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Diverse aqueous environments during Mars' first billion years: the emerging view from orbital visible-near infrared spectroscopy

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Introduction by Paul Mahaffy (NASA Goddard Space Flight Center)
The past decade of Mars missions has been a golden age of Mars exploration with a focus on the habitability of our next-door neighbor planet. With every new set of successful measurements from surface rovers or from orbit a fresh and often surprising perspective emerges on the geological and geochemical processes that brought Mars to its present cold and dry state. In the first contribution of this series (Geochemical News 141) we surveyed the recent progress from several such missions and examined the measurements we hope to make from instruments on a highly sophisticated rover (Curiosity) to be launched in 2011. With the present contribution, Bethany Ehlmann, one of the recent leaders in analyzing and interpreting Mars orbital infrared spectroscopy data will describe these techniques and results and the new view of the history of Mars that is emerging from these studies. (See NASA's illuminating animation at http://mars.jpl.nasa.gov/mro/gallery/video/)

This paper is the second in a series organized by Dr. Paul Mahaffy (Chief, Atmospheric Experiments Laboratory, Solar System Exploration Division, NASA Goddard). In the first installment, Dr. Mahaffy discussed Curiosity, the 900 kg, nuclear-powered rover scheduled to land on Mars in late 2012. He reviewed the rover's landing system and its extensive array of integrated scientific instrumentation. (http://www.geochemsoc.org/publications/geochemicalnews/gn141oct09/sampleanalysisatmars.htm).

Stay tuned for the third paper, which will describe the x-ray diffraction and x-ray fluorescence instruments on Curiosity and how they will help characterize the Martian surface.

Diverse aqueous environments during Mars' first billion years: the emerging view from orbital visible-near infrared spectroscopy

Phyllosilicates, sulfates, carbonates, zeolites, chlorides, perchlorates, and opaline silica: news of discoveries on Mars is starting to read like a mineralogy textbook. With the arrival of orbiting visible/near-infrared (VNIR) spectrometers, first in 2003 on the European Space Agency's Mars Express followed in 2006 by NASA's Mars Reconnaissance Orbiter (MRO), it is now clear that chemical and mineralogic evidence of past aqueous geochemical processes persists to the present, recorded in rocks and sediments. Coupled with data from landed missions, Mars exploration is moving beyond excitement about simply past liquid water towards understanding that ancient Mars probably hosted a diverse array of aqueous environments. Recent data suggest that hydrothermal, lacustrine, and pedogenic settings were part of the Martian landscape during its first billion years. Could one (or more) of these environments have been habitable or inhabited? Using the current data to guide the upcoming set of landed and orbital missions, we may be poised to find out. Here I review recent mineralogic findings, detail the methods, and discuss implications for understanding the first billion years of Mars history-a period in which the geologic record on Earth is sorely lacking.

Following the water...and the minerals

For the past decade, "follow the water" has been NASA's guiding principle for selection of Mars exploration missions and landing sites. The reason is simple: on Earth wherever we find water we find life. Tracing the history of this important Mars volatile may be our best means of understanding whether life could have existed there, as well as understanding the fundamental processes necessary to sustain water-rich worlds like our own through time.

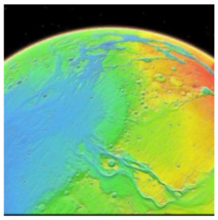
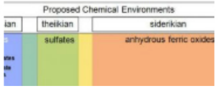


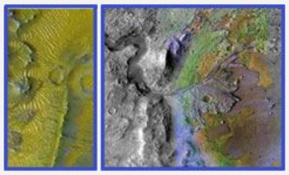
Figure 1

Since the Mariner missions of the late 1960s, it has been known that liquid water was once a powerful force shaping Mars' surface. Since the first Mariner and Viking orbiters, orbital imaging has revealed large outflow channels, valley networks, evidence for crater lakes and, some posited, a possible northern ocean (Figure 1). Yet subsequent missions did not reveal the mineralogy and chemistry one might expect for a once watery world. Elemental composition measurements from landers and rovers showed rocks of primary volcanic composition. A few tantalizing hints of salts in Mars soils and in Mars meteorites pointed to at least small amounts of liquid water, but the basaltic rocks had not altered to clays or oxides. There appeared to be no secondary rocks, e.g. carbonates, that on Earth precipitate in large bodies of water and that should precipitate on Mars from waters in equilibrium with its 95% CO2 atmosphere.

But in 2004, following the water took an exciting, chemical/mineralogical turn. The Opportunity Mars Exploration Rover discovered sulfate-rich sedimentary rocks at Meridiani Planum, most likely deposited in shallow surface waters (Squyres et al., 2004). Then the Observatoire pour l'Minéralogie l'Eau les Glaces et l'Activité (OMEGA) visible/near-infrared imaging spectrometer on Mars Express began finding hydrated minerals from orbit (Bibring et al., 2005; for methods, see 'Identifying minerals from orbit' below). One class was the sulfate salts, such as at Meridiani, found in rocks from Mars' middle epoch, the Hesperian, approximately 2.9-3.7 Gyr. The second class was phyllosilicates, in this case Al-, Fe-, and Mg- smectite clays, found in the most ancient Noachian rocks, >3.7 Gyr. The youngest Amazonian terrains, <2.9 Gyr, had none of these hydrated minerals. This suggested a directional evolution for Mars, traceable through mineralogy (Bibring et al., 2006). A wet, circum-neutral pH clay-forming epoch ("phyllosian") was followed by a drier, more acidic sulfate-forming epoch ("theiikian"). By three billion years ago, only anhydrous alteration processes persisted over large scales ("siderikian").



The higher spatial and spectral resolution NASA follow-on to OMEGA, the Compact Reconnaissance Imaging spectrometer for Mars (CRISM; Murchie et al., 2007) on MRO has discovered many more occurrences of hydrated minerals than previously known as well as refined the detections of phyllosilicates and sulfates to reveal extraordinary mineralogic diversity



About the Author

Bethany Ehlmann will receive her Ph.D. in Geological Sciences from Brown University in May 2010. She studies planetary surfaces, especially areas that may have hosted ancient life forms. She collaborates with the CRISM instrument team, which is responsible for the visible-infrared imaging spectrometer on NASA's Mars Reconnaissance Orbiter. From January to September 2004, she helped direct the Mars Exploration Rovers Spirit and Opportunity. She received her B.A. at Washington University in St. Louis and holds masters' degrees from Brown and Oxford Universities.

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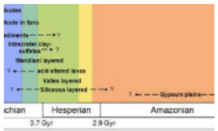


Figure 2

phyllosilicates and sulfates to reveal extraordinary mineralogic diversity within these classes as well as new mineral classes (Table 1). It is now possible to perform meters-scale geologic mapping from Mars orbit that includes both morphological and mineralogical properties of the units. By understanding the context and associations of these diverse alteration minerals, we are better able to distinguish the geological environment in which they formed. Coupled mineralogy with morphology allowed the identification of distinct chemical environments and their rough time ordering (Figure 2; Murchie et al., 2009), which we detail further below ('Mineralogic clues to the first billion years').

Table 1. Minerals resulting from aqueous alteration, discovered on Mars through January 2010. All mineral phases are observed from orbit with VNIR spectroscopy except for phases in italics, which have been reported by other orbiting and landed missions.

Class	Group/mineral	Formula	References
Phyllosilicates	Fe/Mg smectites (e.g., nontronite, saponite)	$(Ca, Na)_{0.3-0.5}(Fe,Mg, Al)_{2-3}(Si, Al)_4O_{10}(OH)_2$	Poulet et al., 2005; Mustard et al., 2008
	Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2$	Poulet et al., 2005; Mustard et al., 2008
	Kaolin group minerals (e.g. kaolinite, halloysite)	$Al_2Si_2O_5(OH)_4$	Bishop et al., 2008; Ehlmann et al., 2009
	Chlorite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	Mustard et al., 2008; Ehlmann et al., 2009
	Serpentine	$(Mg, Fe)_3Si_2O_5(OH)_4$	Ehlmann et al., 2009
	High charge Al,K phyllosilicate (e.g. muscovite or illite)	$KAl_2AlSi_3O_{10}(OH)_2$	Mustard et al., 2008; Ehlmann et al., 2009
Other hydrated silicates	Prehnite	$Ca_2Al(AlSi_3O_{10})(OH)_2$	Clark et al, 2008; Ehlmann et al, 2009
	Analcime	$NaAlSi_2O_6 \cdot H_2O$	Ehlmann et al., 2009
	Opaline silica	$SiO_2 \cdot H_2O$	Milliken et al., 2008; Ehlmann et al., 2009
Carbonates	Magnesium carbonate (e.g. magnesite)	$MgCO_3$	Ehlmann et al., 2008b
	Calcium carbonate	$CaCO_3$	*Phoenix lander (Boynton et al., 2009)*
Sulfates	Fe/Mg mono- and poly- hydrated sulfates	$(Fe,Mg)SO_4 \cdot nH_2O$	Gendrin et al., 2005
	Gypsum	$CaSO_4 \cdot 2H_2O$	Langevin et al., 2005
	Alunite	$KAl_3(SO_4)_2(OH)_6$	Swayze et al., 2008
	Jarosite	$KFe^{(III)}{}_3(OH)_6(SO_4)_2$	Milliken et al., 2008
	not a named mineral	$FeSO_4(OH)$	Swayze et al., pers. comm.
Chlorides	*chlorides*	*metalCl*	*Thermal Emission Spectrometer (Osterloo et al., 2008)*
Perchlorates	*perchlorates*	$(Mg,Ca)(ClO_4)_2$	*Phoenix Lander (Hecht et al., 2009)*
Fe Oxides	Hematite	Fe_2O_3	Christensen et al., 2000; Bibring et al., 2007
	Goethite	$FeO(OH)$	Farrand et al., 2009

Identifying minerals from orbit

The fundamental advance that led to the discovery of these diverse water-related minerals only recently has been the application of orbital hyperspectral, visible/near-infrared (VNIR) imaging. The 0.4-2.6 µm wavelength region has proven to be most useful for mineral identification on Mars. VNIR spectroscopy is a technique commonly employed in the laboratory that is sensitive to changes in the energy state of transition metals' outer electrons (Fe is especially important in rock-forming minerals) as well as vibrations between atoms chemically bonded in mineral structures. The electrons and vibrating molecules, respectively, absorb radiation at characteristic wavelengths leading to distinctive absorption features in reflected light spectra that are often diagnostic of specific minerals. Usually, the electronic transition absorptions are broad and occur at wavelengths <1.5 µm (Burns, 1993). The fundamental vibrations due to OH, CO3, and H2O occur at much longer wavelengths (3-15 µm), but overtones and combination tones occur in the VNIR range measured by orbiting instruments. While these are weaker than the fundamentals in transmission spectra, light at VNIR wavelengths is multiply scattered in particulate media on planetary surfaces. The result is that the overtones and combinations may sometimes be stronger than the fundamentals that occur in the thermal infrared wavelengths (Clark et al., 1990).

The imaging spectrometers collect light in two different ways. In its infrared channels, OMEGA is a whisk broom imager which scans back and forth across the surface as it passes over, collecting one pixel in 352 wavelengths (0.35-5.1 µm) at a time with a spectral sampling of 7-20nm. CRISM is a push broom imaging spectrometer which collects a single row of pixels in 544 wavelengths (0.4-4.0 µm). Both instruments build up an image, north-south or south-north along the path of their polar orbits. The end result for each observation is the same: an image cube with x and y spatial dimensions and a z spectral dimension so that the VNIR spectrum of each pixel on the surface can be interrogated separately. OMEGA's spatial resolution ranges from 300-4800m/pixel, and global coverage is nearly complete. CRISM will complete a global map of Mars at 200m/pixel and in targeted mode acquires images at up to 18m/pixel.

The raw sensor data are corrected to radiance using laboratory data and data from an onboard calibration sphere. They are then converted to illumination angle-corrected I/F, an effective reflectance, by ratioing to the solar spectrum at Mars distance and dividing by the cosine of the incidence angle of light. To investigate surface mineralogy it is necessary to correct for strong bands resulting from atmospheric absorptions. Although more complex methods exist, most commonly employed is the "volcano scan method" in which each pixel is divided by scaling an atmospheric transmission spectrum to fit the band depth of the CO2 triplet absorption at 2.0 µm. The atmospheric transmission spectrum used is derived by taking observations over the base and top of the 27-km high Olympus Mons volcano and ratioing the difference. Commonly, corrected data from an area of interest on the surface are also ratioed to corrected data from a "boring" area to eliminate residual artifacts from instrument calibration and highlight the distinctive absorption features.

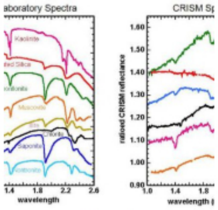


Figure 3

After these corrections are made, individual spectra or spectra averaged over a given region can then be compared to laboratory spectra (e.g. Clark et al., 2007; http://speclab.cr.usgs.gov/spectral.lib06/) to make mineral identifications (Figure 3 and 4). For example, in smectites, the principal absorptions are near 1.4, 1.9 and 2.2-2.3 µm. These are due to vibrations of water and OH, water, and metal-OH structural elements, respectively. Shifts in band position occur, however, when Fe- (1.43, 2.29) vs. Mg- (1.39, 2.32) vs. Al- (1.41, 2.21) is the principal octahedral cation, allowing even structurally similar phases such as nontronite, saponite, and montmorillonite to be distinguished from orbit (Clark et al., 1990; Mustard et al., 2008).

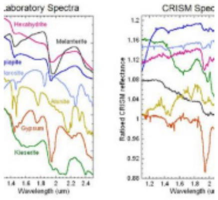


Figure 4

Once identified, by mapping absorption band depth (Pelkey et al., 2007) or using more sophisticated parameters to examine overall spectral shape (Clark et al., 2003), the distribution of VNIR spectral signatures diagnostic of particular minerals can be mapped spatially. The high-resolution mineralogic data can then be combined with high-resolution imaging data sets-down to 25 cm/pixel resolution with MRO's HiRISE camera-to study mineralogy in concert with morphology.

Mineralogic clues to the first billion years

As Figure 2 shows, nearly a dozen new aqueous chemical environments have been identified on Mars and are now the ongoing subject of intensive study (Murchie et al., 2009). A period of particular interest is the Noachian and the Noachian to Hesperian transition. During this period of Earth's history many important events happened: the first crust formation, the first liquid water, late heavy bombardment by meteorites, prebiotic chemistry and events leading to the origin of life. When did the Earth become habitable and when did it become inhabited? The timing and environmental conditions remain shrouded in mystery due to the recycling of the rock record by plate tectonics. Far less than 1% of Earth's rock record is from this period and much of what does exist has been heavily altered by metamorphism, weathering, and more recent biologic activity. However, about half of Mars' crust dates back to before 3.5 Gyr. Moreover, this appears to be the period where liquid water played the greatest role in planetary geologic processes. Little is known about these early conditions and a big question is why did Mars apparently begin to dry by the end of its first billion years. By studying the environments of early Mars, we gain insight into the history of water on Mars and also the earliest watery environments on terrestrial planets.

Environmental history from mineralogy

While some of the minerals on Mars form under a variety of geochemical conditions and at relatively unconstrained temperatures and pressures (e.g. smectites, chlorites, gypsum), some of the minerals form in only narrow temperature, pH or redox conditions (e.g. prehnite, analcime, alunite, jarosite). The recently discovered alteration mineral diversity suggests global Mars trends were modulated by specific local conditions. Moreover, distinctive stratigraphies and morphologies of the mineral-bearing units suggest multiple settings for liquid water. Here are a few of the earliest environments:

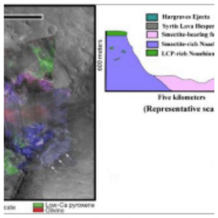


Figure 5

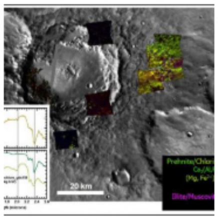


Figure 6

'Deep phyllosilicates': these geologic materials are the oldest altered crust on Mars and, in some areas, such as in the Nili Fossae fracture system, the basement layer of a complex stratigraphy (Figure 5). Here the basaltic materials have been partially altered to materials whose VNIR spectral signature is dominated by that of Fe/Mg smectite clays. The materials are frequently brecciated and sometimes have raised veins and fractures. In this region, these clay-bearing materials are the deepest exposed unit and apparently unaltered mafic materials cap them (Mustard et al., 2009). Elsewhere, hydrated minerals buried deeply in Mars' crust are exposed by craters drilling into the southern highlands and throwing out material. Some of the "deep phyllosilicates" have a distinctively hydrothermal character. Minerals and mineral assemblages indicative of low-grade metamorphism such as analcime, illite, and prehnite are found associated with craters. Figure 6, for example, shows a crater with prehnite- and chlorite-bearing ejecta deposits. Prehnite is a mineral diagnostic of the temperature and pressure of its formation since it only forms at temperatures between about 200-350°C and pressures <3 kbar. That it is in ejecta deposits means that it was most likely transported ballistically during impact, excavating materials from depth, rather than formed in-situ (Ehlmann et al., 2009). "Deep phyllosilicates" may represent the altered component of Mars earliest crust, which was churned by repeated impacts that were a common feature of the early solar system. That the bulk rock and breccia blocks within are altered to smectite clays suggests liquid water was probably stable that time and, at least in some locations, hydrothermal processes were occurring.

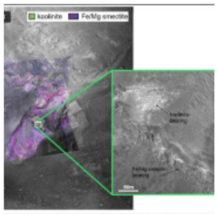
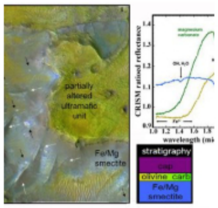


Figure 7

'Layered phyllosilicates': Near the two most areally extensive phyllosilicate deposits on Mars, at Mawrth Vallis and the Nili Fossae, a distinctive stratigraphy is observed, traceable over hundreds to thousands of kilometers. Alumnium phyllosilicates are found overlying Fe/Mg smectites. Figure 7 shows one example from eroded sediments which fill a crater. The bulk of the sediments are Fe/Mg smectite bearing, but a distinctive bright layer tens of meters thick instead has a spectral signature consistent with a kaolin group mineral most likely kaolinite or halloysite. Elsewhere on Mars, in this Al phyllosilicate layer, kaolinite is accompanied by montmorillonite and opaline silica (Bishop et al., 2008). A simple explanation to explain this stratigraphy is top-down leaching by surface and near surface waters that strips a pre-existing smectite unit of Fe, Mg, and Ca cations, leaving behind mostly Al and Si to form kaolinite (Ehlmann et al., 2009). An analog terrestrial setting is pedogenesis of Hawaiian basalts under intermittently wet conditions.



Carbonate and altered ultramafics: in one region of the planet, near the Nili Fossae an areally extensive stratigraphic unit elevated in olivine abundance (>30%) is found circumferential to the Isidis impact basin (Figure 8). The unit is thought to represent either lavas emplaced immediately following basin formation or a melt sheet containing materials excavated from Mars' lower crust and upper mantle by the impact (Mustard et al., 2009). The olivine-bearing bedrock exhibits signs of partial alteration, in most cases to magnesium carbonate and in a few cases to serpentine (Ehlmann et al., 2009). On Mars, these deposits are significant because the existence of carbonate at this site indicates neutral to alkaline aqueous conditions, in contrast to acid conditions indicated at different locations and in younger rocks by the MER rovers

Figure 8

indicated at different locations and in younger rocks by the MER rovers (Ehlmann et al., 2008b). Serpentine is also a tantalizing find because the process of serpentinization leads to the generation of methane. Although these particular rocks formed billions of years ago and do not indicate the source for the methane presently observed in the Mars atmosphere, it points to the fact that processes of methane production from serpentinization did exist in Mars' past.

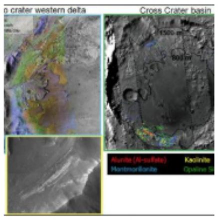


Figure 9

Fluvial/lacustrine sedimentary clays: Craters are topographic lows. A few have hosted crater lakes and still fewer host sedimentary structures that contain alteration minerals. Depending on the basin, however, the preserved sediments differ in mineralogy and implied geochemical conditions. One example is Jezero crater (Figure 9), a putative open basin lake which apparently hosted neutral to alkaline waters. The materials comprising sediments within the crater are Fe/Mg smectite- and Mg carbonate- bearing similar to the materials found in the Jezero basin watershed (Ehlmann et al., 2008a). Elsewhere, the lakes have a distinctly different acidic character. For example, a closed basin in Terra Sirenum, Cross Crater, probably once hosted a crater lake and is filled with sediments containing alunite, an Al-sulfate that forms only at pH <4 (Swayze et al., 2008). Alunite, along with silica and aluminum phyllosilicates, is found within friable layered units ringing the crater (Figure 9).

The sulfate-forming epoch and its many environments: Salts, e.g. sulfates, become increasingly common and clays less common in later time periods. As revealed by in-situ exploration by the Mars exploration rover at Meridiani Planum, the Hesperian sandstones there have been altered by acidic waters in a complex sequence of surface weathering and diagenesis (Squyres et al., 2004). At Gusev crater, the Spirit rover has found evidence for silica and sulfates possibly created by acid hydrothermal systems (Squyres et al., 2008). Furthermore, extensive silica deposits accompanied by sulfates have been found from orbit in the plains surrounding Valles Marineris and massive mounds of sulfate-bearing materials exist within the Valles system (Milliken et all, 2008; Murchie et al., 2009).

The future

All these discoveries point to the fact that Mars has a rich record from its first billion years available for exploration. On Mars, the new news for scientists is to think locally rather than globally. The types of chemical environments that hosted liquid water varied substantially in character through space and time.

The most immediate impact that these new mineral finds will have on NASA and ESA's program of Mars exploration is in the selection of the landing site for the next rover, the Mars Science Laboratory (MSL) that launches in 2011. Environments of paleolakes with sediments with Fe/Mg smectite clays (Holden and Eberswalde, Gale) and layered phyllosilicates (Mawrth Vallis) are currently represented in the suite of four finalists. In light of recent discoveries of the diversity of alteration environments on early Mars, two additional sites , altered ultramafics (Northeast Syrtis) and a plain of sediments of Fe/Mg smectites and chloride (East Margaritifer), were recently targeted for a period of intensive study for their consideration as candidates [for more on this selection process see http://marsoweb.nas.nasa.gov]. Landing site safety is the primary factor that must be fulfilled at the chosen site and efforts are ongoing to characterize any possible hazards. In addition to finding out more about aqueous processes on early Mars, scientists hope that in-situ sample analysis could reveal evidence for organic carbon (Mahaffy, 2009). Scientifically, an intense debate rages over (a) what types of environments early microbial organisms might have been most likely to inhabit and (b) in which types of environments biosignatures of past life-organic carbon, morphologic fossils, mineral disequilibria, or distinctive isotopic fractions- are most likely to be preserved over three billion years.

In spite of all the progress made since 2004, many questions persist about the newly discovered alteration minerals. One basic question is "how much?" Quantification of mineral abundance with VNIR data is a highly nonlinear problem, since texture and grain size also effect spectra, although efforts are beginning to model likely modal mineralogies (Poulet et al., 2008). Mineralogic data have also thrown down the gauntlet for geochemical modelers to use data on the minerals and their assemblages to more tightly constrain geochemical conditions and the rates and processes of mineral formation so as to establish more detailed parameters on Mars' earliest environments.

As VNIR images from OMEGA and CRISM continue to be collected and analyzed, discoveries of still more minerals on Mars may yet be made. By combining orbital data with data from the next generation of landers and rovers, we can make substantial progress in understanding the history of water on Mars, its evolution over billions of years, and perhaps, whether Mars ever hosted the geochemical environments necessary to sustain life.

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Figure Captions

FIGURE 1. Topographic map showing large outflow channels and valleys draining into Mars' northern lowlands. In spite of abundant morphologic evidence for liquid water, until recently orbiting spectrometers, no large deposits of altered minerals had been found.

FIGURE 2. Chemical environments on Mars, adapted from Murchie et al., 2009 with mineralogic epochs from Bibring et al., 2006. The age dates for the Mars epoch boundaries are from Hartmann & Neukum (2001) cratering chronology.

FIGURE 3. Selected hydrated silicate minerals discovered by CRISM (Mustard et al., 2008; Bishop et al., 2008; Ehlmann et al., 2009). Spectra have been colored so as to match CRISM spectral data to the most probable mineralogic match, based on examination of laboratory spectra. In some cases, mineral identifications cannot be made uniquely (e.g. muscovite vs. illite, orange/yellow) or phases on Mars are intermediate between endmember minerals with solid solution series (e.g. Fe/Mg smectite with composition between nontronite and saponite endmembers, blue/cyan)

FIGURE 4. Selected sulfate minerals discovered by CRISM (Swayze et al., 2008; Murchie et al., 2009; Roach et al., 2009)

FIGURE 5. 'Deep phyllosilicates' as exposed in a 600m tall scarp beneath a mafic LCP-bearing cap rock (figures after Mustard et al., 2008; 2009). Arrows indicate that Fe/Mg smectites exposed beneath the younger Syrtis Major lavas. Olivine is present here in as mobile sands. The two CRISM images are overlain on and use to colorize a grayscale, high resolution Context Imager (CTX) image. Uncolored parts of the image do not have CRISM coverage.

FIGURE 6. 'Deep phyllosilicates' as excavated by impact. Mineral mapping from several CRISM images shows that prehnite and chlorite are the spectrally dominant phases in ejecta surrounding this 50km diameter crater (figure from Ehlmann et al., 2009). Where CRISM images are black, no alteration mineral phases were observed during examination of spectra.

FIGURE 7. Example of the layered phyllosilicates. A CRISM parameter map was used to colorize a higher resolution Context Imager (CTX) observation. The 2.3 micron Fe- or Mg-OH absorption in Fe/Mg smectites is mapped as red, the H_2O 1.0 micron band is mapped as blue, and the 2.2 micron Al-OH band is mapped as green. In this filled crater from Nili Fossae, a thin Al-OH bearing unit, identified using spectral data as kaolinite, overlies an Fe/Mg smectitie-bearing unit (figure from Ehlmann et al., 2009).

FIGURE 8. Example of the partially altered ultramafic unit and phyllosilicate/carbonate stratigraphy. CRISM spectra at the upper right correspond to colored units in this CRISM false color plus grayscale HiRISE (23cm/pixel) composite image. Arrows point to raised fractures (white) and breccia blocks (black) in the Fe/Mg smectite-bearing unit (figure from Ehlmann et al., 2009).

FIGURE 9. (left) the western delate of Jezero crater. Sediments within are Fe/Mg smectite and Mg carbonate bearing. The inset shows the wall of the crater in the delta which exposes a 20m crossbedding structure (Ehlmann et al., 2008a). (right) the Cross crater basin hosts layered sediments and where eroded exhibit signatures of alunite, silica, and Al-phyllosilicates (Swayze et al., 2008).

Atmospheric Chemistry of the Gas Giant Planets

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Synopsis

This is a brief description of historical and more recent studies about the composition and chemistry of the giant planet atmospheres, with an emphasis on Jupiter. There are several constraints from the chemistry for the various models of gas-giant planet formation, but our current knowledge remains incomplete, despite the tremendous progress made during the past 100 years of planetary research and technical developments. This article is intended to stimulate some interest in research about the gas-giant planets rather than being a comprehensive review.

Some General Characteristics

The gas-giant planets Jupiter, Saturn, Uranus and Neptune in our solar system are quite different in mass, density, and in chemical composition than the inner terrestrial planets Mercury, Venus, Earth, and Mars. Several physical properties of the gas giant planets and their atmospheres are in Table 1 which illustrates the close kinship of Jupiter and Saturn as well as that of Uranus and Neptune. Jupiter and Saturn, the most massive planets in the solar system are mainly composed of H and He, whereas in the Earth, oxygen is the most abundant element, mainly tied to rock, but also abundant in the oceans and air. The elemental make-up of the giant planets especially that of Jupiter and Saturn, is much closer to the solar photospheric composition than to the terrestrial planets. However, unlike the solar photosphere with relatively 'simple' chemistry of neutral and ionized atoms, the cool outer atmospheres of the giant planets are rich in molecular chemistry.

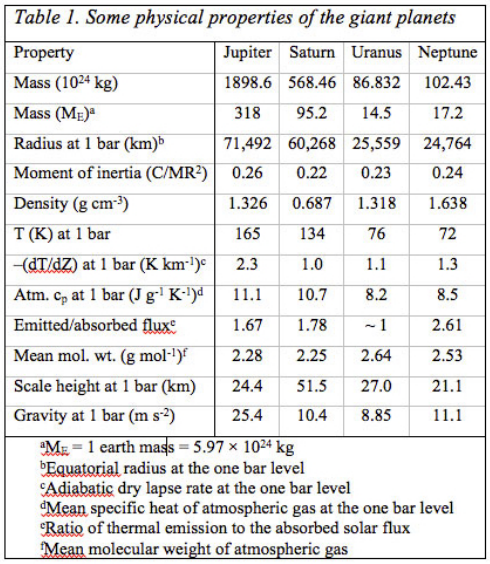


Table 1. Some physical properties of the giant planets

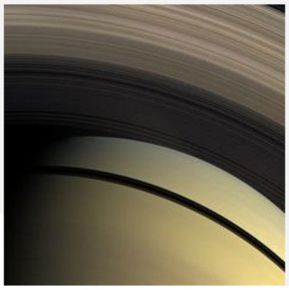
Property	Jupiter	Saturn	Uranus	Neptune
Mass (10^{24} kg)	1898.6	568.46	86.832	102.43
Mass (M_E)[a]	318	95.2	14.5	17.2
Radius at 1 bar (km)[b]	71,492	60,268	25,559	24,764
Moment of inertia (C/MR^2)	0.26	0.22	0.23	0.24
Density (g cm^{-3})	1.326	0.687	1.318	1.638
T (K) at 1 bar	165	134	76	72
$-(dT/dZ)$ at 1 bar (K km^{-1})[c]	2.3	1.0	1.1	1.3
Atm. c_p at 1 bar (J g^{-1} K^{-1})[d]	11.1	10.7	8.2	8.5
Emitted/absorbed flux[e]	1.67	1.78	~ 1	2.61
Mean mol. wt. (g mol^{-1})[f]	2.28	2.25	2.64	2.53
Scale height at 1 bar (km)	24.4	51.5	27.0	21.1
Gravity at 1 bar (m s^{-2})	25.4	10.4	8.85	11.1

[a] M_E = 1 earth mass = 5.97×10^{24} kg
[b] Equatorial radius at the one bar level
[c] Adiabatic dry lapse rate at the one bar level
[d] Mean specific heat of atmospheric gas at the one bar level
[e] Ratio of thermal emission to the absorbed solar flux
[f] Mean molecular weight of atmospheric gas

The giant planets fall into two groups: The larger and gas-rich giants Jupiter and Saturn with more than 50 mass % H and He, and the smaller gas-poor giants Uranus and Neptune with less than 50 mass % H and He. Jupiter's low bulk density (1.33 g cm^{-3}) and Saturn's even lower density (0.69 g cm^{-3}) coupled with their atmospheric composition, size, shape (i.e., their oblateness), and interior structure models are evidence that they are mainly H and He with smaller amounts of heavier elements. Uranus and Neptune have higher densities, and presumably larger contents of compounds containing C, N, and O.

The oxidizing atmospheres of Venus, Earth, and Mars are < 0.01% of the planets' total masses and are terminated by sharp boundaries with their surfaces. In contrast, the reducing atmospheres of the giant planets are significant fractions of the total planetary masses. There are no observable solid surfaces, and (apparently) bottomless atmospheres extend deep into the planets. In absence of something similar to sea-level as on Earth or a mean radius of the solid surface as on the other terrestrial planets to which atmospheric properties are referenced, the reference used is the one bar level in the atmospheres of the giant planets. Their atmospheres extend to great depth, but may turn into liquid metallic H-He deep inside Jupiter and Saturn, while ionic oceans of aqueous ammonia may occur deep inside Uranus and Neptune. All four planets have magnetic fields, which are probably generated by dynamo currents in the electrically conductive fluids (liquid metallic H-He inside Jupiter and Saturn and ionic oceans of aqueous ammonia inside Uranus and Neptune). At least three of the four giant planets emit more energy than they receive from the Sun (Uranus is the apparent exception). The heat emitted by the giant planets comes from their continued gravitational contraction and cooling and also from phase separation and sedimentation of He from H in their deep interiors (on Saturn and Jupiter). In contrast, the terrestrial planets are in radiative equilibrium and emit only as much energy as they absorb from the Sun.

Theoretical models suggest that the observed heat fluxes on Jupiter, Saturn, and Neptune are transported by atmospheric convection. This has been demonstrated for Jupiter by in situ measurements down to 22 bars from the *Galileo* probe (Seiff et al. 1998) and for Saturn, Uranus, and Neptune by determination of P, T profiles down to ~ 10 bars from *Voyager* IRIS data (Lindal 1992, Lindal



The Casssisi spacecraft recently returned this natural-color image of Saturn's inner rings.(NASA/JPL/Space Science Institute)

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et al. 1992). Convection is also necessary to explain observations of CO, PH_3, AsH_3, and GeH_4 at abundances orders of magnitude larger than their thermochemical equilibrium values in the upper troposphere (~ 100mb to ~ 3 bar) where the spectral absorption bands form and the identity of the molecules is revealed though vibrational-rotational transitions.

Discovery Log About Giant Planet Chemistry

It was in the early 1900s when the first spectroscopic investigations were undertaken to find the chemical nature of the gas-giant planets Jupiter Saturn, Uranus, and Neptune. The discovery of the latter two planets itself was not too long ago: Uranus in 1781, and Neptune in 1846 (The dwarf planet Pluto, an icy world which we do not discuss here, was only discovered in 1930).

Obtaining the spectral fingerprints of the chemistry in their atmospheres was not a trivial task. At the time observers had to be chemists as well as astronomers in order to develop emulsions to increase the sensitivity of photographic plates that could capture the planetary spectra they sought. The chemistry did not stop there, however. In 1909, Slipher obtained spectra of the giant planets, only to realize that the identification of the chemical species causing the numerous absorption bands would require further detective work. Slipher noted *'Of the chemical identity of the spectral bands of these four planets almost nothing is certainly known.'* There was a hint of atomic hydrogen absorption, but no firm conclusions were possible. He compared several of the unknown bands to bands at wavelengths that appear in cool stars but he ruled out any similarities to gases there, and others after Slipher came to the same conclusions. Slipher discussed the possible water absorption in Uranus and Neptune but also showed that these water bands are not due to absorption in these planets but instead stem from telluric water vapor instead. Many other bands in the spectra remained a mystery. Slipher concluded: *'The remaining bands in these spectra are yet to be chemically accounted for. The spectra are quite unlike the spectrum of the Earth's atmosphere, but the differences of pressure and temperature between the atmosphere of the major planets and our air are probably large. Until the bands are identified, it is not possible to arrive at satisfactory conclusions of the conditions existing in the atmospheres, although the breadth and diffuseness of the bands suggest high pressure or high temperature or both.'*

By the 1930s, knowledge about the physical conditions and chemical composition of the giant planets was improving. In 1930, Menzel described the two possibilities for the physical state of the giant planets that were popular at the time: *'Either their interiors are hot and gaseous, i.e., greatly distended by high temperature, or the material they are composed of is of relatively low density.'* Up to that time, the first possibility had been widely entertained, but the discovery that the surface temperatures of Jupiter and Saturn were only about 150K, a little higher than expected from radiative balance with solar radiation (Menzel 1923), eventually ruled against the 'hot' giant planet hypothesis. Modern measurements yield temperatures from 165 k(Jupiter) to 72 K (Neptune) at the 1 bar level; see Table 1.

The low observed mean densities and estimates for the mass distribution within the planets derived from the moment of inertia led to the suggestion that the giant planets consist of a central solid core made of rock and metal, surrounded by a layer of ice upon which a large atmosphere is located. The first of such layered structure models was by Jeffreys (1923, 1924) but at that time it was not yet known that the atmospheres are mainly H-He rich followed by smaller amounts of methane and ammonia. Layered structure models, although modified and much refined, of the giant planets are widely accepted today. Often the cores of the giant planets are still referred to as rock and ice. 'Rocky' elements are those usually found in metal, silicate, and sulfide rock (e.g., Ca, Al, Fe, Mg, Si, S) and 'icy' elements (e.g., Ar, C, N, O) are those expected to condense as various ices in the solar nebula. However, whether distinct cores actually exist or all of the 'rocky' and 'icy' elements are dissolved in the molecular and/or metallic H - He phases is unclear at present. At least some of the 'rocky' and 'icy' elements are present in the molecular H - He layers of Jupiter and Saturn because CH_4, NH_3, H_2O, H_2S, AsH_3 (arsine), GeH_4 (germane), and PH_3 (phosphine) are observed in their atmospheres. The *Juno* polar orbiter, scheduled for launch in August 2011, will measure Jupiter's gravitational field with sufficient accuracy to decide whether or not a core exists.

The low densities of the gas giants require that the outer portions are made of compounds of low molecular weight. Jeffreys considered the low-density liquids and solids hydrogen, helium, nitrogen, oxygen, CO, CO_2, CH_4, and C_2H_6. A large gaseous portion was clearly required to account for Saturn's density below that of water. Based on material properties, Jeffeys (1924) suggested that the atmospheres of Jupiter and Saturn probably consist of hydrogen, nitrogen, oxygen, helium, and perhaps methane, and make 9% and 23% of the entire radius of Jupiter and Saturn, respectively. Except for O_2, this idea about which gases are possible in the outer atmospheres is correct. However, the abundances needed to be determined, and other gases, namely He, needed to be added. He also thought that there are clouds of solid CO_2, which is not the case. Still, some types of clouds were necessary since observations indicated that Jupiter (and the other giant planets) do not rotate as rigid spheres but have visible surface features that change.

Menzel (1930) concluded that the outer atmospheres are mainly hydrogen based on the recognition from the previous year, that the sun, like other stars, is mainly composed of hydrogen (Russell 1929). This is in accord with the earlier tentative observation of hydrogen by Slipher. However, the collision induced absorption of H_2 was only found decades later in the 1950s (e.g., see review by Rea 1962).

However, identification of the gases in the atmospheres of the giant planets still remained to be done. What compounds caused the strong absorption bands in the giant planet spectra that Slipher and others had observed? It was quite clear that some strong absorbers turned Uranus and Neptune pale cyan-greenish through absorption at red visible wavelengths. Later it was found that absorptions were strong in the infrared as well - a feature now exploited to hunt and identify possible gas-giant planets around other stars. The culprits causing the strong absorptions in the giant planets - methane and ammonia - were identified by Wildt in 1932. These spectral identifications became more firm later, as more laboratory measurements became available.

The identification of hydride-gases CH_4 and NH_3 made sense as well from the theoretical point of view. They are hydrides of the more abundant elements C and N, and they are stabile at low temperatures. One would also expect the hydride of oxygen, H_2O. However, while detection of water vapor is technically possible, it was not observed (until the 1980s) because all water vapor is frozen out into clouds in the deeper, unobservable regions of the atmospheres of the gas giant planets. The water vapor pressure above the water clouds is very low at the temperatures where observations probe the atmospheres. Indeed, the water abundance on the giant planets still remains an open question (see below).

By the early 1960s, many methane and ammonia absorption features were identified in giant planet spectra (e.g., see review by Rea 1962). Estimates of abundances were made, but these were quite uncertain. Molecular H_2 was first detected in Uranus and Neptune, but then also found in Jupiter and Saturn. The presence of helium on Uranus was inferred on theoretical grounds to match the planet's density with the deduced H_2 abundances. Also identified by that time were ammonia clouds on Jupiter. However, no other compounds had been identified in the gas giant planets up to the early 1960s.

This does not mean that searches for other molecules were lacking. Volatile hydrides of elements such as Si, Ge, P, and As are among the gases that could be present on thermochemical grounds. The abundances of these gases can be used to constrain mixing processes, and therefore place constraints on the interior of the outer planet atmospheres. Detection and quantitative determinations of deuterated molecules such as HD and CH_3D could provide information about the proto-solar D/H ratio (also of interest to cosmologists) because D is destroyed in the sun. Furthermore, the increasing D/H ratios in the giant planets with increasing distance from the sun could indicate ion-molecule chemistry in the outer solar nebula or the efficiency with which cold interstellar materials were homogenized in the outer solar system (see Fegley 1999 for a review). The development of high resolution Fourier Transform Infrared (FTIR) spectrometers led to the discoveries of many other gases from the late 1960s onwards. Table 2 gives the composition of the atmospheres of the gas giant planets compiled from literature data.

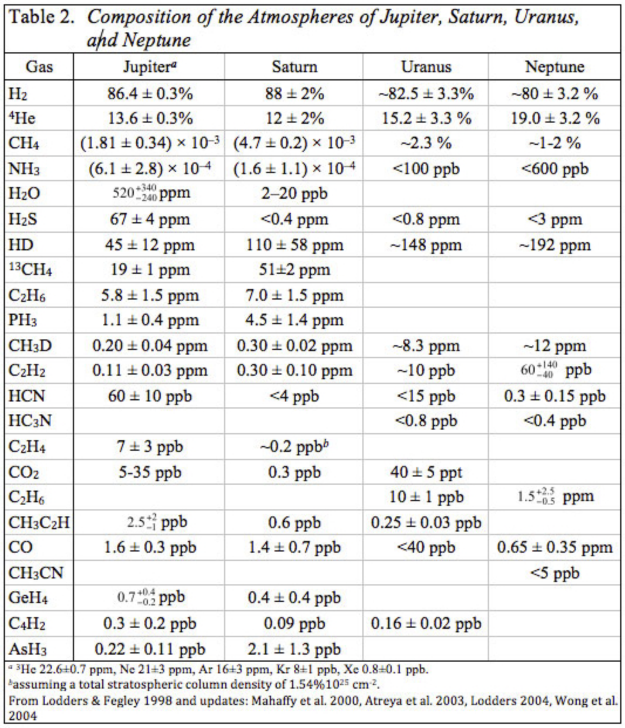
Table 2. *Composition of the Atmospheres of Jupiter, Saturn, Uranus, and Neptune*

Gas	Jupiter[a]	Saturn	Uranus	Neptune
H_2	86.4 ± 0.3%	88 ± 2%	~82.5 ± 3.3%	~80 ± 3.2 %
^4He	13.6 ± 0.3%	12 ± 2%	15.2 ± 3.3 %	19.0 ± 3.2 %
CH_4	$(1.81 \pm 0.34) \times 10^{-3}$	$(4.7 \pm 0.2) \times 10^{-3}$	~2.3 %	~1-2 %
NH_3	$(6.1 \pm 2.8) \times 10^{-4}$	$(1.6 \pm 1.1) \times 10^{-4}$	<100 ppb	<600 ppb
H_2O	520^{+340}_{-240} ppm	2–20 ppb		
H_2S	67 ± 4 ppm	<0.4 ppm	<0.8 ppm	<3 ppm
HD	45 ± 12 ppm	110 ± 58 ppm	~148 ppm	~192 ppm
$^{13}CH_4$	19 ± 1 ppm	51±2 ppm		
C_2H_6	5.8 ± 1.5 ppm	7.0 ± 1.5 ppm		
PH_3	1.1 ± 0.4 ppm	4.5 ± 1.4 ppm		
CH_3D	0.20 ± 0.04 ppm	0.30 ± 0.02 ppm	~8.3 ppm	~12 ppm
C_2H_2	0.11 ± 0.03 ppm	0.30 ± 0.10 ppm	~10 ppb	60^{+140}_{-40} ppb
HCN	60 ± 10 ppb	<4 ppb	<15 ppb	0.3 ± 0.15 ppb
HC_3N			<0.8 ppb	<0.4 ppb
C_2H_4	7 ± 3 ppb	~0.2 ppb[b]		
CO_2	5-35 ppb	0.3 ppb	40 ± 5 ppt	
C_2H_6			10 ± 1 ppb	$1.5^{+2.5}_{-0.5}$ ppm
CH_3C_2H	2.5^{+2}_{-1} ppb	0.6 ppb	0.25 ± 0.03 ppb	
CO	1.6 ± 0.3 ppb	1.4 ± 0.7 ppb	<40 ppb	0.65 ± 0.35 ppm
CH_3CN				<5 ppb
GeH_4	$0.7^{+0.4}_{-0.2}$ ppb	0.4 ± 0.4 ppb		
C_4H_2	0.3 ± 0.2 ppb	0.09 ppb	0.16 ± 0.02 ppb	
AsH_3	0.22 ± 0.11 ppb	2.1 ± 1.3 ppb		

[a] ^3He 22.6±0.7 ppm, Ne 21±3 ppm, Ar 16±3 ppm, Kr 8±1 ppb, Xe 0.8±0.1 ppb.

[b] assuming a total stratospheric column density of $1.54\%10^{25}$ cm^{-2}.

From Lodders & Fegley 1998 and updates: Mahaffy et al. 2000, Atreya et al. 2003, Lodders 2004, Wong et al. 2004

As most information is for the atmospheres of Jupiter (and Saturn), we focus on the largest planet in the solar system. Jupiter has a mass (M_J) of about 10^{-3} that of the Sun, or approximately 318 times that of the Earth (M_E). Saturn is the second most massive gas giant planet with a mass of about 95 M_E. Although quite massive relative to the Earth and other planets in our solar system, Jupiter is much smaller than an object capable of 'burning' deuterium by nuclear fusion which requires at least 13 times Jupiter's mass. The 13 M_J mass limit is widely taken as the boundary between planets (at lower masses) and brown dwarfs (at higher masses).

The molecular H - He layers of Jupiter and Saturn are only a small fraction of each planet. However, these layers are the only regions of the two planets that are observable from the Earth and spacecraft. Our knowledge of atmospheric composition and structure on Jupiter and Saturn is based on a combination of Earth-based and spacecraft observations. The spacecraft which explored Jupiter and Saturn are *Pioneer* 10, *Pioneer* 11, *Voyager* 1 and 2, *Galileo* (7 Dec 1995 arrival at Jupiter and entry probe launch - 21 Sept 2003), and *Cassini* (1 July 2004 arrival at Saturn, and continuing now).

In situ observations of Jupiter's atmosphere by the *Galileo* entry probe (7 December 1995) extended down to ~ 22 bars (at 429 K), about 126 km below the one bar level. Saturn's atmosphere has not yet been explored by entry probes. (The *Huygens* probe on the *Cassini* spacecraft descended to the surface of Titan, Saturn's largest satellite, on 14 January 2005.) The *New Horizons* mission launched in 2007 had a Jupiter flyby en route to the dwarf planet Pluto and its three satellites Charon, Hydra, and Nix.
In general remote sensing observations in the UV, visible, and IR regions sample only the uppermost regions of Jupiter's and Saturn's atmospheres down to pressures of a few bars. Radio wave observations extend deeper to tens or hundreds of bars.

Visually, Jupiter's atmosphere shows dark belts alternating with bright zones. These are the upward (bright zones) and downward (dark belts) arms of atmospheric convection cells. The Great Red Spot (about 32,000 km long and 13,000 km wide) in Jupiter's southern hemisphere exists since at least 1664 when it (or a similar feature) was observed by the English scientist Robert Hooke (1635 - 1703). The Great Red Spot is a long-lived cyclonic storm and its red color is likely due to red phosphorus formed by UV sunlight photolysis of PH_3 gas. Other ovals and spots have also been observed in Jupiter's meteorologically active atmosphere for various periods of time. Inorganic compounds of sulfur and other elements probably are the chromophores coloring the belts in Jupiter's atmosphere. The organic compounds produced by atmospheric photochemistry are colorless and do not provide the observed cloud colors. The bright zones are high level NH_3 ice clouds at about 0.5 bars (138 K). Saturn's atmosphere is less colorful than Jupiter's but has a similar banded structure visible in spacecraft photographs.

Remote sensing observations by the *Voyager* spacecraft and in situ measurements by the *Galileo* entry probe show that Jupiter's atmosphere is convective down to at least 22 bars where the temperature is 429 K. The presence of CO, AsH_3, GeH_4, and PH_3 at abundances orders of magnitude greater than their thermochemical equilibrium values in the upper tropospheres of Jupiter and Saturn shows that convective mixing extends down to at least kilobar levels in their atmospheres. The convective regions (tropospheres) of Jupiter's and Saturn's atmospheres extend up to their tropopauses, which are the radiative - convective boundaries and temperature minima in their atmospheres (~100 mb, 110 K on Jupiter and ~83 mb, 83 K on Saturn). Methane in the stratospheres of the giant planets plays the role that O_3 does in Earth's stratosphere and absorption of UV sunlight by CH_4 heats the stratospheres of the four gas giant planets.

Chemical Processes

Chemistry in the atmospheres of the gas giants is determined by their overall elemental composition, and the stability of chemical compounds at the prevailing temperatures, the (gravity-controlled) total pressures, and where applicable in the atmosphere, the interaction with UV light and charged particles. The following describes some characteristic chemical processes.
Both photochemistry and thermochemistry control atmospheric chemistry on the giant planets. Ultraviolet sunlight and other disequilibrating energy sources such as charged particles (e.g., in Jupiter's magnetosphere) and cosmic rays drive photochemical reactions in the upper atmospheres of all four planets. The heat released by gravitational contraction and cooling (and by He phase separation and sedimentation on Jupiter and Saturn) drives thermochemical reactions in the deep atmospheres. Thermochemical reactions also lead to formation of condensation clouds throughout the observable and deeper, unobservable regions of all four giant planets. There are intermediate regions where both photochemistry and thermochemistry affect the chemistry in the giant planet atmospheres, and the depth of these intermediate regions varies from planet to planet.

Ultraviolet sunlight drives photochemistry in the upper atmospheres of the four giant planets Jupiter, Saturn, Uranus, and Neptune. In turn, photochemistry moves the upper atmospheres of these planets away from equilibrium and produces disequilibrium species (e.g., ethane C_2H_6, acetylene C_2H_2, and ethylene C_2H_4) from methane and hydrazine N_2H_4 from ammonia, the thermodynamically stable forms of carbon and nitrogen in the H_2-rich atmospheres of the giant planets. In addition, photochemistry of NH_4SH and phosphorus compounds is plausibly responsible for the colored belts and bands on Jupiter. The first modern models of hydrocarbon and ammonia photochemistry on Jupiter emerged in the late 1960s.

Many of the gases observed in their atmospheres are hydrides, e.g., CH_4, NH_3, H_2O, H_2S, PH_3, GeH_4, and AsH_3. All of these gases (except H_2O and H_2S) are photochemically destroyed by UV sunlight in the stratospheres of Jupiter and Saturn. Ammonia is removed by formation of NH_3 ice clouds and photolysis above these clouds in the atmospheres of Jupiter and Saturn. Water vapor and H2S condense to form clouds (liquid water, NH_4SH) before they reach the stratospheres where they can be photolyzed by UV sunlight. As shown in Table 2, NH_3 is more abundant than H_2S on Jupiter and NH_4SH condensation removes all H_2S, but not all NH_3 from Jupiter's atmosphere above the NH_4SH cloud. As long as nitrogen and sulfur are equally enriched (or depleted) relative to solar composition this is probably also true on the other giant planets because the atomic N/S ratio is 5.0 in solar composition material.

Hydride gases are important in the atmospheres of all four giant planets because H_2 is the major gas and high atmospheric pressures exist in their hot, deep atmospheres where thermochemical reactions proceed rapidly. Thus, any gases or solids produced by photochemistry in the upper atmospheres of Jupiter and Saturn are rapidly converted back into hydrides by thermochemical reactions deep inside these planets. For example, CH_4 photochemistry forms ethane C_2H_6, which has an abundance of 5.8 - 7 parts per million by volume on Jupiter and Saturn. At ~ 1000 K deep inside these two planets it reacts with H_2 to reform CH_4 via the net reaction $C_2H_6 + H_2 = 2CH_4$. Other photochemically produced species (e.g., C_2H_2, C_2H_4, CH_3C_2H, C_4H_2, N_2, elemental As, Ge, and P) that are transported downward into the hot, high pressure regions of the atmospheres of Jupiter and Saturn also react with H_2 to reform hydrides.

The presence of hydride gases is important for several other reasons. Hydrogen sulfide was first observed and measured in Jupiter's atmosphere by the *Galileo* Probe Mass Spectrometer (GPMS). The observed H_2S/H_2 ratio of ~ 7.8×10^{-5} is about 2.7 times higher than the S/H_2 ratio of ~ 2.9×10^{-5} based on solar elemental abundances. (The S/H_2 ratio and other element/H_2 ratios based on solar abundances are calculated using ½ the H elemental abundance, which gives the equivalent H_2 abundance in solar material.) The presence of H_2S in Jupiter's atmosphere requires depletion of Fe by Fe cloud condensation at high temperatures deep in Jupiter's atmosphere. If Fe cloud formation did not occur, H_2S would be completely absent from Jupiter's atmosphere because FeS (troilite) formation at ~ 700 K would consume all H_2S gas (because the atomic ratio of Fe/S ~ 2 in solar composition material) via

$$H_2S\ (\text{gas}) + Fe\ (\text{metal}) = FeS\ (\text{troilite}) + H_2\ (\text{gas}) \quad (1)$$

Hence, Fe metal condensation clouds form at great depth inside Jupiter according to thermochemical equilibrium models.
Similar thermochemical equilibrium models predict H2S is the dominant sulfur gas in the atmospheres of Saturn, Uranus, and Neptune. Hydrogen sulfide is not observed by remote sensing on these planets because formation of NH4SH clouds (via reaction of H2S with NH3) depletes H2S from the observable regions of their atmospheres. However, observation of H2S by the Galileo entry probe shows that planetary entry probes should be able to detect H2S on Saturn, Uranus, and Neptune.

The presence of CH4 and GeH4 (germane), but not of SiH_4 (silane) on Jupiter and Saturn is due to condensation of magnesium silicates (MgSiO3, Mg2SiO4) deep in their atmospheres. Silicon is much more abundant than germanium in solar composition material (the atomic Si/Ge ratio is ~ 8,700), but it is more refractory than Ge and forms silicate clouds deep in the atmospheres of the giant planets via net thermochemical reactions such as

$$SiH_4\ (g) + Mg(OH)_2\ (g) + H_2O\ (g) = MgSiO_3\ (\text{enstatite}) + 3H_2\ (g) \quad (2)$$

and

$$SiH_4\ (g) + 2Mg(OH)_2\ (g) + H_2O\ (g) = Mg_2SiO4\ (\text{forsterite}) + 4H_2\ (g) \quad (3)$$

Silane is not observed on either Jupiter or Saturn and the observational upper limits for it are about one part per billion by volume (SiH_4/H_2 ratio < 10^{-9}) on both planets). This is 68,000 times smaller than the Si/H_2 ratio of 6.8×10^{-5} from solar elemental abundances. In contrast, the observed CH_4/H_2 ratios of 2.1×10^{-3} on Jupiter and 5.3×10^{-3} on Saturn are 4 to 11 times higher than the C/H_2 ratio of 4.9×10^{-4} from solar elemental abundances. The GeH_4/H_2 ratios of 8.1×10^{-10} (Jupiter) and 4.6×10^{-10} (Saturn) are 0.1 to 0.06 times the Ge/H_2 ratio of 78×10^{-10} from solar abundances. The Ge/H_2 ratios in the atmospheres of Jupiter and Saturn are lower than the solar value because not all Ge in their atmospheres is present as germane. Most Ge condenses out of the atmospheres of Jupiter and Saturn as elemental Ge and Ge chalcogenides at high temperatures.

Aside from photochemically produced gases, the hydride/H_2 ratios in the atmospheres of Jupiter and Saturn give elemental enrichments (or depletions) relative to solar composition. As already seen, carbon and sulfur are enriched and germanium is depleted relative to solar composition in Jupiter's observable atmosphere. Carbon is also enriched on Saturn (~ 11 times solar) but H_2S is not observed as discussed earlier. Nitrogen is enriched 4.9 times solar (with 46% uncertainties) on Jupiter, but only 1.2 times solar on Saturn where condensation of NH_3 into NH_3 ice clouds depletes ammonia in the observable region of its atmosphere. Water is depleted and is only 0.6 times solar on Jupiter. This depletion is observed below the level where water clouds are predicted to form and is probably a depletion of water (and oxygen) throughout Jupiter's atmosphere and interior. On Saturn H_2O is removed by condensation of water clouds below the observable region of Saturn's troposphere. The small amounts of H_2O observed in Saturn's stratosphere are due to oxygen coming into Saturn's upper atmosphere from its icy rings, and provide no information on the water content of the planet.

Phosphorus is enriched 2.2 times solar on Jupiter and 9 times solar on Saturn. Arsenic is depleted on Jupiter (~ 0.6 times solar) and enriched on Saturn (~ 5.8 times solar). Arsine is the major As-bearing gas on Jupiter and Saturn, but condensation of elemental arsenic at 400 K depletes the AsH_3 abundance in the cooler, observable region of Jupiter's atmosphere. Arsenic and phosphorus behave similarly in meteorites and in the solar nebula, so their enrichment factors on Jupiter and Saturn are plausibly the same. This is the case within the uncertainties on the enrichment factors for As and P on Saturn.

These data on hydride/H_2 ratios show that the atmospheres of Jupiter and Saturn are close to solar composition and that Saturn is more enriched in heavy elements relative to solar composition than

Jupiter. This trend is continued at least qualitatively by Uranus and Neptune where CH_4/H_2 ratios are about 57 and 38 times larger relative to solar composition, respectively. Given their mean densities, similar sizes, and uncertainties in the CH_4 observations, it is plausible that Neptune is more enriched than Uranus. Except for photochemically produced gases and isotopomers (e.g., CH_3D), no other hydride gases are observed on Uranus or Neptune. Thus the heavy element enrichment trend on the four giant planets depends on observations of methane.

Chemical reaction rates and vertical mixing rates also explain the abundances of CO, PH_3, GeH_4, and AsH_3 in the atmospheres of Jupiter and Saturn. The abundances of these gases are significantly higher than those predicted at chemical equilibrium in the cool, observable regions of the atmospheres of Jupiter and Saturn. Carbon monoxide and PH_3 are the most dramatic examples because their observed abundances are about 32 to 36 orders of magnitude greater than their chemical equilibrium values. The reason for this is rapid vertical transport of CO and PH_3 from hot, high pressure atmospheric regions where they are more abundant due to favorable chemical equilibria.

For example, consider CO in Jupiter's atmosphere. Carbon monoxide is produced by oxidation of methane via

$$H_2O + CH_4 = 3H_2 + CO \qquad (4)$$

The equilibrium constant for reaction (4) in terms of partial pressures is

$$K = \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}} \qquad (5)$$

If we rewrite this to solve for the CO/CH4 ratio at equilibrium we obtain

$$\frac{X_{CO}}{X_{CH_4}} = K\left(\frac{X_{H_2O}}{X_{H_2}^3}\right)\frac{1}{P_T^2} \qquad (6)$$

Thermodynamic data show that the equilibrium constant for reaction **(4)** increases with increasing temperature. Furthermore, the adiabatic gradient (dP/dT) in the convective lower atmosphere of Jupiter is easily calculated using the temperature dependent heat capacity of H_2 - He gas mixtures. Thus, the CO/CH_4 ratio as a function of temperature (and thus of depth and pressure) can be computed from the observed H_2O and H_2 abundances. These calculations show that the observed CO/CH_4 ratio of $\sim 8.8 \times 10^{-7}$ occurs at about the 1100 K level in Jupiter's atmosphere.

Chemistry and Gas-giant Planet Formation Ideas

What is known about the gas-giant atmospheric composition and chemistry also provides clues to the formation mechanism. The non-solar elemental compositions show that chemical fractionations between the rock, icy, and gases (H_2, noble gases; see below for more about water, Ar, Kr, Xe,) took place. As soon as the first hints of Jupiter's and Saturn's composition became available, the models came. With respect to planet formation, Menzel's line of thought in 1930 was that the giant planets formed at the same time as the sun from the same materials. Density differences among the planets could arise when light gases, especially hydrogen, were lost from giant planets early on, when the planet was extended through heating by release of gravitational energy. These thoughts about formation and modifications of planetary composition *during* planet formation and evolution now find renewed attention in the context of other giant planets discovered outside the solar system. Currently, two competing models portray how the gas giant planets could have formed from the materials in the accretion disk (see, e.g., Pollack et al. 1996, Boss 2001). The core accretion model postulates that such planets form after enough solid and icy materials accumulated to form a core of 5-10 Earth-masses which can gravitationally capture H and He rich gas before the planetary accretion disk is dissipated. This requires rapid accumulation of solids which may be difficult within the estimated lifetime of the solar nebula. Thus the amount of H and He captured depends on the accumulation rate of the 'core' and the rate of capture. The advantage of this model is that it can account for higher heavy element contents than expected for solar composition if capture of H and He is terminated before all gas in the accumulation region of the planet could be acquired by the planet.

The other formation model postulates that planets like Jupiter form through gravitational instabilities in the accretion disk, more similar to the mechanism the sun formed. This allows rapid planet formation. A consequence of this model is that the planet would be made of elements and compounds that are present in the accretion disk without any fractionation of rocky and icy from H and He. However, subsequent fractionation, such as loss of light gases, could also lead to an overall composition which is heavy element rich when compared to the sun.

Lessons From Water and Chemically 'Inert' Gases

The Galileo Probe Mass Spectrometer also observed Ne, Ar, Kr, and Xe in Jupiter's atmosphere (Table 2). The observed noble gas/H_2 mixing ratios are 0.1 (Ne), 2.9 (Ar), 2.4 (Kr), and 2.5 (Xe) times relative to solar composition. Neon and Ge are depleted by the same factor (0.1) but for different reasons - Ne is thought to partition preferentially into helium in Jupiter's interior while most Ge condenses out of Jupiter's atmosphere as elemental Ge and Ge chalcogenides at high temperatures. In contrast, Ar, Kr, and Xe are about as enriched as S (2.7 times) relative to solar composition.

The relatively uniform enrichment of the heavy noble gases (Ar, Kr, Xe) on Jupiter requires that they were not fractionated, which limits the possible scenarios of how these gases were acquired by the planet. One possibility is that they were also captured from the solar nebula when the large amounts of H_2 and He were captured. This, however, requires subsequent fractionation of H_2 from the noble gases because the observed noble gas/H_2 ratio is not solar, i.e., not the ratio that prevailed in the solar nebula. Such fractionation can come from subsequent atmospheric loss of H_2, or removal of H_2 into the liquid and metallic H-He layers deeper in the planet (see Lodders 2004 for a discussion).

Another way to explain the uniform noble gas enrichment is their delivery in icy planetesimals. The heavy noble gases, as well as CO and N_2, can be captured into clathrate hydrate 'cage' compounds $X{\cdot}nH_2O$, where X is the caged atom or molecule, and n, with typical values of 5-7, is the number of water molecules providing the 'cage'. If clathrate hydrates form at sufficiently low temperatures, quantitative removal of the noble gases from solar nebula gas could be achieved, but He and H_2 stay behind. If clathrate-bearing icy planetesimals were captured, a planet accreting such ices receives the same unfractionated noble gas abundances. Such a model is advocated by Gautier et al. (2001).

Similarly, the noble gases may get trapped into amorphous ice, again at low temperatures (Owen et al. 1999). The problem is that quantitative noble gas clathration requires very low temperatures that can only achieved at larger distances from the sun than Jupiter's current location. Formation of crystalline clathrate hydrates may be less likely than amorphous ice formation, but in either case, both crystalline and/or amorphous ices have to quantitatively capture the noble gases and then move inward to be accreted by the planet. This may lead to selective release of light noble gases because the ices get heated as they get closer to the sun. Then the planet no longer receives ices with unfractionated noble gas abundances (see Lodders 2004, Guillot and Hueso 2006 for various arguments). Alternatively, larger water abundances in the Jupiter region might have increased clathration efficiency (Gautier and Hersant, 2005). Yet another model is to assume incorporation of noble gases into clathrates or amorphous ices, inward transport and sublimation of these ices deliver the noble gases unfractionated. Over time as the accretion disk evolves, an enrichment of the noble gases would result in the inner solar system as redistribution of ices from the outermost regions proceeds (Guillot and Hueso 2006). All these models make specific predictions about the heavy noble gas abundances on Saturn, Uranus, and Neptune, but without atmospheric entry probes measuring these abundances, all these models remain possibilities for the moment.

Another obstacle from accretion of clathrate hydrates or amorphous ice is that large amounts of water are brought to the planet. The expected water abundances are higher than the solar O/H_2 ratio even if all solar O were present as water. The amount of O in the form of water in a solar composition gas available for forming clathrates is barely sufficient to provide 'cages' for the noble gases (see Lodders 2004). Since other gases such as N_2 and CH_4, as well as ammonia-hydrate, NH_3 H_2O, compete for water, the amount of water must be higher than given by the solar value. Enrichment of water ice through cold-trapping in the outer solar system is a very likely possibility, so supply of water for ice formation is not necessarily a problem. However, the ice that carries the noble gases to the planet atmosphere also brings water, thus, a water enrichment should be observed below the water-ice clouds that are present in Jupiter's upper atmosphere.

However, the available observations indicate that the O/H_2 ratio on Jupiter is 0.6, clearly sub-solar. The Galileo probe measurements could be biased since the probe entered a 'hotspot' which is an uncharacteristically dry pocket in the atmosphere caused by meteorological phenomena. However, other observations also indicate a relatively dry atmosphere. If the noble gases where brought in water ice, and/or the planet formed by core accretion of a massive rocky and icy core (see below), water must be somewhere on Jupiter. At the minimum, one should expect a solar complement of oxygen, even if this where still at odds with the enrichment of other rocky and icy elements relative to solar.

The other option is that Jupiter never acquired large amounts of water, but instead, the role of water during planet formation was replaced by refractory organic 'goo' that aided the accretion of a substantial rocky-icy-organic core onto which solar gas was captured (see Lodders 2004 for a detailed description). The decision which formation scenario is 'right' can only be decided by future measurements of the deep water content of Jupiter, preferentially by emerging probes into more characteristic atmospheric regions, but also on the other giant planets. This would not only improve the constraints on gas-giant formation models, but also place constraints on the kind and distribution of planetary building blocks within the forming solar system.

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Complex Organic Carbon on Abiotic Solar System Bodies: Titan as a model

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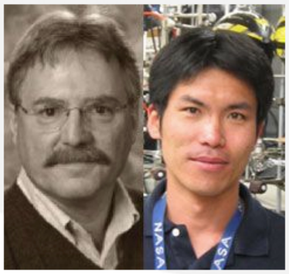
I. Introduction: Complex organic chemistry outside of the terrestrial envelope

The chemistry of the terrestrial environment is dominated by carbon. Carbon plays a critical role in the chemical balance of our oceans, in controlling the optical and therefore thermodynamic properties of our atmosphere and in determining the fundamentals of life. This centrality is partially governed by its unique set of balanced oxidation/reduction properties, its modest but significant tetrahedral valence and its prevalence in the matter that originally formed our solar system. Understanding the more fundamental origins as to why carbon plays an essentially unique and unmatched role in life science and why life, as we know it, has not developed with a greater elemental diversity is a continuing and difficult task. Though terrestrial life provides a broad spectrum of diverse systems of study, it is difficult to objectively study general prebiotic chemistry and gain an understanding of how carbonaceous or organic chemistry developed in an abiotic world or outside of the terrestrial box, so to speak. Biotic carbon is ubiquitous in our immediate world and it has been claimed that there is not a single carbon atom at our disposal on Earth which is not in a form previously influenced by a life process. Nascent carbon is beyond the reach of all of us, and accurate, verifiable simulations of the early organic chemistry of the solar system are fraught with difficulties, limitations and pitfalls.

The ability to observe, in nature, the development of abiotic chemistry, uninfluenced by contact with any life form, is critical to our understanding of the conditions extant during the precipitation of life on Earth or in our Universe. In order to understand the driving forces behind the complex intercouplings of chemical and structural diversity in what we believe to be the earliest life forms, we must understand the driving forces and couplings active in primordial matter. It is not clear how much of the symmetry and structural specificity we see in the chemistry around us has been generated and maintained by the forces, kinetics and thermodynamics of biochemical processes in living organisms and how much can be attributed to the natural chemical and physical forces present in highly complex chemical systems of arbitrary origin. To understand the transition between abiotic matter and a living system may not be as simple a question as we might wish.

If we are to seek the answers to the questions regarding the most fundamental definition of life and its origins it is wise to approach the problem not just from the direction of living examples but also ask, how far can the simple forces of physics and chemistry drive a complex abiotic chemical system? What levels of symmetry are maintained as such abiotic processes evolve to arbitrary complexity and do unbound abiotic systems possess non-equilibrium localities or simply evolve stochastically? The approach of retroanalysis from living matter to the simplest and most primitive biotic chemistry has yet to uniquely reveal the biotic/abiotic boundary. The latter approach beginning at the simplest chemical levels and building in complexity towards a prebiology has not received as much attention as it deserves, partly because it is maddeningly difficult to perform or analyze the correct studies, of sufficient complexity, in the common laboratory and looking for the answers beyond our earthly environment proves even more daunting. Looking outward is the natural approach towards understanding life beginning from the elements and in a way unbiased by the finite examples presented on Earth. In the outer reaches of our galaxy, the study of complex chemistry through observational astronomy has provided many surprises as to the paths complex molecular environments can follow (Herbst and VanDishoek, 2009). Using radio astronomy over the past 40 years alone, scientists have assembled a picture of complex chemistry, again dominated by carbon containing molecules, but including a plethora of molecules not observed in earthbound environments and only difficultly prepared in specific laboratories. At present there are over 150 molecules identified outside of our solar system, with our reach now extending deeper outside of our galaxy. The major chemical environments containing a complex organic chemistry are comprised of the out-flowing chemical clouds about stars, the dense interstellar molecular clouds where stars are born and to a lesser extent the highly rarified environment of the interstellar medium itself. It has become clear that the thermodynamic, radiation and kinetic conditions within these clouds create a unique set of chemical drivers. These conditions produce a chemistry which understandably appears to truncate at an exotic level, rich in functional groups and structures not common to denser media. From an organic or prebiotic chemical perspective, however, the chemistry appears to a simpler level than is expected from a prebiotic system. This picture is certainly highly filtered by the instrumental bias of the astronomical tools currently available. It is clear that if we are going to advance our understanding of molecular chemistry at the prebiotic level of complexity in the near term, it is necessary to look for more general sampling means somewhat closer to home.

Within our own solar system there are a broad range of intriguing and mysterious chemical systems of a complexity well deserving of close scrutiny. Ignoring those where we might seek remnants of a past active chemistry, the most notable thriving chemical environments are present on satellites within our solar system. The Jovian moon, Europa, possesses an ice crust below which appears to be an aqueous ocean thermally driven from the objects thermal core (Greenberg, 2005). Enceladus was recently discovered to be ejecting plumes of water from below its mantle, water which appears to be contributing to, if not responsible for, at least the E ring of Saturn (Hansen, 2006). Also within the Saturnian system lies the moon, Titan, which is the preeminent object of organic chemical interest within our solar system (Brown, 2009). With its rich, dense atmosphere of a few percent methane in nitrogen, its optically thick layers of organic aerosol haze and irrefutable evidence for liquid hydrocarbon lakes, mobile dunes of organic matter mixed with water ice and the presence of a molten sub-mantle aqueous reservoir, this object presents a diverse geochemical organic environment of richness unrivaled outside of Earth. If the pursuit of astrobiology centers about complex organic chemistry, then Titan must currently be accepted as the premier astrobiology laboratory.



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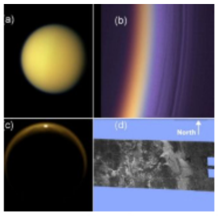


Figure 1

Discovered by Huygens in 1655, Kuyper first detected the presence of carbon, in the form of its methane rich atmosphere in 1944. An object of long chemical interest, the Voyager mission, with Titan fly-bys in 1980 and 1981 revealed the first details of the complex organic nature of its atmosphere, rich in lesser constituents of ethane, ethylene, acetylene, hydrogen cyanide and cyanogen. Covered in an optically dense organic haze, see Figure 1, this shrouded world long defied any understanding beyond a plethora of competing models. However, it was not until the arrival of the Cassini-Huygens mission that the true geochemical mysteries of this object began to emerge (Brown, 2009). Since its arrival in 2005, the continuing Cassini (Saturn) orbiter mission has performed over 65 high altitude fly-bys. These fly-bys probe the Titan atmosphere at greater than approximately 1000 km, high in the ionosphere. In 2005, the Huygens probe was dropped to the Titan surface making the first direct measurements of the lower atmosphere of Titan and the very first direct images of its strange surface. The Huygens measurements have certainly been significant. However, from a chemical perspective, the Cassini data has been overwhelming in diversity, quality and volume. Most significantly, its optical, infrared and radar imagery have provided detailed insights into the physicochemical and geochemical structure of this shrouded world.

With a surface temperature near 95 K, most of the oxygen on Titan is believed to be frozen out as water ice. Yet the complex surface topography suggests that weathering, perhaps by periodic rain of condensed hydrocarbons has occurred in the past. This hypothesis is supported by direct observations of tropospheric cloud dynamics (Griffith, 1995; Roe, 2005; Schaller, 2009) and more recently definitive evidence of liquid hydrocarbon lakes in the northern latitudes (Stephan, 2010). In the equatorial plane are observed dunes believed to be comprised of organic solid particles deposited from the dense upper atmospheric haze layers. Current models suggest these haze layers are comprised of rich C, H and N containing aerosols produced by photochemical and energetic particle induced chemistry from an N_2 and CH_4 origin (Waite, 2009).

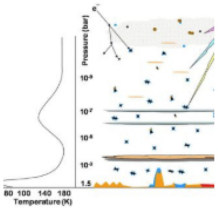


Figure 2

Though less is directly known regarding the haze layers, lying predominantly below the direct reach of Cassini, much is now known regarding the atmosphere above the haze. Using the Ion-Neutral Mass Spectrometer (INMS) on Cassini, we now know that even in the ionosphere, there is a rich and complex organic chemistry unparalleled in any known atmosphere (Waite, 2005; Waite, 2009). Using the Cassini Plasma Spectrometer (CAPS) originally designed to measure properties of the small ions and free electrons in the magnetosphere of Saturn, it has discovered that at the highest altitudes of the Titan atmosphere there exist surprising concentrations of very large charged particles, now believed to be the chemical seeds of the Titan haze (Coates 2007). Chemistry at these levels is driven by the solar extreme ultraviolet radiation (EUV) below 150 nanometers (nm) as well as the more minor energetic electrons entering the atmosphere guided by the strong saturnian magnetic field, as depicted graphically in Figure 2. The dissociation and ionization of nitrogen and methane leads to a reforming plasma which is now known to produce benzene, formimine and other complex molecules at regions of the atmosphere where on Earth only small atoms, ions and diatomics exist (Imanaka, 2007; Imanaka, 2009). The predominant difference being Titan's currently reducing methane rich atmosphere, a condition thought to be relevant however during the prebiotic stages of Early Earth. In fact, when one factors in the 100 times lower solar energy flux received by Titan relative to Earth, the resulting lower atmospheric and surface temperatures, and the positive activation energies of much of the complex neutral chemistry required to generate a prebiological chemistry, one can argue that Titan is geochemically reminiscent of Early Earth in its organic chemistry.

As a result, Titan has become a laboratory whereby planetary organic chemistry from its most fundamental stages is moving towards a palette of organic chemical diversity and complexity unknown in our solar system outside of Earth. We can observe directly the evolution and impact of the production of free atoms and light molecules as they evolve to moderately complex molecules. It is possible to probe this chemical environment for production of condensed molecules of surprising complexity. This developing, and presumably abiotic environment rivals the complexity which must have evolved on Early Earth before the generation of persistent molecular oxygen, the earliest stages of photosynthesis and ultimately life. We now possess a significant and growing set of direct data being used to drive models which can tie the observations together as well as lead to a predictive geochemistry. In addition, enough understanding exists from observation and reliable models to allow the design of significant laboratory studies, under known relevant conditions. These laboratory studies can lead to both model validation and observational interpretation as well as provide extension to systems (such as the Jovian) or conditions (as on Early Earth) for which we have much less understanding and for which direct data is currently not forthcoming.

II. Laboratory studies of Titan chemical processes

A. Atmospheric Chemistry

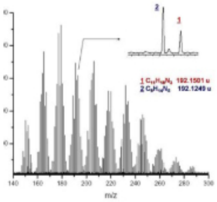
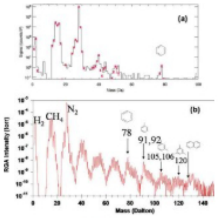


Figure 3

Meaningful laboratory investigations of planetary astrobiology really began with the groundbreaking study of Miller and Urey in the 1950's (Miller 1959). They prepared a gas mixture believed to be representative of the Early Earth atmosphere, containing nitrogen, methane, ammonia and water, and exposed it to an electrical discharge (representative of lightning and uv light) for days. Sampling of the crude resulting mixture revealed the presence of complex organic molecules including 11 of the 20 natural amino acids (in racemic form). Since then, several laboratories, beginning with that of the late Carl Sagan, have applied this approach to the investigation of complex molecule generation under Titan's somewhat simpler atmospheric mix, there being no appreciable ammonia or water in the upper atmosphere and no demonstrable lightning or intense energy sources in the lower. Even in this simpler gas mixture, nitrogen containing a few percent methane being well representative, an incredibly complex mixture of organics (dubbed tholins by Sagan) is formed from exposure to low energy (10's of volts) electrons within minutes. Figure 3 shows a representative solids mass spectrum from an electrical discharge product sample containing thousands of products. Mixtures such as these are believed to be possible analogs to the complex solids, such as the haze material, which form in the Titan atmosphere and settle to the surface. Before going further with solids discussion however, it is useful to take a closer and more controlled look at the beginnings of this chemistry in the highly rarefied environment of Titan's upper atmosphere.



In the earliest flybys of Cassini through the upper atmosphere of Titan, it was clear from the INMS mass spectra, that the atmospheric chemistry contained unimagined complexity. Figure 4a shows a low resolution spectrum from Cassini (using electron impact ionization, therefore producing signals from parent constituents as well as their ionization fragments) which shows a set of moderately complex organic molecules such as ethane, ethylene, acetylene, HCN, cyanogen, but also formimine and very surprising quantities of benzene (Waite, 2005; Imanaka, 2010). The benzene signal observed is 4 orders of magnitude greater than any model predicted at that time. In order to reconcile the discrepancy between model and observation, better understanding of the key contributing chemical processes is necessary and this is where

Figure 4

laboratory studies can contribute. The issue here is not in refinement of the experimentally determined rate values inherent to the models, but here entire chemistries are obviously missing and it becomes critical that new pathways be unveiled through detailed experimental investigation.

Methane/nitrogen mixtures are photochemically inert to wavelengths above or to the red of 140 nm. Thus the primitive or nascent atmosphere absorbs predominantly only deep in the vacuum ultraviolet (VUV), where the first processes produce methane neutral fragments such as CH_3 and CH_2. To even begin exploring the photochemistry relevant to the Titan upper atmosphere, it is necessary to employ intense VUV and EUV (wavelengths below the window cutoff near 100 nm) exposure, most readily obtained from synchrotron light. Using the Molecular Dynamics endstation at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, we have at our disposal intense narrow band ($\Delta\lambda \approx 1$ nm) radiation tunable between 150 and 50 nm. This covers the range of methane dissociation, methane ionization, nitrogen dissociation to both ground and excited state N atoms and nitrogen photoionization. Using a windowless photocell we have studied the wavelength dependent photo processes and Figure 4b shows a mass spectrum of a gas mixture produced upon methane/nitrogen exposure to 60 nm radiation, lying energetically above the nitrogen ionization potential. Here it is found that the nitrogen ionization product, N^{2+}, is critical to the efficient production of benzene with a large variety of larger complex aromatics observed (Imanaka 2007; Imanaka 2009; Imanaka 2010).

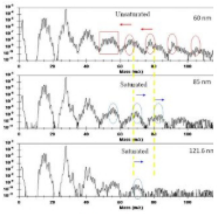


Figure 5

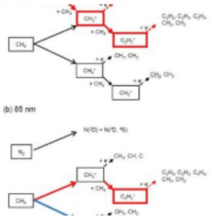


Figure 6

Investigation of the full wavelength dependence of the photochemistry in this region suggests that though methane processes alone contribute to complex hydrocarbon generation, the products are more saturated, with higher hydrogen content, and that nitrogen in this atmosphere acts as an antenna absorbing the bulk of the radiation below its ionization onset at 79 nm (see Figure 5). The resulting N^{2+} then dissociatively ionizes methane to produce CH^{3+} which upon collision with methane produces the first CC bond containing constituent, $C_2H_5^+$ as outlined in Figure 6. At the low pressures of the Titan atmosphere, such bimolecular processes yielding CC bond formation are unique to the ion chemistry and critical to the growth of the carbonaceous chemistry. Subsequent electron-ion recombination can then produce the complex neutral molecules which can begin to participate in these reactive growth processes.

In order to produce a prebiotic chemistry of relevance, it must include fixed nitrogen in the form of nitrogenous organics. HCN has been known to be a significant constituent of the Titan atmosphere, but only since Cassini have more complex nitrogenous molecules been identified. One of the most astrobiologically relevant of these is formimine (CH_2NH). Such simple one carbon nitrogen bearing form from reactions involving methane or methane fragments and the excited forms of atomic nitrogen. Understanding the preparation of the higher possible CHN containing organics, presumed to contribute to Titan's orange tint, is more difficult. We can use synchrotron radiation once again to search for the key photo processes producing the higher nitrogenated species. Once again, production of the one carbon species are indicated at wavelengths where nitrogen is known to dissociate (λ < 95 nm) to atomic nitrogen in both the ground ^4S and excited ^2D states. However a search for higher order nitrogenated species in the gas mixture has been elusive. Using ^{15}N and ^{13}C isotopomers (organic molecules differing only in their isotopic distribution) of methane and nitrogen proves a very sensitive means to determine the C/N content in such muddled low resolution mass spectra as necessarily currently employed in our synchrotron investigations. These demonstrate to reasonable certainty that less that 5% of the product species above 40 daltons (and so, excluding single carbon atom species) in this wavelength region contain nitrogen (Imanaka, 2010). This surprising result contradicts the known N atom photo yields and the chemical expectations.

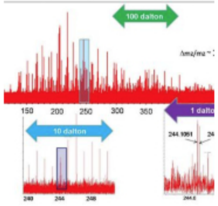


Figure 7

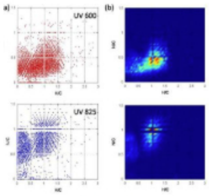


Figure 8

Under our experimental conditions, and those of the Titan ionosphere, the small molecule gas mixture is highly transparent to atomic nitrogen. On Titan, the second surprise of Cassini was the presence of reasonably large negatively charged 'nanoparticles' most likely the organic seeds of the subsequent haze. These particles, ranging to molecular weights near 10,000 dalton, present an appreciable collision target to the atomic nitrogen being produced in their vicinity. Similarly, in the laboratory studies, the hydrocarbon photoproducts rapidly produce a layer of (charged) hydrocarbons on the inside walls of the photocell which play a similar role to the CAPS particles on Titan. Energetic N atoms largely pass through the gas mixture and reactively collide with this organic surface, simulating the interaction of organic aerosol with energetic gas species. The high efficiency of these processes is confirmed by direct observation, through laser scattering, of the growth of the organic product films as well as their direct compositional analysis using laser desorption/ionization (LDI) mass spectrometry, as shown in Figure 7 and 8. The material detected contains a large diversity of very complex organics, essentially every one of which contains at least one nitrogen atom.

B. Aerosol processes

The evidence suggests that a wide variety of energetic precursors are contributing to the growth of the aerosol solids. The thin film solids, or trapped aerosols, possess significant reactive centers on their surfaces such as extended unsaturation, radical centers and charges. The heterogeneous growth process at low temperature does not allow for equilibrium chemistry and so significant chemical potential from the highly exothermic growth reactions locks up significant surface reactivity in the form of strained structure, unsaturation and dangling bonds. As the material grows, presumably this chemical potential is continuously buried resulting in a highly energetic material which never has the freedom to reach any form of local equilibrium.

The resulting aerosol then possesses a reactive potential unmatched by simple mixtures of complex organics. The Titan aerosols, likely formed in a similar reactive intermediate or heterogeneous growth mechanism, must also contain this high potential for subsequent chemistry. Their color is certainly consistent with high nitrogen content and high unsaturation. In the photo field of the upper atmosphere, their charge state must be high and their continual bombardment by open shell radicals and atoms, must lead to considerable open valence. Surface film growth naturally buries and protects much of this structure and potential reactivity in a highly nonequilibrium state that is retained in the solid material. This material slowly settles to the Titan surface (over years) and presents a rich and energetic feedstock for further chemical development. This material is a form of prebiotic fertilizer in many ways. The only problems with its further development are related to the conditions leaving it locked as a solid: the extremely low surface temperatures (near 95°K) and the apparent lack of significant liquid phase which could dissolve and release these active components.

This chemical potential can most easily be explored by investigating the kinetics of chemical reactivity of the dissolved aerosols. Titan is believed to have periodic episodes of liquid water on its cold surface either induced by energetic meteoritic impacts or via cryovulcanism (Jaumann, 2009). The impacts strike the icy surface liberating tremendous energy which models show can produce aqueous melt pools lasting hundreds or even thousands of years. The apparent lack of craters on Titan suggest the viability of this process as the models suggests the result is a set of topographically flat or neutral features composed of frozen water filled craters. Cryovulcanism, another potential source of liquid water on the Titan surface, is believed to originate from the sub-mantle liquid water layer believed to exist as a dense ammonia-water eutectic. This eutectic, when forced to the surface though faults, can present a minus 50 °C cryoflow, eventually freezing as the source flow ceases. Topographic evidence consistent with such flow characteristics have been identified in high resolution, synthetic aperture (SAR) radar images from Cassini. One observes large flat flow fields emanating from apparent caldera domes. In either of these mechanisms, aqueous mixtures are presented to settled aerosol organic 'soil'. The laboratory studies of plasma produced tholins suggest that this material should in general be highly soluble in such mixtures. The solubility releases all but the highest molecular weight insoluble components producing a solution which can undergo new chemistry.

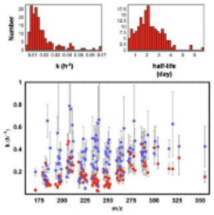


Figure 9

Using the plasma generated tholins we have investigated the reactivity of dissolved tholins in both pure water and in ammonia/water mixtures at low temperatures (Neish, 2008; Neish, 2009; Neish, 2010). Contrary to the much longer timescales of these periodic melts on Titan, tholins in the laboratory are observed to undergo hydrolytic reactions with water mixtures at 0°C and below in minute to hour timescales as seen in Figure 9. The majority of the products possess only a single oxygen atom consistent with simple reactions. However, at longer times, multiple oxygen atom addition occurs. Recently, we have observed production of both amino acids and nucleobases in these hydrolysis mixtures (Neish, 2010; Horst, 2010). Amino acids had been observed in tholin hydrolysis reactions previously, but only under the extremely harsh and unrealistic conditions consistent with stubborn nitrile hydrolysis (pH of 1 at 100°C) (McDonald 1994). Observation of low temperature production of these more complex oxygen functionalities under natural pH is highly surprising, defying textbook models of carboxylic acid generation for instance. Though the structural features driving this unusual chemistry have as yet not been identified, they are clearly supportive of the concept that this material remains highly energetic in its solid phase and that this potential energy can be released to drive astrobiologically important processes under low temperature abiotic conditions.

III. Correlation between laboratory studies and mission data

Titan is arguably the most complex abiotic organic chemical environment in our solar system. In spite of the stunning success of the Cassini-Huygens mission, its data has only provided the smallest glimpse at the chemical environment on Titan. This is no fault of the mission and the certain continuing Cassini data analysis which will occur over the coming decade will do little unfortunately to advance this. The chemical instrumentation on Cassini, and the Huygens probe, was designed only for small molecule analysis. None of the instruments were designed in a way to provide structural information for anything but gaseous species. Of the instruments which provided reliable data, the best we can hope for is correlation between gaseous molecule identification, modeling of formation processes and laboratory validation. These limitations must be eliminated in future missions if we are to advance our understanding of abiotic chemical development to a stage of astrobiological or prebiotic relevance.

This is a daunting task. Flight instruments do not exist currently, which are capable of separating and identifying condensed phase species. Mass spectrometers with 'exact mass' resolving powers allowing absolute molecular formula assignment are not flight capable under current mission constraints. Structural analytic tools which can uniquely identify complex molecules of prebiotic complexity in gross mixtures, as they certainly will be in natural environments, have not been developed. Nor have the chromatographic methods of broad generality been demonstrated which can address the separation demands of these natural mixtures. However, if we are going to succeed in developing an understanding of prebiotic chemistry as it currently exists in abiotic pockets of our world (i.e., most of the universe?) then we must develop these tools as well as missions to take them to these worlds.

These instruments cannot be developed in isolation. An understanding of the nature of the mixtures and the separation problem must be reasonably defined in order to produce an approach with sufficient generality to be successful. The biases contained in the separation, as all techniques possess, must not exclude whole categories of structure or functional group. To approach this, a reasonable model of the environment must exist as well as a sufficient set of laboratory studies of the chemistry under the constraints surrounding those models or past mission observations. As we move towards a field study of prebiotic chemistry, it must be with a completely open mind, an appreciation for how complex organic chemistry in the field can evolve and a full understanding of the extreme difficulty of developing truly general and sensitive analytical tools.

Mass spectrometry has proven itself as a critical part of this analytical approach. Its biases are reasonable and well understood. Recent developments in ionization techniques allow its general application to any phase; gas, liquid, or solid. Coupled with even crude separation technology, its power in resolving gross mixtures is proving itself in current studies of the human body involving proteomics and the inventory of the processes occurring within single cells or even on single cell membranes. But it has become very clear that the next generation of flight capable mass spectrometers, if they are to be used for complex organics, must be 'exact mass' capable. This means that they have resolution values in excess of 10^6, such that exact molecular formulas can be assigned without ambiguity, so that isotope ratios in molecular mixtures can be made molecule specific and that the mass spectrometric identification of molecules can move into the 200 dalton and above prebiotic mass range.

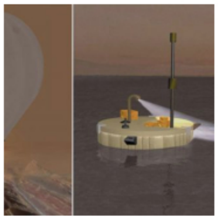


Figure 10

Sampling technology, such as that depicted in Figure 10 for a follow-on mission to the lakes of Titan, must be developed such that molecular mixtures can be removed from their natural environments into that of the analytical instrumentation and presented for separation/identification without chemical alteration. Development ought to be cognizant of the fact that simple covalent structure may not be the only interesting analytical target. It may be that compositional micro-homogeneity, third order structure and paired correlations between components may be target information. Looking for organized chemical systems must go beyond general bulk chemical analysis and must be sensitive to molecular distributions. In life, and likely in pre-life, molecules will be correlated, either as membrane structures, polymeric assemblies or simply as byproduct pools amid a generally homogenous background.

Until now, we have not mentioned the molecular attribute of chirality which exists as soon as you get to reasonably sized organic structures of anything but the most mundane of functionalities. Chirality is a result largely of the tetravalent nature of carbon and is manifested in the observations that chiral molecules possess a handedness. This handedness, or the inability of isomeric forms to be superimposable on their mirror images, has critical importance in life as we know it. Terrestrial life has chosen homochiral pathways in its chemical processes that have no use for molecules of the wrong handedness. Thus only sugars of the right handed form are processed enzymatically and used for energy and only left handed amino acids are produced and used in proteins. The non-utilitarian isomers or enantiomers (the other hands) are largely suppressed in our environment since they are neither made nor used by living organisms. Man-made versions can again be largely ignored by the body as is the case of newer artificial sweeteners which are non-bioactive enantiomers that are sensed as being sweet but are metabolically ignored and therefore non. On the other hand (no pun intended), some can be quite toxic as was found in the 1950's when the unknown chiral isomer of the sedative, thalidomide, was found too late after drug trials on enantiomerically very pure material, to produce severe birth defects when less pure commercial material became available.

when less pure commercial material became available.

Chirality must, and eventually will play a critical role in the advancement of astrobiology (Lunine, 1999). There is no currently accepted explanation as to how terrestrial life developed along homochiral pathways. However, it is felt that a broad search for enantiomeric imbalance in natural organic compounds might be an excellent and simple means to screen for biological origins.

The next decades of space science will increasingly focus upon organic geochemistry. Motivators begin simply with the fact that organic chemistry presents a dimension of geochemistry not well explored in the past and which is ripe for discovery. Our increasing ability to design models and instruments capable of extending our understandings to ever more complex chemistries validate our interests. Naturally coupled to this capability is then a strong motivation to seek extraterrestrial evidence for biologically similar chemistry, prebiotic chemistry on the edge of life or the identification of chemical evidence of life beyond Earth. It is a fascinating time for chemically oriented space mission science and we must seize our opportunities, push our creative imaginations and extend our world beyond its current confines.

IV. Acknowledgements

This work is supported by NASA Exobiology Grant NNG05GO58G and the NASA Astrobiology Institute award NNH08ZDA002C. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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Figure Captions

Figure 1. Composite of Titan images from Cassini. (a) Titan atmosphere as seen in the visible spectrum. (b) Upper atmosphere limb view of the upper atmosphere haze layers (c) Titan at occultation showing the specular reflection of sunlight from a northern surface lake. (d) Radar image of complex surface tomography. (From JPL.NASA.gov)

Figure 2. A schematic illustration of the physical conditions on Titan that affect the diverse chemical processes. Hard ionizing radiation and electrons initiate chemistry in the ionosphere from nitrogen and methane. This rapidly develops a set of complex molecules which ultimately leads to condensate and/or organic chemical hazes. These hazes produce the surface feedstock for surface processes involving frozen water ice, periodic aqueous cryoflows or meteoritic impact melt pools and precipitated hydrocarbon lakes from the dense methane/ethane lower atmosphere.

Figure 3. A representative mass spectrum (electrospray ionization from a methanol/formic acid solution) of the complex mixture of organic solids (tholins) produced upon 50V dc discharge within 5% methane in nitrogen at 10 mbar. The spectrum was taken using a 9.4 tesla Fourier transform ion cyclotron resonance mass spectrometer with a mass resolution $M/\Delta M > 10^6$. Each signal represents a single molecular formula, $C_xH_yN_z$ and each formula can be comprised of a single parent molecule or a mixture of isomeric parents. This spectrum represents in excess of 5000 different parent molecules present in the discharge mixture.

present in the discharge mixture.

Figure 4. (a) Cassini mass spectrum of the Titan ionosphere near 1200 km that shows the presence of moderate size organic molecules. The points (red squares) are a fit to a subset of molecules including benzene (from Waite, 2005). (b) A laboratory mass spectrum of a low pressure 5% methane and nitrogen gas mixture exposed to 60 nm radiation, demonstrating the presence of nitrogen photoionization stimulated production of complex organics including the aromatics.

Figure 5. Averaged mass spectra of neutral gaseous species (EI = 70 eV) obtained by 60 nm, 82.5 nm and 121.6 nm (Lyman α) EUV-VUV irradiation of a N_2/CH_4 (=95/5) gas mixture. Highlighted on the mass spectra is the difference in the degree of saturation evident in the heavier organics, with 60 nm photolysis leading to a greater degree of unsaturated species. The proposed causative mechanism involves catalysis through the photoionization of nitrogen gas below 79 nm, which eventually produces protonated ethylene ($C_2H_5^+$) in methane rich mixtures.

Figure 6. Summary of initial chemical reaction pathways in complex molecule synthesis EUV irradiation of various methane mixtures. The estimated relative ratios of major ion species and other minor ions (hatched area) are also shown.

Figure 7. LDI mass spectrum of a 200 nm thick product thin film produced from 82.5 nm photolysis of a 5% methane in nitrogen gas mixture at 8 x 10^{-2} mbar. The spectrum was obtained from a roughly 10 micron diameter spot, using a single 330 nm laser shot without signal averaging.

Figure 8. Mass spectral information from LDI mass spectra of methane/nitrogen atmosphere EUV photolysis generated aerosol thin films (upper panel 60 nm photolysis; lower panel, 82.5 nm photolysis). (a) Van Krevalen plots of the N/C vs. H/C ratio for each molecular species observed in the mass spectrum, independent of intensity. (b) False color intensity weighted Van Krevalen diagrams for the same data set (approximately 10,000 formula masses) The 60 nm generated solid products appear dominated by an H_2CCN motif while that at 82.5 nm centers about an HCN motif.

Figure 9. Results of variable temperature hydrolysis studies of dissolved laboratory tholins in water and 15% ammonia/water solutions. Upper panels: Rate coefficients and reactive half lives for a set of correlated reactant/product pairs in water at 0°C. Lower panel: Observed hydrolysis rate coefficients for parent loss as a function of parent mass for both water (red squares) and 15% ammonia/water (blue squares) solutions at 0°C. This data demonstrates the rapidity of the initial chemistry in either media near the freezing point as well as the base catalysis observed for a significant fraction of the reactions.

Figure 10. Balloon-borne long term Titan sampling mission design concept. The balloon carries an instrumentation suite that can be lowered to sample (shown here) the physicochemical parameters and chemical composition of a hydrocarbon lake, or perhaps more generally the surface of an organic dune, a cryo-ice flow, or an ice filled crater (from JPL.NASA.gov).

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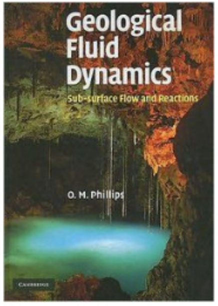
Review of Geological Fluid Dynamics; Sub-surface flow and Reactions By O.M. Phillips



Reviewed by John L. Nieber, Department of Bioproducts and Biosystems Engineering, University of Minnesota

The book Geological Fluid Dynamics by O.M. Phillips provides an excellent reference for researchers and professional working on environmental problems involving groundwater flows, especially flows at large spatial scales that are incited by natural forcing functions. The author presents background material from a very fundamental perspective using physical and mathematical arguments. The book is presented in six chapters consisting of 1) Introduction, 2) Basic Principles, 3) Patterns of Flow, 4) Flows with Buoyancy Variations, 5) Patterns of Reaction with Flow, and 6) Extensions and Examples. The Introduction chapter lays out the approach used in the book and summarizes the topics given in each of the subsequent chapters.

The Basic Principles chapter describes the properties of porous media, the fundamental properties of porosity and permeability, the conservation of mass principle, the stream function, derivation of Darcy's equation, the buoyancy term in the expression for the total potential, the thermal energy balance and chemical balances. A unique feature of this book is that it presents two theorems established by Helmholtz, the uniqueness theorem and the minimum dissipation theory, both of which play important roles in describing phenomena involving flow in porous media.

The chapter on Patterns of Flow describes flow phenomena in both homogeneous and heterogeneous geological formations. It presents the Laplace equation and provides a list of properties of the equation that are directly translated into practical terms. Regional groundwater flow processes are described qualitatively and applications of the Laplace equation to solve for flow patterns are presented. The effect of random heterogeneity of permeability on the flow patterns and ultimately the hydrodynamic dispersion is discussed and analyses given and related to predictions of hydrodynamic dispersion estimated from field scale experiments like the well-known Cape Cod field tracer experiment. The interaction between flows in matrix blocks and adjoining fractures is analyzed to quantity the nature of the flow field as well as solute transport distribution. The chapter ends with a discussion of pressure transients in porous media, either matrix, or media composed of matrix and fracture elements.

The Flows with Buoyancy Variations chapter deals with flow driven by gradients in fluid density brought about by either temperature gradients or salinity gradients. Thermal gradients could arise for instance from the natural geothermal gradient or from buried repositories of radioactive wastes. Salinity gradients can occur for instance when saline water is introduced over the top of fresh water. The author clearly explains that for these flows the uniqueness theorem discussed in chapter 2 does not apply because many different solutions are possible when flow circulations or flow instabilities are involved. The degree of buoyancy is quantified by the Rayleigh number for either thermally driven flows or salinity driven flows. A number of applications are presented for submerged banks and for sloping layers where thermal gradients drive circulations. Salinity driven flows are shown for freshwater lenses and for the phenomenon of gravity currents. Flow instabilities (Rayleigh-Darcy instabilities) caused by thermal gradients and salinity gradients are also discussed in detail. A section is also presented on the unstable flow that can occur when a more dense fluid invades a medium saturated with a less dense fluid.

The chapter on Patterns of Reaction with Flow provides a detailed account of the processes of chemical reactions during the movement of a fluid in porous media. The reaction processes can lead to deposition/precipitation of a chemical on the solid surface, or dissolution of a chemical from the solid surface, or both. The flow pattern is treated as mediating the reaction processes, and three main reaction scenarios are considered: reaction fronts, gradient reactions and mixing zones. The possible alteration of the solid matrix porosity and permeability due to either deposition or dissolution of reactants is considered. Descriptions of field scale reaction phenomena are presented including one that could take place on the time scale of a few years, and another associated with the formation of mineral deposits that are estimated to take tens of millions of years to complete.

The last chapter appears to be more of an appendix than a chapter. It consists of only a few pages with some extra references and a few problem descriptions that end as sample questions to be solved by the reader.

One aspect of the book that was particularly refreshing is that it does not focus on the use of numerical methods for solving the flow and transport equations. Instead it provides quantitative arguments for the significance of particular terms in governing equations and relations, and also provides the derivation of analytical solutions when desired for describing flow and transport phenomena.

Numerous reference books and textbooks exist that cover the topics of flow and transport processes in groundwater systems. Dr. Phillips' book is unique and might become a classic similar to Jacob Bear's Dynamics of Fluids in Porous Media. It certainly should be is a valuable addition to the library of any research or practitioner serious about the processes of flow and reaction transport in geological settings.

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