## thesis

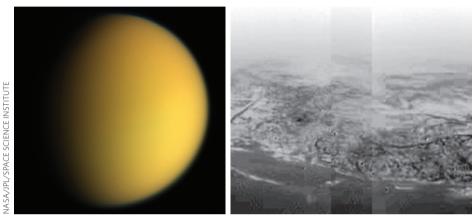
## The organic Solar System

In the second of two essays looking at organic chemistry that can be found in the Solar System, **Bruce C. Gibb** focuses on the gas and ice giants as well as their satellites — concluding the tour on Saturn's fascinating moon Titan.

In the first part of this two-essay series<sup>1</sup> it was pointed out that over 100 different organic compounds have been detected in space, and that there are many locations in the Solar System where complex — and as vet uncharacterized — mixtures of organic molecules can be found. The Galilean moon Europa is a case in point. Its surface is stained with unsaturated polymers called tholins, which are formed by photochemical reactions of the simplest carbon and nitrogen species. To an astrobiologist, if you mix the likes of tholins with liquid water and energy you have the potential for life; and hence Europa, with its mantle of warm water, is an oft-cited target for future exploration (such as the Europa Clipper, a concept mission from NASA).

Is life on Europa too much of a stretch? Let's assume there's nothing in the solar system to overly excite astrobiologists; let's ignore the ingenuity of Mother Nature and the tenacity of life, and resign ourselves to the idea that Earth represents the only haven for life in the Solar System. Even if we do all of this and just consider the emergent phenomena that can arise in even relatively 'straightforward' chemical systems, there are surely startling chemical discoveries waiting to be made in many corners of the Solar System (organic molecules + energy + water + time = a headybrew). So even if conservative scientists are correct and there is nothing to satiate astrobiologists, there is still plenty going on for the average organic chemist to get worked up about.

The 'plausibility of life (POL) on other worlds' scale<sup>2</sup> considers a fluid medium, a source of energy, and constituents and conditions compatible with polymeric chemistry as key to the possibility of life. Based on this scale, five categories of heavenly body can be described that cover the gamut from the ideal (category I, such as the Earth) to the essentially impossible (category V, for example, the Sun). Although most Solar System bodies fall into category V or IV (conditions conducive to life may have been possible at one time but certainly aren't now; Venus for example) there are a surprising number of category II



Titan (left) and a shoreline on Titan (right).

(water + energy + organic compounds) and category III (physically extreme conditions but with a possibility of harbouring very alien life) systems.

The gas giants Jupiter and Saturn are primarily composed of hydrogen and helium, but their interiors contain denser materials. It is estimated that 5% of Jupiter's mass is made up of other elements. The Galileo probe - which descended 100 miles into the atmosphere (pressure = 23 atmospheres; temperature = 153 °C) — as well as other orbiter and ground-based measurements, have so far identified an array of compounds including methane, ethane, benzene, other organics, water, ammonia, silicon-based compounds, hydrogen sulfide, neon, oxygen, phosphine and sulfur. This richness of chemistry led Sagan and Salpeter to propose the presence of life on Jupiter<sup>3</sup> somewhere between the metallic hydrogen core and the cold upper atmosphere - but if it is there, it would likely be devoid of compartmentalization and be really weird<sup>4</sup>.

By the definitions given above, Jupiter falls into category III, but perhaps Jupiter is best classified as a category V body after all. That point ceded, even if Jupiter is only conservatively 0.1% organic, that's nearly  $2.0 \times 10^{24}$  kg of organic molecules; onethird the mass of the Earth! Tossed between high pressure and heat on one side and frigid temperatures and near vacuum on the other, there must be some fascinating chemistry occurring in this turbulent giant. Less is known about Saturn, but methane, ethane, propane, acetylene, ammonia and phosphine have all been detected in the upper atmosphere, so again there are literally Earth-sized quantities of organic chemistry going on deeper down on this category III or V planet.

The ice giants Uranus and Neptune are rich in energy, water and organics, and could be described as category III — or category V if you consider solid surfaces and sharp physical transitions important for supporting life. However, the composition of these two planets is visibly different; Uranus is a pale cyan colour — attributed to the presence of large amounts of methane — whereas Neptune is a vivid azure. The latter is also rich in methane, but there are evidently other compounds that lead it to absorb more in the yellow part of the spectrum than the red. Deeper down, models suggest that both planets have mantles composed of water-ammonia oceans.

For reasons that are not clear, the internal heat of Uranus is very low; it is the coldest planet in the Solar System with an upper atmospheric temperature of -224 °C, some 24 °C colder than more distant Neptune. Nevertheless, in both cases the deepest sections of the mantle are so hot and under such pressure that methane is

decomposed to elemental carbon. The end result of this is the potential for diamond hailstones to continually rain down on a sea of liquid diamond, replete with 'diamondbergs'<sup>5</sup>. Alien indeed. Higher up where conditions are milder, products from the photolysis of methane such as acetylene and diacetylene have been detected on both planets and so there is, yet again, likely to be a lot of interesting organic chemistry (life engendering/enabling or otherwise) going on somewhere between the diamond nucleation zone and the upper atmosphere.

While we're out at the edge of the Solar System it is also worth briefly mentioning Titania and Triton. Titania, the largest moon of Uranus, is largely composed of water. Its water-ice surface shows evidence of the flow of liquid, and one theory is that there is enough ammonia present that a cold (roughly -80 °C) liquid water-ammonia ocean exists under its surface. However, we do not know if Titania has a large amount of organic material. Neptune's Triton is more interesting in that regard. It has a weak atmosphere with what are suspected to be nebulous nitrogen clouds. The troposphere is thought to be composed in large part of simple tholins and its highly reflective surface shows evidence of plate tectonics and cryovolcanism. Volcanoes of ammonia and water seem to have erupted on Triton, at least sometime in the past. If the tholins on the surface that give Triton it's red-brown hue are being internalized into the water-ammonia mantle, then some interesting chemistry would likely ensue.

Like any good guided tour though, the best has been kept for last. Although the gas giants and ice giants contain between them incredibly large amounts of organics in highly complex dynamic systems, how can an organic chemist not be awe-struck by the majesty of Titan<sup>6</sup>. Saturn's largest moon is the second largest in the Solar System (only Jupiter's Ganymede is bigger) and is even larger than Mercury. It is the only natural satellite with a dense atmosphere (approximately 1.5 times that of Earth) and, moreover, it is the only object other than Earth with clear evidence of stable bodies of liquid on its surface.

Although we've been gazing at Titan since its discovery by Dutch astronomer Christiaan Huygens in 1655, its thick, hazy atmosphere shrouds Titan in mystery in much the same way as the clouds of Venus do. Ground-based observations, Voyager, and more recently the Hubble telescope taught us much about the atmosphere, but to peer through it has required something special. That something is the Cassini–Huygens mission, which continues to provide us with a wealth of information about Saturn, its rings, and its satellites. However, it is the exquisite view of Titan provided by Cassini– Huygens that is arguably the great success story of the mission. For planetary scientists, astrobiologists and organic chemists alike, the dozens of Titan flybys by Cassini and the landing of the Huygen's probe on the surface of Titan itself have opened up a wide range of new thinking.

Cassini-Huygens has shown us an alien world eerily reminiscent of Earth. The thick atmosphere is a veritable soup of nitrogen and methane, as well as a wide range of photochemical products from their reactions. Acetylene, hydrogen cyanide and a host of organic cations can be found at the highest levels; benzene and other complex organics up to a mass of roughly 350 Da lie beneath this; negatively charged organic ions of masses of up to 8,000 Da are found lower still; and near the surface there are high concentrations of polymeric tholins. There is a cascade of organic chemistry from 1,000 km above Titan all the way to the surface7-9. In Earth's oxidative atmosphere there is no equivalent to this one-way tholin 'rain'; Dr Seuss' Oobleck - that green sticky goo that rains down on the Kingdom of Didd in *Bartholomew and the Oobleck* — is the closest thing we have.

There is, however, a second rain on Titan that is completely analogous to what we experience here on Earth. Except it's not water of course; not with a surface temperature of -180 °C. Rather the rain on Titan is liquid methane or a methane/ethane mixture — potentially with other organics and nitrogen gas dissolved in it — which intermittently pours forth from the heavens in cloud-bursts and storms (the jury is still out about whether there is lightning on Titan). And just like Earth, the rain and wind on Titan bring about fluvial and aeolian weathering of the surface. This weathering is apparent from an altitude of 8 km, where the hills and mountains look like a winter scene reminiscent of the glaciated, rounded mountains of northern Europe, and it is apparent on the ground where rounded pebbles and stones of ice litter the Huygens landing site. Radar images from Cassini and the Huygens probe also reveal gullies, riverbeds and channels that flow into lakes and seas. Except - and you sometimes have to pinch yourself to remember this we're not talking hydrology, were talking hydrocarbonology (organology would be better but we'd be stepping on the toes of musicians). The lakes and seas, mostly found in the northern hemisphere, come in all sorts of shapes and sizes. The largest methane sea identified so far, Kraken Mare, is somewhat larger than the Caspian Sea and contains hundreds of times the total liquid hydrocarbon reserves of Earth.

Of course the ground of Titan isn't made of minerals. Like many of the moons this far from the sun, Titan is mostly just water and ammonia. And the best evidence for this is that the weathered surface is rock-hard water-ice covered, in part, with tholins. So when you look at those black and white images from the Huygens probe you also have to remember that the 'snow' is the black bits and the bare surface is the white patches. Quite the opposite of what we are used to.

Radar imaging from Cassini also gives tantalizing evidence of cryovolcanoes dotting the solid-ice surface of Titan. Although this remains to be confirmed, there are other Earth-like vet alien geological features on Titan that we're more certain about. In particular, there are large areas of longitudinal 'sand' dunes on Titan; not silicates, but either pulverized waterice coated in organic molecules, or simply solid organic material<sup>10</sup>. Because polymeric tholins are more akin to tar than crystalline or granular materials, perhaps a readily crystallizing compound such as benzene forms these 100-m high and tens-of-km long dunes. If true, these would act as a huge thermodynamic sink modulating equilibria within the tholin cascade.

Not too long ago there was a plan to build on Cassini-Huygens and send a second, more advanced, mission to Titan. One that would release a probe attached to a sizable hot-air balloon so that it could float endlessly around Titan gathering atmospheric and climatic data, and perhaps land once in a while to analyse the surface in a particularly intriguing locale. If this does come to pass, and there is such a thing as reincarnation, I want to come back as an organic chemistry student analysing data from the mission and trying to replicate Titan chemistry in the fumehood for my PhD. Although I must confess that my lunch breaks would take an inordinately long time; whilst eating my sandwich I would definitely be glued to the high-definition video-stream from the probe's Titan Cam. 

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