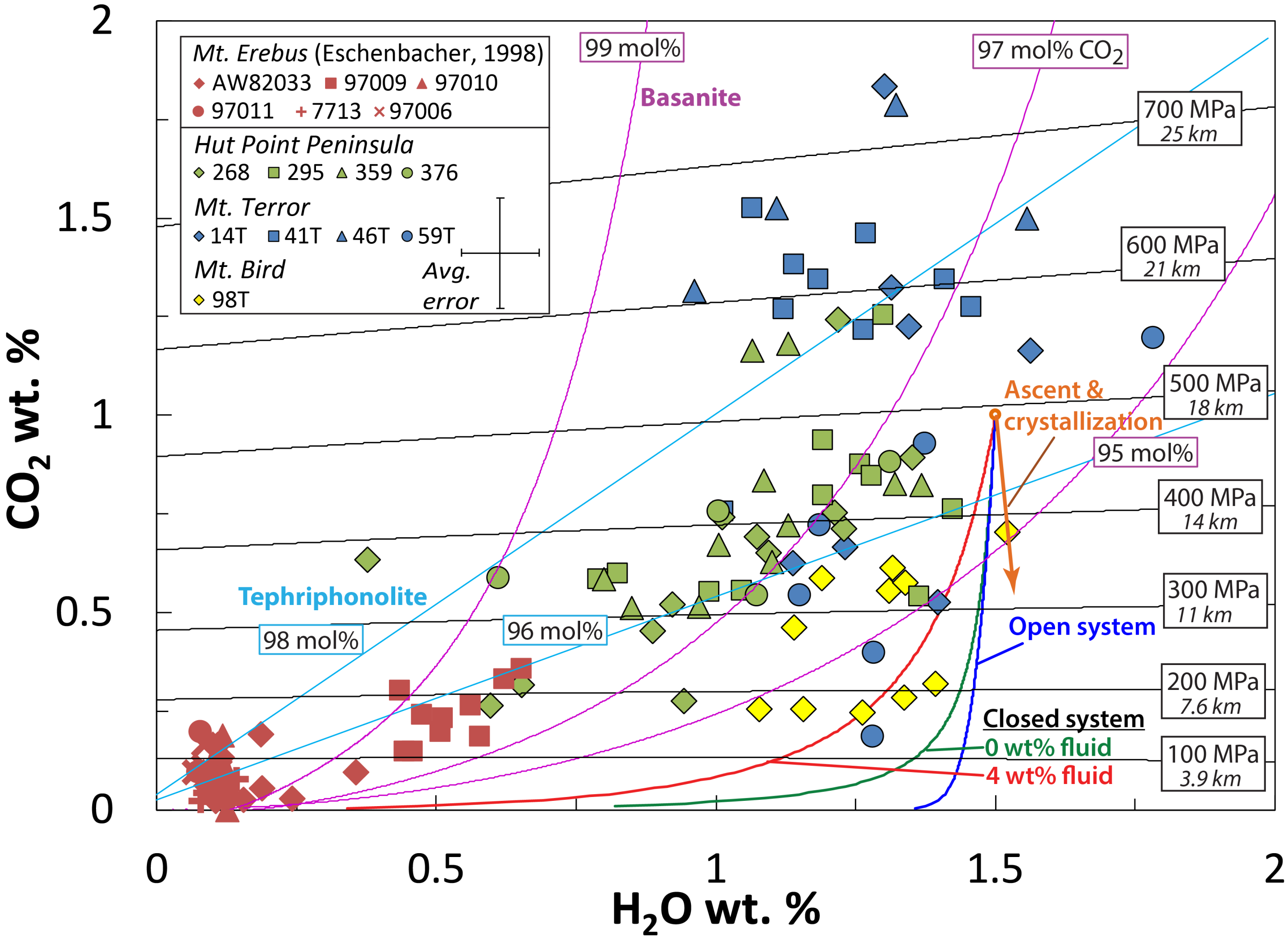
Cascade arc

Mironov et al. (2015)

Aster et al. (2016)

Evidence for very high CO_2 in alkaline magmas

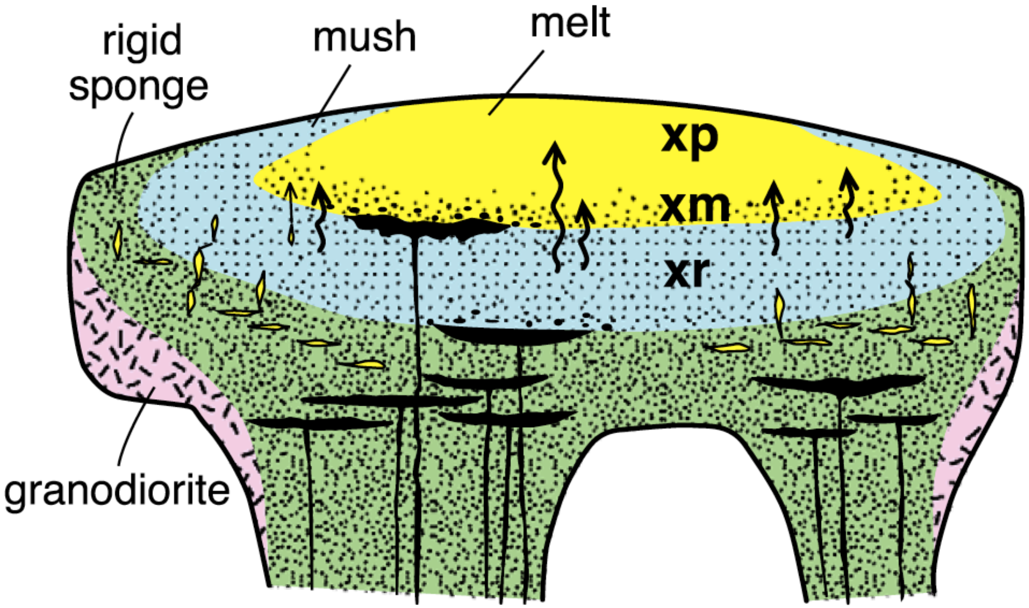
Basanites from Ross Island, Antarctica



Rasmussen et al. (2017)

Mafic magma supplies CO_2 to crustal magmatic systems

- Crustal magmatic systems are fundamentally basaltic
- Basaltic magma transfers volatiles from mantle to crust



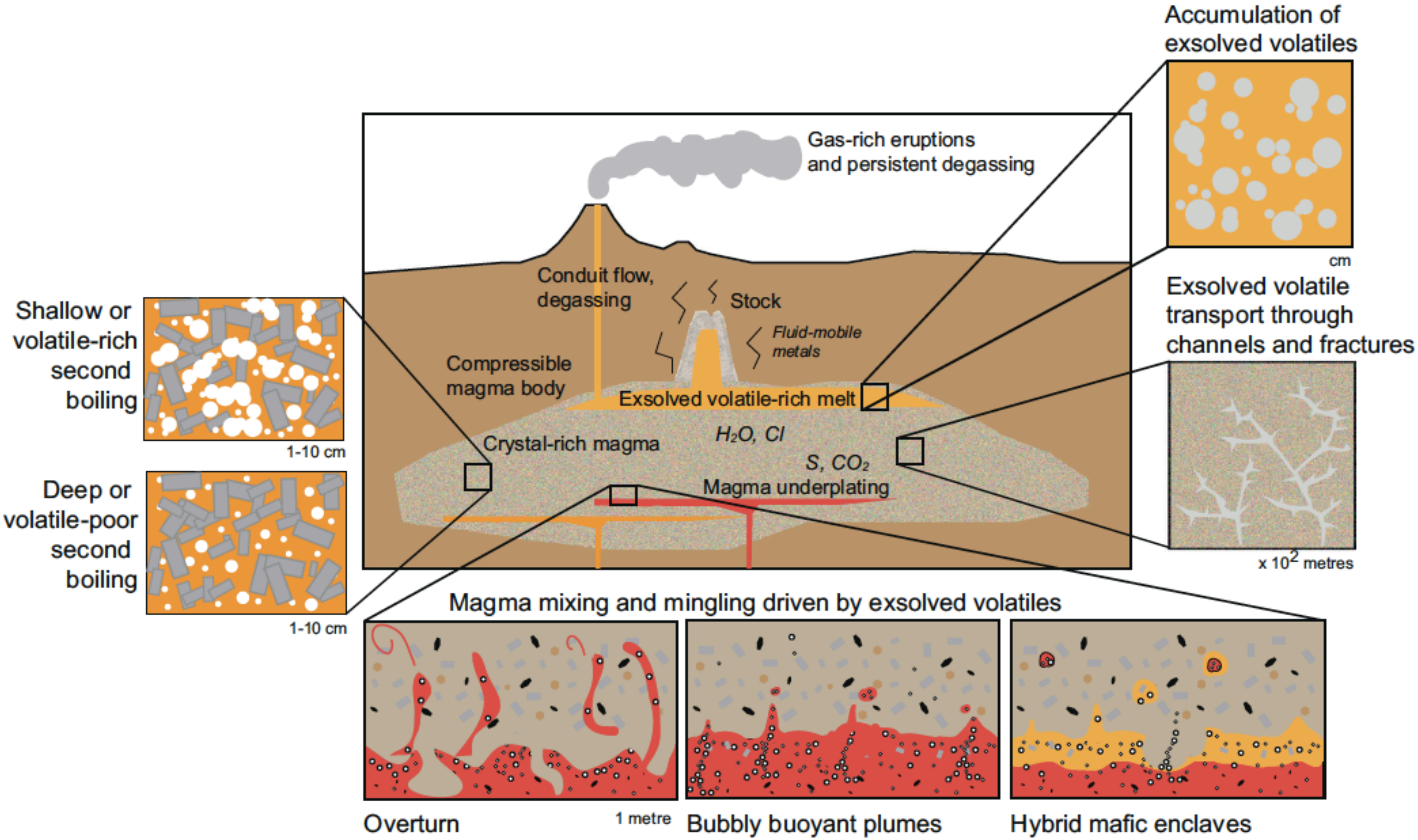
Hildreth (2004)

"Degassing of basalt crystallizing in the roots of these systems provides a flux of He, CO_2, S, halogens, and other components."

"[Stable isotope] data suggest that magmatic fluxes of C and S are dominated by mantle sources"

Hildreth (1981)

Transport & accumulation processes for exsolved vapor



Edmonds & Woods (2018)
Parmigiani et al. (2016)

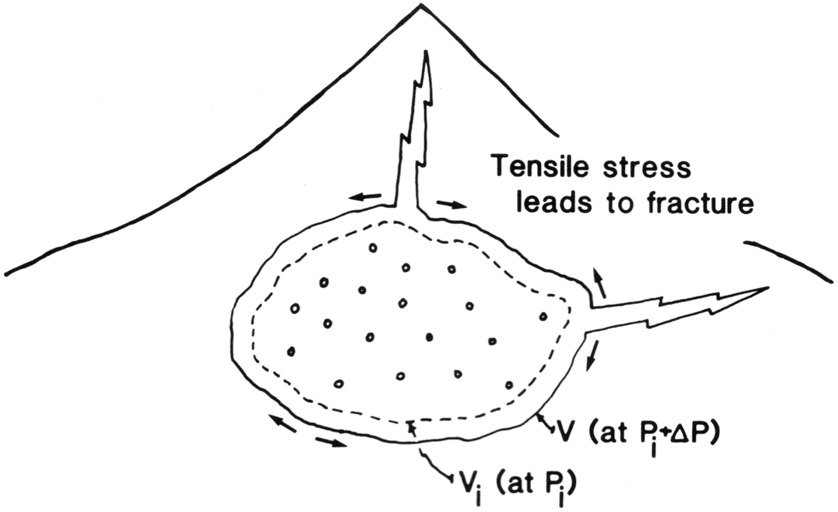
Exsolved Vapor & Eruption Triggering

Presence of exsolved vapor bubbles makes magma compressible

Volume fraction of vapor increases by:

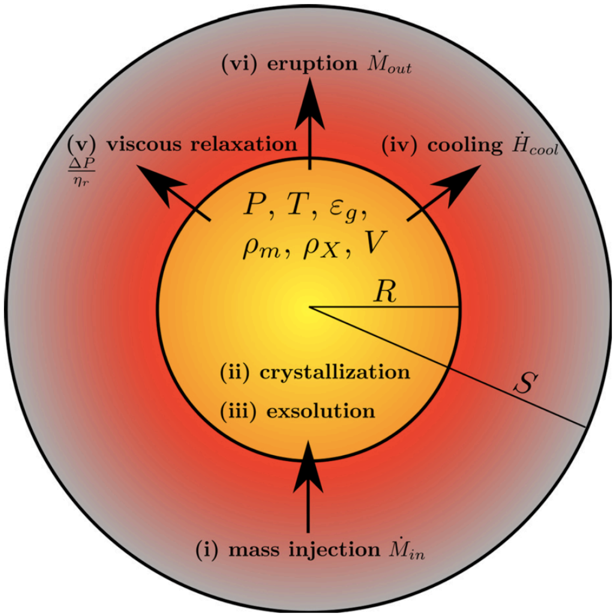
- Fractional crystallization
- Recharge with vapor-saturated magma

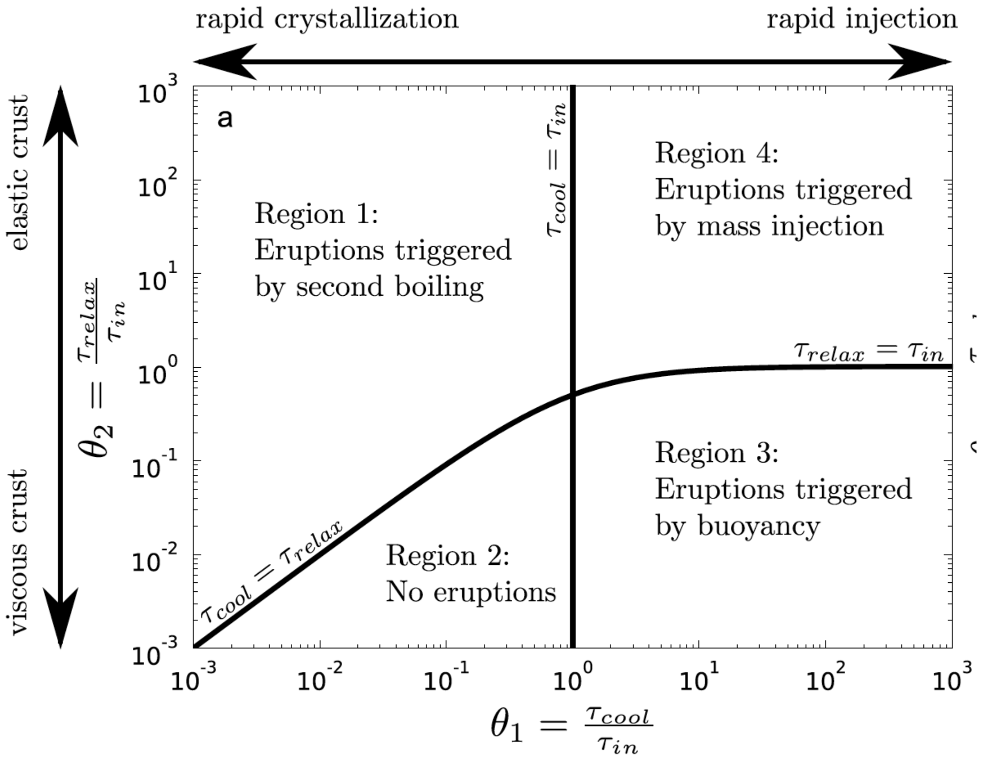
Eruption may be triggered as increase in volume fraction of vapor causes overpressure in magma reservoir



Tait et al. (1989)

Eruption Triggering



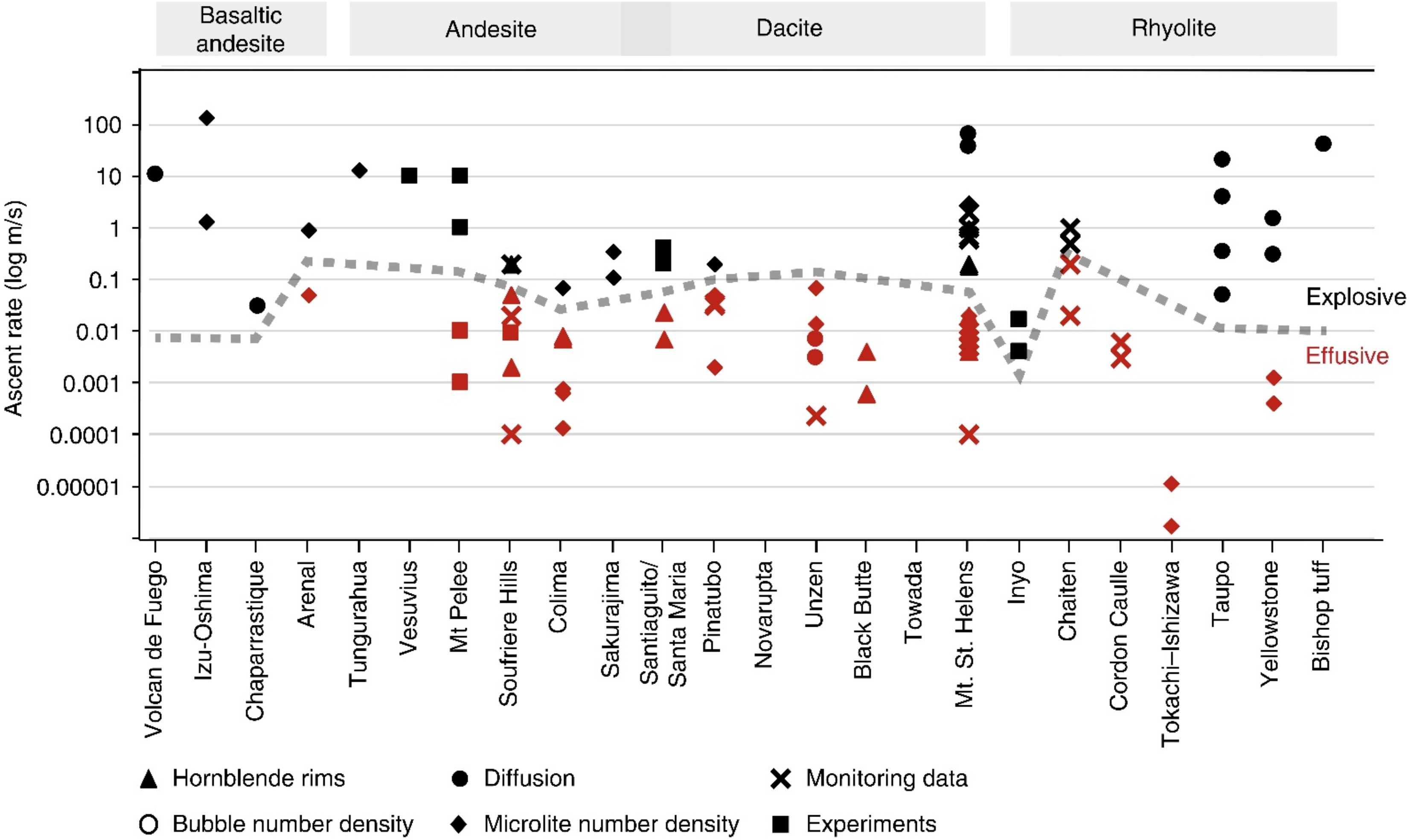


= cooling timescale / injection timescale

- Homogeneous magma mixture cooled by a colder viscoelastic shell.
- When a critical overpressure is reached before mechanical locking, an eruption is triggered.

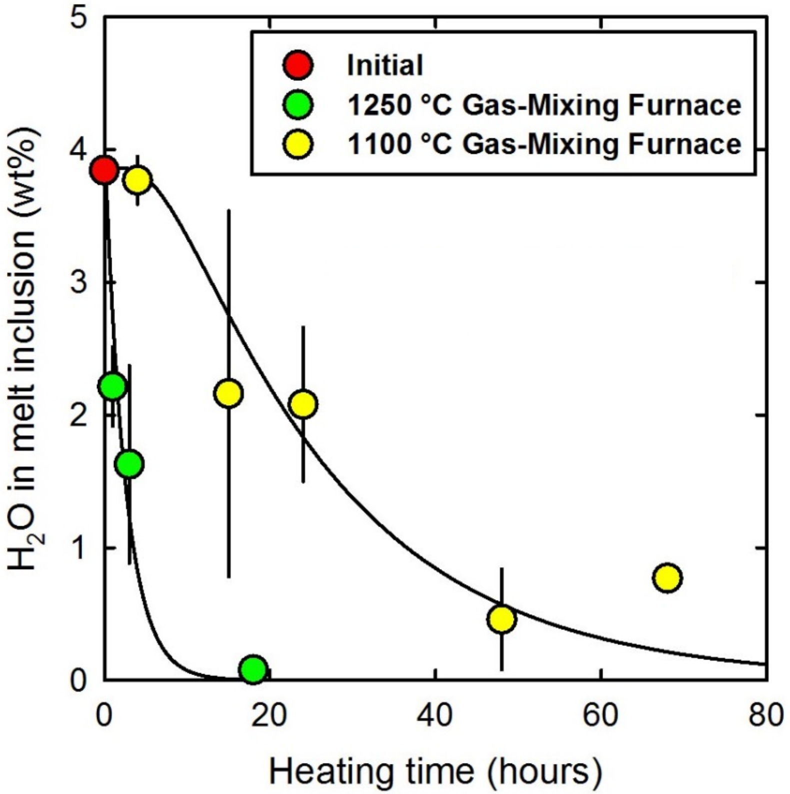
Degruyter & Huber (2014)

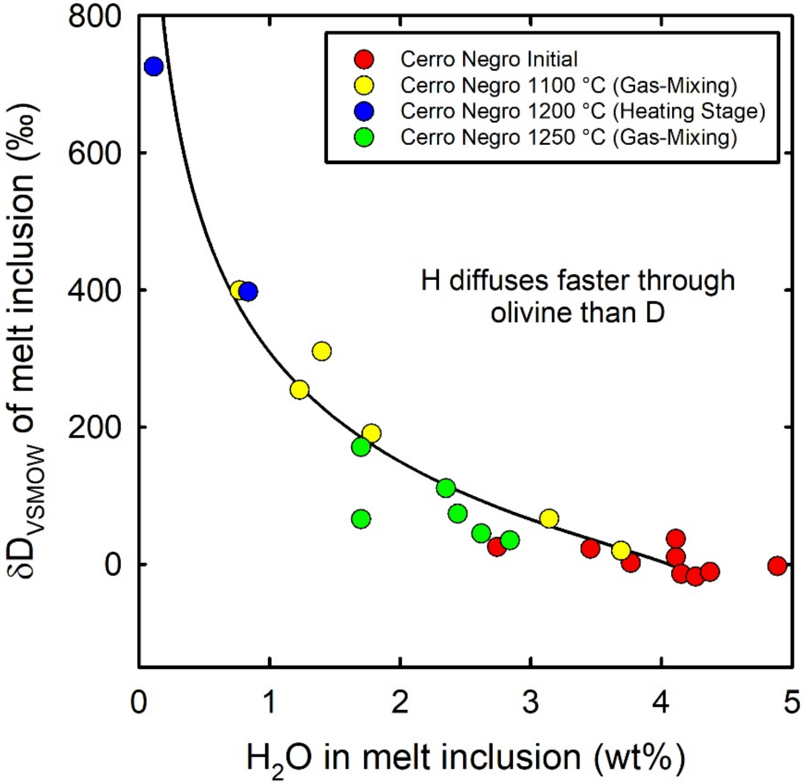
Magma Ascent Rates



Cassidy et al. 2018

Diffusive loss of H from melt inclusions as a geospeedometer

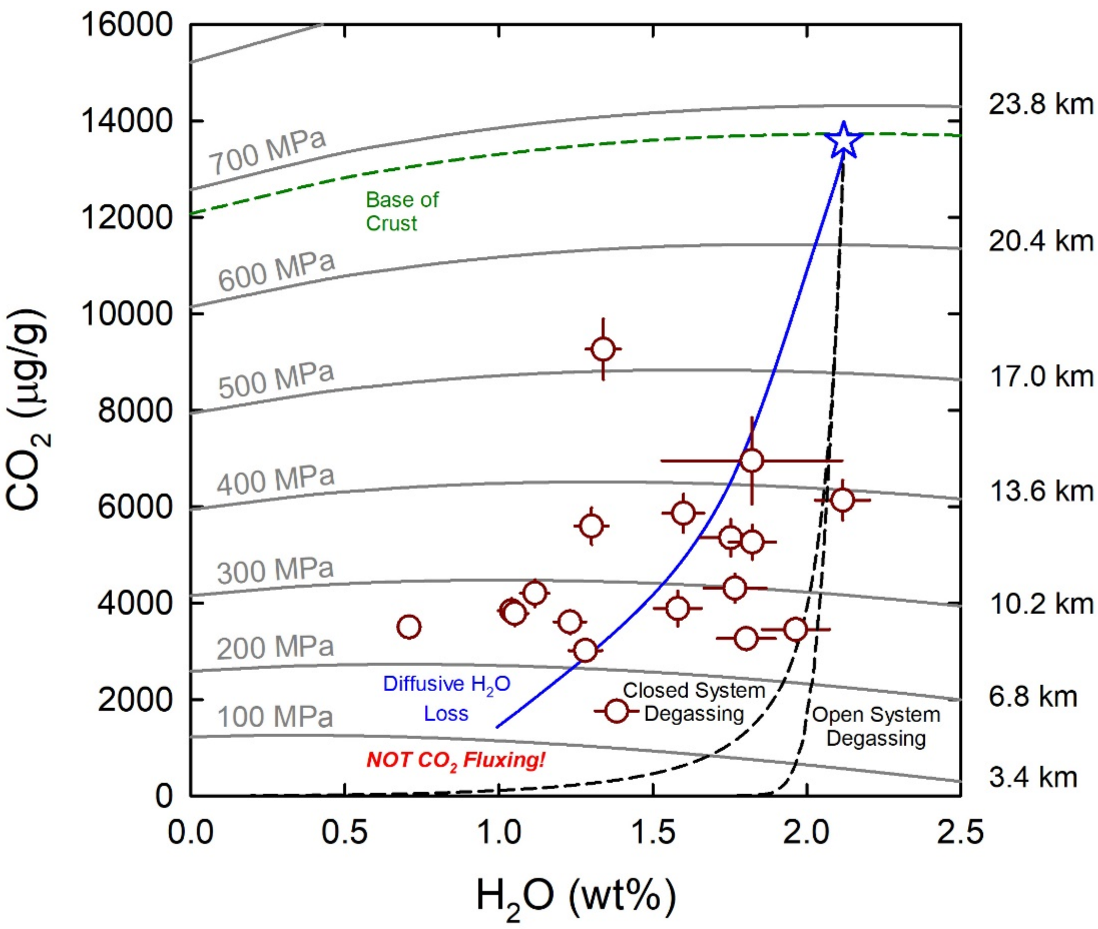


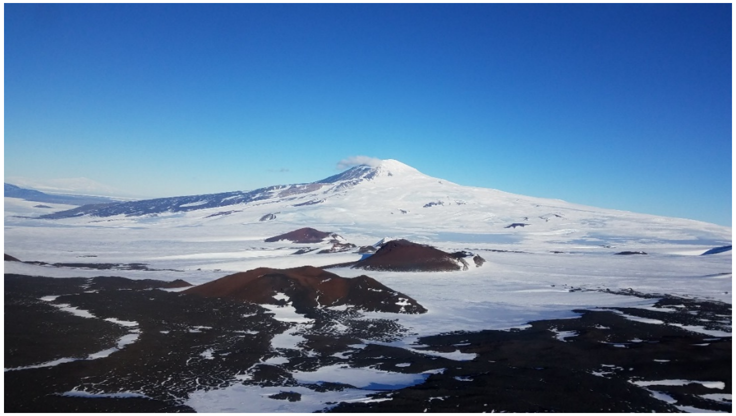


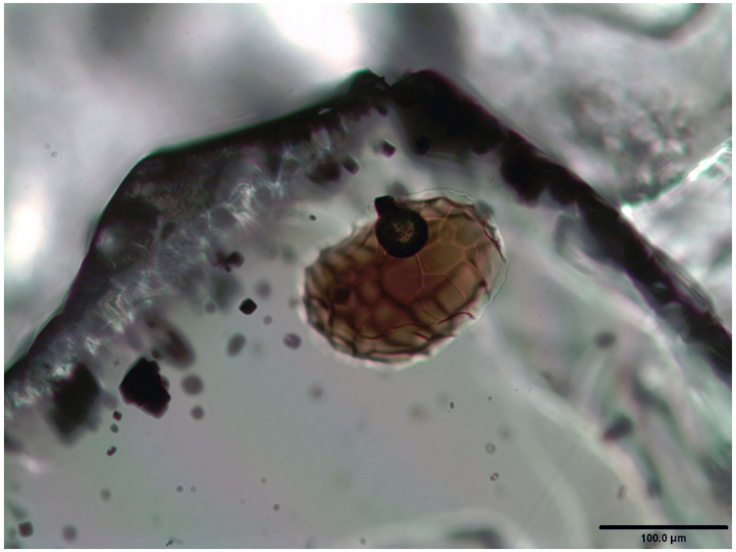
H diffuses faster through olivine than D

Bucholz et al. (2013)

Basanite melt inclusions from Ross Island, Antarctica

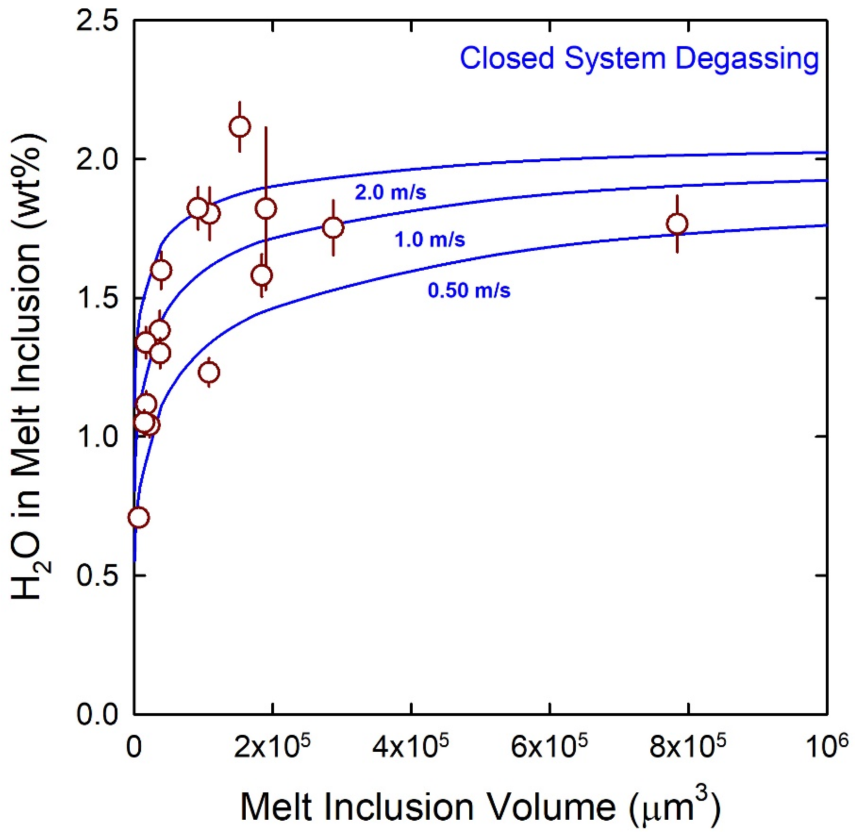


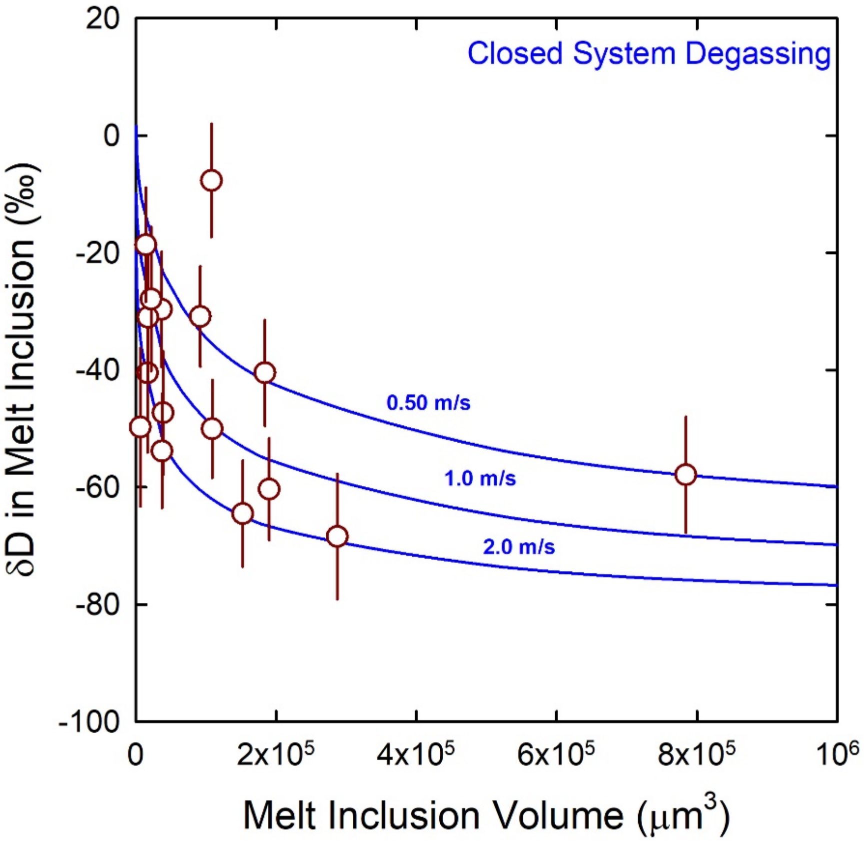




Gaetani et al. (in prep.)

Ascent rates estimated from H_2O and δD variations

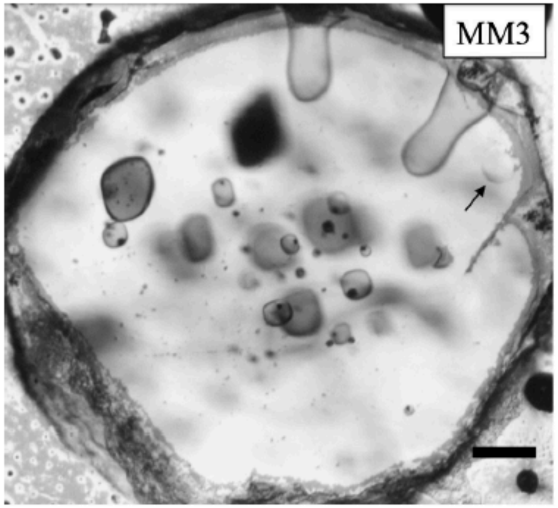


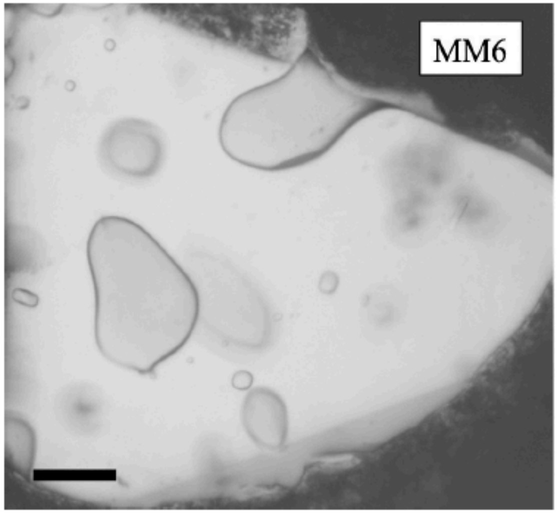


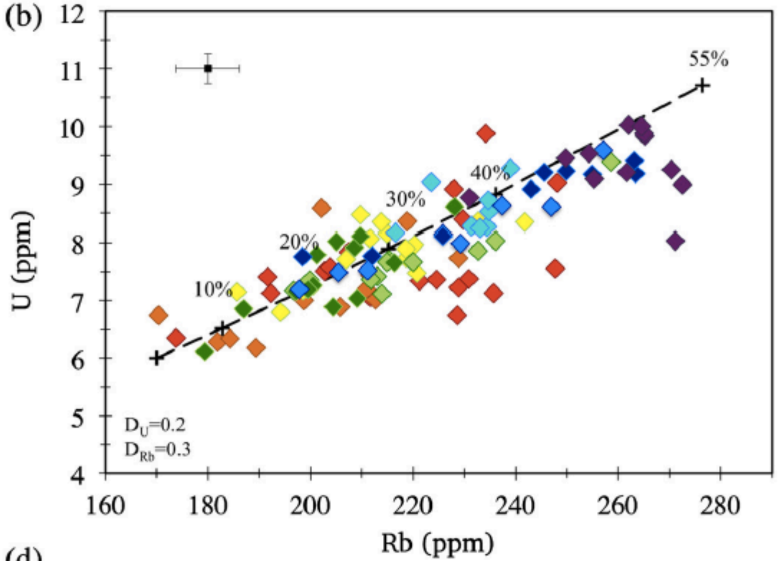
Gaetani et al. (in prep.)

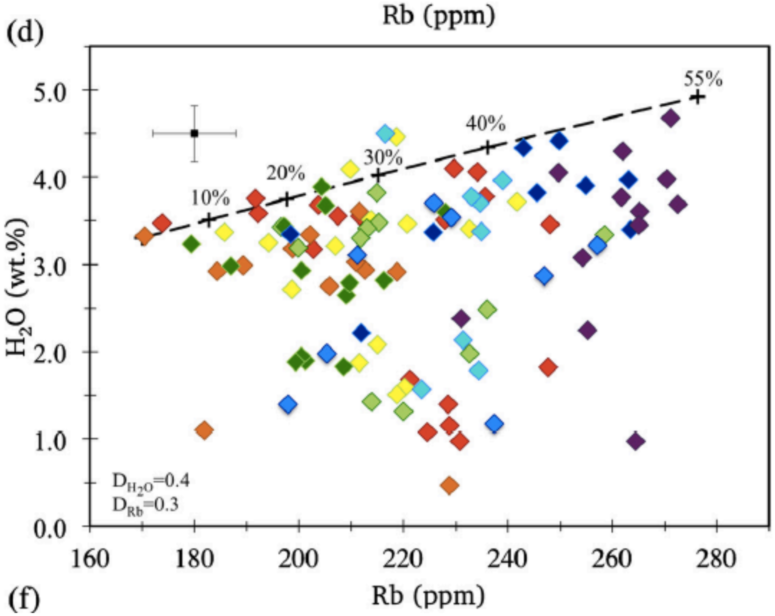
Diffusive H loss from rhyolitic melt inclusions

Huckleberry Ridge Tuff, Yellowstone





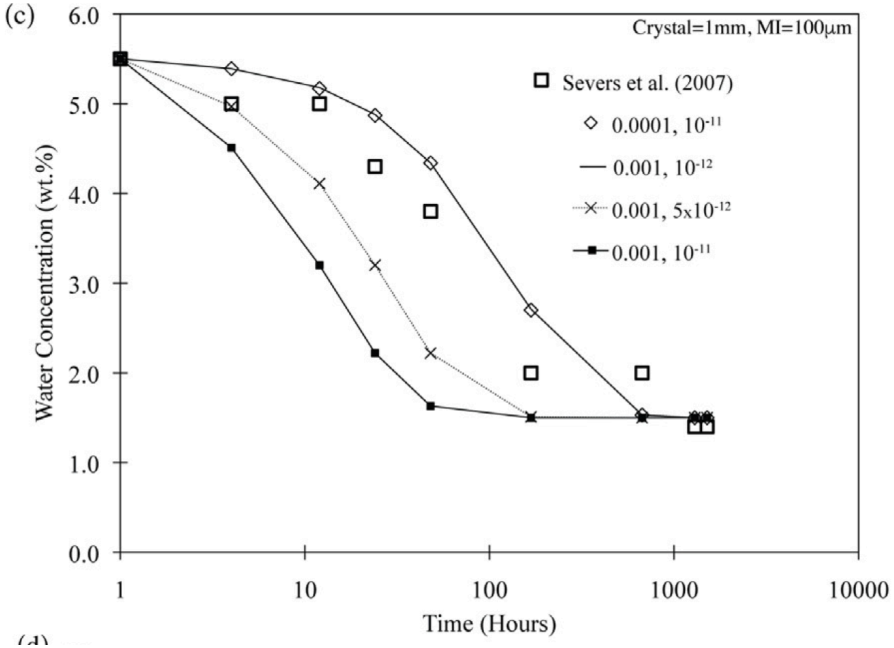


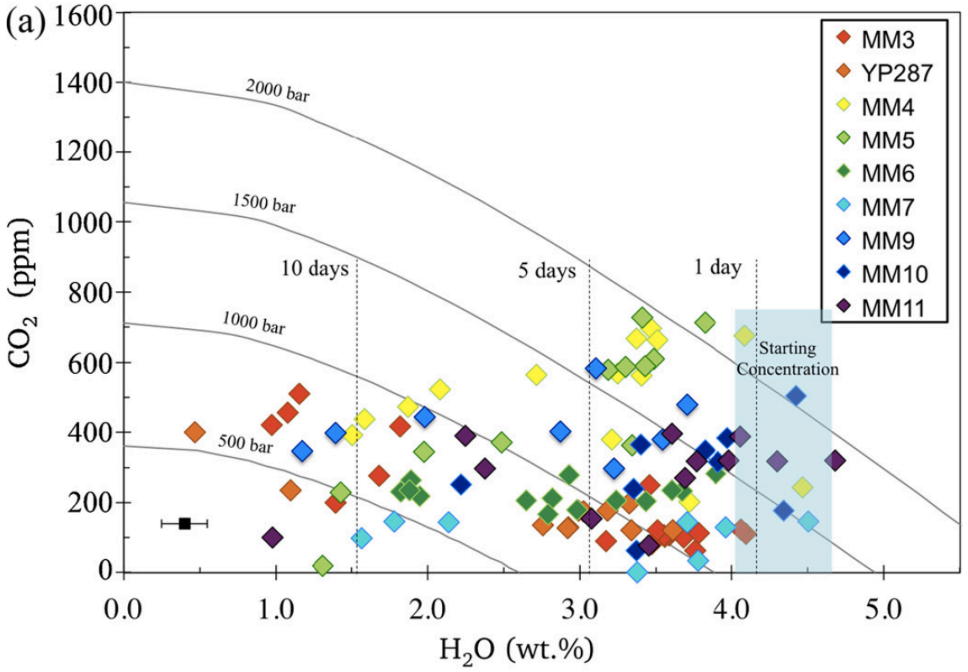


(f)

Myers et al. (2016)

Ascent rates estimated from H_2O variations





- For inclusions that experienced <12 hours of diffusive loss, ascent rates are >0.1 m/s, whereas inclusions that underwent days of diffusive loss ascended much more slowly, at apparent rates of ~0.01-0.005 m/s.

- These slow rates could be the result of either slow, continuous magma ascent or more rapid ascent, with periodic stalling at shallower depths in the conduit.

Myers et al. (2016)

Summary Questions

- How and where are magmas formed?
- How much CO_2 is in mantle-derived magmas & how deep do they become vapor saturated?
- How are magmas stored and transported in the crust?
- How are volatiles transferred through crustal magmatic systems?
- How do eruptions begin, evolve, and end?
- How do feedbacks between volatiles, bubbles, crystals, magma viscosity, degassing and ascent rate determine eruptive style?
- What controls the explosive – effusive transition?