Portable Raman Instrumentation in Geoscience and Exobiology

Jan Jehlička

Charles University in Prague,
Institute of Geochemistry, Mineralogy and Mineral Resources
Prague, Czech Republic

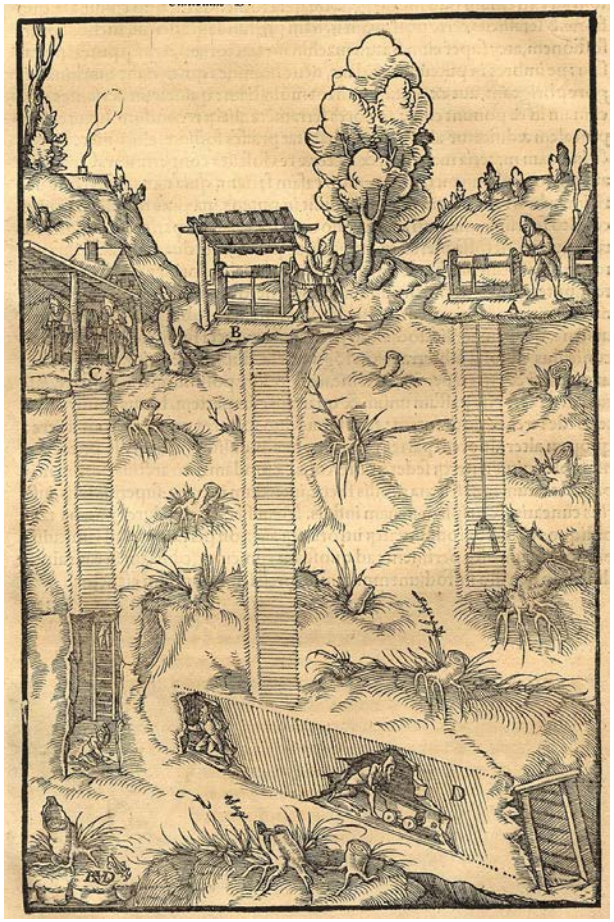
Talk for GeoRAMAN School for students and young scientists

Přírodovědecká fakulta
UNIVERZITY KARLOVY V PRAZE

Techniques of identification/discrimination of phases ?

- In the past ?
- Nowadays…?


A
B


B
C
D

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Novosibirsk, Russia, June 9-15, 2016

Minerals of relevance for geoscience ?

Minerals of relevance for planetary research and exobiolgy ?

Biomarkers of relevance for geoscience ?

Biomarkers of importance for exobiology?

Methods of identification/discrimination of phases

	Advantages	Disadvantages
XRD		
Other diffraction techniques		
Raman spectroscopy		

- How to identify minerals ??

Earth x Planets

geobiology

exobiology

- Miniature instruments

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University of Ljubljana

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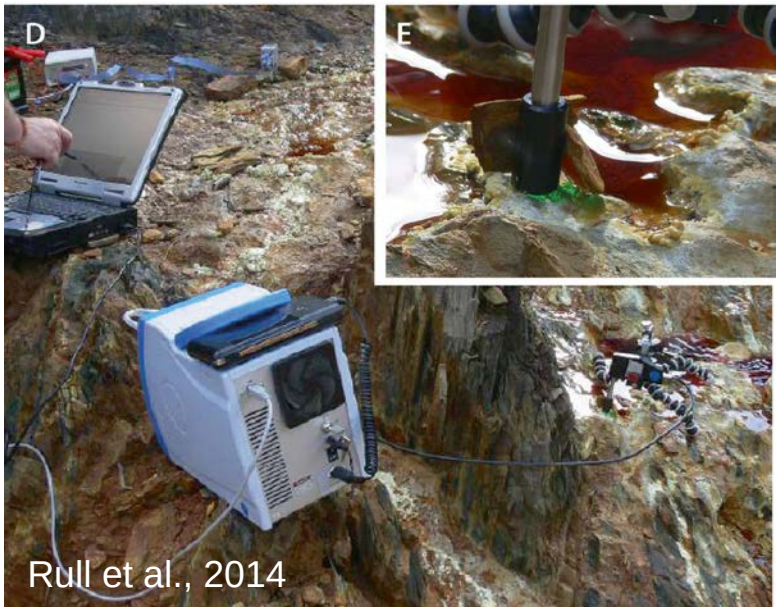
Mobile Raman spectroscopy: Conditions

Temperature, altitude

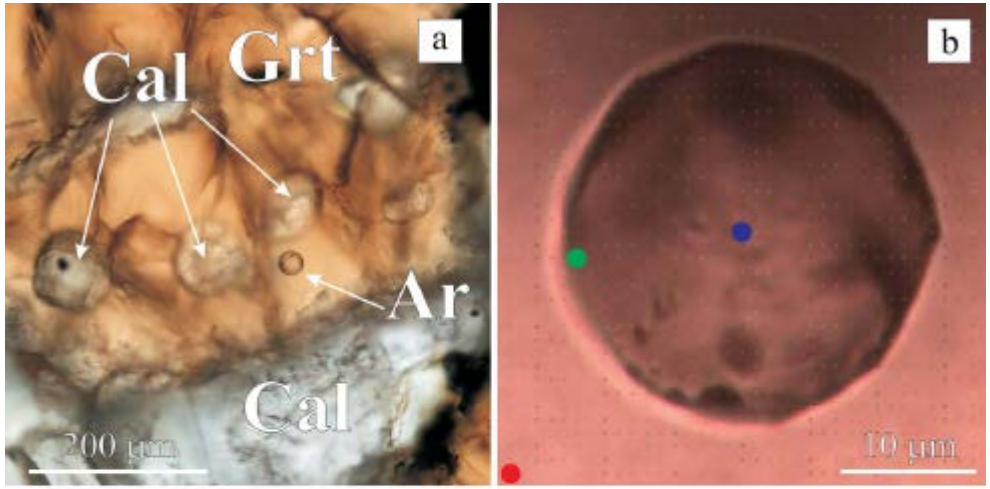

D
E
Rull et al., 2014

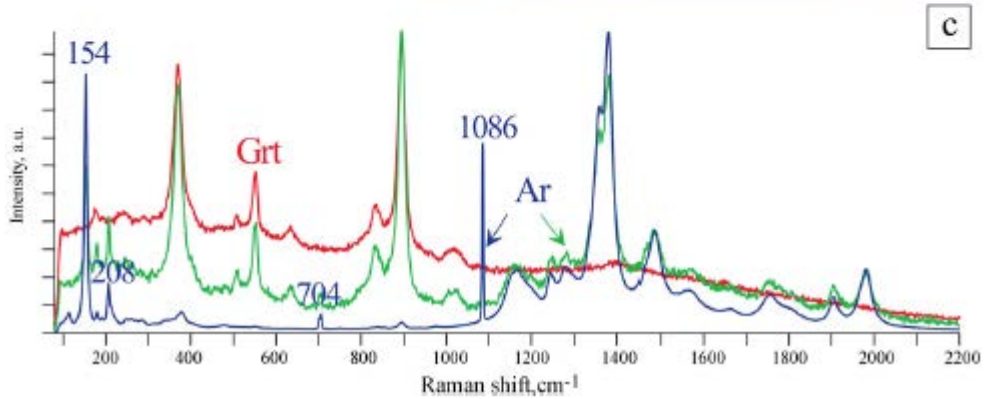

Guimbretière et al. 2016


Kong et al. 2014

what is possible to follow using HR Raman spectrometers

- Mineralogy
- Geobiology





Spectrochimica Acta Part A 80 (2011) 21–26

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

First findings of monocrystalline aragonite inclusions in garnet from diamond-grade UHPM rocks (Kokchetav Massif, Northern Kazakhstan)

Andrey V. Korsakov[a,*], Peter Vandenabeele[b], Maria Perraki[c], Luc Moens[d]

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Raman spectroscopy for the detection of haloarchaea - inlusions

Research Article

JOURNAL OF RAMAN SPECTROSCOPY

Received: 4 October 2008 Accepted: 14 May 2009 Published online in Wiley Interscience: 10 July 2009

(www.interscience.wiley.com) DOI 10.1002/jrs.2357

Raman spectroscopy as a potential method for the detection of extremely halophilic archaea embedded in halite in terrestrial and possibly extraterrestrial samples

Sergiu Fendrihan,[a] Maurizio Musso[b]* and Helga Stan-Lotter[a]

J. Raman Spectrosc. **2009**, *40*, 1996–2003

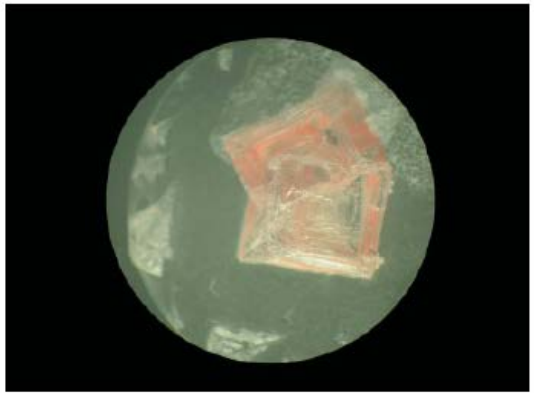

Figure 2. Halite crystals containing embedded haloarchaeal cells (*Halococcus dombrowskii*) on a quartz disk following drying of a cell suspension in 4M NaCl.

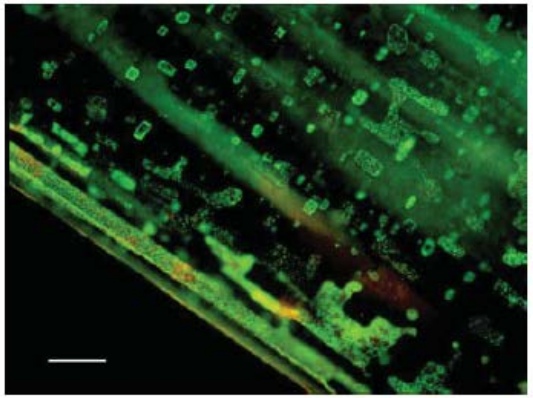

Figure 3. Localization by epifluorescence microscopy of haloarchaea in fluid inclusions embedded in halite, obtained by staining cells of *Halobacterium salinarum* strain NRC-1 with the *Bac*Light LIVE/DEAD kit[48] prior to embedding. Bar: 25 µm.

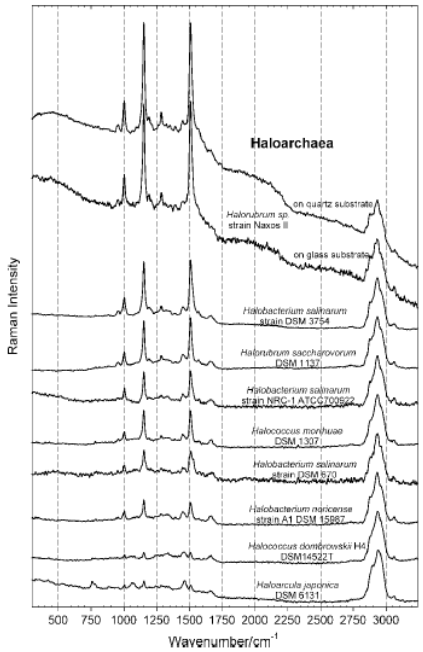

Figure 4. FT-Raman spectra of haloarchaeal strains in the region of 300 cm^{-1} to 3250 cm^{-1}, obtained with an excitation wavelength of 1064 nm, and normalized relative to the height of the peak around 2900 cm^{-1}, attributed to the asymmetric and symmetric CH_3 and CH_2 stretching vibrations.

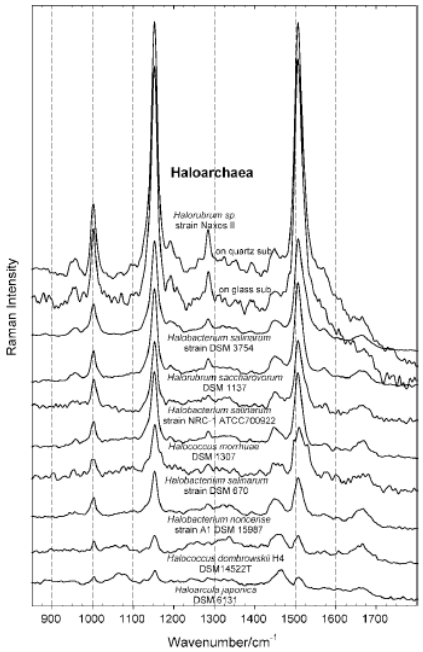

Figure 5. FT-Raman spectra of haloarchaeal strains in the region of 850 cm^{-1} to 1800 cm^{-1}, taken with an excitation wavelength of 1064 nm, and normalized relative to the height of the peak at around 1450–1460 cm^{-1}, attributed to the CH_2 scissors vibration and the asymmetric CH_3 deformation.

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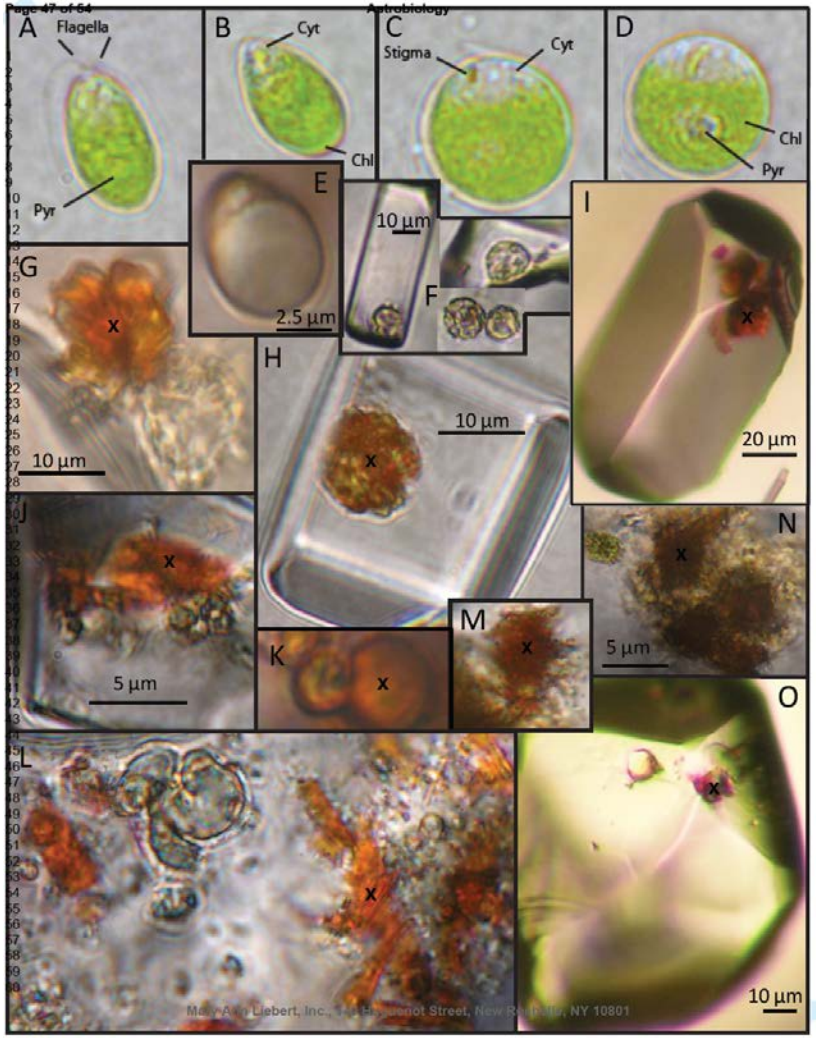
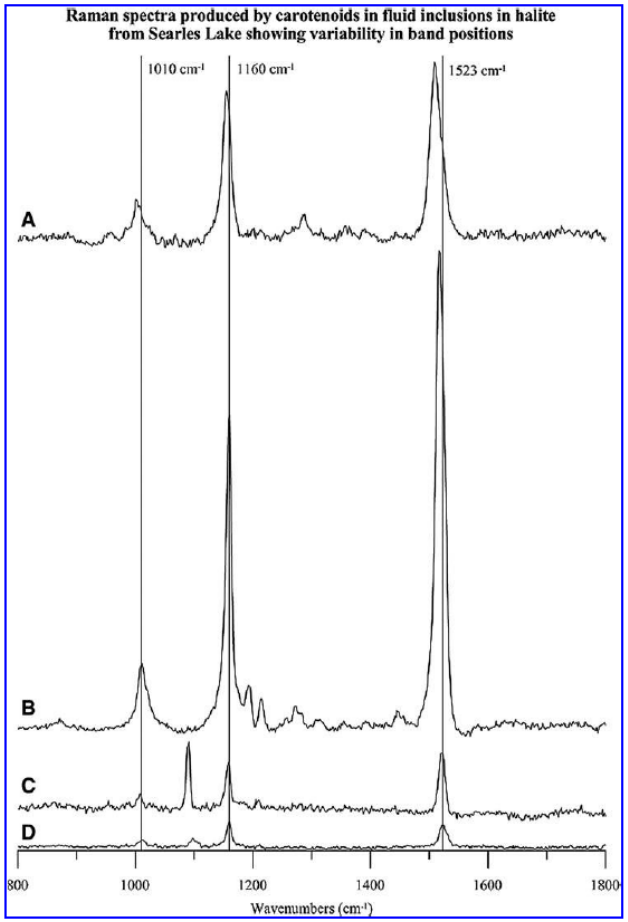
ASTROBIOLOGY
Volume 13, Number 11, 2013

DOI: 10.1089/ast.2012.0952

Identification of Carotenoids in Ancient Salt from Death Valley, Saline Valley, and Searles Lake, California, Using Laser Raman Spectroscopy

Y.D. Winters, T.K. Lowenstein, and M.N. Timofeeff





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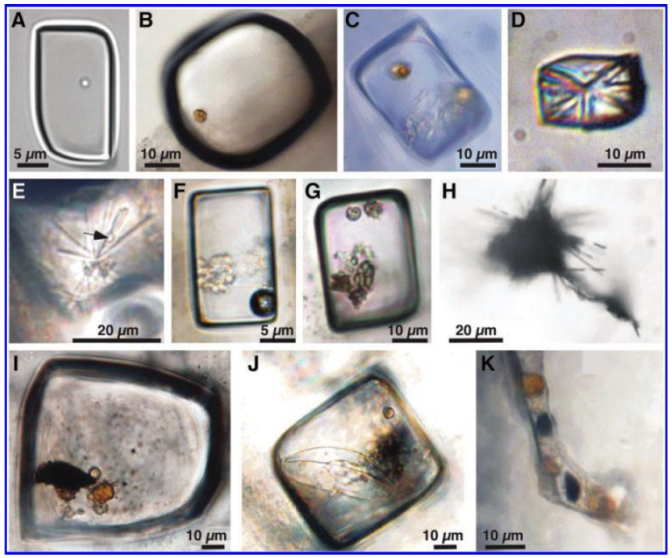
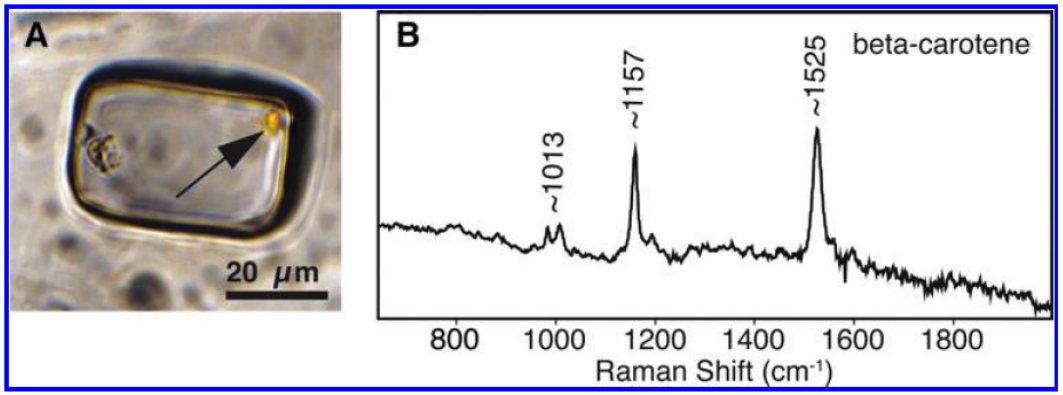
ASTROBIOLOGY
Volume 13, Number 9, 2013

DOI: 10.1089/ast.2012.0956

Acidophilic Halophilic Microorganisms in Fluid Inclusions in Halite from Lake Magic, Western Australia

Amber J. Conner[1] and Kathleen C. Benison[2]





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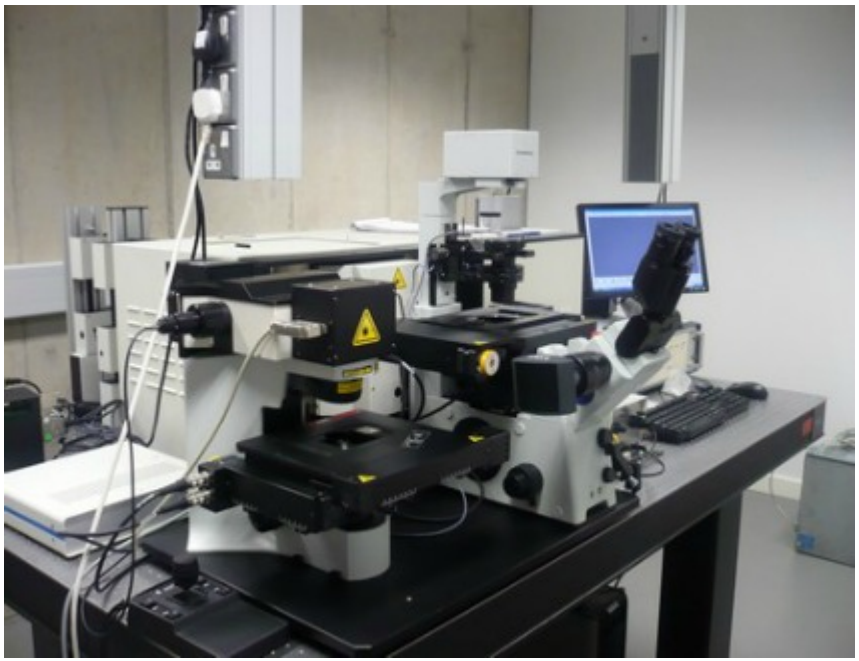
- Raman spectroscopy in the laboratory



HR dispersive Raman spectrometers
FT-Raman spectrometers

~~Raman spectrometry is a technique allowing determination of chemical composition~~

~~Raman spectrometry is a technique allowing determination structural parameters~~

Raman spectrometry permits identifying of phases and their spectroscopic description

Raman spectrum is unambiguous for a given phase

a) spectroscopist – describe the spectrum
describe the bands observed,
propose assignemnts

b) users – asking for identification

How to use Raman spectroscopy

1) Preparation of samples

2) Obtaining Raman spectrum

3) Comparison of obtained spectrum with a database

or

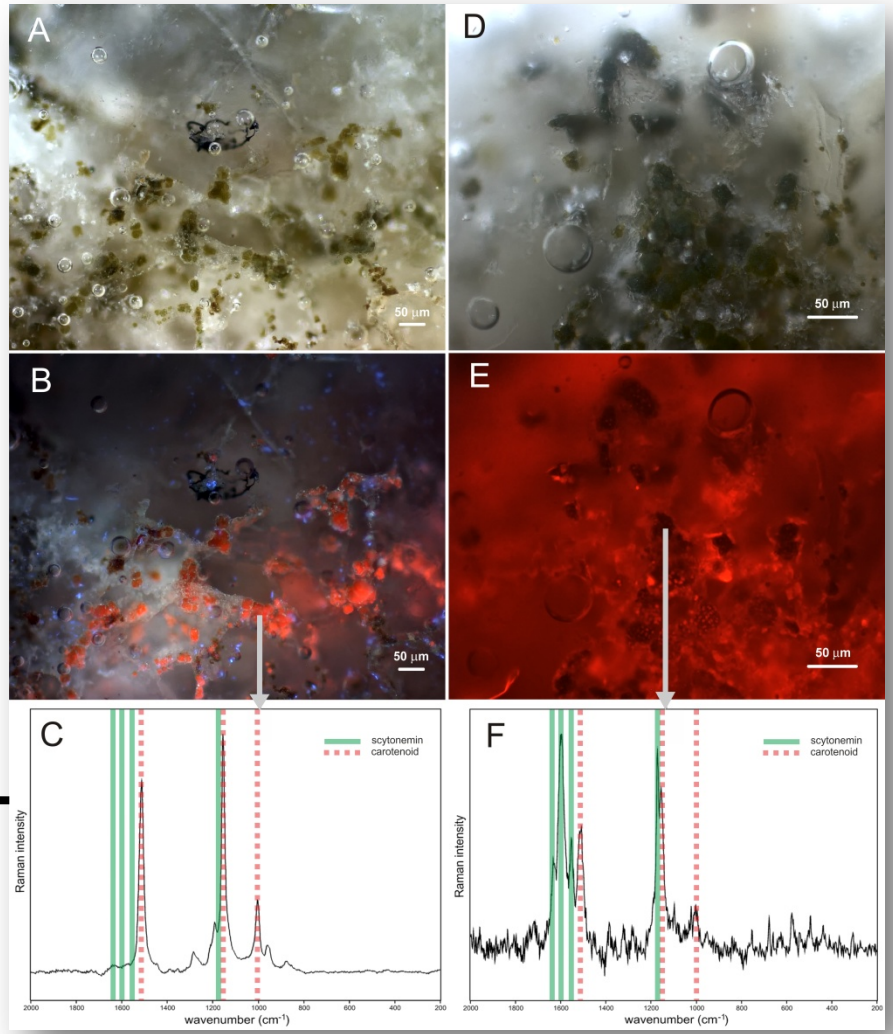
if not included in the database

4) Interpretation of Raman spectrum

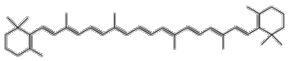
Halite crust – endolithic cyanobacteria

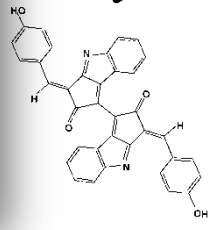
Green cell aggregates

Black cell aggregates

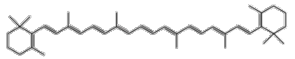


carotenoid





scytonemin + carotenoid



RESEARCH ARTICLE

Distribution of scytonemin in endolithic microbial communities from halite crusts in the hyperarid zone of the Atacama Desert, Chile

Petr Vítek[1], Jan Jehlička[1], Carmen Ascaso[2], Vlastimil Mašek[3], Benito Gómez-Silva[4], Héctor Olivares[4] & Jacek Wierzchos[2]

FEMS Microbiol Ecol **90** (2014) 351–366

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what is possible to follow using miniature handheld Raman spectrometers

- Mineralogy
- Geobiology

Mineralogy ?
Geobiology ?

Miniature Raman spectroscopic instrumentation

Planetary research ?
Exobiology ?

Miniature Raman spectroscopic instrumentation

Raman spectroscopy in the **field**

Miniature Raman spectrometers

Raman spectroscopy with handheld instruments


c)

Portable Raman spectrometers

- Not equipped with optical microscope
- Lower laser power
- Lower spectral resolution

- Laboratory instrumentation and analytical work
- Field analytical work

- Forensic
- Art/archaeology
- Geoscince

- Planetary research

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- Forensic

- Unambiguous detection
- Fast identification

- Drugs of abuse
- Explosives
- Precursors

- Art

- Non destructive analysis onsite

- Materials
- Binders
- Pigments

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Thermo Scientific FirstDefender ex Ahura

Specifications

Thermo (exAhura)

1.8 kg

Spectral range: 250 – 2875 cm-1

785 nm diode laser

Compact, rigid

rechargeable 7.4 V Li battery

Thermo Scientific FirstDefender RM

Specifications
Weight 1.8 lbs (800g)
Size 7.6 x 4.2 x 1.75 in (19.3 x 10.7 x 4.4cm)
Use Mode Point-and-shoot
Spectral Resolution 7 to 10.5cm-1 (FWHM) across range
Laser Output Power Adjustable, 75 mW, 125 mW, 250 mW
Battery Removable and rechargeable lithium ion battery or 123a
(eg SureFire™) batteries; > 4 hours operation
External Power Supply DC Wall Adapter, 12 V 1.25 A

Inspector Raman™
Handheld Raman Spectrometer

DeltaNu

- **785 nm excitation**

Specifications

Range: 100 – 2000 cm^{-1} at 8 cm^{-1} resolution

Laser: 785 nm 120mW

Weight: 2.3 kg (5 lbs)

Laptop PC operated

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FIRSTGUARD
Handheld Raman analyzer

Rigaku

- **532nm excitation**
- Suitable for the detection of carotenoid pigments

Specifications

Range: 200 – 3000 cm^{-1} at ~ 10 – 15 cm^{-1} resolution
Spot size: 10 – 15 micron at 10x lens
Laser: 532nm 0 – 60mW
Size: 33.5 x 12.2 x 28.6 cm
Weight: 2.3 kg (5 lbs)

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BW Tek

Specifications
Dual laser mobile Raman system (785 and 532 nm)
Different lenses: e.g. High N.A., Long W.D.
2 probeheads, no simultaneous measurement
Spectral range: 100-2200 cm^{-1} (785 nm) and 100-3100 cm^{-1} (532 nm)
Battery operated, compact, 5m optical fibre

BRAVO

Handheld Raman Spectrometer

- Dedicated for material verification (industry, pharmaceutics)
- Rugged, lightweight, touch screen operation
- Novel approach for fluorescence elimination
- Duo LASER™ (785 and 1064 nm)
- SSE™ (Sequentially Shifted Excitation)

Specifications

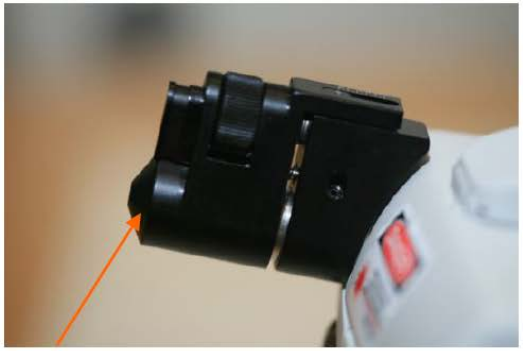
Range: 300 – 3200 cm^{-1} at ~ 10 – 12 cm^{-1} resolution

Spot size: 10 – 15 micron at 10x lens

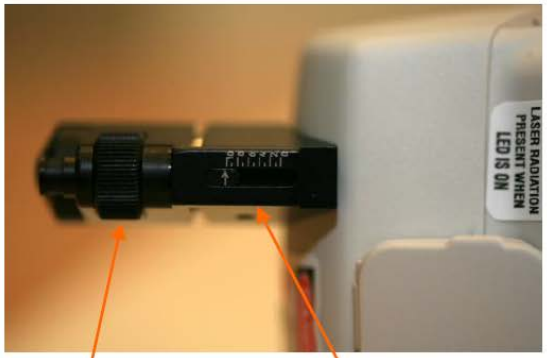
Laser: 700 - 1100 nm (Duo LASER™)

Weight: 1.5 kg (3.3 lbs)

Probe heads



Optical probe tip



Knurled knob

Focal adjustment scale

Mobile Raman spectroscopy: minerals

OUTCROP Plesovice

Delta Nu – RockHunt
Hand-held, 1,8 kg

785 nm diode laser
Notebook operation,
lightweight Raman device
NuSpec software

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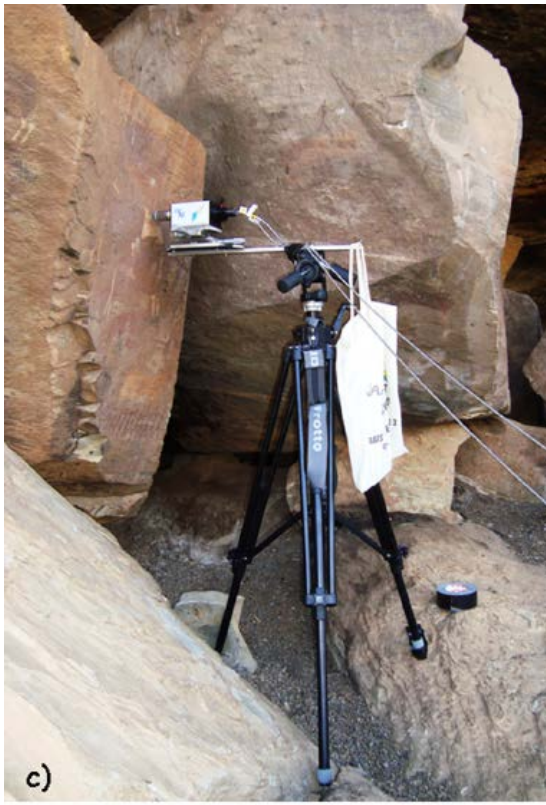
Mobile Raman spectroscopy

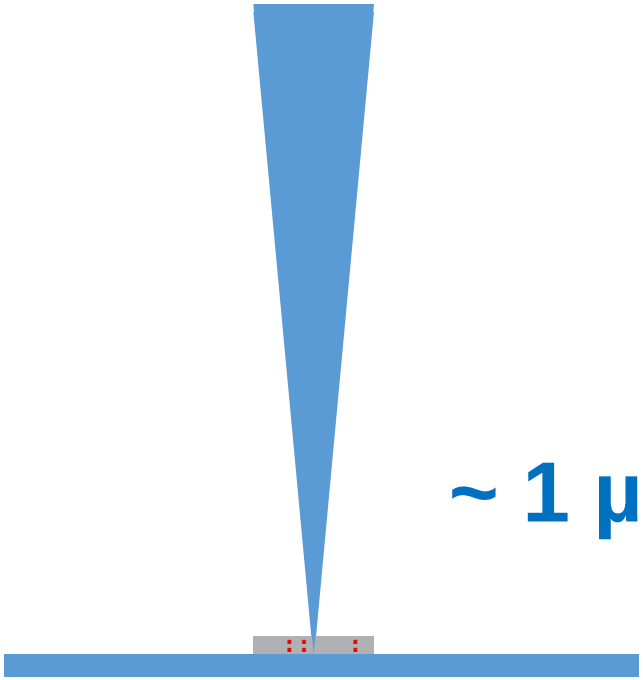
Vandenabeele et al.,
J. Raman Spectrosc.
2014, 45, 114–122

Mobile Raman Spectroscopy: bringing the instrumentation on site

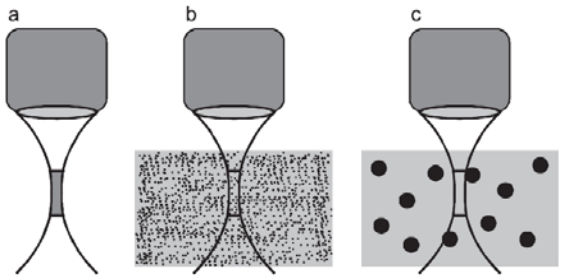
Positioning



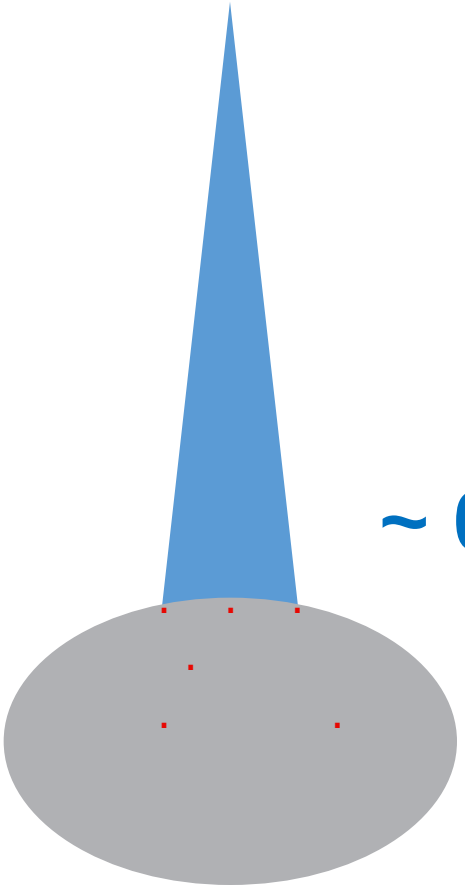
Focusing using micro-Raman



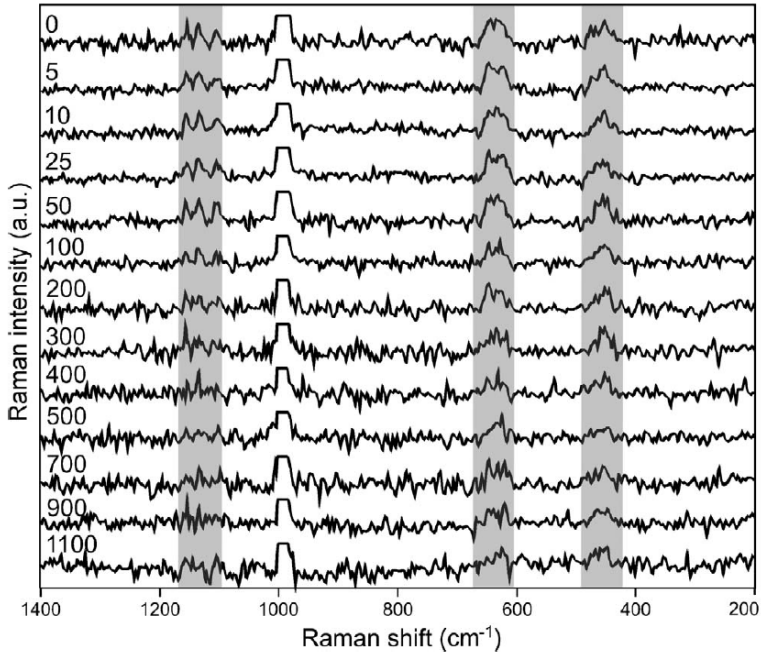
~ 1 µm



Focusing using handheld instruments



~ 0.1 mm



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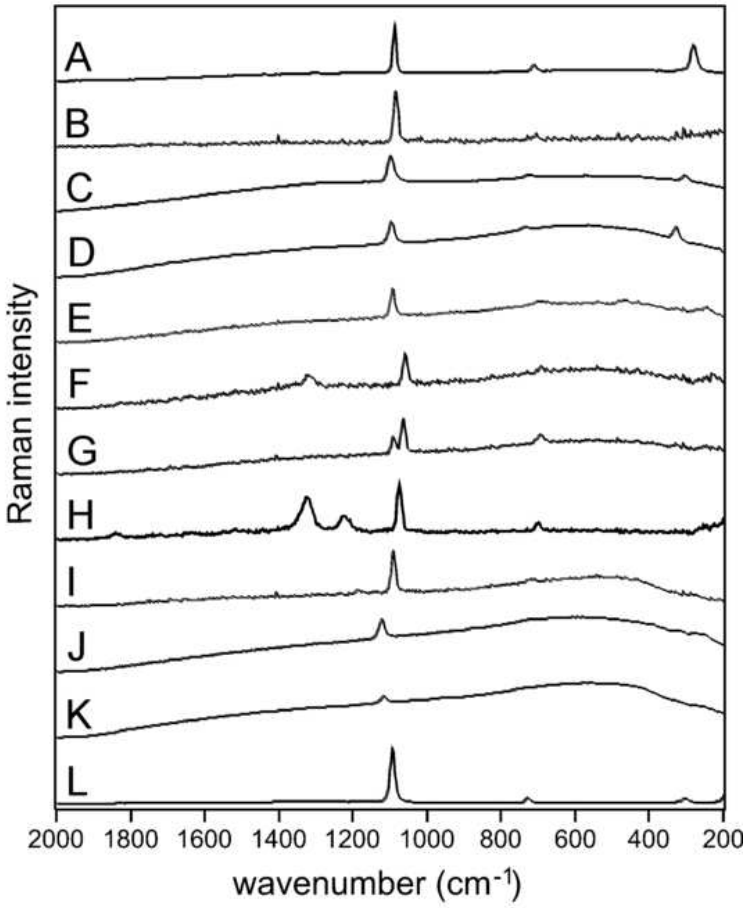
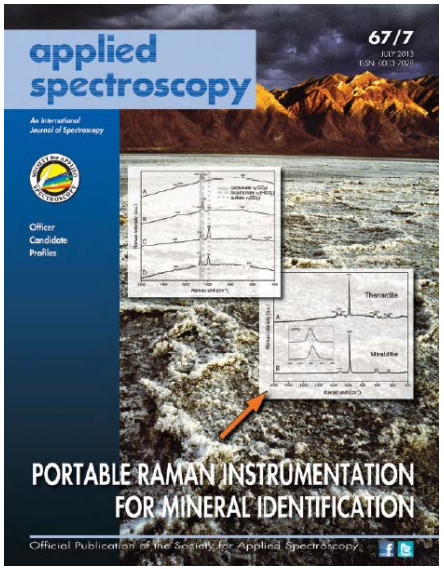


Raman spectra carbonates

A: calcite
B: aragonite
C: dolomite
D: magnesite
E: artinite
F: witherite
G: alstonite
H: stronianite
I: huntite
K: hydromagnesite
L: smithsonite



Practical Considerations for the Field Application of Miniaturized Portable Raman Instrumentation for the Identification of Minerals

Petr Vítek,[a,*] Jan Jehlička,[a] Howell G. M. Edwards[b,c]

[a] *Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic*
[b] *Centre for Astrobiology and Extremophiles Research, School of Life Sciences, University of Bradford, Bradford BD7 1DP UK*
[c] *Department of Physics and Astronomy, Space Sciences Research Centre, University of Leicester, Leicester LE1 7RH UK*

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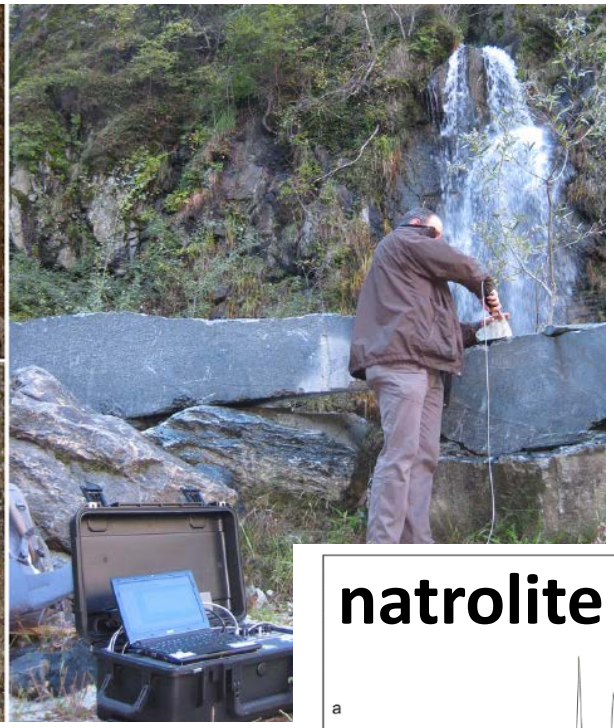
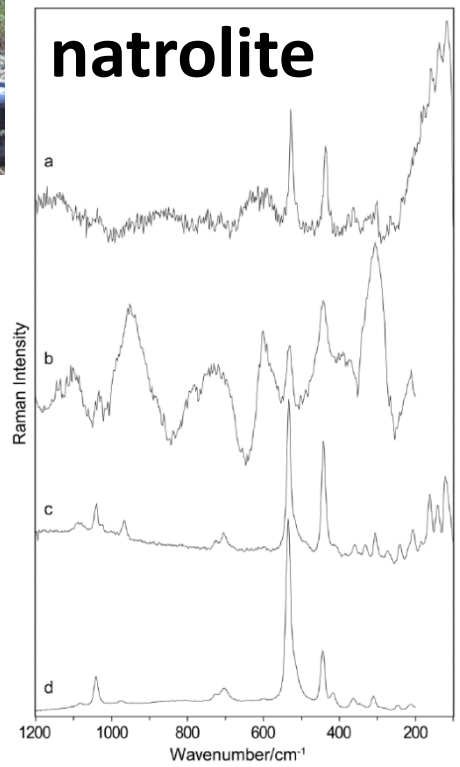
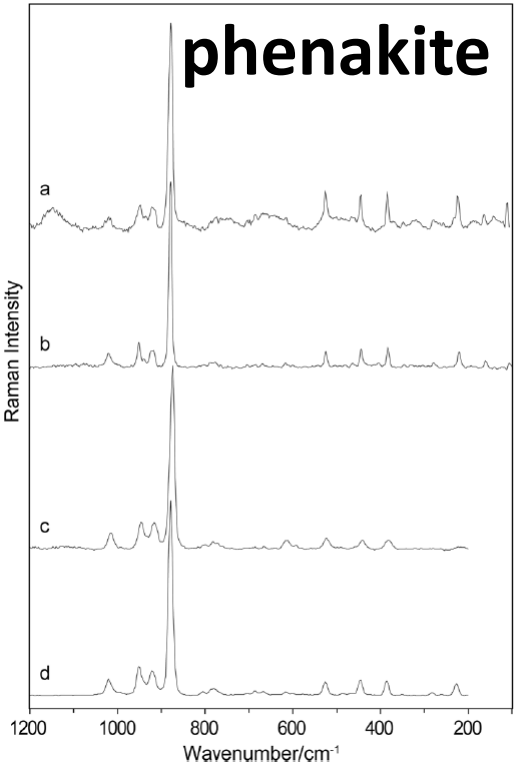
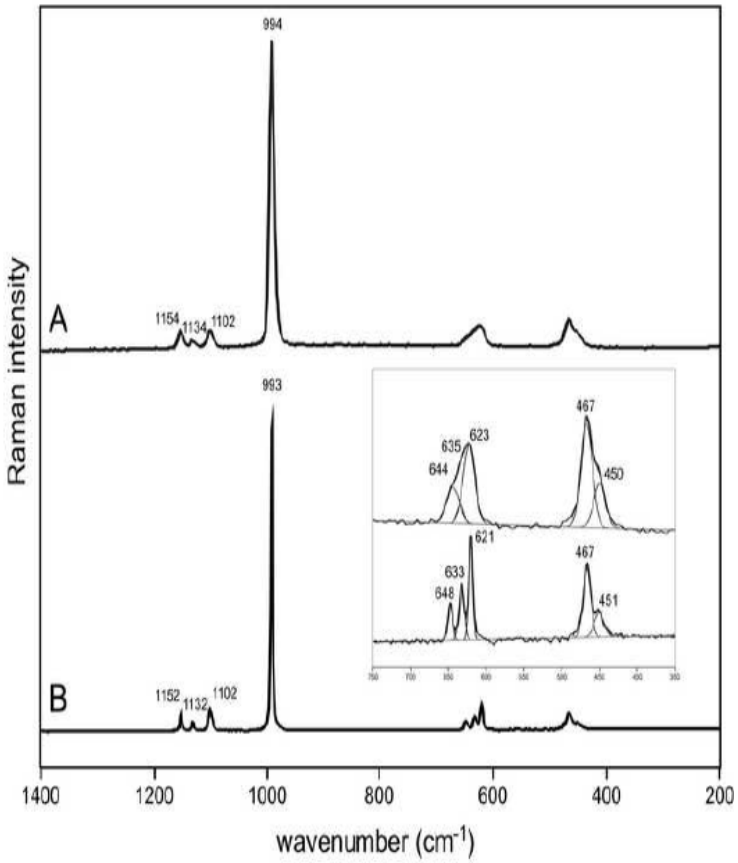
BAS
Rigaku
FastGeard



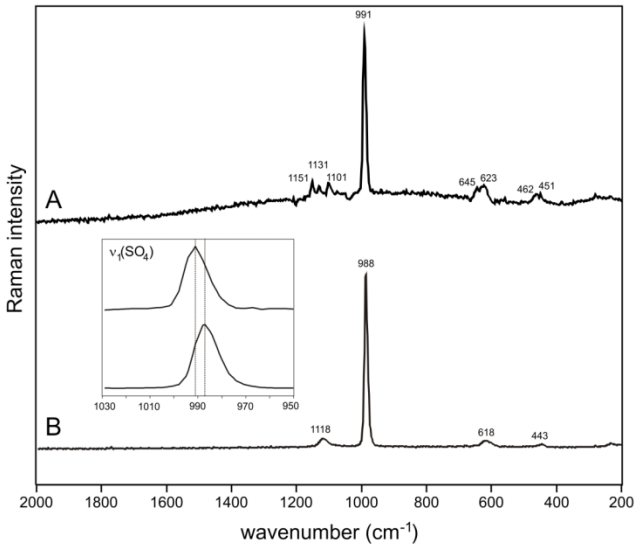

natrolite
a
b
c
d
Raman Intensity
1200
1000
800
600
400
200
Wavenumber/cm-1


phenakite
a
b
c
d
Raman Intensity
1200
1000
800
600
400
200
Wavenumber/cm-1



handheld Raman spectrometer

Bench-top microspectrometer



thenardite

mirabilite

handheld Raman spectrometer, 785 nm

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Valachov – alteration – formation of sulfates

Ostrava – formation of secondary minerals

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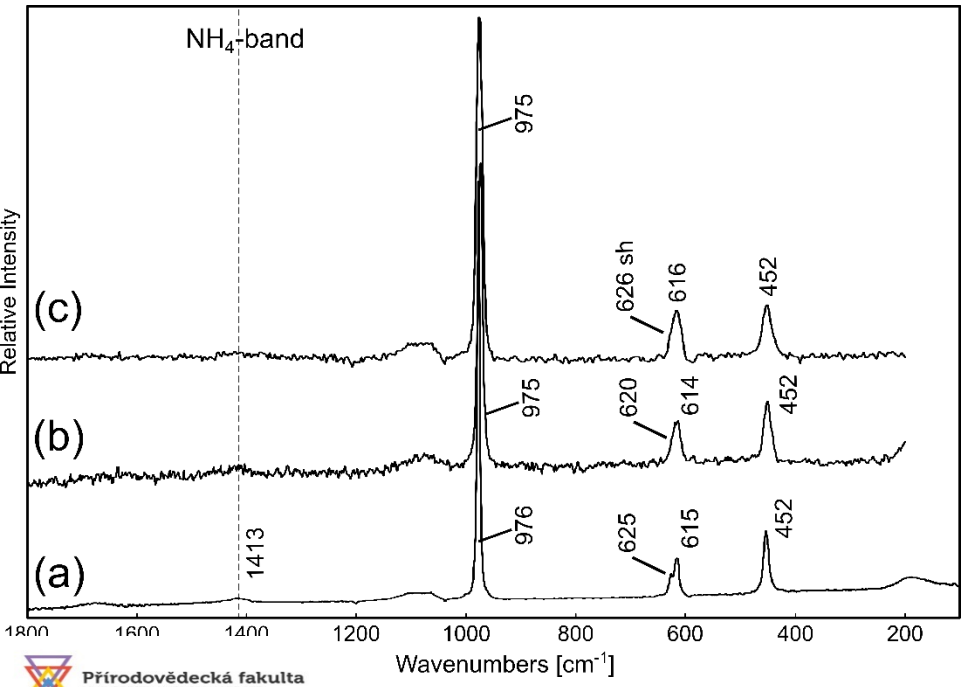
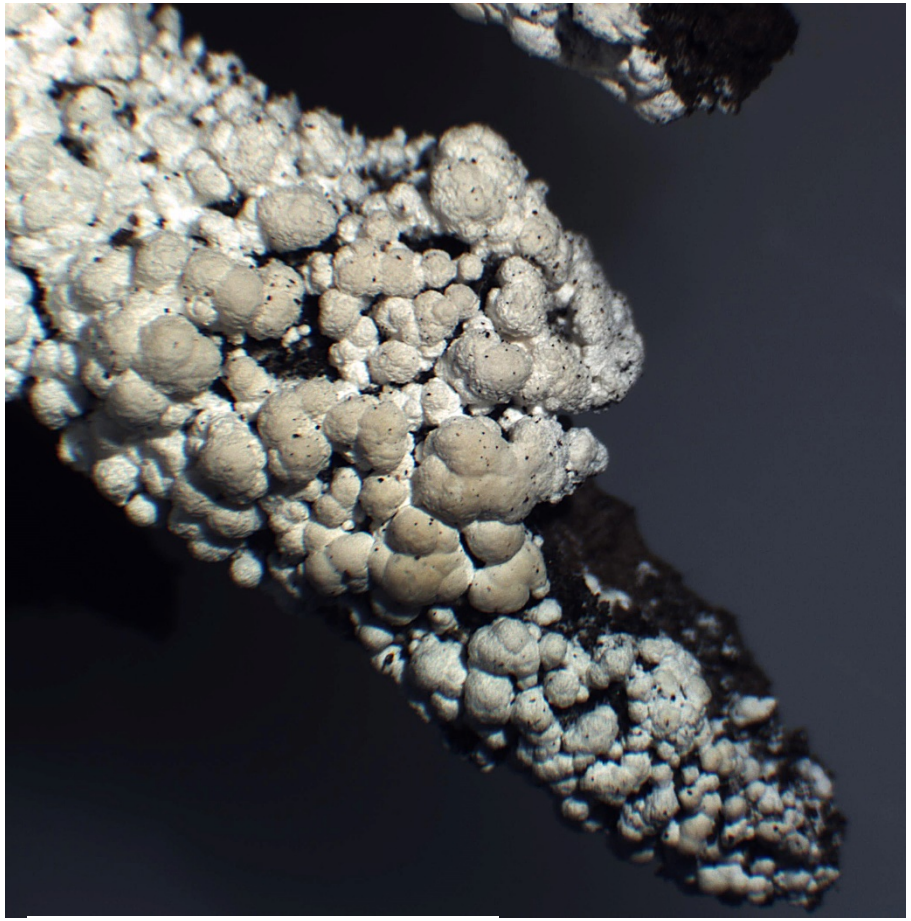
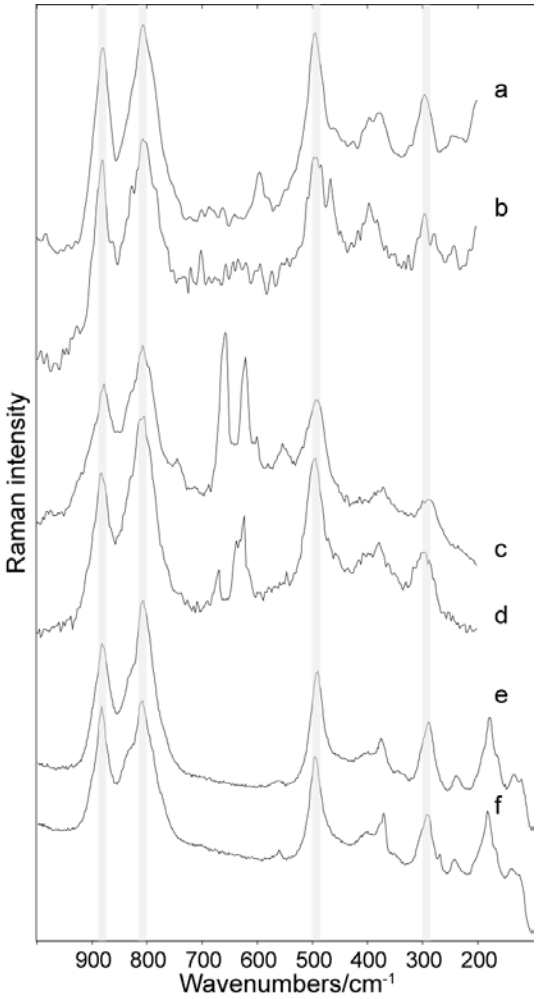
Mascagnite $(NH_4)_2SO_4$

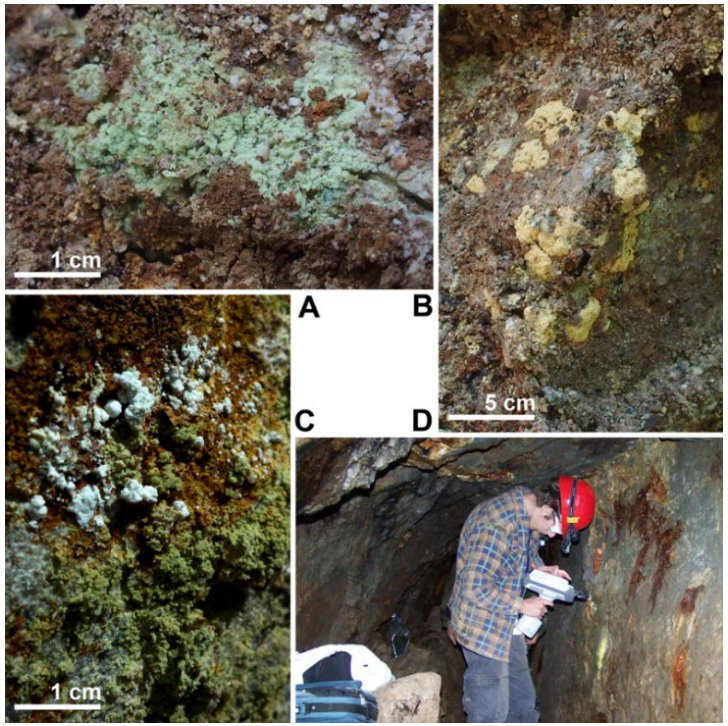




Kaňkite $Fe^{3+}AsO_4 \cdot 3.5(H_2O)$

Zýkaite $Fe^{3+}_4(AsO_4)_3(SO_4)(OH) \cdot 15(H_2O)$





Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 154 (2016) 193–199

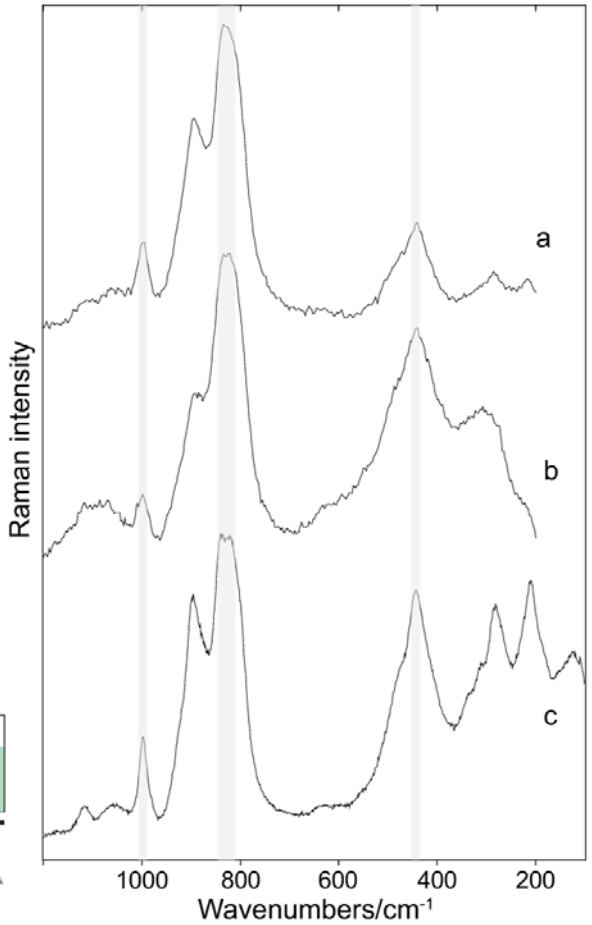
Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Raman spectroscopic identification of arsenate minerals *in situ* at outcrops with handheld (532 nm, 785 nm) instruments

Adam Culka, Helena Kindlová, Petr Drahota, Jan Jehlička *



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Rocks, minerals and gemstones

Gemstones

diamond

oxides
silicates

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diamonds

zirconia

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Diffraction grating spectroscope

Illuminator Polariscope

Single/double refractive gems

http://www.gia.edu/

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Minerals/Gemstones

Precious and Semiprecious

Diamonds and Colored Stones

Organics and Inorganics

Crystalline and Amorphous Materials

Natural and synthetic gemstones

Identification of minerals

Identification of gemstones

- uncommon colours
- resistant, hard

Physical properties

- Raman spectroscopy ? Advantages ?

Raman microspectrometry in gemology

Journal of RAMAN SPECTROSCOPY

JOURNAL OF RAMAN SPECTROSCOPY, VOL. 28, 673–676 (1997)

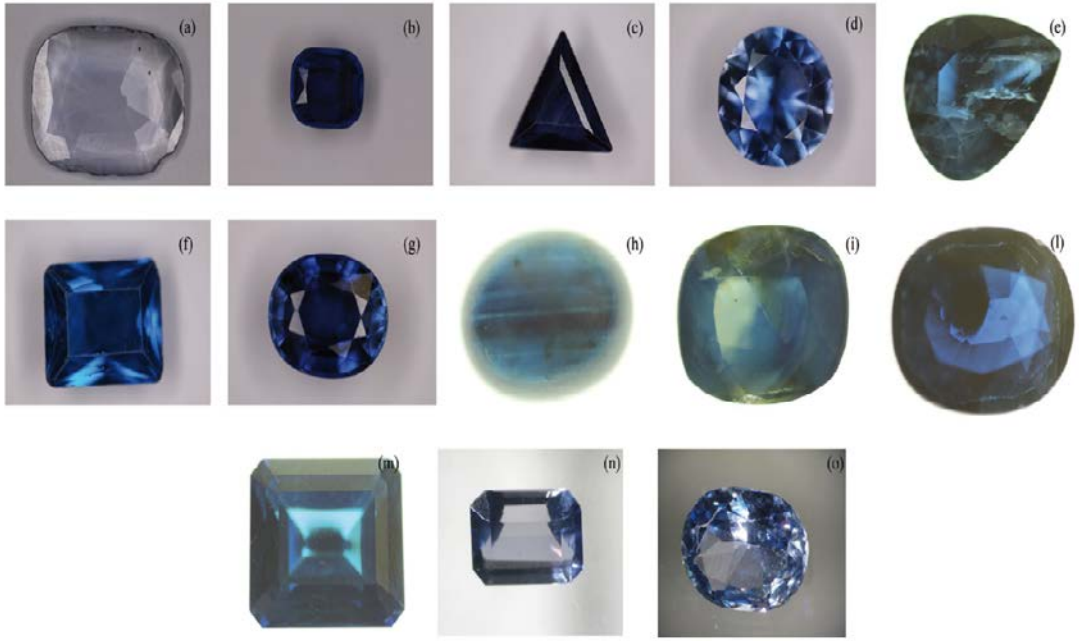
Use of Spectroscopic Techniques for the Study of Natural and Synthetic Gems: Application to Rubies

M. L. Dele,[1] P. Dhamelincourt,[1]* J. P. Poirot,[2] J. M. Dereppe and C. Moreaux[3]

A portable *versus* micro-Raman equipment comparison for gemmological purposes: the case of sapphires and their imitations†

Germana Barone,[a]* Danilo Bersani,[b] Vincenza Crupi,[c] Francesca Longo,[c] Ugo Longobardo,[d] Pier Paolo Lottici,[b] Irene Aliatis,[b] Domenico Majolino,[c] Paolo Mazzoleni,[a] Simona Raneri[a] and Valentina Venuti[c]

J. Raman Spectrosc. **2014**, *45*, 1309–1317



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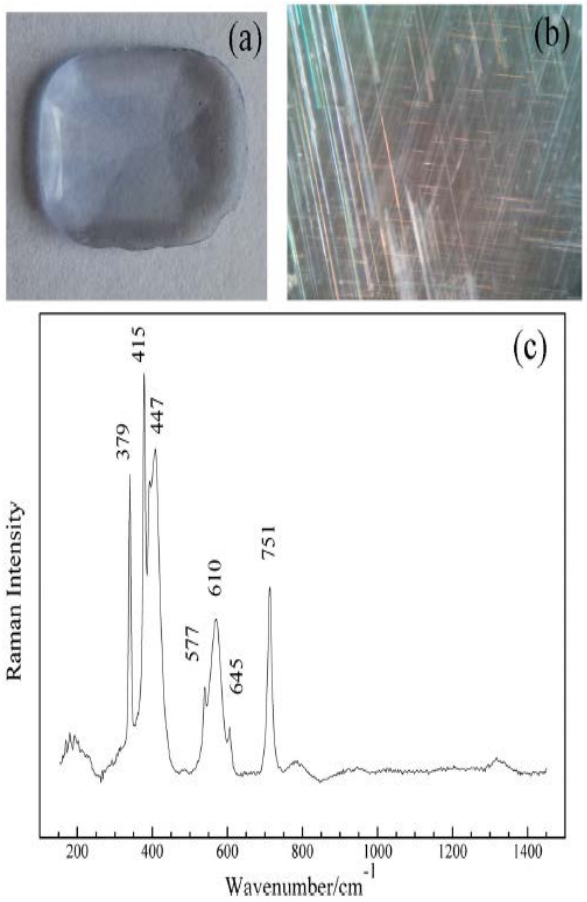
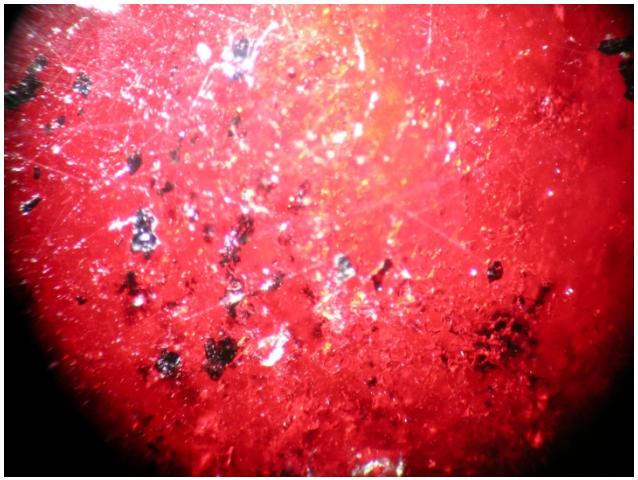


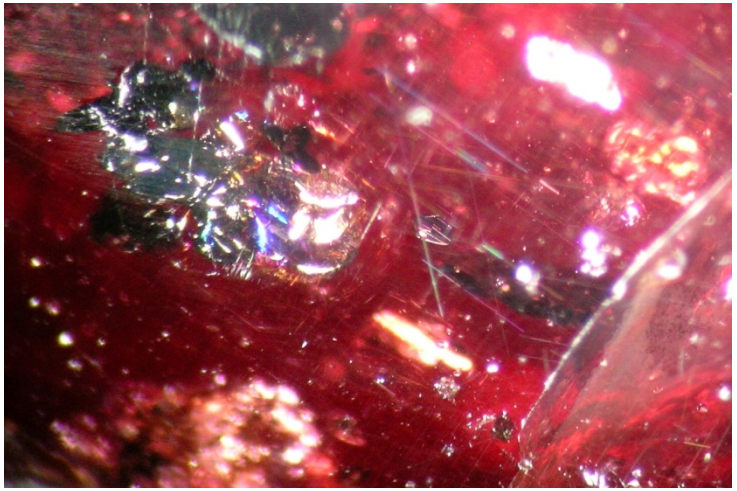
rutile inclusions

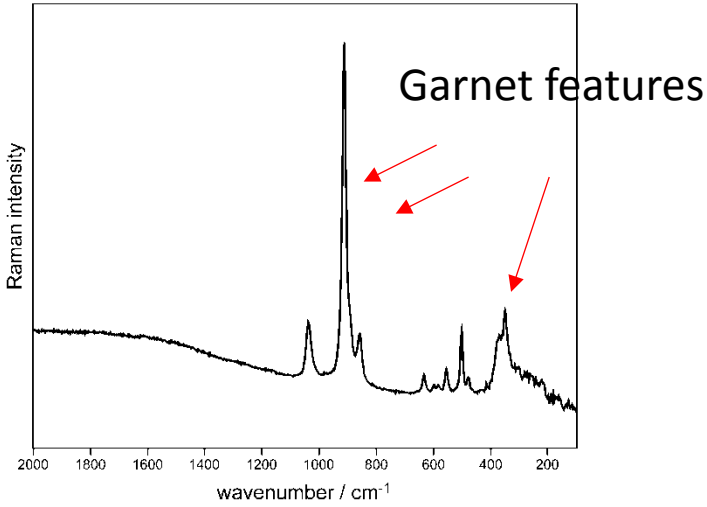
Barone *et al*., 2014

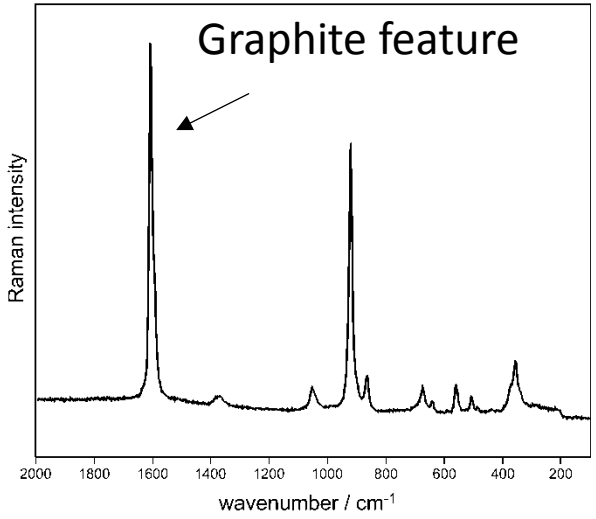
J. Raman Spectrosc. **2014**, *45*, 1309–1317

Inclusions in garnets









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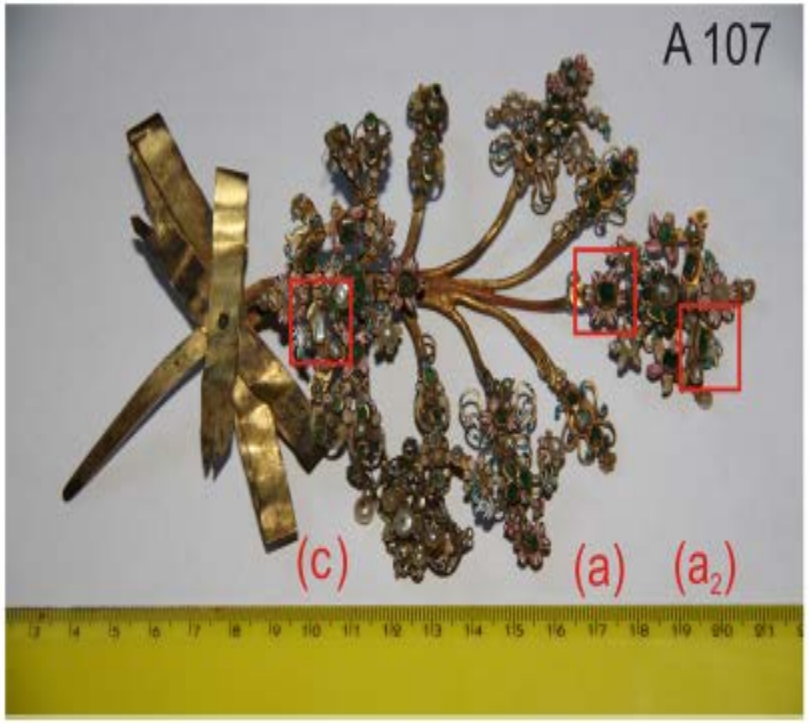
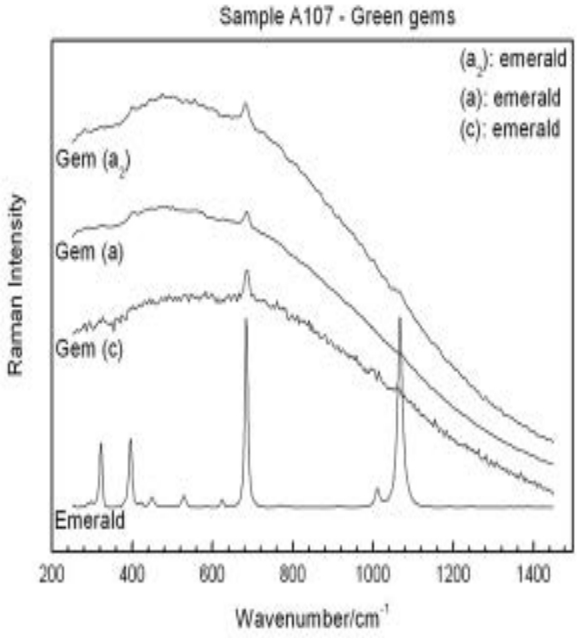
Ancient jewelry

Nondestructive investigation on the 17-18th centuries Sicilian jewelry collection at the Messina regional museum using mobile Raman equipment

G. Barone,[a]* D. Bersani,[b] J. Jehlička,[c] P. P. Lottici,[b] P. Mazzoleni,[a] S. Raneri,[a] P. Vandenabeele,[d] C. Di Giacomo[e] and G. Larinà[e]

J. Raman Spectrosc. **2015**, *46*, 989–995





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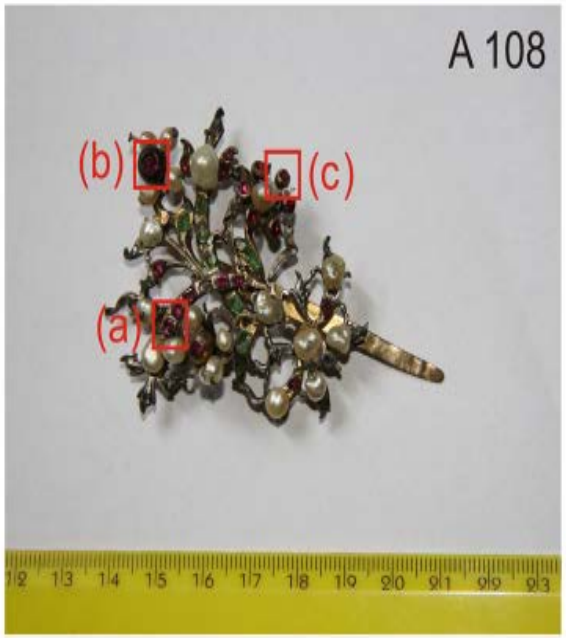

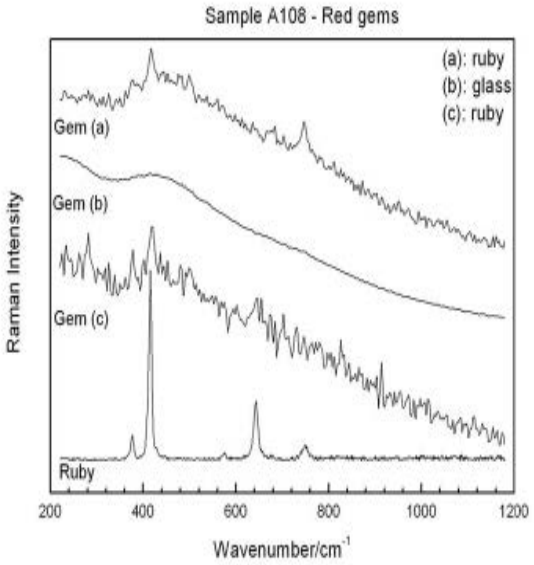

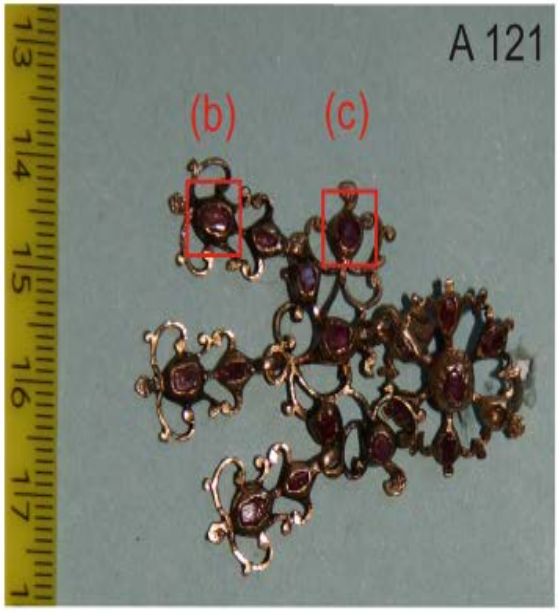

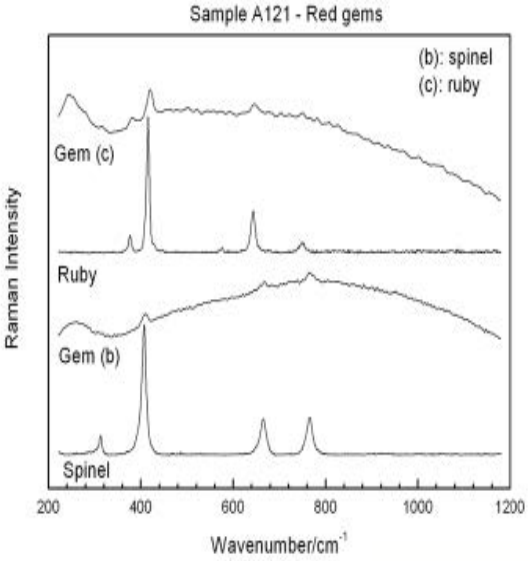

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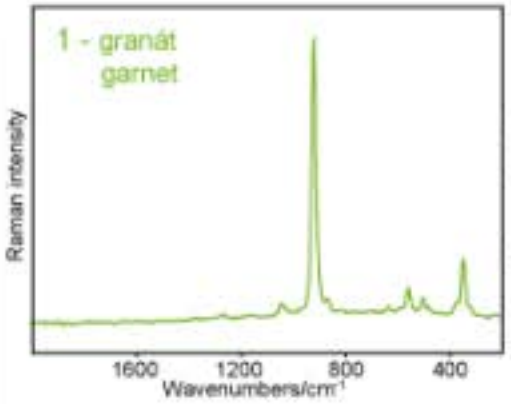
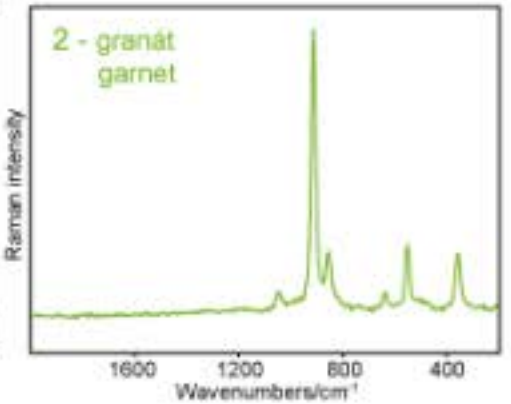
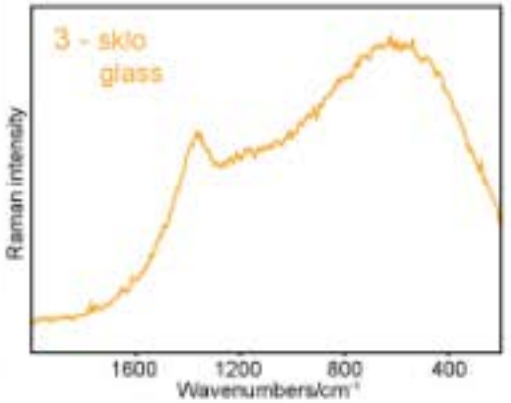
Loreto, Prague







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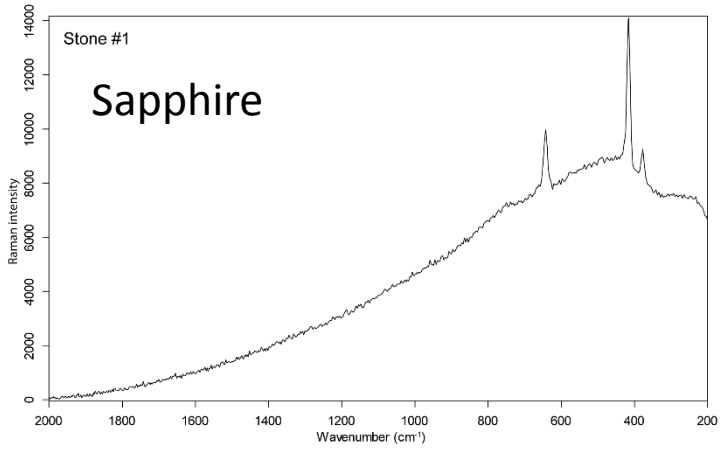
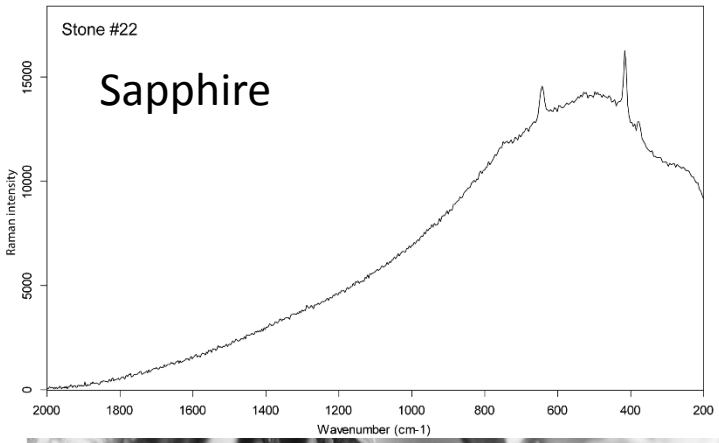
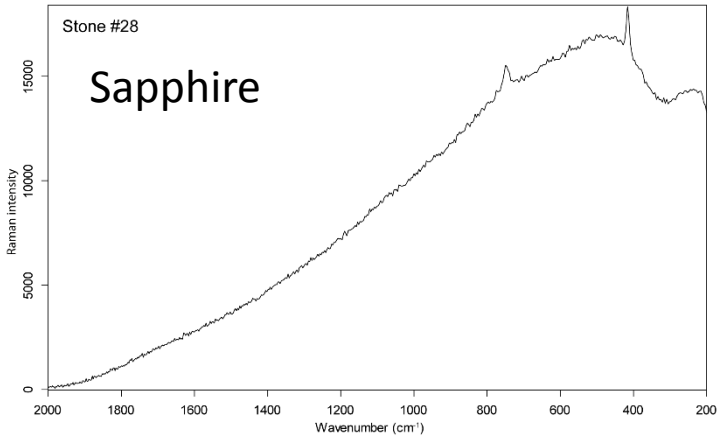
RockHound





XVII.



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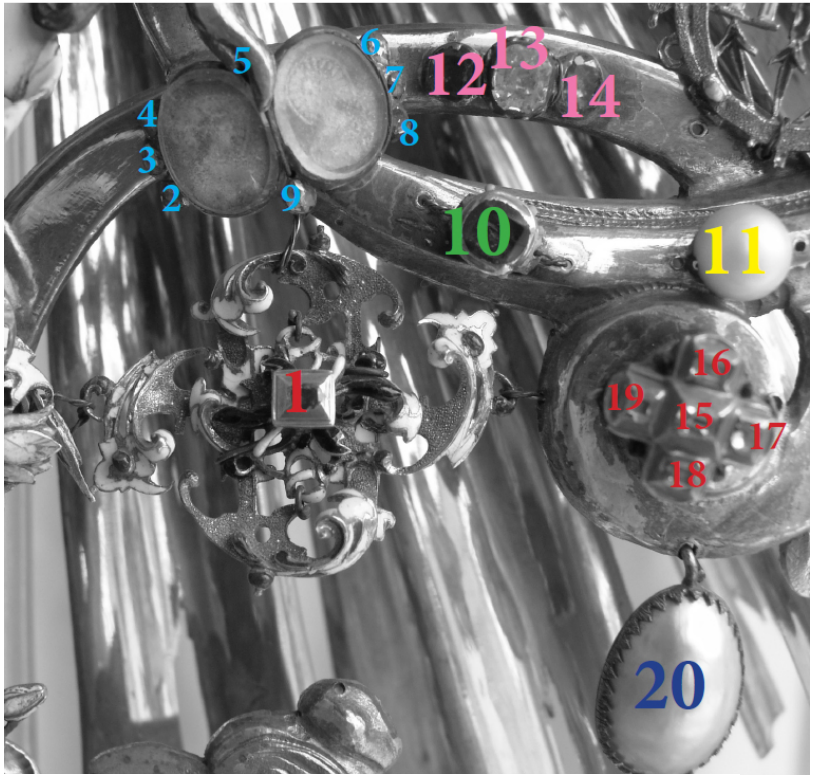
XX.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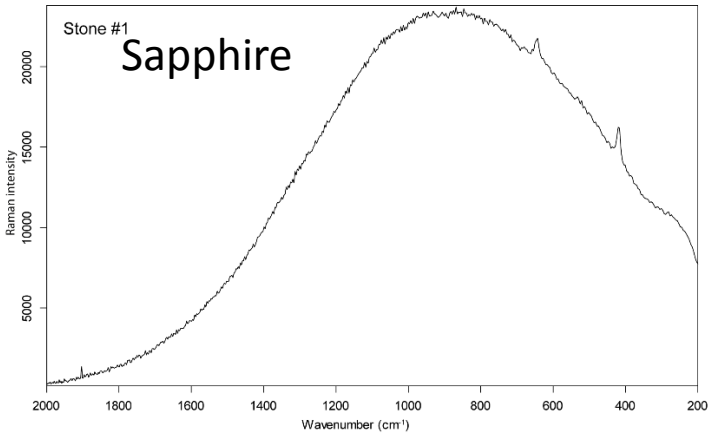
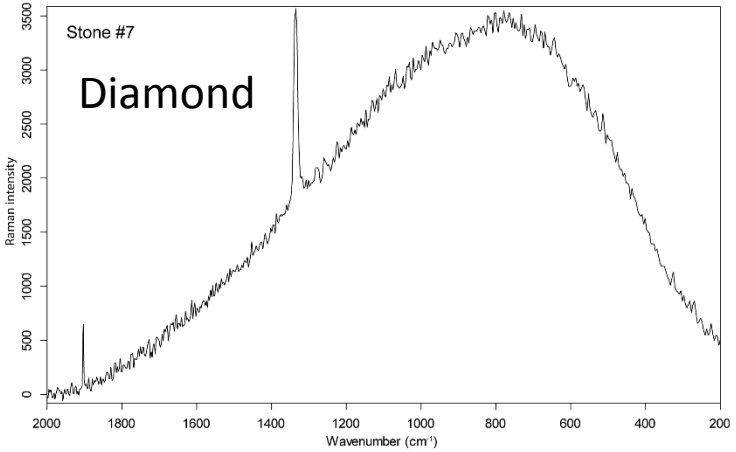
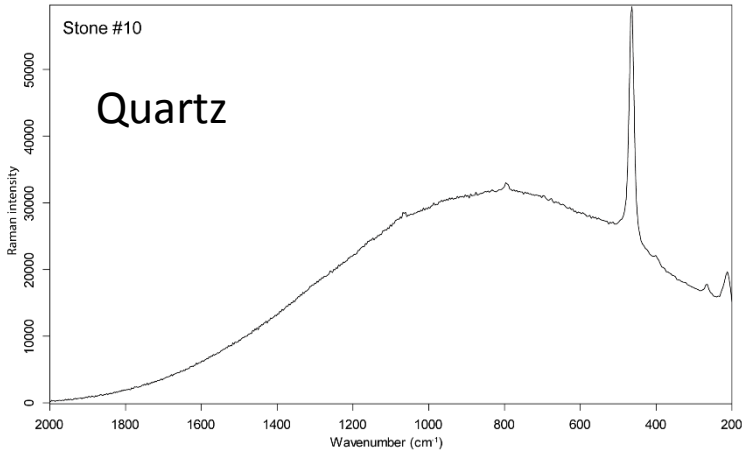
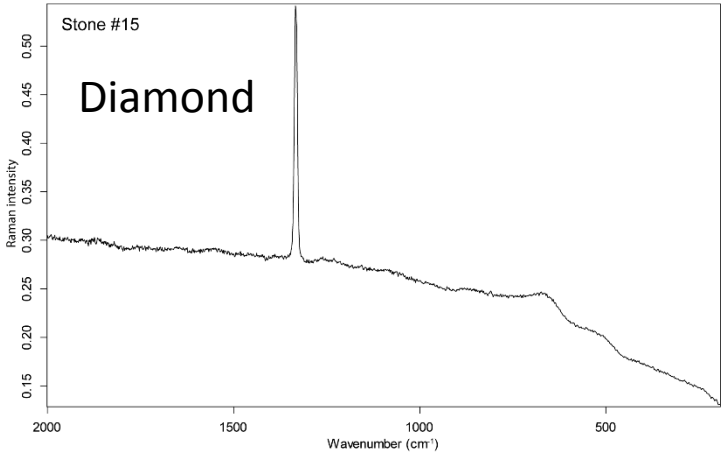
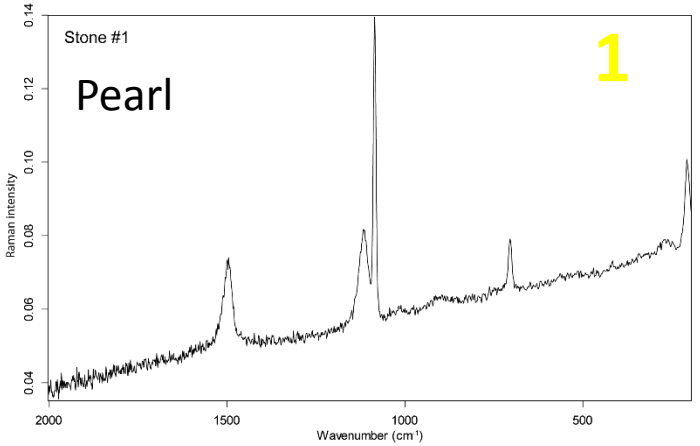

Stone #1
Sapphire
Raman intensity
Wavenumber (cm⁻¹)

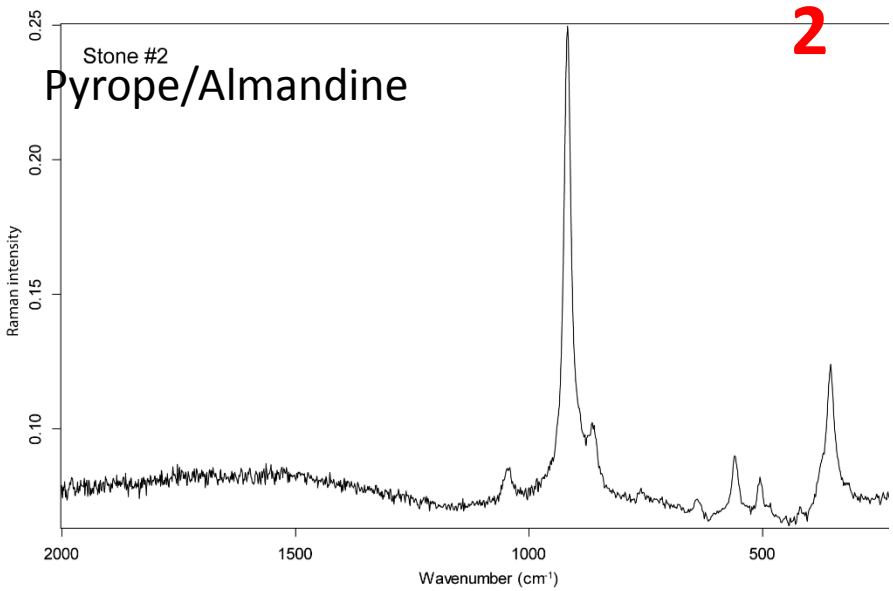

Stone #7
Diamond
Raman intensity
Wavenumber (cm⁻¹)

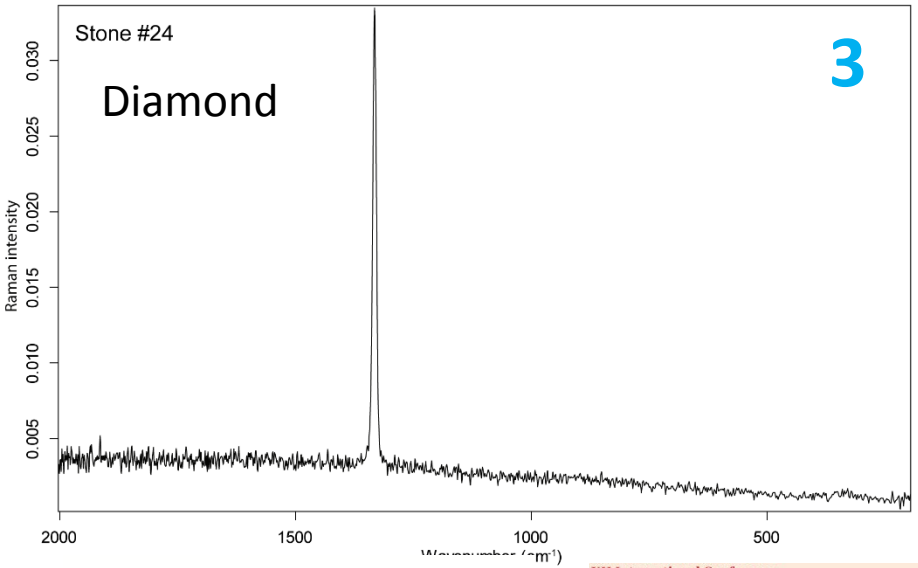

Stone #10
Quartz
Raman intensity
Wavenumber (cm⁻¹)


Stone #15
Diamond
Raman intensity
Wavenumber (cm⁻¹)

XXI.







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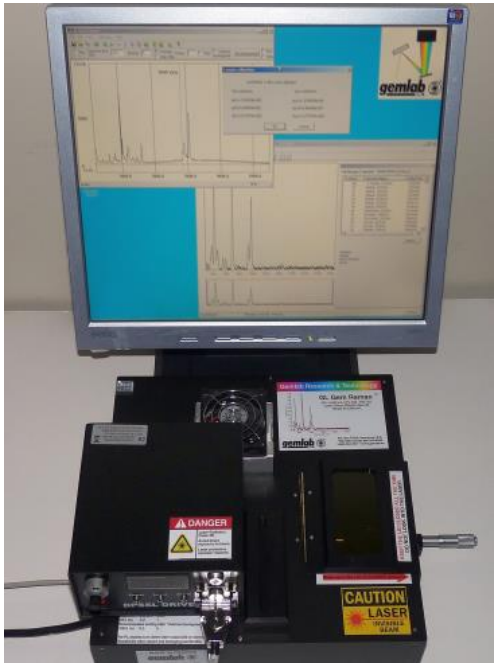
Gemtesting Raman instrumentation

Gemtesting Raman system

The GL Gem Raman™ PL532 TEC



Analytical tool for gemology

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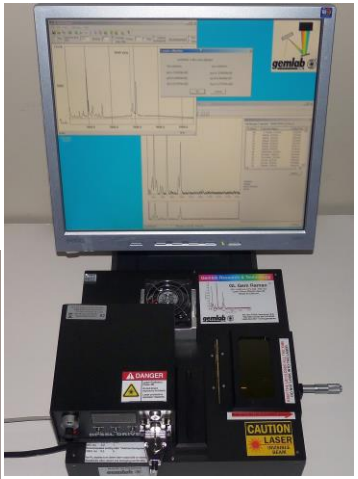
The GL Gem Raman™ PL532 TEC

- Developed for gemological and mineralogical applications
- Cheap cost, very easy to use
- Possible search in the RRUFF mineral database for identification



Specifications

Range: 100 – 5,440 cm-1 at ~ 10 cm^{-1} FWHM resolution
Spot size: 10 – 15 micron at 10x lens
Laser: fan-less, confocal, 532nm regulated 300mW, Class 3B
Size: 33 x 33 x 7.6 cm
Weight approximately 8 kg (18 lbs)
PL Option: 530 - 750 nm (broad scan) is included for experimental applications
Cost: ~ $10,000 USD

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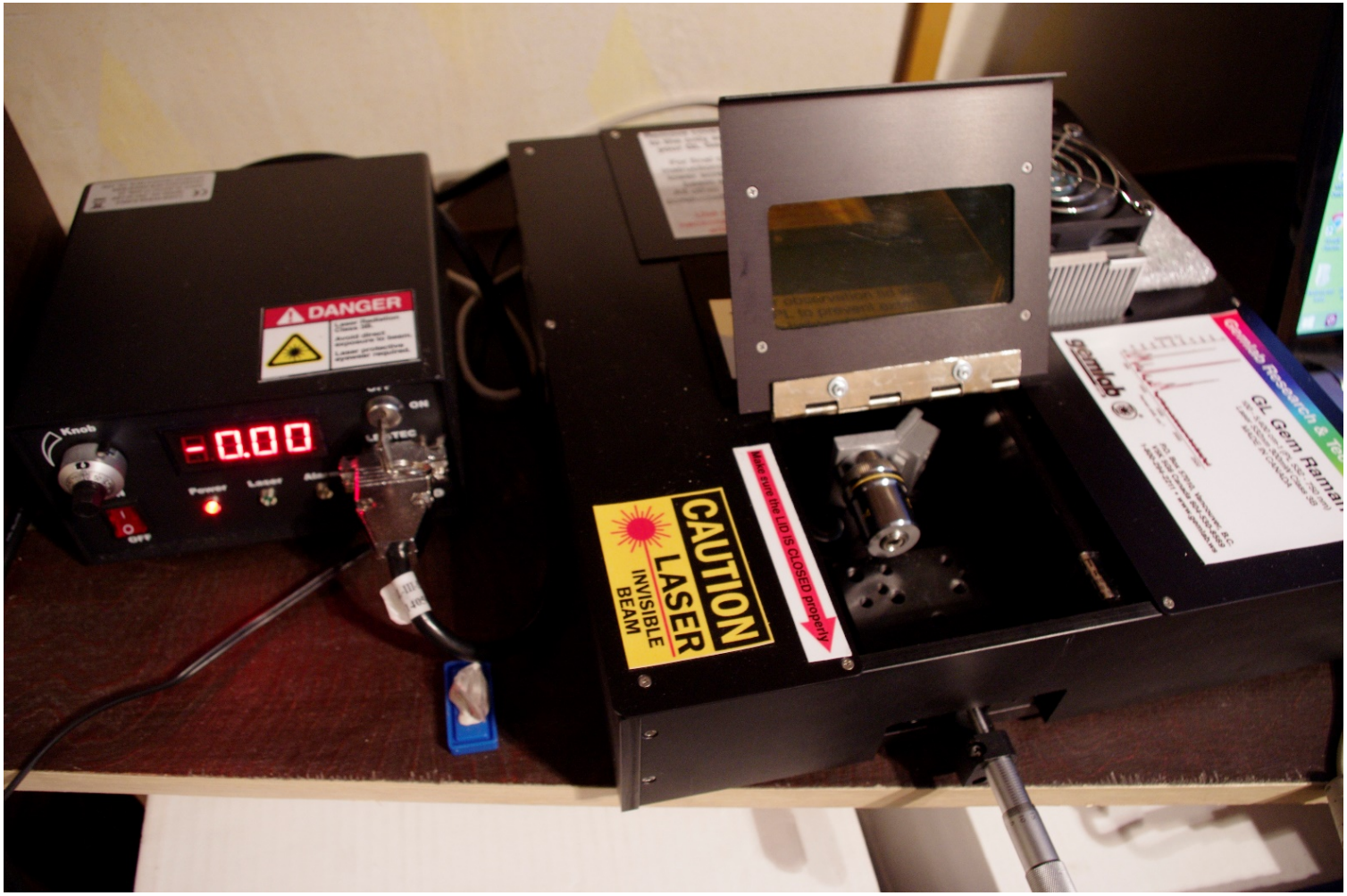
DANGER
CAUTION
LASER
INVISIBLE BEAM
Make sure the LID IS CLOSED properly
Knob
Power
Laser
ON
OFF


DANGER
CAUTION
LASER
INVISIBLE
BEAM
OFF
ON
LD&TEC
Knob
Power
Laser
Alarm
PSU-III-LED
ON
OFF

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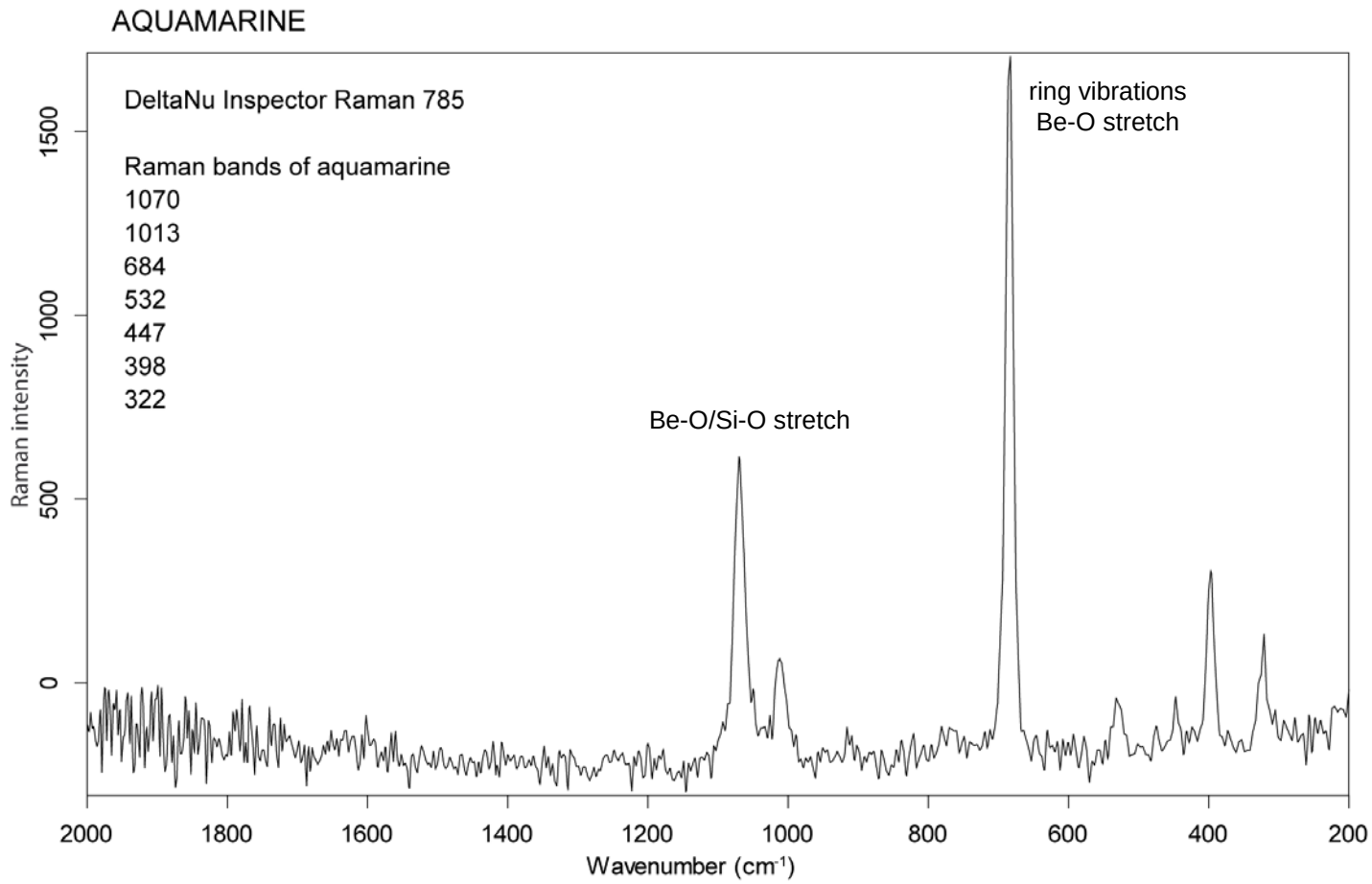
Aquamarine $Be_3Al_2(SiO_3)_6$



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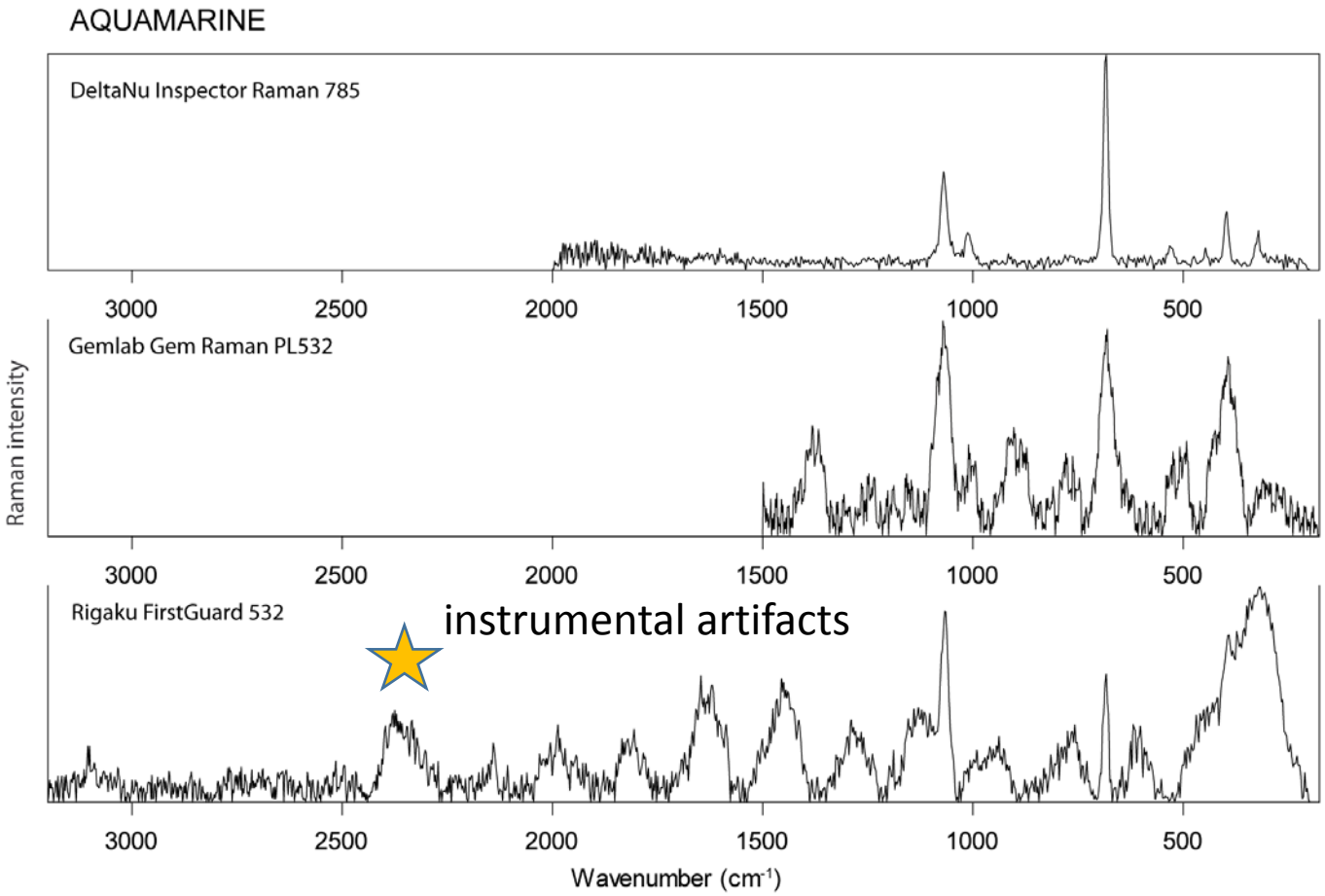

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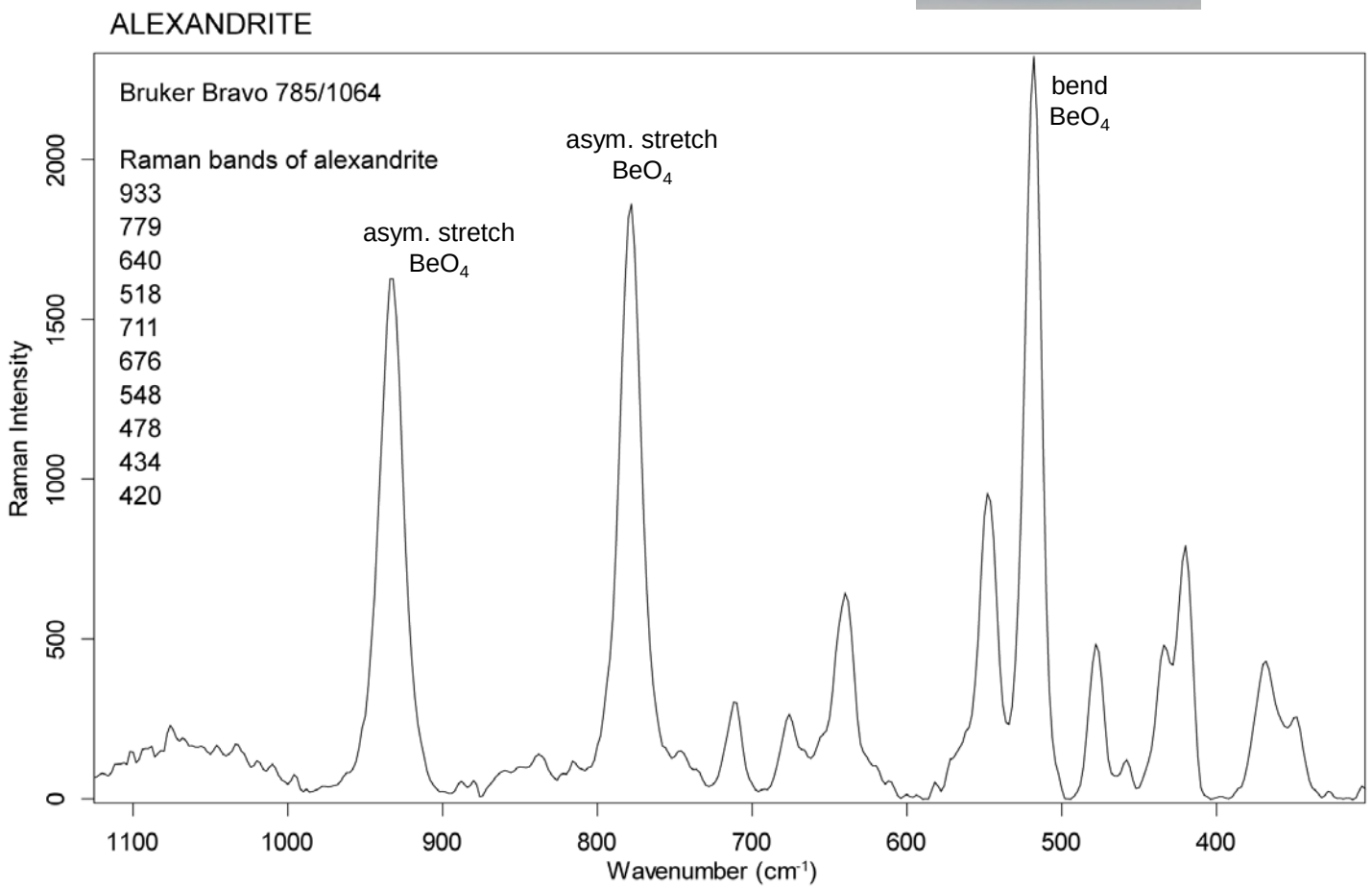
Alexandrite $BeAl_2O_4$



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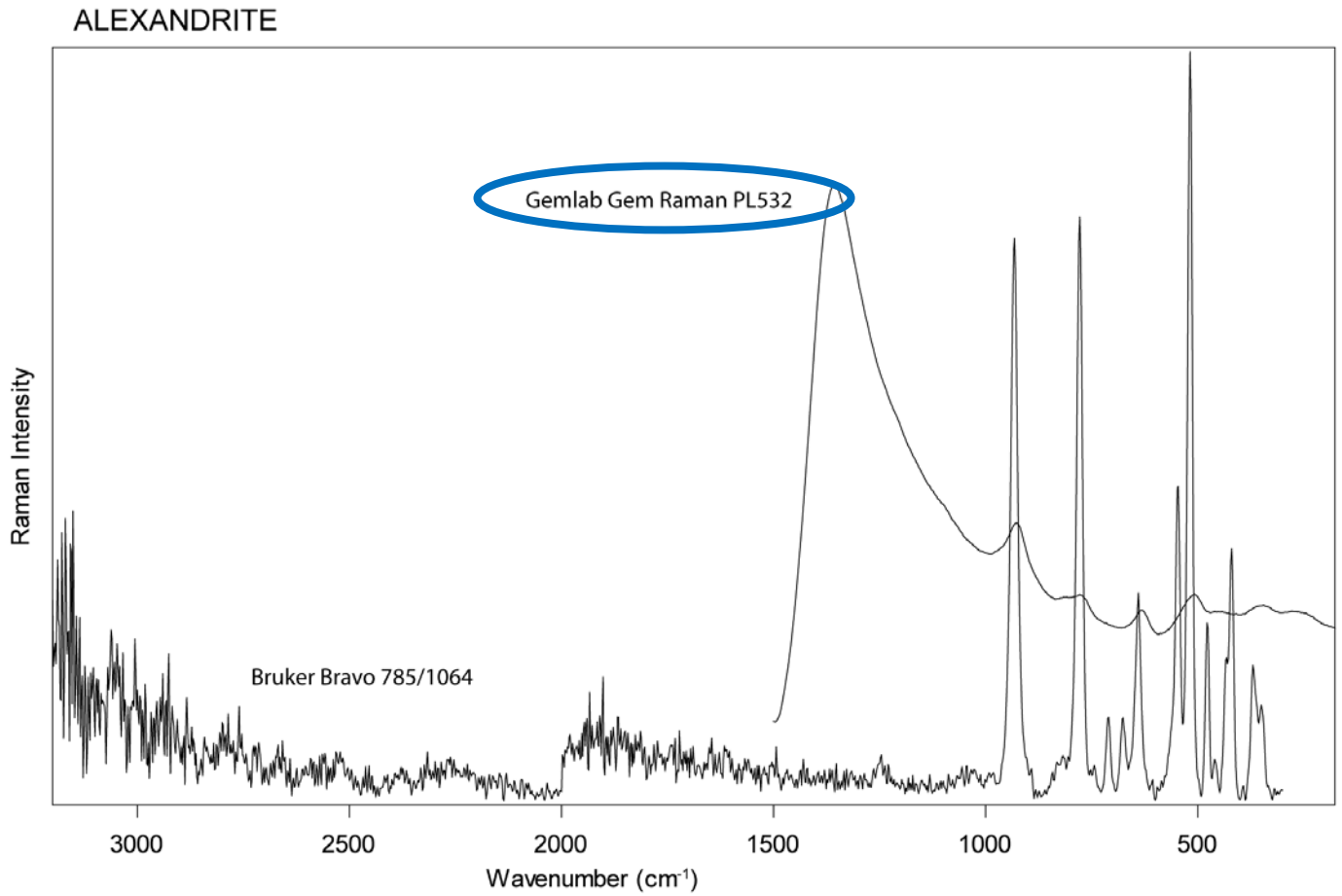

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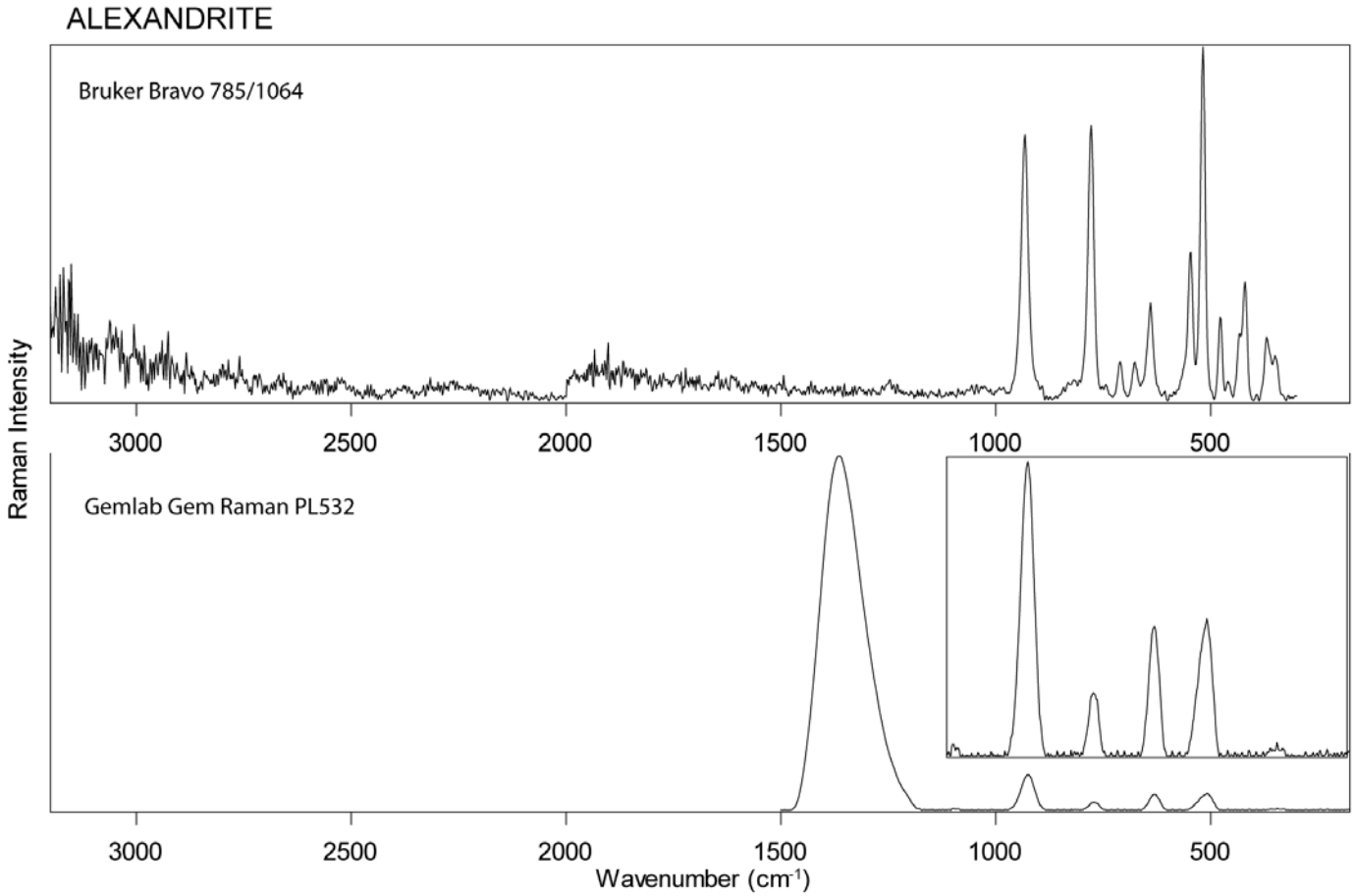

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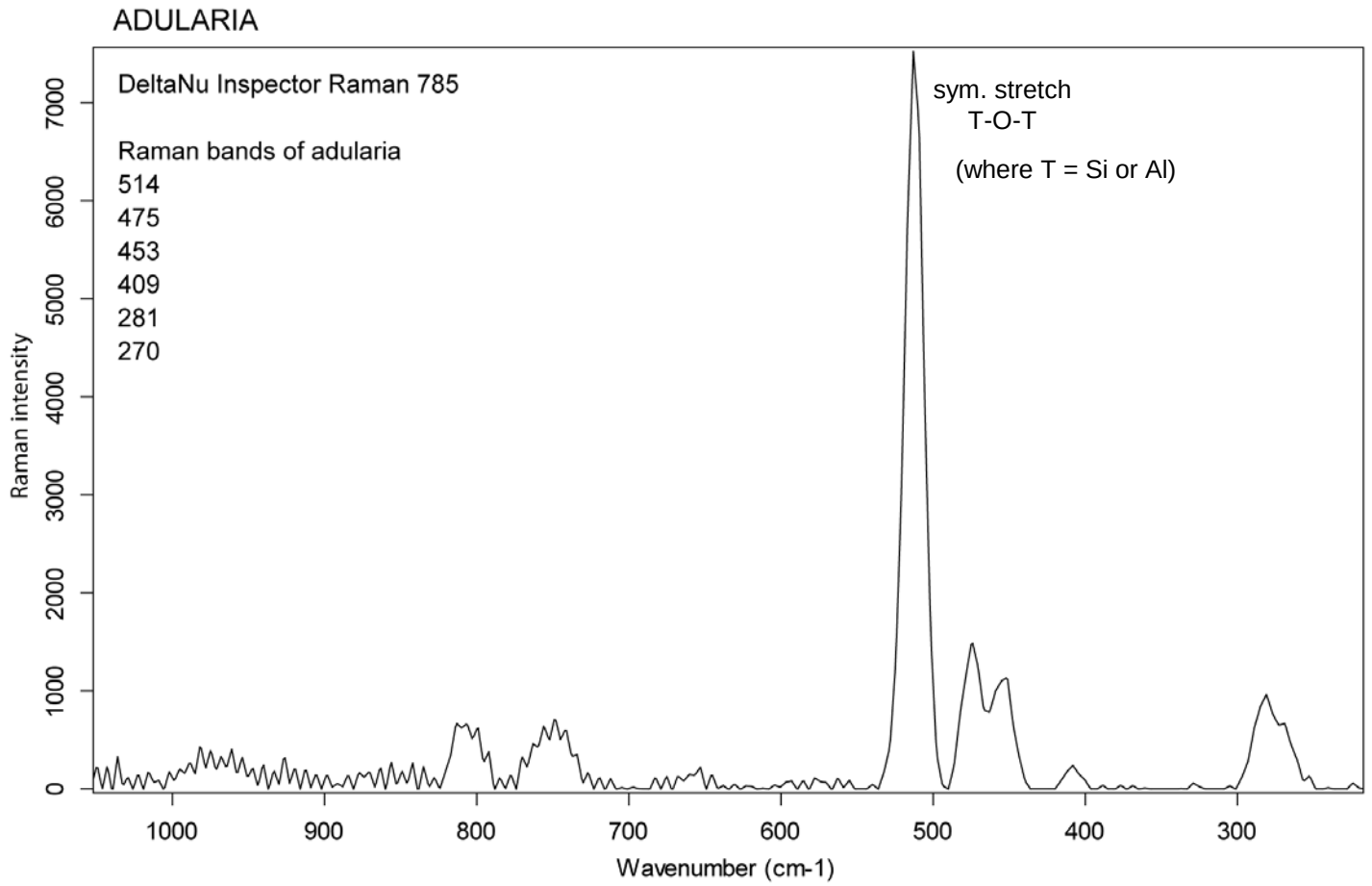

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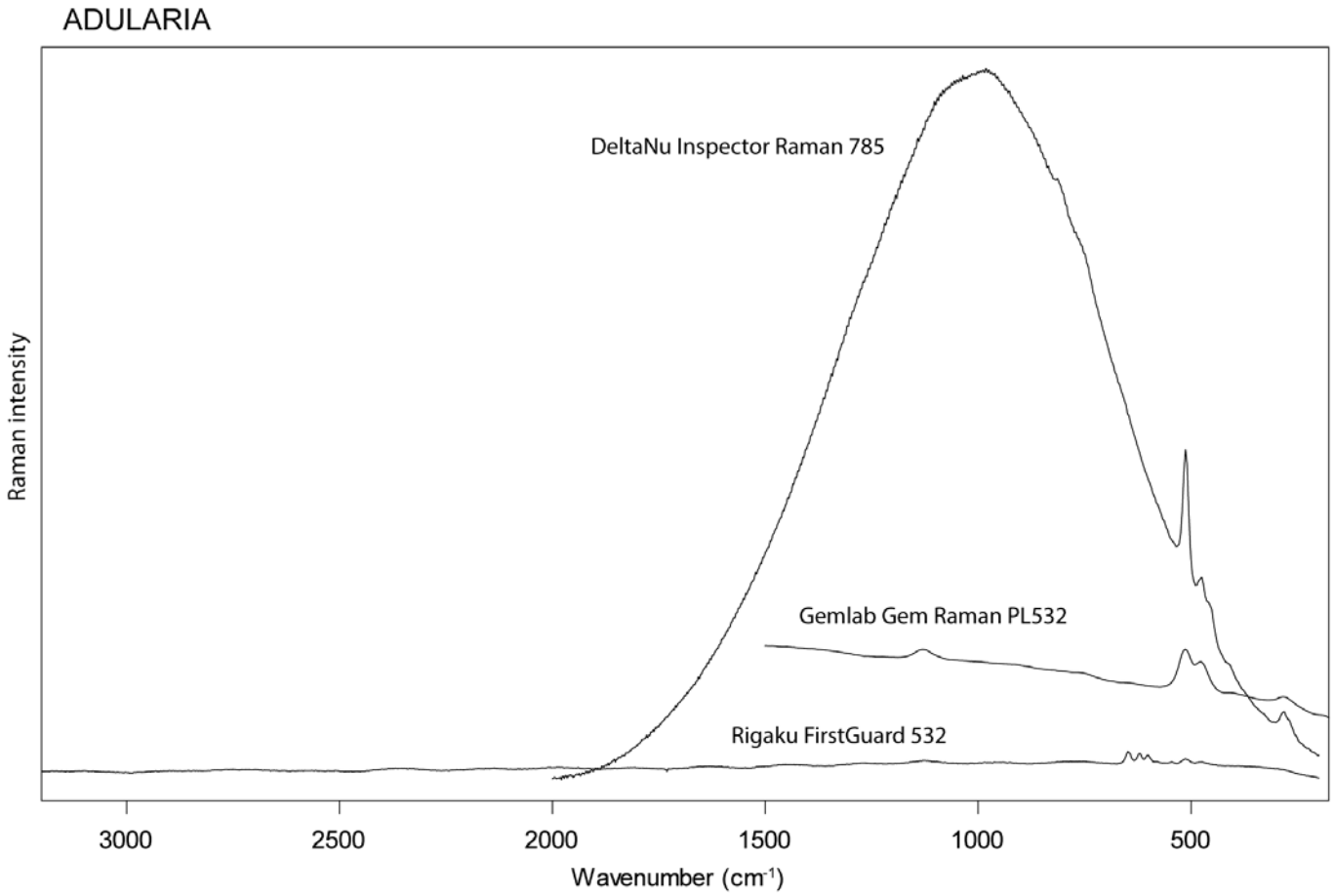

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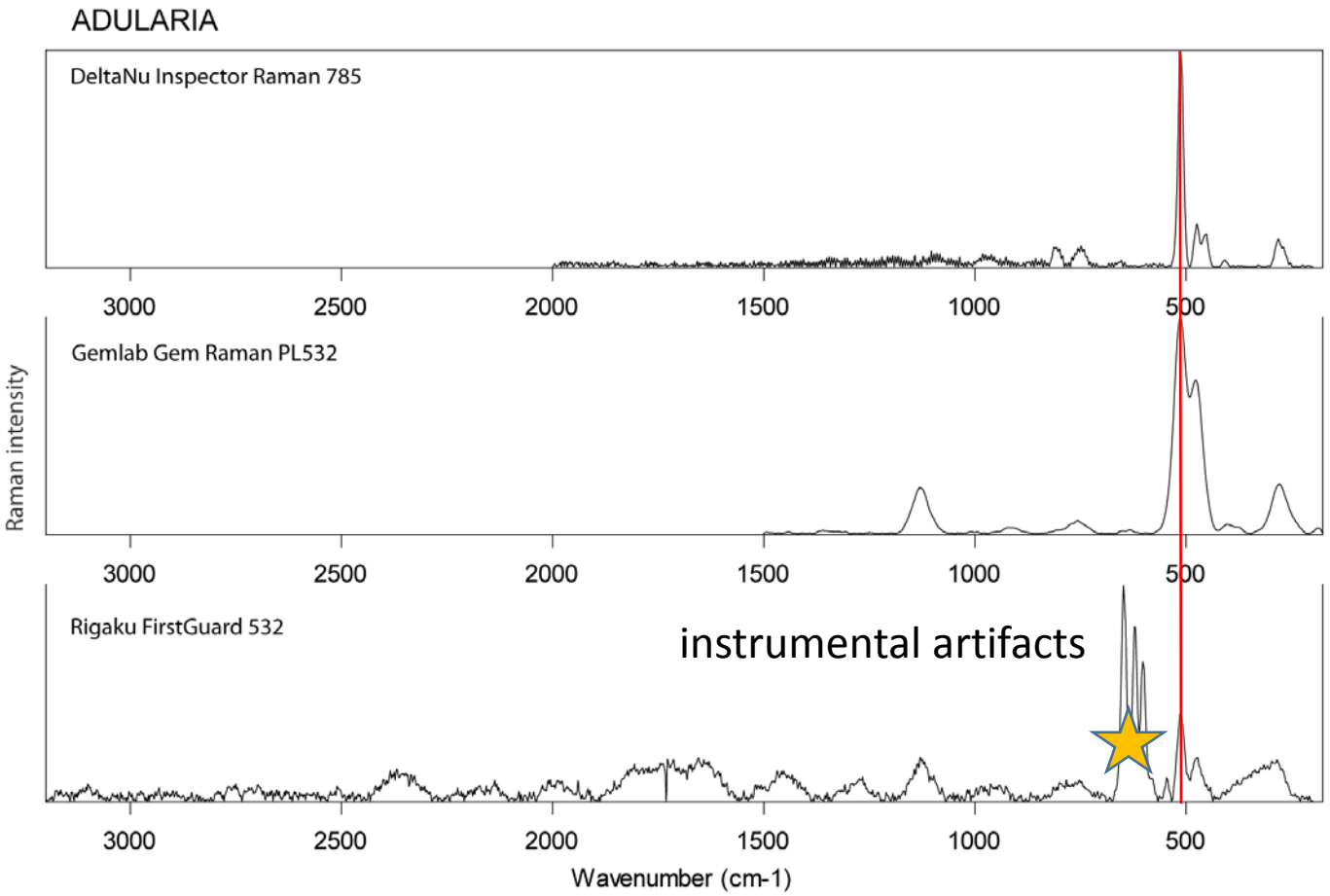

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Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Critical evaluation of a handheld Raman spectrometer with near infrared (785 nm) excitation for field identification of minerals

Jan Jehlička[a,*], Adam Culka[a], Peter Vandenabeele[b], Howell G.M. Edwards[c]

Icarus 243 (2014) 440–453

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Use of miniaturized Raman spectrometer for detection of sulfates of different hydration states – Significance for Mars studies

Adam Culka, Filip Košek, Petr Drahota, Jan Jehlička *

Nondestructive investigation on the 17-18th centuries Sicilian jewelry collection at the Messina regional museum using mobile Raman equipment

G. Barone,[a]* D. Bersani,[b] J. Jehlička,[c] P. P. Lottici,[b] P. Mazzoleni,[a] S. Raneri,[a] P. Vandenabeele,[d] C. Di Giacomo[e] and G. Larinà[e]

J. Raman Spectrosc. **2015**, *46*, 989–995

In situ study of stones adorning a silver Torah shield using portable Raman spectrometers

Kateřina Osterrothová,[a]* Laura Minaříková,[a] Adam Culka,[a] Jaroslav Kuntoš[b] and Jan Jehlička[a]

J. Raman Spectrosc. **2014**, *45*, 830–837

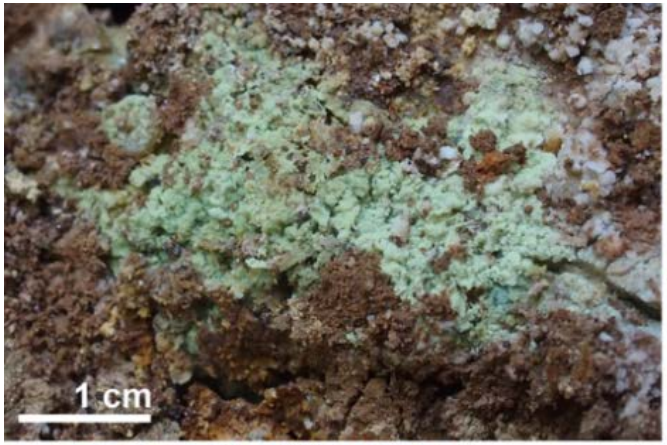
- Geobiology

Carbonates

crystallization

formation of accumulations

relationship matrix - microorganisms



sulfates

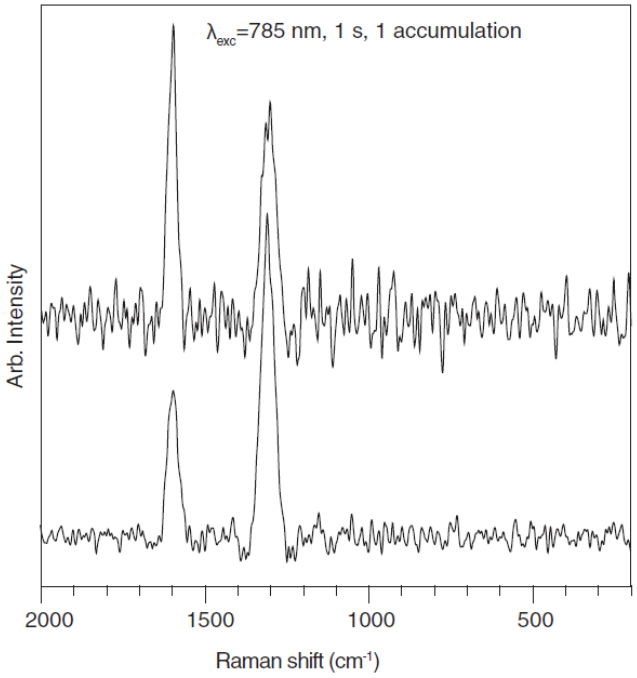
ASTROBIOLOGY
Volume 13, Number 9, 2013

DOI: 10.1089/ast.2013.1026

Rapid Communication

Field-Based Raman Spectroscopic Analyses of an Ordovician Stromatolite

Alison Olcott Marshall and Craig P. Marshall



Carbonaceous matter

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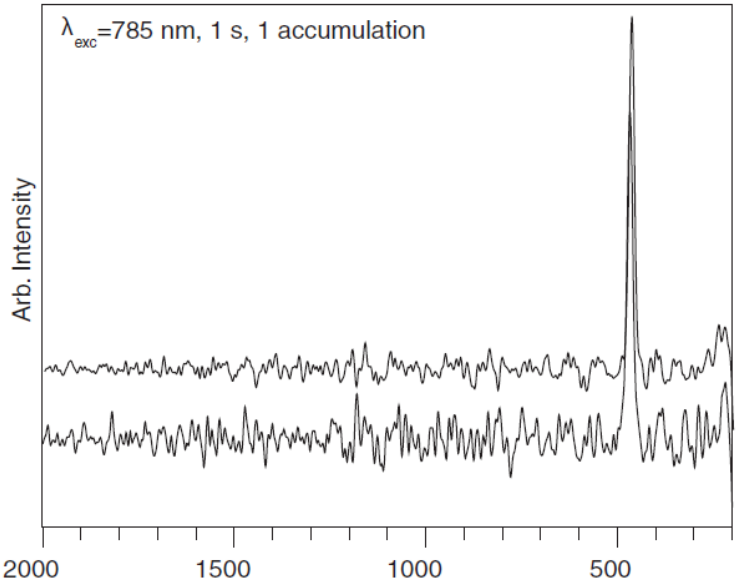
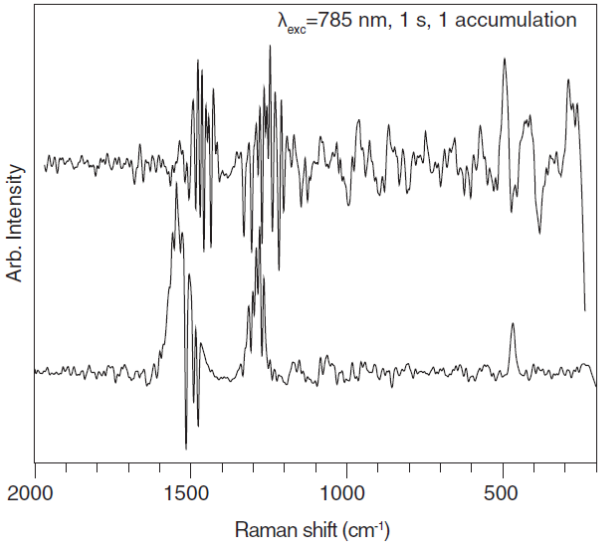
XII International Conference
GeoRAMAN – 2016
Novosibirsk, Russia, June 9-15, 2016

Quartz



Carbonaceous matter



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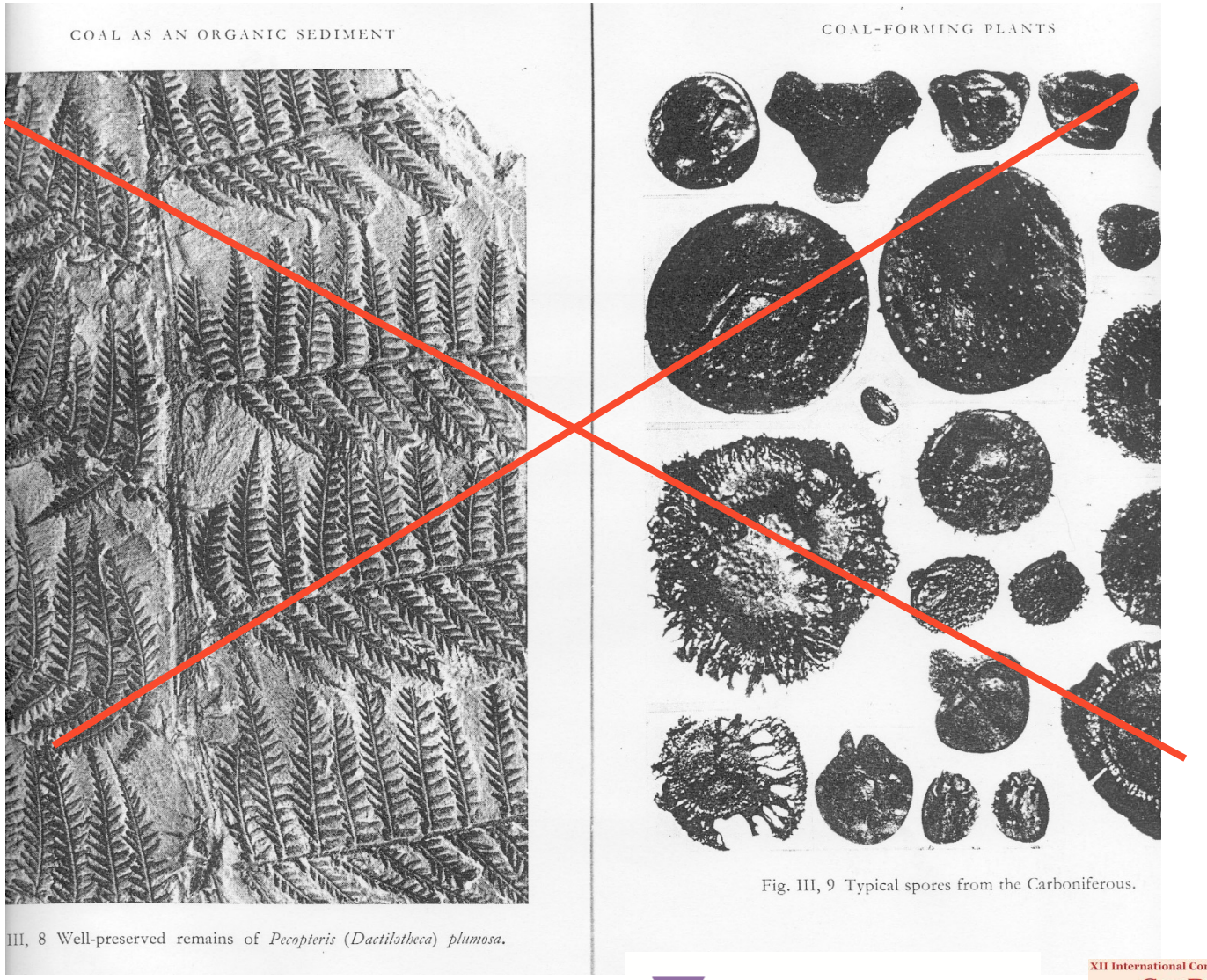
- Exobiology

Fossilised remnants of plants

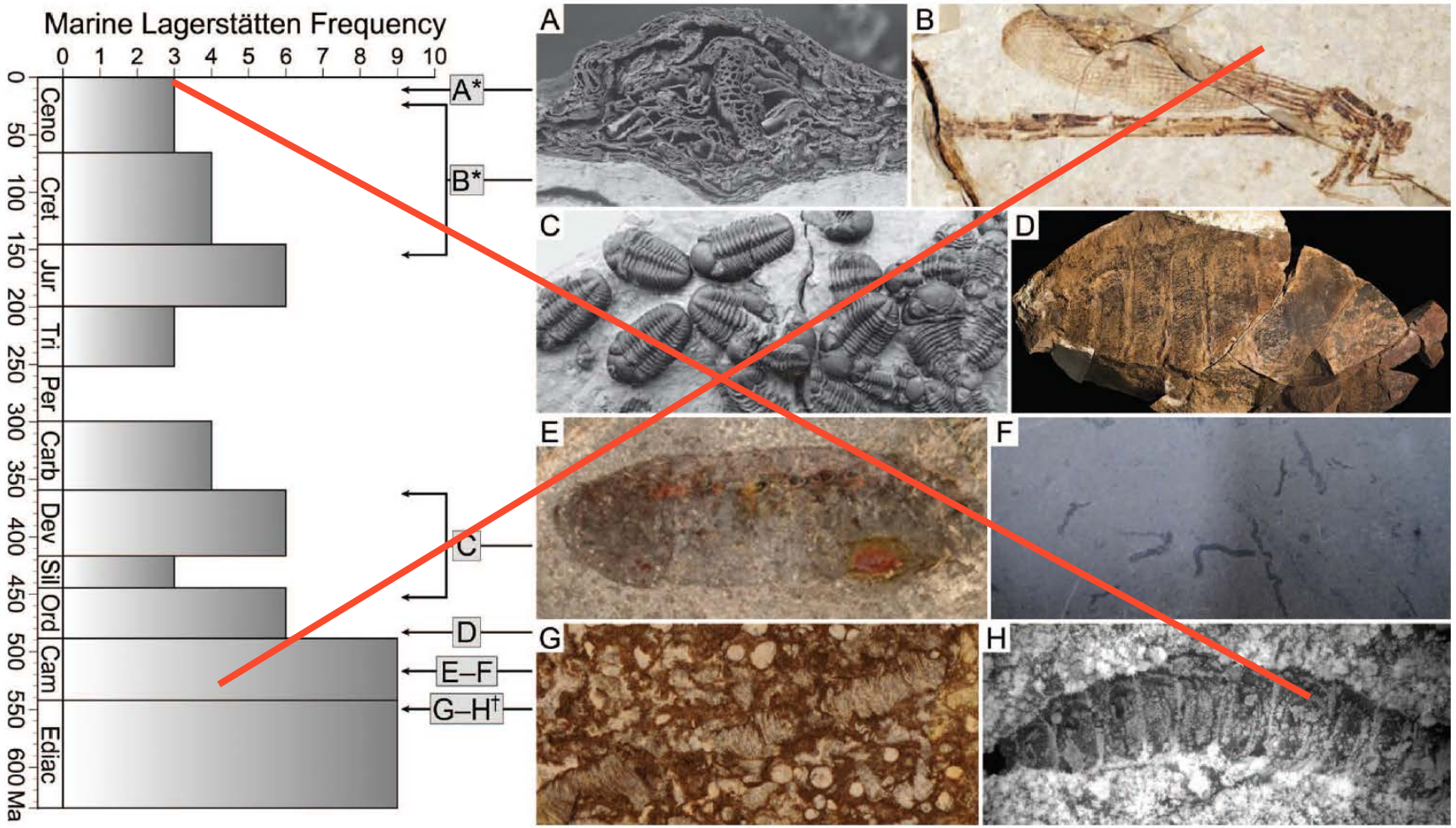


COAL AS AN ORGANIC SEDIMENT

III, 8 Well-preserved remains of *Pecopteris* (*Dactilotheca*) *plumosa*.

COAL-FORMING PLANTS

Fig. III, 9 Typical spores from the Carboniferous.



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Biomarkers

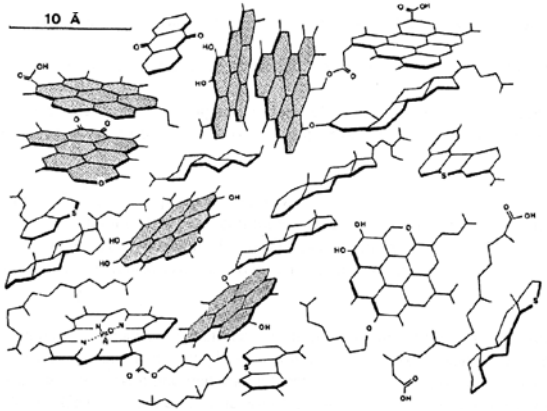
Biomolecules derived from life

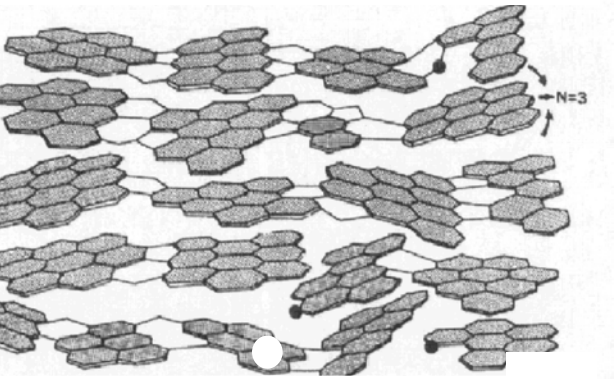
Highly characteristic structure

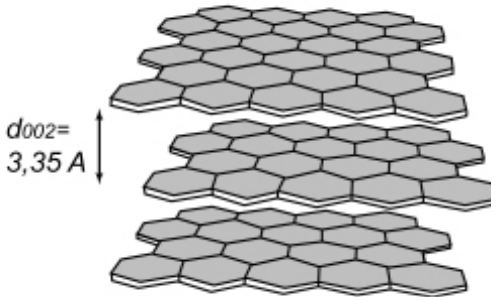
High stability –
(under terrestrial conditions)

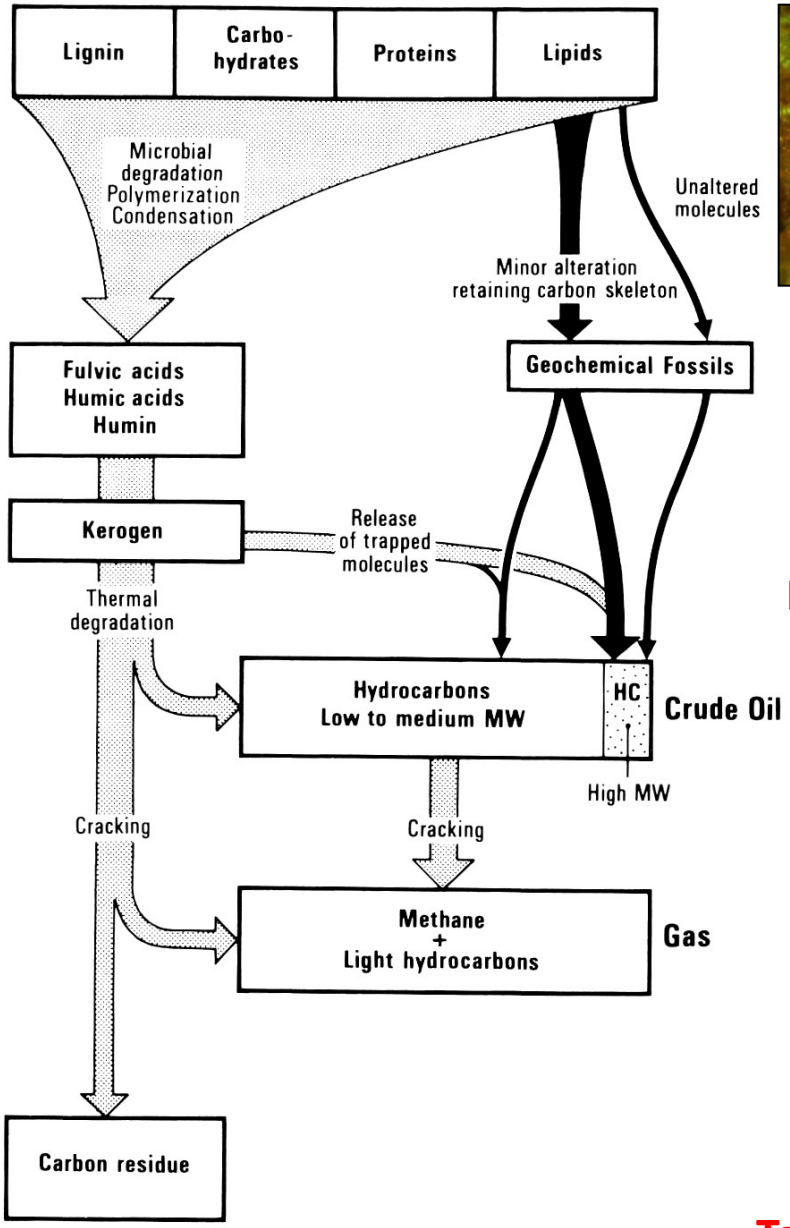
Detection of a given biomarker – indicative for preexisting organisms

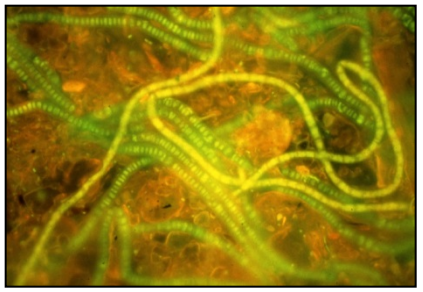
Organic geochemistry……











Diagenesis

Taphonomy

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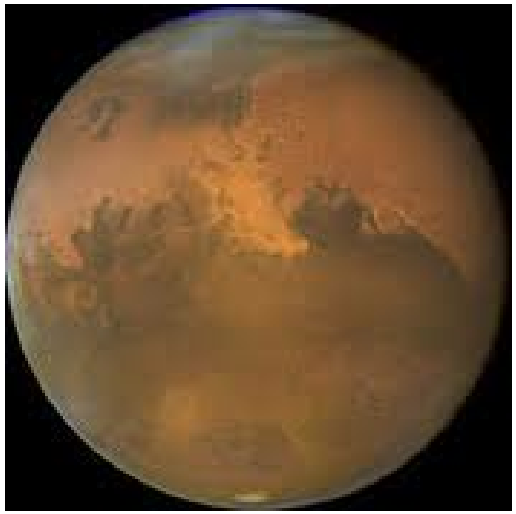
Biomarkers

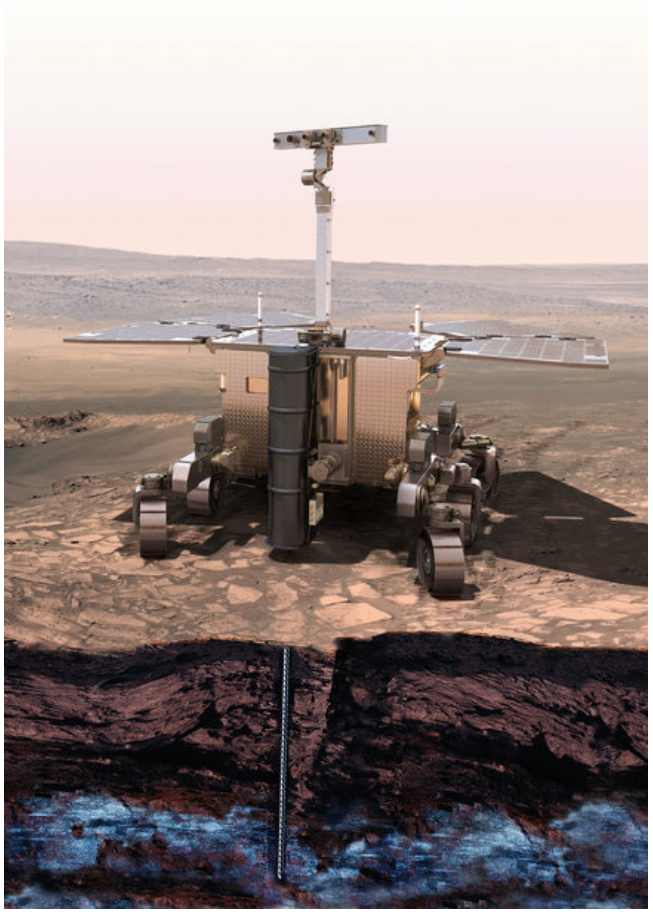
RAMAN SPECTROSCOPY AS A TOOL FOR BIOMARKER DETECTION

why biomarkers ?

pigments ?

Search for life on Mars ?





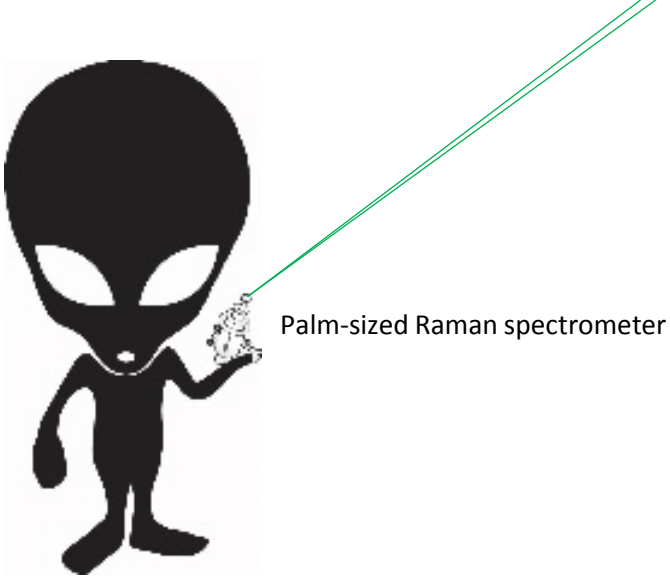
- Planetary research

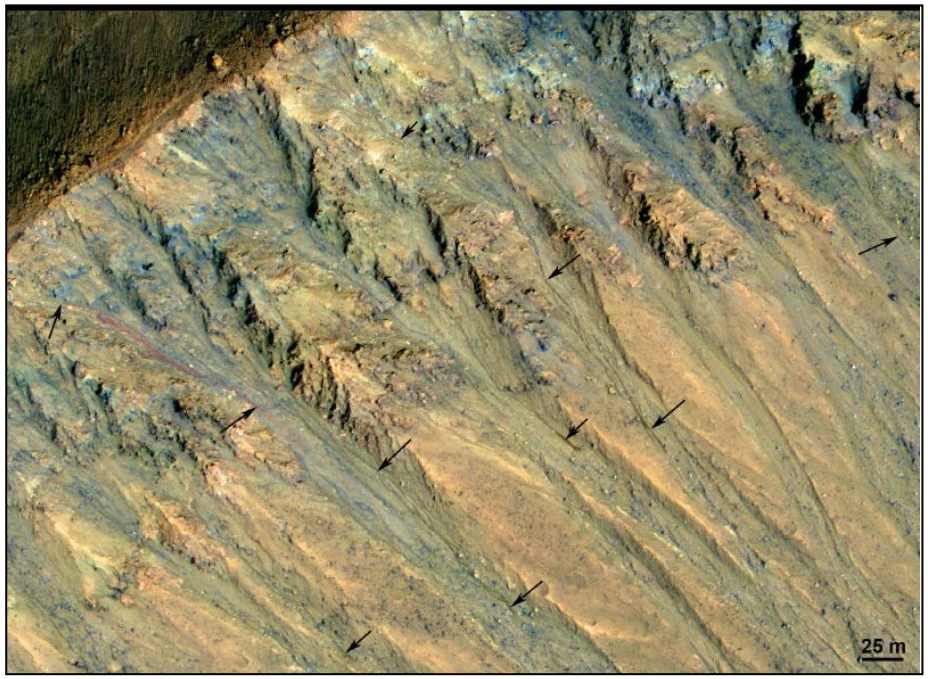
Minerals

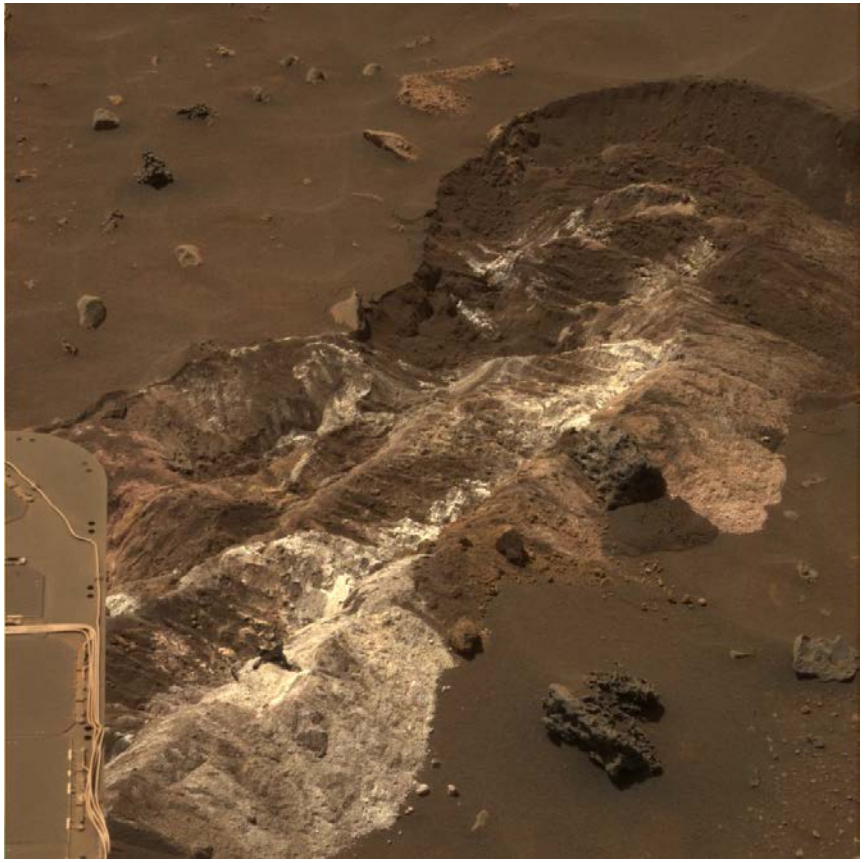
= environments in the past

Biomarkers

= extinct/extant life







Seasonal Flows on Warm Martian Slopes

Alfred S. McEwen,[1]* Lujendra Ojha,[1] Colin M. Dundas,[2] Sarah S. Mattson,[1] Shane Byrne,[1] James J. Wray,[3] Selby C. Cull,[4] Scott L. Murchie,[5] Nicolas Thomas,[6] Virginia C. Gulick[7]

5 AUGUST 2011 VOL 333 SCIENCE www.sciencemag.org

brines - sulfates

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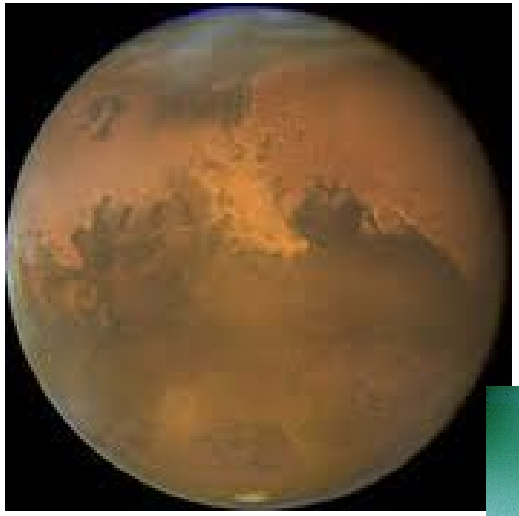
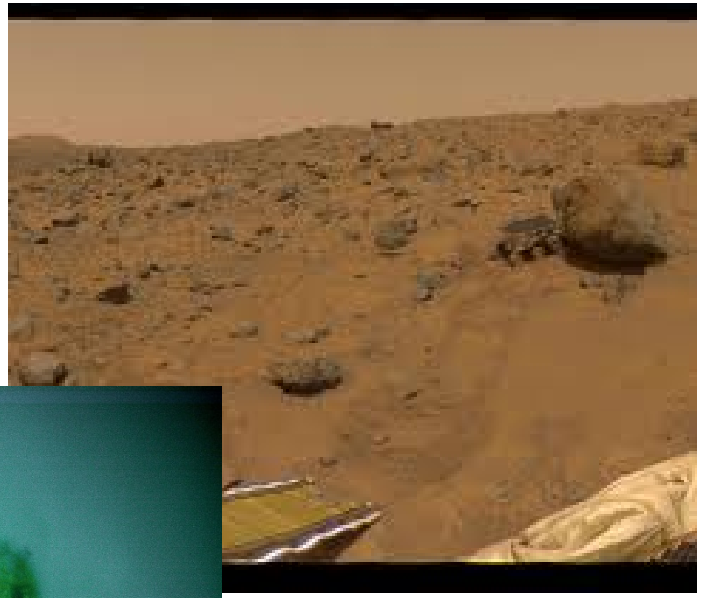
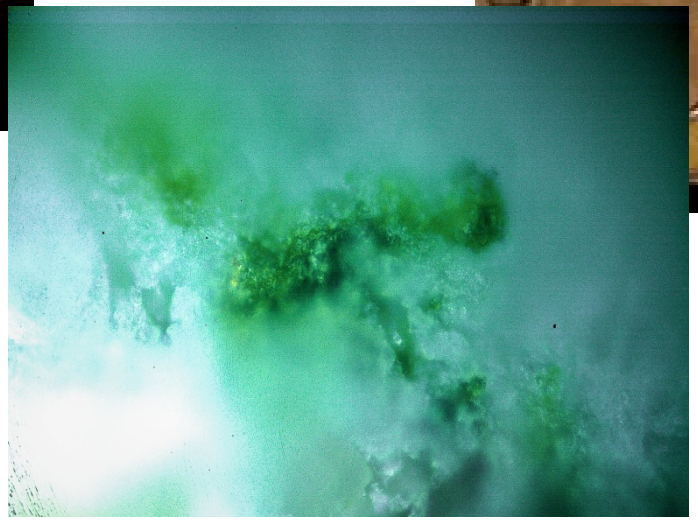






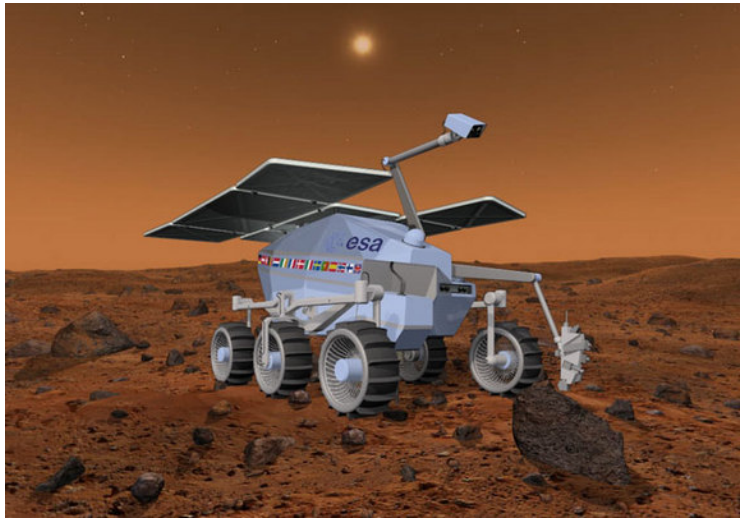
Life on Mars astrobiology

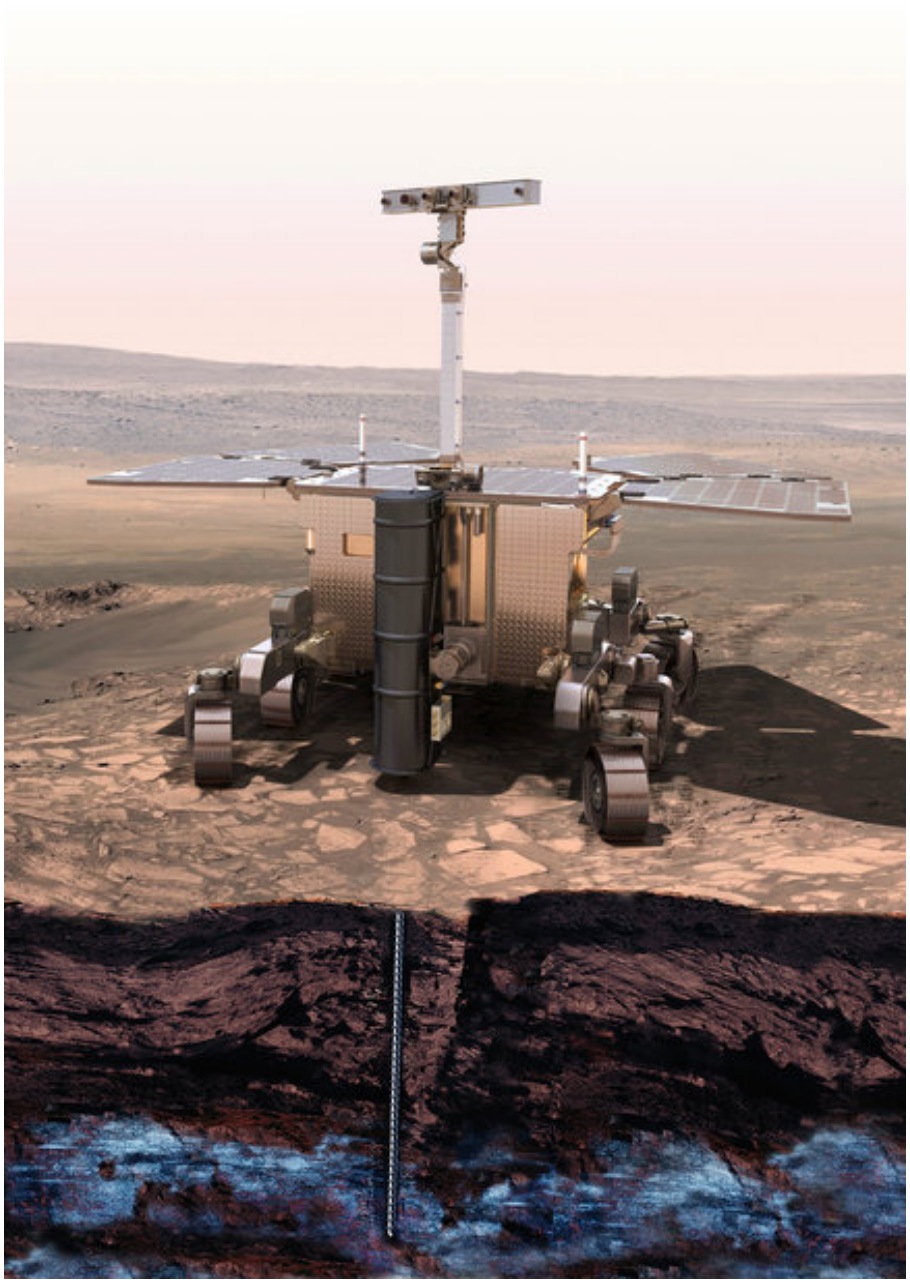
?

Curiosity - NASA

Exomars – ESA/NASA

Minerals - biomarkers





Life on Mars astrobiology

Curiosity - NASA

Exomars – ESA/NASA

ExoMars mission
ESA/Roscosmos

Groups of biomarkers (organic geochemistry)

Raman spectrometry – a preferential technique

Pigments

….chlorophylls

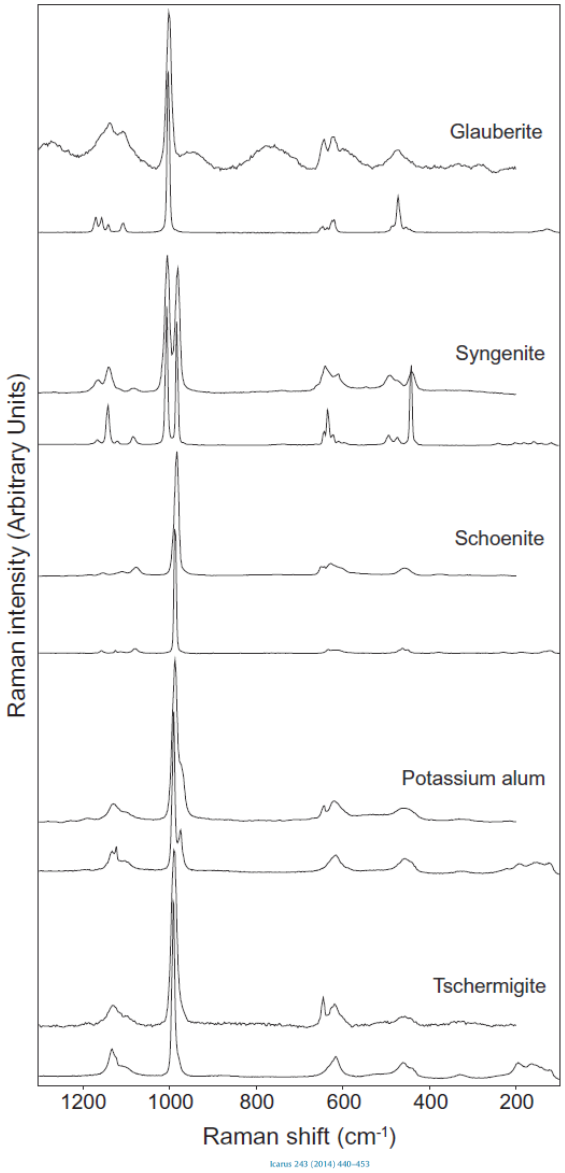
….carotenoids

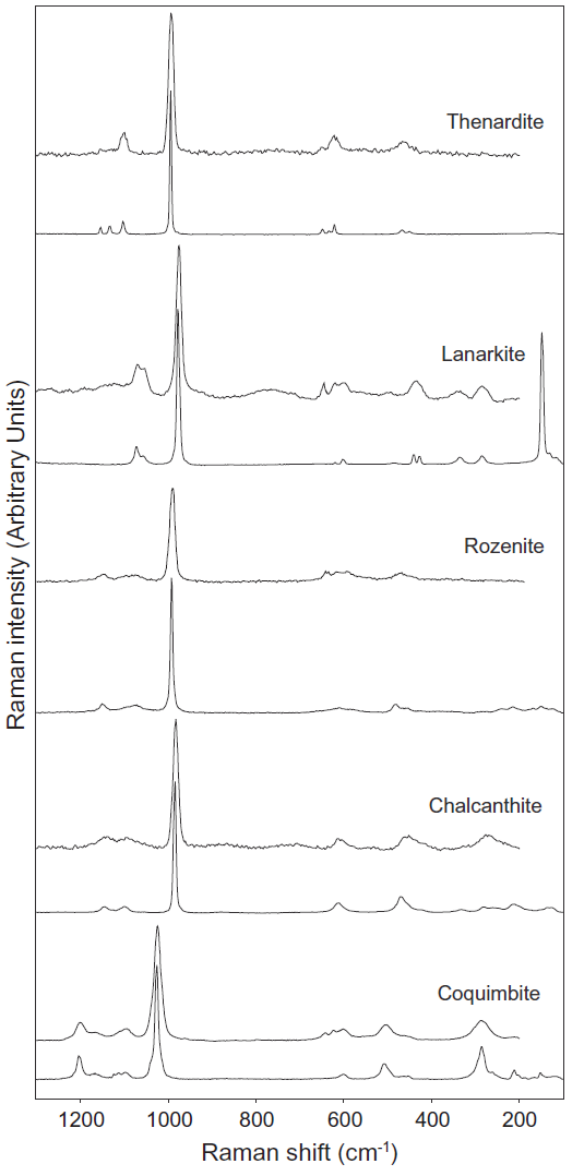
….scytonemins

……


Training on Earth…

Raman spectra sulfates
785 nm





Portable RS
Dispersive laboratory RS

Icarus 243 (2014) 440–453

Contents lists available at ScienceDirect

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Use of miniaturized Raman spectrometer for detection of sulfates of different hydration states – Significance for Mars studies

Adam Culka, Filip Košek, Petr Drahota, Jan Jehlička *

Charles University in Prague, Institute of Geochemistry, Mineralogy and Mineral Resources, Albertov 6, 12843 Prague, Czech Republic

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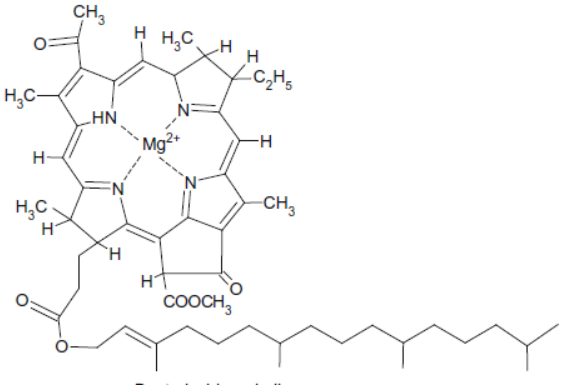
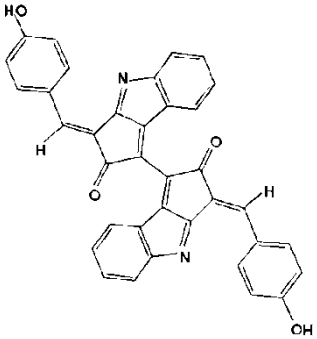
Raman spectroscopy for exobiology

- Biomarkers
- Pigments
- Carotenoids

Bacteriochlorphyll

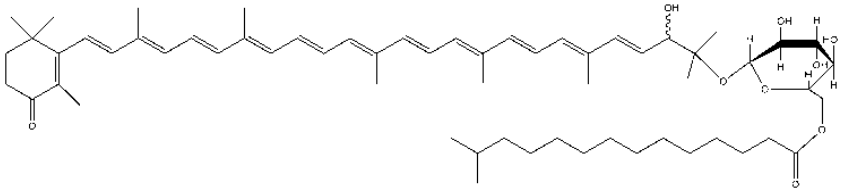


Scytonemin



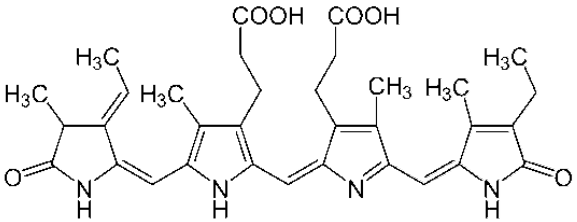
Salinixanthin

Salinibacter ruber



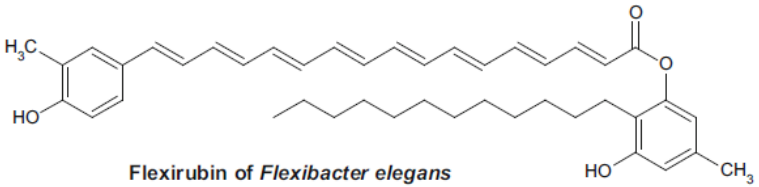
Phycocyanin

Cyanobacteria



Flexirubin

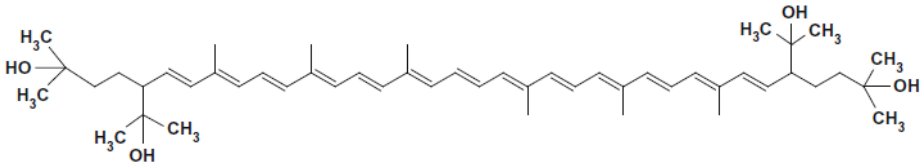
Flexibacter elegans



Flexirubin of *Flexibacter elegans*

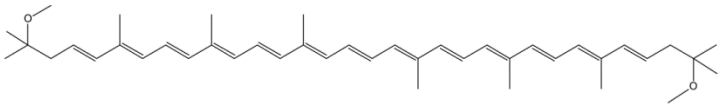
Bacterioruberin

Haloarchaea

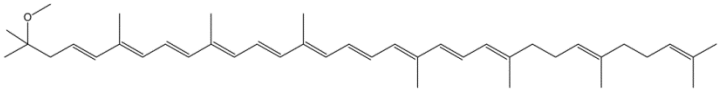


Carotenoids

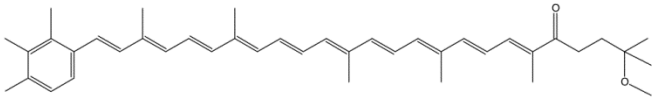
Spirilloxanthin



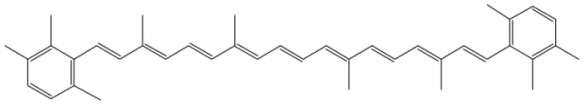
Spheroidene



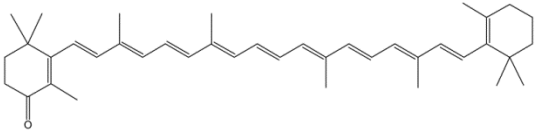
Okenone



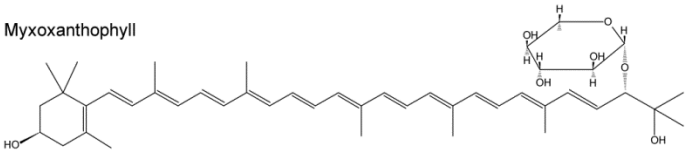
Isorenieratene



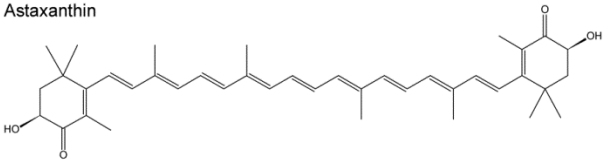
Echinenone



Myxoxanthophyll



Astaxanthin



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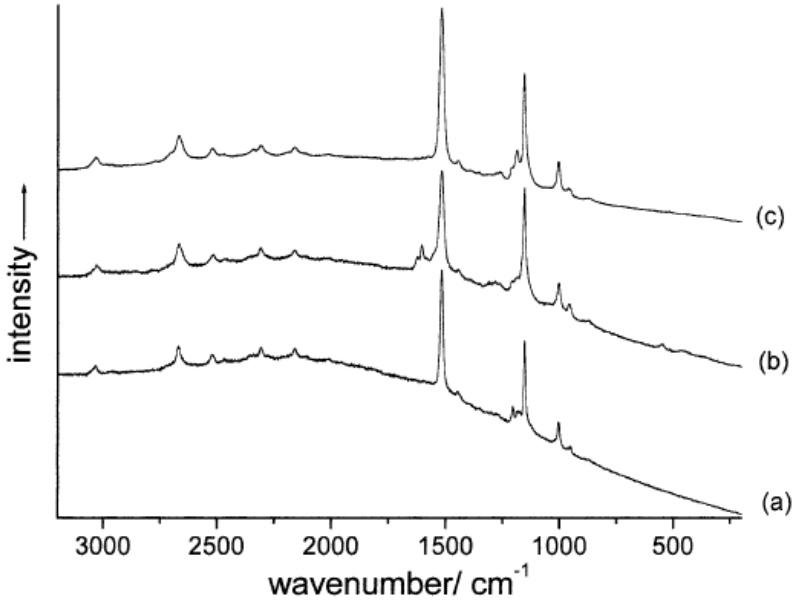
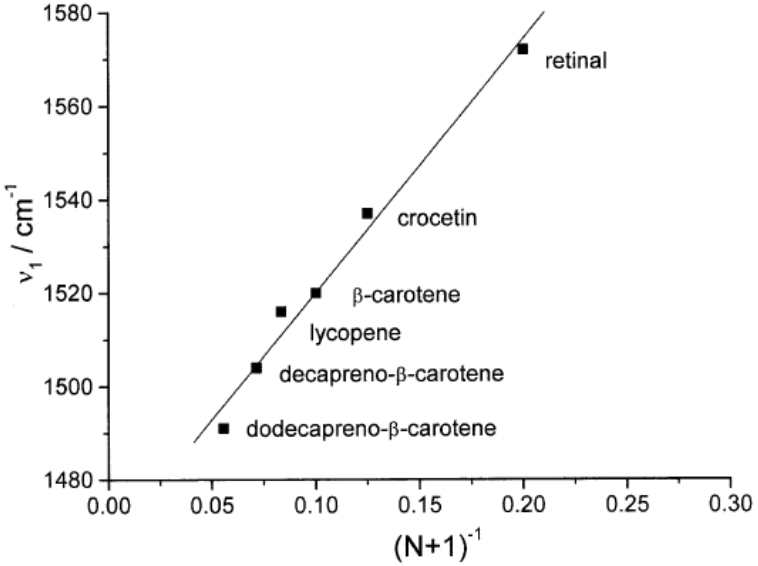
Raman spectra of carotenoids in natural products

Robert Withnall [a,*], Babur Z. Chowdhry [a], Jack Silver [a], Howell G.M. Edwards [b], Luiz F.C. de Oliveira [c]





Potential of miniature Raman spectrometers detect and discriminate

- Pigments in hypersaline environments
- Pigments in endoliths of hyperarid areas
- Pigments of microfungi, yeasts
- Pigments of snow algae
- Pigments of lichens

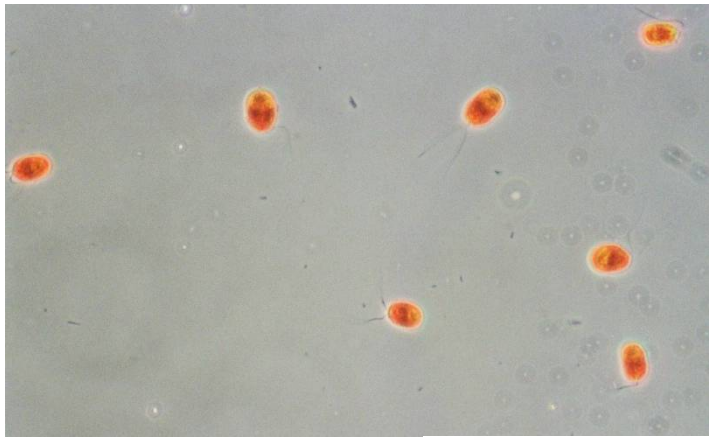
Pigments in hypersaline environments

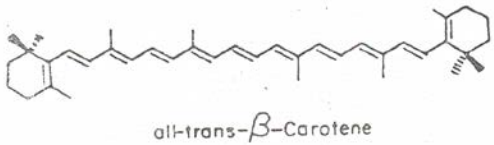

Dead Sea
Eilat

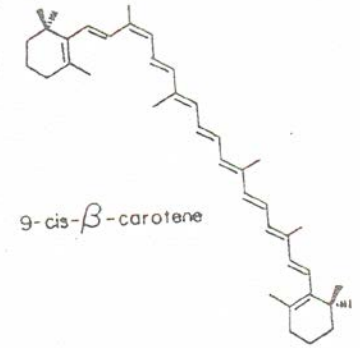
Eilat (Israel), salterns

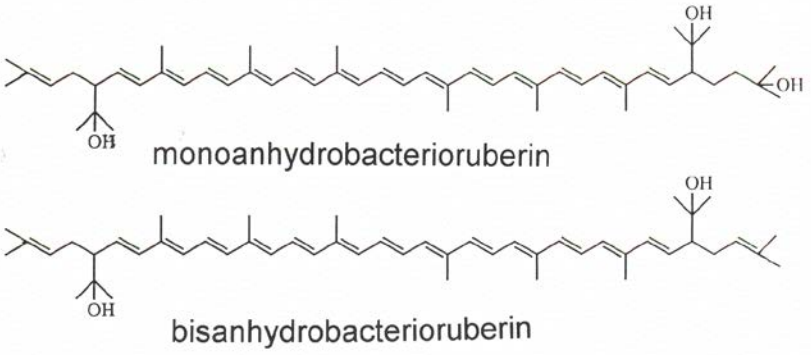
Bottom gypsum colonized layers, saltern pond 200

Pigments in hypersaline environments



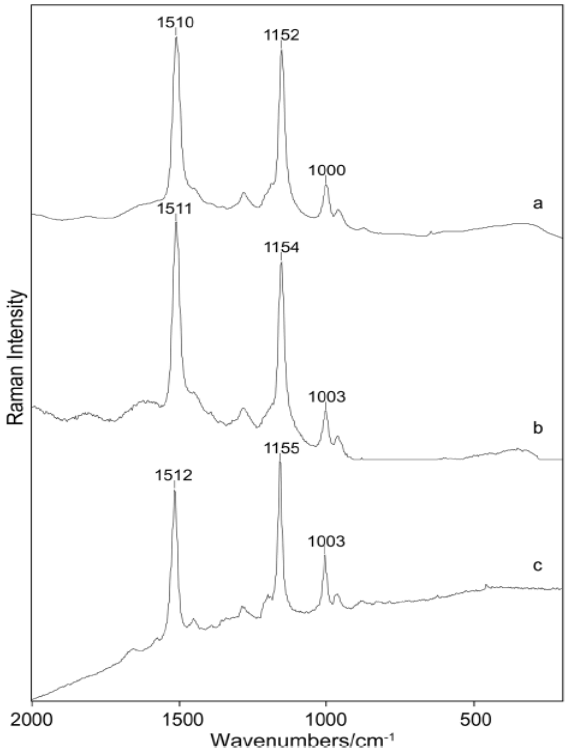


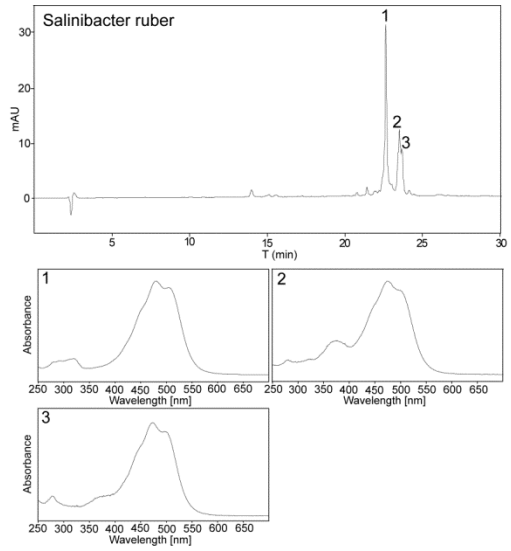


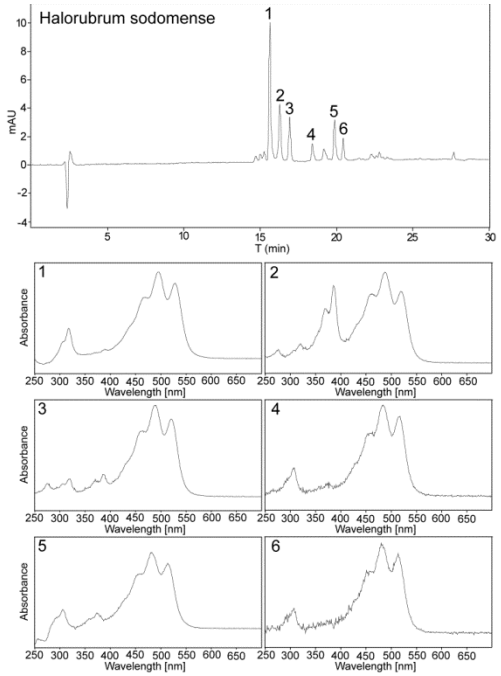


Halophiles

Raman analysis of pigments of different groups of halophiles using handheld instruments testing on pure cultures







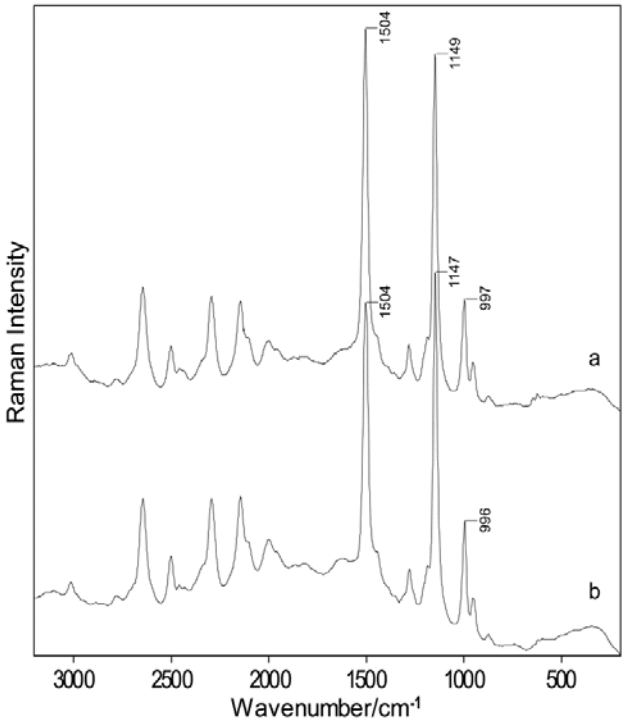
Salinibacter ruber

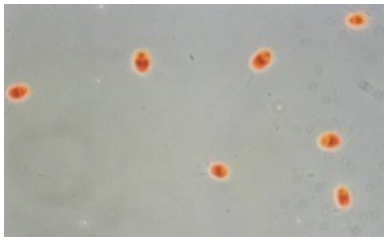
HPLC/UV-VIS sp.

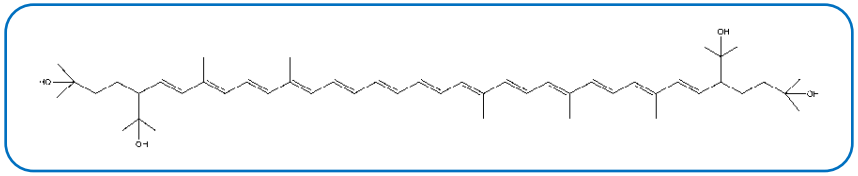
Raman spectra of Archaea, bacteria

Pigments in hypersaline environments

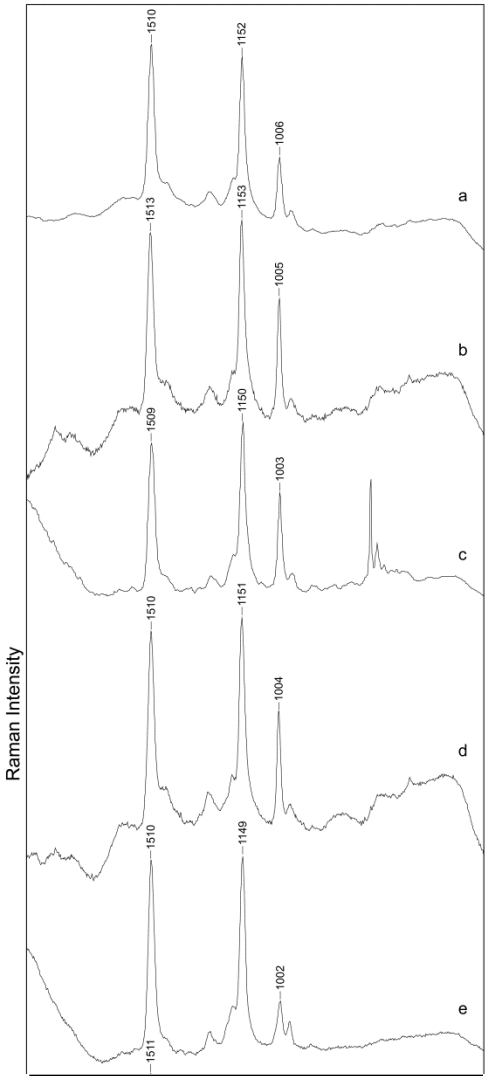
Eilat, pond 200
pellet of plankton







bacterioruberin



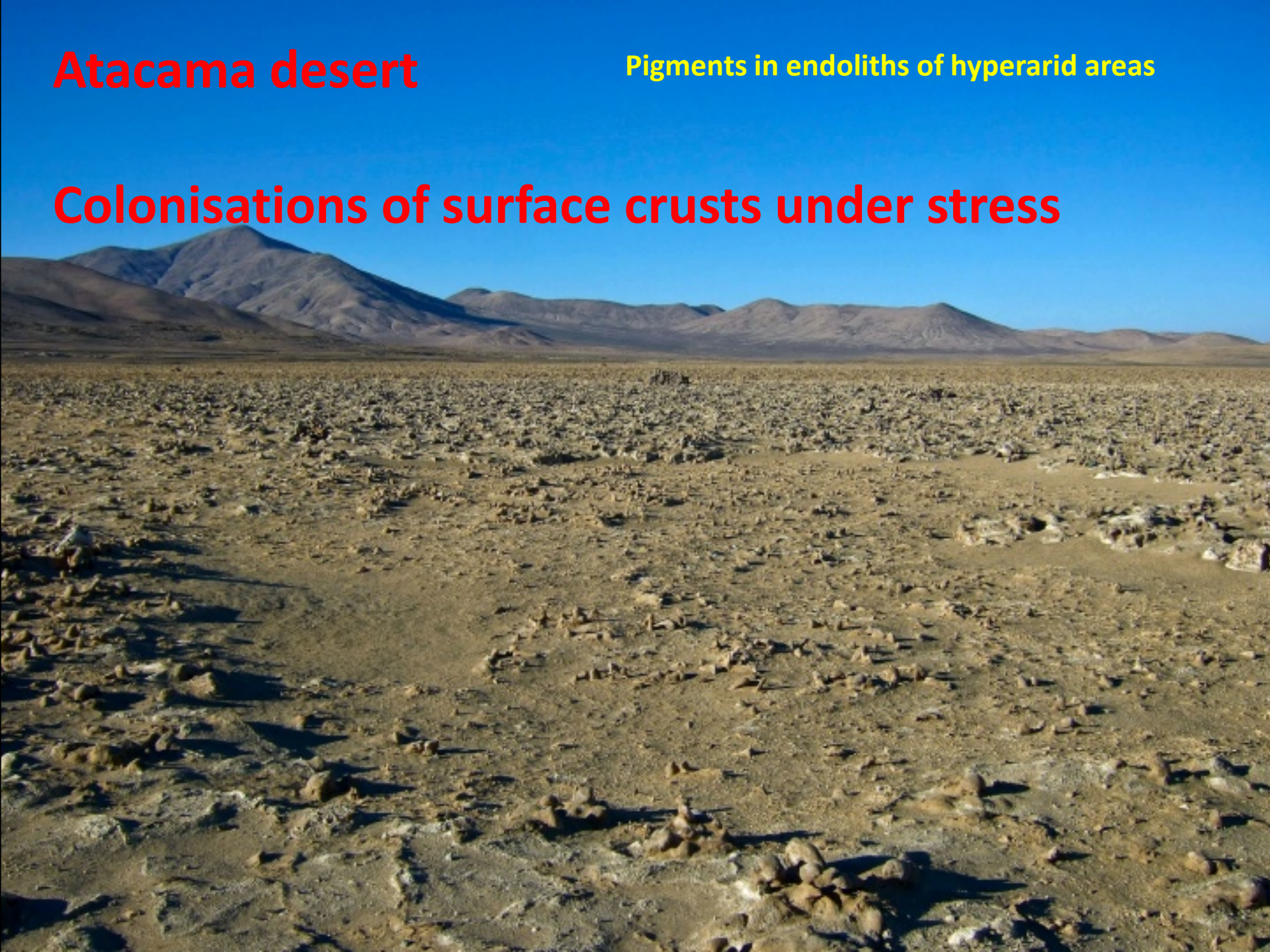
spirilloxanthin

Ectothiorhodospira marismortui
spirilloxanthin

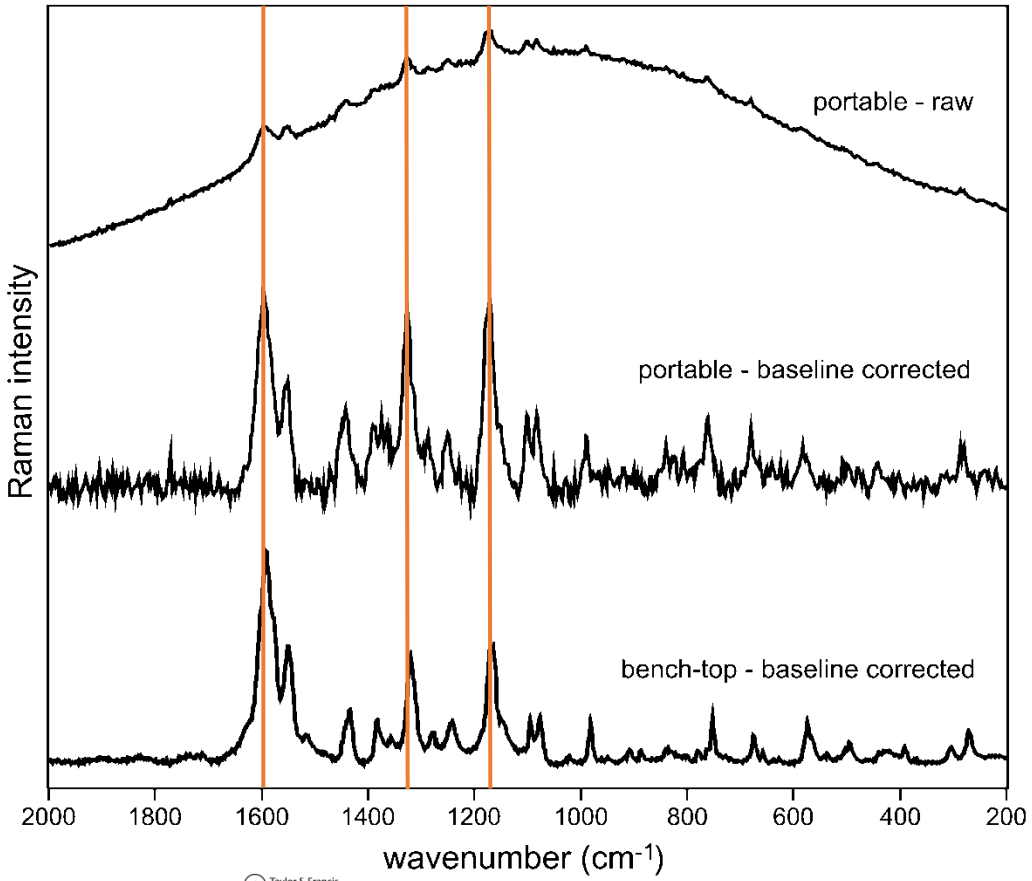
Atacama desert

Pigments in endoliths of hyperarid areas

Colonisations of surface crusts under stress



Atacama desert - Soronal salar gypsum crust



Pigments identified:

Scytonemin

Geomicrobiology Journal (2013) **30**, 399–410

ISSN: 0149-0451 print / 1521-0529 online
DOI: 10.1080/01490451.2012.697976

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Phototrophic Community in Gypsum Crust from the Atacama Desert Studied by Raman Spectroscopy and Microscopic Imaging

PETR VÍTEK[1]*, BEATRIZ CÁMARA-GALLEGO[2], HOWELL G. M. EDWARDS[3], JAN JEHLIČKA[1], CARMEN ASCASO[2], and JACEK WIERZCHOS[2]

[1]*Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Prague, Czech Republic*
[2]*Museo Nacional de Ciencias Naturales, CSIC, Madrid, Spain*
[3]*Centre for Astrobiology and Extremophiles Research, School of Life Sciences, University of Bradford, Bradford, United Kingdom*

Received March 2012, Accepted May 2012

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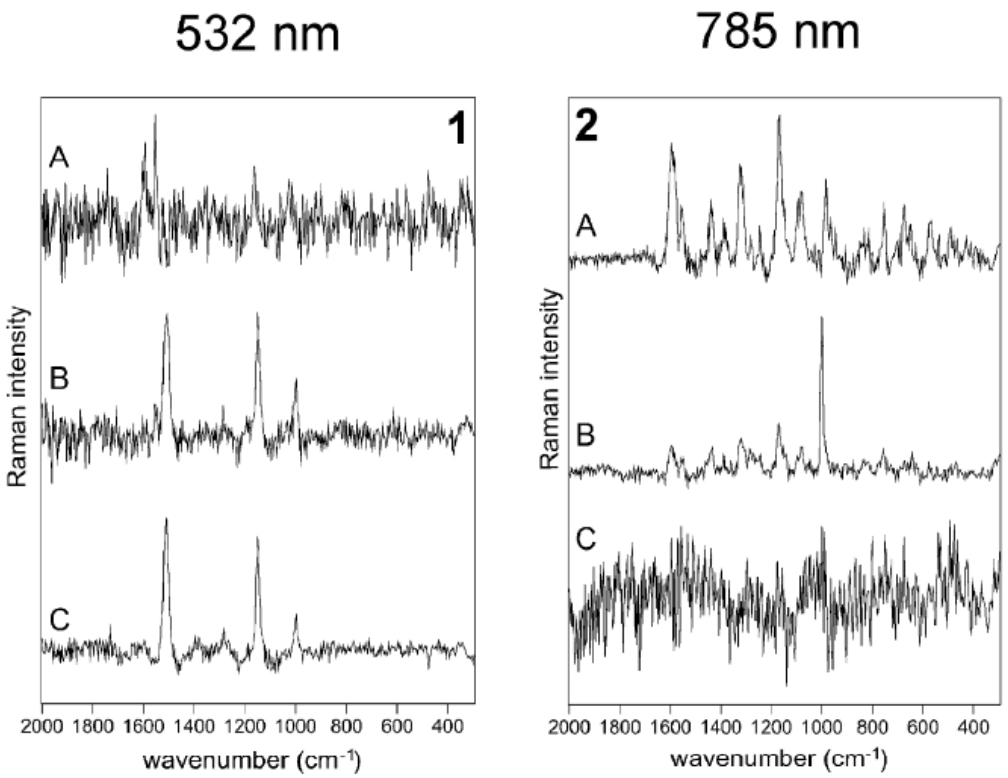
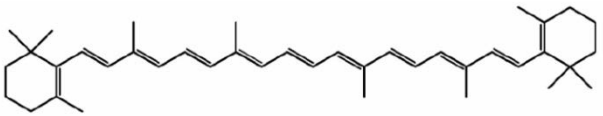
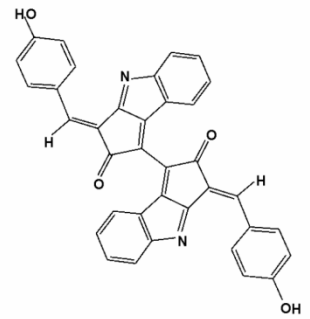
Direct measurement on the raw specimen as sampled



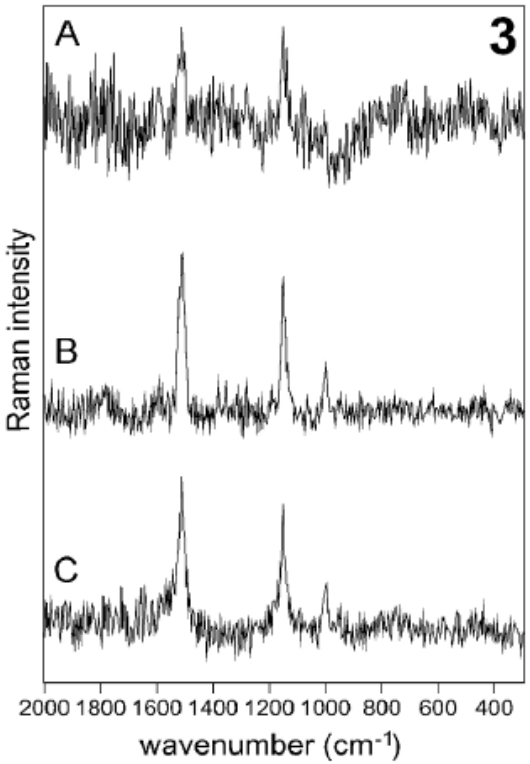


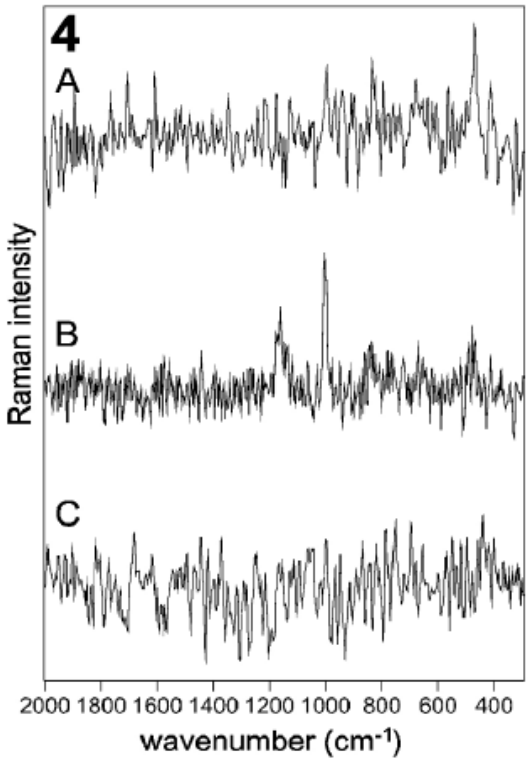
carotenoid



scytonemin

Measurements on powdered sample



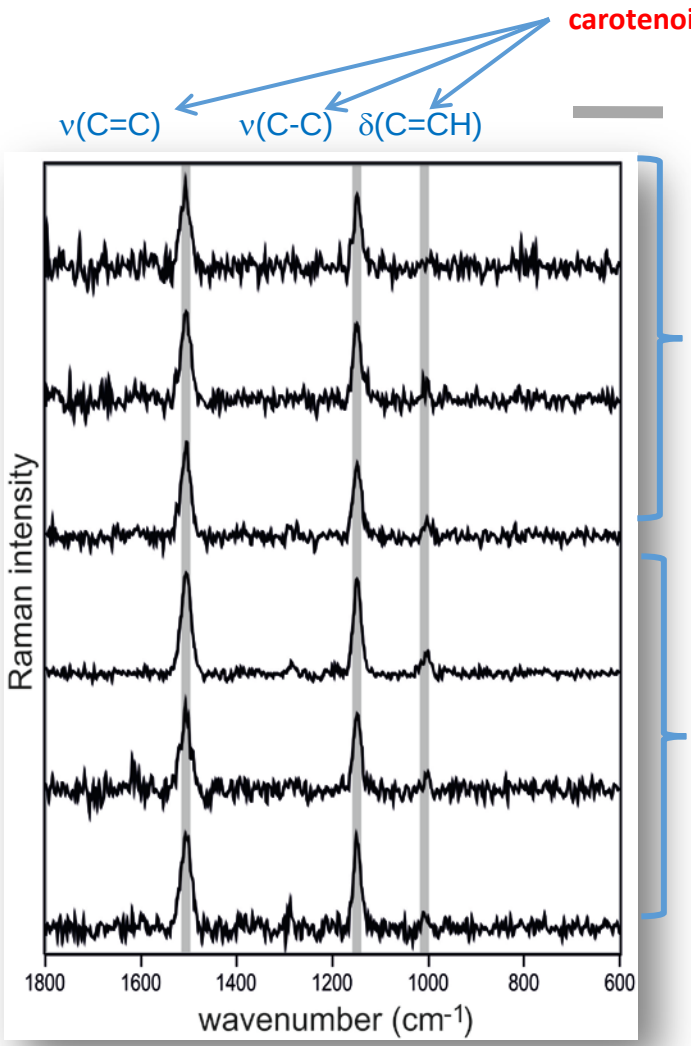


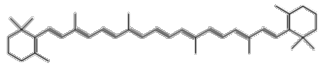
carotenoid

scytonemin

Searles Lake, halite

miniaturized Raman, 532 nm





on the powdered samples

directly on the rock

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Miniaturized Raman instrumentation detects carotenoids in Mars-analogue rocks from the Mojave and Atacama deserts

P. Vítek, J. Jehlicka, H. G. M. Edwards, I. Hutchinson, C. Ascaso and J. Wierzchos

Phil. Trans. R. Soc. A 2014 **372**, 20140196, published 3 November 2014

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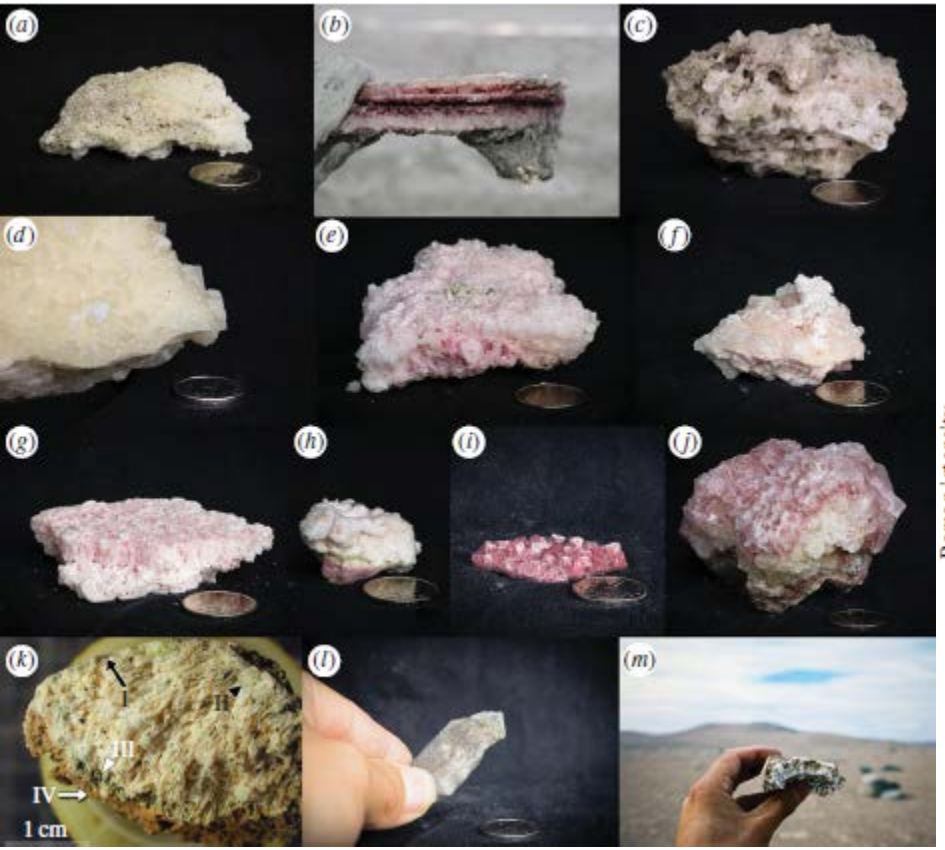
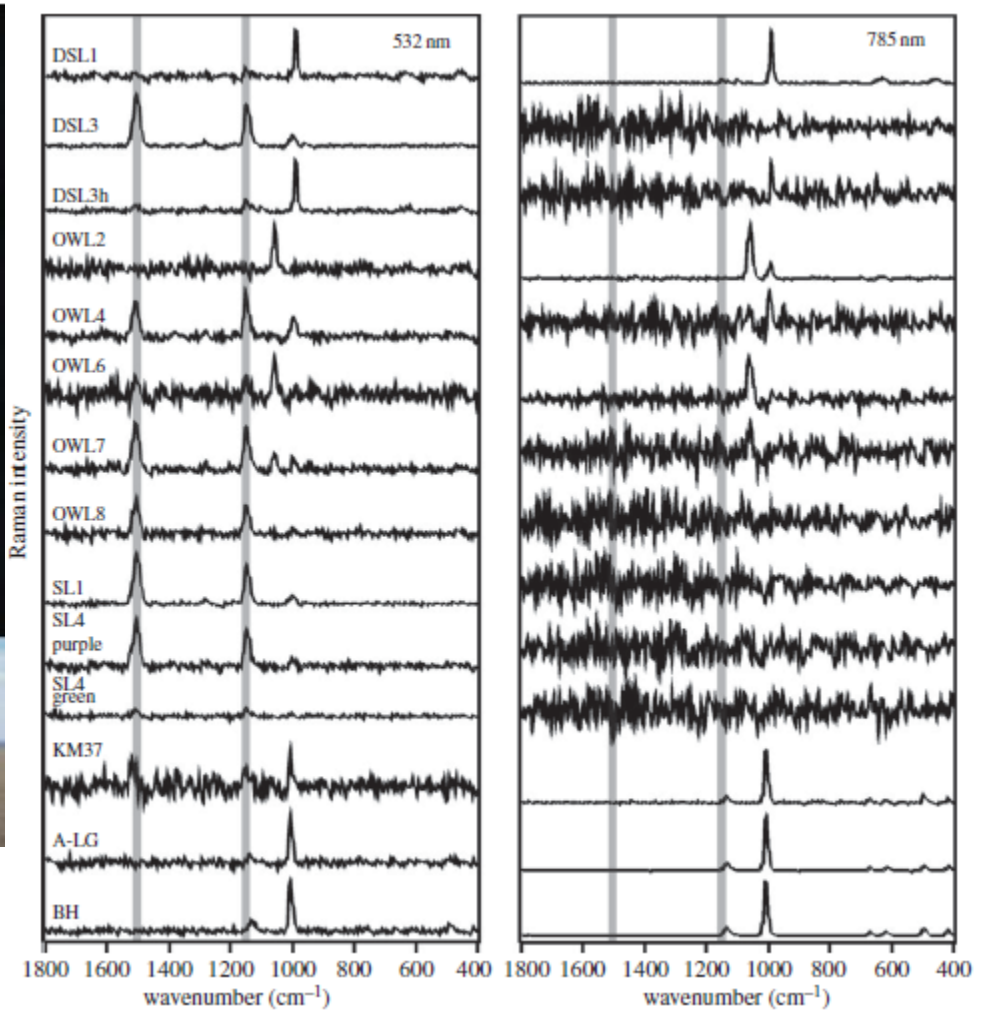
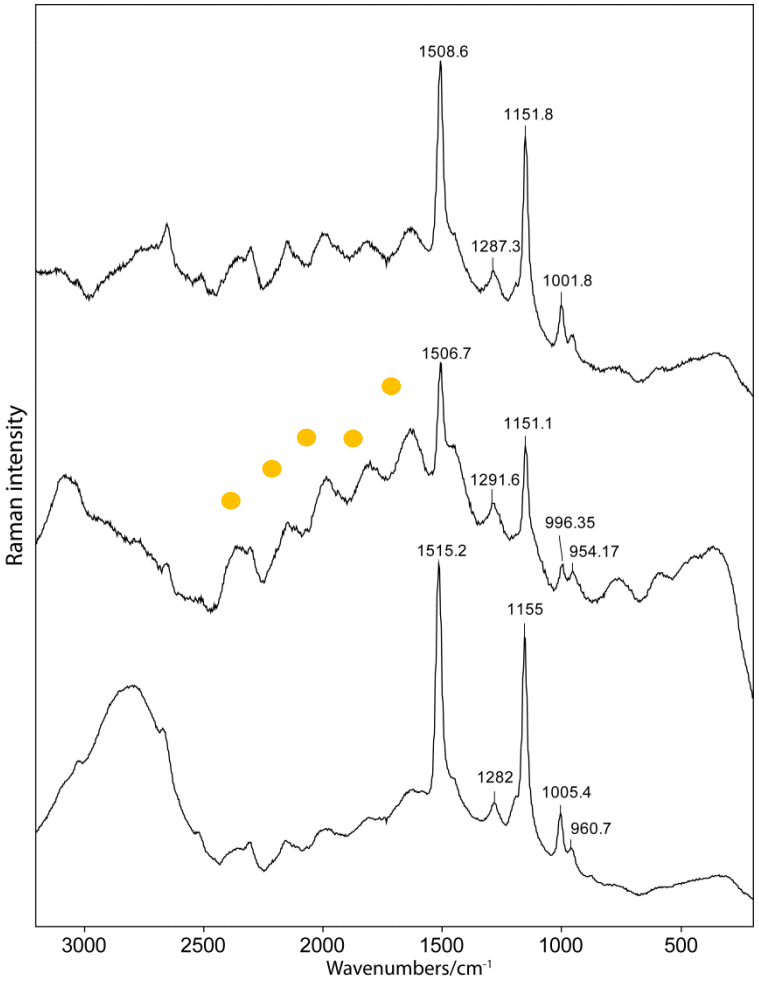

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
I
II
III
IV
1 cm
(l)
(m)


532 nm
785 nm
DSL1
DSL3
DSL3h
OWL2
OWL4
OWL6
OWL7
OWL8
SL1
SL4 purple
SL4 green
KM37
A-LG
BH
Raman intensity
1800 1600 1400 1200 1000 800 600 400
wavenumber (cm−1)
1800 1600 1400 1200 1000 800 600 400
wavenumber (cm−1)

Raman spectra of microfungi pure culture



Rhodosporidium

β-carotene, torulene, torularhodin ????

Rhodotorula glutinis,

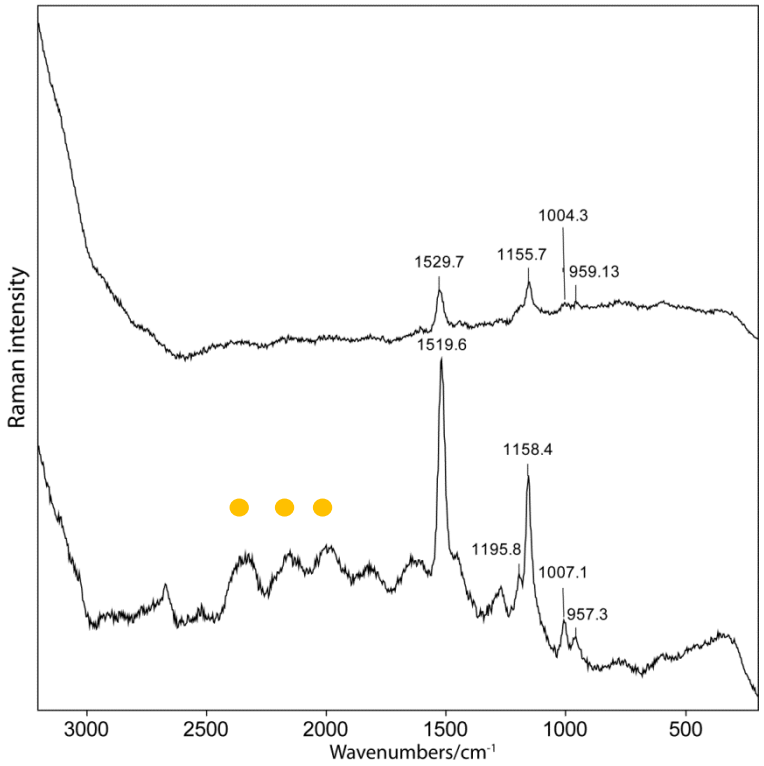
β-carotene, torulene, torularhodin ????

Thelebolus stercoreus

β-carotene

- Instrumental artifacts, Rigaku system

Raman spectra of microalgae pure culture



Botrydiopsis alpina

Lutein, **β-carotene**

Haematococcus pluvialis

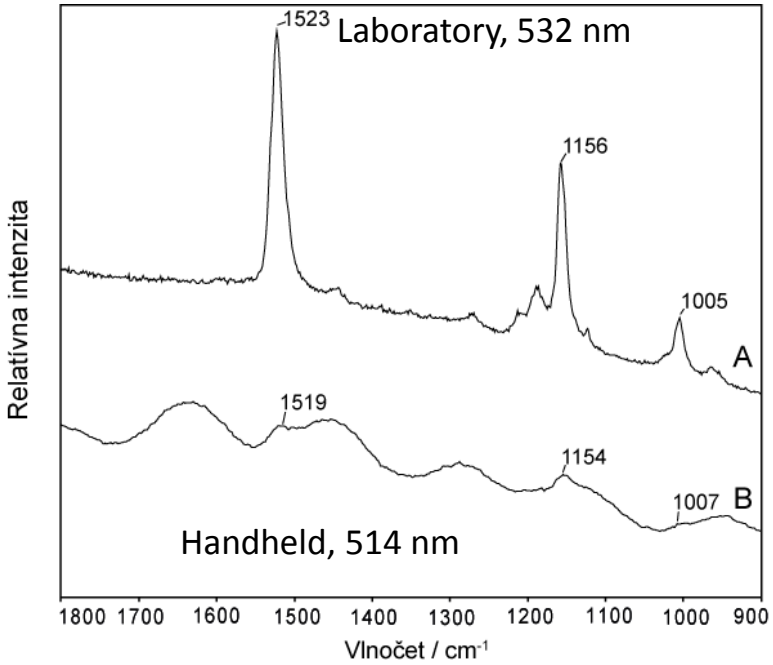
astaxanthin

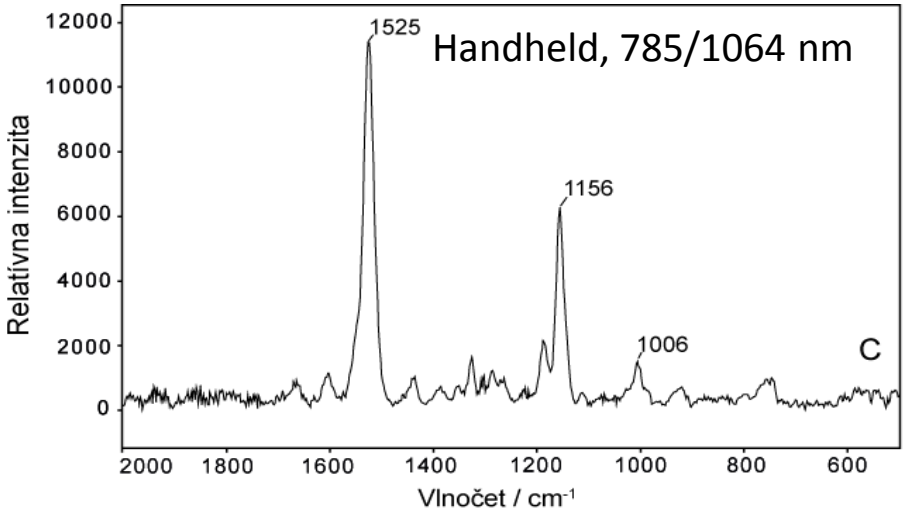
- Instrumental artifacts, Rigaku system

Pigments of lichens

Pseudevernia furfuracea (Modrava - Šumava, hora Medvěd)

Pseudevernia furfuracea (Modrava - Šumava, hora Medvěd)





Pseudevernia furfuracea		
514 nm - A	**532 nm (vlhké) - B**	**700–1100 nm - C**
1523 vs	1519 w	1525 vs
1156 s	1154 w	1156 s
1005 m	1007 vw	1006 m

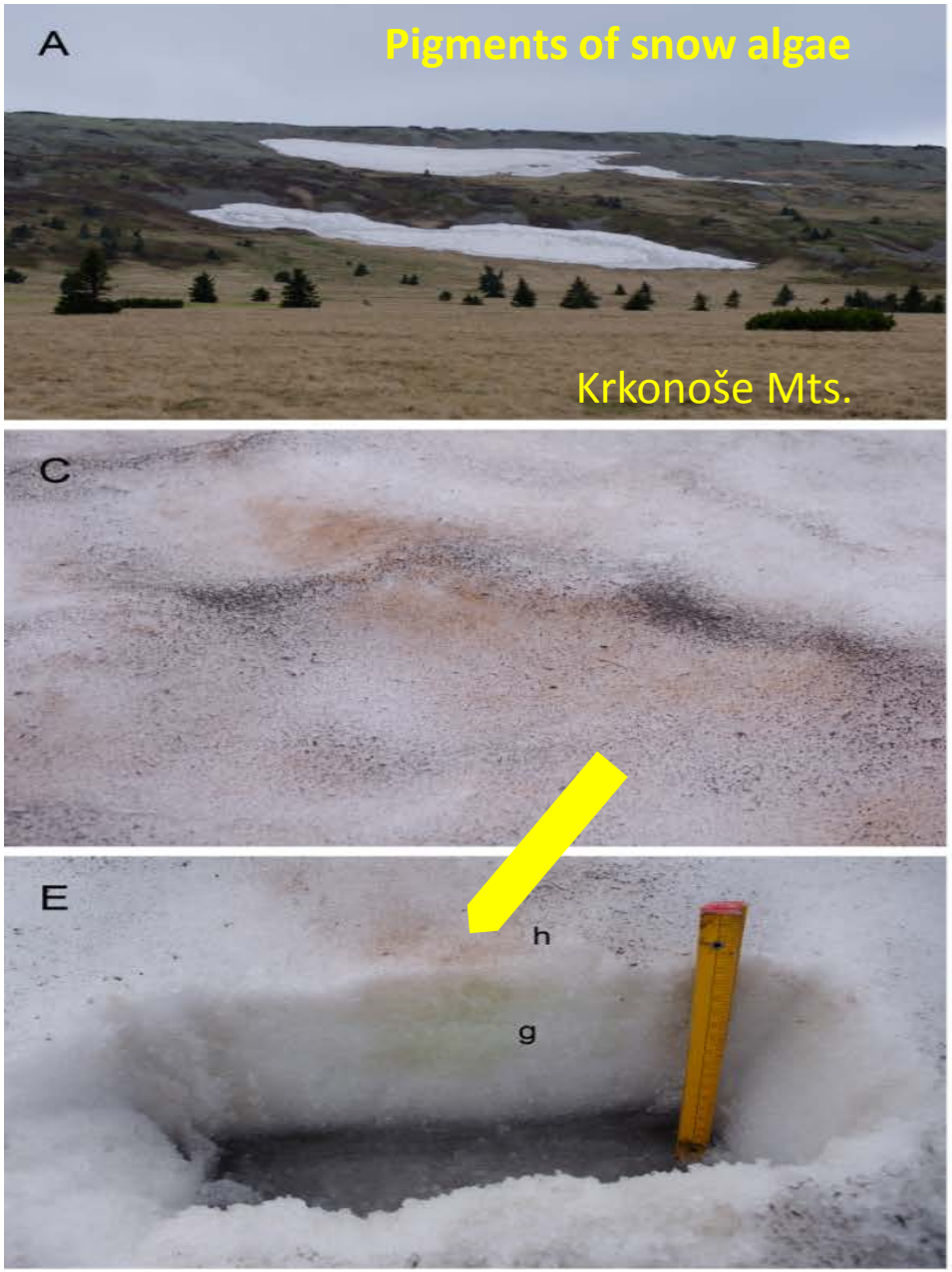
carotenoids……..

Other **pigments** expected – not detected using the current protocol

- chlorophylls, phycobiliproteins

Other **biomarkers** expected – not detected using the current protocol

- chlorophylls, phycobiliproteins



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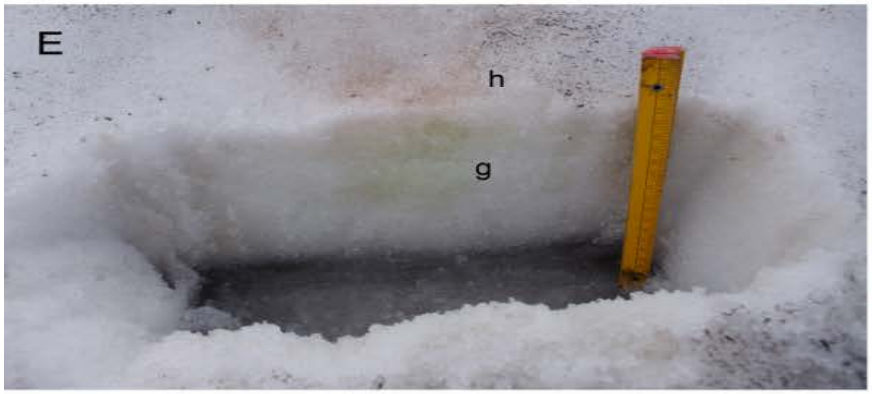

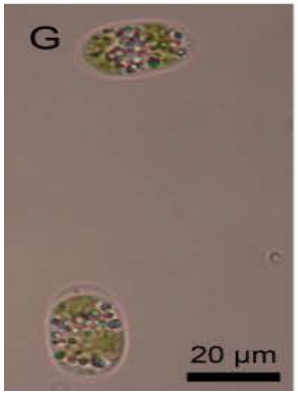

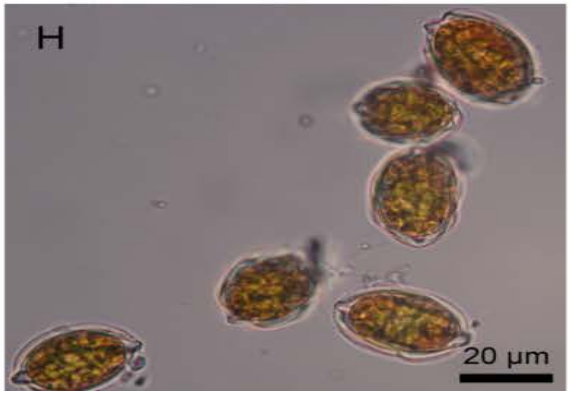

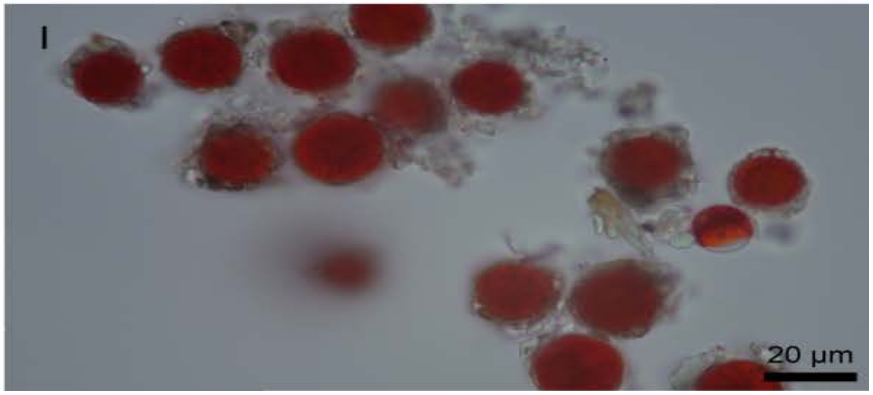

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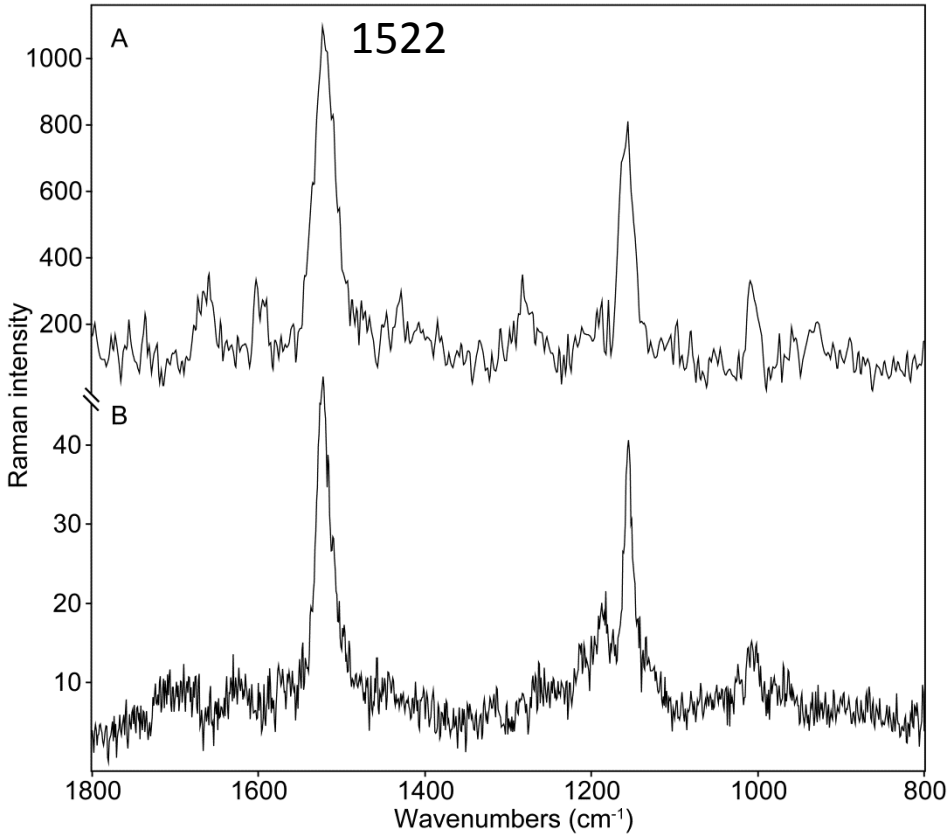
yellow-green snow field with ***Chloromonas nivalis***

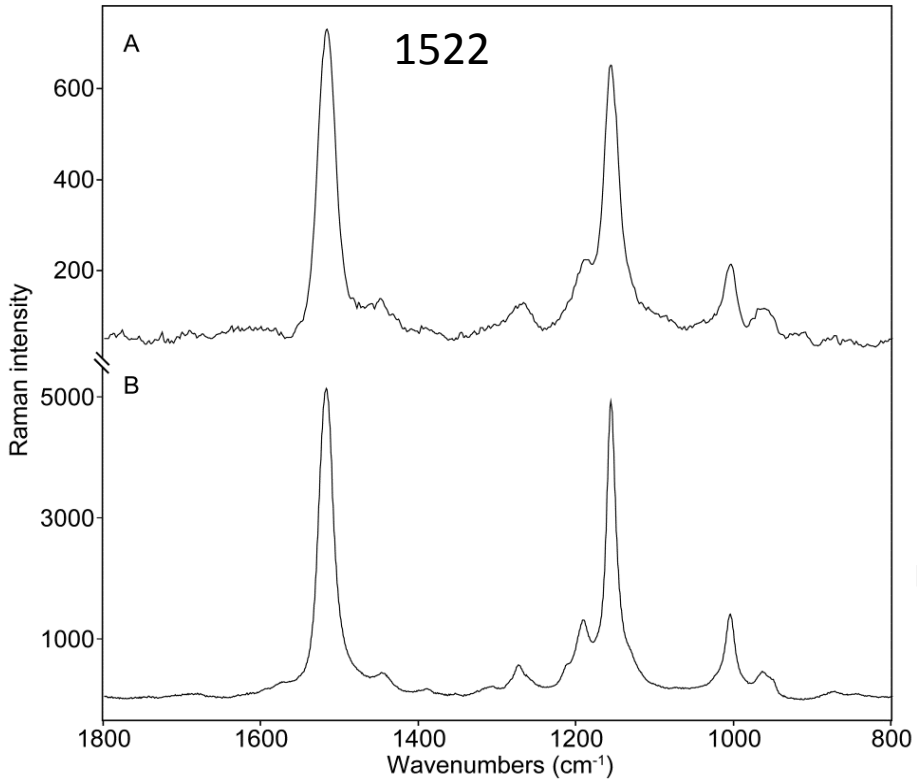


handheld instrument

algal biomass from the melted snow by the laboratory instrument

Krkonoše Mts., β-carotene, chlorophyll/n.i.

snow field containing orange-pink resting stages ***Chloromonas nivalis***

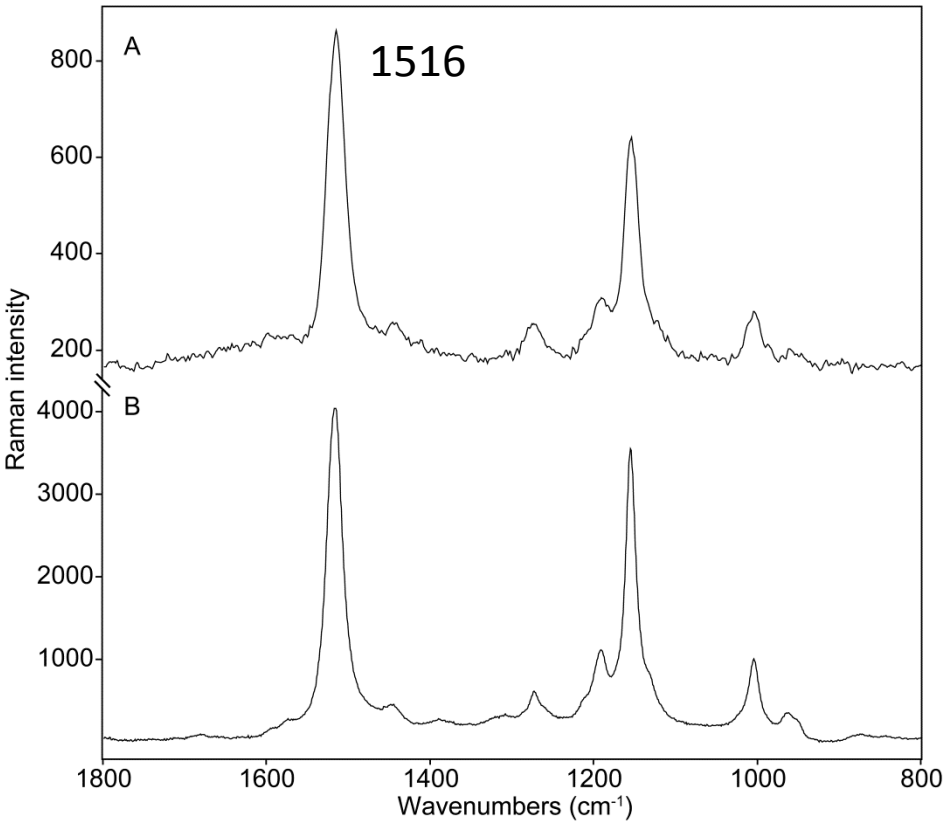


handheld instrument

melted snow by the laboratory instrument

Krkonoše Mts., β-carotene

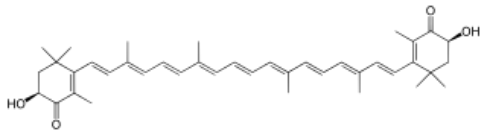
red-violet snow field ***Chlamydomonas* cf. *nivalis*** resting stages



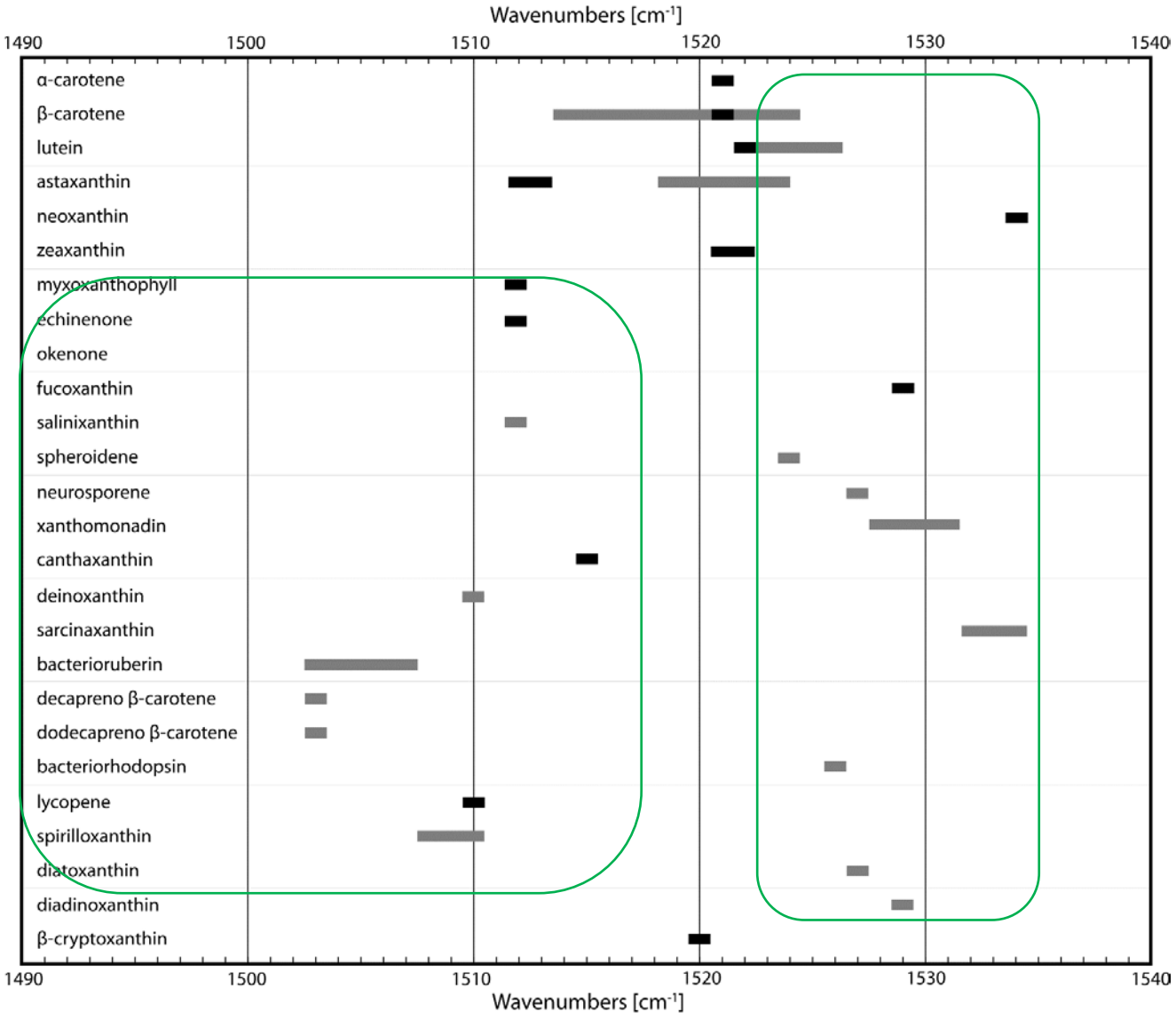
handheld instrument

algal biomass from the melted snow by the laboratory instrument

Rettenbach Glacier, Alps, astaxanthin



Positions of the ν_1 (C=C) bands of carotenoids



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
rsta.royalsocietypublishing.org
Research

Potential and limits of Raman spectroscopy for carotenoid detection in microorganisms: implications for astrobiology

Jan Jehlička[2], Howell G. M. Edwards[2], Katefina Osterrothová[3], Julie Novotná[3], Linda Nedbalová[3], Jiří Kopecký[4], Ivan Němec[5] and Aharon Oren[6]

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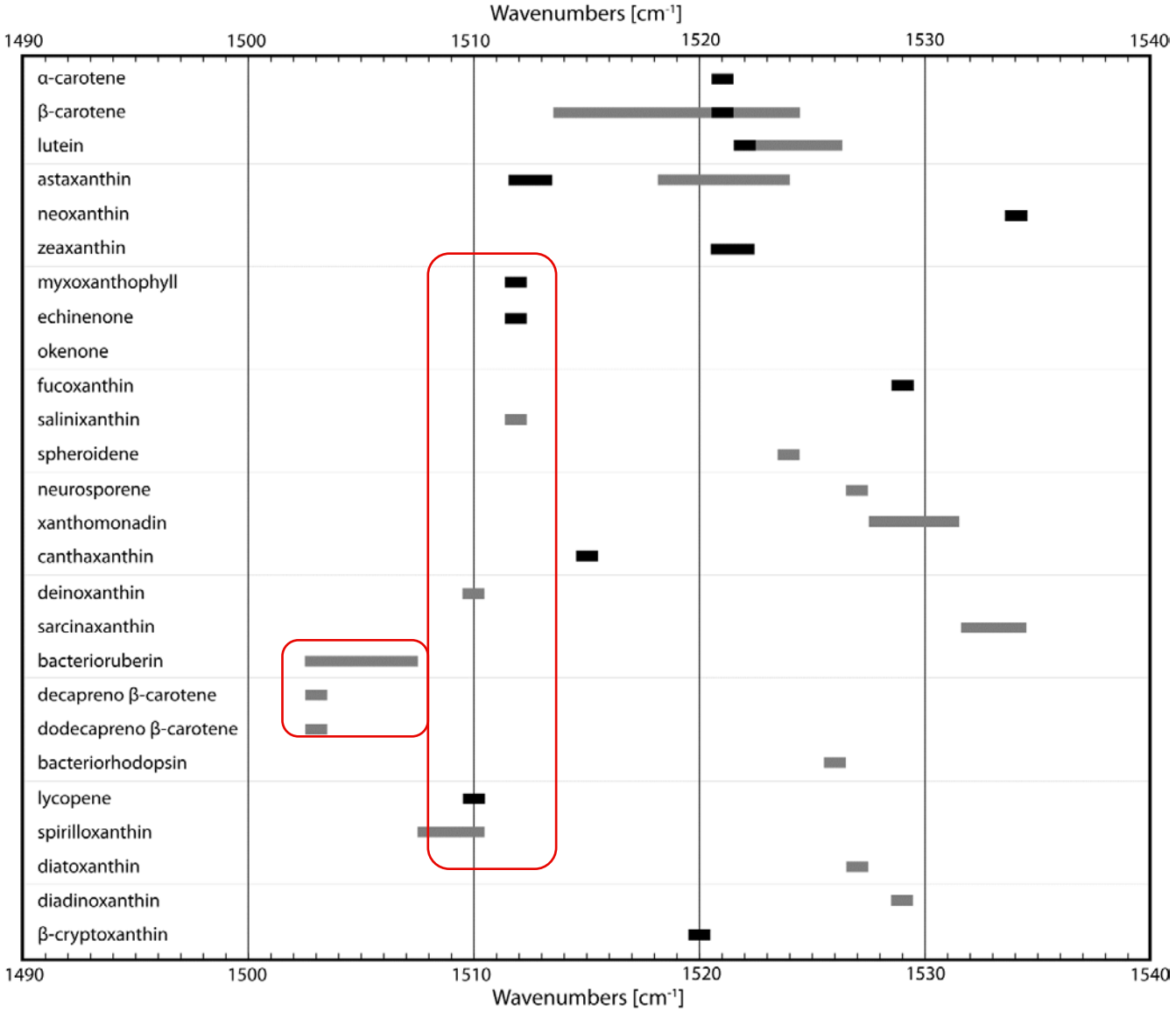
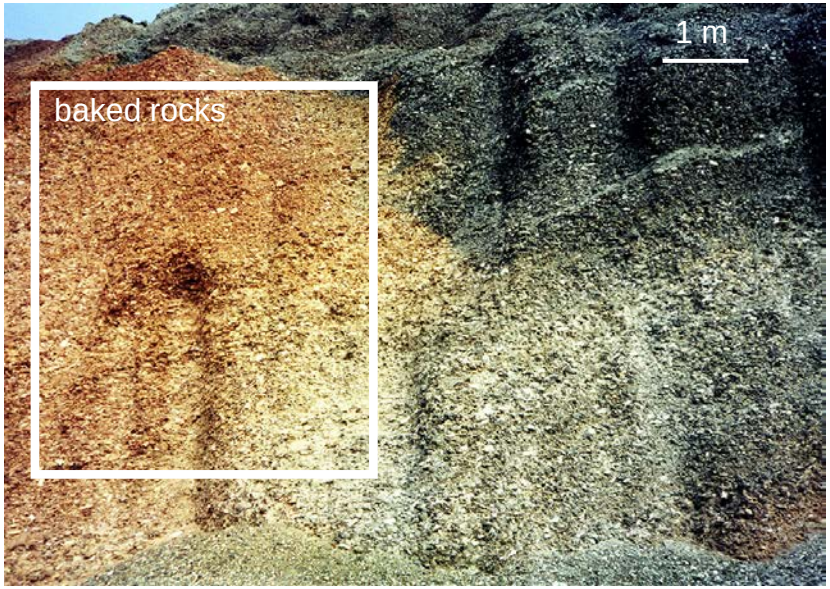
Positions of the ν_1 (C=C) bands of carotenoids



Burning coal heaps

Heřmanice Dump, Ostrava, Czech Republic

Coal fire mineralogy



Kateřina coal-waste pile, Bohemia, 2001 (Klika and Martinec, 2012)

high temperature (~1000 °C)

➔ pyrometamorphism

➔ silicates and oxides

production of toxic and aggressive gas

(SO_2, H_2S, NH_3, HCl, CO_2, CO, org. components)

➔ mineral nucleation around gas vents

Gas vents (GV) mineralogy = pseudofumaroles

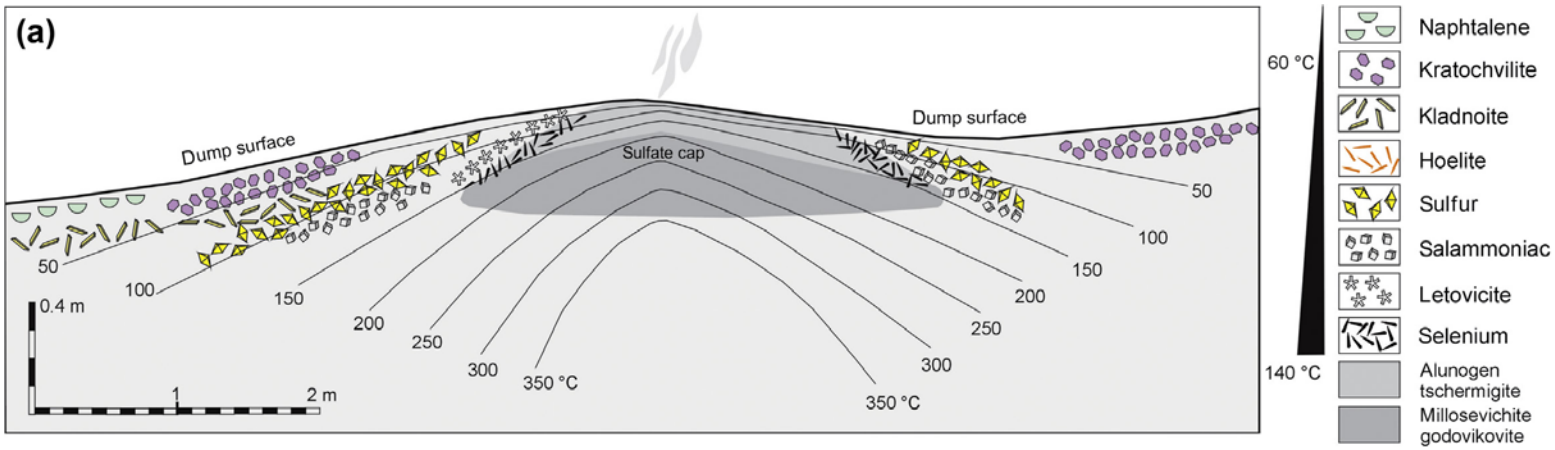
- mineral occurrence driven by **temperature**, time, rock and gas composition

Douro coal field, Portugal, 2007 (Ribeiro et al., 2012)

unique mineralization:

- sulfur and other native elements
- halides and sulfates of ammonia, Fe, Al, Mg, Ca, K and Na, hydrous or anhydrous
- organic compounds

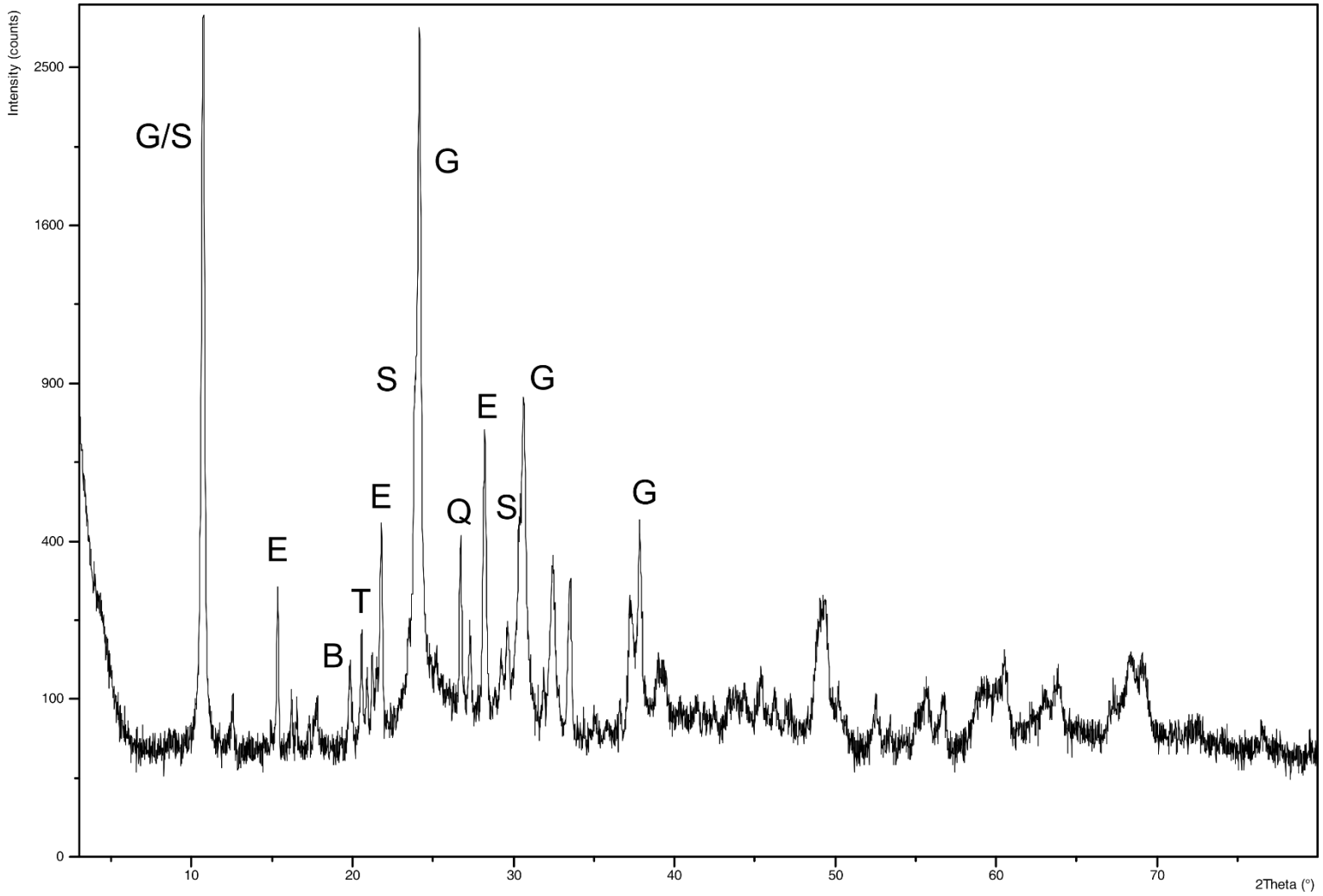
~ comparable with volcanic areas



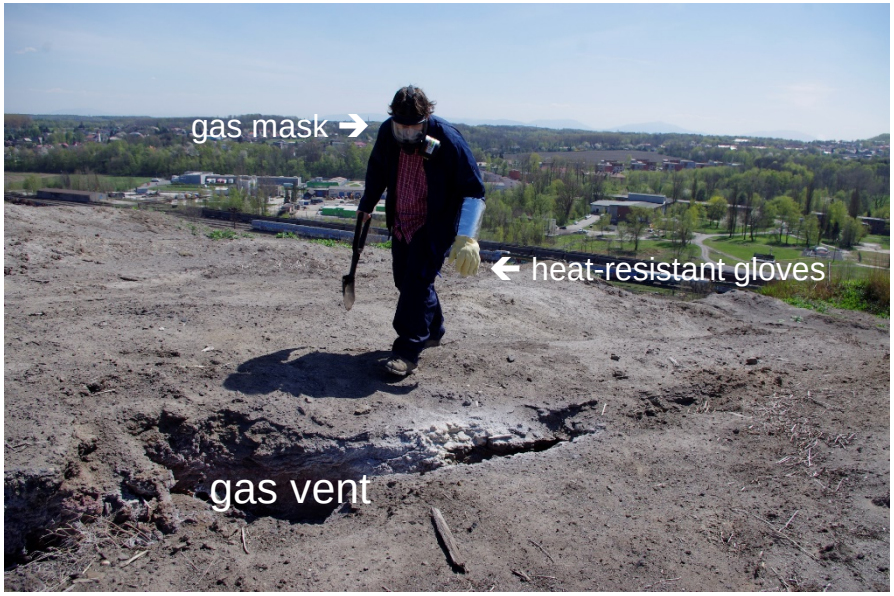
Shoeller Mine near Kladno, Bohemia (Žáček and Skála, 2014)

XRD record of the mixture:

godovikovite, efremovite + sabieite, tschermigite, boussingaultite and quartz



(G) – godovikovite; (E) – efremovite; (S) – sabieite; (T) – tschermigite; (B) – boussingaultite; (Q) - quartz



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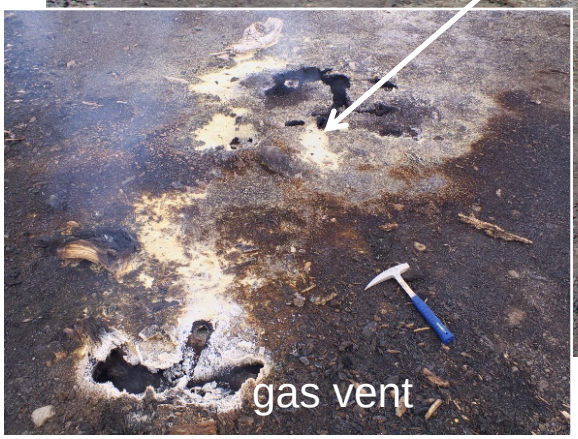
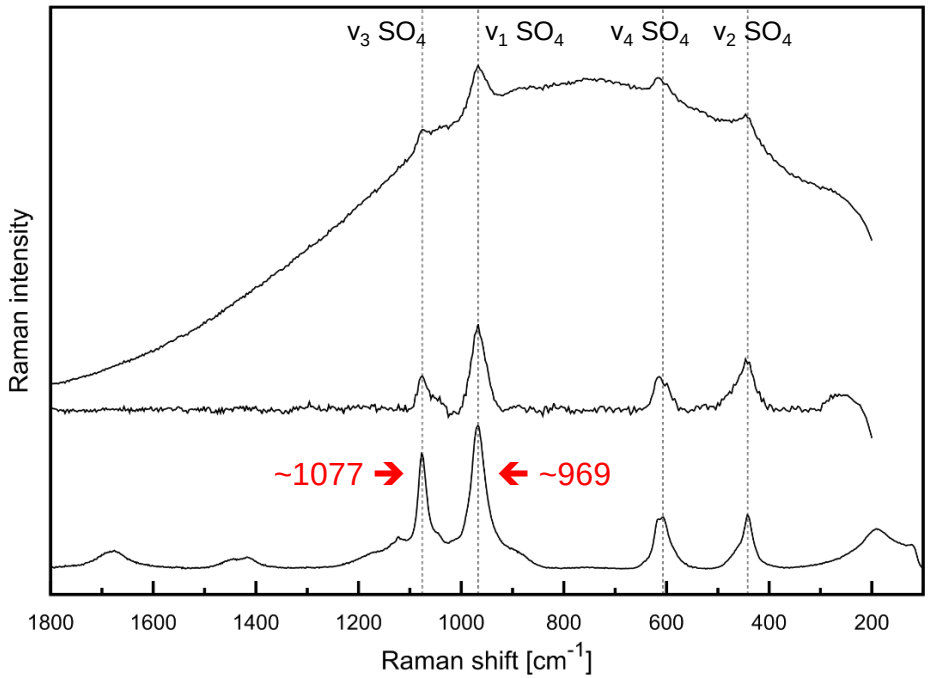
fumarole field on the top

sublimates



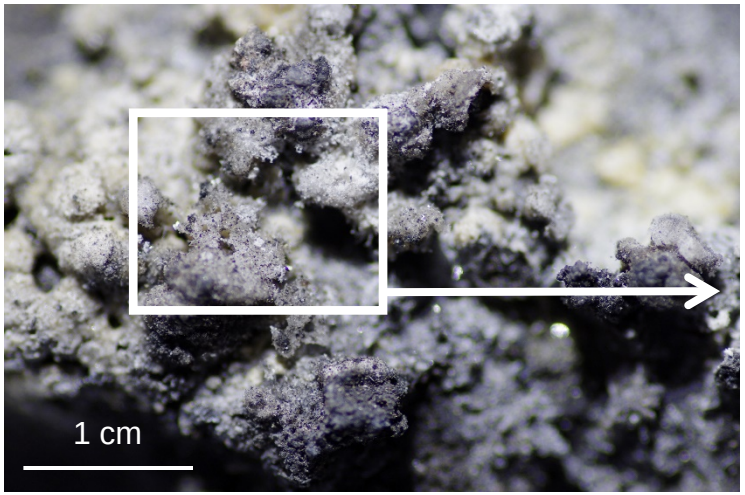
Letovicite $(NH_4)_3H(SO_4)_2$

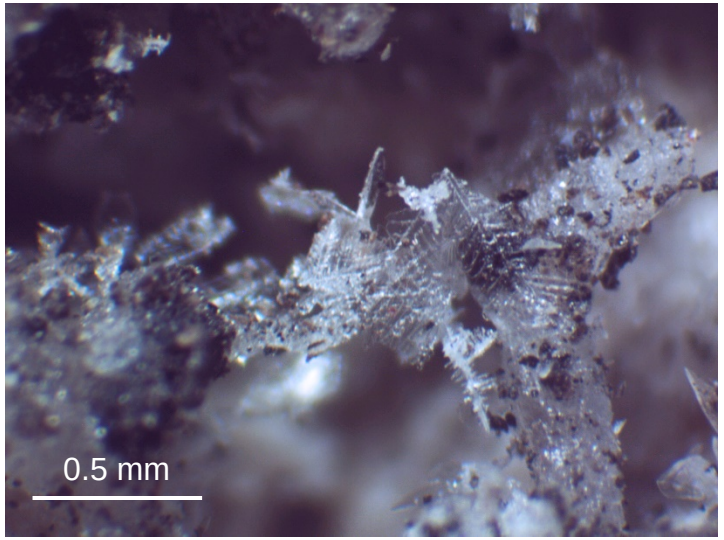


← field raw (DeltaNu)

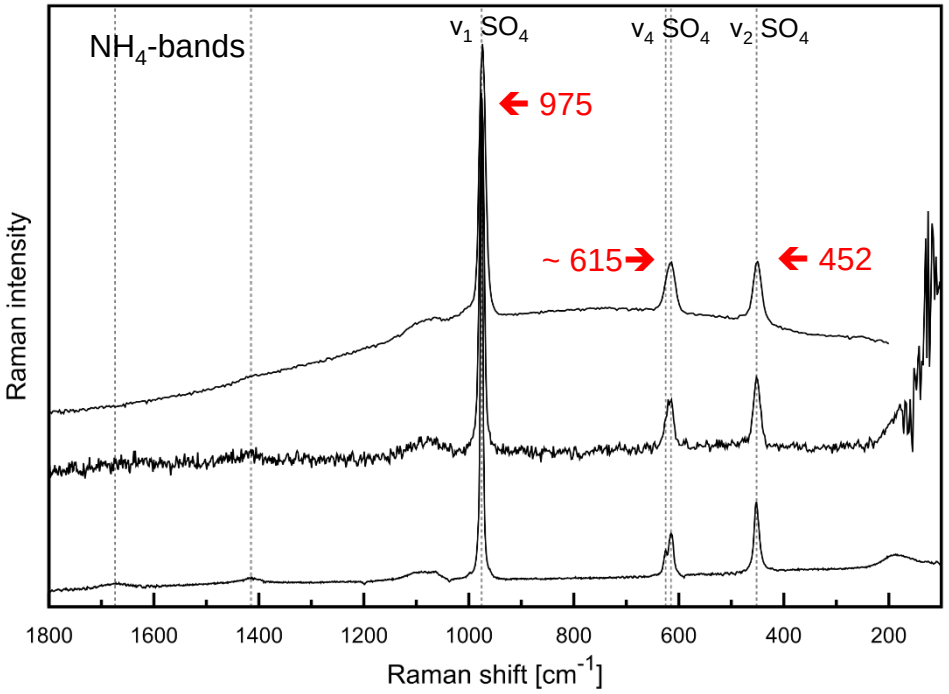
← field corrected (DeltaNu)

← laboratory





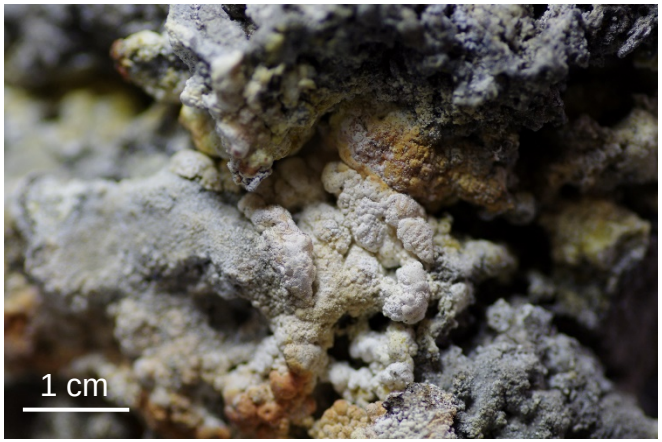
Mascagnite NH_4SO_4



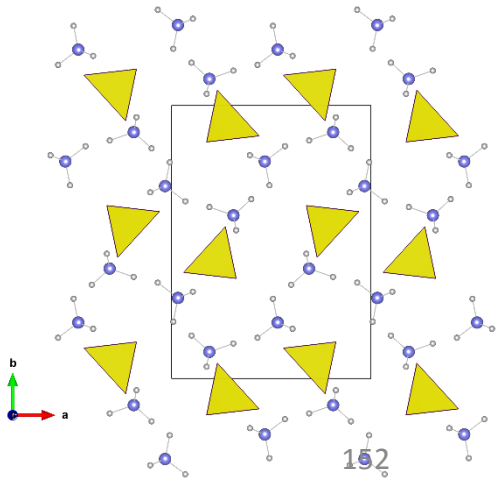
← field raw (DeltaNu)

← field raw (ThermoScientific)

← laboratory



Schlemper and Hamilton, 1966



- Raman spectroscopy – miniatures for mineralogy, exobiology

- Pigments

- Carotenoids

- Detection of phases, carotenoids

- Discrimination of very similar carotenoids

Thanks to

Howell G.M.Edwards

Peter Vandenabeele

Petr Vítek

Adam Culka

Filip Košek

Michal Kovacs

Kateřina Osterrothová

Ivan Němec

Julie Novotná

Jacek Wierzchos

Rachel Bardavid Lewi

Linda Nedbalová

Lilly Mana

Pavel Bašta

Danilo Bersani

Germana Barone

Jiří Kopecký

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