

István Kovács

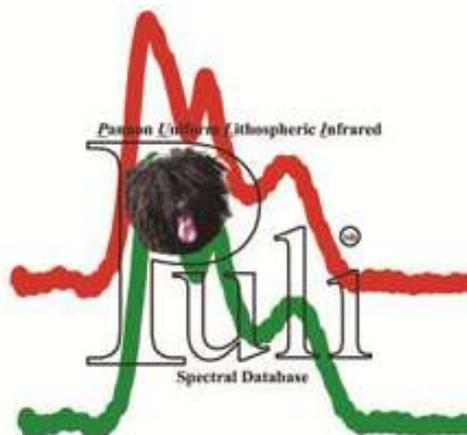
QUANTITATIVE INFRARED SPECTROMETRY OF WATER IN NOMINALLY ANHYDROUS MINERALS: FACTS, DOUBTS AND BELIEFS: AN „EAST SIDE” STORY

Geological and Geophysical Institute of Hungary

Geochemical and Laboratory Department

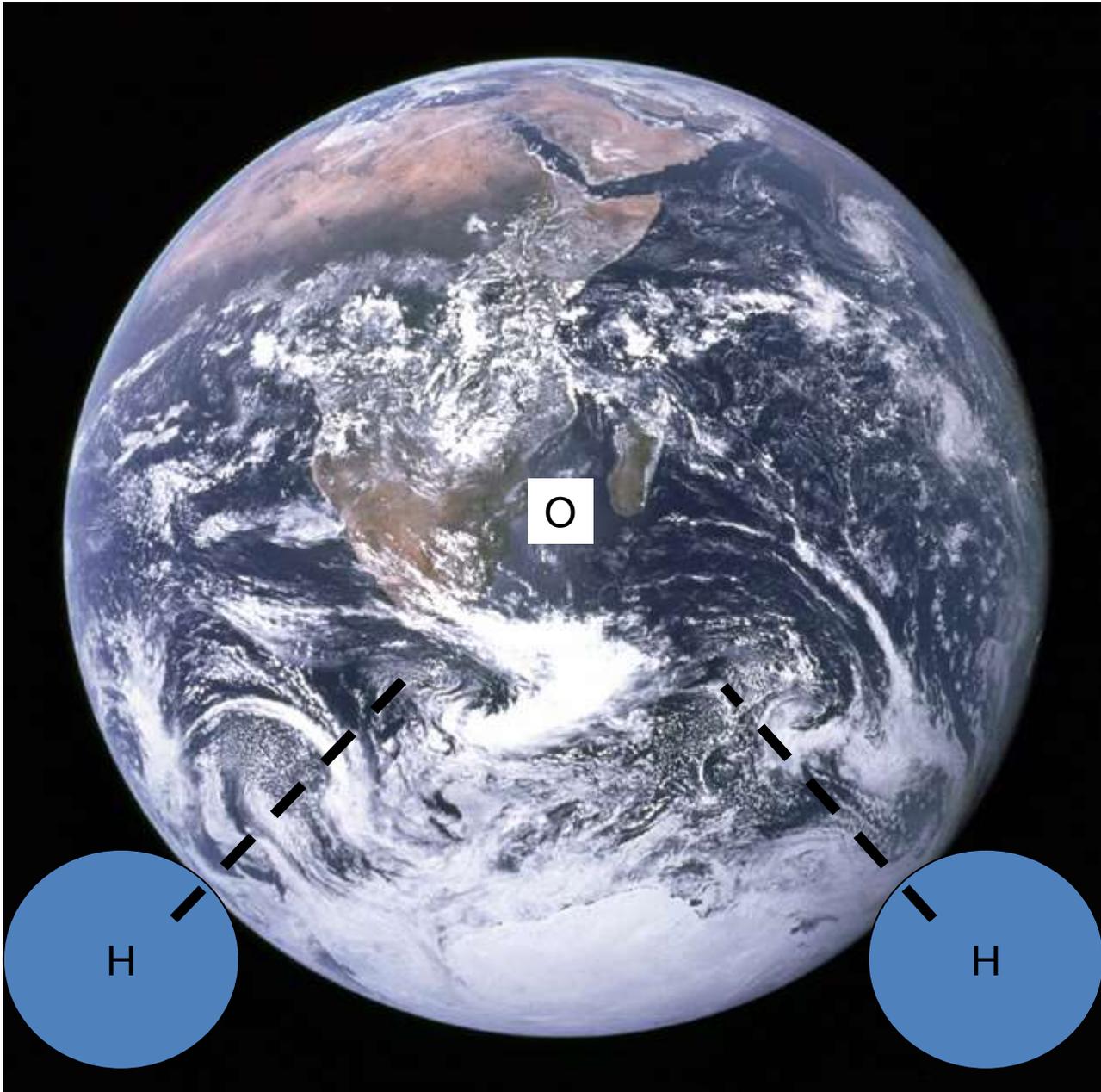
(kovacs.istvan.janos@mfgi.hu)

with the significant contribution of Andrew Berry, Jörg Hermann, Hugh O'Neill, Dave Green, Anja Rosenthal, Qunke Xia, Jannick Ingrin, Roland Stalder, Katalin Kamarás, Judith Mihály, Csaba Németh, Tamás Gál, Judit Sándorné Kovács, Beatrix Udvardi, Zsanett Pintér, Károly Hidas, Tamás Bíró, Lászlóné Kutassy, Pál Lendvai, Tamás Zelei, György Falus, Csaba Szabó, Júlia Dégi, Tamás Fancsik



Bolyai Research Fellowship
OTKA PD101683

“water” = (H⁺, OH⁻, H₂O)



- melting temperature
- rheology
- conductivity
- diffusion

Why FTIR spectrometry?

Advantages

- prices of new “state of the art” FTIR spectrometers and accessories are relatively low (~100 000 €)
- cost of maintenance is low
- low detection limits for different vibrations of H, N, C, S species in various bonds
- sample preparation is simple
- user friendly and easy to learn

Some drawbacks

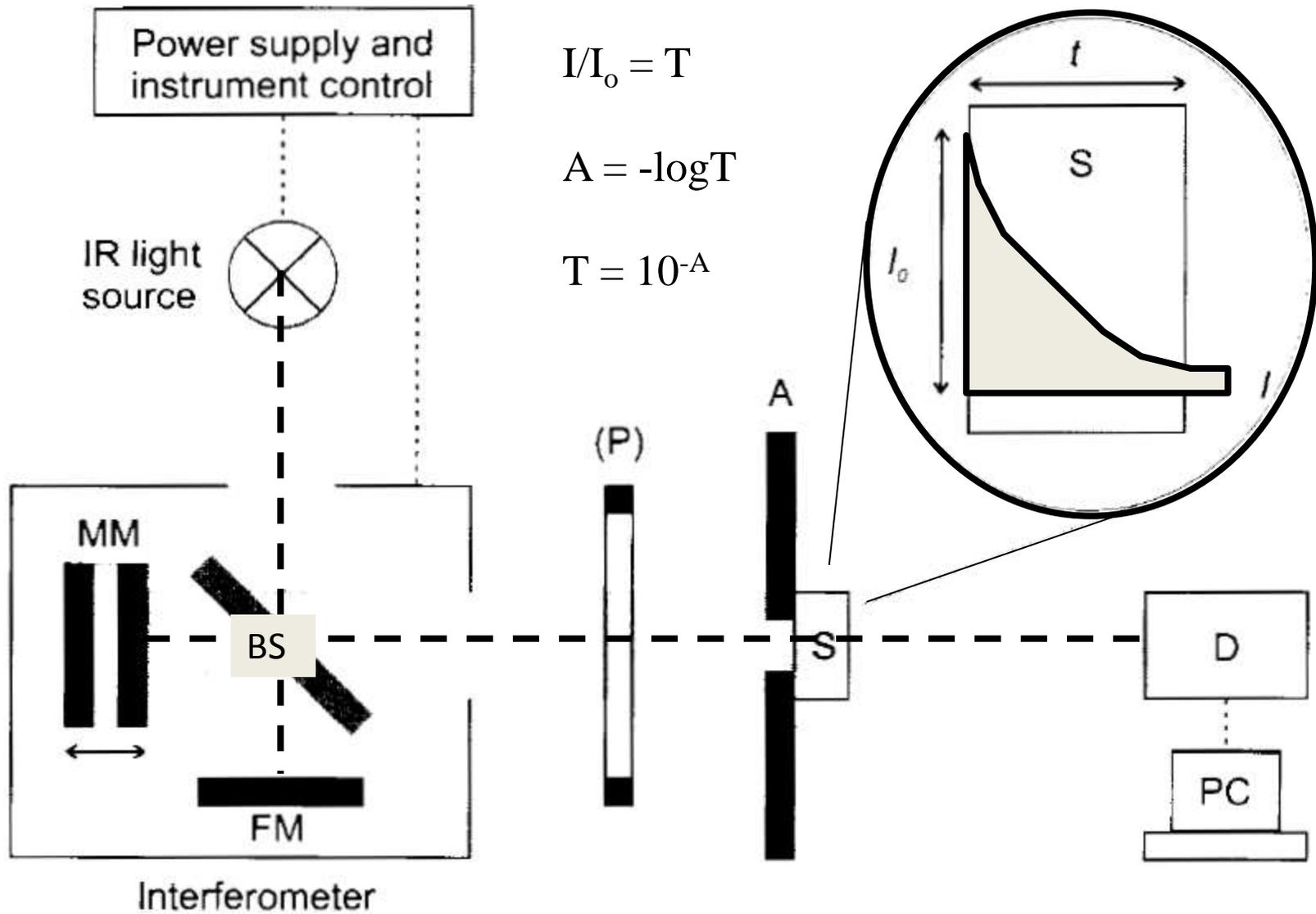
- identification of absorbing species in geological substances may be difficult due to the lack of appropriate spectral libraries
- quantifications bears (significant) uncertainties sine no standard protocol has been established so far

This talk is to give practical information
how to analyse quantitatively “water” in:

- nominally anhydrous minerals (NAMs): olivine, glass and SMIs
- some implications of the method



Principles of IR microscopy – experimental setup



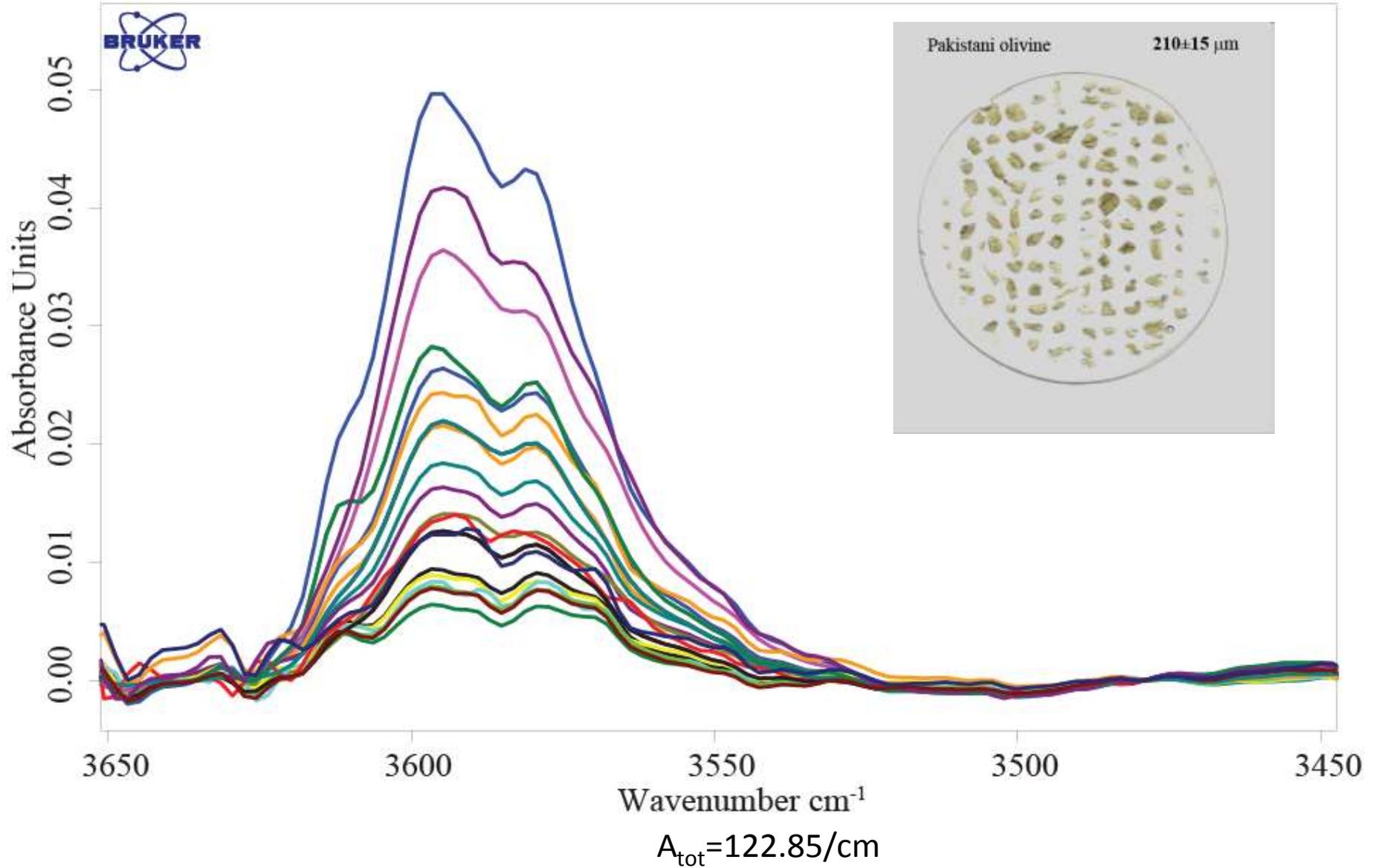
$$I/I_0 = T$$

$$A = -\log T$$

$$T = 10^{-A}$$

(Libowitzky, 2006)

Inter-laboratory measurements



Bruker, Hyperion-Vertex 70, Hungarian Police, Budapest

How much “water” is in NAMs (olivine)?

Beer-Lambert law

$$c = \frac{A_{\text{tot}} M_i}{\epsilon_i \cdot \rho \cdot t} \cdot 100 \quad \text{or in a simplified form } c = k * A_{\text{tot}}$$

Where:

1. A_{tot} total integrated absorbance (peak height or integrated area)/cm

2. ϵ molar extinction coefficient (L/mol*cm) or

k calibration factor [$k = c * M_A / (\rho * \epsilon)$]

c) concentration (ppm wt%)

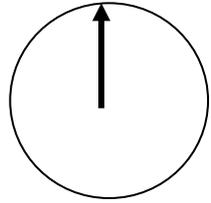
t) sample thickness (cm)

ρ) density (g/L)

M_i) molecular weight (g)

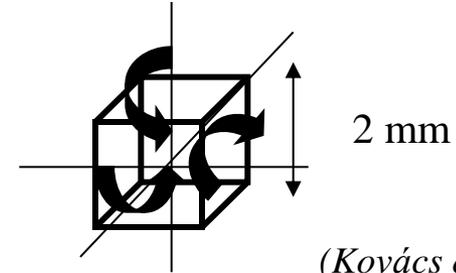
How much “water” is in NAMs (olivine)?

The determination of A_{tot} : the “classical” and more accurate way

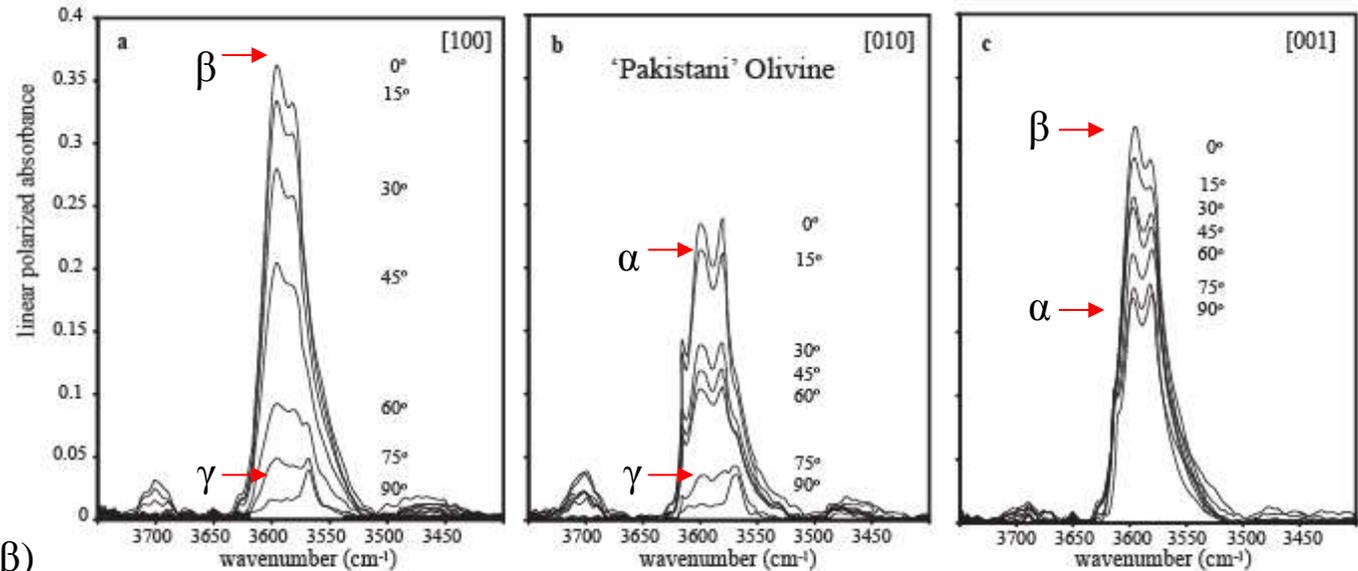
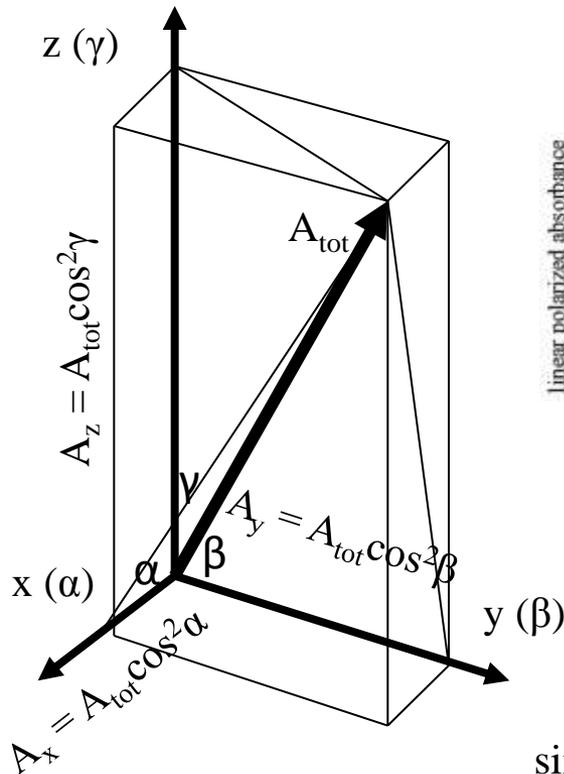


-measurements with polarized IR radiation
(weaker signal, very sensitive to orientation and quality of the polarizer)

-along the principal crystallographic directions
or
-three random but orthogonal sections



(Kovács et al., 2008)



$$A_{tot} \cos^2 \alpha + A_{tot} \cos^2 \beta + A_{tot} \cos^2 \gamma$$

$$A_{tot} = A_a + A_b + A_c$$

since $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$ then

$A_{tot}/\text{cm} = 128.4/\text{cm}$ (Bruker, Canberra)

(Libowitzky and Rossman, 1996)

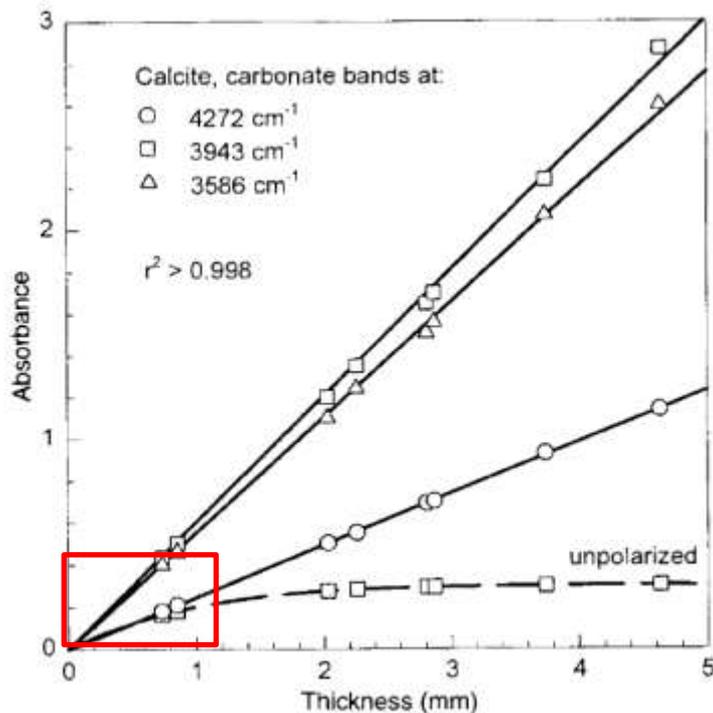
How much “water” is in NAMs?

The determination of A_{tot} : the “economical” but still satisfactory protocol

-measurements with unpolarized IR radiation
(stronger signal, less sensitive to orientation, less precise)

-a number of unoriented grains are needed to make it work

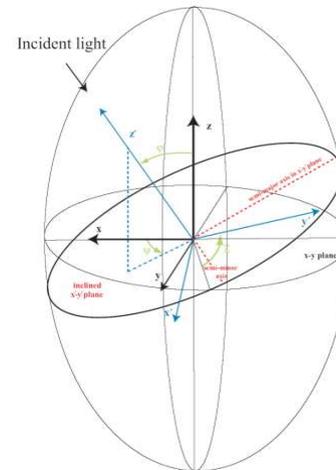
1) Unpolarized absorbance is NOT linearly proportional to thickness, therefore we cannot normalize it to a reference thickness



2) There was no theory similar to refractive index theory to link (unpolarised) absorbance to direction of incident light with respect to principal polarized absorbances

$$T(\varphi, \psi) = T_a \cdot \cos^2 \varphi \cdot \sin^2 \psi + T_b \cdot \sin^2 \varphi \cdot \sin^2 \psi + T_c \cdot \cos^2 \psi$$

$$T(\varphi) = T_a \cdot \cos^2 \varphi + T_b \cdot \sin^2 \varphi$$



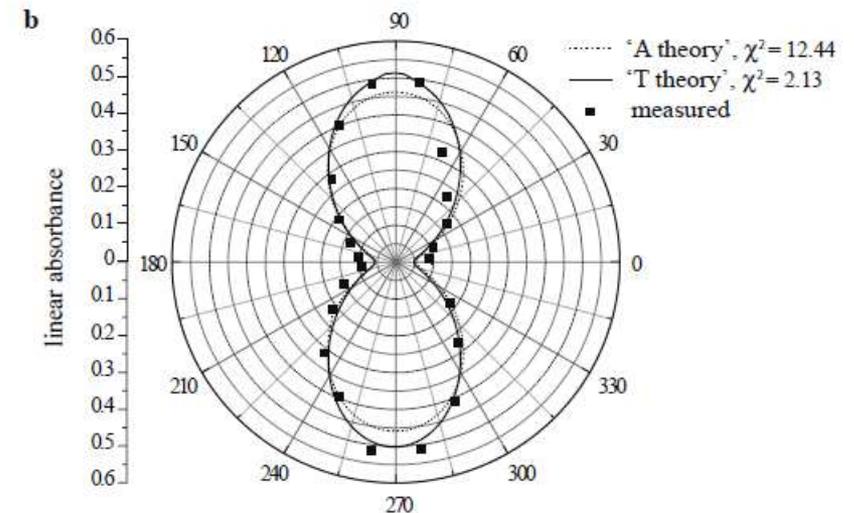
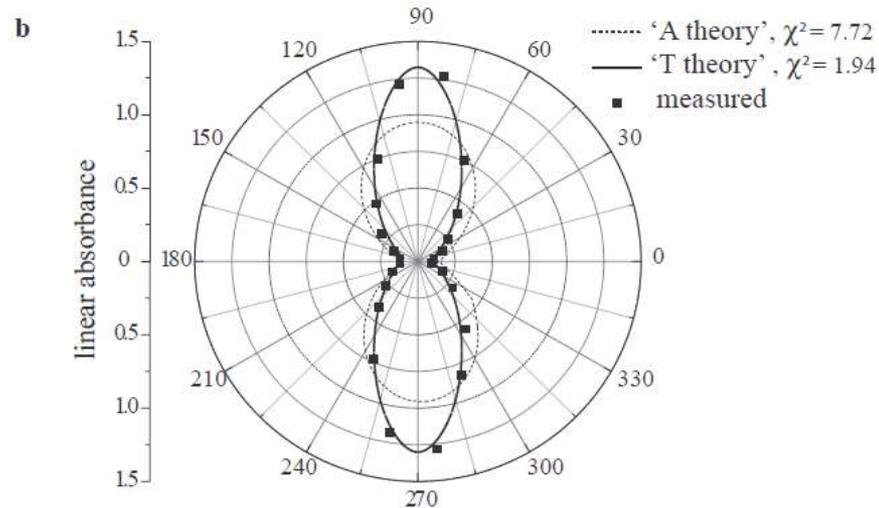
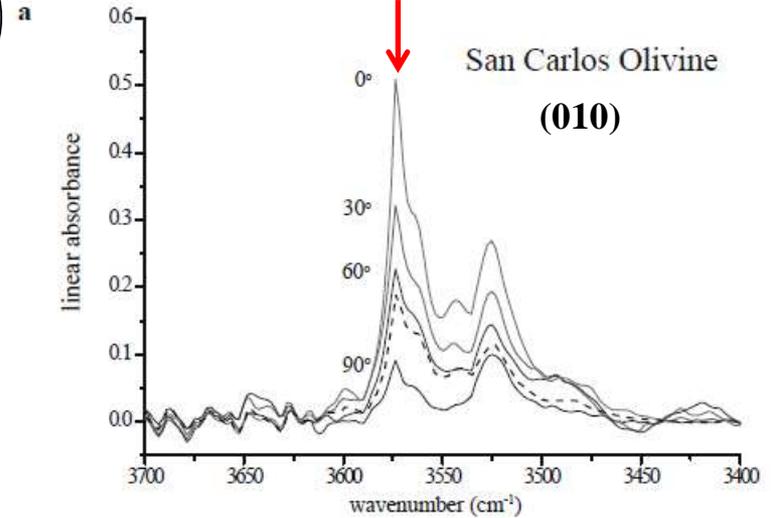
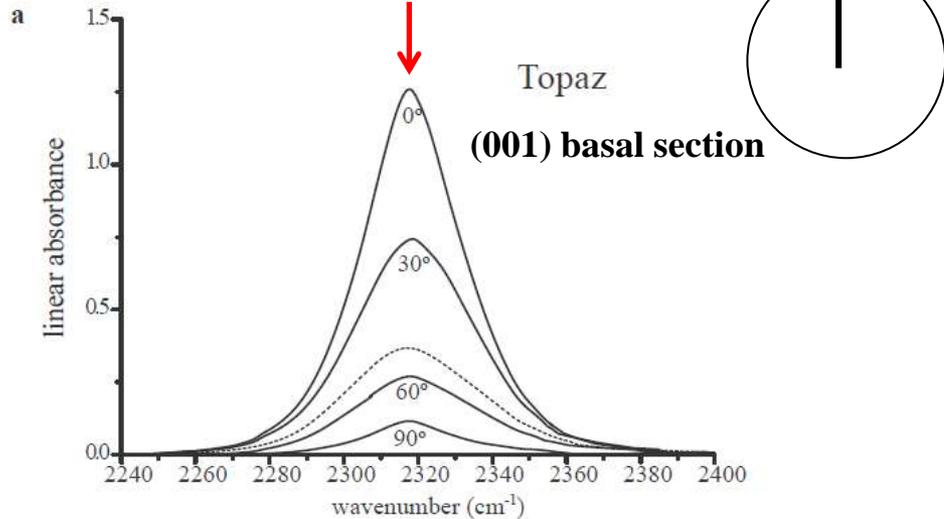
Polarized linear absorbance

$$A(\varphi) = -\log(T_{min} \cdot \cos^2 \varphi + T_{max} \cdot \sin^2 \varphi)$$

“T-theory”

$$A(\varphi) \approx A_{max} \cdot \cos^2 \varphi + A_{min} \cdot \sin^2 \varphi$$

“A-theory”

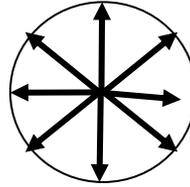


Unpolarized linear absorbance

$$A_{unpol}[T] = -\log \int_{\varphi=0}^{\varphi=2\pi} T_{min} \cdot \cos^2 \varphi \cdot + T_{max} \cdot \sin^2 \varphi$$

$$A_{unpol}[A] = -\log \int_{\varphi=0}^{\varphi=2\pi} A_{min} \cdot \cos^2 \varphi \cdot + A_{max} \cdot \sin^2 \varphi$$

$$\frac{A_{unpol}[A] - A_{unpol}[T]}{A_{unpol}[A]} (A^{max}, A^{min})$$



$$A_{unpol} = 1/2 (A_{pol}^{max} + A_{pol}^{min}).$$

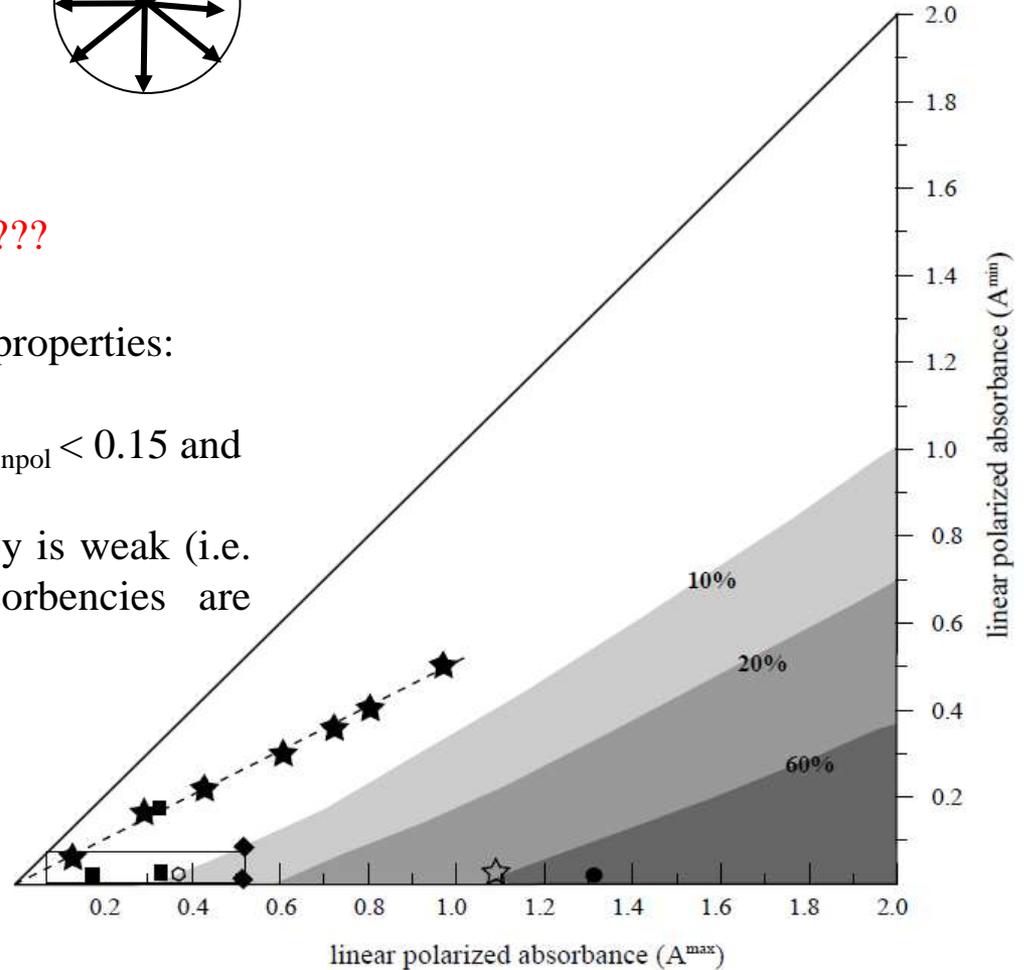
$A_{unpol}[T] \approx A_{unpol}[A]$ under which conditions???

This holds under a wide range of absorbance properties:

-always if the absorbance is low $A_{pol} < 0.3$; $A_{unpol} < 0.15$ and

-also for stronger absorbance if the anisotropy is weak (i.e. the difference between the principal absorbencies are moderate:

$$\frac{A^{max}}{A^{min}} \leq \frac{2}{1})$$



Unpolarized integrated absorbance

A_{tot} can be estimated from A_{unpol}^{avg} : ???

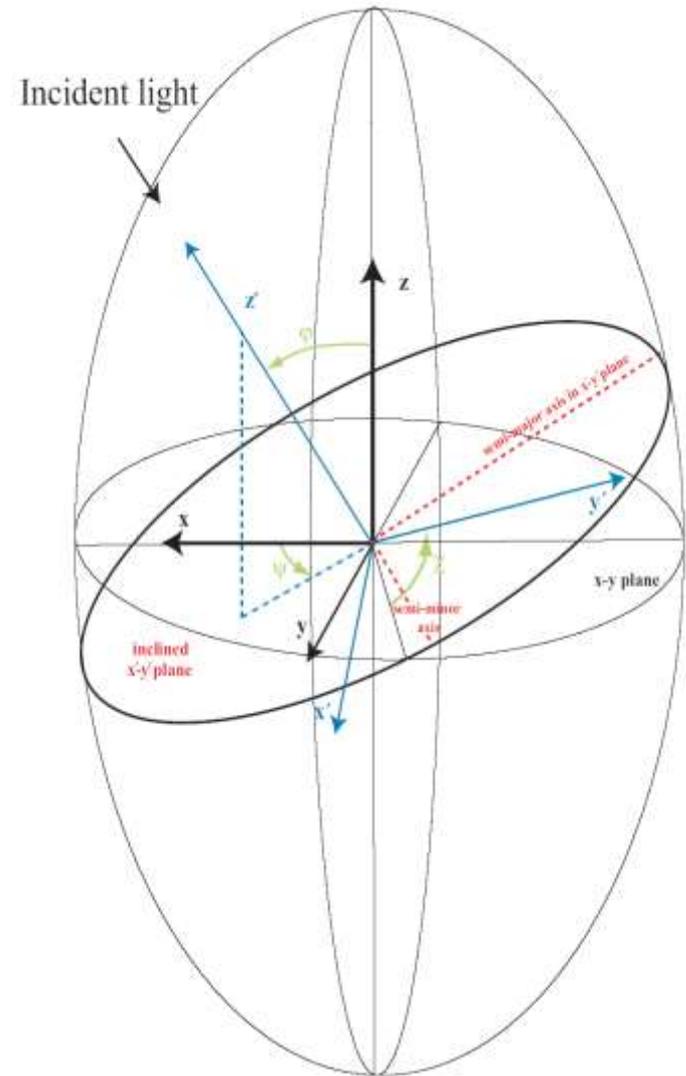
Yes, if:

- distribution of the absorber is homogenous in the analyzed mineral ✓
- the grains are (perfectly) unoriented (i.e. strong preferred orientation) ✓
- enough unoriented grains are considered for the calculation of the average

$$A_{unpol}^{avg} = \frac{1}{3} (A_a + A_b + A_c) = \frac{1}{3} A_{tot}$$

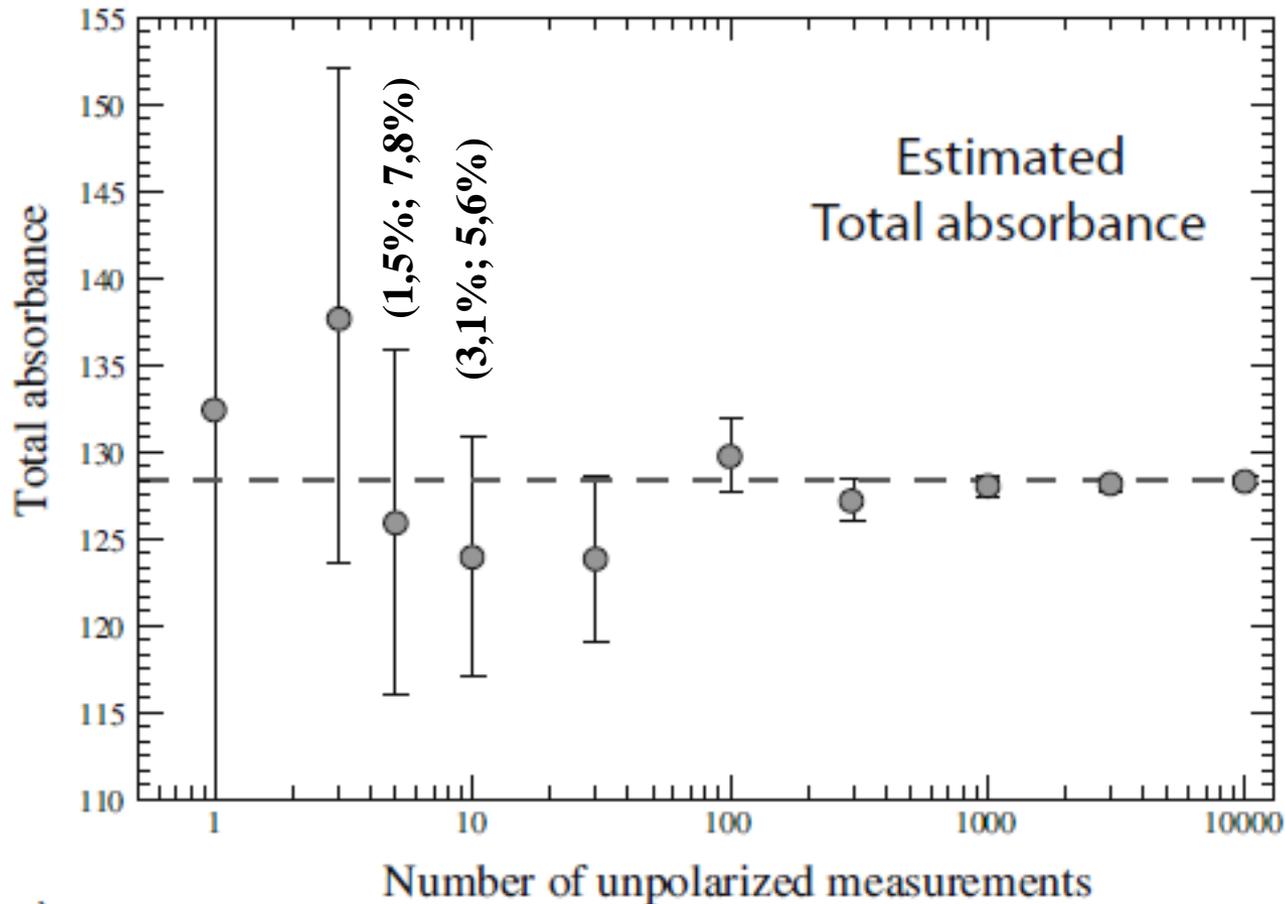
$$A_{unpol}^{avg} = \frac{1}{4\pi} \int_{\psi=0}^{\psi=2\pi} \int_{\varphi=0}^{\varphi=\pi} A(\varphi, \psi) \sin \varphi d\varphi d\psi$$

$$A_{unpol}(\varphi, \psi) = \frac{1}{2} [A_a (\cos^2 \varphi \cos^2 \psi + \sin^2 \psi) + A_b (\cos^2 \varphi \sin^2 \psi + \cos^2 \psi) + A_c \sin^2 \varphi]$$



Unpolarized integrated absorbance

How many grains one needs to achieve reasonable accuracy in A_{tot} if anisotropy is very strong ($\frac{A^{\text{max}}}{A^{\text{min}}} \gg \frac{2}{1}$)?



Unpolarized integrated absorbance

$$A_{unpol}^{avg} = \frac{1}{3}(A_a + A_b + A_c) = \frac{1}{3}A_{tot}$$

,Urban legends': ,orientation factors' or ,correction factors' (Demouchy and Bolfan-Casanova, 2016)

Paterson (1982): Appendix 2. 

Koch-Müller et al. (2001)

the integrated absorbances in the three principal directions in the calculations described above. However, in special circumstances, appropriate quantitative measurements may be obtained on random sections. Table 2 lists the total integrated absorbances of the bands of the unpolarized as well as of the polarized spectra. For the unpolarized spectra the integrated total absorbances have been calculated by multiplying the integrated absorbance by three assuming that there is no preferred orientation of the bands. At least for the samples MKM-

OH Orientation Distribution	Beam Direction	Polarisation	Orientation Factor γ	Remarks
Isotropic	any	any	1/3	Case of Scholze and "gel-type" OH.
OH c axis	c axis	any	0	
"	⊥ c axis	unpolarized	1/2	
"	"	c axis	1	
"	"	⊥	0	
OH ⊥ c axis	c axis	any	1/2	Case of Kats and Brunner et al.
"	⊥ c axis	unpolarized	1/4	
"	"	c axis	0	
"	"	⊥ c axis	1/2	
OH at angle α to c axis	c axis	any	$\frac{1}{2}\sin^2\alpha$	
	⊥ c axis	unpolarized	$\frac{1}{2}\cos^2\alpha + \frac{1}{2}\sin^2\alpha$	
		c axis	$\cos^2\alpha$	
		⊥ c axis	$\frac{1}{2}\sin^2\alpha$	

TABLE 1. — Orientation Factors in Uniaxial Crystals.

Reception: 1) Criticism, skepticism

Withers (2013)

American Mineralogist, Volume 98, pages 689–697, 2013

On the use of unpolarized infrared spectroscopy for quantitative analysis of absorbing species in birefringent crystals

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Department of Earth Sciences, University of Minnesota, 108 Pillsbury Hall, Minneapolis, Minnesota 55455, U.S.A.

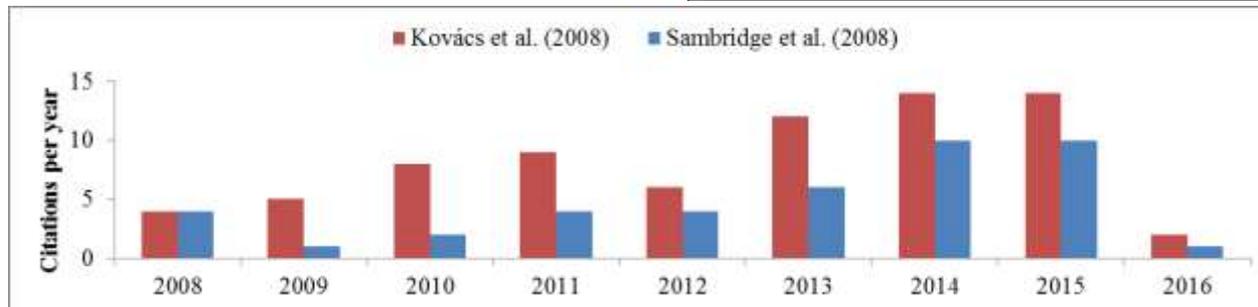
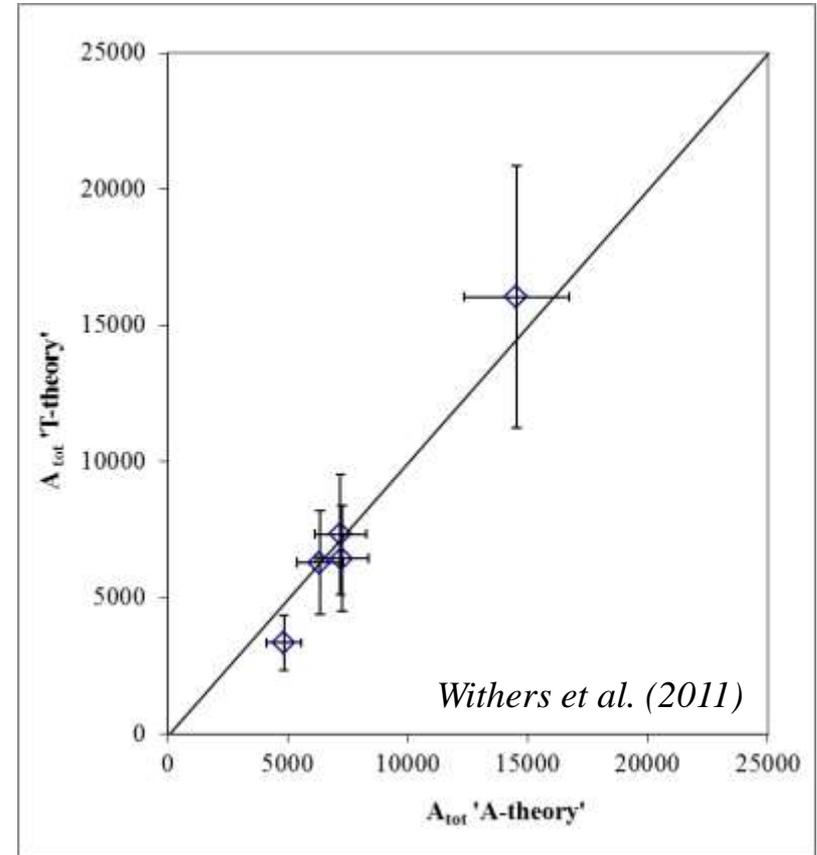
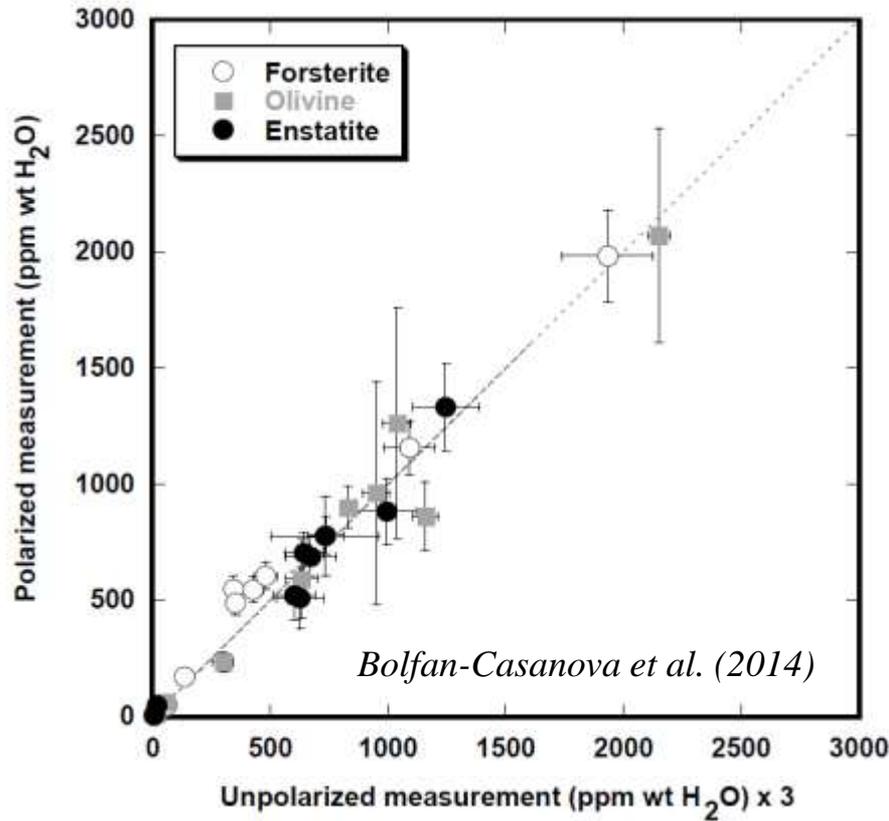
ABSTRACT

There is an understandable desire to use simple unpolarized infrared analysis of unoriented anisotropic samples to extract quantitative information, rather than using more demanding polarized techniques. Owing to the fact that unpolarized infrared absorbance in birefringent media deviates from the Beer-Lambert law, previous studies have either warned against using unpolarized spectroscopy for quantitative purposes, or have used flawed error analysis to justify using simple averages of integrated absorbance of multiple absorbance bands as a proxy for total integrated polarized absorbance in the principal spectra. It is shown here that unpolarized infrared absorbance is correctly calculated by averaging in the transmission domain. The errors in estimates of principal absorbance by averaging of unpolarized absorbance spectra are evaluated using correct theory of unpolarized infrared transmission. Correction schemes for integrated absorbance based on linear-absorbance error calculations are shown to be inappropriate. A theory is developed that allows the sum of the polarized principal absorbance spectra to be estimated from multiple unpolarized measurements of randomly oriented samples. The systematic errors that arise when averaging in the absorbance domain are avoided by use of exact theory rather than an approximation. Numerical simulation shows that applying the new procedure to 10 unpolarized measurements of OH stretching bands in olivine results in convergence of the estimated total integrated principal polarized absorbance to within 10% of the true value for a sample size of 10 measurements, but the technique is limited to spectral regions that do not contain absorption bands that are simultaneously intensely absorbing and strongly anisotropic.

Keywords: Infrared spectroscopy, unpolarized, quantitative, hydroxyl, olivine

Reception: 2) Wide applications demonstrating satisfactory accuracy

Bali et al. (2008); Férot and Bolfan-Casanova (2012); Sokol et al. (2013); Bolfan-Casanova et al. (2014); Doucet et al. (2014); Padrón-Navarta et al. (2014); Bizimis and Peslier (2015)



Reception: 2) Internal inconsistency in Withers (2013)?

Can something be true and false simultaneously?

,Science is politics'

David H Green

CONCLUDING REMARKS

(3) Based on calculations of unpolarized spectra in the OH-stretching region from natural and hydrothermally annealed olivines, averages of >10 unpolarized spectra where the maximum linear absorbance does not exceed 0.3 absorbance units are expected to give a reasonable estimate of A_{tot} . This conclusion is valid only for samples where the average degree of anisotropy in the principal polarized spectra is not significantly greater than that of the examples used in the simulations.

Withers (2013)

ABSTRACT

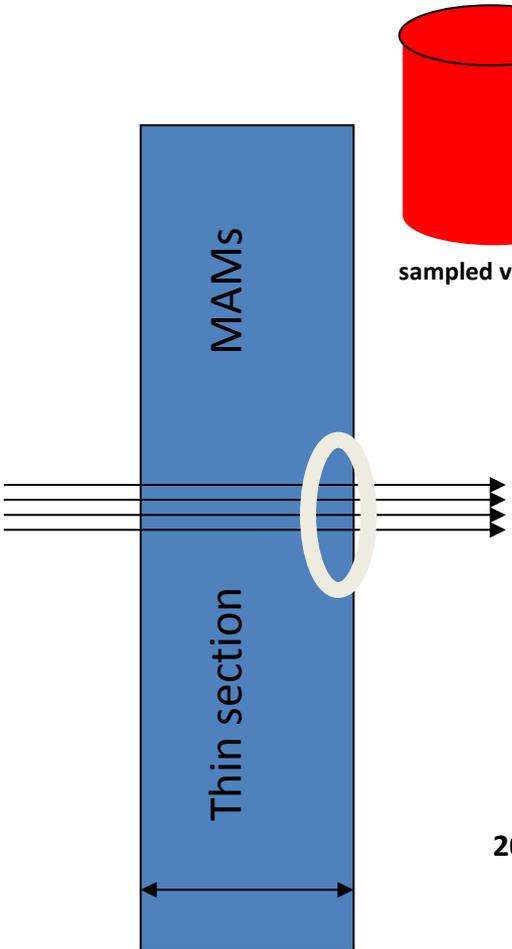
The predictions of the theory of light propagation in weakly absorbing anisotropic minerals are tested against systematic measurements of the infrared absorbance spectra of calcite, olivine, and topaz oriented in both principal and random sections, using both polarized and unpolarized light. We show that if the linear polarized maximum absorbance is smaller than ~ 0.3 , or if the ratio of maximum and minimum absorbance is close to unity, then (1) the polarized maximum and minimum absorbances as well as the unpolarized absorbance are, to a good approximation, linearly proportional to thickness, regardless of the direction of the incident light; (2) the angular variation of polarized light absorption is indistinguishable from the theoretical predictions within the uncertainty of the measurements; (3) for any section the unpolarized absorbance is the mean of the polarized maximum and minimum absorbance; and (4) the average unpolarized absorbance of randomly oriented grains is one third of the Total Absorbance (defined as the sum of the three principal absorbances). Therefore, calibrations relating Total Absorbance to absorber concentration in minerals that have been developed from measurements with polarized light parallel to the principal axes may be applied to measurements with unpolarized light on a population of randomly oriented sections. We show that 10 such measurements are sufficient to achieve a petrologically useful accuracy. The method enables water concentrations in nominally anhydrous minerals to be determined from samples where the preparation of oriented specimens is not feasible, such as high-pressure experimental runs and fine-grained mantle xenoliths. The method may also be used for obtaining quantitative measurements on low-symmetry minerals.

Keywords: Infrared spectroscopy, absorbance spectroscopy, unpolarized light, olivine, calcite, topaz, nominally anhydrous minerals

Kovács et al. (2008)

Instrument setup and sample preparation

Sample compartment



sampled volume

Aperture size ~ horizontal resolution

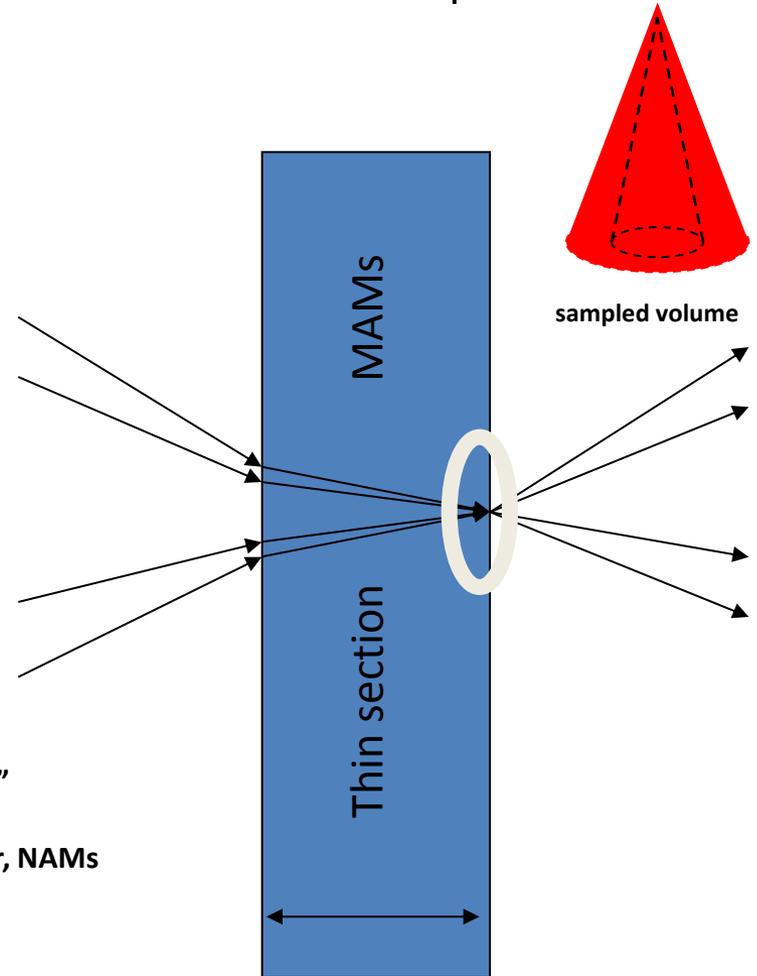
50 μm < for standard NAMs
20 – 50 μm for good quality NAMs
< 20 μm with synchrotron radiation

Sample thickness ~ „integral method”

200 - 300 μm < for standard (i.e. water-poor, NAMs
< 100 μm for synchrotron radiation
and water-rich NAMs

Stronger and even signal, less scattering
and other unwanted optical effects

Microscope

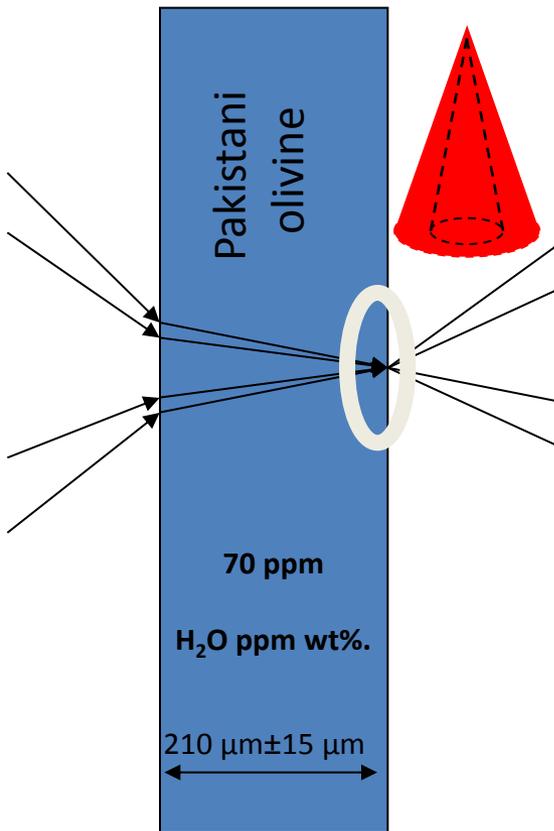


sampled volume

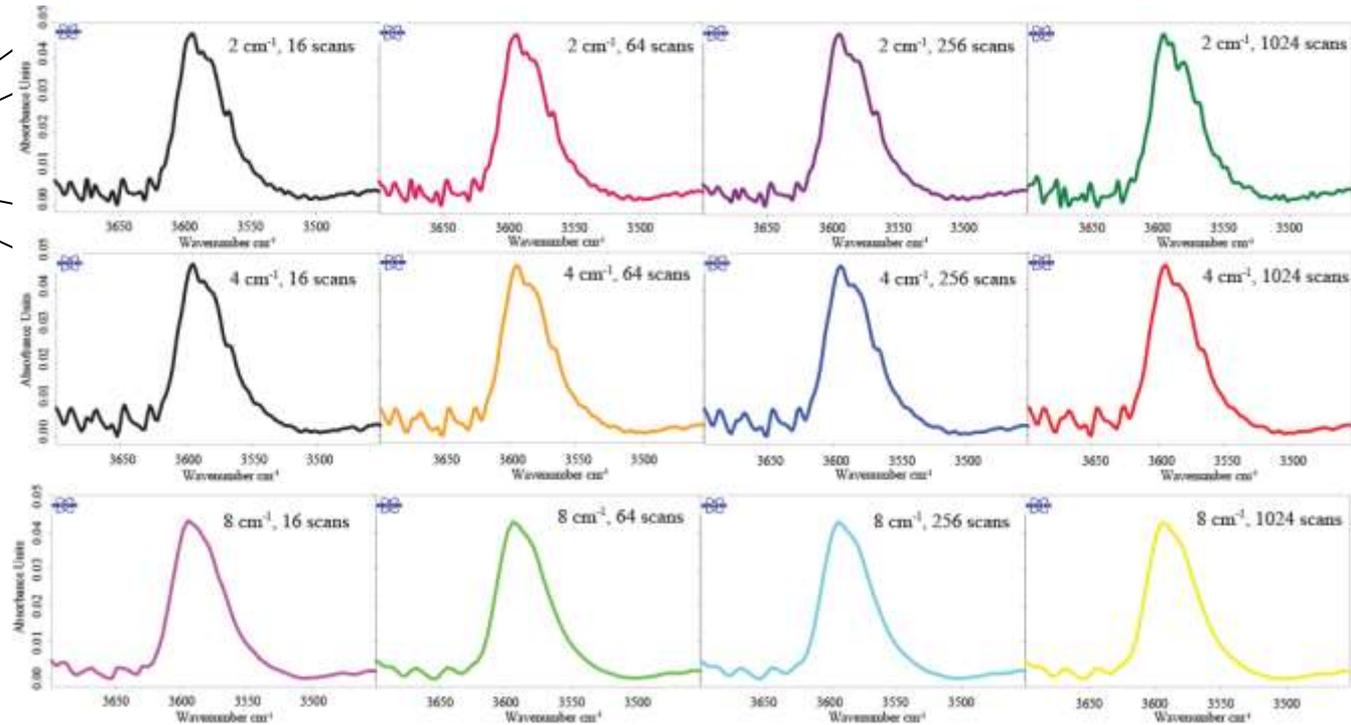
Better suited for small samples,
with higher spatial resolution

Instrument setup and sample preparation

Microscope

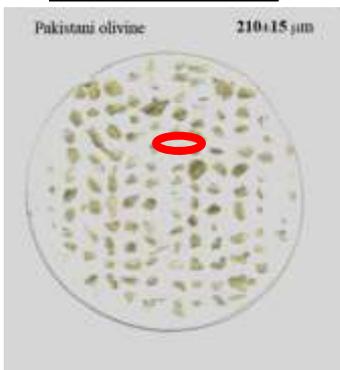


Number of scans and resolution



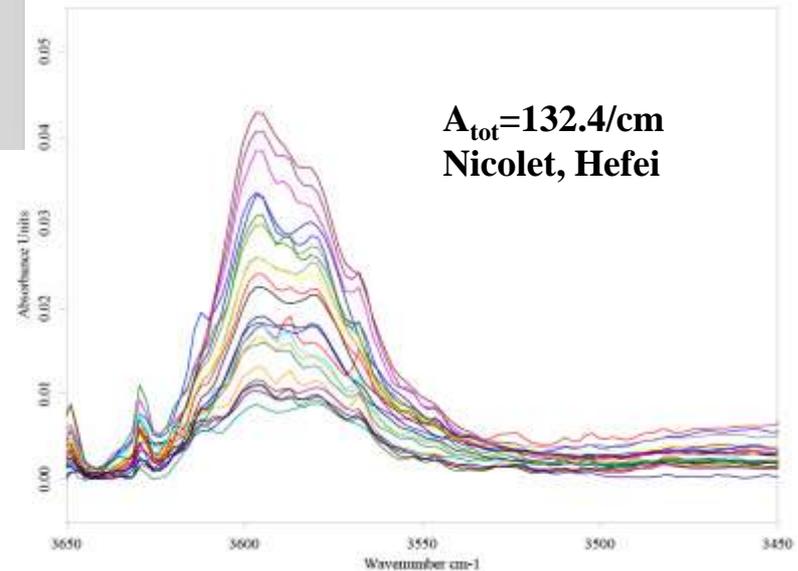
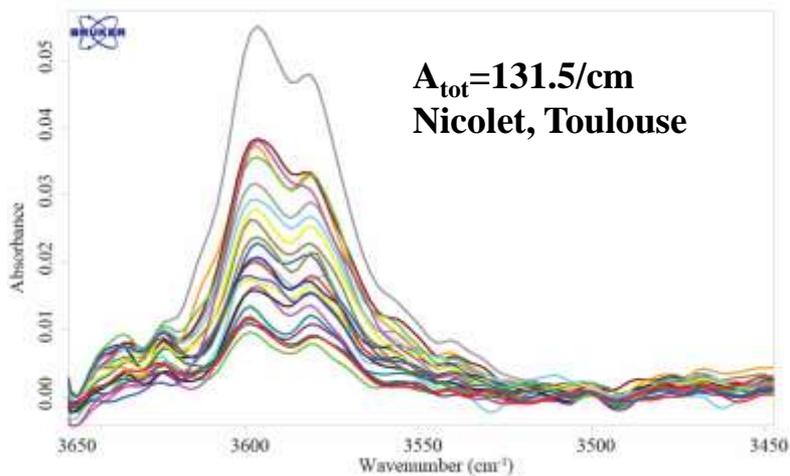
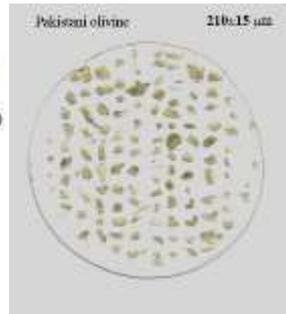
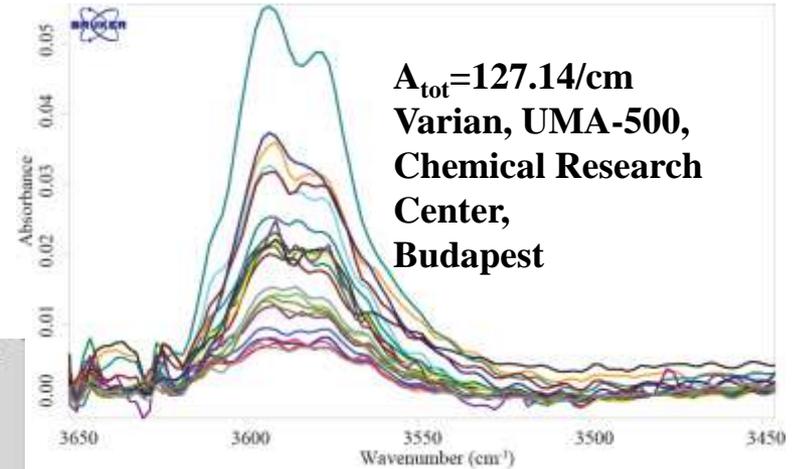
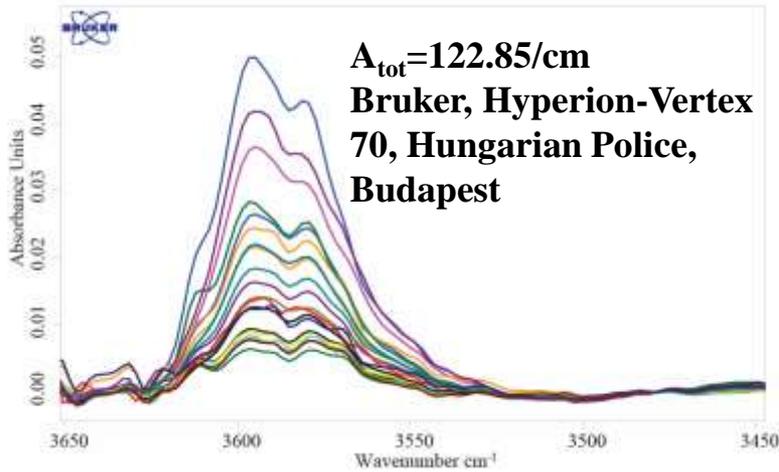
4 cm⁻¹, 256 scans are optimal

Bruker, Hyperion-Vertex 70, Hungarian Police, Budapest



How much “water” is in NAMs (olivine)?

Pakistani olivine, standard’ with 23 grains analysed in more than 10 different laboratories worldwide (Australia, Austria, China, France, Germany, Hungary and Italy) using a range of micro-FTIR microscopes and spectrometers (Bruker, Varian (Digilab); Nicolet) average unpolarised absorbance is within 10% the same, therefore it is not a major source of uncertainty



How much “water” is in NAMs (olivine)?

Beer-Lambert law

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Where:

1. A_{tot} total integrated absorbance (peak height or integrated area)/cm

2. ϵ molar extinction coefficient (L/mol*cm) or

k calibration factor [$k = c * M_A / (\rho * \epsilon)$]

c) concentration (ppm wt%)

t) sample thickness (cm)

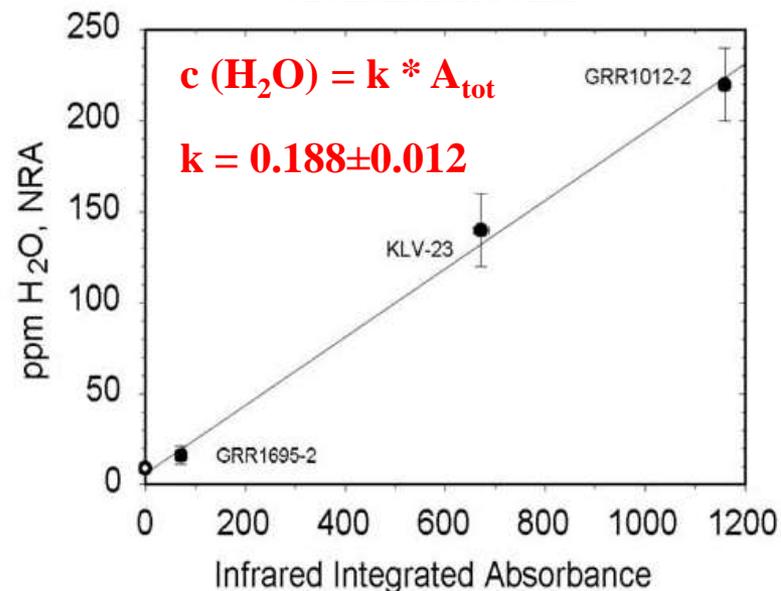
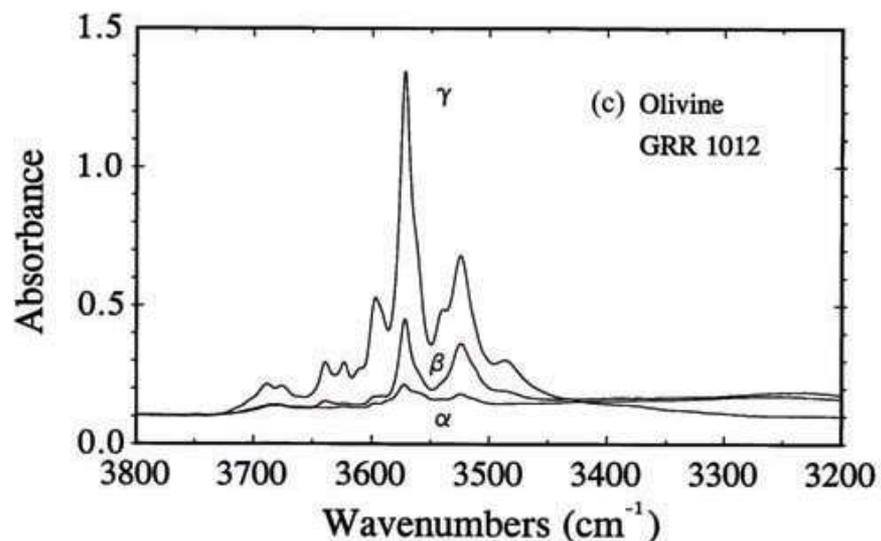
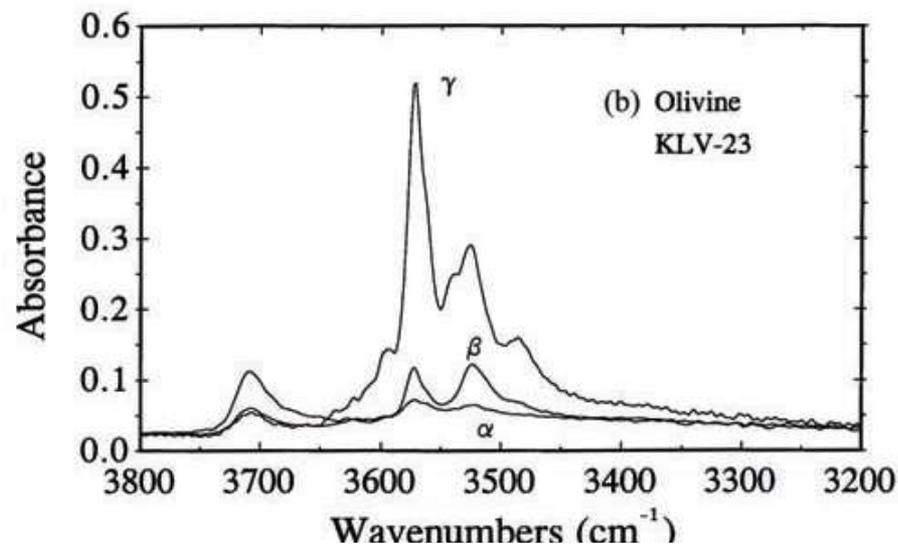
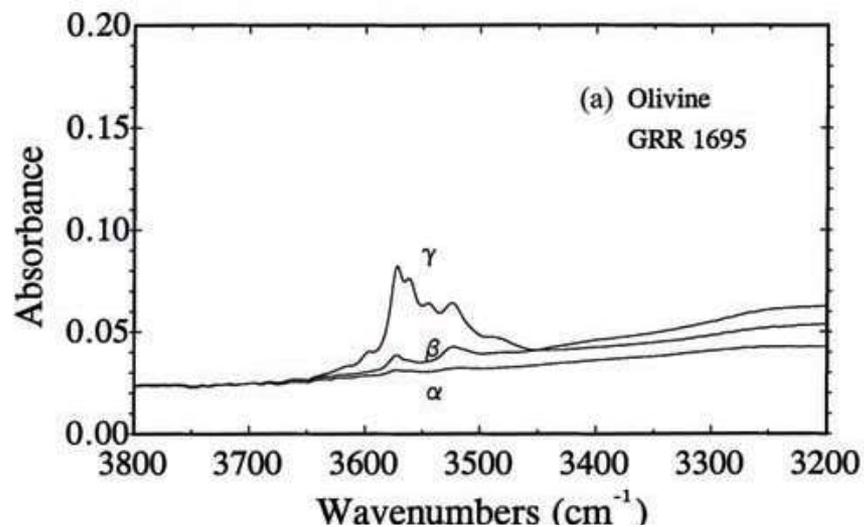
ρ) density (g/L)

M_i) molecular weight (g)

How much “water” is in NAMs (olivine)?

2) The choice of molar extinction coefficient (ϵ) or/and calibration factor (k) to calculate absolute “water” content (ppm wt%) from A_{tot} :

a) the mineral specific approach



Drawbacks

-only suitable for olivines with identical IR spectra

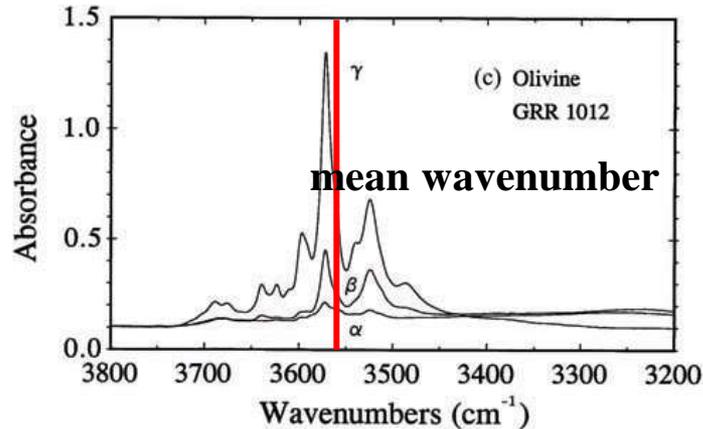
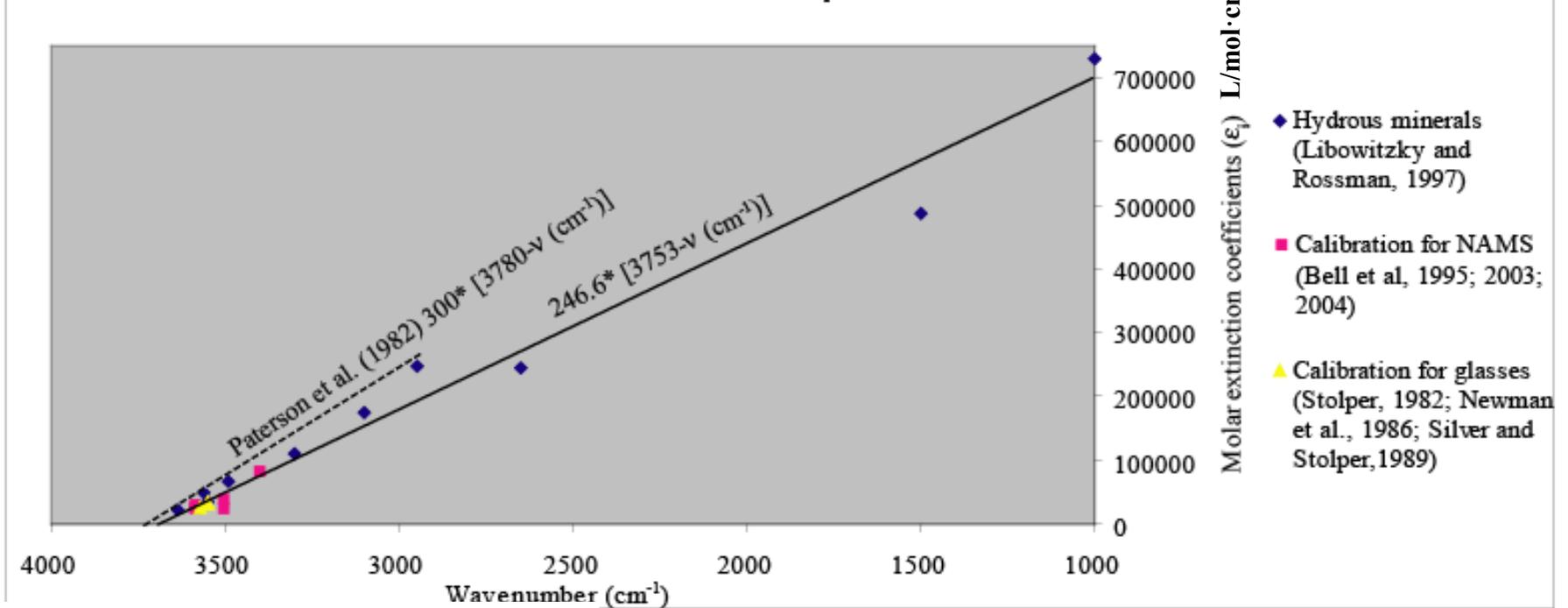
(Bell et al., 1995, 2003, 2004)

How much “water” is in NAMs (olivine)?

2) The choice of molar extinction coefficient (ϵ) or/and calibration factor (k) to calculate absolute “water” content (ppm wt.%) from A_{tot} :

b) wavenumber dependent calibration

Molar extinction coefficient (ϵ_i) vs. wavenumber (cm^{-1})



$$c(H_2O) = \frac{A \cdot M_i}{\rho \cdot t} \cdot 100 \int \frac{1}{\epsilon_i(\nu)} d(\nu)$$

Drawbacks

-it is still not proved whether the calibration is also valid for Nominally anhydrous minerals

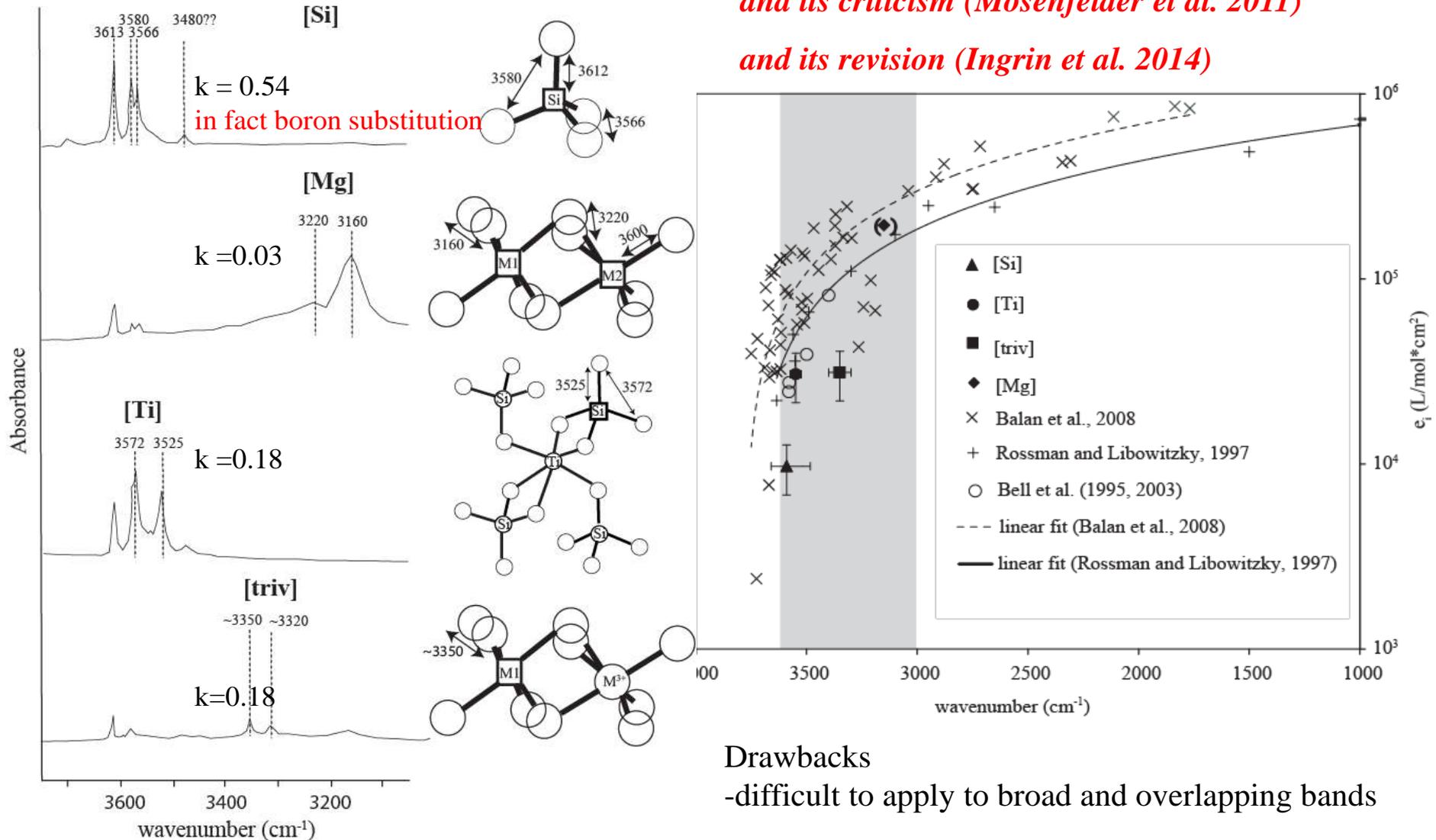
-difficult to apply to broad and overlapping bands

Paterson (1982), Libowitzky and Rossman (1997)

How much “water” is in NAMs (olivine)?

2) The choice of molar extinction coefficient (ϵ) or/and calibration factor (k) to calculate absolute “water” content (ppm wt%) from A_{tot} :

c) substitution specific calibration and its criticism (Mosenfelder et al. 2011) and its revision (Ingrin et al. 2014)

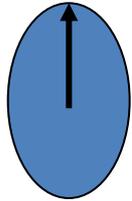


Drawbacks

-difficult to apply to broad and overlapping bands

Kovács (2008); Kovács et al. (2010)

Suggested protocol for quantification



Polarized

(more accurate, weaker signal, very sensitive to orientation and quality of the polarizer)

from three
principal directions

$$A_{\text{tot}} = A_a + A_b + A_c$$



Unpolarized

(less accurate, stronger signal, less sensitive to orientation)

from random
directions

$$A_{\text{unpol}}^{\text{avg}} = \frac{1}{3} (A_a + A_b + A_c) = \frac{1}{3} A_{\text{tot}}$$



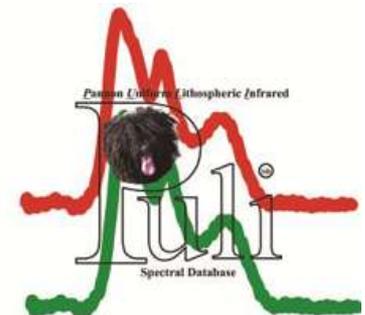
Mineral specific calibrations (olivine, clinopyroxene, orthopyroxene, garnet, feldspar: Bell et al., 1995; 2003; Mosenfelder et al., 2011; Whitters et al., 2012; Mosenfelder et al. 2013a, 2013b, 2015)

-only suitable for minerals with identical infrared characteristics

Substitution-specific calibrations (olivine, Kovács et al., 2010)

-can be utilised generally, however it is often difficult to resolve the contribution of the different substitutions

-it is crucial to make digital version of the original spectra available (puli.mfgi.hu)



Thank you for your attention!

