Raman Spectroscopy in Analytical Astrobiology

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Are we alone… ?

Origin of the Science of Astrobiology

Astrobiology : 1950s
Exobiology : Lederberg , Science ,1960
Bioastronomy : ISSOL , 1990s
Exo/Astrobiology : Compromise – Brack , Horneck and Wynn-Williams , OLEB, 2001
Cosmobiology : EANA, Tokyo , 1998
Astrobiochemistry : not adopted

Astrobiology:

- Astrochemistry
- Astronomy
- Biogeological chemistry
- Remote analytical techniques
- Astrophysics
- Planetology
- Geology
- Palaeontology
- Biology
- Chemistry
- Space engineering
- Meteoritics
- Extreme environments
- Microbiology

"Astrobiology – A New Science for the New Millennium" (Lord Sainsbury , 2000)

Targets :

Solar System – Mars – prime target , planet

Titan– satellite of Saturn

Europa– satellite of Jupiter

Venus , Mercury – too hostile

Renaissance astrobiologists :

Giordano Bruno

Tycho Brahe

Key definition:

What is life?

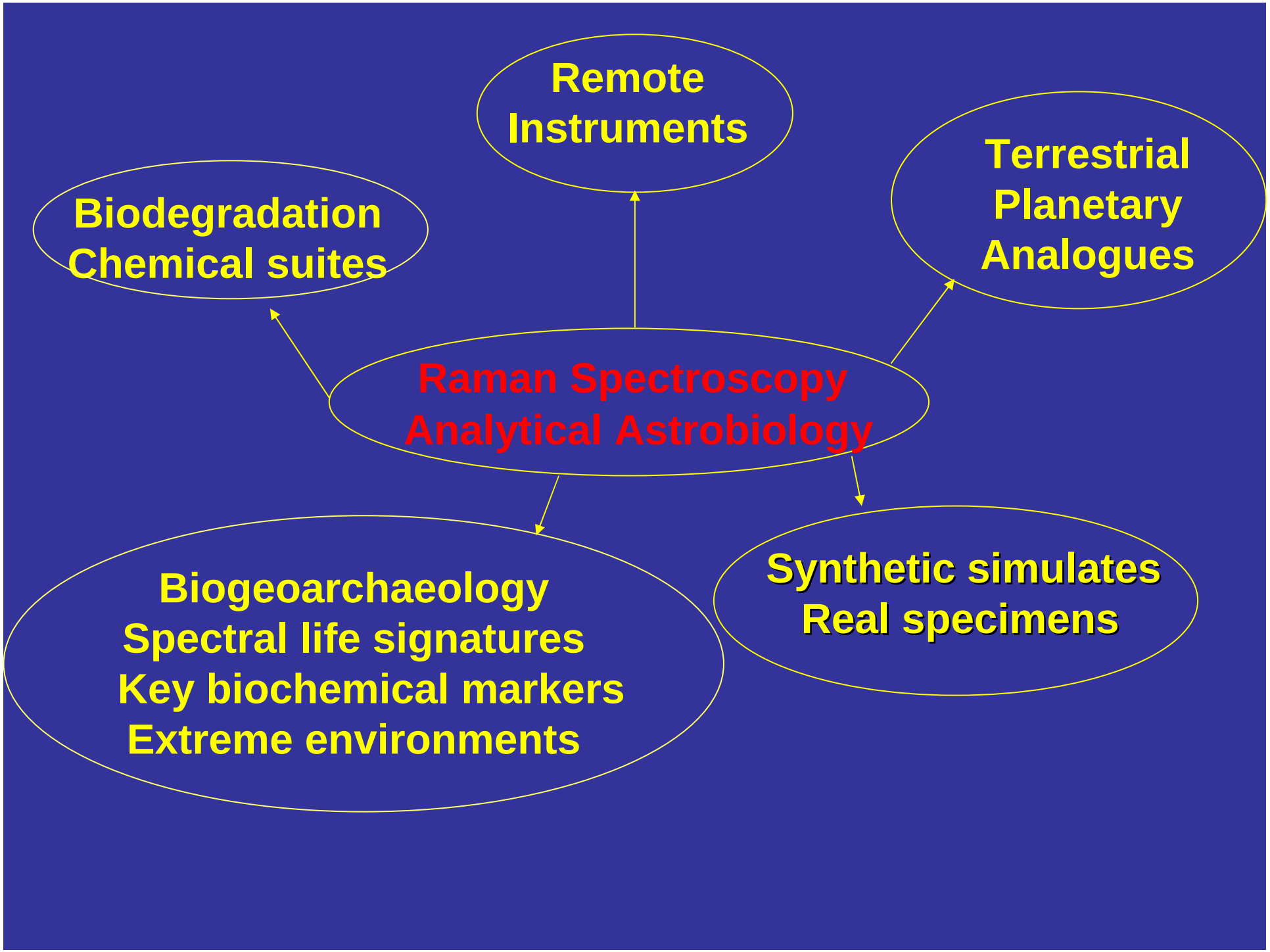
NASA

A self-replicating biological assembly capable of evolution and adaptation to change

How can we recognise life ?

Through the detection of biomarker molecules which are unique to extant or extinct life

Raman spectroscopy and biomolecular spectral signatures


Remote
Instruments
Biodegradation
Chemical suites
Terrestrial
Planetary
Analogues
Raman Spectroscopy
Analytical Astrobiology
Biogeoarchaeology
Spectral life signatures
Key biochemical markers
Extreme environments
Synthetic simulates
Real specimens

Questions for Analytical Raman Spectroscopic Application to Astrobiology

- What materials are present ?
- How much of each component is present ?
- Where did the source materials originate ?
- What changes have taken place with time ?
- What can we use today to simulate the specimen
- Is there evidence of adaptation ?
- Recognition of key spectral biomarker signatures ?

Analytical Raman Spectroscopy and Terrestrial Analogues

- Extreme environments : hot and cold deserts, salterns , caves , volcanoes, mines, deep ocean smokers, geysers, thermal springs , crystal inclusions , natural glasses (desert glasses, fulgurites, volcanic basalts) .

- Laboratory bench , microscopic and miniaturised instrumentation ; recognition of biomarker signatures, database constructiuon .

- In field studies in deserts , salterns , hot and cold locations , glaciers , high and low altitudes, impact craters .

Terrestrial Analogue Sites for Planetary Exploration

- Atacama Desert
- Negev Desert / Dead Sea
- Atlas Mountains /Mauretania
- Arctic/Svalbard
- Antarctic/Dry Valleys
- Glaciers
- Meteorite Impact Craters
- Rio Tinto
- Bahamas Trench
- Death Valley
- Yellowstone National Park

The Terrestrial Record

Clues to extinct or extant life are contained in the geological record

- **Extremophilic organisms colonised early Earth**
- **Geological protective niches**
- **Chemical survival strategies – analytical chemistry – the preservation of biochemicals in the terrestrial geological record**

Extremophile : an organism that can survive
where humans cannot –achieved through the synthesis of a suite of protective chemicals and adaptation of their geological host matrix

The Key to Extremophile Behaviour

“ What doesn’t kill us makes us stronger”

Friedrich Nietzsche

"But with regard to the material world, we can at least go so far as this—we can perceive that events are brought about not by insulated interpositions of Divine power, exerted in each particular case, but by the establishment of general laws."

W. Whewell: *Bridgewater Treatise.*

"To conclude, therefore, let no man out of a weak conceit of sobriety, or an ill-applied moderation, think or maintain, that a man can search too far or be too well studied in the book of God's word, or in the book of God's works; divinity or philosophy; but rather let men endeavour an endless progress or proficience in both."

Bacon: *Advancement of Learning.*

Down, Bromley, Kent,
October 1st, 1859.

ON

THE ORIGIN OF SPECIES

BY MEANS OF NATURAL SELECTION,

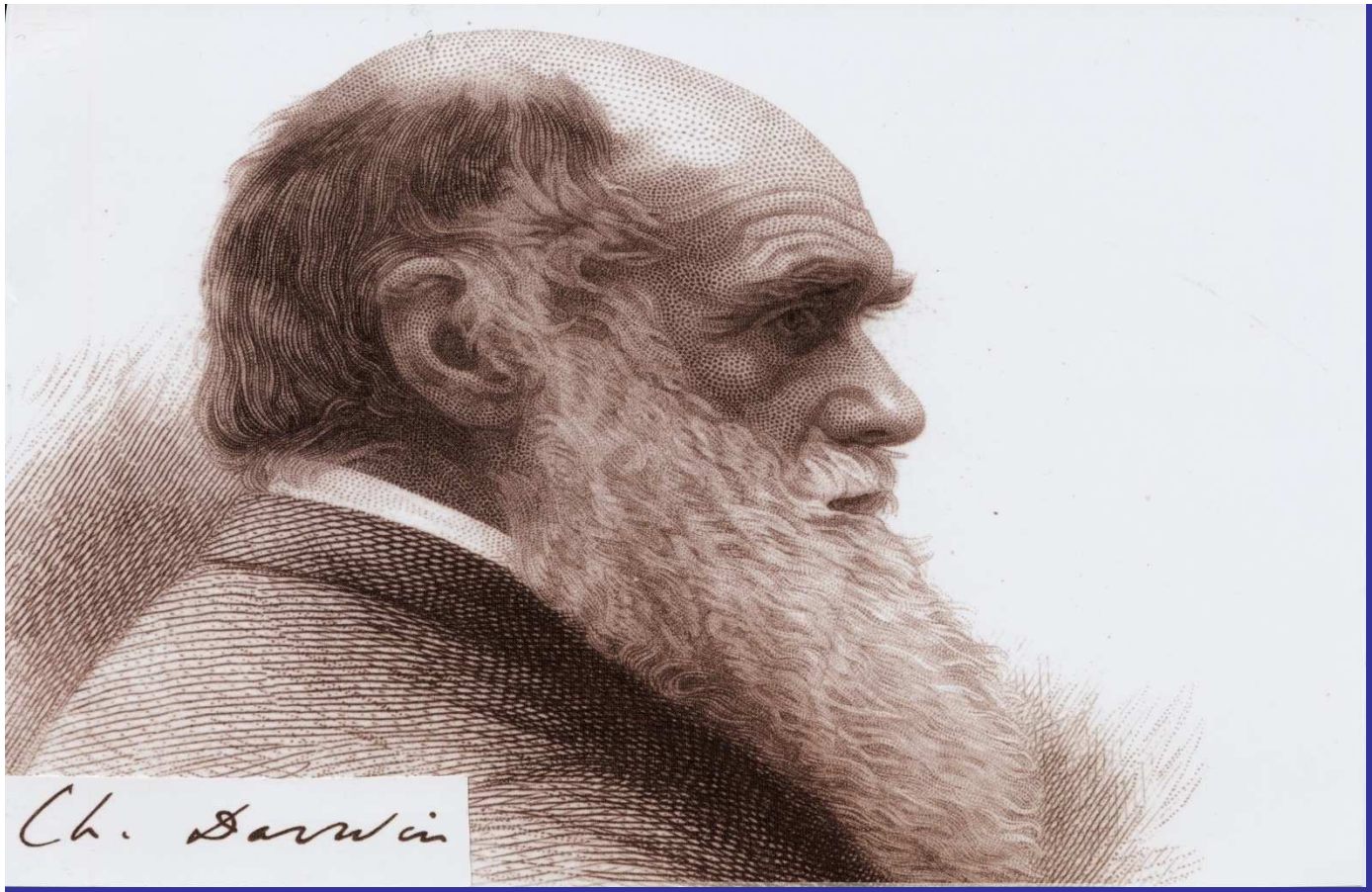
OR THE

PRESERVATION OF FAVOURED RACES IN THE STRUGGLE FOR LIFE.

By CHARLES DARWIN, M.A.,

FELLOW OF THE ROYAL, GEOLOGICAL, LINNÆAN, ETC., SOCIETIES;
AUTHOR OF 'JOURNAL OF RESEARCHES DURING H. M. S. BEAGLE'S VOYAGE ROUND THE WORLD.'

LONDON:
JOHN MURRAY, ALBEMARLE STREET.
1859.



2009 : Bicentenary of Darwin's birth
Sesquicentenary of publication of
The Origin of Species by Natural Selection , 1859

Adaptation to environment is the key to species survival

Evolution only mentioned in 6th Edition , 1879 , p.358

Raman spectroscopy

Laser based analytical technique
Fingerprinting molecular functionality
Organic and inorganic materials (together !)
Water and glass insensitive
Micro and remote capability
Nondestructive – first pass analysis
Databases of minerals and biomaterials
Variable wavelength excitation of laser
Linearity between Raman signal and species concentration

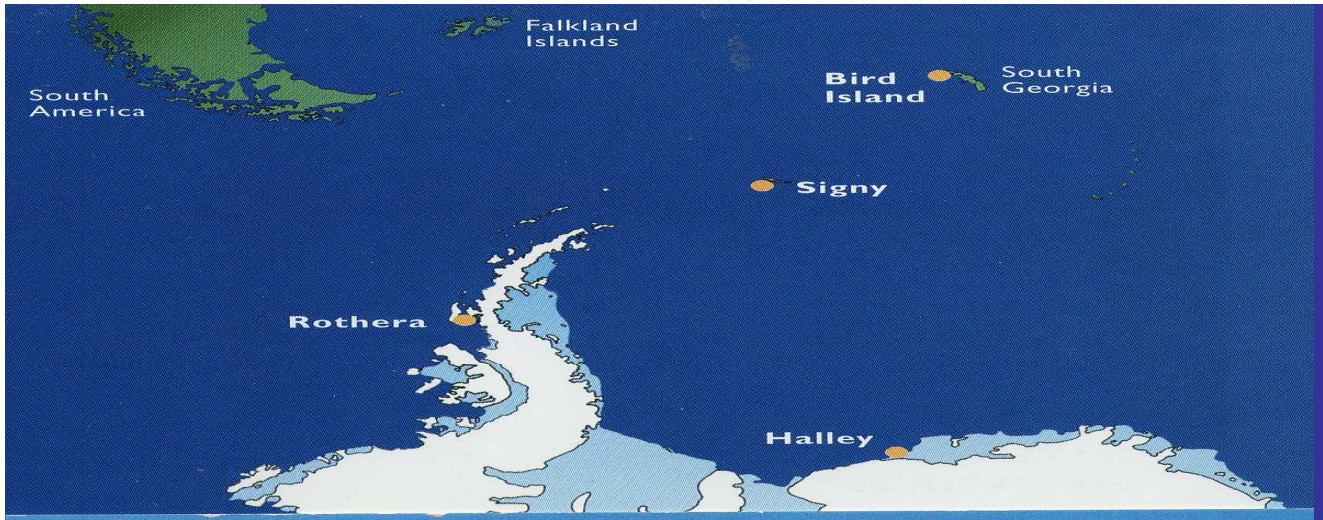
Effect of Cation on Raman Anion Bands

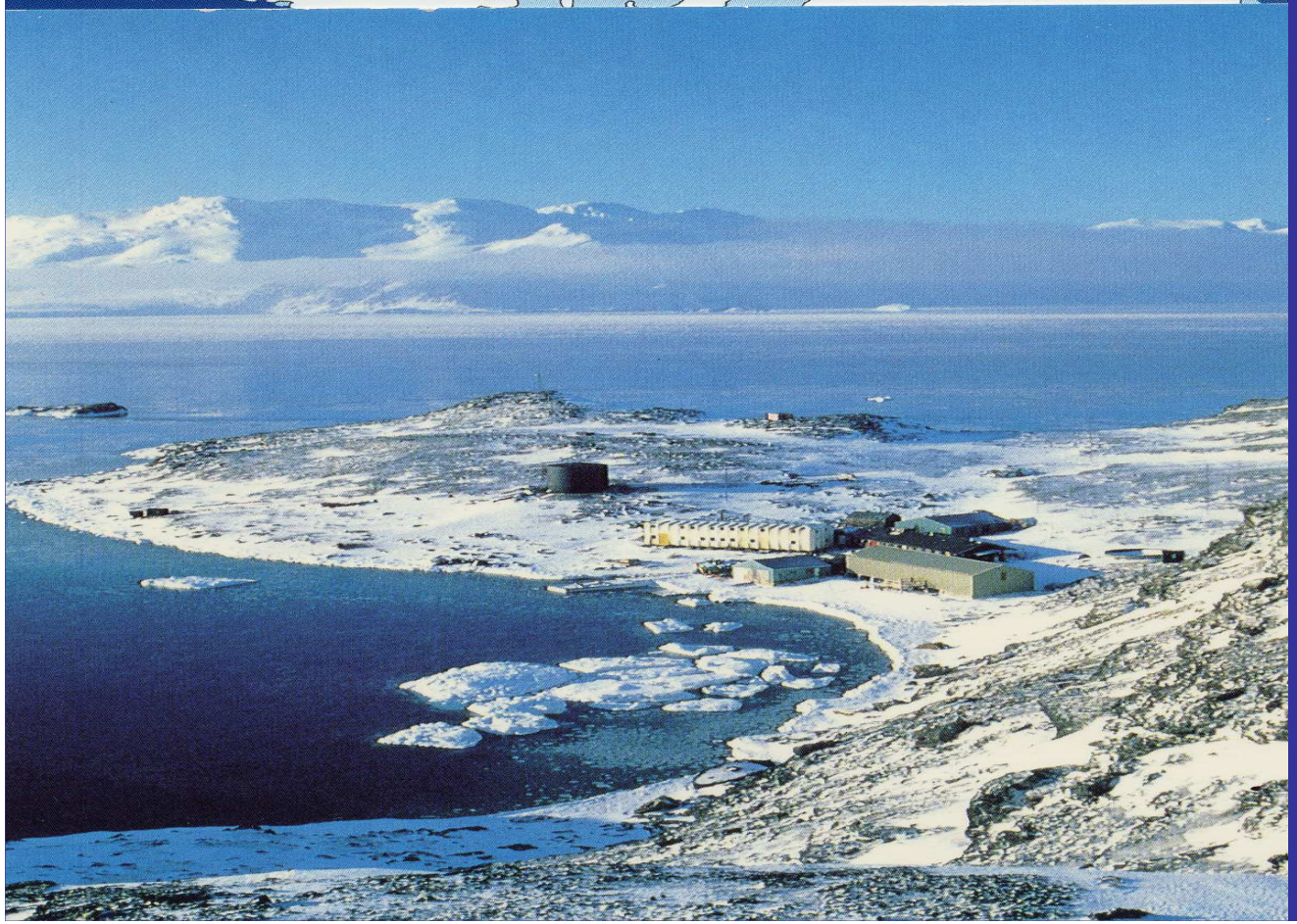
- Calcium carbonate 1086 cm^{-1}
- Dolomite 1094 cm^{-1}
- Magnesite 1117 cm^{-1}

Environment and structure affects observed stretching band wavenumber of carbonate, despite Ca and Mg not being active in the Raman effect

PHYSICAL LIMITS FOR LIFE ON EARTH

Parameter	Limiting Conditions	Type of Organism
Water	Liquid water required	
Temperature	-2°C (31.8 F) minimum	Psychrophiles
	50-80°C (122-176 F)	Thermophiles
	80-115°C (176-239 F)	Hyperthermophiles
Salinity	15-37.5 % NaCl	Halophiles
pH	0.7-4	Acidophiles
	8-12.5	Akalophiles
Atmospheric pressure	up to 110 Mpa	Barophiles





Signy Island , Maritime Antarctica

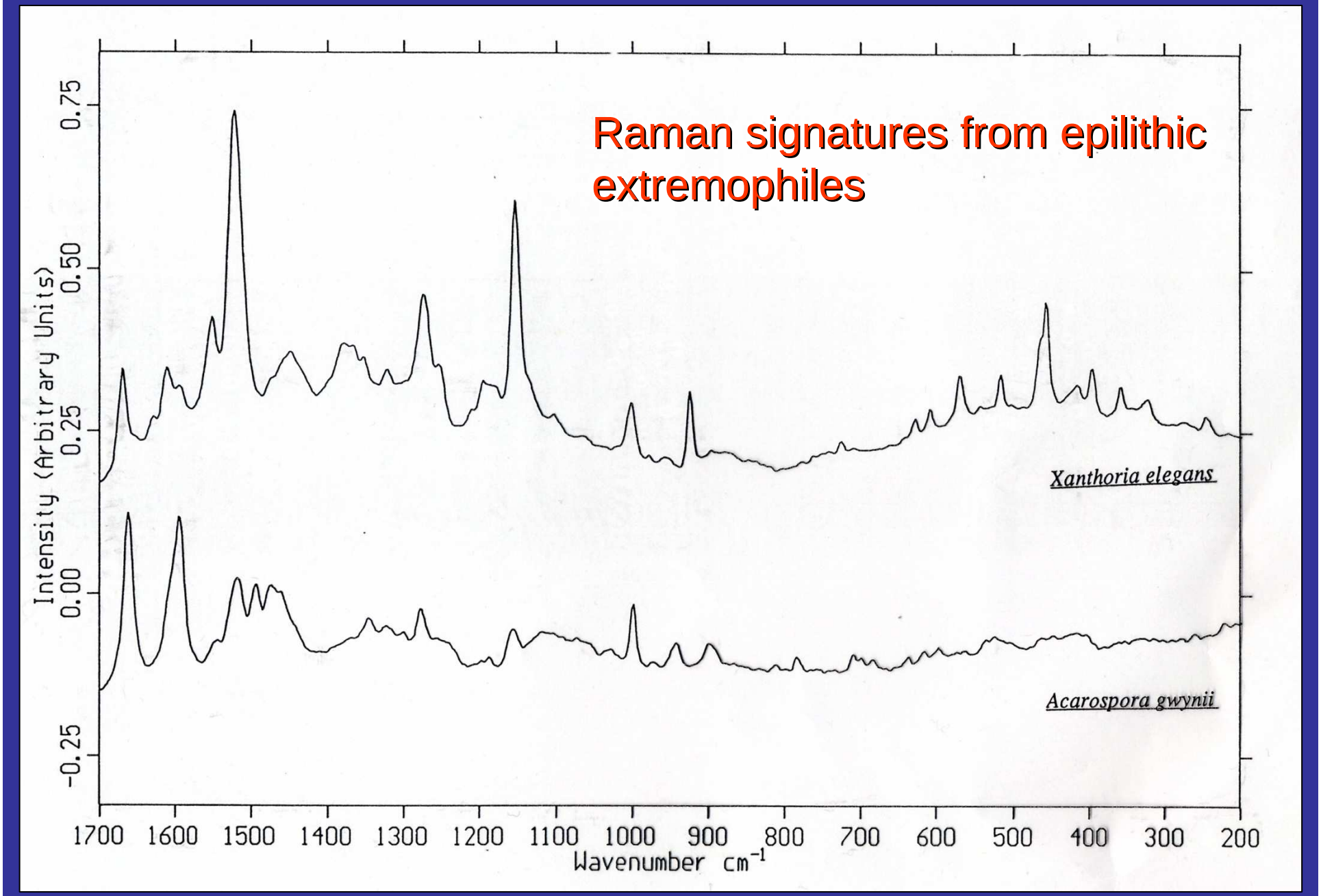
Epilithic lichens : Antarctic Extremophiles

Acarospora gwynii (yellow)

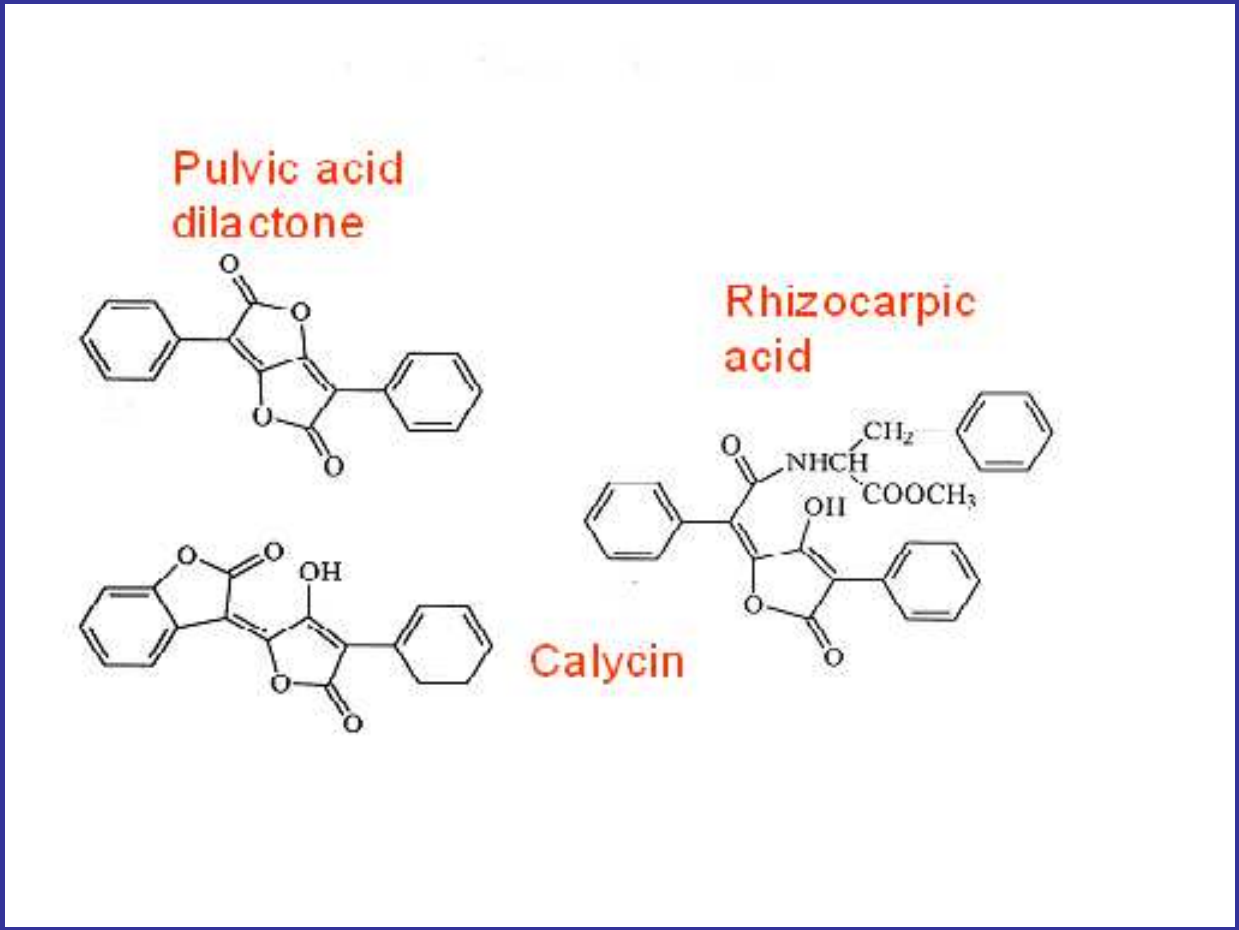
Xanthoria elegans (orange-red)

- Signy Island, Maritime Antarctica

Raman signatures from epilithic extremophiles

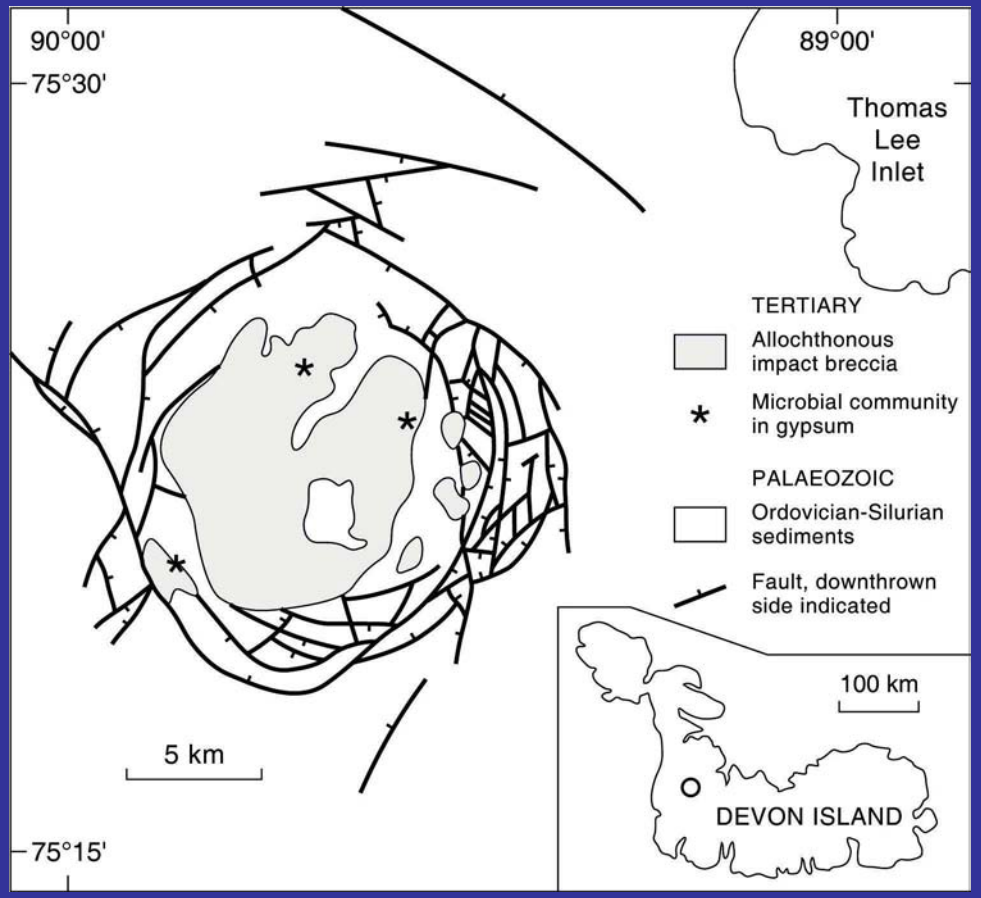


Radiation Protective Chemicals in Desert Epiliths



Haughton Crater

Devon Island , Canadian Arctic



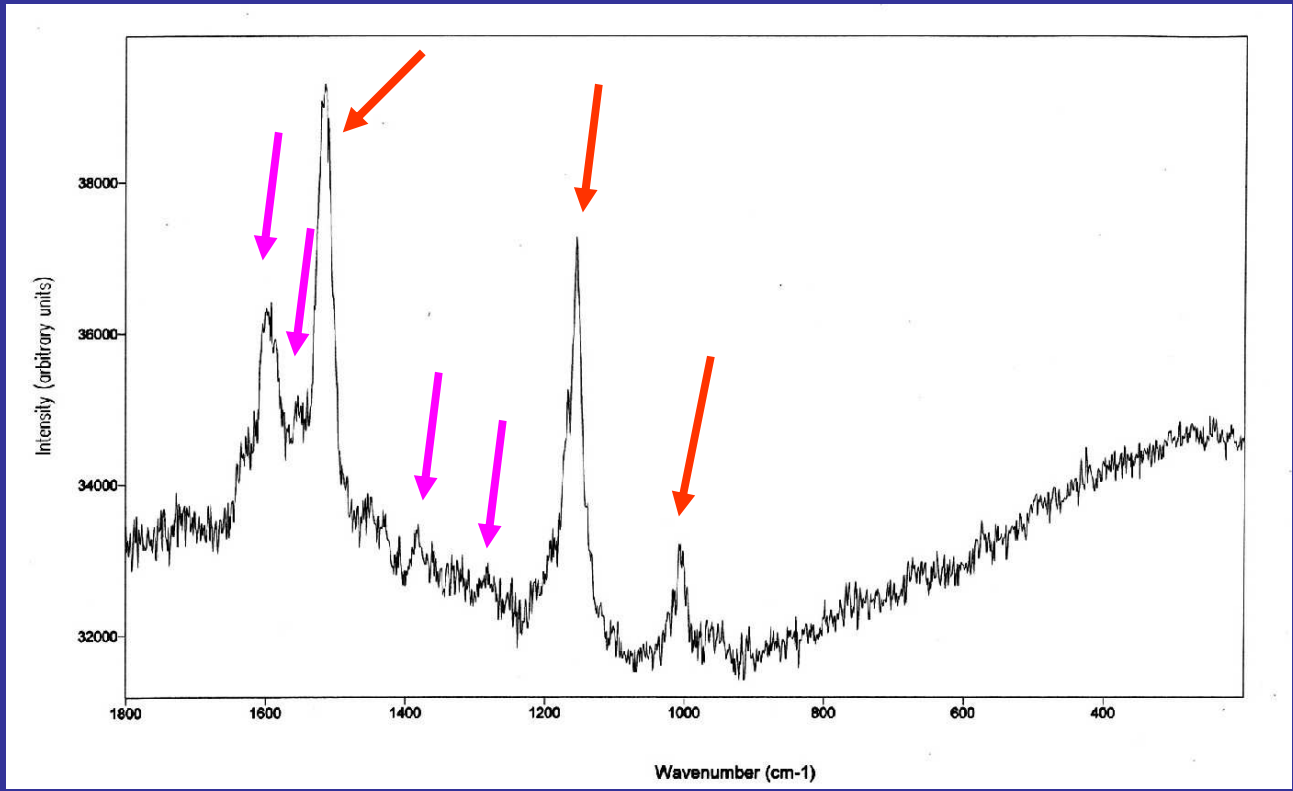
Meteorite impact 26 Mya

Field exposure of coalesced mass of selenite crystals within melt breccia deposits.

Halotroph in selenite crystal

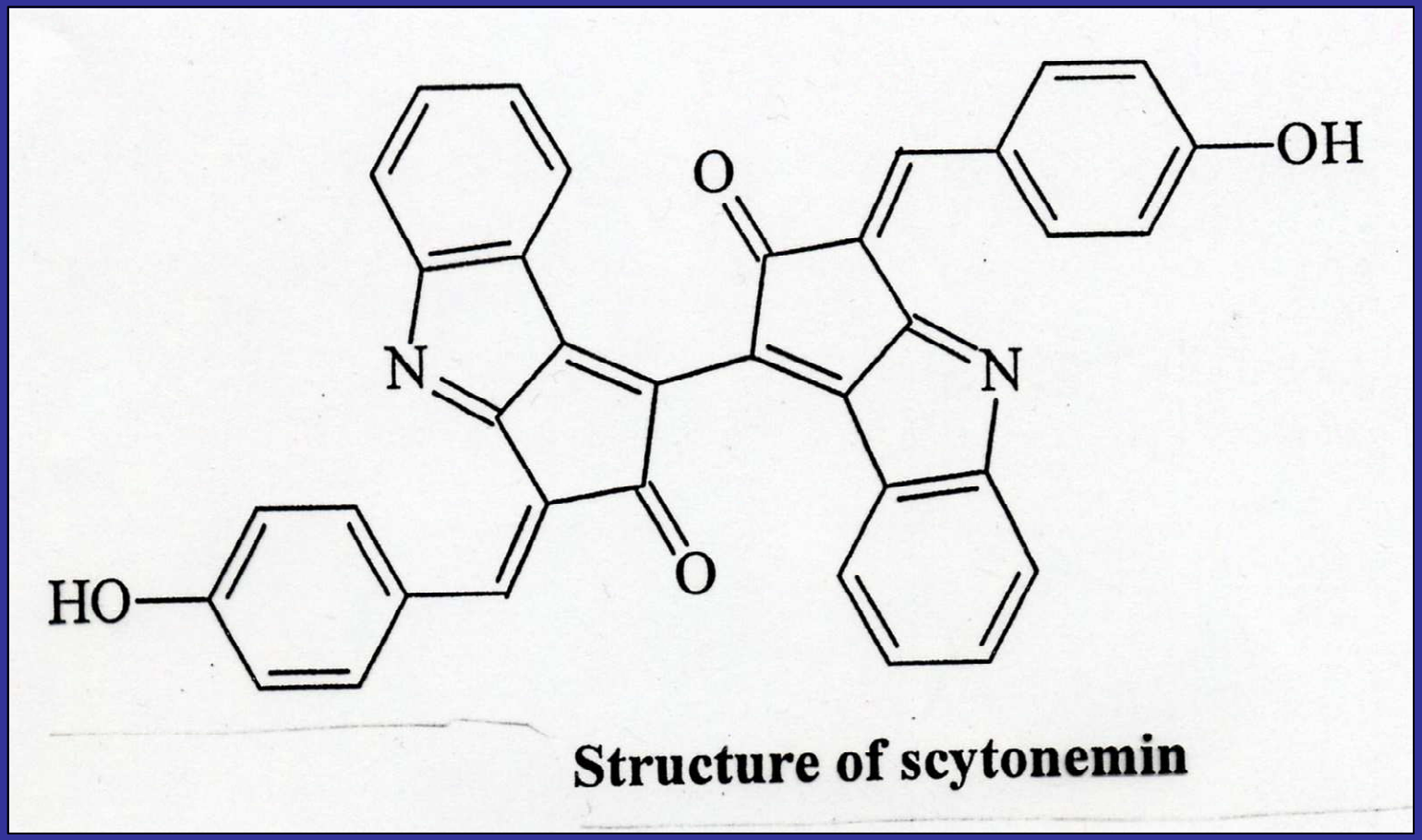
Cyanobacterial colony type I (*Nostoc*)

Raman spectrum obtained confocally by imaging directly into cyanobacterial inclusion ~ 5cm inside crystal

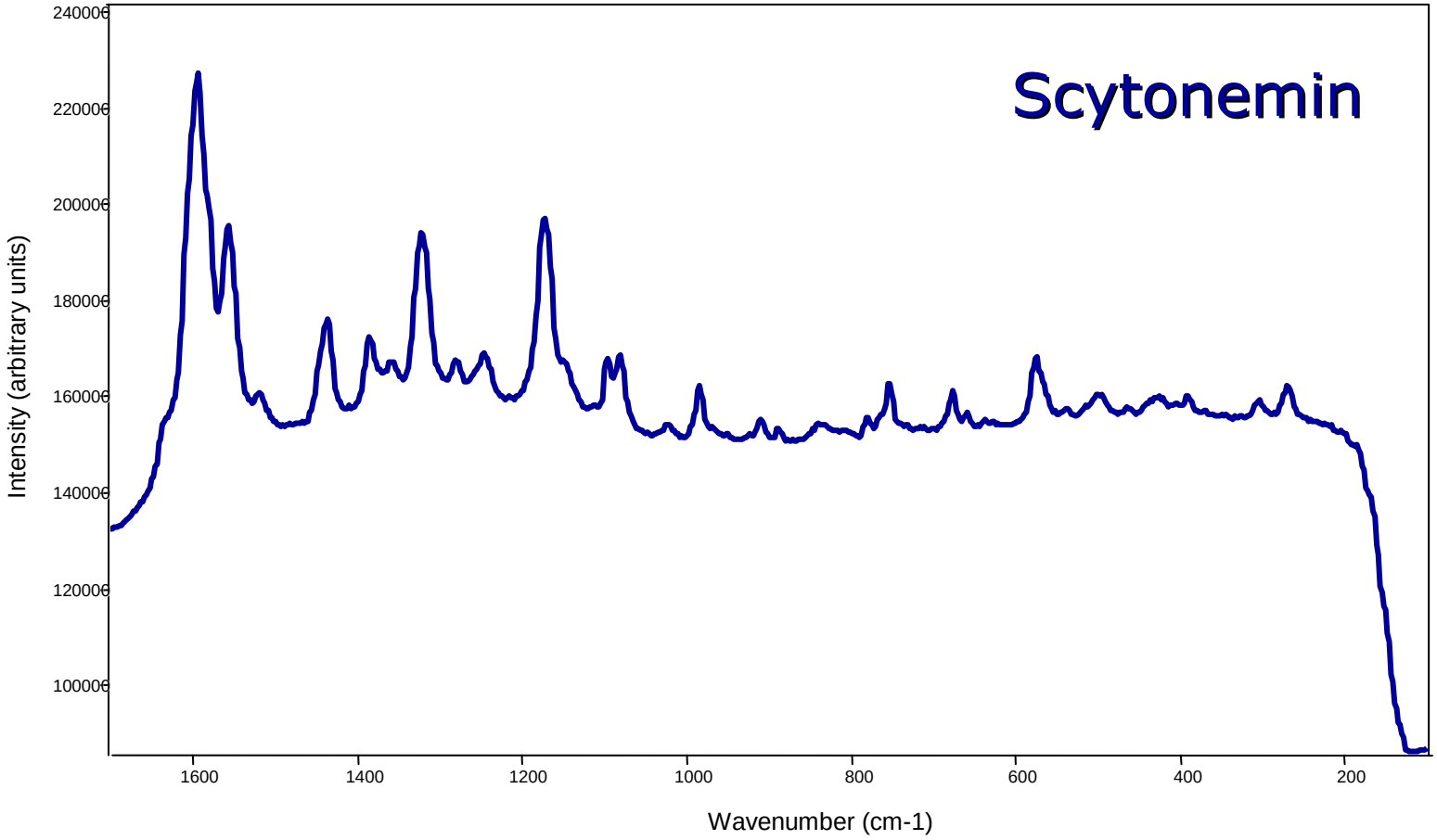


Scytonemin and carotene

The UV-protective pigment scytonemin produced by cyanobacteria.

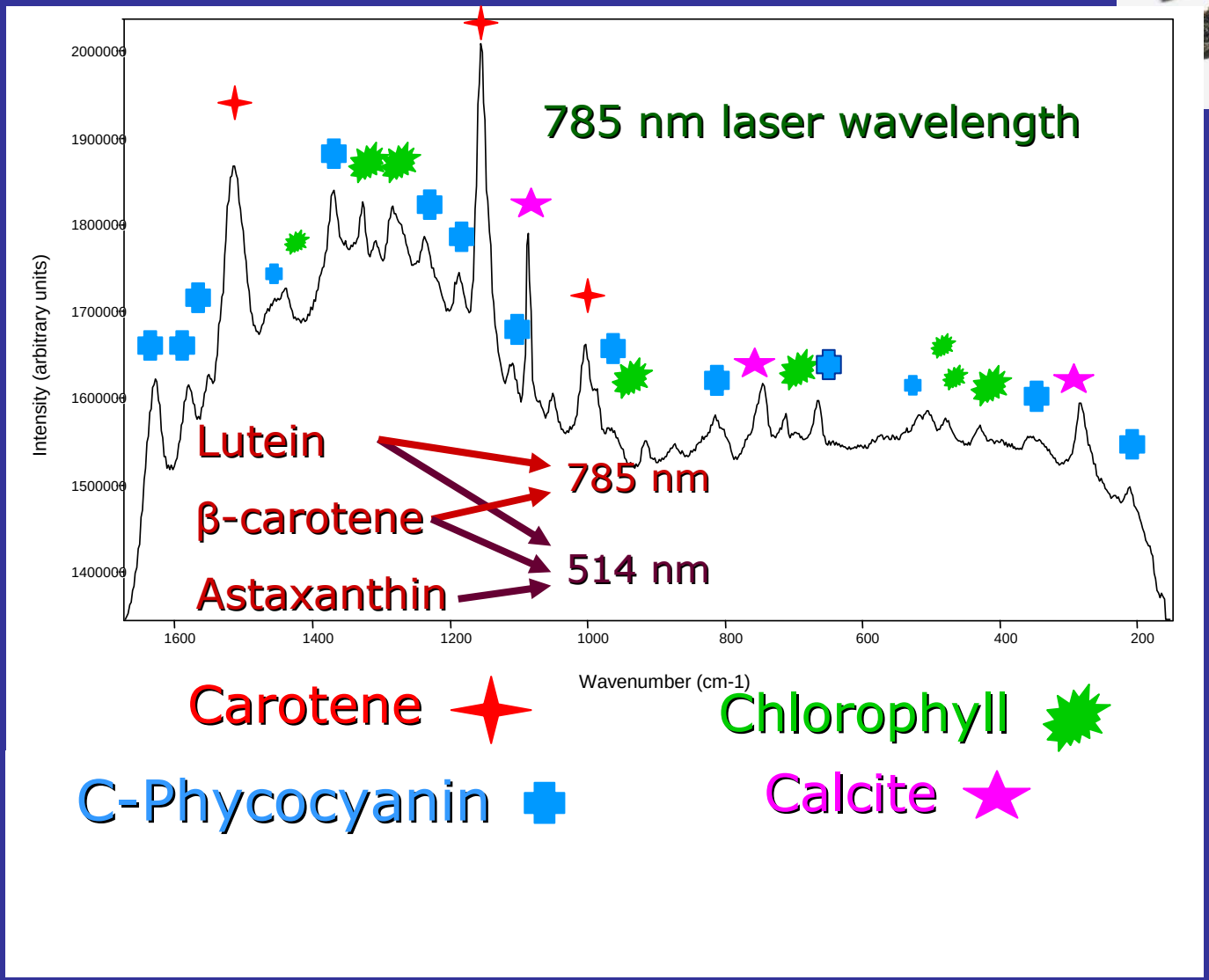


Structure of scytonemin


Scytonemin
Intensity (arbitrary units)
240000
220000
200000
180000
160000
140000
120000
100000
1600
1400
1200
1000
800
600
400
200
Wavenumber (cm-1)

Raman spectrosopy of different microbial types

ENDOLITH



Key Biomolecular & Geological Signatures

Inorganic

Quartz

Carbonates

Metal oxides

Metal silicates

Metal phosphates

Metal sulfides

Metal sulfates

Geological fingerprint

Organic

Oxalates

Chlorophyll

Carotenoids

Anthraquinones

PAH

Polyphenolic acids

Scytonemin

Proteins

Trehalose

Biological fingerprint


Mars –an inhospitable place
UV radiation insolation
Desiccation
Extreme cold
Oxidising surface
Corrosive dust
Limited atmosphere

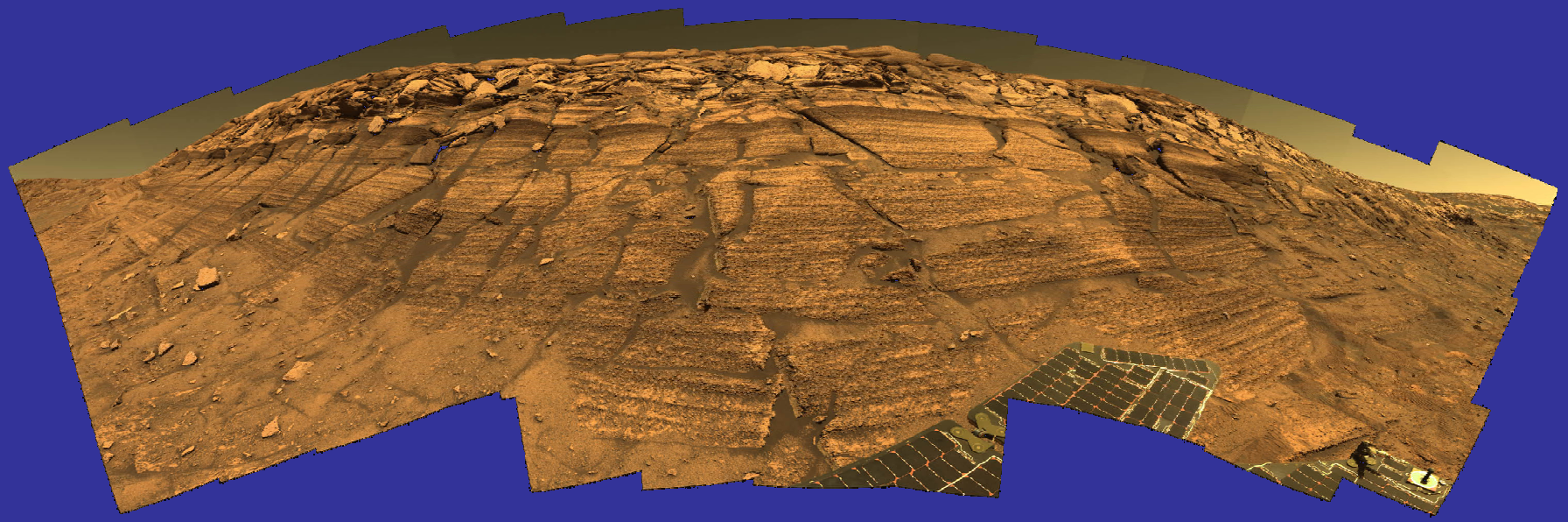
Water on Mars

- Mars believed to be totally desiccated - until photographic evidence from 30 years ago .
- Gradual perception of water presence on ancient Mars from geological features revealed by high-resolution cameras on planetary orbiters.
- Presence of significant water on Mars now realised – subsurface .


Icy ecosystem on Mars ?

Evaporites on Mars

Large sulphate deposits revealed by rovers *Spirit* and *Opportunity*

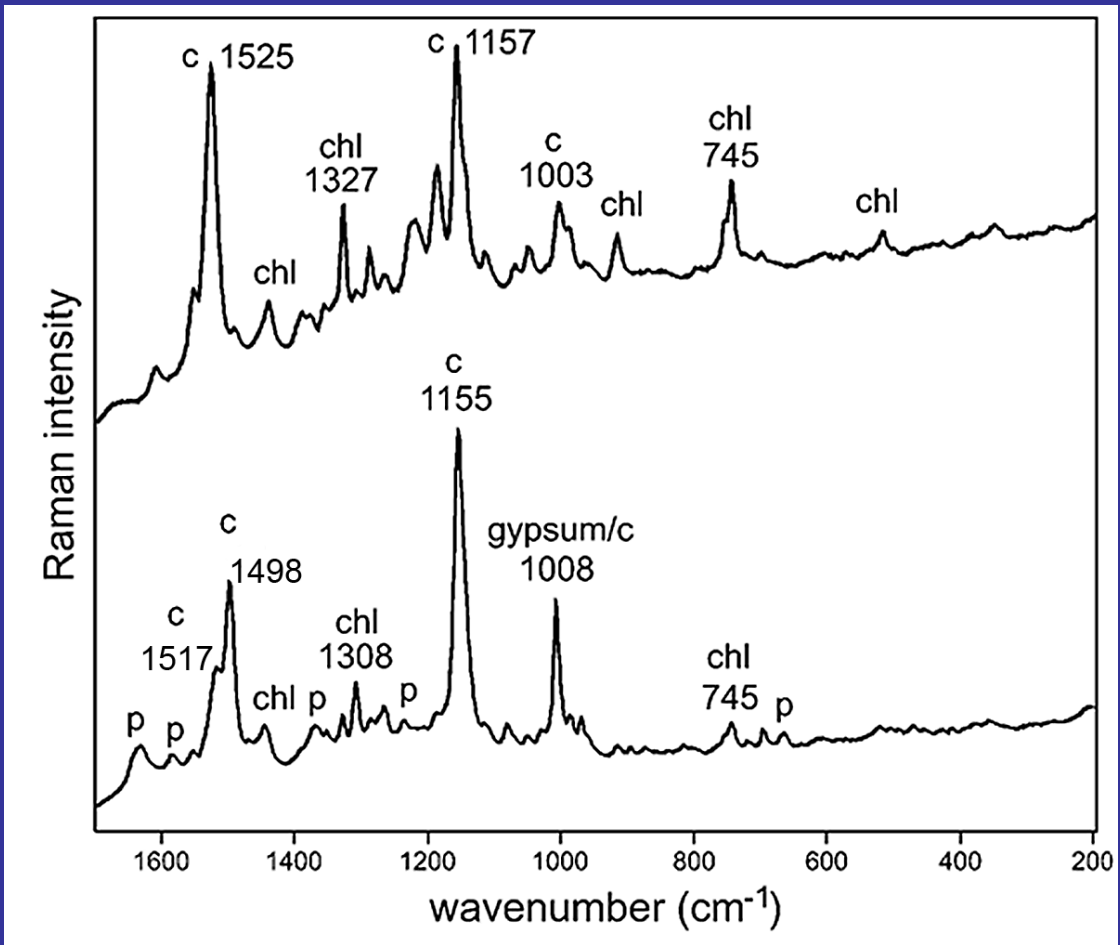


Courtesy NASA/JPL/Cornell

Evaporites as habitats for microorganisms

in pore spaces of evaporitic crusts

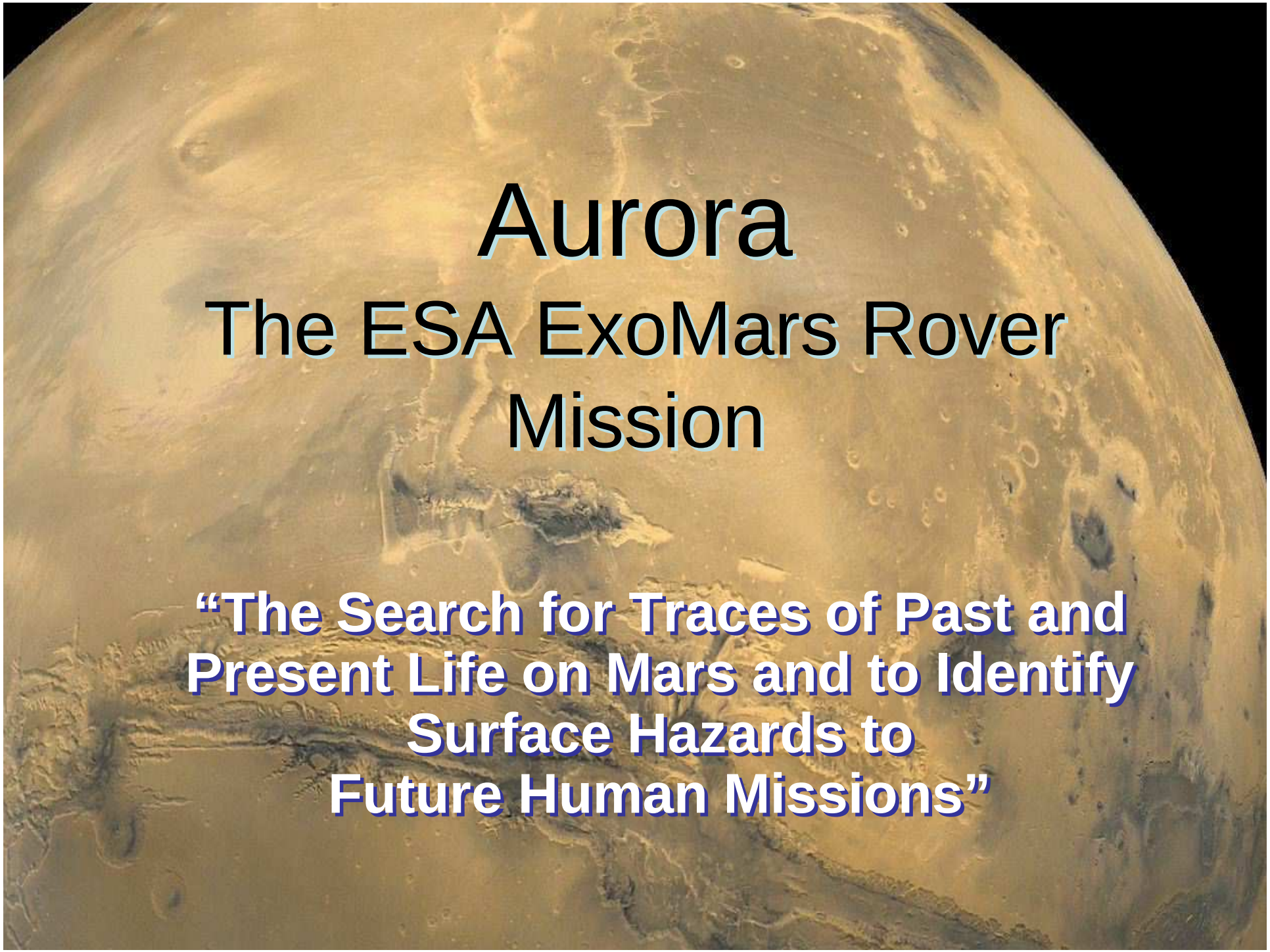
Atacama Desert – gypsum crust



algae

cyanobacteria

c=carotenoids
p=phycobiliprotein
chl=chlorophyll



Aurora

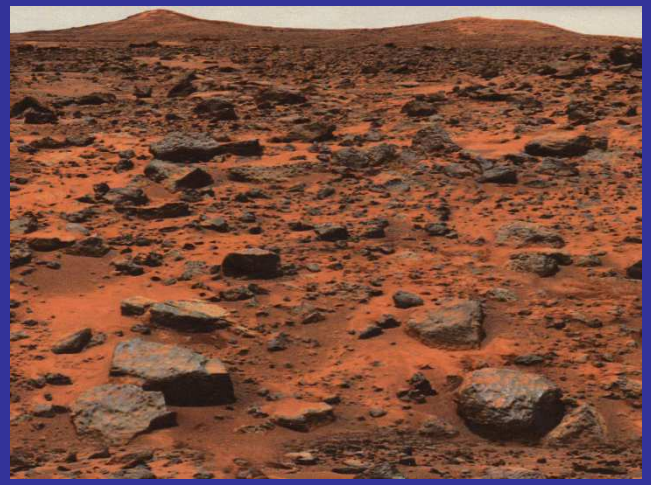
The ESA ExoMars Rover Mission

“The Search for Traces of Past and Present Life on Mars and to Identify Surface Hazards to Future Human Missions”

Sampling challenges: Miniaturisation of Instrumentation

Two possibilities:

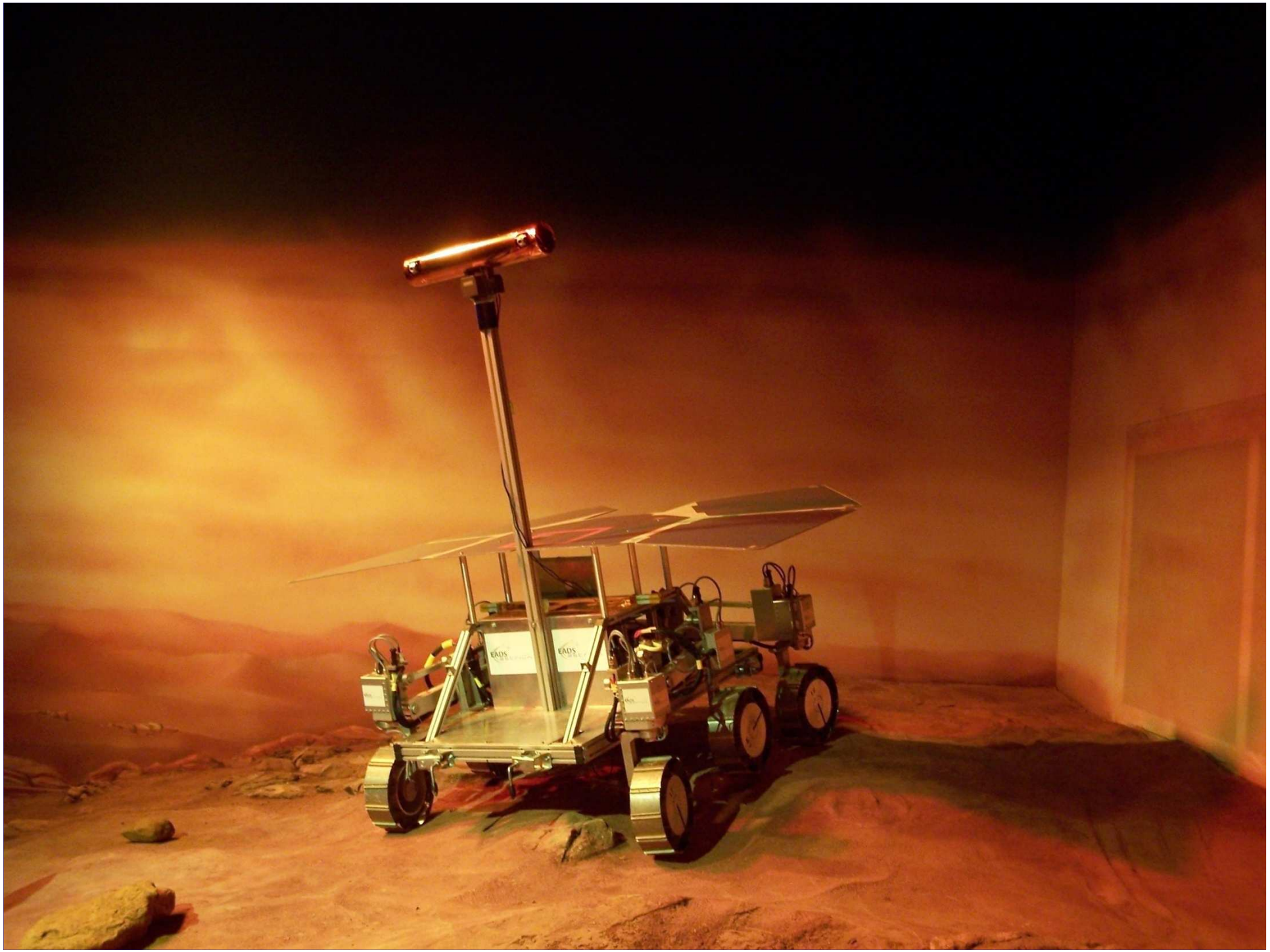
Remove the sample and analyse back in the lab - not always possible!



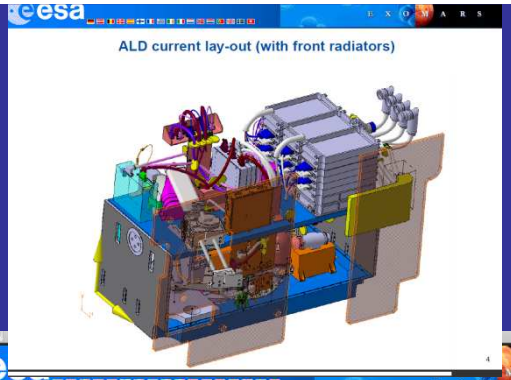
Take the lab (spectrometer) to the analyte

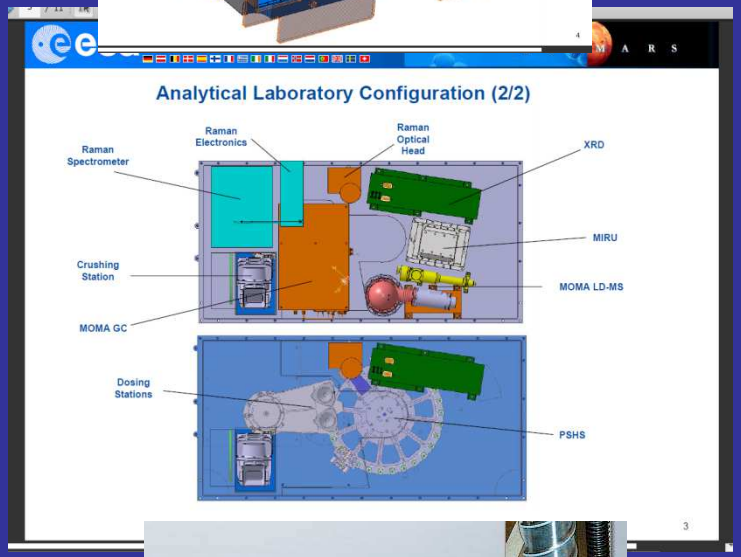
The ExoMars Mission

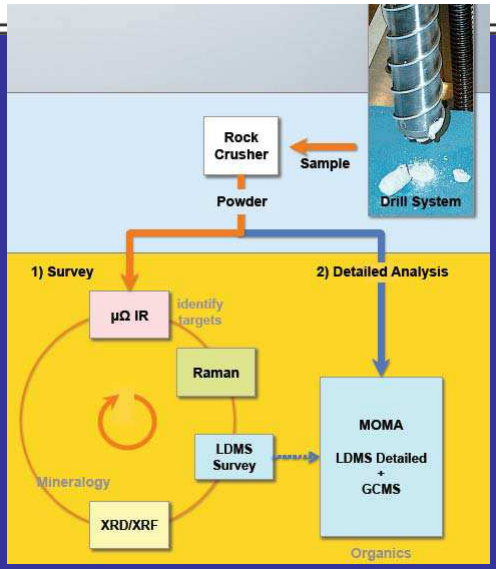
- **The most ambitious analytical exploration of a planet's surface and subsurface yet devised in the search for extraterrestrial life signatures.**
- **Definitive answers will be dependent upon the interpretation of the experimental data from the remote robotic measurements.**
- **An understanding of the behaviour of terrestrial extremophiles and their chemical survival strategies in the geological record is essential.**
- **Link between ANALYTICAL ASTROBIOLOGY and EXTREMOPHILES research.**



EXOMARS Operation Cycle



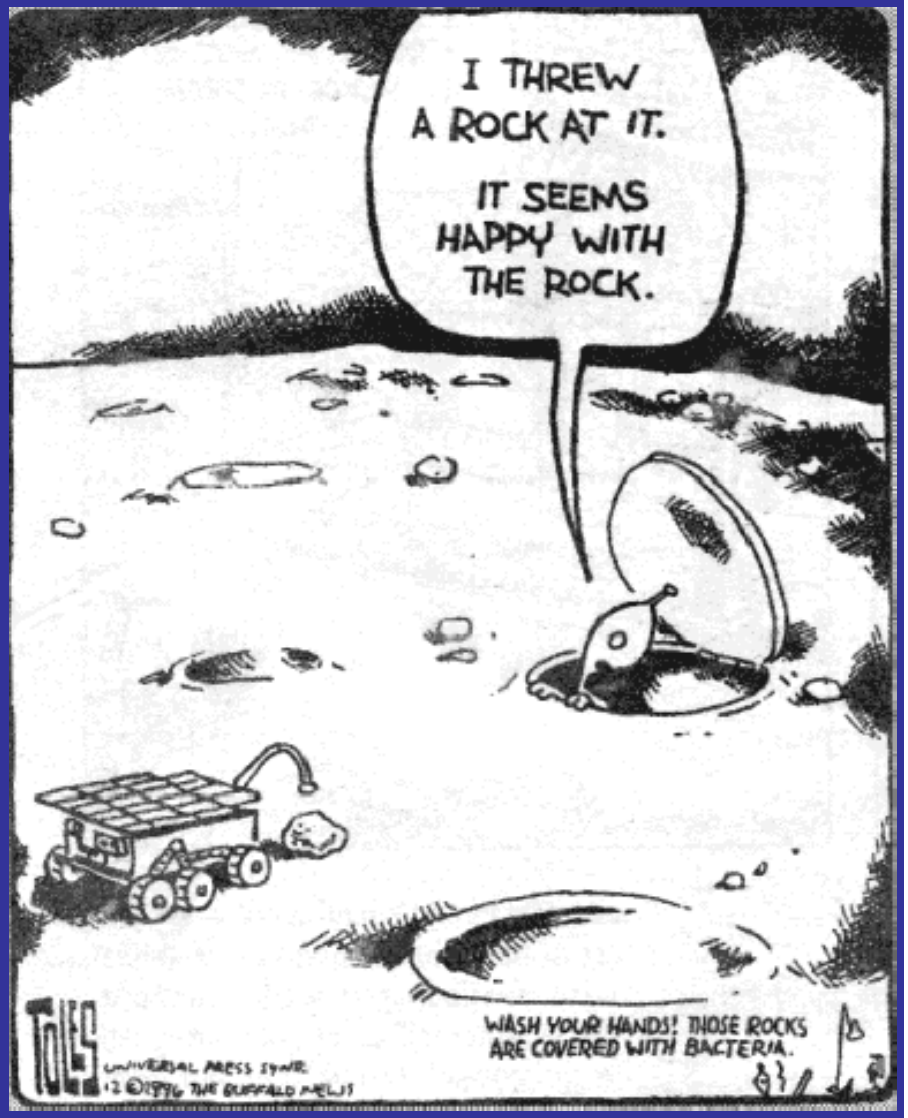




Planetary protection

- We must be able to recognise biosignatures in extraterrestrial locations

- We must ensure that we did not take it there in the first place



The Future

- **Exploration of Other Worlds**
- **A Better Understanding of Our Own World**

- **Making the connection !!**
- **Astrobiology – Raman – Forensic science**

  Astrobiology spectral signatures = forensic biogeoscience

Conclusions

- **Raman spectroscopy is advantageous for the detection of biogeological signatures in rocks .**
- **Wavelength selection is critically important for spectral generation .**
- **Evaluation of novel RS instrumentation on terrestrial extremophiles undertaken prior to mission selection.**
- **Database expansion necessaryfor different scenarios .**
- **Critical lab and field testing of ExoMars mission prototype.**
- **Longevity of biomolecular signatures in geological record ?**

Thank you for your attention