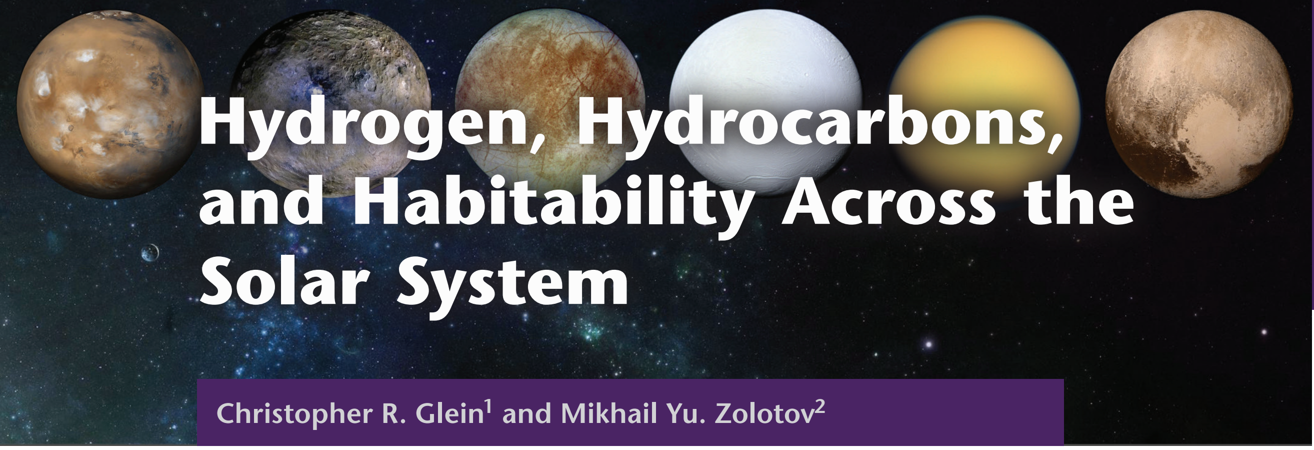

Hydrogen, Hydrocarbons, and Habitability Across the Solar System

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From left to right in the title image (not to scale): Mars, Ceres, Europa, Enceladus, Titan, Pluto.

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The ingredients to make an environment habitable (e.g., liquid water, chemical disequilibria, and organic molecules) are found throughout the solar system. Liquid water has existed transiently on some bodies and persistently as oceans on others. Molecular hydrogen occurs in a plume on Saturn's moon Enceladus. It can drive the reduction of CO_2 to release energy. Methane has been observed in many places: from the dusty plains of Mars, to the great lakes of the Saturnian moon Titan, to the glacial wonderland that is Pluto. Organic molecules are common where volatile elements and reducing conditions prevail: these organic molecules can have diverse origins. Future space missions will attempt to illuminate the "organic solar system" and the role played by possible extraterrestrial life.

Keywords: astrobiology, geochemistry, oceanography, planetary science

INTRODUCTION

The solar system provides an arena for broadening our understanding of geochemistry. Humanity has sent robotic missions to the other terrestrial planets and to the outer solar system to advance fundamental knowledge, to satisfy our curiosity, and to create legacies for inspiration. However, over the past twenty-some years, a fourth aspiration has emerged. We have come to learn that many of our planetary neighbors satisfy at least some of the requirements to support life. When we say "life", what we really mean is "life as we know it", i.e., a variety that bathes in liquid water, constructs itself from a toolbox of essential elements and organic compounds, and harnesses energy from its environment. Planets, moons, and other types of bodies that provide all three of these requirements are said to be habitable.

Reduced compounds, such as H_2 and methane, can support habitability, especially in subsurface systems where sunlight is absent. Their primary biological role is to serve as fuels in reduction–oxidation (redox) reactions that supply sources of metabolic energy. On solid planetary bodies, these electron donors are frequently associated with the subsurface, where conditions are governed by the chemistry of water and rock. Water–rock interaction generates reducing conditions owing to the ubiquity of reduced forms of iron [Fe(0), Fe(II)] in rocks that were originally derived from a swirling disk of dust and H_2-rich gas, known as the solar nebula. Planetary surfaces, in contrast, are prone to oxidation because of the loss of H_2 to space, unless the body is massive like the gas giant planets of the outer solar system. Because organic molecules are rich in hydrogen atoms, they have greater stability in more reduced systems. Reducing conditions can, therefore, enable organic synthesis and persistence in planetary environments without biological photosynthesis. However, H_2 and methane can support metabolism only if they coexist with a suitable electron acceptor.

Here, we present what is known or hypothesized about reduced volatile compounds and organic chemistry, processes associated with these phenomena, and the broader geochemical context for habitability on a number of solar system worlds. We do not attempt to discuss all of these issues for all bodies. Instead, we provide key contextual information for each body, along with more focused discussions on what are considered to be the "hot" topics that are driving current research and defining questions for future exploration. We conclude with brief descriptions of space missions that will seek to shed new light on the organic history and habitability of solar system planets, moons, and other types of bodies, and the possible existence of life beyond Earth.

MARS

Today, Mars is a cold, arid planet with a thin (~6 mbar) CO_2-rich atmosphere. However, the early climate was probably quite different. The occurrence of weathering products (e.g., phyllosilicates, soluble salts, carbonates) on the ancient surface, together with morphological evidence of fluvial processes, demonstrate that surface liquid water was previously present (Fig. 1). Mars may have once had a thicker CO_2 atmosphere that contained significant amounts (a few percent) of H_2 or methane (Wordsworth et al. 2017). These reduced gases would have been needed to provide sufficient greenhouse warming to produce surface temperatures above ~273 K during the Noachian Period (before ~3.7 Ga). Possible evidence for the past presence of atmospheric H_2 or methane may be found in the depleted abundance of atmospheric xenon and its pattern of heavy isotopic enrichment, which could be due to hydrogen escape that drove ionized xenon into space. An alternative climate scenario is that early Mars might have been largely frozen but was punctuated by periods of warming due to impacts and volcanism.

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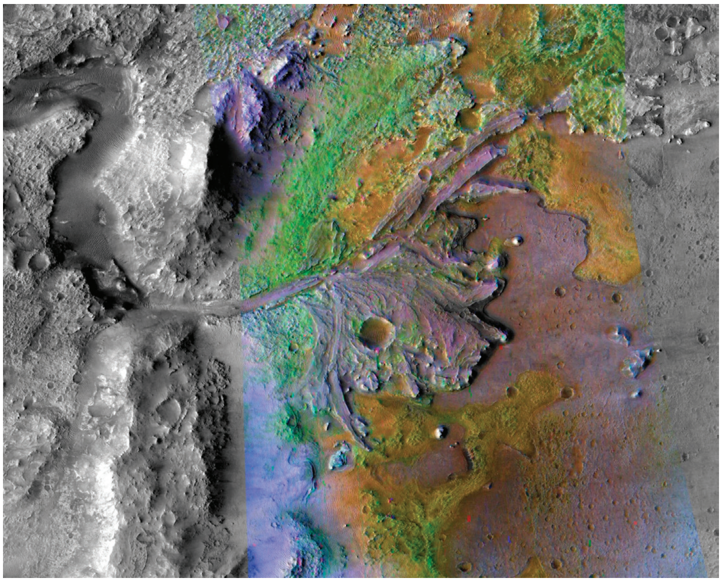

Figure 1 False-color delta deposits in Jezero Crater on Mars, as seen by NASA's *Mars Reconnaissance Orbiter*. The green color shows Fe/Mg smectites deposited in the ancient crater lake. The *Mars 2020* rover is scheduled to explore whether these deposits contain trapped organic biosignatures. Image credit: NASA/JPL-Caltech/MSSS/JHU-APL.

Molecular hydrogen and methane on early Mars could have formed in impact, igneous, or hydrothermal systems hosted in the mafic/ultramafic rocks that dominate the Martian crust. One source of H_2 would have been the degassing of reduced magmas. Another would have been the reduction of water by ferrous iron present in silicate minerals:

$$3FeO_{(in\ silicates)} + H_2O_{(liq)} \rightarrow Fe_3O_{4(magnetite)} + H_{2(aq)} \quad (1)$$

One instance where this reaction occurs is during serpentinization. This is where water alters igneous ultramafic rocks into more hydrated and oxidized rocks containing serpentine and other Mg/Fe-rich phases. Serpentine-bearing rocks have been identified on the surface of Mars from orbit, although they are relatively rare. Martian basalts contain about twice as much FeO as mid-ocean ridge basalts on Earth, and they can also react via Reaction 1. A third source of H_2 that is important in crustal environments is the radiolysis of water, which can be represented by the following:

$$2H_2O_{(liq)} \rightarrow 2H_{2(aq)} + O_{2(aq)} \quad (2)$$

Other reactive oxygen species (e.g., hydrogen peroxide) are also produced. These oxidants are consumed by ferrous iron or sulfide sulfur in the host rock to form ferric oxyhydroxides or sulfate, which are out of equilibrium with H_2. Such disequilibria could provide energy to any extant Martian subsurface life. Radioactive isotopes of K, Th, and U are enriched in the Martian crust compared to bulk silicate Mars; their decay emits radiation that could decompose a small amount of the groundwater that might still occupy any pores/fractures. This process could have been more prevalent during the Noachian when the crust was more radioactive than it is today (Tarnas et al. 2018).

Two recent reports may have profound implications for the habitability and potential presence of life on Mars, both past and present. The *Curiosity* rover detected aromatic, aliphatic, and S- and Cl-bearing organics in pyrolysis products of ~3.5 Ga mudstones at Gale Crater (Eigenbrode et al. 2018). This finding indicates the presence of sedimentary organic matter that may resemble organic matter in kerogens, coals, and carbonaceous chondrites. Previously, indigenous organic matter was found in Martian meteorites. The existence of organic matter at the surface is interesting: current surface conditions do not favor the preservation of organic compounds owing to the intense radiation and the presence of the strong oxidants O_2, H_2O_2, O_3, and ClO_x compounds. However, the environment may have been more benign (e.g., anoxic) when organic matter was deposited. There are a variety of abiotic processes that could account for the presence of organic molecules on Mars, including delivery by interplanetary dust particles or abiotic synthesis in postmagmatic, impact, and other hydrothermal environments. Abiotic synthesis could take place mechanistically by electrochemical CO_2 reduction involving Fe-bearing minerals. A more speculative possibility is an origin of organic matter via biological carbon fixation.

Webster et al. (2018) reported that surface air in Gale Crater had a methane abundance of ~0.4 ppb, which varied from 0.24 ppb to 0.65 ppb with spikes of ~7 ppb. Although these values are small, they are still significant because methane is unstable in the present atmosphere, having an estimated lifetime of ~300 years. Hence, a source of replenishment is implied. And it seems to exhibit temporal variability. Methane may be seeping out of the subsurface, which would be intriguing because biological or geochemical sources could be implicated. This would provide evidence that Mars is biologically or geologically alive. However, initial results from the ExoMars *Trace Gas Orbiter* give an upper limit for methane of ~0.05 ppb in the atmosphere at a few kilometers above the surface. This nondetection appears to be inconsistent with the in situ measurements. Why this is the case is not known. It might mean that there are highly localized sources and that methane is removed from the atmosphere at about a thousand times faster than predicted by present photochemical models. Or, the previous methane data may have been misinterpreted (see Zahnle et al. 2011).

CARBONACEOUS CHONDRITES AND THE DWARF PLANET CERES

Carbonaceous chondrites are organic-rich stony meteorites that originate from asteroids. These meteorites preserve a rich record of water–rock–organic interactions on their parent bodies that occurred within ~6 million years of solar system formation (Zolensky et al. 2018). Chemical reactions occurred in response to radiogenic heating by short-lived ^{26}Al and the melting of H_2O–CO_2 ices in the presence of accreted mixtures of reduced silicates, metals, sulfides, and organics. Water was consumed via hydration and oxidation reactions with minerals, which led to the formation of Fe oxides, Fe/Mg phyllosilicates, and secondary Fe/Ni sulfides. The dominant H_2-producing reaction was

$$3Fe^0_{(in\ Fe\text{–}Ni\ metal)} + 4H_2O_{(liq)} \rightarrow Fe_3O_{4(magnetite)} + 4H_{2(aq)} \quad (3)$$

Because this reaction reaches chemical equilibrium only at high H_2 pressures (>10^3 bar), it should have proceeded until metal or water was exhausted in the interiors of small asteroids. Some H_2 also formed by analogous reactions with Ni^0, sulfides, phosphides, and ferrous silicates. The dissolution of silicates created alkaline solutions that sequestered CO_2 as carbonates, making H_2 the dominant gas in the pore space. Overpressurization by H_2 beyond the fracturing limit (10^1–10^2 bar) could have driven the disruption of asteroids, leading to the escape of H_2-rich gas to space and causing net oxidation of the asteroid.

Increased pressures of H_2 generated a thermodynamic drive for the reduction of inorganic carbon, which would have promoted the synthesis of hydrocarbons by a Fischer–

Tropsch-type process. This is where hydrocarbons are formed from CO_2 or CO by the stepwise hydrogenation and polymerization of carbon atoms on a solid surface. The efficiency of this process depends strongly on transition metal/oxide/sulfide catalysis. Its occurrence in kinetically inhibited (e.g., <400 °C) systems is debated. The decrease in $^{13}C/^{12}C$ ratio with carbon number in chondritic alkanes agrees with Fischer–Tropsch-type synthesis (Yuen et al. 1984), and the pattern is the inverse of that produced by thermal cracking of high molecular weight organic matter. Hence, insoluble organic matter, the major carrier of carbon in chondrites, is unlikely to be the dominant source of alkanes. Chondritic methane is enriched in ^{13}C by ~30‰ relative to insoluble organic matter and is depleted in ^{13}C by ~50‰ relative to carbonate reactants. The latter fractionation is in the expected direction for a kinetically controlled synthesis of methane at low temperatures [e.g., ~0–160 °C in the CM chondrite group (carbonaceous chondrites of the Mighei type)]. Another potential source of light hydrocarbons in carbonaceous chondrites is for them to be trapped in primordial ices and accreted by parent bodies. Cometary ice contains 10^3–10^4 times more methane than is needed to account for the inventory in the Murchison meteorite (e.g., Rubin et al. 2019), so accreting even a small amount of cold ices from the outer solar system could suffice. Such ices would also contain reactive organic species (e.g., formaldehyde, hydrogen cyanide), and the release of these species into aqueous solutions would produce more complex soluble organics. These products include species of prebiotic significance that have been found in carbonaceous chondrites (e.g., amino acids, sugars, nucleobases).

Ceres is the largest asteroid (~940 km in diameter). It was explored by the *Dawn* spacecraft from 2015 to 2018. The surface of Ceres is dark, rocky, and cratered, and its mineralogy indicates a history of aqueous activity. Abundant Mg- and ammonium-phyllosilicates, space-weathered organics, and Mg/Ca carbonates account for ~2 wt% H and 8–14 wt% C in surface materials (Prettyman et al. 2019). The most prominent features are bright spots found in Occator Crater, among others. These features contain sodium carbonates that could have been delivered to the surface through low-pressure boiling of salty water solutions that formed after impacts (Zolotov 2017). Abundant organic matter and ammonium-bearing phases are consistent with Ceres' migration from the outer solar system where organics and ammonia are abundant, as in comets. In this case, methane-bearing ice and other cometary ices might also have been accreted. Because metallic iron corrodes quickly, even in anoxic environments, the advanced alteration of Cerean materials implies major past production of H_2 through the reduction of water by nebular materials (e.g., Reaction 3). It can be hypothesized that high past pressures of H_2 in an impermeable interior of compacted clays would have favored the preservation of primordial aliphatic organic structures and the formation of new C–H bonds via Fischer–Tropsch-type synthesis. However, it is unclear if aliphatic organic matter found in the Ernutet Crater region is endogenous, or if a comet impact delivered this material to Ceres.

EUROPA

Europa, a lunar-sized satellite of Jupiter, is considered to be one of the likeliest places for hosting extant life elsewhere in the solar system. From the inside-out, Europa has a likely metal core, a silicate mantle, a water ocean, and an icy crust. Subsurface liquid water may be delivered to the surface in certain locations (Fig. 2). Little is known about the composition of Europa's ocean. Data from the *Galileo* spacecraft suggested that this ocean contains dissolved salts that make it electrically conductive (Kivelson et al. 2000). Observations of Na and K in Europa's exosphere, and Mg salts on the surface, suggest that these elements occur as cations in the ocean. The anionic chemistry is more enigmatic and depends primarily on the oxidation state of the ocean. Europa's ocean could be rich in sulfate if it is sufficiently oxidized, or it might be relatively reduced and dominated by chloride if appreciable sulfate is absent (Brown and Hand 2013). In both cases, carbonate species could contribute to the anion budget.

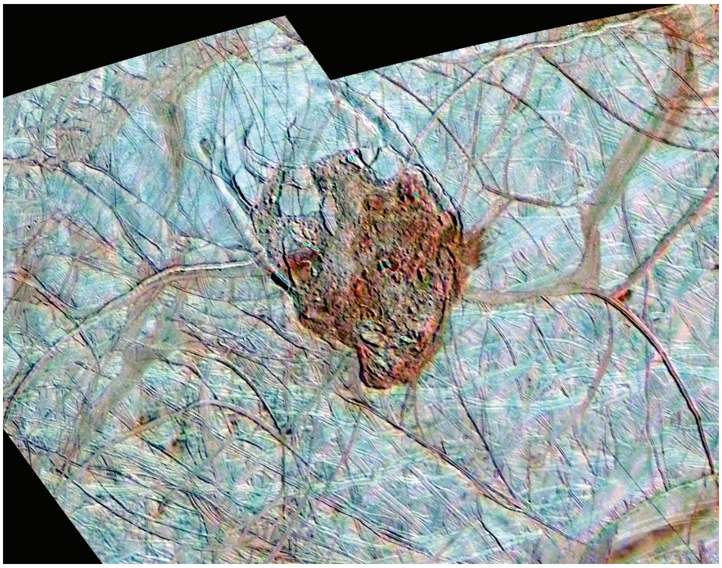

Figure 2 Color-enhanced image from the *Galileo* spacecraft showing Thera Macula, an ~70 km wide "chaos" feature on the surface of Jupiter's moon Europa. A shallow reservoir of liquid water within the ice shell may facilitate resurfacing to deliver subsurface material that becomes colored at the irradiated surface. Whether there is a genetic relationship between any subglacial lakes and the global ocean remains to be clarified by observations from NASA's upcoming *Europa Clipper's* mission to Jupiter's icy moon. Image Credit: NASA/JPL/University of Arizona.

Oceanic redox conditions will be affected by the amounts of oxidants and reductants that can be accessed by ocean water (Vance et al. 2016). Possible oxidants include O_2 or hydrogen peroxide that is either generated by radiation chemistry on the icy surface or as a result of ^{40}K decay within the ocean or seafloor. Reductants would be derived from the silicate mantle. Their sources include ferrous iron and sulfide sulfur in seafloor rocks (e.g., basalt), hydrothermally produced H_2 and hydrogen sulfide, and hydrocarbons that could be synthesized in olivine-hosted fluid inclusions. It is difficult to evaluate the robustness of these sources because they are dependent on poorly understood processes such as burial or subduction of surface material, partial melting of the silicate mantle, or circulation of ocean water below the seafloor. These processes may, in turn, depend critically on the strength, direction, and distribution of gravitational tidal forces acting on the satellite by Jupiter. Europa's habitability could be linked to its gravity tides as they may control the fluxes of redox species into the ocean. The concentrations of reductants and oxidants in the ocean determine the metabolic potential for putative sulfate reducers, methanogens, and other organisms (Zolotov and Shock 2004).

An outstanding issue is whether Europa exhibits current cryovolcanism. Roth et al. (2014) reported ultraviolet observations of exospheric H and O atoms using the *Hubble Space Telescope* and interpreted them as evidence of water vapor plumes. Since then, several more plume searches have been performed using different approaches with *Hubble*, *Galileo*, or the W.M. Keck Observatory (Hawaii, USA): plume signatures have been identified in some observations. These independent lines of evidence suggest that plumes may be real but episodic. However, this conclusion should be considered tentative because the data are sparse, indirect, or close to the detection limits. The existence of plumes would provide easy access to subsurface materials. Neither methane nor H_2 have been detected at Europa, but they would partition into the gas phase if present in a plume source region. Because organic compounds undergo radiolytic oxidation at Europa's surface, plumes would provide opportunities to constrain the organic composition of the interior, where such relatively reduced compounds could be more stable and abundant.

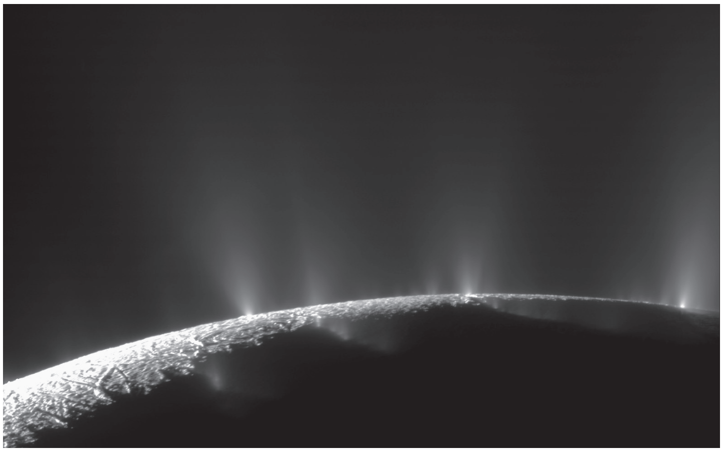

Figure 3 Icy geysers burst from fissures in the south polar terrain of Saturn's moon Enceladus, forming a plume that extends into space over a scale height of 10^2 km. The plume was sampled by the *Cassini* spacecraft. Image Credit: NASA/JPL/Space Science Institute.

ENCELADUS

Saturn's icy moon Enceladus has a diameter of only ~500 km, yet is cryovolcanically active, in contrast to many larger bodies. Observations by the *Cassini* spacecraft revealed that Enceladus has a plume of gases and ice grains emanating from its south polar region. The plume is fed by ~100 jets (Fig. 3) as well as by less distinct "curtains" that erupt along four parallel fissures. These fissures (called "tiger stripes") serve as pathways that connect a subsurface ocean of liquid water to space.

The interior of Enceladus is made up of three concentric layers. The surface is dominated by water ice, and the crustal layer of water ice has a mean thickness of ~20 km. However, the ice thickness is thought to be variable—thickest near the equator, thinner at the north pole, and thinnest at the south pole (Hemingway and Mittal 2019). This variability seems related to heterogeneous gravitational tidal heating. Below the ice shell is a global ocean of ice-cold water. The deepest internal layer is the rocky core, which is expected to be in contact with the ocean because the seafloor pressure (~70 bar) is insufficient to form dense phases of ice. The core is likely to be composed of ultramafic rock if it formed from chondritic material that did not undergo igneous partial melting. The low inferred core density (~2.4 g cm^{-3}) suggests a dominance of phyllosilicates, such as serpentine and saponite.

Plume composition measurements have opened a window into the geochemistry of the ocean and deeper interior. A large population of plume ice grains is rich in NaCl and $NaHCO_3$ or Na_2CO_3 salts (Postberg et al. 2009). The interpretation is that these grains preserve the ion chemistry of the ocean as a result of flash freezing of sea spray, which is driven by low-pressure boiling. The plume gas is dominated by water (>95% by volume), with smaller quantities of H_2, ammonia, CO_2, and methane (Waite et al. 2017). The presence of H_2 indicates the occurrence of redox reactions between water and rock. The H_2 could be produced during water circulation that is driven by gravitational tidal heating in a porous core (Choblet et al. 2017). One possibility is that ultramafic rocks containing abundant ferrous iron are oxidized by water, forming magnetite and molecular hydrogen (Reaction 1). In a general sense, this process may be analogous to H_2 production during serpentinization in ultramafic systems on Earth. Alternatively, if accreted metallic iron is still present deep in the core, then aqueous oxidation of metal could be the dominant source of H_2 (Reaction 3), as on chondrite parent bodies.

The ocean of Enceladus is most likely a habitable environment. Suspected hydrothermal activity would provide a source of chemical energy that could be harnessed by microorganisms. The levels of CO_2, H_2, and methane in the plume appear to be significantly out of thermodynamic equilibrium in the ocean with respect to the reaction:

$$CO_{2(aq)} + 4H_{2(aq)} \rightleftarrows CH_{4(aq)} + 2H_2O_{(liq)} \quad (4)$$

In particular, the abundance of H_2 appears to exceed the equilibrium value for inferred ocean conditions by over four orders of magnitude. This means that methanogenesis (reaction to the right in Reaction 4) is viable and that plume methane could be biotic, although a primordial or geochemical (e.g., thermogenic) origin of methane is not excluded. The Enceladan ocean also contains many of the chemical building blocks that would be needed by life. Diverse organic compounds, including macromolecular material rich in benzene rings (Postberg et al. 2018), as well as N- and O-bearing volatile organic compounds, have been found. These materials could be derived from primordial organic matter, putative biomass, or Fischer–Tropsch-type synthesis. There is also a ubiquitous source of nitrogen in the form of ammonia that could be used to form amino acids. Sulfur may be present as hydrogen sulfide, but its identification in the plume is presently tentative. Regardless, Enceladus' core should contain sufficient sulfur for life if its composition is chondritic. This argument also applies to phosphorus, which has not been detected.

TITAN

Titan is Saturn's largest moon, and the second largest moon in the solar system. It is often referred to as an Earth-like moon because it has a thick (~1.5 bar), N_2-rich atmosphere. However, Titan's atmosphere contains little oxygen, which is mainly present as minor carbon monoxide. An important consequence is that carbon can exist in its fully reduced form. Methane is the second most abundant atmospheric gas (Niemann et al. 2010), and it participates in two processes that shape Titan's chemistry. The first is photochemistry, where ultraviolet photons and other high-energy particles initiate the dissociation of methane and N_2. This process sets off a cascade of chemical reactions involving radicals and ions that lead to the synthesis of complex organic compounds. The second key process involving atmospheric methane is its condensation. It rains liquid methane on Titan. Rainfall commences a meteorological and fluvial cycle that is reminiscent of Earth's hydrological cycle.

Atmospherically derived liquid and solid organic condensates modify the surface of Titan. The most distinct surface features are lakes and seas. Titan has three seas—named Kraken, Ligeia (Fig. 4), and Punga Maria—all located in the north polar region. The lakes and seas contain ~70,000 km^3 of methane-rich liquid (Hayes 2016). Although they are difficult to inventory, surface organic solids appear to be abundant. Liquid methane derived from rainfall can dissolve soluble organic minerals (Glein and Shock 2013). If the liquid is subsequently subjected to changing conditions, mineral precipitation can occur. These changes can be driven by climatic, mixing, or geothermal processes. Despite the absence of ionic solutions, a rich molecular combinatorial solid-state chemistry is likely. Several Titan-relevant molecules (e.g., benzene, ethane) can form co-crystals, in which different molecules are hosted in a single crystal structure. Because this behavior can generate a diversity of new organic minerals, there should be great potential for the mineralogy of Titan to record sedimentary processes.

Where did Titan's atmosphere come from? The geologically short photochemical lifetime of methane (10^7 years) implies replenishment from the interior, possibly by some form of organic or water volcanism. The presence of radiogenic ^{40}Ar in the atmosphere shows that transport from the subsurface has occurred, and geophysical data suggest the presence of a salty water ocean in the interior (e.g., Durante et al. 2019). However, there is no conclusive evidence for cryovolcanoes. It is uncertain whether Titan's ocean is habitable. Given the ubiquity of methane on Titan, reductants and carbon compounds could be available in the ocean. The bigger question is whether there are sufficient sources of oxidants in the ocean. Radiolysis can serve as a long-term oxidant source (e.g., Reaction 2), although its influence depends on how much of Titan's ^{40}K is in the ocean versus the rocky core. Titan's methane could be primordial, as in comets, or it might have been produced internally. The issue is unresolved, but recent data may support the latter hypothesis. That is, the upper limit on Titan's atmospheric $^{84}Kr/CH_4$ ratio ($<10^{-6}$) from the *Huygens* probe is much lower than the value ($\sim 8 \times 10^{-5}$) determined at comet 67P/Churyumov–Gerasimenko by the European Space Agency's *Rosetta* spacecraft (Rubin et al. 2019).

The origin of Titan's nitrogen seems clearer. Combined constraints from the abundance of atmospheric ^{36}Ar and nitrogen isotopes in N_2 implicate two sources of N: ammonia, and primordial C–H–O–N–S organic matter. These materials would have been accreted if Titan formed from comet-like icy planetesimals at temperatures of ~70–100 K. Ammonia could have been converted to N_2 via early atmospheric photochemistry, shock chemistry from comet impacts, or heating of ammonium-bearing minerals in Titan's core. Organic matter in the core would release secondary ammonia during radiogenic heating, which could be oxidized to N_2 under suitable conditions of time, temperature, pressure, pH, oxygen fugacity, and bulk nitrogen concentration (Miller et al. 2019).

TRITON AND PLUTO

Triton, the big moon of Neptune, is thought to be a captured Kuiper Belt Object. Although only ~40% of its surface was imaged closely by the *Voyager 2* spacecraft, the data revealed a youthful and geologically active surface featuring plumes, potential cryovolcanic landforms, and few impact craters. Earth-based spectroscopy shows that the surface is composed of N_2, methane, carbon monoxide, CO_2, and water (Merlin et al. 2018). These compounds exist as ices that maintain a tenuous (~14 µbar) atmosphere by sublimation at ~38 K. Although the internal structure of Triton is unknown, the dynamic geology suggests that an ocean may exist between an ice shell and a silicate mantle. This ocean could have been hydrothermally processed as a result of extreme gravitational tidal heating during the circularization of Triton's orbit after capture by Neptune. Accreted compounds containing carbon or nitrogen could have been transformed in hydrothermal systems, forming new assemblages of aqueous species, including organic compounds that may serve as quantitative probes of potential habitability in an icy ocean world (Shock and McKinnon 1993).

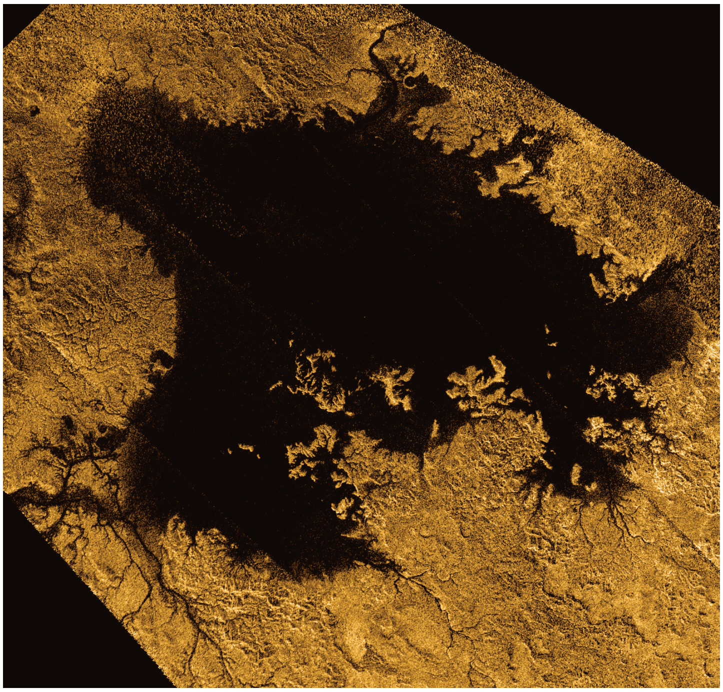

Figure 4 Ligeia Mare is the second largest body of liquid on the surface of Saturn's largest moon, Titan. It has a maximum depth of ~160 m, a volume that is ~3 times that of Lake Michigan (USA), and a major chemical species composition of ~73 mol% methane, ~10 mol% ethane, and ~17 mol% N_2 at 91 K. Radar images from the *Cassini* spacecraft were used to construct this false-color mosaic. Image Credit: NASA/JPL-Caltech/ASI/Cornell.

Pluto is another water–rock–organic body at the edge of the classical solar system. Observations by the *New Horizons* spacecraft revealed a heterogeneous landscape that has been modified by glacial, sublimation, and potential cryovolcanic processes (Moore et al. 2016). The largest glacier (Sputnik Planitia) has an area that is comparable to the country of Pakistan and a depth (~3–10 km) that could rival, or exceed, Earth's oceans. The surface of this ice sheet is dominated by N_2, which flows at the surface temperature of ~37 K. It has been estimated that Sputnik Planitia contains 10^{18}–10^{19} kg of N_2, which could have originated in cometary building blocks (Glein and Waite 2018). The other major volatile on Pluto's surface is methane ice. It sublimes into the thin (~12 µbar in 2015) atmosphere, providing a carbon feedstock for photochemical organic synthesis, as on Titan. This process produces layers of haze that settle onto the surface, which help make it reddish and darker in certain areas. Some of Pluto's methane escapes from the atmosphere and freezes out at the north pole of its largest moon, Charon, where it is also photolyzed into organic materials (Grundy et al. 2016).

LOOKING AHEAD

Numerous opportunities for exploration promise to advance our understanding of reduced volatile compounds and organic evolution on planetary bodies. The *Rosalind Franklin* rover, which is part of the ExoMars mission, will search for organic signs of life in clay-rich rocks after it lands in 2021. The *Mars 2020* rover is also scheduled to land in 2021, and, in addition to in situ investigations, it will cache materials for a future sample return mission back to Earth. The *Hayabusa2* (of the Japanese Aerospace Exploration Agency) and *OSIRIS-REx* spacecraft (from NASA) have already reached their target asteroids, and are anticipated to return samples that may contain organic compounds in 2020 and 2023, respectively. In 2027, the *Lucy* spacecraft (from NASA) will begin making the first flyby observations of several Trojan asteroids, which are dark objects thought to hold clues about the formation of the outer solar system. Also in the late 2020s, the *Europa Clipper* spacecraft will investigate Europa, with an emphasis on the habitability of the subsurface ocean and its possible expression at the surface. The *JUICE* [JUpiter ICy moons Explorer; of the European Space Agency] spacecraft is planned to enter orbit in 2032 around Ganymede, the largest moon in the solar system which is another icy ocean world that might be habitable. The *Dragonfly* mission will send a dual-quadcopter drone through the skies of Titan to study potential prebiotic chemistry at organic-rich landing sites near Titan's equator. It is scheduled to arrive in 2034. No new missions to Ceres, Enceladus, Triton, Pluto or other Kuiper Belt Objects have been approved, but concepts continue to be refined. An ambitious lander concept to search for possible biosignatures on Europa is also under study. The *James Webb Space Telescope*, set to launch in 2021, will offer new views of these worlds in addition to furthering a new era of exoplanetary geochemistry.

In time, we will gain ever deeper insights into universal geochemical phenomena and how they can come together to create habitable worlds, from our cosmic backyard to the far frontiers of space.

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REFERENCES

Brown ME, Hand KP (2013) Salts and radiation products on the surface of Europa. Astronomical Journal 145, doi: 10.1088/0004-6256/145/4/110

Choblet G and 6 coauthors (2017) Powering prolonged hydrothermal activity inside Enceladus. Nature Astronomy 1: 841-847

Durante D, Hemingway DJ, Racioppa P, Iess L, Stevenson DJ (2019) Titan's gravity field and interior structure after Cassini. Icarus 326: 123-132

Eigenbrode JL and 21 coauthors (2018) Organic matter preserved in 3-billion-year-old mudstones at Gale crater, Mars. Science 360: 1096-1101

Glein CR, Shock EL (2013) A geochemical model of non-ideal solutions in the methane–ethane–propane–nitrogen–acetylene system on Titan. Geochimica et Cosmochimica Acta 115: 217-240

Glein CR, Waite JH Jr (2018) Primordial N_2 provides a cosmochemical explanation for the existence of Sputnik Planitia, Pluto. Icarus 313: 79-92

Grundy WM and 40 coauthors (2016) The formation of Charon's red poles from seasonally cold-trapped volatiles. Nature 539: 65-68

Hayes AG (2016) The lakes and seas of Titan. Annual Review of Earth and Planetary Sciences 44: 57-83

Hemingway DJ, Mittal T (2019) Enceladus's ice shell structure as a window on internal heat production. Icarus 332: 111-131

Kivelson MG and 5 coauthors (2000) Galileo magnetometer measurements: a stronger case for a subsurface ocean at Europa. Science 289: 1340-1343

Merlin F, Lellouch E, Quirico E, Schmitt B (2018) Triton's surface ices: distribution, temperature and mixing state from VLT/SINFONI observations. Icarus 314: 274-293

Miller KE, Glein CR, Waite JH Jr (2019) Contributions from accreted organics to Titan's atmosphere: new insights from cometary and chondritic data. Astrophysical Journal 871, doi: 10.3847/1538-4357/aaf561

Moore JM and 41 coauthors (2016) The geology of Pluto and Charon through the eyes of New Horizons. Science 351: 1284-1293

Niemann HB and 9 coauthors (2010) Composition of Titan's lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment. Journal of Geophysical Research: Planets 115, doi: 10.1029/2010JE003659

Postberg F and 7 coauthors (2009) Sodium salts in E-ring ice grains from an ocean below the surface of Enceladus. Nature 459: 1098-1101

Postberg F and 20 coauthors (2018) Macromolecular organic compounds from the depths of Enceladus. Nature 558: 564-568

Prettyman TH and 13 coauthors (2019) Elemental composition and mineralogy of Vesta and Ceres: distribution and origins of hydrogen-bearing species. Icarus 318: 42-55

Roth L and 6 coauthors (2014) Transient water vapor at Europa's south pole. Science 343: 171-174

Rubin M and 20 coauthors (2019) Elemental and molecular abundances in comet 67P/Churyumov-Gerasimenko. Monthly Notices of the Royal Astronomical Society 489: 594-607

Shock EL, McKinnon WB (1993) Hydrothermal processing of cometary volatiles—applications to Triton. Icarus 106: 464-477

Tarnas JD and 6 coauthors (2018) Radiolytic H_2 production on Noachian Mars: implications for habitability and atmospheric warming. Earth and Planetary Science Letters 502: 133-145

Vance SD, Hand KP, Pappalardo RT (2016) Geophysical controls of chemical disequilibria in Europa. Geophysical Research Letters 43: 4871-4879

Waite JH and 12 coauthors (2017) Cassini finds molecular hydrogen in the Enceladus plume: evidence for hydrothermal processes. Science 356: 155-159

Webster CR and 43 coauthors (2018) Background levels of methane in Mars' atmosphere show strong seasonal variations. Science 360: 1093-1096

Wordsworth R and 7 coauthors (2017) Transient reducing greenhouse warming on early Mars. Geophysical Research Letters 44: 665-671

Yuen G, Blair N, Des Marais DJ, Chang S (1984) Carbon isotope composition of low molecular weight hydrocarbons and monocarboxylic acids from Murchison meteorite. Nature 307: 252-254

Zahnle K, Freedman RS, Catling DC (2011) Is there methane on Mars? Icarus 212: 493-503

Zolensky ME and 6 coauthors (2018) Physical, chemical, and petrological characteristics of chondritic materials and their relationships to small solar system bodies. In: Abreu N (ed) Primitive Meteorites and Asteroids: Physical, Chemical, and Spectroscopic Observations Paving the Way to Exploration. Elsevier, Amsterdam, pp 59-204

Zolotov MY (2017) Aqueous origins of bright salt deposits on Ceres. Icarus 296: 289-304

Zolotov MY, Shock EL (2004) A model for low-temperature biogeochemistry of sulfur, carbon, and iron on Europa. Journal of Geophysical Research: Planets 109, doi: 10.1029/2003JE002194