

## **On-Surface Measurements Primer**

## **Mineralogy Techniques**

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## **KISS Study on**

In Situ Science and Instrumentation for Primitive Bodies

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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	$\checkmark$	×	O potentially	×	×
Raman	$\checkmark$	×	$\checkmark$	×	×
APXS	×	<ul> <li>&gt; Na and lighter elements with alpha mode</li> </ul>	O potentially	×	$\checkmark$
Mid-IR	O sometimes	×	O potentially	Penetrates dust	×
NIR	O sometimes	×	$\checkmark$	×	$\checkmark$
Gamma Ray	×	$\checkmark$	×	$\checkmark$	×
Neutron	×	Limited to H	×	$\checkmark$	×
Mossbauer	O Good for Fe –containing minerals	×	×	×	$\checkmark$
XRF	×	✓ > Na	<b>O</b> potentially	×	X Included w/XRD
LIBS	×	$\checkmark$	Opotentially	<b>~</b> 10-100 μm	×



## **X-RAY DIFFRACTION (XRD)**

ELASTIC SCATTERING OF X-RAYS IN SOLIDS

## **Basic Technique**

 Collimated x-rays are incident on a crystalline sample and the scattered x-rays produce an XRD pattern. Peak positions can be determined by Bragg's law of diffraction. Peak positions and relative intensities reveal structure and composition of nearly all crystalline materials.



- X-rays interact with electron clouds unlike neutrons which interact with nuclei. Neutron scattering better for light elements (e.g. H and D).
- Powder XRD (variable  $\theta$  / monochromatic source)
  - Transmission requires sample preparation
  - Reflection can be done without sample preparation, but requires small grain size and random orientation of grains.
- Laue XRD (variable  $\lambda$  / broadband source)
  - Useful for or single- or large- grain material
- X-ray Sources
  - Synchrotron high intensity (~ 10<sup>10</sup> 10<sup>12</sup> photons/sec), narrow line-width.
  - Tube source (electrons impinge on a solid target like Cu, Mo, Co and produce characteristic x-rays) typical 20-40 kV producing up to 10-20 KW.
  - Radioactive Source lower intensity but huge power savings.
- In Situ Science and Instrumentation for Primitive Bodies, April 30, 2012

### **Measurement Capability**

- **Typical Laboratory Specifications** 
  - \* 35 KV tube source
  - \* 50 µm beam
  - \* <1° 2 $\theta$  and °0. 001 resolution are achievable
  - \* detection limit can be as low as 0.01% in some

Svnchrotron Laue

Wild 2 (Stardust

Sample Return)

[Ref: Hagiya et al.

LPSC 20071

particle from Comet

\* 1.6 µm beam size

XRD of 10 µm



## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

- CheMin on MSL transmission powder diffraction [Ref: Yen et al. LPSC 2012]
  - \* 28 KV Co tube source
  - \* 10 Kg
  - \* 50 μm beam
  - \* 5°-55° 2 $\theta$ , 0.35 ° 2 $\theta$  resolution,
  - \* detection limit > 3% by weight for crystalline phases.



#### DEVELOPED INSTRUMENTS

 Mars-XRD on ExoMars 2018 - Reflection Powder Diffraction [Ref: Marinangeli et al. DPS 2011]
 <sup>\* 55</sup>Fe radioactive source, < 1.5 Kg, 6° - 65° 2θ</li>



#### FUTURE INSTRUMENTS

• Combined reflection powder and Laue diffraction can look at both small and large grains without sample preparation (e.g. Dave Blake)

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## **RAMAN SPECTROSCOPY**

#### INELASTIC SCATTERING OF LIGHT BY PHONONS (VIBRATIONAL MODES IN MATTER)

**Measurement Capability** 

### **Basic Technique**

- A laser is incident on the sample, and is scattered by phonons or vibrational modes in the material.
- Because each band in a Raman spectrum represents interaction of light with a vibrational mode, it is highly specific for a given material. Raman can be used for identification and structural characterization of unknown samples (much like XRD).



Raman is inherently weak (~10<sup>-8</sup> of the incident laser intensity is Raman scattered). Scattering efficiency varies as  $1/\lambda^4$ , so infrared Raman is much weaker than visible and UV Raman.

- Non-destructive and requires no sample prep.
- Can be directed at a specific target sample (or microscopic grain) within the context of its natural mineral setting.
- Laser source can be focused to a very small spot size (< 1µm) comparable to mineralogical grains</li>
  - Foundation for 2-D Raman mapping





State-of-the-art Laboratory Raman (typical):

- \* <1 cm<sup>-1</sup> resolution
- \* Multi-excitation λ (e.g. 325, 532, and 785 nm)
- \* <1 µm spot size
- \* Spectral coverage variable (gratings can be easily changed out). Can go as low as 10 cm<sup>-1</sup> from laser line.
- \* Quick surface mapping



metamorphism)] [Sandford et al. Science 314 (2006)]

# Raman map of a slice of a lunar meteorite

200 µm LPSC 2 Calcite Pyroxene Olivine plagioclase

## **On-Surface Versions**

 Raman spectroscopy addresses a primary goal of mineralogical analysis of planetary bodies: determination of structure and composition. It is a prime candidate for many future missions.

#### **DEVELOPED INSTRUMENTS**

• Raman Laser Spectrometer (RLS) on ExoMars 2018 [Ref: Rull et al. LPSC 2011]



- RLS on ExoMars:
- $\sim$  6 10 cm<sup>-1</sup> resolution
- λ = 532 nm
- 50 µm spot size
- Spectral range coverage
   ~150 to 3800 cm<sup>-1</sup>
   ~ 2.5 kg
- Proposed for MERLIN Discovery-class mission to Mars' moon Deimos [Murchie et al. LPSC 2012]
- Developed for Mars Exploration Rover (MER) but de-scoped [Wang et al.,JGR 2003]
- Proposed for SAGE New Frontiers mission to Venus [Clegg et al. LPSC 2011]





#### FUTURE INSTRUMENTS

- *Remote Raman and LIBS* [Sharma et al., Spectro. Acta. Part A, 2009]
- *Microscopic Time-Resolved Raman and LIBS* [Blacksberg et al., Applied Optics 2010]. Eliminates background fluorescence and allows daylight operation.



## **MÖSSBAUER SPECTROSCOPY**

#### RECOIL-FREE RESONANT ABSORPTION AND EMISSION OF GAMMA RAYS IN SOLIDS

## **Basic Technique**

- A solid sample is exposed to a beam of gamma rays and a detector measures the intensity of the transmitted or reflected beam.
- While many spectroscopic techniques probe electronic energy levels, Mössbauer (MB) is a very sensitive technique that probes transitions between nuclear energy levels.
- The chemical environment of the nucleus affects the energies of the nuclear transitions and therefore the positions of the Mössbauer lines.
- Radioactive isotopes are used as gamma ray sources, and must be matched to the element being probed (e.g. <sup>57</sup>Co decays to <sup>57</sup>Fe and is chosen to probe Fe in Fe-bearing minerals).



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

- **Measurement Capability**
- Backscatter geometry is used for planetary surface instruments to avoid the need for sample preparation.
- Fundamental MB parameters (IS isomer shift, QS – quadrupole splitting, and B<sub>hf</sub> – magnetic hyperfine field) must be known for the common rock-forming minerals in order to correct for material-dependent effects (analogous to matrixcorrection effects).
- MB parameters vary with valence state (e.g. Fe<sup>0</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>) and coordination number which are not necessarily distinguishable for all phases.
- Planetary Mössbauer has poor counting statistics relative to the laboratory which often uses transmission geometry.





## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

 MIMOS II on MER Rovers, Mass 0.55 kg, 2.0 W Phases detected: olivine, pyroxene, hematite, magnetite, nanophase ferric oxide, ilmenite, goethite, ferric sulfate, jarosite.



MER Mossbauer Sensor Head





- Beagle 2 (lost)
- MIMOS II on Phobos-Grunt (lost)



## **X-RAY FLUORESCENCE (XRF)**

#### ELEMENTAL ANALYSIS BY DETECTING CHARACTERISTIC X-RAYS

### **Basic Technique**

- An electron is ejected from its atomic orbital by an incident x-ray of sufficient energy.
- An electron from a higher energy orbital drops down and emits a photon. The emitted x-ray is a "characteristic x-ray" of the element.



- Measurements of both x-ray energy and intensity provide quantitative elemental analysis.
- Lighter elements have lower energy x-rays compared to heavy elements. They are often absorbed within the sample making them more difficult to detect.
  - \* Be K edge ~ 0.11 keV
  - \* Pu K edge ~ 122 keV L edge ~ 22 keV
- Difficulty: matrix effects Intensity depends on absorption/enhancement of x-rays by other elements present within the sample, as well as microscopic inhomogeneity. Calibration is needed to achieve accurate quantification. This is not always possible for samples of unknown composition and morphology.
- Line overlap can be a problem for mixtures.

## Measurement Capability

- Typically used for element 11 (Na) and above.
- Elemental detection limits as low as few ppm.
- Like in XRD, a synchrotron source is used where increased sensitivity is required.



#### Synchrotron XRF Maps of a Stardust track (SSRL 2006)



## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

- Viking 1&2 (1975): <sup>55</sup>Fe and <sup>109</sup>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): <sup>55</sup>Fe and <sup>238</sup>Pu radioactive sources.

$\begin{array}{c} \mbox{Elemental Concentration of a Mar} \\ \mbox{Regolith Sample from Viking} \\ \mbox{Mg} & 5.0 \pm 2.5 \\ \mbox{Al} & 3.0 \pm 0.9 \\ \mbox{Si} & 20.9 \pm 2.5 \\ \mbox{Cl} & 0.7 \pm 0.3 \\ \mbox{K} & < 0.25 \\ \mbox{Ca} & 4.0 \pm 0.8 \\ \mbox{Ti} & 0.51 \pm 0.2 \end{array}$	Viking XRF: * ~ 2 kg, 3.5 W * Calibration standards * Samples delivered by Surface Sampler * Detection limit ~ 30 ppm to ~ 0.1 %			
Fe $12.7 \pm 2.0$ L† $50.1 \pm 4.3$ X‡ $8.4 \pm 7.8$ Rb $\leq 30 \text{ ppm}$ Sr $60 \pm 30 \text{ ppm}$ Y $70 \pm 30 \text{ ppm}$ Zr $\leq 30 \text{ ppm}$ Ref: Clark et al. 1977	$\begin{array}{cccc} SiO_2 & 45.1 \pm 3.0 \\ TiO_2 & 1.59 \pm 0.45 \\ Al_2O_3 & 15.8 \pm 3.0 \\ FeO & 9.3 \pm 2.2 \\ MnO & 0.2 \pm 0.1 \\ MgO & 11.4 \pm 6.2 \\ CaO & 7.1 \pm 0.96 \\ K_2O & 4.0 \pm 0.63 \end{array}$			
Venus surface composition of a collected sample	$\rightarrow \begin{array}{c} \text{S} & 0.65 \pm 0.4 \\ \text{Cl} & < 0.3 \\ \text{Ref: Surkov 1997} \end{array}$			

- measured by Venera 13
- CheMin on MSL (2011): XRF descoped but data will still be available on a best effort basis.
   Sensitive to Z above 15 (P)
- Related: Used as remote sensing from orbit

#### DEVELOPED INSTRUMENTS

- Mars-XRD on ExoMars 2018 XRF in addition to Reflection Powder Diffraction [Ref: Marinangeli et al. DPS 2011] Elements 13 (Al) to 25 (Mn)
- XRS on Beagle 2 (lost): 340 g , 5W FUTURE INSTRUMENTS
- *Micro-XRF* uses small spot size to obtain XRF within geological context (Allwood, LPSC 2011)



## ALPHA PARTICLE X-RAY SPECTROSCOPY (APXS)

#### SIMILAR TO XRF BUT USING AN ALPHA PARTICLE SOURCE INSTEAD OF AN X-RAY SOURCE

### **Basic Technique**

• 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.
- *Alpha mode:* Detect backscattered alpha particles. Also known as Rutherford Backscattering Spectroscopy (RBS) in the laboratory.
- Lab instruments use MeV He ion accelerators.
- MicroPIXE is a non-destructive multi-element microprobe technique with detection limits down to ppm. It uses a tightly focused beam < 1um to analyze individual mineral grains.



### **Measurement Capability**

- MSL A full analysis with detection limits of 100 ppm for Ni and ~ 20 ppm for Br requires 3 hours, while quick look analysis for major and minor elements at ~ 0.5% abundance, such as Na, Mg, Al, Si, Ca, Fe, or S, can be done in 10 minutes or less.
- MER X-ray mode sensitive to major elements, e.g. Mg, Al, Si, K, Ca, and Fe, and minor elements, e.g. Na, P, S, Cl, Ti, Cr, and Mn. Alpha mode sensitive to lighter elements, e.g. C and O. Depth of analysis varies with atomic number, ranging from ~ 10 to 20  $\mu$ m for Na, to ~ 50 to 100  $\mu$ m for Fe. Detection limit typically 0.5 to 1 weight percent, depending on the element. Insensitive to small variations of the geometry of the sample surface.





## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

- Mars Pathfinder APX (1996), Mass = 0.57 kg, 0.3 W
- Russian Mars 96 APXS (lost)
- Russian Phobos-Grunt (lost)



- APXS on MER: 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. Time for measurement ~ 10 h.
- APXS on MSL: 1.7 cm sample area. Major improvements compared to 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". Only X-ray mode, no alpha mode.
- APXS on Rosetta Philae Lander: Predecessor of the MER APXS. The compositional data of the APXS may confirm similarities of the dust component to elemental ratios of CIs or other carbonaceous chondrites. Na to Ni in X-ray mode and lighter elements (except H and He) using alpha mode.

Alpha mode is enhanced for airless bodies. C and O can be detected in contras to Mars where CO<sub>2</sub> interferes. Will be lowered to the comet surface by special deployment device [Ref: Klingelhofer 2007] Mass: 0.64 kg, 1.5 W





## **NEUTRON SPECTROSCOPY**

#### NEUTRON SCATTERING TO DETECT WATER

## **Basic Technique**

- Neutrons are produced by cosmic rays (passive source) or a focused active neutron source such as a Pulsing Neutron Generator (PNG).
- With each collision the neutrons transfer part of their kinetic energy to the scattering nucleus (like billiard balls). More kinetic energy will be transferred to a lighter nucleus. Slow neutrons may even be captured by a light element like H.
- Hydrogen (in the form of H<sub>2</sub>O or hydrated minerals) absorbs more kinetic energy in the scattering process than other elements.



- Low neutron fluxes can therefore be correlated with higher  $\rm H_2O$  concentrations .
- Cosmic-ray produced neutrons give poor depth resolution compare to PNG-produced neutrons.



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### **Measurement Capability**

- Popular terrestrial use for pulsed neutron tools include Mineral exploration, water well drilling, oil and gas well drilling
- Neutron and gamma ray spectra are both measured 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



## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

- To date there have been no on-surface neutron measurements. The first will be from DAN on MSL (< 5 Kg)</li>
- Phobos Grunt (lost) ~ 4.0 kg
- 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% - DAN is also designed to perform an in-situ analysis of the layering structure of hydrogen bearing minerals (or water) in the Martian subsurface, with horizontal resolution up to 1 m. It will resolve layers of water and ice beneath the surface up to 2m. It does not include a gamma ray spectrometer



PI: Igor Mitrofanov, Space Research Institute (IKI), Russia

Neutron source is a compact linear accelerator that produces neutrons by fusing isotopes of hydrogen together. It is a vacuum tube with tritium and deuterium. Accelerating voltage causes a nuclear fusion reaction generating 10<sup>7</sup> neutrons per pulse with energy 14 MeV neutrons.



## **GAMMA RAY SPECTROSCOPY**

#### GAMMA RAY LINE SPECTRA OF THE ELEMENTS PRESENT

## **Basic Technique**

- When a neutron impinges on the surface, a transition between nuclear levels occurs. A gamma ray is emitted that is specific to the nucleus which produced it.
- 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.
- Can detect all major rock-forming elements and some volatiles (C, H, O, S)
- Passive mode can measure the content of natural radioisotopes K, Th, U.
- Can be integrated with a penetrator.



### **Measurement Capability**

- Can be performed from orbit (using ambient cosmic ray flux as a source) or on-surface (using an active source) for detailed mapping.
- Can detect up to a depth of tens of centimeters (passive source) to meters (active source).
- Rich history of orbital gamma ray spectrometers (Mars Odyssey, GRaND on DAWN, Mercury Messenger).
- Using PNG increases the S/N and can differentiate between the active source and ambient cosmic ray flux. Produces neutron flux many orders of magnitude above background flux.



NAGRS SAGE Gamma Ray Test Data from representative Venu Soil Sample [Mitrofanov EPSC 2010]

## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

 GRS on Venera-Vega Venus missions measured K, U, Th, sensing an area ~ 1m below the lander and a few cm in depth.

#### Table 1

Contents of K, U, and Th in Venus surface material measured by the gamma spectrometry technique (Surkov, 1997)

Lander	Venera 8	Venera 9	Venera 10	Vega 1	Vega 2
K (mass%) U (ppm) Th (ppm)	$4.0 \pm 1.2$ $2.2 \pm 0.7$ $6.5 \pm 0.2$	$0.5 \pm 0.1$ $0.6 \pm 0.2$ $3.7 \pm 0.4$	$0.3 \pm 0.2$ $0.5 \pm 0.3$ $0.7 \pm 0.3$	$\begin{array}{c} 0.45 \pm 0.22 \\ 0.64 \pm 0.47 \\ 1.5 \pm 1.2 \end{array}$	$\begin{array}{c} 0.40 \pm 0.20 \\ 0.68 \pm 0.38 \\ 2.0 \pm 1.0 \end{array}$



K-Th from GRS for Venus - similar trend to Mars, Earth. Comparatively, Lunar and HED achondrites are K depleted [Basilevsky et al. LPSC 2006]

- *GRS on NEAR Shoemaker* landed on Eros surface where GRS was 10x more sensitive than in orbit.
- Phobos Grunt (lost) neutron and gamma ray, 1-2m penetration depth - 5.5 kg.

#### DEVELOPED AND FUTURE INSTRUMENTS

- *NAGRS on SAGE* (upper 1 m) uses PNG and detects both neutrons and gamma rays.
- Trojan asteroids: C, O, N, S, H buried beneath the surface.



## MID-INFRARED SPECTROSCOPY

#### REFLECTANCE SPECTROSCOPY AT $\lambda \simeq 2 - 25 \ \mu m$

## **Basic Technique**

- · An infrared source is incident on a sample and absorption is measured vs. wavelengths.
- Infrared source can be passive (solar reflectance) or active (broadband light source).
- Absorption is by fundamental vibrations characteristic of the target material.



- Narrow line-widths and rich spectral detail.
- Often uses Fourier Transform Infrared (FTIR) Spectroscopy technique.
- Often requires sample preparation (many solids are measured in transmission after diluting in a non-absorbing matrix like KBr). Can also use reflectance or attenuated total reflectance techniques. In the lab, transmission spectra of thin sections are common for complex natural

samples.



- **Measurement Capability**
- In principle, infrared spectroscopy from ~ 2 25 um probes the same vibrational states as Raman spectroscopy (but with different selection rules)
- In practice, IR spectroscopy requires more complex calibration and is more sensitive to sample morphology.



Ref: Morlok 2005

## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

• Mini-TES on MER : Mast-mounted, Passive source (thermal emission), FTIR with Michelson interferometer,  $\lambda = 5 - 29 \,\mu\text{m}$  (10 cm<sup>-1</sup> resolution), Remote mineralogical measurements on surface. Thermal IR can penetrate dust coatings. Thermal IR well identifiable for carbonates, sulfates, phosphates, silicates. 2.4 kg



#### FUTURE INSTRUMENTS

• In Situ FTIR with active source and sample preparation [Anderson et al Rev. Sci. Instr. 2005]



## **NEAR-INFRARED SPECTROSCOPY**

#### REFLECTANCE SPECTROSCOPY AT $\lambda$ ~ 0.8 – 2.5 $\mu m$

## **Basic Technique**

- Active source (usually broadband light source) or passive source (sunlight), often combined with visible imaging and spectroscopy.
- Can be reflection or transmission.
- Instruments can be Dispersive (grating) or FTIR using an interferometer.
- Near-Infrared imaging spectrometers are commonly used in remote sensing (Earth and planetary orbiters).
- Typically for minerals, mid-infrared offers a much richer spectrum (most relevant vibrational modes lie in the mid-IR). However, with well-developed calibration and fitting, much useful information has been gleaned from NIR spectra (particularly from orbit).
- 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.



### **Measurement Capability**

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



#### LABORATORY CRISM **SPECTRA SPECTRA** Kaolinite Hvdrated silica Montmorillonite tance ped reflect CRISM r Chlorite 2.2 1.0 1.4 2.2 1.8 2.6 1.8 Wavelength (um) Mustard et al., Nature 454 (2008)

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## **On-Surface Versions**

#### DEVELOPED INSTRUMENTS

 MicrOmega on ExoMars 2018 (0.9 to 3.5 um) miniaturized near infrared hyperspectral microscope using a monochromater Monochromator based on an acousto-Source optical tunable filter spatial sampling 20 AOTE µm and spectral Imaging optics sampling of 20 cm<sup>-1</sup> **MicrOmega** [Pilorget EPSC 2011]. Pixel spectrum of the

Pixel spectrum of the matrix material Pixel spectrum of a subhate-ich grain of the subhate-ich g

•CIVA M/I on Rosetta Lander – Visible microscope and NIR hyperspectral imager, active source (white light), monochromater, spatial sampling 40  $\mu$ m, spectral sampling 10 nm at 4 $\mu$ m, MCT detector passively cooled, 450 g.

#### FUTURE MISSIONS

 In Situ Vis-NIR Spectrometer with Moon Mineralogy Mapper (M3) heritage and compact optics [D. Blaney, et. Al. LPSC 2012], Mastmounted ~ 2Kg.



## LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

#### ATOMIC EMISSION SPECTROSCOPY OF LASER-CREATED PLASMA AT SURFACE

### **Basic Technique**

- A high power pulsed laser is focused on the surface and ablates a small amount of material (e.g. ng). A plasma is created near the surface. Continuum radiation is emitted. After some time (typically μs) the continuum dies down and sharp atomic emission lines characteristic of the elements present can be detected.
- Can be performed close-range (microscopic) or remote (meters).
- A time-resolved detector increases the signal to noise by 'gating out' or eliminating the continuum radiation and collecting only the atomic emission spectra



### **Measurement Capability**

- Can detect all elements, with varying degrees of sensitivity (e.g. high sensitivity to K, Na, Ca, Ba and 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.
- Sensitive to atmosphere and pressure. Can be used on an airless body with proper calibration.
- Quantitative analysis of mixtures can be challenging due to large number of peaks. Relative peak heights are sensitive to the plasma conditions and change with target material, laser power, pressure. Calibration is very important.

#### Photon Machines 'Insight' Laboratory LIBS





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### **On-Surface Versions**

#### FLIGHT INSTRUMENTS

• ChemCam on MSL – remote sensing on the surface (1-7 m). LIBS and remote micro-imager. 200 – 500 um spot size. Spectral range 240 – 850 nm. High laser irradiance removes weathering layer (~ 0.4 to 100  $\mu$ m per pulse depending on material). Carries calibration targets. Does not have a time-gated detector. Mass ~ 5.6 kg





#### **DEVELOPED INSTRUMENTS**

• ExoMars (De-scoped from combined LIBS-Raman)

#### FUTURE INSTRUMENTS

- SAGE Venus
- MarcoPolo-R lander
- Considered for Mars, Venus, Titan, Asteroids
- Microscopic LIBS combined with Raman



## Comparison of Gas Phase Techniques

Technique	Noble gases & their isotope ratios	Gas Abundances	Stable isotope ratios in CHNOS	Low H2O, NH3, CH4	Complex Organics	Chirality	pH, ions, salinity, conductivity, etc
TLS	×	~	✓ No interferences	$\checkmark$	×	×	×
Mass Spec	$\checkmark$	$\checkmark$	✓ Mass interferences	×	$\checkmark$	×	×
GC	×	(✓)	×	×	$\checkmark$	$\checkmark$	×
Wet Chemistry	×	×	×	×	$\checkmark$	$\checkmark$	$\checkmark$

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Chris Webster, JPL



## **TUNABLE LASER SPECTROSCOPY**

#### IR ABSORPTION IN GASES AND VAPORIZED LIQUIDS AND SOLIDS

## **Basic Technique**

• Optical depth of IR absorption lines (individual vibration-rotation transitions) give abundances according to Beer's law:

#### $T = I/I_{o} = 10^{-EcL}$

I= transmitted intensity,  $I_{o}$ =initial intensity,  $\epsilon$ =absorption coefficient, c=concentration, L=pathlength



- IR light (1-30 μm) in the form of narrow-band scanning tunable laser is absorbed by IR-active molecules in gas phase;
- Ultra-high spectral resolution provides high sensitivity (deep lines) that is enhanced by detection techniques (second-harmonic for SNR and cavity-ringdown for extended path);
- Good for all IR-active molecules (including weak transitions in N<sub>2</sub> and O<sub>2</sub>), but cannot be used for atoms nor for noble gases;
- Especially good at high-precision isotope ratios in CHNOS without interferences of mass spec;
- Gas phase detection of gases directly or produced from liquid or solid pyrolysis or combustion;
- Targets specific spectral lines in narrow scan with resulting limited survey capability;
- Absorbing path can be in sealed cell (Herriott cell or cavity ringdown cell) or open atmospheric path.

## **Measurement Capability**

**Typical Laboratory Specifications** 

- \* Herriott mulitpass cells of typically 50 m path;
- \* Cavity ringdown detection extends path to km;
- \* Absolute gas abundances to 2% with calibration gases; 20-50 kg field-portable systems;
- \* Picarro single isotope ratio cavity-ringdown precisions for 15 mins:
  - \* delta- $^{13}$ C in CO<sub>2</sub> to 0.1 per mil
  - \* delta-<sup>13</sup>C in CH<sub>4</sub> to 0.5 per mil for 1800 ppb





- \* Extensive use in Earth balloon, aircraft missions to study ozone photochemistry, heterogenous (aerosol, polar cloud) chemistry, cloud physics
- \* Typical gases: HCl, HF, NO, NO<sub>2</sub>, HNO<sub>3</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, SO<sub>2</sub>, OCS, H<sub>2</sub>S, HCN, C<sub>x</sub>H<sub>x</sub>,;
- \* Laser sources operating at room temperature are now available: tunable diode lasers, quantum-cascade lasers, interband-cascade lasers.
- \* Because laser power is high (>1 mW cw), roomtemperature detectors (e.g. InAs) are used, and system sensitivity is limited by optical interference fringes, not detector noise;
- \* Traditional Herriott cell can accommodate up to 6 laser channels with one set of mirrors, whereas cavity ringdown needs one (highly reflective) set of mirrors for each wavelength.

## **On-Surface Versions**

#### FLIGHT INSTRUMENTS

- Flown on Mars 98 lander and DS-2 probe that both crashed
- TLS in SAM on MSL tunable laser spectrometer for gas detection in Mars atmosphere or evolved from solid pyrolysis and combustion;
  - \* 5 mW lasers
  - \* Two-channels
  - \* 3.7 kg, 10 W
  - CH<sub>4</sub> to 1 ppb
     or much less with
     pre-concentration
- \* Isotope ratios in H, C, O to 2-5 per mil
- \* C and  $H_2O$  in rocks to  $10^{-10}$ wt%





#### FUTURE INSTRUMENTS

- Mars aircraft (long path to ground)  $\rm NH_3$ ,  $\rm CH_4$ ,  $\rm SO_2$
- Venus, Saturn, Uranus entry probes to profile gases and isotope ratios on descent;
- Primitive bodies on-surface analysis;



## **MASS SPECTROMETRY**

### IDENTIFYING MASS/CHARGE for ATOMS and MOLECULAR FRAGMENTS

## **Basic Technique**



- Gas sampled is produced from a variety of techniques including direct atmosphere, GC, LC, ion traps, pyrolysis, combustion, laser ablation, derivatization, wet chemical and microfluidics;
- Gas sample is ionized by a variety of methods including electron impact, laser ionization, chemical ionization (CIMS), MALDI, secondary ion MS (SIMS);
- Mass discrimination is based on m/z dispersion in a variety of basic methods:
  - Magnetic sectors including IRMS
  - Ion traps, such as the linear quadrupole mass spectrometer (QMS), Paul trap, and Orbitrap
  - Time of Flight (TOF) and reflectron- or multi-bounce- TOF
- Detection is continuous or sequential using electron multipliers, Faraday cups, microchannel plates, CCD direct ion detector arrays, or as induced AC current in orbitrap plate pairs.

## **Measurement Capability**

- Surveys all gases over wide mass range
- Records m/z spectra for neutrals (NMS) or ions (INMS)
- Essential for noble gases and noble gas isotope ratios
- Suffers from mass interferences in water, methane, ammonia, and stable isotopes:
  - N<sub>2</sub> = 28 = CO
  - HDO = 19 = H<sub>2</sub><sup>17</sup>O
  - <sup>13</sup>CO<sub>2</sub> = 45 = <sup>17</sup>OCO
  - <sup>18</sup>OCO = 46=<sup>17</sup>O<sup>13</sup>CO
  - <sup>13</sup>CH<sub>4</sub> = CH<sub>3</sub>D (diff. = 0.003 amu)
  - ${}^{15}N^{14}NO = 45 = {}^{14}N^{15}NO$   $N_2O = 44 = CO_2$
  - ${}^{34}SOO = 66 = {}^{32}SO^{18}O$  so need  ${}^{18}O/{}^{16}O$
- Current planetary mass spectrometers (Mars, Venus, primitive bodies):
  - Measure noble gas abundances 3-20%
  - Measure noble gas isotope ratios to 1% (typical) to 5-10% for light Xe isotopes
  - Interferences limit abundances of CH4, NH3, H2O to 5-20%,
  - Isotope ratio D/H in H2 to 20%; D/H precision in H2O, CH4, NH3 not useful; 15N/14N about 30%; 13C/12C around 10-100 per mil.
- Enhanced capability mass spectrometers:
  - Measure noble gas abundances
  - Tailored for clumped isotopic analysis?

## **On-Surface Versions**

Technology	Planetary Missions			
QMS	<ul> <li>MSL, Huygens</li> <li>Ptolemy GC-IRMS on Rosetta Lander</li> </ul>			
Magnetic Sector	<ul><li>Viking, Phoenix</li><li>ROSINA on Rosetta</li></ul>			
Paul Trap	VCAM on ISS, MOMA on ExoMars			
TOF	<ul> <li>ROSINA, COSIMA on Rosetta</li> </ul>			
Orbitrap	Under development			

#### Ptolemy on Rosetta Lander





## **GAS CHROMATOGRAPHY (GC)**

### SEPARATING OUT LARGE MOLECULES AND FRAGMENTS

## **Basic Technique**



- Used to separate volatiles that can be vaporized without decomposition;
- Mobile phase is carrier gas like He
- Stationary phase is microscopic layer of polymer on inside of column
- Separation in He gas flowed through tempcontrolled (30-250°C) chromatographic columns (CC, metallic capillary tubes).
- Column polarity should match sample;
- Detectors are flame ionization detectors (FIDs- destructive) or thermal conductivity detectors (TIDs- non-destructive);
- Detection by nano-thermal conductivity detectors (TCD- similar to COSAC Rosetta) with a dynamic and linear response area, suited to melting ratio ranging from a few hundreds to a few.
- Non-destructive detectors allow feed to MS with a lower detection threshold

## **Measurement Capability**

- Wide variety of organic and inorganic compounds.
- Relative concentrations (abundances) to typically 10%
- SAM's GC on MSL has six columns:
- <u>Column 1</u>: devoted to "atmospheric gases", as rare Gases (Kr, Ar...) + N2 + O2 + CO + CO2 + H2O + CH4;
- <u>Column 2</u>: devoted to low molecular weight VOC (C1-C3) and sulfur compounds (SO2...);
- <u>Columns 3 and 4</u>: Classical or "universal" columns that give access to a wide range of products- devoted to pyrolysis products and lighter derivatized products :
- <u>Column 5</u>: devoted to products of derivatization (they are heavy after this sample preparation and need a specific column);
- <u>Column 6 :</u> devoted to chiral compounds, could be also a backup if one of the (3+4 columns) couple fails.



## **On-Surface Versions**

- COSAC on Rosetta has 2-column GC and includes chirality
- SAM on MSL has 6-column GC including chirality



### MSL-SAM 6 column GC- M.Cabane



COSAC on Rosetta 2-column GC- Goesmann , MPI



## **MICROFLUIDICS and WET CHEMISTRY**

### IDENTIFYING COMPONENTS AND CHEMICAL PROPERTIES BY LIQUID ADDITION

## **Basic Technique**

- Wet chemical analytical methods determine properties of solids (soils) and liquids, including: pH (acid, alkaline), concentration, conductivity, salinity, specific gravity, density, viscosity and moisture content.
- Dissolution in water or solvent is followed by elemental analysis nitrogen, chloride, bromide, fluoride, nitrates, sulfates, phosphates
- High Purity Liquid Chromatography (HPLC):
  - Velocity of each component depends on its chemical nature, the nature of the stationary phase (column) and composition of the mobile phase.
  - Widely used for analysis of beverages, forensics, pharmaceuticals and drug testing, environmental, industrial and petrochemical analysis.
- Microcapillary Electrophoresis (µCE):
  - Lab-on-a-chip technologies developed at UC Berkeley and JPL
  - Identifies chirality (handedness)





## **Measurement Capability**

- Liquid chromatography and microcapillary electrophoresis allow separation, identification and analysis of chirality in large molecules like amines;
- MECA Wet Chemistry Lab:
  - Conductivity, pH (3 sensors), Cl<sup>-</sup> (2 sensors), Br<sup>-</sup> (2 sensors), I<sup>-</sup> (2 sensors)
  - NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Na+
  - Pb/Cu/Cd/Zn/Fe (ASV)
  - Cyclic Voltammetry
  - ORP (redox potential)







Graphene cover slip allows observation of wet chemistry in progress -LBNL

## **On-Surface Versions**

• MECA characterizes the soil of Mars. By dissolving small amounts of soil in water, the wet chemistry lab (WCL) determines the pH, the abundance of minerals such as magnesium and sodium cations or chloride, bromide and sulfate anions, as well as the conductivity and redox potential.

MECA- Soil is delivered through funnel and added to water stored in a metal tank. The bottom section contains electrochemical sensors.



 UREY on ExoMars (cancelled) would have combined lab-on-a-chip organic analysis (LIF, μCE) with soil reactivity sensors to characterize the biotic capacity of Martian

