

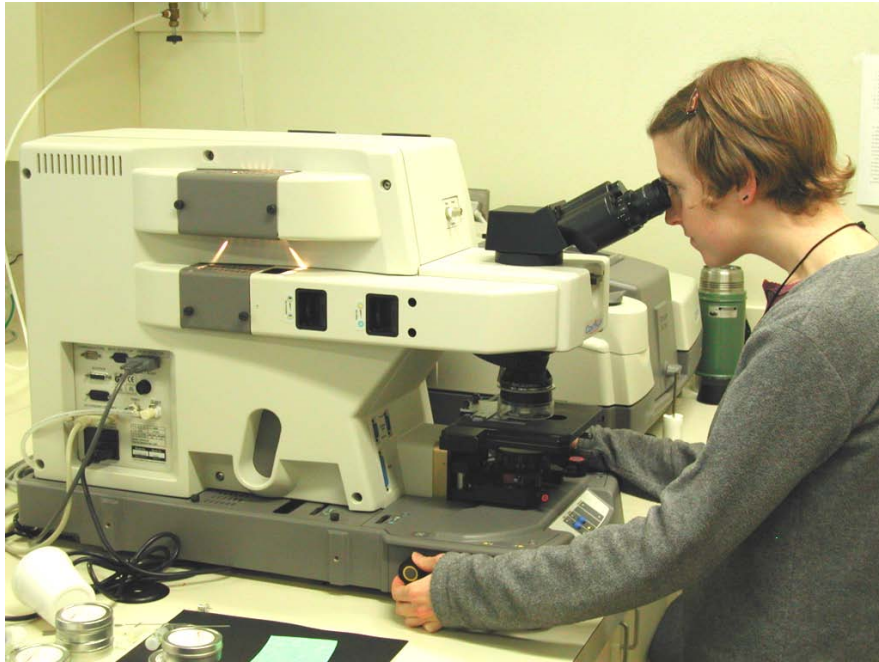
# How do we analyze glasses & melt inclusions for volatiles?

- Secondary ion mass spectrometry (SIMS or ion microprobe)  
H<sub>2</sub>O, CO<sub>2</sub>, S, Cl, F
- Fourier Transform Infrared (FTIR) spectroscopy  
H<sub>2</sub>O, CO<sub>2</sub>
- Electron microprobe  
Cl, S, F (H<sub>2</sub>O can be estimated “by-difference”)
- Confocal micro-Raman spectroscopy  
H<sub>2</sub>O
- Nuclear microprobe  
CO<sub>2</sub>
- Larger chips of glass from pillow rims or experimental charges  
can be analyzed for H<sub>2</sub>O and CO<sub>2</sub> using bulk extraction techniques  
e.g., Karl-Fischer titration, manometry

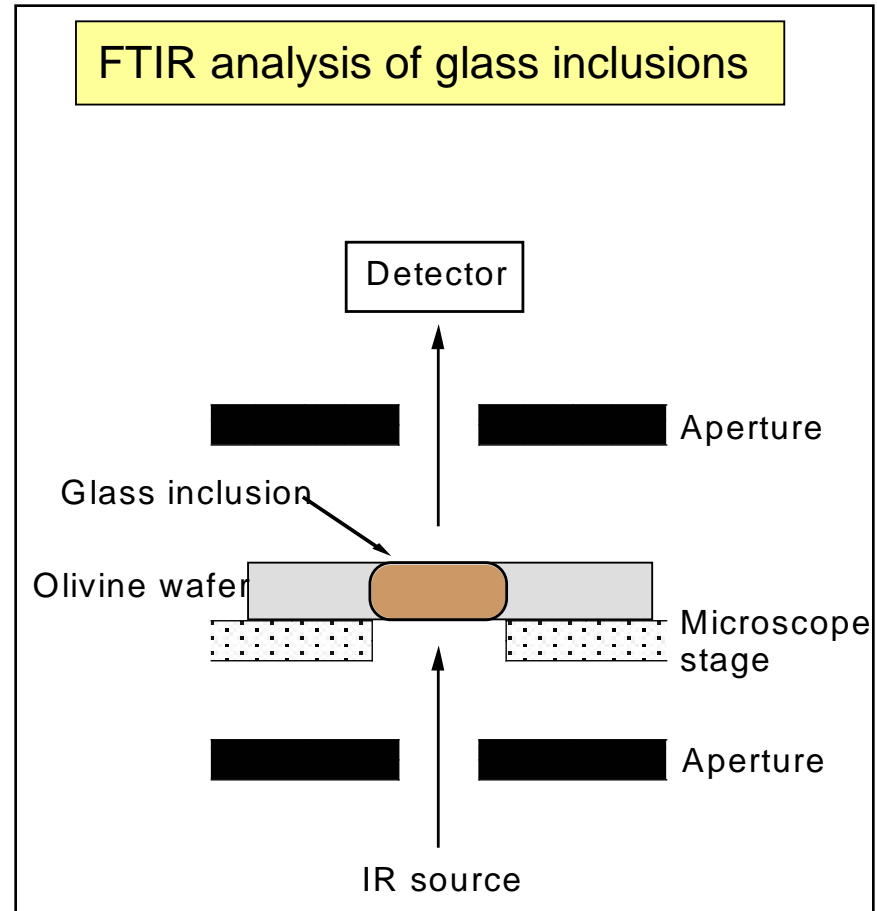
# Infrared Spectroscopy

- Molecules have specific frequencies at which they vibrate corresponding to discrete energy levels

## FTIR Microscope



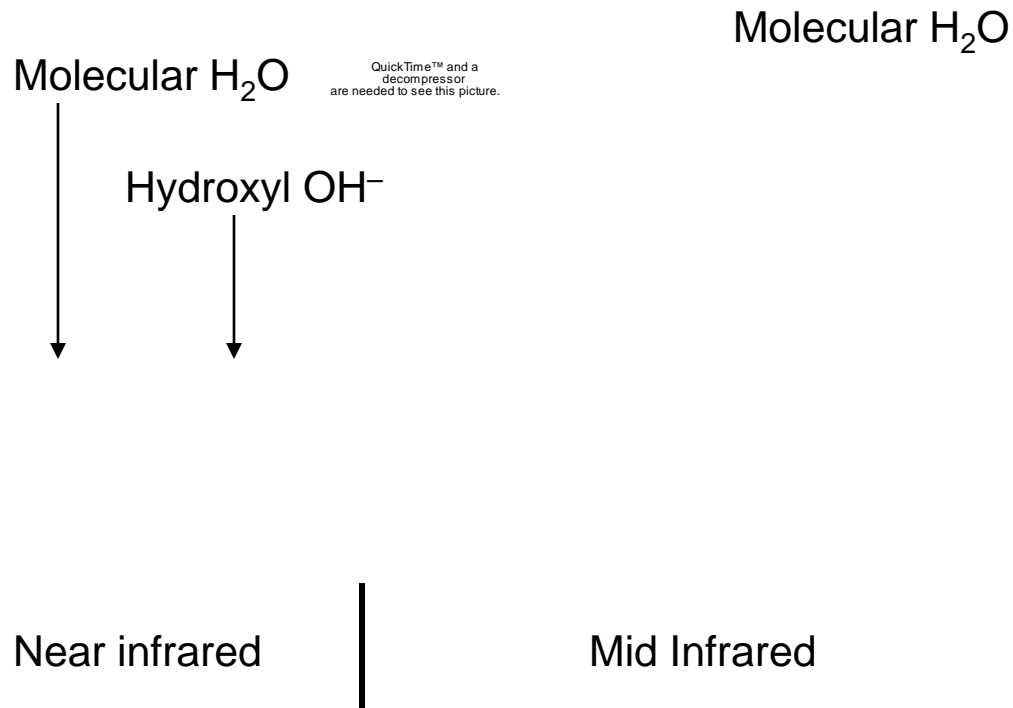
Fourier transform infrared (FTIR) spectrometer interfaced with an IR microscope



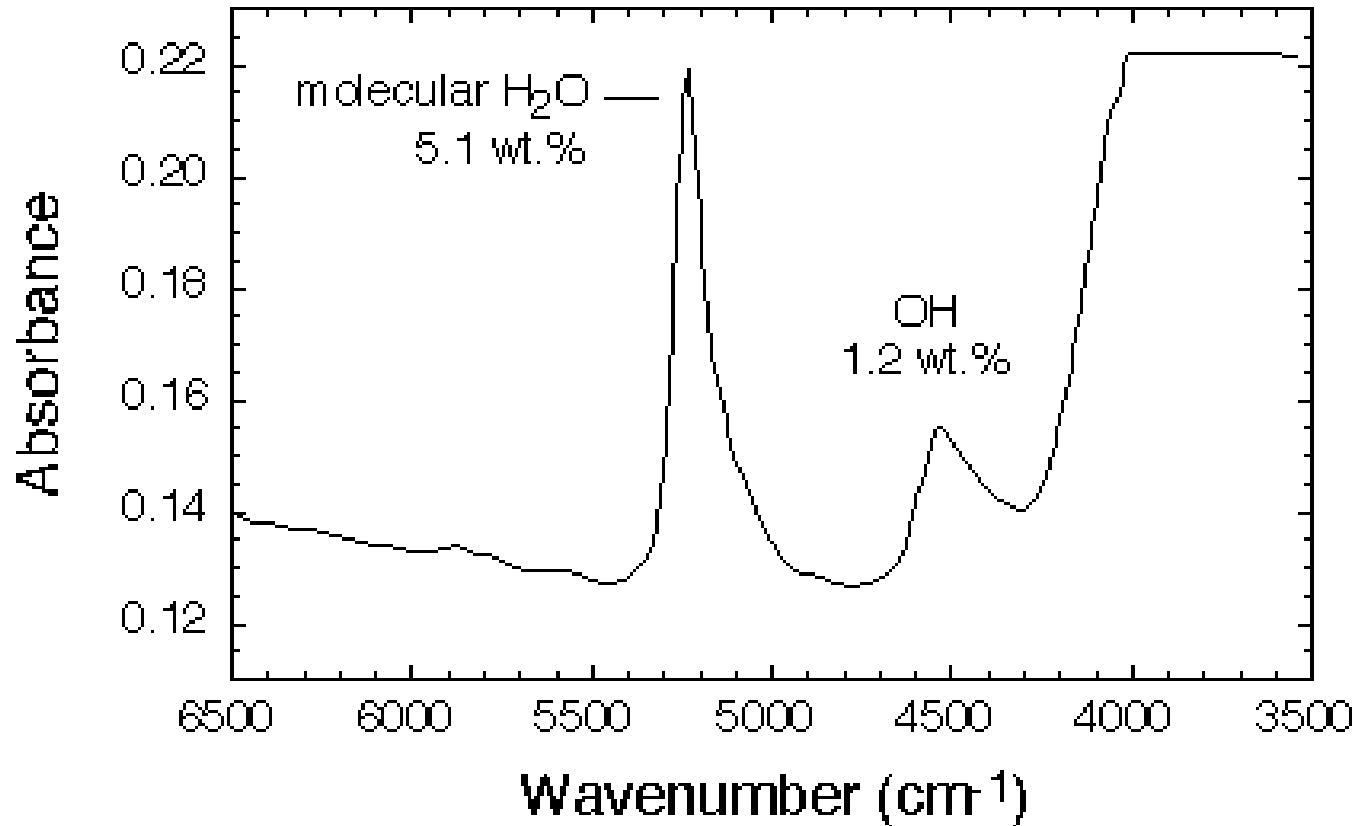
Note: Wafer thickness must be measured independently

# Infrared spectrum of rhyolitic glass

Fundamental O–H stretching vibration



# Near-IR hydroxyl (OH<sup>-</sup>) & molecular H<sub>2</sub>O peaks

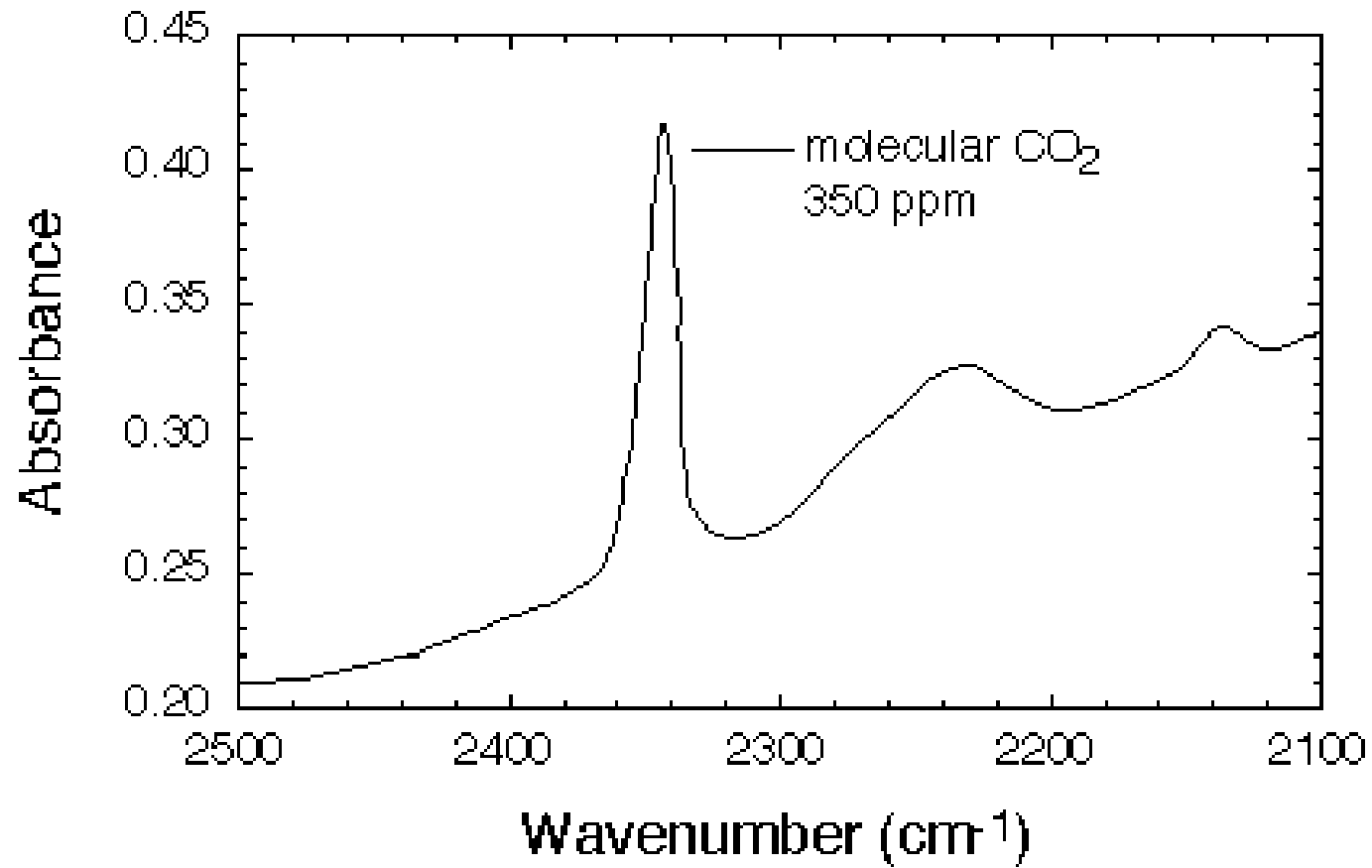


Pinatubo melt inclusion

# Water speciation in glasses determined by FTIR

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

# Molecular CO<sub>2</sub> in rhyolitic glass



Pinatubo melt inclusion

# Carbonate ( $\text{CO}_3^{2-}$ ) in silicate glasses

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

# Background beneath carbonate doublet

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



# Carbon Speciation in Silicate Glasses

- Basalt to nephelinite glass – carbonate
- Rhyolitic glass – molecular CO<sub>2</sub>
- Andesite glass – both species are present
- Both species have also been observed in a synthetic rhyolite, but natural rhyolite-composition glasses have only molecular CO<sub>2</sub> (Leschik et al., 2004)

# Background Subtraction

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

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decompressor  
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# Calculation of species concentrations using Beer–Lambert Law

$$C = \frac{M A}{\varepsilon \rho d}$$

C = weight fraction of absorbing species

M = molecular weight of species of interest

$\varepsilon$  = molar absorption coefficient (or extinction coefficient)

$\rho$  = room temperature density of glass; depends on glass composition & H<sub>2</sub>O content

d = path length (thickness of wafer)

- Absorption coefficients have to be determined using standard glasses for which total H<sub>2</sub>O and CO<sub>2</sub> have been measured using an independent technique, typically manometry (H<sub>2</sub>O & CO<sub>2</sub>) or Karl-Fischer titration (H<sub>2</sub>O)

# Comparison of H<sub>2</sub>O measured by FTIR & manometry

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

# Electron Microprobe Analysis of Volatiles

- Uses a focused electron beam to generate X-rays via electron transfer between inner orbitals in the target atoms
  - The wavelength of the resulting X-radiation is chemically diagnostic
  - The intensity of a particular X-ray is a function of the concentration of the element that produced it within the target volume.
  - Can be used to analyze S, Cl, and F and to estimate H<sub>2</sub>O by difference. Also used to analyze major & minor elements in MI & host crystals
- See excellent summary in Blundy & Cashman (2008)

# Electron Microprobe Analysis of Volatiles

## Sulfur

- Need relatively long counting times (several minutes on peak & background)
- Beam currents of 25 to 50 nA
- Can achieve detection limits of ~25 to 50 ppm & precision of  $\pm 10\%$  (or better) at the 1000 ppm level
- Wavelength of S  $K\alpha$  peak shifts with oxidation state. Need to take this into account because sulfide or sulfate standard will have different peak positions than glass unknowns (Carroll & Rutherford, 1988; Wallace & Carmichael, 1994)
- Can measure the S  $K\alpha$  peak position & use it to estimate oxygen fugacity. Wavelength scans take ~1 hour per scan.

# Sulfur Speciation

QuickTime™ and a  
TIFF (Uncompressed) decompressor  
are needed to see this picture.

Minerals

QuickTime™ and a  
TIFF (Uncompressed) decompressor  
are needed to see this picture.

Basaltic glasses

# Electron Microprobe Analysis of Volatiles

## Chlorine & Fluorine

- Also need relatively long counting times (as much as 400 seconds on peak) to achieve maximum precision
- Beam currents of 50 to 100 nA
- Can achieve precision of  $\pm 5\%$  for Cl and  $\pm 10\text{--}20\%$  for F (e.g., Davis et al., 2003). Detection limit for Cl can be as low as 10 ppm (e.g., Michael & Cornell, 1998).
- Must correct for interference of Fe on F. In basaltic glasses, the interference can be 3x as large as the F peak itself.



# Electron Microprobe Analysis of Volatiles

## Alkali migration

- Migration of Na & K caused by electron beam irradiation occurs during analysis of hydrous glasses
- Causes Na (& K) to be low, and Si & Al to be high
- Can be mitigated by using low sample currents (2-4 nA) and analyzing Na, K, Al, and Si first
- Best method is to count in short intervals and extrapolate counts per second back to zero time.

## H<sub>2</sub>O by difference

- Calculated as 100% – sum of all analyzed elements
- Can achieve values within 0.5 to 0.7 wt% of true H<sub>2</sub>O (Devine et al., 1995; Roman et al., 2006; Humphreys et al., 2006).