Analytical Techniques in Double Walled Isolator and BLS4+ Sample Return Facilities

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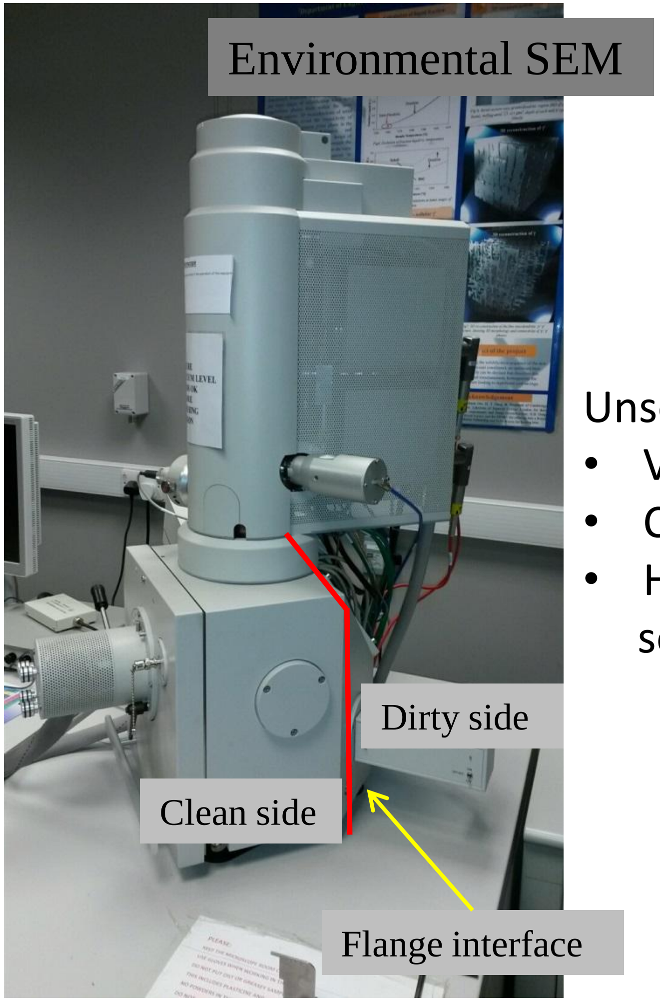
DWI Interfaces

Working with Thales Alenia Space, the University of Leicester are now developing generic interfaces for science instruments that are required to operate either fully or partially inside a Double Wall Isolator (DWI).

For example, an SEM might be seen as a necessary and decisive instrument early in the analysis chain of a returned Mars sample.

A DWI will be designed such that a stainless steel flange will seal the body of the SEM to the wall of a DWI allowing it to open in the isolated working area but the bulk of the instrument and its ancillaries remain safely, external to the DWI.



Unseen challenges:

- Vacuum systems
- Chillers
- High voltage power sources

How we Analyse Planetary Materials
- use nakhlite as an example

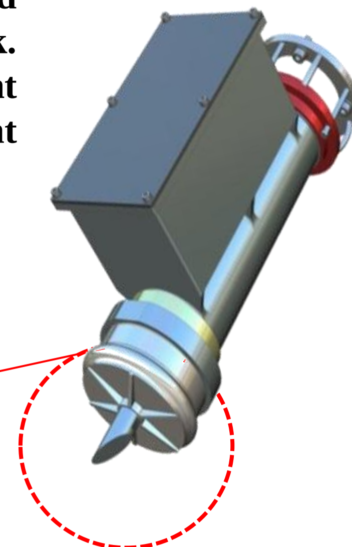
Analytical Workflow

- Rock cutting (or splitting)
- High resolution optical microscopy
- Sample polishing
- CT scanning
- Thick and thin sections
- Environmental SEM (ESEM) for high resolution imaging, compositional analysis of rough and polished samples
- Focused Ion Beam (FIB-SEM) for preparation of ~80 nm thick wafers for subsequent TEM
- Transmission Electron Microscopy (TEM) – nm to Å scale analysis of wafers prepared in FIB
- Gas Chromatography-Mass Spectrometry

<u>Mobile technology Needed</u>

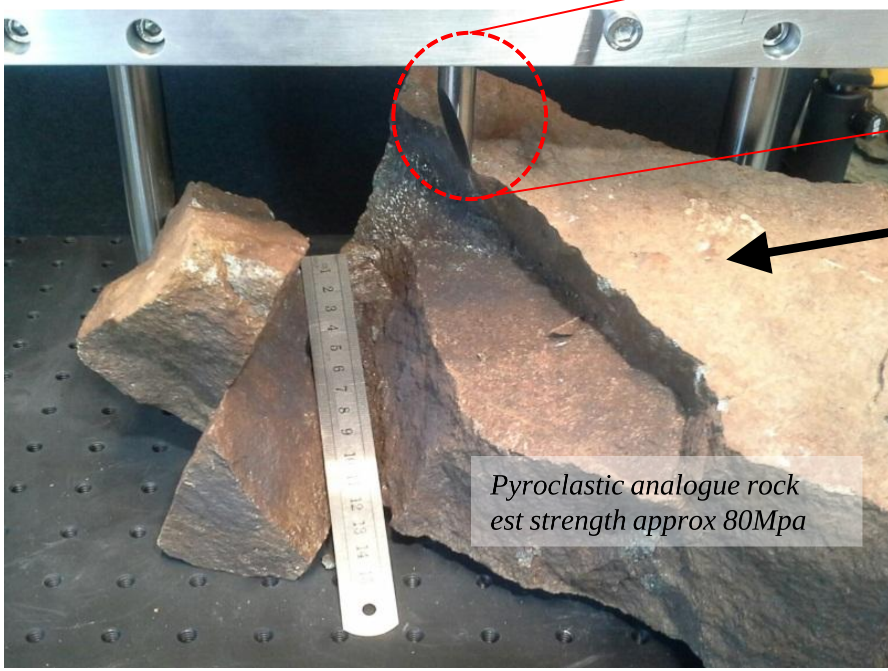
- XANES – X-ray absorption microscopy, synchrotron analyses
- Ion Probe – stable isotope analyses
- TOF-SIMS, desorption techniques for organic analyses, biomarkers e.g. protein analyses

SPLIT breaks a target rock exactly as a field geologist would with a hammer to expose a deep internal surface of the rock. Complementary to other tools, SPLIT facilitates subsequent targeted sampling and extends sampling depth of current technologies.



Flight Type Design

Mass:	*1kg to 1.8kg*
Power:	*15W – 20W*
Length:	*≈260mm*
Diameter:	*≈ 65mm*



Basis Breadboard Model

The basic breadboard model here is used to simulate the impact mechanism used in SPLIT, a motor driven inclined helical cam mechanism to store energy in a machined spring.

Results

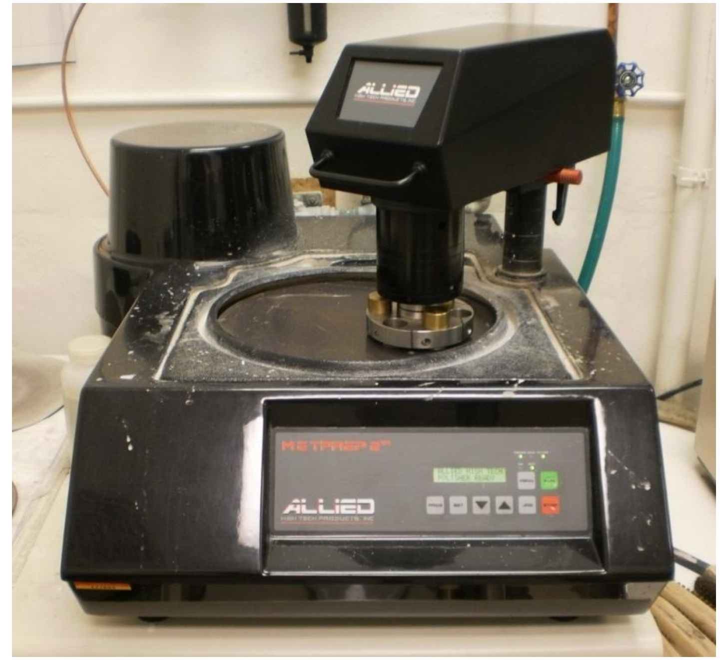
Impulse frequency 0.5Hz

Time = 1min

Images from SRC, University of Leicester

Sample Preparation

- Sample cut or split
- Polished thin sections and polished blocks, for use in transmitted and reflected light microscopy and electron microscopy.
- 30 μm thick slice of rock.
- Rock slice set between epoxy layers, on a glass slide or in a resin block.
- Grinder can be used to obtain the correct thickness.
- Use diamond [1 -0.5 μm] polycrystalline polish to eliminate any mechanical damage to the surface.

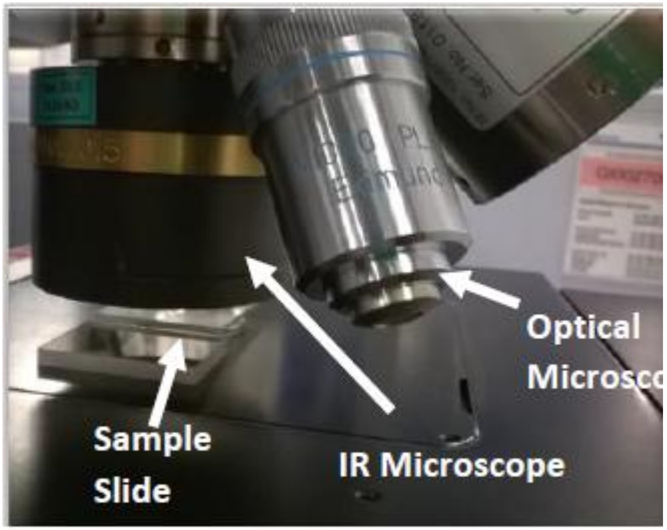


▲ Geological thin section polishing

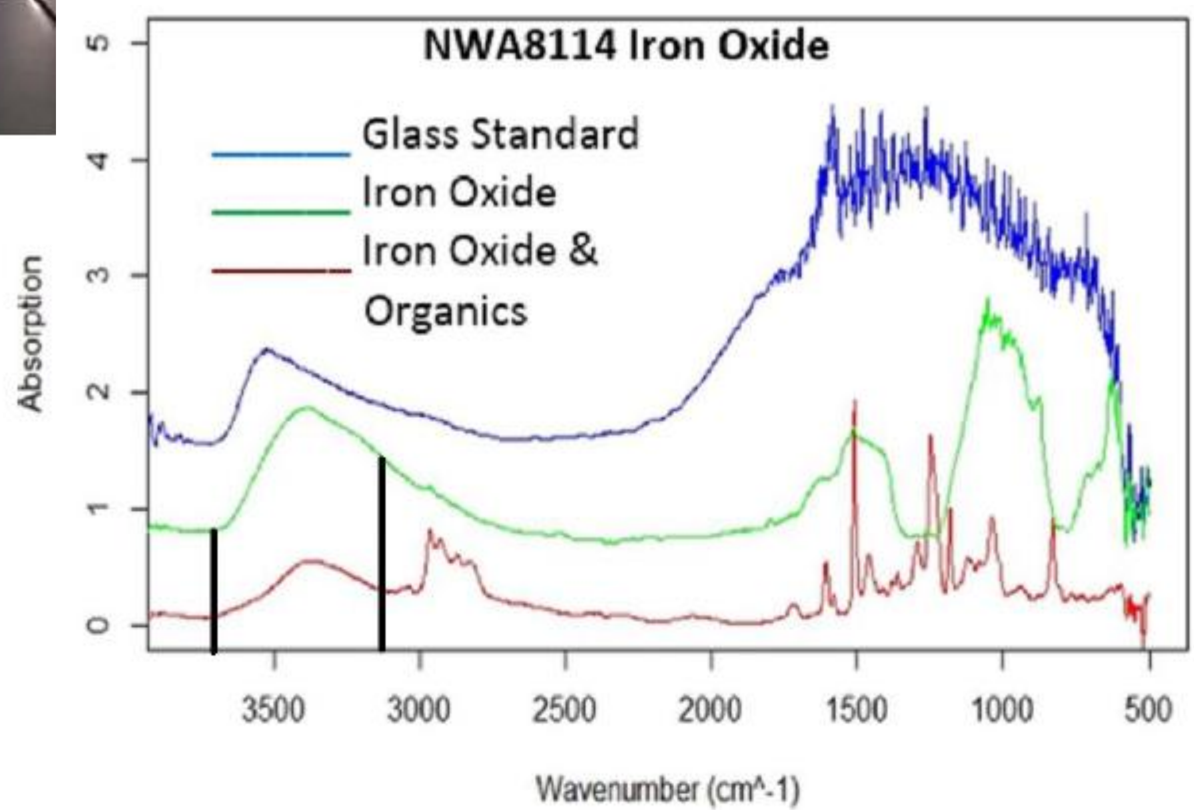
▲ Olympus BX51 petrographic microscope

▲ Nikon Shuttlepix P-MFSC optical microscope

IR Spectroscopy

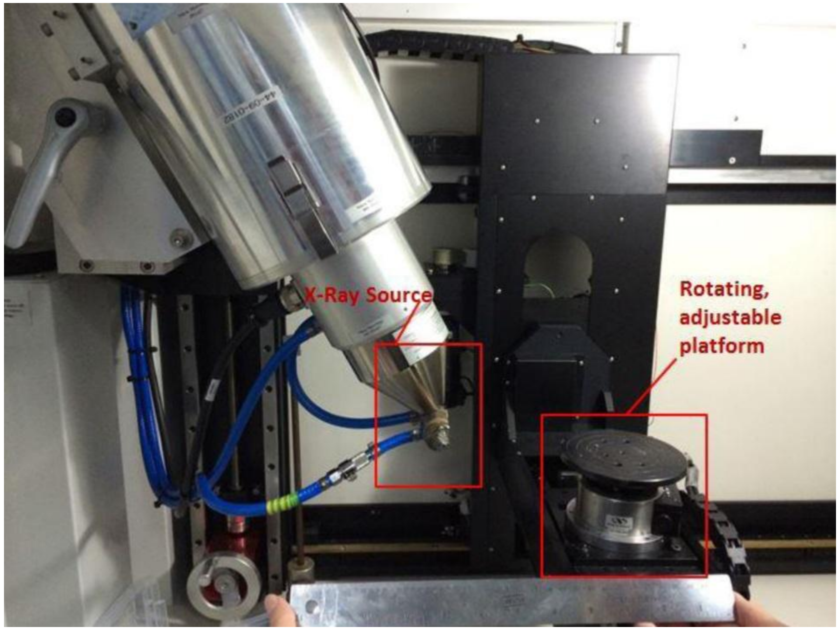


Easiest on polished sections but can be done non destructively on rough samples

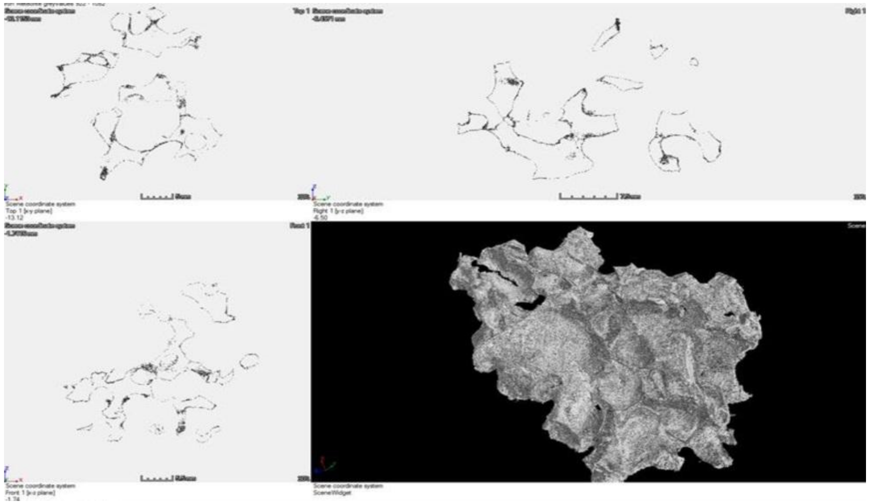


X-ray Micro Computerised Tomography (CT scanner)

- Uses X-rays to cross section a 3-D object.
- Maximum size 23 x 33 cm.
- Produces a virtual model without destroying the sample.
- Capable of resolving structures down to 1 µm
- Example NWA 8114 (‘Black Beauty’) martian breccia

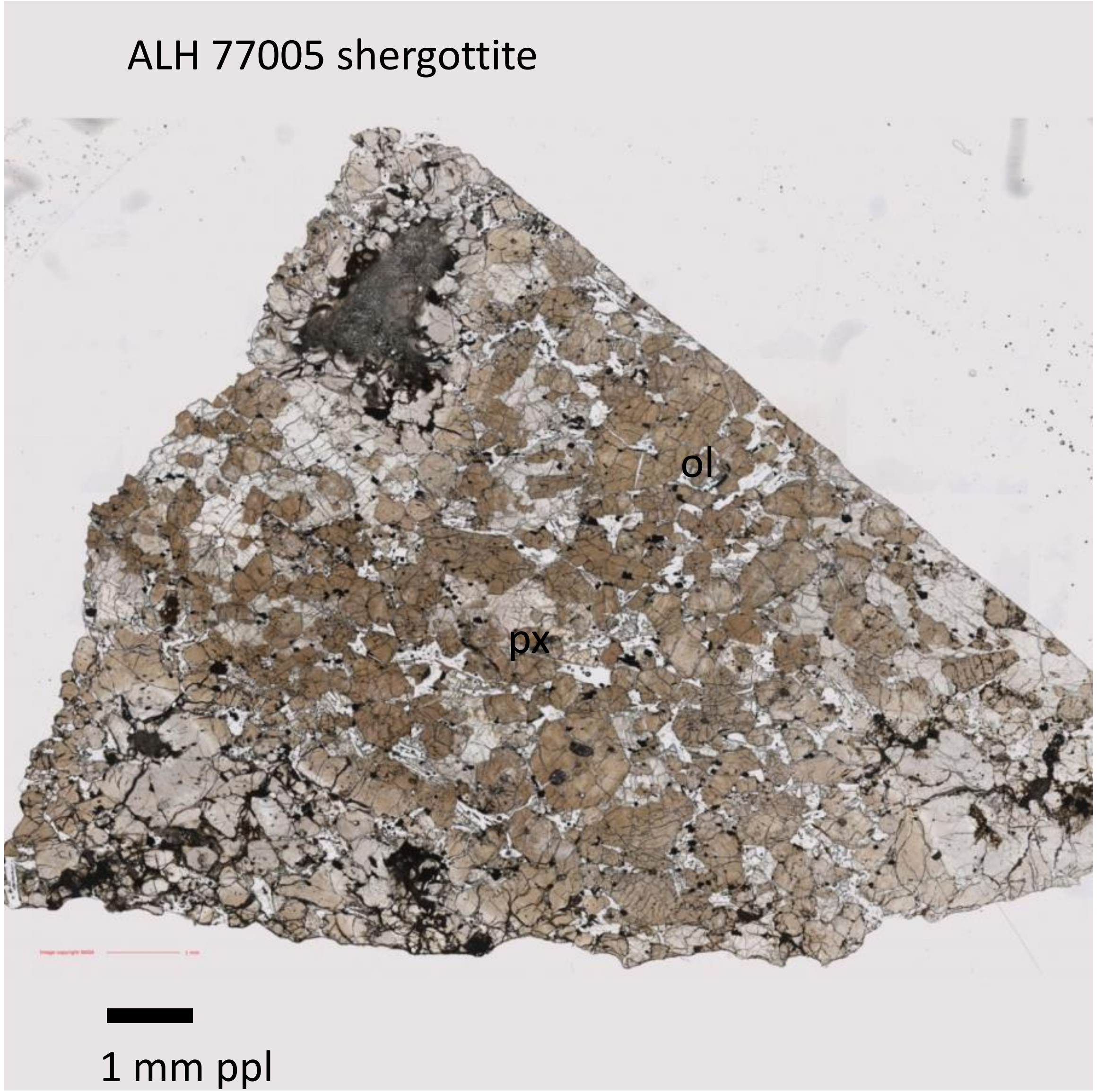


▲ Nikon Metrology XT H 225 (UoL)

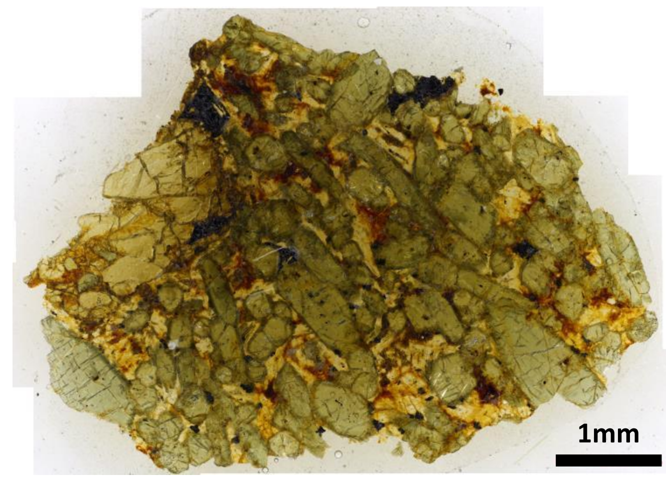


▲ Iron meteorite

Optical Microscopy – polished sections



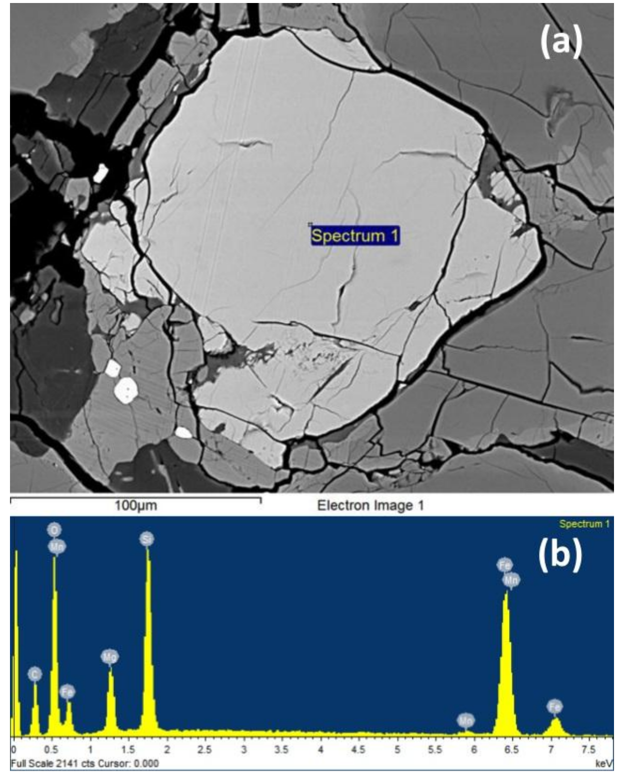
- Plane Polarised optical microscopy
- Identify minerals and textures
- Requires polishing



▲ Transmitted microscopy (Nakhlite)

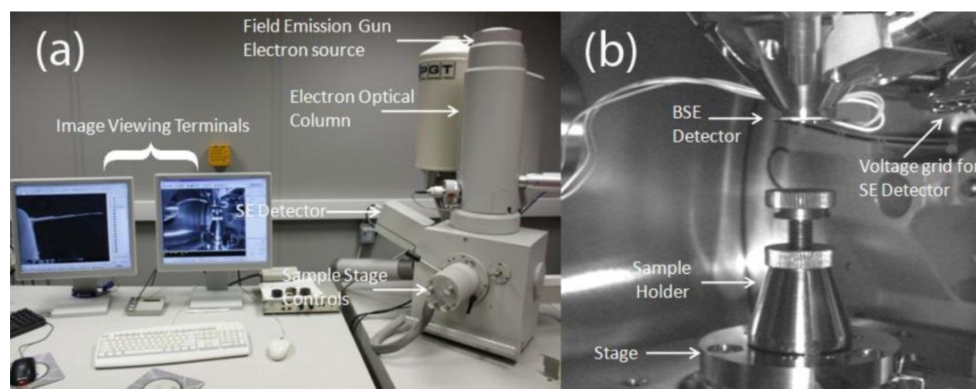
Scanning Electron Microscopy (SEM)

- Environmental (ESEM) and Field Emission Gun (FEG-SEM).
- Usually vacuum pressures ranging 10^{-4}-10^{-5} mbar, sometimes 10^{-1} mbar
- Suitable sample viewing parameters:
  - 15-20 kV
  - Spot size 5 (~1.0 nA)
  - Working Distance (WD) ~10 mm
- Techniques include:
  - Secondary Electron (SE) imaging
  - Backscattered Electron (BSE)
  - Energy Dispersive X-ray (EDX), for quantitative analysis of chemical compositions and elemental mapping.



◀ Point & ID analysis on nakhlite using EDX analyses

▼ FEG-SEM chamber

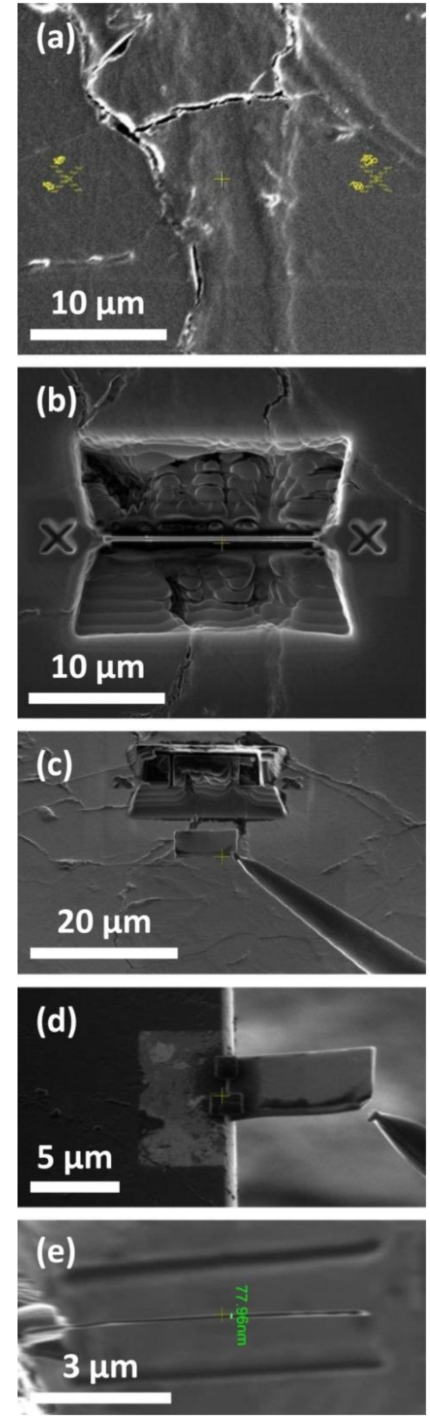


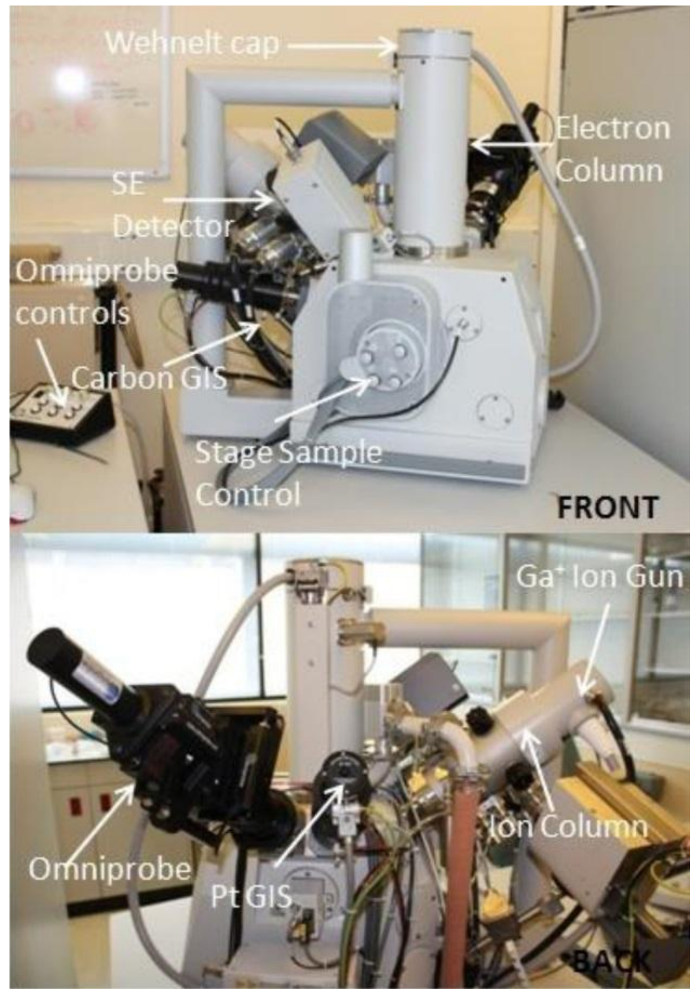
▲ Sirion 200 FEG-SEM (UoL)

Focussed Ion Beam (FIB)

- Dual Focussed Ion and Electron Beam (FIB-SEM).
- Liquid metal ion source (LMIS) of gallium (Ga^+), capable of exceeding sample surface binding energy.
- Gas Injection System (GIS), including carbon and platinum.
- *Omniprobe* tungsten probe tips for extracting FIB-TEM sections.
- Techniques (and ion beam current settings) include:
  - Imaging (10 pA)
  - C deposition (30 pA)
  - Pt deposition (0.30 nA)
  - Sample thinning (0.10 nA)
  - cutting/milling (>0.30 nA)

▶ Extraction of ultra-thin FIB-TEM section measuring ~5×15 µm, and <100 nm thick

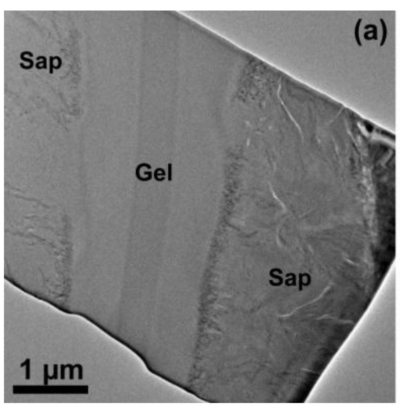


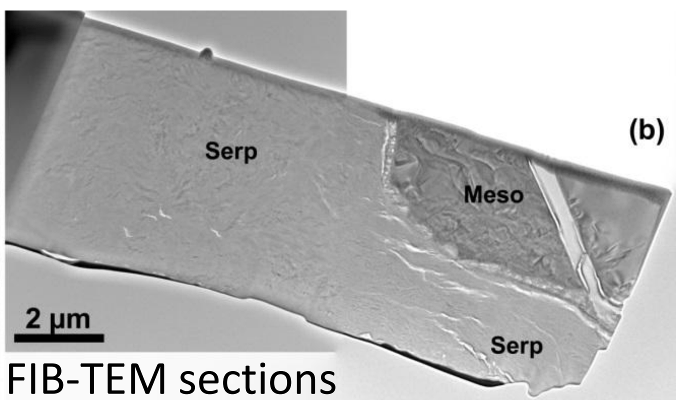


▲ FEI Quanta 200 3D FIB-SEM (UoL)

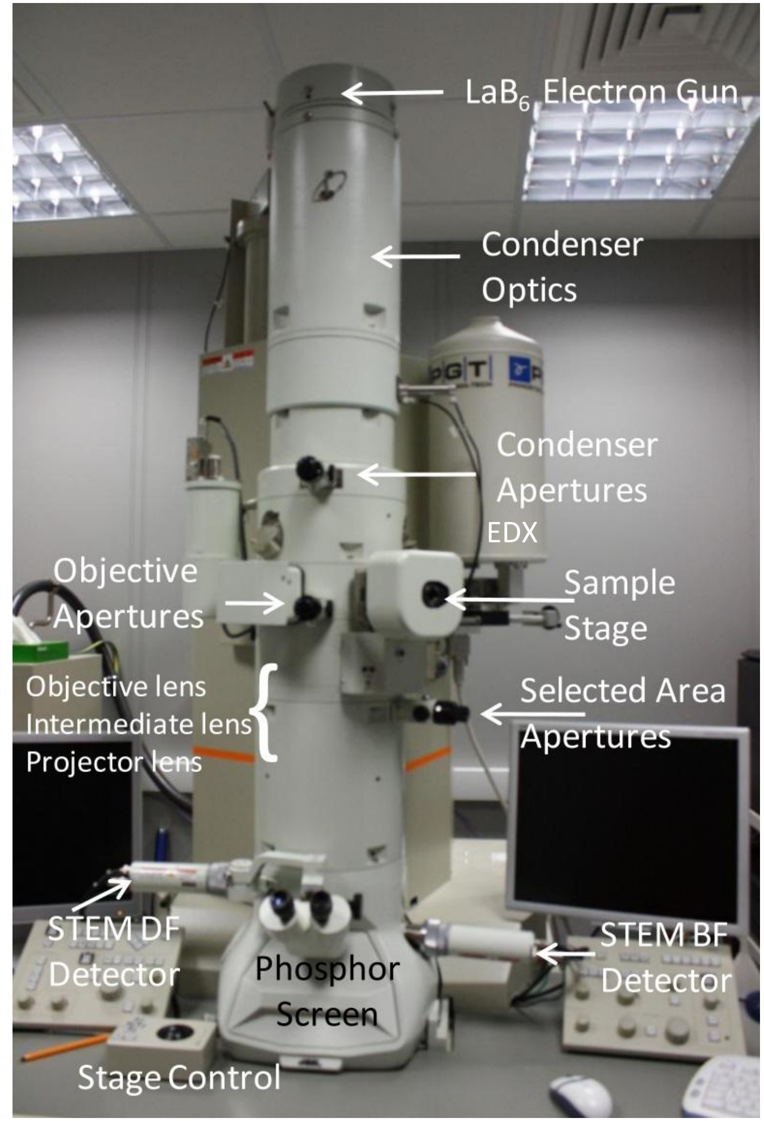
Transmission Electron Microscopy (TEM)

- LaB_6 thermionic source
- Acceleration voltage 200 kV; Beam current ~110 µA; Camera length 21.15 cm.
- Techniques include:
  - Bright/Dark Field High Resolution (HRTEM). Capable of resolving Angstrom (Å) scale crystal lattice spacings.
  - EDX chemical composition.
  - Selected area electron diffraction (SAED).





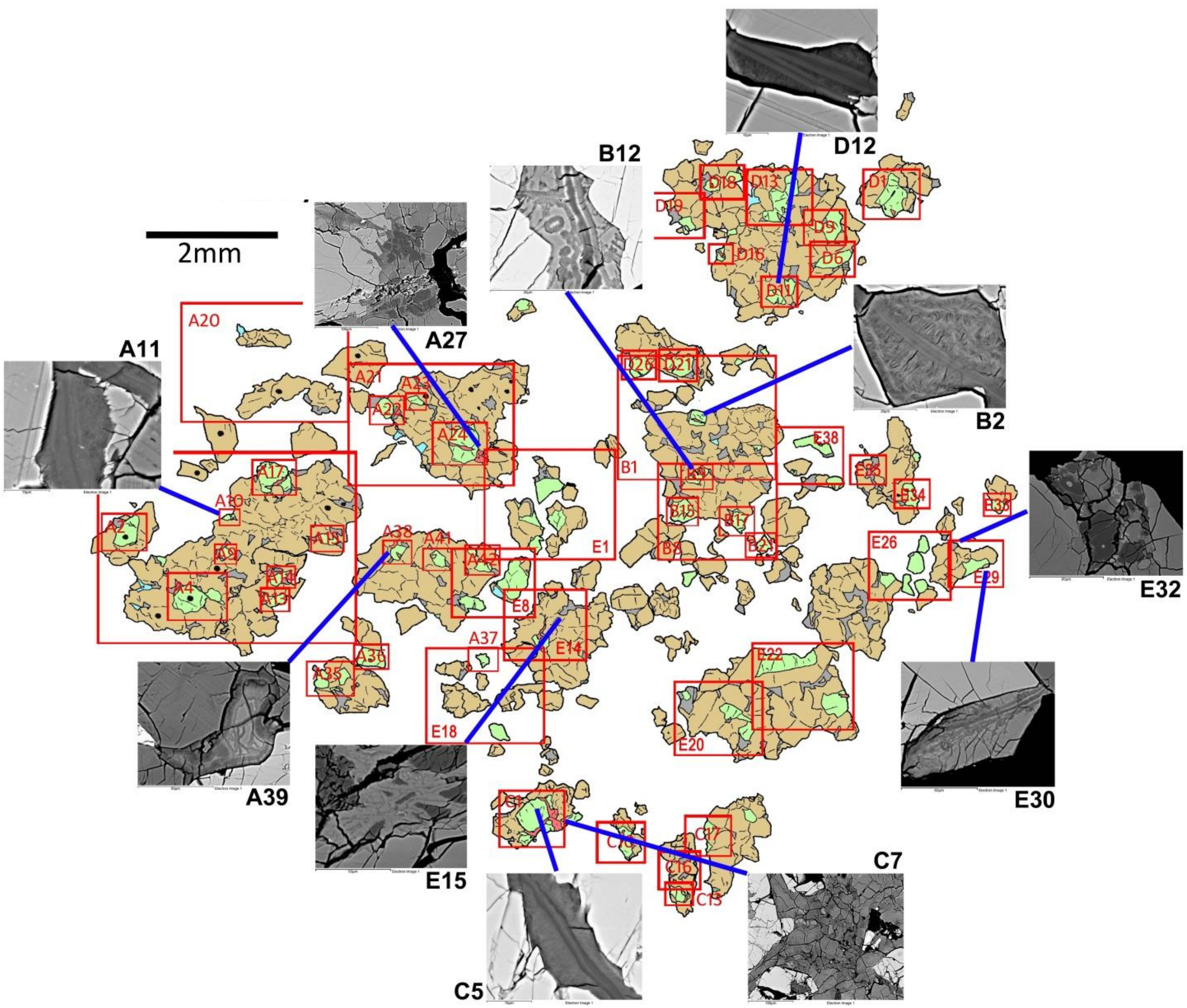
FIB-TEM sections

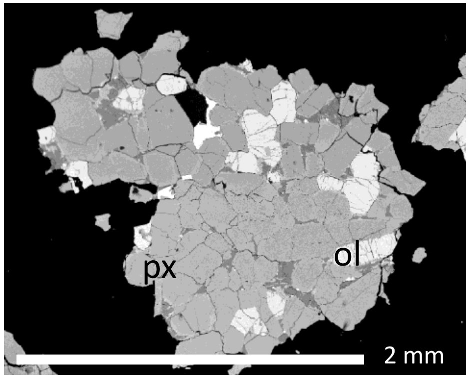


▲ JEOL 2100 TEM (UoL)

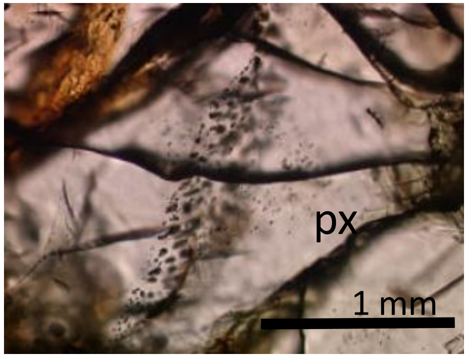
▲ Note pumps, chiller etc not shown!

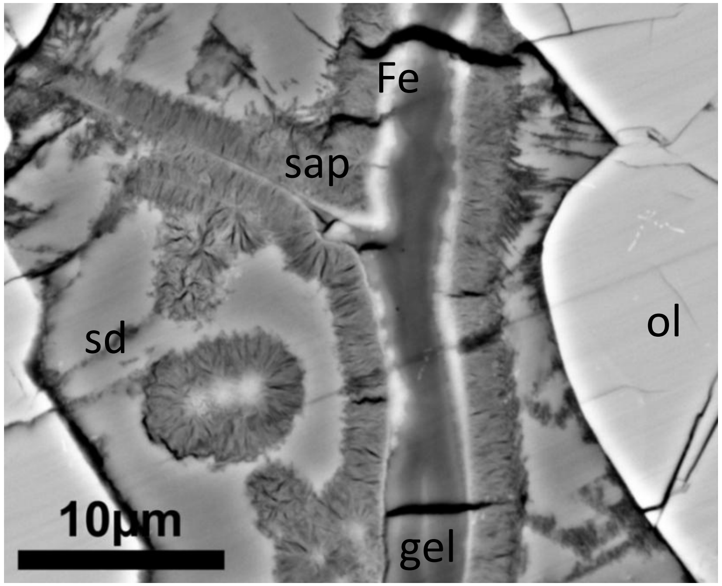
The Nakhlites: Lafayette Example



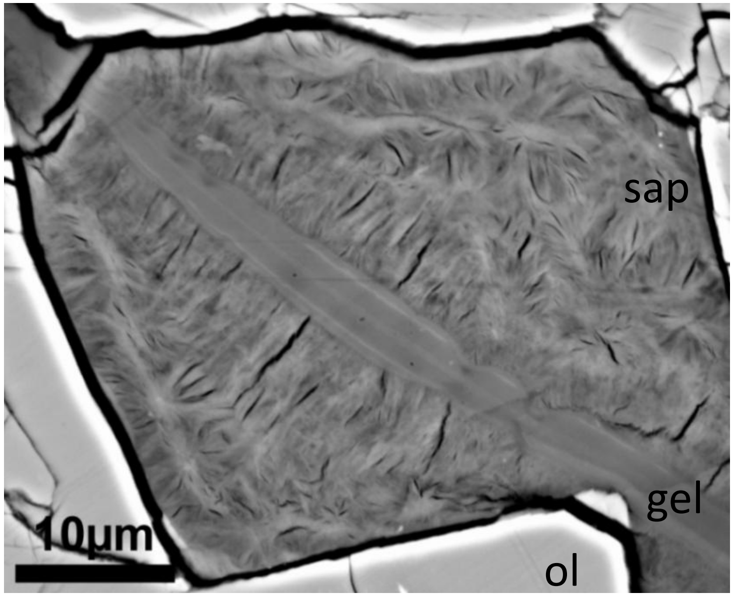


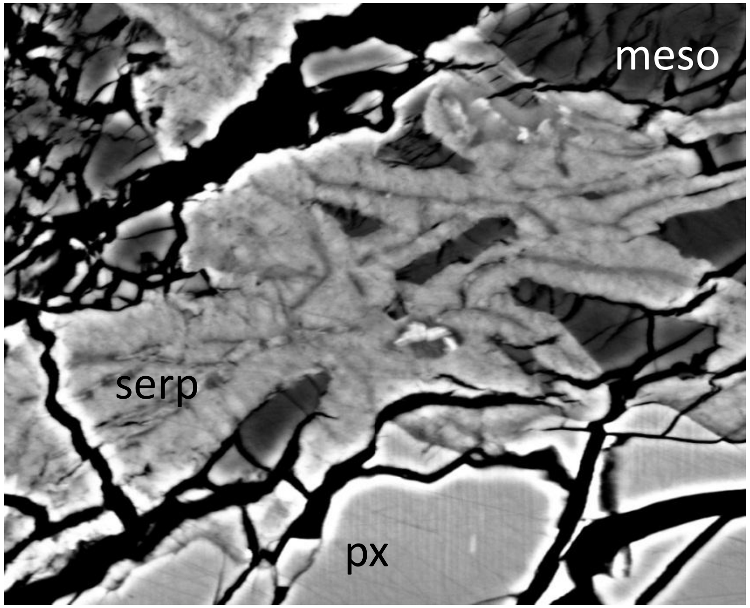
- Fluid path seen in brittle fractures in olivine & mesostasis





- Siderite-smectite/serpentine-gel ± salt assemblage
  - 9 nakhlites studied: Lafayette, NWA998, G. Valadares, Nakhla, Y000593/749, NWA5790, NWA817, Miller Range03346

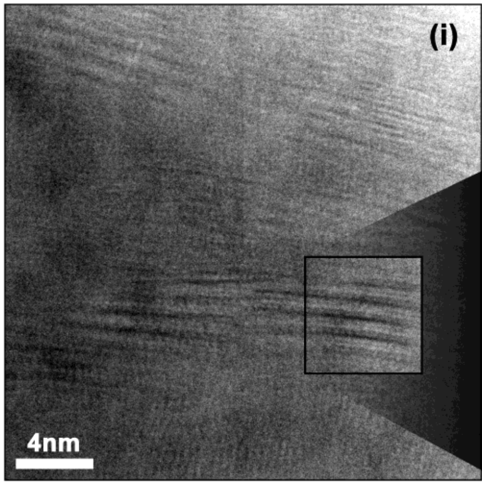


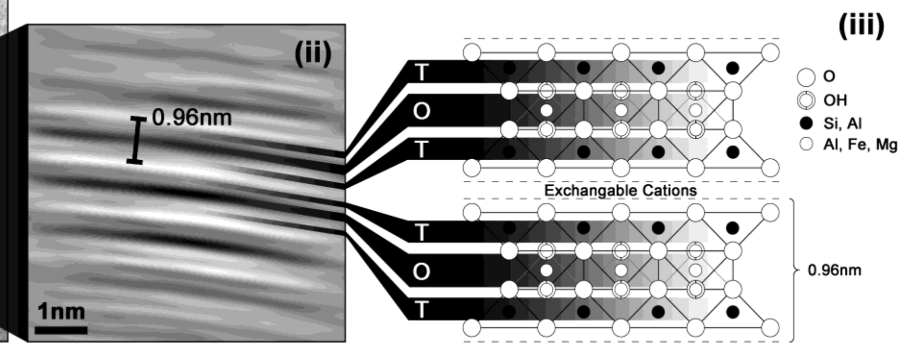


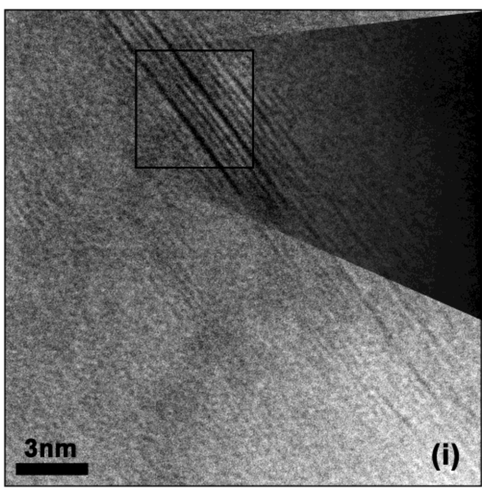
Lafayette

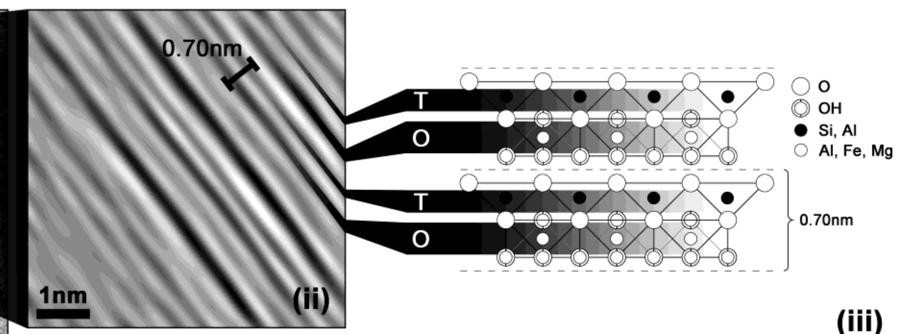
FIB-TEM to Measure Lattice Spacings to identify clays

2:1 T:O:T sites
Saponite $(Ca_{0.2}K_{0.1})_{\Sigma 0.3}(Mg_{2.6}Fe^{2+}{}_{1.3}Fe^{3+}{}_{1.7}Mn_{0.1})_{\Sigma 5.7}[(Si_{6.7}Al_{0.9}Fe^{3+}{}_{0.4})_{\Sigma 8.0}O_{20}](OH)_4.nH_2O$









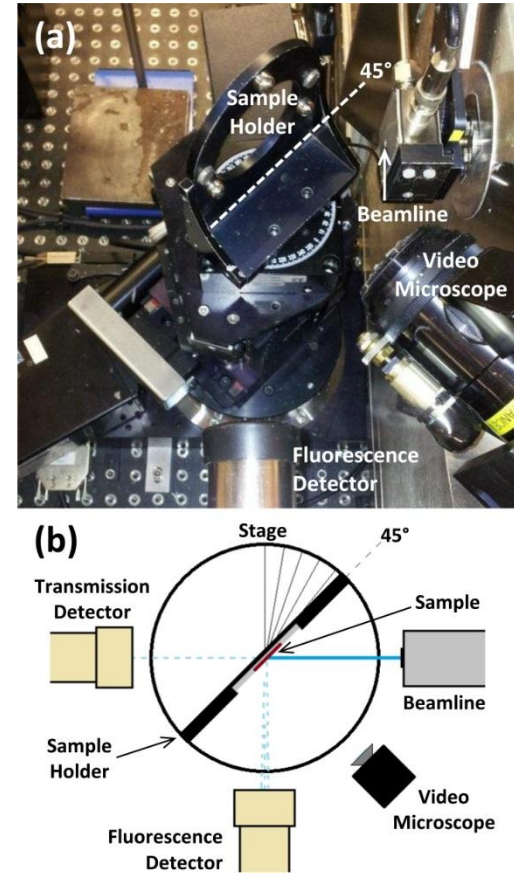
1:1 T:O sites
Serpentine $(Ca_{0.1}Mg_{0.7}Fe^{3+}{}_{1.0}Al_{0.4})_{\Sigma 2.2}[Si_2O_5]OH_4$

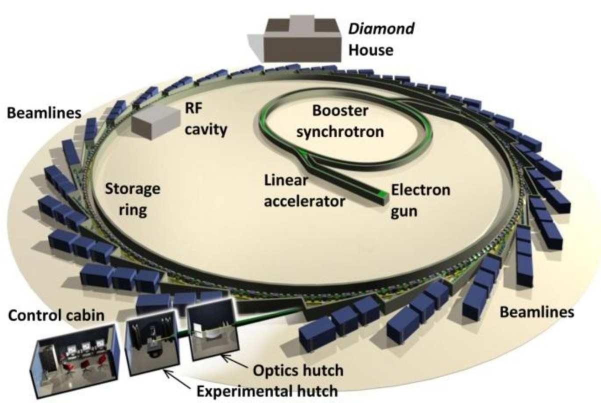
Hicks, Bridges and Gurman 2014

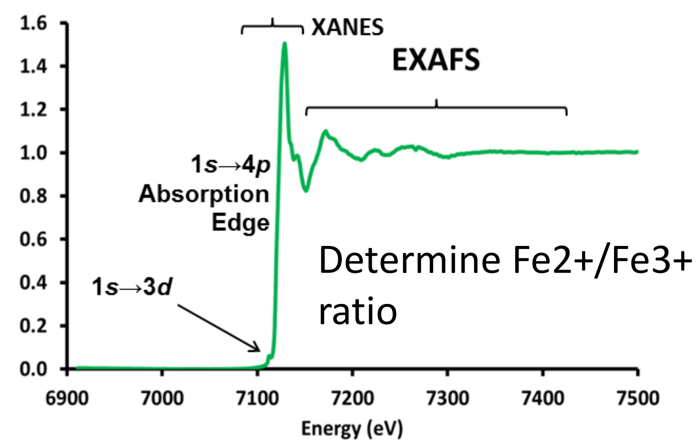
XANES

I18 Microfocus Spectroscopy Beamline at the UK *Diamond Light Source* Synchrotron.

- Spatial resolution of 2 x 2.5 µm.
- Energy resolution of 0.1 eV.
- Energy range of 2.0 keV – 20.7 keV:
    - K-edges from Phosphorus (Z=15) to Molybdenum (Z=42)
    - L_3-edges from Strontium (Z=38) to Plutonium (Z=94)
- Techniques include:
    - X-ray fluorescence (XRF) mapping
    - X-ray absorption near-edge structure (XANES)
    - Extended X-ray absorption fine-structure (EXAFS)
    - Transmission X-ray diffraction (XRD)







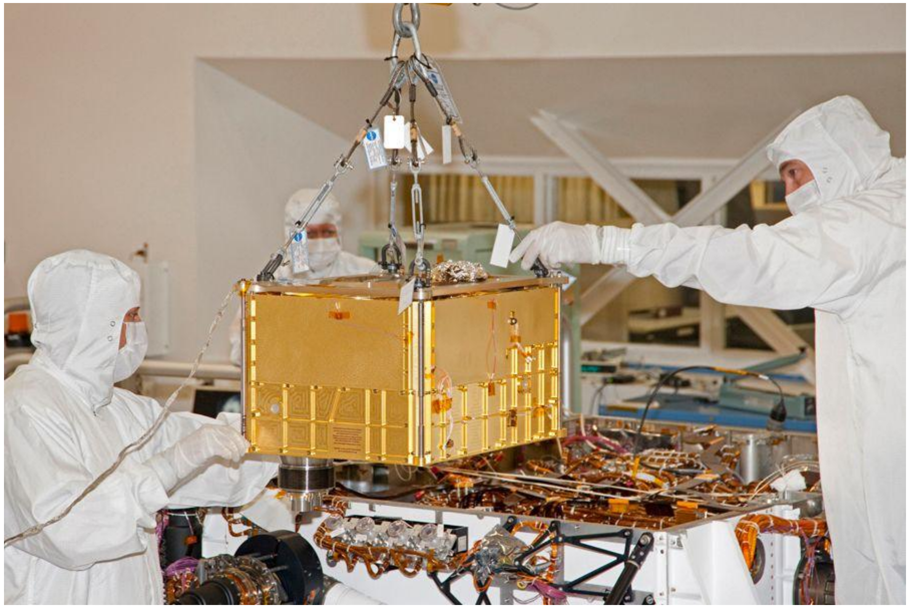
Ion probe NanoSIMS (secondary ionization mass spectrometry)

- O or Cs or Ar primary beams
- Spatial resolution ~ 50 nm+
- SIMS gives isotopes e.g. $\delta^{17}O$
- Molecules e.g organics, elements to ppb level
- Ultra high vacuum e.g. 10E-7 torr

http://www.open.ac.uk/science/ukcan/nanosims.html

Gas-Chromatography Mss Spectrometry

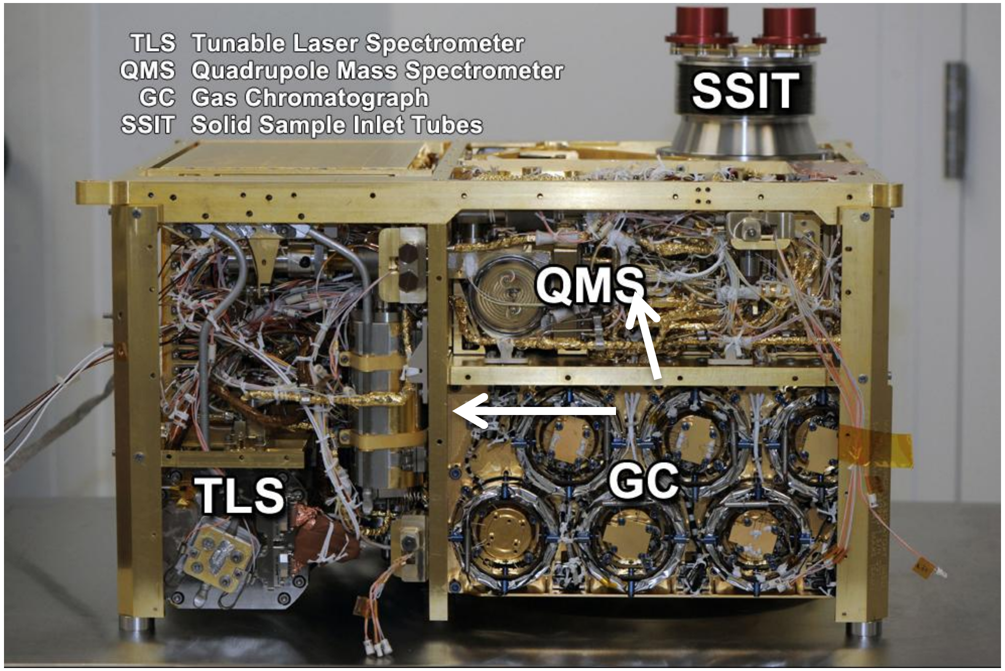
SAM: Mars Science Laboratory GCMS



- Stable isotopes
- Organic and volatile analyses
- Pyrolysis e.g. CO_2, H_2O release versus T
- Gas and solid analyses
- ~100 W
- Vacuum pumps

CURIOSITY

SAM Gas Chromatography (GC)-Mass Spectrometer (MS) &Tuneable Laser Spectrometer (TLS)



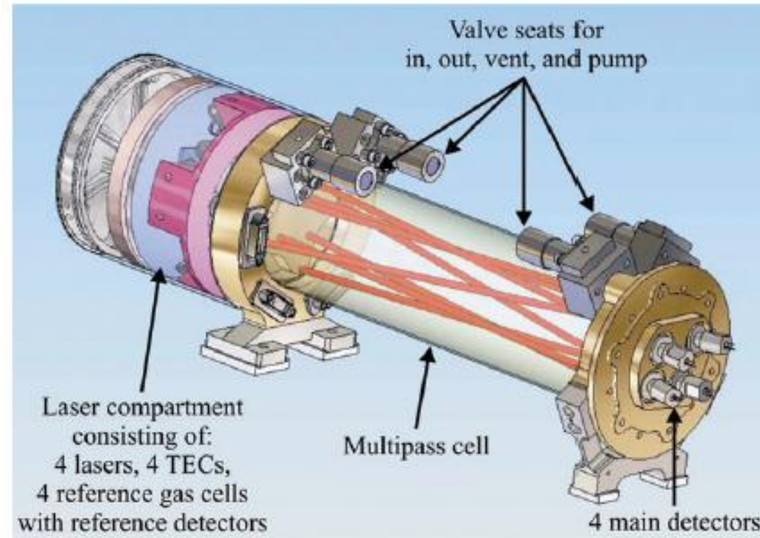
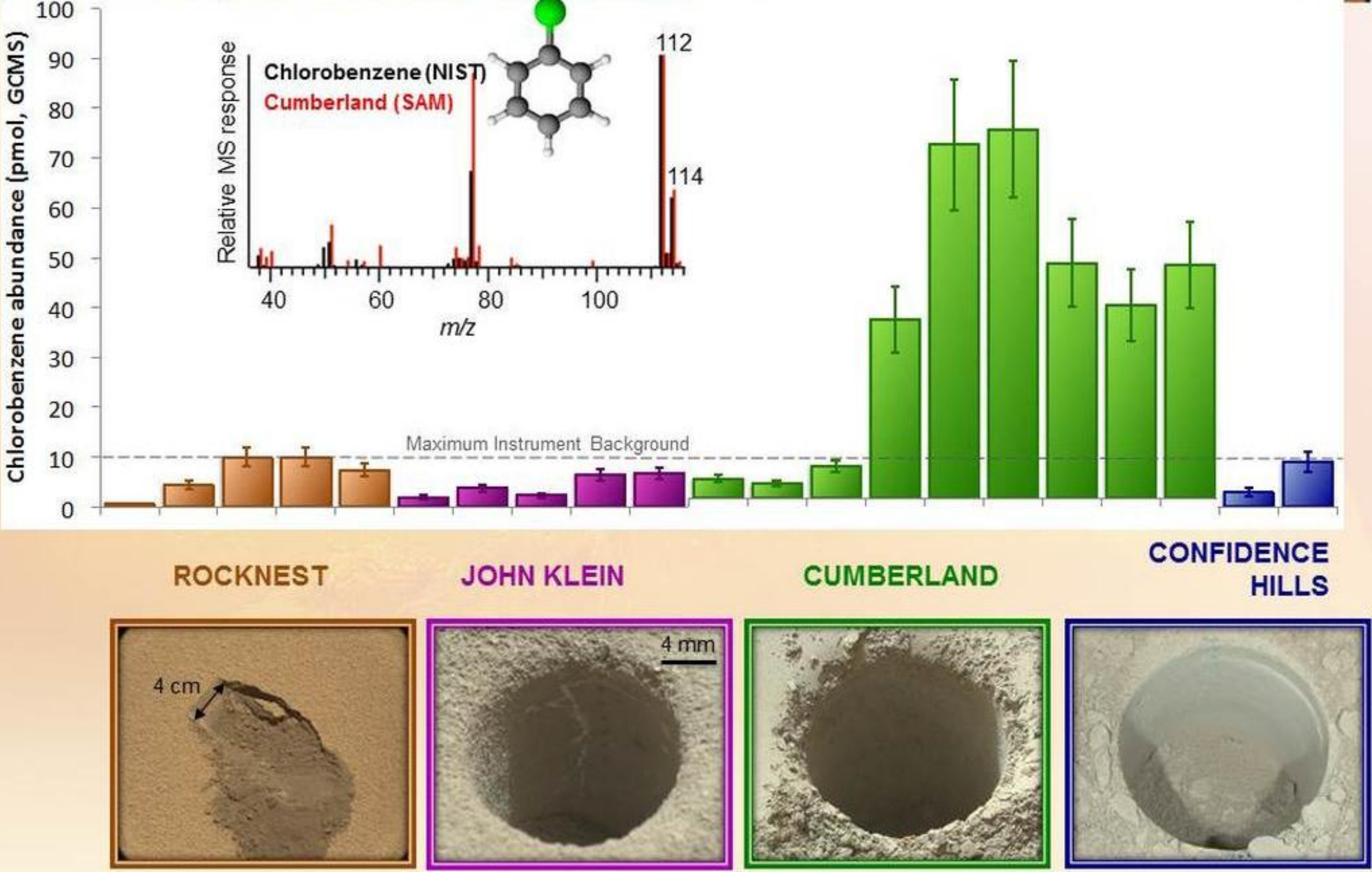


Fig. 1. TLS of the SAM analytical suite on the MSL mission.

Table 1. TLS Laser Wavelengths, Target Gases, and Isotope Ratios

Laser Type	Wavelength (μm)	Target Gas	Target Isotopes Ratios	Limit of Detection[a]
NIR diode	2.64	H_2O	D/H, $^{18}O/^{16}O$, $^{17}O/^{16}O$	1 ppmv
NIR diode	2.78	CO_2	$^{13}C/^{12}C$, $^{18}O/^{17}O/^{16}O$	1 ppmv
IC	3.27	CH_4	$^{13}C/^{12}C$	1 ppbv
QC	7.8	H_2O_2, N_2O	—	2 ppbv and 5 ppbv



Benzene organics were detected in the Cumberland drilled sample

Future Work and Summary

- We will test some of these techniques with a new DWI facility at University of Leicester
- Only a subset of techniques can reasonably be planned for this type of analytical environment
- There is a typical analytical work flow for planetary materials that we will want to follow as far as possible for sample return and test in a DWI facility
  - Optical microscopy on hand specimens
  - Spectroscopy e.g. FTIR, Raman
  - CT scanning
  - GC-MS – for sample characterisation e.g. organics, isotopes and life detection e.g. chirality
  - Thin sections ? – this involves sample loss, and use of resin, polishing fluid
  - Scanning Electron microscopy – can be done on rough or polished samples

- Other techniques e.g. Synchrotron XRD, XANES, TEM, SIMS will need to be done outside the facility if declared non hazardous