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

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Melt Inclusions

What are they?

How to use them → volatiles

What information can we get from

What information can we **NO**

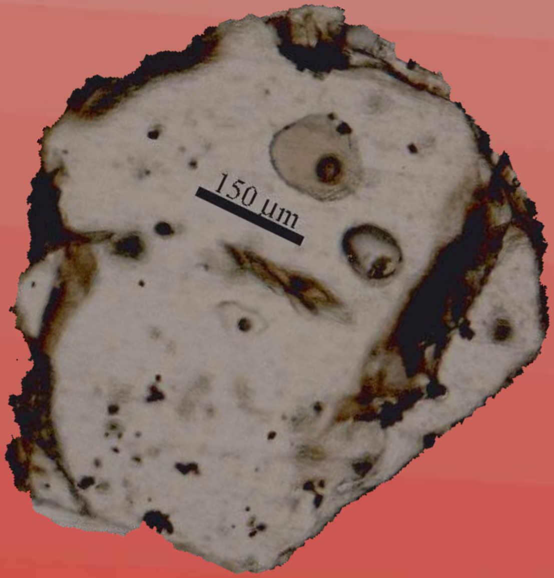
Examples

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)

Plagioclase – Montserrat
Mann et al. (2013)



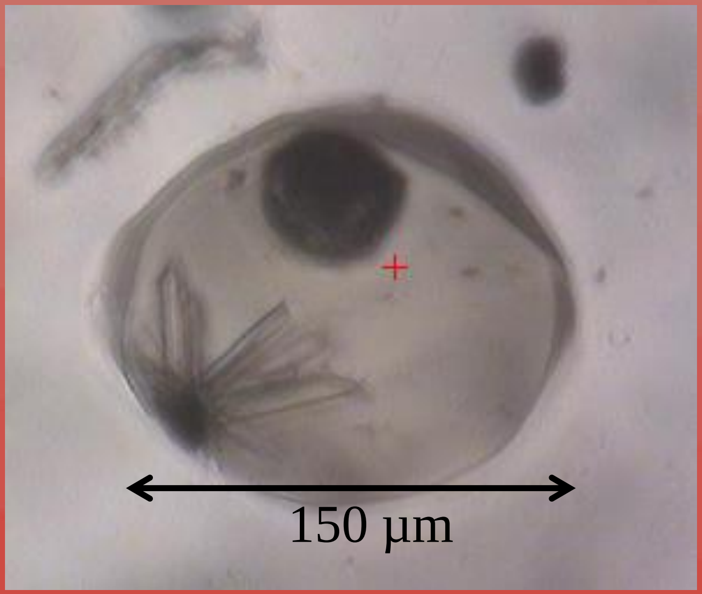
Olivine - Popocatepetl
Roberge et al. (2009)

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?

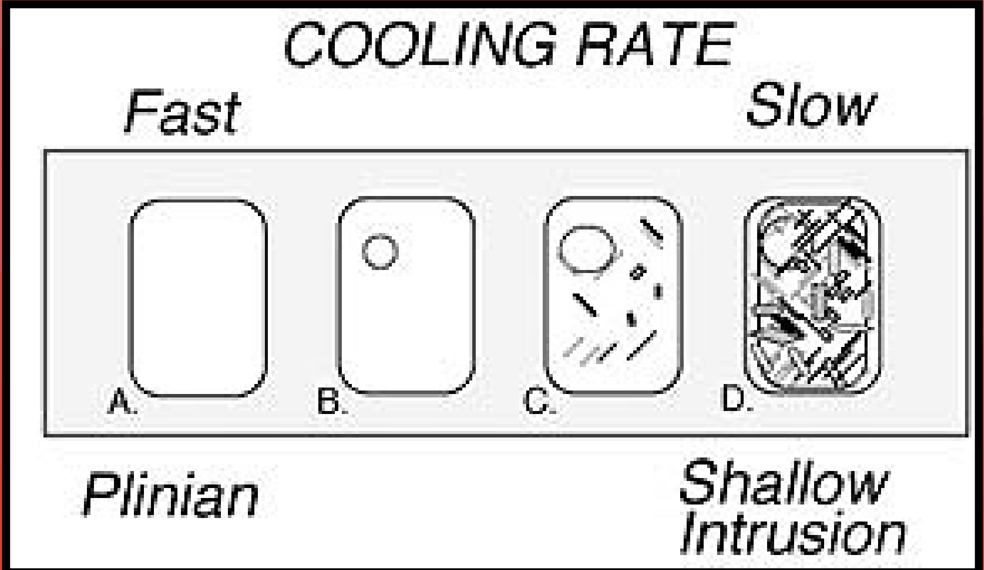
or fully crystallized

Qz – Pantelleria
Lowenstern (1994)

Crystallized = Crystals grew
from melt

Devitrified = Crystals grew
from glass

Depending on cooling rate

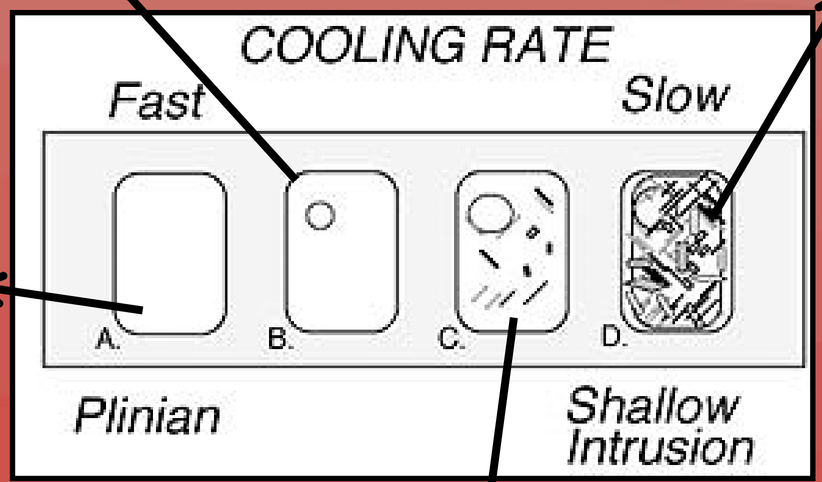


Melt Inclusions – What are they?

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

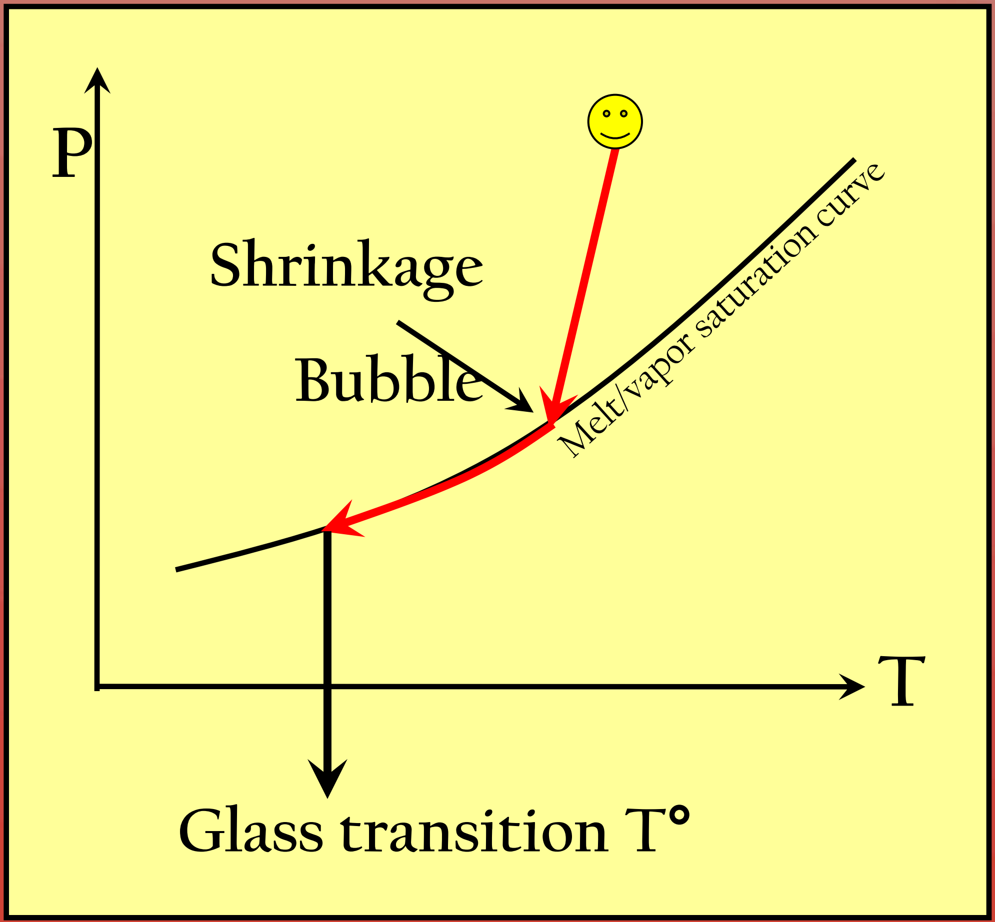
Rapid cooling, no crystals nor bubble form



Diffusion during slow cooling allows the bubble to grow and the melt to partly crystallize

Melt Inclusions – What are they?

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

Melt Inclusions – What are they?

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

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)

Solubility Vs P

Volume of volatile-rich melt « Volume of volatile-free melt + volatile phase (bubbles)

Push reaction to side with smaller volume

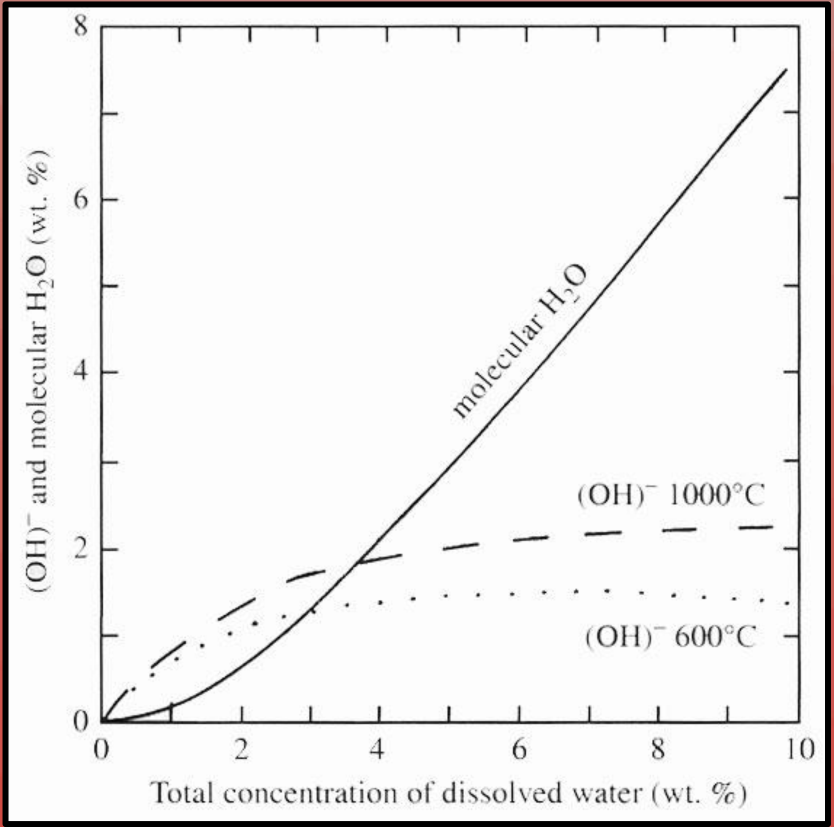
What happens with increasing P?

This means that solubility increases with pressure

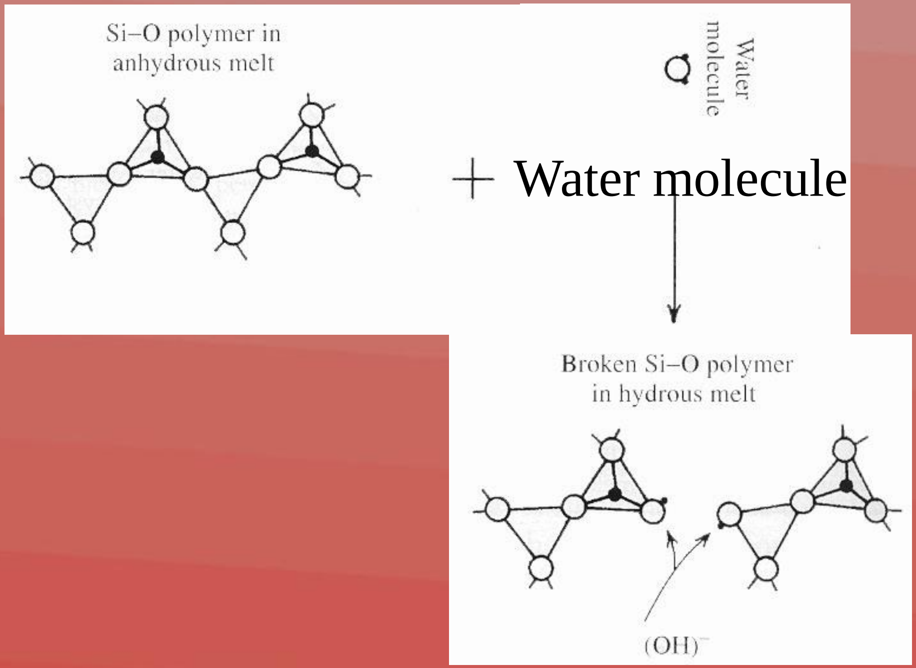
soda analogy

Solubility Vs Composition

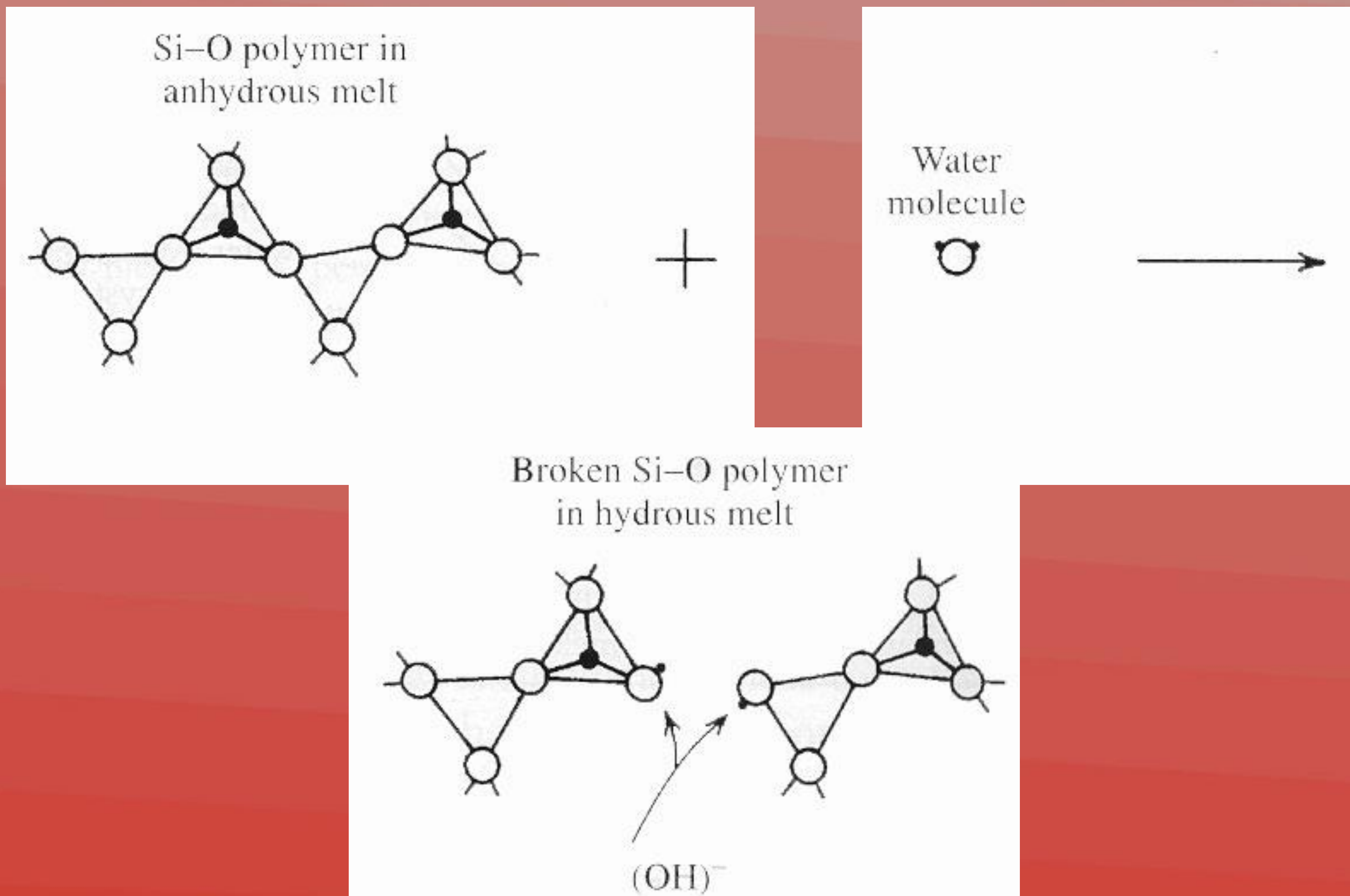
Water speciation in Silicate Melts



From Silver et al., 1990

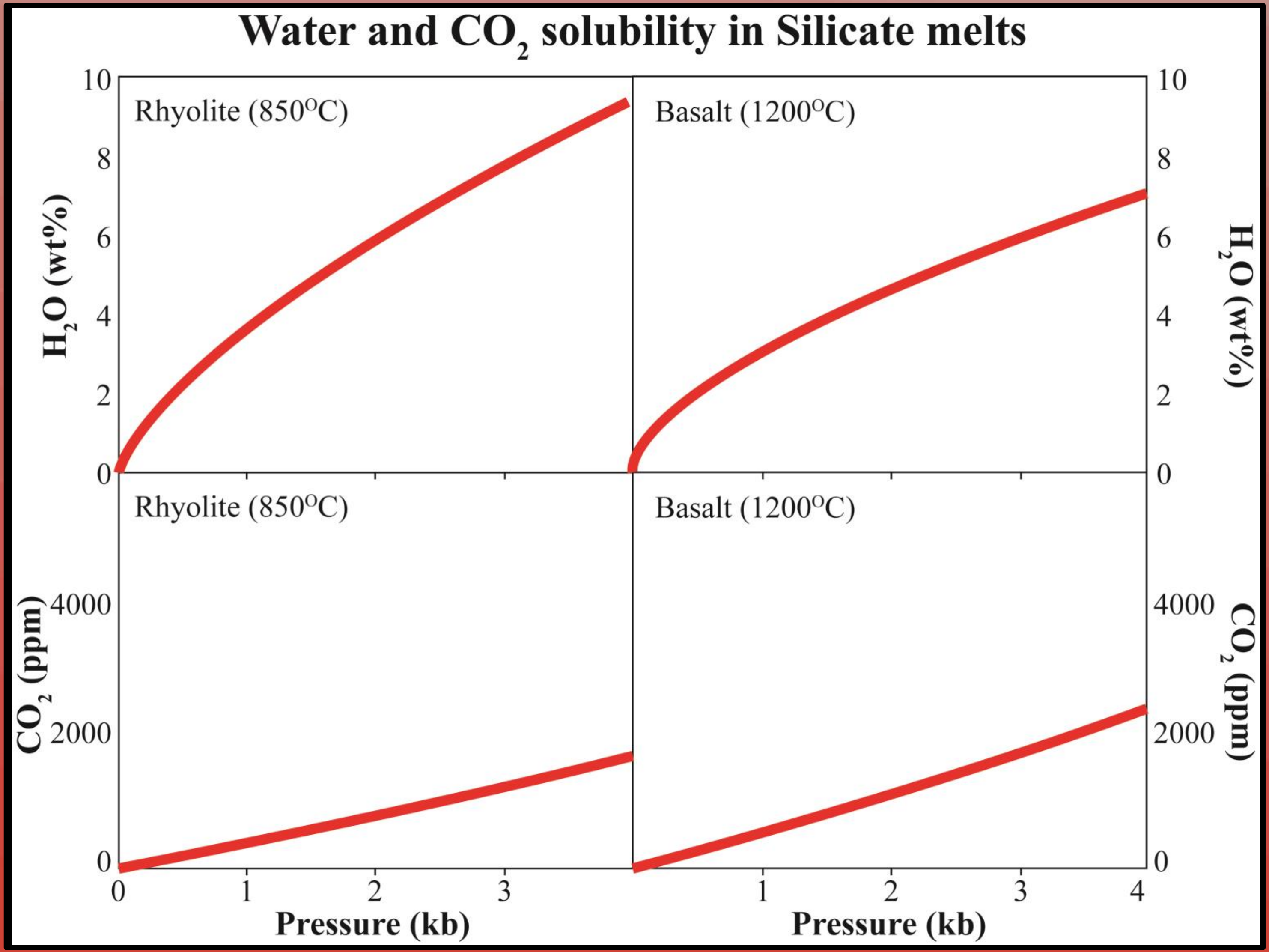


Depolymerization of Silicate Melts



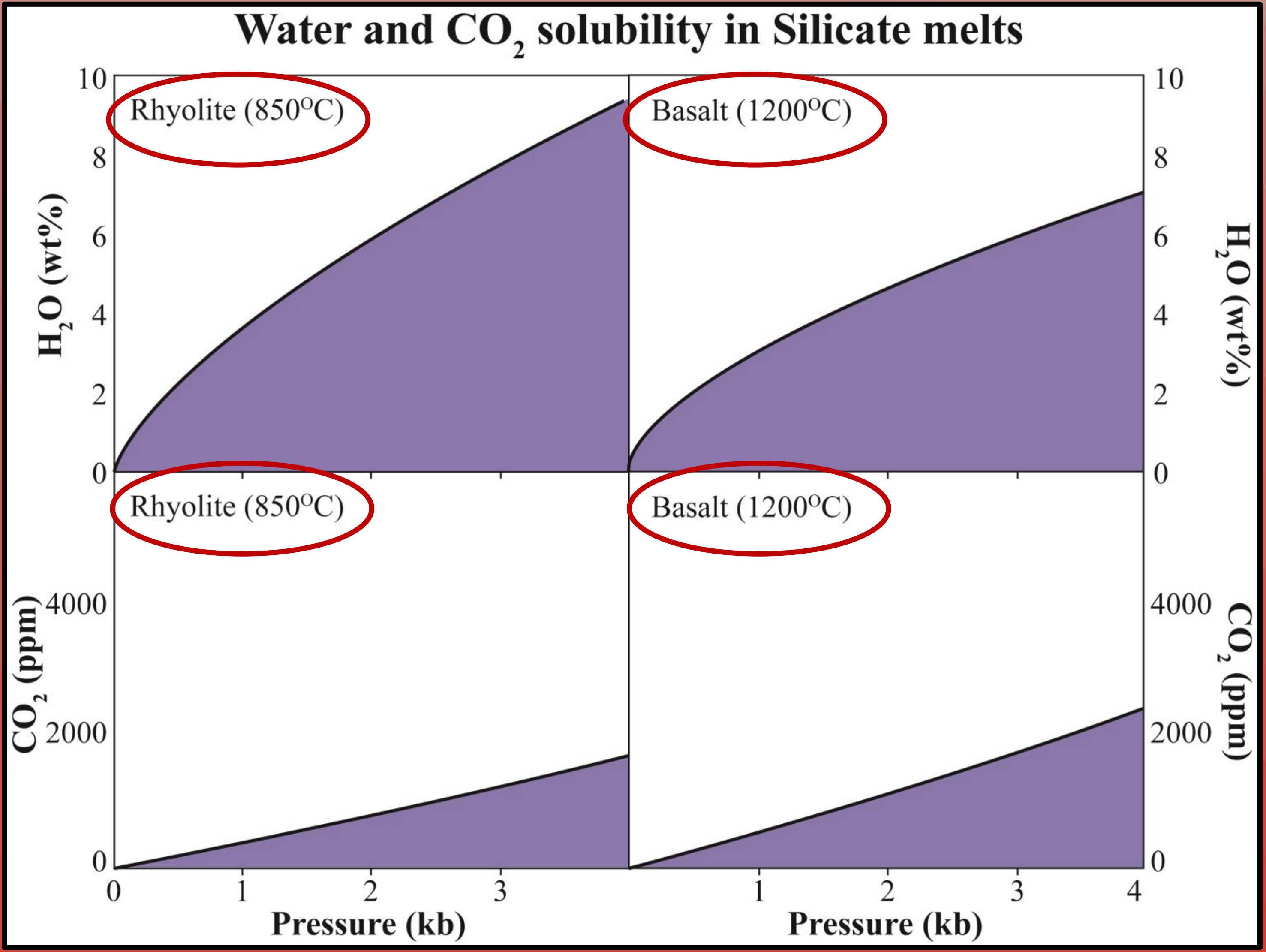
Solubility

Saturated



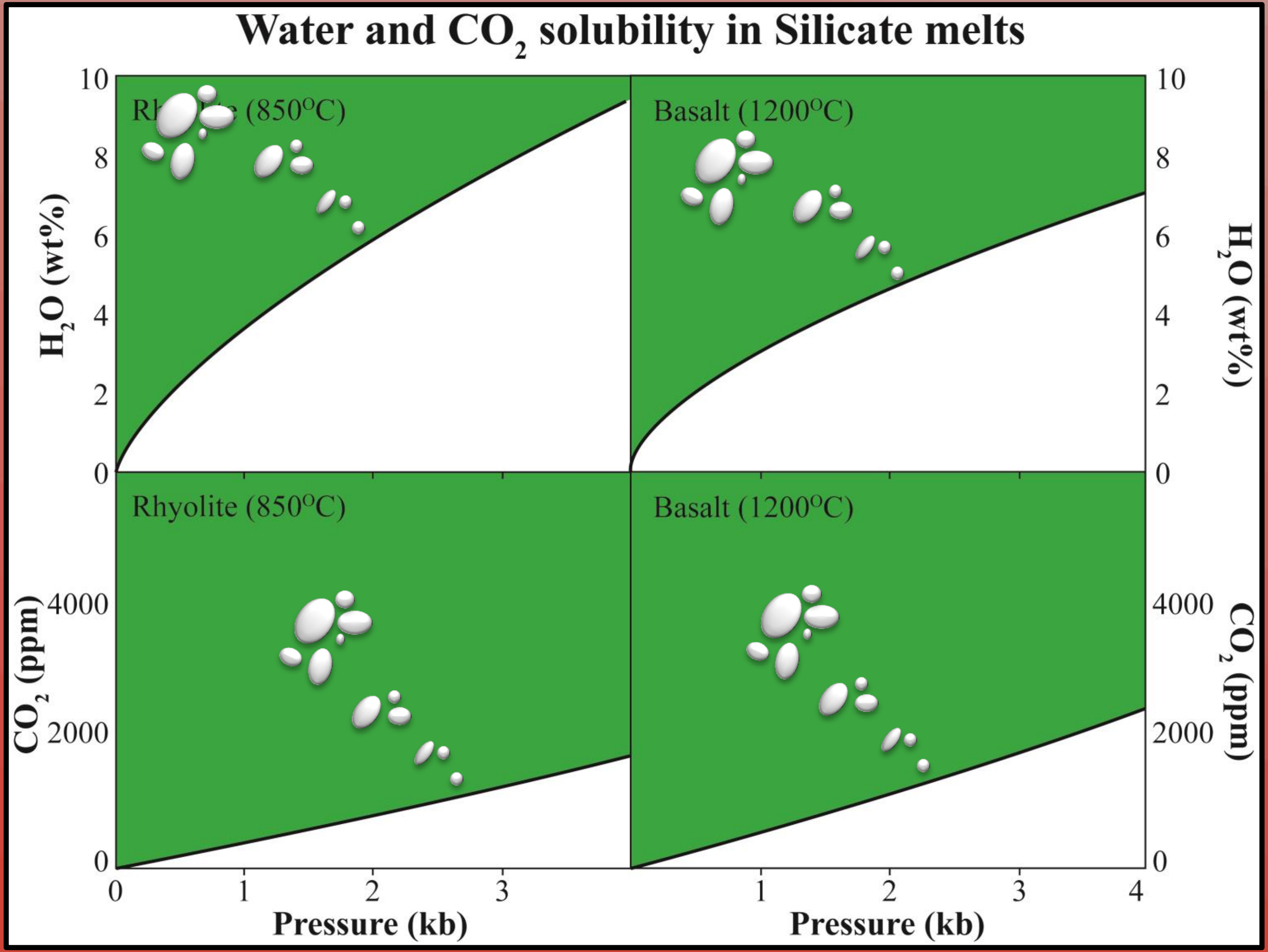
Solubility

Undersaturated

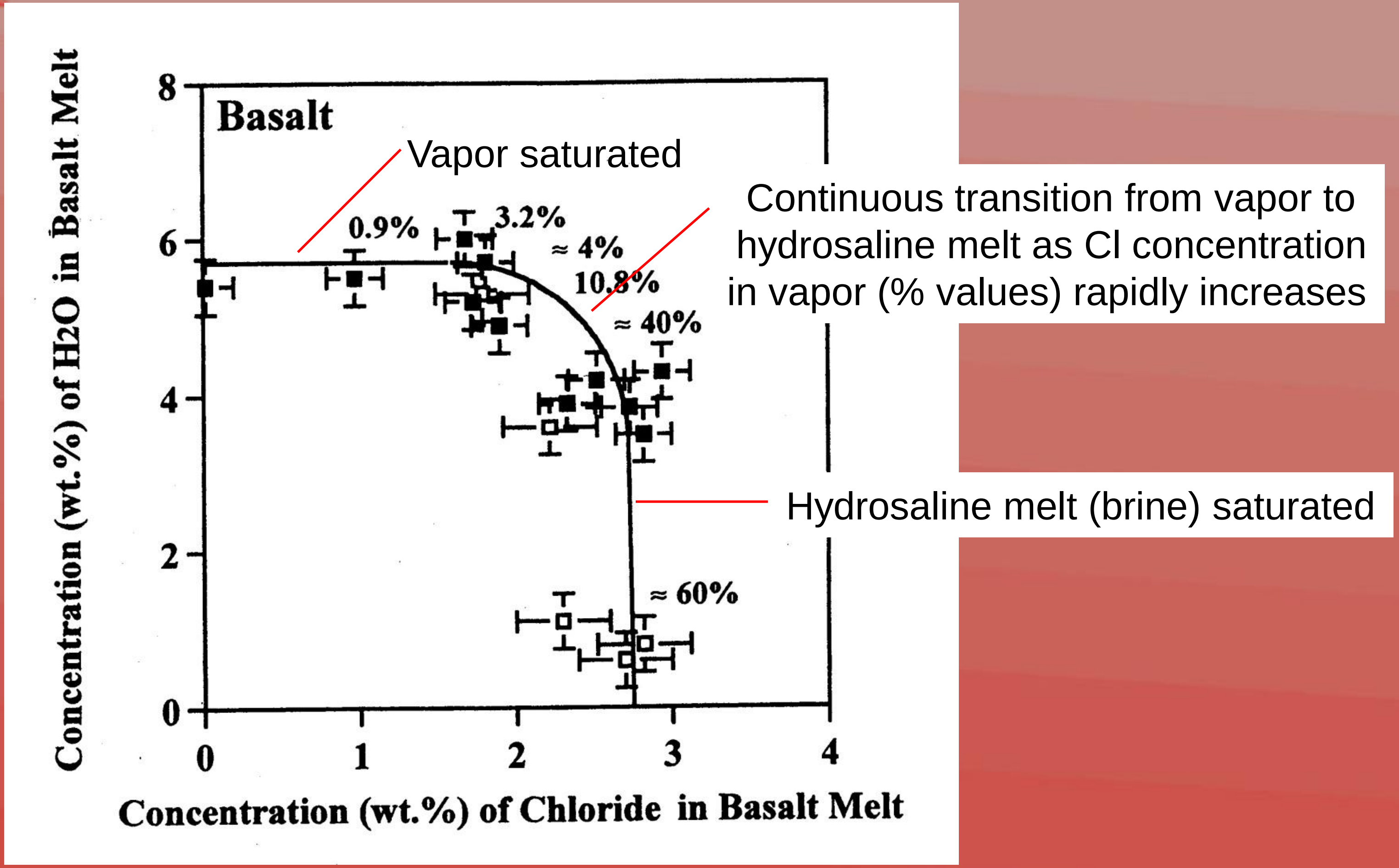


Solubility

Oversaturated



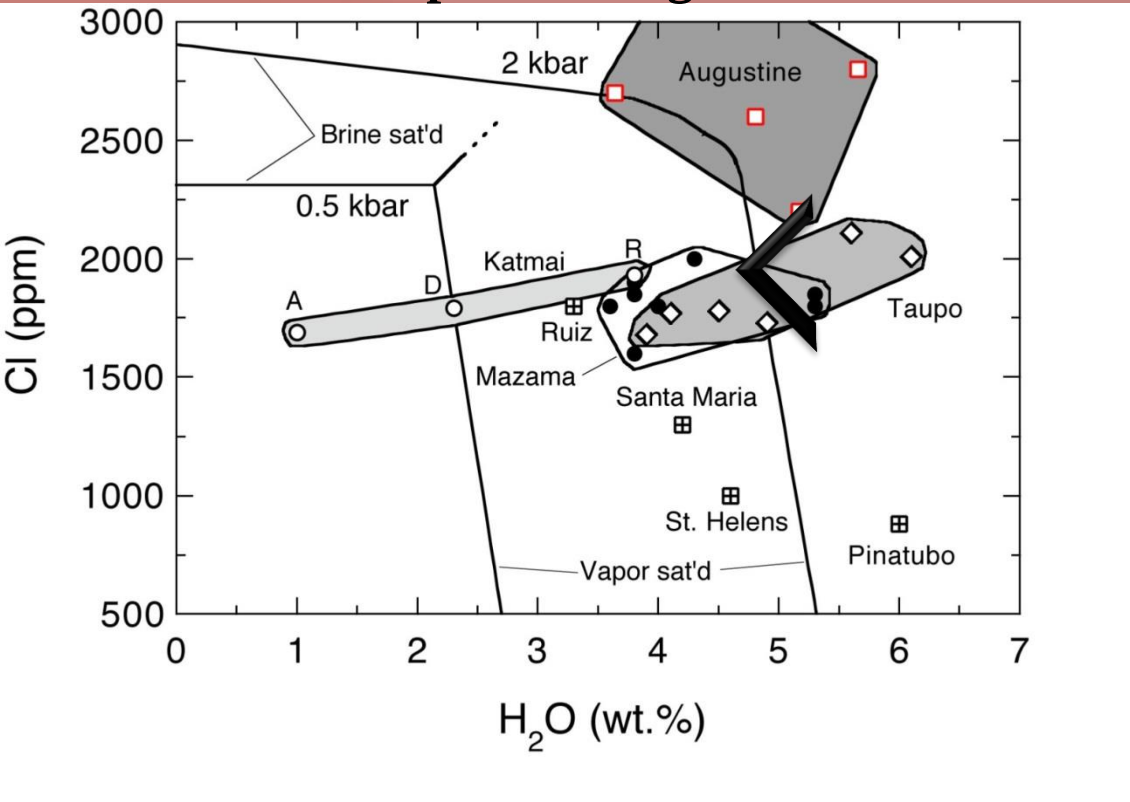
Chlorine Solubility



From Webster et al., (1995)

Chlorine in rhyolitic melts

Note: x and y axes have been switched from previous figure

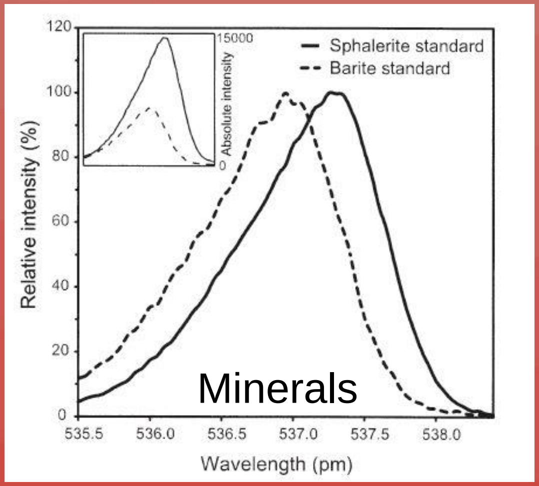


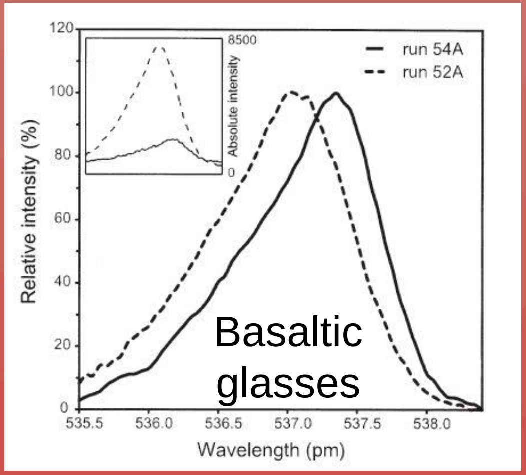
Cl solubility is <u>much</u> lower in rhyolitic melts compared to basaltic melts

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

- S solubility is more complicated because of multiple oxidation states
- Dissolved S occurs as either S^{2-} or S^{6+}
- Solubility is limited by sat’n with pyrrhotite, Fe-S melt, anhydrite, or $CaSO_4$ melt
- S in vapor phase occurs primarily as H_2S and SO_2

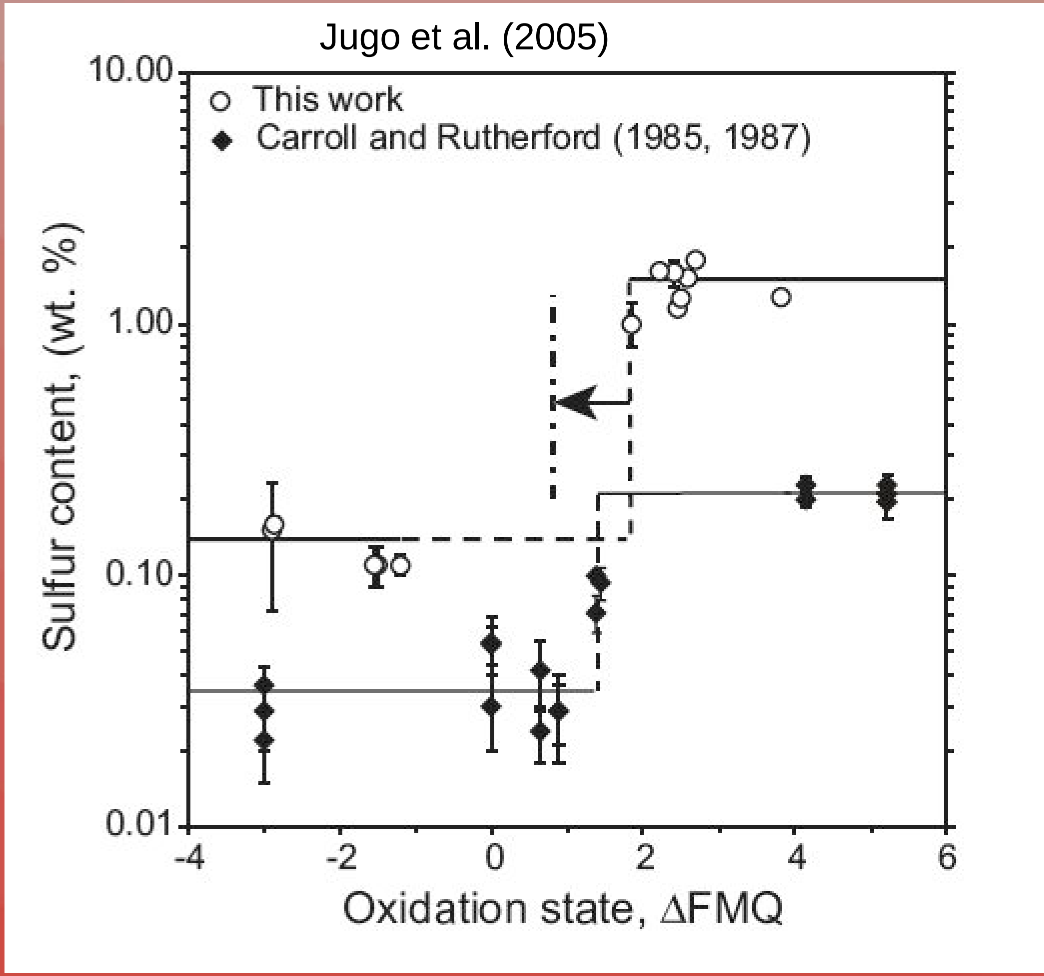




From Jugo et al. (2005)

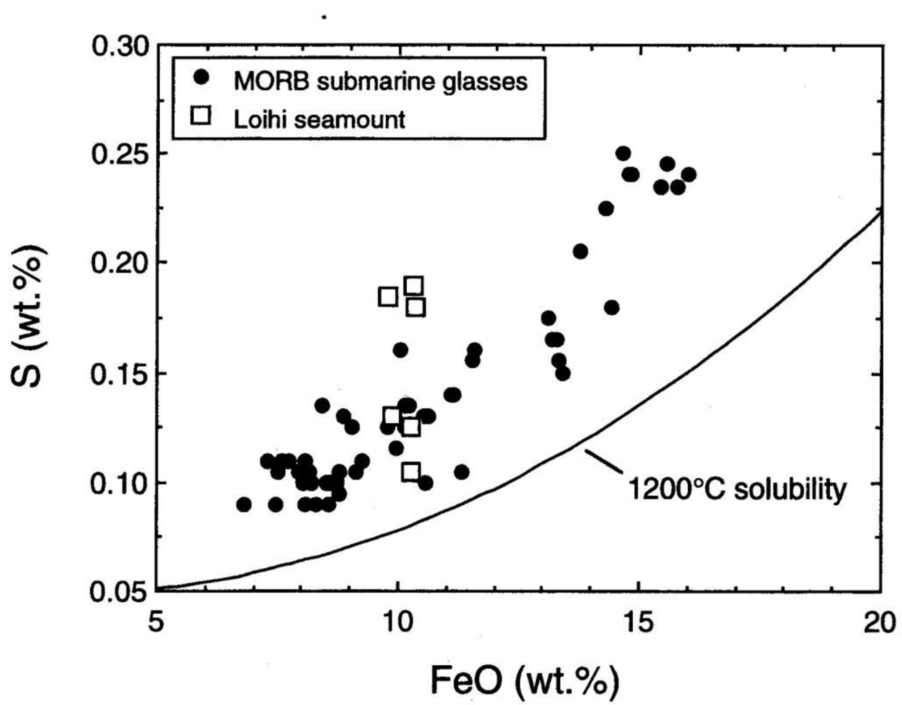
- Measure the oxidation state of S in minerals & glasses by measuring the wavelength of S Kα radiation by electron microprobe

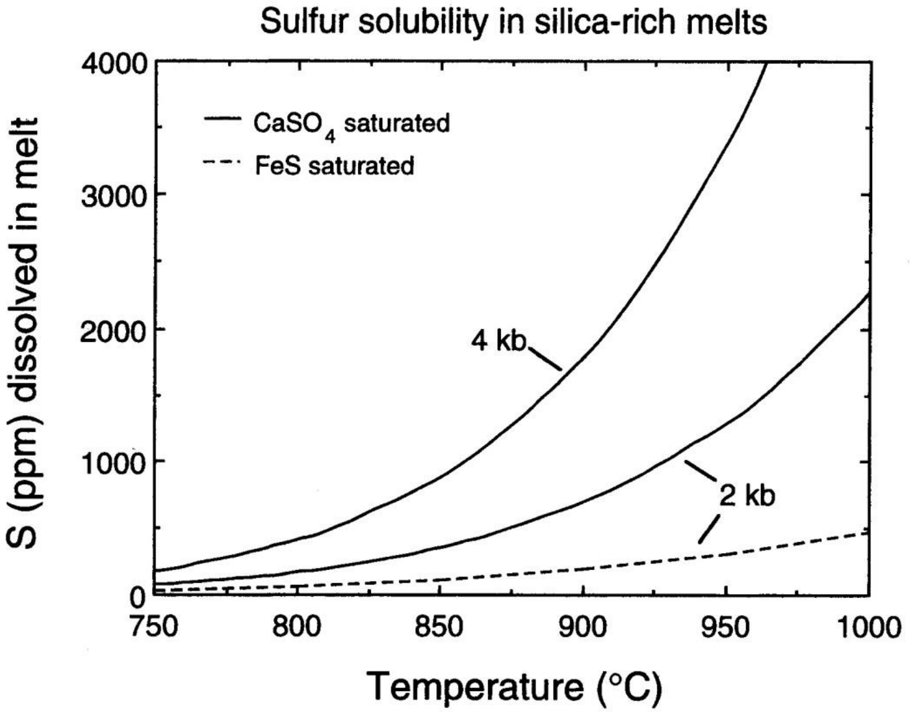
Effect of oxygen fugacity on S solubility



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

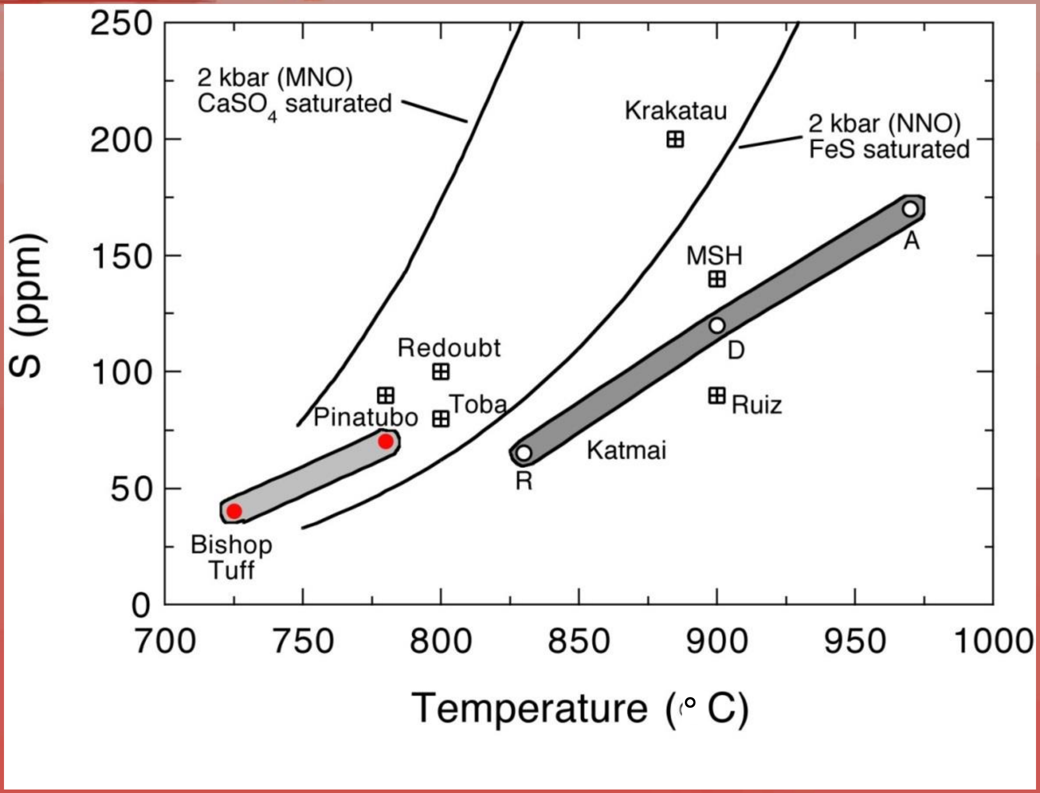




S solubility at low oxygen fugacity S^{2-} is the dominant species

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

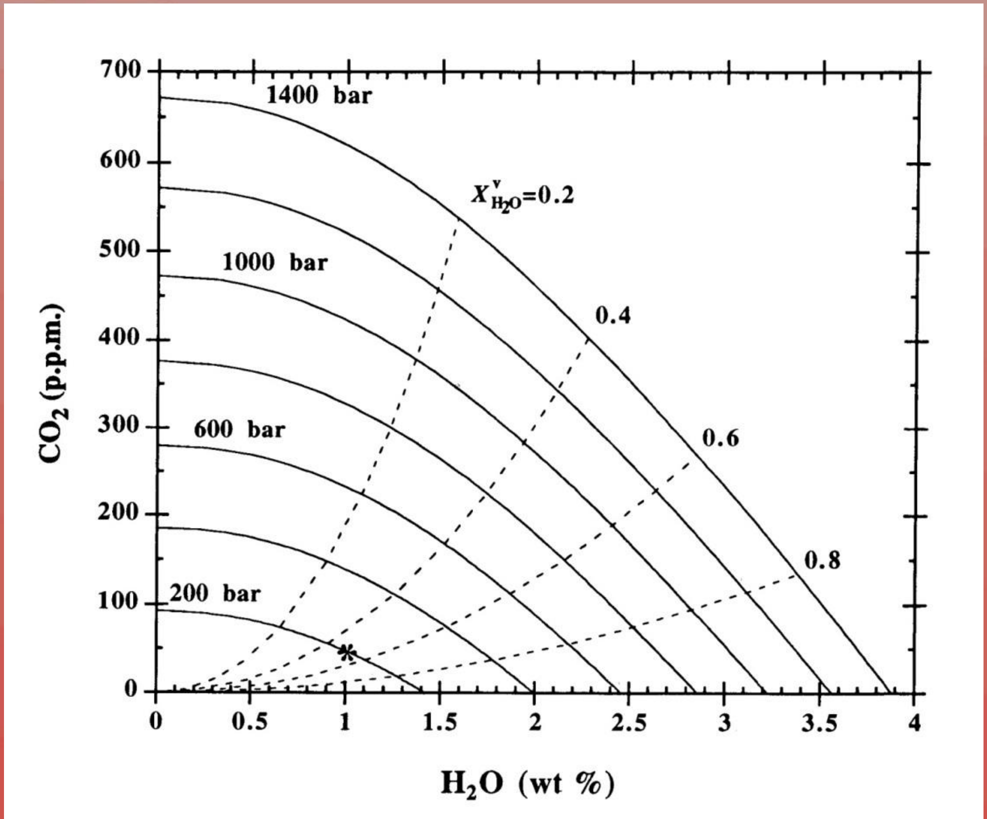
S solubility in intermediate to silicic melts



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

Solubilities with more than 1 volatile component present



From 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

Solubility

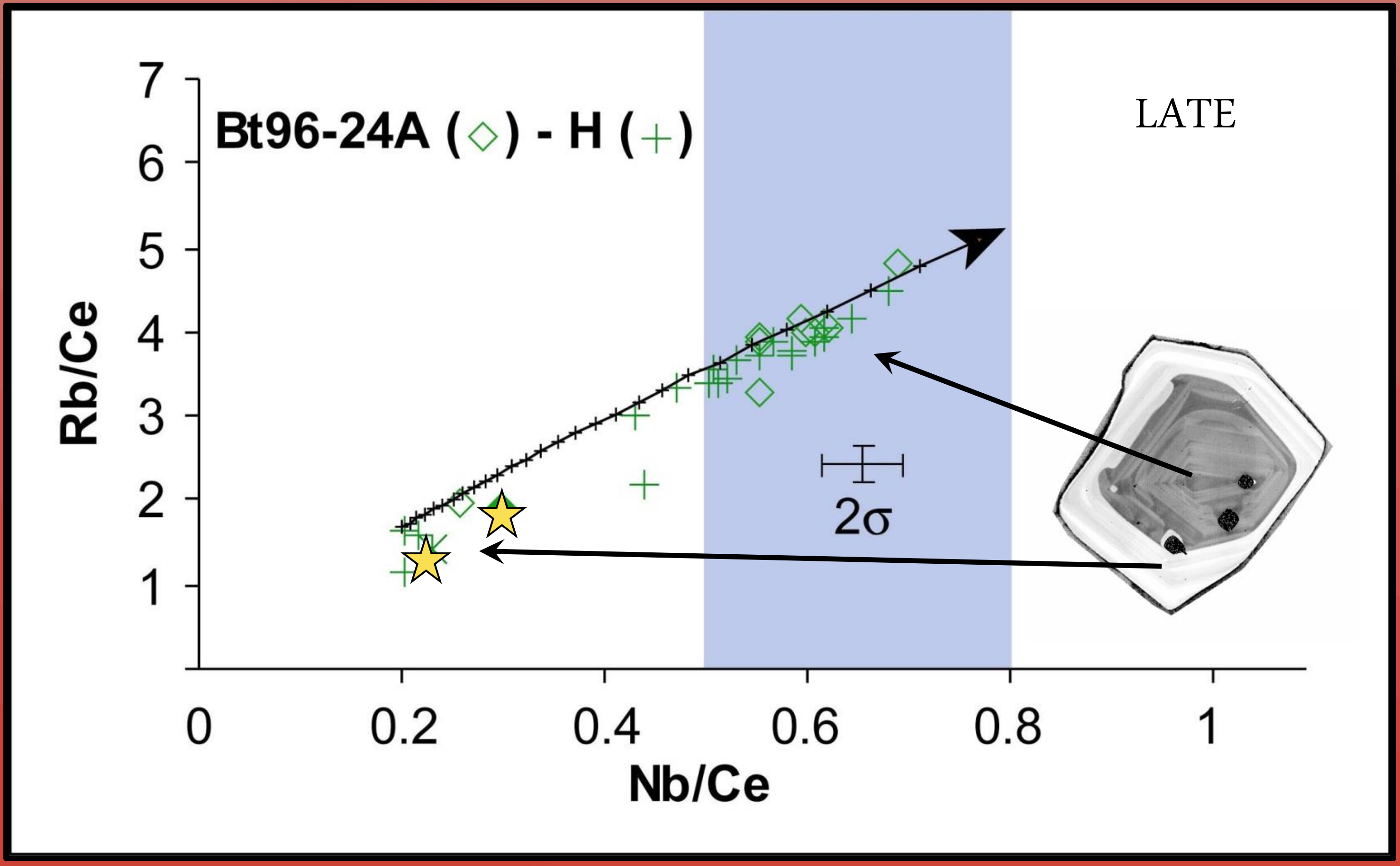
$$CO_2 \ll H_2O < S < Cl$$

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

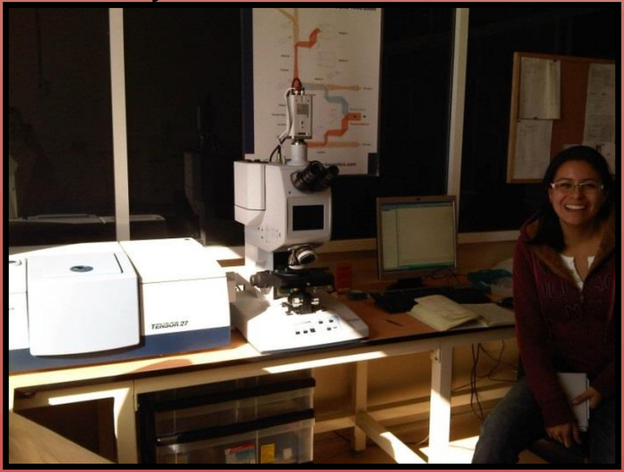


Data NOT obtainable from M.I.

- 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?

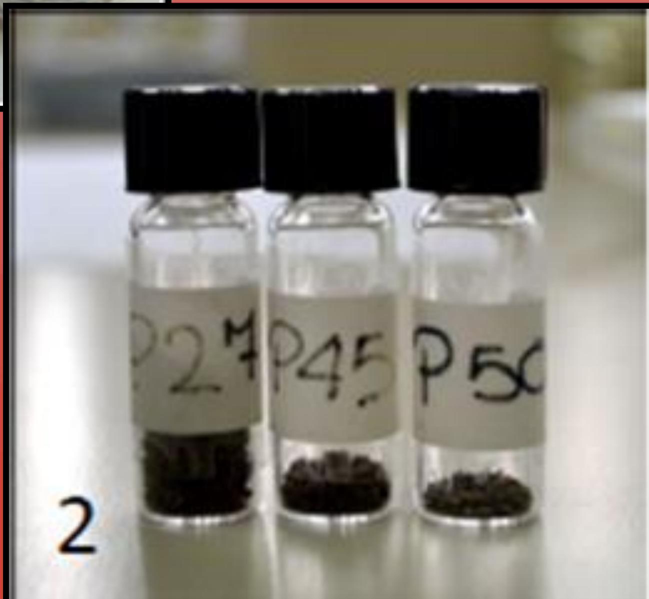
H_2O, CO_2 → FTIR



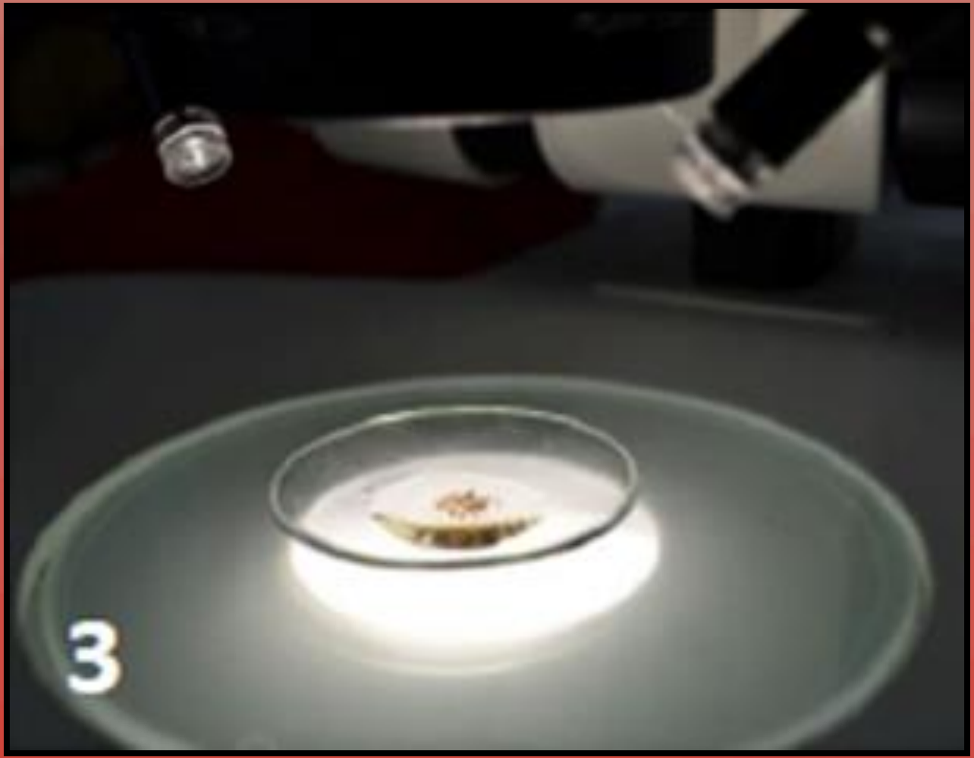
Cl, S, F → Microprobe

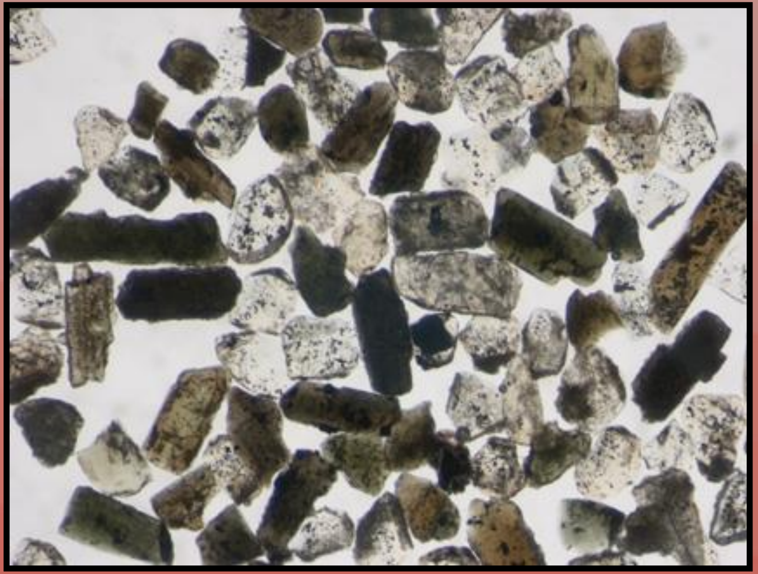
H_2O, CO_2 Cl, S, F→ SIMS

Sample Preparation



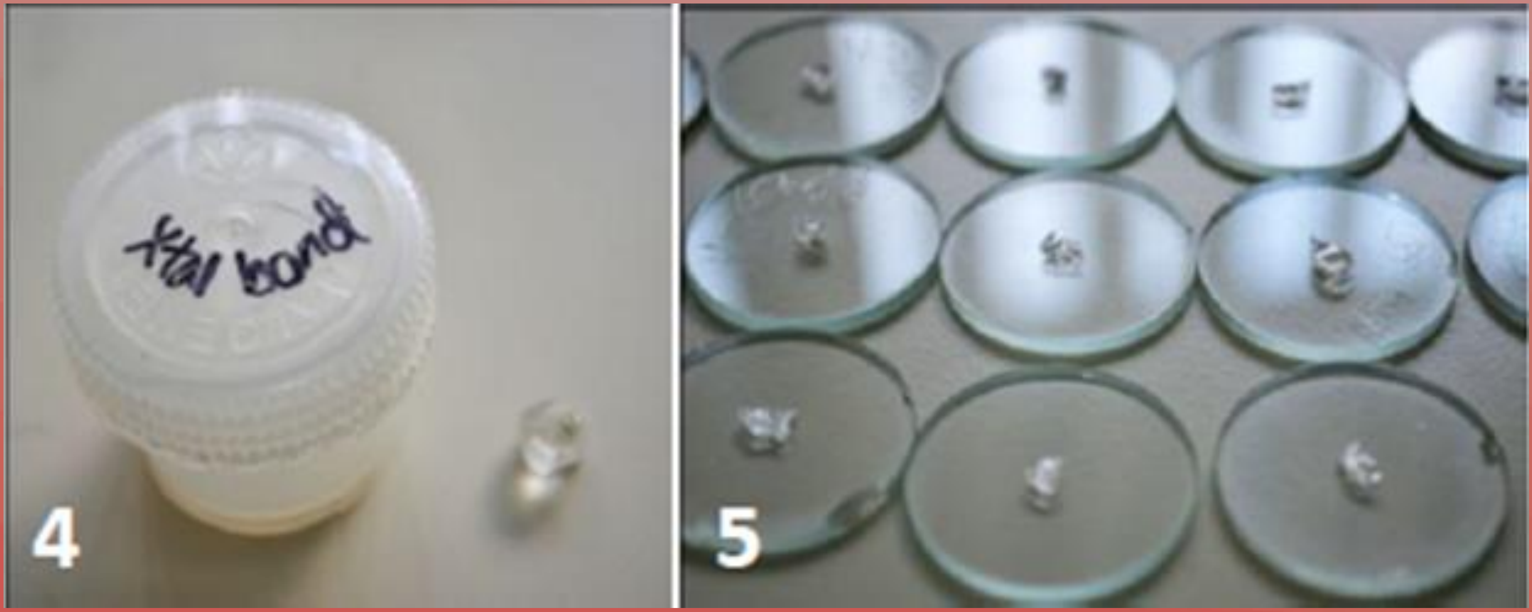
Sample Preparation

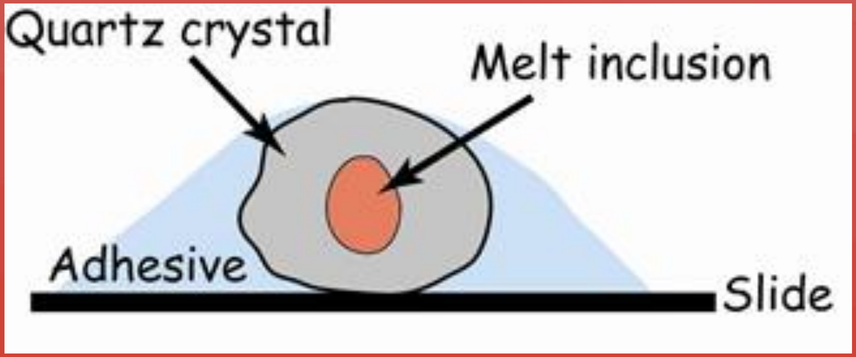




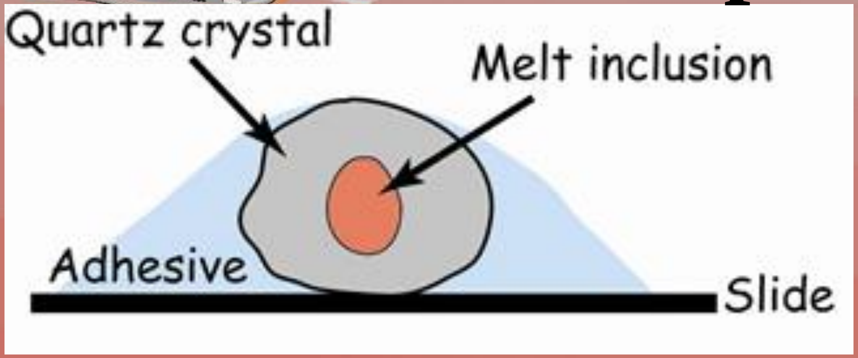
Sample Preparation

Mount selected crystals in dissolvable crystal bond

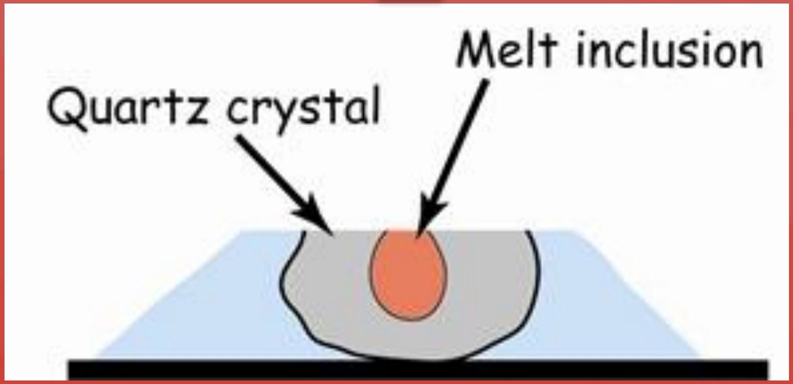




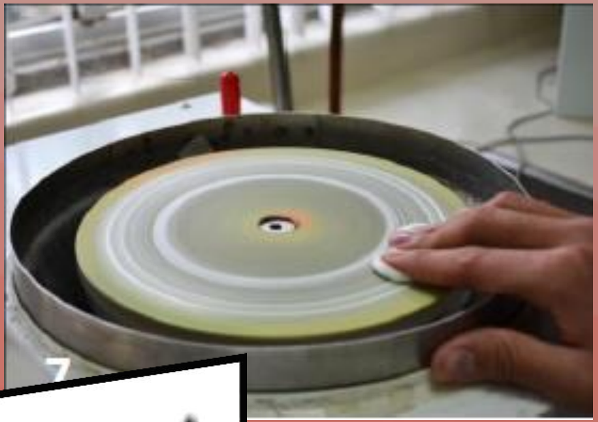
Sample Preparation



Grind until incl
intersected



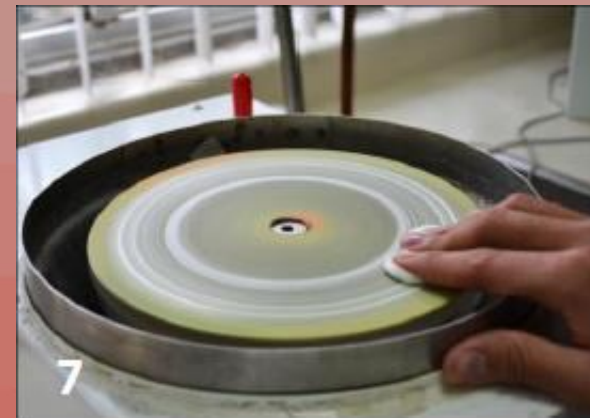
Flip the crystal



l Polish

Sample Preparation

Flip the crystal

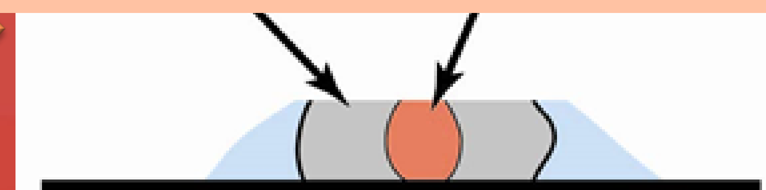


Final Polish

Grind until inclusion is intersected (second

Remember

… Melt inclusions (MI) are small < 100 µm) …



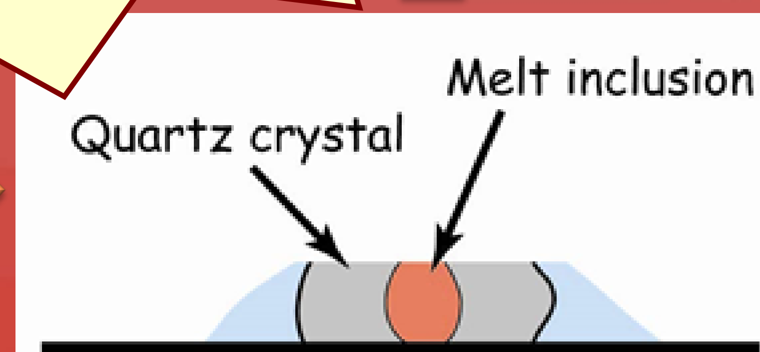
Sample Preparation

Flip the crystal

Grind until inc

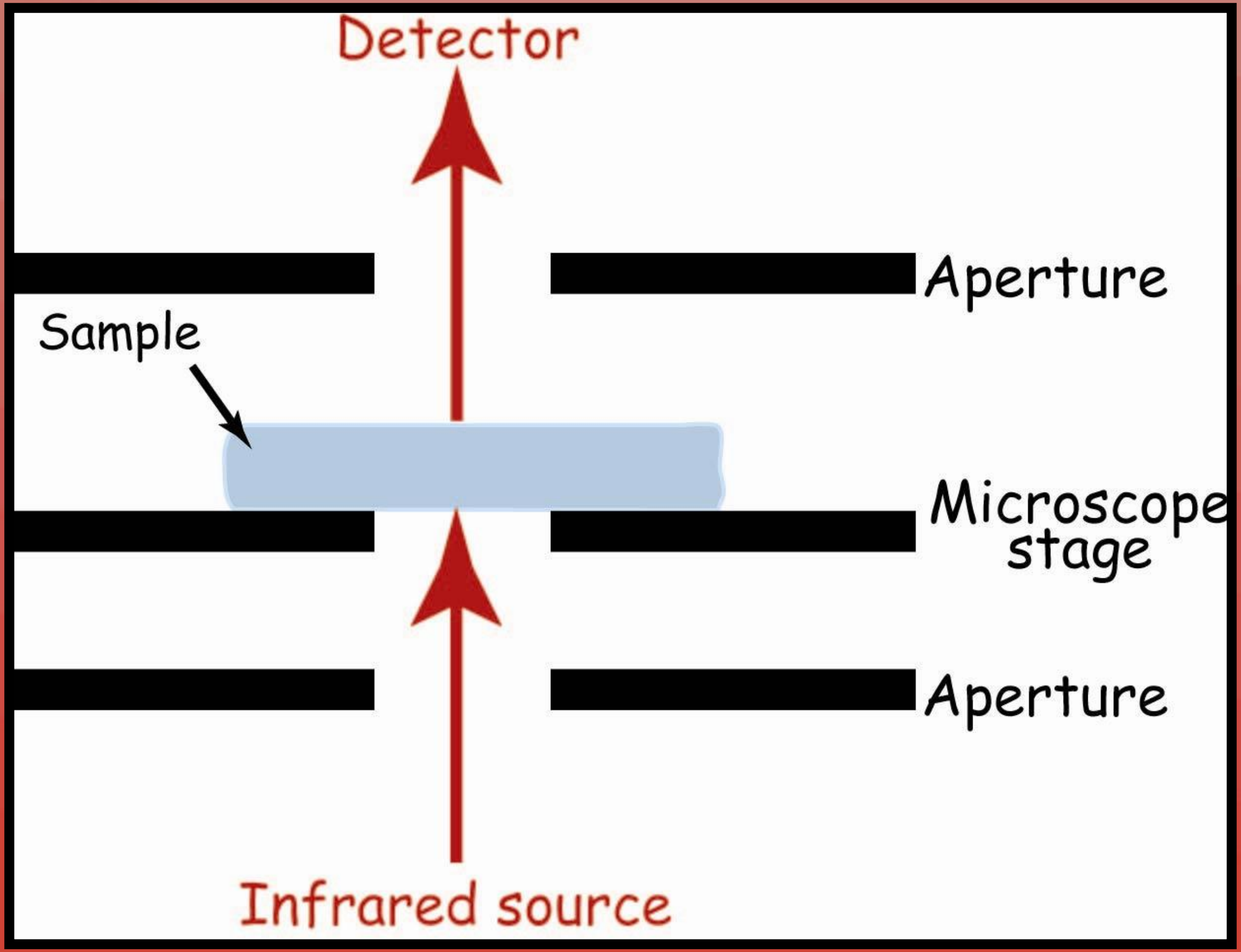
intersected

Handle with care!!



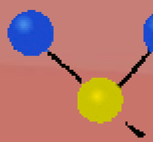
FTIR analysis

The transmitted light reveals how much energy was absorbed at each wavelength

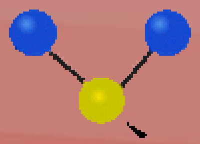


Infrared Vibrational Modes

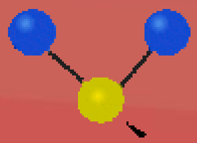
Symmetrical stretching



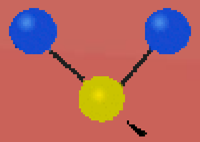
Antisymmetrical stretching



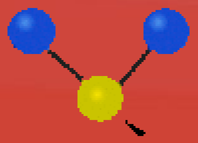
Scissoring



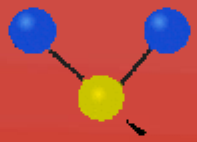
Rocking



Wagging



Twisting



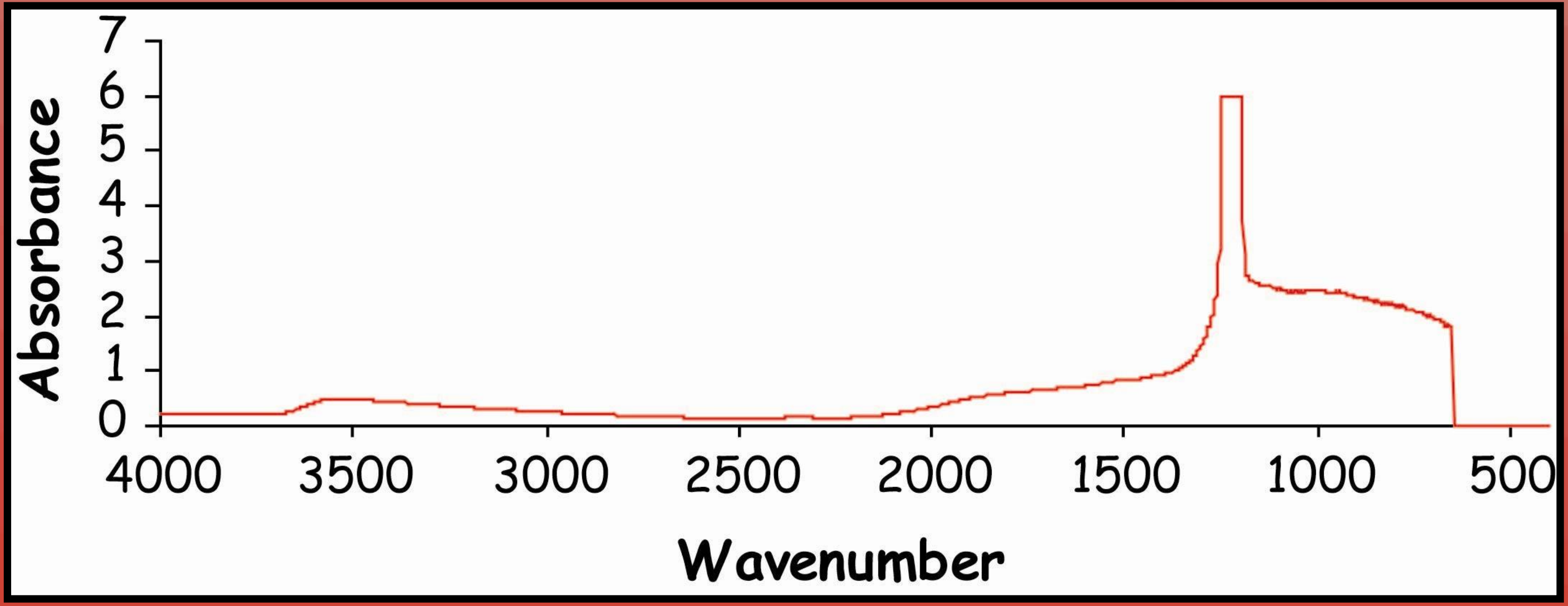
FTIR analysis

Fourier transform allow to measure all wavelengths at once,

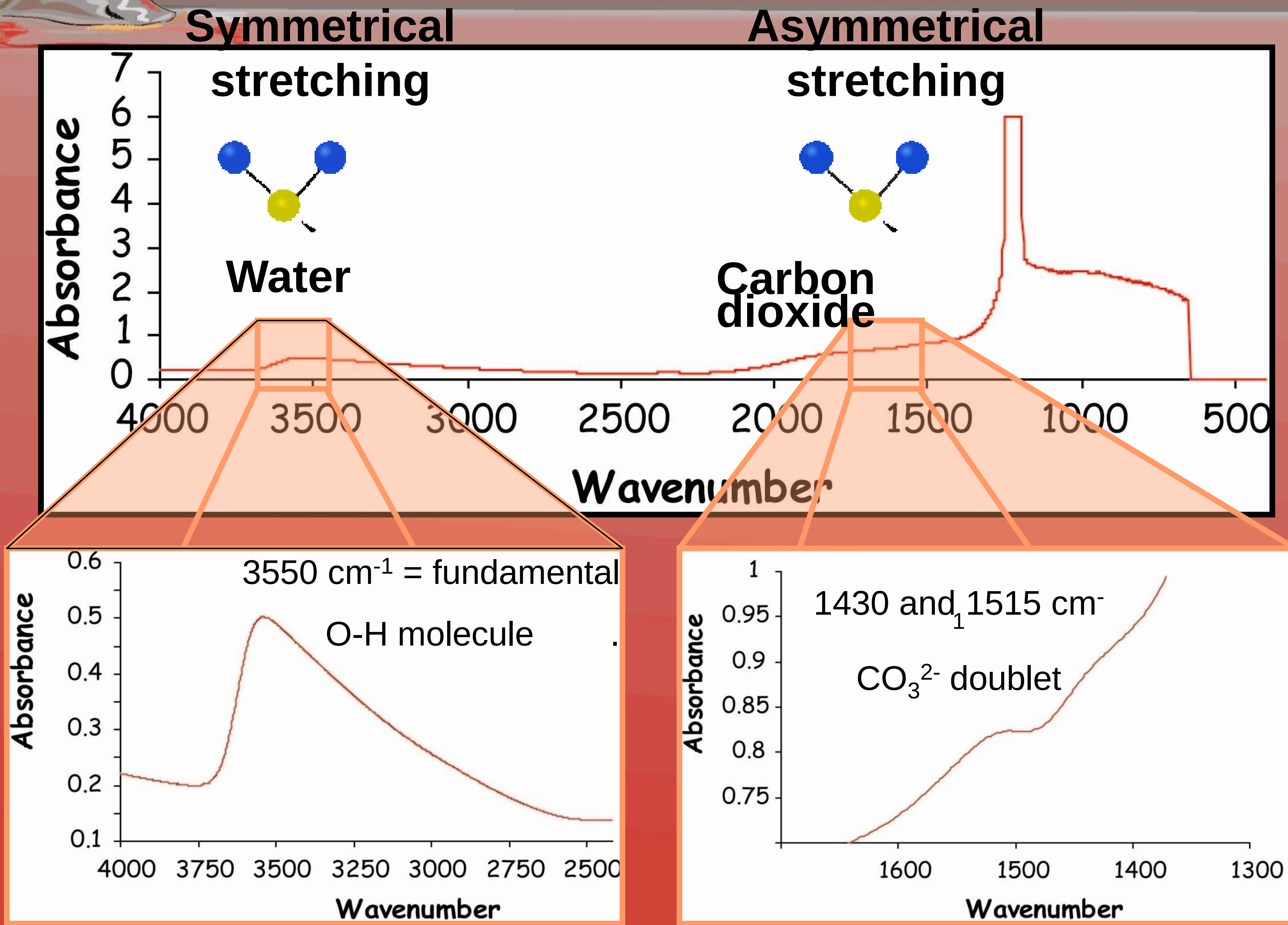
and

produced the absorbance spectrum

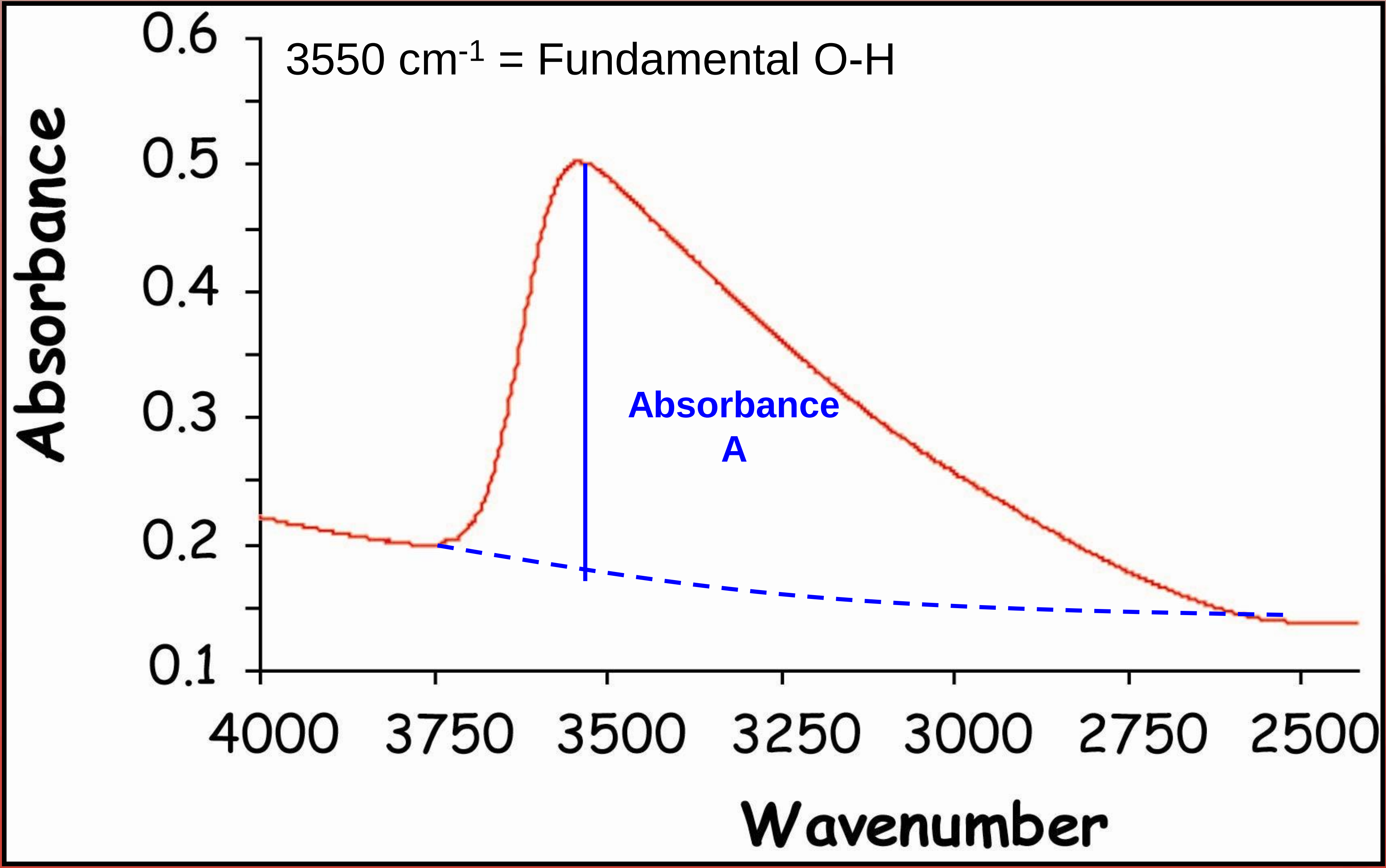
showing at which IR wavelengths the sample absorbs



Acquiring Data

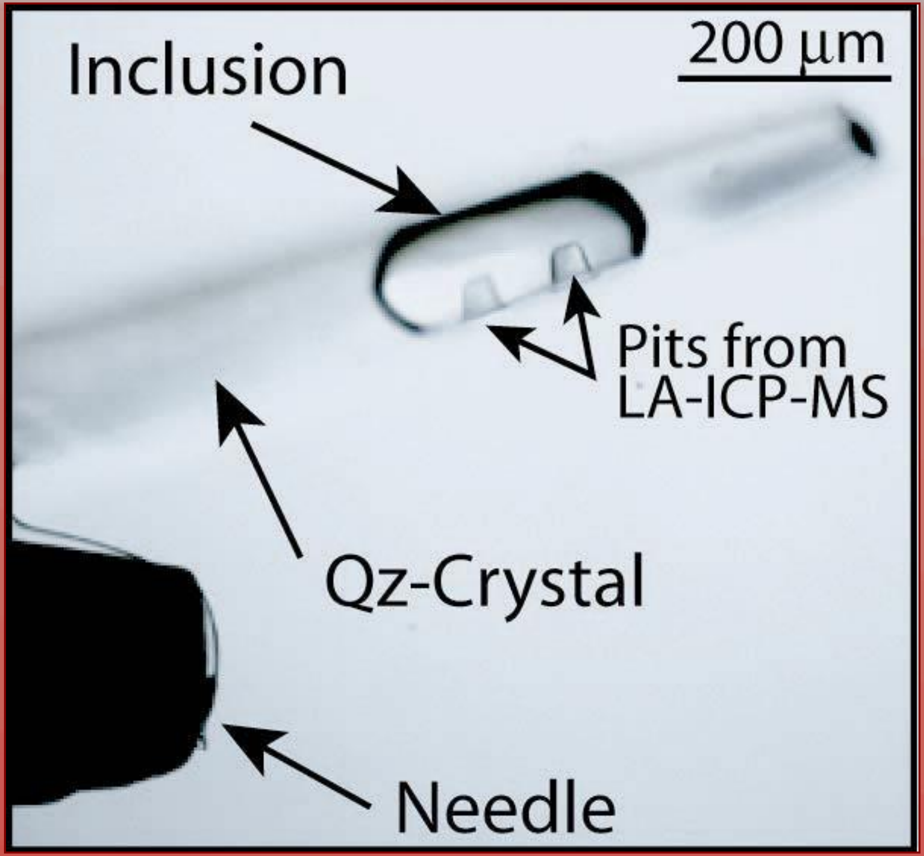


Data reduction



Beer's Law

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



M = Molecular weight

A = Absorbance

ρ = density of the glass at 25°C

d = Thickness of the waffer

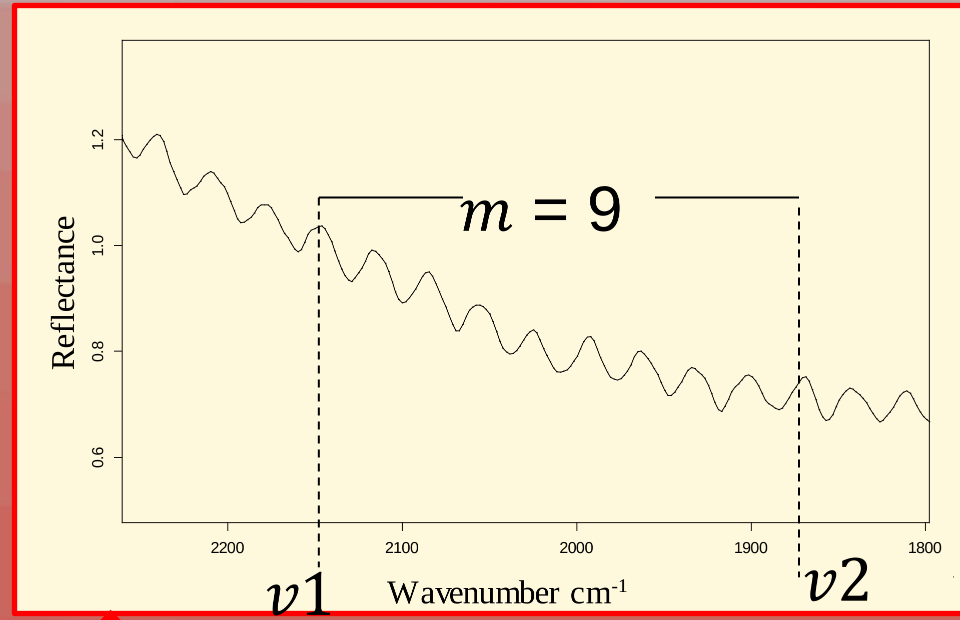
ε = Molar absorption coefficient

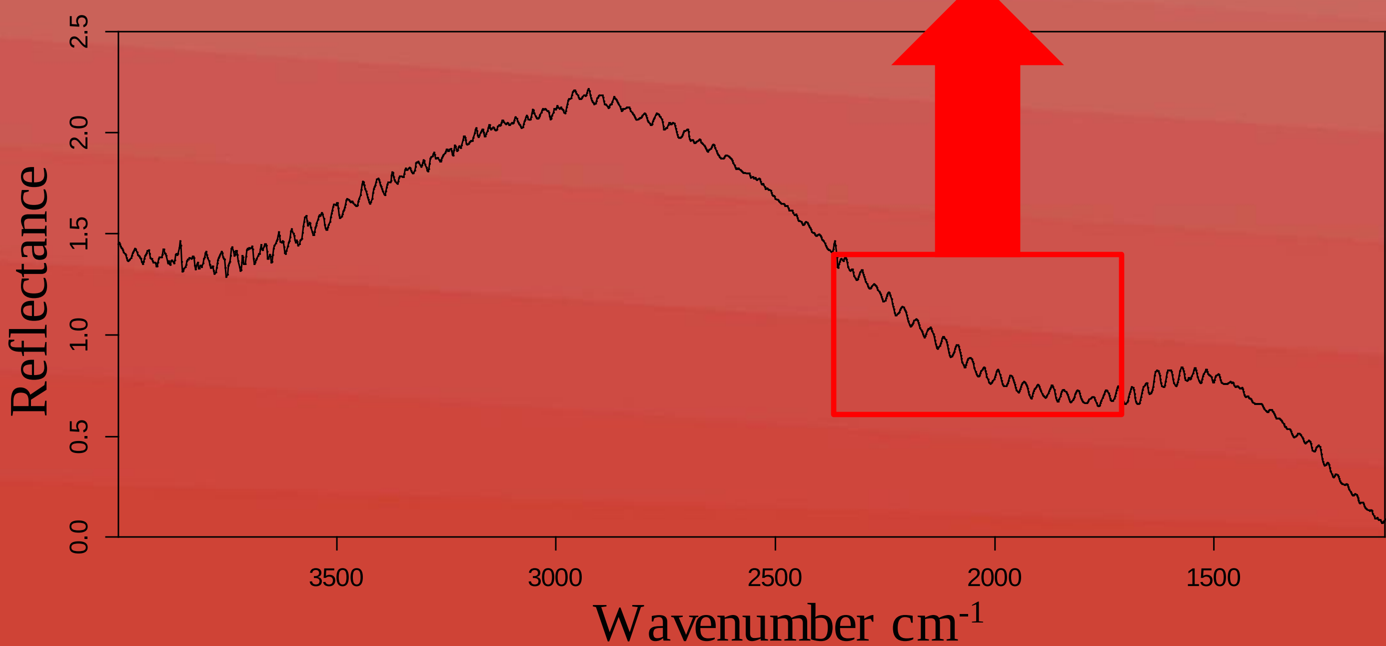
Thickness of the wafer

The reflection method

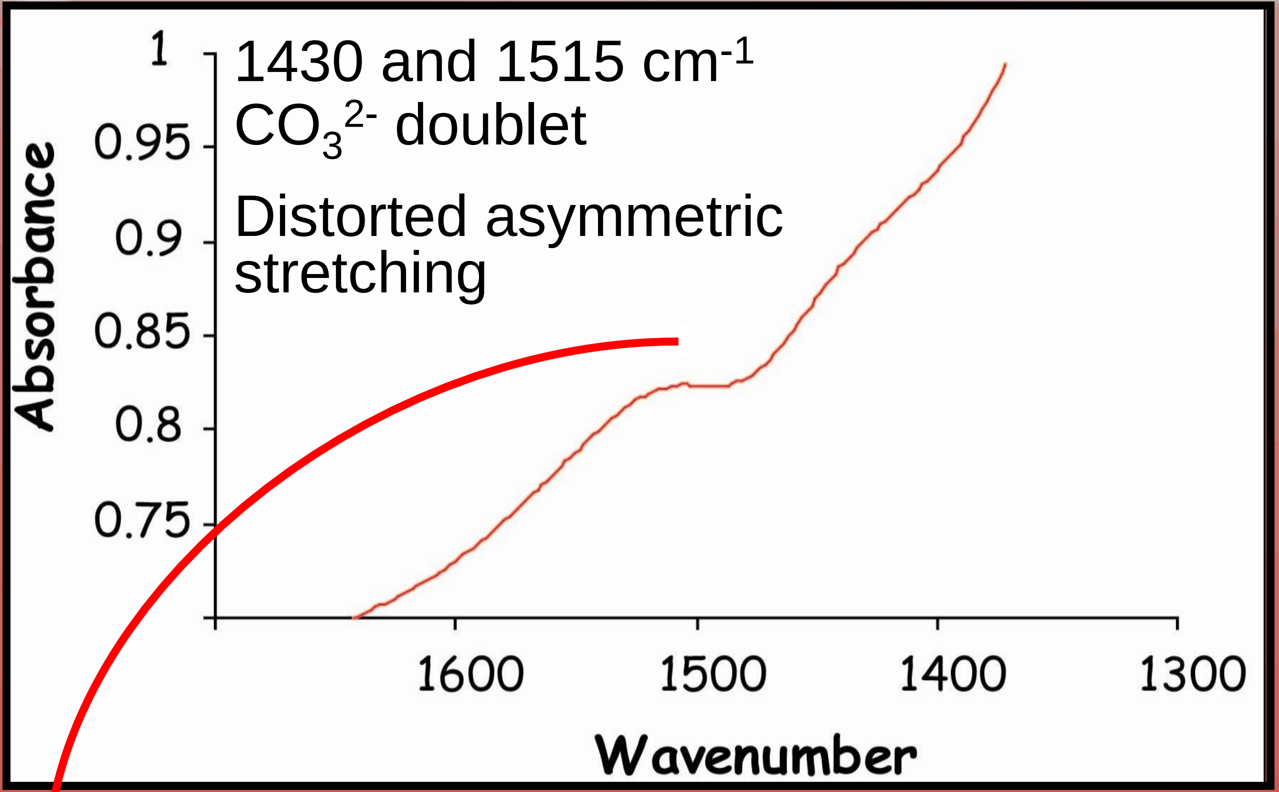
Wysoczanski & Tani (2006)

$$\partial = \frac{m}{2n\,(v1 - v2)}$$





Data reduction - Carbon Dioxide



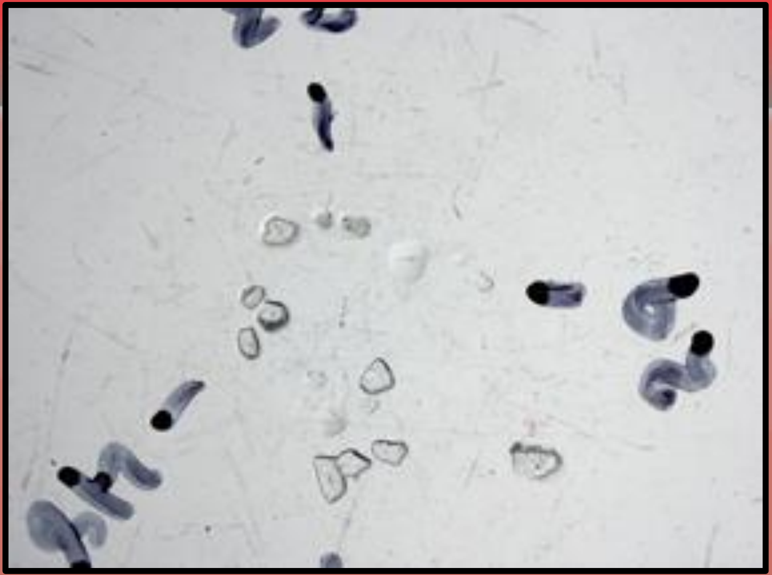
Shape of the background is complex → **Necessary to subtract a carbonate-free reference spectrum (Dixon et al., 1995)**

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_2O
- Fit to a pure carbonate doublet

*** Unpublished program by Sally Newman**



Inclusions	FTIR	Microprobe	LA-ICP-MS
	H2O – CO2	Major, S, Cl F	Trace
#1	✓	✓	✓
#2	✓	✗	✗
#3	✗	✓	✓

Popocatépetl is the site of open vent degassing since the begining of its new eruption phase in 1994

Open vent degassing:

- Release of large masses of gas (CO_2, SO_2)
- Short explosive activity

Need a large masses of degassing magma below the volcano.

New data on Popocatépetl

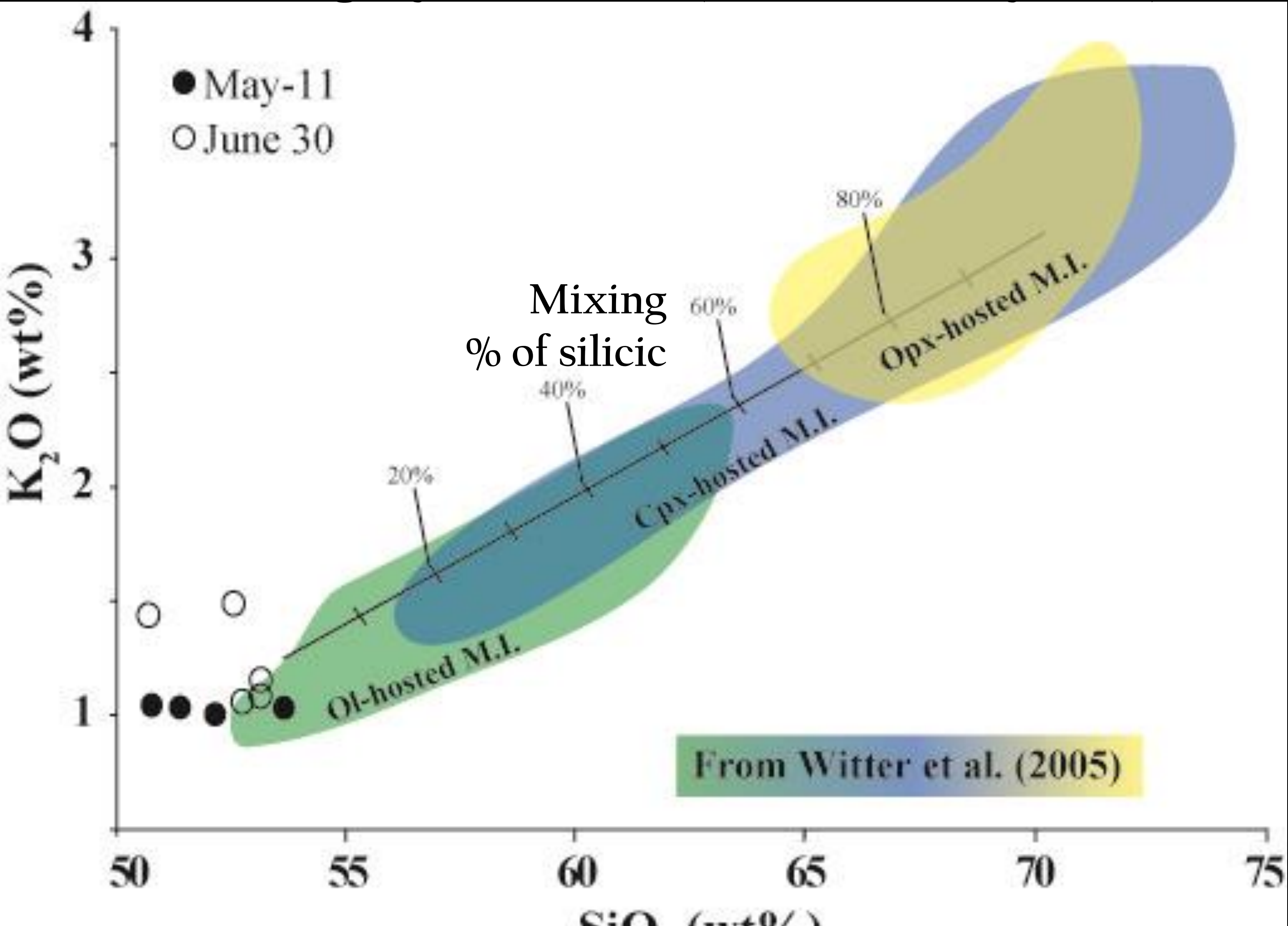
+

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 Fo_{87-90}

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

Similar to Straub and Del Pozzo (2001)

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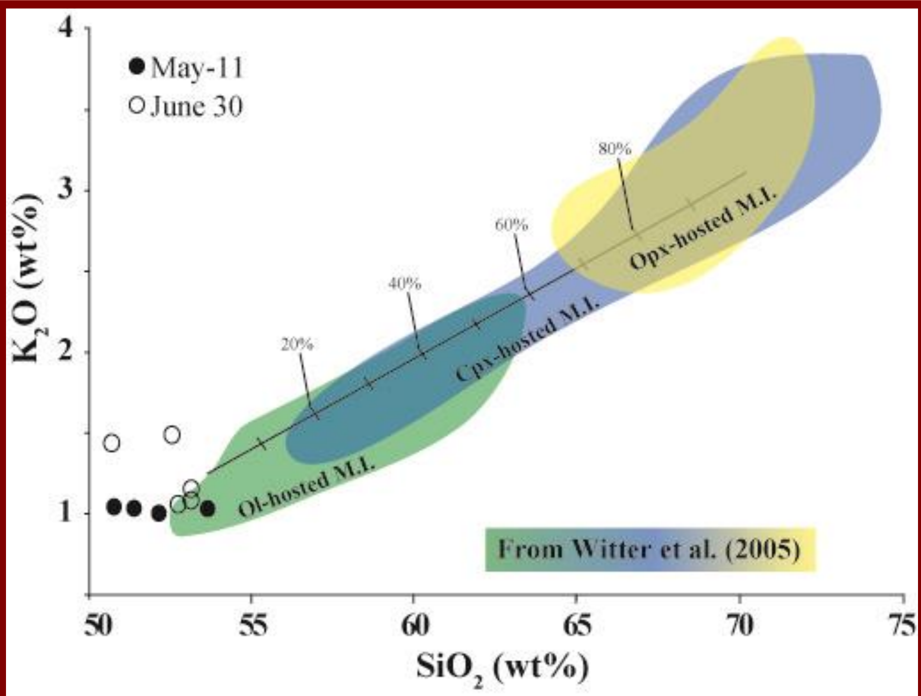


New Ol-hosted M.I.

Basalt –basaltic andesite

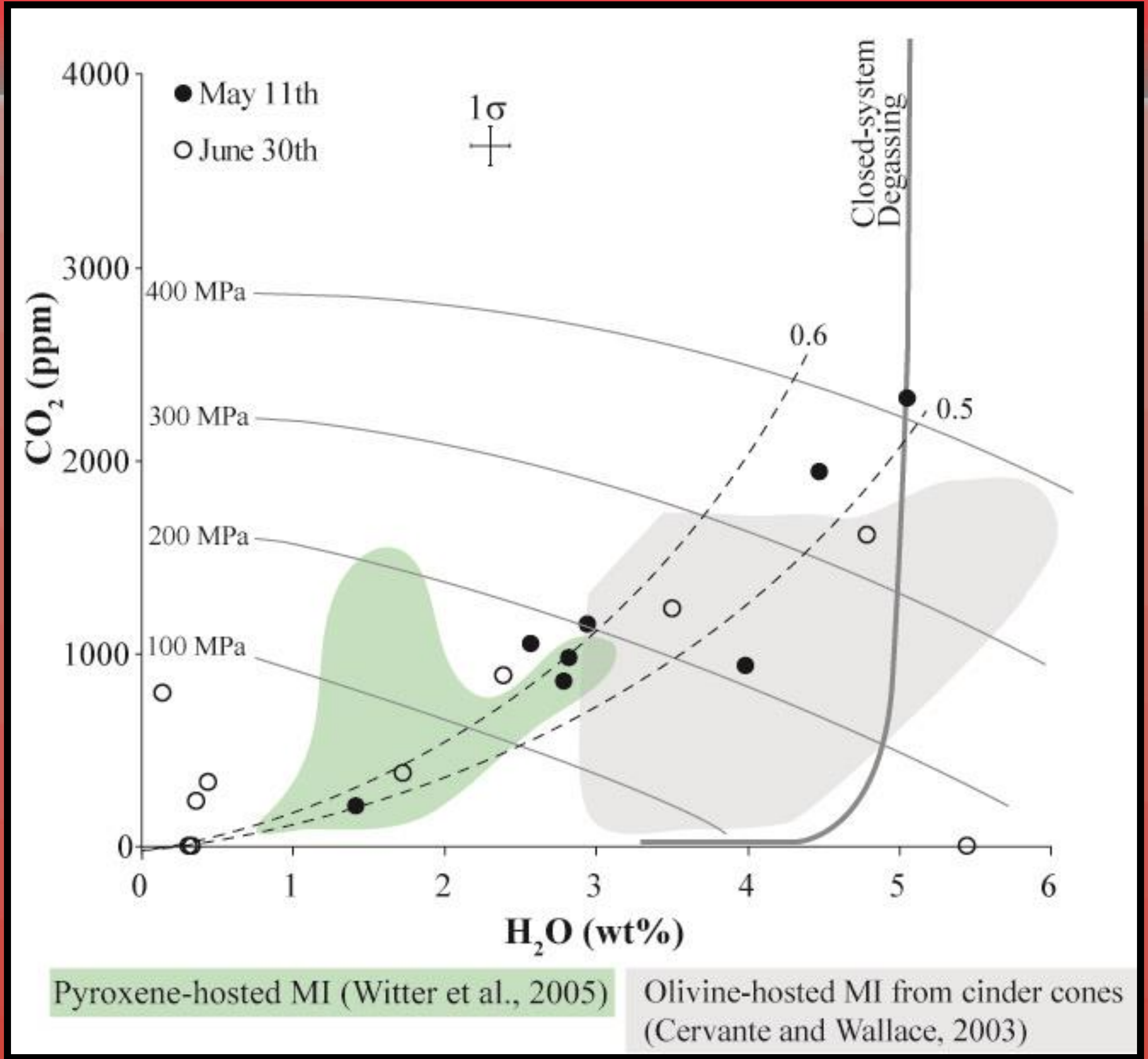
mafic melt that resupply and thermally sustain Popo’s system

Parent to more evolved components

MI trapped varably degassed melts over a wide range of pressures

+100-200MPa

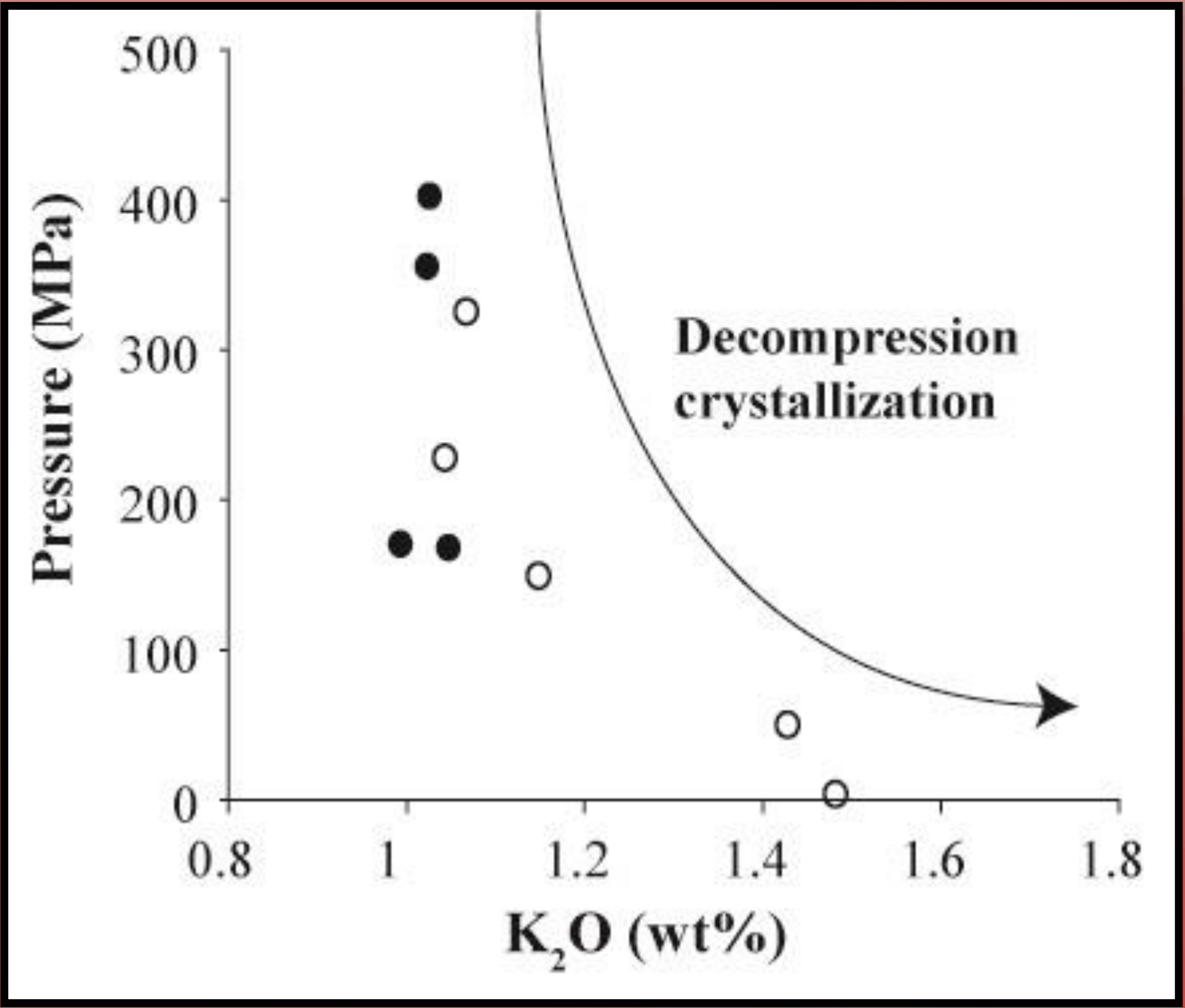
Depth, beneath the summit down to 17 km



From Roberge et al. (2009)

Not equilibrium degassing

Degassing induce crystallization of olivine



From Roberge et al. (2009)

Sat. Pressure ↓
As
Crystallization ↑

Degassing Model

Emission rates: (Delgado Granados, unpublished data)	SO_2	CO_2	
	7200 t/d	33280 t/d	April 23
	6150 t/d	37240 t/d	June 19

	April 23	June 19
CO_2/SO_2	4.6	6

} 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

Calulating the CO_2/SO_2 mass ratio of gas at equilibrium with the basaltic melt (M.I.) as a funcion of Pressure

Using

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

Degassing Model

Model Inputs:

Melt composition - average of all M.I.

T° - average of 1140°C from Sagawara, 2000

H_2O content

S - >150 MPa = 2000ppm, <150 linear varition with P

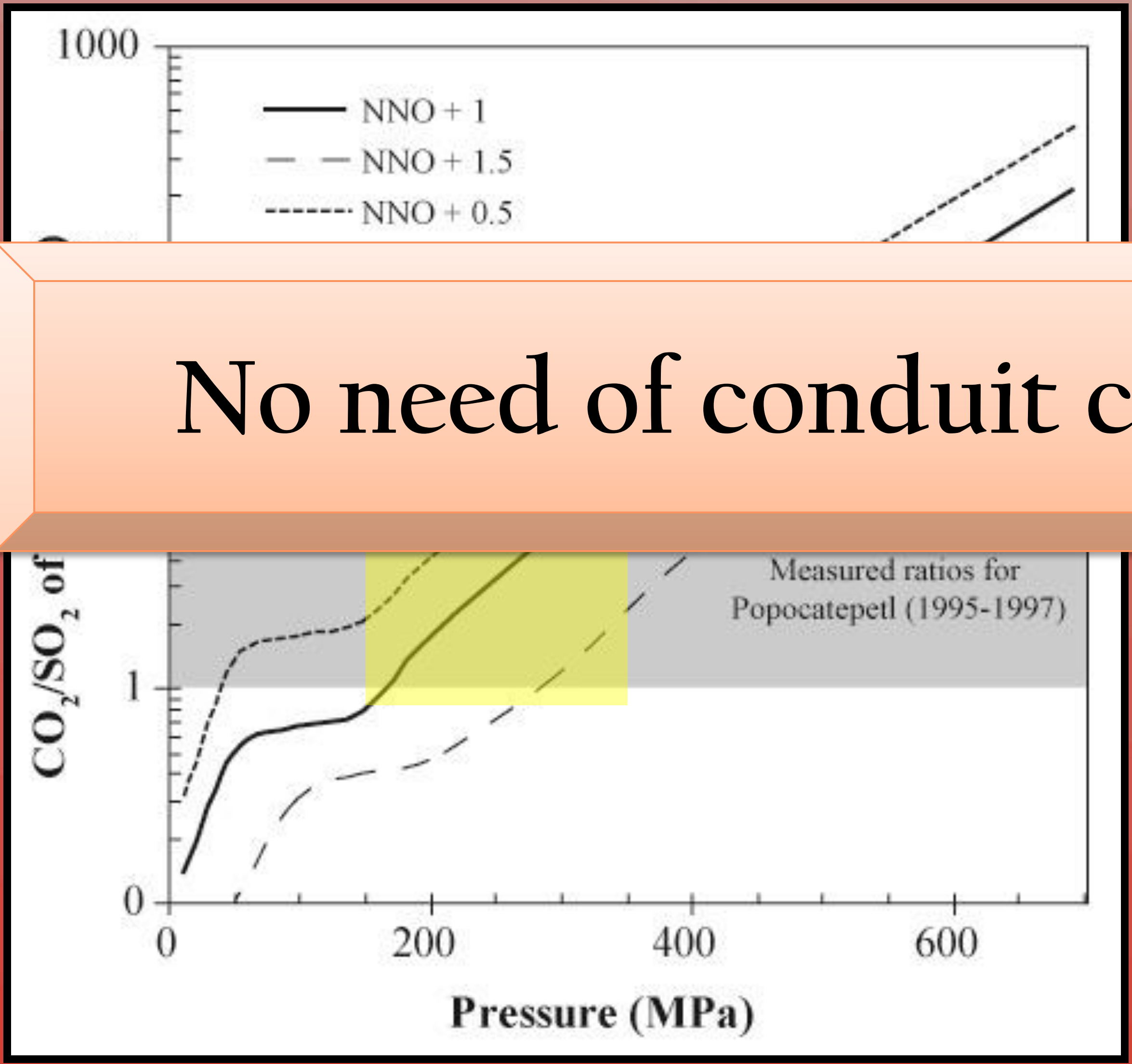
f_{O2} - Used range between NNO+0.5 to NNO+1.5 because f_{O2} directly related to the mole fraction of SO_2 in gas BIGGEST UNCERTAINTY OF THE METHOD

Degassing Model

Varied Pressure and
used the method of Pichavant (2005)
to get f_{SO2}

Converted f_{SO2}
in mole fractions using the
Redlich-Kwong equation of state

Degassing Model



From Roberge et al. (2009)

Degassing of mafic magma between ~150 and 350 MPa beneath

No need of conduit convection

comparable to the measured values (1-8)

Similar to Stromboli + Etna (Scaillet and Pichavant, 2005)

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

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Summary

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

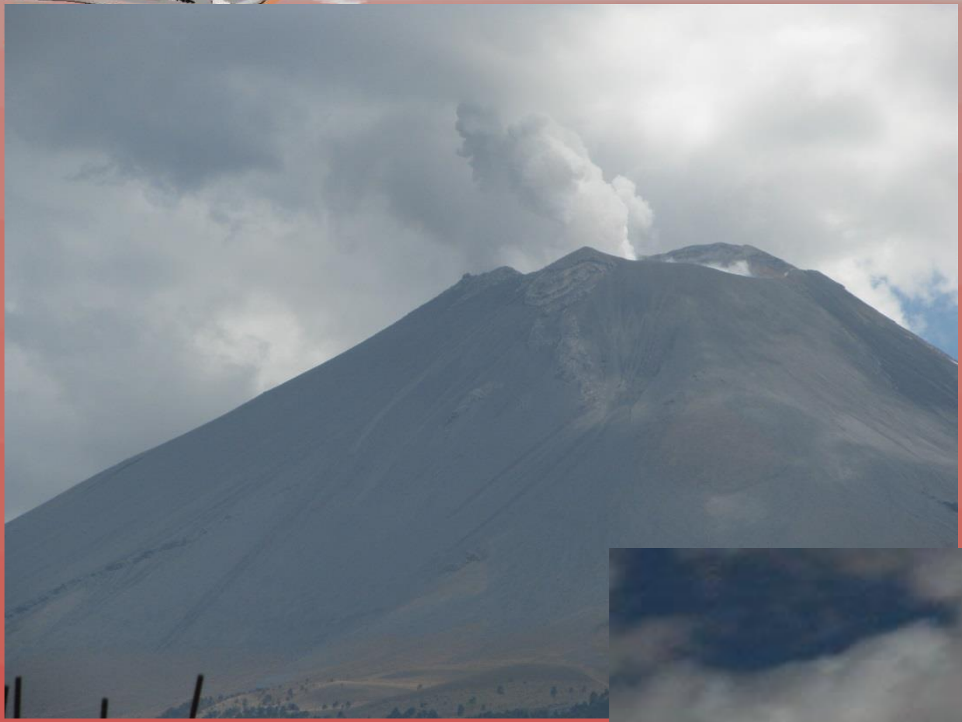
Degassing at Popocatepetl

What about the hypothesis of limestone assimilation proposed to explain the short-lived (0.5-3 hr), very high ($\leq$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, 2012



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.