Chapter 9: Sample handling and instruments for the in-situ exploration of ice-rich planets

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9.1 Introduction

NASA's key science goals for the exploration of the solar system seek a better understanding the formation and evolutionary processes that have shaped planetary bodies and emphasize the search for habitable environments. Efforts are also made to detect and quantify resources that could be used for the support of human exploration. These themes call for chemistry and physical property observations that may be best approached by in situ measurements. NASA's planetary missions have progressively evolved from remote reconnaissance to in situ exploration with the ultimate goal to return samples. This chapter focuses on the techniques, available or in development, for advanced geophysical and chemical characterization of icy bodies, especially Mars polar areas, Enceladus, Titan, Europa, and Ceres. These astrobiological targets are the objects of recent or ongoing exploration whose findings are driving the formulation of new missions that involve in situ exploration.

After reviewing the overall objectives of icy body exploration (Section 9.1) we describe key techniques used for addressing these objectives from surface platforms via geophysical observations (Section 9.2) and chemical measurements (Section 9.3).

9.1.1 Science Rationales for the Exploration of Mars' Polar Regions

Mars is the 4th planet from the Sun, the 2nd smallest planet in the Solar System, after Mercury, and it is a neighboring body to Earth. It was named after the Roman god of war, and it is also known as the "Red Planet" because of its reddish appearance resulting from form the iron oxide that is prevalent on its surface. Polar temperature ranges from −143°C to -125°C and operating on its surface requires the use of mechanisms that can tolerate low temperatures. Its surface contains thin atmosphere with a pressure of about one-hundredth of Earth's atmosphere and it is filled with impact craters, and the volcanoes, valleys, deserts, and polar ice caps. Its rotational period and seasonal cycles are somewhat similar to those of Earth, as is the axial tilt that produces the seasons. For its potential of harboring life in some form including extinct, Mars has been one of the most attractive bodies for planetary exploration. This includes the five orbiting spacecraft: 2001 Mars Odyssey, Mars Express, Mars Reconnaissance Orbiter, MAVEN and Mars Orbiter Mission; and the landed missions: Mars Exploration Rovers Spirit and Opportunity, Phoenix lander, and the Mars Science Laboratory Curiosity. In particular the Phoenix mission deployed a lander at high-latitude where ice was found as well as perchlorates [Hecht et al. 2009]. Several missions [e.g., Ice Breaker by McKay et al. 2015; Cryobot by Aharonson et al. [http://web.gps.caltech.edu/~oa/simulations.shtml] have been proposed to gain further insight into the structure of Mars polar caps and their isotopic makeup. The latter can help constrain the origin of Mars' ice, which bears implications to constrain the origin of Earth's water and organics.

9.1.2 Enceladus Exploration

Saturn's Moon Enceladus was discovered in 1789 by William Herschel. Enceladus is only about 500 kilometers (310 mi) in diameter and has been extensively studied, first by the two Voyager spacecraft that passed nearby in the early 1980s, and more recently, since 2004, by the Cassini-Huygens Mission. Enceladus' surface reflects almost all the sunlight that strikes it and it is mostly covered by clean ice with a surface temperature as low as −198 °C. In 2005 the Cassini orbiter discovered a water-rich plume venting from Enceladus's South Polar Region. Large rifts located around the South pole, called "Tiger Stripes" shoot geyser-like jets of water vapor, other volatiles, and solid material, including sodium chloride crystals and ice particles, into space, at approximately 200 kilograms (440 lb) per second [Hansen et al. 2006]. More than 100 geysers have been identified [Porco et al., 2015] whose activity is driven by the tidal stress exerted by Saturn. Some of the water vapor falls back as "snow", whereas the rest escapes, and may be the source of most of the material making up Saturn's E ring [Kempf et al., 2008]. The heat production inferred from surface temperature measurements at the Tiger Stripes is about 15 GW [Spencer and Nimmo 2013] has not been explained yet. Further, in 2014, Cassini data provided evidence for a large south polar subsurface ocean of liquid water within Enceladus with a thickness of around 10 km [Iess et al., 2014]. These observations make Enceladus a major target for in situ exploration with focus on the South Polar Region and sampling of the plumes by geochemistry instruments during high-velocity flybys [Lunine et al. 2015]. Landers for Enceladus exploration have been proposed [e.g., Konstantinidis et al. 2015] that could help further the assessment of Enceladus' habitability potential.

9.1.3 Titan's Surface Exploration

Saturn's largest satellite Titan was discovered by Christiaan Huygens in 1655 and the fact that it had an atmosphere was established by Kuiper in 1944, who detected absorption bands due to methane at infrared wavelengths from ground-based observations. Sixty years later the Cassini-Huygens mission unveiled Titan's complex world very much akin to Earth in many regard but shaped by the cycle of hydrocarbons and especially methane.

Decades of modeling efforts, validated by ground-based, and spacecraft observations (*Voyager I*, 1980, and *Cassini-Huygens*, since 2004), elucidated the complex chain of UV-induced photochemical reactions that take place in the atmosphere and the rates at which they proceed [e.g. Yung et al., 1984; Coustenis et al., 1991; Coustenis et al., 2003; Wilson and Atreya, 2004; Lavvas et al., 2008]. Using these constraints, Lavvas et al. [2008] established a refined photochemistry model of the atmosphere, and Cordier et al. [2009] used the outputs to estimate the fluxes of photochemical products to the surface. This information establishes two essential starting points about Titan: 1) the dominant products of the photochemistry are *ethane* C_2H_6 *and propane* C_3H_8, which are in *liquid state* at Titan's surface conditions (1.5 bar of N_2, 92-94 K); 2) the higher molecular weight compounds would be in the solid state on the surface, where they may form the observed dunes [e.g. Lorenz et al., 2008), and/or contribute to evaporitic materials tentatively detected by the VIMS instrument [e.g. Barnes et al., 2011]. These solid organic compounds are thus expected to form a blanket cover on the presumed water ice bedrock. A recent study discusses the possibility of the emergence of a form of life not based on liquid water in Titan's hydrocarbon lakes [Stevenson et al., 2015].

Titan, and particularly its lakes, has been identified as a high-priority target by the NRC Planetary Science Decadal Survey "Visions and Voyages" for 2013-2022. Several mission concepts have been suggested for the follow-on exploration of Titan with focus on the habitability potential of its surface and subsurface. The Titan and Saturn System Mission concept developed in 2008 [Coustenis et al., 2009] introduced an architecture involving an orbiter, balloon, and surface element. More recent concepts have focused on landers and especially lake landers [e.g., Stofan et al., 2013; Mitri et al. 2014], and even submarines [http://www.gizmag.com/nasa-titan-submarine-concept/35960/].

9.1.4 Europa Exploration

Europa is the smallest of Jupiter's Galilean satellites and the 6th largest moon in the Solar System. Its average surface temperature is about −171°C. It was discovered by Galileo Galilei in 1610. Ground-based observations (e.g., radar) and flybys by the Voyager spacecrafts have revealed a complex surface dominated by ice and salt compounds associated with tectonic features (e.g., ridges). The Galileo mission, launched in 1989, provided the majority of the current data on Europa, revealing a geologically young surface, as indicated by the variety of tectonic features and the scarcity of impact craters. *Galileo* also uncovered the presence of a deep ocean from the detection of an induced (time-variable) magnetic field. That same technique also led to the discovery of deep oceans in the other Galilean moons Ganymede and Callisto. Because of its active geology and expected high tidal heat input, Europa's ocean is believed to be relatively close to the surface (<25 km, Pappalardo 2010) and in contact with a rocky core, while the thick hydrospheres of Ganymede (~800 km) [Vance et al. 2014] and Callisto (~200-400 km) [Schubert et al. 2004] suggest the presence of high-pressure ice phases at the interface with the rocky core. Ongoing analyses of Galileo datasets over the past 20 years continue to reveal surprises at Europa, including evidence for subduction of the brittle upper crust of Europa's ice, a key feature of plate tectonics on Earth [Prockter and Kattenhorn 2014]. Also recently, Hubble Space Telescope observations of Jupiter's magnetosphere in the vicinity of Europa have revealed the evidence for transient water vapor plumes [Roth et al. 2014]; these have yet to be confirmed by subsequent observations (Roth et al. 2015).

Because of the strong likelihood of having a global ocean in contact with a rocky mantle, Europa is a primary target for future exploration, as illustrated by the numerous mission concepts developed since even before the end of the Galileo mission (**Figure 1**). These missions all focus on getting a better understanding of Europa's internal structure and surface composition. Several concepts have considered some form of in situ platform, such as penetrators [Gowen et al. 2010] and legged landers [Pappalardo et al. 2013].

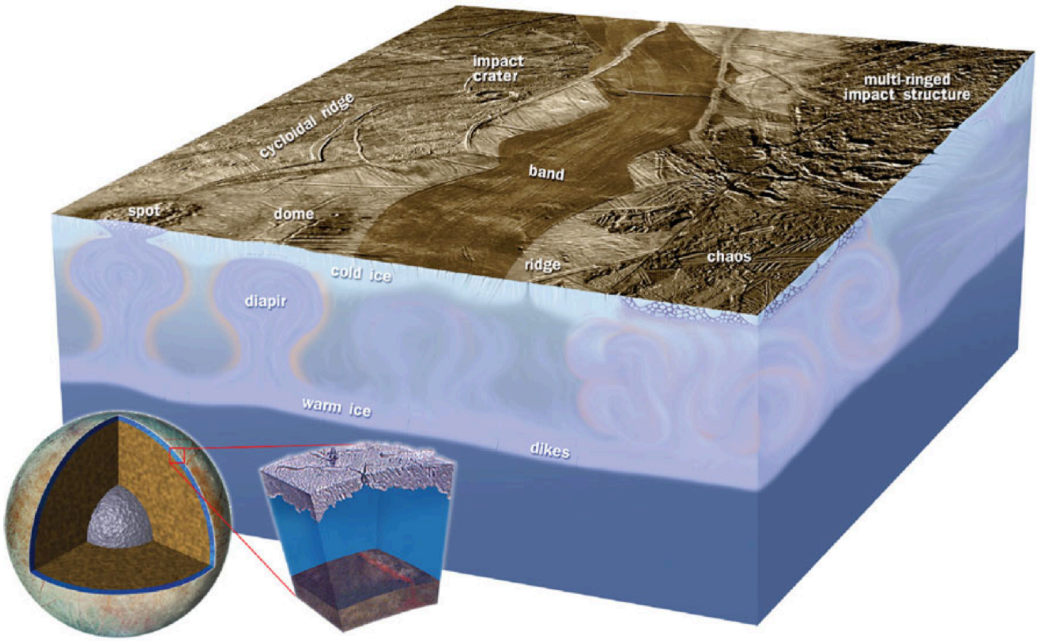


Figure 1: Europa's hydrosphere structure based on the current state of knowledge inferred from observations by the Galileo Mission. Image credit: NASA/JPL-Caltech.

9.1.5 Ceres Exploration

Ceres is the largest body in the asteroid belt. It was also the first asteroid to be discovered when it was observed by Giuseppe Piazzi in 1801. Ceres' density suggests it contains about 50% of ice in volume [McCord et al. 2011]. Most of our knowledge of Ceres to date comes from ground-based and Earth-orbiting telescopes, especially the NASA's *Hubble* Space Telescope [Thomas et al. 2005]. An extended vapor cloud at Ceres was detected with the Herschel Space Telescope [Kueppers et al. 2014]. This is evidence for the presence of ice in Ceres' subsurface that was predicted by Thomas et al. [2005] Ground-based infrared observations enabled the discovery of carbonates and possibly of brucite [Rivkin 2006], which are signatures of formation in a hydrothermal environment. The Dawn mission achieved rendezvous at Ceres early March 2015 and will carry out in-depth investigations of Ceres' chemistry and geology that will help answer questions on Ceres' origin and habitability potential. The prospect of shallow ice tables or even cold traps in shadowed craters have already prompted interest for surface exploration as a possible precursor to a Europa lander [Poncy et al. 2011]. While the Dawn mission is in its early stage at Ceres it is expected that it will obtain critical data needed to formulate a follow on in situ mission.

9.2 Geophysical Exploration Techniques

This section reviews key geophysical techniques that have been developed with the objective to characterize the physical properties of outer planet satellites with in situ platforms. Such techniques complement global scale observations of the gravity and magnetic fields. These techniques are: acoustic radar with application to the characterization of Titan's lake; seismometry with application to Europa's deep interior; and ground-penetrator radar with application to Enceladus in particular. Other techniques are notable, such as electric fields, induction, etc.

9.2.1 Sonar - Acoustic radar

Conceived at a time when it was widely thought that Titan had a global ocean, the Surface Science Package (SSP) carried by the Huygens probe, and deployed by the Cassini Orbiter in January 2004, had the ability to measure the sound velocity (Zarnecki et al. 2000). This measurement could have been used to determine the relative amounts of methane and ethane in the ocean. It also had a limited ability to do sonar measurements.

The key challenges to using sonar, also known as Acoustic Radar, is to employ piezoelectric transducers that are operational at such extremely low temperatures (~90K), that is specifically applicable to Titan's lakes. The issues involve a very large thermal expansion mismatch that may be associated with the construction materials and the composition of the liquids (methane/ethane) in these lakes. To address the challenges, one needs to take advantage of the piezoelectric materials that can potentially be used to serve as transmitters and receivers of acoustic waves. The required transducer needs to perform optimally at the temperature of 90K. Also, the operation in liquid methane/ethane requires addressing the related physics that affects the response and performance of the sonar as an analyzer. Combining the use of transducer array and phase control, one may be able to scan the terrain without physically moving the transducer. Combing the use of an array and phase control as well as vehicle movement, 3D mapping can be made, which is scientifically desirable.

Sonars can be used to perform ultrasonic analysis for investigating Titan's wet subsurface beneath and around its hydrocarbon lakes [e.g. Stofan et al., 2007; Hayes et al., 2008]. Such a scientific instrument, based on the transmission and reception of acoustic waves by one or more piezoelectric transducers, can be installed on an in-situ platform (lander, floater, submarine, rover, etc.) and measure the bathymetry of the lakes. This ultrasonic analyzer may be essential to measure directly the structure of the subsurface, and its interactions with the lakes: depth of liquid percolation, stratigraphy (porosity gradients and/or discontinuities between subsurface materials), existence and thickness of the organic deposits blanket, location of bedrock beneath, connectivity of the lakes, existence and extent of a deep-seated aquifer.

One sonar for Titan exploration has been reported in the literature. It was part the Meteorology and Physical Properties Package (MP3), conceived at John Hopkins University / Applied Physics Laboratory [Lorenz et al., 2012], and proposed as part of the scientific payload for the Titan Mare Explorer (TiME), a *Discovery 12* Step 2 mission concept. This sonar of the MP3 package was solely dedicated to measuring bathymetry of Ligeia Mare, using standard (low-efficiency) PZT transducers. Alternatively proposed by JPL, and described herein, is the use of recent developments of high-efficiency piezoelectric transducer technology to achieve similar capabilities with less power. Such an instrument would enhance the scientific return of an ultrasonic analyzer by enabling the capability of sounding the subsurface beneath the hydrocarbon lakes (**Figure 2)**. The terrain beneath the piezoelectric transducer can be scanned without physically moving the transducer. This can be accomplished by the use of a transducer array and phase control. The image of the lake bottom and the subsurface can be made in 3D by combining the operation of the sounding device with the vehicle movement.

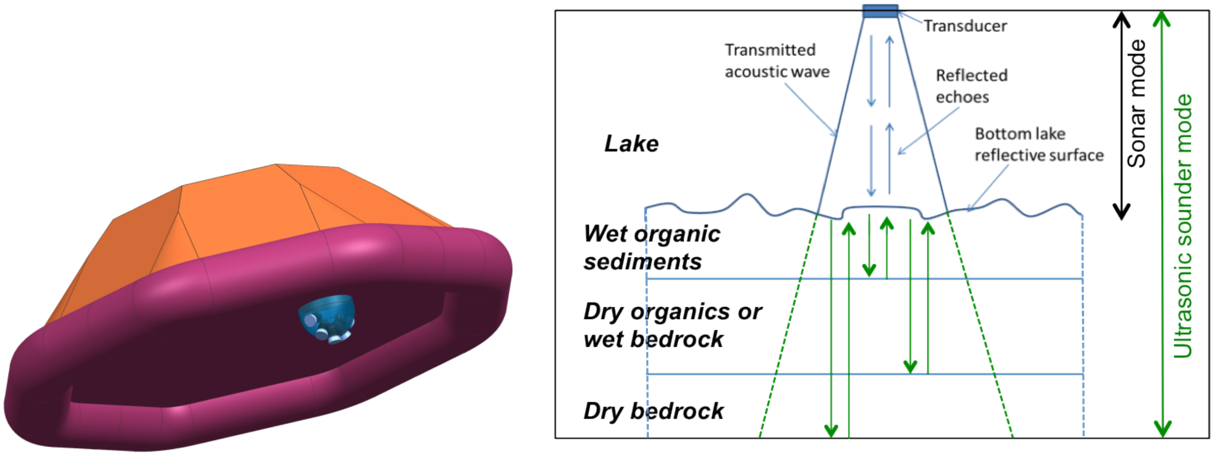


Figure 2: The envisioned marine lander and the ultrasonic analyzer for the exploration of Titan (*left*) and illustration of the instrument operation as compared to conventional sonars (*right*).

The sonar as an analytical instrument can be used to emit and receive sound waves, where the reflected or backscattered echoes from acoustic interfaces are used to measure the distance of objects by analyzing the travel time between the transducer and the objects/layers. This principle is also used in Navy sonars but the focus in this application is beyond mapping the lake bottom surface and immersed objects. It is interesting to note that the same principle is also widely used in diagnostic medical imaging and nondestructive testing. The main differences between medical imaging and underwater sonar are the operating frequency and the power level. In general, megahertz ultrasound (1-10 MHz) is used for non-destructive testing and medical imaging for high resolution, and this type of ultrasonic test does not require high power level (typically much less than 1 watt). In contrast, for great distance range finding and imaging sonar transducers use higher power with low to moderate frequencies in the Hz - kHz. This is also a requirement for an ultrasonic instrument, that may be used as an analyzer for the subsurface of Titan's lakes but the frequency needs to be focused on the ~ 1 - 100 kHz range.

9.2.1.1 Transducer composition, and behavior at cryogenic conditions

Piezoelectric transducers convert applied electrical signals into acoustic radiation and they are designated as projectors. Further, transducers that convert received acoustic radiation into electrical signals are designated as hydrophones. The performance criteria for projectors and hydrophones are quite different; for example, the major concern of projectors is high power output, while that of hydrophones is high sensitivity (signal-to-noise ratio). Piezoelectric transducers can serve as both projectors and hydrophones, in which the performance is greatly dependent on the properties of the piezoelectric materials such as mechanical Q_m (inverse of mechanical loss) and electromechanical k coupling. High values of these coefficients allow generating broad bandwidth signals and provide high sensitivity and increased power efficiency. Currently, the majority of piezoelectric materials for such transducers are ferroelectric materials due to their high electromechanical properties, which arise from the two types of contributions; the intrinsic (lattice effects) and extrinsic contributions (the motion of ferroelectric–ferroelastic domain walls) in ferroelectric materials. One of the most important characteristics of this kind of materials is the morphotropic phase boundary (MPB), which refers to the boundary between two compositions where the two phases are present in equivalent energy states. MPB is an important concept for ferroelectric materials as MPB compositions offer enormously high dielectric and piezoelectric properties as a result of enhanced intrinsic contributions. Lead Zirconate Titanate PZT is one of the most widely used piezoelectric materials because of the MPB characteristics [Jaffe et al., 1971].

The piezoelectric response contains not only the intrinsic contribution, but also an extrinsic contribution caused by movement of non-180° domain walls, which is strongly temperature dependent. MPB-based PZTs are generally tailored with dopant ions, which impede or facilitate domain wall movements. Importantly, in PZT ceramics, more than 50% of the net piezoelectric responses arises from these extrinsic contributions; therefore, when PZT materials are used at cryogenic temperatures, most of the extrinsic contributions are frozen out, consequently, the materials lose their piezoelectric performance; for example, the piezoelectric d coefficient was reported to decrease from 760 pC/N to 220 pC/N when the operating temperature was decreased from 300K to 30K (Park et al., 1999; Hackenberger et al., 2008). This indicates the necessity for appropriate piezoelectric materials to be used to make ultrasonic analyzer for operation at cryogenic temperatures. It is interesting to note that the transducer of the JHU/APL sonar is made of PZT-5A (Lorenz et al., 2012).

Recently, domain engineered <001> relaxor-PT single crystal family, such as PZN-PT, PMN-PT and PIN-PMN-PT, has been studied extensively due to their extremely high piezoelectric responses, strain over 1.7%, piezoelectric constant d_{33} over 2000 pC/N, electromechanical coupling factor k_{33} over 90%, with almost non-hysteretic strain-field behavior (Park et al., 1999). Of particular significance is that, in contrast to PZT ceramics, the mechanical Q_m values can be tailored by the crystallographic orientation, being on the order of 200 and >800 for <001> and <011> oriented PMN-PT crystals, respectively, without sacrificing the electromechanical *k* coupling. Since the origin of such high electromechanical properties of relaxor-PT single crystals is polarization rotation effect, (i.e., intrinsic contributions), the property degradation at cryogenic temperatures is much lower than in PZT ceramics, making them promising candidates for cryogenic transducers from the perspective of bandwidth and power efficiency of transducers (Fu and Cohen, 2000). The relaxor-PT single crystal transducers, specifically <110> oriented binary PMN-PT or ternary PIN-PMN-PT, can be used to produce a probe that can potentially sustain the very cold conditions, be inert to potential chemical reactions and constructed of materials with minimal thermal mismatch.

9.2.1.2 Estimates for the operation of sonar on Titan

The estimation of detection range for sonar transducer for a given input power is one of the most important considerations for the success of research related to potential missions to Titan. In order to accurately estimate the detection range for mapping the topography of Titan's lake, the elastic properties of propagating media need to be known. **Table 1** shows reference properties of various media from several sources, which allow for the estimation of the transmission range and/or transmission loss of acoustic waves from sonar using a given input power.

Table 1: Material properties used for assessing the ability of the proposed ultrasonic analyzer to detect subsurface interfaces.

Material	Vp (km/s)	Vs (km/s)	elastic modulus (GPa)	Attenuation
Methane (94 K)	1.520 (94 K – [Singer 1969] 1.490 (96 K – [Straty 1974]	---	0.9-1.9 GPa [Marx 1984, Shimizu 1996])	Alpha/f^2x 10^17: 5.6-6.2 cm^{-1}/s^{2} [Singer 1969, Straty 1974]
Ethane (95 K)	1.974 [Tsumura & Straty1977]	---		

H_2O ice (90 K)	4.2 [Proctor 1966]	1.98 [Proctor 1966]	5-9 GPa Young modulus for polycrystalline ice.	~ 1 db/100 m at -25°C for 35 and 60 MHz [Johari & Charrette 1975]
Benzene (solid, 170 K)	~2.8 [Heseltine et al., 1964]	-	5.72 GPa. Linear extrapolation yields 6.5 at 90 K [Heseltine et al., 1964]	~ 2-4 db/cm at 255 K. [Heseltine et al., 1964]; 3.1x10^5 cm/s at 273 K [Liebermann 1959]

For the detection of acoustic wave from a sonar, the signal-to-noise (SNR) ratio should be higher than the detection threshold (DT), i.e., SNR > DT, where SNR can be written as follows:

$$SNR \; = \; L_S\text{-}L_N = (SL - 2TL) - (NL - DI) \qquad (1)$$

where SL is source level, DI is the directivity index, in the case of omni-directional, DI=1, TL is one way transmission loss and NL is background noise level. The value of detection threshold of sonar transducer is dependent on the transducer performance and signal processing method.

The source level (SL) is defined as the intensity of the radiated acoustic wave relative to the intensity in medium referenced to 1 micropascal at 1 m, given in the Eq (1).

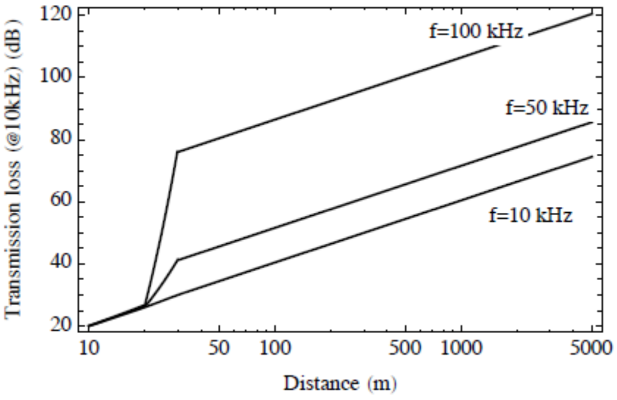
$$SL = 10\log(\frac{I_S}{I_0}) = 10\log(Wa) + 168.9 \text{ dB re}: 1\mu\text{Pa at} 1\text{m} \qquad (2)$$

where W_a is acoustic output power. I_o is the reference sound intensity of methane, referenced to 1 micropascal at 1 m.

The transmission loss (TL) includes all the effects of the energy losses, such as geometric losses (spreading, spherical or cylindrical), and attenuation due to scattering, viscosity, and adsorption. The main source of attenuation is generally associated with absorption, where acoustic energy is converted to heat energy. In this estimation, only spreading and absorption losses are considered and these are the main causes of transmission loss of acoustic waves. Transmission loss due to the effects of spreading and absorption can be expressed as follows:

$$TL = 20\log(x) + \alpha x \qquad (3)$$

where x is distance and α is attenuation coefficient. Note that the attenuation coefficient has a strong frequency dependence, much greater losses at higher frequency. In addition, the attenuation is also temperature dependent; generally increasing with decreasing temperature. Unfortunately, the attenuation coefficients of most materials at 90K are not available; thus, from this estimation we used the attenuation values given in **Figure 3**.



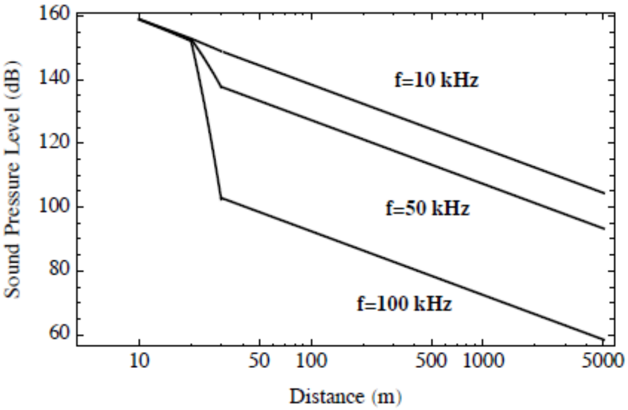


Figure 3: Diagrams showing transmission loss (top) and sound pressure level (bottom) of sound wave through our nominal subsurface model for an ultrasonic analyzer using 10 W input power.

The materials presented in **Table 1** are used as reference to estimate one-way sound pressure level (SPL) at distance through the structural model presented in **Figure 4**. Using a given 10W input power, the transmission loss and pressure level of the acoustic wave (predicted by Eq. (2) and (3), respectively) can be estimated as a function of distance with different frequencies (see Figure 2). From the figure, it can be seen that the most dominant factor for the transmission loss is spreading loss for sonar range (<10 kHz); however, with increasing frequency (ultrasound >20kHz), the attenuation coefficient factor becomes a significant factor in figuring the transmission range. Although this is a rough estimation, it is promising that if we design the sonar below 20 kHz, it is possible for sounding the subsurface beneath Titan's lakes with 10 W.

If we assume that the transducer can detect the sound when DT>0, we can also estimate the detection range with Eq. (1) for a given input power, assuming that NL-DI is 0, which is shown in **Figure 4**. From the figure, it can be seen that the sonar transducer can detect the sound up to 50 kHz for a given 10 W. Therefore, using a frequency of a few tens of KHz, the sonar as an ultrasonic analyzer can enable to transmit sound through the various layers of Titan subsurface, down to several hundreds of meters, providing detailed information on its structure.

The use of acoustic radar to perform analysis on Titan may enable detection of various anomalies and discontinuities as well as the characterization of material properties. Generally, the detection requires acoustic properties mismatch between the propagating medium and the presence of other materials such as cryo liquids, sediments, run-off, etc.

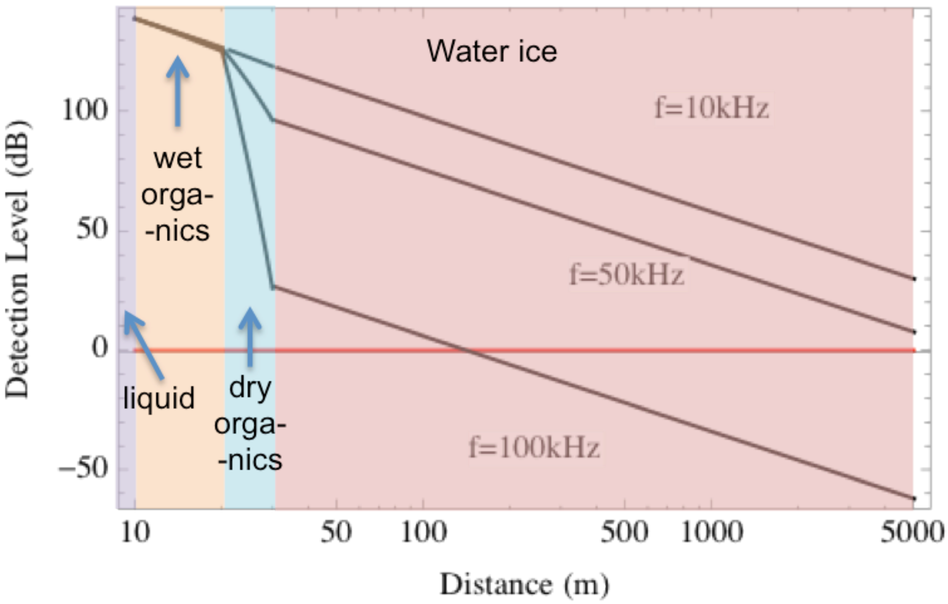


Figure 4: Influence of the operating frequency on the threshold detection level, using a nominal 10 W input power, for our nominal subsurface structural model. This assumes no significant suspended elements from wind or wave action.

9.2.1.3 Pulse-Echo versus Phase Shift Techniques

Successful mapping of targets in a Titan's lake requires effective signal processing and analysis. The most widely used methods of transmitting and receiving ultrasonic signals are the pulse-echo and the phase shift techniques. For the case of pulse-echo technique, the same transducer is used for both a projector and a hydrophone, where the accuracy depends on the accurate measurements of time-of-flight (ToF) value between two successive echoes; the distance of the object is estimated from the product of the ToF and the sound velocity when the path is homogeneous. Although it is proven to be simple and inexpensive, the difficulties arise from the fact that the received signals may contain significant noise and additional reflections from various sources. Potential noise sources include ambient lake noise, internal probe noise, preamplifier noise, and the reverberation from the lake surface. These unwanted echoes make the measurement of the ToF difficult.

In a phase shift method, the projector generates a continuous wave, whose echo is detected by a separate hydrophone. In this case, the distance information is determined by comparing the phase-shift between the transmitted and reflected wave. Although better performances than with pulse-echo can be obtained as the transducer can be optimized for only projecting or receiving acoustic signals, complex hardware is required to measure phase shift. To effectively extract the distance and directional information from the received signals in real time, various signal processing methods and algorithms need to be investigated including cross-correlation analysis and deconvolution for time-frequency analysis.

9.2.2 Ground Penetrating Radar (GPR)

Ground penetrating radar (GPR) is a nondestructive testing method that is based on the use of radar pulses to examine and image the subsurface for geophysical characterization. The technique is based on measuring the reflection of electromagnetic radiations in the microwave band (UHF/VHF frequencies) of the radio spectrum.

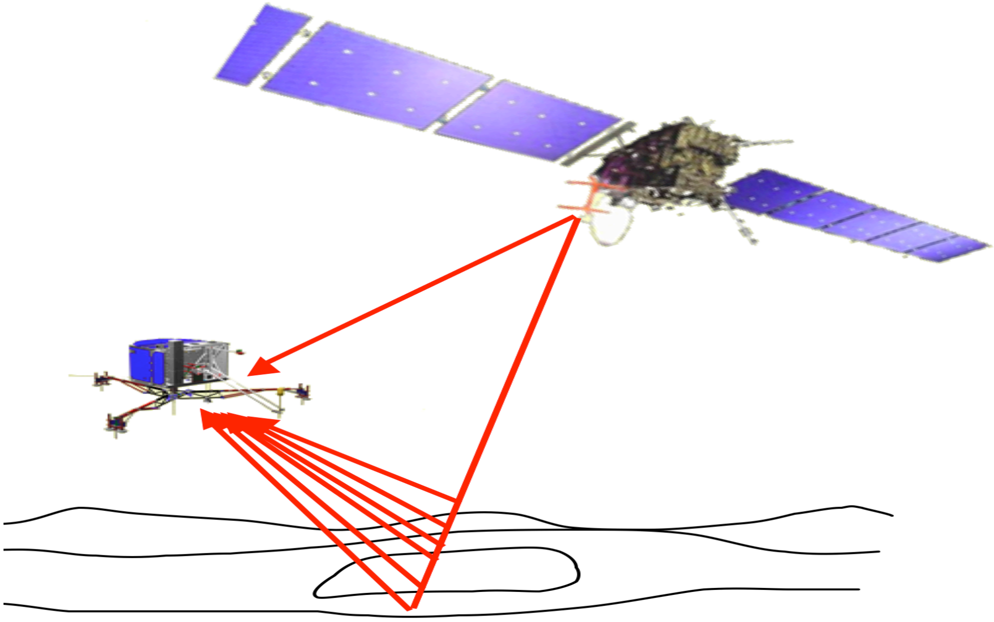


Figure 5. Illustration of the geometry of the CONSERT experiment part of the Rosetta mission (after Trautner 2012).

Given that this approach is based on electromagnetic radiation, the method is operational at low temperatures. Generally, this method is applied for use in various media including rock, soil, ice, and water and it can be used to detect subsurface objects, changes in material properties, and voids and cracks [Conyers, 2004; Daniels, 2004; Jol, 2009]. The technique involves transmitting high frequency radio waves in the range of 10 MHz to 1 GHz into the ground. When a boundary between materials having different dielectric constants is encountered, reflection takes place and a signal is returned to the surface. An antenna is used to receive the returned signals and the response provides information about the ground content. The operation principle is somewhat similar to seismic and ground sonar tests, except that electromagnetic energy is used instead of acoustic energy. Like seismometry, described below, the timing of the reflected signal yields information on the geometry (thickness, slope) of stratifications. The signal amplitude, compared to the amplitude of the source, carries information on the properties of the probed material. The material response to electromagnetic radiation is generally referred to in terms of "transparency." A pure water ice layer is transparent to the signal while a material rich in impurities tends to scatter and attenuate the signal, so that its recorded amplitude may be a small fraction of the source intensity. The effective depth of penetration of GPR is limited by the transmitted center frequency, the electrical conductivity of the ground, and the radiated power. The higher the frequency the lower the penetration depth but the higher the resolution that can be obtained and in choosing the operating frequency one needs to do a trade-off between resolution and the depth of penetration. In addition, higher electrical conductivity of the subsurface is associated with higher attenuation and therefore decreased depth of penetration. Generally, using low frequencies provides depth of subsurface penetration that can be achieved with GPR testing can be as much as several kilometers for pure water ice. When testing dry soils and hard rocks like granite and limestone, which have relatively low conductivity, the depth of penetration is limited to several meters. On the other hand, moist soils having high electrical conductivity leads to penetration that is in the range of few centimeters.

Ground penetrating radar measurements have been used on Earth for characterizing the thickness and structure of ice sheets [e.g., Legarsky et al., 2001]. This technique has also been applied to Mars during two ongoing missions: the MARSIS experiment on ESA's Mars Express mission and the SHAllow RADar investigation on the Mars Reconnaissance Orbiter [Seu et al., 2004]. While its penetration into Titan's surface is limited to a few centimeters, the Cassini Orbiter Ku-Band radar returned significant information on the surface properties of this singular world: radiometry (for temperature), altimetry, synthetic aperture radar imaging, and dielectric properties (e.g., Elachi et al. 2006; Hayes et al. 2010; Lorenz et al. 2014). The Cassini Orbiter also performed bistatic radio science experiments (Cassini-Titan-Earth geometry) providing information on the volumetric properties of Titan's surface (Marouf et al. 2014)

While the latter are remote observations, more recently GPR was used as part of the bistatic radar, COmet Nucleus Sounding Experiment by Radiowave Transmission (CONSERT) of the Rosetta orbiter and its lander Philae (**Figure 5**). CONSERT did not meet its primary objectives following the half-successful landing of Philae. However, measurements acquired during Philae's descent returned partial permittivity mapping of comet 67P (Plettemeier et al. 2015). Those are under analysis at the time this chapter is written.

In situ ground penetrating radar experiments have been suggested for several Mars missions, including the WISDOM radar [Ciarletti et al. 2011] proposed to the ESA's Exo-Mars mission that was eventually descoped. The Mars 2020 payload includes a radar called RIMFAX (Radar Imager for Mars SubsurFAce eXperiment) (**Figure 6**) that will be used to search for buried ice on Mars as part of the mission thrust for characterizing Mars' habitability and identifying potential samples of interest for return to Earth. In situ GPR was also suggested for the exploration of Enceladus [e.g., Konstantinidis et al. 2015] for characterization of the ice shell. It is remarkable that the most recent generation of that type of instrument is less than 1kg and requires less than 1 W of power [Kim et al. 2012]. While still under development, the projected penetration depth for that class of radar is of the order of a few hundred meters for pure ice down to a few meters if ice is mixed with rocks.

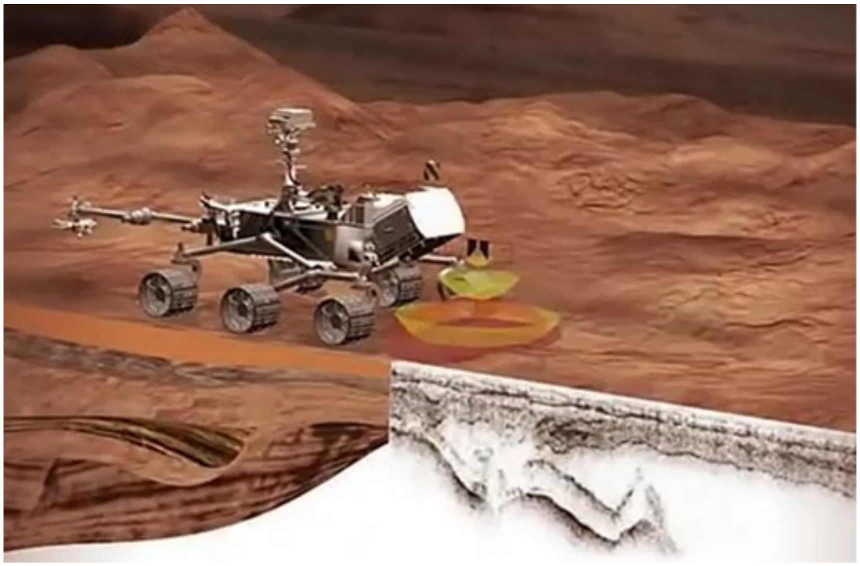


Figure 6: Illustration of the observations to be obtained by the RIMFAX radar planned for NASA's Mars 2020. Credit: Hamran et al. (2014).

9.2.2.1 Dielectric properties of planetary surfaces

The interaction of material with electromagnetic waves is described via two properties: (1) the electrical permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ (or dielectric constant when measured relative to the value for air) and (2) the magnetic permeability $\mu = \mu' - i\mu''$, where prime and second refer to the real and imaginary parts of these complex parameters, respectively. The real part is a measure of how much energy is stored and radiated by the material, while the imaginary part is a measure the amount of energy that is lost in the material as a consequence of energy attenuation effects generally a function of temperature and physical and chemical properties and impurities.

When a radar pulse reaches the boundary between two materials of differing dielectric properties, a portion of the incident energy is reflected backwards, while the remainder is transmitted forward. As successive dielectric interfaces are encountered, the signal experiences additional reflections and losses by absorption (affecting both the transmitted and reflected portions of the signal) until its strength is so attenuated that the reflected signal can no longer be detected above the ambient noise.

The penetration depth is primarily a function of the nature and temperature of the sounded terrains. Penetration depth can be estimated from observations at terrestrial analogs and experience gained from measurements at Mars (e.g., Phillips, 2008). Mars Advanced Radar for Subsurface and Ionospheric Sounding (MARSIS) aboard the European Mars Express spacecraft has demonstrated very low attenuation within the Mars polar ice, although Mars polar ice is believed to contain up to 20% non-ice impurities. The primary reason for low bulk attenuation is the cold temperature of the ice.

Both Antarctica and Mars polar caps are relevant analogs to Titan's and Enceladus' subsurface because they associate water ice and clathrate hydrates (gas molecules encaged by water molecules, e.g., Choukroun et al. 2013), which are predicted to be major constituents of both Titan's and Enceladus' icy shells [e.g., Tobie et al., 2006; Kiefer et al., 2006; Fortes, 2007]. On the other hand, limited knowledge of Titan's surface composition and structure, e.g., porosity at various scales, precludes a firm prediction of the penetration depth that would be achieved. Ground-penetrating radar investigations at terrestrial ice sheets for the same range of frequencies considered for these instruments (mean frequency and bandwidth of a few tens of MHz) have reached depths of up to 3 km [e.g., Studinger et al., 2003; Holt et al., 2006]. SHARAD's observations have achieved penetration depths of 0.1 km (in porous regolith) to 1.5 km at Mars' North polar layered terrains. The very low temperatures (i.e., < 200 K) at the Saturnian satellites would enhance the transparency of the material and the radar signal penetration. Based on these results, the expected cold ice temperature expected at both Titan and Enceladus would make it possible for radar detect horizons as deep as many tens of kilometers.

The SHARAD instrument (SHAllow RADar on Mars Reconnaissance Orbiter) was used as a reference for assessing the science return expected at Enceladus from in situ radar. The instantaneous bandwidth equal or greater than 10 MHz would yield a vertical altimetry resolution of 10 meters and would allow the resolution of horizons Enceladus' crust with the same level of accuracy. Preliminary study developed for the Titan and Saturn System Mission [Coustenis et al. 2009] suggests that a mean frequency of 20 MHz, is representative of the range of frequencies that can achieve the required spatial resolution of a few kilometers as well as subsurface sounding a few kilometer deep in an icy body like Enceladus.

9.2.3 Seismology

Seismic investigations offer the most comprehensive view into the deep interiors of planetary bodies. Developing missions (InSight and Europa Lander) have identified seismometry as a critical measurement to constrain interior structure and thermal state of astrobiological targets. By pinpointing the radial depth of compositional interfaces, seismic investigations can complement otherwise non-unique composition and density structures inferred from gravity and magnetometry studies, such as those planned for the NASA's Europa mission and ESA's JUICE mission. Seismic investigations also offer information about fluid motions within or beneath ice, which complement magnetic studies, and they can record the dynamics of the shell, which would shed new light on crack formation and propagation. Characterizing the internal workings of oceanic icy moons will figure prominently in the next Planetary Science Decadal Survey, and seismic investigations offer the best view into their deep internal structure—the compositions and radial extent of their icy layers, rocky mantles and metallic cores, if present. Such information is needed if NASA will seriously consider putting a submarine into a deep ocean. The evidence for salty oceans within Europa, Ganymede, Callisto, Enceladus, and Titan has produced intense public and scientific interest in the possibility of life in extraterrestrial oceans. Seismometry's utility for addressing these problems of intense public interest thus it a key tool for future icy moon exploration.

The highest priority goals of both NASA's Europa mission and ESA's JUICE mission are to "characterize the ice shell and any subsurface water, including their heterogeneity, and the nature of surface-ice-ocean exchange," and to "characterize the extent of the ocean and its relation to the deeper interior," respectively. The studied Europa Lander (Pappalardo et al. 2013) would also address these goals, using a multi-band seismometer (MBS; 0.1- 50 Hz and 125-250 Hz) based on the Exomars and Insight instruments. The architecture for doing this called for 3-axis seismometers in each of the lander's six legs, with required spacing between them of several meters or more.

9.2.3.1 Identification and Modeling of Possible Seismic Sources

Tides may be a major source of seismicity in icy moons, as they are in Earth's moon (Bulow et al., 2007; Weber et al., 2009, 2011), where almost all deep-focus lunar seismic events are clearly related to tidal stress. The locations are identical within the ability of the seismic network to locate them, and the waveforms of the repeat events are almost identical. It thus appears that there are some "special locations" where the tidal stress triggers slip on pre-existing fault planes. Tides also trigger a small part of Earth's seismic activity, such as in the well-studied Cascadia subduction zone (Royer et al., 2015; Houston, 2015). Europa's ice may see more tidally generated activity; its ice is likely more brittle than the lunar mantle rock (Nixon and Schulson 1987, Schulson 2001), but the driving tides, while stronger, have a much longer period. Forced librations in longitude—periodic variations in rotation rate, driven by the torques acting on a triaxial body—very likely create fluid motions in sub-surface oceans in librating icy satellites (Le Bars et al., 2015). In Europa and many other icy moons, gravitationally forced librations will create volume-filling turbulent flow, a possible seismic source similar to that seen from turbulent flow in terrestrial rivers (Tsai et al., 2012; Gimbert et al., 2014; Chao et al., 2015). Riverine flows and flows through glacial channels (Tsai and Rice 2012) may also be useful models for the downflow of dense brines from chaos regions on Europa into its underlying ocean (Sotin et al. 2002). Turbulent flows in Europa's ocean may result from natural currents as well (Soderlund et al. 2014), providing a potential source of seismic information.

In the case of Europa a major source of seismic waves comes from the tidal opening and closing of fractures [Lee et al. 2003, 2005], or slip along subduction-like features [Kattenhorn and Prockter 2014]. Estimated signal strengths up to 100 Hz for impact and fracture sources span a range of ±80 dB relative to 1 J/Hz (Lee et al. 2003), and are detectable using available technology [e.g., Kovach and Chyba 2001; Pappalardo, Vance et al. 2013].

Previous analyses of seismology on Europa (Cammarano et al., 2006; Panning et al. 2006) have concentrated on low frequency signals (0.001 to 0.1 Hz) for which a normal mode analysis is relevant. They concluded that events with magnitude 5 or larger could occur, and that mm accuracy displacement measurements would suffice to characterize thickness of the ice shell, and depth of the ocean. They note that penetration of seismic waves originating near the surface, in to the sub-oceanic silicate region would be limited, but seismic sources within the silicate region would allow determination of the deeper structure, as has been done for the Moon (Goins et al., 1981; Garcia et al., 2011). Seismic techniques to determine the internal structure of a body in the past have require three or more seismic stations in order to locate the event (e.g. Mars and Lunar Network missions; Moquet et al. 1998). The InSight mission to Mars has determined a way to avoid this by measuring travel times of surface waves that travel more than one time around the planet, or possibly detecting the location of impacting meteoroids that produce seismic events with orbital imaging. Active seismology, using an artificial seismic source has been proposed (e.g., Scheeres et al. 2011), although it is difficult to implement. Ambient noise seismology is the new frontier and enables investigations of structure without quakes or active sources but requires sophisticate processing. Jennifer Jackson and Zhongwen Zhan at campus have been doing experiments on terrestrial ice flows that are relevant to Europa and Titan. A previously unconsidered aspect is generation of acoustic signals in the ocean itself. Earth's oceans generate a weak seismic hum (Kedar 2011, Ardhuin 2015). Tidal flexure and librational response can be modeled to quantify forced motion in Europa's ocean, as well as seismic sources associated with collisions.

The architecture study, commissioned by NASA (Science Definition Team 2012 Study Report; Pappalardo, Vance et al. 2013) assumed 3-axis seismometers on each of the lander's six legs. The investigation would probe the detailed structure of Europa's ice and ocean (Kovachs and Chyba 2001; Lee et al. 2003, 2005; Cammarano et al. 2006; Panning et al. 2006) during a nominal mission lasting 9 eurosols (32 days). A multi-band seismometer model payload instrument, with capabilities based on Exomars that have also been adopted for Insight: low-pass 0.1-75 Hz and high-pass from 125-250 Hz. The Europa Lander architecture is achievable in spite of Europa's intense radiation, but its seismic investigation warrants further analysis. The study referred to implementing such a multi-seismometer approach, but did not assess the improvement in accuracy of having at least three of the lander's feet firmly coupled to the underlying ice. Seismic investigations of Antarctic ice shelves as well as ice sheets with subglacial lakes provide the best analogue for Europa, as noted in the Europa Lander study (Robin 1958, Bentley 1974, Roethlisburger 1972). Observations from Antarctic ice shelves suggest that certain phase amplitudes are very different than expected, for example with some phases being more strongly attenuated than might initially be assumed, and other phases being enhanced by resonance effects.

In Summary, the state of the literatures so far suggests the suitability of probing seismo-acoustic signals at frequencies from mHz to 100 kHz. Frequencies lower than 0.1 Hz could probe very long wavelength modes correlated global geophysical processes. A sufficiently accurate low frequency seismometer would also measure the tidal changes in local gravity (Kawamura et al., 2015). Measurements of the tidal Love numbers (Latychev et al., 2009) would provide additional information about internal structure and a check on gravity science measurements.

9.2.3.2 Broadband Seismometers – Status Quo

A seismometer can be thought of as mass suspended on a spring with a natural frequency of

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

where k is the spring constant and m is the suspended mass. When the ground moves at a frequency much higher than f_o, the suspended mass remains stationary, and relative displacement between the mass and the ground is measured as the seismic signal. When frequency of ground motion is much lower than f_o, the suspended mass moves with the ground and the seismometer loses its sensitivity. Therefore a figure of merit for a broadband seismometer is f_o; the lower its value the better.

Two classes of are relevant to icy satellite applications: Very Broadband (VBB) high-dynamic range sensors and MEMS sensors. Each class of sensors has its own set of challenges.

VBB's: The larger, typically more sensitive, yet more complex VBB's are similar to top-of-the line terrestrial VBB's (**Figure 7**), typically comprised of a large spring-mass system and highly sensitive feedback electronics. The InSight VBB's seismometer to be launched in March 2016 was developed by France's CNES (Centre National d'etudes spatiales) and IPGP (Institut de Physique du Globe de Paris) with input from JPL. InSight's VBB has been tested extensively, for Mars conditions down to -65°C. However, the seismometer is not designed to operate in the icy moon temperature (~-160°C) and radiation environment. Its projected sensitivity is 10^{-10}g/√Hz at 0.01-1Hz.

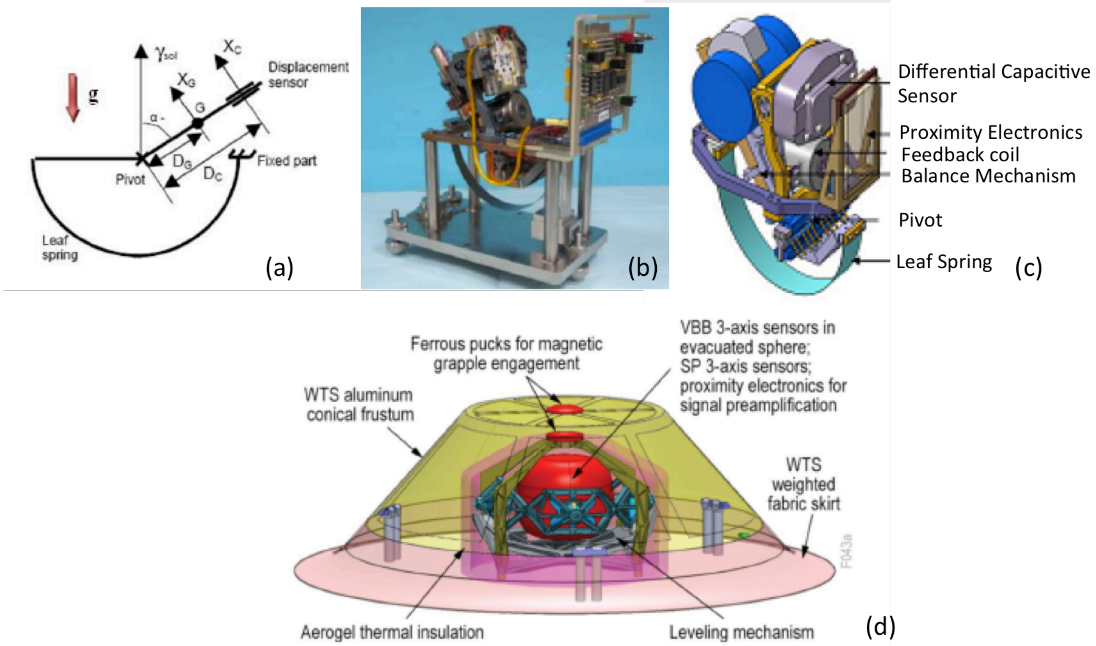


Figure 7: Insight's SEIS inverted-pendulum seismometer. (a) Principle; (b) Single-axis prototype; (c) Block diagram; (d) Shown within the whole seismometer and wind/thermal shield (WTS) system.

MEMS seismometers: Micro-Electro-Mechanical Systems (MEMS) accelerometers are widely used for both industrial and scientific applications. Nevertheless, only a handful of candidate MEMS technologies have the potential of meeting the projected sensitivity performance of highly sensitive broadband seismometers. As an example the *InSight SEIS Short Period (SP) Seismometer* is etched out of a single Silicon wafer and employs a double cantilever spring support of a proof mass whose motion are recorded by a capacitive transducer. Its projected sensitivity is 10^{-9}g/√Hz at 0.04-0.11Hz.

9.3 Chemical Measurements

Here we address instrumentation that is optimized for *in situ* chemical analyses of icy planetary environments. This includes standoff and contact techniques to elucidate the composition of planetary targets such as Titan, Europa, Enceladus, Ceres, and small icy bodies. Not included in this discussion are remote sensing techniques, which typically are not required to meet specific operational constraints as implied by cryogenic conditions.

The operating conditions for the majority of *in situ* flight instruments are generally controlled by the spacecraft to be within the range of -40 to +50°C, with survival conditions as low as -60°C. It is assumed in this section that the adaptation of these instruments to operate at cryogenic conditions is not the most efficient path towards technology development, given the success and robustness of current instrument lines and the other technical challenges present. Rather, we focus here on the interface through which the environment is interrogated and the sample is acquired and processed for delivery to the instrument, which is maintained in the spacecraft within the normal range of operating temperature.

9.3.1 Airless Bodies

Enceladus, Europa, Ceres, and other small icy bodies differ in important ways that can give us clues to the formation, differentiation, and evolution of our solar system. These environments provide a few key similarities, however, that enable the use of instrument techniques and technologies that are compatible with cryogenic temperatures and high vacuum. Generally, opportunities for *in situ* investigations of the chemistry of these bodies are sufficiently sparse or infrequent to merit a comprehensive analysis of their chemistry at every opportunity. Future mission architecture studies have included flybys, orbiters, surface landers, and even ice penetrators. As a result, development efforts of instrumentation designed to analyze the composition of these planetary environments need to consider various candidates for sample presentation. A flyby or orbiting instrument may encounter, for example, rarified neutrals and ions originating from the planetary surface, dust or ice particles originating from the sub-surface due to plume activity, or ejecta generated by a secondary impactor. In contrast, a lander may encounter loose regolith, consolidated bedrock, ice formations, or plume ejecta on the surface of a planetary body. For those outer planet satellites that are thought to possess salty oceans, a deep ice probe (e.g., Philberth probe or Cryobot) could encounter a high pressure, saline, aqueous sample. Two limiting cases that are most likely to be encountered in the next ten to twenty years are: (1) neutrals, ions, dust, and ice from orbit and (2) loose regolith and condensed ice and rock on the surface.

9.3.1.1 Orbital Instruments: Neutrals, Ions, Dust, and Ice

The quantitative abundances of these species in the vicinity of a planetary body will of course depend on the specific characteristics of the target body. In general, however, low number densities of these species, and an altitude-dependent density gradient, are expected for airless bodies. Successful analyses of exospheric species have been performed in past missions to the Moon [Mahaffy et al. 2014a], Venus [Niemann et al. 1980], Enceladus [Waite et al. 2009], and comets [e.g., Nordholt et al. 2003]. The design of these experiments are not explicitly driven by the cryogenic conditions of the surface, so further discussion of these measurements is outside of the scope of this volume and will not be included here.

Lofted surface dust and ice grains present an opportunity to characterize surface and subsurface materials from orbit, but *in situ* analysis implies the need to capture and ingest the dust particle into an instrument, such as a mass spectrometer. The scientific return on dust composition measurements is considerable: these dust and ice grains may be more representative of surface composition than sputtered neutrals, and in addition, the mineral or ice matrix of the dust particle could serve to protect encapsulated organics from damaging ultraviolet or energetic particle radiation that may be characteristic of the orbital environment. Along with these compelling reasons to measure composition of dust and ice grains from orbit, there are challenges in these measurements as well. In general, any flyby or orbiter will encounter the planet with a relative speed of several kilometers per second. This can be detrimental to the spacecraft structure itself, but of direct consequence to *in situ* analyses, impact speeds of this magnitude can pose challenges to the ingestion or acquisition of exospheric constituents by analytical instrumentation.

Experiments supporting and subsequent to the Stardust sample return mission to comet Wild 2 [Brownlee 2014] have shown that high impact speeds can alter or volatilize constituents of the dust particles [Burchell et al. 2012]. Even with this limitation, key measurements on Earth of the returned samples detected a variety of organic species [Sandford et al. 2006]. For certain *in situ* analyses, high impact speed is an advantage. For example, several dust analyzers have used the high impact speed to promote dissociation of the dust particles for elemental analysis [Srama et al. 2004; Horyani et al. 2008, 2014; Colangeli et al. 2007]. For those investigations, however, that aim to understand the molecular composition of indigenous organics or mineral composition, a softer collection or ingestion approach is preferred. Where possible within mission constraints, a combined strategy is adopted of minimizing orbital speed, where possible, and employing capture surfaces that impart low momentum to the dust particle during capture.

9.3.1.2 Landed Instruments: Loose Regolith, Condensed Ices, and Consolidated Rock

A landed mission offers a rich regime for conducting *in situ* investigations of composition of a region of a planetary surface. The surface is naturally stationary with respect to the payload, which provides a key advantage for instrumentation. Standoff techniques can be employed for survey analyses, and precise sample selection and acquisition for detailed chemical and mineralogical analyses become possible. Several flight instruments serving as examples of the following *in situ* techniques are currently in use on Mars, as part of the Mars Science Laboratory [Grotzinger et al. 2012], and at Comet 67/P Churyumov-Gerasimenko, as part of the orbiter and lander architecture of the Rosetta mission [Glassmeier et al. 2007].

9.3.1.2.1 Standoff Measurements

Standoff techniques that do not fundamentally require the instrument to contact the surface to be studied include: x-ray fluorescence and spectroscopy, reflectance imaging and spectroscopy, Raman spectroscopy, laser-induced breakdown spectroscopy, and laser ablation mass spectrometry.

Reflectance imaging and spectroscopy, even for an active instrument, only requires the interaction of a photon source with the surface under study. Photon response of the surface is measured at a single-pixel or array detector plane and can indicate composition by probing electronic transitions, surface refraction, or rotational-vibrational resonances of elements, minerals, and molecules [Rieder et al. 2003; Christensen et al. 2003; Morris et al. 2004; Edwards and Christensen 2013]. X-ray spectroscopy is a particular class of instrument that uses an illumination source to generate characteristic X-rays that indicate the elemental composition of a solid sample. Traditionally, high-Z, rock-forming elements are detectable using a Cm-244 source, but new techniques are enabling the ability to detect elements as low as carbon using low-energy electron sources, often coupled to electron microscopy capabilities [Feldman et al. 2003]. New instruments now in development are allowing for unprecedented spatial resolution for application on planetary surfaces, such as for PIXL (Planetary Instrument for X-RAY Lithochemistry) on the Mars 2020 Rover (Allwood et al. 2015). Particle detection, in general, can also be similarly employed to assign elemental composition to characteristic gamma rays and neutrons generated either passively or actively from surface and sub-surface layers.

Minimal heat is imparted to the sample by these instruments, and often only a fixed working distance or range of working distances is required for these standoff measurements. In some cases, the electrical potential of the planetary surface would need to be defined as ground, but that electrical contact can be established outside of the analytical field of view. Under some conditions, the illumination of a cryogenic sample with intense infrared emission from an illumination source may volatilize some of the most labile constituents of an icy sample, and this effect would require environmental testing of the instrument during development. An environment rich in aromatic organics is a natural target for ultraviolet fluorescence detection [Bhartia et al. 2008].

A special category of reflectance spectroscopy is Raman spectroscopy, in which the use of a continuous-wave or pulsed laser allows very precise excitation of individual phonon or vibrational modes of a sample constituent. This produces extremely narrow spectroscopic features that are diagnostic of minerals and molecules with greater specificity than with traditional light spectroscopy and has been of interest for *in situ* planetary surface investigations for several decades [Wang et al. 1998; Marshall and Marshall 2014]. The Raman instrument traditionally has required close placement of its optics to the surface under study, but no ingestion of the sample is required. Recent advancements have relaxed the proximity requirement, and in fact, remote Raman spectroscopy has been demonstrated in planetary analog surfaces in the laboratory and in a field-portable configuration [Sharma et al. 2003]. A recent field study of water ice crystalline structure in terrestrial icebergs has demonstrated the operation of a Raman spectrometer using visible illumination at 532 nm at working distances up to 120 m [Rull et al. 2011]. For cryogenic environments that are expected to be particularly rich in aromatic organics or certain sedimentary minerals, special measures may be required, such as through time-resolved gating techniques [Blacksberg et al. 2010], to mitigate effects of fluorescence that can diminish the sensitivity of the instrument.

Also benefitting from recent advances in *in situ* laser technology is the implementation of laser-induced breakdown spectroscopy (LIBS) [Weins et al. 2012]. This standoff technique is capable of inducing photon emission from an ablated plume with characteristic energies to allow identification of primarily inorganic elemental composition of a rock surface at a distance of several meters. Such a technique is, in principle, compatible with deployment in a cryogenic environment, with provisions for temperature control of the laser and spectrometer subsystems. For a planetary surface dominated by water ice, the need for localized sample volatilization can lead to a temperature dependence in analyte yield. Reduction in signal is also expected to accompany operation on an airless body, due to lower plasma temperature and more rapid expansion of the plume into a vacuum environment. For highly pure water ice containing only trace minerals or salts, the effective transparency of the target deserves consideration in selecting laser wavelength and assessing expected instrument performance and effective penetration depth. For example, the laser wavelength used on Mars by ChemCam is the fundamental frequency of a pulsed Nd:KGW solid state laser, and the use of similar near-infrared wavelengths has been demonstrated on icy sample compositions relevant to the Mars polar regions [Arp et al. 2004] and Europa [Pavlov et al. 2011].

Laser mass spectrometry has also been considered in a standoff configuration and shown to be viable in laboratory testing and simulation [Brinckerhoff et al. 2000; Li et al. 2012]. In such an instrument, a laser is focused beyond the dimensions of the instrument body to promote ablation and ionization of elemental species from a planetary surface. On an airless body, ions can be generated at distances up to 100 cm between the planetary surface and the inlet of the mass spectrometer and guided into a time-of-flight mass analyzer for elemental identification.

9.3.1.2.2 Measurements Employing Sample Ingestion

A subclass of instruments can enable detailed, highly precise compositional analyses of ingested solid sample. These instrument types and techniques include: gas-phase mass spectrometry, evolved gas analysis, tunable laser spectroscopy and cavity ring-down spectroscopy, gas chromatography, and liquid chromatography and capillary electrophoresis, laser desorption/ionization mass spectrometry, and X-ray diffraction.

Mass spectrometry has been the gold standard for *in situ* analysis of the chemical composition of planetary environments since the dawn of solar system exploration. Mass spectrometers provide a robust tool and nearly-universal detection of variety of environmental constituents across a wide range of concentrations that can approach eight orders of magnitude. Mass spectrometers have been dispatched to a variety of exotic extraterrestrial environments: to discover argon and helium on the lunar surface, measure noble gases in Jupiter's high pressure atmosphere, probe the depths of the Venus pressure cooker, and explore the organics at the top of the Titan atmosphere, to name but a few examples. An assortment of mass spectrometer types have been utilized in planetary exploration, including magnetic sector [Biemann et al. 1976], quadrupole [most recently, Mahaffy et al. 2012, 2014a, 2014b], time-of-flight [Balsiger et al. 2007], and ion traps [Brinckerhoff et al. 2013].

A method that has found wide use in the generation of gas-phase sample from a solid powder is pyrolysis. Typically, powdered sample is generated by a robotic crusher and delivered to an oven. When connected to an analytical instrument, evolved gas analysis can be used to elucidate classes of minerals that may be present, the presence and nature of bound water, and surface-bound or preserved organics that may have been encapsulated in solid surfaces. The challenge of working on a cryogenic surface is principally in the acquisition and processing of sample without imparting excess heat to the sample. However, surface ices that feature a highly volatile component may offer elegant hardware solutions to conducting evolved gas analysis, in that lower maximum temperatures of the heating elements may be required to analyze the condensed species on a cold surface. This could allow for new implementations in heating elements that interact directly with the surface, via a heated probe for example, to produce gas-phase analyte for subsequent ingestion and analysis.

The options for gas-phase analysis of evolved volatiles are numerous. Several types of gas-phase analyzer are discussed briefly here, but this list should not be construed to be comprehensive. An example of gas-phase analyzer that can provide high sensitivity to certain key compounds is Tunable Laser Spectroscopy (TLS). In this technique, a sample cavity with opposing mirrors on each end, known as a Herriot Cell, is filled with evolved gas. A laser pulse of known wavelength is reflected between the mirrors for a large number of passes, and for a molecule that absorbs resonantly at the laser wavelength, the abundance of the targeted species can be quantified very precisely [Tarsitano et al. 2007; Mahaffy et al. 2012].

Alternatively, the gaseous products can be directed to a gas chromatograph. This technique is widely used to study labile organic composition in a variety of terrestrial samples. With sufficient temperature control of the analytical column, gas chromatography (GC) provides separation of a complex organic gas-phase mixture by compound via interactions with a stationary resin coating the interior of the GC column. Chiral separation of amino acids has also been designed into *in situ* instrumentation [Mahaffy et al. 2012; Goesmann et al. 2007].

When starting with an icy planetary surface, an alternative to complete volatilization to the gas phase can be considered. Melting the ice into the liquid state offers new opportunities in instrumentation. Liquid-phase analysis is typically more sensitive for the study and quantification of certain classes of compound that require further processing to be analyzed by GC, such as amino acids and nucleobases. These prebiotic compounds typically possess functional groups that often preclude intact volatilization for gas-phase analysis without the use of a derivatizing agent. Derivatization can be done *in situ* [Mahaffy et al. 2012; Goesmann et al. 2007] but this step adds complexity and risk for a mission in which the existence and abundance of organic species is poorly constrained. Alternatively, analysis of the liquid by capillary electrophoresis or liquid chromatography can be considered as a more optimized approach for the *in situ* search and identification of prebiotic organic species. The challenges in implementing these liquid techniques lie in the requirements to maintain stable optimal operating temperatures and the transport of solvents during mission cruise phase without loss to leakage or alteration of the solvent or buffer chemistry after launch.

A class of instruments employing a laser to directly investigate the composition of a solid planetary sample offers an alternative to these highly capable but involved analytical techniques. Laser desorption/ionization is under development for the Mars Organic Molecule Analyzer (MOMA) mass spectrometer 2018 ESA/Roscosmos ExoMars mission [Brinckerhoff et al. 2013]. A laser desorption/ionization mass spectrometer (LDMS) offers some particular advantages for use on an airless body. For example, a mass spectrometer that benefits from high vacuum for sensitivity reasons, such as a quadrupole mass filter or time-of-flight mass analyzer, can operate at an airless body without the need for a supplementary vacuum pump or the need to transport a sample into a dedicated vacuum enclosure. An unprepared solid powder, chip, or core can be presented at the focal plane of the instrument for direct interrogation of the sample composition. A pulsed laser, particularly with a wavelength in the ultraviolet range, can desorb and ionize inorganic and organic species directly from a solid sample [Brinckerhoff et al. 2005; Wurz et al. 2012]. Additional features, such as extraction, chromatographic separation, and laser post-ionization, can be employed in advanced instrument concepts for higher performance as required by the mission.

9.3.1.2.3 Challenges to Instruments Requiring Sample Ingestion

For instruments that require ingestion of a sample, there are a few key common challenges presented by handling regolith in icy environments. The regolith will be composed of particulate and adsorbed species with varying degrees of volatility; for comprehensive, quantitative regolith analysis, care must be taken to avoid fractionation of the sample during acquisition and processing. In addition, for some planetary targets, the acquisition mechanism will need to operate in a microgravity environment. Heritage mechanisms for sample crushing and portioning, such as have been developed for Mars Science Laboratory, are not suitable for a microgravity environment. Missions in operations and in development have devised approaches to address these challenges, but more work is required.

A range of sample handling requirements are represented by the instruments listed above, but the degree of regolith handling can be divided into the following categories: scooping and portioning, melting, and pyrolyzing. For all mechanisms, the icy or cryogenic regolith will contact the hardware, and the extent to which that hardware is maintained at ambient temperature will determine the degree of loss of volatile species during handling. For instruments optimized for liquid analysis, such as liquid chromatography, ion chromatography, and capillary electrophoresis, melting is a key approach to introducing sample into a fluidic subsystem. Airless bodies present a particular constraint on this process, in that sublimation heat loss can dominate the heating process at low pressures. Therefore, melting must be done in a hermetically sealed container to prevent loss of key constituents into the gas phase. Furthermore, even for a sealed system, a fraction of condensed analyte will be lost to produce the head pressure during the initial melting process. A gas pressurization subsystem may then be considered to counteract quantitative losses due to the combined effects of change of phase and dead volumes of the hardware.

Consolidated icy surfaces present a particular challenge to sampling hardware, not previously encountered in predecessor missions to the Moon or Mars: water ice is extremely hard, especially at cryogenic temperatures. This aspect will be discussed in detail in Chapter 10. Once the mechanical requirements of surface drill are addressed, additional challenges arise due to sample volatilization and differential adhesion or cohesion properties of the acquired materials. In the following section, we treat the specific case of surface solids and liquids on Titan to allow the presentation of surface material to an *in situ* analyzer.

9.3.2 Titan surface and liquids

Here we explore some of the challenges and possible solutions for probing the composition at the surface environment of Titan, which provides an array of sampling reservoirs such as cryogenic fluids and frozen surface materials, and in which a quantitative investigation of the chemical inventory is paramount. Regardless of the ‘flavor’ of instrumentation deployed, for many instruments, there is a requirement that the components for analysis be gas-phase ions prior to introduction into the analyzer. For atmospheric investigations this entails careful design of the inlet, dictated by the sampling environment and ambient pressure. Sampling of solid and liquid phases necessitates an additional step to get analytes into the gas phase, with optional complementary separation approaches prior to introduction into the mass spectrometer. The sample capture and preparation approach needs to be tailored to both the conditions particular to the exploration environment as well as the instrument requirements.

9.3.2.1 Sampling Lakes and seas on Titan

Exploration Titan’s lakes and seas, thought to be composed primarily of methane and ethane, represents a primary science goal for Titan and Outer Planet science. Titan lake and sea landers have been studied as a potential element in the Titan Saturn System Mission [ESA 2009], as a stand-alone mission concept [Vision and Voyages 2011], the *Discovery 12* Step 2 mission concept Titan Mare Explorer (TiME) [Stofan et al., 2013], as well as exploration concepts described above. Primary science goals for measurements of the Titan seas include the determination of the chemical make-up of the liquid with the isotopic compositions of major elements, the inventory of dissolved gases, and the identification of trace molecules and suspended solids that result from the active CH_4 photochemical cycle. Furthermore, the lakes in the South Pole in particular may exhibit seasonality (Hayes et al. 2011), and so a temporal investigation of the composition over the long (~7.5 yr/season) seasonal cycle on Titan would be desirable.

Mass spectrometry, as a 'universal' detector, is likely to play a major role in future *in situ* investigations of the Titan lakes. We therefore frame this discussion using mass spectrometry as a strawman analyzer to facilitate the following discussion of sampling from a cryogenic liquid. The primary challenges for sampling the lakes for compositional analysis are: (1) the sampling mechanism must function in the cryogenic fluid at approximately 90 K; and (2) the acquired liquid sample must be converted to gas and transferred to the ion source of the mass spectrometer, and the conversion of the sample to the gas phase must preserve the integrity of the sample to ensure proper quantitative analysis. This must be accomplished despite a wide array of unknowns, such as the bulk composition, which drives the range of boiling points and specific heats, as well as the particulate load and sizes and the liquid viscosity (Lorenz et al. 2010).

The challenge of developing a sampling system that is compatible with the cryogenic fluids may be the most straightforward to address. The propulsion, medicine, food, and aerospace industries have developed cryogenic fluid management technologies that operate well within the conditions of the Titan seas. Valves that function at the cryogenic temperatures are commonly designed to operate with LN_2 (77 K), LO_2 (55 K), or LHe (4 K). NASA has led efforts to advance cryocooler technologies using LHe in support of Earth and Space Science Missions, with a recent push for the James Webb Space Telescope instrumentation. Given the mass, power, and volume constraint of planetary instruments, miniaturized automated valves designed for other spaceflight applications will be necessary components for *in situ* fluid sampling on Titan. Materials typically used in cryogenic valves, metals (e.g., stainless steel, copper, brass, aluminum, and its alloys) and plastics (Teflon®, Vespel®, Torlon®), should be robust in the hydrocarbon liquids, which are not particularly corrosive. However, any proposed valve system would need to be tested against relevant mixtures for possible degradation of mechanisms or valve seats.

Cryogenic seals for the valve and inlet ports that may protrude from the spacecraft for sampling are well understood, and have been used in every single flight project and mission that has involved liquid cryogens. The most common method of creating a cryogenic seal uses indium wire that is compressed into a groove. Indeed indium uniquely preserves its malleability to very cold temperatures so the sealing properties are retained. Indium seals have proven effective in past missions such as COBE, SHOOT, ASTRO-E I and ASTRO-E II. The testing programs on these past projects, on the ground and in flight, have proven the versatility, repeatability, and maturity of designs that use indium to create cryogenic seals. Conflat flanges can also be used to achieve a cryogenic seal, but these types of seals require far more mass and have higher He leak rates, although that may not be an issue in the liquid hydrocarbons.

Mass Spectrometer Gas Analysis and Sample Vaporization

The conversion of the acquired liquid sample into the gas phase for measurement, while preserving the sample fidelity, is a much greater challenge to the proper investigation of the sea composition. There are a variety of thermal complications that arise when sampling from a multi-component cryogenic lake, including the provision of proper insulation of the spacecraft to minimize heat flow through the spacecraft skin to prevent local vaporization and thus compositional changes in the sea [Lorenz 2015]. Then, provided that a sampling port on the exterior of the spacecraft has access to unaltered fluid, the sampling apparatus must be maintained at the sea temperature during capture. A warm enough sampling reservoir that drives the fluid to the onset of boiling will alter the sample composition and may lead to rapid gas expansion that drives fluid out of the open port. This requires proper thermal coupling to the cryogenic sea, with limited thermal coupling to the interior of the spacecraft during sampling. Further, during sample capture there should be either no heat generated by the mechanism itself or such heat should be redirected and dissipated away from the sampling region.

This is particularly the case if the quantification of the bulk composition of the lake is a required science measurement. The phase diagram in **Figure** demonstrates the limited tolerance for temperature increases at the conditions of the Titan Sea before the sample begins to fractionate due to vaporization. Here, the bubble point is defined as the temperature (at a given pressure) where the first bubble of vapor is formed. The vapor will have a different composition than the parent liquid. Correspondingly, the dew point is the temperature (at a given pressure) at which a vapor will being to condense into liquid. For a pure compound, the bubble point and dew point are equivalent. This simple approximation based on Raoult's Law for mixtures indicates that if the temperature of the sample is raised 40 K, the CH_4 will begin to preferentially enter the vapor phase enough to change the sample composition by nearly 50%. With a slightly more complicated model for the sea composition such as that proposed by Cordier et al [2009] and Tan et al [2013], temperature changes of even a few K could lead to significant loss of the N_2 and dissolved noble gases in the system (see **Table 2**). An update to the thermodynamic analysis suggest that the ethane component may be slightly higher, which will only serve to increase the viscosity [Cordier et al 2013].

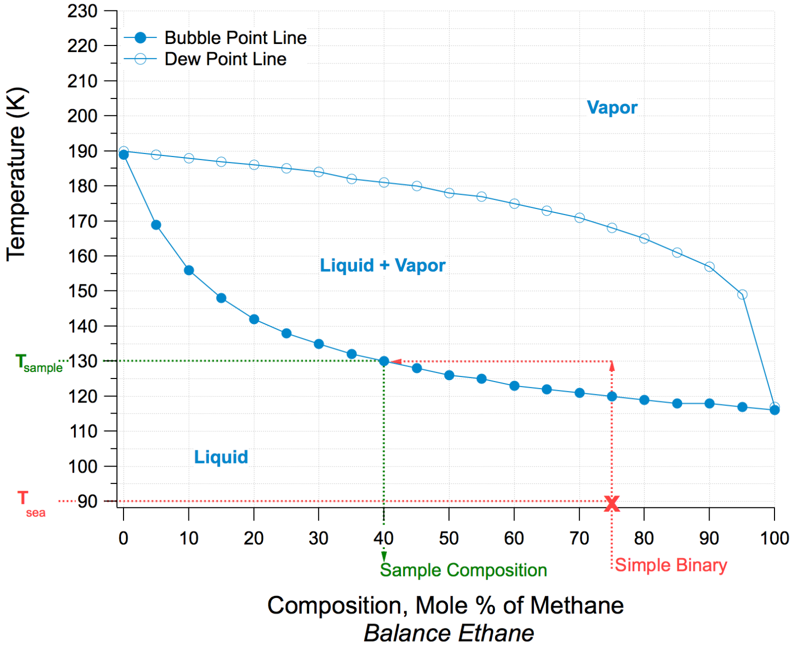


Figure 8: Phase diagram for CH_4 and C_2H_6 mixtures at 1500 mbar pressure show the tolerance of the cryogenic hydrocarbons against warming by the sampling mechanism. An example is made with the "Simplified Ligeia Binary" mixture of 25% C_2H_6 and 75% CH_4 (Table 9.4-1).

Temperature increases above the bubble point in **Figure** will lead to rapid fractionation and alteration of the liquid sample. Above the dew point (boiling point) the composition of the vapor phase will reflect the composition of the original liquid sample. Below the bubble point, temperature increases will lead to preferential evaporation of the more volatile component (**Figure**)

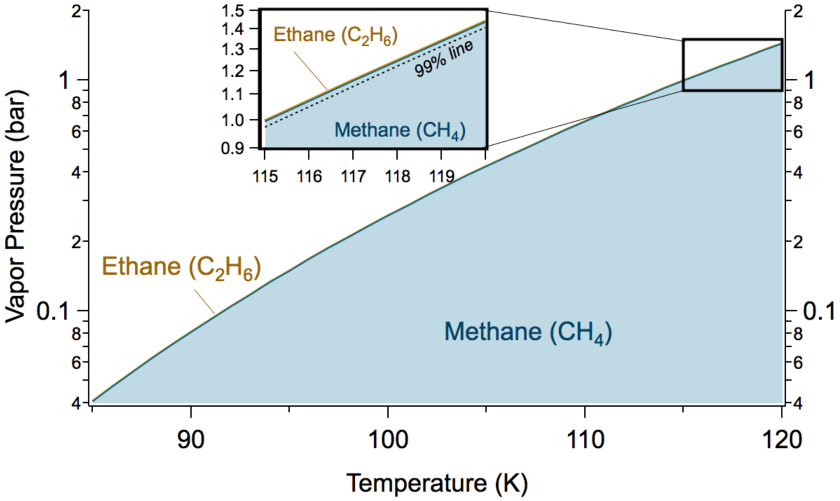


Figure 9: The vapor pressure curve for the "Simplified Ligeia Binary" mixture of 75% methane and 25% ethane. The headspace vapor of the liquid is dominated by the more volatile component, methane, which leads to sample fractionation even at temperatures below the bubble point. The dashed line in the inset indicates that > 99% of the vapor phase is composed of CH_4 even just up to the bubble point.

Table 2: Candidate lake compositions and thermochemical properties. Adapted from Lorenz et al (2010). X denotes the mole fraction of each component.

	Pure CH_4	Pure C_2H_6	Simplified Ligeia[a] Binary	Cordier et al (2009)
$X\,[CH_4]$	1		0.75	0.10
$X\,[C_2H_6]$		1	0.25	0.74
$X\,[N_2]$				0.005
$X\,[C_3H_8]$				0.07
$X\,[C_4H_{10}]$				0.085
Bubble Point (K)[b]	116	189	120	150
Specific heat C_p (kJ/kg K)	3.29	2.27	3.04	2.4
Viscosity at 94 K (µPa s)	208	1141	305	1423
Expansion ratio at 250 K, 1.5 bar	388:1	295:1	344:1	282:1

[a] From Mastrogiuseppe et al. (2014); Malaska et al. (2014)

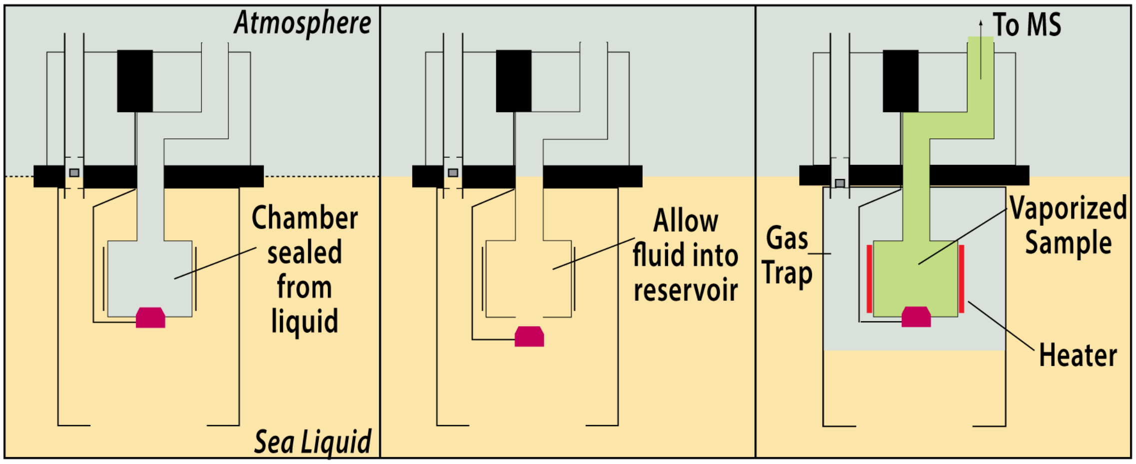
[b] Assumes ideal mixture, P_{surf}= 1500 mbar.

One approach is to design a valve that also serves as the sample chamber and vaporization region, minimizing the transfer of cryogenic fluids into the warm spacecraft and thus mitigating issues with sample fractionation. A concept for this type of all-in-one cryogenic inlet was developed for coupling to a neutral mass spectrometer on a Titan lake lander [Trainer et al. 2012]. For the NMS inlet concept, a custom valve was designed at the bottom of a sampling chamber that was completely submerged in the sea and thus thermally coupled to the sampling region. The valve seal utilizes geometries discussed above for cryovalves, but the actuation mechanism and other temperature-sensitive components are housed internally to avoid large temperature fluctuations. This design thus has the benefit of maximizing the use of high heritage components. The concept of operations shown in **Figure 10: (a) A cryogenic fluid inlet concept for quantitative sampling of the bulk composition of a Titan sea with a mass spectrometer or other gas analyzer. (b) Testing at NASA Goddard Space Flight Center in cryogenic fluid demonstrated the duty cycle of this approach,**

demonstrates this type of sampling approach. With the chamber surrounded by fluid during sample acquisition it is easily held at the sea temperature for capture of a high-fidelity, non-fractionated sample. The valve then seals the chamber from the sea to perform sample vaporization. The temperature of the captured fluid is not raised until the seal from the environment is made preventing premature boiling and escape. The small amount of cryogenic sea that is heated by the inlet chamber (right panel) serves as an insulation pocket to minimize the power applied during heating. An inlet modeled after this concept has been designed and tested to flight-readiness [Trainer et al. 2012]. Repeated sampling capability and robust leak-tight seals in a model cryogenic fluid was demonstrated in a laboratory system (**Figure 10: (a) A cryogenic fluid inlet concept for quantitative sampling of the bulk composition of a Titan sea with a mass spectrometer or other gas analyzer. (b) Testing at NASA Goddard Space Flight Center in cryogenic fluid demonstrated the duty cycle of this approach,**

This inlet allowed for rapid (< 1 hr) re-cooling due to excellent thermal connectivity to the sampling fluid. The cryogenic valve maintained the required seal through repeated sealing/heating cycles with no loss of sample gas at high pressures. The volume of sample captured is driven by the chamber dimensions and tailored to the needs of the sampling instrumentation, with excess gas diverted through an exhaust line. The rapid vaporization approach drives the majority of the sea components into the vapor and through heated lines in the spacecraft and thus provides quantitative sampling of the fluid. Following sample vaporization, additional enrichment steps using flight heritage approaches can take place in the gas processing line to target specific analytes.

(a)



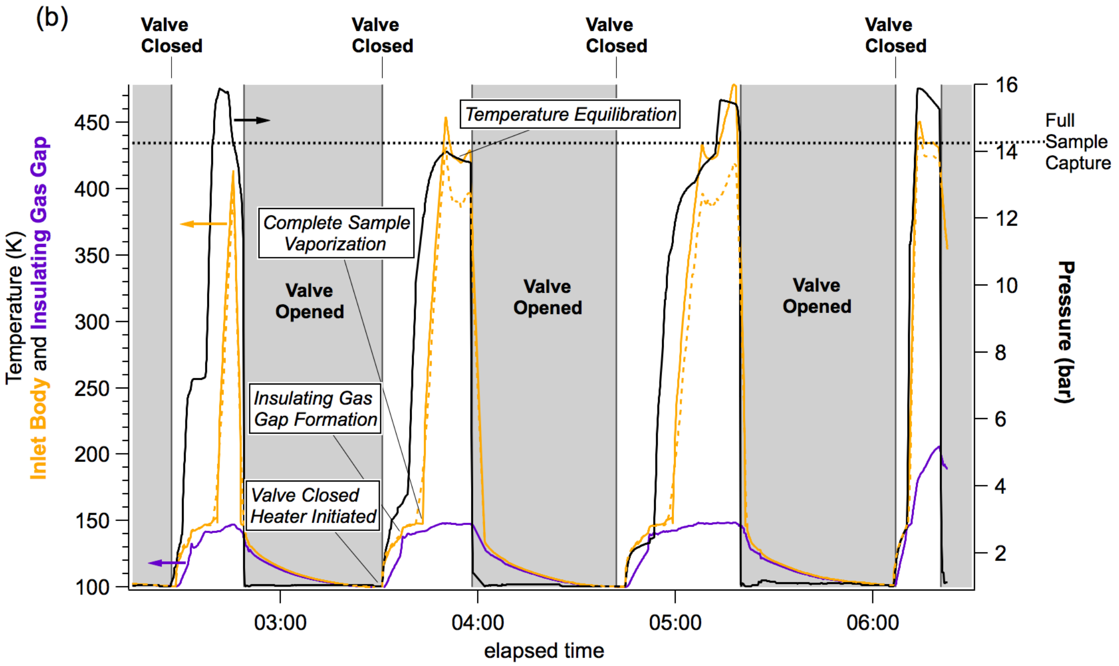


Figure 10: (a) A cryogenic fluid inlet concept for quantitative sampling of the bulk composition of a Titan sea with a mass spectrometer or other gas analyzer. (b) Testing at NASA Goddard Space Flight Center in cryogenic fluid demonstrated the duty cycle of this approach,

For science investigations in which the bulk composition of the sea fluid is not a high priority, such care does not need to be taken to maintain the sample at the ambient temperature during capture. Rather, following acquisition it may be advantageous to boil off the major species in the sea sample (CH_4, C_2H_6) to concentrate the less abundant, less volatile compounds for analysis. In this case, care should be taken to account for the expansion ratio of the liquids (**Table 2**), possibly including pressure relief valves, to ensure that the generated pressures do not overwhelm the valving and plumbing system.

9.3.2.1.1 Liquid Sample Distribution and Analysis

Other approaches for chemical analysis may require maintenance of the sea fluids in the liquid state for analysis, and thus could utilize cryogenic valves that are maintained at cold temperatures without concerns for resistance to heating. The use of piezoelectric valves and liquid distribution systems for Titan sea fluids has been explored [Sherrit et al. 2014]. The advantages of utilizing piezoelectric actuation in a cryogenic fluid distribution system is that this approach allows proportional flow control and is capable of generating high force with low power consumption, on the µW – mW scale (Park et al. 2008). A major disadvantage of piezoelectric actuation is its small stroke, even for large voltages. At cryogenic temperatures, the displacement is further reduced due to degradation of the piezoelectric coefficient. One proposed solution to overcome this challenge is the fabrication of a large effective perimeter in the valve plate of the MEMS device [Brosten et al. 2007]. The use of relaxor-PT single crystal, discussed in Section 9.2.1.1, also shows promise to make the use of piezoelectric microvalves feasible for fluid management.

A liquid distribution system would rely on a pumping mechanism to draw in and move fluid through a controlled system. For very small volumes, the development of cryogenic micropumps for cooling systems on satellites, detector arrays, and superconducting magnets may be leveraged for liquid sampling on Titan. Micropump designs that utilize electrohydrodynamic (EHD) pumping, in which the throughput and power requirements are proportional to the dielectric properties of the fluid, may have a range of performance dependent on the liquid characteristics (e.g., composition, density, temperature, and viscosity) [Darabi and Wang 2005]. A mechanical pump developed for high energy physics applications could provide higher throughput, and may be more robust against a variety of fluid properties [Grohmann et al. 2005]. These and other proposed pumping solutions need to be vetted and tested for function in simulated Titan sea conditions.

Liquid distributions systems could be designed to interface with a variety of analyzers. Some that could provide valuable scientific investigations in the Titan seas are Nuclear Magnetic Resonance (NMR) spectroscopy, capillary electrophoresis, or even liquid chromatography or supercritical-fluid chromatography coupled to MS, common in the petroleum industry [Barman et al. 2000]. For instance, solution-state NMR spectroscopy can provide high resolution structural analysis of complex mixtures and large compounds, but can also provide quantitative analysis in a nondestructive manner. This approach has been used to analyze the chemical structure of analogs of Titan photochemical aerosol [He and Smith 2014]. Microfluidic capillary electrophoresis has been demonstrated as a viable technique for separating and identifying nitrogen functional groups in complex Titan-like organics [Cable et al. 2014]. However, there are no flight-ready cryogenic instruments for liquid analysis currently available.

In addition, as discussed above, if quantitative analysis of the bulk composition were not a priority measurement, the fluid could also be passed through this type of distribution system and heated for introduction into a gas analyzer. Moreover, if the sample is distilled as described above, the fluidic analysis can be performed at accordingly higher temperatures, relaxing the cryogenic temperature requirements on the instrumentation.

9.3.2.1.2 Challenges to In Situ Liquid Sampling

The composition of the Titan lakes and seas is unknown, since there are many environmental components that could be present in the liquid or solid phases in these reservoirs. A significant fraction is likely made of methane, ethane, propane, and even nitrogen; although the surface is not cold enough for formation of liquid nitrogen, as the dominant atmospheric component (~94% at the surface [Niemann et al. 2010]) this gas will be incorporated into precipitable fluids and surface liquids. There are additional trace compounds, such as benzene, hydrogen cyanide, and acetonitrile which may also be present as liquids or solutes. Competing models suggest a variety of compositional mixtures in equilibrium with the atmosphere at the surface [Cordier et al. 2009, 2013a; Tan et al. 2013]. Recent Cassini observations have indicated that the northern sea Ligeia Mare is primarily composed of methane [Mastrogiuseppe et al. 2014]. However, the liquid compositions of Titan’s surface liquid reservoirs may vary significantly and even differ from one lake to the next. Further, density and other fluid variations could lead to stratification within the lakes and seas, rather than a homogeneous mixture. Thus, the possible exploration targets for analysis of the cryogenic liquids on Titan could vary spatially, vertically, and temporally. The compositional variation alone presents a significant challenge in that the properties of the fluid and constraints placed on sampling an analysis may not be tightly bound, and developed sampling mechanisms and instrumentation will need to function in a wide array of conditions (e.g., Table 9.4-1). As discussed above, the integrity of captured and processed samples may have tight operating margins, particularly for the more volatile fluid components. Moreover, the uncertainty in the measured properties of candidate liquids at Titan-relevant conditions is high [Cordier et al. 2013b].

Particulates could be composed of deposited haze aerosols (Tomasko and West 2009) or precipitated organic solutes [e.g., Malaska and Hodyss 2014b]. Evidence of "evaporite" deposits in dry lake beds suggests that, at least in evaporating bodies, suspended matter is likely [Barnes et al. 2011; Cordier et al. 2013b]. These suspended particulates provide challenges to the integrity and efficacy of sampling systems. Particulate matter is a particular hazard to valve seals in all conditions, and may prove more damaging at cryogenic temperatures where materials are more hardened and brittle. For microfluidic sampling of the fluid, particulate matter could also lead to clogging, as particle diameters of hundreds of nm to several μm are on the order of the fluid channel or valve conductance dimensions. Typically particle filters are used to protect valve seats and other small channels from clogging. However this approach may be limiting for scientific investigations in which the suspended material may itself be the target analyte. In addition, the filter lifetime will be a limiting factor and must be considered depending on the required number of samples and mission duration.

A heavy particulate load may also have implications for the fluid viscosity, and therefore the sampling and fluid handling mechanisms. Although viscosity is expected to vary substantially as a function of composition, and thus may vary from sea to sea, or at different times of year, the calculated dynamic viscosities for different candidate sea compositions ranging from 150 to ~2000 μPa s [Lorenz et al. 2010]. This is a manageable range given that it does not greatly exceed that of water (894 μPa s) or blood (3000 – 4000 μPa s) at 25°C, two common fluids used in lab-on-a-chip microfluidics. However, high concentrations of suspended particulates may greatly increase the viscosity, to the point of producing a mud-like slurry of fluid. The range of conditions or target lakes or seas, and the effect on cryogenically adapted pumping and fluid management systems is not well characterized. Fluid viscosity is not normally a consideration for cryogenics where viscosities are quite low (much less than water) and particulates are filtered out, and will need to be taken into consideration for any sampling system developed for Titan.

9.3.2.2 Ice and organic surfaces on Titan

The solid surface of Titan is also a high priority exploration target, with a large variety of geologic units including alluvial systems, dunes, mountains, and cryovolcanic flows [Aharonson et al. 2013]. The general surface composition has been proposed to be water-ice bedrock covered in hydrocarbon and organic deposits, such as the aforementioned atmospheric aerosol and lake evaporites. The only *in situ* explorer sent to Titan's surface to date, the Huygens Probe, landed in what was later determined to be damp ground [Lorenz et al. 2006]. The Huygens GCMS detected a release in volatiles upon landing and subsequent warming of the surface, suggesting a surface saturated in atmospheric constituents such as ethane, acetylene, and carbon dioxide [Niemann et al. 2010].

The discussion of potential stand-off and *in situ* compositional measurements for airless bodies in Section 9.3.2 above covers the types of instrumentation appropriate for exploration of the Titan surface. The environmental challenge of operating such instrumentation on Titan's surface as compared to an airless body is the high atmospheric pressure, ~ 1.5 bar. The dense atmosphere provides challenges for instrumentation that requires low pressure or vacuum conditions. Mass spectrometers, for example, would require high conductance pumps to maintain low pressures inside the mass analyzers. This has been accomplished previously for short timeframes on Titan using chemical getter and ion pumps [Niemann et al. 2002]. For extended missions requiring instrument evacuation on Mars, hybrid turbomolecular pumps have been used to provide the necessary vacuum conditions [Mahaffy et al. 2012]. A laser desorption/ionization mass spectrometer, such as the MOMA instrument under development for ExoMars, would be well-suited for the analysis of Titan's organic surface materials. MOMA-MS utilizes a fast-actuating solenoid aperture valve to enable LDMS operations at Mars ambient pressures (4 – 8 mbar) without requiring a vacuum seal to the sample [Arevalo et al. 2014]. Both of these components are designed to work at Mars ambient pressures and spacecraft-controlled temperatures (-45°C for the aperture valve). Though the pressure conditions at Titan are several orders of magnitude higher, similar technologies may be adapted through the use of differential pumping with secondary pumps.

9.3.2.3 Example of Application: Tunable Laser Spectroscopy for low temperature atmosphere on Titan

Tunable laser spectroscopy has developed over the last three decades as a powerful way to understand planetary climate cycles. TLS in-situ instruments have participated in measurement campaigns using airplanes, helicopters, balloons, ground vehicles and on foot. Most recently a tunable laser spectrometer visited the surface of Mars aboard the Curiosity mission as part of the Sample Analysis at Mars suite. TLS-SAM has begun addressing questions about the loss of water from the atmosphere [*Webster et al.* 2013a] and the possibility for present-day release and uptake of methane [*Mumma et al.* 2009, *Webster et al.* 2013b].

In the case of Titan, rapid, direct, and sensitive hydrocarbon characterization is needed for future aerial exploration of the atmospheres of the outer planets, or in situ exploration of Titan. A planetary alkane TLS (PA-TLS) could investigate Titan's complex interplay of the geology, hydrology, and meteorology by assessing isotopic and compositional fractionation associated with exchanges across the multiple hydrocarbon reservoirs (**Figure 11**). Such an instrument would be a natural outgrowth from the successful Mars TLS, but it would require attention to sample handling to characterize the range of relevant conditions found on Titan, as discussed above. For example, isotopic characterization of methane is optimal for at mbar pressures found on Mars, where line broadening is minimized. A cryogenic vacuum would thus need to be included, which could also prove helpful for analyzing liquids sampled from Titan's lakes.

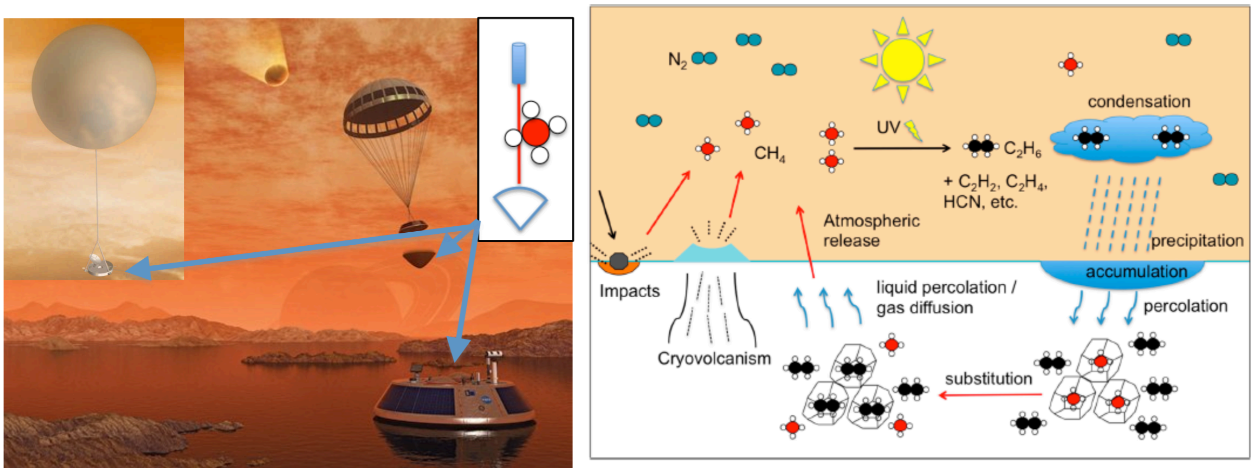


Figure 11: In Titan's earth-like hydrocarbon cycle, alkanes move between gas, liquid, and solid reservoirs on Titan [right: adapted from *Choukroun and Sotin* 2012]. Rapid, direct, and sensitive measurements of these and other molecules in Titan's atmosphere using tunable diode laser spectroscopy (middle schematic) could track Titan's hydrocarbon cycle, with high spatial and temporal fidelity needed to distinguish among the various processes. This approach would fit well on a probe, balloon, or surface explorer (left image).

Evaporation and precipitation of liquids and vapors also fractionate the isotopic composition of atmospheric gases due to their different diffusion rates. *Craig* [1961] describes a "meteoric line" for water in Earth's atmosphere: the linear relation between D/H and $^{18}O/^{16}O$. They couple this information with studies of evaporation of water in the laboratory similar to what we propose to do here. A PA-TLS can assess the relation between $^{12}C/^{13}C$ and D/H in methane (as CH_3D) and also for ethane with cryogenic hydrocarbon liquids.

The isotopic tracer concept applies across the series of hydrocarbons with increasing chain length. *Telling et al.* [2009] point out that the trend in $^{12}C/^{13}C$ and D/H in molecules in terrestrial hydrocarbon deposits indicates chemical processes occurring at shallow crustal depths. In general, heavy-isotope enrichment increases with hydrocarbon molecules size. Measuring the trend of the $^{12}C/^{13}C$ or D/H ratio can reveal the chemical processes that generate the molecules. Processes occurring at high temperature and pressure, and in low-pressure gas-phase conditions, produce molecules where the heavier isotope is depleted as molecular sizes increase. The decreasing ratio is consistent with a free-radical formation mechanism.

Equations of state for fluid-gas systems under planetary conditions [Tan et al. 2013, Glein and Shock 2013] provide the tools for modeling transport and exchange of hydrocarbons on other planets.

Figure shows methane absorption in the region of interest for PA-TLS, based on the development of the Mars TLS instrument [Webster and Mahaffy 2011]. Methane absorbs more strongly in this region than ethane or propane, and has well separated absorption lines for both ^{13}C and D isotopologues, providing unambiguous isotope ratios. A PA-TLS instrument would incorporate a 3057 cm^{-1} laser for measuring methane under conditions obtained in planetary atmospheres. The strongest lines at $3057+\{0.58,0.69,0.98\}$ cm^{-1} allow sensitive measurements absolute abundances of $\{CH_3D, {}^{12}CH_4, {}^{13}CH_4\}$.

The well-characterized 3057 cm^{-1} region serves as a reference for determining ethane compositions in the 2979 cm^{-1} and 2968 cm^{-1} regions, by subtracting methane absorbance effects [*Harrison et al.* 2010]

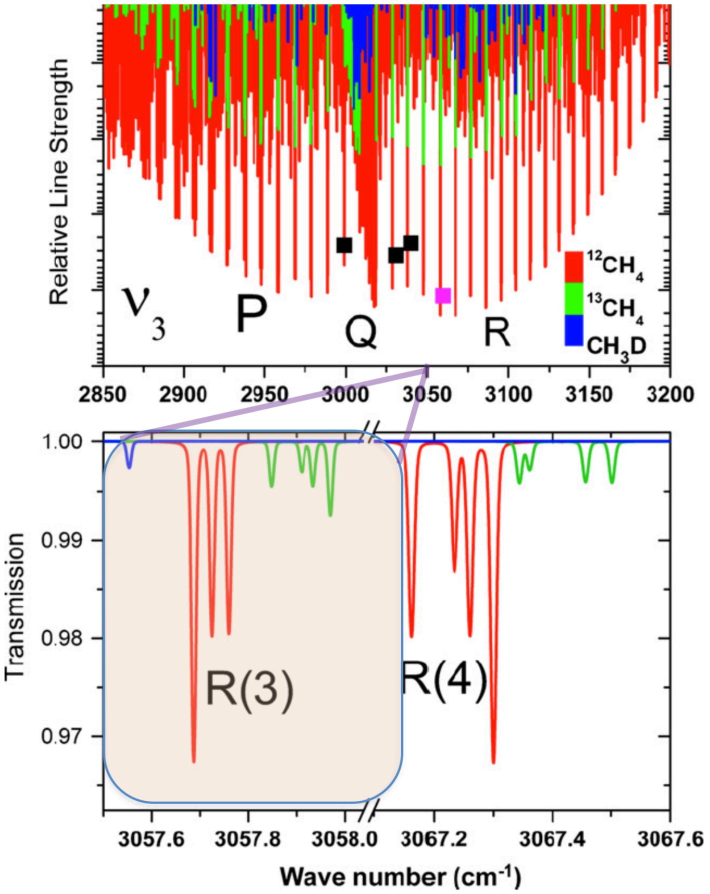


Figure 12: methane absorption in the region of interest for PA-TLS, based on the development of the Mars TLS instrument

9.4 Summary/Conclusions

This chapter has highlighted some of the many techniques that are becoming available for the in situ exploration of icy bodies, driven by discoveries achieved by recent missions. Many of the geophysical techniques are similar to those used on Earth for ice sheet exploration and provide powerful approaches for characterizing the thermophysical properties of planetary bodies. High-resolution chemistry measurements have to handle the challenges that come with sample handling and processing but big science questions at Titan and other icy bodies are motivating the development of innovative technologies. The past ten years have seen an increased number of concepts about observing icy bodies from in situ platforms as the natural next step in our exploration of these objects, driven by the decadal science objectives to improve our understanding of their origin, evolution, and potential habitability for life.

9.5 Acknowledgement

Some of the research reported in this Chapter was conducted at the NASA Goddard Space Flight Center (GSFC). Further, some of the research reported in this Chapter was conducted at the Jet Propulsion Laboratory (JPL), California Institute of Technology (Caltech), under a contract with the National Aeronautics and Space Administration (NASA). The authors would like to thank Robert Hodyss, and James Cutts, Jet Propulsion Lab (JPL)/Caltech, Pasadena, CA; and Tibor

Kremic, NASA's Glenn Research Center, Cleveland, OH, for reviewing this chapter and for providing valuable technical comments and suggestions.

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