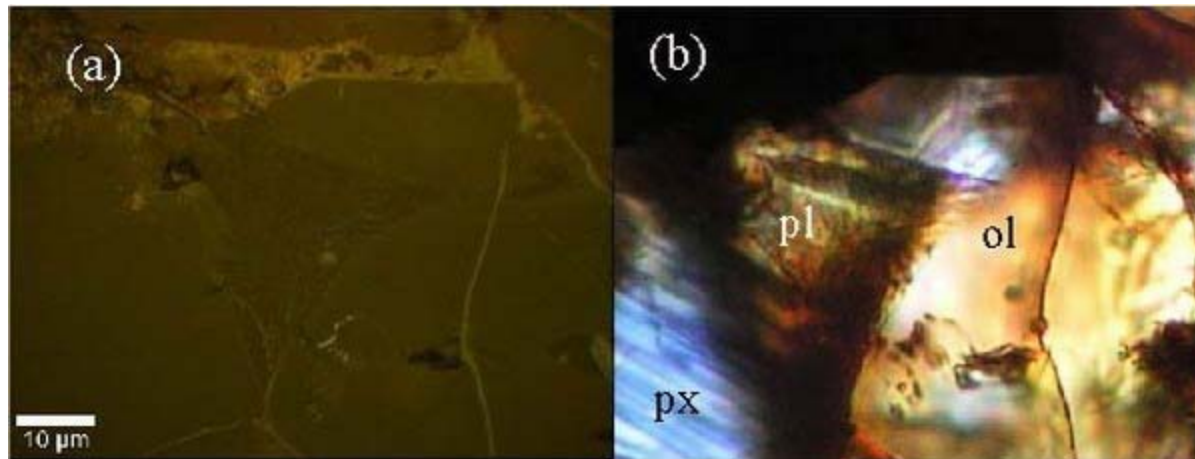


Spectroscopy: Lecture 6

Infrared spectroscopy and Its Applications in Geophysics and Materials Sciences

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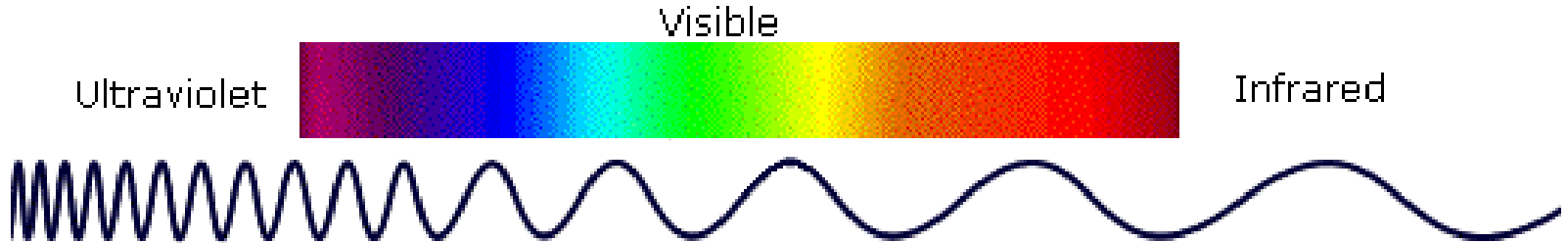


Outlines

Infrared Spectroscopy

- **Absorption Spectroscopy**
- **Near Normal Reflectance Spectroscopy**
- **Diffuse Reflectance Spectroscopy**
- **Thermal Emission Spectroscopy**

EM Spectrum in the UV-IR Spectral Range



Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Frequency, ν (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related: and *where* c is the speed of light, 3×10^{10} cm/sec.

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu} \quad \dots\dots\dots (i)$$

Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda} \quad \dots\dots\dots (ii)$$

Where h = Planck's constant, 6.6×10^{-34} joules-sec
Note that energy is directly proportional to frequency and inversely proportional to wavelength.

The IR region is divided into three regions: the near, mid, and far IR. IR spectra are sometimes reported in μm , although another unit, $\bar{\nu}$ (nu bar or *wavenumber*, cm^{-1} , ($1/\lambda$ where *wavelength is in cm*)), is currently preferred.

IR Spectroscopy

- **IR Absorption Spectroscopy**

Laboratory characterization of minerals and materials

- **Near Normal Reflectance Spectroscopy**

Laboratory applications for determining both n and k as a function of λ

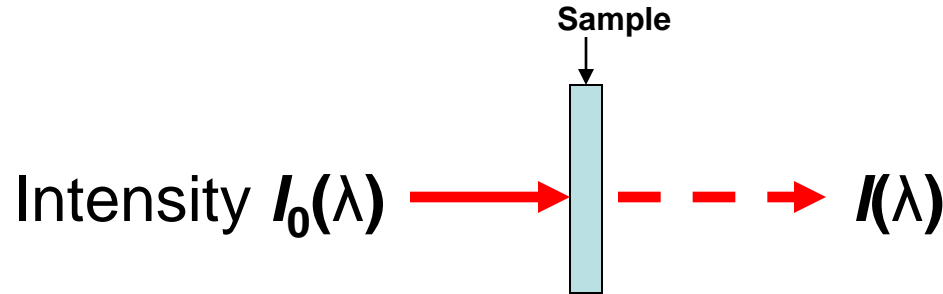
- **IR Reflectance Spectroscopy**

Diffuse Reflectance or Bi-directional Reflectance spectroscopy has both laboratory and remote sensing applications

- **Thermal IR Emission Spectroscopy**

Has both laboratory and remote sensing applications

Absorption of infrared light



- **Excitation of molecular vibrations, & phonons (quanta of lattice vibrations) in a crystal.**
- ▶ **Identification of molecular bonds, crystal structures, morphology**

When photons enter an absorbing medium, they are absorbed according to Beers Law:

$$I = I_0 e^{-kx} \quad (i)$$

where I is the observed intensity, I_0 is the original light intensity, k is an absorption coefficient and x is the distance traveled through the medium. The absorption coefficient is traditionally expressed in units of $1/\text{cm}$ (inverse cm) and x in cm. Equation (i) holds for a single wavelength. At other wavelengths, the absorption coefficient is different, and the observed intensity varies. The absorption coefficient as a function of wavelength is a fundamental parameter describing the interaction of photons with a material.

Specular & Diffuse Reflection and Thermal Emission

- **Near Normal reflection** is the mirror-like reflection of light. The Fresnel's equation for the reflection of normal incident radiation is
$$r = (n - ik - 1) / (n + ik + 1) = r e^{i\theta}$$
Where n and k are the real and imaginary part of refractive index, and θ = phase angle
Reflection $R = (r)^2$
Using Kramer-Kronig analysis¹ values of both n and k as a function of λ can be calculated from reflectivity data.
- **Diffuse reflectivity or bi-directional reflectivity** is measure 10-degree off normal or the light source to avoid back-scattered light and to maximize the intensity of the absorption bands. In diffuse reflection photons may get multiple reflection or scattering in between the grains, some may get absorbed and some escape from the surface. These escaped photons (diffusely reflected) photons carry information about the absorption of the material or the chemical fingerprints. Diffuse reflectance spectroscopy in the visible and near infrared (VNIR) spectral region has been successfully used for remote sensing of minerals.
- **Thermal Emission spectroscopy (TES)**³ measures thermal radiation emitted from the surface of an object which is due to the object's temperature relative to a blackbody that is at the same temperature as the sample.

¹Philipp & E. A Taft, Phys. Rev. **113**, 1002-1005 (1959).

²Gaffey, S. J., Amer. Mineral. **71**, 151-162 (1986).

³Ruff, S.W. et al., J. Geophys. Research, **102**, (B7), 14,899-14,913 (1997).

Sample Preparation for IR Absorption Spectroscopy

1. *LIQUIDS:*

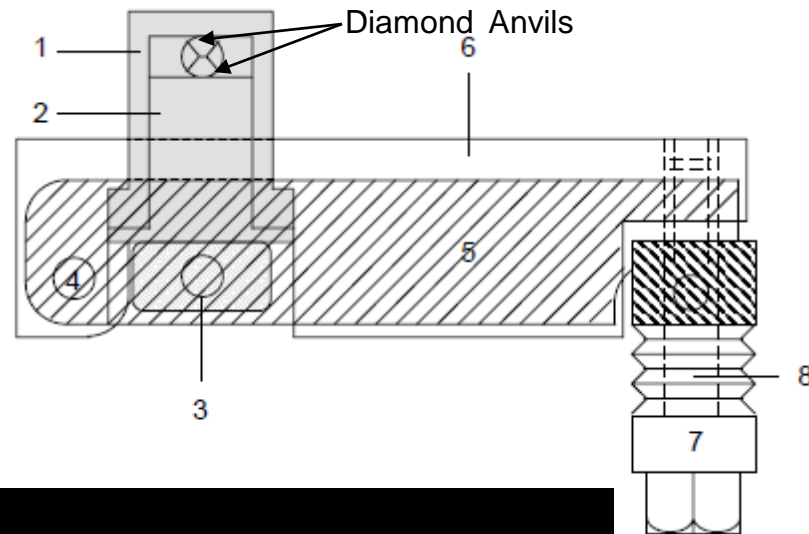
- Place a small drop of the liquid compound on one of the KBr or NaCl plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum. If the sample is too concentrated, separate the plates and wipe one side clean before putting them back together.

2. *SOLIDS*

- A mull is prepared by grinding the sample with mineral oil and sandwiching the resultant paste between sodium chloride plates.
- The solid can be dissolved in a solvent and placed in a special cell, called a solution cell, which is made of sodium chloride. This gives what is called a solution spectrum.
- A KBr pellet is prepared by grinding the solid sample with solid potassium bromide (KBr) and applying great pressure to the dry mixture. Again, KBr is chosen because it is transparent to infrared radiation. If the pellet is prepared properly, one can actually see through it, as through a pane of glass.
- Prepare a thin film of the solid samples by compressing powdered samples between diamond anvils of a high pressure diamond anvil cell.

Diamond Anvil Cells

Schematics of the Mao-Bell type diamond anvil cell. The cylinder-piston assembly is labeled (1) and (2) Pressure is generated by tightening the drive screw (7). Other parts include: (3) thrust block, (4) fulcrum, (5) lever, (6) main body and (8) Belleville washers.



Typical the high pressure anvil face is ~0.8 mm diameter, thickness 2 mm, and base ~3 mm diameter.

Ray Path in Diamond Anvil Cell Used for High Pressure Raman Scattering

Diamond Refractive index

$$n_{\text{diamond}} = 2.4195 \text{ at } 589.3\text{nm}$$

Critical angle for diamond:

$$\theta_c = \text{Sin}^{-1} (1/ n_{\text{diamond}})$$

$$\theta_c = 24.4^\circ$$

If the height of diamond anvil is h and the radius of opening is r

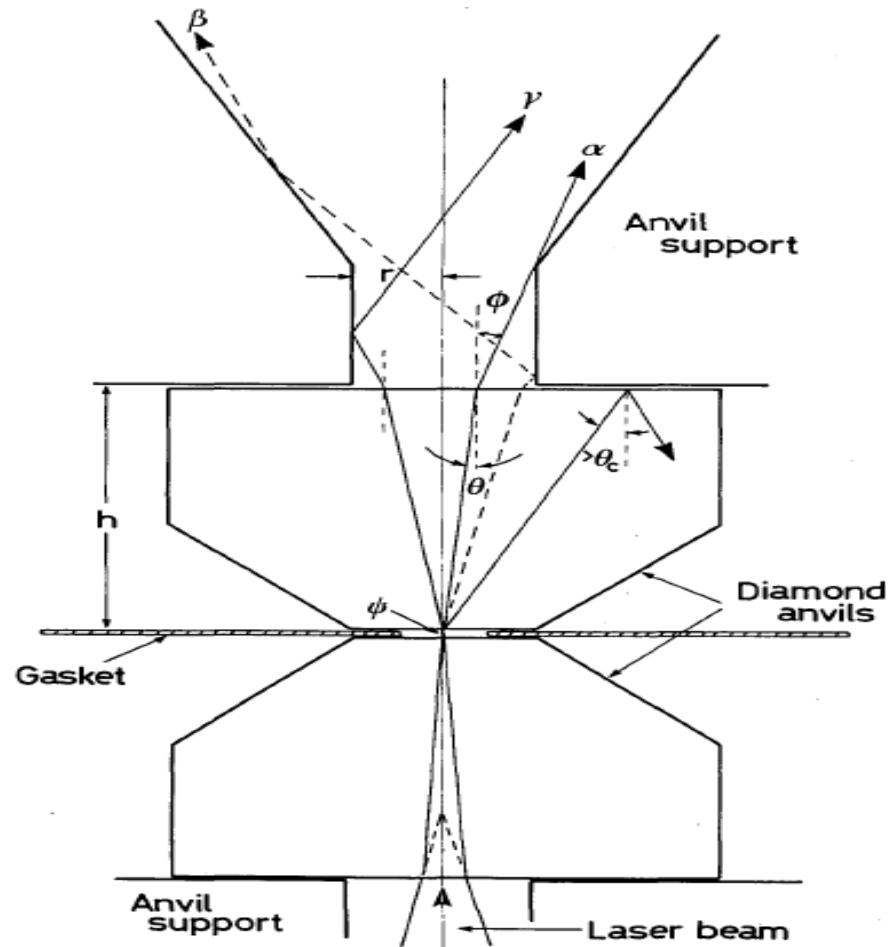
$$\theta_D = \tan^{-1} (r/h)$$

Typically $r = 1 \text{ mm}$ and $h = 2 \text{ mm}$

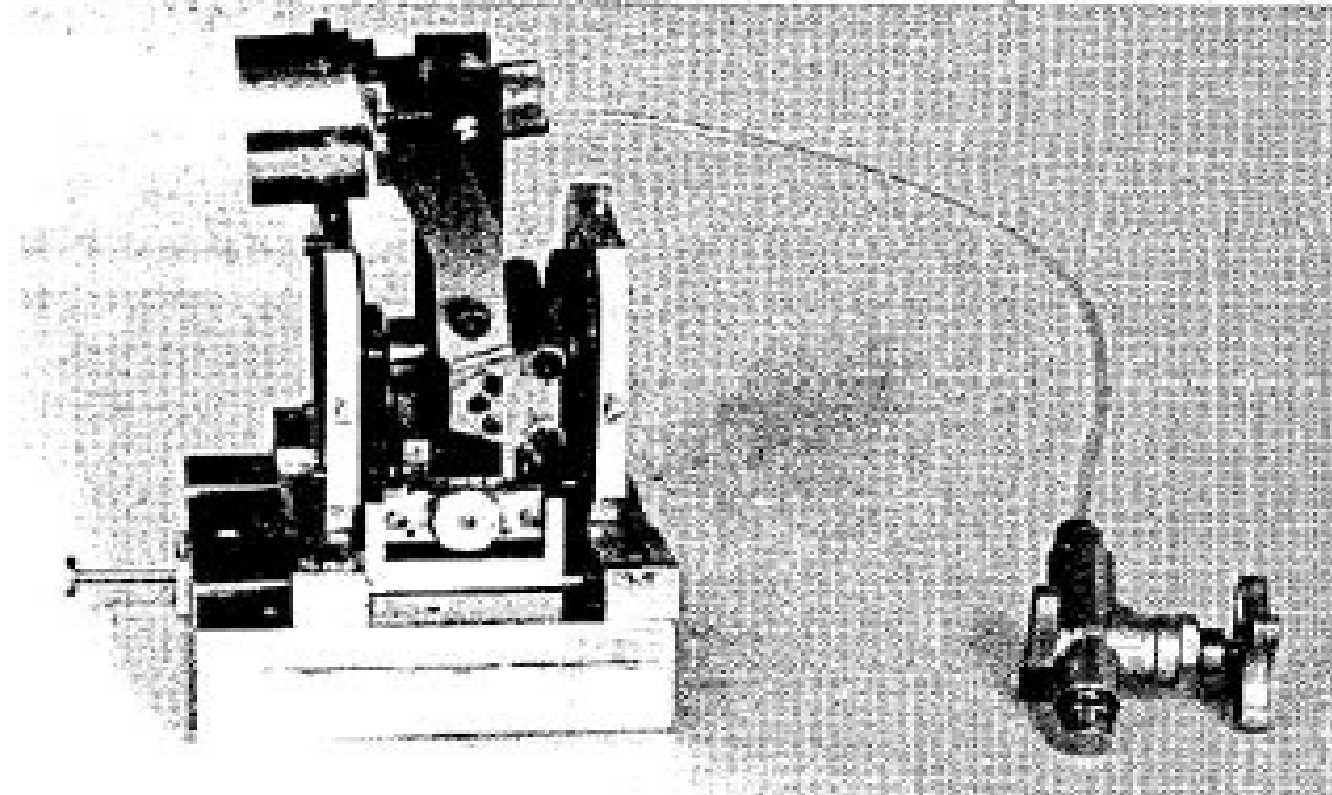
$$\theta_D = 12.7^\circ \text{ and } \Phi = 32.1^\circ$$

$$NA_t = 0.53$$

Only rays with $\theta < 5.80$ will pass directly out of the cell (e.g., ray α) but others (e.g., rays β and γ) with $5.8 < \theta < 12.70$ will be collected after reflection from the walls of the support material.



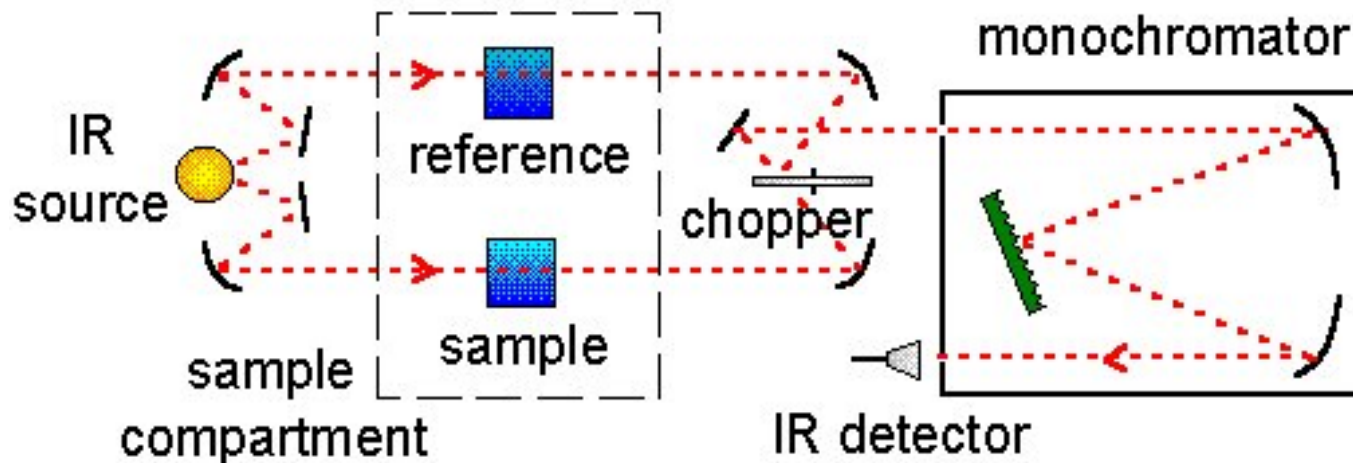
Diamond Anvil Cell with KBr Lenses for IR Absorption Spectroscopy



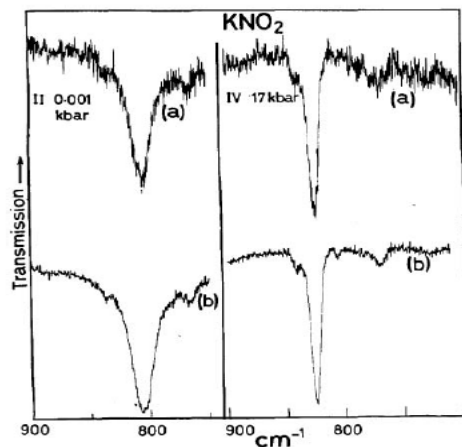
The beam condenser: right, the condenser lens (40-mm diam) and left, the collection lens (KBr, 25-mm diam); .

Adams, D. M. & S. K. Sharma *J. Phys. E.*, **10**, 838-842 (1977); *Appl. Optics*, **18**, 594-595 (1979).

Dispersive IR spectroscopy Instrumentation



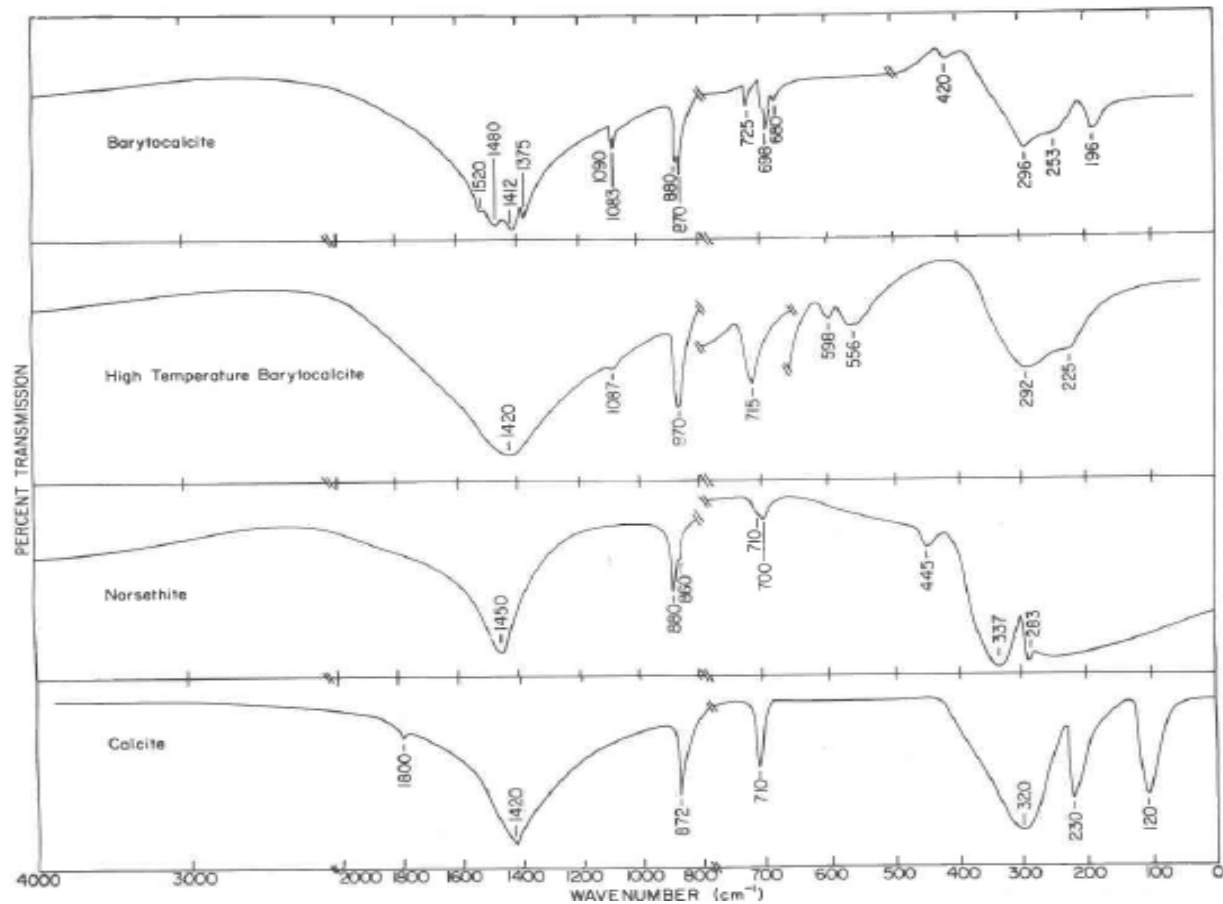
©1995 CHP



The $\delta(\text{NO}_2)$ region of KNO_2 in a gasketed DAC. Gasket, 0.1-mm thick Inconel; hole, 0.4-mm diam. The reference beam was attenuated with a mask having a 0.4-mm diam hole, and $\times 20$ scale expansion was used. Spectral slit width 3.7 cm^{-1} . Over-all transmission of sample $\sim 0.86\%$. At ambient pressure the sample is in phase II but has transformed to phase IV by 1.7 GPa (10 kbar = 1 GPa). (a) Single scan without beam condenser; (b) Single scan with beam condenser.

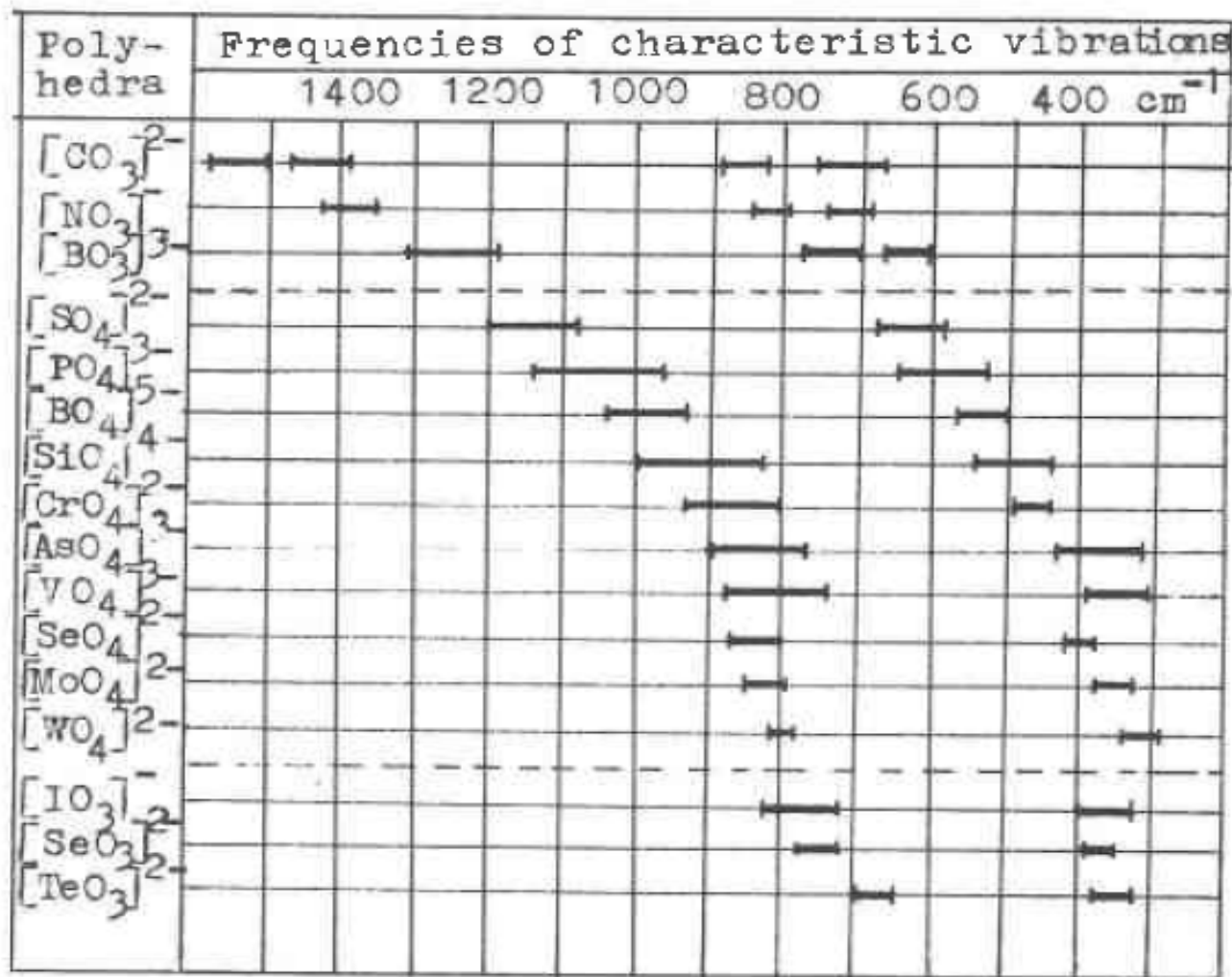
Adams & Sharma, *Appl. Optics*, **18**, 594-595 (1979).

IR Spectra of carbonate minerals in KBr pellets



Scheetz, B. E. and White, W. B., *American Mineralogist*, **62**, 36-50 (1977)

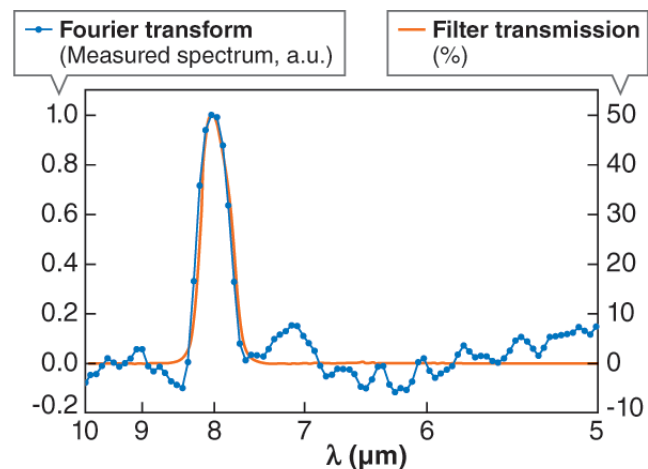
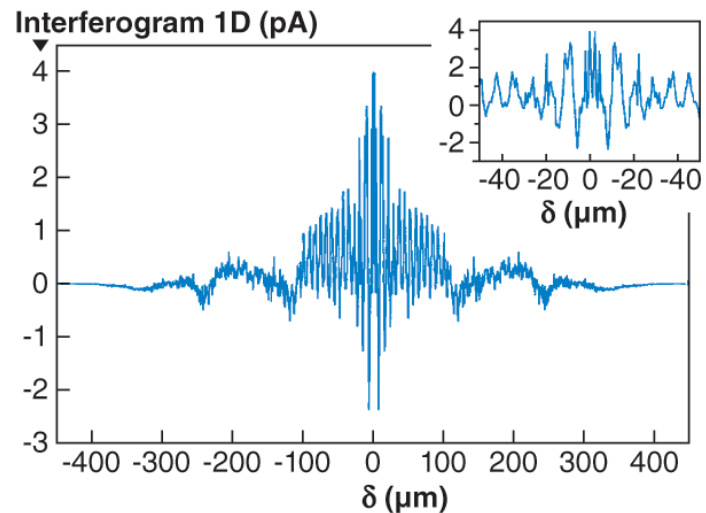
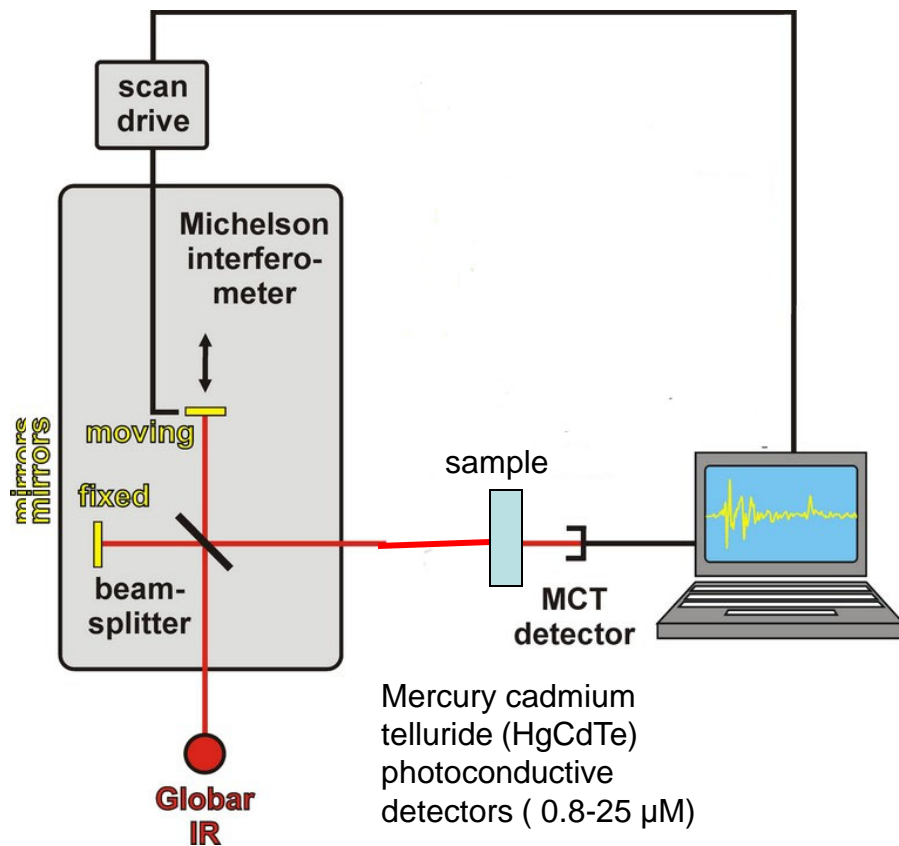
Characteristic IR Absorption Frequencies of closed Polyhedra



The limits of characteristic vibrations of "closed" and "open" atomic polyhedra in minerals

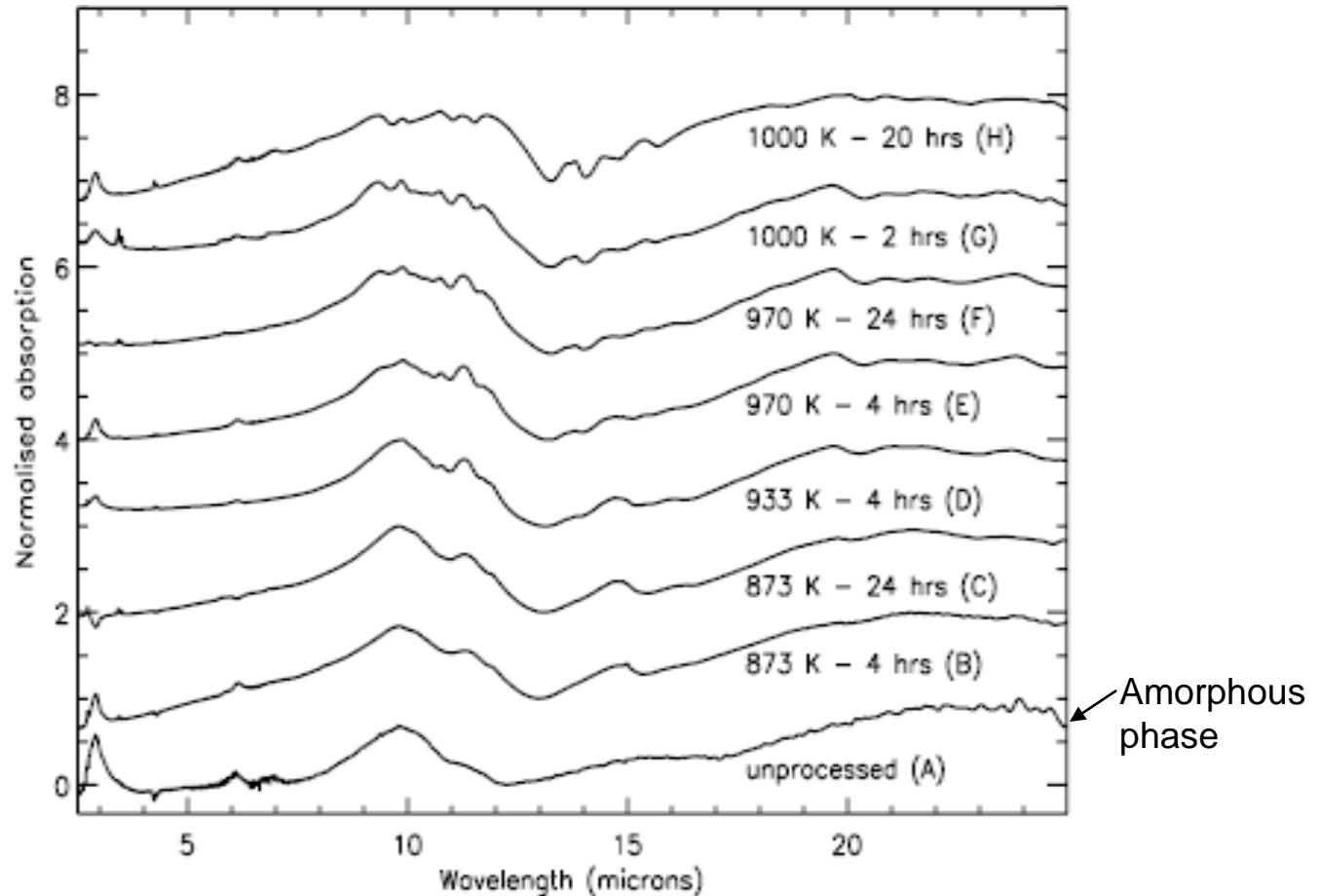
Classes or radicales	Frequencies of characteristic vibrations		Classes or radicales	Frequencies of characteristic vibrations	
	ν_3	ν_4		ν_3	ν_4
Carbonates	1570-1500 1475-1390	765-675	Beryllates	850-700	400-320
Nitrates	1430-1350	750-695	Aluminates	840-760	460-380
Borates	1315-1190	680-605	Titanates	800-690	?
Sulphates	1200-1080	680-580	Ferriates	660-540	-
Phosphates	1140-960	650-525	Magnesiates	620-500	170-130
Orthoborates	1040-940	570-500	Zincates	570-450	140-100
Silicates	1000-830	540-435	LiO ₄ ⁷⁻	460-370	-
Chromates	930-800	400-360	FeO ₄ ⁶⁻	400-320	-
Arsenates	900-760	420-310	SiO ₄ ³⁻	880-670	?
Vanadates	880-740	390-310	AlO ₆ ⁹⁻	700-580	200-140
Selenates	870-800	415-375	TiO ₆ ⁶⁻	580-430	-
Molibdates	850-790	375-330	FeO ₆ ⁹⁻	560-400	-
Wolframates	815-785	340-295	MgO ₆ ¹⁰⁻	420-300	130
Iodates	825-720	400-320	ZnO ₆ ¹⁰⁻	370-270	-
Selenites	770-720	390-350	LiO ₆ ¹¹⁻	320-230	-
Tellurites	700-650	375-315			

FT-IR Spectroscopy Instrumentation



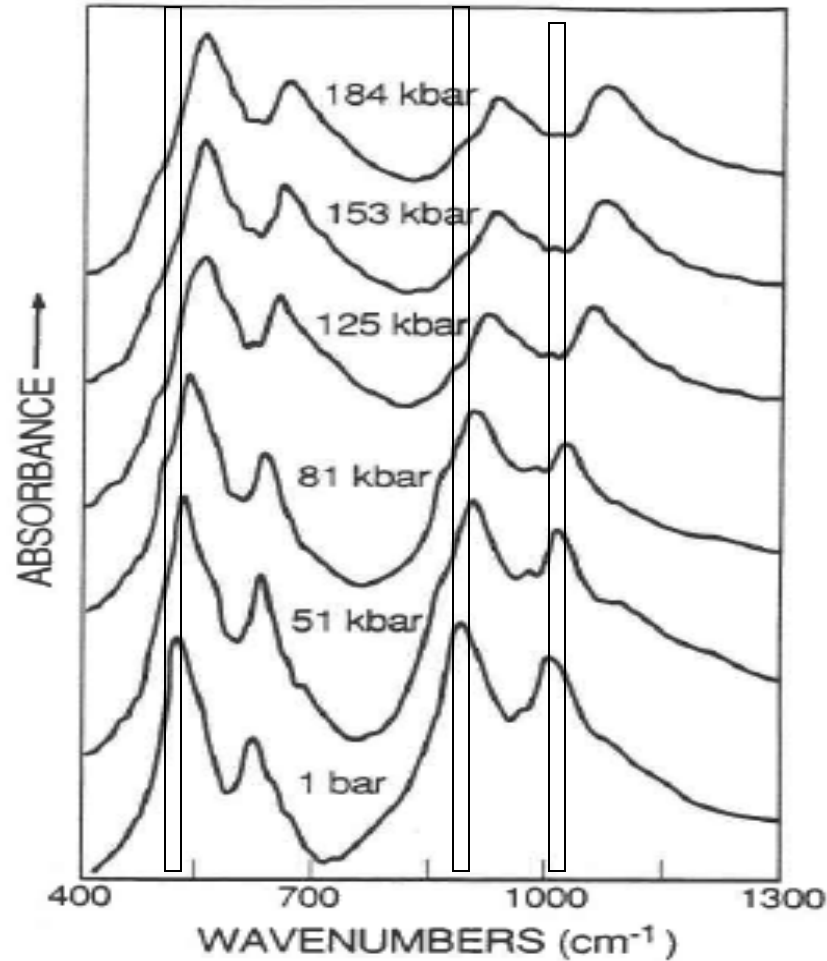
Normalized IR spectra of MgSiO₃ annealed at various temperatures

Crystallites with many different Si-O stretching Modes around 10 μm ,
Amorphous state gives broad Si-O band.



S. P. Thompson et al. (2002) *Astronomy & Astrophysics*, **395**, 705–717.

FTIR Spectra of Mg_2SiO_4 (Fo) at High Pressures



Wang et al., *Amer. Mineral.*, **78**, 469-476 (1993).

Reflectance Spectroscopy

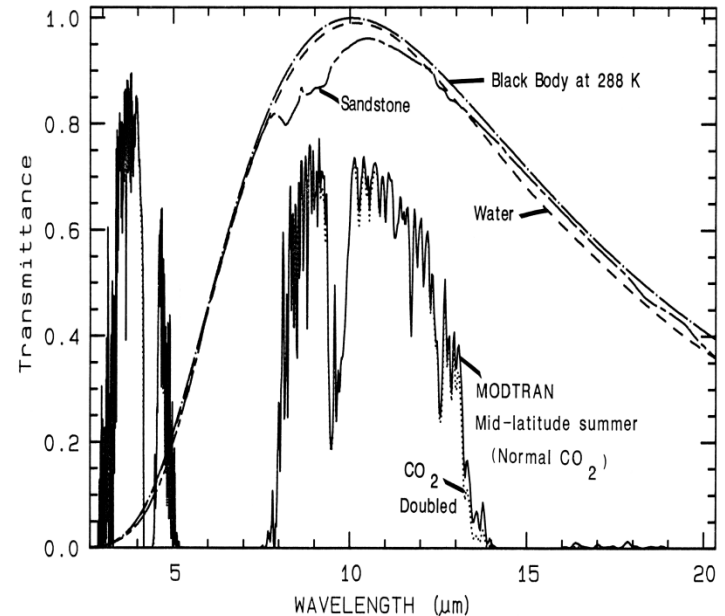
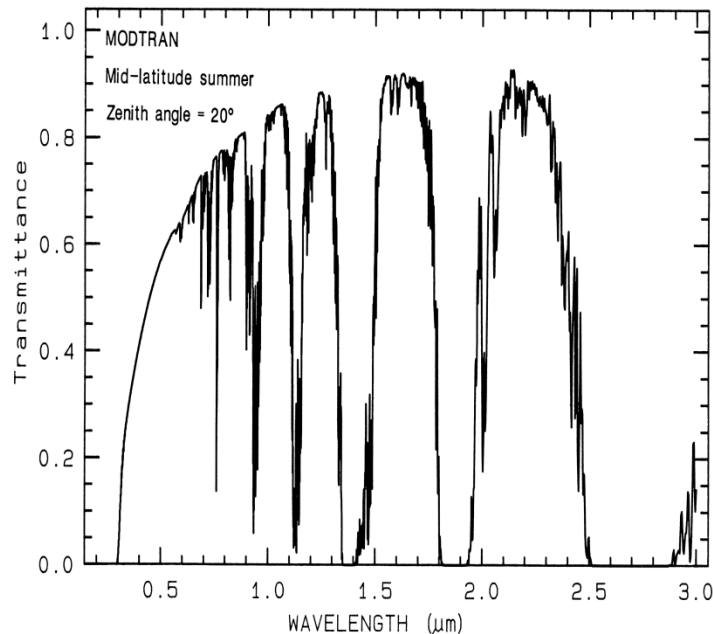
- A lot of initial development work in the field of reflectance spectroscopy was done in the Planetary Science Group at UH
- Paul G. Lucey uses reflectance airborne spectroscopy in the 7.5-11.5 microns range

<http://www.higp.hawaii.edu/~lucey/>

- Roger N. Clark at USGS is one of the leading scientist in the use of reflectance spectroscopy for remote sensing.

<http://speclab.cr.usgs.gov/>

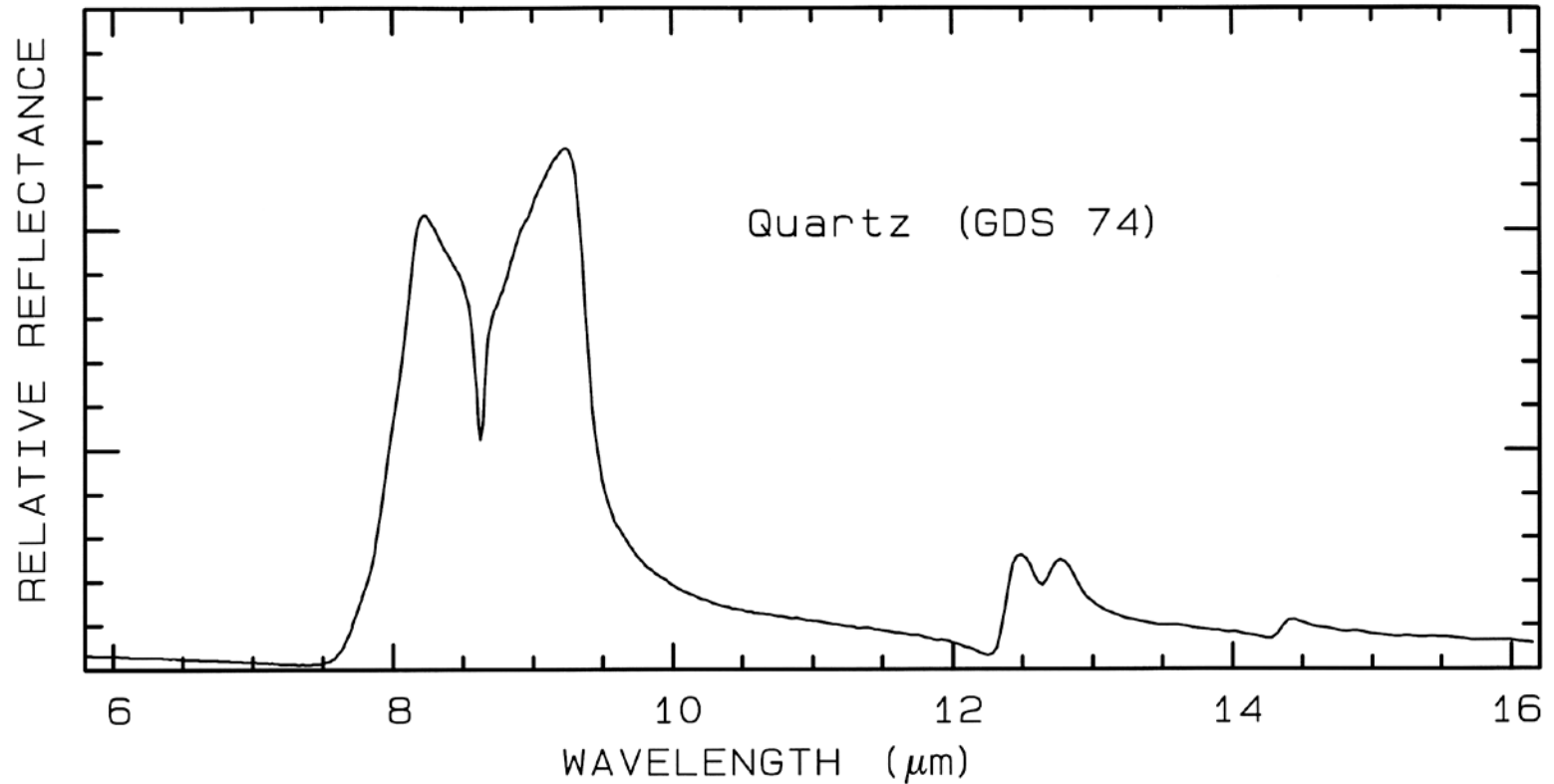
Atmospheric Transmission of Radiation



The drop in transmission toward the ultraviolet is due to scattering and strong ozone absorption at wavelengths short of 0.35 μm. Ozone also displays an absorption at 9.6 μm. Oxygen absorbs at 0.76 μm in a narrow feature. CO₂ absorbs at 2.01, 2.06, and a weak doublet near 1.6 μm. Water causes most of the rest of the absorption throughout the spectrum and hides additional (weaker) absorptions from other gases.

The mid-IR spectrum in shows the effect of doubling CO₂, which in this case is small compared to the absorption due to water. While we will see that the spectral region near 1.4 and 3 μm can be diagnostic of OH-bearing minerals, we can't usually use these wavelengths when remotely measuring spectra through the Earth's atmosphere.

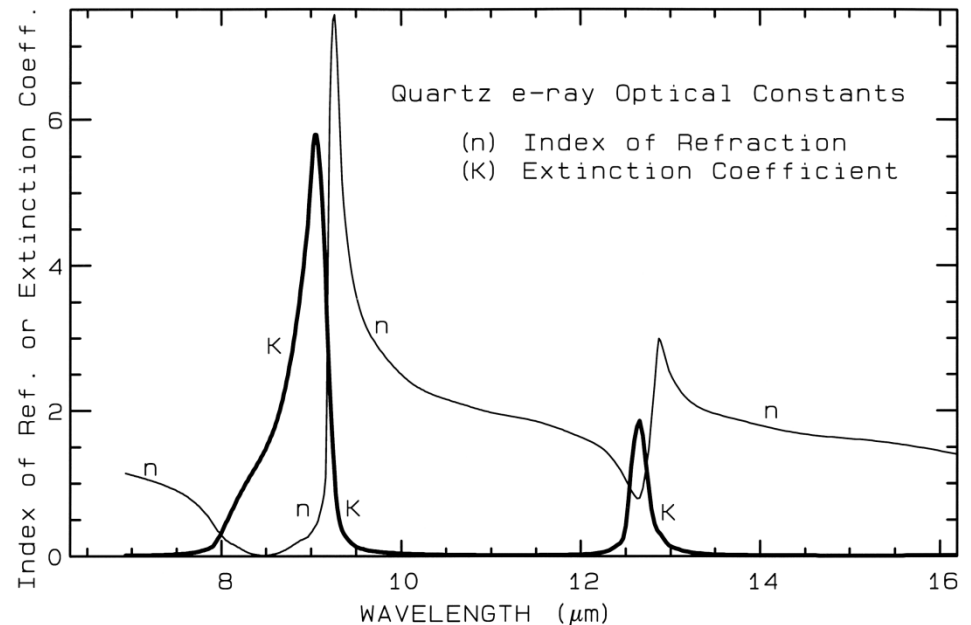
Relative Reflectance of Powdered Quartz Sample



The reflection maxima are called the restrahlen bands: the location of fundamental vibrational stretching modes in the near and mid-infrared. The combination of n and K at these wavelengths often results in high reflectance.

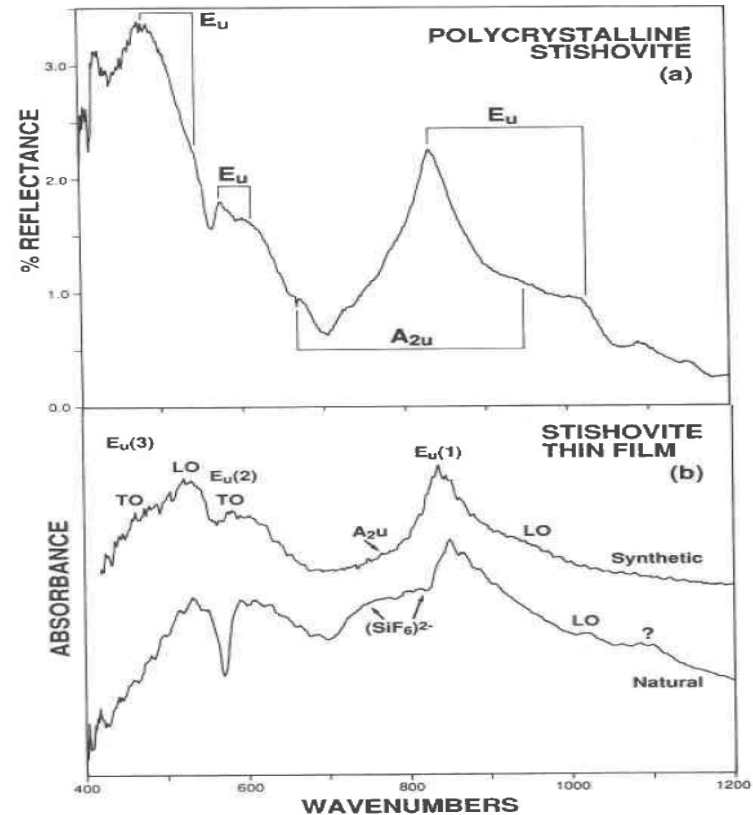
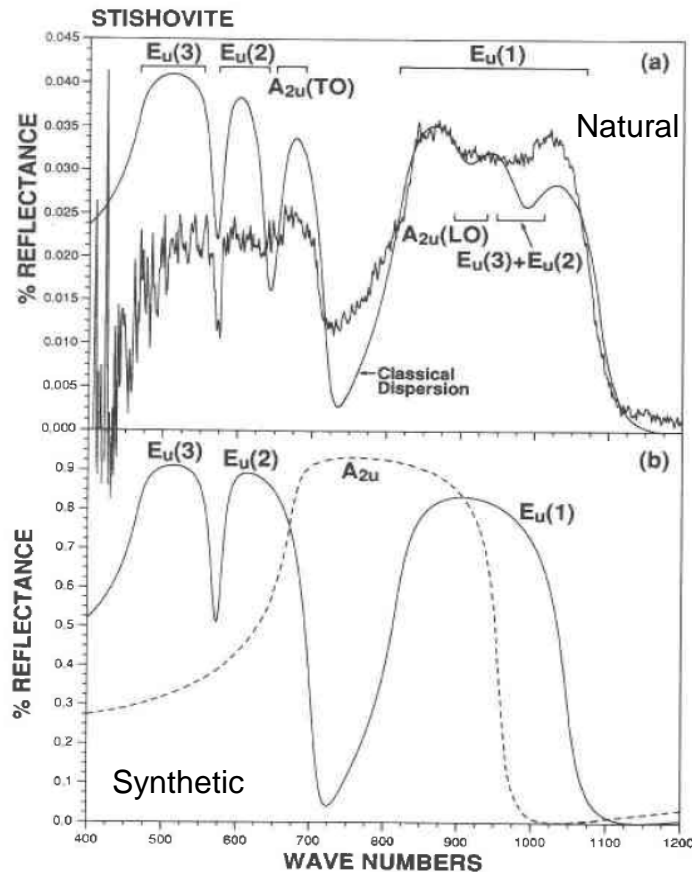
Index of Refraction & Extinction Coefficient from Reflectance Spectrum of Quartz

The complex index of refraction in Figure shows important properties of materials. The index of refraction decreases to a minimum just before a sharp rise (e.g. at 8.5 and 12.6 μm). The minimum is often near or even below $n = 1$. The wavelength where $n = 1$ is called the Christensen frequency. This reflection maximum is called the restrahlen band: the location of fundamental vibrational stretching modes in the near and mid-infrared. The combination of n and K at these wavelengths often results in high reflectance.



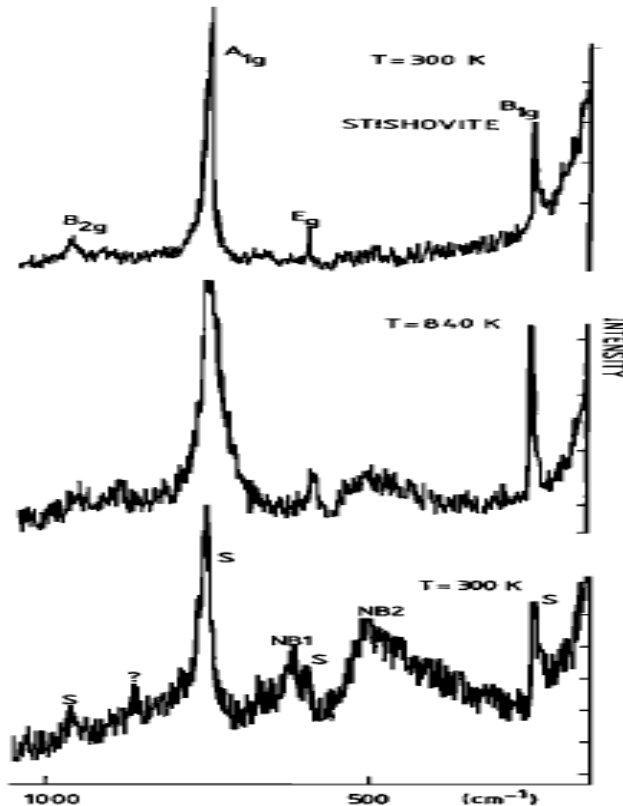
Hapke (1993) *Introduction to the Theory of reflectance and Emittance Spectroscopy* for details).

IR Normal Reflectance and Absorption Spectra of Stishovite Measured with a FT-IR Spectrometer



Hofmeister, A. M., *American Mineralogist* 75, 951-955 (1990).

Raman Spectra of Stishovite



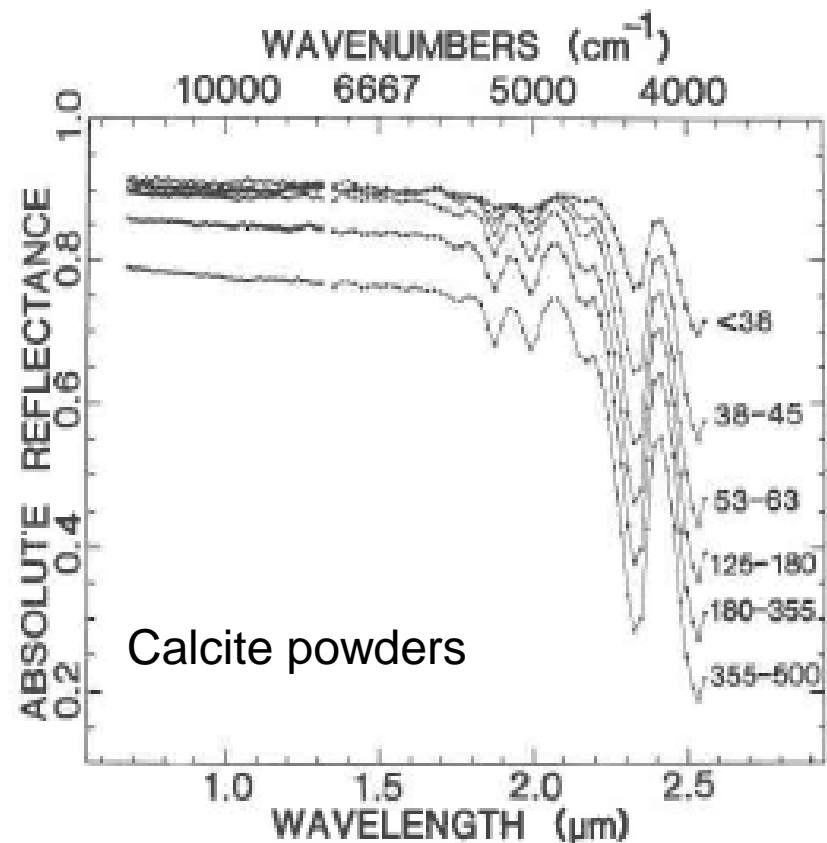
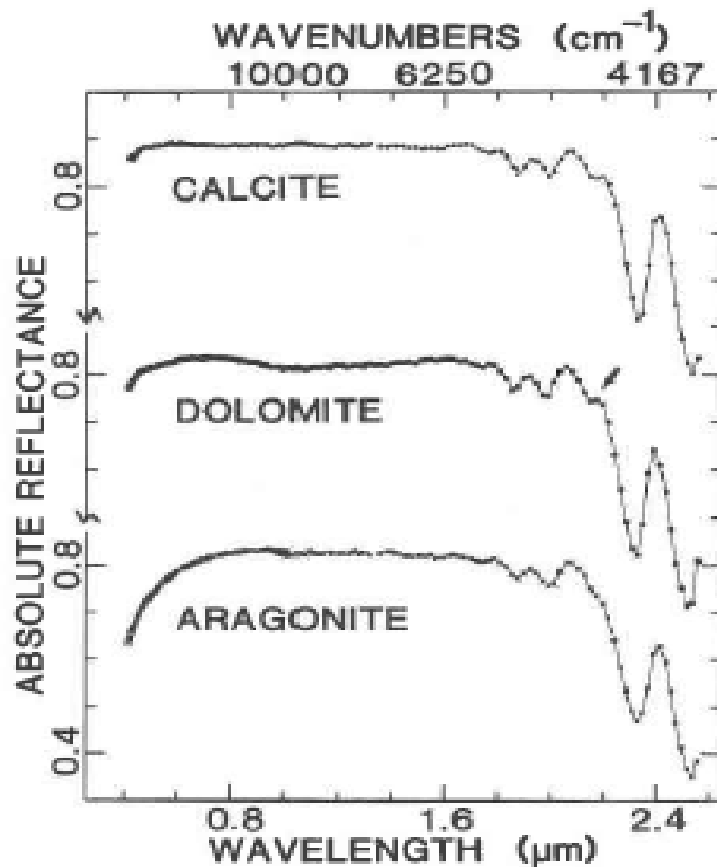
Stishovite tetragonal (rutile-type structure) have two formula units in the primitive cell and the irreducible representation

$$\sum_{op} = A_{1g}(R) + A_{2g}(IR) + A_{2u}(IR) + B_{1g}(R) + B_{2g}(R) + 2B_{1u}(IR) + E_g(R) + 3E_u(i.a.)$$

Raman spectra of stishovite. The lower spectrum has been recorded on a sample heated at 800 K and subsequently quenched at room temperature. Note the new bands (NB1 and NB2) superimposed on those of perfect stishovite (S). NB1 and NB2 are characteristic of silica glass with Si in four-fold coordination.

Gillet, P. et al. (1990) *J. Geophys. Res.*, 95 (B13), 21,635–21,655

Reflectance Spectra of Carbonates

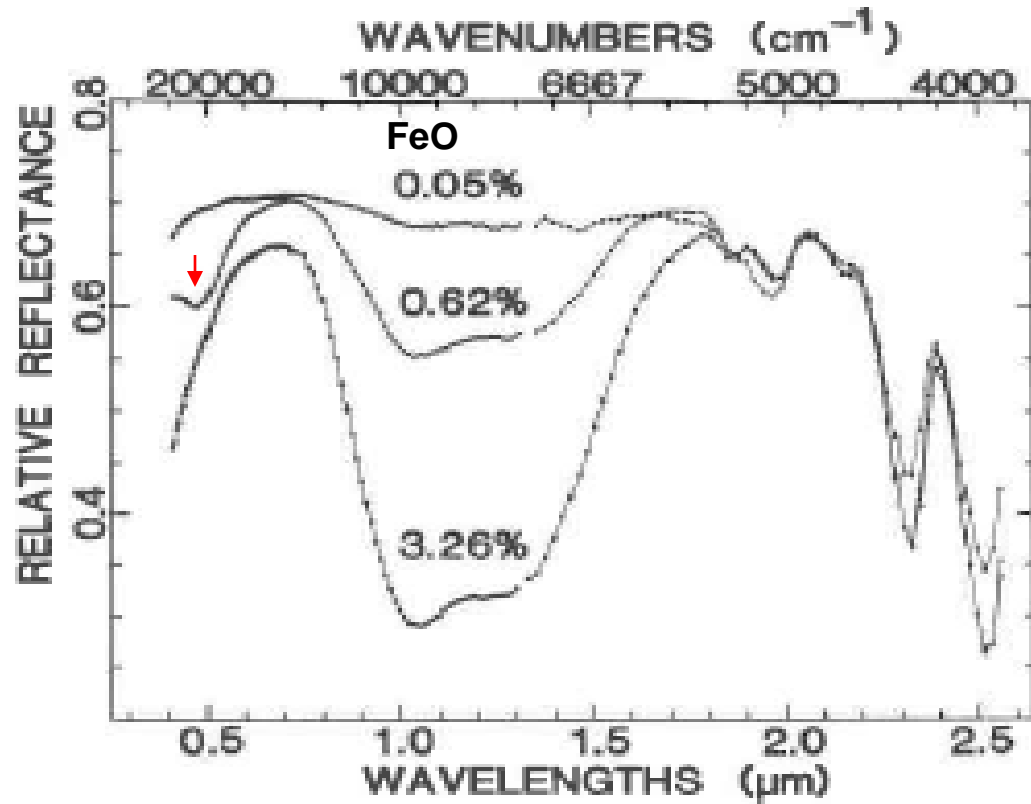


Combination and overtone bands of the CO_3 fundamentals occur in the near IR. The two strongest are $\nu_1 + 2\nu_3$ at 2.50-2.55 μm (4000-3900 cm^{-1}), and $3\nu_3$ at 2.30-2.35 μm (4350-4250 cm^{-1}). Three weaker bands occur near 2.12-2.16 μm ($\nu_1 + 2\nu_3 + \nu_4$ or $3\nu_1 + 2\nu_4$; 4720-4630 cm^{-1}), 1.97-2.00 μm ($2\nu_1 + 2\nu_3$; 5080-5000 cm^{-1}), and 1.85-1.87 μm ($\nu_1 + 3\nu_3$; 5400-5350 cm^{-1}). The band positions in carbonates vary with composition.

Gaffey, S.J., *J. Geophys. Res.* **92**, 1429-1440 (1987)

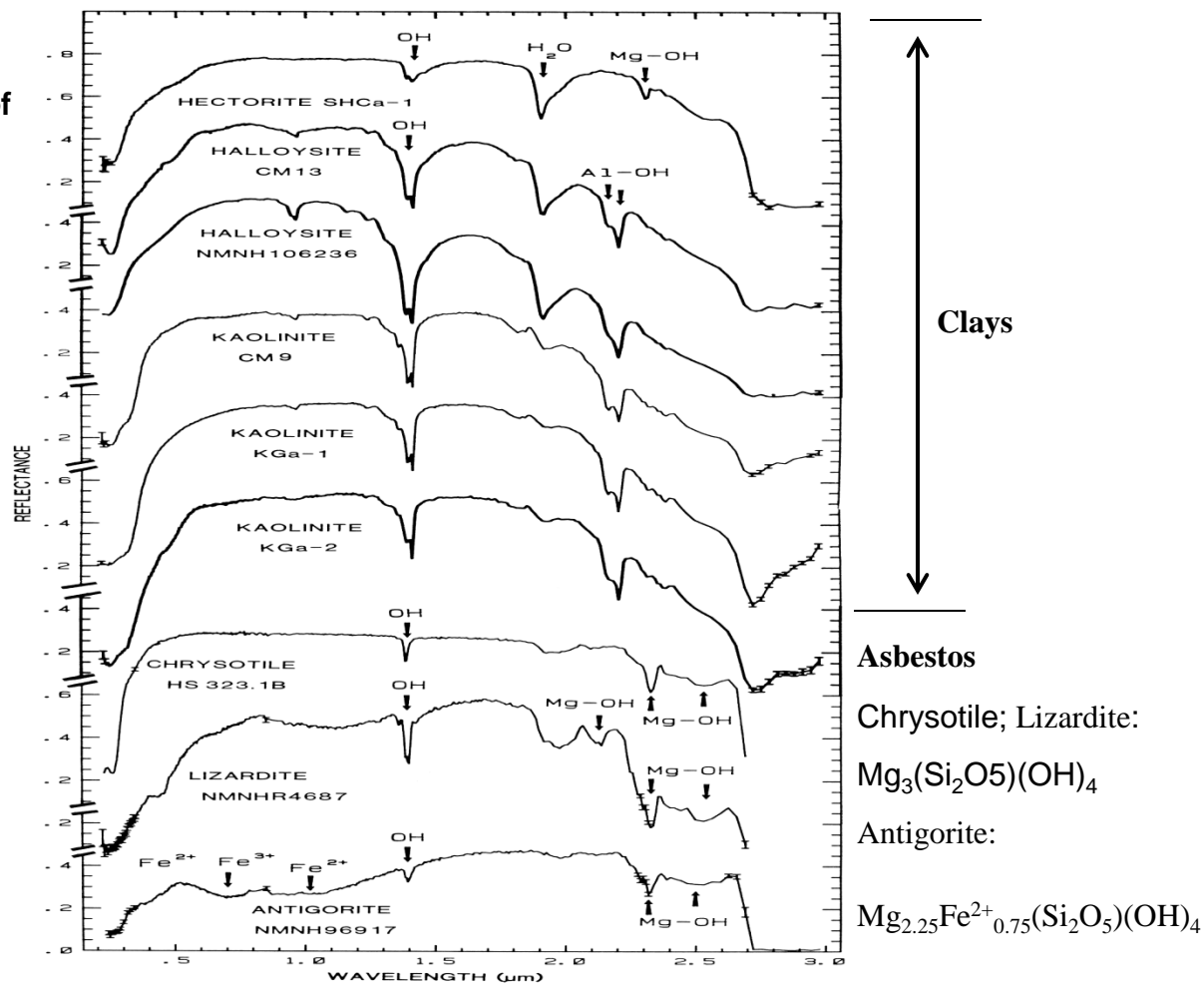
Spectra of three dolomite samples with different iron contents

FeO in wt.% in $\text{CaMg}(\text{CO}_3)_2$ determined by X-ray fluorescence spectroscopy. Feature near $0.45\mu\text{m}$ in second spectrum due to Fe^{3+} in the sample formed by weathering



Reflectance spectra of hectorite, halloysite, kaolinite, chrysotile, lizardite, and antigorite showing vibrational bands due to OH

The overtones of water are seen in reflectance spectra of H₂O-bearing minerals. The first overtones of the OH stretches occur at about 1.4 μm and the combinations of the H-O-H bend with the OH stretches are found near 1.9 μm. Thus, a mineral whose spectrum has a 1.9-μm absorption band contains water (e.g. hectorite and halloysite in Figure, but a spectrum that has a 1.4-μm band but no 1.9-μm band indicates that only hydroxyl is present (e.g. kaolinite in Figure) has only a small amount of water because of the weak 1.9-μm absorption but a large amount of OH).



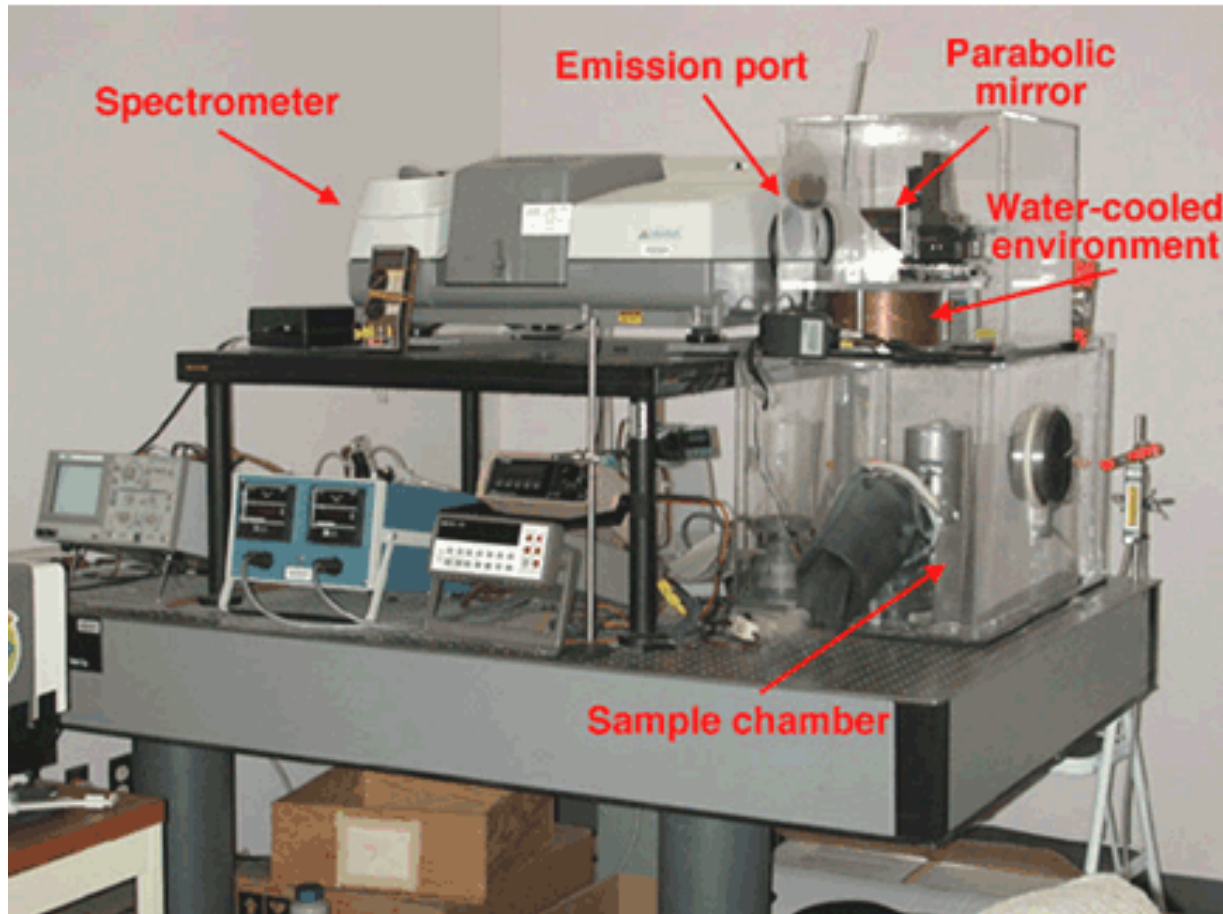
Hectorite: $Na_{0.4}Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$; Halloysite: $Al_2Si_2O_5(OH)_4$ (monoclinic); Kaolinite: $Al_2Si_2O_5(OH)_4$ (Triclinic)

Clark, R.N., et al., *J. Geophys Res.* **95**, 12653-12680 (1990).

Thermal Emission Spectroscopy

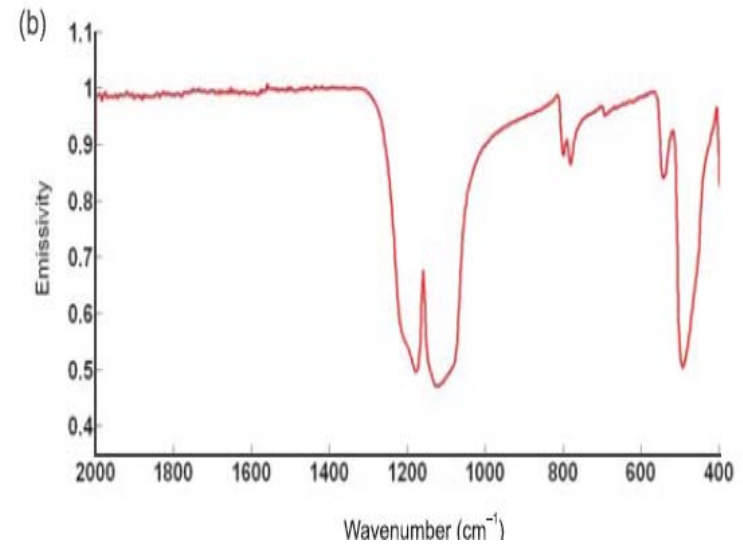
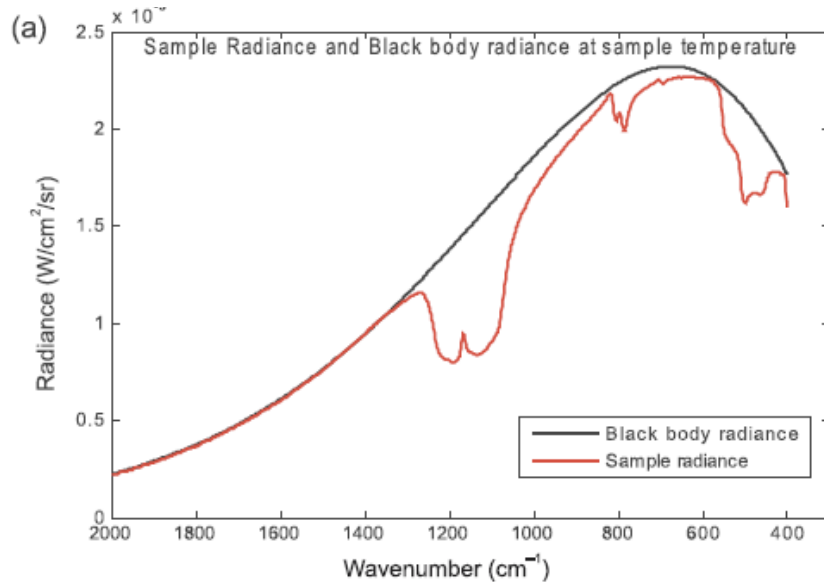
Thermal IR Spectrometer

Spectrometer at Arizona State University



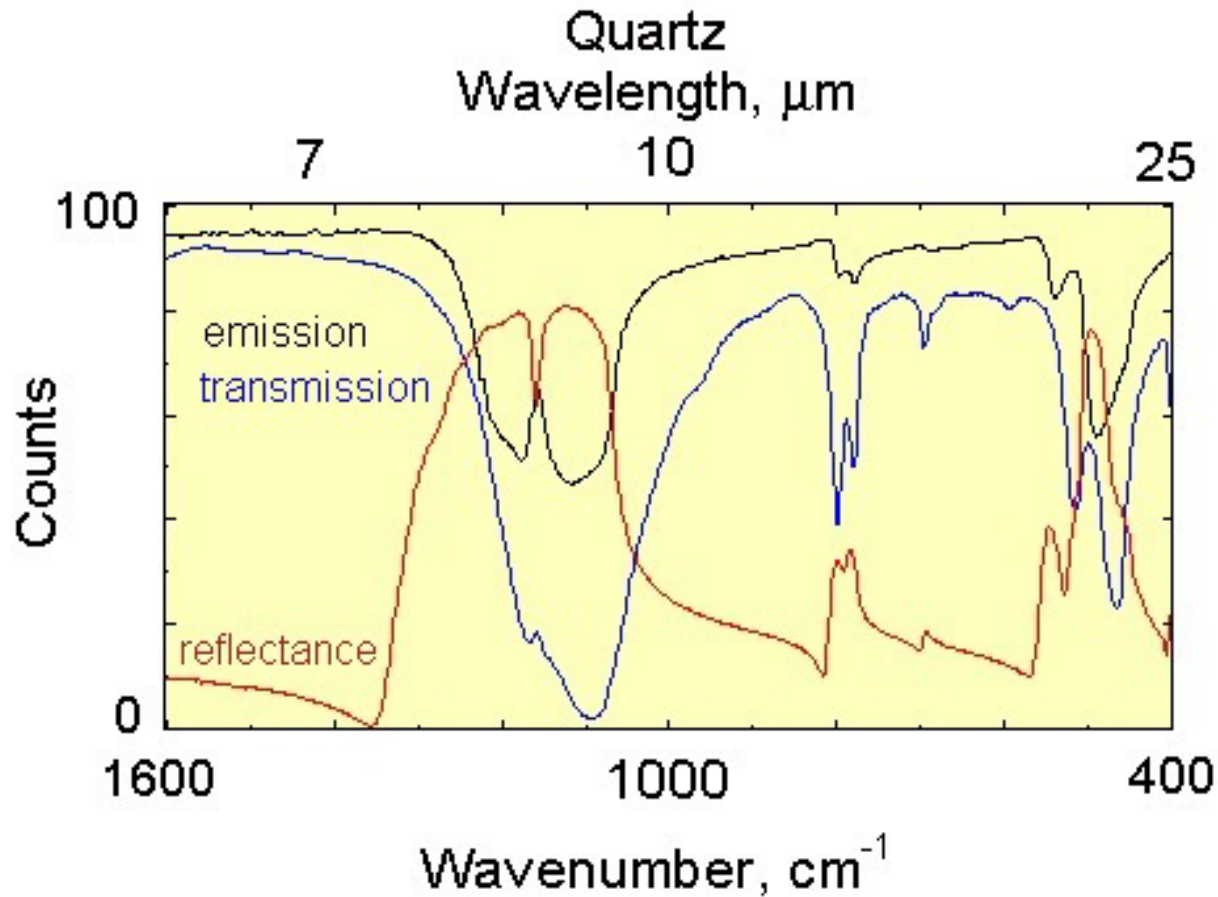
(Photo courtesy of Joshua Bandfield, Arizona State University.)

Thermal Emission Spectrum of quartz

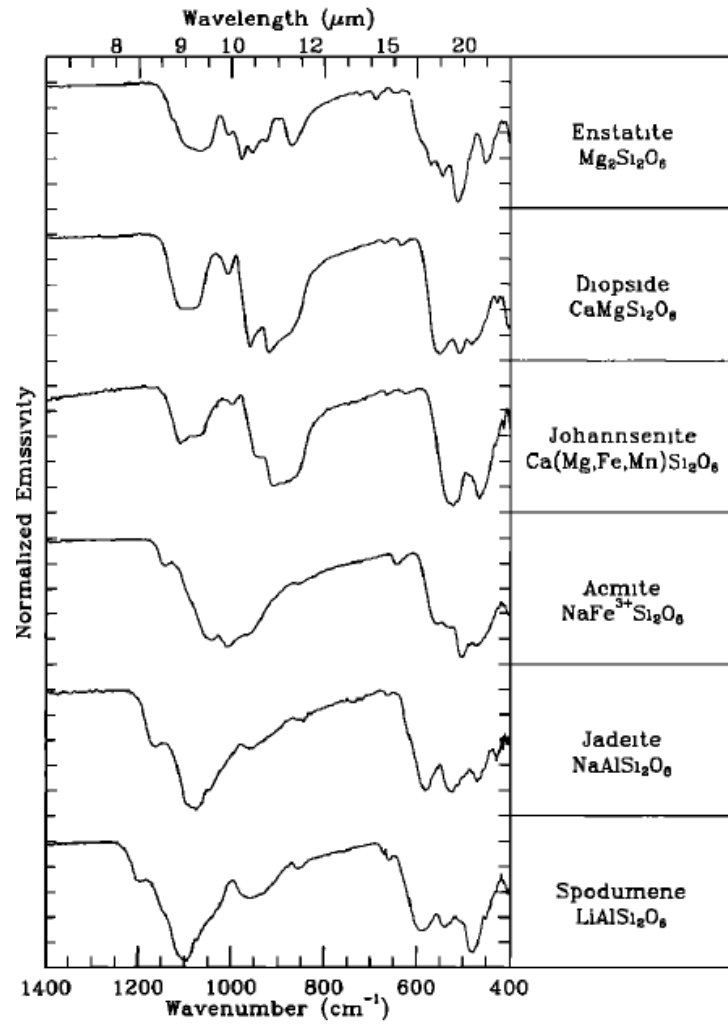
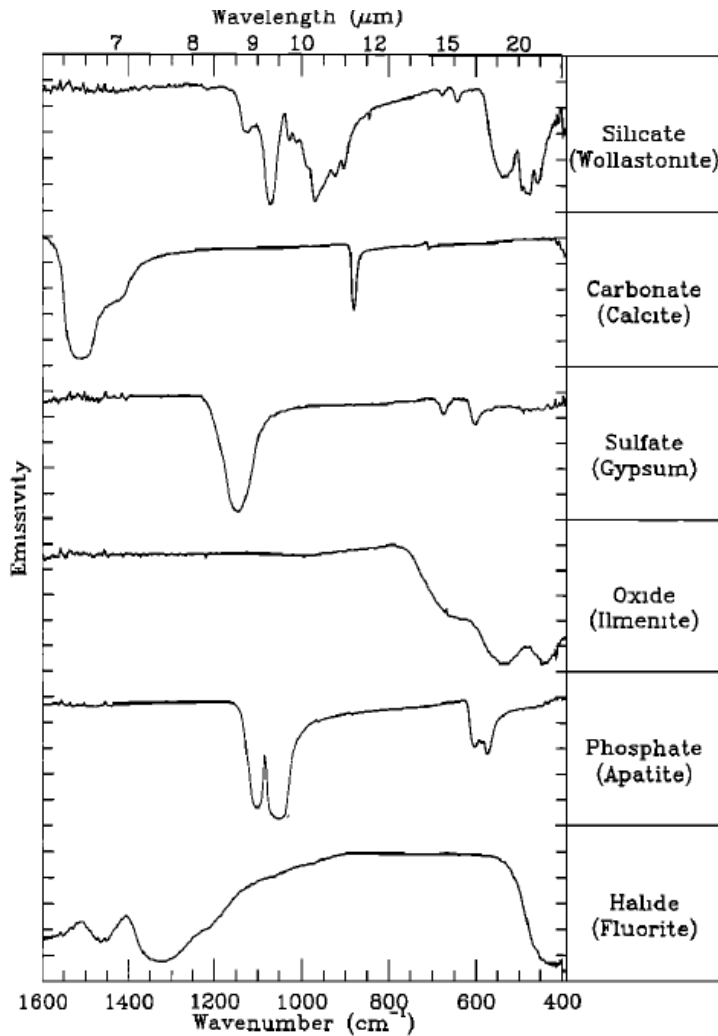


$$\text{Emissivity, } \epsilon = \epsilon_{\text{sample}}(T) / \epsilon_{\text{blackbody}}(T)$$

α -Quartz IR Emission, Reflectance and Transmission Spectra



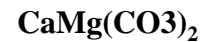
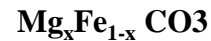
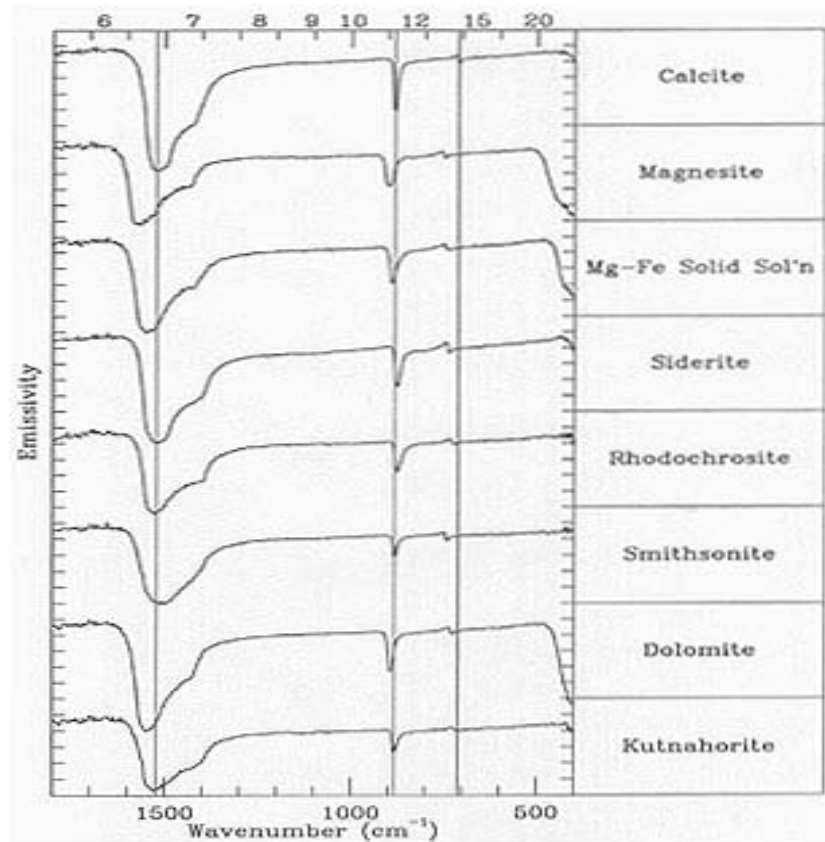
Thermal Emission Spectra of Minerals



¹Christense, Philip R., et al., *J. Geophys. Res.* **105**, (E4) 9735-9739 (2000).

²Hamilton, Victoria E., *J. Geophys. Res.* **105**, (E4) 9701-9716 (2000).

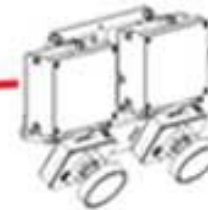
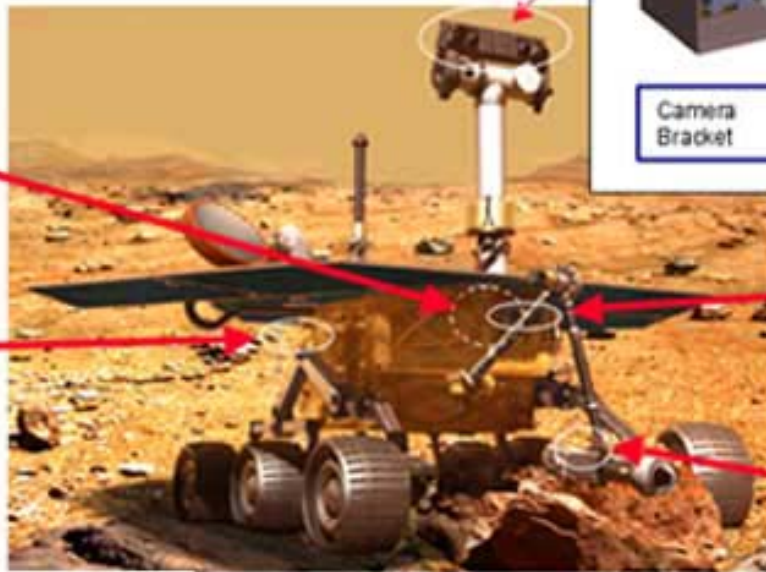
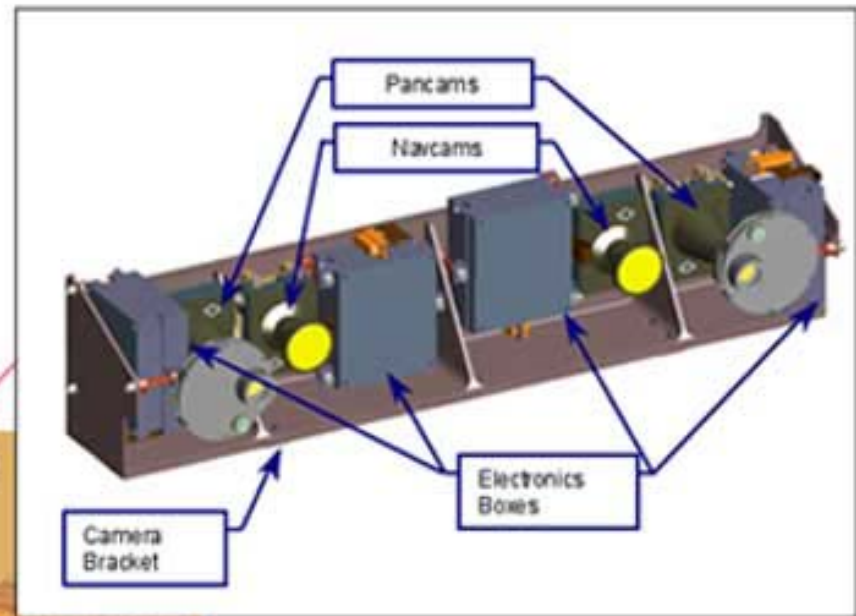
Thermal Emission Spectra of Carbonate Minerals



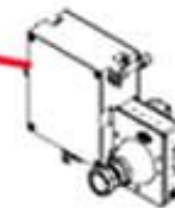
(Figure from Lane, M.D. and P.R. Christensen (1997) Thermal infrared emission spectroscopy of anhydrous carbonates, *J. Geophys. Res.*, 102, p. 25581-25592.)

Mars Exploration Rover (MER) Sensing System

- The MER Remote Sensing System includes:
 - 10 Cameras
 - 3 Science (2 Pancams + 1 Microscopic Imager)
 - 6 Surface Navigation Cameras (4 Hazcams + 2 Navcams)
 - 1 EDL Imager on the lander
 - 1 Thermal Infrared Spectrometer
 - Mini-TES
 - Pancam Mast Assembly (Pancam/Navcam/Mini-TES pointing)
 - Various calibration targets
 - 1 Pancam calibration target
 - 2 Mini-TES calibration targets (internal and external)



Front Hazcam Pair



Microscopic Imager

http://marsrovers.jpl.nasa.gov/mission/spacecraft_surface_instru.html

Mini-TES Electronics

Mini-TES Electronics

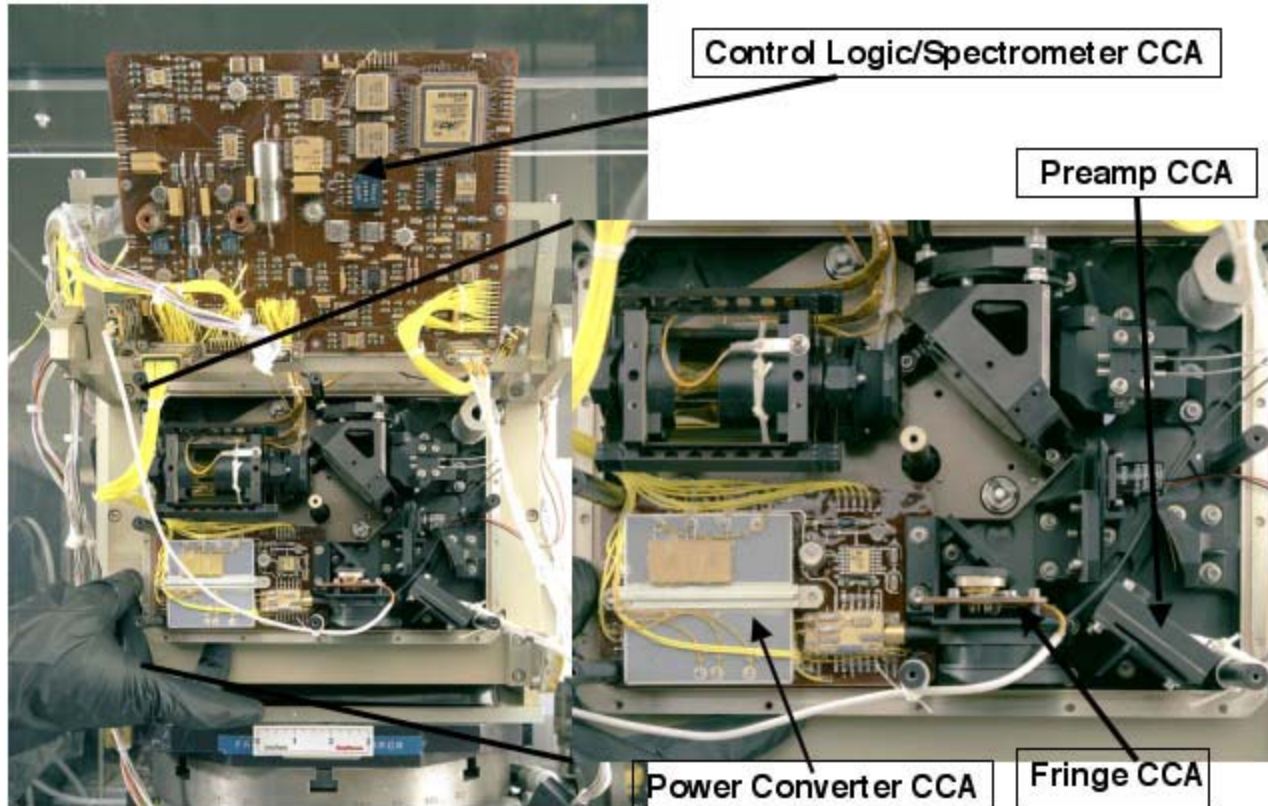
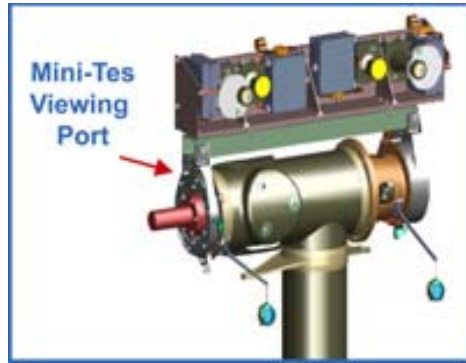


Image credit: NASA/JPL/SBRS/ASU

Mini-TES Optical Bench



Mini-TES is located in the body of the rover at the bottom of the "rover neck," known as the Pancam Mast Assembly (PMA). Scanning mirrors located in the Pancam Mast Assembly act like a periscope to send light down to the instrument. This structure allows Mini-TES to see the terrain around the rover from the same vantage point as Pancam. Mini-TES looks one way, and the Pancams look the other way. To make observations of the same location from both of the instruments, the Pancam Mast Assembly (the rover's neck) must be commanded to swivel. Mini-TES telescope is a 6.35-cm diameter Cassegrain telescope

Mini-TES Optical Bench

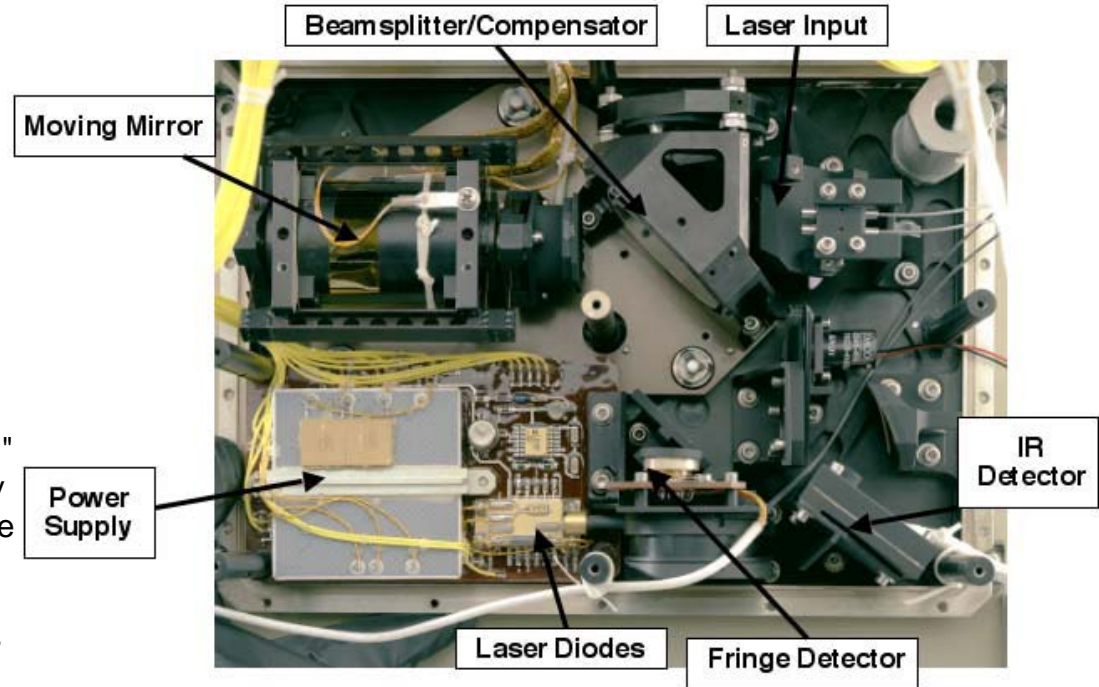


Image credit: NASA/JPL/SBRS/ASU

Mineral Hematite



Polished Mineral Slice of Banded Hematite



Globular Hematite



Speckled Hematite $\text{Fe}^{3+}_2\text{O}_3$



Goethite $\text{Fe}^{3+}\text{O}(\text{OH})$

If the hematite on Mars formed under wet conditions, Mini-TES may find Goethite.

Mineral Magnetite ($\text{Fe}^{3+}_2\text{Fe}^{2+}\text{O}_4$)



Magnetite granules

If the hematite on Mars formed under dry conditions, Mini-TES may find Magnetite but no Goethite.

Thermal IR Spectra of Minerals on Mars

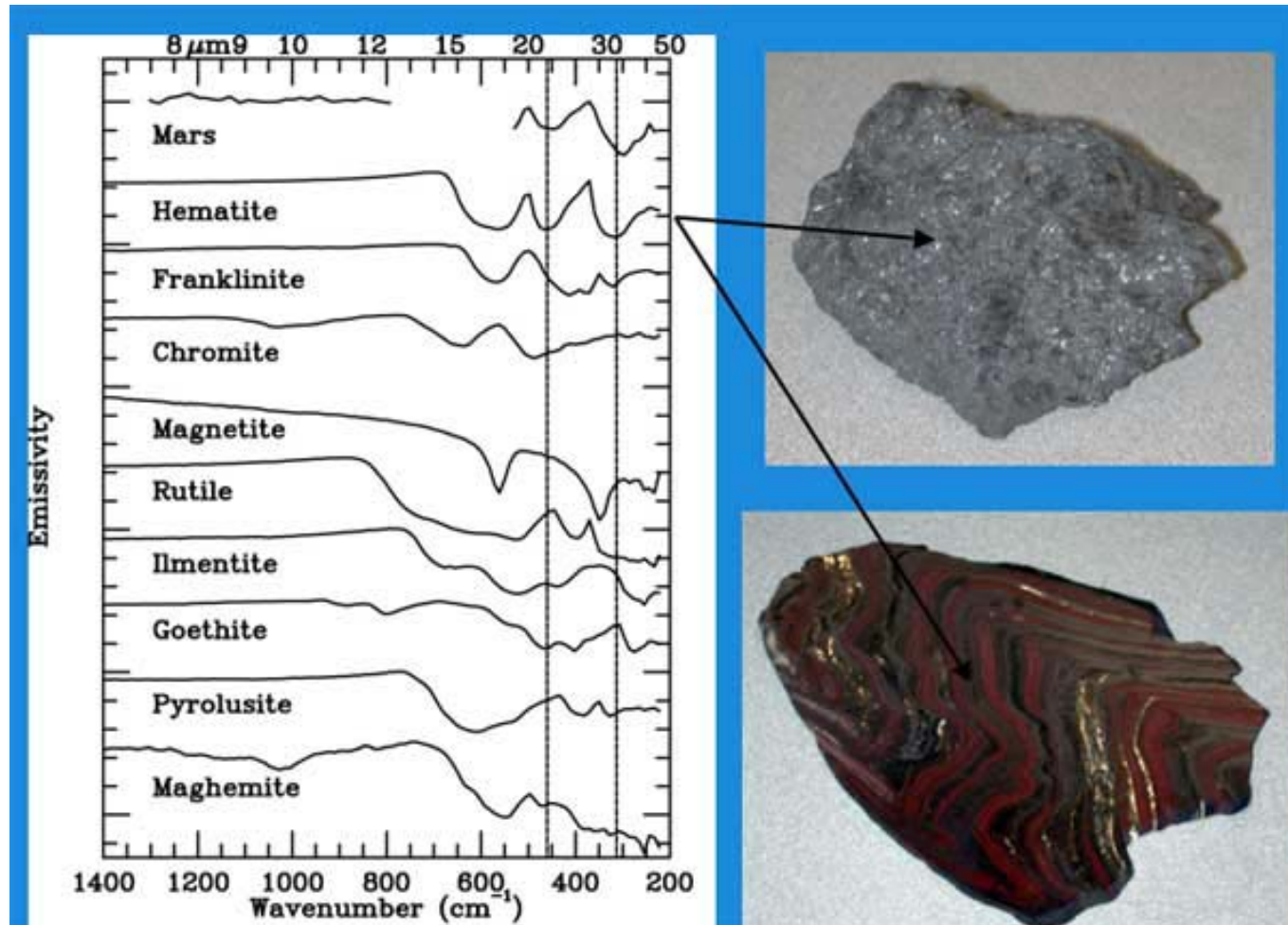


Image credit: ASU

Mini-TES can identify a variety of minerals by recording their infrared spectral signatures

Summary

Infrared absorption spectroscopy can be used to identify synthetic and natural minerals and glasses from their IR fingerprints.

Diffuse reflectance in the near and mid-IR can be used in the laboratory and remote sensing of mineral classes.

Thermal emission spectroscopy (TES) in the mid-infrared is being used successfully in the laboratory as well as for remote sensing of minerals.

Home Work

Reading:

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<http://speclab.cr.usgs.gov/spectral-lib.html>
- Thermal emission spectra of minerals Database
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