Future Missions to Titan: Scientific and Engineering Challenges

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Team Leads:

Julia R. Greer
California Institute of Technology
jrgreer@caltech.edu

Jennifer M. Jackson
California Institute of Technology
jackson@gps.caltech.edu

Jonathan I. Lunine
University of Arizona
Jonathan.I.Lunine@jpl.nasa.gov

Mohammad M. Mojarradi
Jet Propulsion Laboratory, California Institute of Technology
mohammad.m.mojarradi@jpl.nasa.gov

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Acronyms and Abbreviations

ASN	Ambient seismic noise
BiCMOS	Bipolar junction complementary metal-oxide-semiconductor
CCN	Cloud condensation nuclei
CE	Capillary electrophoresis
CNT	Carbon nanotube
CTE	Coefficient of thermal expansion
DAP	Diallyl phthalate
DOSY	Diffusion ordered spectroscopy
FID	Flame ionization detector
FT-ICR	Fourier transform-ion cyclotron resonance
GaAs	Gallium arsenide
GC	Gas chromatography
InP	Indium phosphide
IC	Integrated circuits
LC	Liquid chromatography
MEMS	Microelectromechanical system
MER	Mars Exploration Rovers (NASA)
μTAS	Micro-total-analysis systems
MSL	Mars Science Laboratory (NASA)
NMR	Nuclear magnetic resonance
PAH	Polycyclic aromatic hydrocarbon
PMT-PT	Lead magnesium niobate/lead titanate crystal (low-T piezo material)
PSN-PT	Lead scandium niobate/lead titanate crystal (low-T piezo material)
PTFE	Polytetrafluoroethylene (Teflon)
RHU	Radioisotope heater unit
RTG	Radioisotope thermoelectric generator
SAM	Sample Analysis on Mars (MSL)
SEM	Scanning electron microscopy
SiGe	Silicon germanium
SP	Short period
SPU	Sample processing unit
TAG	Thermal desorption aerosol GC/MS-FID
TCR	Thermal coefficient of resistance
TEG	Thermo electric generator
TOF	Time of flight
TRL	Technology readiness level
UHV	Ultra-high vacuum
ULE	Ultra-low expansion
VBB	Very broad band
VCAM	Vehicle Cabin Atmosphere Monitor (NASA)

1. Executive summary

Saturn's largest moon, Titan, has been an enigma at every stage of its exploration. For three decades after the hazy atmosphere was discovered from the ground in the 1940s, debate ensued over whether it was a thin layer of methane or a dense shield of methane and nitrogen. Voyager 1 settled the matter in favor of the latter in 1980, but the details of the thick atmosphere discovered raised even more intriguing questions about the nature of the hidden surface, and the sources of resupply of methane to the atmosphere. The simplest possibility, that an ocean of methane and its major photochemical product ethane might cover the globe, was cast in doubt by Earth-based radar studies and then eliminated by Hubble Space Telescope and adaptive optics imaging in the near-infrared from large ground-based telescopes in the 1990s. These data, however, did not reveal the complexity of the surface that Cassini-Huygens would uncover beginning in 2004. A hydrological cycle appears to exist in which methane (in concert with ethane in some processes) plays the role on Titan that water plays on Earth.

Channels likely carved by liquid methane and/or ethane, lakes and seas of these materials—some rivaling or exceeding North America's Great Lakes in size—vast equatorial dune fields of complex organics made high in the atmosphere and shaped by wind, and intriguing hints of geologic activity suggest a world with a balance of geologic and atmospheric processes that is the solar system's best analogue to Earth. Deep underneath Titan's dense atmosphere and active, diverse surface is an interior ocean discovered by Cassini and thought to be largely composed of liquid water.

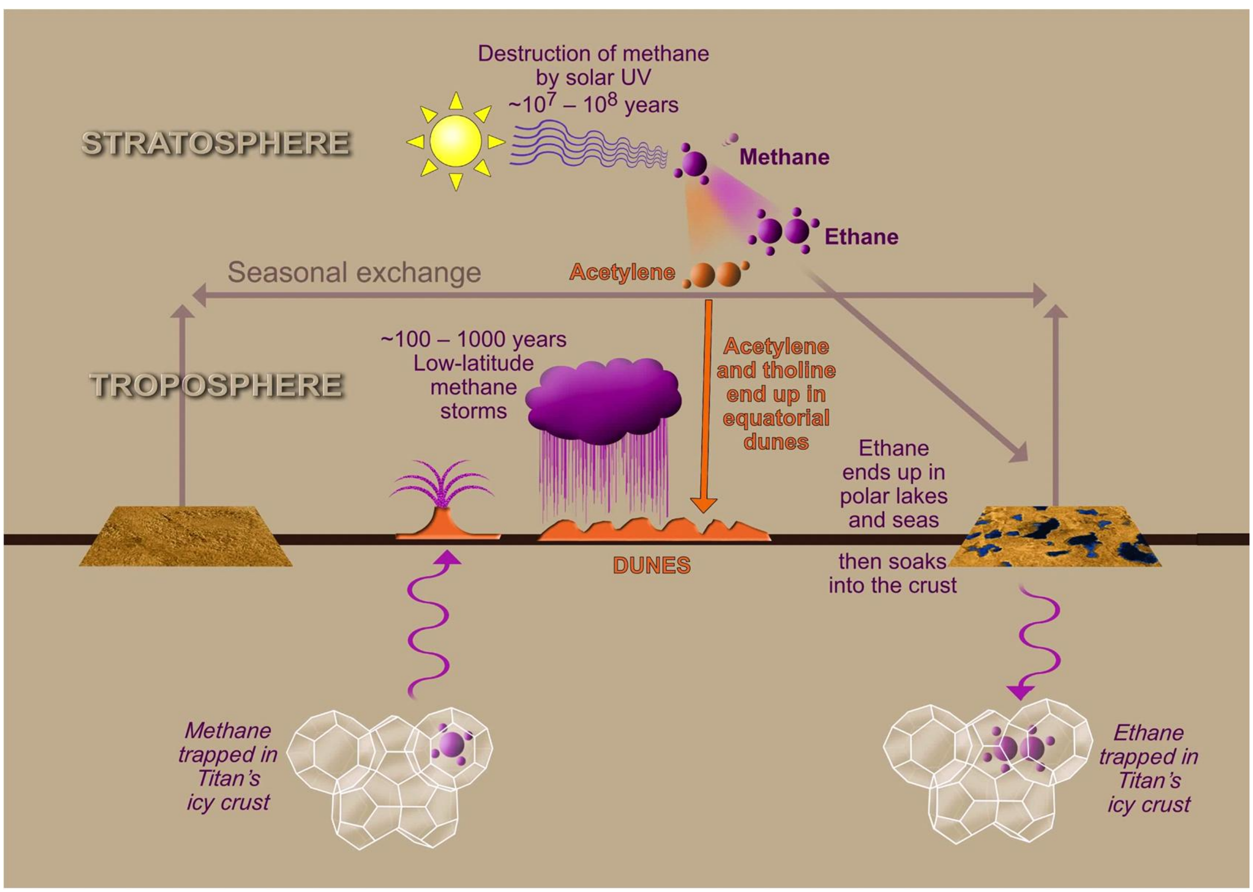


Figure 1-1. A schematic view of the methane cycle on Titan shown with rough timescales for the various processes.

Cassini-Huygens has provided spectacular data and has enabled us to glimpse the mysterious surface of Titan. However the mission will leave us with many questions that require future missions to answer. These include determining the composition of the surface and the geographic distribution of various organic constituents. Key questions remain about the ages of surface features, specifically whether cryovolcanism and tectonism are actively ongoing or are relics of a more active past. Ammonia, circumstantially suggested to be present by a variety of different kinds of Cassini-Huygens data, has yet to be seen. Is methane out-gassing from the interior or ice crust today? Are the lakes fed primarily by rain or underground methane-ethane aquifers (more properly, "alkanofers") and how often have heavy methane rains come to the equatorial region? We should investigate whether Titan's surface supported vaster seas of methane in the past, and whether complex self-organizing chemical systems have come and gone in the water volcanism, or even exist in exotic form today in the high latitude lakes. The presence of a magnetic field has yet to be established. A large altitude range in the atmosphere, from 400–900 km in altitude, will remain poorly explored after Cassini. Much remains to be understood about seasonal changes of the atmosphere at all levels, and the long-term escape of constituents to space.

Other than Earth, Titan is the only world in our solar system known to have standing liquids and an active "hydrologic cycle" with clouds, rains, lakes and streams. The dense atmosphere and liquid lakes on Titan's surface can be explored with airborne platforms and landed probes, but the key aspect ensuring the success of future investigations is the conceptualization and design of instruments that are small enough to fit on the landed probes and airborne platforms, yet sophisticated enough to conduct the kinds of detailed chemical (including isotopic), physical, and structural analyses needed to investigate the history and cycling of the organic materials. In addition, they must be capable of operating at cryogenic temperatures while maintaining the integrity of the sample throughout the analytic process. Illuminating accurate chemistries also requires that the instruments and tools are not simultaneously biasing the measurements due to localized temperature increases. While the requirements for these techniques are well understood, their implementation in an extremely low temperature environment with limited mass, power and volume is acutely challenging. No such instrument systems exist today.

Missions to Titan are severely limited in both mass and power because spacecraft have to travel over a billion miles to get there and require a large amount of fuel, not only to reach Titan, but to maintain the ability to maneuver when they arrive. Landed missions have additional limitations, in that they must be packaged in a sealed aeroshell for entry into Titan's atmosphere. Increases in landed mass and volume translate to increased aeroshell mass and size, requiring even more fuel for delivery to Titan. Nevertheless, missions during which such systems and instruments could be employed range from Discovery and New Frontiers class *in situ* probes that might be launched in the next decade, to a full-up Flagship class mission anticipated to follow the Europa Jupiter System Mission. Capitalizing on recent breakthroughs in cryo-technologies and smart materials fabrication, we developed conceptual designs of sample acquisition systems and instruments capable of *in situ* operation under low temperature environments.

The study included two workshops aimed at brainstorming and actively discussing a broad range of ideas and associated challenges with landing instruments on Titan, as well as more focused discussions during the intervening part of the study period. The workshops each lasted ~4 days (Monday-Thursday/Friday), included postdoctoral fellows and students in addition to the core team members, and generated active engagement from the Caltech and JPL team participants, as well as from the outside institutions. During the workshops, new instruments and sampling methodologies were identified to handle the challenges of characterizing everything from small molecules in Titan's upper atmosphere to gross mixtures of high molecular weight complex organics in condensed phases, including atmospheric aerosols and "organic sand" in dunes, to highly dilute components in ices and lakes. To enable these advances in cryogenic instrumentation breakthroughs in a wide range of disciplines, including electronics, chemical and mechanical engineering, and materials science were identified.

Four sub-groups with their respective tasks and participants were identified at the first workshop and continued their work between workshops 1 and 2.

Group 1: In situ chemical analysis (Lead: J. Lunine assisted by P. Beauchamp)

This group had the responsibility for determining the most promising measurement techniques, individually and in combination, for organic and (secondarily) inorganic materials, and the state of the art available in the coming 5 years (but not yet space qualified at that time).

Group 2: Sample handling (Lead: J. R. Greer assisted by A. Shapiro)

This group had the responsibility to determine how samples would be pre-selected, collected and prepared for chemical analysis. Materials capable of surviving the ambient environment on Titan were also explored by this group.

Group 3: Physical and geophysical measurements (Lead: J. Jackson assisted by C. Sotin)

This group had the responsibility of identifying measurement techniques for geophysical and physical properties, as well as determining capabilities and system integration for extreme environment operations that would be state of the art in the following five years.

Group 4: Low temperature electronics & packaging (Lead: M. Mojarradi assisted by E. Kolawa)

This group had the responsibility for determining technology needs and availability for operation of the instruments and sampling devices in the Titan environment. Packaging of electronic devices was also a key consideration.

Each sub-group had monthly telecon meetings, with the findings recorded and disseminated among the leads during their (additional) telecons. Several sub-groups also met face-to-face in the Keck Institute throughout the course of the study. The sub-groups presented their results to all the participants at the second workshop for further discussion. As a result, some of the conclusions of this second workshop were unexpected and had not been previously considered:

1. ***Solution State Nuclear Magnetic Resonance is a perfect instrument for non-destructive identification of organic functional groups because it works better under Titan conditions.***

   Such an NMR would satisfy the design challenge of providing "out of the (thermal) box" analytic instrumentation and actually benefit from the low temperature surface conditions of Titan. The critical design issue is the fabrication of the permanent solenoid magnet.

2. ***A Sample Processing Unit (SPU), composed of a Sample Bus and a Miniaturized Chemical Laboratory (mini chem lab), can be designed for automating sample handling (gas or liquid) between instruments as well as enabling separations and extractions.***

   Even very simple chemical analyses involve complex sample handling. By taking a systems engineering approach to this fundamental issue, we have devised a Sample Processing Unit, comprised of a sample bus interfaced to a miniaturized chemical laboratory, which processes small sample volumes while satisfying mass and power constraints. The SPU is modular and reprogrammable allowing for adaptive sample transfer to/from various instruments, and also functions as a wet chemistry bench, performing functions such as extraction, dilution, labeling reactions, or even chromatographic separations. The incorporation of lasers/optical detectors in this unit also makes the SPU an instrument in its own right, capable of ultra-high sensitivity detection of specific functional groups, including but not limited to amines, carboxylic acids and ketones. Hence, a single integrated reprogrammable SPU could be capable of performing and enabling a suite of chemical analyses to generate a complex picture of the chemistry on the Titan surface.

3. ***Advances in high resolution, high sensitivity Mass Spectrometry have enabled a path for simplifying the overall complexity of a chemical analysis suite by eliminating the need for complicated gas chromatography.***

   Mass spectrometry has long been identified as the key technique for a thorough chemical analysis of complex surface organic species on Titan. However, obtaining the mass resolution and sensitivity required to accomplish this goal within the mass and power constraints of a probe payload has been elusive. However, recent developments in mass spectrometry now place this goal within the realm of possibility. A laboratory-based technique, the Orbitrap mass analyzer, is now routinely used to obtain mass resolution of $\geq 10^5$ and has been shown to be capable of teasing apart Titan organic simulants without the use of a gas chromatograph. This simplifies the instrument and with the flight demonstration of a Paul ion trap, which can be used as an injection system, the path to developing a flight instrument is now clear, although some challenges in obtaining the ultra-high vacuum required for mass spectrometer operation still remain.

4. ***Physical measurements of aerosols in Titan's atmosphere are possible even if they differ from those in common use for Earth atmospheric measurements.***

   Key questions can be answered by two well-established measurement methods; electrical mobility analysis and optical scattering. From these we can learn the size distribution of the aerosol particles, how the clouds are formed, the optical properties of the aerosol and whether the aerosols undergo any physical transformations. A model was developed during the study to explore charge distributions under conditions of the Titan atmosphere, which should be applicable to other planetary atmospheres. Future work is needed to ensure that the measurement sensitivities are possible within the mass constraints and to develop these instruments for use in the Titan environment.

5. ***A single seismometer is closer to being possible for studying the interior and dynamic surface processes of Titan than we had thought.***

   While the concept of using one seismometer to study planetary interiors and dynamic surface processes was recognized amongst all the participants of the second workshop as a potentially "revolutionary" concept, it still must be demonstrated within the seismological community. As a true success of the KISS geophysics study group's efforts and the second workshop, much more focus and attention has been put on this concept -- an action that would not have happened without the hard efforts of everyone involved over the last few months within the KISS framework. Even within the seismological community, this concept is relatively new, but the team felt the research behind this technique should continue with Titan in mind.

6. ***Designing electronics that perform well at 95 K is possible and progress has been made in recent years, but developing low power circuits that meet the demands of many of the in situ instruments at these low temperatures is still a work in progress.***

   To reduce mass and power, all the instruments described above benefit from electronics that can function at ambient Titan temperatures. Circuit building blocks and the corresponding low temperature integrated circuit infrastructure have been designed for application-specific electronics, e.g., for amplification of sensor signals, sample acquisition and drive-and-control of motors. However, for ultra-low power electronics at these temperatures, SiGe-based technology will not yet support the micro-power operation and the signal-to-noise ratio requirements of the instruments. New developments are required for such methodologies.

7. ***Light weight power sources continue to be a major challenge for long-life landed missions to Titan.***

   To support long-life missions to Titan, a fresh look at emerging power technologies is needed. For example, parallel arrays of small size modular radioisotope power sources could produce higher power levels. These small devices may not require large radioisotope sources and could become critical components of smart power systems. At the system level we may also take advantage of power-aware electronics, which use a small power source to run essential functions of the mission and trickle charge an energy storage system with rechargeable energy storage elements to momentarily support applications with higher power demand.

8. ***Possible packaging materials for long-life, low temperature in situ Titan missions are available, but design of substrates and the characterization and testing of novel materials is critical.***

   Ceramics, polymers and metals all have lifetime difficulties at Titan surface temperatures. However, solutions to overcome these difficulties were proposed by the team members, which now need to be developed and tested. In addition, over the past five years significant attention has shifted to vertically oriented carbon nanotube (CNT) arrays (a.k.a., CNT forests, mats, or films) as promising packaging materials that have been demonstrated to produce thermal contact resistances that compare favorably to state-of-the-art materials. The benefits of these CNT materials is that they operate over a large temperature range, are chemically stable, are effective absorbers of mechanical energy, and have low thermal interface resistance and high mechanical compliance. Two groups within the study team started working together to explore the deformation mechanics of CNT arrays fabricated by one of the groups. Continued work in this area has the potential for providing promising packaging materials that could be used for Titan electronics.

To effectively explore and understand the complex environment on Titan, novel techniques must be cultivated to address the physical challenges of these conditions while providing robust, sensitive chemical analysis. We believe the revolutions in NMR spectroscopy, mass spectrometry, aerosol analysis, and instrument system integration enabled by the sample bus and mini chem labs outlined here will establish the analytical arsenal needed to fully investigate the chemistry of Titan. Novel power and electronics will relieve the need for Earth-like conditions within the spacecraft power and electronics housings. Bold use of materials such as carbon nanotubes and other nanostructured materials will enable new capabilities. Continued examination of geophysical techniques to explore Titan's interior without multiple networked stations is crucial given the distance to Titan and the resulting expense per kilogram of launch weight. However, although the novel geophysical techniques are important to explore (and the research should continue), it became apparent from this study that, at this present point in time, developing low mass and power chemical analysis system for novel Titan missions is more valuable. It is through characterization of the chemistry of Titan that we may begin to understand this mysterious moon.

We have found this KISS study, comprised of two workshops inter-spaced with a study period, to be remarkably strategic and productive. With data still pouring in from Cassini and the next Discovery class mission to Titan in the works, the timing for this study was ideal to generate revolutionary technologies for the next generation *in situ* mission.

2. Study goals

Meeting NASA's scientific goals for *in situ* planetary exploration relies on revolutionizing current instrument technologies to achieve high resolution and sensitivity with low mass and power requirements.[1] In this context, Titan (with extremely low surface temperatures ranging from 90 to 94 K[2]) represents a tremendous challenge for mission design and implementation, particularly when the scientific goals involve an analysis of the physical and chemical processes taking place. Detailed chemical analysis requires the acquisition and handling of samples without chemically or physically perturbing them in the process. Current state-of-the-art sample acquisition systems demonstrated on the warmer Martian surface (with average surface temperatures of ~210 K and pressures of ~0.01 bar) require elaborate environmental control systems and have only been utilized on solid samples taken at extremely shallow depths. It is not straightforward to simply re-design sample handling systems – or instrument systems – for exploration of the colder, denser, and more thermally conductive Titan environment because of the extreme penalties incurred in terms of system mass and power (missions to the Saturnian system are highly mass constrained because of the distance travelled and the amount of fuel required). Furthermore, the process of acquiring a complex sample from one of Titan's wide-ranging environments (lakes, dunes, possible cryo-volcanoes, and atmosphere) and transferring it to a warmer spacecraft interior inherently induces physical and chemical alteration of the sample, which has to be accounted for and understood.

Our team, comprised of scientists and engineers possessing expertise in all facets of exploration of extreme environments, believes that the only way to support these future NASA missions to Titan and other cold bodies is by fundamentally changing the technology paradigm of *in situ* exploration. We set out to, and succeeded in, formulating revolutionary technology breakthroughs that would enable the development of sample acquisition systems and relevant instruments capable of *in situ* operation during NASA's missions to extremely cold environments, with Saturn's moon Titan as the exemplar. **The focus of our KISS Study Program was identifying those technologies that have the potential to develop innovative ideas and exploration approaches for future space missions based on our strategy that includes a unique cross-fertilization of key experts from multi-institutional backgrounds: Caltech, JPL, industry, and other academic institutions.** The two workshops, separated by a study period, provided opportunities for junior members of the community to get involved and enabled the promotion of JPL-Caltech-external collaborations.

2.1. Why Titan?

Saturn's largest moon, Titan, has been an enigma at every stage of its exploration. For three decades after the hazy atmosphere was discovered from the ground in the 1940s,[3] debate ensued over whether it was a thin layer of methane or a dense shield of methane and nitrogen. Voyager 1 settled the matter in favor of the latter in 1980,[4] but the details of the thick atmosphere discovered raised an even more intriguing question about the nature of the hidden surface, and the sources of resupply of methane to the atmosphere. The simplest possibility, that an ocean of methane and its major photochemical product ethane might cover the globe, was cast in doubt by Earth-based radar studies[5, 6] then eliminated by Hubble Space Telescope and adaptive optics imaging in the near-infrared from large ground-based telescopes in the 1990s.[7] These data, however, did not reveal the complexity of the surface that Cassini-Huygens would uncover beginning in 2004. A hydrological cycle appears to exist in which methane (in concert with ethane in some processes) plays the role on Titan that water plays on Earth.[8, 9] Channels likely carved by liquid methane and/or ethane, lakes and seas of these materials—some rivaling or exceeding North America's Great Lakes in size[10]—vast equatorial dune fields of complex organics made high in the atmosphere and shaped by wind,[11] and intriguing hints of geologic activity suggest a world with a balance of geologic and atmospheric processes that is the solar system's best analogue to Earth.[12, 13] Deep underneath Titan's dense atmosphere and active, diverse surface is an interior ocean discovered by Cassini and thought to be largely composed of liquid water.[14]

Cassini-Huygens has provided spectacular data and has enabled us to glimpse the mysterious surface of Titan. However the mission will leave us with many questions that require future missions to answer. These include determining the composition of the surface and the geographic distribution of various organic constituents. Key questions remain about the ages of surface features, specifically whether cryovolcanism and tectonism are actively ongoing or are relics of a more active past. Ammonia, circumstantially suggested to be present by a variety of different kinds of Cassini-Huygens data,[15] has yet to be seen. Is methane is out-gassing from the interior or ice crust today? Are the lakes fed primarily by rain or underground methane-ethane aquifers (more properly, "alkanofers") and how often have heavy methane rains come to the equatorial region? We need to learn whether Titan's surface supported vaster seas of methane in the past, and whether complex self-organizing chemical systems have come and gone in the water volcanism, or even exist in exotic form today in the high latitude lakes. The presence of a magnetic field has yet to be established. The chemistry that drives complex ion formation in the upper atmosphere was unforeseen and is poorly understood. A large altitude range in the atmosphere, from 400–900 km above the surface, will remain poorly explored after Cassini. Much remains to be understood about seasonal changes of the atmosphere at all levels, and the long-term escape of constituents to space.

KISS Study Outcome: Target the DUNES as well as the LAKES

Prior to this study, the dunes of Titan's equatorial region were not a major objective for an *in situ* lander. We suggest the potential for high science return from these interesting features that cover 20% of Titan's surface.

Key Questions

- **Composition** – How do the small, 'fluffy' aerosol particles turn into the large, sandy particles that comprise the dunes? Are the interdunes made of different material than the dunes?
- **Surface chemistry** – Is there active chemistry, such as tribochemistry (induced by electrostatic discharge from wind-driven particles) occurring on the surface?
- **Seismology** – Are there booming dunes on Titan? Is there a subsurface ocean?

2.2. New science

Other than Earth, Titan is the only world in our solar system known to have standing liquids and an active "hydrologic cycle" with clouds, rains, lakes and streams (Figure 2-1). However, at the extremely low temperatures in Titan's environment, the working fluids are not water, but methane and ethane.[9] Titan's climate system differs from the Earth's in lacking an ocean and having different working fluids, but has much to offer in terms of learning planetary volatile cycles under

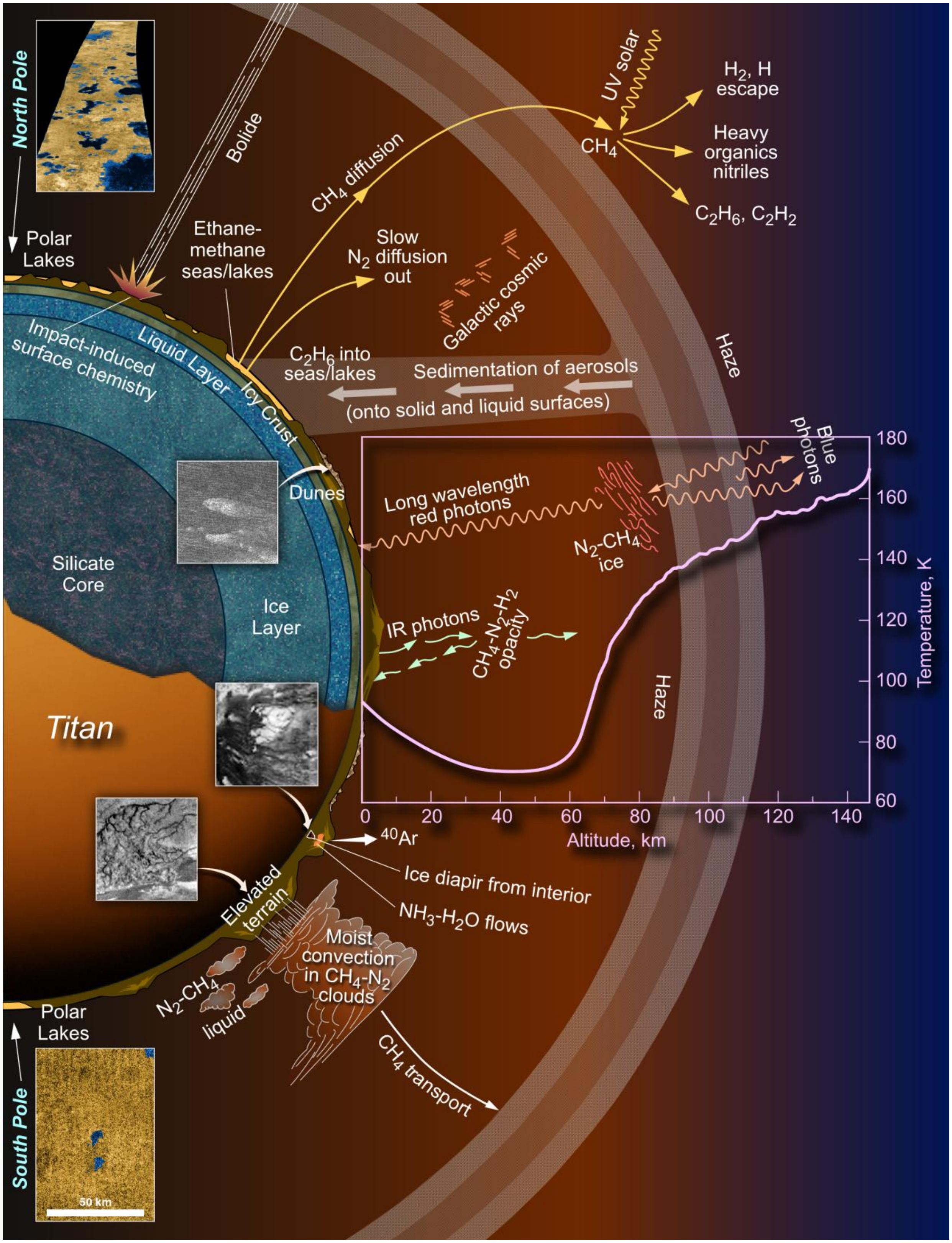


Figure 2-1. Diagram of the subsurface, surface and atmosphere of Titan, demonstrating the relevant chemistry in each region and how all three are interconnected.

different conditions. In addition, the wealth of organic molecules in Titan's atmosphere and on its surface, combined with the occasional presence of liquid water generated by meteoritic impacts and cryovolcanism, means that prebiotic organic chemistry over long timescales and large spatiascales may be occurring.[16-18] The Cassini-Huygens mission has proved to be an enormous success in revealing the complex chemistry and active liquid cycles on the surface and in the atmosphere of Titan. Chemical processing of methane and nitrogen in the upper atmosphere over long time-scales is expressed on the surface in the form of deposits of solid organics organized into dunes, and lighter hydrocarbons such as ethane (in the lakes),[19] acetylene, and other hydrocarbons and nitriles.[20] It is those surface deposits that are of particular interest now because Cassini-Huygens was not designed to provide information on the surface chemistry of Titan, particularly if these organics have been in contact with liquid water. Further, the surface deposits are intimately connected with the interior of Titan and learning more about the geophysical processes occurring on Titan also informs the outcome of chemical compositional studies, since Titan is a prebiotic chemical system with the atmosphere, surface and interior playing integral roles.

KISS Study Outcome: A Miniaturized Sample Processing Unit

The KISS Study Team recognized the need to develop a sample handling platform capable of addressing the unique challenges of the Titan environment.

This resulted in the concept of a **Sample Processing Unit (SPU),** composed of:

- Sample bus
- Miniaturized chemical laboratory (mini chem lab)

The SPU operates as both the fluid transfer center to/from various instruments and the wet chemistry bench (extraction, dilution, separation, LIF detection). The technology is modular, reprogrammable and capable of manipulating small fluid volumes using very low power and mass, making it ideal for *in situ* missions.

2.3. New technology

The dense atmosphere and diverse organic deposits on Titan's surface can be explored with airborne platforms and landed probes, but the key aspect ensuring the success of future investigations is the conceptualization and design of instruments that are small enough to fit on the landed probes and airborne platforms, yet sophisticated enough to conduct the kinds of detailed chemical (including isotopic), physical, and structural analyses needed to investigate the history and cycling of the organic materials. In addition, they must be capable of operating at cryogenic temperatures while maintaining the integrity of the instrument and sample throughout the analytic process. Illuminating accurate chemistries also requires that the instruments and tools are not simultaneously biasing the measurements due to localized temperature increases.

While the requirements for these techniques are well understood, their implementation in an extremely low temperature environment with limited mass, power and volume is challenging. Titan missions during which such systems and instruments could be employed range from Discovery and New Frontiers class *in-situ* probes that might be launched in the next decade, to a Flagship-class mission anticipated to follow the Europa Jupiter System Mission. Capitalizing on recent breakthroughs in cryo-technologies and smart materials fabrication, we developed conceptual designs of sample acquisition systems and instruments capable of *in-situ* operation at low temperature. Novel engineering solutions provided by our study may determine the next type of probe we send to Titan: lake-lander, dune-lander, balloon or other possibilities (Figure 2-2).

During the workshops, new instruments and sampling methodologies were identified to handle the challenges of characterizing everything from small molecules in Titan's upper atmosphere to gross mixtures of high molecular weight complex organics in condensed phases, including atmospheric aerosols and "organic sand" in dunes, to highly dilute components in ices and lakes. To enable these advances in instrumentation, breakthroughs in a wide range of disciplines including electronics, chemical and mechanical engineering, and materials science are critical. Recent research activities of NASA, Caltech, JPL, other key universities, and industry studying extreme environment technologies have demonstrated the feasibility of building materials/sub-components with the capability to operate directly in the wide temperature range environments of future NASA missions. Some recent developments include: miniaturized chemical laboratories involving small volume chemical analysis of Titan-analog samples (Willis e*t al.* [21]); wide range, low-temperature integrated electronics, such as SiGe based circuits; solid-state mechanical properties and microstructures at the nano-scale; and measurements of phase stabilities of candidate species under Titan's environmental constraints. Our team explored the fundamental technological limits, barriers and inadequacies of current mission-qualified instrumentation (e.g., constrained sample handling, limited mass range and resolution of compact mass spectrometers) for making *long life, low power, and lightweight* systems capable of performing demanding analytical tasks while operating under extremely cold temperatures.

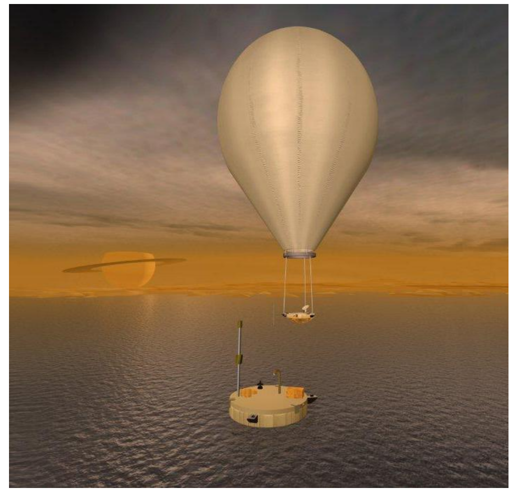


Figure 2-2. Examples of probes to send to Titan; a montgolfière balloon and a lake lander.

2.4. Scope of the study

The study included two workshops, 5 months apart, and consisted of introducing the scientific and technical issues followed by brainstorming and actively discussing a broad range of ideas and solutions to the challenges of sending instruments to Titan. During the intervening period more focused discussions were held, trade studies performed and new concepts developed. The workshops lasted 4-5 days (Monday-Thursday/Friday), included post-docs and students in addition to the core team members, and generated active engagement from the Caltech and JPL team participants, plus experts from the outside institutions. The main topics of discussion were: (1) what type of analysis would be most important to conduct on Titan (i.e. chemical, geological, etc.), what instruments would carry out these analyses (Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS), ambient noise seismometer, etc.), and how such analyses would be integrated into an automated payload; (2) what type of lander would be required (i.e. a balloon vs. a lake lander); (3) what are some of the major issues in terms of electronics and packaging (what devices and materials can still function properly at ~95 K); (4) what would be a feasible source of power (RTGs, low-T batteries, capacitive charging, etc.); and (5) data handling and storage. Presentations on each of these topics including necessary corollary thrusts were made by the study team members with ample time for discussion to ensure a more interactive (rather than conference-like) atmosphere. In the time period between the two workshops, each of the 4 leads guided a group of study participants in their efforts to generate an informed body of knowledge on the 4 particular topics: (1) *in-situ* chemical analysis; (2) sample handling and materials; (3) physical and geophysical measurements; and (4) low-T electronics and packaging.

3. Components of the study

3.1. Study organization and goals

> **KISS Study Outcome: Geo Challenges**
>
> During the study period, we introduced the concept of using a single seismometer to obtain information of Titan's interior, as opposed to a network of sensors.
>
> After further exploration of this concept, it was decided that this revolutionary idea needs an Earth-based proof of concept and might be better suited for use on other planetary objects (i.e., Enceladus).

The study consisted of opening and closing workshops held at the Keck Institute on the 6th floor of the Millikan building, in May (21-25) and November (1-4) 2010, respectively, as well as a series of engaged interactions through 4 focused study groups led by each of the study leads. There were roughly 30 participants in both workshops, with each person carefully chosen to bring a particular expertise relevant to the overall program. Beyond the senior-level scientists (academic, JPL and industrial), several post-docs and graduate students were involved, which proved to be a very successful and enjoyable decision. Notably, the workshops intentionally had discussion/open forum time in the spirit of a "Gordon conference" to facilitate "out of the box" thinking and allow for non-experts to familiarize themselves with each topic. During the first morning of the opening workshop, Jonathan Lunine presented a short course (open to the Caltech and JPL community) to provide a scientific overview on Titan, so that all participants understood the issues and the complexity of the technical challenges. The remainder of the workshop involved a more detailed overview of some of the particularly salient Titan features (the hydrological cycle, the dunes and lakes and their compositions, the unique chemistry, etc.) and the technological challenges that atmospheric and landed missions face. Also during this first workshop we identified the critical thrusts to be explored in the on-going individual study groups. The final workshop was more focused, with the discussions aimed primarily at the information generated through the efforts of the individual study groups with the goal of defining the direction for the Phase II KISS proposal and identifying the revolutionary concepts which could be proposed. Specifically, the four sub-groups with their respective tasks and participants as identified at the first workshop are described below:

Group 1: In situ chemical analysis (Lead: J. Lunine assisted by P. Beauchamp)

This group had the responsibility for determining the most promising measurement techniques, individually and in combination, for organic and (secondarily) inorganic materials, and the state of the art available in the coming 5 years (but not yet space qualified at that time). Special attention was focused on integration of these instruments into a single system capable of automated operation on Titan. It included the following subgroups identified at the workshop: (1) Raman: Hayes, Hodyss, Willis; (2) NMR: Cody, Manohara; (3) GC-MS: J. Beauchamp, Hurst, Smith, Willis; (4) LC-MS: J. Beauchamp, Henion, Hodyss, Smith, Sturhahn, Willis, Cable; and (5) XRF: Hodyss, J. Beauchamp.

Group 2: Sample handling (Lead: J.R. Greer assisted by A. Shapiro)

This group determined how samples would be pre-selected, collected and analyzed. It included the following subgroups identified at the workshop: (1) Solid sample handling: Cody, Hodyss, Holland, Zimmerman; (2) Liquid sample handling: J. Beauchamp, Cody, Hodyss, Holland, Willis, Zimmerman; (3) Aerosol and atmosphere sampling from a balloon: J. Beauchamp, Flagan, Hall; and (4) Materials challenges for extremely cold environments (i.e., ductile-to-brittle transition): Greer, Shapiro.

Group 3: Physical and geophysical measurements (Lead: J. Jackson assisted by C. Sotin)

This group had the responsibility of identifying measurement techniques for geophysical and physical properties by using remote sensors, determining capabilities and system integration for extreme environment operations that would be state of the art in the following five years. Subgroups included: (1) Seismology: Aharonson, Blalock, Chen, Cressler, Jackson, Johnson, Kolawa, Manohara, Shapiro, Sotin, Sturhahn, Tsai, Zhan; (2) Sonar: Manohara, Willis; (3) Electrical conductivity: Manohara, Shapiro; (4) Remote sensors and quickscan: Lorenz; (5) Geosaucer: Reh, Zimmerman.

Group 4: Low temperature electronics and packaging (Lead: M. Mojarradi assisted by E. Kolawa)

This group had the responsibility for determining technology needs and availability for operation of the instruments and sampling devices in the Titan environment. Specifically, (1) Low temperature batteries/power: Brandon, Kolawa, Manohara, Samuele, M. Brown; (2) Low temperature electronics: Blalock, Cable, Cody, Cressler, Johnson; (3) Titan chamber development: P. Beauchamp, Hodyss, Sotin, Willis; (4) Data transfer: Cressler, Mojarradi; and (5) Packaging: Johnson, Shapiro.

Each sub-group had monthly telecon meetings, with the findings recorded and further disseminated among the leads during their (additional) telecons. Several sub-groups met face-to-face in the Keck Institute throughout the course of the study taking advantage of the inspiring location, extremely helpful KISS staff, and the convenience of the presentation/dial-in setup.

3.2. Education and public engagement

The two workshops served as unique vehicles to bring together experts from a variety of fields and academic/professional levels. In particular, the inclusion of postdoctoral fellows and graduate students in these workshops provided a welcome influx of new ideas in addition to expanding the horizons of these young scientists and engineers. There are precious few settings such as this where young scientists and engineers are able to participate as equals with the principal architects of the field. Further, the open nature of this study encouraged all participants to think ‘out of the box’ and challenge current perceptions, forming a comfortable atmosphere that fostered new collaborations (see section 4.6.1).

Figure 3-1. Oded Aharonson answers questions during his public lecture entitled ‘Titan: A Strange Yet Familiar New World’.

The entire study team was highly conscious of the impact of this effort, not just on the planetary science community but on the population as a whole. Thanks to the resounding success of the Cassini-Huygens mission Titan has become a popular topic in the general media, and we saw KISS as the perfect conduit to capture that interest and redirect it towards thoughts of the future discoveries on Titan. The resulting short course given by Jonathan Lunine and public outreach lecture given by Oded Aharonson (short course and lecture videos available for download from the KISS website here: http://kiss.caltech.edu/workshops/titan2010/schedule.html) were well received, as evidenced by the large audiences (~70 attended the short course and ~200 attended the evening public lecture) and excellent questions after each talk (Figure 3-1).

4. Taking Earth-based techniques to Titan: Challenges facing future missions

In addition to the cryogenic temperatures at the surface of Titan, future *in situ* missions will also have to contend with the complexity of samples obtained on this moon that is teeming with organic chemistry. Appropriate sample acquisition/handling and chemical analysis protocols must be devised to optimize science return while addressing the unique challenges of the Titan environment. With the lakes, dunes, atmosphere and putative cryovolcanic flows as potential sampling targets, the study team generated an instrument suite with multiple capabilities. It was also recognized that some techniques benefit from the Titan environment and can be used *in situ* (i.e., NMR spectroscopy is better at lower temperature), while others are necessary to provide insight into the chemical nature of the complex organic samples (i.e., wet chemistry, mass spectrometry). The mass and power constraints for a landed mission were also factors for consideration, and led the study team to focus on technologies capable of miniaturization or requiring small sample aliquots with maximum science return.

As we anticipate solid, liquid and aerosol samples, the instrument platform will involve multiphase sample analysis (Figure 4-1). Liquid samples, which could be a lake aliquot or icy regolith/ cryovolcanic meltwater, will first be analyzed using NMR spectroscopy (as this is non-destructive) prior to chemical interrogation with miniaturized chemical laboratories and finally obliteration with a mass spectrometer. Aerosol samples will be analyzed at ambient Titan conditions using electrical mobility analysis and optical scattering (see section 4.3) prior to condensation and introduction into the sample processing unit (SPU). Solid samples from a Titan dune or lake sediment layer will undergo melting, extraction or solubilization into a liquid mobile phase before analysis. Gas and/or vapor samples will be analyzed directly by mass spectrometry.

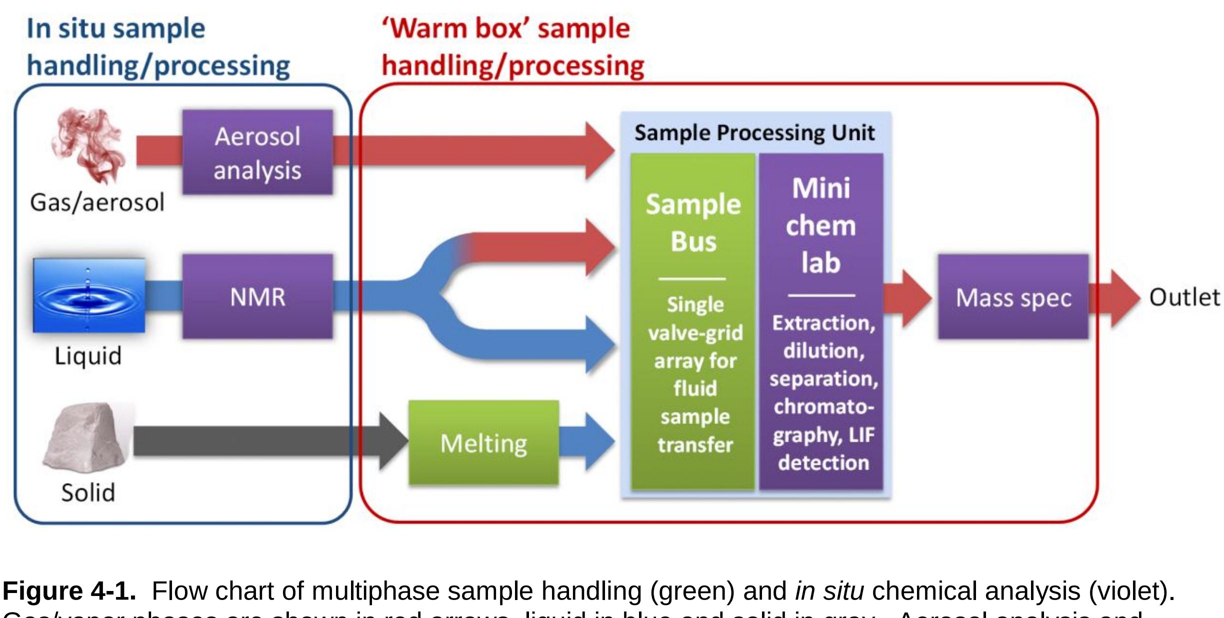


Figure 4-1. Flow chart of multiphase sample handling (green) and *in situ* chemical analysis (violet). Gas/vapor phases are shown in red arrows, liquid in blue and solid in gray. Aerosol analysis and solution state NMR can both be performed in the ambient Titan environment prior to entry into the lander 'warm box'. Sample transfer between downstream instruments (mini chem lab and mass spec) will be performed using an automated reprogrammable valve array (sample bus), which handles both gas and liquid phases so volatiles from vaporized liquid samples (forked arrow) are also captured. Abbreviations: nuclear magnetic resonance spectroscopy (NMR), laser-induced fluorescence (LIF).

Even performing very simple chemical analyses involves complex sample handling inside a probe's instrument systems, requiring at least many tens of valves. By taking a systems engineering approach to this fundamental issue, we have devised a Sample Processing Unit (SPU), comprised of a sample bus interfaced to a miniaturized chemical laboratory, which can tie together the different instruments we have identified as essential for the future exploration of Titan. This automated system is modular and can be reprogrammed if the analytical approach, sample flow, or even the instruments themselves are altered or removed from the analysis. Additionally, by designing this instrument system interface monolithically (i.e., from a single valve-grid reprogrammable array), the mass and power constraints so critical to exploration of Titan are satisfied. This "universal" interface is ideally suited for handling the very small sample volumes associated with laser-induced fluorescence (LIF) and mass spectrometry analyses, and is additionally capable of performing wet chemistry modifications to the samples, such as extraction, solvent exchange, dilution, labeling with molecular tags, or even chromatographic separations. By incorporation of power supplies and lasers/optical detectors in this analytical system prior to delivery to the other subsystems, the Sample Processing Unit can become an instrument system in its own right, capable of ultra-high sensitivity detection of specific functional groups (amines, carboxylic acids, ketones, etc.). Hence, a single integrated SPU could be capable of performing and enabling a suite of chemical analyses to generate a complex picture of the chemistry on the Titan surface.

4.1. Sample acquisition and handling

Getting a sample from the Titan surface (at ambient conditions) and into an *in situ* lander instrument suite for analysis is one of the key challenges addressed in this study. Section 2 of this report provided the foundation for understanding sampling requirements. A subset of the critical science requirements which have fed into our sampling and sample delivery approaches are as follows:

i. Characterize the chemistry/composition and physical structure of lakes/lake shore

- Determine stratification/structure of benthic environment (liquid sampling);
- Record the temperature profile, major component compositions vs. depth, turbidity, refractivity, lake shore composition, particle size, currents and any lake shore erosion (liquid/solids filtration and sampling);
- Determine the mass flux from lake to atmosphere, or vice-versa (aerosol sampling);
- Search for chiral compounds, ordered chemistry, remnants of pre-biotic markers (liquid/solid sampling);

ii. Characterize the chemistry/composition of the surface near lakes or in the dunes

- Characterize composition and physical properties of surface (layering, hardness, adhesion properties obtained during solids sample acquisition);
- Develop an organic/inorganic inventory (liquid/solid sampling);
- Analyze material properties--crystal structure, porosity, permeability, strength, embedded liquids, clathrate (solid sampling);

To meet the above science requirements, the KISS team examined potential ways to obtain solid, liquid and aerosol samples.

Sample acquisition/handling process

Sample acquisition during descent through the atmosphere and at the surface boundary layer will require periodic injection of Titan atmosphere into a column or chamber which allows analysis of temperature, pressure, density, suspended particulates, and, finally, chemical composition. Both solid and liquid sampling of surface material (e.g., dunes) or lakes will require forced injection of material into a column by either impact (i.e., the lander impact with the surface or a penetrator) or differential pressure (i.e., reducing the pressure in the column similar to sucking on a straw and using ambient pressure to force liquid up the column). The solid/liquid sample would then be parsed to the analysis instrument suite of NMR spectroscopy, wet chemistry (miniaturized chemical laboratories), and mass spectrometer using cryogenic valves and the sample processing unit. The primary stages of sample acquisition/transfer and analysis are:

1. Sample acquisition-
   - For aerosols- lowering of pressure in the column to cause gas/vapor to move into the interrogation chamber(s);
   - For solids/liquids- either lowering the pressure inside the sample column or actively forcing the sample into the column (i.e., penetration of the surface);
2. Sample handling- changing pressure or temperature to either move gas/vapor through the interrogation zone, or changing the phase/state of a sample to allow it to move into the sample processing unit (e.g., melting a solid sample and pumping the liquid into an interrogation zone);
3. Sample preparation using the **sample processing unit (SPU)** – separation of particulates, extraction of solids, solvent exchange, chemically tag elements of the sample (e.g., UV markers), addition of reagents, change physical state (e.g., move sample from liquid state to vapor state);
4. Chemical analysis instrument suite derived from this study:
   - NMR spectroscopy;
   - Wet chemistry (miniaturized chemical laboratories);
   - High resolution, high sensitivity mass spectrometry;
5. Sample transfer to next triage instrument using the sample processing unit;
6. Sample disposal;
7. Purge/clean system to prevent cross contamination (e.g., flush/clean via dilution).

Sample acquisition and transfer of solids/liquids

The capability to acquire atmospheric samples has been demonstrated (Huygens Titan probe) and will not be discussed here. The ability to acquire solid and liquid samples under Titan surface environmental conditions has not been demonstrated. Laboratory research on both passive- drop and pyro-activated penetrators (J. Jones, W. Zimmerman, 2004) have demonstrated that 1-10 cc ice samples can be obtained from ice cooled to 90 K. Figure 4-2 shows the design concept developed for the pyro-activated penetrator.

For the purposes of this KISS study, we assume that the lander instrument delivery platform will be stationary (either sitting on the dunes or in a lake). A reasonable solid sample acquisition approach for sampling dune material would be to use the lander impact momentum to force solid material up into a deployed hollow column. The column would then be retracted, rotated over a seal, and then heated to allow the sample core to be melted and pumped to the instrument suite. Similarly, once the lander is on the surface, a pyro-activated penetrator could be deployed off a pivot arm and, again, rotated over a seal to allow the material to be melted and retrieved. In the above scenarios and as suggested by Figure 4-2, maximum sampling depth would be limited to 10-15 cm with cores not exceeding 1 cm in diameter.

In the liquid sampling case, the sampling column would be lowered in the lake off the floating platform to move sample into the column and then pumped to the instrument suite. Cryo-pumping technology already exists for moving small sample volumes over distances of 10's of cm. Piezoelectric actuated micro-peristaltic pumps have been built and tested at JPL.[22] Piezo actuation is particularly attractive for extreme cold environments because piezo crystal materials retain their strain properties over a very large temperature range. Low temperature piezo materials like lead magnesium niobate/lead titanate (PMN-PT) and lead scandium niobate/lead titanate (PSN-PT) crystals have demonstrated excellent strain properties down to 77 K.[23] The actuator footprint is approximately 10 mm x 10 mm and while the voltage requirement is high (~150 V), current requirements are very low which allows actuation in the range of <10 W. By setting up a frequency in the crystal, the periodic crystal distortion provides the driving force for a solid state actuator. The piezo flexure sets up a traveling wave between a stator surface and the piezoelectric ceramic. This traveling wave causes a pressure front to form which compresses either atmospheric gas or liquid and essentially pushes the fluid along the sample column.

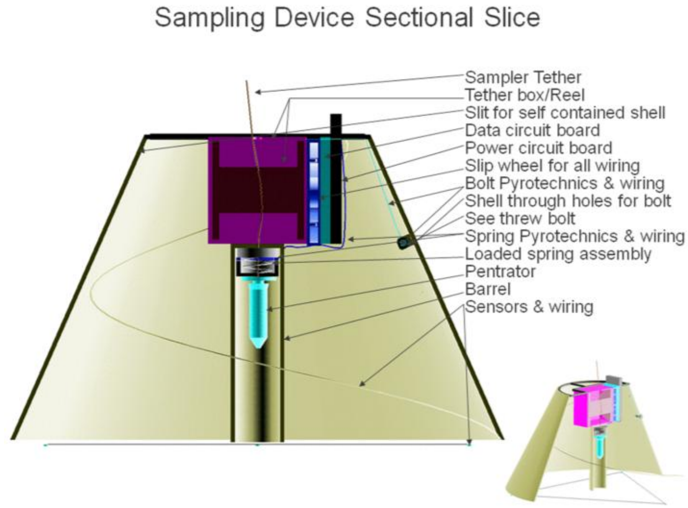


Figure 4-2. Pyro-activated penetrator capable of dune sampling on Titan.

While piezo actuators/pumps and piezo micro-valves have been demonstrated and PMN-PT type materials show promise for operation at cryogenic temp-eratures, this technology has not been rigorously tested for flight environments like Titan. Considerable characterization/life testing are required of the materials, followed by actual laboratory demonstration of a sample transfer system under Titan-like environmental conditions.

A cryogenic liquid sampling system for Titan's lakes which exploits the large barometric head provided by Titan's atmosphere can be developed using Thorleaf Research's design concept, with an example configuration shown in Figure 4-3. This would pump cryogenic liquid samples from the lake up to the surface through a small diameter tube, where it then passes through the sampling valve. This would allow the sample to first pass through the miniaturized permanent magnet proton NMR for non-destructive analysis, then through the Sample Processing Unit which would allow a small portion of the sample to be injected into the miniaturized chemical laboratory and

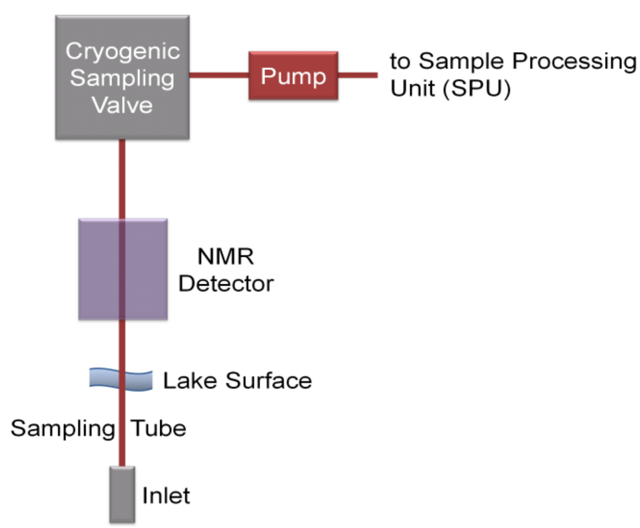


Figure 4-3. Example of a cryogenic liquid sampling system for Titan lakes.

subsequently the mass spectrometer, while a much larger volume of the sample could be collected at the outlet of the sampling pump for other processing and/or discard. Since the sampling path is thoroughly flushed with cryogenic liquid sample, this helps avoid cross-contamination between successive samples.

This concept potentially allows cryogenic liquid sample collection to be made at a wide range of different depths in Titan's lakes in order to investigate variations in chemical composition related to mixing or stratification. By providing capability for sample injection and the collection of larger cryogenic sample volumes, a variety of sample post-processing and analysis schemes can be accomodated.

Use of a monolithic valve-grid array for automated sample handling

Following NMR analysis at ambient Titan temperatures, samples will then be transferred to the Sample Processing Unit (SPU) for chemical modification/interrogation (mini chem labs) and distribution to the high resolution mass spectrometer. For automated sample handling, the SPU will contain a Sample Bus to relay sample rapidly and without introducing contamination. Efficient handling of both gas and liquid phases makes the SPU versatile and capable of addressing samples from the complex Titan environment, including lake samples that may be volatilized upon entry into the 'warm box'. Tubes and capillaries, such as those in the cryogenic sampling system discussed previously (see section 4.1), are extremely facile to connect to a fluidic sample routing device. Microfabricated monolithic membrane valves formed in three-layer glass/PDMS hybrid microdevices enable rapid (100 nL/s) fluidic routing with low dead volumes (< 20 nL) using minimal power.[24, 25] Further, 'bus valves' (in analogy to an electronic bus), which continuously allow fluidic connection and regulate connections between the bus channel and input/output channels, offer an effective means of flushing the channel to prevent contamination.[26, 27]

Key scientific and technical points for concern

Sample Filtration - Small solid or sticky particles may be present in the lake's liquid and could interfere with the liquid flow, potentially impacting the NMR spectrometer operation and performance, and the cryo-pump and valve operations. Therefore, filtration of the sample must take place prior to transfer into the sampling tube and the instruments. To our knowledge, separation of the solid particles from the liquid stream has not been studied or tested at Titan temperatures.

Monitoring/Preservation of Sample's Properties - Accurate quantitative analysis of the sample is one of the scientific objectives in Titan surface studies (both solid as well as lake samples). Therefore, NMR analysis of the lake samples will be performed at ambient Titan conditions (94 K and 1.5 bar) to preserve the intrinsic physical properties of the samples. Pressure, temperature, viscosity, and flow velocity sensors coupled with a closed loop environmental control system must be developed along with the sample acquisition components/materials (sampling tube, pumps, valves, actuators for sample transfer, filters, etc.) to demonstrate the capability to preserve the sample's original physical state.

Roadmap for technical development

The following steps are critical to developing both the component and system technologies needed for the sample acquisition and delivery system:

- Develop a complete model of fluid behavior of Titan-like liquids under Titan environmental conditions, e.g., viscosity changes as a function of small pressure/temperature changes, particle suspensions in fluid flow and to what degree different filter grids affect fluid flow.

- Develop Titan liquid organic analogs and test how the analogs change as a function of changes in environmental control variables. The intent here is to understand how sensitive samples are to small environmental changes during sample transfer and to investigate whether it is feasible to predict those changes and, therefore, derive the original sample properties.
- Determine the appropriate solvent treatments necessary to effectively solubilize and study the chemical and physical properties of Titan organic analogs.
- Set up and test component technologies/materials (valves, actuators, housings, solid state peristaltic pumps, sensors, filters, control system electronics, etc.) under expected Titan environmental conditions.
- Prototype both solid/liquid sample acquisition and delivery systems to demonstrate end-to-end sample transfer integrity under Titan-like environmental conditions.
- Validate the integration of the valve-grid sample bus with mini chem labs for both gas and liquid samples.
- Integrate/test the sample acquisition and delivery system with laboratory (i.e., non-flight) quality instruments.

4.2. In situ chemical analysis

We investigated many *in situ* chemical analysis techniques (Table 4-1), and selected the following for application on Titan: (1) NMR spectroscopy, (2) miniaturized chemical laboratories and (3) high resolution, high sensitivity mass spectrometry.

Table 4-1. Experimental techniques chosen for Titan *in situ* chemical analysis

Technique	Included?	Advantages/Disadvantages for Use on Titan
NMR spectroscopy	Yes	Non-destructive; excellent for identifying various functional groups; better at lower T (Boltzmann factor, enhanced polarization); tiny data sets; capable of miniaturization
Miniaturized chemical laboratories	Yes	Required due to complexity of sample; low mass/power/volume; capable of separating and identifying aromatics and many functional groups. Facilitates sample preparation and manipulation.
Mass spectrometry	Yes	Required due to complexity of sample; provides empirical formulae of all components (including unlabeled and nonfluorescent species); Orbitrap can be miniaturized
X-ray fluorescence spectroscopy	No	Can only determine the elemental composition for light elements; can detect metals, but limit of detection on Titan is an issue
Raman spectroscopy	No	Can only find oxygen-containing species if they are > 1%; limited characterization of tholins; sensitivity is a problem

We will address each analysis technique selected and why this technology is ideally suited for use on Titan, paying particular attention to revolutionary designs on the horizon.

4.2.1. Solution state NMR spectroscopy

Liquid state NMR can aid in unraveling Titan's chemistry, because it can determine the functional groups of major constituents. This, in turn, informs the scientist whether this sample warrants further investigation. Due to its non-destructive capabilities for chemical analysis, its potential low power and mass and small data sets, the KISS team decided to use this technique to triage the samples in a landing instrument suite for a Titan lake or when other liquid sample are available. In addition, the recent advancements of light-weight permanent magnets and the modern designs of solution state Nuclear Magnetic Resonance (NMR) spectrometry have made this technology feasible for flight.

Benefits of Solution State NMR

- Non-destructive to sample
- Low power and mass
- Superior performance at ambient Titan temperatures (enhanced polarization), so can operate outside of 'warm box'
- Very small data sets (512 K)
- No moving parts
- Can detect functional groups of major constituents (down to ~1%)

Introduction

One of the striking aspects of Titan is the existence of ephemeral lakes and seas (mares) demonstrating an active "hydrologic" cycle. Given the low surface temperatures and likely atmospheric chemistry, thermodynamic calculations suggest that the mare are composed of a mixture of hydrocarbons,[28] although the precise composition is not known. It is possible that the mare are chemically stratified through a combination of evaporative and recharge processes. Analyzing Titan mare composition is clearly a major objective of any surface analysis mission. It is recognized that integral to any subsequent analyses, a Titan mare liquid sampler will be required.

As an outcome of the KISS Titan workshop a number of participants initiated a sub-study to investigate the feasibility of integrating a low power solution state NMR for the analysis of Titan mare liquids at the point of extraction, under ambient Titan surface temperature. This "out of the (thermal) box" instrument would actually benefit from the low temperature surface conditions of Titan. As a point of explanation, NMR is a radiofrequency spectroscopy that utilizes a fixed external magnetic field to align nuclei with the property of spin, e.g. ^{1}H and ^{13}C, such that they may resonantly absorb radiation (in the radiofrequency range) and once promoted to an excited state such nuclei emit an RF signal with a frequency that records the local electronic environment associated with a given nuclei yielding a spectrum. This study focused on (1) whether a low field NMR based on a design employing rare earth permanent magnets would be able to provide sufficient spectral resolution to characterize the major constituents of Titan Lake fluids, and (2) what the design characteristics would be to achieve the spectral resolution required.

Arguments for using solution state NMR for the bulk chemical analysis of Titan mare

- An "out of the (thermal) box" solution state NMR would provide a low mass, low power instrument capable of performing multiple analyses of Titan mare liquid composition. The data size of NMR spectra are low relative to other methods of organic analysis.
- A solution state NMR has no moving parts and can easily be integrated into a liquid sampling system that would be required for any other analytical instrumentation (e.g. gas-chromatograph mass-spectrometers).
- The ambient cooling of electronics including amplifier(s), RF coil, and pre-amplifier can *improve* performance through reduction of thermal electrical noise.

Potential solution state NMR designs

Analytical Requirements

In order to assess the analytical requirements for a solution state Titan NMR we started with a thermodynamic analysis by Corider *et al.*[28] who estimates that ethane is the predominant species, followed by subsidiary quantities of methane, propane, butane, butene, and acetylene (Figure 4-4). The critical design specification of any NMR, therefore, must be the ability to detect and quantify the abundance of each of these species.

Design specifications

The critical design issue for the proposed NMR is the permanent solenoid magnet. Currently, the highest fields possible with rare earth magnets are on the order of 1.4 T. Ideally, a doubly tuned RF system capable of exciting both ^1H and ^{13}C (with ^1H decoupling) is preferred. Integration into the fluid handling aspects of the system (i.e., minimum diameter of the sampling straw) places a constraint on the minimum internal diameter of the magnet-RF coil assembly. Low power transmitter RF amplifiers, filters, and preamplifier constitute the main electronic components of the NMR. If analysis of polymeric species is desired, additionally a Z-gradient coil and a DC pulsed Z-gradient amplifier will be necessary in order to perform Pulsed Gradient Spin Echo spectroscopy to obtain diffusion ordered spectroscopy (DOSY).

Key scientific and technical points for concern

In principal there exist no physical issues confronting the fabrication of a Titan lander solution state NMR. Most of the necessary electronics have been fabricated previously in various concept studies of miniature NMR for space missions. The critical technical point for concern is establishing a highly *homogenous* magnetic field in the RF coil region. Standard field homogeneity for solution NMR as routinely performed in chemistry laboratories is on the order of 1 part in 10^9. Simulations performed as part of this study reveal that establishing a field homogeneity of 1 part in 10^7 would be sufficient to resolve the resonance bands of the major Titan Mare hydrocarbon species. It is noted that such field homogeneity has not yet been achieved with rare-earth-based miniature NMR magnets, but is considered possible.

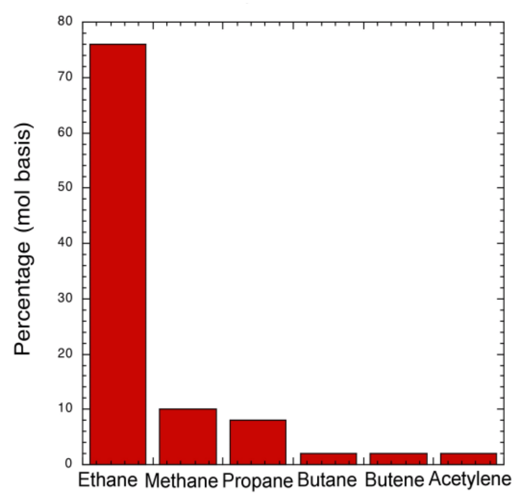


Figure 4-4. Composition of Titan lakes. Reproduced from Cordier *et al.* 2009.[24]

Roadmap for technical development

- Numerical modeling of field homogeneity for various magnet designs implementing shimming to achieve minimum field homogeneity requirements, and minimum solenoid diameter including RF coil and sample tube.
- Fabrication of permenant rare earth solenoid magnet, RF coil, sampling tube for testing first at ambient conditions.
- Design and fabrication of integrated Titan mare sampling system including pumps, sample loops, and sampling straw.
- Testing of Titan Mare NMR under cryo-conditions with liquefied hydrocarbons.
- Integrating Titan Mare NMR and Titan mare sampler under cryogenic conditions.

4.2.2. Miniaturized chemical laboratories

Introduction

Benefits of Mini Chem Labs

- Low power and mass constraints
- Liquid separations performed using electro-osmotic flow (no high pressure)
- Functions as a wet chemistry bench (dilutions, mixing, labeling reactions, etc.)
- Very small sample size (nL to µL)

One of the major themes of this workshop was to identify and develop key revolutionary technologies capable of high science return while meeting the unique challenges of the Titan environment. The primary goal is to understand the *chemistry* going on at the surface (lakes, dunes, cryovolcanic flows, etc.), and consequently the KISS team focused on generating a complete chemical analysis platform including target analytes and instrumentation. One technology that offers high sensitivity with low power and mass constraints involves is that of micro-total-analysis systems (µTAS), or 'lab on a chip'. These devices require very small sample volumes and are able to perform wet chemistry *in situ*, such as dilutions, labeling reactions and chromatographic separations. In this sense, these devices serve as **miniaturized chemical laboratories (mini chem labs)**. They can also be coupled to various detection techniques both on and off the chip, ranging from laser-induced fluorescence to mass spectrometry. A future mini chem lab device, or multiple devices, could be capable of performing a suite of chemical analyses to generate a complete picture of the chemistry on the Titan surface. Further, as these devices can move small volumes of sample efficiently and with low power, microfluidic technology also represents an effective means of **sample transfer** between instruments, as described in section 4.1.

Mini chem labs are ideally suited to a future Titan mission as they are based on liquid chromatography. Thermal decomposition and possible reaction between tholins – Titan aerosol analogues – during heating makes pyrolysis and other gas chromatography-based techniques not ideal for separating and characterizing such samples.[29] Liquid-based separations, in contrast, are less destructive and can provide a more comprehensive analysis of the sample with judicial choice of solvent. Further dimensions such as introducing concentration gradients or performing multiple extractions also enhance the capability of this technique.

Understanding Titan chemistry with miniaturized chemical laboratories

We are exploring use of mini chem labs in an effort to produce a fully automated device that can identify key functional groups present in a Titan sample. Knowledge of the type and distribution of compounds on the surface can provide a basis for understanding how particular regions evolved, or if they are still evolving. For instance, the presence of oxygen-containing species such as aldehydes, ketones and carboxylic acids in organic material on the surface (if absent in aerosols) would indicate reaction of precipitated material with the water-ice regolith, in effect a 'smoking gun' for active chemistry on the surface. Surface science may also help us understand the methane cycle on Titan by providing clues to the source of methane replenishment in the atmosphere.[9]

Protocols have been developed to detect a variety of functional groups using µTAS devices, with limits of detection in the picomolar to nanomolar range for most targets.[30-32] These compounds can either be detected directly using laser-induced fluorescence (polycyclic aromatic hydrocarbons, PAHs) or via labeling with a fluorescent dye (amino acids, primary amines, aldehydes, ketones and carboxylic acids). The revolutionary step will be to achieve this sensitivity on a fully automated system capable of operating on the Titan surface.

Key scientific and technical points for concern

We have demonstrated at JPL the ability to perform sequential dilutions and labeling reactions in a microfluidic device, in addition to analyzing multiple liquid samples on the same device (manuscript in preparation). Currently, these mini chem labs are only operational at or near room temperature due to the physical capabilities of the materials that comprise the pumps and valves, and because many labeling reactions are not thermodynamically viable at low temperature. Further, the appropriate solvents (determined from the sample handling/preparation roadmap specified in section 4.1) must be tested and optimized to generate a stable nano-electrospray for coupling of the mini chem lab to a high resolution mass spectrometer.

Roadmap for technical development

If we assume that these lab-on-a-chip devices will be operating inside a 'warm box' of the lander, the technology simply needs to be validated using Titan-like samples. Preliminary work using tholins, complex organic compounds produced in a simulated Titan atmosphere, indicates that separation using capillary electrophoresis (CE) is possible in certain solvents (see Figure 4-6). Further work will involve detection on a µTAS device with the various labeling protocols, and coupling the min chem lab to a mass spectrometer using nanospray ionization for analysis of unlabeled species. As a result of this KISS study, we are currently working with Mark Smith and Hiroshi Imanaka at the University of Arizona to optimize our detection techniques using a poly-HCN compound as a 'tholin standard,' as individual tholin samples can vary significantly in their properties. We will then perform separation and characterization studies of tholin samples.

We will also investigate adapting our devices using Fluorocur and Teflon polymers to perform non-aqueous CE, as many tholins are not soluble in water. By judicial choice of solvent, we could also operate the device at temperatures approaching that of the Titan surface (~90 K), thereby minimizing sample perturbation and maximizing retention of volatiles. This idea in particular was a direct result of 'out of the box' discussions from the two workshops of this study, and may very well lead to a microfluidic device capable of performing tholin separation and characterization at ambient Titan surface conditions.

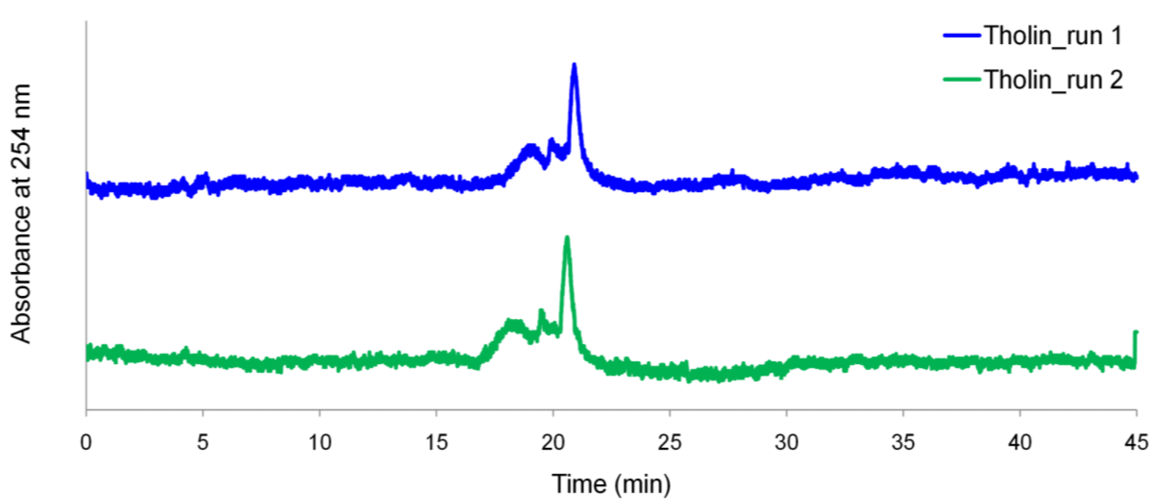


Figure 4-6. Capillary electrophoresis chromatograms of 4.25 mM tholin in DMSO, 20°C. Tholin samples donated from M. Smith *et al.* for analysis as part of this KISS study.

4.2.3. High resolution mass spectrometry

Many studies have shown that Titan sample analysis requires a high resolution, high sensitivity mass spectrometer. After examining all techniques it became clear to the KISS study team that a future flight-qualified Paul-trap Orbitrap MS system would be ideal for analysis of the complex organics present on Titan. Using a high resolution mass spectrometer minimizes or eliminates the need for sample pre-processing steps such as functionalization; even direct analysis of complex mixtures is routine in terrestrial labs.

Benefits of Orbitrap Mass Spectrometry

- Versatile (empirical formulas for all compounds that carry a charge)
- High resolution ($\geq 10^5$), high sensitivity
- Low mass (no RF or magnets)
- Little or no pre-processing necessary

Introduction

The complex mixture of organic matter occurring on Titan, and often simulated in the laboratory by plasmas or photochemically (tholins), demands a technology capable of positively identifying the different classes of molecules produced using accurate mass determination. The KISS study team examined the Orbitrap mass spectrometer as a means of obtaining this high resolution, high sensitivity data and concluded this was capable of being developed for flight. While in rotational motion about the z-axis, the axial frequency oscillations of ions in the Orbitrap are monitored by the outer split-electrode. Since the frequency of oscillation is directly proportional to the mass-to-charge ratio of the ion, a high resolution mass spectrum is obtained.[33] One of the major results of this KISS study was that with the advent of high resolution, high sensitivity mass spectrometers such as the Orbitrap, a GC column is unnecessary, which substantially reduces the complexity of the instrumentation.

A future flight qualified system is not out of reach in light of the previous delivery of flight ion trap instruments by JPL. A Paul-trap-Orbitrap system is conceptually sound and would provide the high resolution and accurate mass determination capabilities that are required for analysis of complex organic mixtures on Titan. Construction of such a system is not without challenges. Chief among these is immaturity of high vacuum technology for operation on the surface of Titan. A future effort would draw upon vacuum technology advancement currently underway on the Sample Analysis on Mars (SAM) instrument on the Mars Science Laboratory (MSL) and other missions.

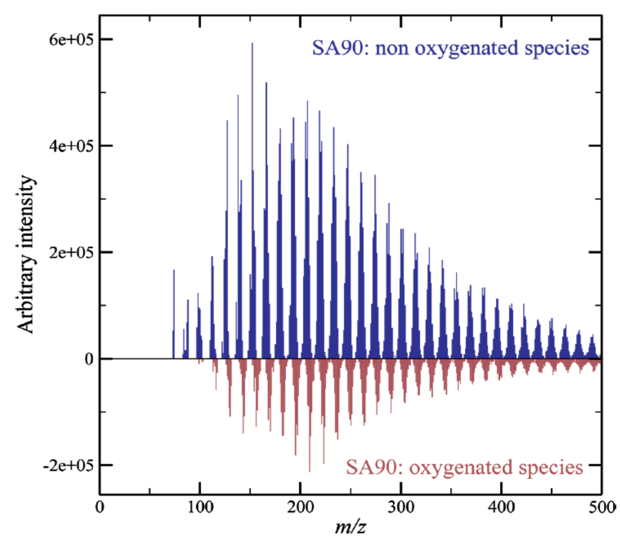


Figure 4-7. Plot showing capability of Orbitrap MS for analysis of tholins, with separation of oxygenated and non-oxygenated species differentiated and no sample pre-processing. Figure from Pernot *et al.* 2010.[34]

Analysis of tholins using an Orbitrap-MS

Analysis of complex organics found in the Titan tholins by mass spectrometry presents several unique challenges not encountered when studying simpler chemical systems. Mass spectrometers of modest resolution are incapable of providing meaningful analysis of a mixture without sample pre-processing, such as gas chromatography. However, in modern laboratories, high resolution mass spectrometry analysis, mostly Orbitrap or FT-ICR based, of tholins, have allowed us to unravel the complex chemicals found in tholins. Using an Orbitrap[33] which has a mass resolving power >100,000 allows for the separation of classes of compounds within complex mixtures. The utility of a high resolution instrument for tholin analysis, and specifically an Orbitrap-based instrument,[34] is widely accepted and the Orbitrap has been identified as the 'right tool for the job' when analyzing tholin mixtures (Figure 4-7).

Key scientific and technical points for concern

As compared to other high resolution mass spectrometers when considered for space flight applications, the Orbitrap has a number of advantages. Chief among these is no requirement for radio frequency electronics and no magnet, greatly reducing mass and power requirements. The Orbitrap is DC-field based, and does require fast high-voltage switching for operation. Packetized injection of ions into the Orbitrap for analysis is a critical requirement, and a method which is feasible for this is using a 3D ion trap (Paul trap) for ion injection into the Orbitrap.

Despite the advantages and strong capabilities for implementation of such a system, some open engineering challenges remain. Chief among these is the requirement for ultrahigh vacuum (UHV) inside the orbitrap. The orbitrap analyzer must be maintained at a pressure of less than 10^{-10} mbar for adequate ion lifetime, and in terrestrial laboratories this is achieved using some form of differential turbomolecular pumping. High vacuum pumping technology would mature along with mass analyzer development for a Paul trap orbitrap-MS system, and several candidate pumping technologies currently exist (flight-qualified turbomolecular pumps as used on the SAM instrument for MSL, sputter-ion pumps, and cryogenic pumps) which could also be implemented.

Roadmap for technical development

Fast injection of ion packets into a time-of-flight (TOF) instrument was demonstrated previously.[35] A Paul-trap based injection system for the orbitrap would prove advantageous since JPL has already developed and delivered a flight-rated Paul-trap instrument in the form of the Vehicle Cabin Air Monitor (VCAM). Having essentially half the mass analyzer complete in build-to-print form, as well as the maturity of the driving electronics,[36] provides a strong starting point for a future effort to construct and implement a Paul-trap orbitrap instrument system for use on Titan. Figure 4-8 is a conceptual cartoon of such an instrument, which has sound operating principles.

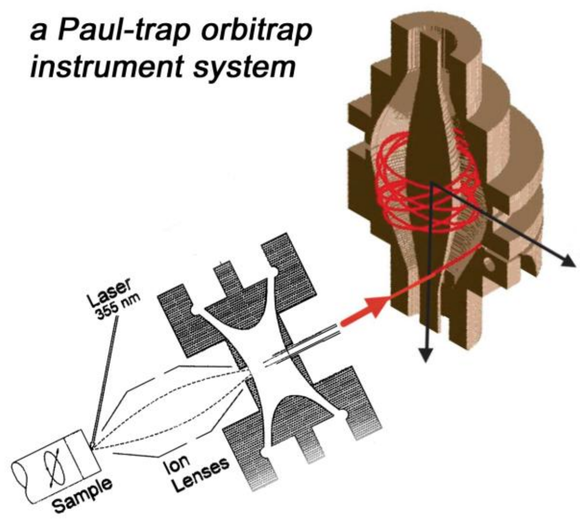


Figure 4-8. Concept for a Paul-trap Orbitrap system, where fast injection of ion packets into the Orbitrap is achieved using a Paul-trap instrument as a 'front end' to the Orbitrap mass analyzer. Image from Hu *et al.* 2005.[29]

4.3. Physical measurements: Aerosols

The atmospheric chemistry of Titan is complex. Cassini-Huygens will capture the low and high altitude atmospheric data, but there will be no measurements available at altitudes from 400-900 km which has often been termed the 'ignorosphere'. In addition, the aerosol collector on Huygens did not work so there is a dearth of information on the aerosols, which play a critical role in the chemistry and physics of both the atmosphere and the surface. In contrast to Earth, Titan's atmosphere has not one but many vapors, which can lead to many types of clouds and complex phase behavior. At the heart of Titan's atmospheric investigation is the reason why Titan is so difficult to study from orbit: the aerosols.

Aerosol Analysis: Key Questions

- What is the size distribution of the aerosol particles?
- How are the clouds formed?
- Do the aerosols undergo any physical transformations?
- What are the aerosol particle optical properties?

By understanding the physical properties of the aerosols, we will better understand the microphysics and dynamics of the atmosphere, and generate a more accurate model of this complex system. Two techniques were selected to probe the physical properties of the Titan aerosols based on the scientific requirements and the constraints placed on the techniques by the atmospheric conditions at Titan: electrical mobility analysis and optical scattering (Table 4-2).

Introduction

The measurement of aerosols in the Titan atmosphere has, to date, been limited to remote sensing of the haze and clouds. The KISS study team identified approaches for *in situ* characterization of the particles that builds upon experience in probing aerosols in the atmosphere of Earth, but recognizing the constraints of a Titan mission. The ability of aerosol particles to serve as cloud condensation nuclei (CCN) is determined by their size and chemical composition, so the measurement strategy focuses on probing these properties of the aerosol. Such measurements of aerosols in Earth's atmosphere have enabled quantitative modeling of aerosol and cloud evolution. The extreme conditions of Titan's atmosphere and the severe constraints of a Titan mission will, however, require different approaches to making similar measurements. Promising strategies were identified during the course of the study, and while different from those in common use in Earth atmospheric measurements, they build upon well-established measurement methods.

Electrical mobility analysis

Differential mobility analysis[37, 38] is the mainstay of measurements of submicron particles within the atmosphere of Earth, but was considered to be impractical for a Titan mission, as several flows must be precisely controlled and small numbers of transmitted particles must be counted. To simplify the instrument and reduce mass and power consumption, we propose to develop a condenser analyzer in which a single gas flow is controlled. Particle detection will be based upon measurement of the charge carried by the particles to an electrode detector.

Two modes of particle charging can be employed to probe different size regimes. The first involves exposing the aerosol to gas ions in a gas with a net neutral charge and determining the size distribution of the particles by making a series of measurements at different electrical field strengths. Due to multiple charging of particles above a threshold size, this method is limited to measurement of small particles (< 1 µm). The second method uses a unipolar diffusion charging

Table 4-2. Experimental techniques discussed for Titan aerosol physical analysis

Technique	Included?	Advantages/Disadvantages for Use on Titan
Electrical mobility analysis	Yes	Can be simplified using a condenser analyzer with single gas flow. Can determine the size distribution of small aerosol particles (submicron).
Optical scattering	Yes	Can measure both cloud condensation nuclei (CCN) and aerosol particles. Can determine the size distribution of larger particles.
Differential mobility analysis	No	Can precisely measure particles in sub-micron size regime. Too complex to operate remotely in Titan ambient conditions.
Particle into liquid sampler (PILS)	No	Use of methane condensed from atmosphere to concentrate larger organic particles. Can be coupled to microfluidic or mass spec system. Determined to be too complicated and energy-intensive.
Nephelometer	No	Not enough detailed information provided by this technique.

method and detects particles above this threshold, so by combining the two methods, size distribution measurements can be extended over a wide size range.[39] Design of an instrument for performing such measurements will require understanding of the charging kinetics in the Titan atmosphere. The recently developed aerosol charge-transfer model will be used to develop this understanding. Another possibility for mobility-based measurements in the Titan atmosphere involves making measurements at the natural charge state of the atmospheric aerosol.[37]

Measurement of Titan cloud condensation nuclei

In contrast to Earth aerosols, multiple condensable species may contribute to cloud droplet formation in the Titan atmosphere. Methane is the dominant organic in the atmosphere, and because it has a much lower molecular weight than does the major gas species – nitrogen – an approach that has revolutionized CCN measurements in the Earth atmosphere[40-42] could be adapted to enable a simple CCN counter. Because of its low molecular weight, methane in the Titan atmosphere or water on Earth diffuses faster than heat. Supersaturation can be produced by gently heating a wet-walled tube, enabling activation and growth of particles in the flow. For measurements on Titan, methane would condense into a sorbent layer on the inside of the tube, either by cooling, capture of precipitation, or compression of atmospheric gases within the tube and then allowing thermal equilibration. Particles that are activated grow to sufficient size to be detected optically and counted.

Aerosol sampling for chemical analysis

The chemical composition of the atmospheric aerosol can be measured with the methods that are proposed for measuring the atmospheric and lake compositions (see sections 4.1 and 4.2), provided samples can be collected and efficiently delivered to the respective analytical instruments. Following well-established methods for probing particle compositions in the Earth aerosol, e.g., Thermal Desorption Aerosol GC/MS-FID (TAG),[43] we propose to collect particles on a small substrate by inertial impaction or electrostatic precipitation. The collected sample would then be thermally desorbed into the gas for analysis using a high resolution mass spectrometer.

Optical particle size distribution measurements

Particle size distributions can also be measured optically. A sample of particle-containing gas is drawn into an instrument where it is illuminated with a laser. The light scattered from individual particles as they pass through a highly focused beam is related to the particle size and refractive index. Many so-called optical particle counters are commercially available and could be adapted for use in a Titan mission.

KISS Study Outcome: New Aerosol Ideas

- **Modeling** – An atmospheric model was developed to explore charge distributions in Titan conditions. A manuscript is in preparation.
- **New thinking** – This study stimulated new ways of thinking about approaches for *in situ* measurements of aerosols in remote atmospheres.
- **Collaborations** – A new approach to measuring carbon nanotube carpet surface areas was conceived, leading to a collaboration between Julia Greer and Rick Flagan.

Key scientific and technical points for concern

A critical issue in optical particle sizing on Titan will be thermal management to prevent size changes due to evaporation. Instruments that measure particles as they pass by the instrument are also possible, though such instruments are generally limited to particles larger than several tenths of a micron.

Roadmap for technical development

- Use physics models to determine the aerosol characteristics as a function of altitude and particle size for the Titan atmosphere. Parameters to be probed include the steady-state charge distribution for bipolar and unipolar diffusion charging, the aerodynamic relaxation time, and condensational growth rates as a function of supersaturation.
- Determine attainable electrometer sensitivity under conditions of measurements in the Titan atmosphere. There is a direct trade-off between sensitivity and instrument size: the more sensitive the electrometer can be made, the smaller the sampling rates (and hence the instrument) that will be required to make quantitative measurements of the Titan aerosol.
- Perform computational fluid dynamics/aerosol dynamics simulation of instrument concepts to critically evaluate instrumental concepts.
- Measure ion distributions for simulated Titan atmospheric conditions and different charger designs.
- Evaluate scaled prototype instruments in the laboratory.
- Develop data analysis/inversion methods to enable validation of measurement capabilities.

4.4. Geophysical measurements

Another major focus of this study was the interior structure of Titan. The study group led by Jennifer Jackson was focused on "Geophysical and Physical Properties of Titan". The following related concepts were outlined at the end of the first workshop: electrical conductivity, remote sensors, "GeoSaucer", and seismology. The four-month study period began about one month after our first workshop, and we quickly narrowed the focus to seismology opportunities on Titan. The successful application of seismology to Titan provides a real opportunity to study the models of formation volatile cycling, degree of tectonic activity, amount of tidal dissipation interior, surface processes of an icy body, and assess the presence of a liquid layer (Figure 4-9). Existing gravity data has limited capability in determining accurate crustal thickness, boundary layers, and/or core composition. Through seismology, one also has the great potential to gain concrete information on the interior properties of icy and/or terrestrial-like planetary bodies in our planetary system and in particular, to understand the potential connection between the interior of Titan and its atmosphere. For example, Earth's tectonic activity heavily controls the surface topography and volatile budget. The KISS study team therefore investigated revolutionary technologies based on seismology as part of an instrument package for the next Titan lander.

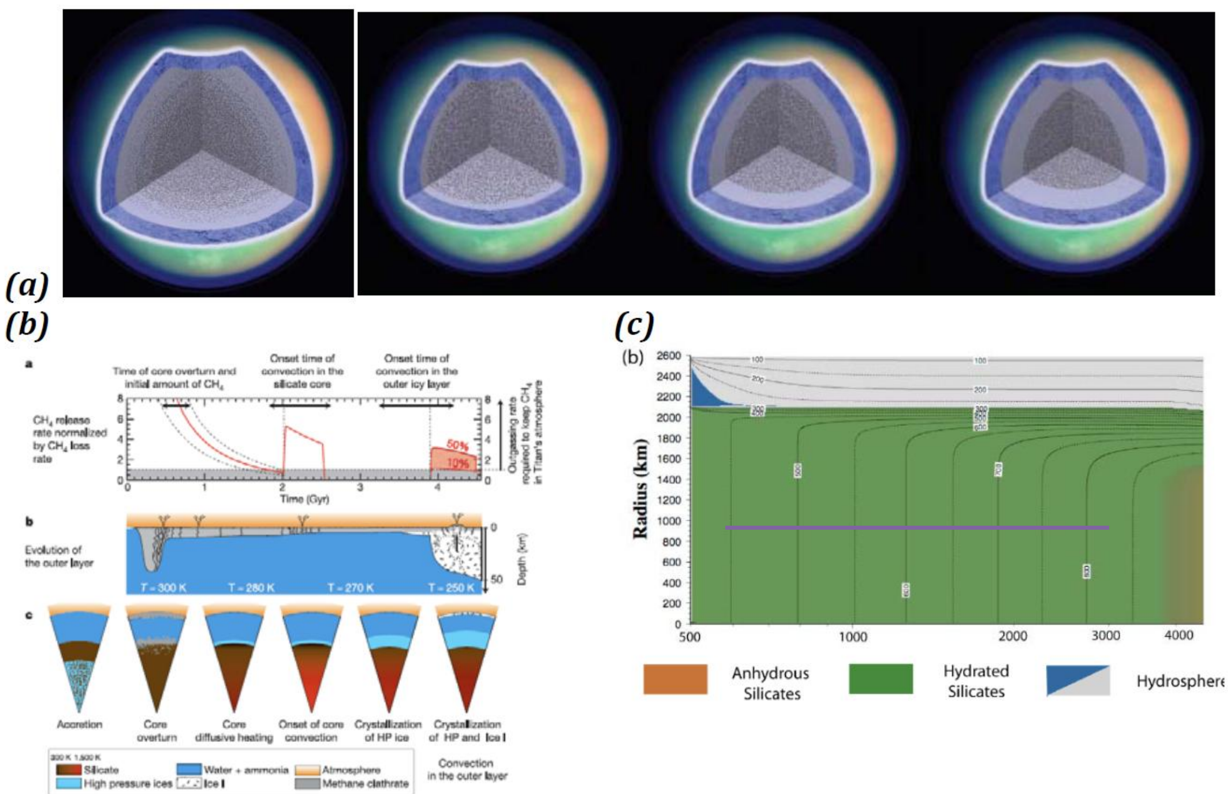


Figure 4-9. (a) Global gravity field and shape data suggest that rock and ice are incompletely separated within Titan's deep interior, overlain by a water ice/liquid shell that may contain a cold water-ammonia ocean (blue), sandwiched between high-pressure water ice below (gray) and a floating ice/clathrate shell above (white). The three smaller images show that the extent of separation of rock from ice would depend on the rock density that is predominantly affected by the amount of silicate hydration[44, 45] Formation model scenarios of Titan's interior proposed by (b) Tobie *et al.* 2006[46] and (c) Castillo-Rogez and Lunine, 2010.[47]

4.4.1. Non-traditional seismology using ambient noise

Introduction

After discussions during our study period on the physical processes that are either occurring or thought to occur on Titan's surface, Jackson proposed the use of a non-traditional means of coupling a measurement that would be sensitive to Titan's crustal structure and environmental processes: *ambient noise*.[48] For example, one could learn a lot about the interaction of Titan's lake dynamics (meteorological cycle)[2, 9, 10, 19, 20, 49-63] and subsurface properties (porosity, presence of an alkanifer, presence of a sub-surface ocean)[64, 65] through applications of ambient seismic noise on Titan (Figures 4-10 to 4-12).

Potential Sources of Titan Ambient Noise

- Weather and cloud formation
- Lakes
- Global radial contraction
- Tidal effects
- Cryovolcanism

Jackson gave an oral presentation on this topic at the 2010 AGU Union session "Innovative Approaches to Planetary Seismology"[48]

Non-traditional seismology methods: Ambient seismic noise (ASN)

The use of cross-correlation of ambient seismic noise to several Earth and planetary applications was recently highlighted in *Physics Today*.[66] The Green's function between two stations can be extracted from the cross-correlation of the noise field recorded by them.[67-73] For example, surface and body waves can be generated from wind and seasonal lake-loading and dynamics (freeze/thaw) in Canada[71] and the Earth's crust/mantle boundary was detected from the cross-correlation of ASN in Canada's Great Slave Lake region.[73]

At the second workshop, a full afternoon was organized for talks focused on Titan's interior, how to access its properties using non-traditional sources, and development of mini-seismometers that can operate under Titan's extreme environment. The session was organized by Jackson and Christophe Sotin (JPL). The following talks were presented: Motivation for Ambient Seismic Noise studies on Titan (Prof. Jennifer Jackson, Caltech), Interior of Titan (Dr. Christophe Sotin, JPL), Ambient Seismic Noise applications on Earth (Ph.D. student Zhongwen Zhan, Caltech), Seismometer designs and concepts (Dr. Harish Manohara, JPL) and Mini-seismometer in an ice-core (Prof. Oded Aharonson, Caltech). Dr. Bruce Banerdt (JPL) made a guest visit during this session and contributed his expertise and interest in applying such a method not only to Titan, but to other terrestrial-like planetary bodies.

Why now?

- Non-traditional seismology can be an alternative to "networks".
- Potential to revolutionize seismology on other planetary bodies and on Earth.
- Microelectromechanical systems (MEMS) and cryo-technology appear ripe for realizing the required sensitivity in the environmental conditions of Titan.
- Observations on Titan show indications of ASN sources.
- Seismology is a low-power possibility that could link processes: surface dynamics (lake circulation, atmospheric coupling), crustal structure.
- Immediate applications on Earth: seismology, remote/hazard environments, oil prospecting, and surveillance.

Key scientific and technical points for concern

- Signal strengths are not well known.
- Surface properties to which we embed (melt) the seismometer are not well constrained.
- Miniaturizing a seismometer that is sensitive enough and can operate under Titan conditions will be challenging.
- Tests on Earth have yet to demonstrate that auto-correlation on one seismometer yields a unique solution for crustal structure over a limiting time-frame.
- It is not clear if it is possible to auto-correlate one station's ASN to deliver a "one-seismometer" concept to the solar system.

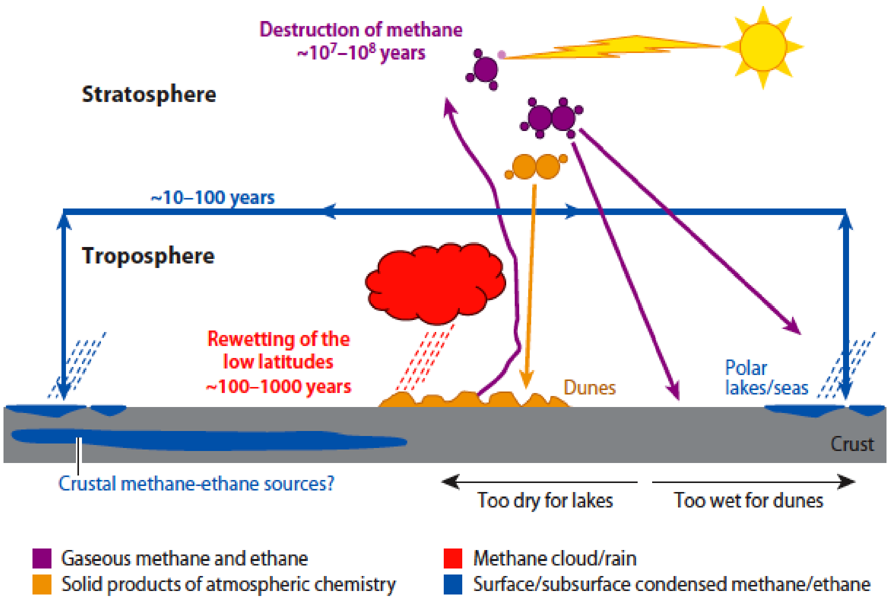


Figure 4-10. Elements of Titan's methane cycle known or strongly suspected to be present, with timescales for various processes.[24] Such activity may provide an ambient seismic noise signal that is measureable.

Roadmap for technical development

While the concept of using one-seismometer to study planetary interiors and dynamic surface processes was recognized amongst all the participants of the second workshop as a potentially "revolutionary" concept, it still must be demonstrated within the seismological community. As a true success of the KISS geophysics study group's efforts and the second workshop, much more focus and attention has been put on this concept – an action that would not have happened without the hard efforts of everyone involved over the last few months within the KISS framework. There are significant hurdles that must be overcome for the one-seismometer concept, and it is not yet clear which planetary body would benefit the most from such an instrument. Titan provides a unique atmospheric noise source, but other bodies may produce higher tidal source signals. Most importantly, the expected signal strengths from various sources as a function of time, especially in the case of using ambient seismic noise, are not yet well-established. Even within the seismological community, this concept is relatively new. The one-seismometer concept should wait until a much better understanding is achieved, and this would likely take a few years. Faculty and students in the Seismo Lab at Caltech are continuing to work in this area, along with others in the field of geophysics.

4.4.2. Micro-seismometers

Introduction

Existing miniaturized seismometers lack the sensitivity and/or capability to operate effectively *in situ* on the Titan surface. As a result, two high sensitivity microseismometer concepts were developed under the Titan KISS study, one using a high-Q (low damping) microresonator and the other using a field emission-based high-sensitivity vacuum device. The measurement requirements drawn from past literature and discussions with seismologists in the study group point to a broad frequency range of 10 mHz to 100 Hz with uniform sensitivity of 10^{-9} m.s^{-2} Hz$^{-0.5}$.

State-of-the-art seismometers for planetary applications

The state-of-the-art broad band seismometers use two separate seismometers. The package consists of two Very Broad Band (VBB) seismometers, in opposite sensing directions and two Short Period (SP) sensors made using MEMS techniques. Targeted performance of these two together is as follows: VBB (<10^{-9} m.s^{-2} Hz$^{-0.5}$ from 10^{-3} up to 10 Hz) and SP (< 5 x10^{-8} m.s^{-2} Hz$^{-0.5}$ from 10^{-2} up to 100 Hz).

State-of-the-art miniature seismometers

Traditional MEMS seismometers use cantilevers that support a proof mass. The seismic wave induced motion of this proof mass is capacitively measured and converted to a corresponding force. Pike *et al.* have developed and demonstrated this type of double cantilever design (schematic shown in Figure 4-11).[74] These are technologically mature and flight-capable. They operate in a closed loop mode thus increasing their sensitivity. The MEMS seismometers have shown a sensitivity of 5x10^{-8} m.s^{-2} Hz$^{-0.5}$.

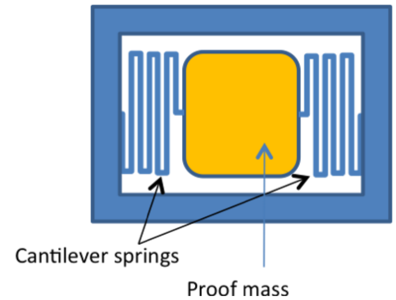


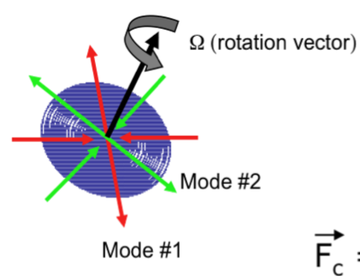
Figure 4-11. Schematic of a double cantilever MEMS seismometer design.[74]

Miniature Seismometers for Titan

Two new MEMS seismometer concepts were developed under the KISS study for Titan applications. One employs high-Q microresonator that operates in closed loop mode. The second uses a vacuum device with carbon nanotube field emitters whose change in emission current is proportional to the seismic forces.

Microresonator seismometer

In this design, a disc resonator is anchored at its center and the change in radial vibration (which is proportional to seismic forces) is measured using a force-balancing approach. In operation, this is similar to that of a disc resonating gyroscope and allows force-feedback to enhance the sensitivity of the measurement. The concept is based on Coriolis force coupling. As shown in Figure 4-12, a disc resonator whose mode #1 is driven, will excite mode #2 in a rotating reference frame due to Coriolis force when the resonator experiences an external force. The amplitude of this motion is proportional to the rotational rate. The high-sensitivity of this design is the result of the high Q of the resonator.



$$\vec{F}_c = 2\, m\vec{v} \times \vec{\Omega}$$

Figure 4-12. Schematic showing the principle of Coriolis force coupling in a disc resonator.

A resonator fabricated from low coefficient of thermal expansion (CTE) material such as quartz or ultra-low expansion (ULE) glass inherently has a high Q because of the high value of its material and temperature dependent component of Q. Quartz microresonators built at JPL have demonstrated Q in the range of 10^6. According to the *root acceleration-noise power density* relation (see equation below), to achieve a sensitivity of 10^{-9} m.s^{-2} Hz$^{-0.5}$ on Titan, the MQT_s factor should be greater than 0.03 kg-s ("kT" product for Titan is 1.3×10^{-21} joules). For a resonating MEMS seismometer with Q of 10^6, M of 1 g and T_s of 1 ms, MQT_s is approximately 1.0, which makes it suitable for high sensitivity measurements.

$$\sqrt{\frac{\alpha^2(t)}{\Delta f}} = \sqrt{\frac{8\pi kT}{MQT_s}}$$

KISS Study Outcome: Miniature Seismometer Concepts

- **Microresonator seismometer** – Disc resonator made of quartz or ultra-low expansion glass.
  External force ⇨ Coriolis force ⇨ signal
- **Field emission-based miniature seismometer** – Field emitter based on carbon-nanotubes.
  External force ⇨ vibration of proof-mass ⇨ change in current ⇨ signal

Field emission-based miniature seismometer

In this design, a carbon nanotube (or another type of robust) field emitter-based vacuum diode is created (see Figure 4-13). Under an applied field (CNTs have a low threshold field, as low as 0.7 V/µm) there is a continuous field emission current being collected at the anode, in this case a flexible membrane with or without a proof-mass (depending on the design requirements). A seismic event causes the membrane to vibrate with respect to the CNT cathodes. The change in gap between anode and cathode due to this vibration exponentially changes the emission current. These types of seismometers, when arranged such that they are sensitive to three axes, is anticipated to provide the necessary measurements to the sensitivity required. The measurement can be done in closed loop mode in this design also by nullifying the steady-state emission current and only measuring the differential signals.

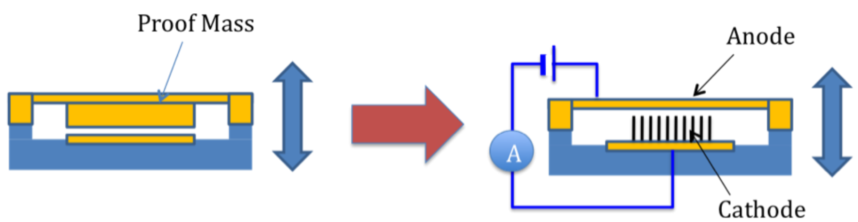


Figure 4-13. Schematic showing the concept of field emission-based seismometer.

Key scientific and technical points for concern

Out of the two miniature seismometer concepts proposed here, the quartz resonator concept has been developed as a microgyroscope and has been demonstrated. While the fabrication and packaging aspects can be drawn from that development, the resonator geometry modification for seismometry, electronics integration, and testing are still in the design phase. The field emission-based seismometer is still in a concept stage from its application point of view. The structure itself has been fabricated for vacuum gauging applications; however, changing the anode to a membrane with proof-mass design, integrating measurement electronics, and testing require considerable efforts. Moreover, both designs must undergo extensive testing (i.e., exposure to cryogenic temperatures, thermal cycling, 'shake and bake' testing) to ensure effective operation on the surface of Titan. The sensitivity of these technologies must also be validated in terms of the expected seismic activity of Titan to be sure that any seismic events will be detectable.

Roadmap for technical development

- Build prototypes of both miniature seismometer designs.
- Compare sensitivity to models of expected seismic activity on Titan.
- Test prototypes in simulated Titan conditions.
- Integrate technology into a landed surface science package.

4.5. Electronics and materials

Our KISS study was motivated by understanding the *in situ* chemistry of Titan, but this goal is ultimately bounded by the capabilities of the electronics and materials used. Every instrument concept discussed requires robust and reliable packaging, particularly those that will operate at ambient Titan conditions. A key objective in this study was therefore to investigate electronics and materials with the potential to bring these technologies into the cryogenic-capable regime (Figure 4-14). Such a revolutionary advancement would consequently **enable future missions** to other low-temperature targets, such as Enceladus, the Galilean moons of Saturn (Europa, Ganymede, Callisto and Io) or comets.

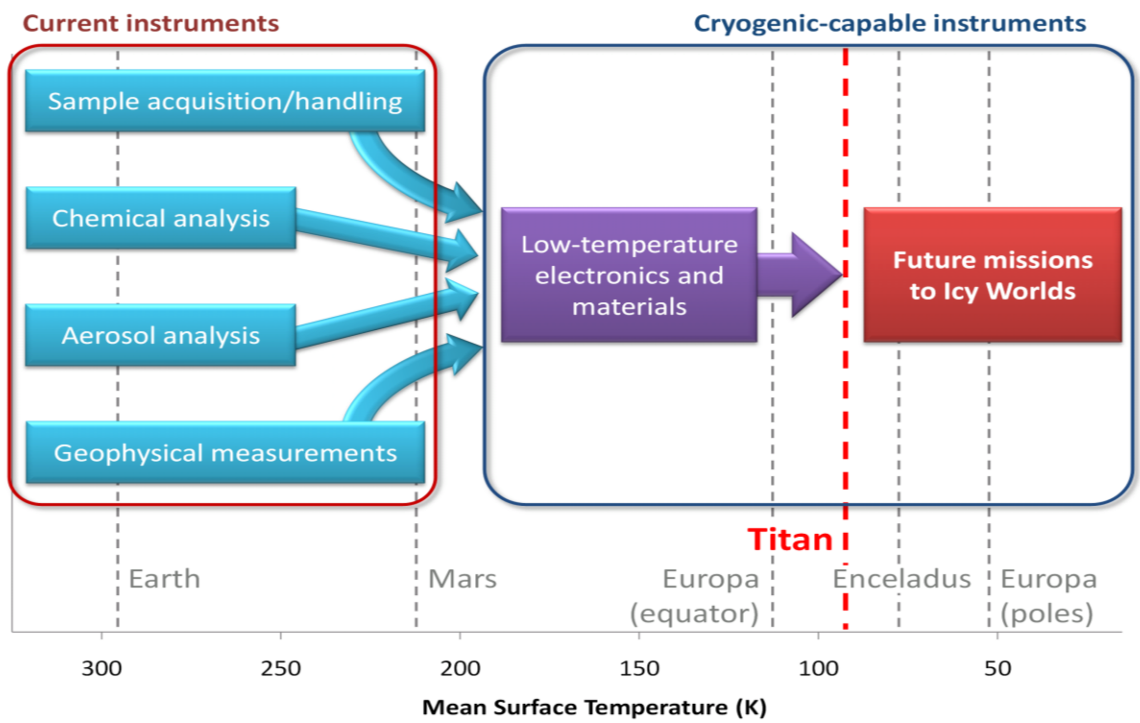


Figure 4-14. Goal of KISS study in terms of electronics and materials. All current instruments required for (1) sample acquisition and handling, (2) chemical analysis, (3) aerosol analysis and (4) geophysical measurements which have been designed to operate at Earth or Mars ambient temperatures, must be adapted to operate in the cryogenic conditions of the Titan environment (red dashed line). This will enable future missions to other icy worlds such as Europa and Enceladus.

4.5.1. Low-temperature electronics

Assumptions:

- Instruments/electronics will *not* be placed inside a warm electronics box unless necessary for experimental reasons. This will minimize mission mass, volume, and power requirements while enhancing science capability.
- Electronics have to survive and operate with very small amounts of available power.
- Design and fabricate micro-powered electronics for instruments/actuators that will survive the ambient environment (90 K).

Electronic technology

Electronic circuit technology choices for Titan are a function of the utilities available for the mission. For mission scenarios with an abundant supply of Radioisotope Heater Units (RHUs), commercial low-power electronics could be considered. For the majority of instruments and avionic functions, commercially available electronics could be kept at Earth-like temperatures with the help of the RHUs. Depending on the mission architecture, certain application-specific electronics (for example electronics for amplification of signal from sensors, sample acquisition and drive-and-control of motors) may need to be designed to operate at 90 K (the Titan surface temperature). A low-temperature library of SiGe bipolar junction complementary metal-oxide-semiconductor (BiCMOS) electronics circuit blocks capable of operating at 90 K (Titan surface temperature) has already been demonstrated under a grant from NASA Exploration Technology Development Program (Figure 4-15). This library was fabricated on the commercial IBM 500-nm SiGe BiCMOS technology using "low-temperature-by-design" techniques. Circuit building blocks and the corresponding low temperature integrated circuit design infrastructure developed by this grant are adequate for construction of circuits for such as low temperature sensor amplifiers and motor control electronics. Powering of missions with available RHU's could also leverage conversion of excess heat from RHUs into electricity using Thermo Electric Generators (TEG) in addition to a combination of primary and secondary batteries that are force-kept at Earth-like temperatures.

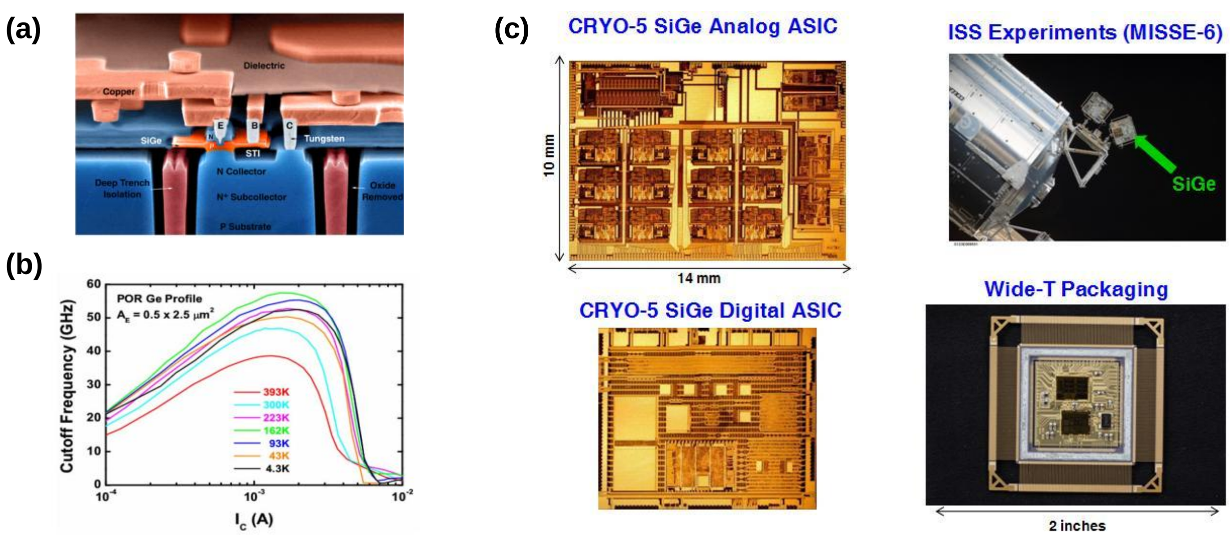


Figure 4-15. (a) Cross section of SiGe transistors. (b) SiGe transistor current vs. temperature. (c) Low temperature SiGe IC's and packaging developed by NASA.

For mission scenarios with limited or no RHUs, power dissipation of the electronic systems becomes a critical design constraint. In these type of energy-constrained missions, power consumption associated with maintaining an Earth-like operating temperature for the electronics cannot be afforded. Instead, the limited available power needs to be shared across the new generation of instruments and avionics electronics subsystems that are designed with ultra-low-power electronics and are capable of directly operating at 90 K. The low temperature capable SiGe-based technology is still an ideal candidate for energy constrained Titan missions. However, the circuit functions in the currently available SiGe low temperature library will not support the combination of micro-power operation and signal-to-noise ratio requirements of the instrument electronics, as well as the ultra-low-power needs of the avionics systems for the mission. Developing ultra-low-power low-temperature circuits for this purpose will require leveraging higher resolution SiGe BiCMOS technologies such as the 130-nm IBM 8HP technology and micro-power design techniques.

Communication systems

Titan missions can benefit from low power communication systems that are capable of working at low temperatures. Fortunately the development of low temperature, low power communication systems is also yielding promising results. Through a NASA grant, JPL/Kansas State University developed a micro-powered RF transponder that was tested at 150 K (−120 °C) for Martian applications. This radio needed 2 W (as compared to a traditional 40-W radio) of power for communication between surface-to-orbit. The electronics used on this radio were fabricated using a commercial silicon-on-sapphire technology and "low-temperature-by-design" techniques. There is no theoretical barrier in developing a similar radio to operate at 90 K for Titan.

Key scientific and technical points for concern

Room temperature-based micro-power circuits are already in use in many applications including biomedical prosthetics (hearing aids, pacemakers, neural implants, etc.), cell phones and many other applications. These circuits operate at significantly lower bias current levels with transistors that are biased in their sub-threshold region of operation. However, it is not clear that these techniques can readily map to lower temperatures and support the low noise levels needed for instrument applications. For example, at 90 K, the increased threshold mismatch of sub-threshold transistors will require development of new active offset cancellation methods. Also, the additional supply voltage needed to compensate for the increase in transistor threshold voltage will give rise to increased power consumption that may need to be considered as well.

Roadmap for technical development

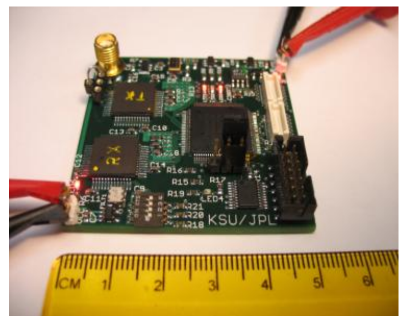
- Identify application-specific electronics that will be needed for the next *in situ* Titan mission and focus on technology innovation in these areas.
- Develop low temperature, low power communication systems similar to Mars that are capable of operating in Titan conditions (~ 90 K) or develop a new system.
- Investigate high resolution SiGe BiCMOS technologies together with ultra-low-power circuit design techniques for making ultra-low-power, low-temperature circuits for long life, power-starved Titan missions.
- Integrate electronics with the instrument package (NMR, mini chem labs, mass spec) and the Sample Processing Unit for automated sample transfer, analysis, data storage/relay and power management.

4.5.2 Power systems for Titan

Power sources continue to be a major challenge for missions to Titan. The Huygens Probe used $LiSOCl_2$ based primary batteries as its power source and deployed thirty-five RHUs to force-keep its primary power source and electronic systems at Earth-like temperatures. The use of the primary batteries significantly limited the lifetime of the Huygens Probe and its science return. Today, advances in low temperature primary batteries such as SO_2ClF:$CHClF_2$ (demonstrated operating as low as 140 K) could minimize the need for the RHUs (by force-keeping the power system at the lower temperature). However, low temperature batteries alone only incrementally raise the mission lifetime and hence the science return.

Table 4-3. Performance comparison between C/TT-505 and Mars Microtransceiver (image at right).

Characteristic	C/TT-505	Microtransceiver
Mass	2000 g	10 g
Volume	2000 cm^3	10 cm^3
Power (RF out)	10 W	0.01/0.1/1 W
PDC (RX/TX)	5 W/45 W	0.05 W/0.1 to 3 W
Operating temp	-55 °C to 75 °C	-125 °C to 120 °C



Key scientific and technical points for concern

To support the long-life missions to Titan, a fresh look at emerging power technologies is needed. For example, at the system level one may be able to take advantage of power-aware electronics. Power-aware systems use a small power source to run essential keep-alive functions of the mission and to trickle charge an energy storage system with rechargeable energy storage elements to momentarily support applications with higher power demand. Both energy generation (power source) and energy storage (i.e. rechargeable batteries and/or capacitors) are essential components of power-aware systems. For efficient power systems for the Titan application, these components need to support low temperature operation as well.

i. Radioisotope power sources.

Radioisotope power sources are still the most attractive potential source for powering electronics for Titan. With a very long lifetime, these sources can operate independent of the ambient temperature and produce both electricity and heat. Historically, RHUs have been predominantly used to produce heat for Titan missions. However, thermoelectric generators can convert excess heat from RHUs into electric energy. A more efficient form of this system, called the Radioisotope Thermoelectric Generator (RTG), is optimized for conversion of thermal energy to electricity. A major issue with both RTGs and RHUs is the very limited availability of the radioisotope source (usually plutonium-238). Small size modular RTGs at an approximate mass of 350 g have now been demonstrated to produce 50 mW of electrical power (Figure 4-16). A parallel array of these small RHUs can produce higher power levels. These small RTG's do not require a large radioisotope source and could become a critical component of smart power systems for long-life Titan missions.

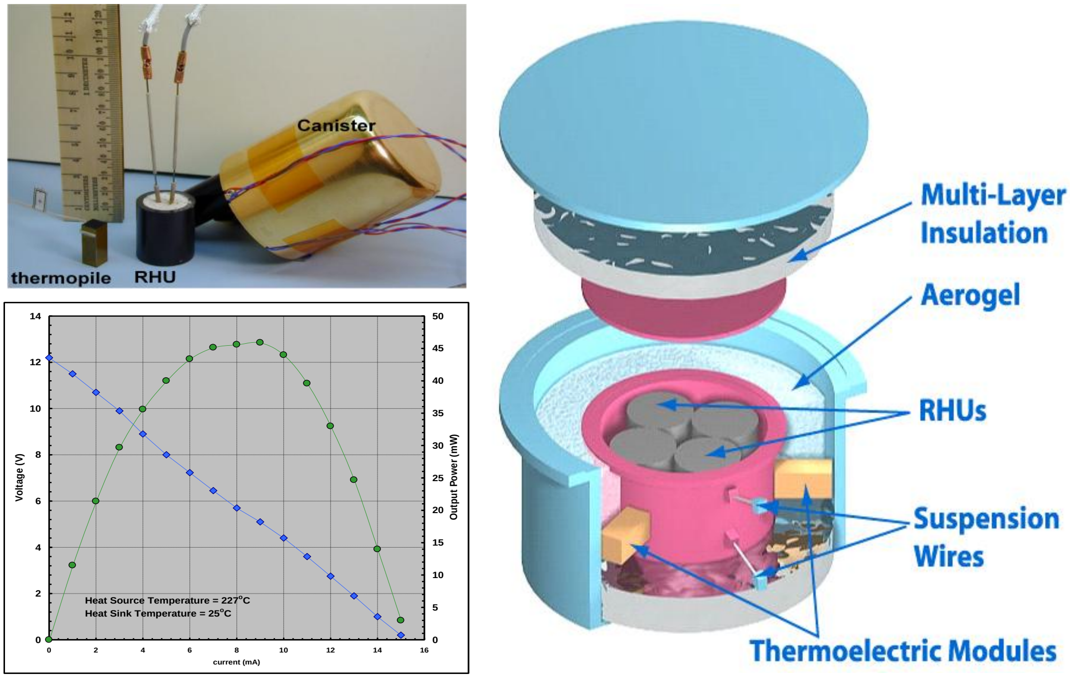


Figure 4-16. Micro RTG and its characteristics. Top left: Photo showing scale of micro RTG. Bottom left: Current-voltage-power characteristics of micro RTG; voltage (V) in blue, output power (mW) in green (heat source 227 °C, heat sink 25 °C). Right: Diagram of components of micro RTG.

ii. Rechargeable batteries.

Rechargeable batteries are one of the major components of an optimally designed power aware system. Unfortunately, the power handling capacity and performance of traditional Li-Ion batteries has a very strong temperature dependency. For example, the Mars Exploration Rover (MER) rechargeable batteries are set to operate at 250 K. However, recent low temperature battery discharge experiments (Figure 4-17) with Gel Polymer Electrolyte Li-Ion cells (with methyl-butyrate) is showing that this type of rechargeable battery is capable of holding 85% of its capacity at 210 K (~−60 °C). Future optimization of the electrolyte may prove to further reduce the operating temperature of rechargeable Li-Ion batteries. Low temperature rechargeable batteries can also be thermally isolated. Force keeping them at lower temperatures will significantly reduce the amount of energy necessary for this purpose. One exercise showed that 10% of the energy stored in the battery was necessary to feed a servo system to self heat a rechargeable battery to 230 K (−40 °C).

iii. Capacitors as energy storage elements.

A new generation of high density, double layer capacitors that store charge on high surface area carbon electrodes in place of high dielectric constant materials are now enjoying a very high energy density. These capacitors can also act as energy storage elements in a power aware system and be used to support peak power operation. Compared to batteries, high density capacitors can be charged and discharged for a very long time. High density capacitors have been tested at temperatures as low as 193 K (−80 °C). The discharge voltage and capacity of these high density capacitors is also a function of temperature. Similar to rechargeable batteries, they have to be force-kept at minimum temperature if used for Titan power applications.

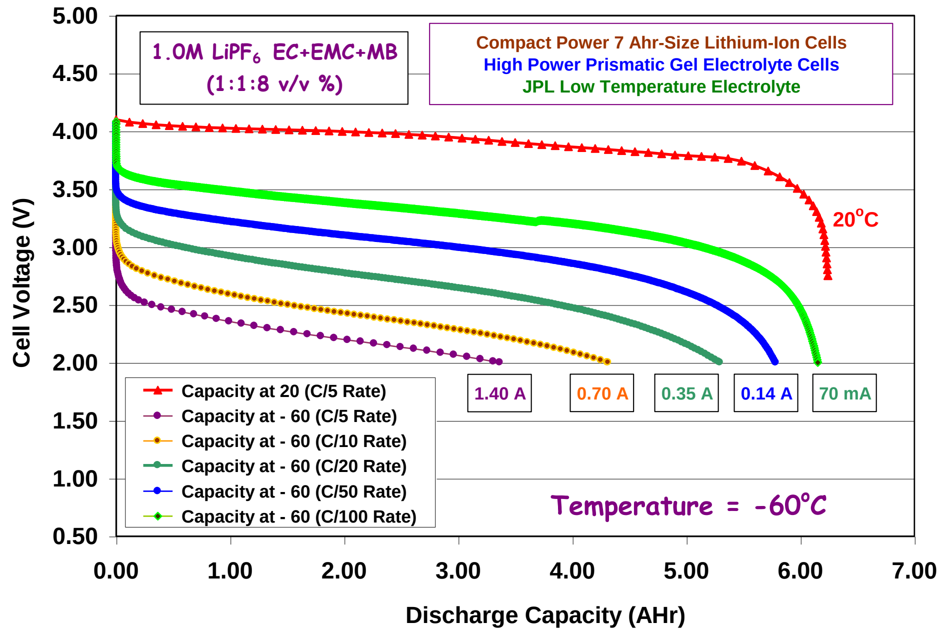


Figure 4-17. Performance testing of high rate, Gel Polymer Electrolyte Li-Ion battery cells and performance of Ester-Based Electrolytes at low temperatures.

Roadmap for technical development

Barring any unforeseen breakthroughs in power technologies, any long-life mission to Titan would require a radioisotope power source, most likely in the form of multiple modular RTGs to minimize plutonium consumption and maintain low spacecraft mass. Low-temperature rechargeable batteries and capacitors can be utilized to support peak power operation, but significant development of these technologies must still be undertaken. It feasible to envision building a long life power-aware Titan mission that has low temperature instruments made with SiGe micro-powered electronics, low temperature micro-powered radio, and power system that would use an array of mW-RPS sources and trickle charged thermally isolated low temperature batteries. This type of a mission could potentially last years instead of hours and days and could have breakthrough science implications.

4.5.3. Packaging materials

Theme

- Design and fabricate electronics for instruments/actuators that will survive the ambient environment (90 K).
- Assume that there will be instruments/electronics not inside a warm electronics box.

Packaging materials

The following list and accompanying drawing (Figure 4-18) provide the most commonly used materials in electronic assemblies and packaging. Items with strikethrough were determined to be not suitable for electronic assemblies in the 90 K environment. Items in underlined in italics and followed by a question mark should be considered for further study.

Materials in electronic assemblies and packaging suitable for the Titan environment:

- IC: Si, SiGe, GaAs, InP, SiC
- Passives (L,C,R): Magnetics, Cu wire, ~~epoxy~~, silicone, encapsulants, *$BaTiO_3$?, various dielectrics?*, contacts, Ag, Ni, solder, C, *$Ru0_x$?*
- Wirebond: Au, Al, Cu
- Chip attach: ~~Bismaleimide Resin:75-85% Silver Flake Filled~~, solders
- Solder Mask: ~~Polyurethane~~, Silicone
- Substrate material: ~~BT, FR4, G10~~, Al_2O_3, AlN, B_2O_3-CaO-SiO_2 , *PI?, BCB?, LCP?*
- Interconnect: Cu, Au, Ag
- Via: Cu, Au, Ag
- Mold Compound: ~~Biphenyl Epoxy Resin: 80-85% Spherical Fused Silica Filled~~, *Silicones?*
- Solder ball (Flip Chip or Package): $Sn_{63}Pb_{37}$, SnPb, AgCuSn, InPb
- Connectors and Cables: *BeCu?, DAP?, Al, PI?, PTFE?*

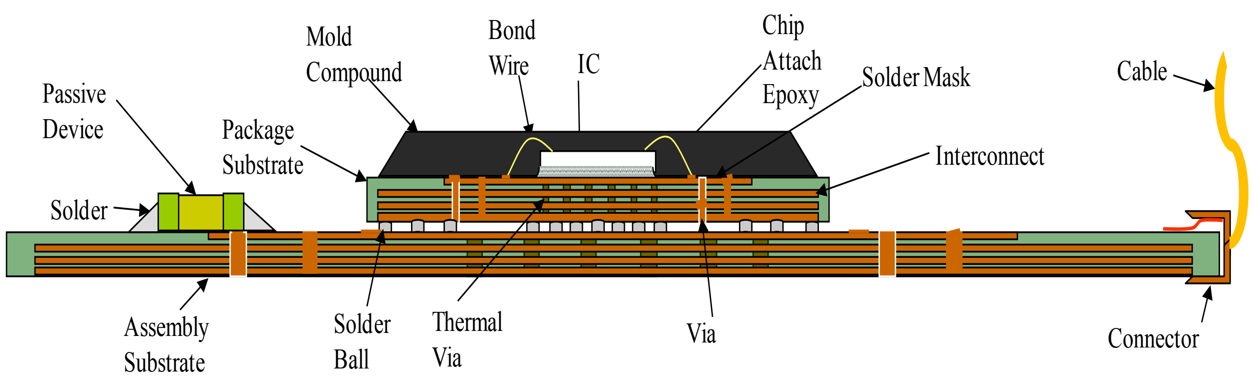


Figure 4-18. Commonly used materials in electronic assemblies and packaging.

Key scientific and technical points for concern

The KISS study team investigated three major packaging materials in terms of their relevance to Titan: ceramics, polymers and metals. The issues with each material were discussed, along with potential solutions to enhance that materials' capability for adaptation to cryogenic temperatures (see Table 4-4). Though further research and development is needed, we believe this study has established a baseline for materials research for *in situ* operation on Titan, and that the goals outlined in this report will enable such technologies for use on other icy worlds.

Roadmap for technical development

Future work will concentrate on developing and testing the solutions proposed in Table 4-4, paying particular attention to the unique conditions of the Titan environment and the specified requirements for sample collection (i.e., sipping from a lake) and chemical analysis.

Table 4-4. Problems and solutions for packaging materials at cryogenic temperatures.

Material	Problems	Solutions
Ceramics	• **Dielectric response.** Storage mechanism in capacitor dielectrics can 'freeze-out.' • **Charge storage.** Mechanical distortion mechanisms for polarization charge storage may not be available at cryogenic temperatures. • **Thermal resistive response (TCR).** The thermal coefficient of resistance may be non-linear and will need to be empirically characterized as conduction mechanisms may shift at low temperatures.	• Improve the design of substrate materials (dielectric build-up substrates, multilayer ceramic substrates). • Standardize performance and properties of ceramic-based substrates.
Polymers	• **Fracture and glass transitions.** Most polymers will become brittle at low temperatures. • **Coefficient of thermal expansion (CTE) matching.** Polymers will display non-linear CTE performance at low temperatures. • **Large thermal expansion.** If the zero-stress point is set at 300 °C, the typically large thermal expansion of polymers (~100 ppm/K) will impart significant stresses on electronics.	• The safest way would be to eliminate most polymers from a low-temperature design. • **Use silicones.** Some silicones have very low glass transitions (below 170 K) and have low modulus, possibly making them suitable for die attach and overcoating. • Studies of wiring with PTFE (Teflon) and using diallyl phthalate (DAP) in connectors should be conducted to assure reliability.
Metals	• **Phase transitions going cold.** Most metals undergo phase transitions when going cold. Tin in particular, a primary constituent of solders, has both an allotropic phase transition and a ductile-brittle transition somewhere below 285 K. Metals in electronics undergoing these transitions will fail catastrophically. • **Empirical knowledge only.** The nature and actual transition temperature of these transitions is not known (there are many conflicting data sets published). Long term reliability is also unknown – if only a small portion of the interconnect metals undergoes the phase transition, it is unknown if they will survive.	• **Micro-measurements over temperature range.** Measurements of nano-pillars should be conducted to characterize alloys of interest and to gain fundamental understanding of the transitions. This will enable the engineering of alloys to suppress the transitions to well below 90 K. • **Bulk measurements.** Bulk measurements should also be performed (toughness and tensile or compression) to correlate with the mechanisms determined by the micro-measurements. • **Atomistic modeling.** Extensive modeling is the final tool in the engineering of alloys for the best performance at low temperatures. This will give the predictive ability for optimum alloys that can be verified by micro and bulk measurements.

4.5.4. Carbon nanotube-based packaging

Benefits of Carbon Nanotube Materials

- Large temperature range
- Chemically stable
- Effective absorbers of mechanical energy
- Low thermal interface resistance
- High mechanical compliance

Introduction

Over the past five years significant attention has shifted to vertically oriented CNT arrays (a.k.a. CNT forests, mats, or films) as promising packaging materials that have been demonstrated to produce thermal contact resistances which compare favorably to state-of-the-art materials.[75] Such configurations possess a synergistic combination of high mechanical compliance and high effective thermal conductivity – in the range of 10-200 W/mK.[76-78] Their ability to conform to nearly any topology is particularly advantageous for absorbing mechanical energy[79-82] and addressing mismatches in coefficients of thermal expansion that can cause material delamination and device failure. Also, in contrast to most traditional packaging materials, CNT array interfaces are dry and chemically stable in air from cryogenic to high temperatures (~ 450 °C), making them suitable for extreme-environment applications (see, for example, Xu *et al.*, 2010[80]).

Arguments for using carbon nanotube-based protective layers on Titan

- CNT arrays can absorb and dissipate mechanical energy over a large range of temperatures, protecting delicate electronics and package connections from failure due to forces encountered during the impact of landing on Titan.
- CNT arrays can have high mechanical compliance to mitigate deleterious effects of stress induced by thermal expansion differences in packaging materials.
- CNT arrays are chemically stable from below Titan temperatures to temperatures well above expected device maximums and recent work has demonstrated that the mechanical properties of CNT arrays can be invariant in this temperature range.
- CNT arrays have been demonstrated to produce low thermal interface resistance, which lessens temperature gradients and resulting stress between connecting materials.

Potential CNT array packaging structures

Figure 4-19 shows a candidate packaging arrangement that utilizes CNT arrays. The one- and two-sided configurations require CNT arrays to be grown directly on the chip or protective housing (or transfer printing of the arrays to the material surfaces) while the foil interposer coated with CNT arrays on both sides can be inserted between structures. The CNT-coated foil interposer would be closer to a technology readiness level (TRL) of 5 or 6 because it can be inserted with existing devices and structures.

Key scientific and technical points for concern

- Mechanical deformation of CNT arrays is highly dependent on array morphology and thus must be studied further, especially at Titan temperatures.
- Adhesion of CNTs to substrates requires more detailed quantification.
- Thermal transport at CNT-substrate contacts at Titan temperatures requires experimental characterization.
- Performance of CNT-based packaging must be tested over several thermal cycles in simulated Titan environment.

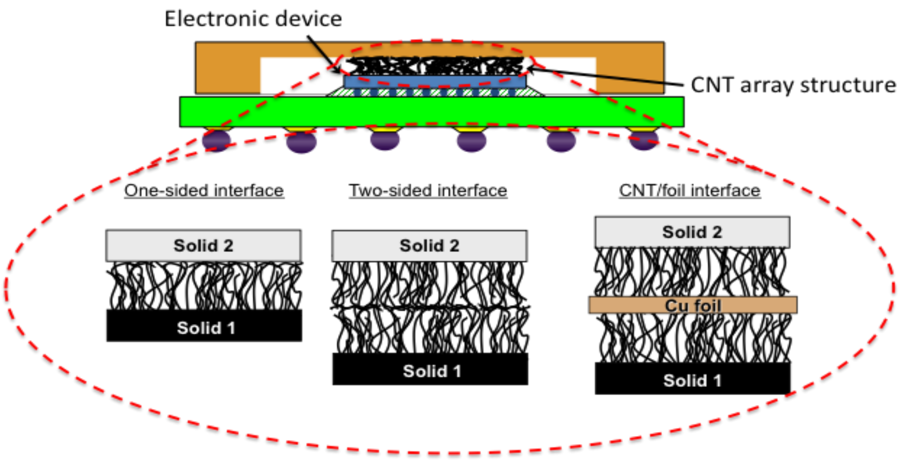


Figure 4-19. Potential packaging arrangement using CNT arrays

Roadmap for technical development

- Study mechanical deformation of CNT arrays as a function of array properties with in-situ SEM experiments and modeling to determine array morphologies that produce temperature-invariant elastic, post-elastic, and time-dependent deformation.
- Quantify strength of adhesion between CNT arrays and supporting substrates using mechanical peel test and sonication to attempt to dislodge CNTs from the substrate .
- Measure thermal resistance of CNT array interface materials at Titan temperatures using a transient technique that can resolve total and intra-interface resistances to provide information about thermal transport at CNT-substrate contacts.
- Characterize the thermal and mechanical performance of CNT-coated foil interposers in a low-temperature electronics package under anticipated mission conditions.
- Assess lifetime capabilities of CNT arrays under in-service conditions.

Future work with CNTs

As a result of the KISS study the Greer Group at Caltech has recently used their in-situ scanning electron microscopy (SEM) to study the deformation mechanics of CNT arrays fabricated by the Cola Group (Georgia Tech). Three different array morphologies were studied and one exhibited highly recoverable deformation, representing a desirable characteristic for packaging materials. The two groups will continue to work together to understand the key parameters that affect the deformation mechanics of CNT arrays in order to develop predictive capabilities.

4.6. Inspired investigations and developments

4.6.1. New collaborations

P. Willis (JPL) and M. Smith/H. Imanaka (U. of Arizona)

The discussions of Titan organic chemistry during the KISS study sparked a collaborative effort between the miniaturized chemical laboratory team, headed by Peter Willis, and the experts of tholin (Titan organic analogs produced on Earth) mass spectrometry, Mark Smith and Hiroshi Imanaka. Future work will involve optimizing tholin separation and characterization techniques using a poly-HCN compound provided by H. Imanaka as a 'tholin standard.'

J. Greer (Caltech) and B. Cola (Georgia Tech.)

One of the potential candidates for electronic device packaging for the Titan mission is relatively dense carbon nanotubes (CNT), as they are able to dissipate and absorb mechanical energy, thereby preventing the impact onto the sensitive electronic instruments. Through this collaboration, Cola's group will pursue synthesis and growth control of these CNT forests while the Greer group will conduct uniaxial compressive and tensile testing on these materials to elucidate their mechanical robustness, deformation modes, and lifetime expectations.

J. M. Jackson (Caltech) and C. Sotin (JPL)

Jackson and Sotin co-authored a book chapter in 'Exoplanets' on terrestrial planet interiors. The collaboration continues with future modeling efforts in the area of Super Earth interiors. 'Exoplanets' was released in December 2010.[83]

A. Shapiro (JPL) and J. Greer (Caltech)

Solders for the electronic circuits ubiquitously used on Earth are generally In-based and are generally well characterized at room temperature and above. Unfortunately, at low temperatures these materials undergo a ductile-to-brittle phase transition, the mechanism for which is poorly understood even today. In order to construct electronic circuits for the Titan instrument package, it is essential to find a non-failing solder material which would not lose its functionality even at such large temperature fluctuations. To address this issue, the Shapiro group will synthesize a variety of promising solder alloys while the Greer group will construct a cryogenic module inside their in-situ nano-mechanical testing instrument, SEMentor, and conduct nano-mechanical testing on these alloys at room and below temperatures. These measurements will be instrumental in identifying the ductile-to-brittle transition, as well as the microstructural mechanism responsible for it.

4.6.2. Proposal opportunities

Study team members have taken advantage of a number of direct and indirect opportunities to write proposals related to the subjects addressed in the workshop. Peter Willis led a proposal to the NASA Planetary Instrument Definition and Development Program (PIDDP) for an integrated and miniaturized laboratory for Titan's lakes (see Executive Summary in Appendix D). Jonathan Lunine was deputy PI of a NASA Discovery proposal to send a lander to one of the large seas of Titan, and PI of an ESA concept study proposal for a Titan balloon. Baratunde Cola submitted a Phase III proposal to the DARPA Nanothermal Interfaces (NTI) Program to expand work on carbon nanotube-coated foil interposers for RF electronics at Titan temperatures, and also led another proposal to Air Force Research Laboratory (AFRL) Thermal Sciences and Materials Branch (RXBT).

Several graduate students associated with the KISS study submitted or are in the process of submitting NASA graduate fellowship proposals. Ryan Diestlhorst, with mentors Mohammad Mojarradi and John Cressler, will work on developing low temperature electronics. Andrew Shapiro and Julia Greer will co-mentor a student exploring cold-temperature solders, and Harish Manohara and Julia Greer are also planning to work with a student on CNT-based packaging.

4.6.3. Publications and conference proceedings/sessions

Peter Willis has a manuscript in preparation on a fully automated mini chem. lab device for submission to *Lab on a Chip*.

Christophe Sotin chaired a session at the 2010 American Geophysical Union (AGU) Fall Meeting entitled 'Titan: The Methane Cycle and Potential for Watery Warm Spots.'
Jennifer Jackson, with co-authors Zhan and Tsai (members of the KISS study team) gave a talk entitled 'Ambient seismic noise applications to Titan' at the 2010 Fall AGU Union session 'Innovative Approaches to Planetary Seismology' as a way to inform the scientific community of our study group efforts and the idea of bringing seismology to extreme environments.[48]

Daniel Thomas, a student working with Jack Beauchamp at Caltech, presented two posters of his work on Titan dune chemistry at the 2010 AGU Meeting and the Gordon Conference, respectively.

Julia Greer had two group members give talks at the Materials Research Society (MRS). Shelby Hutchens, a graduate student, presented her work entitled 'Mechanical Deformation Mechanisms in In-situ Uniaxial Compression of Carbon Nanotube Forests Through Phenomenological Finite Element Modeling' in Symposium Z. KISS postdoc Sid Pathak gave a talk entitled "In-situ SEM Micro-compression of Dense Carbon Nanotube Brushes" in Symposium P.

Pat Beauchamp will co-convene (with Athena Coustenis and Jean-Pierre Lebreton) a session on Scientific Instrumentation at the International Planetary Probe Workshop #8, in June 2011, which includes instrumentation for Titan landers and balloons.

Pat Beauchamp and Jonathan Lunine will co-convene (with Athena Coustenis) a session entitled, 'Titan as a Prebiotic Chemical System' at the joint international conference of the European Planetary Science Congress (EPSC) and American Astronomical Society, Division of Planetary Science (DPS), in Nantes, France in Oct. 2011.

Morgan Cable is lead author on a review article on Titan tholins with several of the workshop participants as co-authors.

4.6.4. Moving forward

The ideas and excitement generated in the study make it highly likely that key participants will move forward with a Keck Phase II proposal to do specific technical studies on the chemistry package, electronics/power and low temperature materials. The KISS study allowed interactions to occur among people working in diverse areas and who probably would never have met had it not been for their participation in the workshops. Many fruitful collaborations have already begun and are planned to continue. During the months between workshops, some research was conducted, testing performed, models derived and papers written. Proposals for external funding have been submitted by some participants and others are planning to do likewise. Studies will continue this year with other funding sources in order to gauge the feasibility of the ambient seismic noise single seismometer concept for planetary bodies and future KISS opportunities. In fact, Jackson, Zhan and colleagues have evaluated the autocorrelation of seismic noise from a single station in Antarctica and see promising results for the ice-structure from one month of data. However, there is still much work to be done if NASA is to be pre-eminent in developing *in situ* techniques for outer planet missions, in particular those of Titan. KISS funding would allow Caltech and JPL to develop novel approaches and emerge as leaders in the field.

5. Conclusions

5.1. Study evaluation

We have found this KISS study, comprised of two workshops interspaced with a study period, to be remarkably strategic and productive. With data still pouring in from Cassini and the next Discovery class mission to Titan in the works, the timing for this study was ideal to generate revolutionary technologies for the next generation *in situ* mission.

Although it may have seemed unconventional to some at the beginning of the study, having an interdisciplinary team with experts ranging from geology and materials science to electronics and chemistry, was a significant contributor to the success of this study. Together our study team was able to form a complete and comprehensive picture of the challenges involved with operating on the Titan surface, and the technological revolutions necessary to address these challenges. Regardless of the questions posed or the directions the discussions took, we always had an expert of that subject present.

We discovered that having two workshops as opposed to one was an excellent format for this study. The first workshop allowed all participants to come up to speed with the scientific and technical issues and the second workshop allowed us to further develop specific goals and ideas identified in the first workshop, with the interim time used for brainstorming, modeling and experimentation. We recommend this model for future KISS studies, in particular those involving mission concept design and technology developments.

Another aspect we found beneficial in this study was the inclusion of young scientists and engineers as part of the study team. The graduate students and postdoctoral fellows who participated in the workshops provided valuable contributions in coming up with revolutionary ideas for Titan surface science. In addition, we hope that the exposure to such a progressive forum with the top minds in the field will inspire these young scientists to excel in the future.

5.2. Concluding remarks

Titan is an incredibly complex and dynamic world. The data sent back by the Cassini-Huygens mission has enhanced our ability to model the atmosphere, but we still know very little about what happens on the surface. We need to return to Titan with innovative experiments that enable an *in situ* mission. These revolutionary technologies must be robust and versatile to meet the unique demands of the Titan environment, whether we focus on the lakes, dunes, putative cryovolcanic flows or icy regolith.

The KISS study allowed us to consider new possibilities. In the past ESA has been responsible for Titan *in situ* experiments. This study allowed us to think deeply about the technical issues involved in meeting the scientific goals of a future mission where NASA might take the lead in that scientific arena. The conclusions of this KISS study were often unexpected and some had not been previously been considered:

1. ***Solution State Nuclear Magnetic Resonance is a perfect instrument for non-destructive identification of organic functional groups because it works better under Titan conditions.***

   Such an NMR would satisfy the design challenge of providing “out of the (thermal) box” analytic instrumentation that would actually benefit from the low temperature surface conditions of Titan. The critical design issue for the proposed NMR is the fabrication of the permanent solenoid magnet.

2. ***A Sample Processing Unit, comprised of a Sample Bus and a Miniaturized Chemical Laboratory, can provide the ability to perform automated complex movement of samples between instruments as well as provide separations and extractions.***

   The Sample Processing Unit (SPU) is capable of functioning both as an instrument (mini chem lab) and a sample transfer system. The low power requirements and high sensitivity of this device makes it ideal for a landed mission. As an analysis tool, the SPU is able to perform wet chemistry *in situ*, such as dilutions, labeling reactions and chromatographic separations, which can help us form a more complete picture of the chemistry occurring on the surface of Titan. As a sample transfer system, the SPU can be easily coupled to a cryogenic sampler for fluidic transfer to/between instruments, such as the solution state NMR, mini chem labs and high resolution mass spectrometer.

3. ***Advances in high resolution, high sensitivity Mass Spectrometry have enabled a path for simplifying the overall complexity of a chemical analysis suite by eliminating the need for complicated gas chromatography.***

   Mass spectrometry has long been identified as the key technique for complete chemical analysis of complex surface organic species on Titan. However, obtaining the mass resolution and sensitivity required to accomplish this goal within the mass and power constraints has been elusive. However, it is now within the realm of possibility. A laboratory-based technique, the orbitrap, is now routinely used to obtain mass resolution of $\geq 10^5$ and has been shown to be capable of teasing apart Titan organic stimulants without the use of a gas chromatograph. This simplifies the instrument system and with the flight demonstration of a Paul ion trap, which can be used as an injection system, the path to developing a flight instrument is now clear, although some challenges in obtaining the ultra-high vacuum still remain.

4. ***Physical measurements of aerosols in Titan's atmosphere are possible even if they differ from those in common use in Earth atmosphere measurements.***

   Key questions can be answered by two well-established measurement methods; electrical mobility analysis and optical scattering. From these we can learn the size distribution of the aerosol particles, how the clouds are formed, the optical properties of the aerosol and whether the aerosols undergo any physical transformations. A model was developed during the study to explore charge distributions under conditions of the Titan atmosphere, which should be applicable to other planetary atmospheres. Future work is needed to ensure that the measurement sensitivities are possible and to develop these instruments for use in the Titan environment.

5. ***A single Seismometer is closer to being possible for studying the interior and dynamic surface processes of Titan than we had thought.***

   While the concept of using one seismometer to study planetary interiors and dynamic surface processes was recognized amongst all the participants of the second workshop as a potentially "revolutionary" concept, it still must be demonstrated within the seismological community. As a true success of the KISS geophysics study group's efforts and the second workshop, much more focus and attention has been put on this concept -- an action that would not have happened without the hard efforts of everyone involved over the last few months within the KISS framework. Even within the seismological community, this concept is relatively new, but the team felt the research behind this technique should continue with Titan in mind.

6. ***Designing electronics that perform well at 95K is possible and progress has been made in recent years, but developing low power circuits that meet the demands of many of the in situ instruments at these low temperatures is still a work in progress.***

   To reduce mass and power, all the instruments described above benefit from electronics that can function at ambient Titan temperatures. Circuit building blocks and the corresponding low T integrated circuit design infrastructure have been designed for application-specific electronics e.g. for amplification of sensor signals, sample acquisition and drive-and-control of motors. However, for ultra-low power electronics at those temperatures, SiGe-based technology will not yet support the micro-power operation and the signal-to-noise ratio requirements of the instruments. New developments are required to develop such methodologies.

7. ***Light weight power sources continue to be a major challenge for long-lived landed missions to Titan***

   To support long-life missions to Titan, a fresh look at emerging power technologies may be needed. For example, parallel arrays of small size modular radioisotope power sources could produce higher power levels. These small devices may not require large radioisotope sources and could become a critical component of smart power systems. At the system level one may also be able to take advantage of power-aware electronics, which use a small power source to run essential keep-alive functions of the mission and to trickle charge an energy storage system with rechargeable energy storage elements to momentarily support applications with higher power demand.

8. ***Possible packaging materials for long-lived, low temperature in situ Titan missions are available, but design of substrates and the characterization and testing of novel materials is critical.***

   Ceramics, polymers and metals all have lifetime difficulties at Titan surface temperatures. However, solutions to overcome these difficulties were proposed by the team members, which now need to be developed and tested. In addition, over the past five years significant attention has shifted to vertically oriented carbon nanotube (CNT) arrays (a.k.a. CNT forests, mats, or films) as promising packaging materials that have been demonstrated to produce thermal contact resistances that compare favorably to state-of-the-art materials. The benefits of these CNT materials is that they operate over a large temperature range, are chemically stable, effective absorbers of mechanical energy, have low thermal interface resistance and high mechanical compliance. Two groups within the study team started working together to study the deformation mechanics of CNT arrays fabricated by one of the groups. Continued work in this area has the potential for providing promising packaging materials that could be used for Titan electronics.

The extreme complexity of the chemistry on Titan forces us to innovate. Novel techniques must be cultivated to address the physical challenges of these environments while providing robust, sensitive chemical analysis. We believe the revolutions in NMR spectroscopy, mass spectrometry, aerosol analysis and mini chem. lab technologies outlined here will establish the necessary analytical arsenal to fully investigate the chemistry of Titan. Novel power and electronics will relieve the need for Earth-like conditions within the spacecraft power and electronics housings. Bold use of cutting edge materials such as carbon nanotubes will enable new capabilities at the surface of Titan. Continued examination of geophysical techniques to explore Titan's interior without multiple networked stations is crucial given the distance to Titan and the consequent expense per kilogram of launch weight. However, although the novel geophysical techniques are important to explore (and the research should continue), it became apparent from this study that, at this present point in time, developing low mass, low power chemical analysis system for novel Titan missions would be more valuable. It is through characterization of the chemistry of Titan that we may begin to understand this mysterious moon.

Acknowledgements

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Appendix A: Workshop agendas

Workshop 1 – May 25-28, 2010

Tuesday, May 25th: Short Course; Instruments				
Time	**Event**			**Speaker**
8:00 - 8:30	Coffee and refreshments			
Start of Short Course in Hameetman				
8:30 - 8:45	Welcome and brief introduction			
8:30 - 12:00	Short Course on Planetary Science of Titan			Jonathan Lunine
	8:45 - 10:30: Basic Characteristics of Titan 10:30 - 11:00: Break 11:00 - 11:30: Key questions about Titan and classes of measurements 11:30 - 12:00: Q&A on Titan and group discussion			
12:00 - 1:00	Sandwich lunch provided by KISS			
Start of Workshop in Millikan Building, 6th Floor				
1:00 - 1:30	Check-in for Titan participants			
1:30 - 2:00	Introduction to the Keck Institute, logistics			Tom Prince Michele Judd
2:00 - 2:30	Goals of workshop			
2:30 - 3:00	Introduce yourselves			
3:00 - 3:30	Break			
3:30 - 5:45	Plenary on Sampling Instruments & Science			Convener: Mohammad Mojarradi
	Approximate order: presentations (~10min each) with discussion on: Lab-on-a-Chip (P. Willis), overview of GC-MS and chemistry instruments (J. Beauchamp), complex organic chemistry (M. Smith), constraints & necessary science goals (P. Beauchamp)			
6:00 - 8:00	KISS Reception on lawn at the Athenaeum			
Wednesday, May 26th: Sample Handling				
Time	**Event**			**Speaker**
8:00 - 8:30	Coffee and refreshments			
8:30 - 10:00	Plenary on Extraterrestrial Sample Handling Overview			Convener: Jennifer Jackson
	Approximate order: presentations (~10min each) with discussion on solids (G. Cody), liquids (R. Hodyss), gases (R. Flagan)			
10:00 - 10:30	Break			
10:30 - 12:30	Air Team	Sea Team		Land Team
	1, 2) Compile list of open science issues in this domain from Short Course & Plenary; Brainstorm measurements. 3) Compile list of instruments to address measurements	1, 2) Compile list of open science issues in this domain from Short Course & Plenary; Brainstorm measurements. 3) Compile list of instruments to address measurements		1, 2) Compile list of open science issues in this domain from Short Course & Plenary; Brainstorm measurements. 3) Compile list of instruments to address measurements
12:30 - 2:00	Buffet lunch at the Athenaeum provided by KISS			
2:00 - 4:00	Plenary on Materials & Technologies			Convener: Peter Willis
	Approximate order: presentations (~10min each) with discussion on materials (J.R. Greer), electrical systems (M. Mojarradi), Future of Low T electronics (J. Cressler)			
4:00 - 4:30	Break			

4:30 - 5:00	4) Formulate Sampling Approaches (if needed) for Instruments	4) Formulate Sampling Approaches (if needed) for Instruments	4) Formulate Sampling Approaches (if needed) for Instruments
5:00 - 5:45	Reconvene for group discussion		
6:00 - 7:30	Dinner at the Athenaeum		
8:00 - 9:00	Public Lecture in Hameetman Auditorium, Cahill Building		Oded Aharonson
Thursday, May 27th: Titan Missions			
Time	**Event**		**Speaker**
8:00 - 8:30	Coffee and refreshments		
8:30 - 10:30	Plenary on Titan Missions		Convener: Jonathan Lunine
	Presentation on TSSM and other mission architectures (K. Reh, ~30min); Titan Mare Explorer "TiME" (O. Aharonson, ~10min) followed by discussions		
10:30 - 11:00	Break		
11:00 - 12:30	Mini presentations with discussion		
	Approximate order: solid handling (W. Zimmerman, ~10min) and liquids (A. Hayes, ~10min) Interim Missions to a Simulated Titan: Group Discussion on the Design of a Standardized Titan Planetary Simulator Testbed		
12:30 - 2:00	Lunch on your own		
2:00 - 3:30	5) Identify Science and Tech Hurdles for Measurements/Sampling Approaches	5) Identify Science and Tech Hurdles for Measurements/Sampling Approaches	5) Identify Science and Tech Hurdles for Measurements/Sampling Approaches
3:30 - 4:00	Break		
4:00 - 6:00	6) Formulate R&D approaches to address needs and summarize all results	6) Formulate R&D approaches to address needs and summarize all results	6) Formulate R&D approaches to address needs and summarize all results
6:00 - 8:00	Southwestern Dinner Buffet on lawn at the Athenaeum		
Friday, May 28th: Planning for Future Titan Exploration			
Time	**Event**		**Speaker**
8:00 - 8:30	Coffee and refreshments		
8:30 - 10:00	Compile and Organize Results	Compile and Organize Results	Compile and Organize Results
10:00 - 10:30	Break		
10:30 - 11:00	Group summary presentation: Air Team		Richard Flagan
11:00 - 11:30	Group summary presentation: Sea Team		Patricia Beauchamp
11:30 - 12:00	Group summary presentation: Land Team		George Cody
12:30 - 2:00	Buffet lunch at the Athenaeum provided by KISS		
2:00 - 3:30	7) Putting it all together: Formulation of tech development strategies, wrap up & team assignments		Mohammad Mojarradi
3:30 - 3:45	Checkout logistics		Michele Judd
4:00	End of Study		

Workshop 2 – November 1-4, 2010

Monday, November 1st		
Time	**Event**	**Speaker**
8:30 - 9:00	Coffee and refreshments	
9:00 - 9:10	Welcome and brief overview of logistics	Michele Judd Tom Prince
9:10 - 9:30	Keck Phase II proposal process and guidelines	Michele Judd Tom Prince
9:30 - 10:30	Discussion of the process, outcomes and expectations and for the workshop	Jennifer Jackson Mohammad Mojarradi
10:30 - 11:00	Break	
11:00 - 11:45	Discussion continued...	Jennifer Jackson Mohammad Mojarradi
12:00 - 1:30	Buffet lunch at the Athenaeum provided by KISS	
1:30 - 2:00	Seismology Talk	Jennifer Jackson
2:00 - 2:30	Seismology Talk	Christophe Sotin
2:30 - 3:00	Seismology Talk	Zhongwen Zhan
3:00 - 3:30	Break	
3:30 - 4:00	Seismology Talk	Harish Manohara
4:00 - 4:30	Seismology Talk	Oded Aharonson
4:30 - 5:45	Discussion	ALL
6:00 - 8:00	KISS Reception at the Athenaeum	

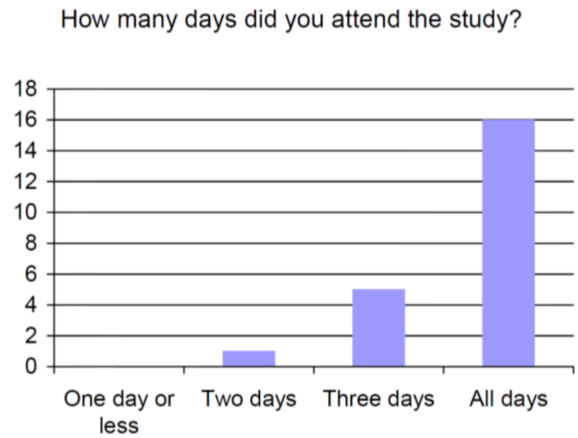
Tuesday, November 2nd		
Time	**Event**	**Speaker**
8:30 - 9:00	Coffee and refreshments	
9:00 - 9:30	Orbitrap	Evan Neidholdt
9:30 - 10:30	NMR	George Cody Soon Sam Kim
10:30 - 11:00	Break	
11:00 - 11:45	Lab-on-a chip	Peter Willis
12:00 - 1:30	Buffet lunch at the Athenaeum provided by KISS	
1:30 -3:00	Assess what is needed to bring each technique/theme up to TRL 5 or 6 (sample handling, etc);	Facilitator: Peter Willis
3:00 - 3:30	Break	
3:30 - 5:45	Homework for theme selection	Facilitator: Peter Willis

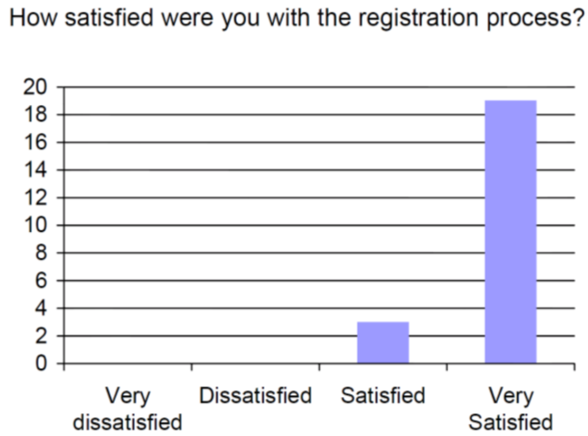
6:00	Mijares Mexican Restaurant - Cash dinner, spouses are invited. All participants are encouraged to attend. Michele to pay for all grad students and postdocs.	

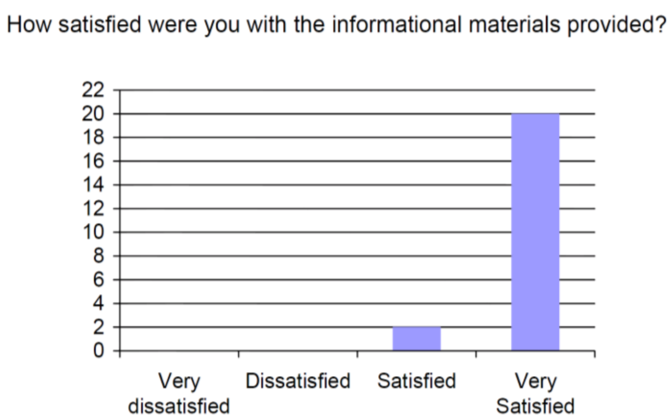
Wednesday, November 3rd		
Time	**Event**	**Speaker**
8:30 - 9:00	Coffee and refreshments	
9:00 - 10:30	Discuss and select theme for Keck Phase II proposal	Facilitator: Peter Willis
10:30 - 11:00	Break	
11:00 - 11:45	Discussion continued...	Facilitator: Peter Willis
12:00 - 1:30	Lunch on your own	
1:30 - 3:00	Electronics/power: Decide on key technologies to be included in a Phase II proposal based on science theme.	Facilitator: Mohammad Mojarradi
3:00 - 3:30	Break	
3:30 - 5:45	Continued...	Facilitator: Mohammad Mojarradi
6:00 - 8:00	KISS Dinner Buffet at the Athenaeum - Spouses, Significant Others are welcome (sign them up on Monday at the workshop)	

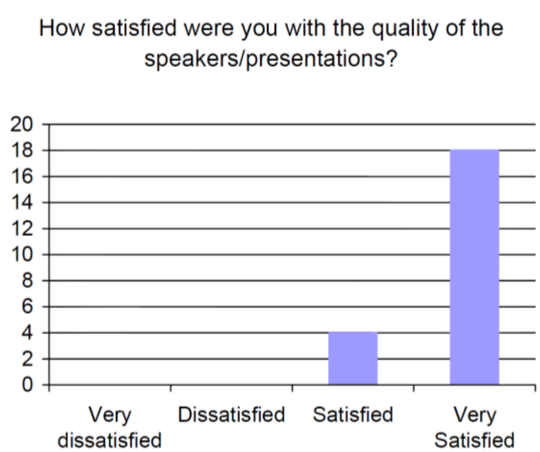
Thursday, November 4th		
Time	**Event**	**Speaker**
8:30 - 9:00	Coffee and refreshments	
9:00 - 10:30	Materials and packaging: Discuss specifics in the context of a Phase II proposal.	Julia Greer
10:30 - 11:00	Break	
11:00 - 11:45	Conclude Workshop	Jennifer Jackson
11:45 - 12:00	Checkout logistics	Michele Judd
12:00	End of Study	

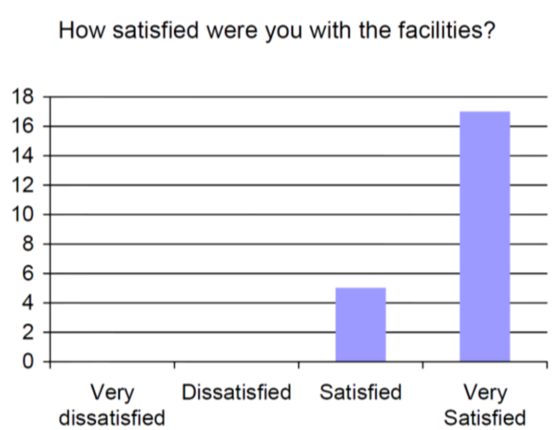
Appendix B: Workshop survey results

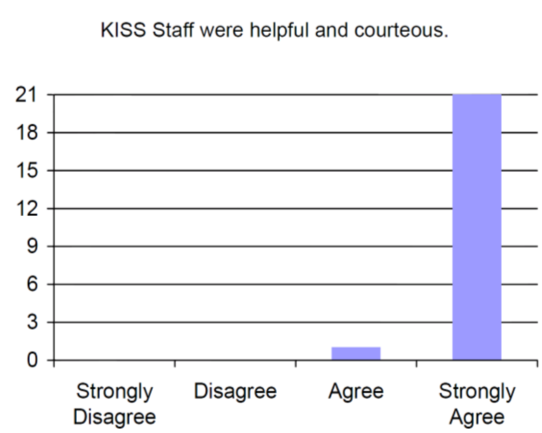








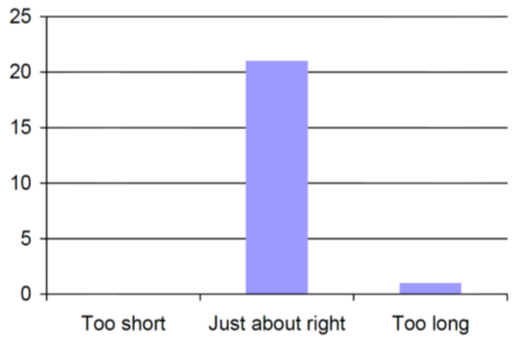




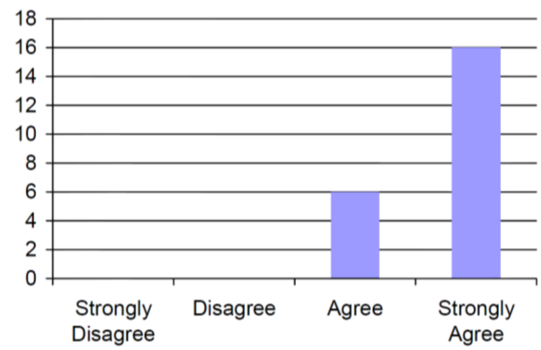
Open comments regarding Institute facilities:

- I thought the location (and view) were phenomenal. I enjoyed that the area was small enough so that people were close together. On the other hand, if the location could be perfect - I would remove the elevators and the bathrooms from the center of the floor so that the two ends of offices were not separated by any barriers.
- It would be nice if there were better chairs or a larger variety of chairs in the study room. I know multiple attendees had back problems that resulted in some of them being extremely uncomfortable or even standing rather than sitting.
- It would be nice to have an easel for large format paper charts.
- The office and seminar rooms are quite well equipped and nice for interactions.
- Seems to work well.
- Having an office was a nice a touch, and more useful than I thought it would be. Seating in the conference room was a little tight...a bit more room would be nice.
- Having Break rooms to interact with other participants was very conducive to building a team environment.
- It was especially nice being centrally located on the Caltech campus. Also, having shared office space worked out very well and helped foster collaboration.
- I loved it there!
- I really, really enjoyed the Millikan location - especially the break room with a gorgeous view. The seminar room was OK but it would be nice if it had some standing workstations - like maybe a couple of tall tables. This would be really helpful for people with bad backs who prefer to stand. I ended up standing by the wall, and people were tripping on my computer wire as they were exiting the room. (Otherwise, the facility was perfect!)
- Need more whiteboards in the conference room.
- I particularly liked the room with the sofas and comfortable chairs. It was nice during the session breaks to take a load off, sip some coffee and enjoy the view of the mountains!
- Good supply of munchies and coffee - actually critical to prevent people wandering off to Starbucks. Email policy is challenging (did indulge in checking incoming mail but tried to avoid replying during sessions). The fact is people always have fires to put out. Maybe you should jam the wireless signal in the room...
- Certainly the offices with windows were very nice. So was the break room. Very comfortable. I have already sent specific suggestions about the meeting room in my earlier email to Tom and Michele.
- The facility worked well.
- The general layout provided a very stimulating environment.

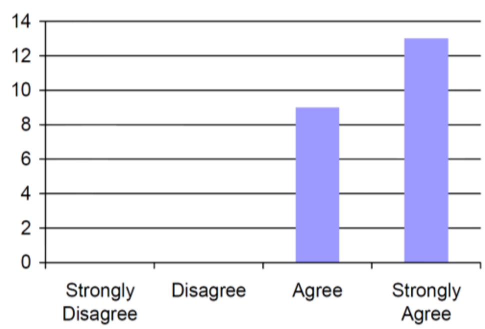
Did you feel the length of the study was too long, just about right, or too short?



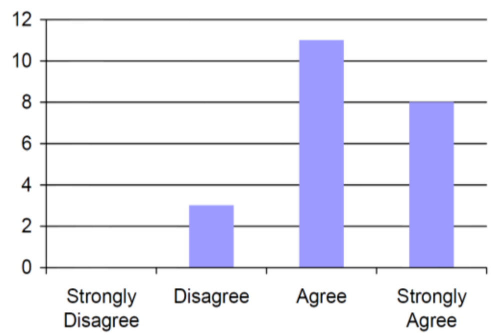
The content of sessions was appropriate and informative.



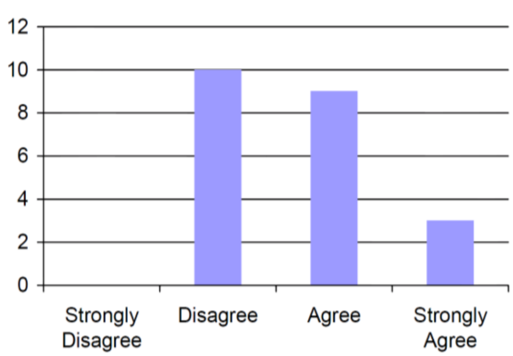
There was good representation at the workshop by the various industries, agencies, organizations and academia involved in this work.



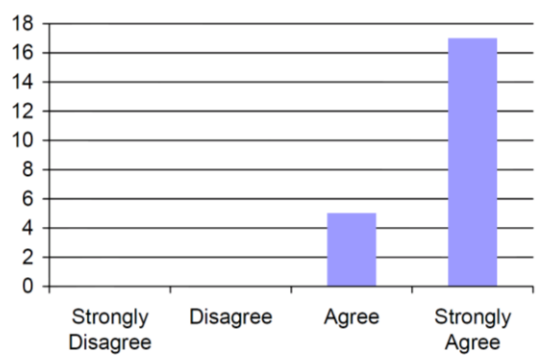
There was enough time allotted during the study for informal discussion and interaction.

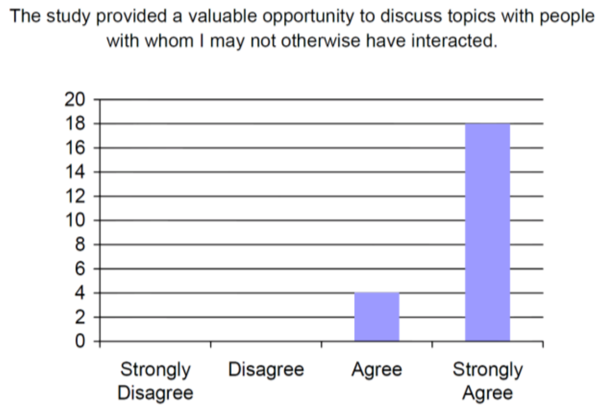


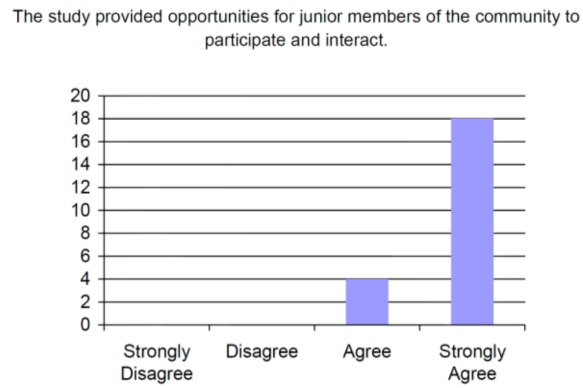
There was enough "open" time during the study for solo study time.

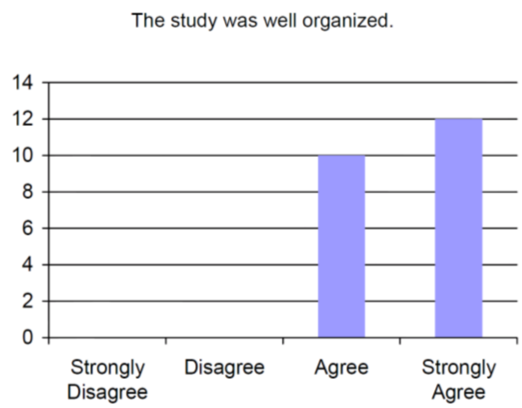


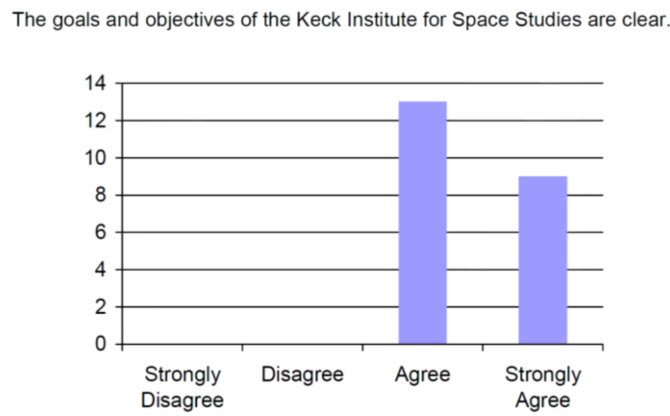
The group meals are important opportunities for informal interaction.











What was the most valuable aspect of the study?

Diversity of Participants

- Getting people from a variety of fields to talk to each other about the goals of Titan exploration and the numerous roadblocks to achieving those goals.
- Interacting with so many people that I had never met, in such a fascinating field that I am only now learning about.
- The close, informal interactions with such a diverse and extremely talented workshop participants.
- Meeting and interacting with amazing colleagues not in my field of study. Michele was also a terrific organizer, mentor, and leader. I am so grateful for this opportunity - although now that we are all so invested in it - it's going to take some hard work!
- As a new postdoc, the most valuable aspect for me was to interact with so many influential people over such a long period of time. By the end of the study, I felt I knew them well, and I learned so much about Titan!
- The opportunity to engage with Low-T electronics people and analytical chemists, disciplines I do not normally encounter.
- Information exchange between members of the Titan community who otherwise tend to work in isolation.

- The interdisciplinary interactions.
- Meeting people that I would not have otherwise met, with the strong potential for future collaborations in a field that is not currently one that I have been involved with in the past.
- Having all the primary individuals involved in Titan research and mission design in one place at the same time.

Topics of Discussion

- The exposure to all the aspects of a Titan mission especially the people involved with developing said ideas.
- Exposure to a wide variety of issues for a future mission to Titan, coupled with an opportunity to directly interact with other scientists. This resulted in expanding my perspective on designing exploration approaches for Titan (e.g. use of low temperature electronics and other components).
- This study provided opportunities to hear many views from many vantage points and to explore the challenges of the measurement campaign that was discussed.
- Understanding the significance of Titan mission and the challenges to overcome. Interacting with recognized authorities to develop technology concepts for the future Titan mission.

Workshop Format

- Plenary brainstorming with represents of multiple disciplines.
- The structured meeting of the minds on a difficult issue.
- I answered ' disagree' with question #12 because that was not the purpose of this workshop. That is what we will do between Workshop 1 and Workshop 2. This workshop was to get everyone up to speed and working off the same page. This is not a negative.
- The ability to closely interact with people over a several day period.

In what ways could this study have been improved?

Organization of Study

- The study could have been shorter. It is unclear how that would be possible with that many attendees/information.
- A bit more organization from the start. It wasn't until day three that I felt things started coming together. After day two I wasn't sure what our goals were. I also felt that people kept stressing "out of the box" thinking, while not actually allowing it to happen. Ideas were shot down rather quickly, and that may have suppressed additional creative thinking.
- I would have liked a more formal product to have emerged at the end of the study.
- Provide more concrete action items for the next few months of the study.
- Possibly an inevitable consequence of (1) the breadth of participants and (2) the intent to generate out of the box ideas, but more background on Titan fundamentals and what mission studies have been pursued and what factors

constrained them might have focussed the discussion a little more. But maybe I'm jaded by having done this stuff too long - the discussion was refreshing, at least.

- This study was a bit awkward in the sense that KISS wants to fund studies where we "don't know the answer" but a Titan in situ mission has received so much attention from other studies that many people think we know the answer already. This tension was never completely resolved, I think, and impeded efforts to focus the workshop. More clear direction at the outset could have avoided that confusion.
- In retrospect, it would have been very informative to have someone dealing with the "power problem" first hand. I will try to address this for the final workshop.

Lack of Independent Study Time

- I would have liked a bit more personal time. We had wonderful offices, but I never had the chance to use it! Also, having a computer nearby with internet access would have been nice. I left my laptop at home so I wouldn't be distracted, but I would have liked the opportunity to check my email during the breaks.
- The study was really great! Some allocation of independent study time to prepare for following sessions would have helped people like myself who are new to the problems of a Titan mission. But, overall, this was really a good experience for me.

Timing of Workshop

- Initially, I had no clue about the nature of the workshop. This made it quite challenging to decide what to present. Consider the academic calendar in scheduling the workshop. End of term is a very busy time.

Facility and Food

- Standing up tables in the workshop room + more healthy snacks (the fruit was good but the rest of the snacks - not so much...)
- Smaller tables at lunch for more interactions.

Miscellaneous

- I thought this workshop went very well and achieved what we need to do. I think the critical time is the period between workshops and keeping the momentum going.
- I don't know of any obvious ways to have improved on this study.

Appendix C: Workshop participants

Leads

Julia R. Greer
Assistant Professor, Materials Science and Mechanics
California Institute of Technology

Jennifer M. Jackson
Assistant Professor, Seismological Laboratory
California Institute of Technology

Jonathan I. Lunine
Professor, Physics
University of Rome, Tor Vergata

Mohammad M. Mojarradi
Group Supervisor, Instrument Electronics and Sensors
Jet Propulsion Laboratory, California Institute of Technology

Participants

Oded Aharonson
Associate Professor, Geological and Planetary Sciences
California Institute of Technology

Patricia M. Beauchamp
Strategic Missions and Advanced Concepts Office
Jet Propulsion Laboratory, California Institute of Technology

Jesse L. Beauchamp
Professor, Chemistry
California Institute of Technology

Benjamin J. Blalock
Associate Professor, Electrical Engineering and Computer Science
University of Tennessee

George D. Cody
Senior Staff Scientist, Geophysical Laboratory
Carnegie Institution of Washington

John D. Cressler
Ken Byers Professor, Electrical and Computer Engineering
Georgia Institute of Technology

Richard C. Flagan
Professor, Chemical Engineering
California Institute of Technology

Jeffery L. Hall
Senior Engineer
Jet Propulsion Laboratory, California Institute of Technology

Robert P. Hodyss
Planetary Ices Group
Jet Propulsion Laboratory, California Institute of Technology

Paul M. Holland
President
Thorleaf Research, Inc.

R. Wayne Johnson
Professor, Electronics and Computer Engineering
Auburn University

Elizabeth Kolawa
Instruments Electronics and Sensors Section
Jet Propulsion Laboratory, California Institute of Technology

Ralph D. Lorenz
Applied Physics Laboratory
Johns Hopkins University

Harish M. Manohara
Technical Group Supervisor, Instrument Electronics and Sensors
Jet Propulsion Laboratory, California Institute of Technology

Kim Reh
Program Manager, Solar System Exploration Directorate
Jet Propulsion Laboratory, California Institute of Technology

Rocco Samuele
System Engineer, Integrated System Engineering
Northrop Grumman Aerospace Systems

Andrew A. Shapiro
Division Technologist, Enterprise Engineering
Jet Propulsion Laboratory, California Institute of Technology

Mark A. Smith
Professor, Chemistry and Biochemistry
University of Arizona

Wolfgang Sturhahn
Senior Technologist, Instrument Systems Implementation and Concepts
Jet Propulsion Laboratory, California Institute of Technology

Peter A. Willis
Senior Engineer, Microdevices Lab
Jet Propulsion Laboratory, California Institute of Technology

Wayne F. Zimmerman
Chief Engineer, Instruments and Science Data Systems Division
Jet Propulsion Laboratory, California Institute of Technology

Postdocs

Morgan L. Cable
Postdoctoral Fellow, Microdevices Lab
Jet Propulsion Laboratory, California Institute of Technology

Bin Chen
Postdoctoral Scholar, Geological and Planetary Sciences
California Institute of Technology

Graduate students

Alexander G. Hayes
Ph.D. Candidate, Geological and Planetary Sciences
California Institute of Technology

Sarah M. Horst
Ph.D. Candidate, Lunar and Planetary Laboratory
University of Arizona

Andrew T. Jennings
Ph.D. Candidate, Materials Science
California Institute of Technology

Appendix D: Proposals

Planetary Instrument Definition and Development Proposal (PIDDP)

Principle Investigator: Peter Willis

Title: Definition and Demonstration of a Titan New Frontiers Chemical Analysis Instrument Suite

Relevance to KISS study

This proposal was written as a direct result of discussions and collaborations initiated during the KISS workshops. Some of the work performed as described in this proposal that aligned with the KISS interim study period was reported during the second workshop and had a constructive impact on discussions of surface chemical analysis and instrumentation.

Executive Summary

We propose to define an in situ chemistry instrument package that will enable future New Frontiers mission robotic explorers on Titan to compile detailed chemical inventories of complex organic materials present in Titan's atmosphere, lakes, shorelines, dunes, and cryovolcanic flows. The complex methanological, photochemical, and geological processes taking place in Titan's reducing environment produce a wealth of condensed phase and solid macromolecular organic materials present in atmospheric aerosols and also as surface deposits. In a very real sense, the complex planetary processes at play on Titan are "encoded" into these materials at the molecular level. However, at present, even here on Earth, we do not even have a comprehensive approach for analyzing these complex materials in order to acquire this information. Therefore, using tholins (i.e. laboratory-generated Titan organic simulants) as the starting materials for analysis, we will develop end-to-end, flight-automatable methods for performing detailed compositional, elemental, and isotopic analyses *in situ*. We will benchmark our methods against pyrolysis GC-MS, which is the current state-of-the-art for analysis of complex organics. The Aerosol Collector and Pyrolyser (ACP) system on the Huygens probe to Titan was designed to utilize this technique, by collecting and pyrolysing organic aerosol particles during descent, and then sending the pyrolysis products to a GC-MS for analysis. Pyrolysis GC-MS was also specified as the primary organic analysis method in the Titan Saturn System Mission (TSSM) study as well as the Titan Lake Probe (TLP) Decadal survey study. However, we believe pyrolysis GC-MS is inherently limited in its ability to analyse tholins, since complex inter- and intra-molecular reactions occur in the material during heating. This leads to drastic chemical alteration of the sample and confounds our ability to recreate the parent structure from a consideration of the fragments. We posit here that liquid extraction prior to analysis gives rise to a much clearer chemical picture of the chemistry of Titan.
The philosophy behind our proposed liquid analysis approach is to gradually dismantle the original sample and analyze the chemical state at each step along the way. The original solid sample is subjected to a series of increasingly powerful liquid extractions. Liquid samples from each extraction step are analyzed using state-of-the-art experimental methods existing in the laboratories of the experimenters, as well as microfluidic lab-on-a-chip systems under development at JPL. Different methods are used to acquire different levels of understanding of a sample. Commercial high-resolution mass spectrometry and NMR instruments at University of Arizona will be used as gold standard analyses in the development of our instrumental protocol. In the end, the entire sample has been consumed and analyzed chemically. By consolidating all the data sets together, a detailed inventory of species present in the original sample can be reconstructed. We will compare these chemical data sets to those originating from tholins via

pyrolysis GC-MS. This information is absolutely necessary in order to rationally design a chemical analysis instrument suite for chemical exploration of Titan. In particular, this analysis will enable us to determine if liquid extraction is required for the most detailed measure of Titan chemistry (which we posit) or if solid-based MS techniques alone will suffice. The final product of this proposal will include, thus, a simplified analysis protocol and proposed instrument for future, higher TRL level development. This instrument definition will also contain a list of descopes and the effect of each descope option upon the scientific return of a flight instrument capable of unlocking the fundamental planetary science that dictates the past, present, and future of Titan.

Appendix E: References

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