

Mon. Feb. 19, 2018

- Reading:
 - Jump ahead to first part of Ch. 8 -- Digital Image Processing for lab next week.
 - Pg. 255 - 269 except
 - Skip over map projections -- we'll cover that in more detail later
 - Just skim descriptions of old scanning/digitizing technology
 - DO understand DN (Data Number, Digital Numbers) and Histograms / Contrast Stretch
- Theory of mineral absorptions (not in text)

Spectroscopy of Rocks & Minerals

- Eventually, mineral absorption bands
- But first:
 - Vibration + rotation bands for gas molecules
 - Complications for solids
 - ices
 - silicates

Electronic, Charge Transfer, Crystal Field bands

Spectroscopy of Rocks and Minerals, and Principles of Spectroscopy

Book chapter by Roger Clark – available at

<http://speclab.cr.usgs.gov/PAPERS.refl-mrs/refl4.html>

Electronic and “Charge Transfer” Bands
primarily in the UV and visible

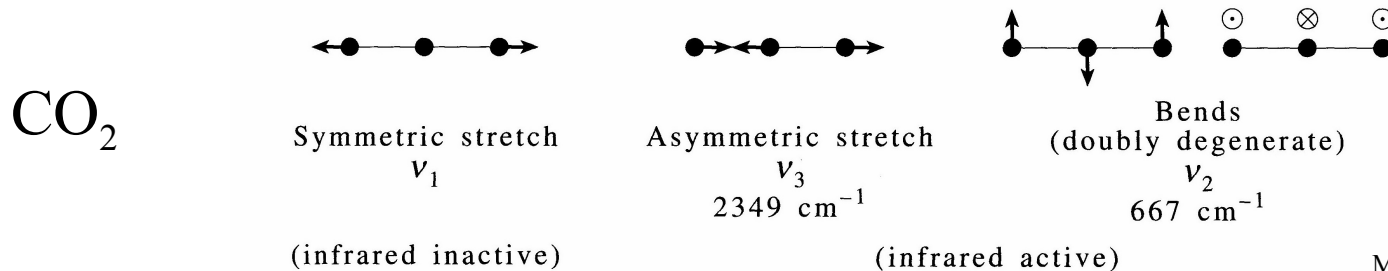
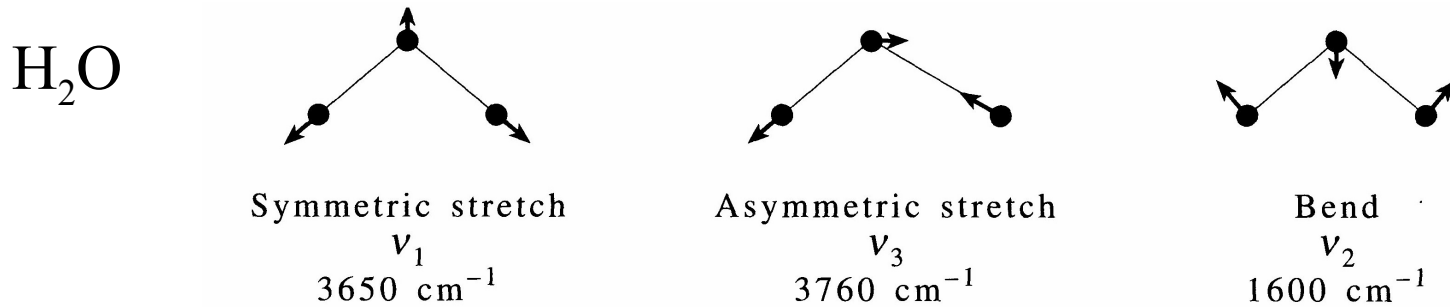
Vibration bands

For silicates primarily in the mid infrared
OH and H₂O bands dominate near 3 microns

Crystal Field Bands

Mostly from Fe, dominate in the 0.9-2.0 μm range

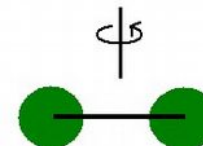
Vibration (and Rotation) Bands



McQuarrie & Simon, 1997

- Classically, molecules like to vibrate in certain “normal modes”, at well defined frequencies ν_{vib}
- From quantum mechanics, vibration “amplitudes” are quantized, with energy levels spaced distance $\Delta E = h\nu_{\text{vib}}$ apart.
(Remember for photon, we also have $E = h\nu_{\text{photon}}$)
- We therefore get absorption/emission at $\nu_{\text{photon}} = n \times \nu_{\text{vib}}$ for $n=1,2,3, \dots$
- For these frequencies, units of Hz are not convenient. Instead use “Wavenumber”
 $\nu = c / \lambda$ Define “wavenumber” = $1 / \lambda$ with λ in cm. So $\nu = c \times$ “wavenumber”

Rotational Lines



- Rotational energy also quantized
 - Classically $E_{\text{rot}} = \frac{1}{2} I \omega^2$
 - where I = moment of inertial, ω = angular rotation rate
 - Quantum mechanically, $E_{\text{rot}} = B J (J+1) \approx B J^2$ for large J
 - where J = rotational quantum number and $B = h^2/(2I)$
- E_{rot} (and ΔE_{rot}) are much smaller than E_{vib} , with energies in the radio range
- H_2O : Microwave ovens tuned to water rotational line
- Both E_{rot} and E_{vib} can change, giving total ΔE slightly above (for $\Delta E_{\text{rot}} > 0$) or slightly below (for $\Delta E_{\text{rot}} < 0$) that expected from ΔE_{vib} alone.

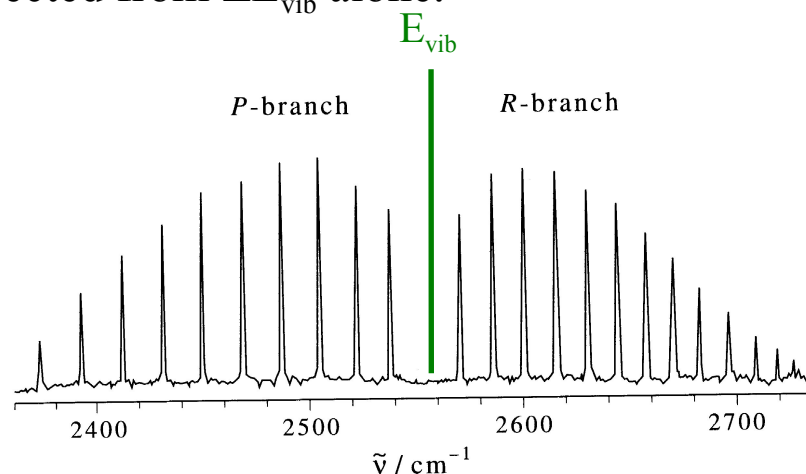
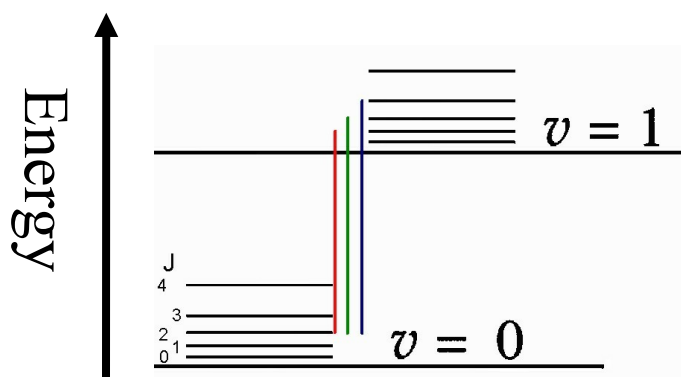
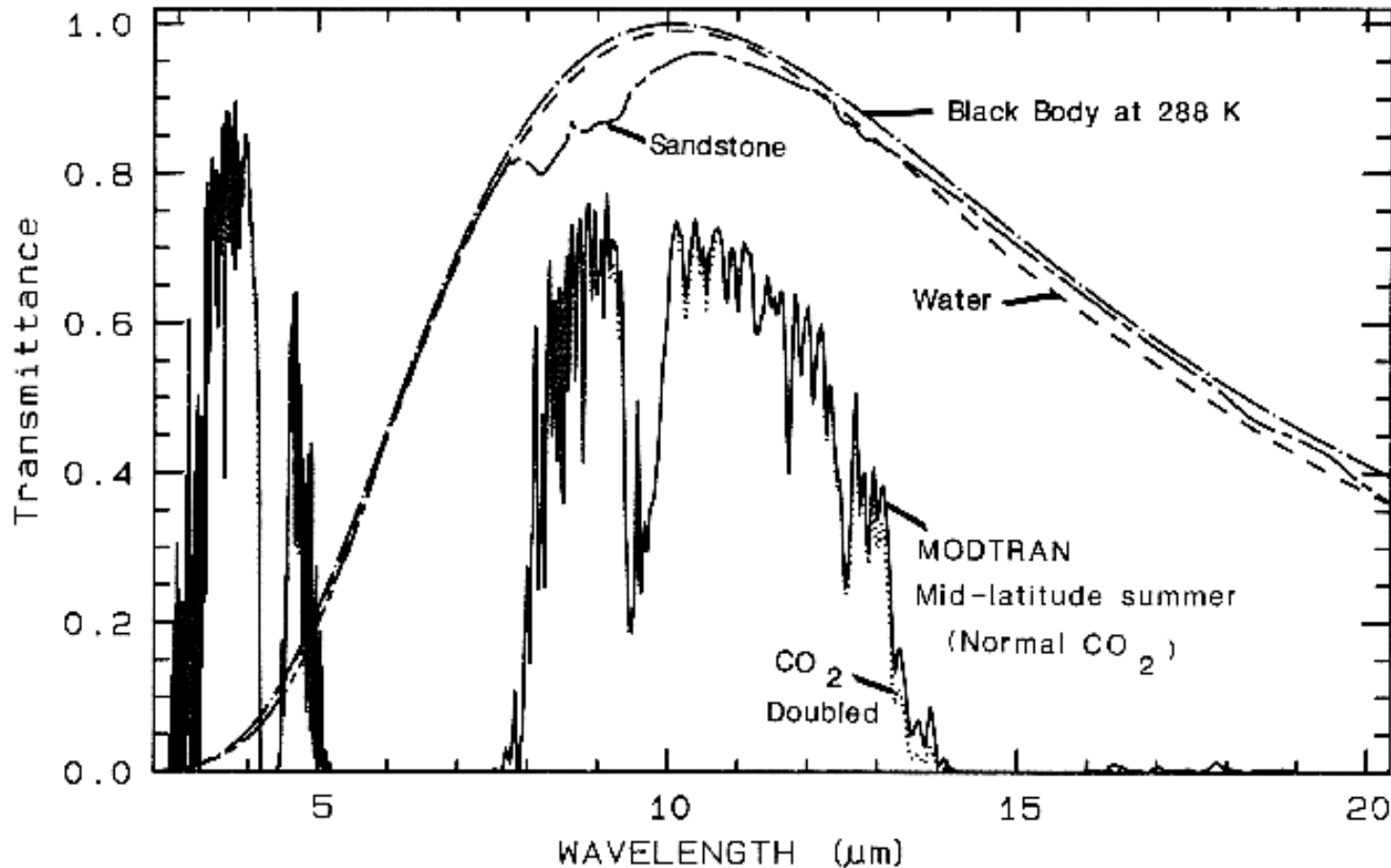


FIGURE 13.2
The rotational-vibrational spectrum of the $0 \rightarrow 1$ vibrational transition of $\text{HBr}(\text{g})$. The R branch and the P branch are indicated in the figure.

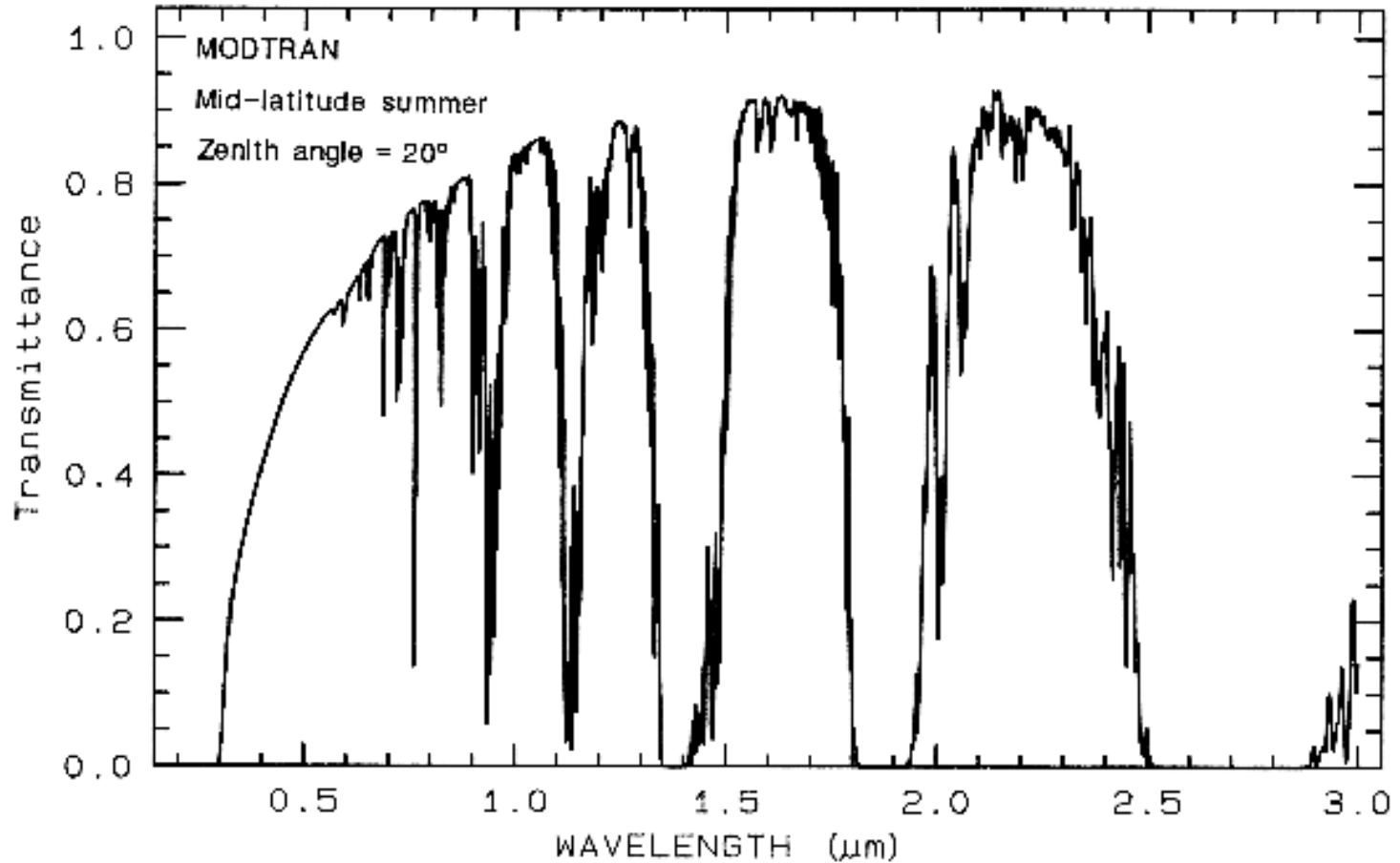
From McQuarrie

Atmospheric Transmission, to 20 μm



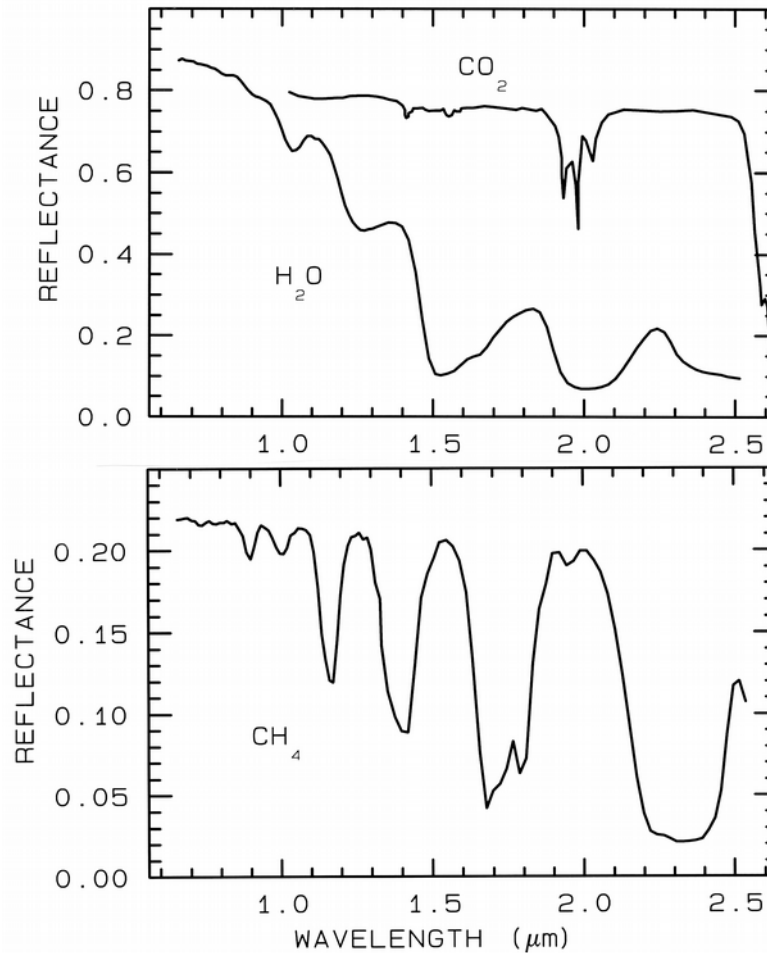
Most absorption due to H_2O and CO_2 rotation-vibration bands
 O_3 causes band at 9.8 μm

Atmospheric Transmission, to 3 μm



Most absorption due to H_2O and CO_2 rotation-vibration bands

Bands in Ices



In ices, vibration of molecules still possible (but at slightly different ν)
Rotation inhibited (some twisting occurs) and rot. lines smeared out.

Mineral Spectra

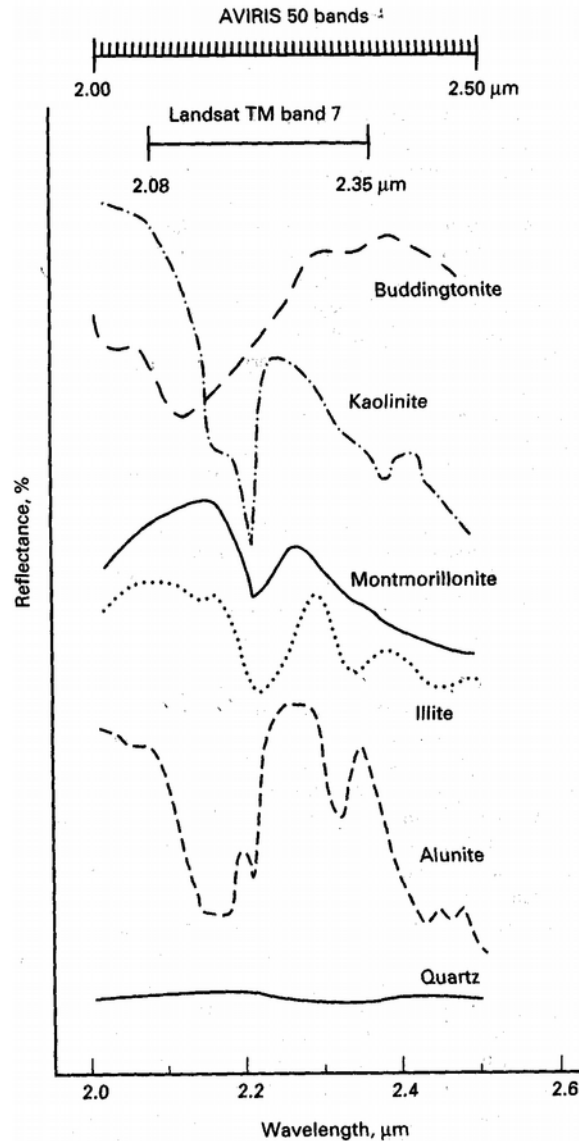


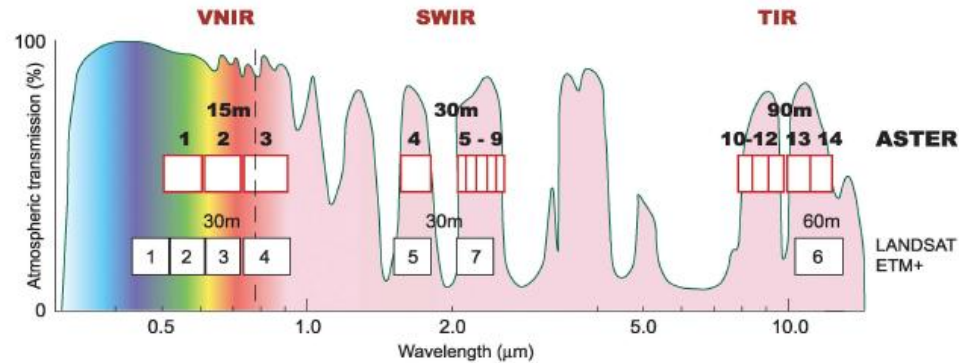
Figure 11-17 Laboratory spectra of alteration minerals in the atmospheric window from 2.0 to 2.5 μm . Spectra are offset vertically for clarity. Bandpasses of AVIRIS and TM band 7 are shown.

Clays have OH incorporated in structure

Generally darken towards $3\mu\text{m}$ where water absorbs strongly.

Detailed structure of 2.0 – 2.5 bands depends upon detailed mineral structure.

Multispectral vs. Hyperspectral



AVIRS: Airborne Visible / Infrared Spectrometer

(don't confuse with AVHRR – radiometer on weather satellites.)

Flown on NASA U2 at 20 km altitude

Swath width 10.5 km, spatial resolution 20 m

0.4 – 2.5 μm, 224 bands, 0.010 μm = 10 nm resolution

Images for ~1/5 of bands shown on pg. 24 and Plate 1B

Hyperion: On board EO-1 (NASA 2001 experimental satellite)

0.4 – 2.5 μm, 220 bands 7.5 km by 100 km images

Electronic, Charge Transfer, and Crystal Field Bands

- Electronic bands: Electron jumps from lower energy level to upper energy level
 - Typical spacing of energy levels means these usually occur in blue or UV
 - Special exception below for “Crystal Field Bands”
 - Currently of limited use in terrestrial remote sensing
 - Atmosphere not transparent in UV (but can be used for planetary remote sensing)
 - Many absorption features not unique and so not diagnostic
- Charge transfer bands
 - Electron moves from one site to another
 - Example: In mineral with both Fe^{+2} and Fe^{+3} sites (magnetite), e^- moves from one Fe to the other
- Crystal Field Bands
 - Special case where “crystal electric field” creates slightly separated electron levels
 - Very important for sensing composition of pyroxene, olivine, and other minerals

Need moderately separated energy levels for NIR absorption: Role of transition elements

Orbitals:

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f 5g
6s 6p 6d 6f 6g ...

nD 's fill after $(n+1)S \Rightarrow$ Transition Elements

nF 's fill after $(n+2)S \Rightarrow$ Inner Transition Elements

1s
2s
3s
4s
5s
6s
7s

2p
3p
4p
4d
5d
6d
7p

Table A-16 Periodic Table of the Elements

Group	Transition Elements																Noble Gases																						
IA(1)	VIII										IIIA(13)	IVA(14)	VA(15)	VIA(16)	VIIA(17)	(18)																							
1 H 1.008											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18																							
2 Li 6.941	3 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95																					
3 Na 22.99	12 Mg 24.31																					19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.7	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
4 K 39.10	20 Ca 40.08	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3																						
5 Rb 85.47	38 Sr 87.62	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)																						
6 Cs 132.9	56 Ba 137.3	89** Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	114 Uuq (285)	116 Uuh (289)	118 Uuo (293)																									
Inner Transition Elements																																							
Lanthanide Series		6	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0																							
Actinide Series		7	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)																							

D Orbitals

Transition elements (including Fe) have partially filled D orbitals

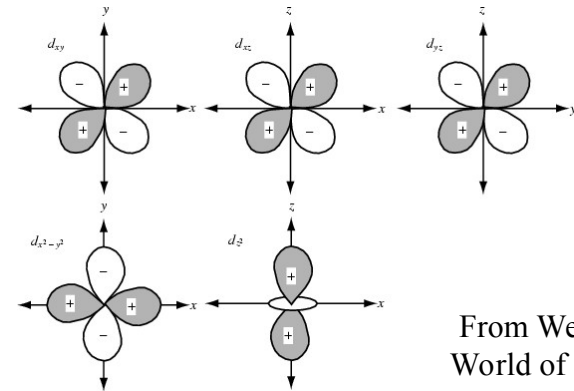
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7	87 Fr (223)	88 Ra 226.0	89** Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	113 Uut (284)	114 Uuq (285)	115 Uup (288)	116 Uuh (289)	117 Uus (293)	118 Uuo (293)

Atomic masses are based on carbon-12. Numbers in parentheses are mass numbers of most stable or best-known isotopes of radioactive elements.

Inner Transition Elements

Lanthanide Series	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
Actinide Series	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	232.0	231.0	238.0	237.0	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)



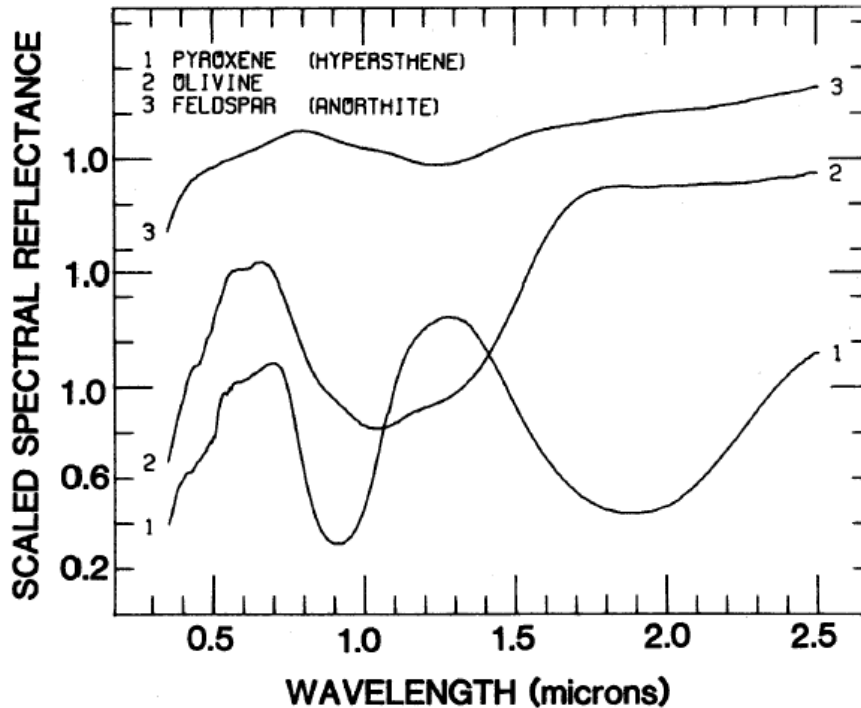
From Weisstein World of Physics

Their energy levels are “degenerate” in absence of external E field

In presence of external E field energy levels split slightly.

“Crystal field” from adjacent atoms provides E field.

Fe Crystal Field Bands



Different crystals have different E fields so different Δ Energy

Strength of E field can shift as composition of crystal changes (eg. as Fe is replaced by Mg)

Some crystals have different types of crystal sites where Fe can be located, so multiple sets of bands.

Olivine One Fe site \Rightarrow one band near 1.05 μ m

Pyroxene Two Fe sites \Rightarrow two bands (0.90 μ m 1.90 μ m in low Ca Pyroxene)

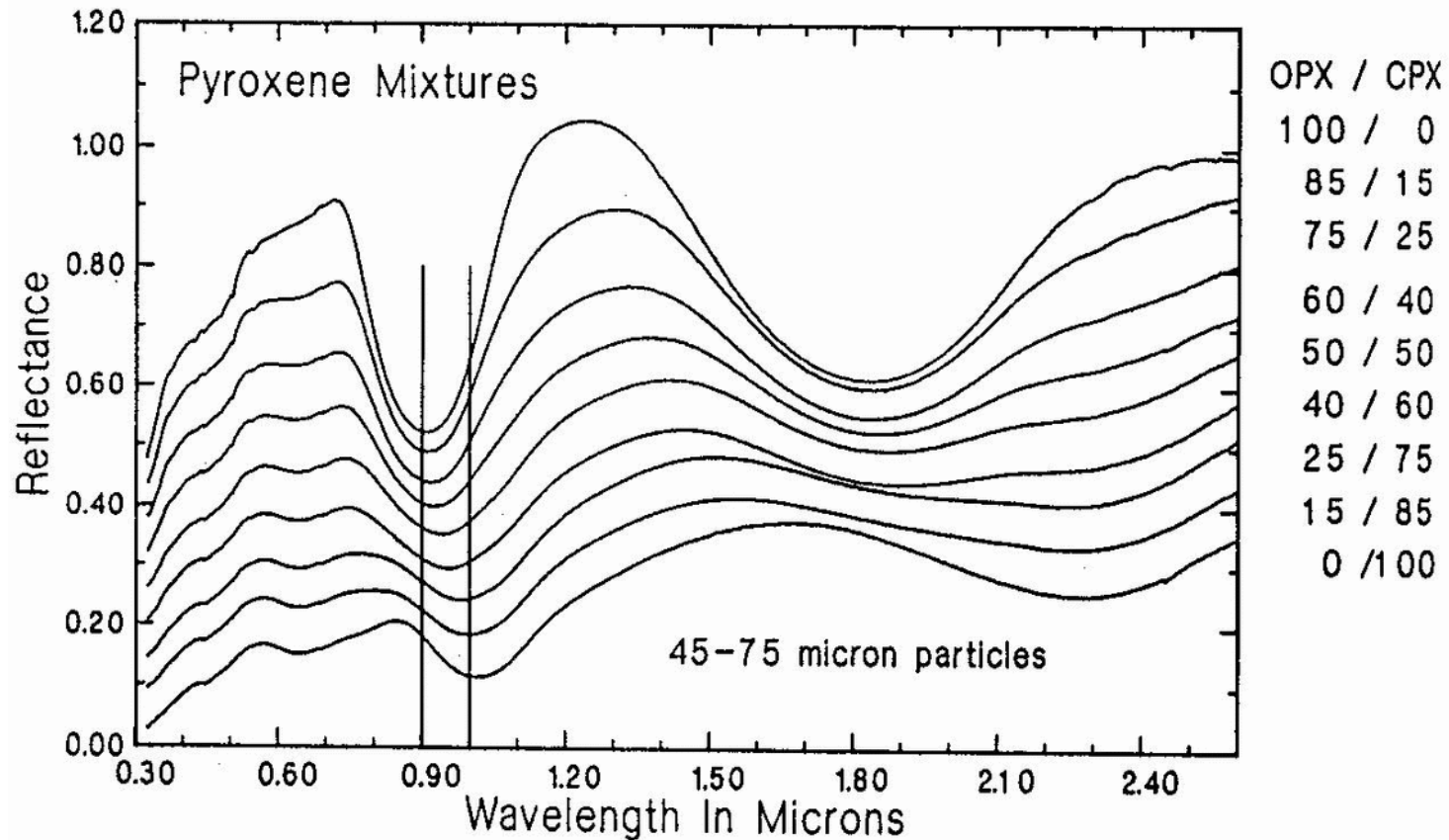
Position depends upon E field strength so upon crystal composition

(On Io position of bands suggests Mg rich crystal)

Anorthosite Due to trace Fe \Rightarrow weak. Broad feature near 1.25 μ m

Shock destruction of crystal lattice can eliminate band

Band Shifts for Pyroxene



Pieters 1993

Increasing Opx/Ca means increasing crystal (electric) field strength
Energy levels more separated, so band moves to shorter wavelength (higher energy)

Note: Bands artificially offset vertically to show them clearly.

Near Infrared Spectroscopy of Lunar Minerals

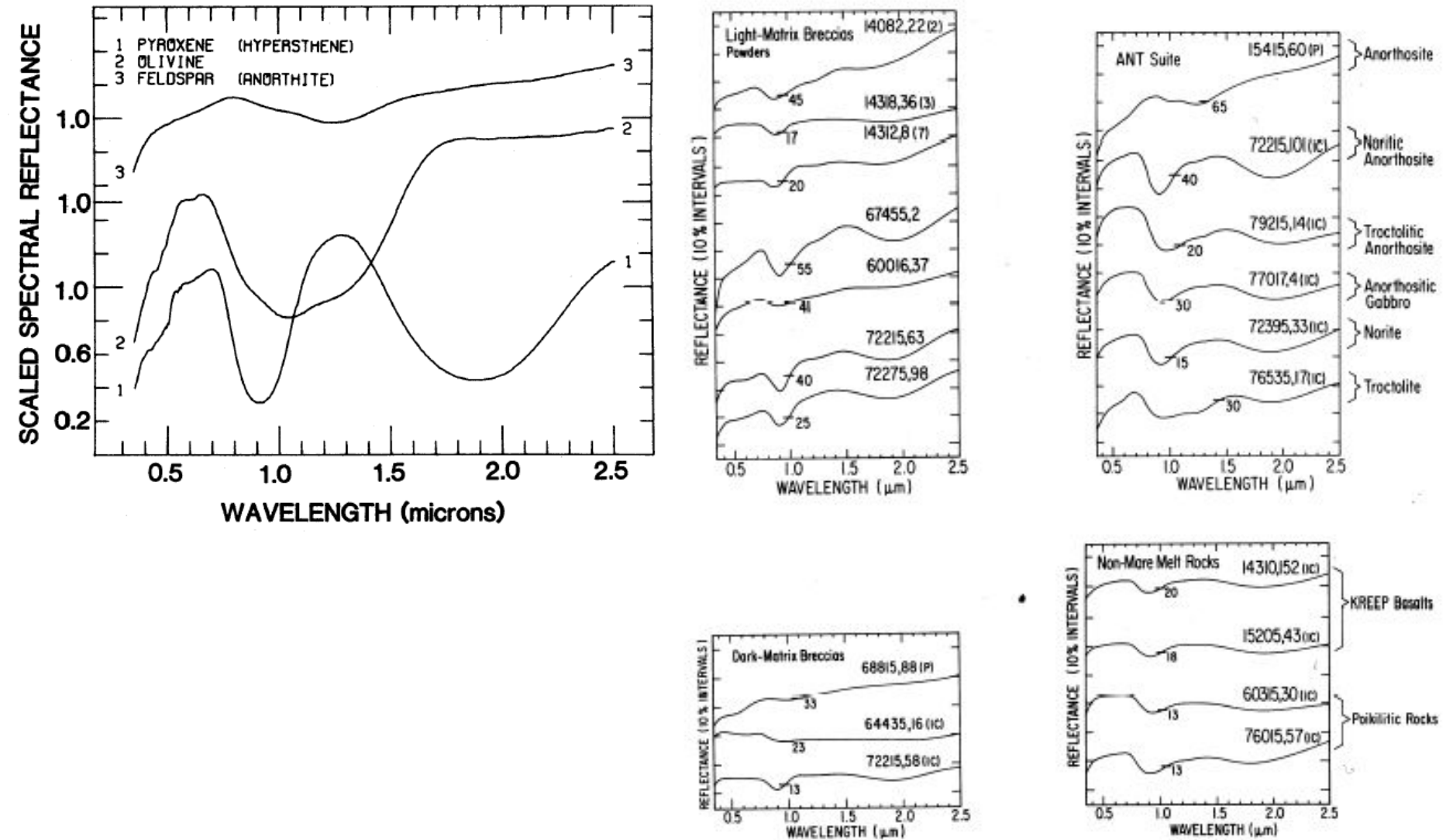
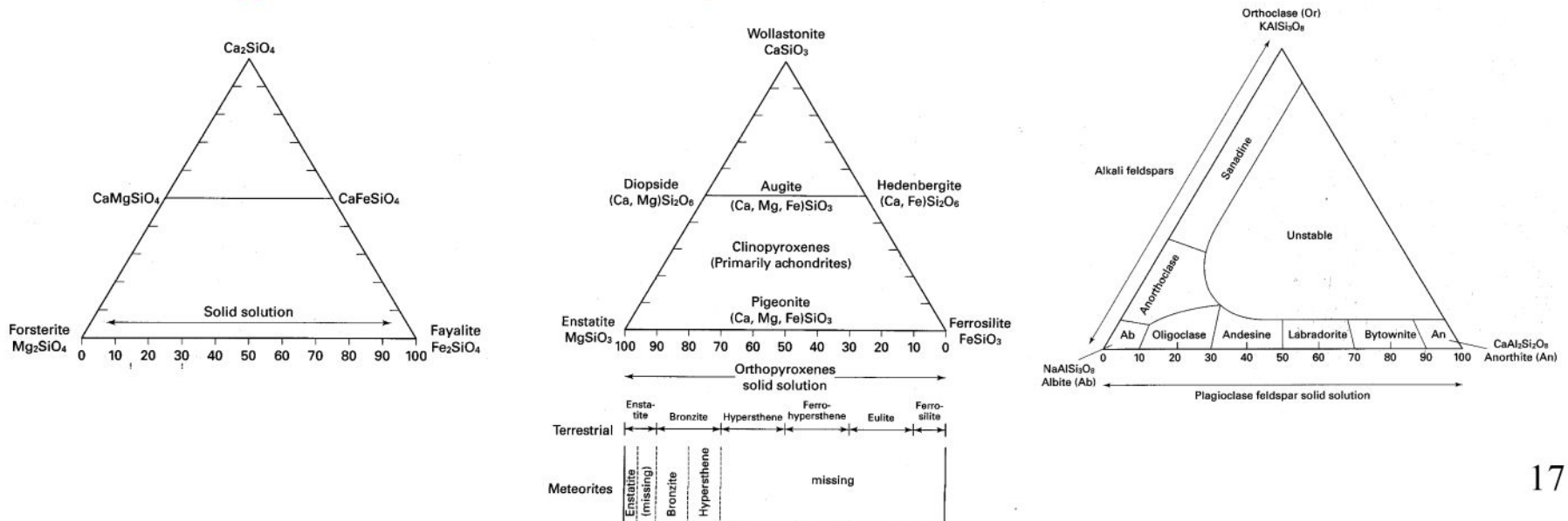


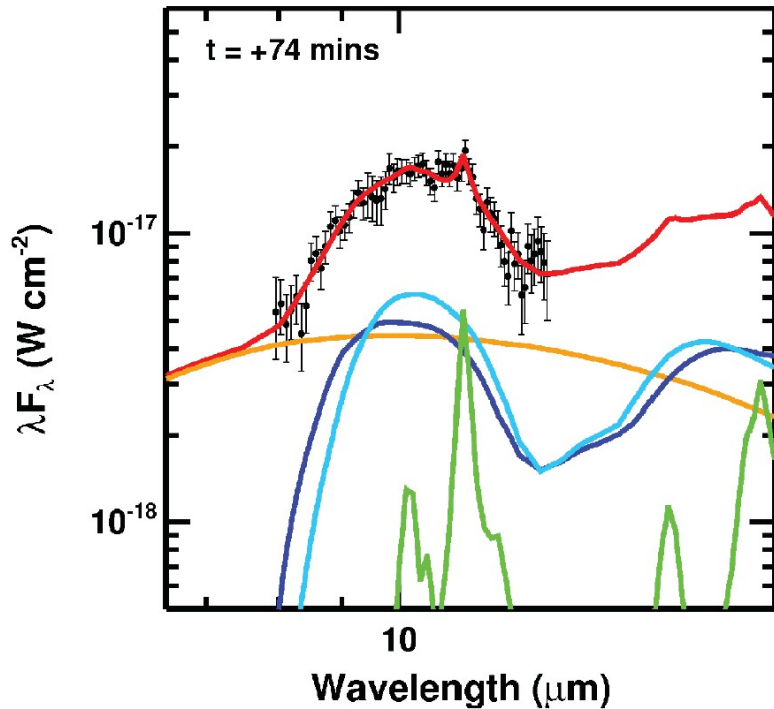
Fig. 3. Diffuse reflectance spectra of returned lunar highland rock interior chips (IC) and powders (P) measured in the laboratory [from Charette and Adams, 1977]. The spectra are offset vertically with the short horizontal bar indicating the reflectance at that wavelength. The classification scheme referenced here has since been updated by Stoffler et al. [1980] (see text).

Common Lunar Minerals

- olivine** isolated tetrahedra with 0 oxygen shared $\text{Si} + 4 \times \text{O} \Rightarrow \text{SiO}_4$
 plus Mg, Fe cations to maintain charge neutrality
- pyroxene** 1-D chains with 2 oxygen shared $\text{Si} + 2 \times \frac{1}{2}\text{O} + 2 \times \text{O} \Rightarrow \text{SiO}_3$
 plus Mg, Fe, Ca cations to maintain charge neutrality
- feldspar** In the quartz 3-D framework, Al^{+3} can replace Si^{+4} in the center of some of the tetrahedra, as long as appropriate cations like K^{+1} , Na^{+1} , and Ca^{+2} are also added to preserve charge neutrality. (This substitution by Al also happens to some of the Si in mica)

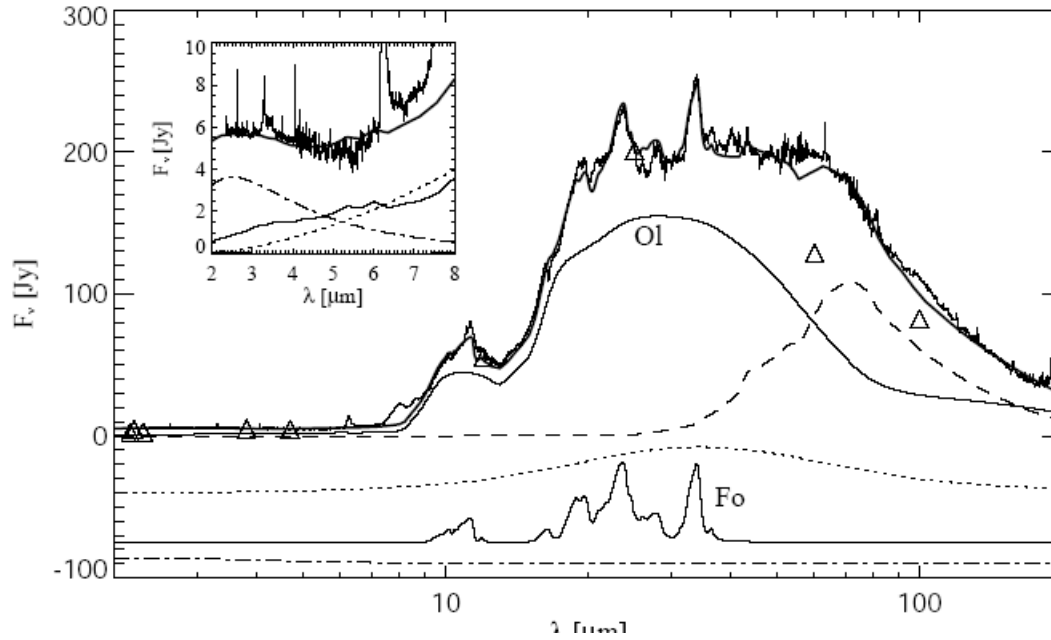


Comet Spectra: 10 μm Features



- Green: Crystalline olivine
- Cyan: Amorphous olivine
- Blue: Amorphous pyroxene
- Red: Observed dust emission from Comet Tempel after Deep Impact
- Orange: Nucleus emission (black body curve)
- Figure from Kelly et al 2009, data from Harker et al. 2007

Stellar Dust Spectra



- HD100546 from Bouwman et al. 2003

Mineral Spectra: Silicate bands

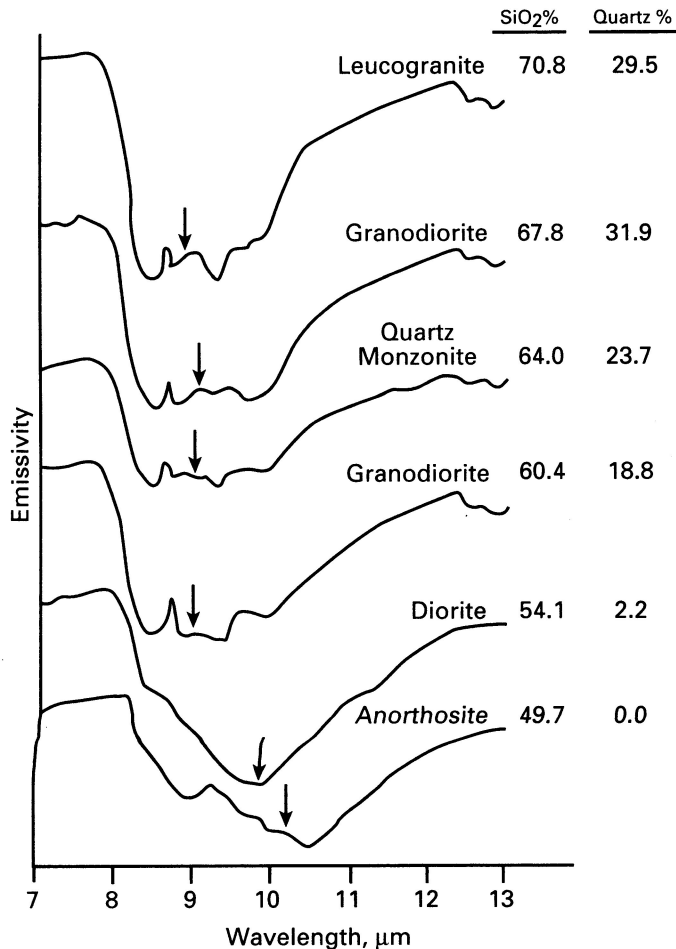


Figure 5-35 Emissivity spectra of igneous rocks with different silica and quartz contents. Arrows show centers of absorption bands. Spectra are offset vertically. From Sabine, Realmuto, and Taranik (1994, Figure 3, revised).

Emissivity to be defined later, in Chapter 5.

- For now: Lower emissivity means it produces less thermal emission than you would otherwise expect.

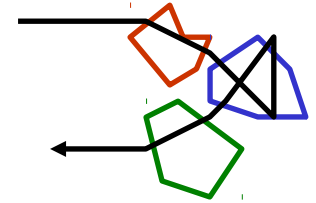
- Location of lowest emissivity point shifts with composition:

- “Mafic” components have minimum at longer wavelengths,

- Silicic components have minimum at shorter wavelengths

Material Properties and Effect on Spectra

- **Grain Size:** Larger grains have comparatively more volume \Rightarrow absorption and less surface \Rightarrow reflection
 - Finely ground powders (“streak”) typically lighter than solid material



- **Macroscopic (checkerboard) mixing:**

If you have two or more types of surface within a pixel, but separated enough that photons either bounce off one or the other, but not between them, then if

R_i is reflectance of each and f_i is fraction of surface area for each:

$$R = f_1 R_1 + f_2 R_2 + f_3 R_3 + \dots$$

$$1 = f_1 + f_2 + f_3 + \dots \quad (\text{so with just two } f_2 = 1 - f_1)$$

Example: 40% snow ($R_1=0.9$) and 60% dirt ($R_2 = 0.1$):

$$R = 0.4 \times 0.9 + 0.6 \times 0.1 = 0.36 + 0.06 = 0.42$$

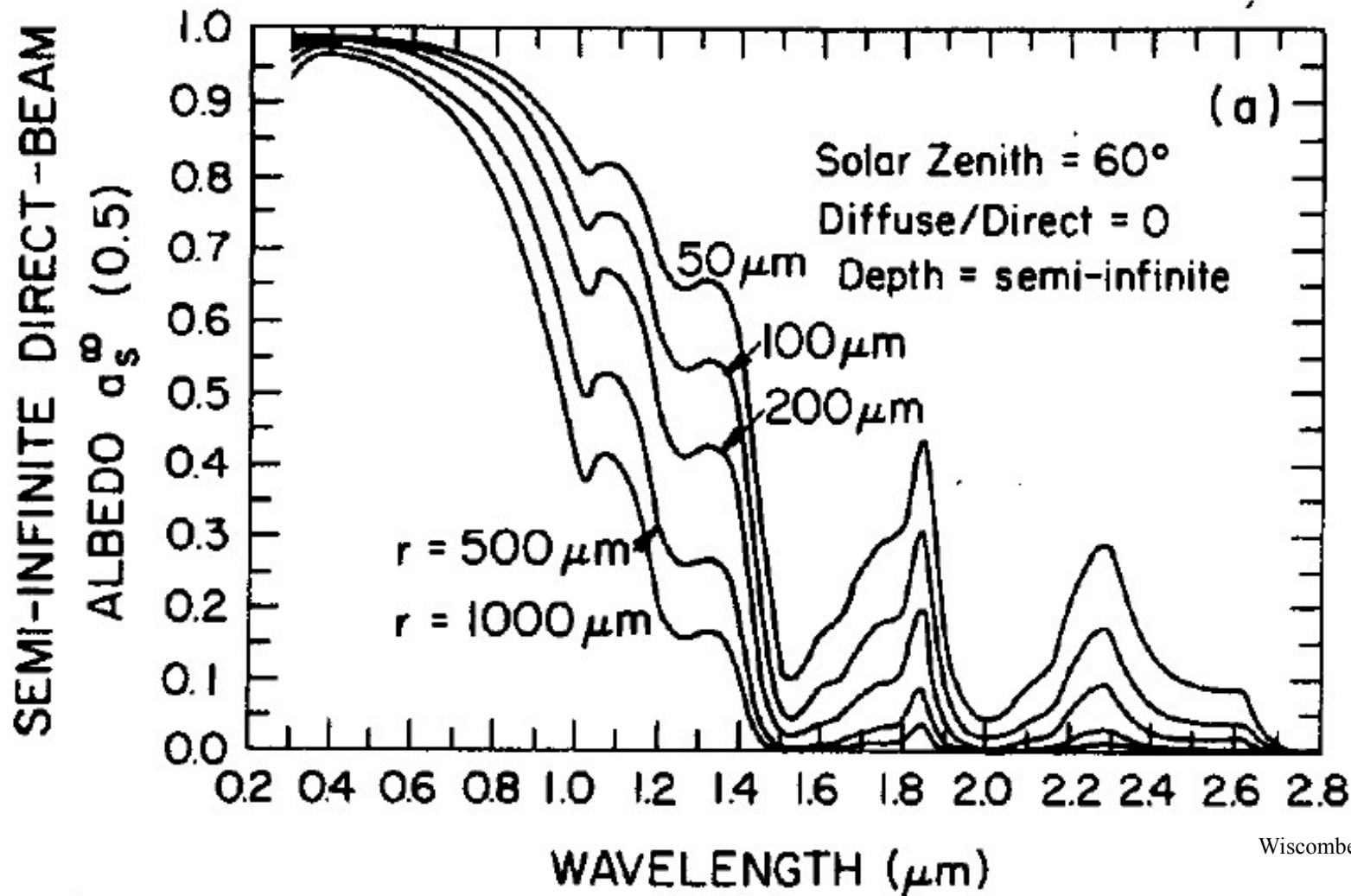
Even if mixing isn't macroscopic, we often assume this as a first approximation, since the math is “easy”

- **Microscopic (Intimate) Mixing**

Two or more materials mixed on such a fine scale that the photons bounce off of more than one type of material, before they exit the surface.

- The darker material always dominates
- (It takes only a little dark pigment to color a white paint base)
- IF it only bounced off Grain 1 then Grain 2 the net reflectance would be:
 $R = R_1 \times R_2$ With multiple bounces the math is messy

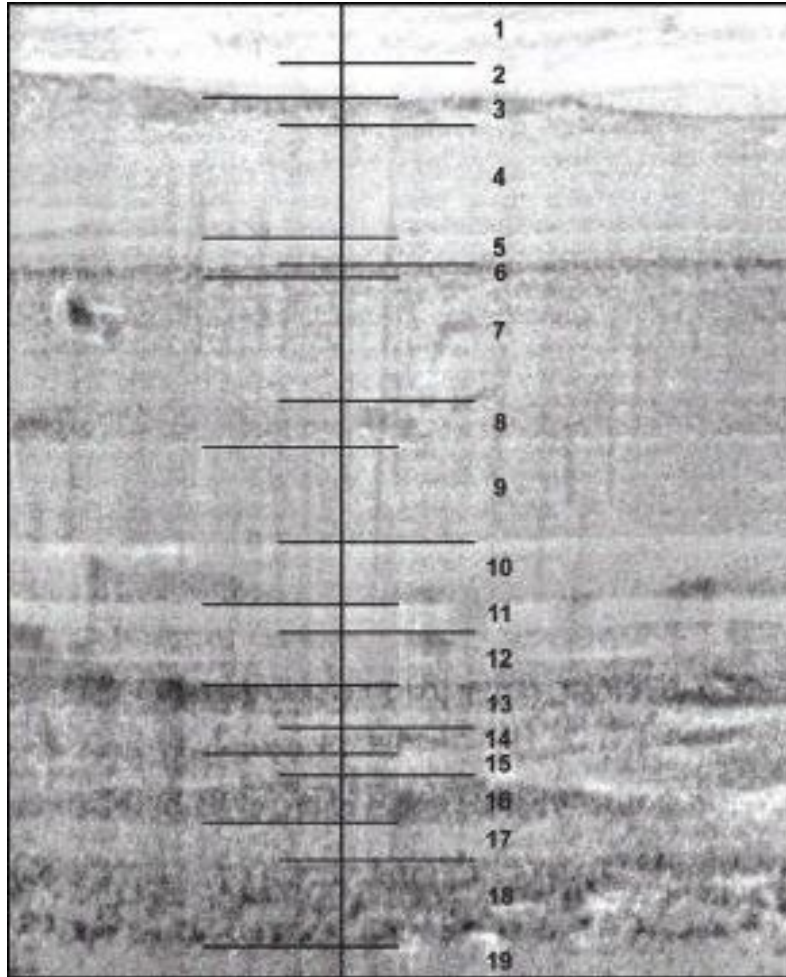
Ice spectra for varying Grain Size



Wiscombe and Warren, 1980

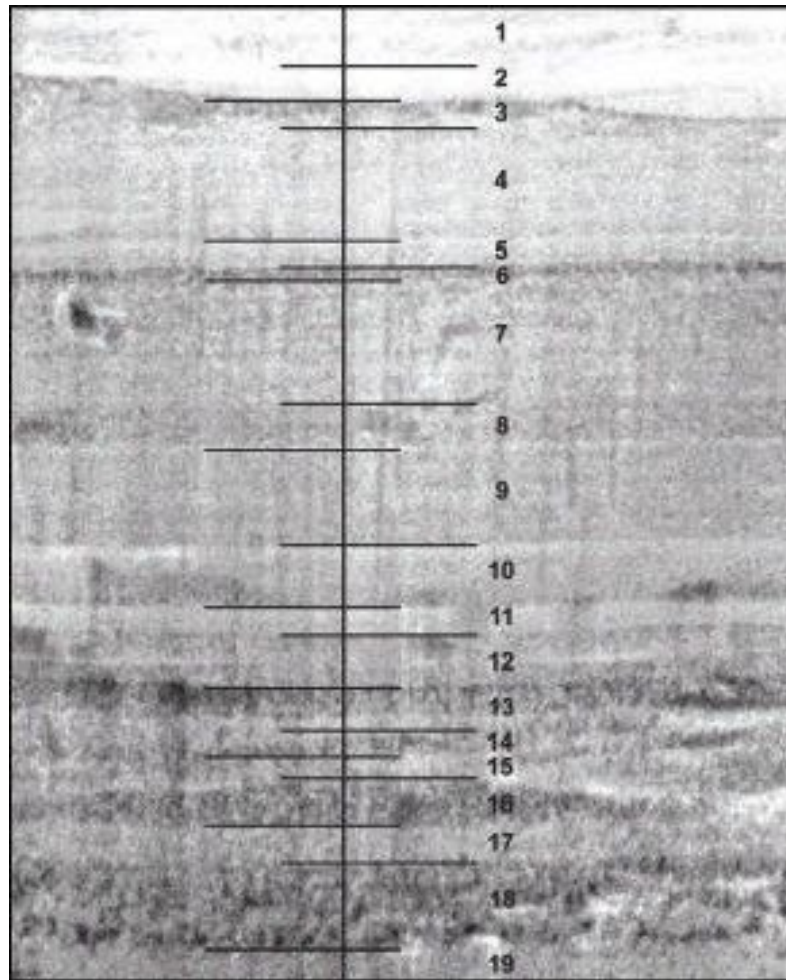
- Absorptions stronger with larger grains

Snow pit profiles with IR images

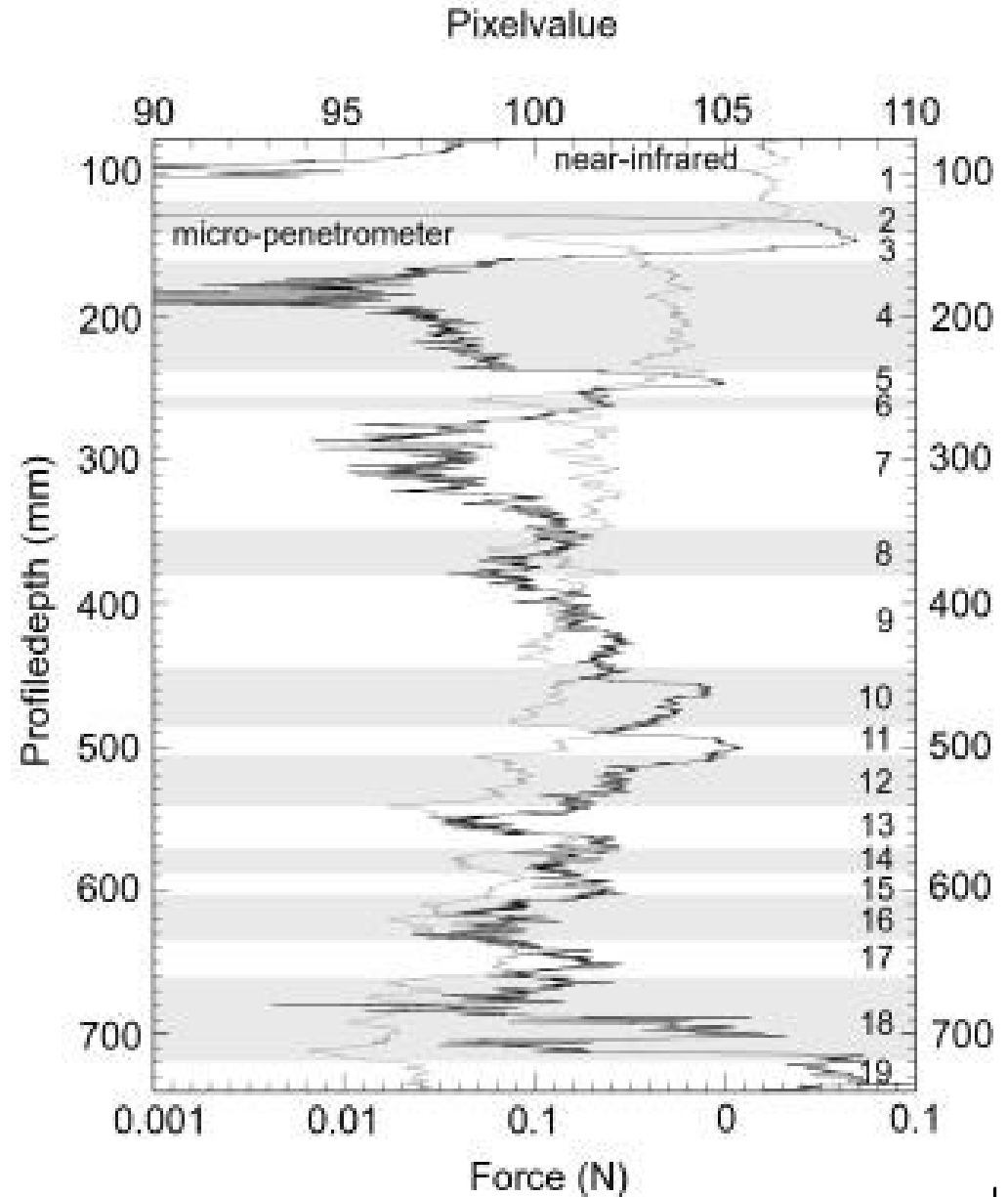


- Modify standard digital camera (replace usual IR blocking filter to see $0.84 - 0.94 \mu\text{m}$)
- Horizontal layers layers ID'd by eye
- Matzl and Schneebeli at Swiss Federal Institute for Snow and Avalanche Research
- Some work supported by NASA Mars Polar Science programs

Snow pit profiles with IR images

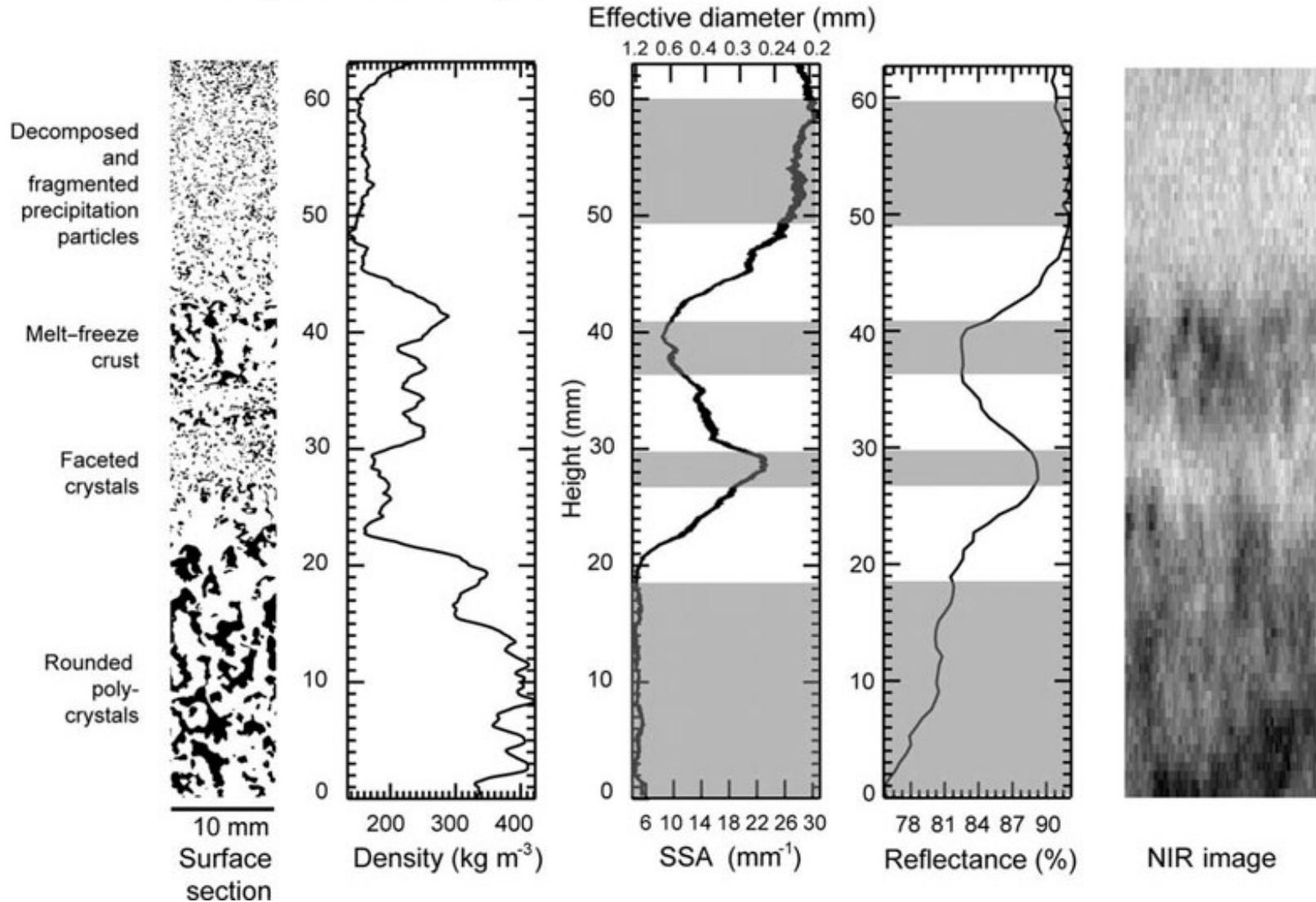


Matzl and Schneebeli, 2003 3rd Mars Polar Science Conference

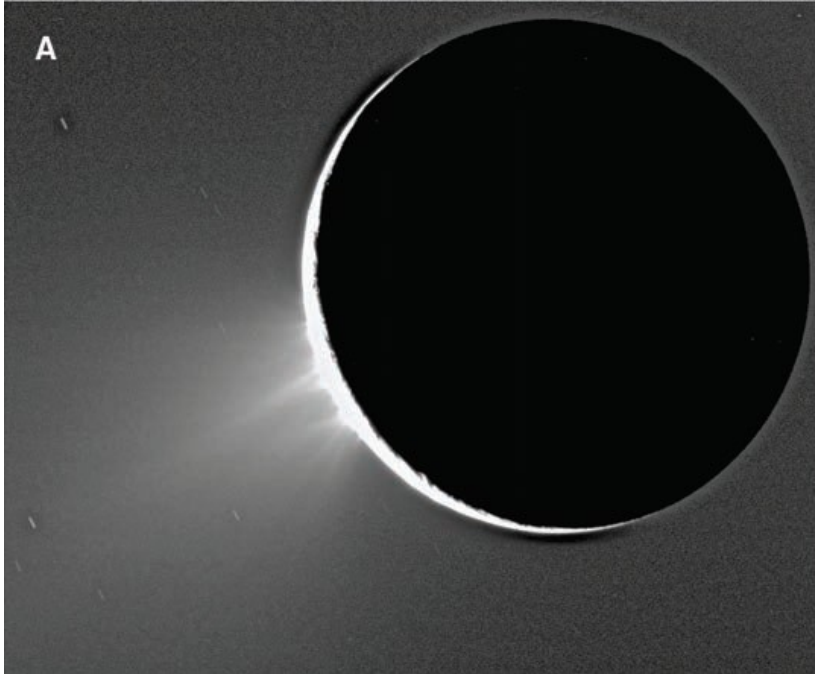


Snow profile

Sample 2: A sequence of decomposed precipitation particles, a melt-freeze crust, faceted crystals and rounded poly-crystals

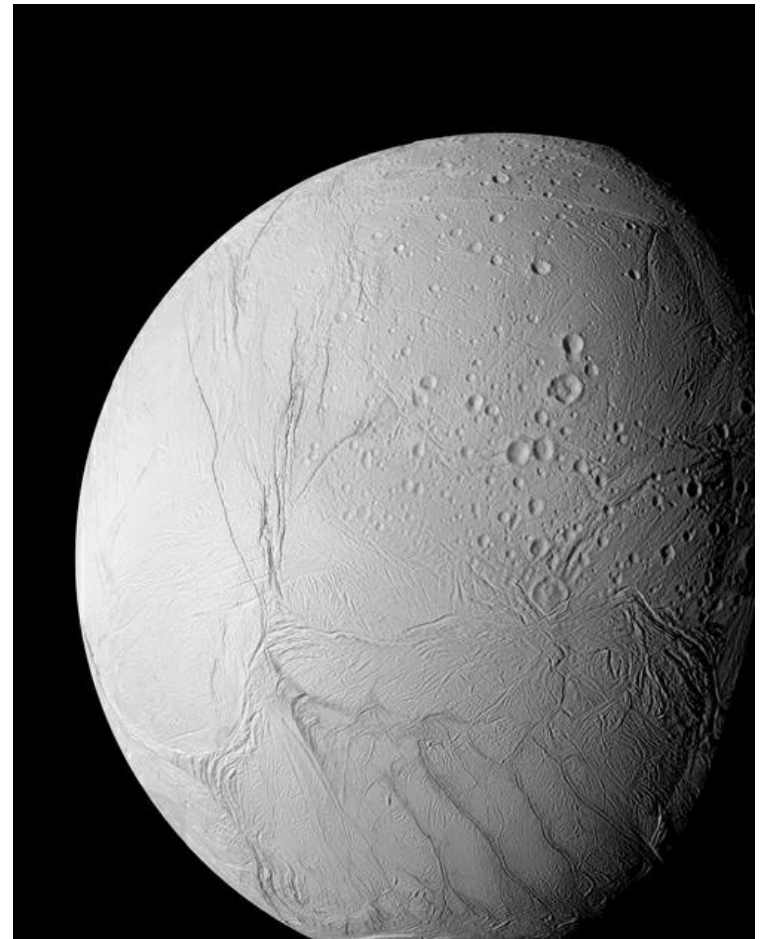


Enceladus: Active moon of Saturn

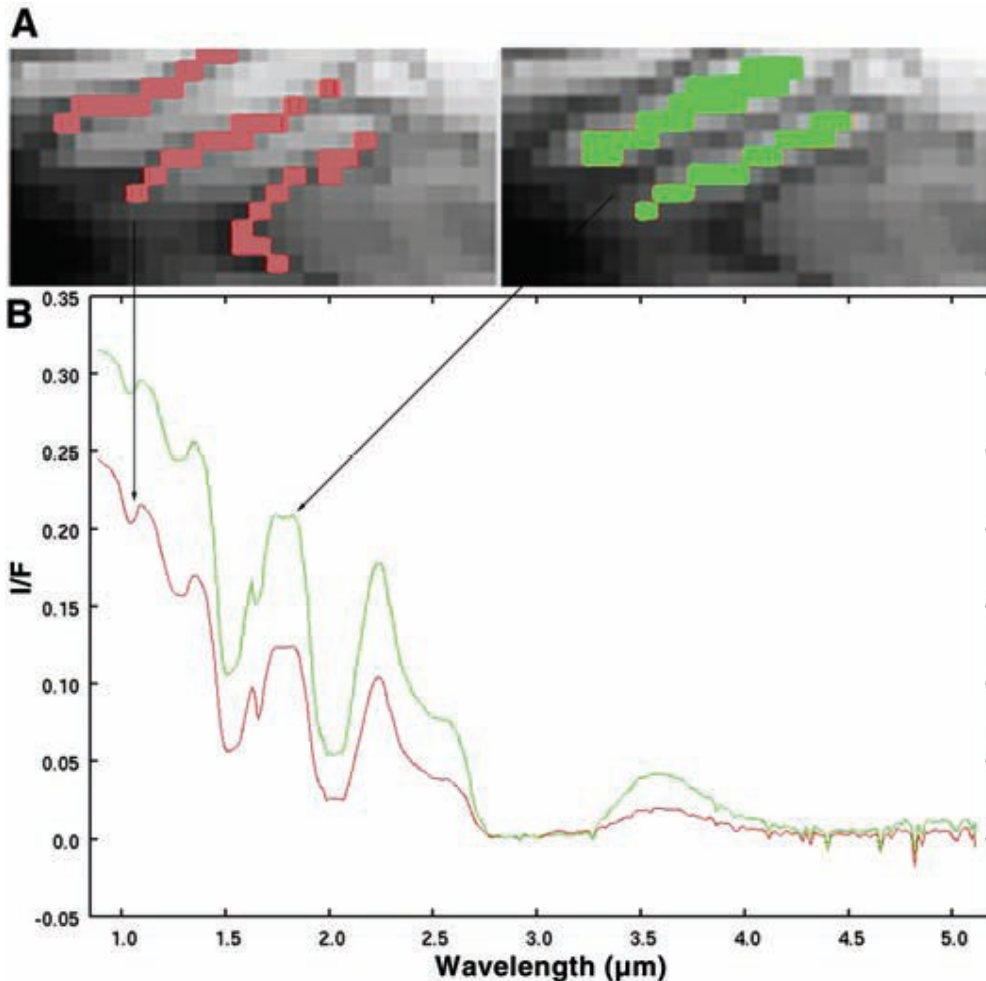


Porco et al. 2006

- 504 km diameter
- Plumes from south pole “tiger stripes”



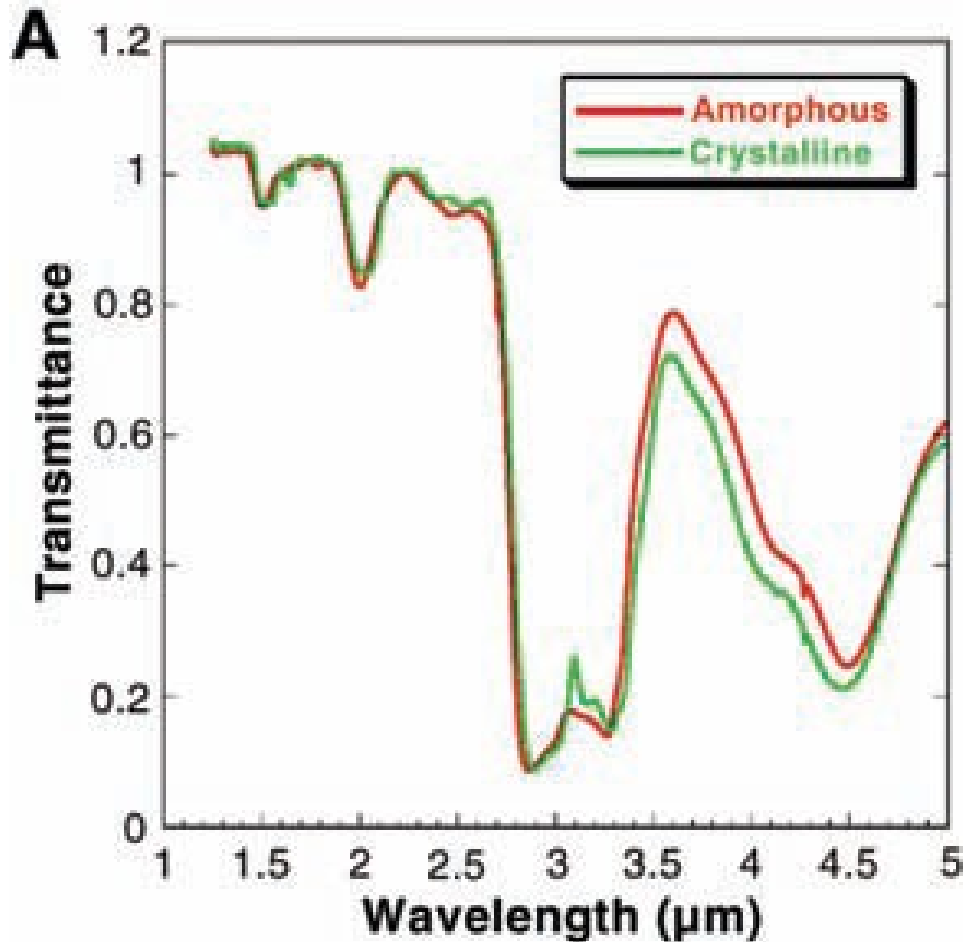
Enceladus Spectra from Cassini VIMS



Brown et al. 2006

- VIMS: Visible and Infrared Mapping Spectrometer (on Cassini spacecraft)
 - 0.5 – 5.1 μm range
 - 352 spectral channels
 - 0.5 mrad pixel size
- Red coded regions
 - Tiger stripes
 - 100 – 300 μm grains
- Green coded pixels
 - Between tiger strips
 - 50 – 150 μm grains

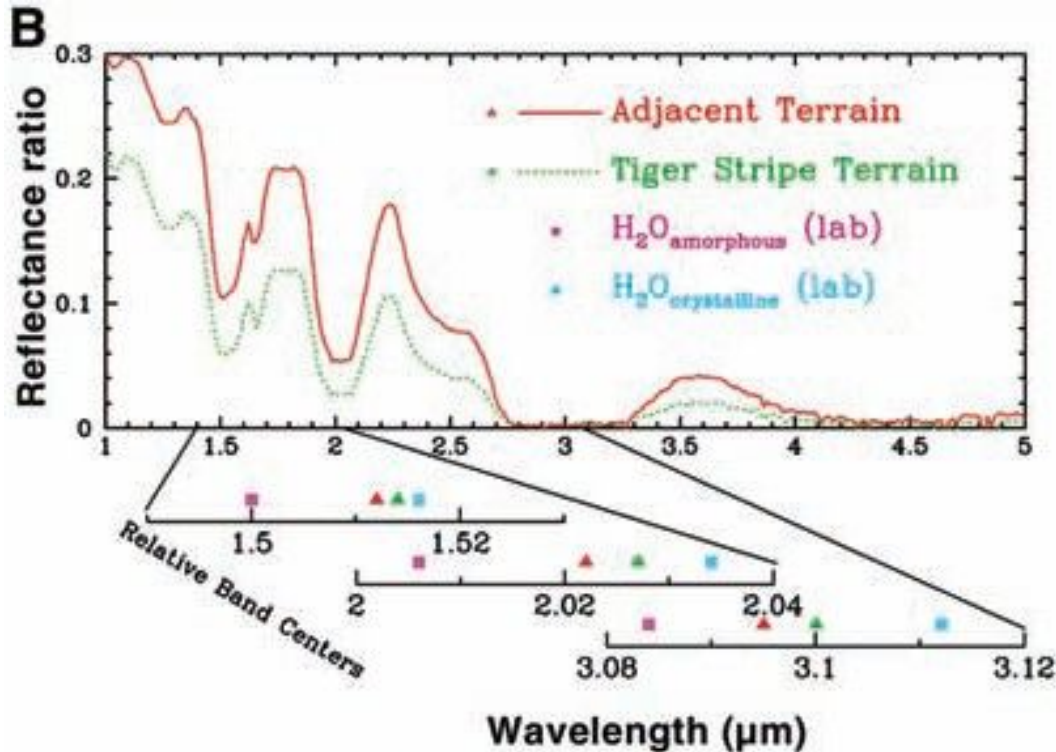
Crystalline vs. Amorphous Ice



- Color code reversed from first slide
- Red = Amorphous ice
- Green = Crystalline ice
 - Stronger 1.65 μm feature
 - Stronger “Fresnel” peak at 3.1 μm
 - (In general features sharper for crystals)
 - Wavelengths also shift
- Amorphous ice forms from direct vapor condensation at these temperatures
- High radiation can also make ice amorphous
- Amorphous ice converts irreversibly to crystalline ice when temperature is raised to ~ 150 K.

Brown et al. 2006

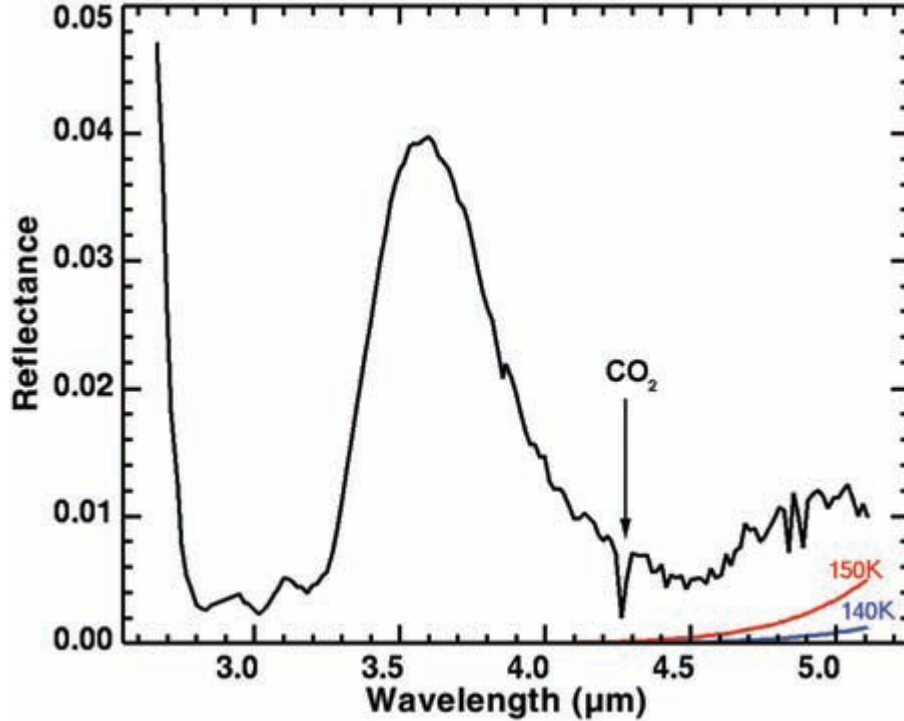
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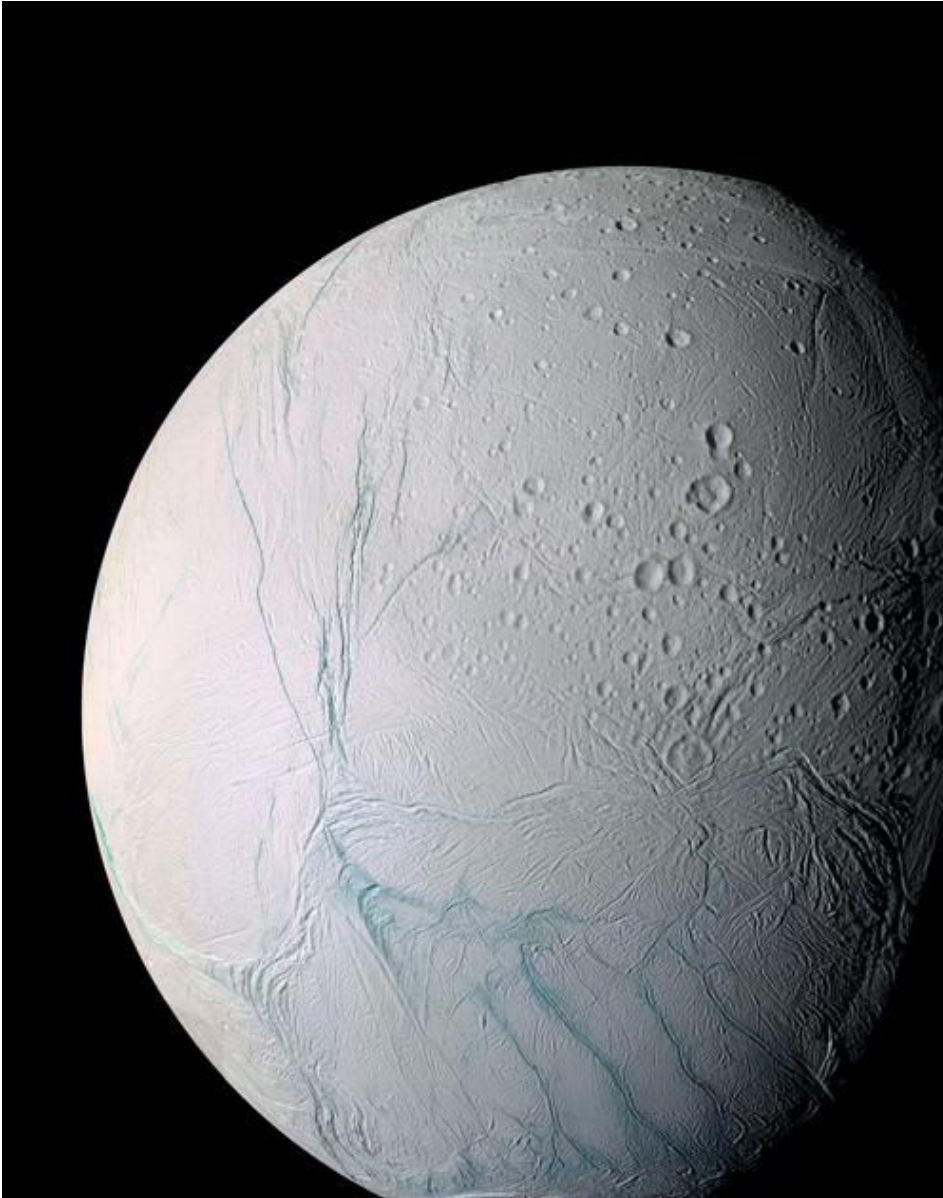
CO₂ molecules in water matrix



Brown et al. 2006

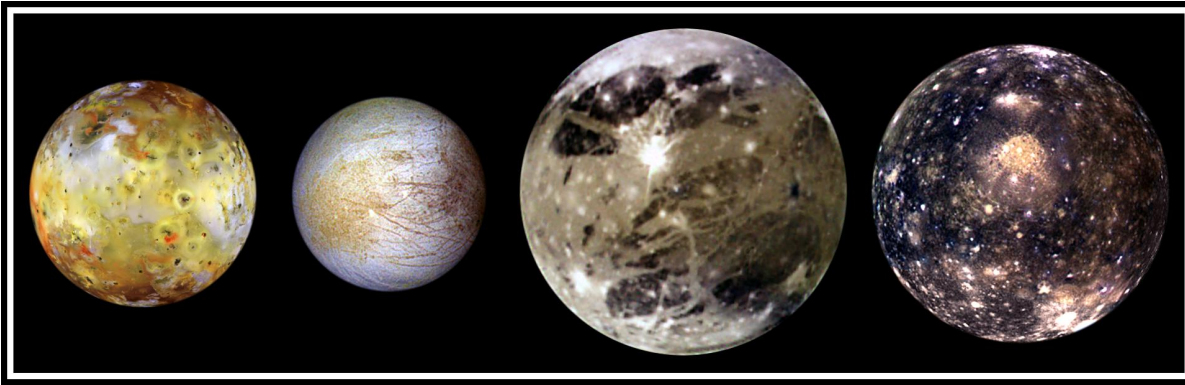
- Observed CO₂ wavelength of 4.26 μm is shifted from CO₂ ice value:
- CO₂ molecules embedded in some other (probably H₂O) matrix
- CO₂ ice is much more volatile than H₂O ice. It probably evaporates rapidly, leaving behind only the CO₂ trapped in H₂O

ISS (visible wavelength results)



- Blue color codes larger grains as sensed by the visible wavelength CCD camera (ISS)

Galilean (Jupiter) Satellites: Dirty Ice



- Io
- Europa
- Ganymede
- Callisto

