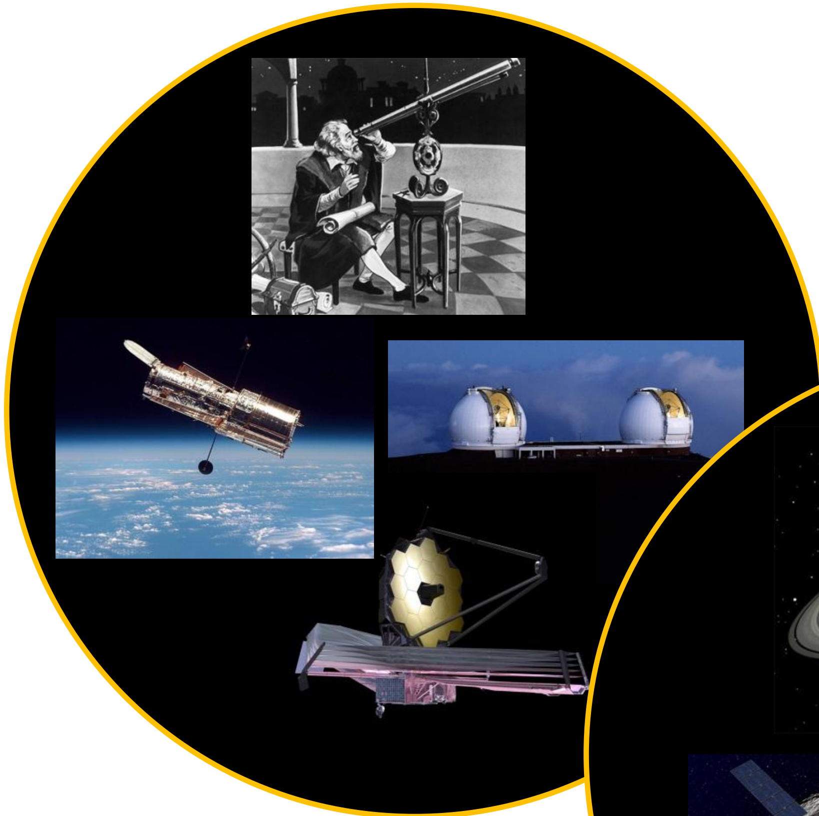
On-Surface Measurements Primer:
Mineralogy



KISS Workshop on
In Situ Science and Instrumentation
for Primitive Bodies
April 30th, 2012

Jordana Blacksberg
Jet Propulsion Laboratory

What can we measure on the Surface?

- **Elemental & Isotopic Composition**
  - Rock forming elements
    - Elemental ratios of rock forming elements can be used to classify primitive materials in the solar system, e.g. Metallic Fe/ Total Fe, Al/Si, Ca/Si, Fe/Si, FeO/(FeO + MgO) in olivine and pyroxene
  - Volatiles and Organics
    - Comets are a likely a combination of rock and ice. Need to measure rock-forming elements plus volatiles. C, H, O, N, S important (elemental and isotopic)
- **Crystal Structure & Morphology**
  - Phases of minerals present and their morphology inform the history of an object (e.g. temperature, pressure, atmospheric composition, surface composition)
- **3D Mapping**
  - Provides geologic context as well as the ability to look below any surface layers altered by weathering
    - Surface maps
    - Drill down
- **Atmospheric Chemistry**
- **Bulk Physical Properties**
  - e.g. dielectric constant, thermal conductivity - used for large scale modeling and validation of results from dynamical models of a body

Measurement Techniques for on-Surface Mineralogy

'Definitive Mineralogy': Structure and Composition

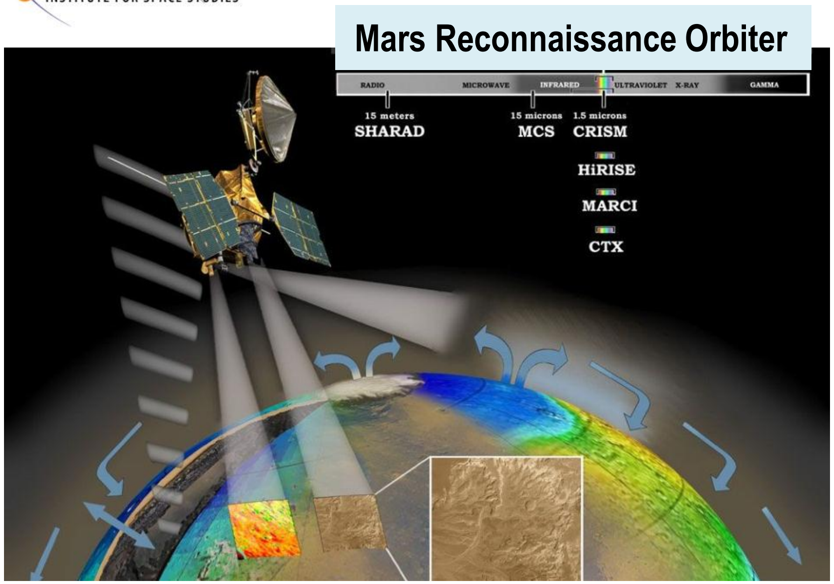
- X-ray Diffraction (XRD)
- Raman Spectroscopy
- Mössbauer Spectroscopy (sometimes)

Elemental Composition

- X-ray Fluorescence (XRF)
- Alpha Particle X-ray Spectroscopy (APXS)
- Gamma Ray / Neutron Spectroscopy
- Infrared Reflectance Spectroscopy
  - Passive Source (reflected sunlight)
  - Active Source (broadband light source, LED, laser)
- Laser Induced Breakdown Spectroscopy (LIBS)

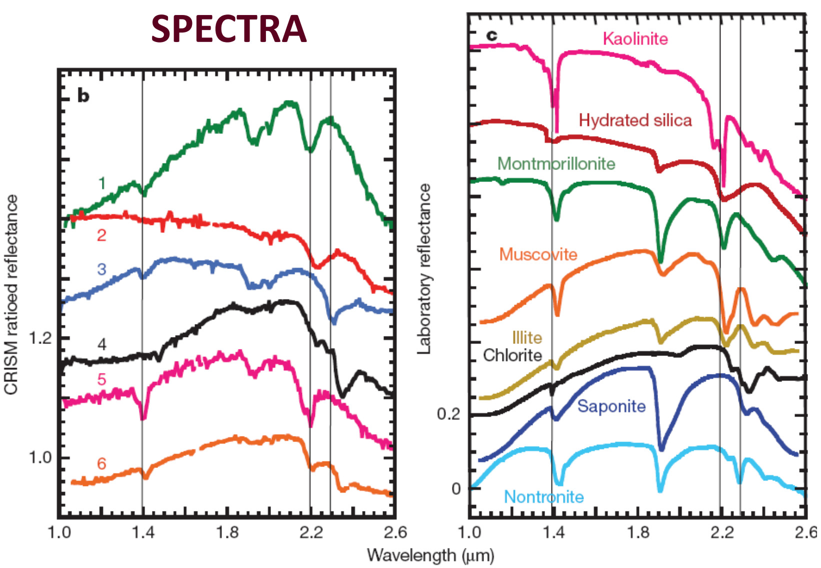
And more ….

Mars is a Good Example

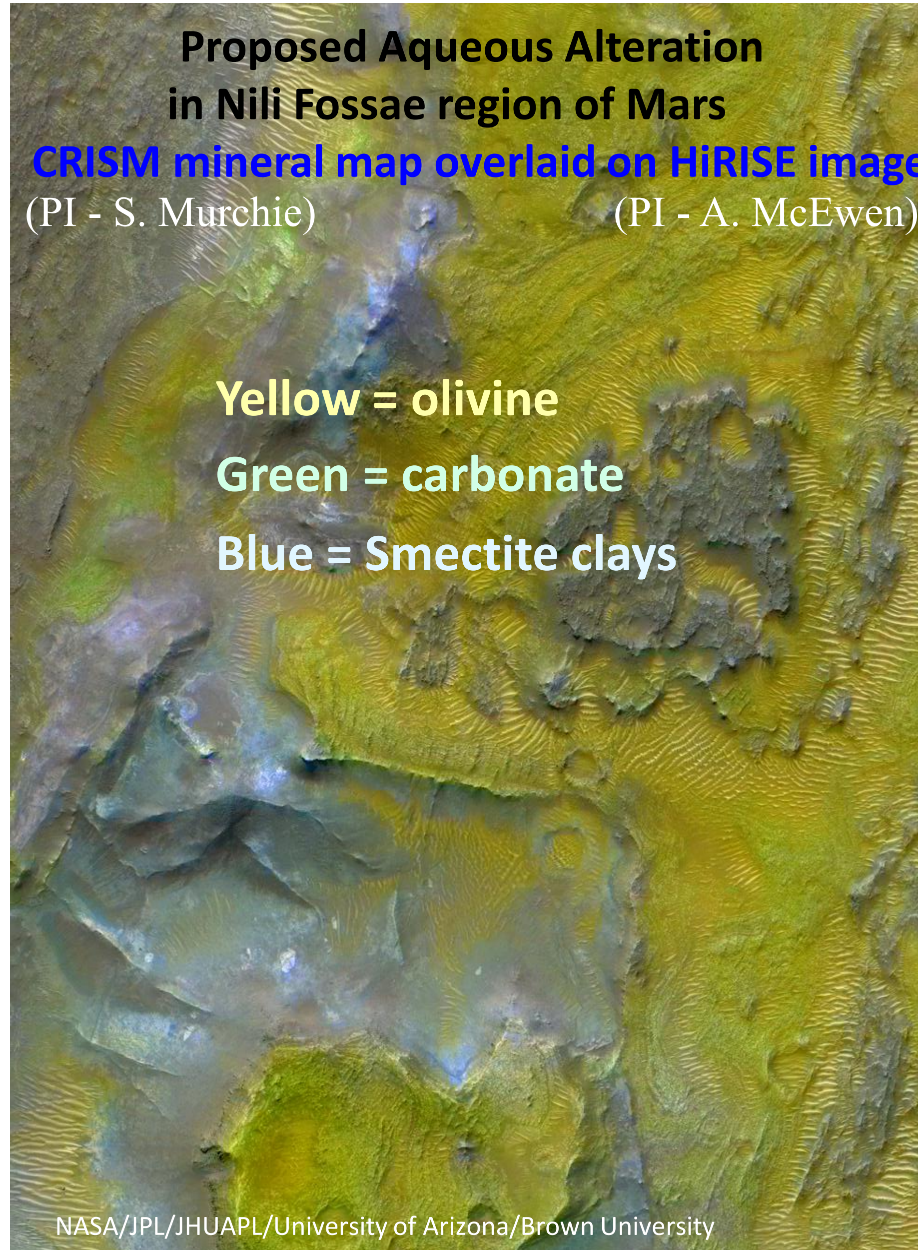


CRISM SPECTRA

LABORATORY SPECTRA

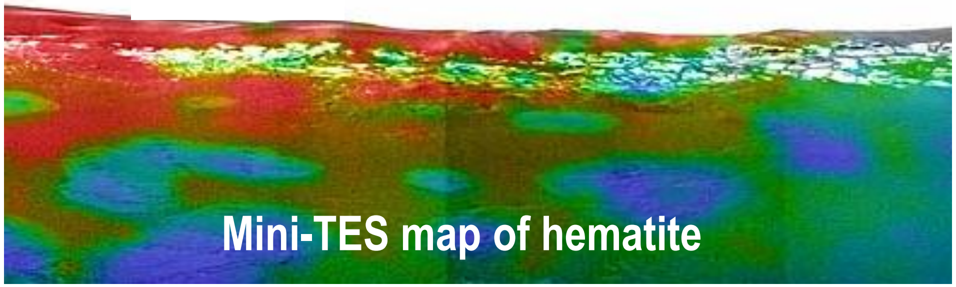


Mustard et al., Nature **454** (2008)

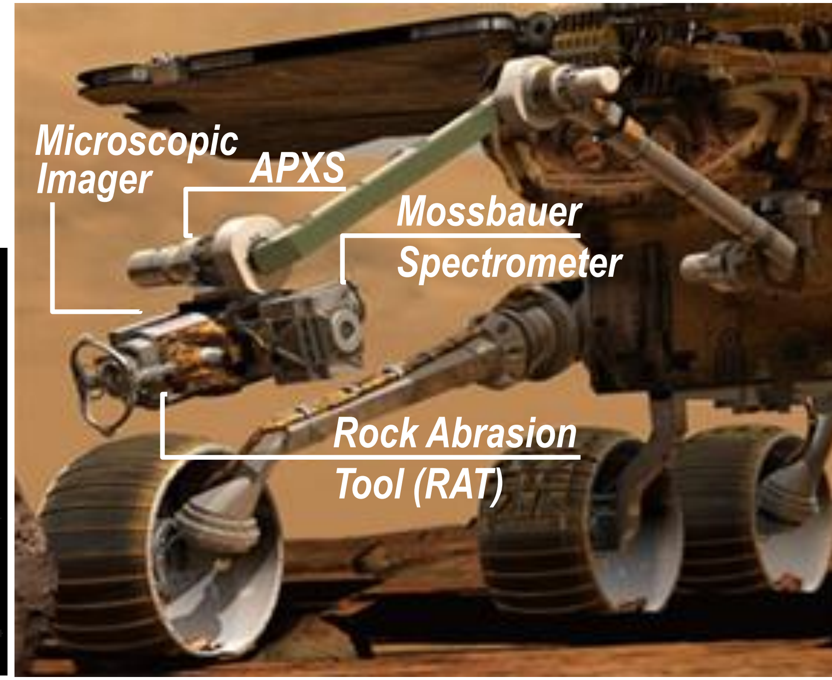


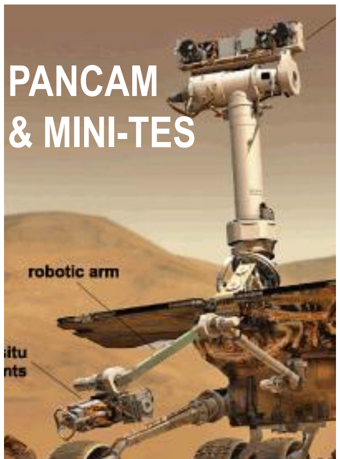
On-Surface Planetary Mineralogy with MER

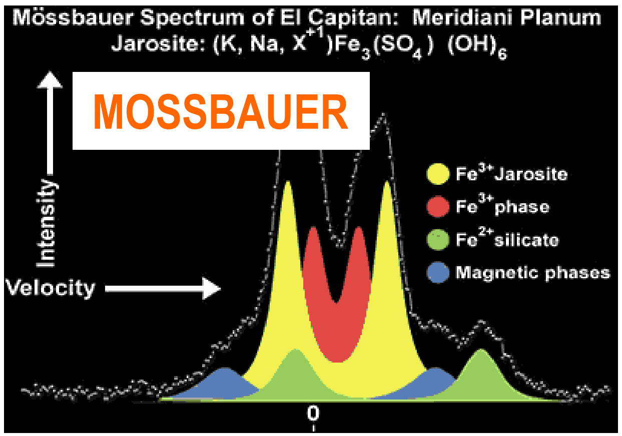
MINI-TES



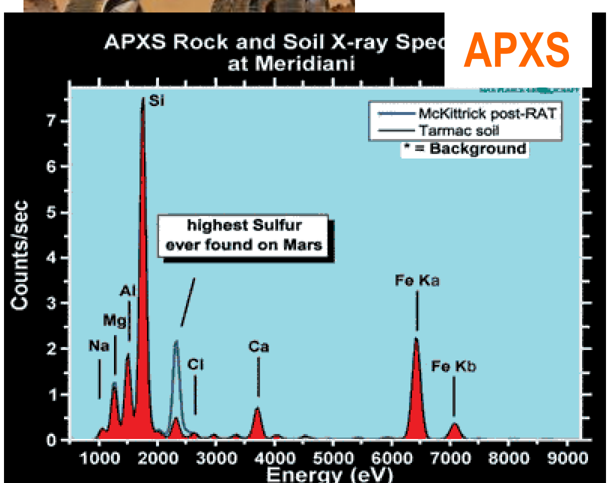
Instruments on Mars Exploration Rover Arm



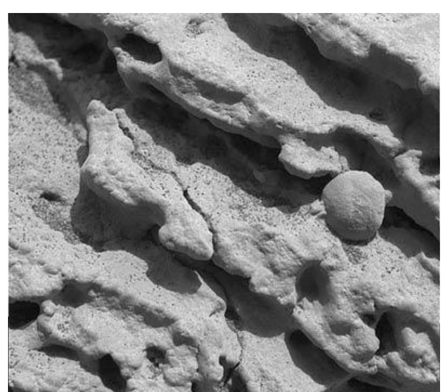




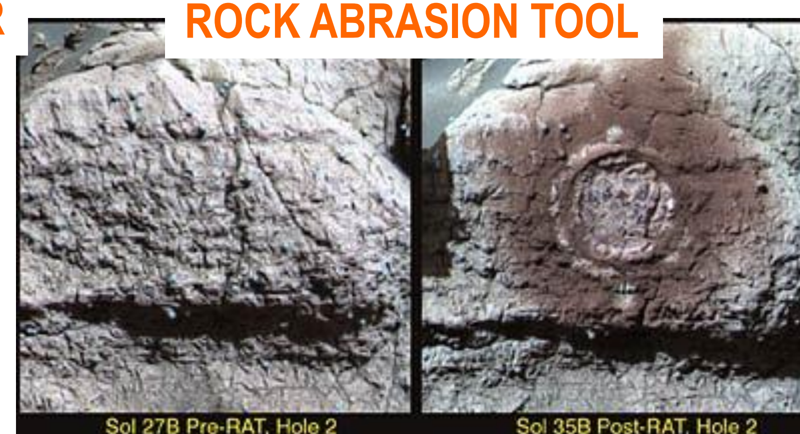
APXS



MICROSCOPIC IMAGER



ROCK ABRASION TOOL



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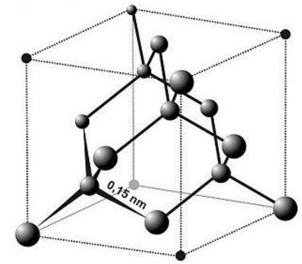
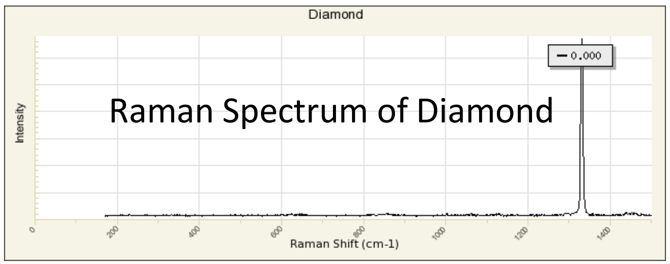
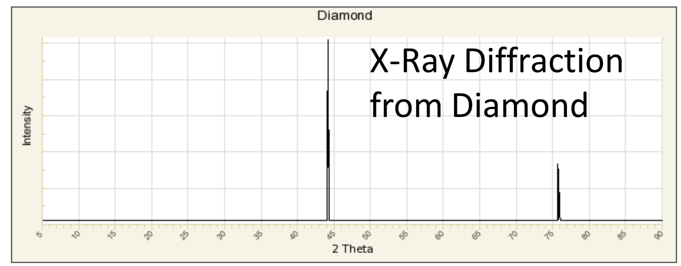
Determining Mineral Structure and Composition

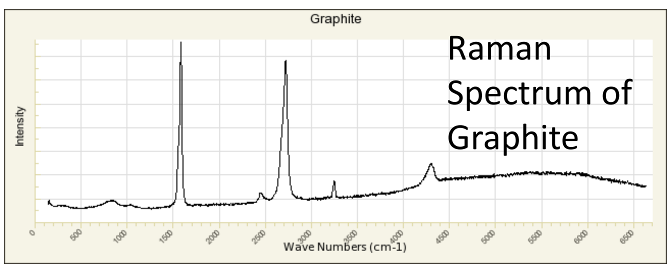
Elemental Analysis: Carbon

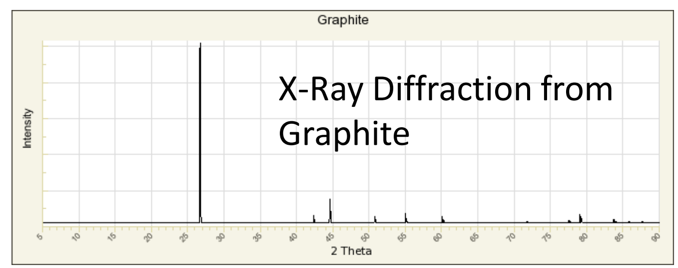
Diamond



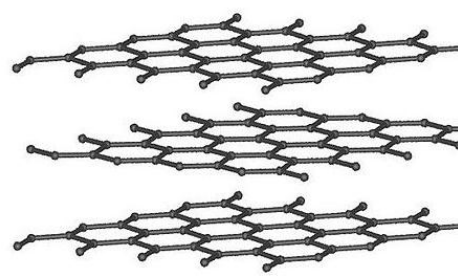








Graphite



Determining Mineral Structure and Composition

SILICATE MINERALS CONTAINING Fe AND Mg

OLIVINE
$(Mg,Fe)_2SiO_4$

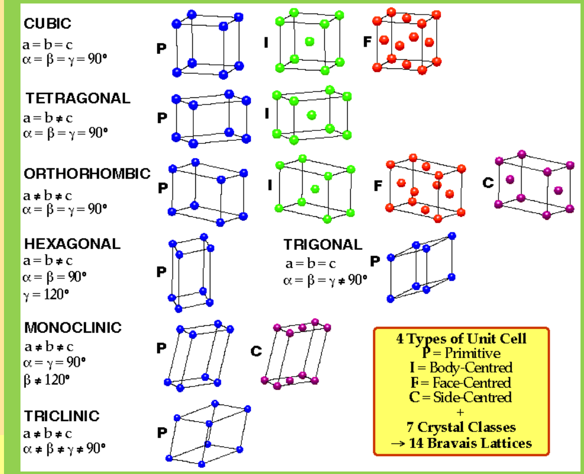
Mg-Fe PYROXENE
$(Mg,Fe)SiO_3$

Forsterite
(Mg_2SiO_4)

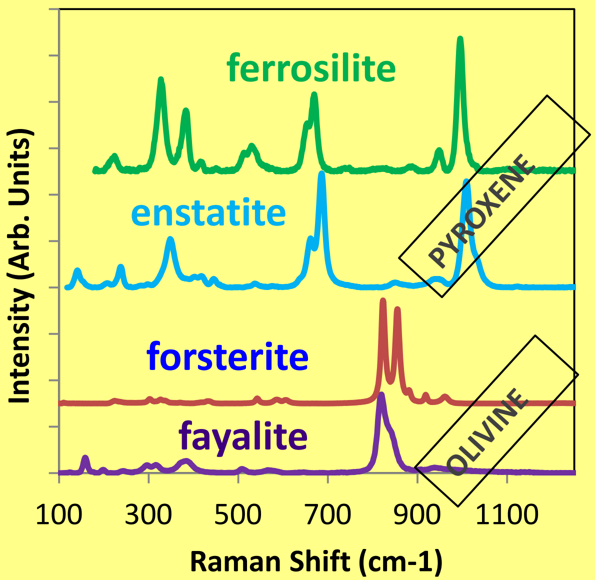
Fayalite
(Fe_2SiO_4)

Enstatite
$(MgSiO_3)$

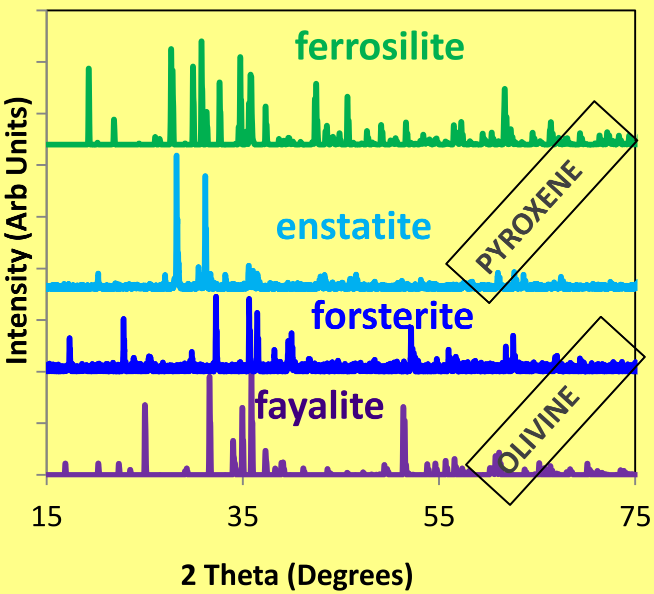
Ferrosilite
$(FeSiO_3)$



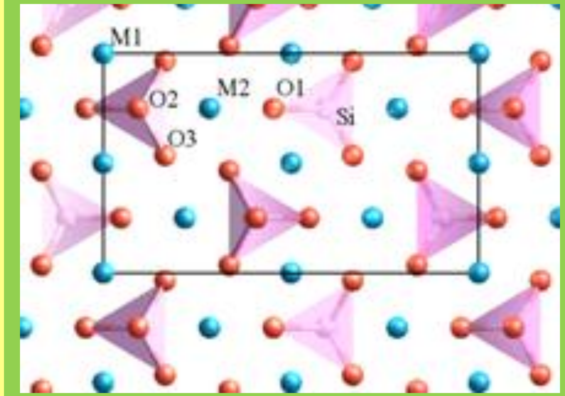
RAMAN SPECTROSCOPY



X-RAY DIFFRACTION



ORTHORHOMBIC UNIT CELL OF OLIVINE

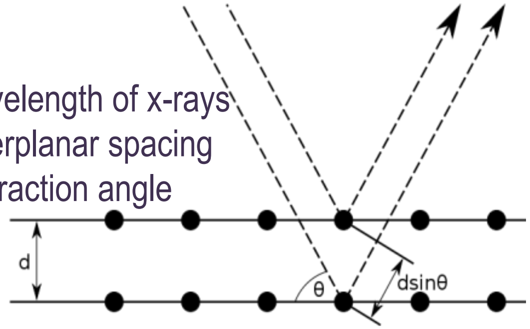


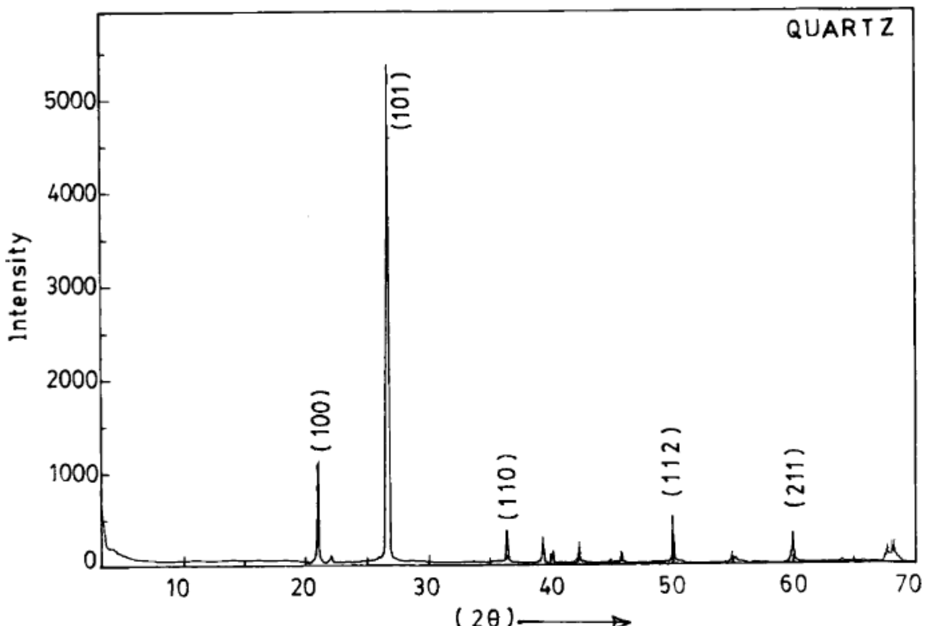
X-Ray Diffraction (XRD)

ELASTIC SCATTERING OF X-RAYS IN SOLIDS

Bragg's Law
$n\lambda = 2d\sin\theta$

λ = wavelength of x-rays
d = interplanar spacing
θ = diffraction angle





Ref: Debnath 2006

- X-rays incident on a crystalline sample
- Scattered x-rays produce an XRD pattern
- Peak positions and relative intensities give structure and composition of nearly all crystalline materials.
- Powder XRD (variable θ / monochromatic source)
  - * Requires small un-oriented grains or sample preparation
- Laue XRD (variable λ / broadband source)
  - * Useful for or single- or large- grain material
- For high intensity, small beam size, and narrow line-width, synchrotron radiation is used (e.g. identified olivine a pyroxene in Stardust samples)
- Lab instruments sufficient for most measurements, and can quantitatively determine phases present in mixtures

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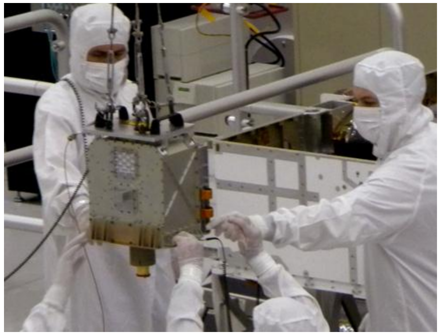
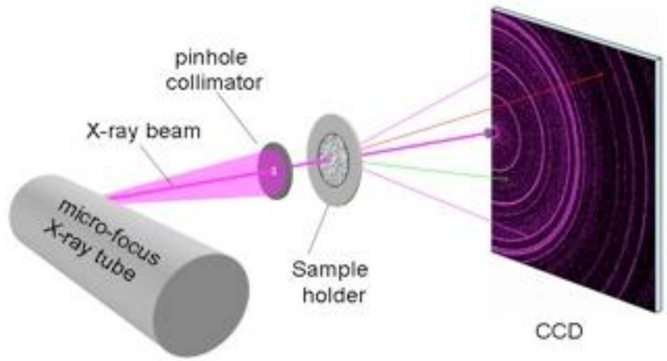
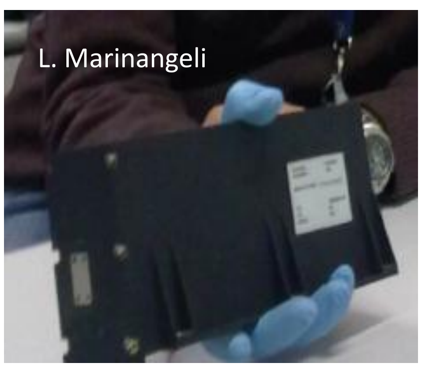
XRD going to Mars

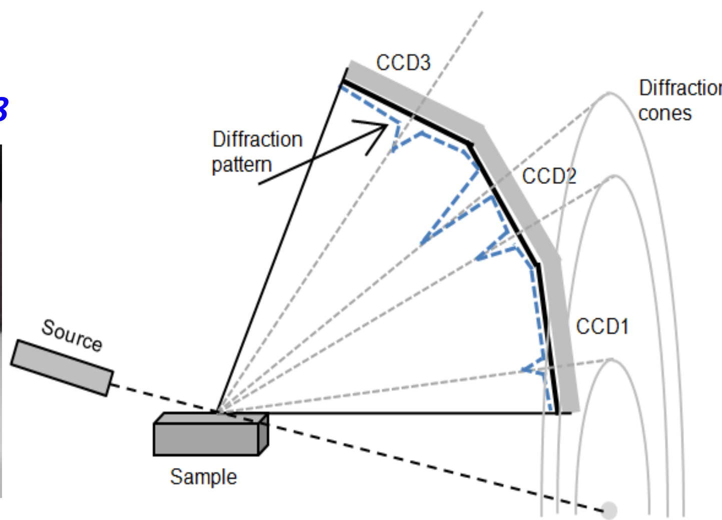
CheMin on MSL





Mars-XRD on ExoMars 2018





CheMin on MSL

- Transmission powder diffraction
- Sample collected and powder delivered to sample cells for analysis
- Combined with X-ray fluorescence (best-effort basis)
- X-ray tube source
- Typical analysis 10 hours

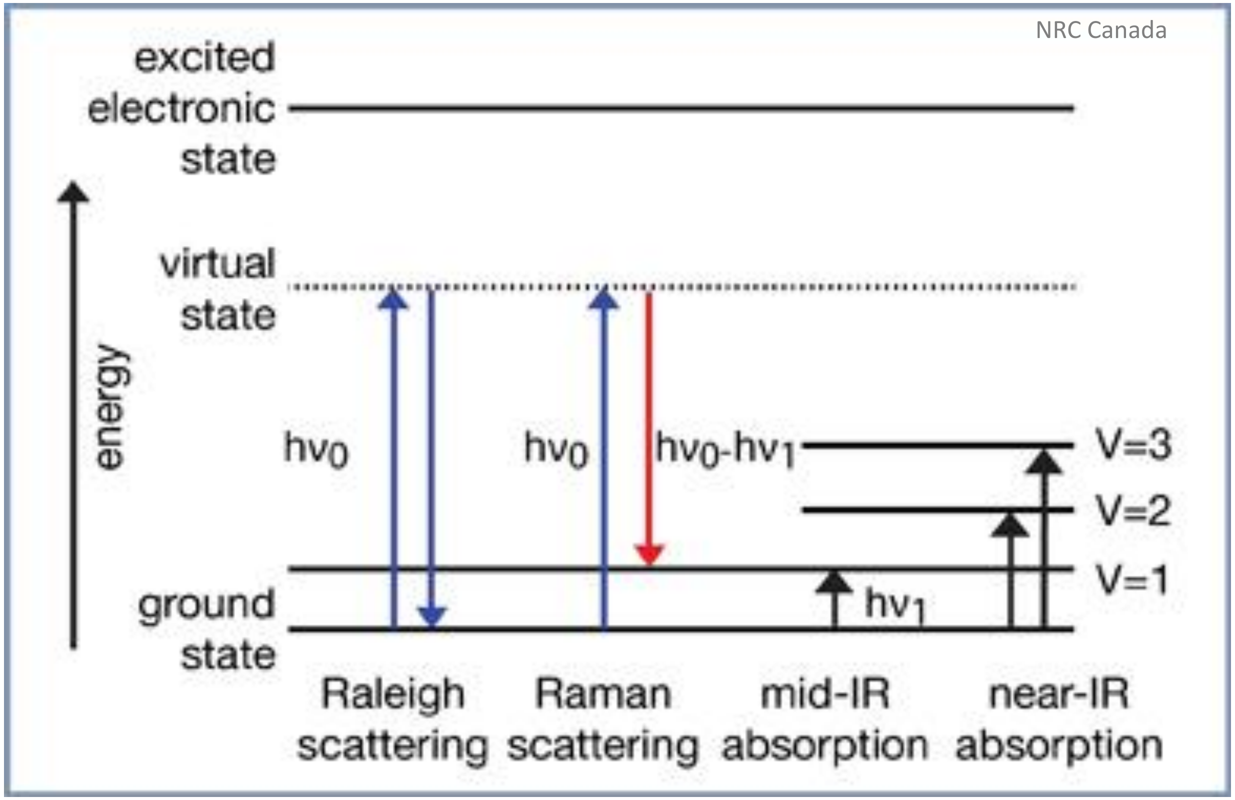
Mars-XRD on ExoMars 2018

- Reflection powder diffraction
- No sample prep
- Combined with XRF
- Radioactive source

Future Instruments

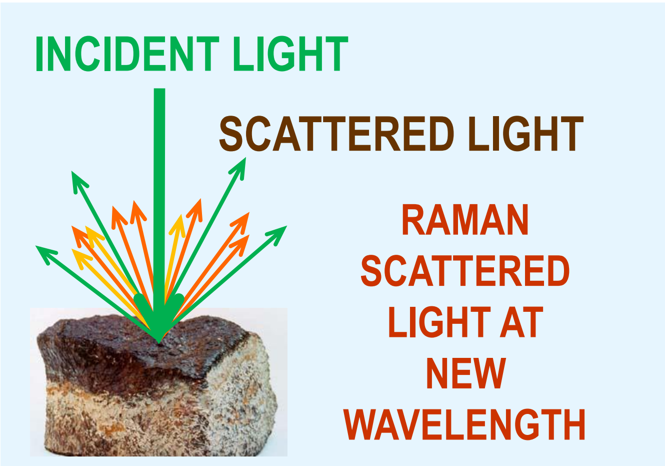
- Combined reflection Powder and Laue XRD for sampling fine grained and single crystal material

A Word About Vibrational Spectroscopy

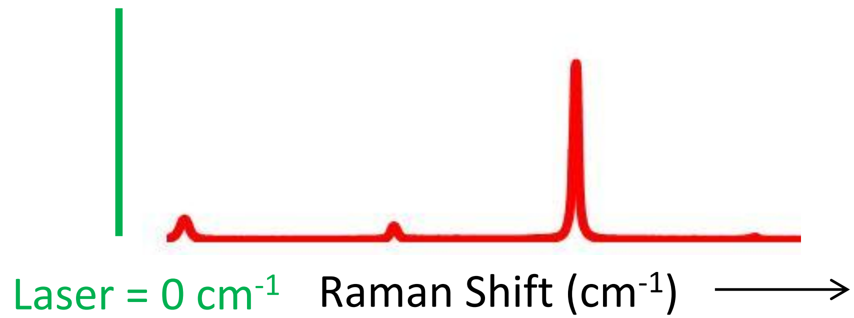


Raman Spectroscopy

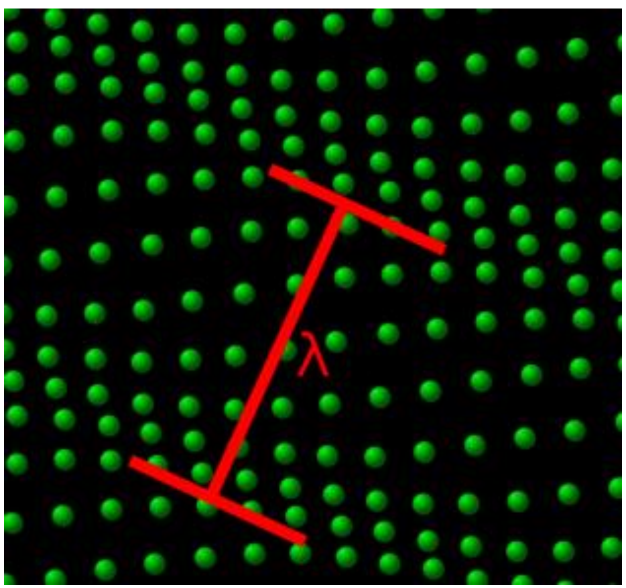
INTERACTION OF LIGHT WITH VIBRATIONAL OSCILLATIONS IN MATERIALS



- Laser incident on sample scattered by phonons
- Each band in a Raman spectrum represents interaction of light with a vibrational mode - highly specific for a given material and can be used for identification and structural characterization of unknown samples (much like XRD).



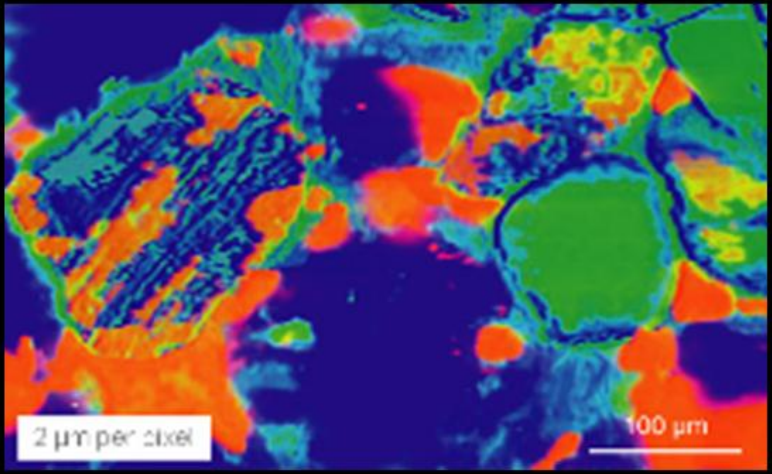
- Non-destructive, no sample preparation
- Retains context of natural mineral setting
- Microscopic imaging of select grains
- Can identify the majority of minerals, but some are notoriously difficult (e.g. sulfides and clays)



Raman 2-D Mapping

- Laser source can be focused to a very small spot size comparable to mineralogical grains (< 1 μm)
- This is the foundation for 2-D Raman mapping

Example (from Renishaw):
Sandstone from Loch Torridon, Scotland



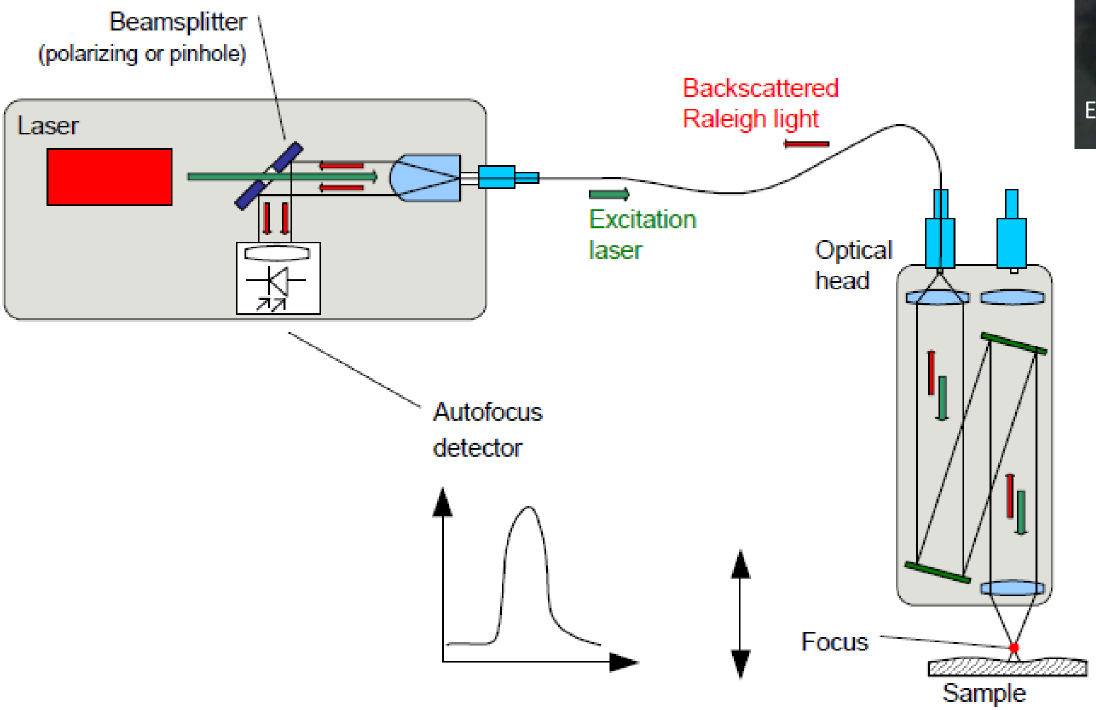
Anatase (TiO_2) (red)
Quartz (SiO_2) (green)
Haematite (Fe_2O_3) (blue)

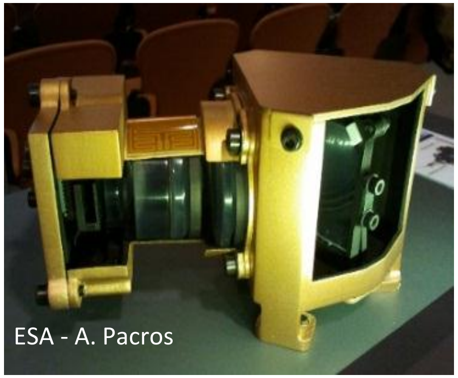
Area of section: 500 μm x 320 μm
Spectra generated: 67,200
Acquisition time: 20 minutes

Raman for Flight

- Never flown before but planned for ExoMars 2018
- proposed for other missions, e.g. to Venus (SAGE), Deimos (MERLIN)

Raman Laser Spectrometer (RLS) on ExoMars 2018

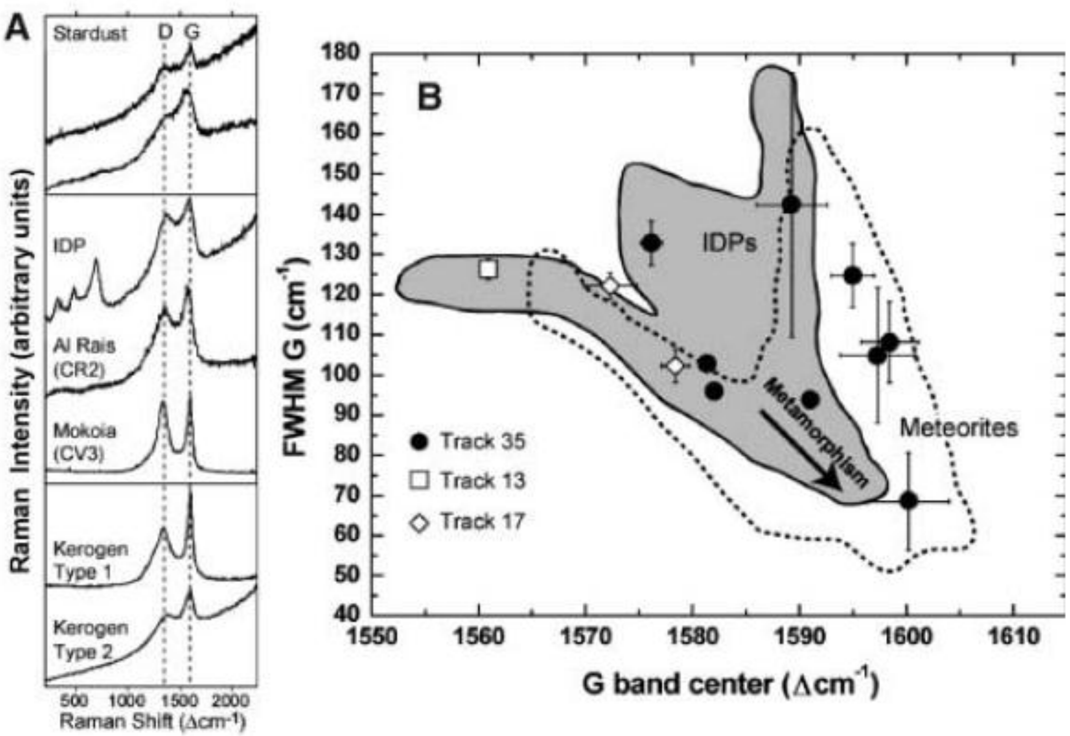




* ~ 6 - 10 cm-1 resolution
* λ = 532 nm
* 50 µm spot size
* Spectral range coverage ~150 to 3800 cm-1
* ~ 2.5 kg

Raman Spectroscopy - Examples

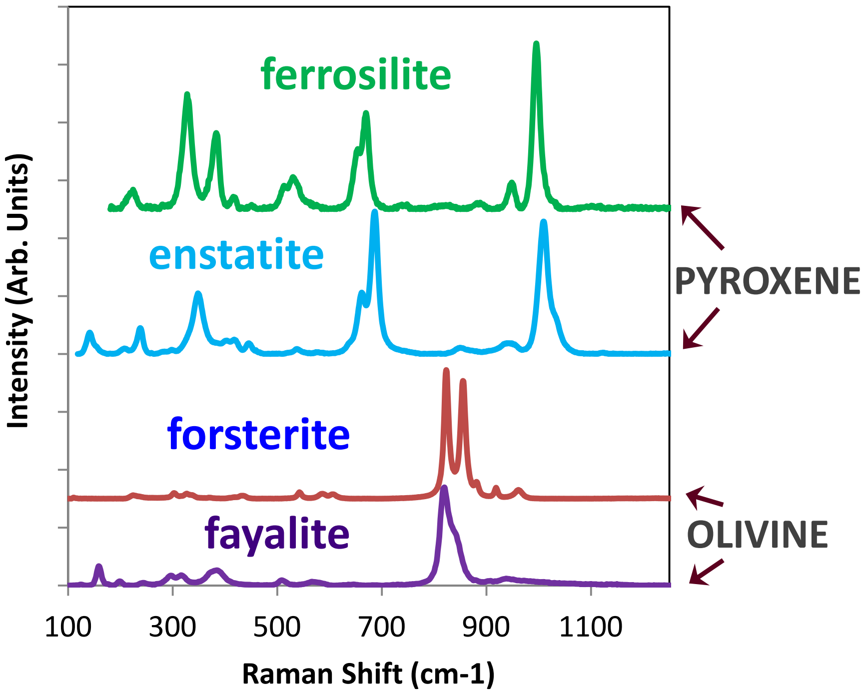
Cometary Samples: Raman of Stardust particles



Sandford et al. Science 314 (2006)

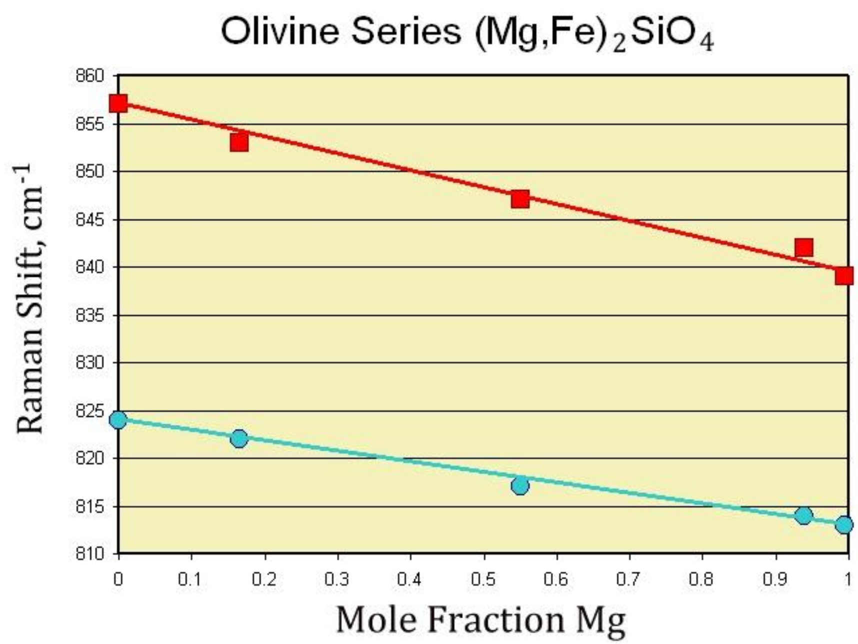
- Raman bands in carbonaceous material reflect disorder and therefore the degree of thermal metamorphism
- Dashed boundary shows range of values for more than 40 chondritic meteorites
- Shaded boundary shows range of values for 40 IDPs
- Highly thermally metamorphized meteorites plot in the lower right
- Points in upper left are primitive
- Organics in Stardust samples span the entire range seen in IDPs and meteorites – unclear if this is due to heterogeneity or variable processing during aerogel capture.
- **At least some stardust material is very primitive**

Raman Spectroscopy - Examples



RRUFF Database

Forsterite to Fayalite:

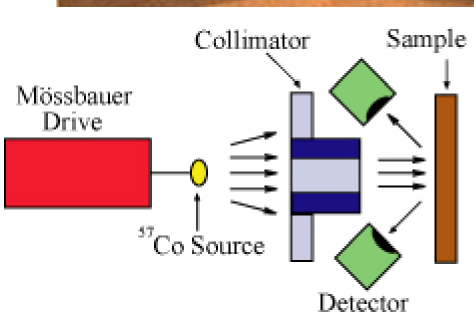


Courtesy of G.R. Rossman, 2012

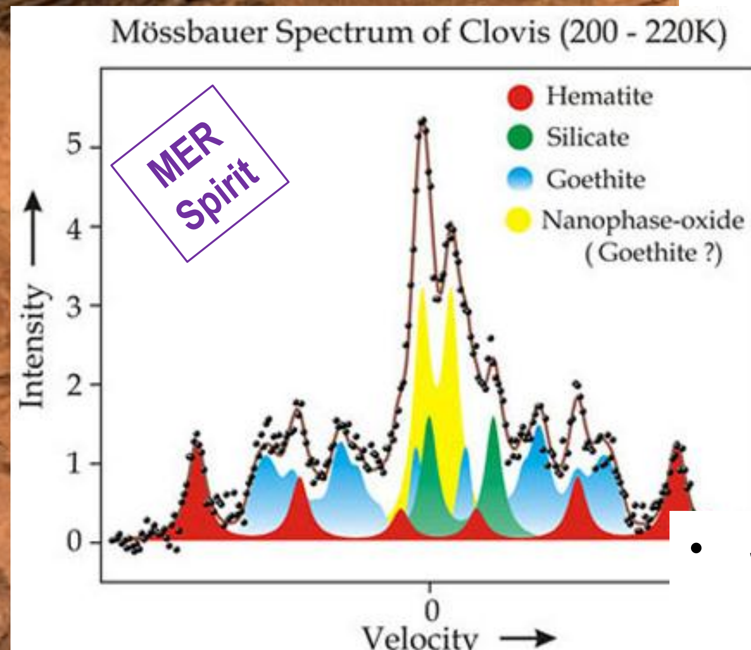
- The ratio of FeO / (FeO + MgO) in olivine and pyroxene is one of the classic discriminators among the chondritic meteorite groups.
- Raman would require ~ $4 cm^{-1}$ or better resolution to determine this ratio accurately.

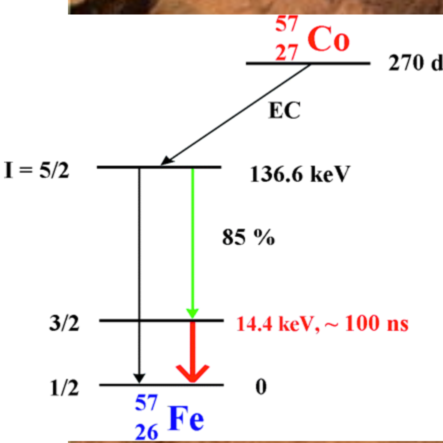
Mössbauer Spectroscopy

RESONANT ABSORPTION AND EMISSION OF GAMMA RAYS IN SOLIDS

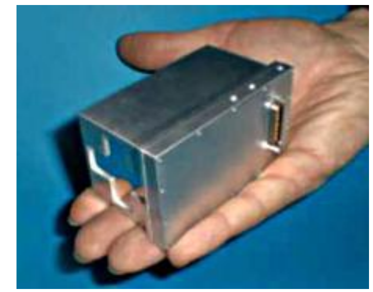


Source is moved rapidly (e.g.13 mm/s), causing a Doppler shift in the gamma rays emitted





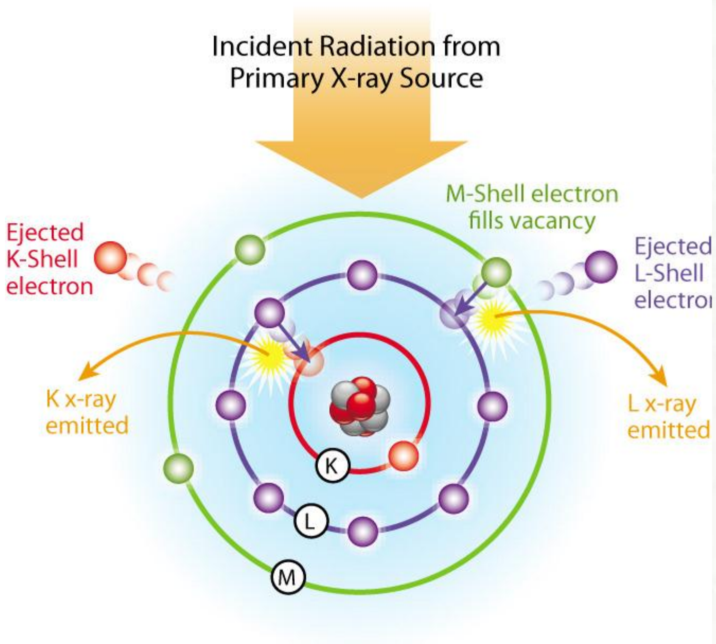
MER Mossbauer Sensor Head

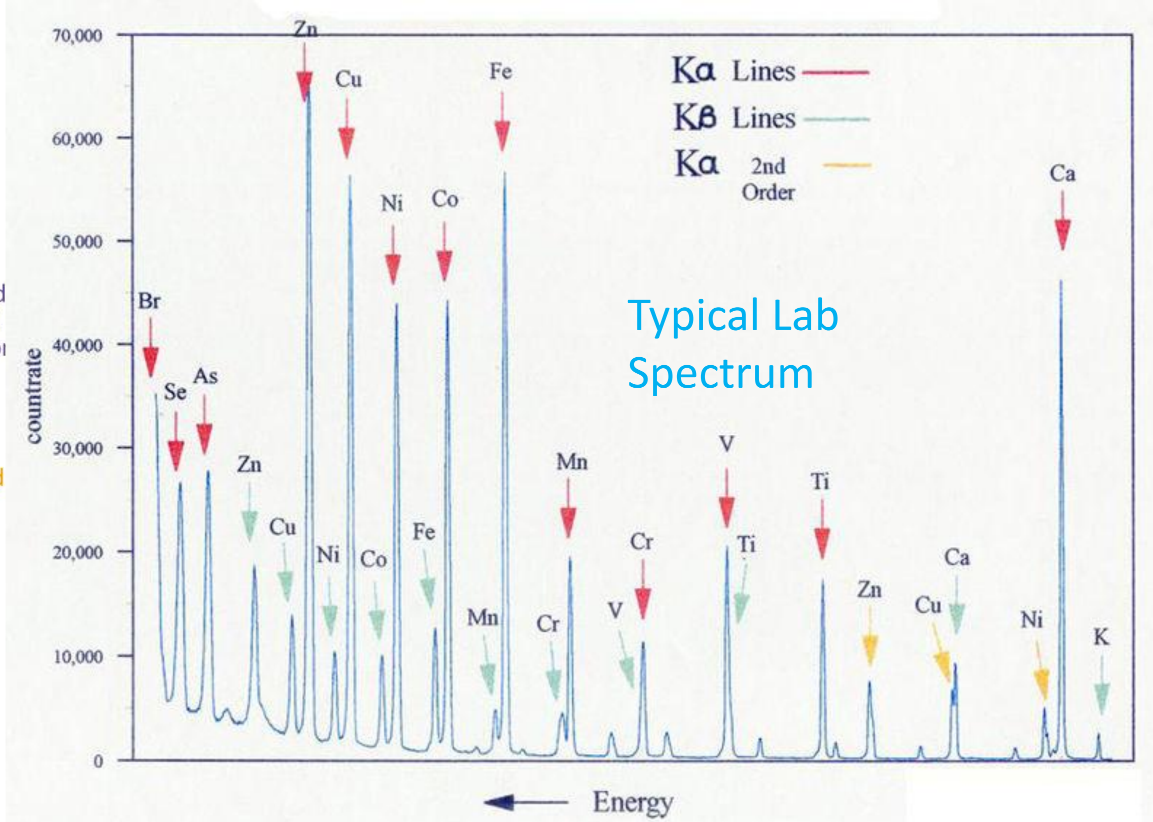


- **Source chosen so that gamma rays are in resonance with a particular element (e.g. Fe)**
- **Moving gamma ray source allows a range of energies to be scanned corresponding to Fe nuclei under various conditions**
  - Identification of Fe-bearing phases
  - Distribution of Fe among its oxidation states
  - Magnetic properties

X-Ray Fluorescence (XRF)

ELEMENTAL ANALYSIS BY DETECTING CHARACTERISTIC X-RAYS





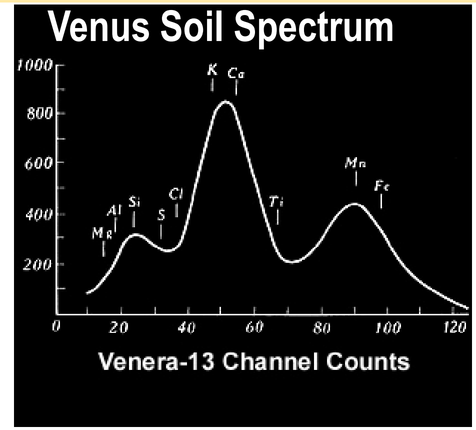
- Electron ejected from its atomic orbital by an incident x-ray
- Electron from higher level drops down and emits an x-ray
- Quantitative elemental analysis (typically Na and above).
- Low X-ray yield for light elements
- Matrix effects can cause difficulties (absorption / enhancement by other elements present and microscopic inhomogeneity)

XRF For Flight

Viking 1&2 (1975): ^{55}Fe and ^{109}Cd radioactive sources produce x-rays with energies of 5.9 KeV, 22.2 KeV, and 87.7 KeV.

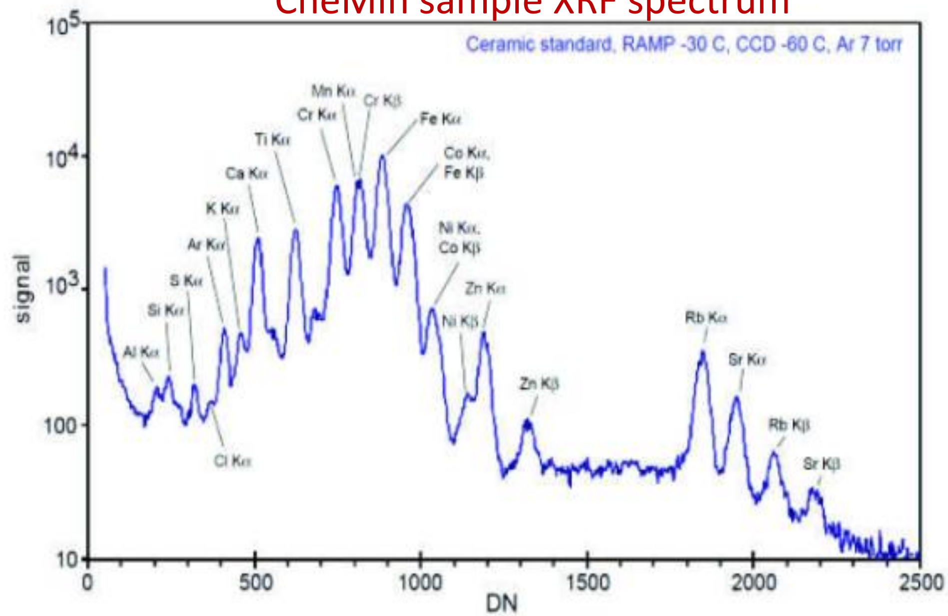
Detectors and window limit detection to elements above Na

Venera 13&14 (1981): ^{55}Fe and ^{238}Pu radioactive sources



- Stand-alone XRF has long flight heritage
- Recent instruments like CheMin on MSL and Mars-XRD on ExoMars combine it with XRD
- Future instruments will look at μ-XRF to obtain measurements within a microscopic geological context

CheMin sample XRF spectrum



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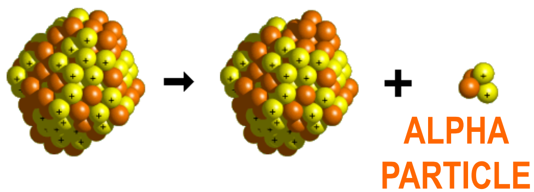
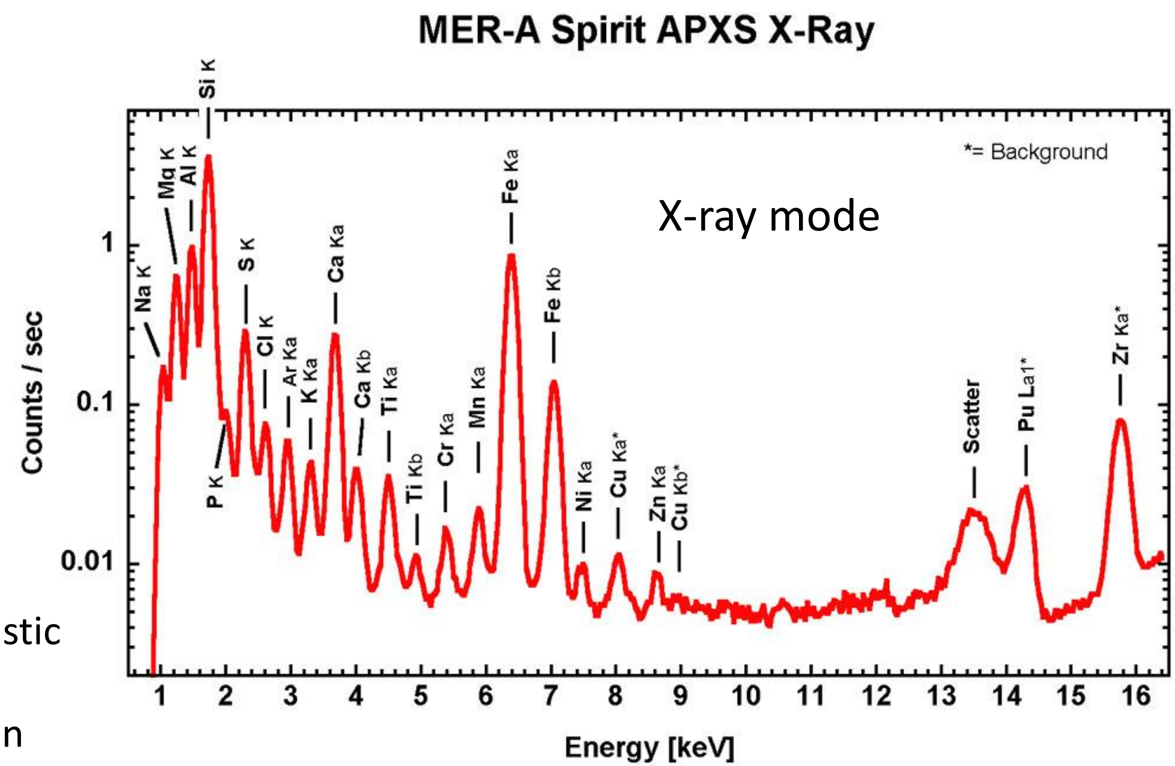
Alpha Particle X-ray Spectroscopy (APXS)

* Same as XRF but using an alpha particle source instead of an X-ray source

$$^{242}_{96}\mathrm{Cm} \longrightarrow {}^{238}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He}$$



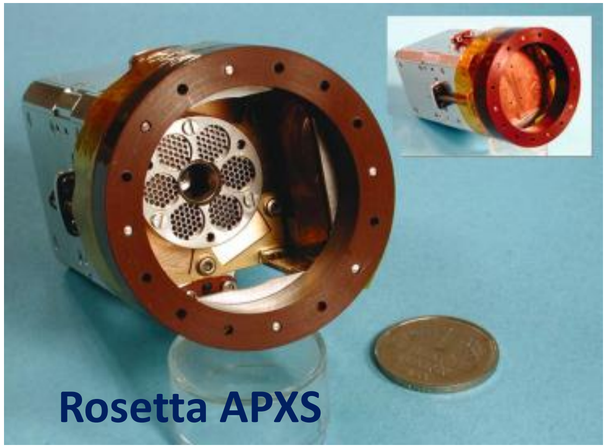


- Alpha particles (Helium nuclei) generated by radioactive decay interact with surface atoms, scatter and generate characteristic x-rays
- *X-ray mode*: Detect characteristic x-rays (XRF). Also known as Particle Induced X-ray Emission (PIXE) in the laboratory. MicroPIXE can probe a very small spot on the sample (< 1μm)
- *Alpha mode*: Detect backscattered alpha particles. Also known as Rutherford Backscattering Spectroscopy (RBS) in the laboratory.
- Lab instruments use MeV He ion accelerators, and flight instruments use radioactive sources

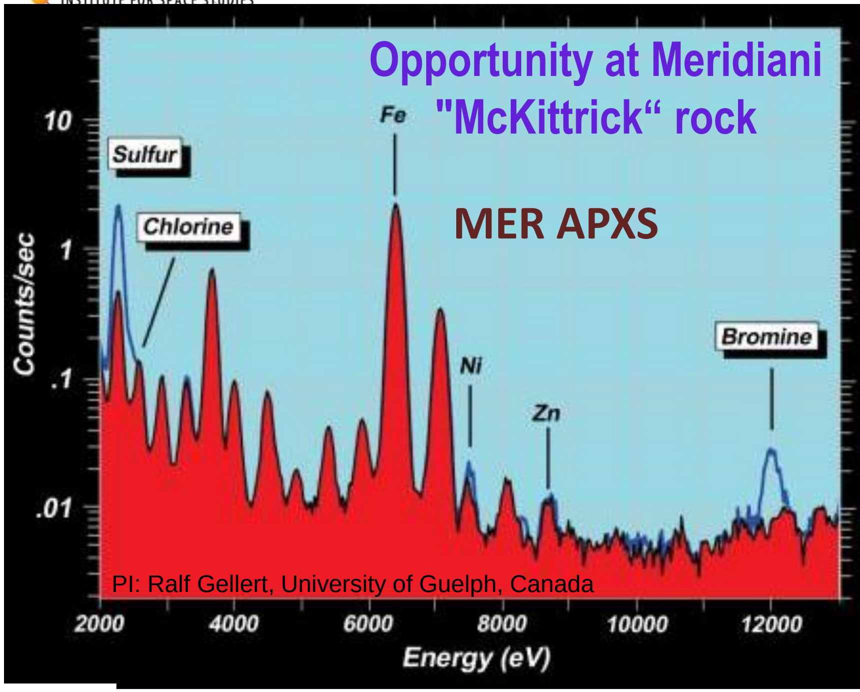
APXS for Flight

APXS has extensive flight heritage (typically ~ 0.5 kg):

- Mars Pathfinder APX
- APXS on MER
- APXS on MSL
- APXS on Rosetta Lander
    - May confirm similarities of the dust component to elemental ratios of primitive CIs or other carbonaceous chondrites.
    - X-ray and Alpha mode
    - Alpha mode is enhanced for airless bodies.
    - C and O can be detected in contrast to Mars where CO2 interferes.



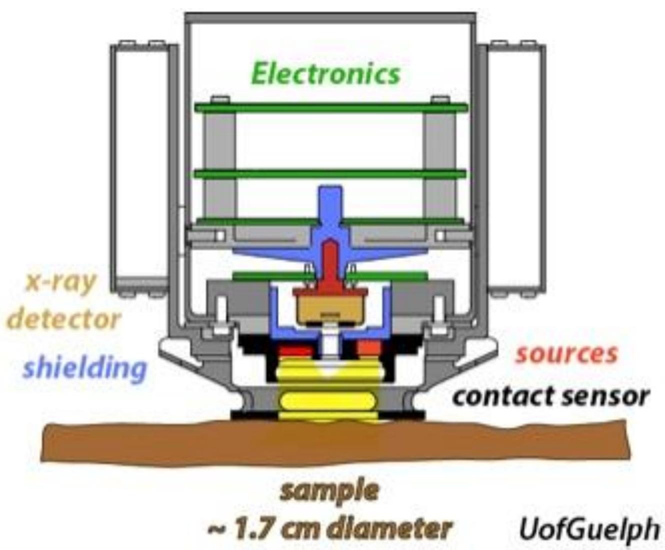
APXS For Flight



Can detect Na and above

High sensitivity to S, Cl, and Br

indicative of slowly evaporating watery brine where various salt compounds are precipitated in sequence.



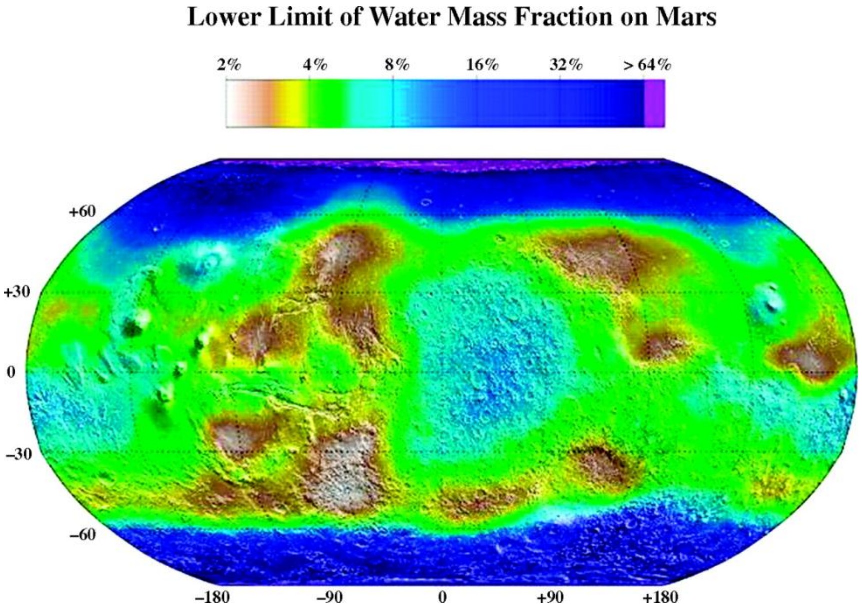
Major improvements on MSL compared to the MER APXS are:

- Stronger source – improved sensitivity
- Daytime operation by using Peltier cooler for the X-ray detector
- Dedicated basaltic calibration target mounted on the rover
- Compressed short duration X-ray spectra (~10 seconds) can be used to steer the arm movement in a “proximity mode”

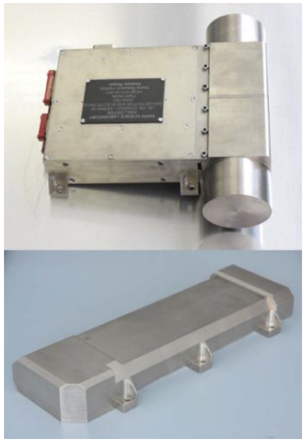
Neutron Spectroscopy

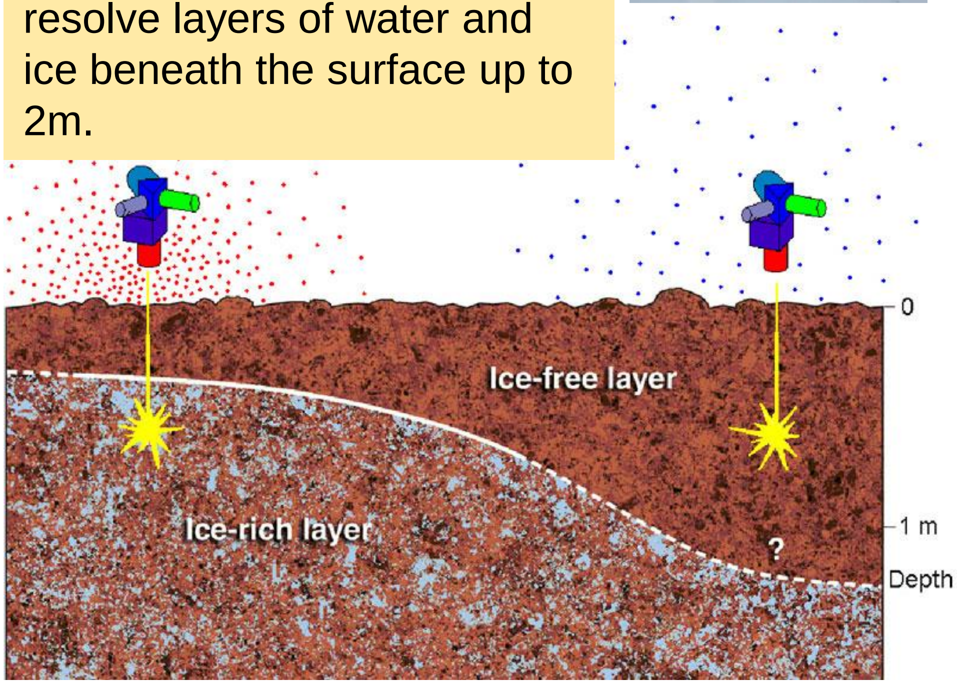
NEUTRON SCATTERING TO DETECT WATER

Neutron spectrometers on *Mars Odyssey*



First on-surface neutron measurement will be ***Dynamic Albedo of Neutrons (DAN)*** *on MSL* Will use a focused neutron source and be sensitive enough to detect water content as low as 0.1% - will resolve layers of water and ice beneath the surface up to 2m.

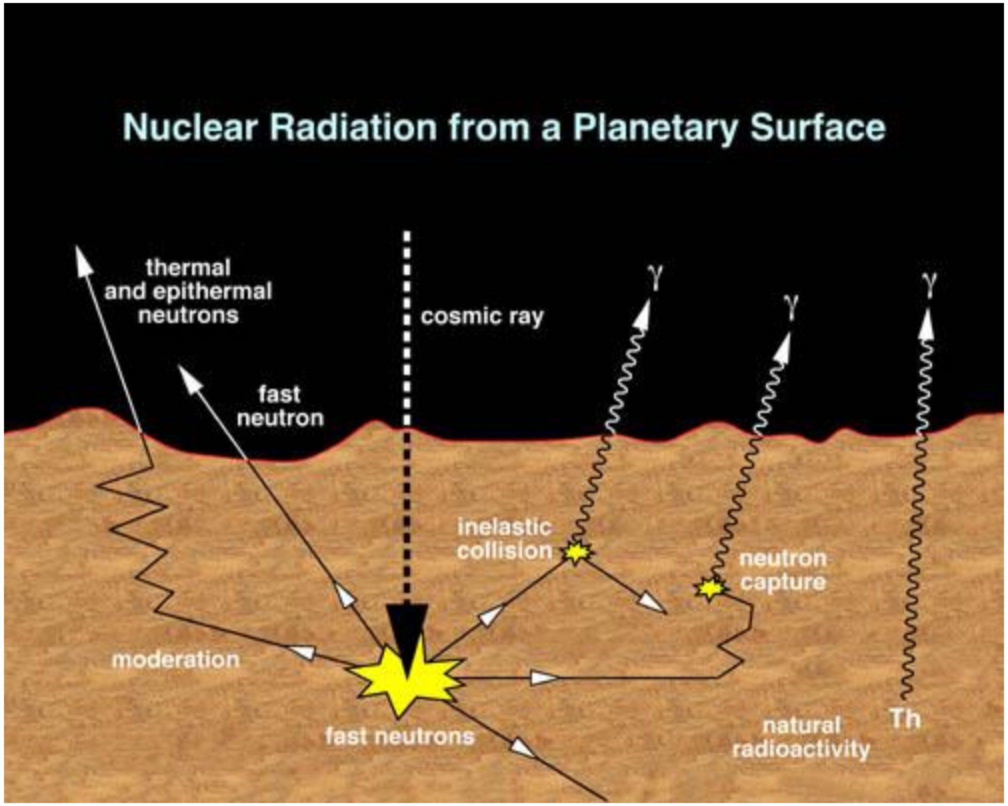




- Cosmic rays produce neutrons
- Neutrons are absorbed by hydrogen (in the form of H_2O)
- Low neutron fluxes can be correlated with higher H_2O concentrations
- Cosmic-ray produced neutrons give poor depth resolution

Gamma Ray Spectroscopy

GAMMA RAY LINE SPECTRA OF THE ELEMENTS PRESENT



- Neutrons impinge on a surface and a transition between nuclear levels occurs. A gamma ray is emitted that is specific to the nucleus that produced it.
- Passive source = ambient cosmic ray flux
- Active source = PNG
- Can detect up to a depth of tens of centimeters (passive source) to meters (active source)
- Active Source: Pulsing Neutron Generator (PNG) produces high energy neutrons which impinge on the surface and sub-surface. Secondary neutrons (detected by neutron spectroscopy) and gamma rays (detected by gamma ray spectroscopy) are produced.
- Rich history of orbital gamma ray spectrometers (Mars Odyssey, GRaND on DAWN, Mercury Messenger)

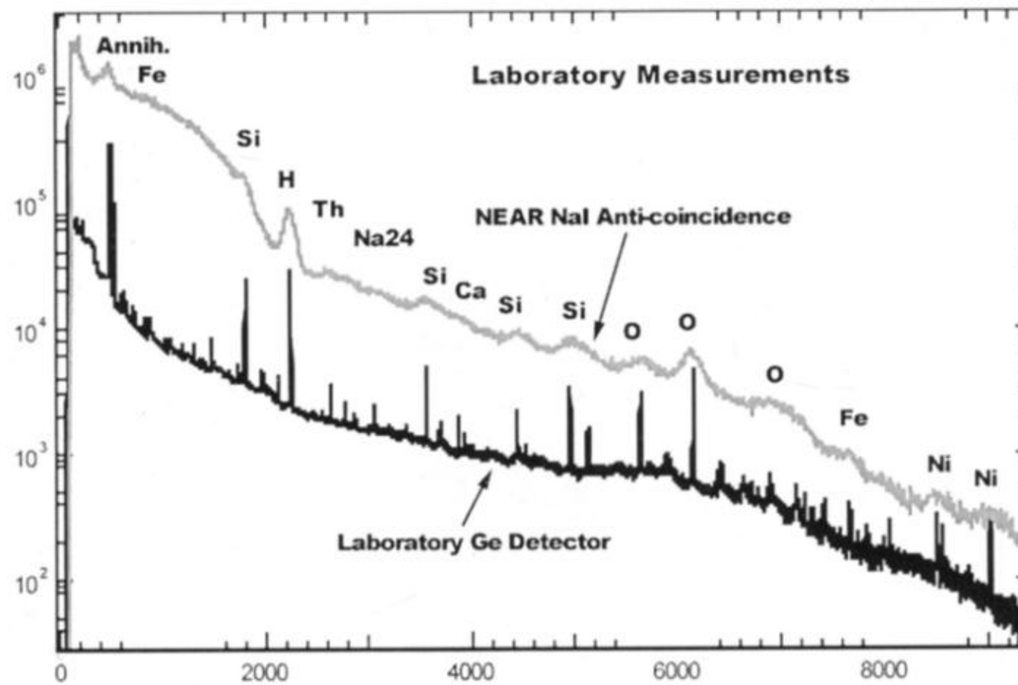
Gamma Ray Spectroscopy for Flight

On-surface Flight instruments:

- Venera 8 (Venus)
  - * Passive source
- NEAR landed on Eros
  - * Passive source
- Phobos-Grunt (lost)

Future Instruments:

- NAGRS on SAGE (proposed)
  - * Active source (PNG)
  - * Detects both neutrons and gamma rays
  - * Probes upper 1m
- Considered fort Trojan asteroids
  - * C, O, N, S, H buried beneath the surface

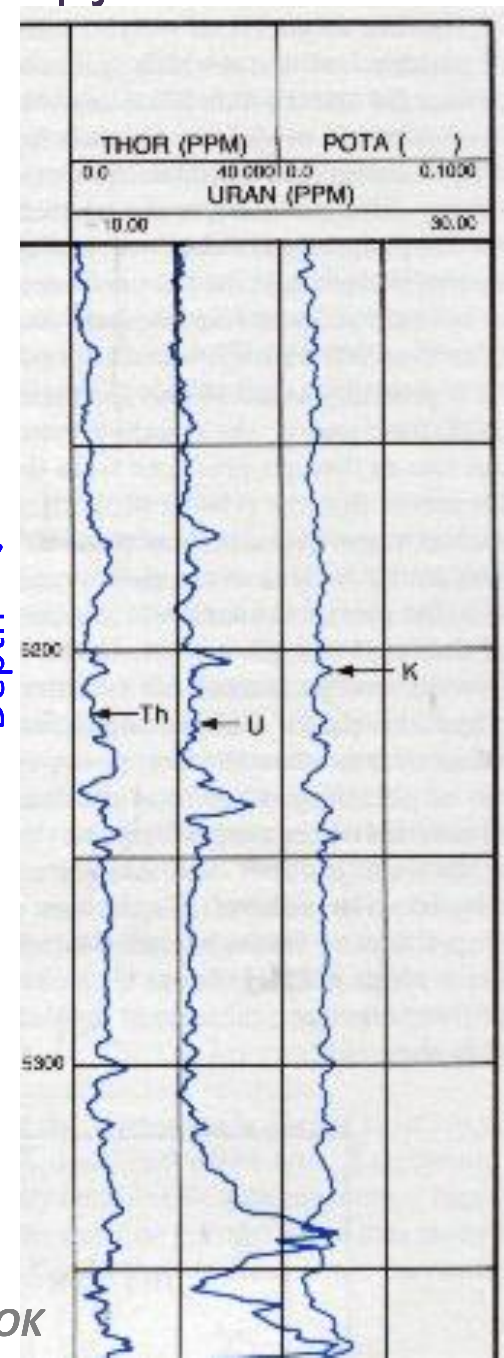


Gamma Ray / Neutron Spectroscopy for Terrestrial Applications

Alton Anderson (USGS, New York) prepares spectral gamma tool.

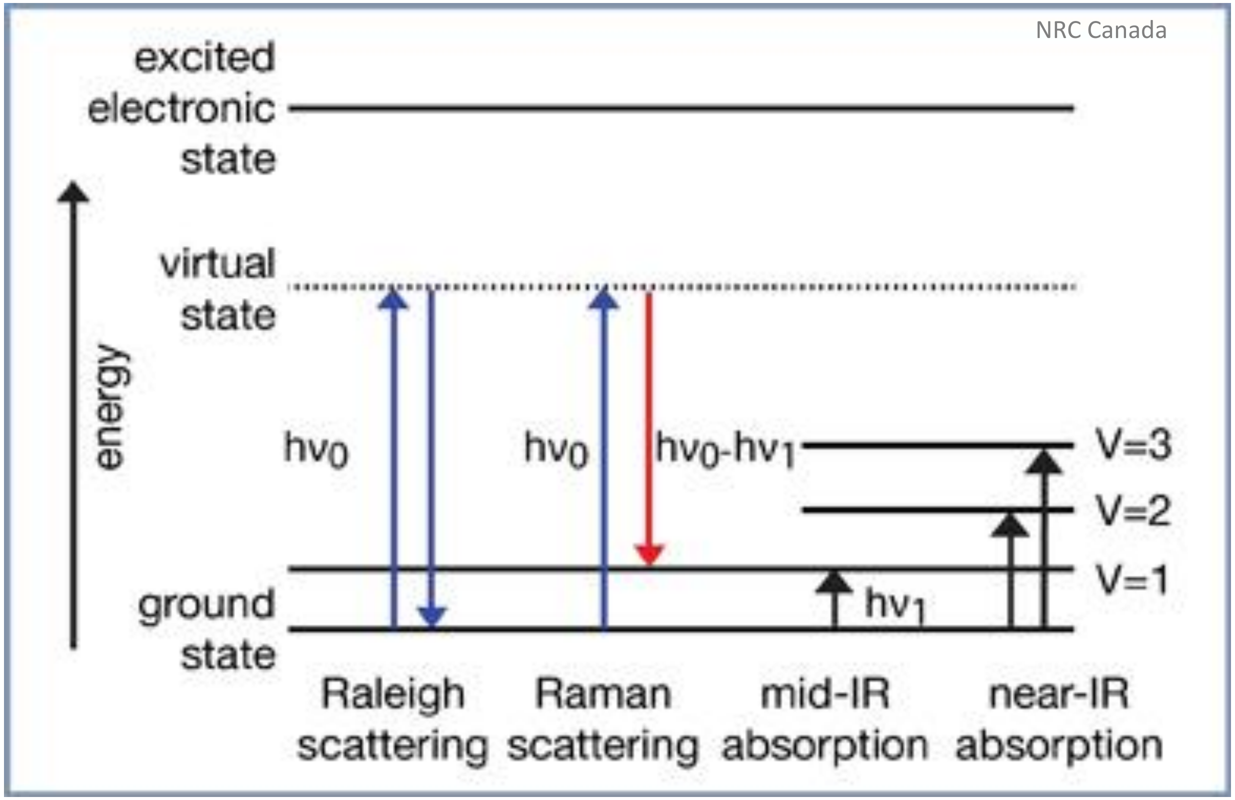
- Mineral exploration, water well drilling, oil and gas well drilling
- Neutron and gamma ray spectra as a function of depth in a bore hole
- Can calculate the partial contributions from the basic oil-, water- and rock-forming element nuclei (C, O, H, Si, Ca, Fe, Cl, etc.)
- Can infer filtration-capacity parameters, rock lithology, and fluids (oil, water) which saturates them.

Depth



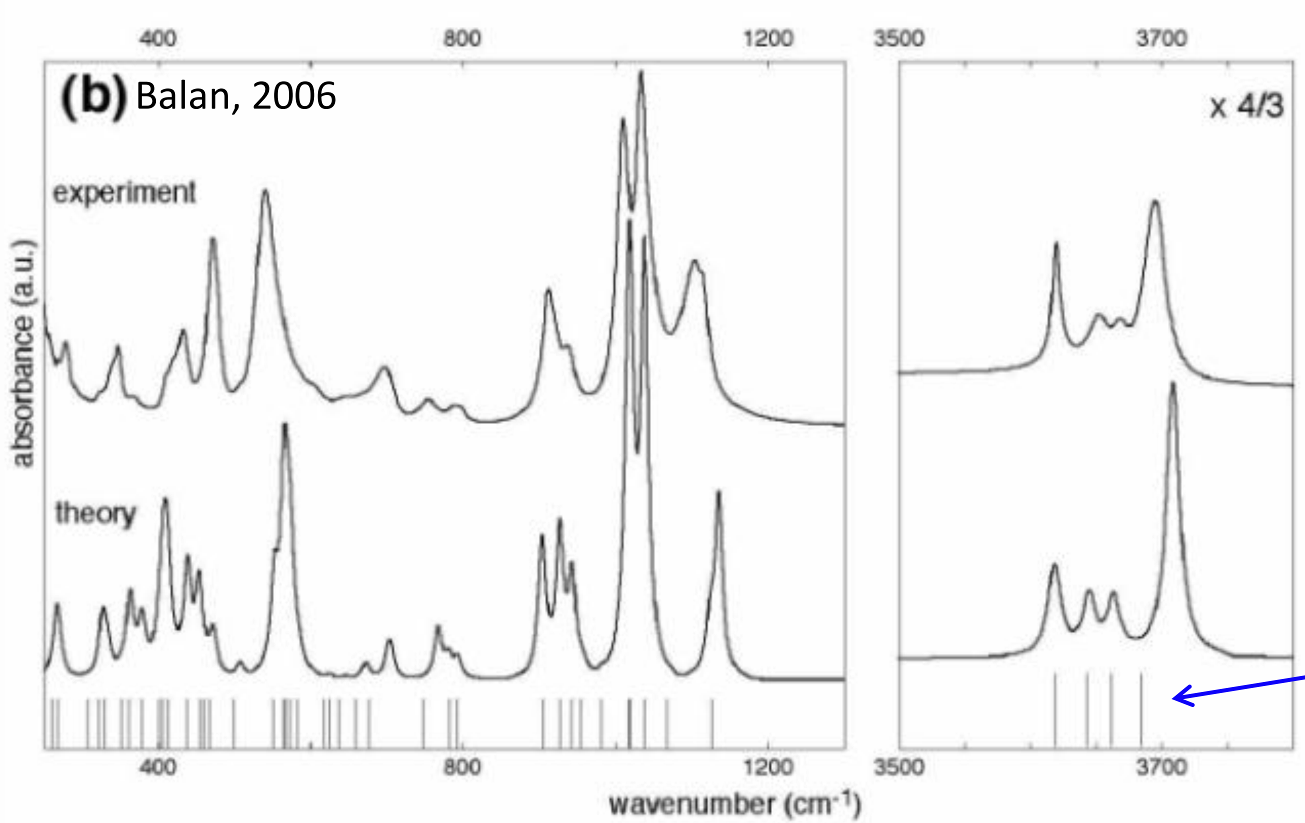
Source: *CRAIN'S PETROPHYSICAL HANDBOOK*

A Word About Vibrational Spectroscopy



Mid-Infrared Spectroscopy

REFLECTANCE SPECTROSCOPY AT λ ~ 2 – 25 μm



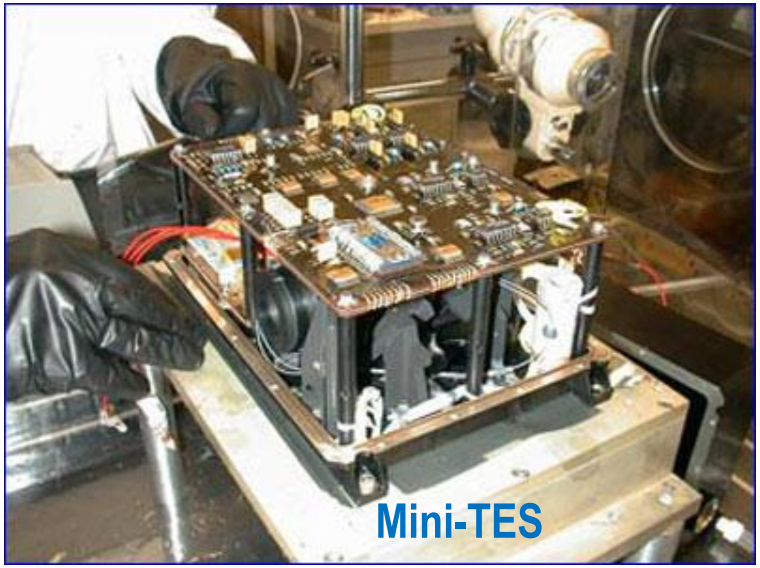
Infrared vibrational spectrum of kaolinite ~ 2 – 25 μm

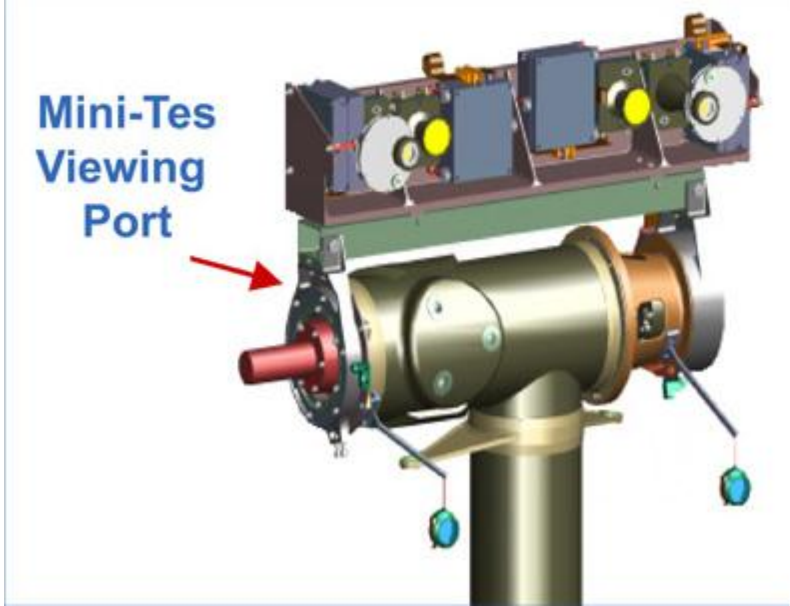
vertical bars are phonon frequencies

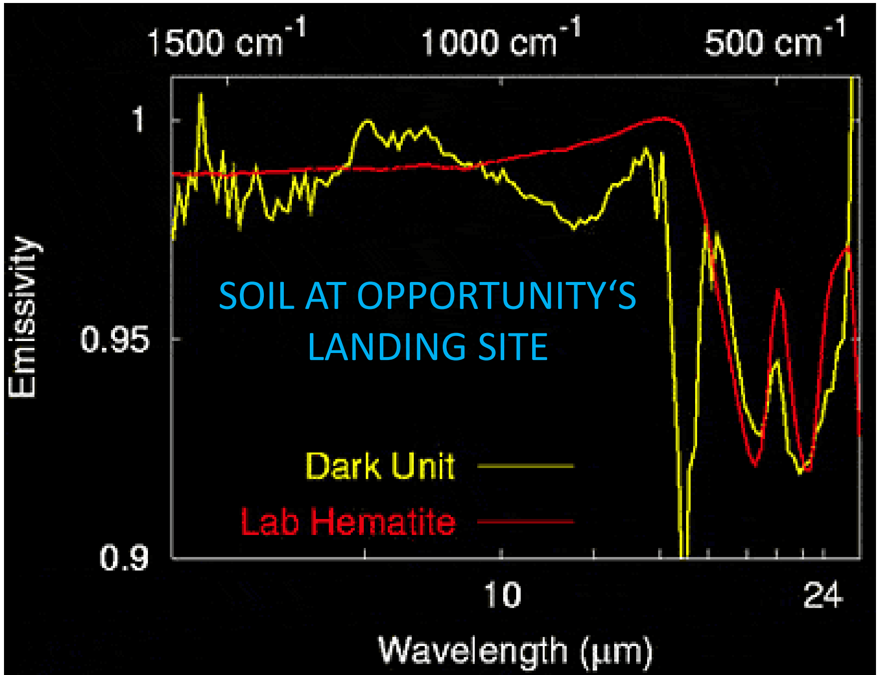
- Absorption by fundamental vibrations
- In principle same as Raman but with different selection rules
- Narrow line-widths and rich spectral detail
- Often requires sample preparation
- In practice, IR spectroscopy requires more complex calibration and is more sensitive to sample morphology.

Mid-Infrared Spectroscopy For Flight

- Mini-TES on MER is a passive thermal emission FTIR spectrometer
- Located on the body of the rover with a mast-mounted viewing port
- λ = 5 - 29 µm
- Remote mineralogical measurements on the surface
- Good for carbonates, sulfates, phosphates, and silicates
- Future instruments may consider active source and sample preparation



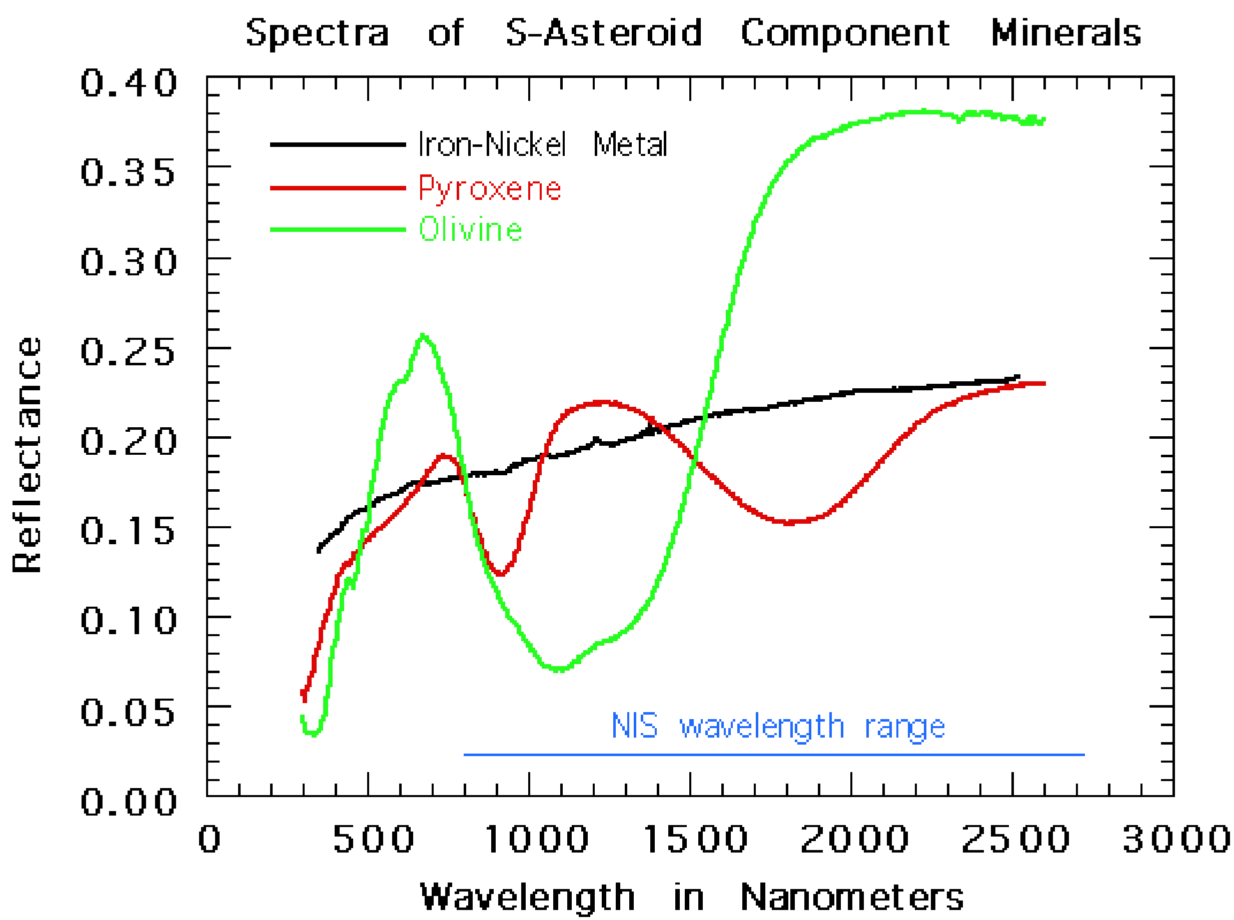




Near-Infrared Spectroscopy

REFLECTANCE SPECTROSCOPY AT $\lambda \sim 0.8 - 2.5\ \mu m$

- Commonly used in remote sensing (Earth and planetary orbiters).
- For minerals, mid-IR offers a much richer spectrum
  - most relevant vibrational modes lie in the mid-IR
- With well-developed calibration and fitting , much useful information has been gleaned from NIR spectra (particularly from orbit).



Ref: NIS Team (NEAR Shoemaker)

Although NIR spectroscopy is difficult to interpret due to wide line-widths and lack of specificity, it has become increasingly popular due to simplicity of sampling and non-invasive nature.

Near-Infrared Spectroscopy for Flight

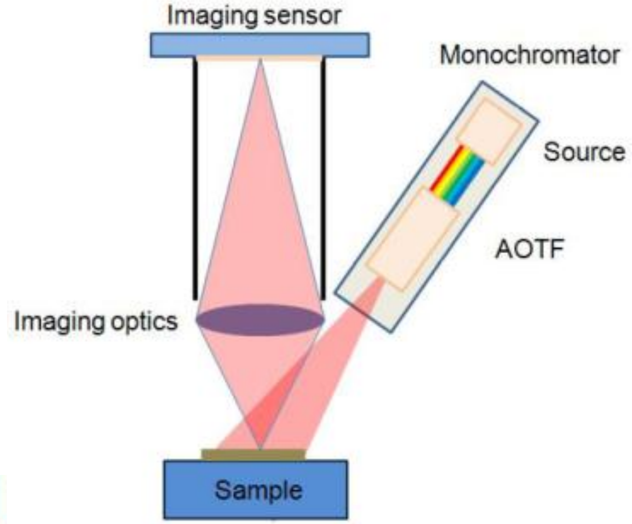
MicrOmega on ExoMars 2018

- Miniaturized NIR hyperspectral microscope
- spatial sampling 20 µm
- 0.9 to 3.5 µm

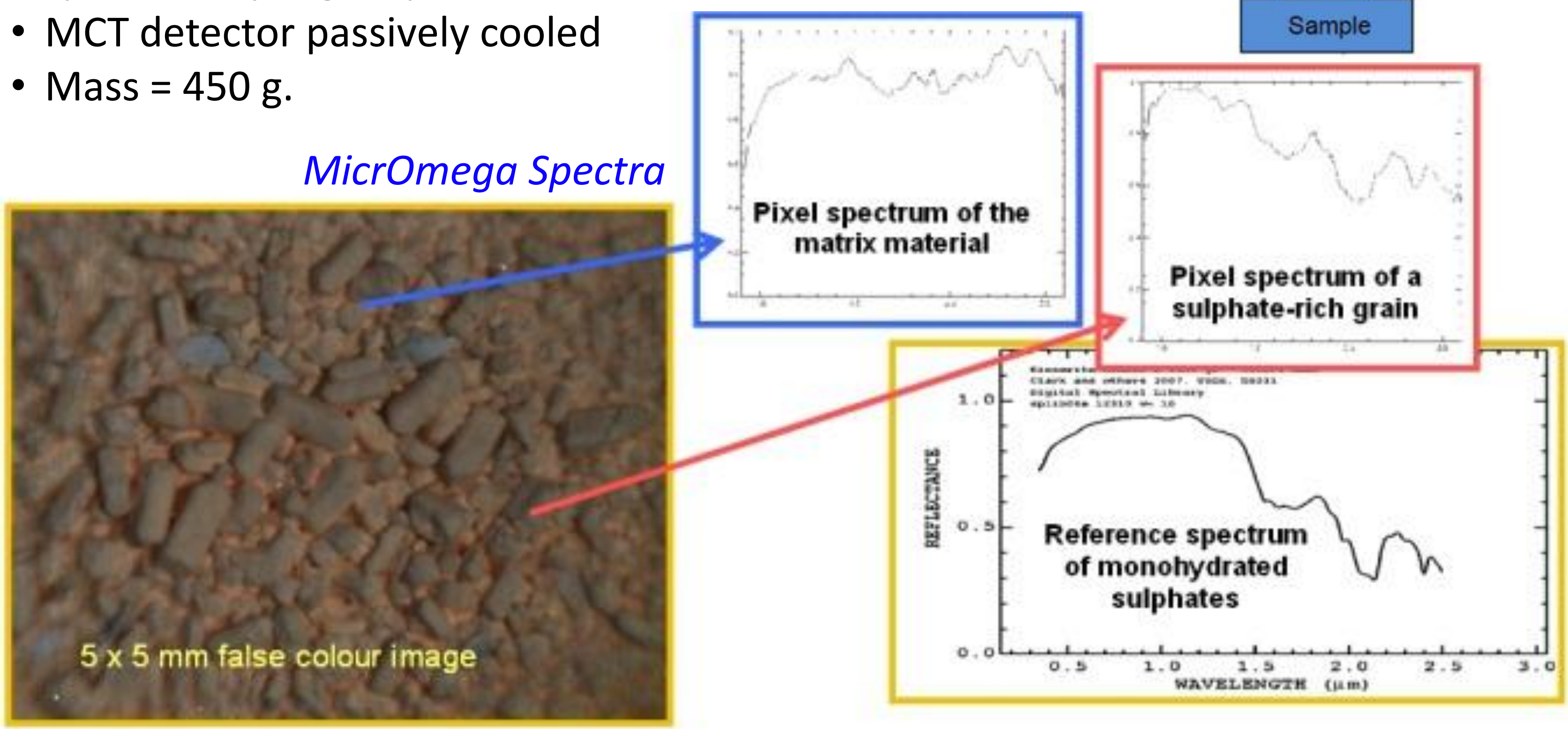
CIVA M/I on Rosetta Lander

- Visible microscope and NIR hyperspectral imager,
- active source (white light)
- spatial sampling 40 µm
- MCT detector passively cooled
- Mass = 450 g.

MicrOmega on ExoMars 2018



MicrOmega Spectra



Near-Infrared Spectroscopy and Primitive Bodies

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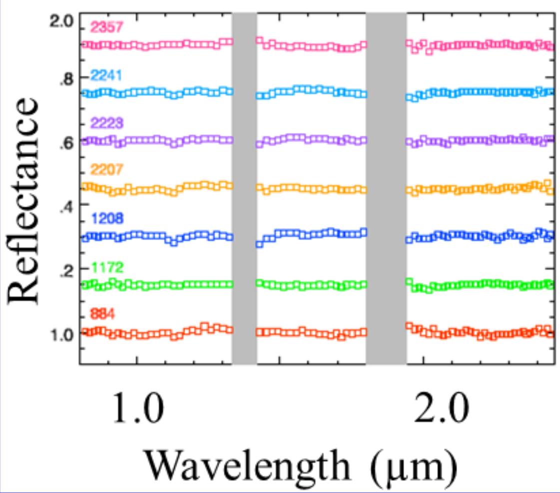
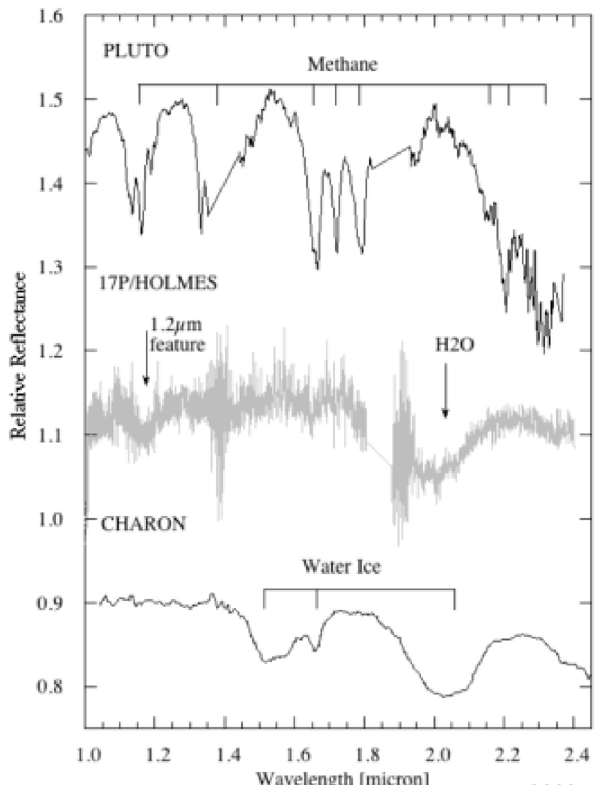
- Near-IR spectroscopy of primitive bodies is difficult (ground-based and remote). Spectra are often featureless. Microscopic on-surface measurements may be similar.

ASTEROIDS & COMETS ... COMPARE TO MARS

Featureless Reflectance Spectra of Trojan Asteroids

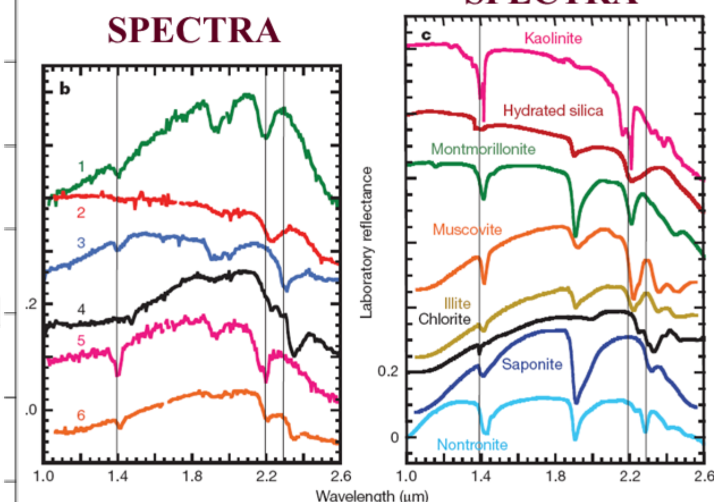


NASA Infrared Telescope Facility 3m telescope / SpeX , Mauna Kea, Hawaii.
Ref: Yang and Jewitt, The Astronomical Journal, March 2011



Yang 2009

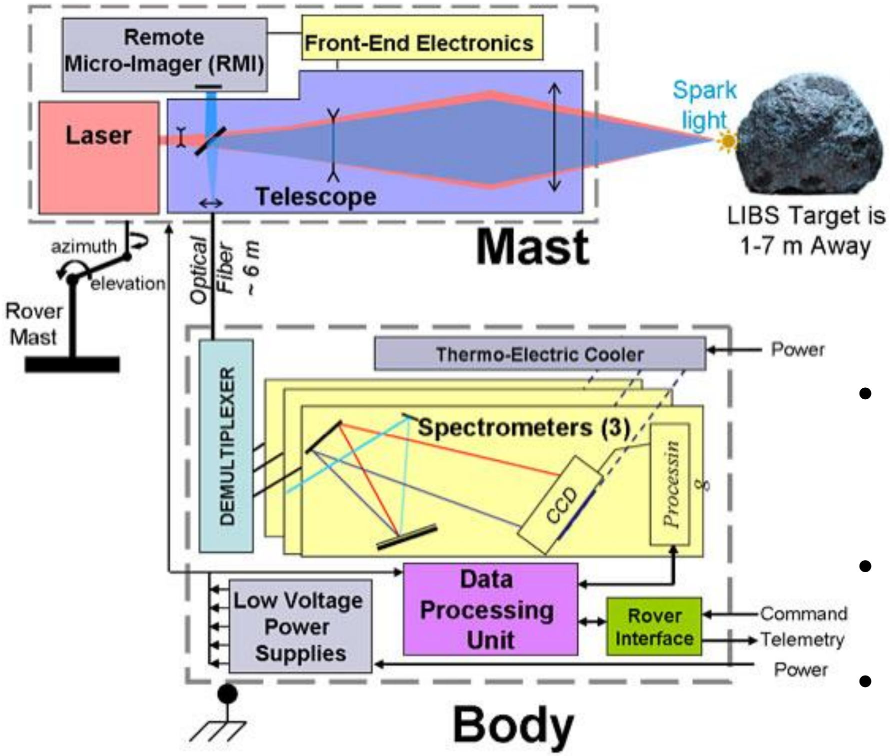
CRISM SPECTRA **LABORATORY SPECTRA**



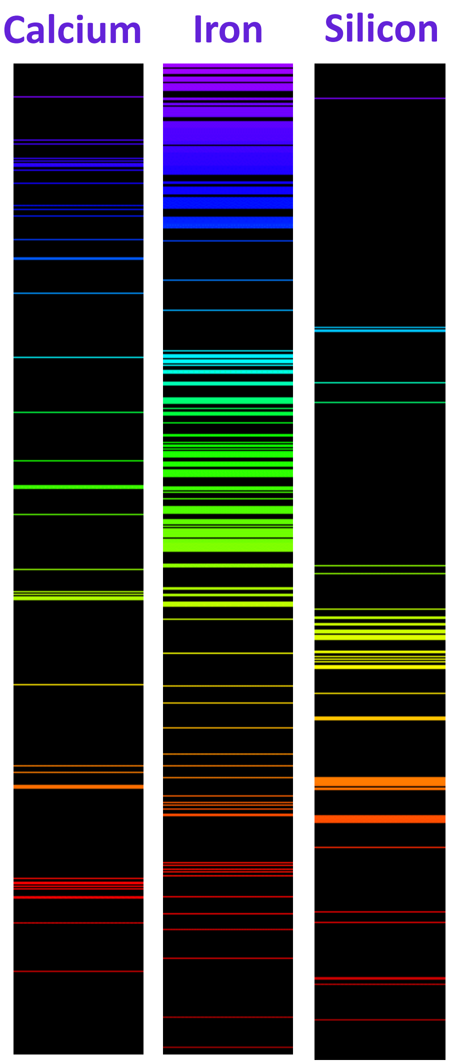
Mustard et al., Nature **454** (2008)

Laser Induced Breakdown Spectroscopy (LIBS)

ATOMIC EMISSION SPECTROSCOPY OF LASER-CREATED PLASMA AT SURFACE



- Detects all elements, with varying degrees of sensitivity
- high sensitivity to K, Na, Ca, Ba
- poor sensitivity to S, Cl, F.



- Detection limits vary from ~0.1% ~0.001%.
- Unlike X-ray techniques it is sensitive to the light elements (H, Li, Be, B, C, N, O).
- APXS is better for sulfur and halogens.
- Challenges: Relative peak heights are sensitive to the plasma conditions and change with target material, laser power, pressure. Calibration is very important.

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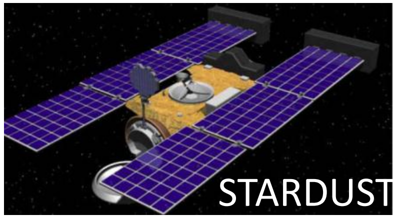
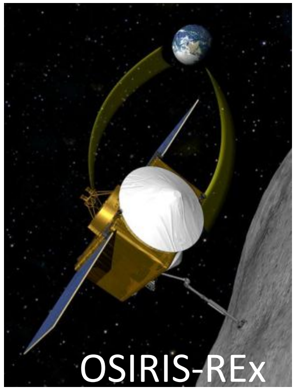
Missions to Primitive Bodies: In Situ and Sample Return

- **NEAR Shoemaker**– Asteroid Eros (s-class) – 23 Km asteroid (touched down on Eros in 2001)
  - Gamma Ray Spectrometer collected data 4-inches from the surface and was 10x more sensitive than in orbit
- **Genesis** – solar wind (samples returned in 2004)
- **Stardust** – comet Wild 2 (samples returned 2006)
  - Dust collector (mass spec) in situ
  - On Earth: Synchrotron-based x-ray microprobes (SXRM - a form of XRF) for Z > 16 , TOF-SIMS and SEM-EDX for lower z elements e.g. Mg, Al, Raman Spectroscopy, TEM and Electron diffraction, Synchrotron XRD
- **Hayabusa** – Asteroid Itokawa - 500 m, s-class asteroid (sample returned in 2010) consistent with thermally processed ordinary chondrite meteorites – bullets never fired but some dust collected anyway (MINERVA mini-Lander lost)
- **Hayabusa 2** - primitive NEA (2015) – C-type asteroid is potential target, impactor will make a small crater and samples collected from subsurface material – small lander / rover planned (possible payload includes Ion Laser Mass Analyser, Evolved gas analyser, APXS, Mossbauer, Camera with microscopic IR spectrometer, ATR, Penetrator, u-seismometer, Radar)



Missions to Primitive Bodies: In Situ and Sample Return (Cont'd)

- **Rosetta** (Philae Lander delivery 2014) – Comet 67P/Churyumov-Gerasimenko
  - APXS Alpha Proton X-ray Spectrometer
  - ÇIVA / ROLIS Rosetta Lander Imaging System
  - CONSERT Comet Nucleus Sounding
  - COSAC Cometary Sampling and Composition experiment
  - MODULUS PTOLEMY Evolved Gas Analyser
  - MUPUS Multi-Purpose Sensor for Surface and Subsurface Science
  - ROMAP RoLand Magnetometer and Plasma Monitor
  - SD2 Sample and Distribution Device
  - SESAME Surface Electrical and Acoustic Monitoring Experiment, Dust Impact Monitor
- **OSIRIS-REx** – B-type primitive asteroid (2016) – sticks out an arm to grab samples – relies on regolith
- **MarcoPolo-R** Dark binary Asteroid (2020-2024) – sample return from a primitive NEA. Sampling area will be selected after inspection from orbit. Will collect 5 orders of magnitude more material than stardust. In situ measurements will be required to provide local and global geological and physical context (possible lander payload includes LIBS, VIS-IR microscope and hyperspectral IR imager, thermal probe, Radar)



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Comparison of Mineralogy Techniques

Technique	Phase or structural Identification 'Fingerprint'	Elemental composition	Microscopic (grain scale) Geological Context	Subsurface penetration	Currently < 1 Kg
XRD	✓	✗	○ potentially	✗	✗
Raman	✓	✗	✓	✗	✗
APXS	✗	✓ > Na and lighter elements with alpha mode	○ potentially	✗	✓
Mid-IR	○ sometimes	✗	○ potentially	✓ Penetrates dust	✗
NIR	○ sometimes	✗	✓	✗	✓
Gamma Ray	✗	✓	✗	✓	✗
Neutron	✗	✓ Limited to H	✗	✓	✗
Mossbauer	○ Good for Fe –containing minerals	✗	✗	✗	✓
XRF	✗	✓ > Na	○ potentially	✗	✗ Included w/XRD
LIBS	✗	✓	○ potentially	✓ ~ 10-100 µm	✗