KISS Lunar Volatiles: NIR working group findings

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November 4, 2013

What do we want to know?

from last time

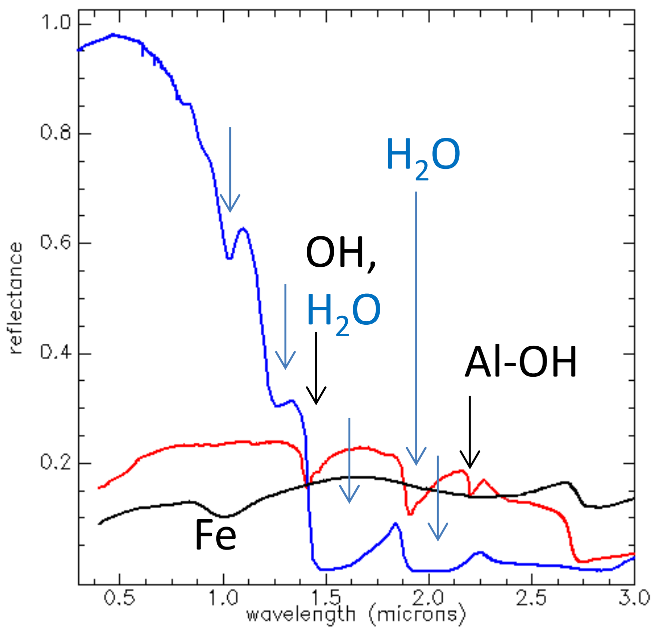
- **Where** is the H_2O(ice,bound)/OH? (Where is each?)
- **How much?** (and how much variation?)
- **What else** is there (regolith, H_2S, NH_3, etc.)?
- **What is the isotopic ratio**?

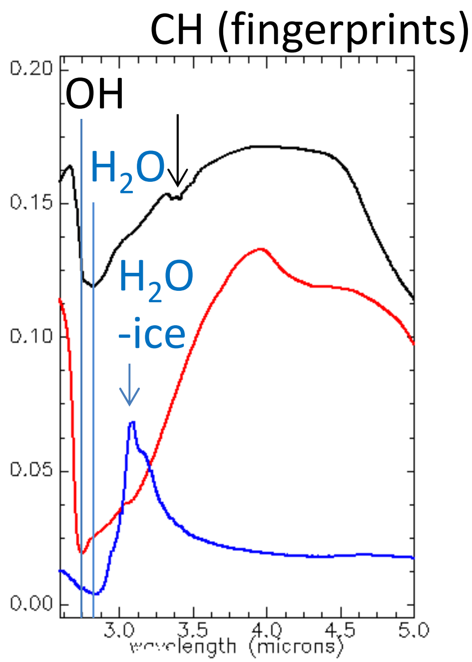
More focused questions for observation requirements

1. How many spectral bands and with what spectral resolution do we need to distinguish H_2O-ice from OH-bearing silicates?
2. What is the relationship between band depth of H_2O-ice and mixing ratio with other lunar materials and/or ice's physical form? What detectability requirements does this place on instruments?

IR spectroscopy H_2O (ice), H_2O (bound), OH (structural)

from last time





Montmorillonite [w/OH, not on Moon]
$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

Water ice
H_2O

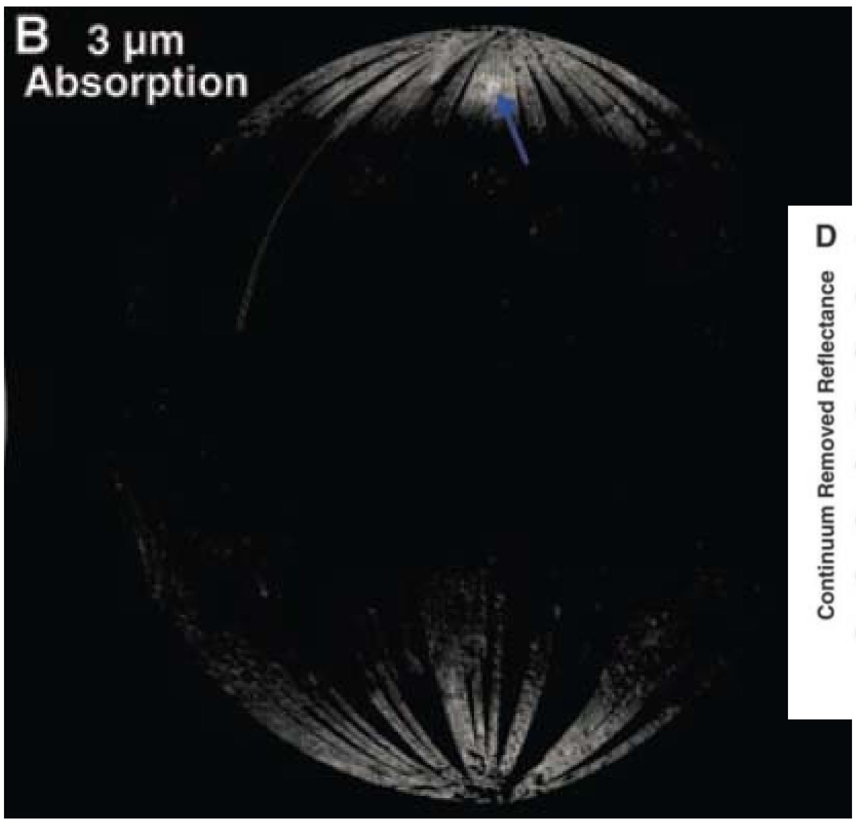
Pyroxene (Augite)
$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$

- OH vs. H_2O-bound and H_2O-ice can be discriminated with appropriate spectral sampling and SNR
- Hard to study OH vs. H_2O question on Earth because too much water

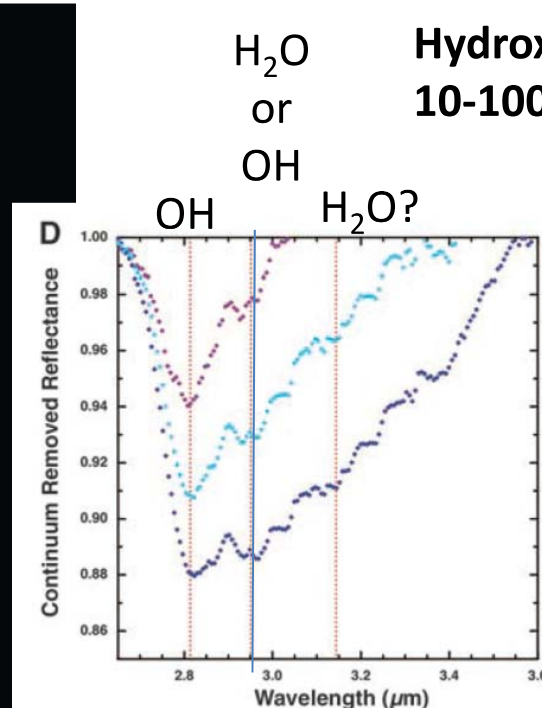
Where is the H_2O(ice,bound)/OH? Where is each?
Recent results: VNIR reflectance

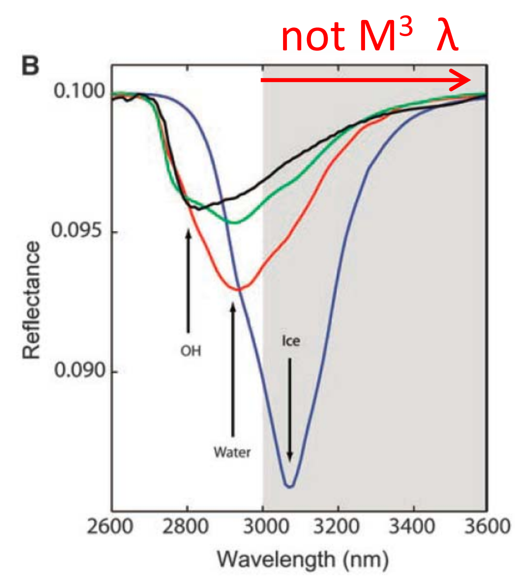
from last time

- Three NIR instruments detect 3-µm absorption (M^3, VIMS, HRI-IR)
- Certainly OH, possibly bound H_2O (deleted) (10-1000ppm)
- Possibly diurnal variation (but difficult to calibrate thermal contribution)
- Highest spatial res (M^3) doesn't have wavelength range to verify H_2O-ice



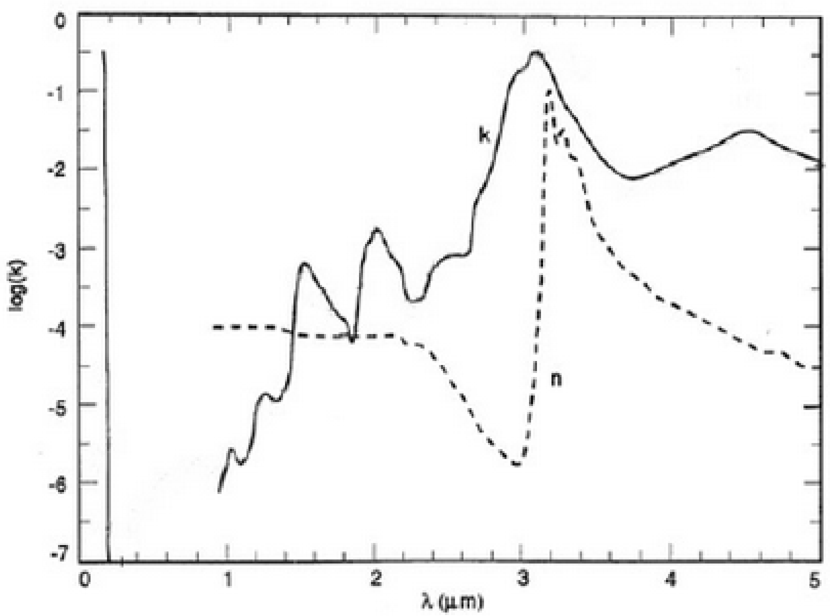
Hydroxylated/hydrated phase: 10-1000ppm and locally higher

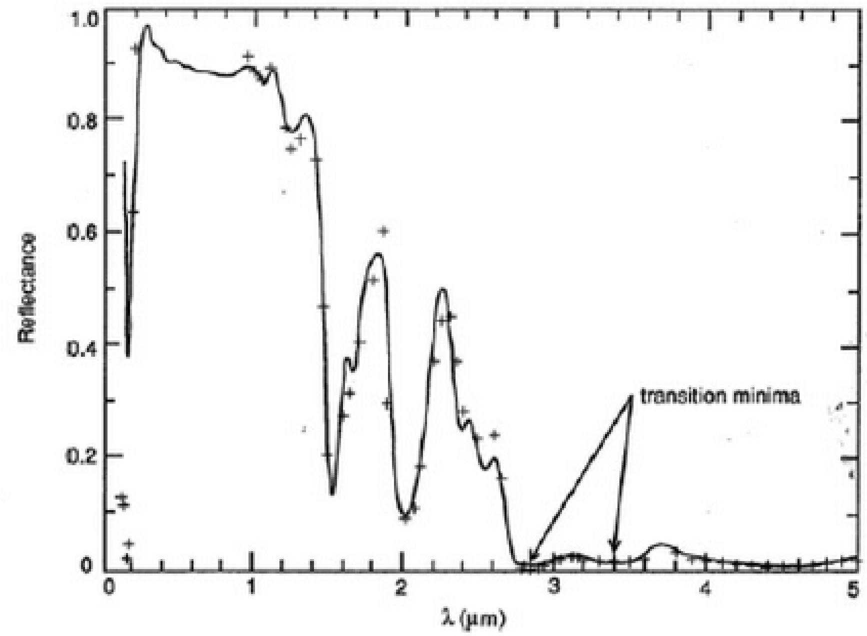




Pieters et al.; Sunshine et al.; Clark et al.; 2009, Science

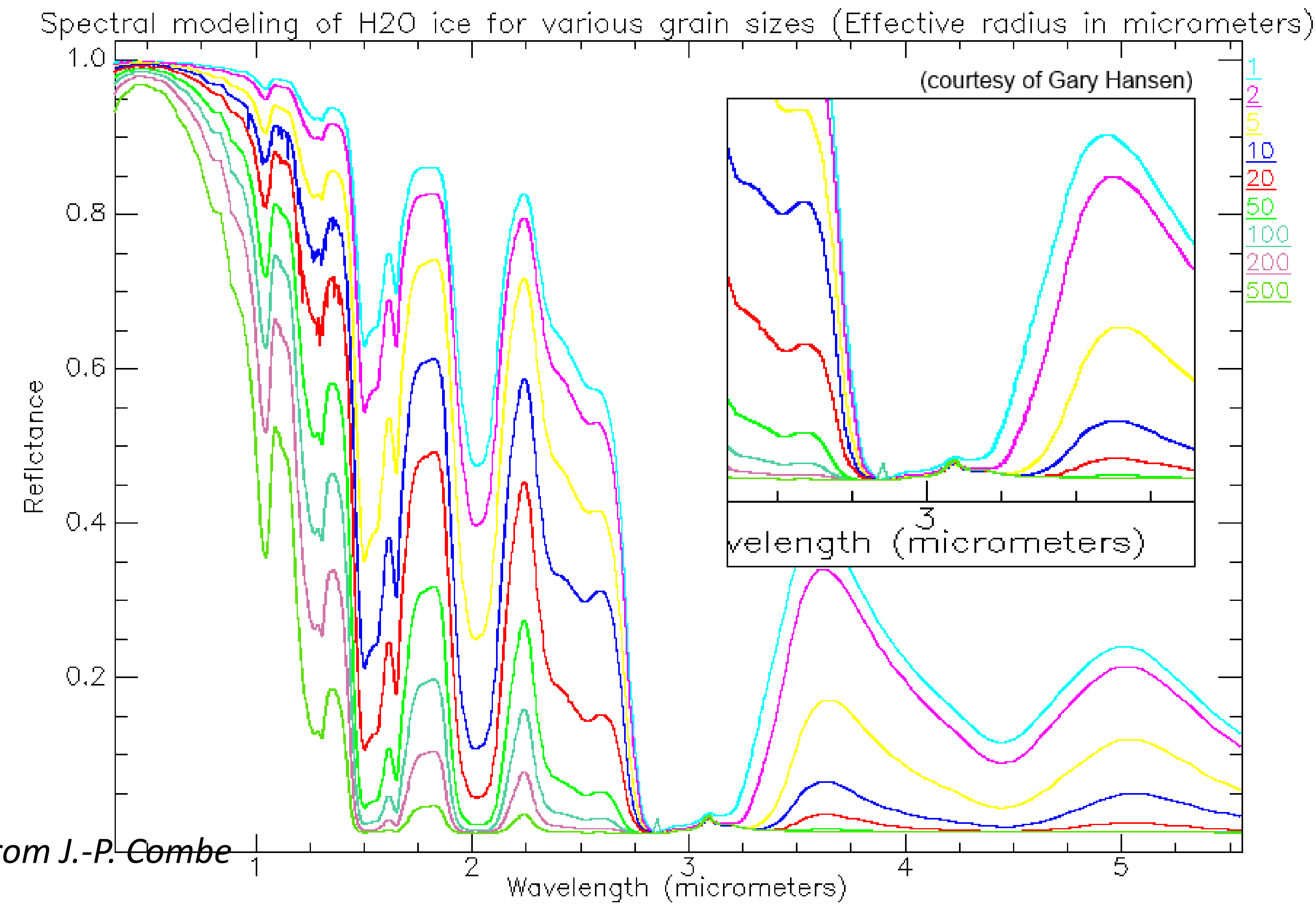
First, to answer the question from last workshop: What governs the shape of the 2.8-3.4µm H_2O ice absorption?





As k increases, at first the reflectance decreases because photons get more absorbed within the grains (volume-scattering regime). As k continues to increase, the reflectance begins to be dominated by the specular reflection off the grains (because most photons that enter the grains are absorbed; weak surface scattering regime). The specular reflection depends on n (real part of the optical constant) and k (imaginary part). When k is "small", the specular reflection is constant because the influence of n dominates. However, as k increases, the specular reflection term begins to evolves with k (increases with k) (strong surface scattering regime). So at the end, when k begins to be quite high, the reflectance tends to re-increase. This is the case around 3.15 microns in water ice, which creates a local maximum that varies in intensity according to temperature and crystallinity.

Grain size effects on band shape



from J.-P. Combe

Dependence to temperature of H_2O ice absorption bands

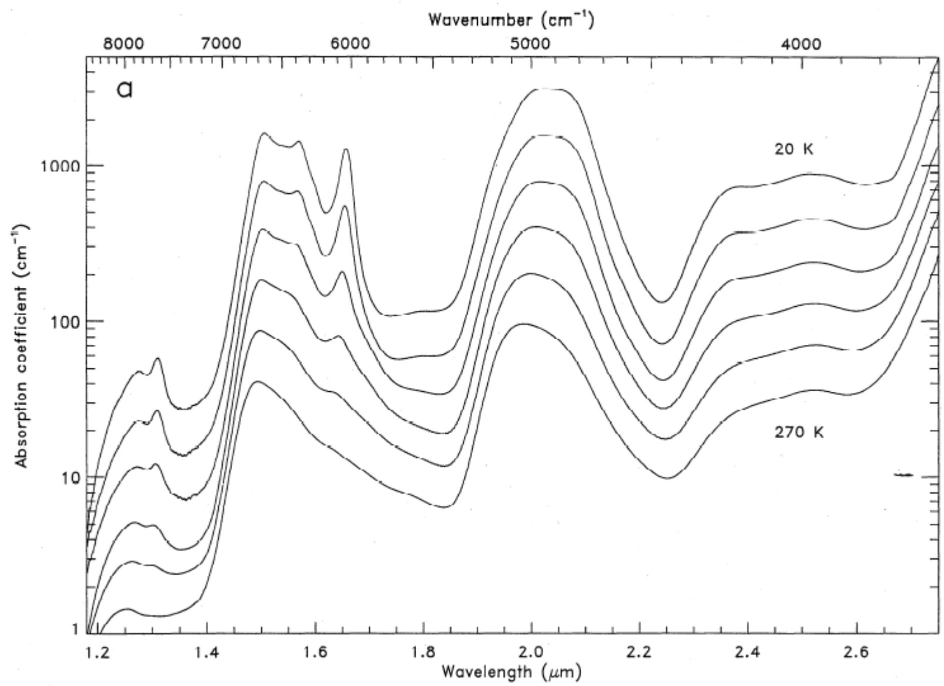


Figure 2. Illustration of the temperature dependence of our H_2O ice absorption coefficients. (a) Spectra shown at 50 K intervals from 20 to 270 K. The ordinate is labeled for the lowest curve, with higher temperature curves shifted upward by successive powers of 2. (b) Enlargement of the band complex around 1.6 μm, showing the shape changes and wavelength shifts of the component bands. All 26 of our H_2O ice spectra (every 10 K, from 20 to 270 K) are plotted, superimposed at the same scale.

from J.-P. Combe

Grundy et al., 1998, JGR 103

Shifting of absorption bands as function of temperature

Table 1. Near-Infrared Bands of Crystalline Water Ice

Average Position	Peak Position		FWHM,	Peak,	$\frac{d\nu}{dT}$,
λ, μm	$\bar{\nu}$, cm^{-1}	λ, μm	cm^{-1}	cm^{-1}	cm^{-1} K^{-1}
1.04	9540±40	1.048	830	0.33	+0.8
1.27	7809±10	1.280	760	1.5	+0.66
1.31	7628±3	1.311	104	0.61	+0.04
1.37	7213±50	1.386	330	0.55	+0.75
1.5	6664±5	1.501	134	17.	+0.32
1.52	6567±10	1.523	340	25.	+0.21
1.56	6371±20	1.570	115	13.	+0.57
1.6	6362±20	1.572	650	21.	−0.75
1.65	6037±1	1.656	87	30.	+0.32
1.8	5568±10	1.796	330	3.2	−0.05
1.99	4949±20	2.017	260	46.	+0.59
2.02	4952±20	2.019	430	19.	−0.07
2.06	4810±20	2.079	140	29.	+0.47
2.36	4242±5	2.357	157	8.1	−0.05
2.52	3961±5	2.525	540	27.	−0.01

Table shows various parameters for 15 Gaussians fitted to the absorption coefficient spectra. The first column shows the wavelength of each Gaussian, averaged over the full temperature range from 20 to 270 K, for identification purposes. The second and third columns show the frequencies and wavelengths of each Gaussian at 20 K. The fourth and fifth columns give the full widths at half maximum (FWHM) and peak absorption coefficients of each Gaussian at 20 K. The last column shows the shift in position with temperature, evaluated using a linear fit to the data between 100 and 200 K.

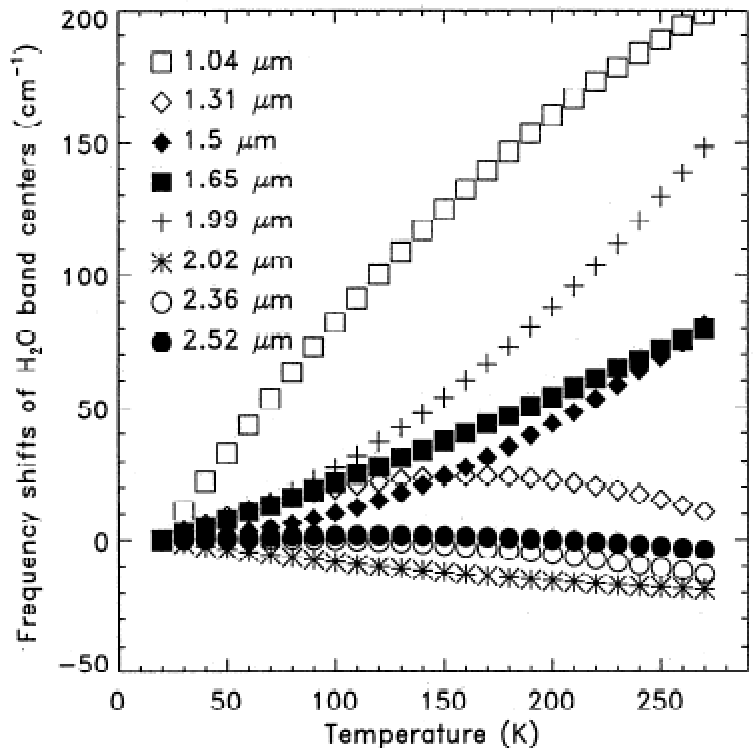


Figure 5. Examples of the temperature dependent shifts in frequency of several of our 12 well-constrained absorption bands, relative to the 20 K values which are tabulated in Table 1. These curves result from fitting Gaussians to the different components of the spectrum at each temperature, as described in the text.

Grundy et al., 1998, JGR 103

Temperature change 50K → 200K:
13nm shift at 1.65 µm

from J.-P. Combe

Amorphous and crystalline solid H_2O ice

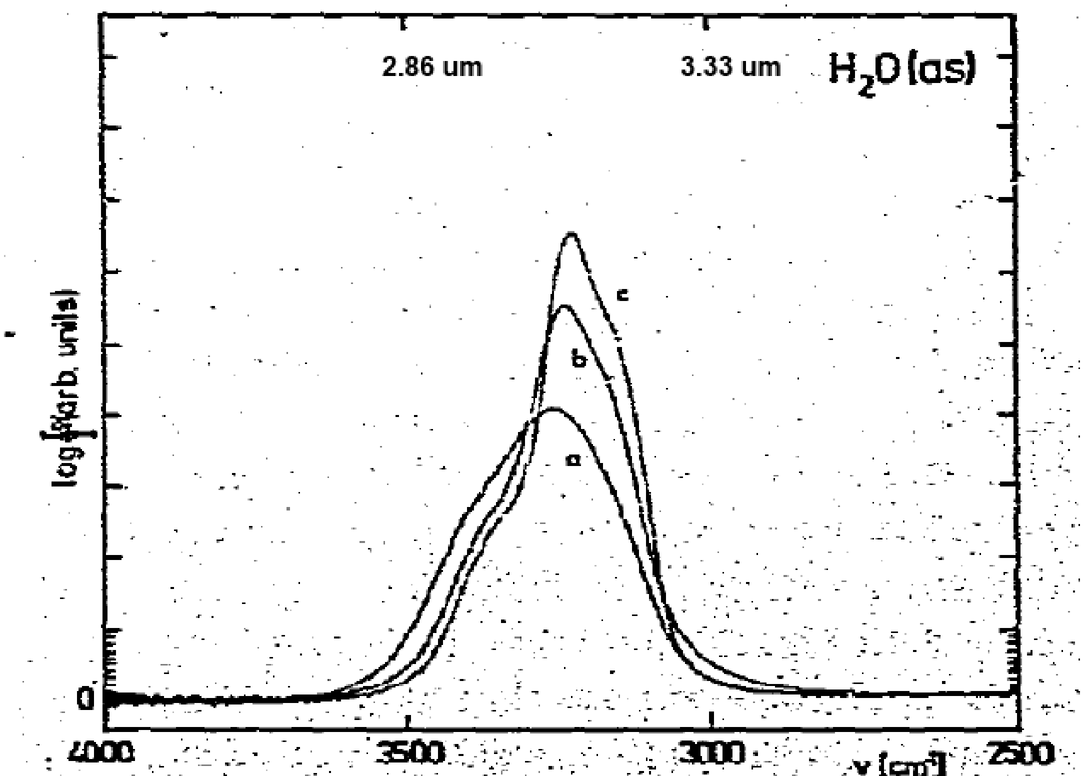


Fig. 1. Infrared absorbance spectra (OH-stretching band) of (a) solid H_2O(as) immediately after deposition at 10 K, (b) the same sample completely annealed at 130 K, and (c) the same sample after recooling to 10 K.

from J.-P. Combe

Hagen, 1981, Chem. Phys. 56

Temperature annealing of H_2O ice

3.05810

3.06748

3.07692

3.08642

3.09598

3.10559

3.11526

Hagen, 1981, Chem. Phys. 56

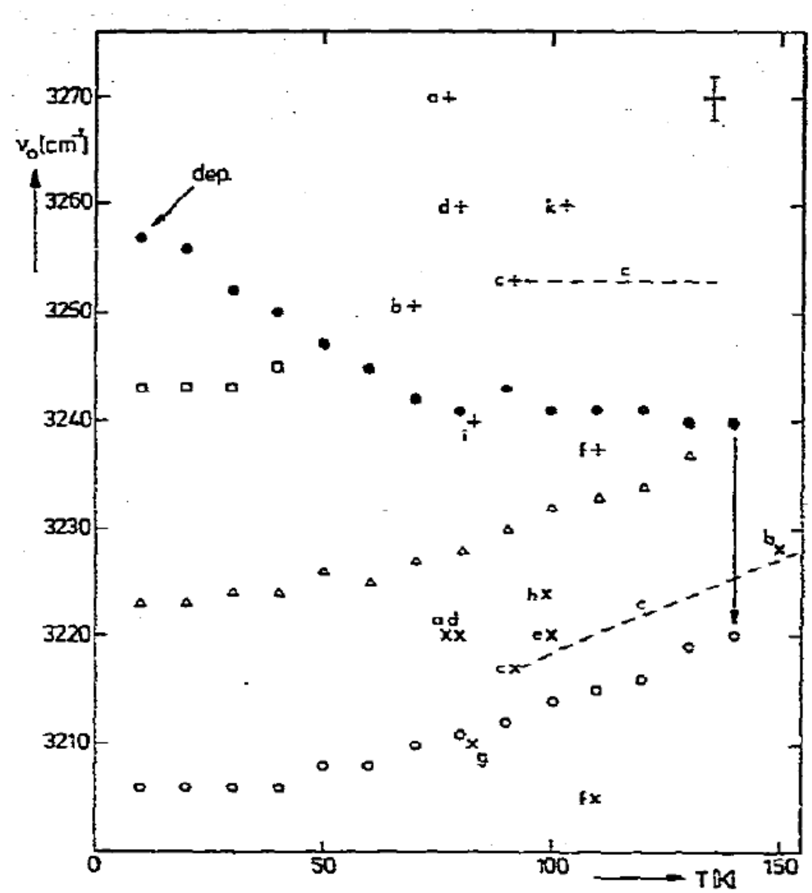


Fig. 5. Peak frequency ν_0 (OH-stretching band) as a function of temperature of solid H_2O deposited at 10 K. Full circles indicate the annealing of solid H_2O(as) from the deposition at 10 K until the phase transformation to H_2O ice I_c at 140 K; the arrow indicates the irreversible transformation of H_2O(as) to H_2O I_c at 140 K; open symbols show the reversible temperature dependent behaviour of partially (to 50 K) annealed H_2O(as) (squares), completely (up to 130 K) annealed H_2O-(as) (triangles), and H_2O I_c (circles) respectively. Literature values are marked with + for H_2O(as) or × for H_2O I_c and I_h, and a letter indicating the reference. The dashed lines are from ref. [17]. Error bars are indicated in the right hand corner. (a) Ref. [8], (b) ref. [17], (c) ref. [18], (d) ref. [19], (e) ref. [20], (f) ref. [21], (g) ref. [22], (h) ref. [23], (i) ref. [24], (k) ref. [25].

from J.-P. Combe

Other trace consituents identified by LCROSS

	H_2O	CO_2	SO_2	H_2S
ν_1	3.17 μm			3.92 μm
ν_3	2.96 μm	4.37 μm		3.80 μm
$2\nu_1$			4.36 μm	
$2\nu_2$				4.28 μm
$2\nu_3$			3.77 μm	
$\nu_2+\nu_3$	2.02 μm			
$\nu_1+\nu_2$				2.69 μm
$\nu_1+\nu_3$	1.52 μm	2.7 μm	4.07 μm	
$2\nu_2+\nu_3$	2.8 μm			
$\nu_1+\nu_2+\nu_3$	1.25 μm			
$3\nu_3$	1.02 μm	1.43 μm		
$\nu_1+2\nu_2+\nu_3$		2.0 μm		
$2\nu_1+\nu_3$		1.97 μm		
$2\nu_1+2\nu_2+\nu_3$		1.58 μm		
$\nu_1+3\nu_3$			1.96 μm	
$3\nu_1+\nu_3$			2.10 μm	

Used successfully on NIMS

Pilorget, 2012

How much ice might there be?

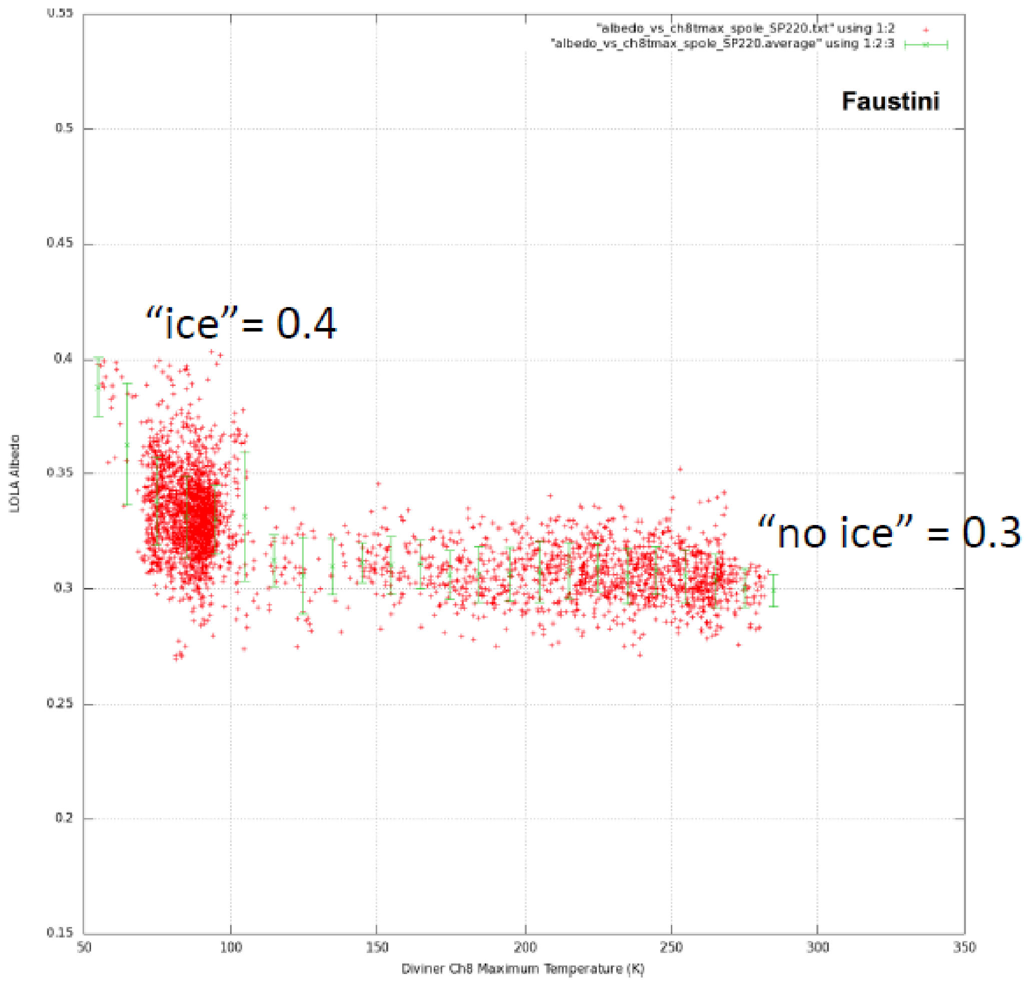
- Two methods
  - Calculate from LOLA reflectance near 1um
  - Determine M3 detection threshold near 2um

LOLA Method

- So far, the LOLA (laser altimeter) reflectance measurements at 1064-nm are the best evidence for this surface water ice
- The approach here is to quantify the abundance of the putative ice using a radiative transfer model along with the LOLA data
- We then look at the water ice absorption bands in order to quantify relative band depth and place requirements on signal-to-noise ratios

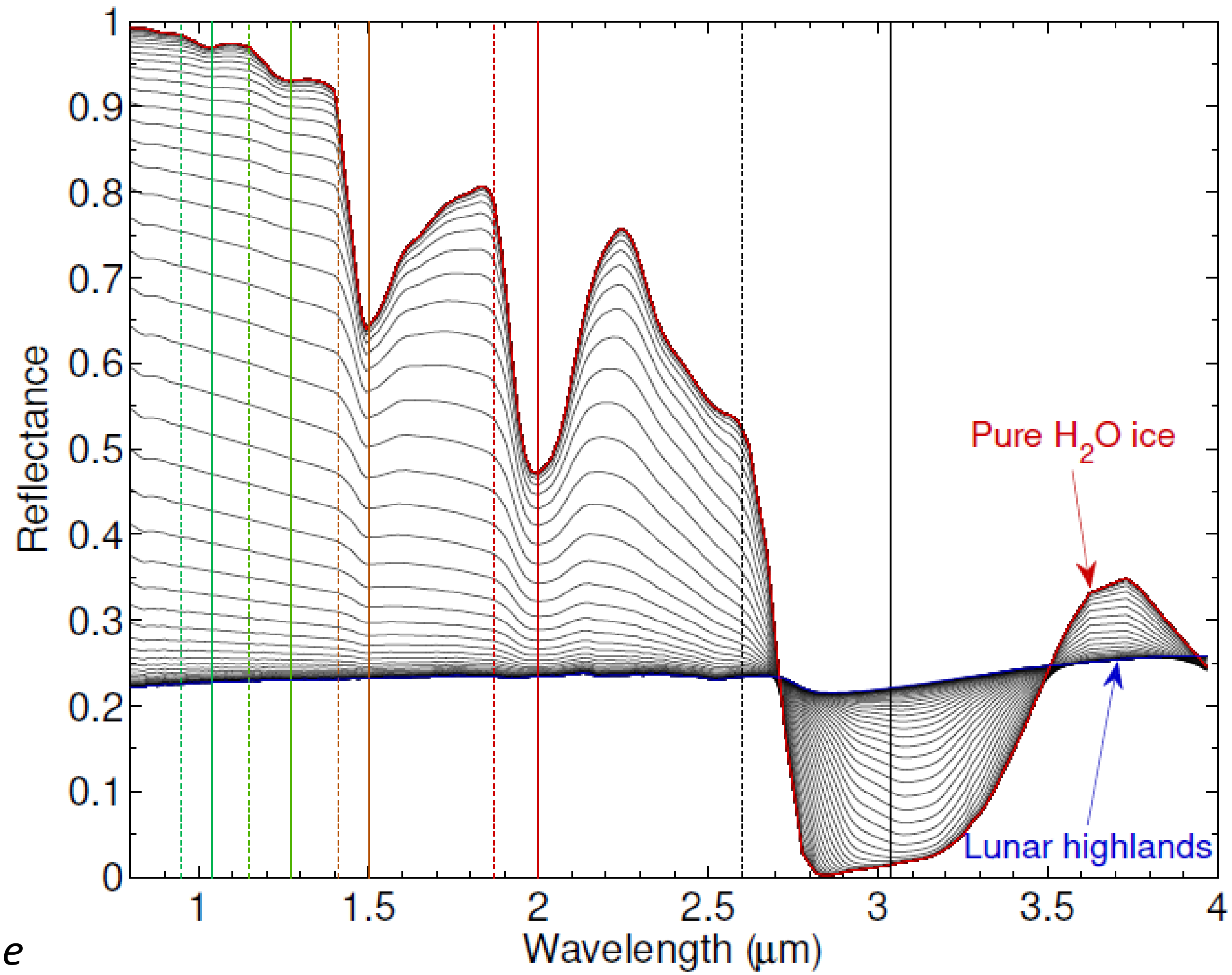
from P. Hayne

LOLA Albedo vs. Diviner Temperature



from P. Hayne

Thin Water Ice Films on Simulated Lunar Highlands Material

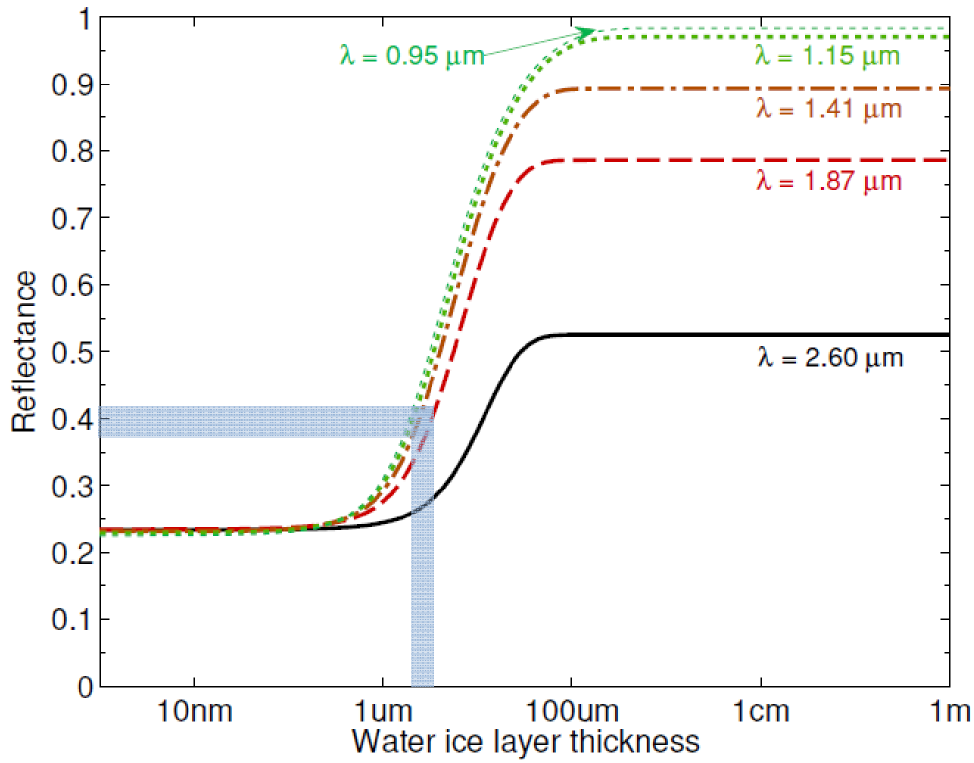


R_{eff}=1μm for H_2O ice

R_{eff}=? for regolith

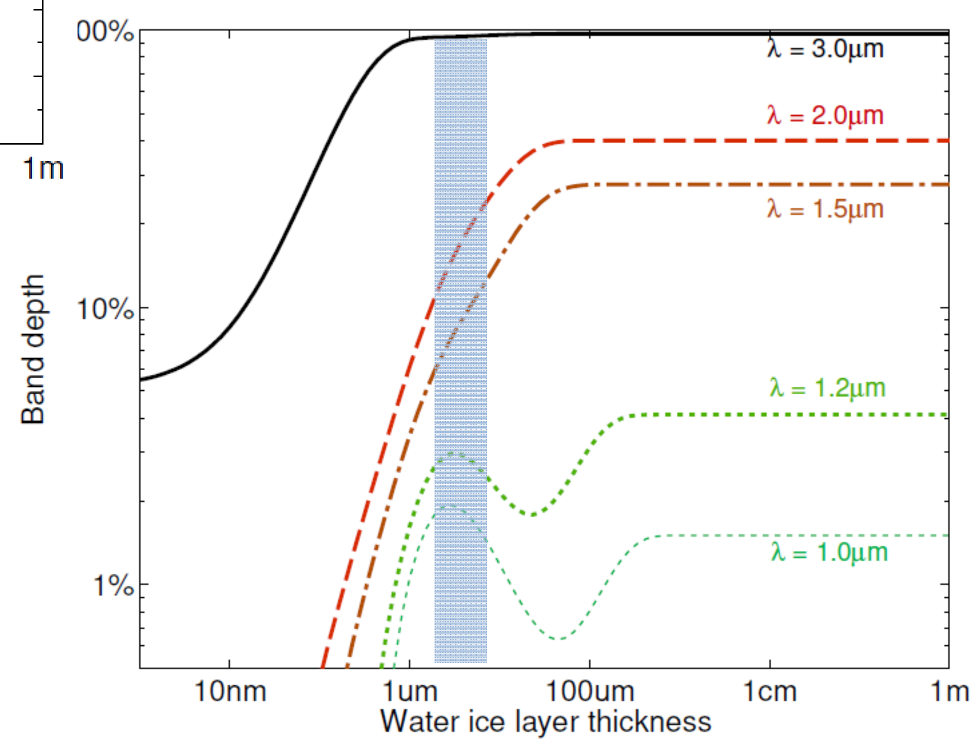
from P. Hayne

Case #1: Thin film of ice on lunar regolith



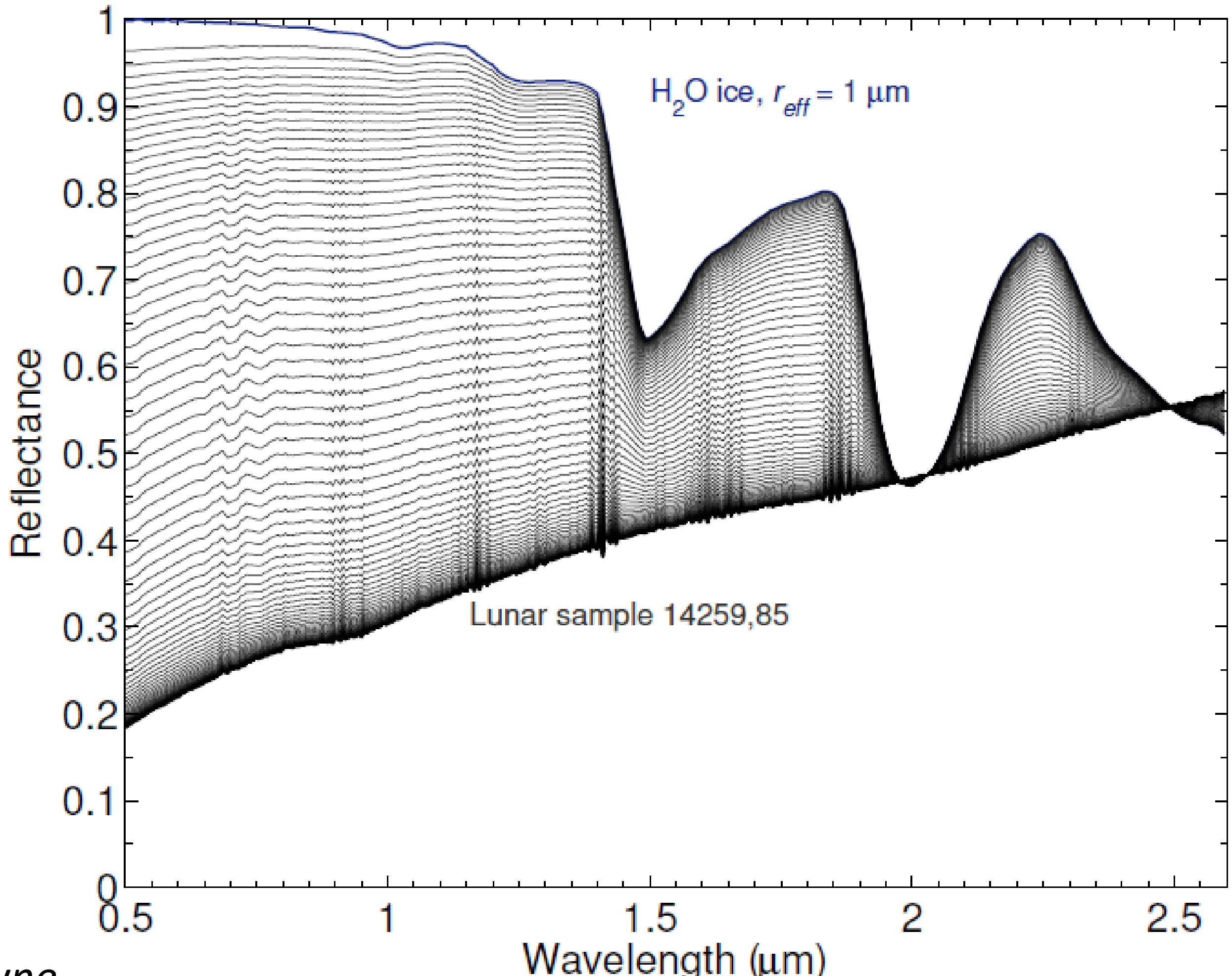
Would predict band depths of >10% for the three longest H2O bands

Not observed at 2um: because of lack of illumination for M3 or absence?



from P. Hayne

Ice Intimate Mixtures w/ Lunar Soil: 0.5 – 2.5 Micron Region

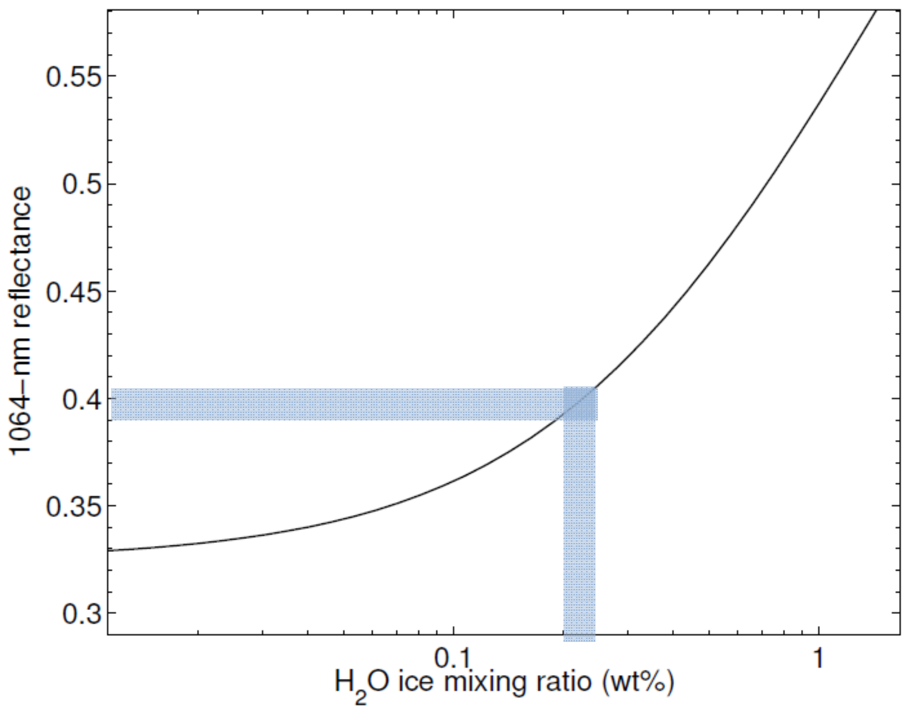


R_{eff}=1μm for H_2O ice

R_{eff}=? for regolith

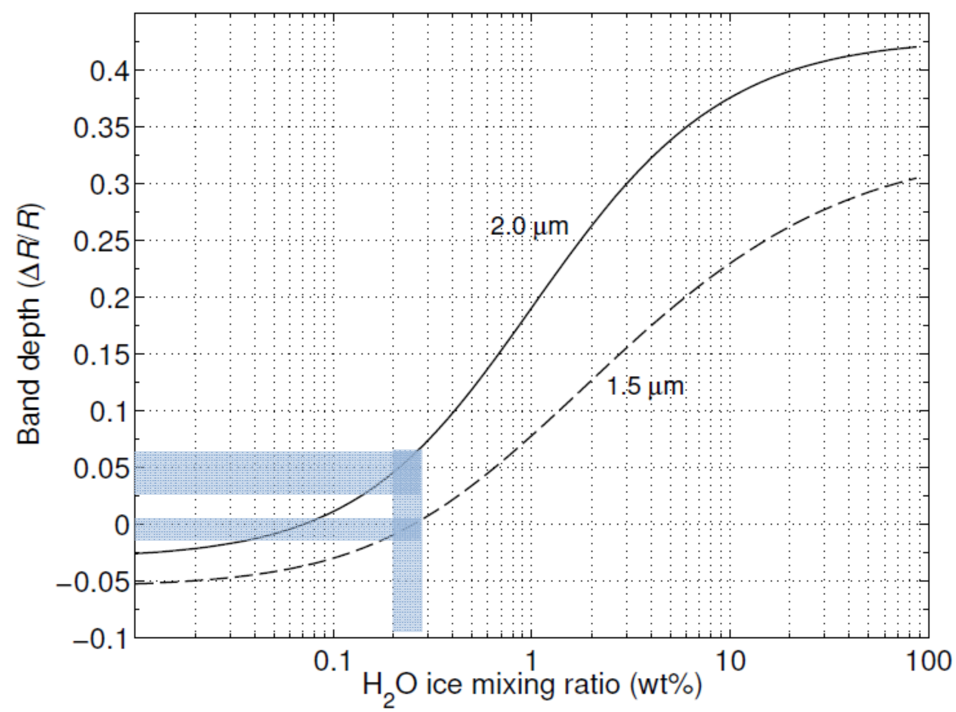
from P. Hayne

Case #2: Ice with lunar regolith



Would predict band depths of 5% at 2um; unobservable bands at 1.5um

Not observed: because of lack of illumination for M3 or absence?



from P. Hayne

Band depth summary

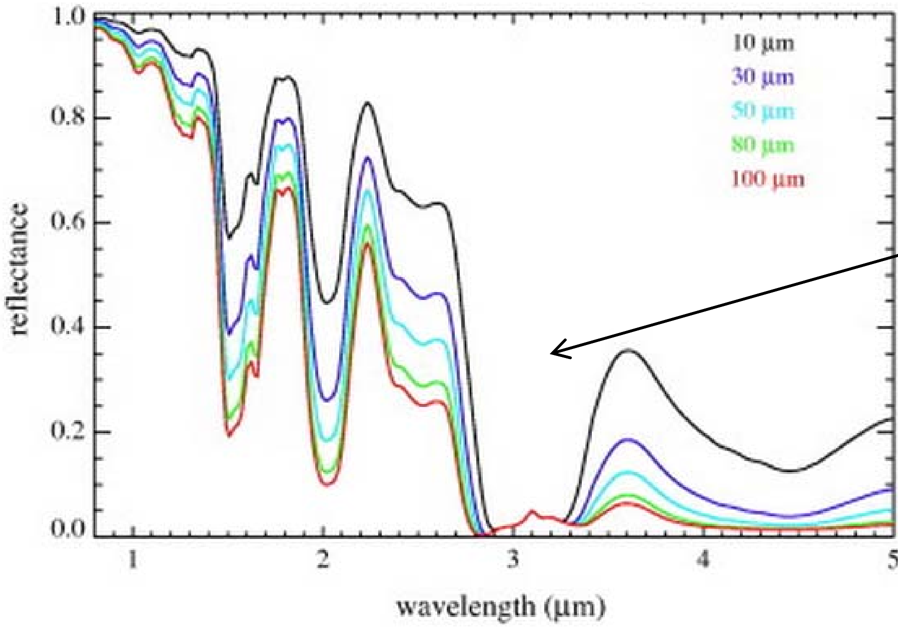
	Band depth in % (reflectance value at λ)				
Scenario	3µm	2µm	1.5µm	1.2µm	1µm
Thin film (2µm) on highlands regolith	100 (.25)	20 (.35)	10 (.4)	3 (.4)	2 (.4)
Intimate mix (0.2%; r=1µm) with Lunar Regolith		5 (.45)	0 (.4)		

Monte Carlo Method (simulating M3 bands)

- Monte-carlo Hapke models of a mixed volume of particles, simulations with
  - Basalt + no ice OR 1vol% ice OR 10vol% ice
  - basaltic glass + no ice OR 1vol% ice OR 10vol% ice
  - "lunar soil" + no ice, + no ice OR 1vol% ice OR 10vol% ice
    - Lunar soil = M^3 spectra , assumed grain size 20µm, extrapolated to long wavelengths. Note: very approximate!
- Regolith grain sizes approximate lunar distribution observed by Apollo
  - power law, r^{-3}, grain size between D_{grain}=20 and 400 microns, g=0.3
- Grain sizes of water ice: D_{grain}=20 microns or 100 microns
  - g=0.5

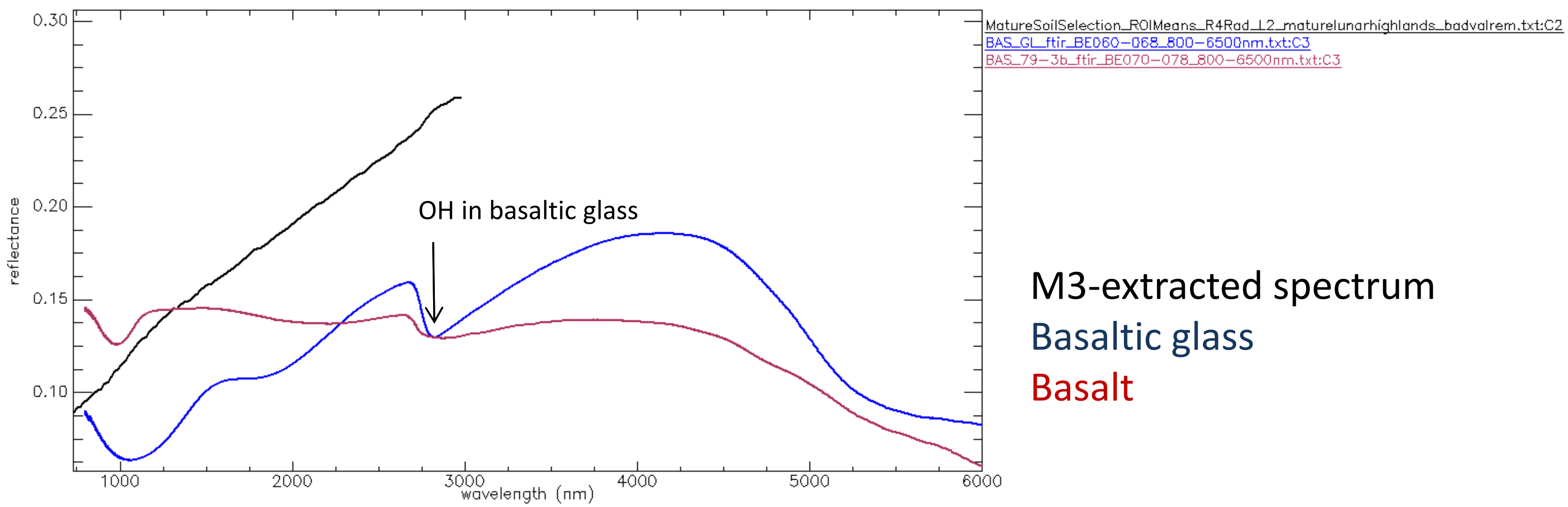
from C. Pilorget

Endmember Spectral Properties



H_2O-ice spectra

Note H_2O ice feature (2.8-3.4µm) has greater width and different shape vs OH feature



M3-extracted spectrum

Basaltic glass

Basalt

Simulations of the 2 μm band

Basalt (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
Water ice, grain size=**20 microns**, g=0.5

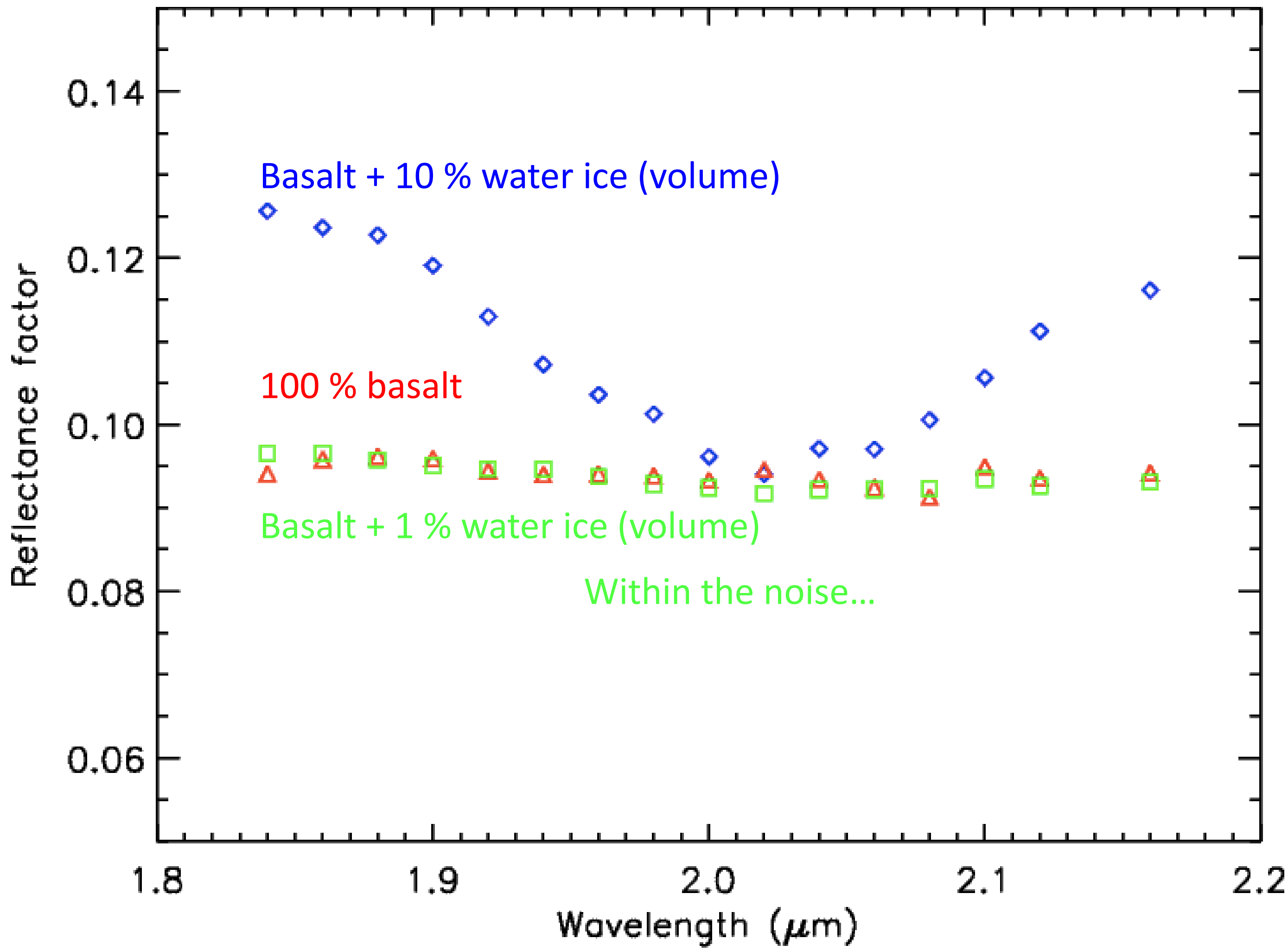
i=45°
Observation at nadir

All simulations with 4e6 photons, except 1% water ice case (2e7 photons)

p_{basalt}=3g/cm^3
p_{water}=1g/cm^3

Case 1% water ice (volume) corresponds to 0.33 % (mass)

Case 10% water ice (volume) corresponds to 3.6 % (mass)



from C. Pilorget

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Observation at nadir

All simulations with 4^e6 photons,
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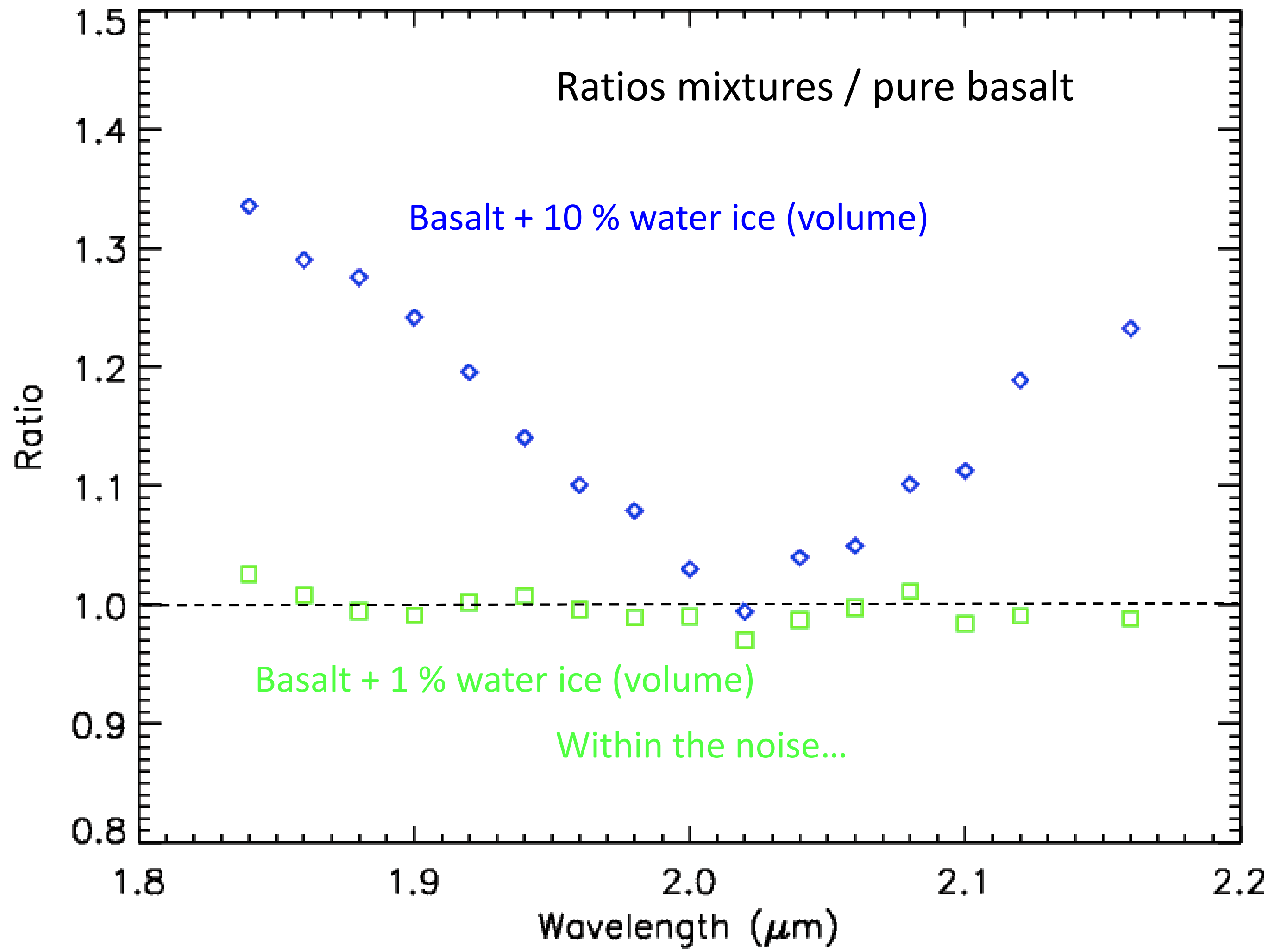

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Basalt (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
Water ice, grain size=**100 microns**, g=0.5

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Observation at nadir

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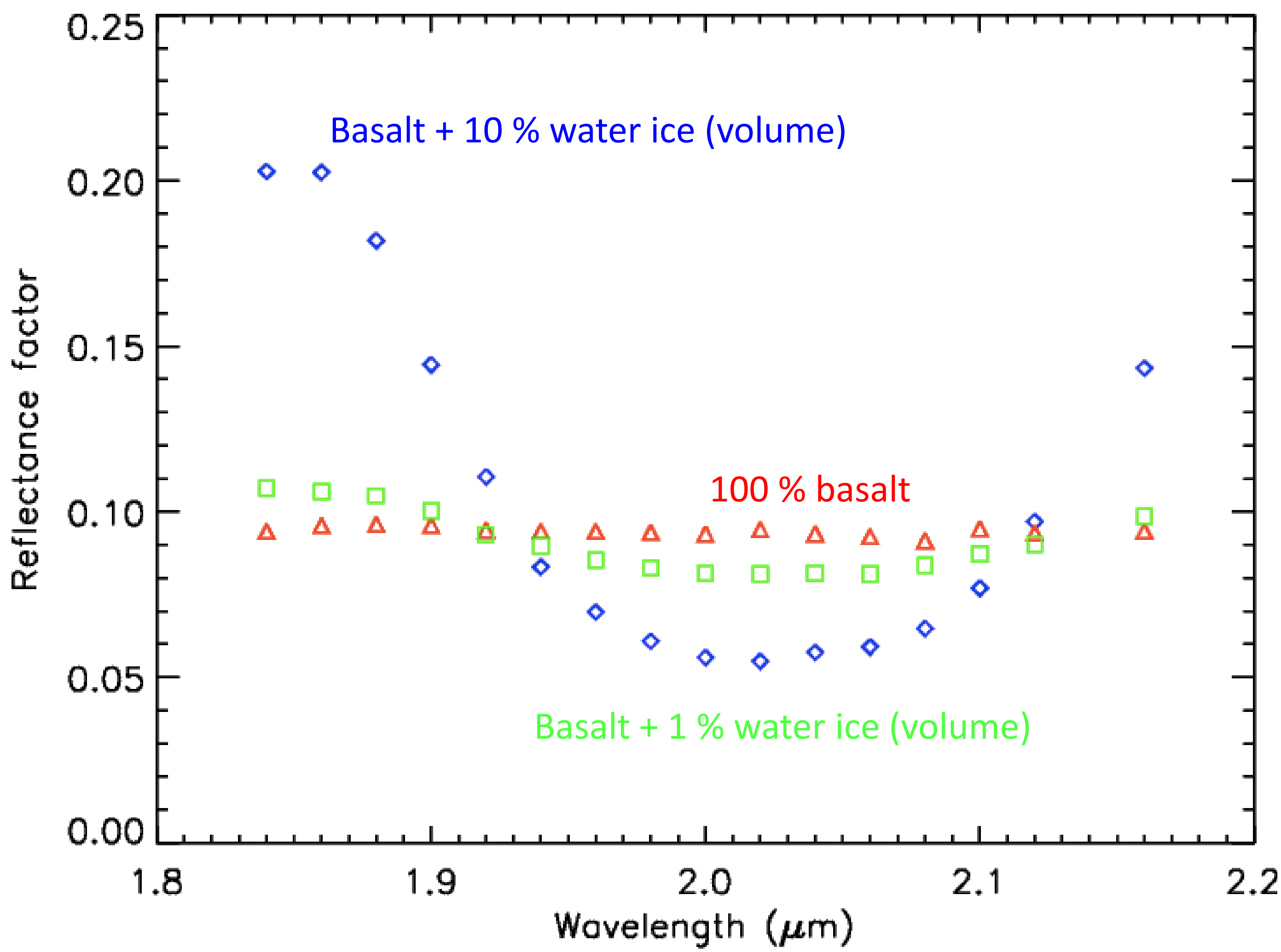

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100-micron grain size is detectable; considering only the small size hereafter

from C. Pilorget

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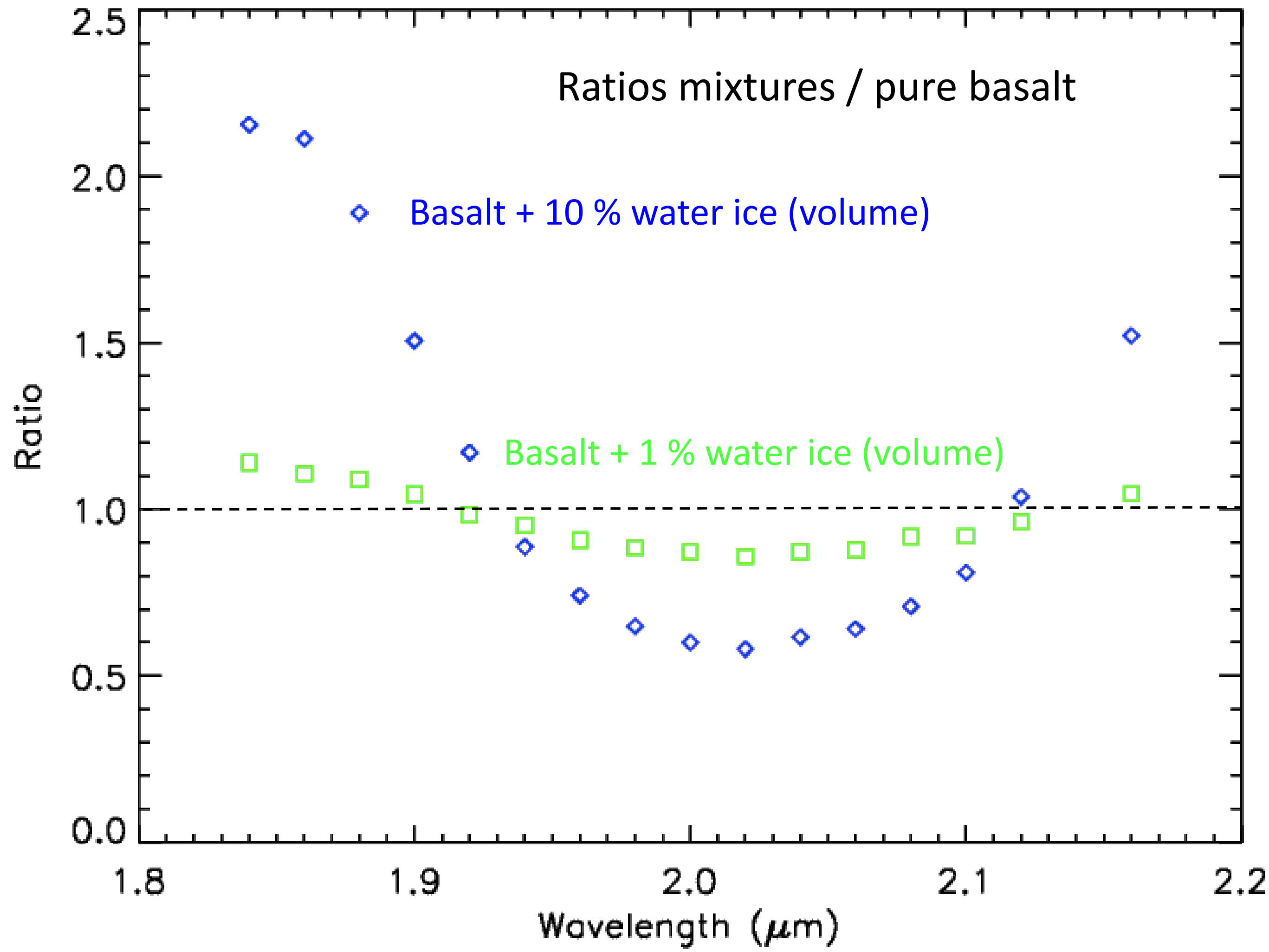

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Basaltic glass (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
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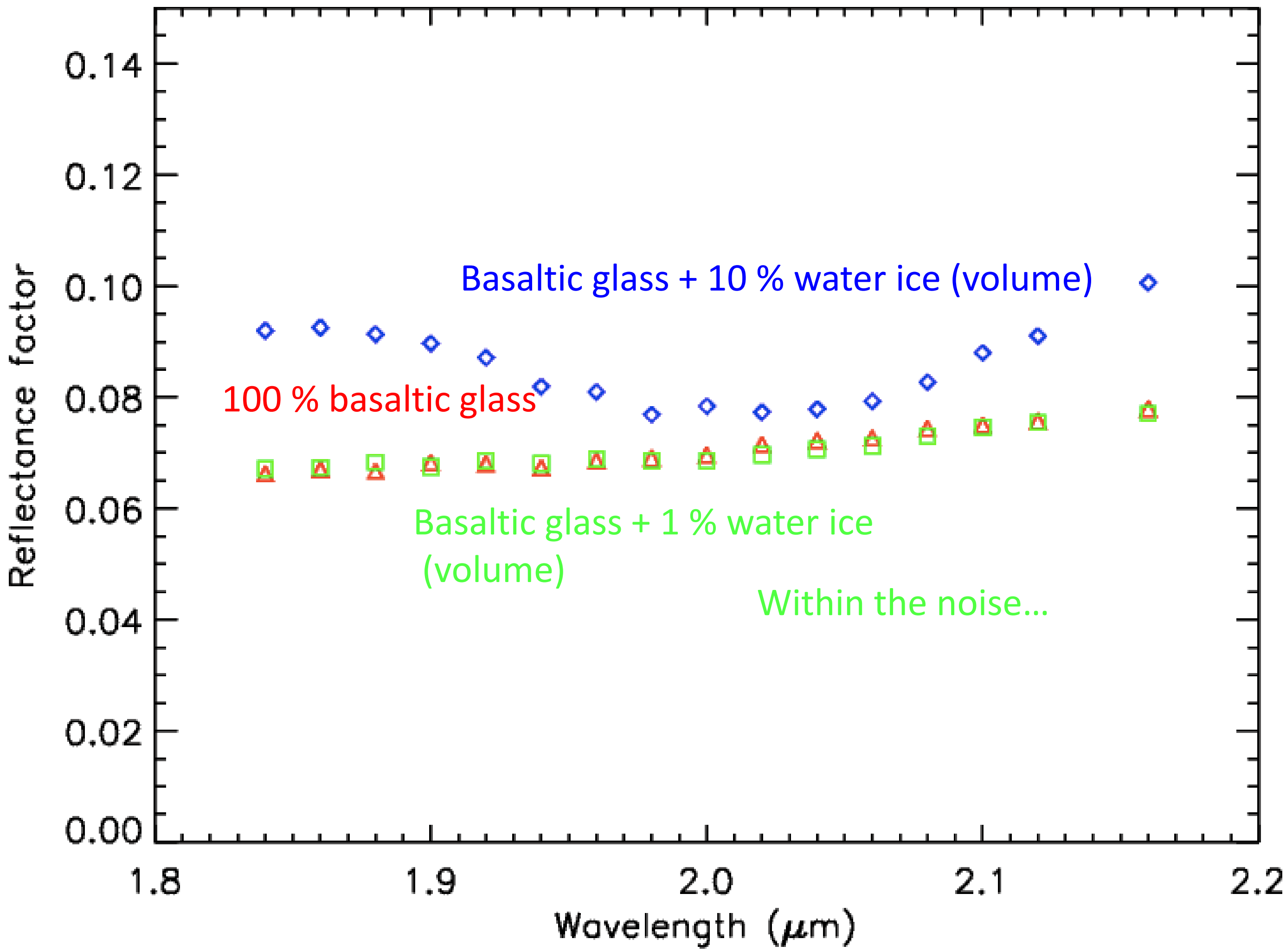

$\rho_{basaltic\ glass}$=2.75g/cm^3
ρ_{water}=1g/cm^3

Case 1% water ice (volume)
corresponds to 0.37 % (mass)

Case 10% water ice (volume)
corresponds to 3.9 % (mass)

from C. Pilorget

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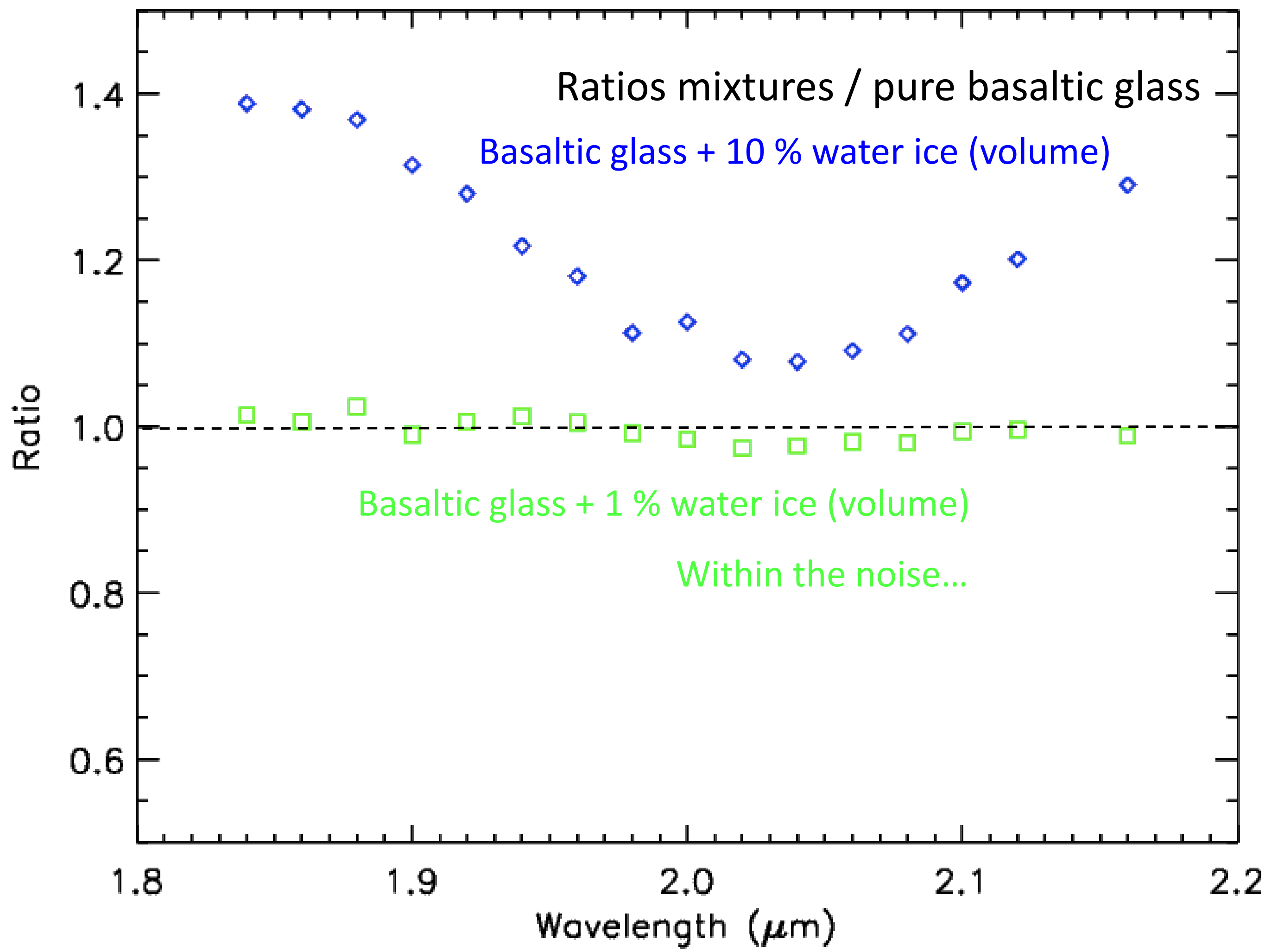

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from C. Pilorget

Lunar soil 1 (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
Water ice, grain size=**20 microns**, g=0.5

i=45°
Observation at nadir

All simulations with 4e6 photons,
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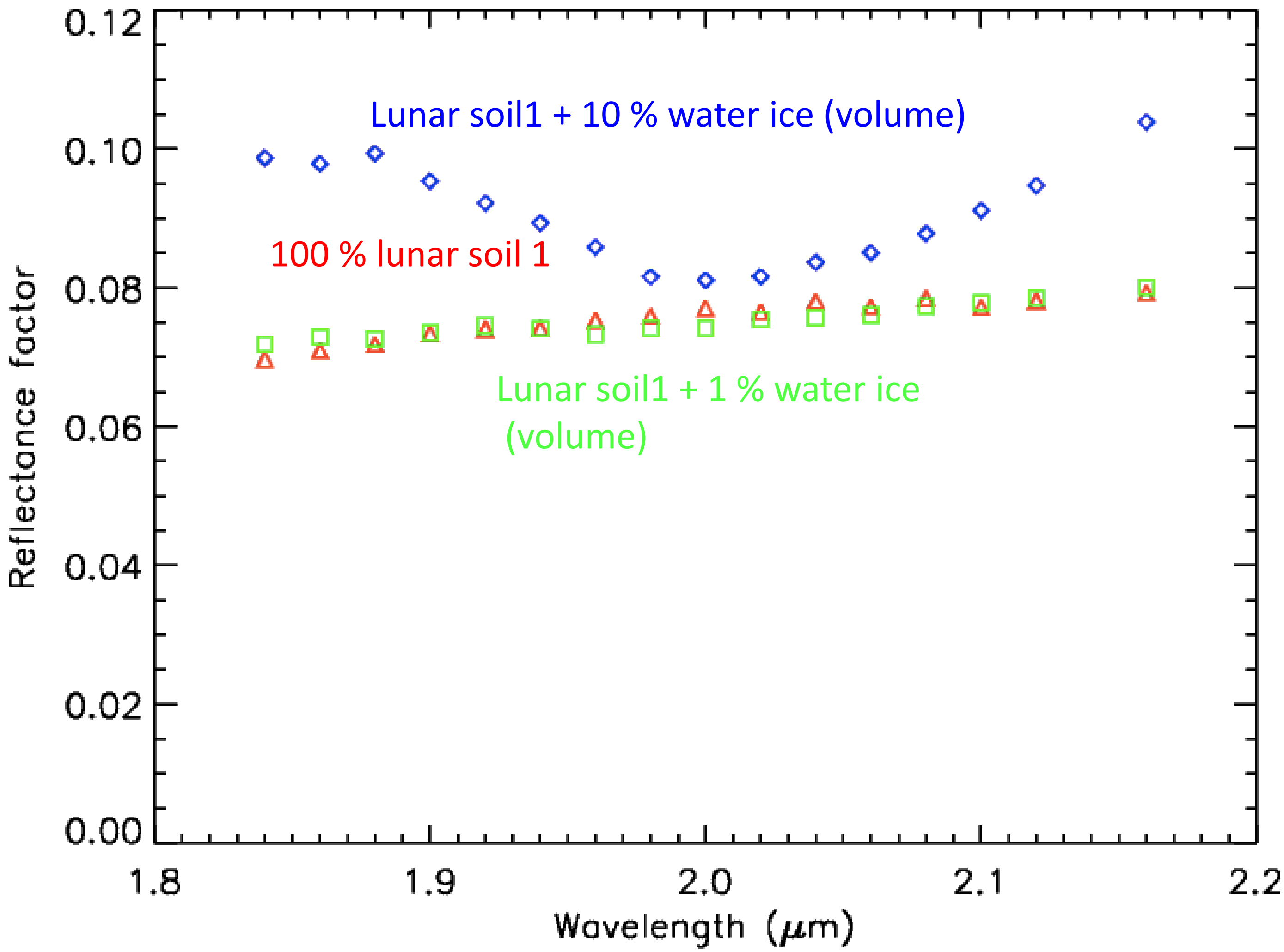

$\rho_{lunar\ soil\ 1}$=2.75g/cm^3 ?
ρ_{water}=1g/cm^3

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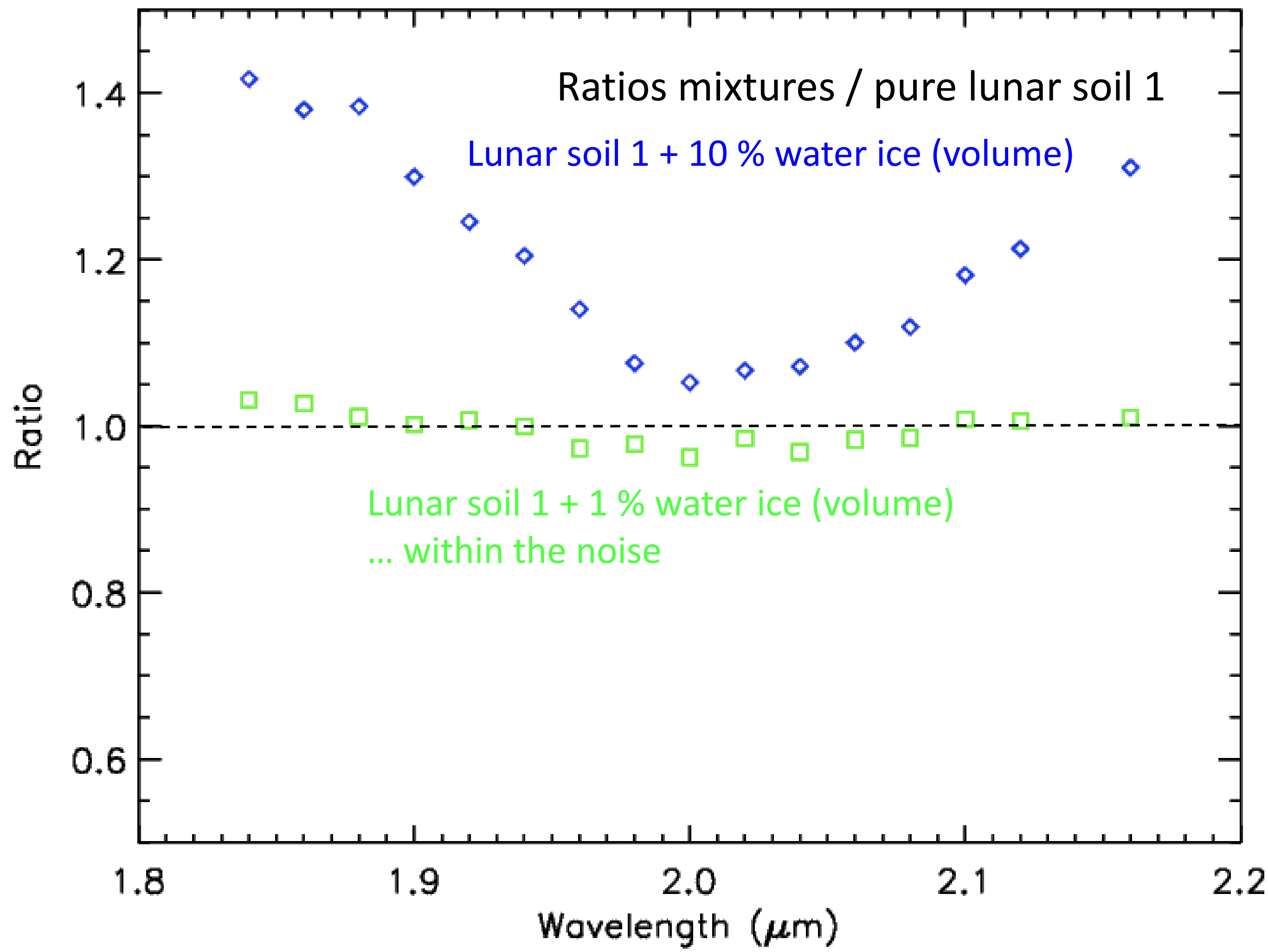

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from C. Pilorget

Simulations of the 3 μm band

from C. Pilorget

Basalt (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
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Observation at nadir

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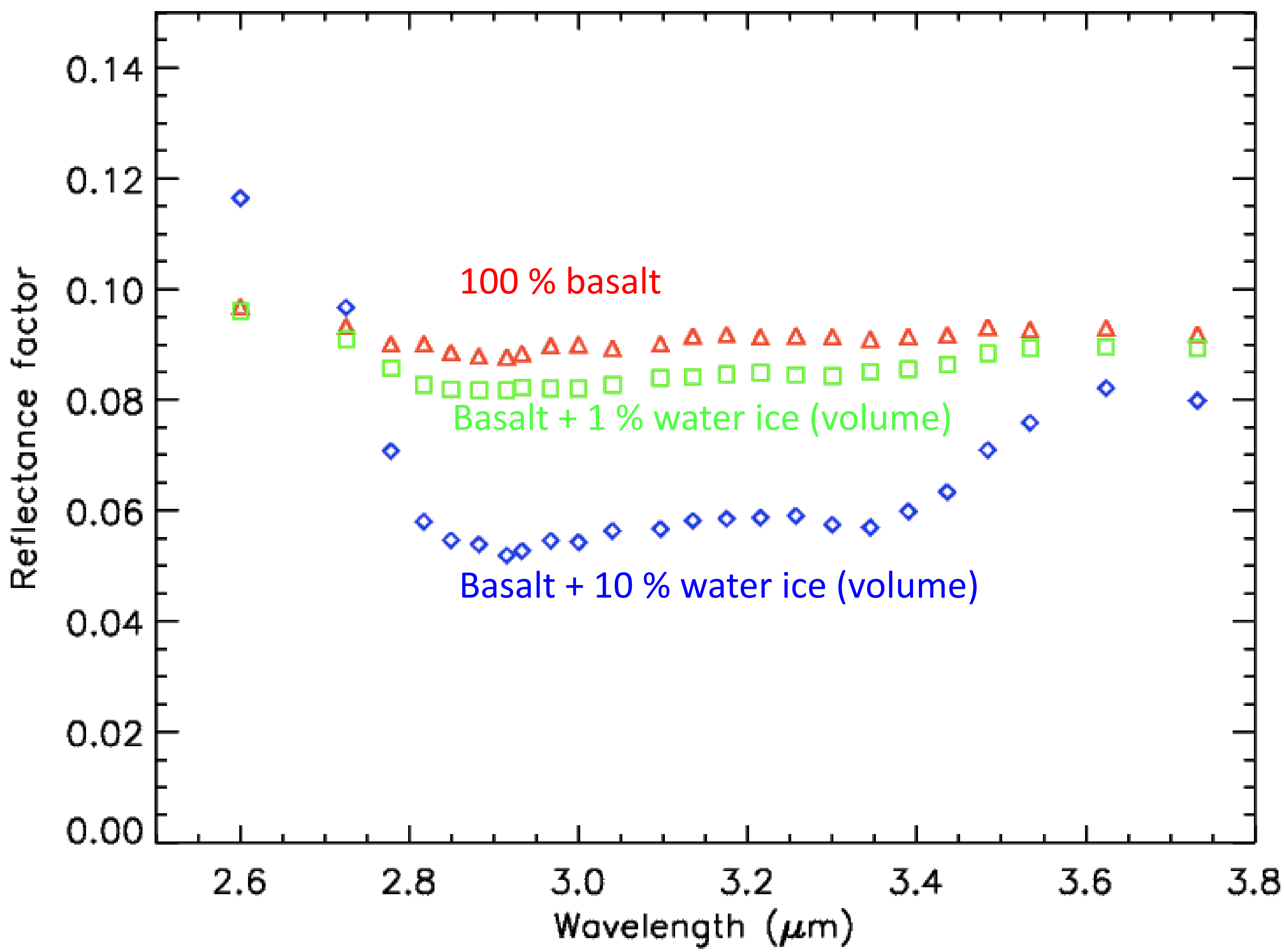

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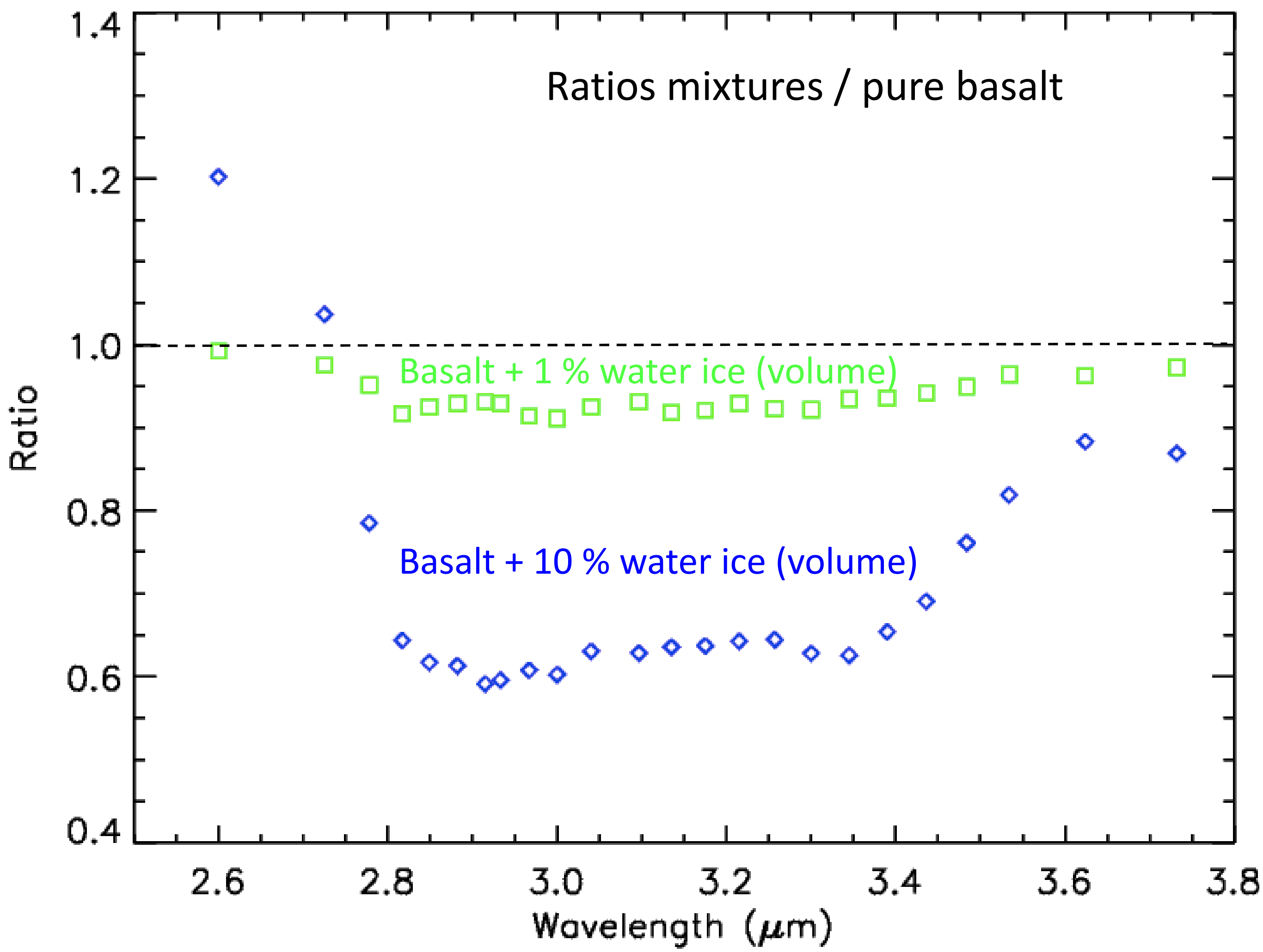

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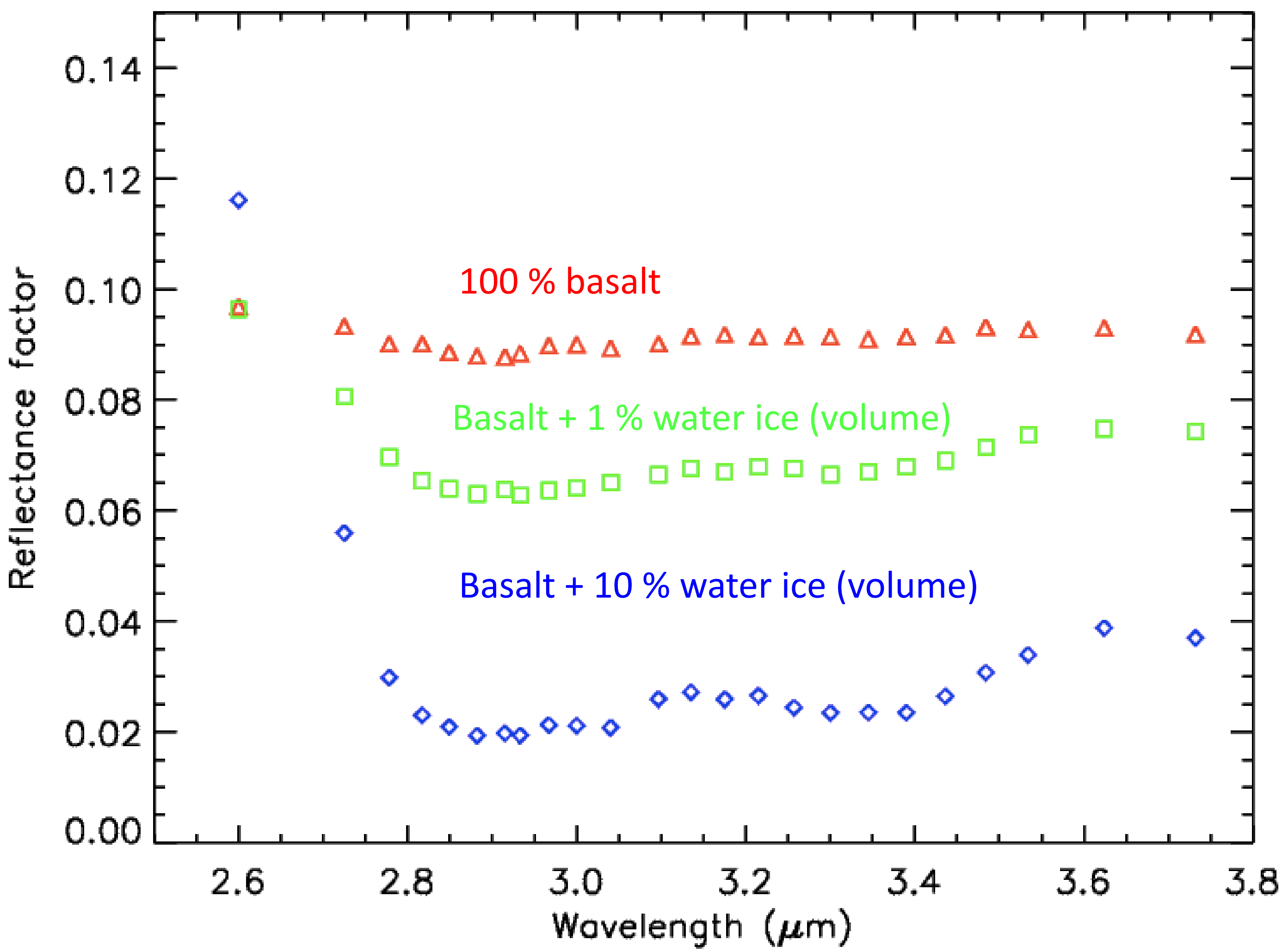
Water ice, grain size=**100 microns**, g=0.5

i=45°
Observation at nadir

All simulations with $4^{e}6$ photons,
except 1% water ice case ($2^{e}7$ photons)



$p_{basalt}=3g/cm^3$
$p_{water}=1g/cm^3$

Case 1% water ice (volume) corresponds to 0.33 % (mass)

Case 10% water ice (volume) corresponds to 3.6 % (mass)

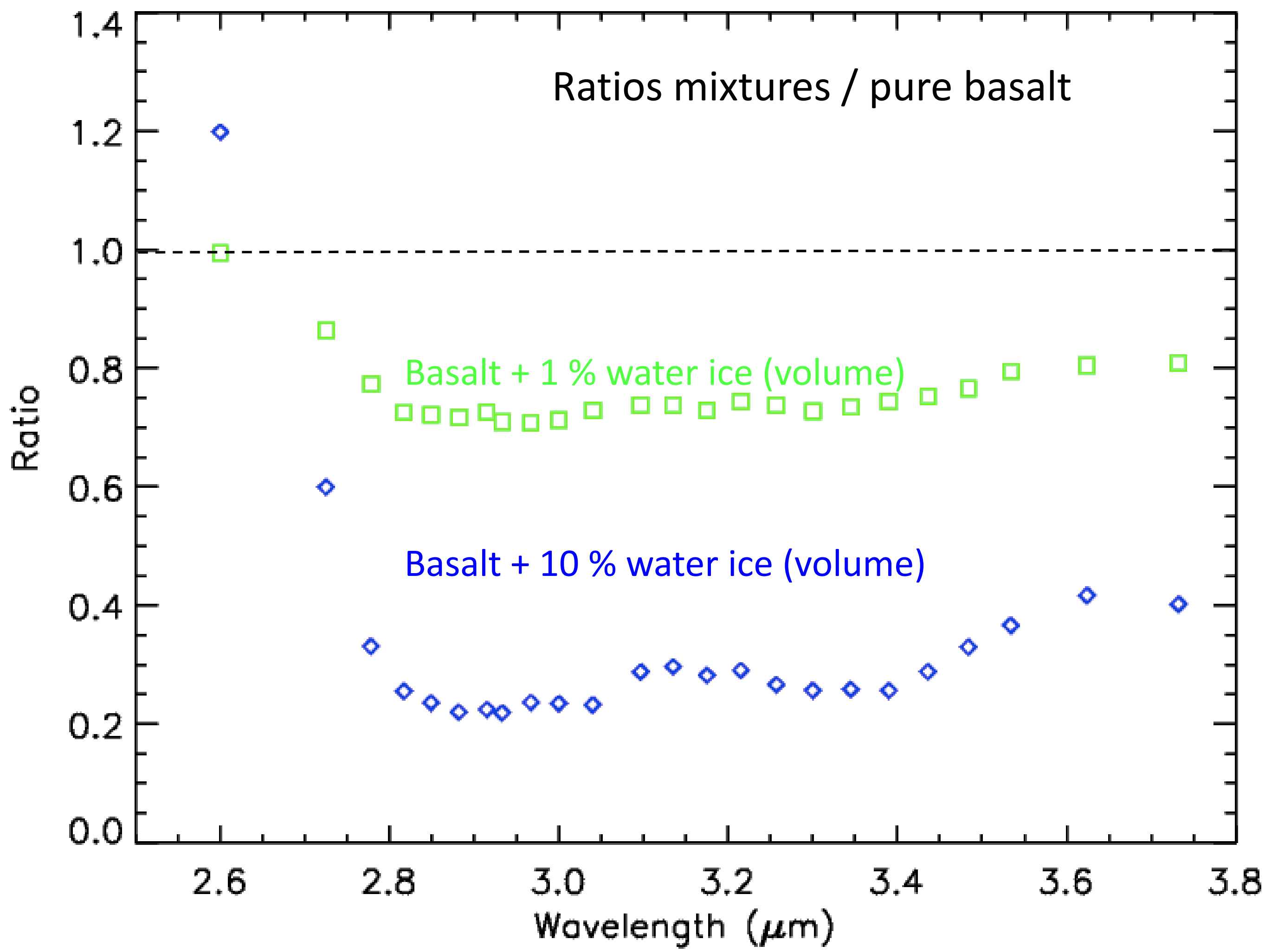
100-micron grain size is detectable; considering only the small size hereafter

from C. Pilorget

Basalt (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
Water ice, grain size=**100 microns**, g=0.5

i=45°
Observation at nadir

All simulations with 4e6 photons,
except 1% water ice case (2e7 photons)



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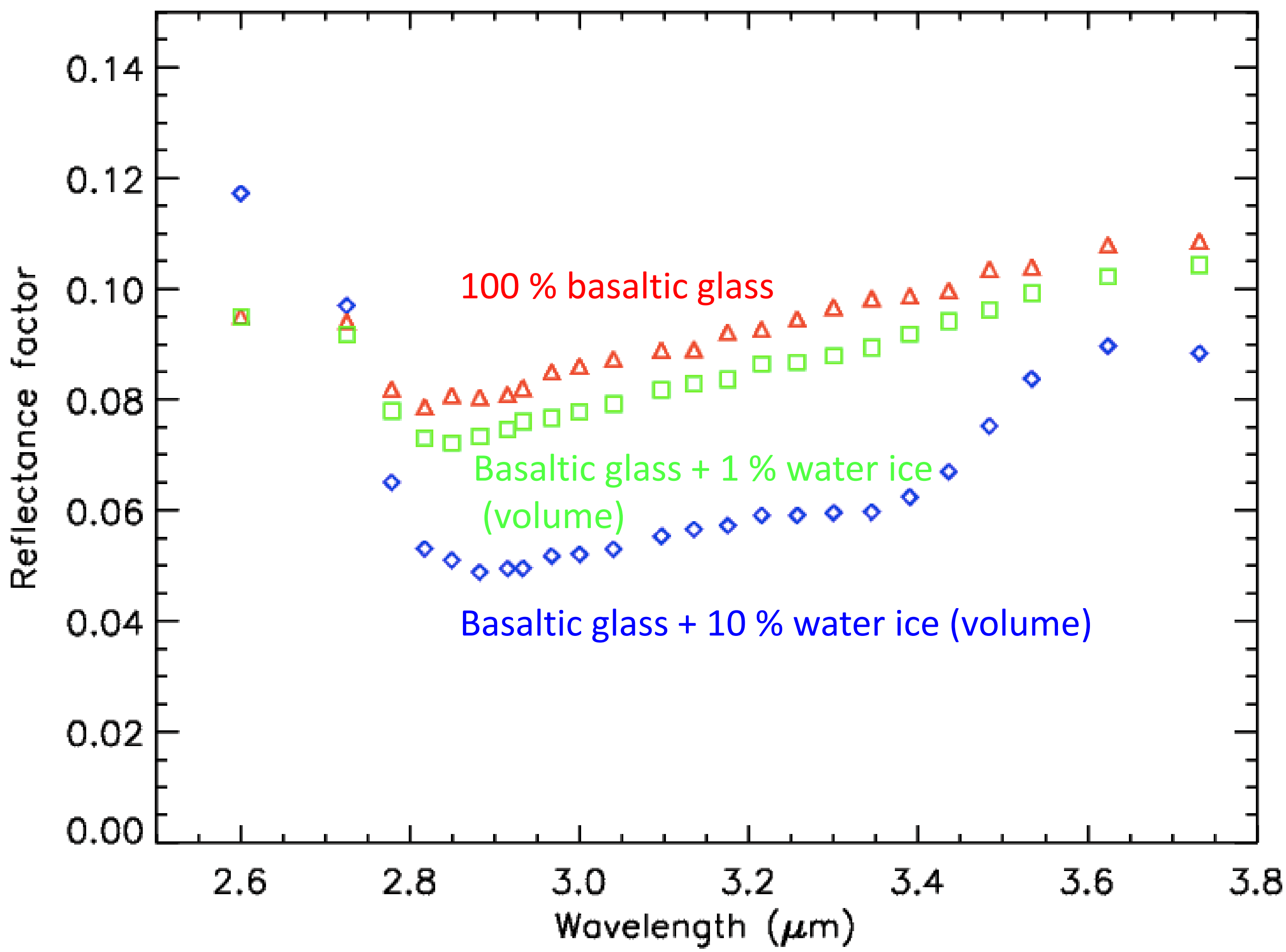

$p_{basaltic\ glass}$=2.75g/cm^3
p_{water}=1g/cm^3

Case 1% water ice (volume) corresponds to 0.37 % (mass)

Case 10% water ice (volume) corresponds to 3.9 % (mass)

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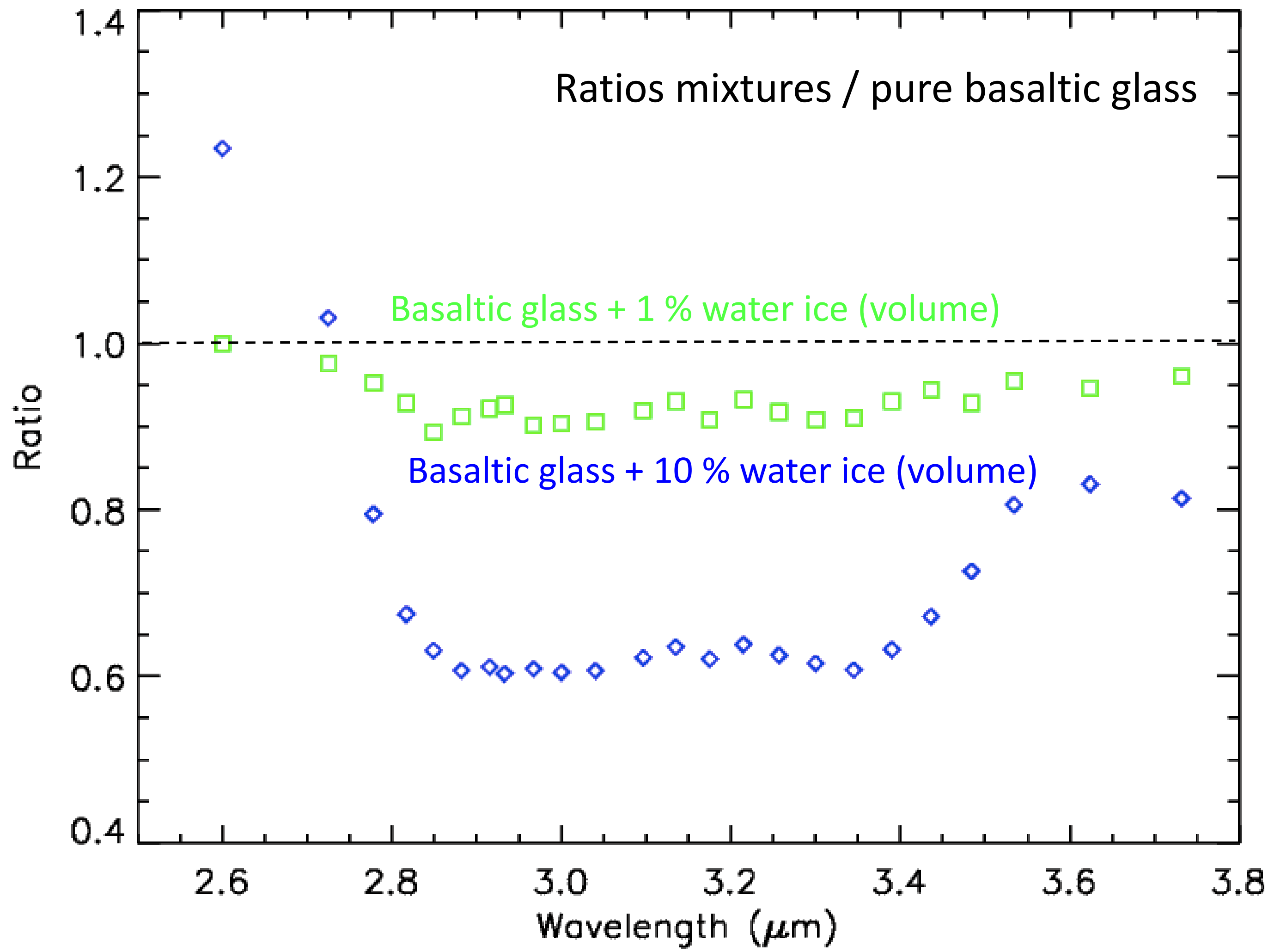

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Lunar soil 1 (power law, r^{-3}, grain size between 20 and 400 microns), g=0.3
Water ice, grain size=**20 microns**, g=0.5

i=45°
Observation at nadir

All simulations with 4e6 photons,
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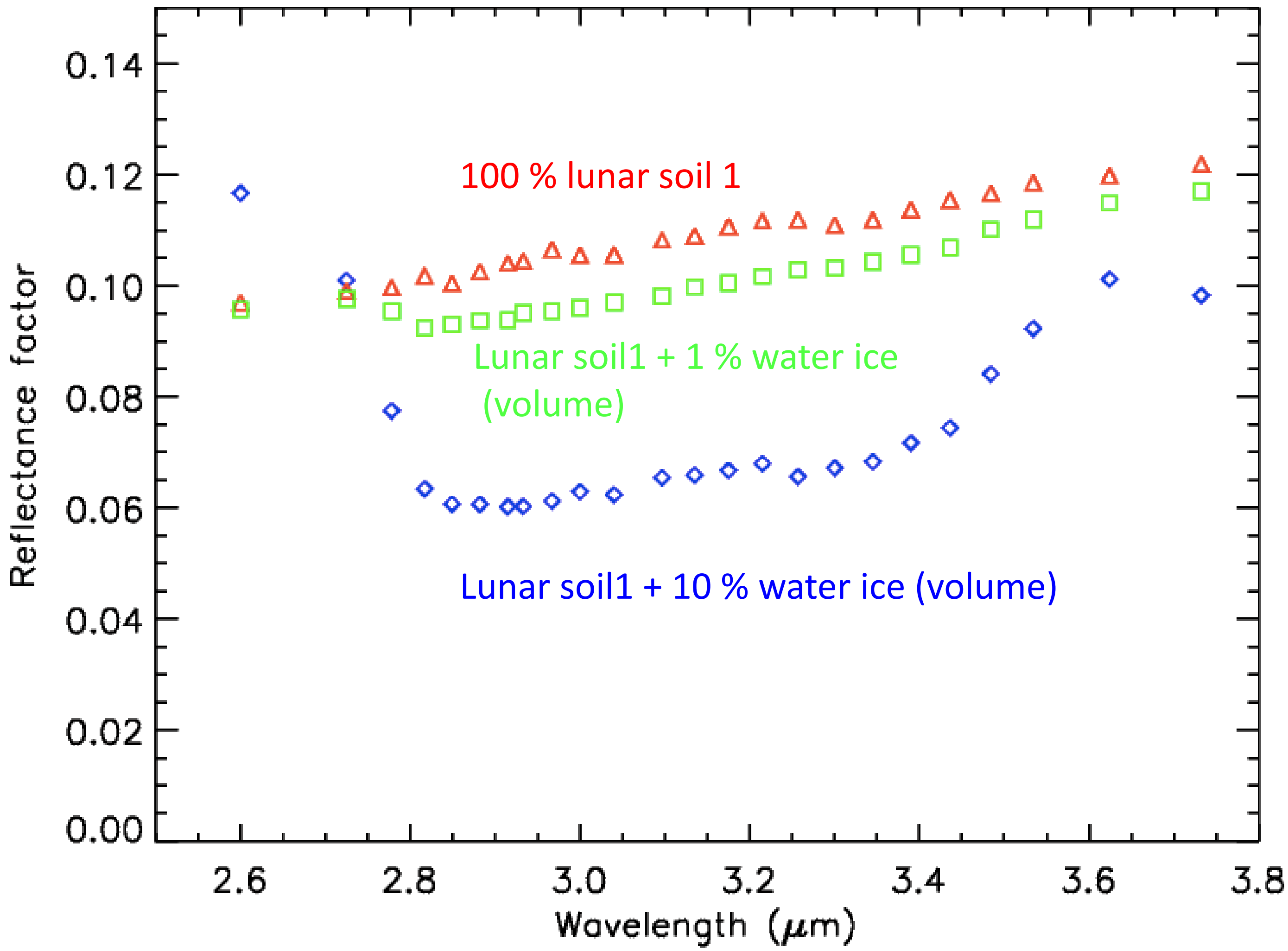

$\rho_{lunar\ soil\ 1}$=2.75g/cm^3 ?
ρ_{water}=1g/cm^3

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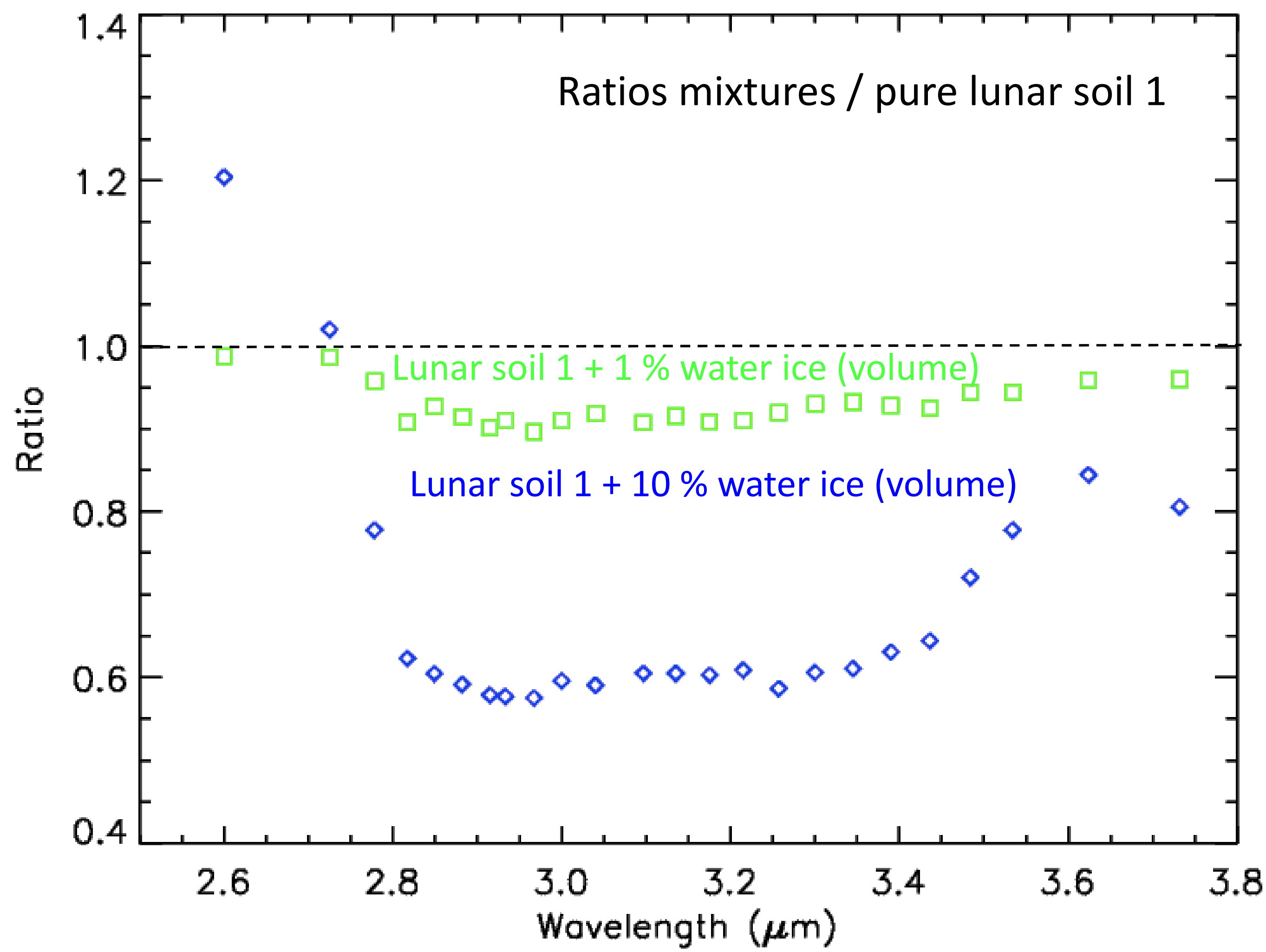

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from C. Pilorget

Band depth summary

	Band depth in % (reflectance value at λ)				
Scenario	3µm	2µm	1.5µm	1.2µm	1µm
Thin film (2µm thick) on highlands regolith [Mie]	100 (.25)	20 (.35)	10 (.4)	3 (.4)	2 (.4)
Intimate mix (0.2wt%; r=1µm) with Lunar Regolith (R=?) [Mie]		5 (.45)	0 (.4)		
Intimate mix (0.33wt%; r=20µm) with Lunar Regolith (R=Apollo) [MC]	10 (.1)	~1 (.08)			
Intimate mix (3.3wt%; r=20µm) with Lunar Regolith (R=Apollo) [MC]	50 (.06)	25 (.1)			
Intimate mix (0.33wt%; r=100µm) with Lunar Regolith (R=Apollo) [MC]	40 (0.06)	75 (.2)			

Most sensitive; how much depends on model

Quite model dependent

Summary

- **Ice grain size/form assumed and RT model matters** for calculating detection thresholds for plausible abundances
  - Regolith with 1% D_{grain}=20µm ice not detectable at 2µm; but 10% band depth at 3µm
  - But finer ice with a different type of lunar grain size is detectable

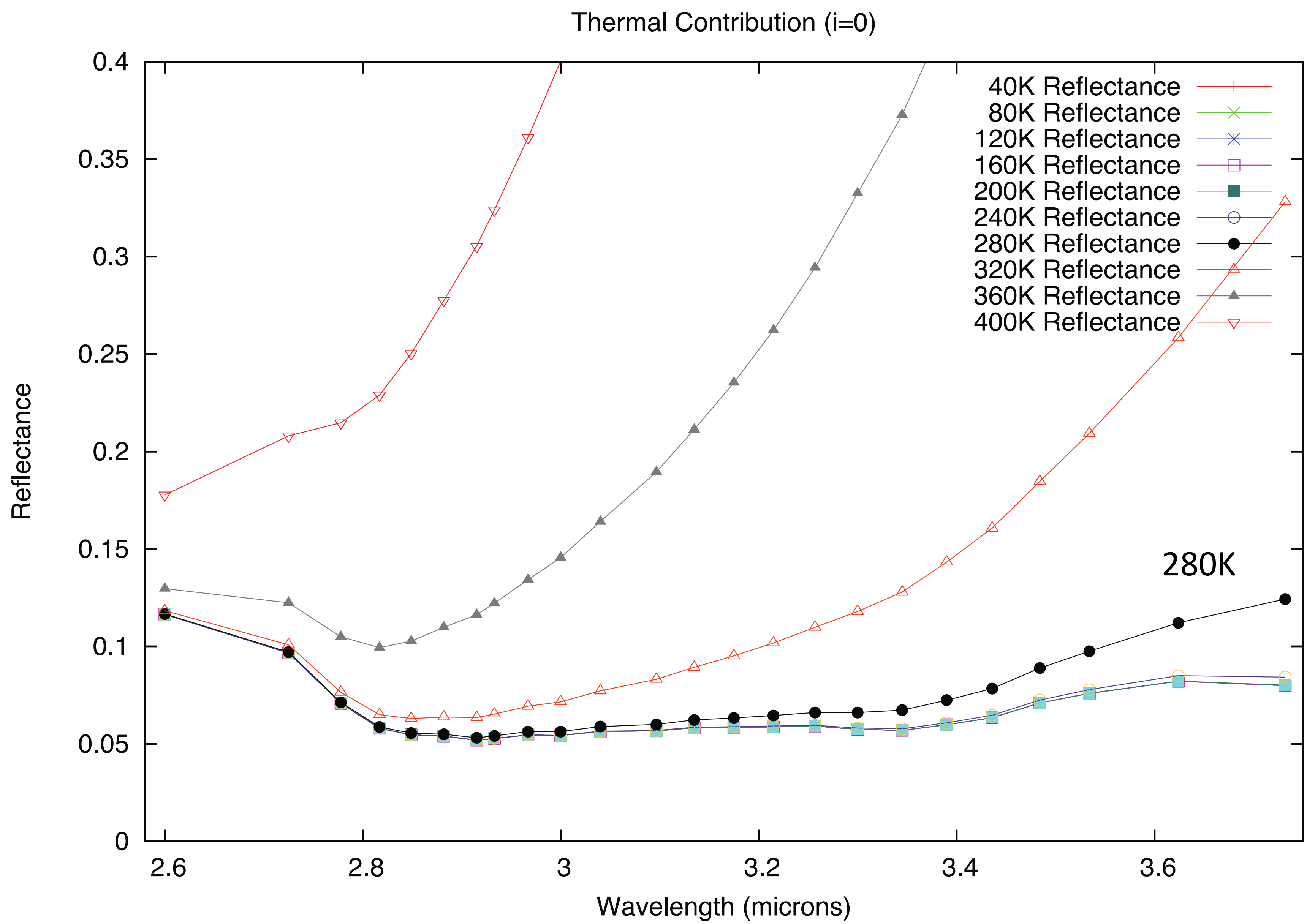
➔ Key question: what do we expect about the nature of the ice? This impacts the choice of required instrument sensitivity

Also a temperature effect?

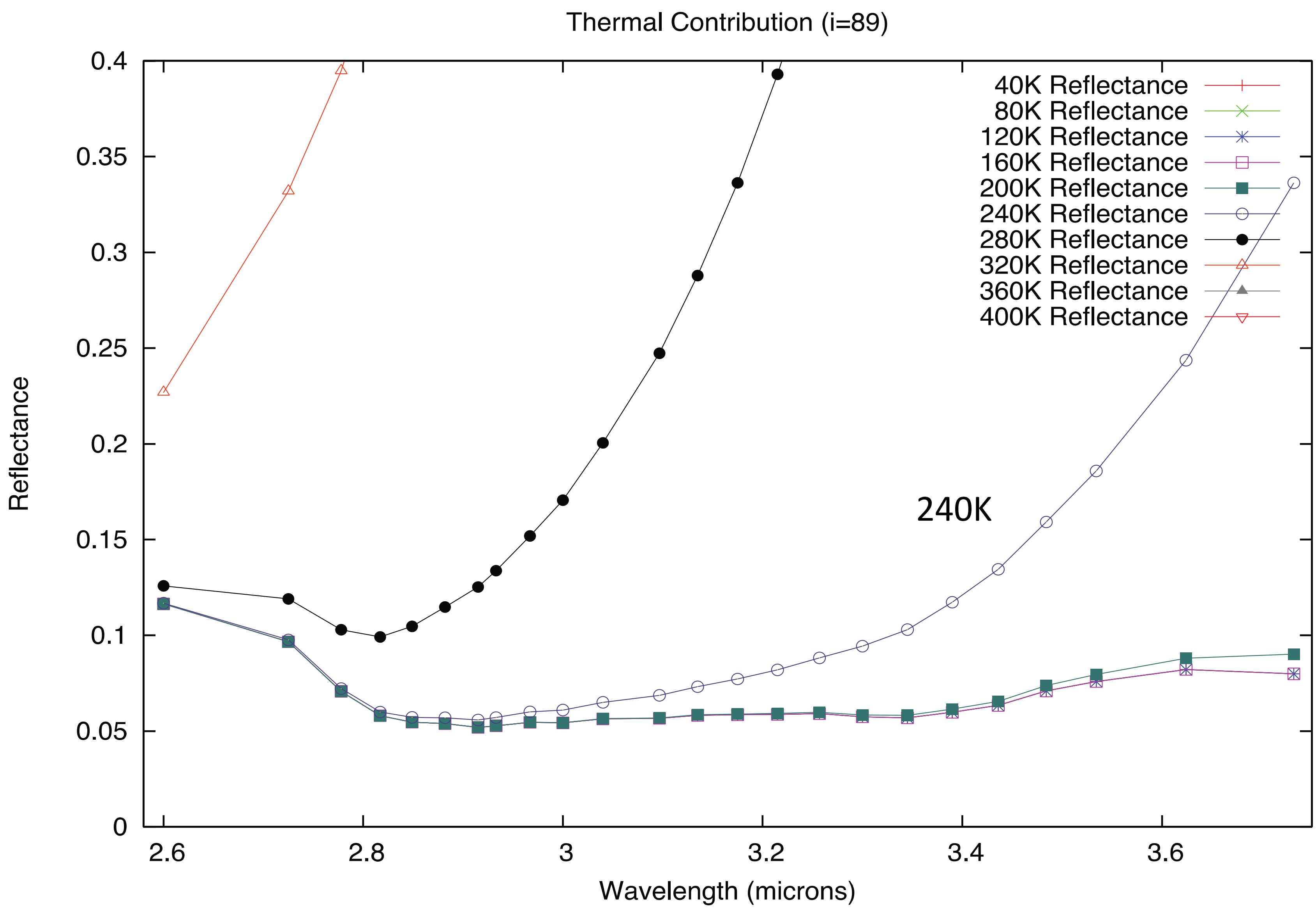
- Thermal emission can decrease band strength further
- Since there is no solar incidence we chose 3 different incidence angle extremes to test parameter space

1. Calculate Blackbody curves for T from 40-300K
2. Multiply the BB * (1 - Input Reflectance)
   – Yields the thermal contribution including emissivity effects
3. BB/solar flux/cos(incidence angle)*PI
   – Returns our calculated thermal contribution to “reflectance” units
4. Add the Input Reflectance to the thermal contribution/”reflectance” spectra

from C. Edwards & C. Pilorget



from C. Edwards & C. Pilorget



from C. Edwards & C. Pilorget

Also a temperature effect?

- Thermal emission can decrease band strength further… but not likely to matter for T<240K

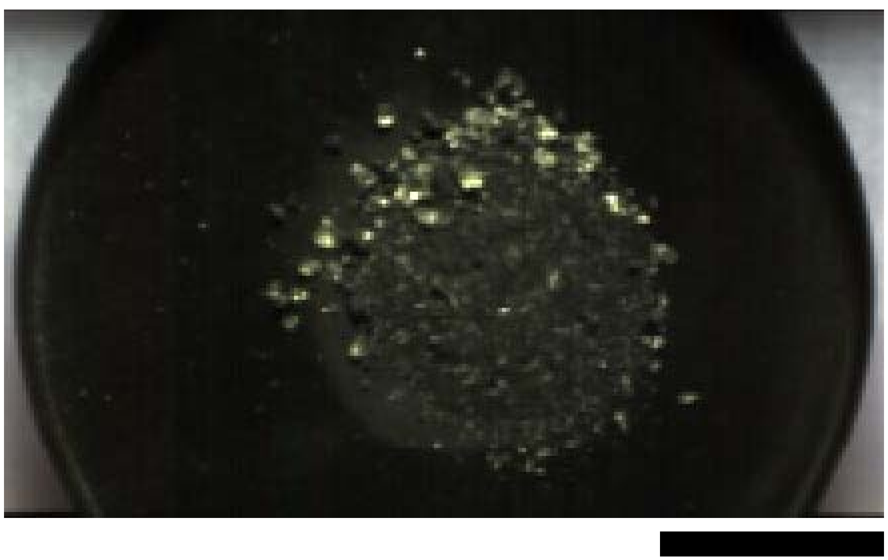
Conclusions – For Detection Lunar Ice

	Essential	Nice-to-have
Spectral range	**2.6-3.6µm** (H2O ice width at most sensitive band)	**1-6µm** (regolith comp; trace ice; better thermal correction)
Spectral resolution	**20nm** (H2O ice band structure)	**10nm** (better resolution of H2O ice band structure)
Signal/sensitivity	1% at 0.1 albedo (10x minimum band strength for 0.33% water ice) ***very model dependent**	
Spatial resolution	<500m/pixel from orbit; more likely to have ice at discrete pixels if near surface (bulk assumption does not apply)	

-Being able to distinguish the ~3.15µm maximum (present in most grain sizes) and the band width is important for distinguishing from H_2O

Of course, spatial scale matters – orbit to in-situ

- Landed investigations can benefit from very high detection limits from in situ study
- Example from cordierite mixed with basalt (1wt%), VISIR hyperspectral camera (~75um/pixel)



1 cm