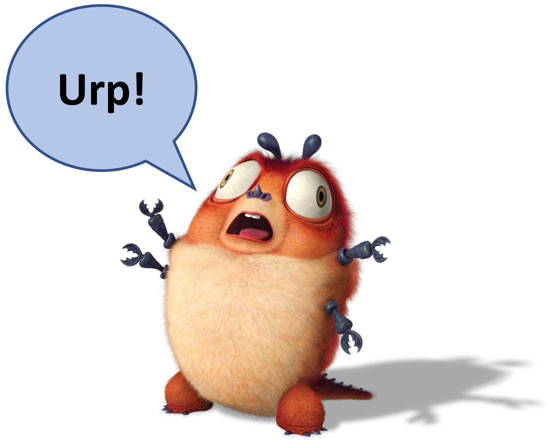
Mostly Mass Spec

Development of ^ Life Detection Technologies for Planetary Science Missions @ NASA GSFC

Will Brinckerhoff and Cast of Colleagues*

NASA/GSFC



CAPS 2020 Fall Meeting

Sep. 16-17, 2020

Cast of Colleagues

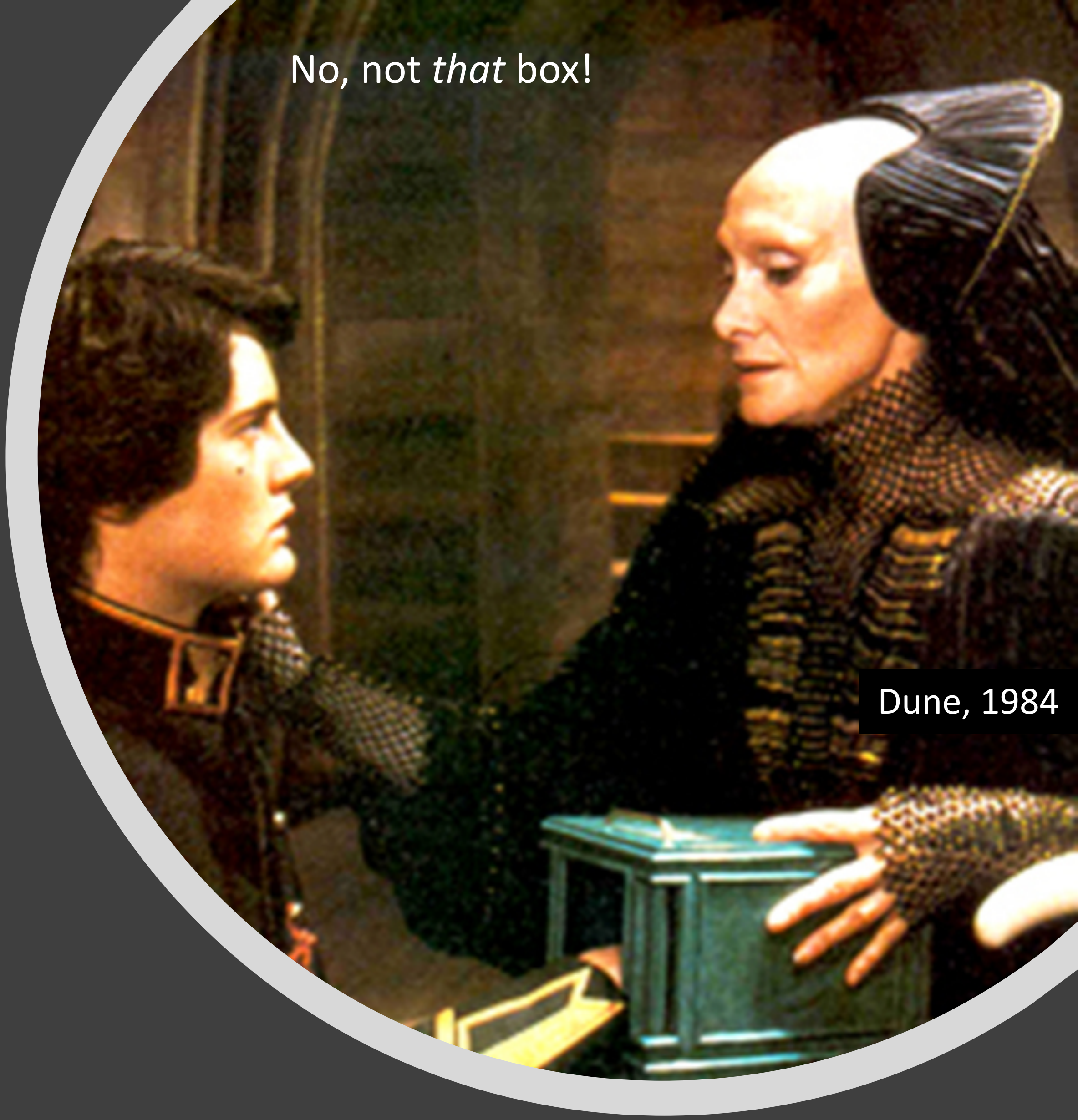
Many people at Goddard working on or toward life detection technologies but special thanks for slide inputs from…

@Goddard - Paul Mahaffy, Stephanie Getty, Rick Arevalo, Andrej Grubisic, Desmond Kaplan, Ryan Danell, Jen Eigenbrode, Heather Graham, Lu Chou, Victoria DaPoian, Conor Nixon, Jen Stern, Ish Aslam, Dina Bower, Charles Malespin, and the Goddard Center for Astrobiology

@Everywhere - Peter Willis & OCEANS team; Tony Ricco & SPU team; Justin Spring & LEM team; Cyril Szopa, Caroline Freissinet & GC team; Fred Goesmann & MOMA team; Sarah Johnson & LAB team; Tori Hoehler & CLD team

What's in the Box?

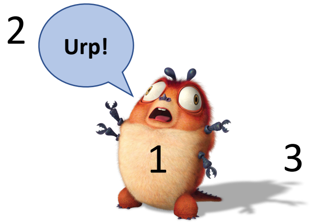
- Commentary on life detection
- Role of mass spectrometry
- Martian Technologies - SAM, MOMA, LITMS
- ICEE-2 Technologies - CADMES, CORALS, EMILI
- TOF-MS Technologies – L2MS, MACROS, RAMS
- Non-MS Technologies - Raman, Nanopore, Biobarrier



Commentary Up Front (from a physicist)

For the purpose of highlighting life detection technologies, we assume we are talking about direct or indirect detection of organisms:

1. An organism or pieces thereof or the processed remains thereof
   - Microscope may image a single-celled microbe; Sensor may detect biomolecule
   - Maybe includes motility - presence of organism via its variation with time
2. The products of organisms (ranging from CH_4 to airplanes)
3. The effects of organisms (e.g. chemical or physical imprints left on the environment, perhaps via alteration by their products)

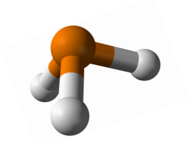


Biosignature - a feature or measurement result whose existence within a defined context *requires* biology. If you see it under the relevant conditions, it is biogenic for sure!

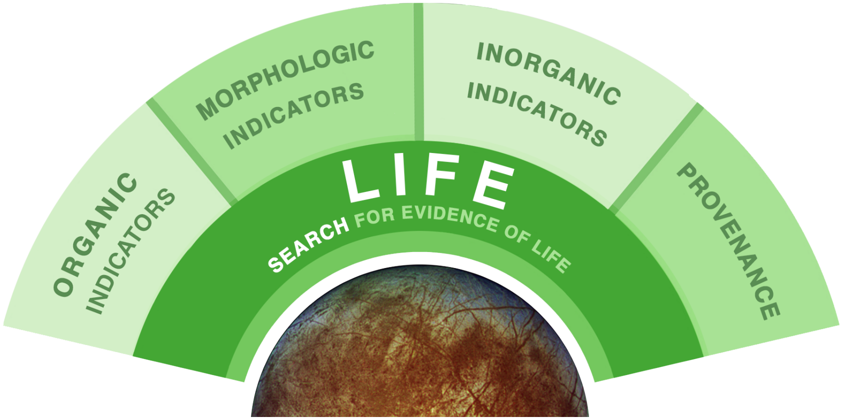
- Part of life detection science is to identify biosignatures, which may be typically *composite*.
- If your so-called biosignature merely provides “evidence” for a biological process, it is *incomplete*.

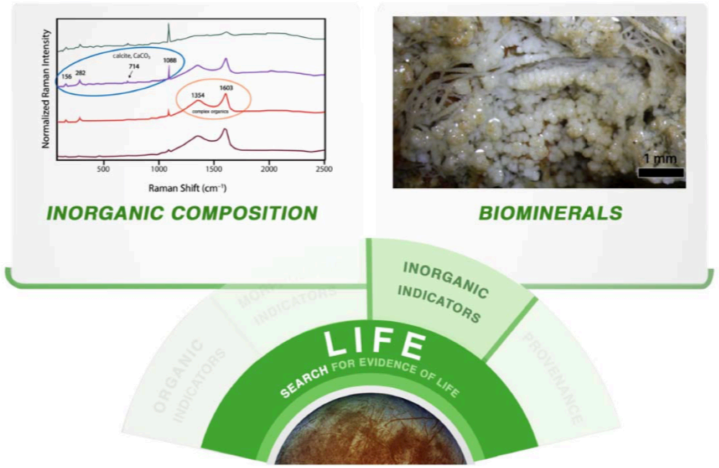
The discovery of alien life likely won’t happen with either a bang or a whimper, but with a series of mid-volume conversations spread over spacetime and expensive scientific-journal PDFs.

- Sarah Scoles, Wired, Sep. 14, 2020



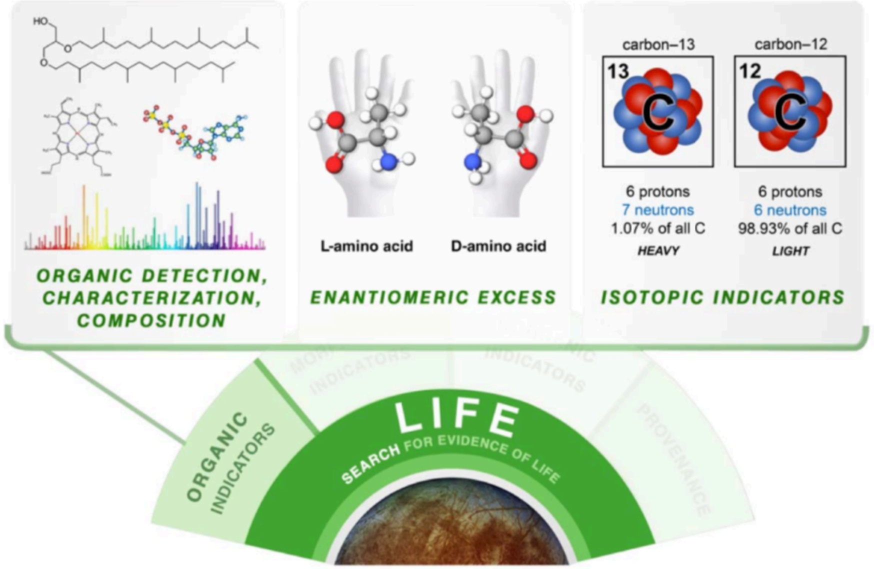
Potential Biosignatures that you can detect!





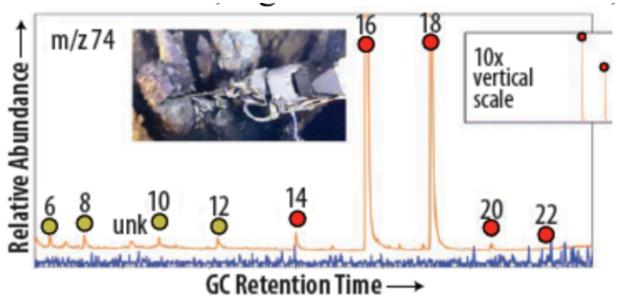
mineralogy, chemistry

e.g. Raman Spectrometer



organic chemistry, isotopes

e.g. Separation Mass Spectrometer

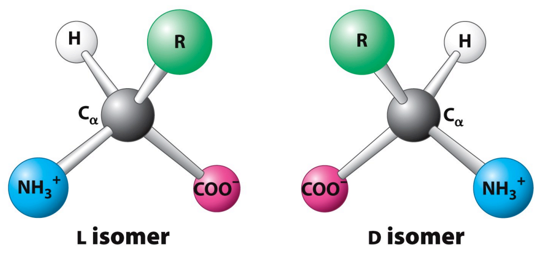


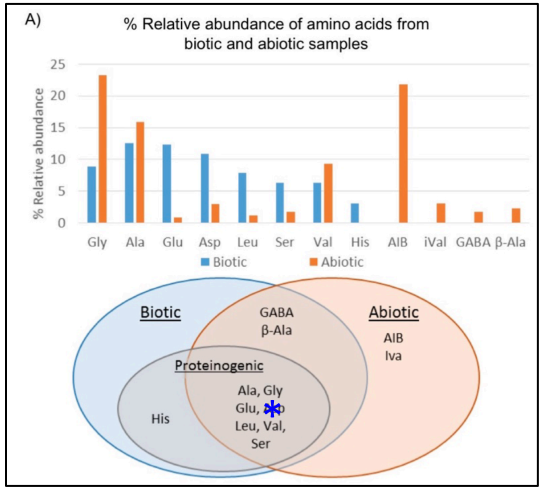
A “potential molecular biosignature” (PMB)

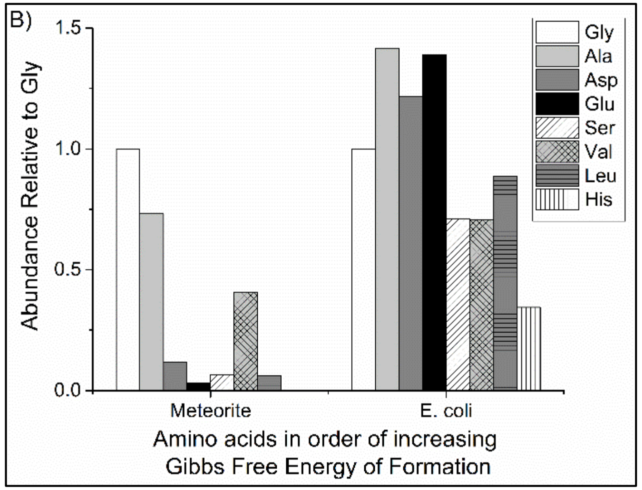
Potential Molecular Biosignature: amino acid type, abundance, and enantiomeric excess

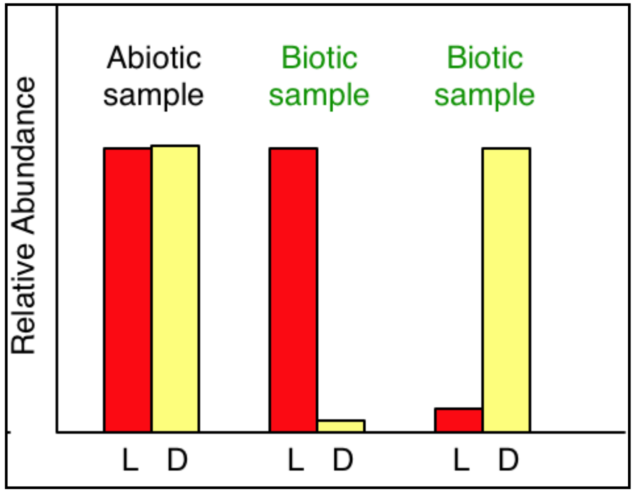
- **Amino acids (AA) are a high priority target for life detection missions. They are fundamental building blocks of terrestrial biology, making up peptides and proteins.**
- **Individual amino acids are not biosignatures (nor are they generally very good “potential biosignatures”) but multiple lines of observation of a collection of amino acids do comprise a very strong potential biosignature, approaching certainty.**
  - distribution/variety of amino acid types (comparable to terrestrial?)
  - ratios of AA to Glycine (most > 0.75 vs. < 0.25 across distribution?)
  - enantiomeric excess (EE) of AA group (avg. EE ≫ 0.2)

Valine





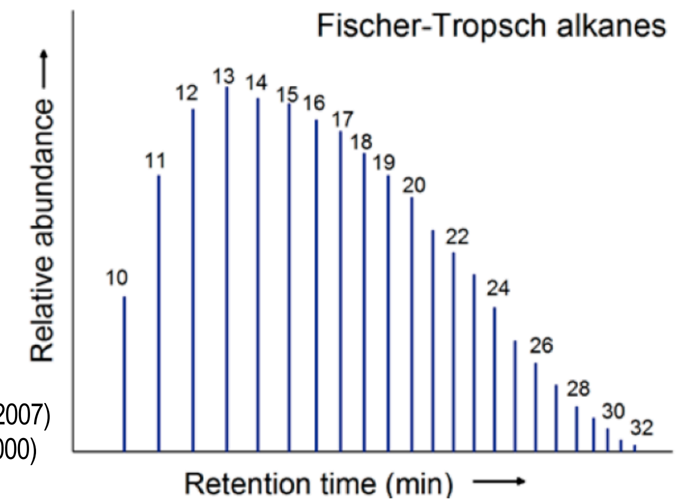




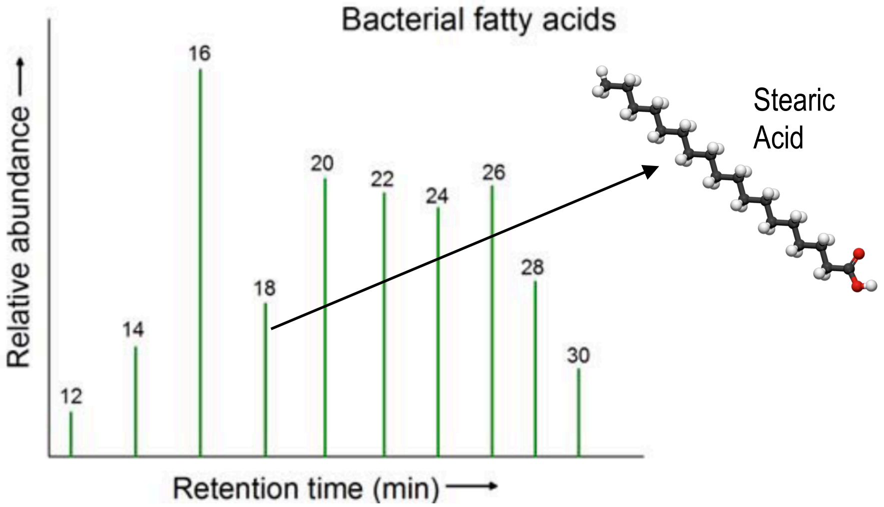
Potential Molecular Biosignature : carboxylic / fatty acid chain length pattern and preference

- **Fatty acids (FA) are a high priority target for life detection missions. They are fundamental building blocks of terrestrial biology, making up cell wall membranes.**
- **Individual fatty acids are not biosignatures (nor are they very good "potential biosignatures") but multiple lines of observation of a collection of fatty acids do comprise a very strong potential biosignature, approaching certainty.**
  - Strong bias to non-random subset of possible chain lengths (e.g. even:odd ≫ 1)
  - Distribution of molecular weights: "mean is large, width is narrow"

Abiotic organic synthesis
Low specificity



Biological organic synthesis
High specificity



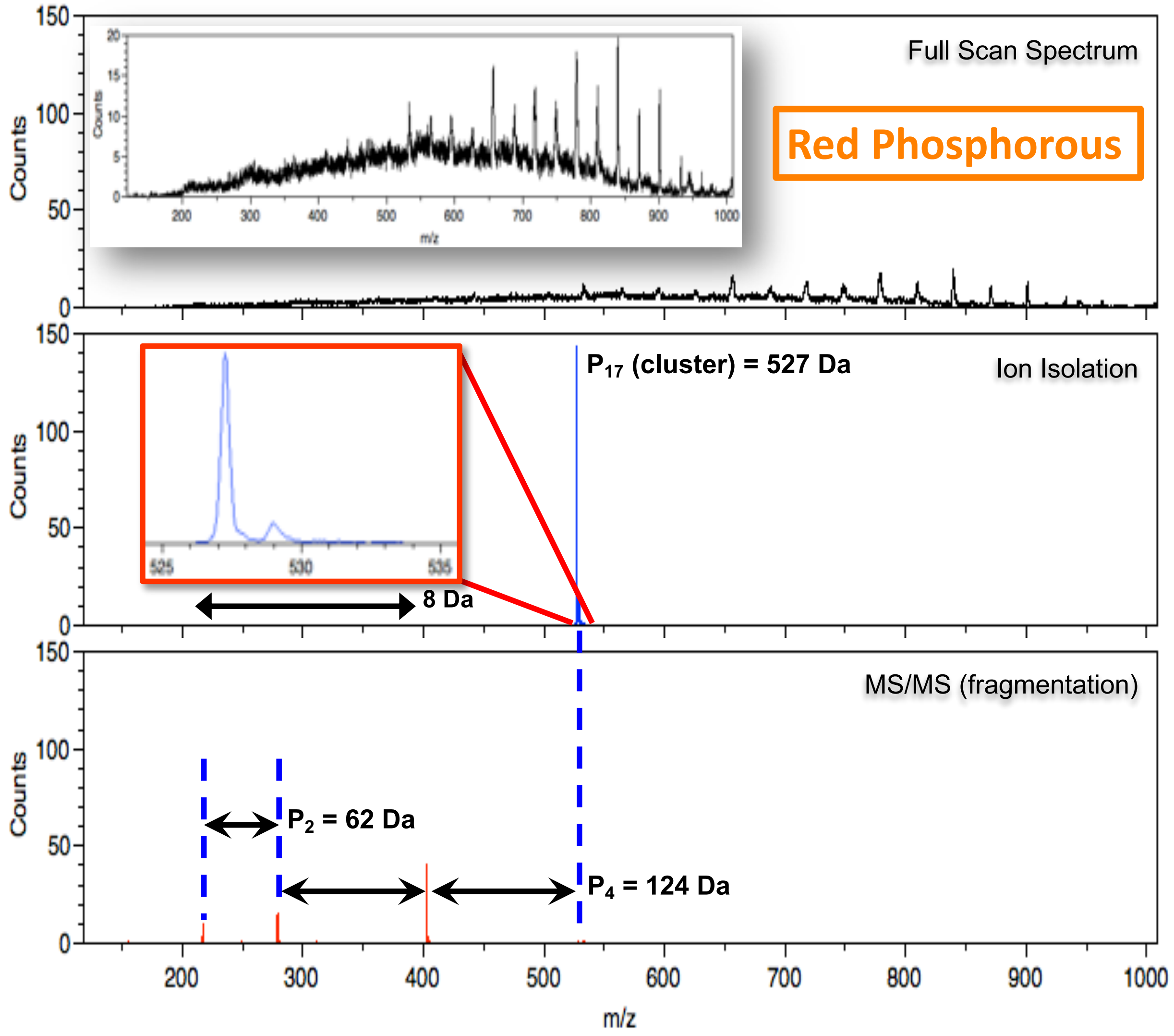
McCollom et al. (2007)
Hartgers et al. (2000)

Potential Molecular Biosignature : complex organic structures and distributions

- **Extraterrestrial biomolecules may be very different in detail than terrestrial biomolecules, but are still expected to reflect a pattern of "nonrandom" structural features and distributions.**
  - Lego® Principle: life uses finite number of common molecular "bricks" to build complex biomolecules
    - Earth: -C_2H_4- (acetogenic lipids) and -C_5H_{10}- (polyisoprenoids) are specific examples
  - Oligomerization/polymerization; branching degree is low
  - Non-equilibrium / skewed distribution of molecular weights
  - Use/expression of only one or few structural isomers of many possible
- **Evidence of individual complex compounds of sufficient *pathway complexity* (Marshall et al. 2017) may be strong potential molecular biosignatures**
- **Thinking about unexpected molecular patterns representing "life-as-we-don't-know-it" has really gotten serious attention lately with the concept of Agnostic Biosignatures.**
  - The Laboratory for Agnostic Biosignatures (LAB) team of the Network for Life Detection (NFoLD), PI Sarah Johnson, Gerogetown; DPI Heather Graham, GSFC, is a multi-year program that includes numerous lines of research including mass spectrometry that is supported by some of the Goddard technologies.

Marshall SM, Murray ARG, Cronin L (2017) "A probabilistic framework for identifying biosignatures using Pathway Complexity" Phil. Trans. R. Soc. A **375**:20160342. http://dx.doi.org/10.1098/rsta.2016.0342

Example Technique - Tandem Mass Spectrometry (a.k.a. MS/MS)

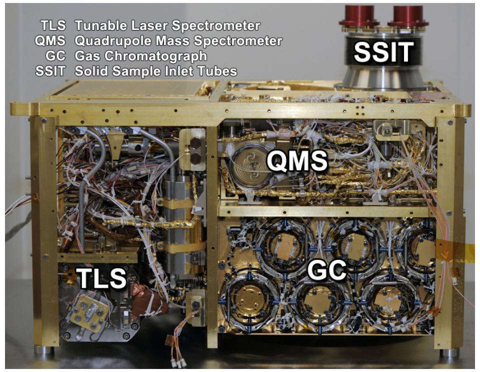


- Isolation and fragmentation of selected mass spec peaks (normally one by one)
- Reveals nature and detailed structure of complex molecules
- Can be used to detect polymers as well as sequence chains such as peptides/proteins
- Might help reveal a truly “alien” biosignature
- Implemented on MOMA and DraMS. Planned for future instruments.
- “Autonomous MS/MS” - use of automatic gain control and peak picking routines to select and analyze individual peaks without ground-in-the-loop could vastly increase mission science throughput.
- Enabled by development of stored waveform inverse Fourier transform (SWIFT) for linear ion traps under the MOMA-MS project

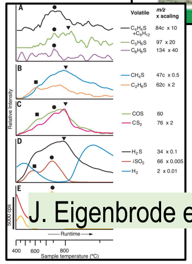
Martian Life Detection Technologies @ GSFC

SAM
Sample Analysis at Mars
MARS SCIENCE LABORATORY

PI P. Mahaffy, DPI C. Malespin



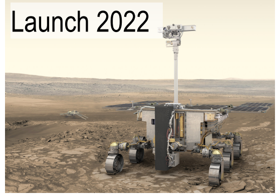
C. Freissinet et al. 2015



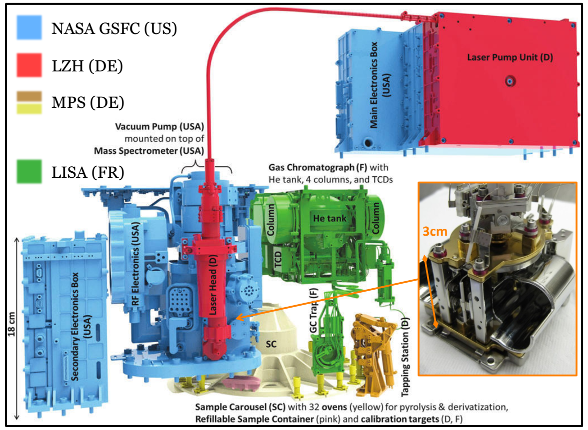
J. Eigenbrode et al. 2018

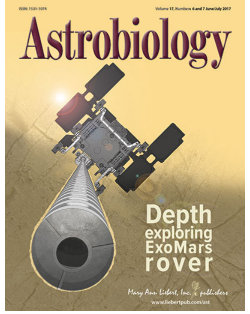
- An integrated, high-performance chemical analysis lab for MSL (TRL 9!)
- Demonstrated many technologies and methods needed for future life detection instruments - pyrolysis and gas handling; wet chemical GCMS; laser absorption spectroscopy; sample handling; valves, pumps, electronics
- While not designed for life detection, SAM has helped reveal Mars habitability

The Mars Organic Molecule Analyser Instrument



PI F. Goesmann, DPI F. Raulin



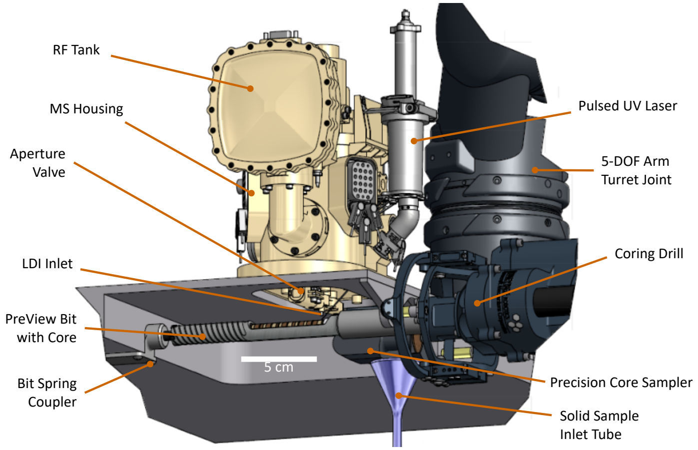


J. Vago et al. 2018

- Combines GCMS (SAM and Rosetta heritage) with laser desorption (LDMS)
- Novel miniature linear ion trap MS enables dual source as well as tandem MS/MS
- MS/MS for molecular structural analysis
- Supports ExoMars rover life detection in samples acquired by drill down to 2 meters
- Supported by MicrOmega, Raman, others

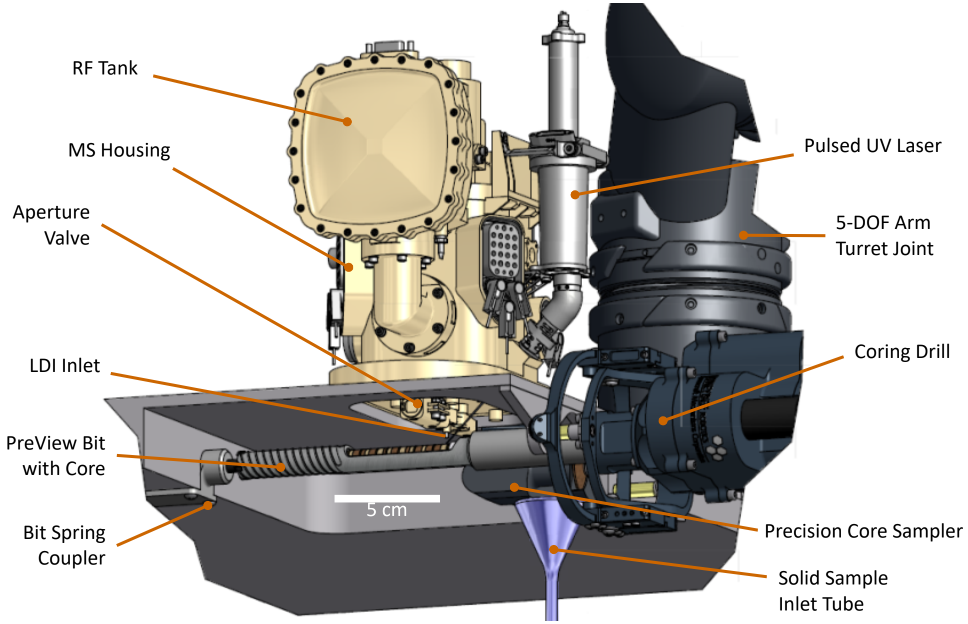
Linear Ion Trap Mass Spectrometer (LITMS)

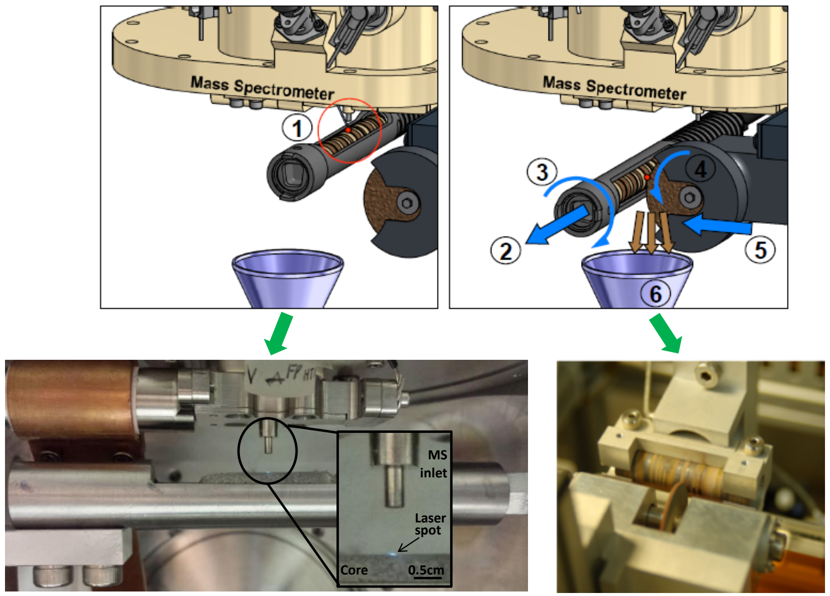
PI W. Brinckerhoff

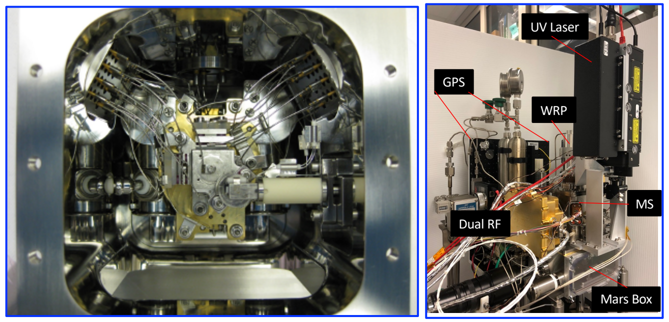


- MatISSE-developed "MOMA 2.0" for future Mars surface mission and beyond
- Precision analysis of core samples
- Higher resolution, wider mass range
- Positive and negative ion detection
- Advanced laser, pyrolysis, and GCMS capabilities compared to MOMA
- More on next slide!

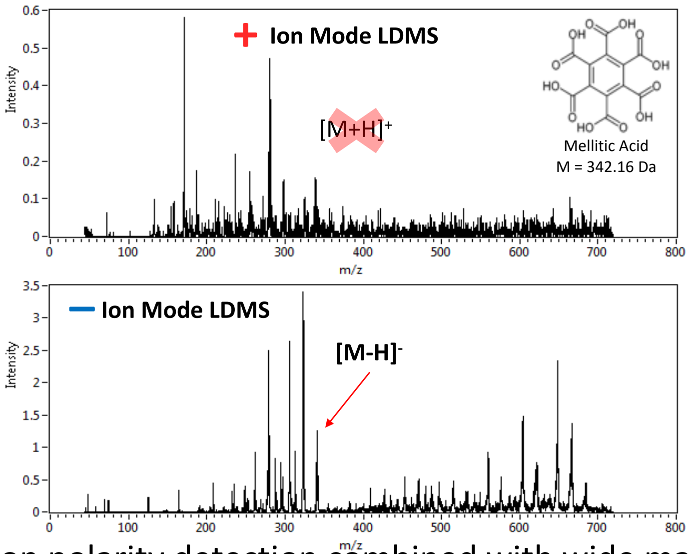
Linear Ion Trap Mass Spectrometer (LITMS)



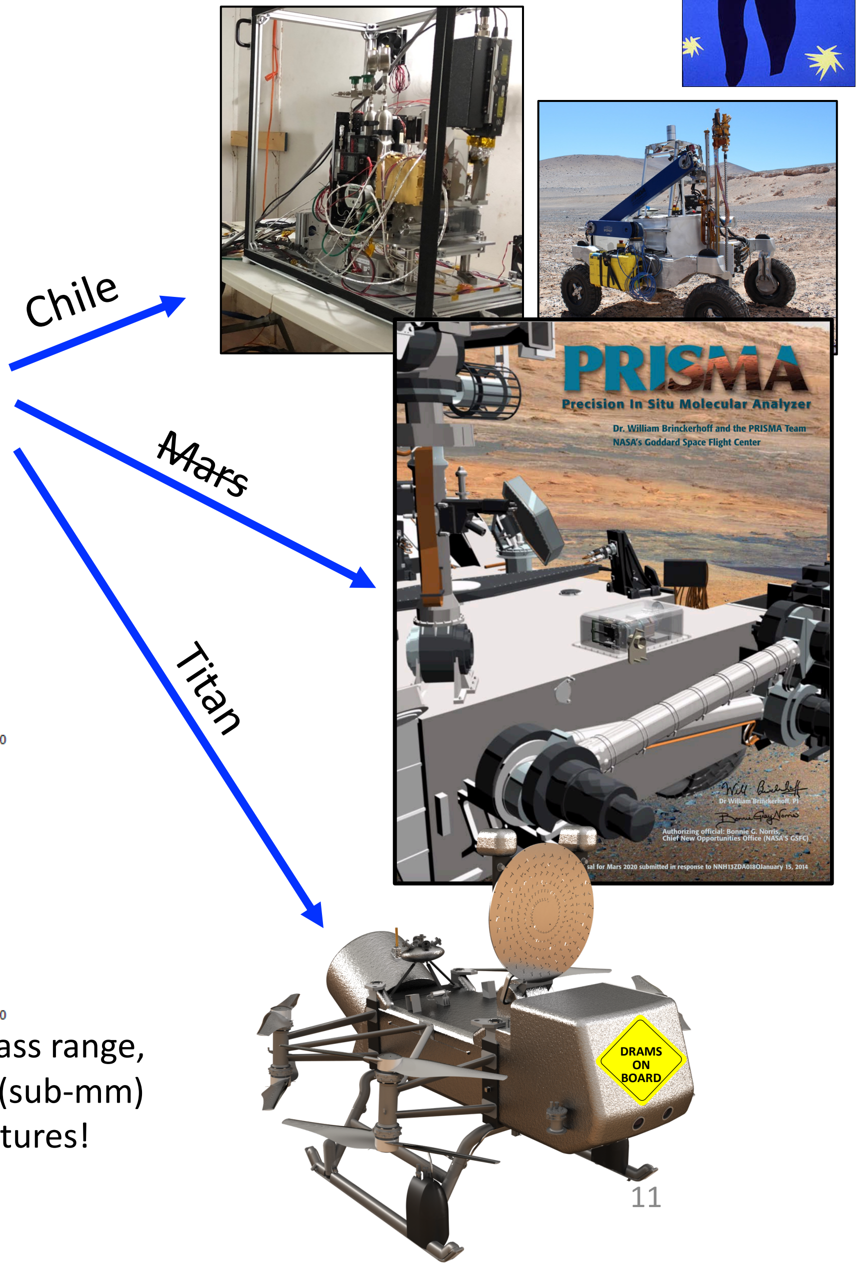




(Left) close up of ion trap "guts"
(Right) TRL 6 LITMS prototype under test



Dual ion polarity detection combined with wide mass range, molecular structure determination, and fine-scale (sub-mm) sampling to identify isolated potential biosignatures!



COLD & ICEE-2 Life Detection Technologies @ GSFC

CADMES

PI C. Malespin

CADMES

Collaborative Acceptance and Distribution for Measuring Europan Samples

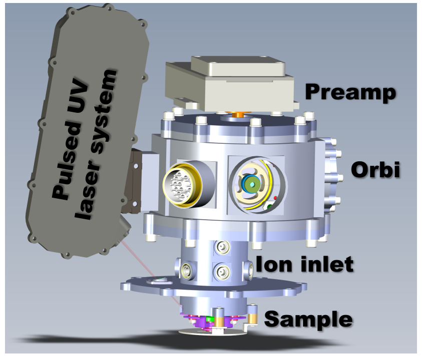
- Critical bridging technology between sample acquisition and measurement instruments on Europa Lander
- Meets requirements for handling all samples - number, volume, position, cleanliness, temperature, etc.
- Prototype under development in collaboration with Lander Pre-project and supported by Honeybee Robotics

CORALS

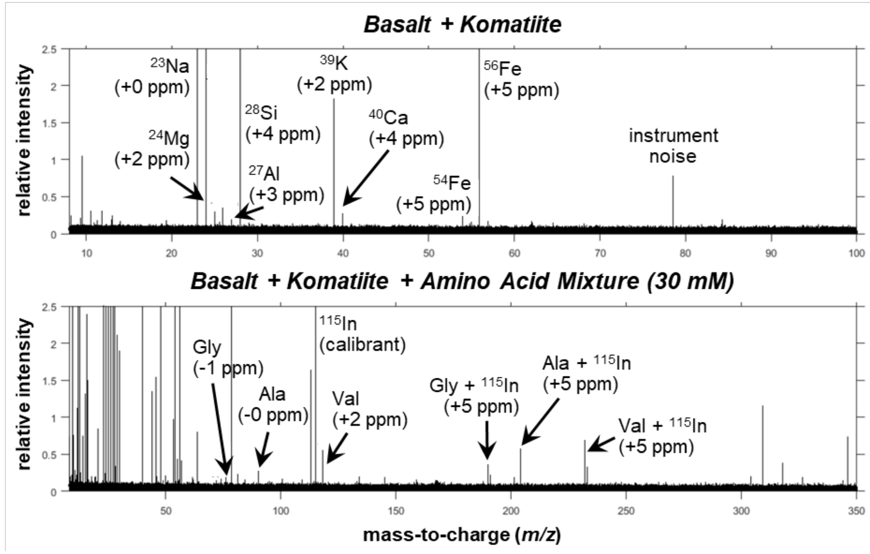
Characterization of Ocean Residues and Life Signatures

PI R. Arevalo (University of MD)

Collaboration with GSFC, Thermo, and French Cosmorbitrap Team

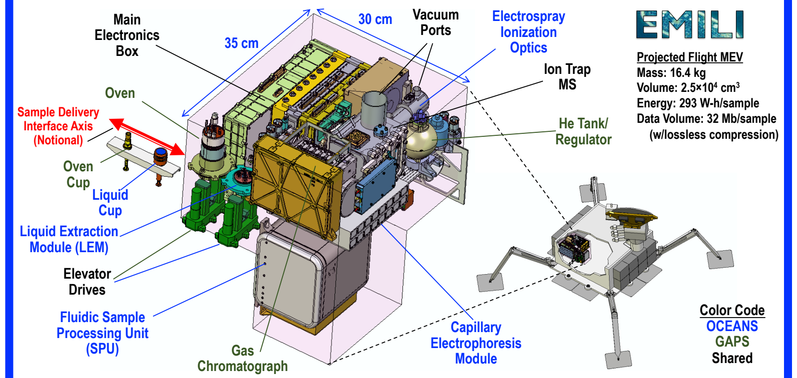


- Laser desorption Orbitrap MS
- Ultra-high resolution (> 10^5) and mass accuracy - directly distinguish molecules with different atomic composition
- Well-suited for hard vacuum conditions of Europa



EMILI

PI W. Brinckerhoff; DPI P. Willis (JPL)

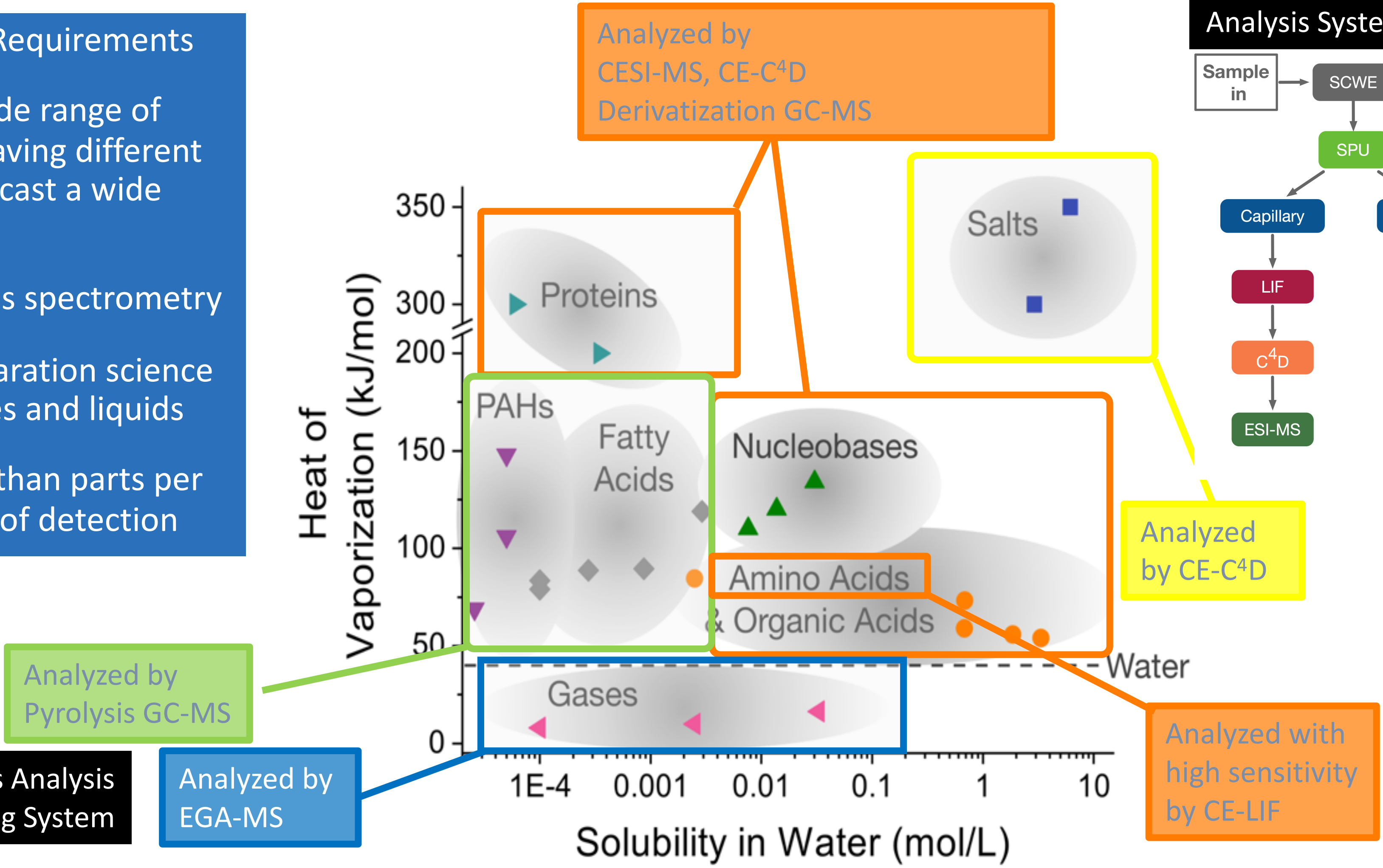


- Combines highly complementary molecular analysis techniques for comprehensive life detection focus
- Meets Europa Lander Organic Composition Analyzer requirements
- Newly-demonstrated coupling of capillary electrophoresis and mass spectrometry for polar organics
- Goddard-JPL-Ames collaboration

Europan Molecular Indicators of Life Investigation (EMILI) for ICEE-2
EMILI = GAPS + OCEANS

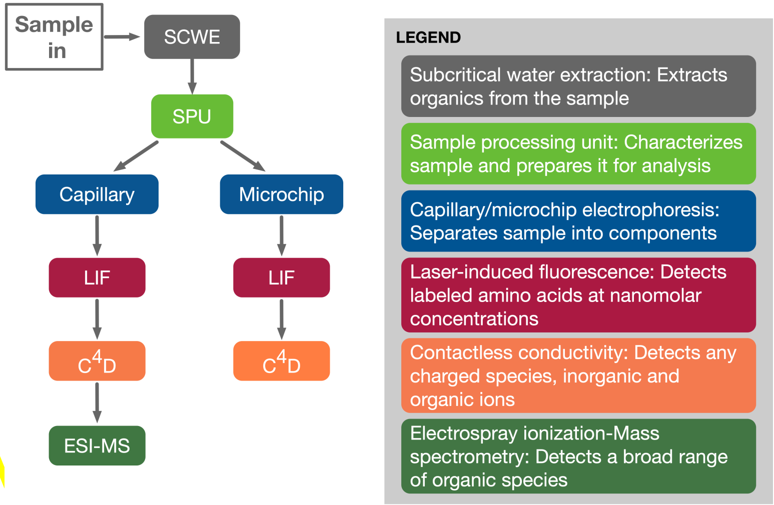
Key and Driving Requirements

1. Analyze a wide range of molecules having different properties ("cast a wide net")
2. Perform mass spectrometry
3. Perform separation science on both gases and liquids
4. Have better than parts per billion limits of detection



GAPS – Gas Analysis Processing System

OCEANS - Organic Capillary Electrophoresis Analysis System

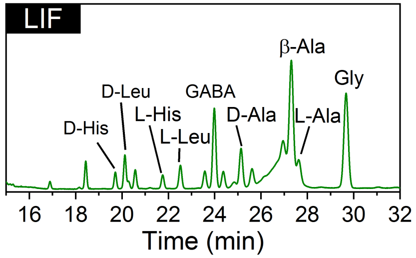


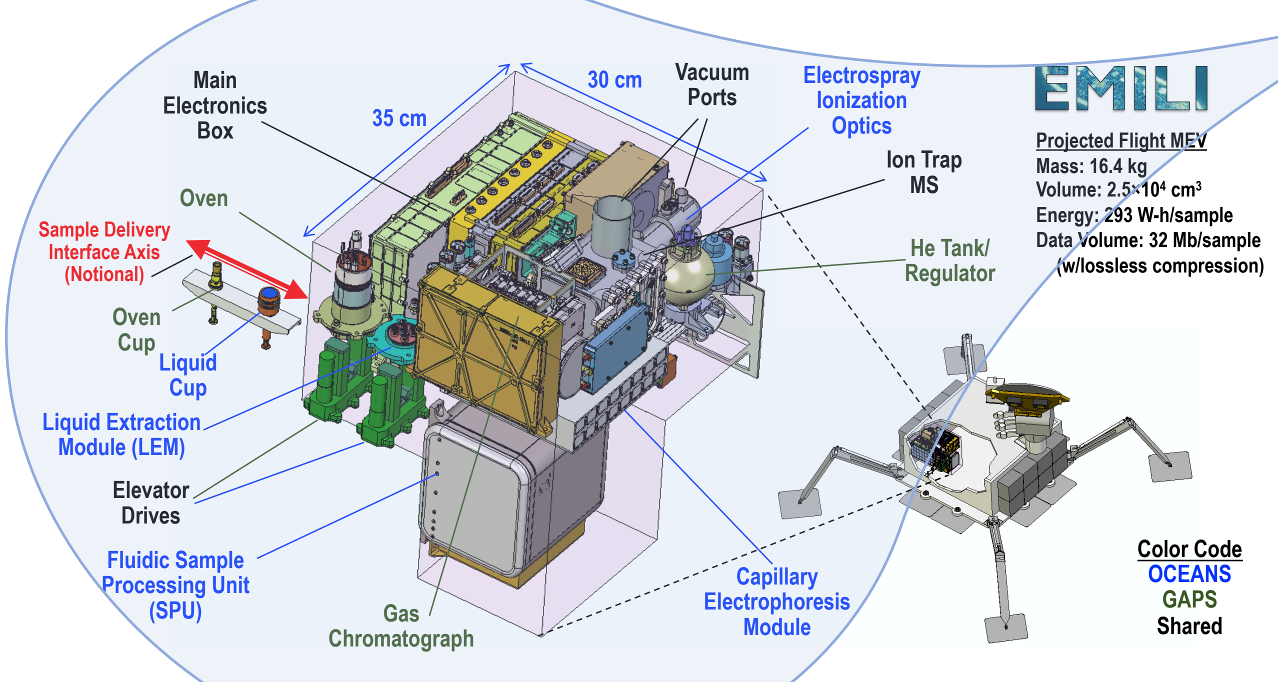
High-Precision In Situ Molecular Biosignature Analysis on Enceladus, Europa, and Beyond

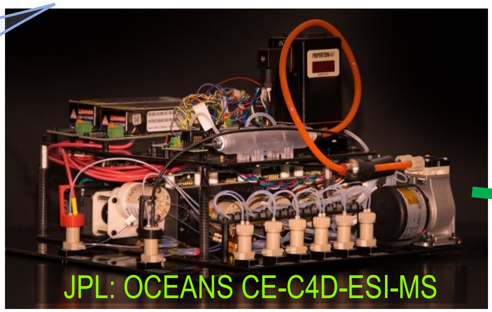
A Life Detection Technology Partnership between Goddard, JPL, Ames, Honeybee Robotics, and Others [POC: W. Brinckerhoff, GSFC]

Newly-developed and demonstrated (COLDTech, ICEE-2) technology combines complementary liquid and gas sample processing with exquisitely sensitive, precise, and broad molecular characterization methods (mass spectrometry, laser-induced fluorescence, conductivity)

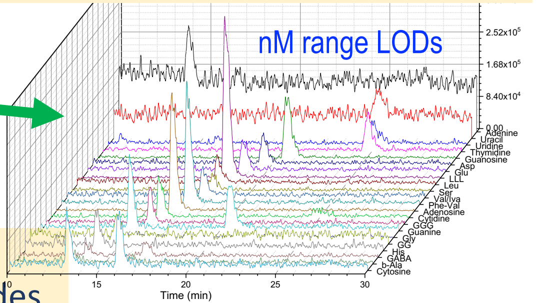
Demonstrated
1-5 nM amino acid limit of detection (LOD) with CE-LIF



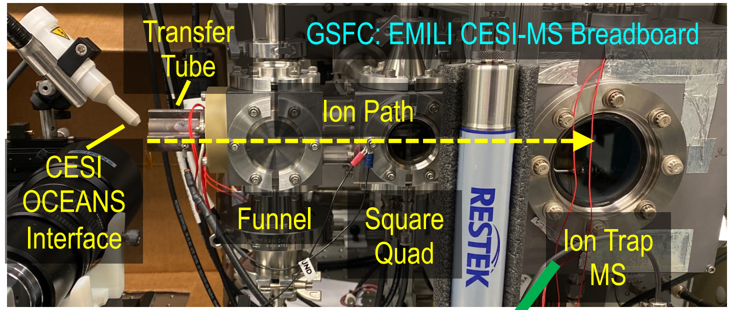


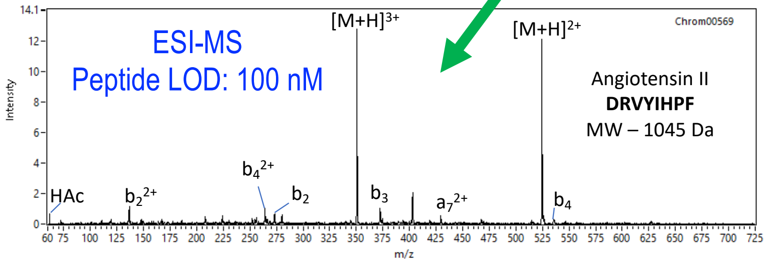


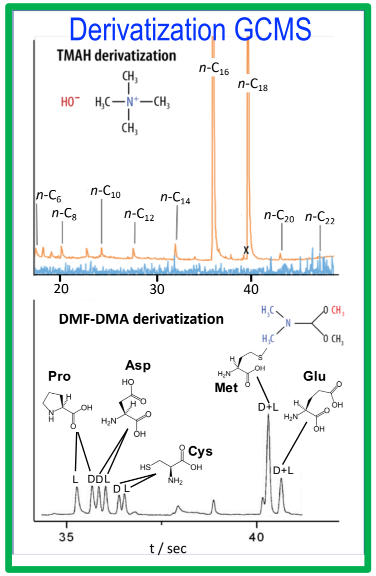
Demonstrated
Integrated & automated CE-C4D-ESI-MS



Demonstrated
Wide mass range ESI-MS analysis of peptides







Europan Molecular Indicators of Life Investigation (EMILI)

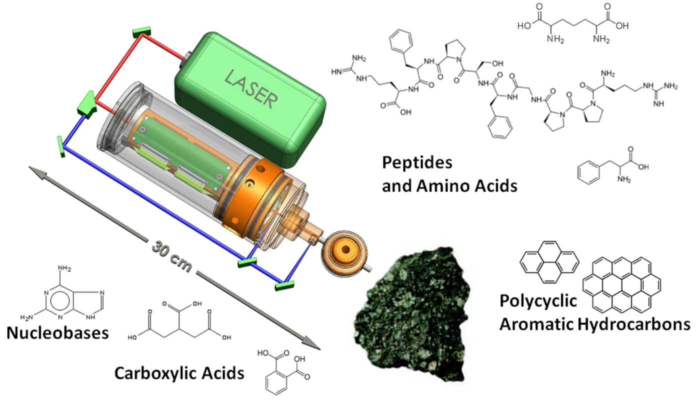
Complete analysis of organic compounds (amino acids, peptides, carboxylic acids, aromatics, …), light volatiles, and salts in ocean world samples. Merges Capillary Electrophoresis (CE), Laser Induced Flurorescence (LIF), Gas Chromatography (GC), and Ion Trap Mass Spectrometry (ITMS) on track to TRL 5/6 meeting all Europa SDT objectives and **fully adaptable to Enceladus**.

TOF-MS+ Technologies @ GSFC

L2MS

Two-Step Laser Mass Spectrometer

PIDDP PI S. Getty

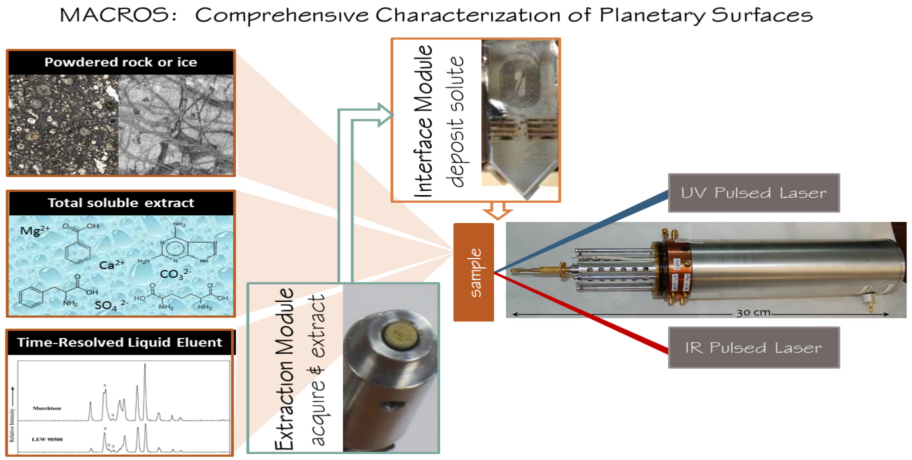


- Highly-miniature (5-6 kg) laser-based time-of-flight mass spectrometer
- “Unbounded” mass range 1-10^5 u
- Direct vacuum sample interrogation
- Two-step laser method (IR desorption, UV ionization) is exquisitely sensitive to aromatics - far greater than LDI or GCMS
- Tunable laser technology can enable selective analysis of other organics

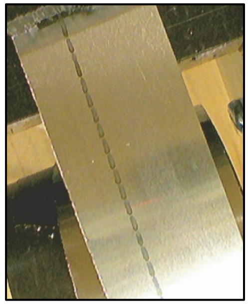
MACROS

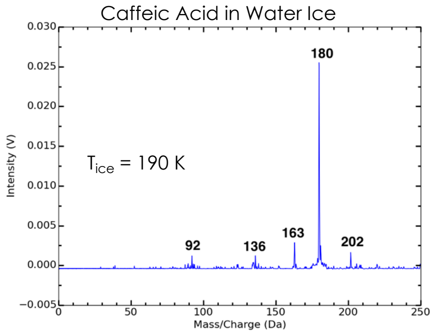
Molecular analyzer for Complex Refractory Organic-rich Surfaces

PICASSO PI S. Getty



Significantly expands L2MS capability by adapting to liquid extraction/deposition front end for LC-TOF-MS or MALDI-TOF-MS - deposition in vacuum!

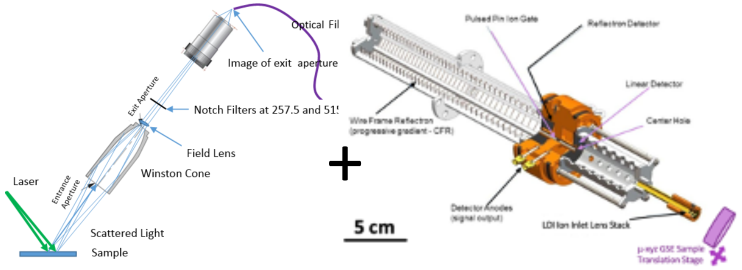




RAMS

Raman Mass Spectrometer

PICASSO PI A. Grubisic



- Combines highly complementary molecular analysis techniques for comprehensive life detection focus
- Meets Europa Lander Organic Composition Analyzer requirements
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RAMS: RAMAN - MASS SPECTROMETER FOR PLANETARY EXPLORATION

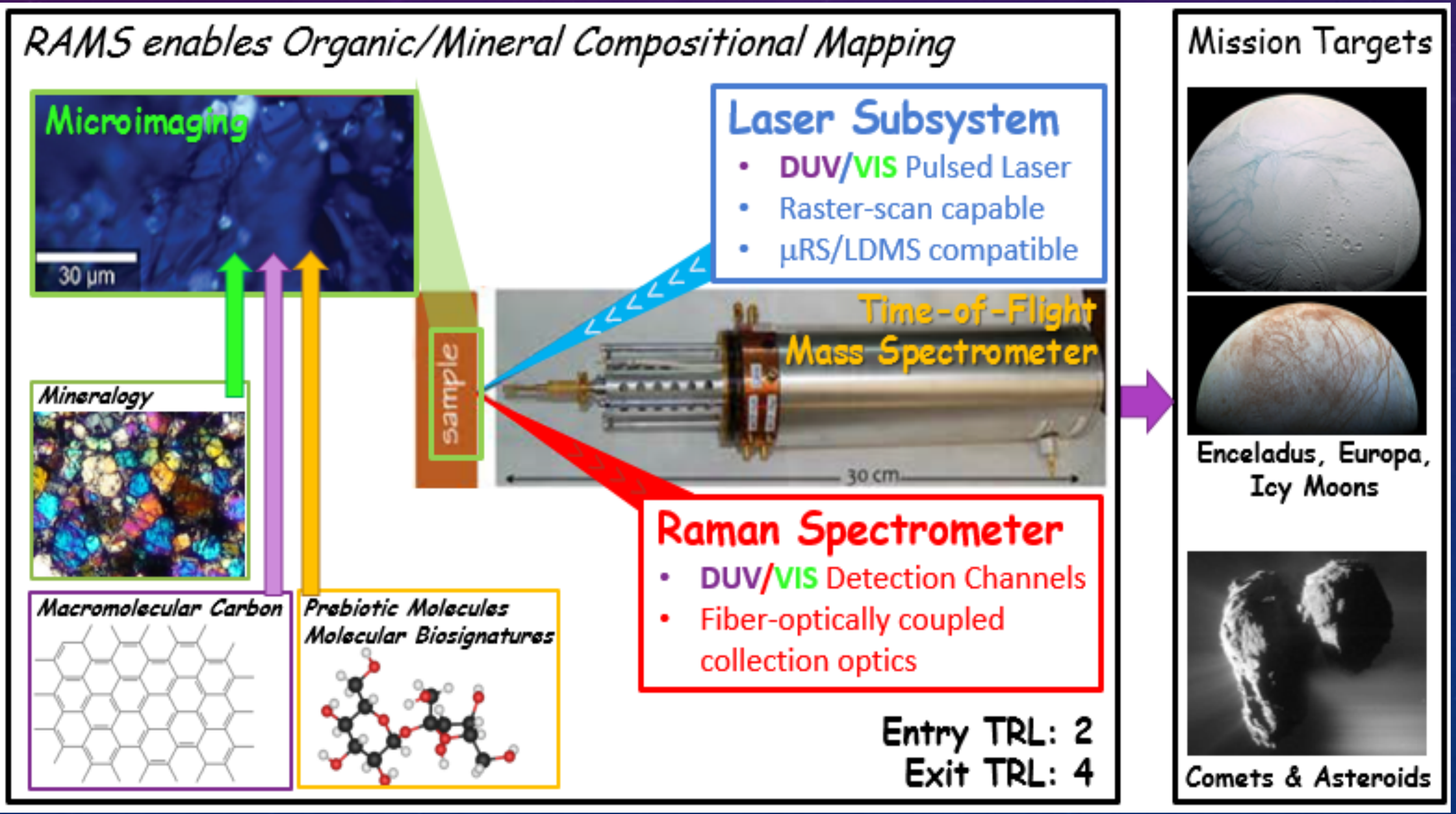
Planetary Instrument Concepts for the Advancement of Solar System Operations (PICASSO), PI Andrej Grubisic, NASA/GSFC

Target:

- RAMS is a hybrid instrument combining Raman Spectroscopy (RS) and Laser Desorption Mass Spectrometry (LDMS) for microimaging surfaces of airless planetary bodies, including ocean worlds, comets, and asteroids.

Science:

- Enables comprehensive characterization of organic (LDMS) and inorganic (RS) composition of planetary surface samples.
- Capable of detection of habitability indicators, molecular biosignatures (amino acids, nucleobases, lipids, and biopolymers), macromolecular carbon, as well as contextual geologic information.



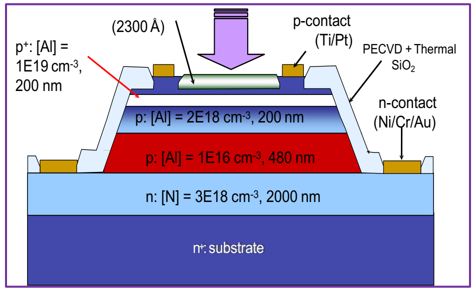
Ultra-Violet Detector Innovation for Raman Exploration and CharacTerization (UV-DIRECT) of Ocean Worlds

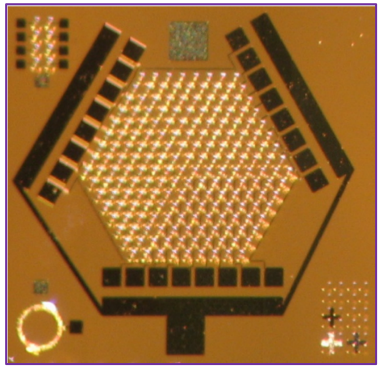
PI: Dina M. Bower (UMD/GSFC)

Co-PI: Shahid Aslam (GSFC)

Co-I's: Tilak Hewagama (GSFC), Anand Sampath and Jonathan Schuster (ARL), Nicolas Gorius (CUA)

UV-DIRECT utilizes 4H-SiC sensor geometry to improve upon existing avalanche photodiode (APD) detector technologies to enable UV-Raman spectroscopy and spectroscopic imaging



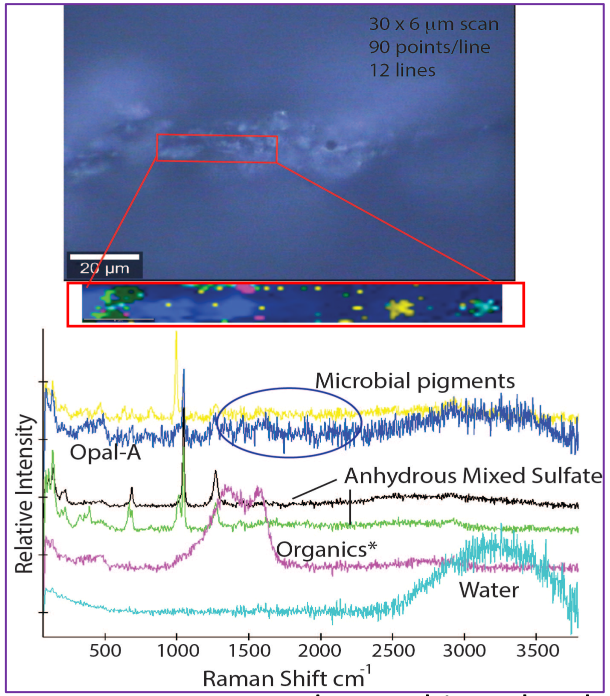


Top: SiC sensor schematic based on current detector used by Army Research Labs
Bottom: Image of detector array

UV-DIRECT Enables

- The assessment of habitability on icy moon/ ocean world surface environments by detecting and characterizing oxidants, salts, aqueous minerals, organics, and brinicles in deposits from subsurface.
- The search for life by detecting biomarkers such as organic compounds, and chemical species containing CHNOPS elements.

UV-DIRECT encompasses the development of a compact, energy efficient, ruggedized linear detector array that is impervious to extraneous visible light with ppb sensitivity for in situ surface exploration using Raman spectroscopy

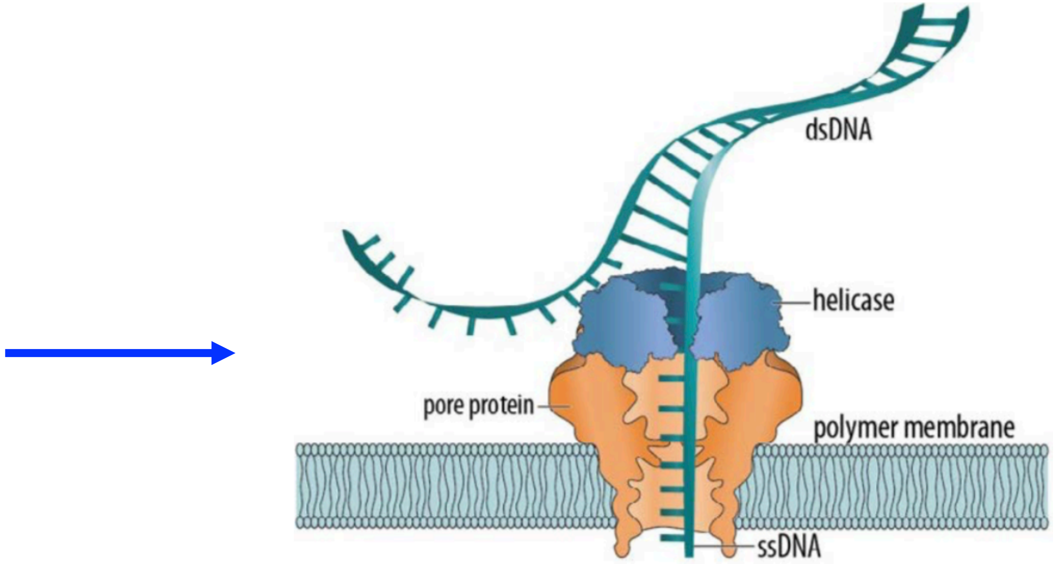


Raman spectroscopy detects biomolecules, minerals, and hydrated species. Raman imaging goes further by revealing the spatial relationships of each component, map colors (red box) match spectra

Project Duration: Oct 2020 – Sept 2023; TRL 2 -3

Planetary Instrument Concepts for the Advancement of Solar System Operations (PICASSO)

“What about me?” squeaked the nanopore.



It’s a whole separate talk but several aspects of the development of nanopore sequencing technology are under development at Goddard, in collaboration with Georgetown University and other NASA centers. Supported in part by the NAI Goddard Center for Astrobiology (PI Mumma) these have included projects, led by college interns Mark Sutton and Maggie Weng, to examine the robustness of nanopore sequencing under spaceflight-relevant conditions, including radiation degradation and high salt concentrations.

Contamination Control Technology Study for Life-Detection Missions

ELSAH Technology Study Team, funded by New Frontiers Program, 2018-2020

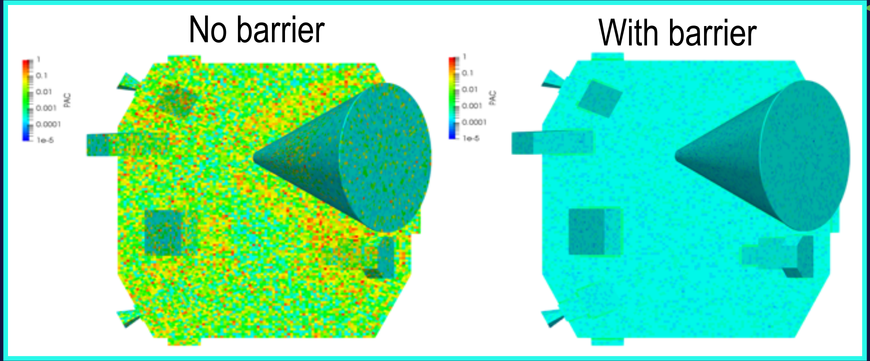
Life-detection missions require extensive mitigation efforts to reduce the risk of terrestrial biosignatures (viable, dead and partial cells, biomolecules, other interferences) compromising measurements by extremely sensitive instruments.

Study Aims:

1) Spacecraft barrier (video)
2) Model particle & molecular contamination transfer on ultraclean surfaces (right image; warm colors = higher particle numbers)
3) Quantitatively evaluate the effectiveness of mitigation approaches

Key Results:

- Barrier reduces particle contamination (likely biological) from fairing to the spacecraft by 2-3 orders of magnitude (image below)
- In-flight cleaning processes of sample collector reduced molecular contamination from spacecraft by 12 orders of magnitude.



Cleanable & Repairable Spacecraft Barrier Prototype & Test

Conclusion: Both barrier and inflight cleaning are key Technologies enabling us to meet the super stringent cleanliness requirements for life detection science (femtomole level of individual biomolecules)

Advanced Molecular & Particulate Contaminant Transport Modeling

POCs: J. Eigenbrode, NASA GSFC (Jennifer.Eigenbrode@nasa.gov)

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NASA funded projects

SAM and MOMA	Mars Exploration Program
LITMS	Maturation of Instruments for Solar System Exploration (MatISSE)
CADMES, CORALS, EMILI	Instrument Technologies for Europa Exploration 2 (ICEE-2)
L2MS	Planetary Instrument Definition and Development Program (PIDDP)
MACROS, RAMS, UV-DIRECT	Planetary Instrument Concepts for Solar System Observations (PICASSO)
Nanopore research	NASA Astrobiology Institute (NAI) Goddard Center for Astrobiology (GCA)
LAB	Network for Life Detection (NFoLD) Research Coordination Network (RCN)

Goddard's Internal Research and Development (IRAD) program provided seed funding for some of the concepts described here.

Acronyms

CADMES	Collaborative Acceptance and Distribution for Measuring Europan Samples
CE	Capillary Electrophoresis
CESI-MS	Capillary Electrophoresis Electrospray Ionization Mass Spectrometry
CLD	Center for Life Detection
CORALS	Characterization of Ocean Residues and Life SIgnatures
C4D	Contactless Capacitively-Coupled Conductivity Detection
EMILI	Europan Molecular Indicators of Life Investigation
GAPS	Gas Analysis and Processing System
GC	Gas Chromatograph
ITMS	Ion Trap Mass Spectrometer
LAB	Laboratory for Agnostic Biosignatures
LDI	Laser Desorption / Ionization
LDMS	Laser Desorption Mass Spectrometry
LEM	Liquid Extraction Module
LIF	Laser Induced Fluorescence
LITMS	Linear Ion Trap Mass Spectrometer
L2MS	Two-step Laser Mass Spectrometer
MACROS	
MOMA	Mars Organic Molecule Analyzer
MS/MS	Tandem Mass Spectrometry
OCEANS	Organic Capillary Electrophoresis Analysis System
RAMS	Raman Mass Spectrometer
SAM	Sample Analysis at Mars
SCWE	Sub-Critical Water Extraction
SPU	Sample Processing Unit
SWIFT	Stored Waveform Inverse Fourier Transform