Hypothesis Paper

Many Chemistries Could Be Used to Build Living Systems

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ABSTRACT

It has been widely suggested that life based around carbon, hydrogen, oxygen, and nitrogen is the only plausible biochemistry, and specifically that terrestrial biochemistry of nucleic acids, proteins, and sugars is likely to be "universal." This is not an inevitable conclusion from our knowledge of chemistry. I argue that it is the nature of the liquid in which life evolves that defines the most appropriate chemistry. Fluids other than water could be abundant on a cosmic scale and could therefore be an environment in which non-terrestrial biochemistry could evolve. The chemical nature of these liquids could lead to quite different biochemistries, a hypothesis discussed in the context of the proposed "ammonochemistry" of the internal oceans of the Galilean satellites and a more speculative "silicon biochemistry" in liquid nitrogen. These different chemistries satisfy the thermodynamic drive for life through different mechanisms, and so will have different chemical signatures than terrestrial biochemistry. Key Words: Carbon, hydrogen, oxygen, and nitrogen life—Planetary liquid— Silicon. Astrobiology 4, xxx–xxx.

INTRODUCTION

There is a famous book published about 1912 by Lawrence J. Henderson . . . in which Henderson concludes that life necessarily must be based on carbon and water, and have its higher forms metabolizing free oxygen. I personally find this conclusion suspect, if only because Lawrence Henderson was made of carbon and water and metabolized free oxygen. Henderson had a vested interest.

—Sagan (1973)

DISCUSSIONS of nonterrestrial life generally assume that the biochemistry of life will be similar to that which we see on Earth. Almost all writers assume that carbon is the central element in any plausible biochemistry, and that its combination with hydrogen, nitrogen, and oxygen is the core of any living system. They argue that carbon, hydrogen, nitrogen, and oxygen (CHON) chemistry is essentially the only chemistry of life. This is an understandable assumption, but not necessarily correct, for reasons eloquently summed up by Sagan (1973) in the quotation above. Because we have one extremely complex and refined example of biochemistry to work

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from, it is difficult to imagine others that could approach its flexibility and power. We are therefore drawn to suppose that there is something unique about our biochemistry, a view recently supported by Pace (2001), but echoed by many other writers, if for no other grounds than that a search for life must assume some properties of life to search for and we might as well assume what we know to be true (Chyba and Phillips, 2001). However, this could be chemical parochialism (Clarke, 1972).

The "CHON" description oversimplifies terrestrial biochemistry. Sulfur and phosphorus play central roles as well, and many "inorganic" components, such as iron-sulfur complexes, are essential to biochemistry. But it is the enormous flexibility of carbon chemistry that is considered the pivot of terrestrial biochemistry, and almost all our biochemicals are built on backbones of carbon-carbon or carbon-heteroatom bonds. Many molecules appear in the metabolic map (ExPasy, 2002) that have no oxygen, or no nitrogen, and most have no sulfur or phosphorus. But only phosphate ions, hydrogen peroxide, ammonia, and the elements themselves contain no carbon.

Carbon can form stable polar and non-polar single bonds with many other non-metals, and double and triple bonds with itself and a few other, non-metallic elements, forming complex functional groups that can bond to all other elements (with the possible exception of the noble gases). Carbon can also form polymers, bonded to itself or to other elements, that can be decorated with an immense variety of side groups to provide information storage and catalytic effect.

Pace (2001) went further, suggesting that many specifics of terrestrial biochemistry are to an extent "universal," in that peptides, sugars, and nucleic acids are the most likely biological components to be built from CHON. This may be so, but our present knowledge of physics and chemistry does not suggest that it is necessarily the case.

The description above is a "builders' specification" (M. Russell, personal communication) or the "parts list" (Bains, 2001) for life—it describes what life is, rather than what life does. This paper argues that the CHON "builders' specification" is unnecessarily narrow, that many other chemistries could be rationally considered as candidates for the basis of life depending on the chemical, physical, and energetic environment in which they could form, and that "functional specifications" can flow from this. It is the nature of

the liquid system in which the chemistry arises, and not limitations on chemistry itself, that will direct the biochemistry of non-terrestrial living things. A speculative estimate is provided as to whether conditions for a non-water biochemistry are probable on a galactic scale, and the type of chemistry that might be possible under those conditions is discussed.

WHAT IS LIFE?

A basic problem with identifying where life might occur is defining what life is (Conrad and Nealson, 2001). We observe life to be energy-using, growing, and having structure that is characteristic of each incidence of life and of evolutionary history. Both the physical structure and the control structure of the chemistry of life are diagnostic.

A basic feature of this is the capability for environmentally adapted coded replication. Living systems grow and replicate so that the replicants are similar to their progenitor(s). However, this is not just "a self-sustained chemical process that can undergo Darwinian evolution" (Joyce, 1994); there is an internal program that directs how the chemistry operates. The concept of chemical self-replication can be applied with some justification to other catalytic, self-sustaining physicochemical process, such as forest fires. However, the nature of a fire is determined by the material that is burning, not what started it. We only fancifully consider fire to have "life": Its "metabolism" is determined by the substrates on which it grows, and has no internal control.

By contrast, the nature of a living system is determined by the coded pattern contained within that system, and is constant in a variety of environments. The living system converts energy and a variety of materials into more living systems. Growth and reproduction are chemical, but not chemically defined. There is a code, program, or blueprint that describes what each species should be like.

The mapping from code to organism is arbitrary; the genetic code had to be discovered, and could not be deduced from the nature of the organisms it coded for. Hence it can be changed. The genetic code is not a law of nature, but a true "program" that is interpreted by the organism. The implementation of the plan is adaptable, so that propagation can continue under changed cir-

cumstances: Because no permanent information copying process can ever be 100% accurate, replication inevitably involves mutation, and hence candidature for evolution. Evolution is not a requirement for life (arguably, the entire genetic apparatus is an attempt to provide genetic stability, and hence prevent evolution), but is an inevitable consequence of the programmed, rather than template-patterned, replication.

The other basic feature of life is its ability to capture and transform energy to power this process. The accuracy of this replication is primarily a function of how much energy is expended in getting it right, showing the centrality of energetics to living. Life requires many other functions, such as the capture and processing of materials and structural integrity. All these must be highly specific, but also flexible enough to function when the underlying "program" is changed. This leads to the requirement of a general method for generating a wide range of arbitrary chemicals, and *not* generating many others that are not wanted. This points to the absolute requirement for a battery of specific catalysts. (I assume throughout that life is chemical: Non-chemical life, such as life patterned into magnetic or gravitational fields in space or built of nucleons on the surface of a neutron star, is an interesting hypothesis but one with so little theoretical or factual support that I ignore it here.) The synthesis of the catalysts themselves must be guided by catalysts, which would imply the need for an infinite number of catalysts unless the catalyst–synthesis system assembles some modular, preformed units as directed by the "program." This leads to a requirement for polymeric catalysts, as well as polymeric "program." The polymers are non-repetitive, as they must be capable of almost arbitrary chemistry. So a key feature of the *functional structure* of the chemistry of life can be seen to be highly specific, non-repetitive macromolecules and their smaller components or interaction mediators.

This description does not tell us about the other components of living systems, such as spatial boundaries or structural integrity elements. These could in principle be composed of small or large molecules, or crystalline or amorphous solids, and all of these are used in terrestrial biology. Such spatial organization is essential for both the origin and the maintenance of life. Life is not just chemistry—it is chemistry that dissipates energy and is organized. Fundamental considerations suggest that any chemical system that is organized in space and far from equilibrium will generate complex, non-linear behavior (Nicolis and Prigogine, 1977). Mitchell (1976) emphasized the role of "vectorial chemistry" in the life process. So such structural elements are essential for life. However, their chemical nature is not constrained by this requirement.

For a system of many interacting macromolecules to be physically stable and yet capable of chemical activity, the molecules must (a) interact flexibly, which in practice means that they be able to move with respect to each other, but (b) be kept in consistently close proximity. A solid will not fulfill the former requirement, and a gas or suspension in a gas will probably not fulfill the latter, so chemical life is dependent on its molecular components being suspended in a fluid of comparable density of the macromolecules, most plausibly a liquid or a supercritical fluid. The same requirements apply to self-assembling chemical systems in the laboratory, and lead to the same requirement for a liquid in which the components can move and interact (Whitesides and Grzybowski, 2002). The only accessible fluid on Earth is liquid water.

This paper postulates that:

1. Liquid environments in which biochemistry must take place are common on a cosmic scale, and that neutral pH, "Earth-like" oceans are not the only such environments.
2. Different liquid environments can be compatible with different basic chemistries.
3. Those chemistries can be used to assemble extremely complex and flexible chemical systems, with analogues within those systems for central functions of biochemistry.
4. Those chemistries can provide a route by which a "biochemistry" could arise.

LIQUIDS IN OUR SOLAR SYSTEM

On Earth, the only accessible common liquid is water, and water is compatible with an enormous diversity of carbon chemistry, and specifically CHON polymer chemistry. Water, as much as carbon, is essential for terrestrial life. Conventionally, the circumstellar habitable zone (HZ) has been considered that region where liquid water could be stable on the surface of a planet (Hart, 1979), and the concept has been extended to a

"Galactic HZ" being the region of a galaxy where stars could exist that have planets on which liquid water is stable (Gonzalez and Brownlee, 2001). The discovery of an extensive, deep subsurface biota on Earth (Pedersen, 1993), which can exist solely on chemolithotrophy (Stevens, 1997), and the likely involvement of deep sea vents in the origins of life suggest that subsurface water could also be a source of and support for life.

Recently, evidence has accumulated that liquid water occurs in other places in our Solar System. There is evidence for "oceans" of water and water/ammonia within Callisto and Europa, and these may also be present in Titan (Showman and Manotra, 1999). These "oceans" are expected to be extremely basic, conditions under which the terrestrial nucleic acids and proteins would be rapidly hydrolyzed and most terrestrial biochemistry would be thermodynamically unworkable.

Liquid water/ammonia mixtures also exist in the giant planets. Conditions 10–20 km below the cloud base of Jupiter (rather deeper in Saturn) allow for formation of large quantities of water/ammonia droplets (Chamberlain and Hunten, 1987). However, cloud circulation carries such droplets into regions where all but simple carbon-containing molecules are destroyed by thermal dissociation (Guillot, 1999). Similarly, the haze droplets on Venus are probably too aggressive an environment for CHON biochemistry (but for ideas on how life could arise and survive on Venus, specifically in mid-level haze or at the poles, see Cockell, 1999; Irwin and Schulze-Makuch, 2001; Yamauchi et al., 2002).

A wide variety of liquids, including organic solvents, ammonia, HF, BF_3, N_2O_4, sulfuric acid, and a range of molten salts are used to facilitate a huge range of synthetic laboratory chemistry (Housecraft and Sharpe, 2001), so differing solvent systems are not *a priori* incapable of sustaining complex chemistry. The questions are: Which, if any, of these exists as a liquid in a cosmic context? What chemistry that includes complex, heterogeneous macromolecular synthesis and catalysis could those liquids and chemistries sustain? Do considerations of energetics suggest that life could reasonably arise in such environments?

COSMIC ABUNDANCE OF LIQUIDS

Such speculation is pointless if substantial amounts of these liquids do not, or cannot, exist on a cosmic scale. We know that at least one body in the Solar System has a large volume of liquid water on it. At least two and possibly three others have large bodies of very cold water/ammonia mixtures on or in them. The existence of surface oceans of ethane and methane on Titan has been postulated (Taylor and Coustenis, 1998), and although infrared surveys show that the surface is not covered with ocean (Meier et al., 2000), substantial bodies of ethane/methane liquid in lakes (Lorenz, 1994) or near-surface reservoirs (Lara et al., 1994) are still suggested by the high levels of photochemically labile methane in Titan's dense atmosphere. Plumes in the atmosphere of Triton have been interpreted as geysers of nitrogen (Soderblom et al., 1990), which could be generated when sunlight shining through a "greenhouse" of translucent nitrogen ice on the surface of the moon melts and then vaporizes the nitrogen at the base of the solid layer, causing subsurface ponds to form and then erupt [although other explanations are possible (see Kirk et al., 1995, for review)].

Are these liquids likely to be cosmically common, and what other liquids could exist at all in cosmically significant levels?

Table 1 shows the relative cosmic abundance of the most common 10 elements, and gives a crude estimate of the frequency with which volatile and chemically stable combinations of them might exist. A crude estimate of the relative abundance is given by the relative frequencies of the elements concerned; thus we would expect H_2O to be more common than H_3N, and both to be more common than NO_x. The rank order suggested by Table 1 is similar to that seen in interstellar ices (Tielens and Whittet, 1997) and near-Earth comets (Bockerlee-Morvan, 1997), with the caveat that both environments are likely to enrich for relatively non-volatile CO_2 and deplete for CH_4. The only substantial anomaly is that Table 1 suggests the existence of relatively high cosmic levels of silanes.

Fractionation in the protostellar cloud and within the planet results in bodies richer in some of these volatiles than others. So the chance that any of these "cosmically common" compounds exists as a substantial volume of liquid on a planet depends on the nature and history of the planet. What are the chances for the possible combinations of the liquids in Table 1 and the plausible size and structure of planets that might exist in other planetary systems?

TABLE 1. RELATIVE ABUNDANCE OF THE 10 MOST ABUNDANT ELEMENTS, AND
COMBINATIONS OF ELEMENTS THAT CAN FORM VOLATILE COMPOUNDS

Element	Cosmic abundance (H = 1)	Volatile elemental form	Volatile compounds formed with more abundant elements
H	1.000	H_2	(See below)
He	0.787	He	—
O	0.139	O_2	H_2O
Ne	0.104	Ne	—
C	0.087	—	CH_4, C_2H_6 (etc.), CO, CO_2, and nitrogen compounds
N	0.056	N_2	HCN, HC_nN, NH_3, NO_x
Si	0.046	—	SiH_4
S	0.038	—	H_2S, NSH, CS_2
Ar	0.023	Ar	
P	0.007	—	PH_3

This is a question beyond the scope of this paper to answer rigorously, as illustrated by the complexities of terrestrial atmospheric and tectonic physics and chemistry that allow liquid water to exist on the Earth. Terrestrial surface conditions are a balance of surface and atmospheric heat balance, and the chemistry of the carbonate/silicate cycle, which modulates atmospheric CO_2. (For discussion of the evolution of the carbonate/silicate cycle, see Kasting, 1988; Kasting *et al.*, 1993; Sleep and Zahnle, 2001, and references therein). However, boundaries can be put on the HZ, the distance from a planet's primary where surface liquid water is stable (Hart, 1979). The inner limit is where the stratosphere is sufficiently warm to allow significant amounts of water vapor to accumulate there, and so escape into the upper atmosphere where it can be photolysed by solar ultraviolet. The resulting hydrogen escapes into space, and the oxygen (under equilibrium conditions) will react with surface rocks. This depletes the planet of water, and a runaway greenhouse can start. The HZ outer limit is where the stratosphere is cold enough for CO_2 to freeze out (as happens at the martian poles), thus destroying its ability to act as a greenhouse gas (Kasting *et al.*, 1993). For our Sun, the inner limit is around 0.85 AU, the outer around 2.4 AU.

One might imagine similar feedback cycles stabilizing other planets at very different temperatures. However, we would have to know a lot about the atmospheric, surface, and interior chemistry, as well as the physics of crust, subcrustal zones, and climate, to be able to model such cycles accurately.

A more feasible model is the simplistic one that planets and their atmospheres are chemically and tectonically inert. Calculation of the possibility of a material being liquid on or in a planet then depends solely on physical properties, which we can compare between planets to obtain the *relative* frequency of liquids. This can then be compared with the *actual* frequency observed in the Solar System.

If we regard a planet and its atmosphere as chemically and tectonically inert, then the only requirement we have for liquid to exist is for there to be an environment in which the liquid does not boil and does not freeze. Whether a pure liquid freezes is determined solely by temperature (at pressures of relevance to surface or near-surface bodies of liquid). Whether it boils depends on the pressure and the temperature. The need for pressure implies a substantial solid body: Asteroids and comets are unlikely to be able to retain enough internal pressure or any significant atmosphere to stabilize liquid. So we can estimate the relative likelihood of the existence of a "planet" that can hold substantial liquid by estimating (1) what is its surface temperature and (2) whether it big enough to retain a substantial atmosphere at that temperature.

Surface oceans and lakes

The condition for a surface ocean or lake to exist is that the surface temperature is above the freezing point of the liquid, and below the boiling point, the latter being determined by the surface pressure. The surface temperature of a

rapidly rotating object, *i.e.,* one at thermal equilibrium, at distance d from a star is:

$$T_d = T_s \frac{\sqrt[4]{(1-A)}}{\sqrt{d/r_s}} \quad (1)$$

where T_d is the (black body) surface temperature of the planet at distance d from the star, T_s is the surface (black body) temperature of the star, r_s is the radius of the star, and A is the albedo of the object. Bodies with non-zero albedo can maintain lower temperatures closer to the star, moving the inner boundary at which a liquid boils closer to the star. However, greenhouse effects in the atmosphere that are necessary to stabilize a surface liquid will increase surface temperature, moving the inner boundary of the layer outwards (Franck *et al.,* 2000). On Earth, these two effects cancel out (to rough approximation). The combined effect is represented by a "pseudoalbedo" A':

$$A' = 1 - \left(\frac{T_o}{T_b}\right)^4$$

The distribution of A' is obtained from observed T_o (the observed planetary surface temperature) and T_b (the black body temperature). In practice, pseudoalbedo is very close to actual aldebo in most cases.

Almost all the non-giant bodies in our Solar System have a substantial atmosphere, *i.e.,* surface pressure >0.1 bar, if their atmosphere parameter (A) is <1:

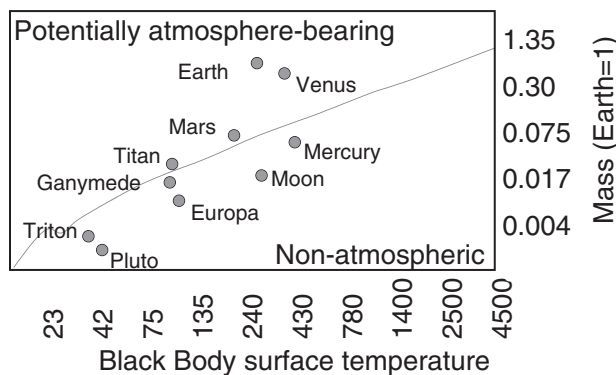$$\frac{(\log(R) = T^{1.25})M_e^{-1.25}}{30,000} = A \le 1 \quad (2)$$

where M_e is the mass of the body relative to Earth $= 1$, and R is the absolute rate of loss of atmospheric mass from the planet due to the thermal (Jeans mechanism) energy of the molecules in the upper atmosphere (Yung and DeMore, 1999). The predictions of Eq. 2 are shown in Fig. 1 with respect to some non-giant bodies in the Solar System, and shown to accurate with the exception of Mars.

R is calculated by

$$R = \frac{J \times R_e^2 \times MW}{2.9 \times 10^8}$$

where MW is the molecular weight of the principal molecular species in the atmosphere (which is itself limited by what is the heaviest molecular species that will not solidify under the surface temperature); J is the Jeans escape rate, *i.e.,* the expected rate at which molecules will escape the planet due to their thermal energy per square centimeter; R_e is the radius (Earth $= 1$); and J is calculated exactly (Yung and DeMore, 1999).

For bodies that are not embedded in a more powerful magnetic field than their own (in our Solar System, this criterion excludes Io, whose atmosphere is dominated by the jovian magnetic field), it is empirically true that

$$T_a = L \times M_e - \sqrt{5.9 - \frac{2.2}{R_e}} + 1.03T_d$$
$$+ \frac{R_e \times T_d \times \sigma}{L} + \frac{L - 6.45}{5.7} + 78$$

where R_e is the radius of the body (Earth $= 1$), and L is the period of rotation (length of day, Earth $= 1$), *i.e.,* the excess temperature of the top of the thermosphere is related to the temperature of the ground and two parameters that are related to the likely interaction of the body's magnetic field with the solar wind: the mass and rate of rotation of the body.

Subsurface liquids

We can assume that subsurface liquid must be denser than the material on top of it, and have a melting point that is not higher than the material on top of it (Fig. 2). This is true for water and water ice, but none of the other liquids listed in Table 1 has ices that are less dense than the liquids from which it is formed. Table 2 lists the combinations of liquids from Table 1 for which it is possible for

FIG. 1. Predictions of whether a planet will have a dense atmosphere. The continuous line represents the boundary between $A > 1$ and $A < 1$. See text for details.

FIG. 2. Requirement for a subsurface liquid ocean.

such a liquid/crust relationship to occur. (Densities and melting points are for Earth surface pressures—depth compression will alter both, an effect not taken into account here.) It is assumed that a mass of at least 2% of that of the Earth (approximately the mass of Europa) is needed to sustain a subsurface "ocean." By definition, the surface temperature must be lower than the freezing point of the liquid concerned (as otherwise surface oceans will form), and observationally a surface temperature of <60% of the freezing point of a liquid appears to mean, in our Solar System, that substantial subsurface reservoirs of that liquid do not form. In addition, the surface temperature must be suitable for a "crust" of solid material of a lower density than the liquid to form, as summarized in Table 2.

The distribution of accessible volume, *i.e.,* non-rocky core, of mid-size ("terrestrial"/"galilean")

bodies >1,000 km in diameter at distance D from their parent star is $\alpha \times r^{-1.5}$ [both for our Solar System (see Fig. 3) and for the dust disc around nascent solar system Vega-type stars such as Beta Pictoris (Artymowicz, 1997)]. The number of bodies is a power function of their mass, such that

$$M \propto \frac{1}{N}$$

where M is the mass of the object and N is the relative number.

Planets of arbitrary size cannot form at arbitrary distances from a star. Beyond some critical distance (around 50 AU for our Sun) the nebula from which the star condenses will be too thin for there to be enough time for planets to form before the star's own radiation drives the components into interstellar space (Artymowicz, 1997; Morbidelli and Jacob, 2002). So very large bodies did not form, and in most models of planetary formation are unlikely to form, outside the orbit of Neptune. However, smaller bodies can and did, and larger ones could have been ejected from the inner Solar System to form the core of trans-Neptunian "giants." Gravitational lensing observations hint that "planets," *i.e.,* bodies of substellar mass, may populate both the fringes of stellar systems and the space in between them, at least in globular clusters (Sahu *et al.,* 2001), having been ejected there by close stellar encounters. There is increasing uncertainty in estimates of the density of planets further from the Sun.

TABLE 2. COMBINATIONS OF CHEMICALS FOR WHICH AN ICE CAN FLOAT ON A LIQUID AT THE SAME TEMPERATURE

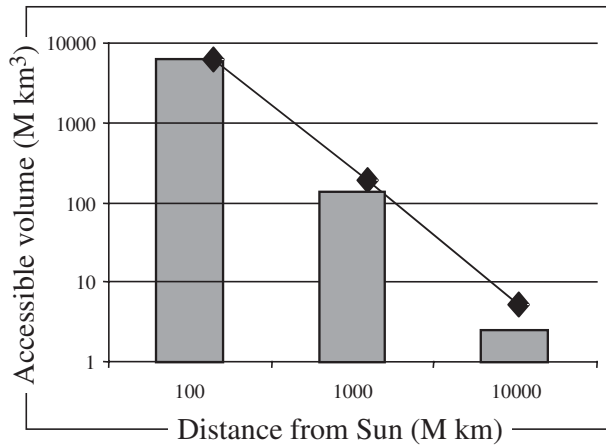|	Candidate for surface "crust"									
	^4He	H_2	Ne	N_2	Ar	CH_4	C_2H_6	NH_3	H_2O	H_2SO_4
Solid density (kg/m^3)	190	86.7	1,400	947	1,624	500	525	821	900	~1,900
Liquid density (kg/m^3)	125	70.8	1,204	808	1,400	423	446	681.8	958	1,840
Melting point (K)	—	13.96	24.6	63.2	83.8	90.7	101.1	195.5	273	283
Boiling point (K)	4.224	20.39	27.1	77.36	87.3	111.7	185.2	239.8	373	563.2
Candidate for subsurface liquid										
He		√								
H$_2$										
Ne				√		√	√	√	√	
N$_2$						√	√			
Ar						√	√	√	√	
CH$_4$										
C$_2$H$_6$										
NH$_3$										
H$_2$O									√	
H$_2$SO$_4$										

FIG. 3.   Number of the upper 100 km of bodies at least 100 km in diameter in the Solar System, excluding Jupiter, Saturn, Uranus, and Neptune. The solid line is the line to fit the number to $5 \times 10^6 \times r^{-1.5}$, where r is the distance from the Sun.

Both of these estimates assume that the planet is uniformly heated. If it is tidally locked to the local source of heat, then substantial differences in surface temperature could exist. In reality, tidal locking is only likely to occur in planets the size and solar distance of Mercury, which would be depleted of volatiles on formation, so the speculation of Niven (1975) that cryogenic environments could exist on the "cold side" of Mercury (even if it were in a 1:1 orbit:rotation resonance with the Sun, not 3:2) is questionable.

ESTIMATES OF THE RELATIVE FREQUENCY OF LIQUIDS

Given these assumptions, we can estimate the relative frequency of a liquid of given melting and boiling points and density, at different distances from a star, as well as the characteristics of gasses which could form an atmosphere at those temperatures. Figure 4 illustrates the calculation of the relative probability of liquid "oceans" of water in our Solar System, as surface oceans and subsurface reservoirs. (The "sawtooth" form of some curves under this model is a reflection of the modeling granularity, and not of actual structure in proposed "habitats.")

Five points can be made with regard to the predictions in Fig. 4:

1. First, the range of areas in which liquid water is likely (>0.05 probability) is 0.5–1.6 AU, which differs in absolute magnitude but is very similar in range to that predicted by Kasting *et al.* (1993) on more rigorous grounds. Because the CO_2 greenhouse is ignored, the range is shifted sunward.
2. Related to this range shift, Venus is predicted here to potentially have a substantial surface ocean of liquid water. This is incorrect, because of runaway greenhouse effects.
3. The Earth is at the innermost limit at which a subsurface, ice-covered ocean is predicted to be possible. It is believed that the Earth's
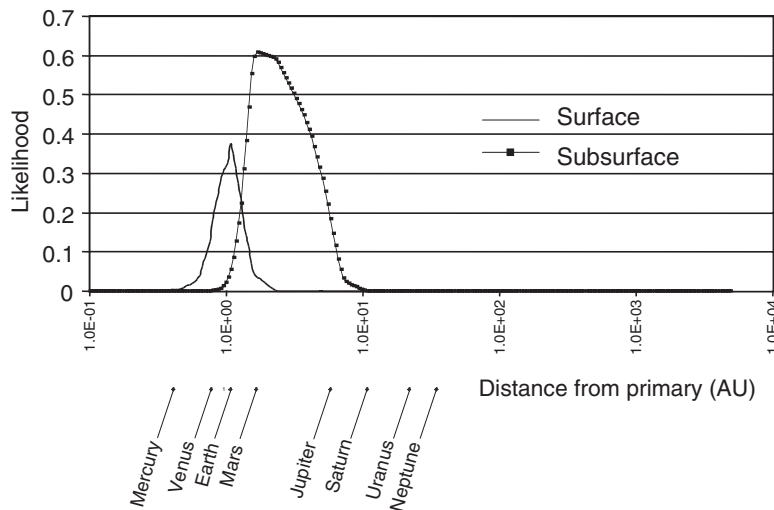
FIG. 4.   Relative probability of bodies containing liquid water as surface oceans or as subsurface reservoirs as a function of distance from the Sun.

oceans did indeed freeze over almost completely in the neoproterozoic epoch (Hyde *et al.,* 2000). A "snowball Earth" is not geologically stable, in agreement with the prediction that such a geology is at the edge of the possible; the black body temperature of the Earth is around 310 K, and so a "snowball Earth" can only be created if the Earth's albedo is very low.

4. Mars is just within the surface ocean zone, suggesting that Mars does not now have surface water because of its small size rather than its orbit. [Mars is also the only planet to violate Inequality 2; it is possible, therefore, to postulate that Mars had both atmosphere and oceans in the geologically recent past, something that Mars' geography would also suggest (Carr, 1996).]

The summed probability of an internal, ice-capped ocean is at least as high as that of a surface ocean in our Solar System. This is borne out in practice; at least three bodies are believed to have internal oceans of water in our Solar System (Europa, Ganymede, and Titan), and the volume of Titan's internal ocean alone might be as high as 1.8×10^{10} km^3 (Grasset *et al.,* 2000), enough to cover the Earth to an average depth of 35 km.

Figure 5 shows the likely frequencies of several different liquids as a function of distance from a star of the same luminosity as the Sun. (Note that this is not a frequency plot of the likelihood of liquids *in our Solar System,* as it does not assume that there are planets in orbits identical to those of our planets. Rather, it is what we might expect of an "average" solar-type-system, should such a thing exist.) Liquid ethane
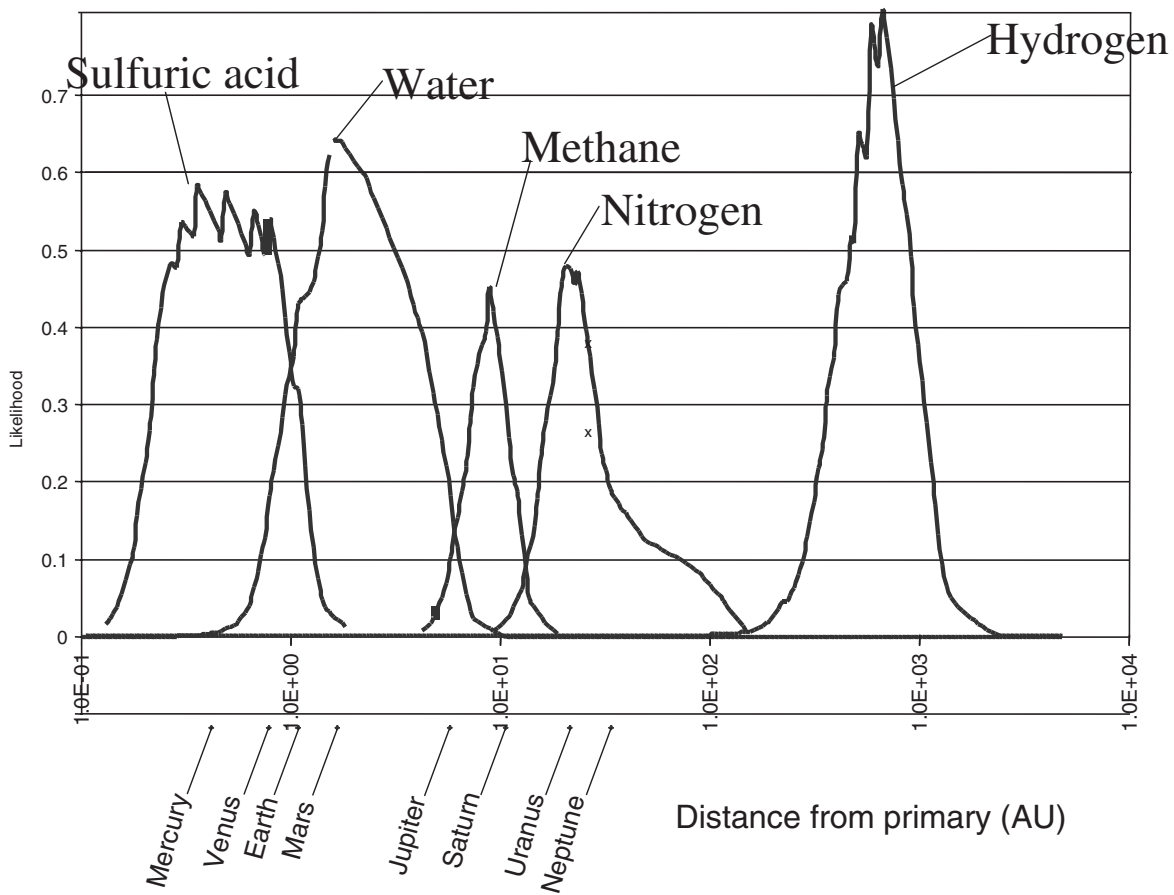
FIG. 5. **Probability distribution for occurrence of different liquids as a function of distance from a Sun-like star.** The *x*-axis represents distance, and the *y*-axis represents probability (summed probability of surface and subsurface liquid). Note that the *x*-axis is a log axis, so that area in this graph is not linearly proportional to probability in Tables 3 and 4.

and methane appear as highly probable around the orbit of Saturn and Uranus. Liquid nitrogen is predicted to be possible, and not unlikely, around the orbits of Uranus and Neptune, which is in line with current thinking that liquid nitrogen may be present at least occasionally below the surface of Triton (Soderblom *et al.,* 1990).

Thus this simple model makes predictions that are broadly in line with what is observed in our Solar System, with respect to the *relative* frequency of liquids, and even gives some correlation with the observed orbital distribution of bodies on which liquids are found.

LIQUIDS IN OTHER SOLAR SYSTEMS

It is now evident that planetary systems are relatively common (Schneider, 2003), although their dynamics may differ from ours. If "hot giant planet" systems are common, this means that liquid water may be less common than our Solar System suggests. The presence of a giant planet near the star effectively prevents the formation of Earth-sized planets in the water zone. Even 47 Ursae Majoris, which has two giant planets in nearly circular orbits, with the innermost giant planet 2.1 AU from its primary—a close analogue of our Solar System—is unlikely to have a planet in the HZ. The orbit of a planet in the HZ is stable (Cunz *et al.,* 2003), but the presence of the giant makes its formation unlikely (Laughlin *et al.,* 2002). The only way these systems could have water-bearing planets is if they were the moons of the giant worlds (Williams *et al.,* 1997).

Hot giant planet systems may represent systems formed from protoplanetary clouds with high metallicity, in which case systems formed from clouds of intermediate metallicity will be more like our Solar System (Charles and Lineweaver, 2001).

As we do not know the "average" distribution of planets around an "average" star, the assumption can be made that our planetary system is typical with respect to the distribution of nongiant planets. From this assumption it is possible to estimate the global probability of liquid around other stars by performing calculations similar to those shown in Figs. 4 and 5 for stars of different luminosity, with scaled families of planets around them following an inverse power law on size and a $d^{-1.5}$ proportionality for the mass of the "surface" layers of bodies with respect to distance from the primary.

There is an effective outer limit to bodies of relevance to life at 2,000 AU (solar system measures), corresponding to the inner section of the Kuiper belt. Beyond this the Oort/Opik cometary "cloud" is significantly perturbed by galactic tides, passing molecular clouds, and is penetrated by passing stars on a time scale of around 500 My. Objects in this zone can be expected to suffer substantial orbital change on a paleontological time scale due to gravitational interactions (Napier and Clube, 1997). In practice, this does not affect our calculations as stellar heating is insufficient to melt even hydrogen at such extreme distances.

The calculations illustrated in Figs. 4 and 5 were scaled for the observed frequency distribution of stars in the stellar neighborhood (Fig. 6), ← F6
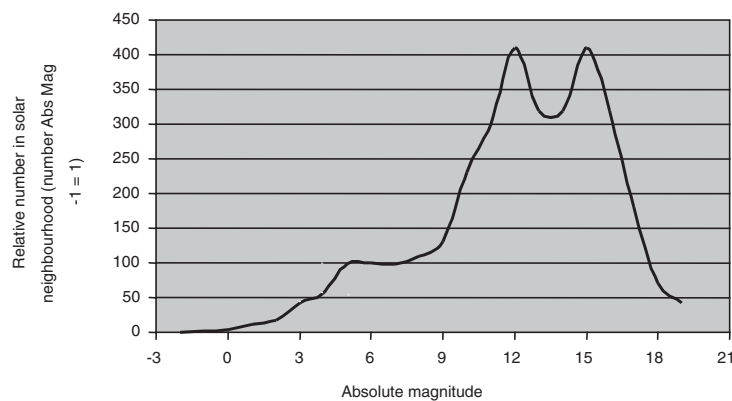
FIG. 6. **The frequency distribution of stars in the Sun's neighborbood.** Data derived from the Gliese survey (Jahreiß and Gliese, 1993), with additional data from the Hipparcos database (http://astro.estec.esa.nl/hipparcos). Mass/luminosity relationships for lower mass stars are taken from Zuckerman (2000).

TABLE 3. RELATIVE PROBABILITIES OF LIQUIDS ON
BODIES >1,000 KM IN DIAMETER AROUND
ANY STAR IN OUR STELLAR NEIGHBORHOOD

Liquid	Relative probability
Ammonia	0.25
Argon	1.56
Carbon disulfide	1.33
Ethane	1.25
Hydrazine	0.26
Hydrogen	4.53
Hydrogen cyanide	0.14
Hydrogen sulfide	1.31
Methane	0.62
Neon	2.44
Nitrogen	1.96
Nitric (II) oxide	1.48
Sulfuric acid	0.42
Water	1

Given are values for assumed pressures of 1, 0.333, and 0.1 atmosphere. Most volatiles sublime at 0.1 atmosphere pressure, and so the probability of an ocean is 0.

their different luminosity, mass (directly related to luminosity for main sequence stars), and hence presumed mass of solar disc and of the gravitationally bound segment of the Kuiper belt.

This calculation is done for stars of less than 3 times the mass of the Sun [which are likely to have main sequence lifetimes of >500 My (Franck *et al.,* 2000)]. The "methane dwarf" class of brown dwarfs (≤1,500 K surface temperature, spectral classification L6 and cooler) are not included, as they do not sustain sufficient internal fusion to maintain stable conditions on any body orbiting them over geological time scales (Basri, 2000). White dwarfs are also not included here.

Tables 3 and 4 illustrate the result. On the basis of their physical properties, many chemicals (some chemically implausible, some cosmically unlikely) have a significant relative probability of being present as bulk liquids on planet-sized bodies in our stellar neighborhood. Indeed, the only obvious liq-

uid that is missing from the list is helium. This is because, with a boiling point of 4.2 K (^{4}He) at 1 atmosphere pressure, there is no reasonable set of conditions where a planet's surface is likely to be cold enough to maintain a temperature of <4.2 K *and* where the planet is massive enough to maintain a significant atmosphere. This is in part because the cosmic microwave background radiation has a "temperature" of 2.7 K, and so this is the minimum temperature that can be attained anywhere without special cooling.

The apparent likelihood of liquid hydrogen and neon is unexpectedly high. However, this is an extrapolation. The surface temperature of such cold worlds as predicted here is also most likely incorrect, as heating from cosmic rays and internal radioactivity will be a significant part of their heat budget. Thus the frequency calculations for liquid hydrogen or neon must be regarded as even more speculative than those for other liquids. The uncertainties in all aspects of this calculation as applied to hydrogen are too large to consider liquid hydrogen further in this paper.

Table 3 assumes that liquids occur essentially pure. Earth's water (and Triton's liquid nitrogen) may be atypical in this respect. The water/ammonia oceans of the galilean moons, Titan's presumed methane/ethane lakes, and the sulfuric acid clouds of Venus are all mixtures. Table 4 summarizes probabilities for the most likely mixtures, based on the calculations from Table 3 and the cosmic abundances from Table 1. Figure 7 shows the distance distribution that this implies for bodies with methane/ethane/nitrogen oceans, in comparison with "pure" liquid nitrogen. Other mixtures are likely: While surface liquid on Titan is likely to be a methane/ethane mixture, this will dissolve substantial amounts of nitrogen from the atmosphere, altering its properties significantly (Thompson *et al.,* 1992; Lorenz and Lunine, 2002). Thus the properties listed in Table 3, and solu-

TABLE 4. RELATIVE PROBABILITIES OF MIXED LIQUID ON BODIES >1,000 KM IN
DIAMETER AROUND ANY STAR IN OUR STELLAR NEIGHBORHOOD

Liquid	Relative frequency	Assumed melting point (K)	Assumed boiling point (K)	Assumed density
Water/ammonia	1	240	325	900
Methane/ethane	1.4	90	180	475
Silane/phosphine	1.46	100	184	700

The probabilities depend on the density of the liquid and its melting and boiling points—assumed values are given.
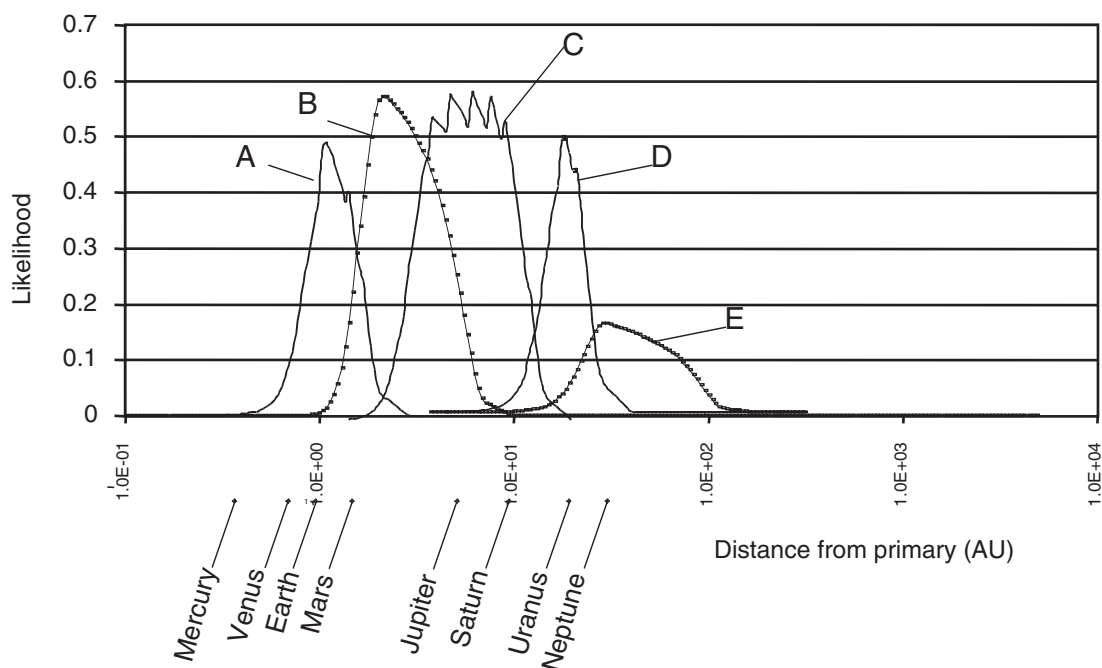
FIG. 7. Expected distance distribution for water/ammonia, methane/ethane, and nitrogen "oceans" in our Solar System: curve A, water/ammonia surface lakes; curve B, water/ammonia subsurface; curve C, methane/ethane surface lakes; curve D, surface nitrogen; and curve E, subsurface nitrogen.

bility properties discussed below for pure nitrogen, must only be taken as rough approximation of planetary environments. The details of when it rains on Titan will depend, as on Earth, on the specifics of planetary physics, atmospheric and "ocean" chemistry, and local chemistry and physical properties.

BIOCHEMISTRY IN "EXOTIC" LIQUIDS

Terrestrial biochemistry in liquids other than (clean) water

If life is possible in water/ammonia, methane/ethane, or nitrogen, it must have different biochemistry from Earth's life. Clearly terrestrial biochemistry could not function in non-aqueous environments. Most intermediary metabolites will not be soluble in cryogenic solvents, and many will be unstable at the high pH of the internal oceans of the galilean moons (or the low pH of the acid clouds of Venus). DNA and RNA would be hydrolyzed rapidly at the very high pH of Europa or Callisto (RNA in seconds), and even if the low temperature protected them from chemical attack the pH would denature them. Alkaline

conditions are used *in vivo* and in industry to accelerate breakdown of lipids and fats—alkaline hydrolysis of fatty acid esters of glycerol (the base component of storage lipids and many cell membranes) has been used for centuries to generate the free acids for use as surfactants, under the name of saponification.

So terrestrial biochemistry could not be exactly replicated in a galilean environment, nor in the more exotic liquids of Titan or Triton. Could an essentially terrestrial chemistry adapt to those conditions? This has been the subject of some speculation, often based on the idea that, even if life did not originate, for example, on Europa, it could have been transferred from Earth and subsequently flourish there.

Terrestrial organisms have proven to be enormously adaptable, essentially surviving anywhere where water is liquid. However, the conditions inside Europa would challenge even this adaptability. While a terrestrial organism that could survive at such high pH is not impossible, we must note that the maximum pH range of even the extremophile terrestrial organisms is 0–10 pH units (see, for example, Yeo *et al.,* 1998; Bond *et al.,* 2000; Edwards *et al.,* 2000; Takai *et al.,* 2001). Most pH-extremophiles survive by main-

taining a more neutral pH inside their cells than outside (see, *e.g.,* von de Vossenberg *et al.,* 1998). Tolerance of very low pH is greater than very high pH (7 pH units below neutrality as opposed to 3 units above neutrality), primarily because all organisms have potent mechanisms for pumping protons *out* of cells. So, while terrestrial life can survive at "unusual" pH, it does so as a specific adaptation.

The pH of the internal ocean of Europa is probably >11. [It is not trivial to estimate what the pH of a solution of 15% ammonia is at 240 K when other materials and minerals are present, but as a 1.7% ammonia (1 N solution) has a pH of 11.6 (Budavari *et al.,* 1996) it is unlikely that 33% ammonia will have a substantially lower pH.] No terrestrial organism could survive this, let alone flourish. This is only in part because such extreme conditions are rare on Earth. It is equally because the energy needed to maintain a pocket of "Earth-normal" conditions in which terrestrial DNA, RNA, lipid, and metabolites could survive could be greater than the total energy available to the cell.

Terrestrial life in liquid methane or nitrogen seems even less likely (although it is not impossible that some terrestrial enzymes could work in liquid nitrogen, a point currently undergoing investigation).

So the idea that a biochemistry that was chemically very similar to Earth's could flourish in all the exotic liquids, which my previous calculations suggest, may be cosmically common seems pretty unlikely. If terrestrial biochemistry is all that exists, then we are back with the argument that only oceans of largely "clean" water could be abodes for life.

BIOCHEMISTRY IN THE GALILEAN SATELLITES

There has been substantial discussion of the potential of the water/ammonia "internal oceans" of the galilean satellites to support life. These oceans are expected to be 30%–40% ammonia by weight, and hence extremely basic.

Raulin *et al.* (1995) suggested that an ammoniated version of terrestrial biochemistry, with most oxygen atoms replaced by NH, would be stable and suited to the highly reducing conditions. Though they only sketch the idea, it is extensible in many ways to start to build a realistic, alternative biochemistry.

Thus phosphate—an essential component of energy metabolism in our chemistry—can be replaced by ammonophosphate analogues that are stable in water and ammonia, can lose protons to hold multiple negative charges, and can form stable amide-like bonds with carbon molecules (Aspinall *et al.,* 2002). The central energy transactions of most terrestrial processes use "high-energy" phosphate bonds, which this alternative chemistry could provide.

Terrestrial biochemistry transforms metabolic energy via what Mitchell (1976) called "proticity"—the accumulation of differences in proton concentration and the flow of protons—as a fundamental energy generation mechanism, coupled to phosphate energetics via the membrane ATPase complex. Ammonochemistry can also use protons in this way, as protons are hydrated in solutions with relatively low water activity almost as well as in pure water. However, this need not be the only energy "currency" of an ammonobiochemistry. Free electrons are highly unstable in water, rapidly forming hydroxyl ions and hydrogen. However, they are stable in liquid ammonia. Alkali metals can dissolve in pure liquid ammonia to form metal$^+$ e$^-$ solutions that can be stable for months, with the electrons remaining as a genuine solution, being highly mobile, and hence allowing the solution to conduct (Audrieth and Kleinberg, 1953). It is unlikely that electrons could be as stable in the oceans of Europa as in the laboratory on Earth, as the chemistry of solvated electrons depends on the ammonia being dry—Freed and Thode (1939) offered a vivid description of how dry it has to be at terrestrial temperatures to form stable sodium solutions. But at 240 K the stability is enhanced, and we might consider that "electricity" rather than "proticity" is a reasonable energy transaction for ammono-life. This would make searching for the characteristic intermediates of terrestrial oxidative phosphorylation as a signature of life (Crawford *et al.,* 2001) rather moot.

This, then, would be an environment where a CHON-based but non-terrestrial biochemistry would be structurally stable. Is there an energy source that would allow such a biochemistry to function?

Cryogenic environments could be compatible with the energetics of life

It has been argued that the amount of free energy available under conditions where methane,

ethane, nitrogen, or (more speculatively) hydrogen or neon is liquid would be too low to allow life to develop.

Light is a valuable source of "free" energy for living processes, which can be processed locally, *i.e.*, within one molecule. Photosynthesis on Earth is relatively inefficient: In the most energy-rich environments (tropical daytime) photorespiration causes loss of a substantial fraction of the energy captured, and requires special biochemistry for plants to accumulate a net balance of sugars at all. In dim light terrestrial photosynthesis is more efficient. Photosynthesis on Titan is not implausible. Even if the hazy atmosphere absorbs 99% of the light from the Sun, the energy flux in the visible is still around 1 W/m^2. This is sufficient to provide a photosynthetic energy source for even terrestrial organisms (Moe and Sullivan, 1985), and other energy sources may be available as well.

In addition, the relatively small amount of visible light falling on bodies in such an environment can be used more efficiently than the same light falling on Earth (Sagan, 1973), because of the lower ambient temperature. With a greater temperature difference between energy source (the Sun) and energy sink (Titan), higher thermodynamic efficiency is possible. Energy from near-infrared radiation is also available to capture as chemical free energy, which it is not under terrestrial temperatures, meaning that for biochemistry operating at cometary temperatures, the whole inner Solar System—planets, asteroids, zodiacal dust, *etc.*—would be a source of photosynthetic power (Sagan, 1973).

Life in subsurface oceans on the galilean moons is unlikely to be able to use photosynthetic energy. Light itself will only penetrate a few tens of meters of ice, and photolysis products such as hydrogen peroxide, superoxides, and oxygen generated at the surface will only be subducted to the interior in sporadic cataclysmic events or by extremely slow "tectonic" processes. Other energy sources would be needed for life in such circumstances.

Chemolithotrophy—the use of the chemical potential of environmental minerals to drive biochemistry—is certainly likely to be available in any liquid environment. Fortes (2000) estimated that the total energy available from chemolithotrophy within Titan is $\sim5 \times 10^8$ W (based on a radiogenic heat flow of $4–5 \times 10^{11}$ W, of which 1% is translated into volcanic activity at the

"ocean" floor, of which 10% is available as chemical energy to a biosphere), which would allow a microbial yield of $\sim1.5 \times 10^{13}$ g/year of new microbial biomass, or $\sim6 \times 10^{22}$ g of accumulated biomass over 4 Ga. This makes many assumptions, and equates the total cumulative mass of living things since the origin of the Solar System with the "biosphere" (although this is not unreasonable, as the aim of many such calculations is to see whether we can *detect* living processes, current or past, rather than whether they are still going on).

Heat flow is not the only determinant of the chemical power available for biochemistry. As reviewed by Gaidos *et al.* (1999), much of the energy available for terrestrial chemolithotrophy derives from processes linked with the tectonic recirculation of the crust. Without this recirculation, upper crustal chemistry would fall into redox equilibrium with the ocean, and cease to be a source of energy for life. This is not true of all chemical energy sources: Iron can act as an oxidant in appropriate conditions, in chemistry that is not dependent on plate tectonics. However, this again points to a different biochemistry from any found on Earth.

Other energy sources, such as the radiation generated in giant planet magnetospheres (Chyba, 2000), might increase this amount substantially, although many such calculations assume the generation of energy-rich chemicals on the surface and their subsequent turnover to the interior. Recent modeling suggests that such exchange may be very limited, if it happens at all (Shenk, 2002). But with at least two energy sources available for biochemistry (and photosynthesis for surface life on Titan), conceiving of the galilean moons as a home for a non-terrestrial biochemistry is not unreasonable.

Life's origination in cryogenic environments

Russell and Hall (1997) provided an eloquent description of how life's origination on Earth was not only possible, but almost inevitable, and that our biochemistry is a result of the chemical processes that drove its origin. A key aspect is the development of a redox front between the reduced mantle of the early Earth and the atmosphere and ocean, which would be oxidized by solar ultraviolet lysis of water and ammonia. Analogous atmospheric chemistry is known to happen in the atmospheres of Titan and Triton,

where ultraviolet photolysis of methane generates higher hydrocarbons, alkenes, and alkynes. The redox chemistry at the interface between this atmosphere and the likely solid rock substrate of the galilean moons will not be the same as Earth's, and it is not clear whether, during the early moon's history, an ammonia/water ocean would be oxidized or reduced. But it would be one or the other, and so provide, either at its surface or its base, an energy and pH interface that could be coupled to the emergence of complex, self-sustaining chemistry.

Can chemistry happen fast enough in such cold environments for life to start, and to be maintained? Reaction rates for the initiation of life will be limiting—simple reactions such as polymerization of HCN, believed to be important in some scenarios of terrestrial biogenesis, happen on time scales of the same order of magnitude as the age of the Solar System at Titan's surface temperature (Raulin *et al.*, 1995). However, catalysis—even very weak general acid/base catalysis—can speed this up dramatically. If such chemistry was possible, then selection of chemistry that was self-catalyzing would ensure the development of more efficient catalysts. This is the route by which peptides and proteins are created in Russell's scenario.

Terrestrial enzymes can catalyze reactions extremely efficiently, such that some apparently abolish the activation energy entirely so that the enzyme-catalyzed reaction rate approaches the diffusion-limited maximum possible rate (see, *e.g.*, Forman and Fridovich, 1973; Jez *et al.*, 2000; Oh *et al.*, 2000; reviewed in Stroppolo *et al.*, 2001), as do other processes such as protein folding in some circumstances (see, *e.g.*, Bashford *et al.*, 1988; Karplus and Weaver, 1994; Hagen *et al.*, 1996) as well as the more obviously diffusional protein:protein binding interactions. Diffusion-lim-

ited chemistry is not unfeasibly slow in liquid ethane, nitrogen, or hydrogen, because values of the diffusion-limited reaction rate constant k_x are linearly proportional to temperature (T) and inversely proportional to viscosity (η) (Hague, 1971) as illustrated in Table 5.

Terrestrial enzymes have been shown to be catalytically active down to temperatures of $-100°C$ (170 K), using a variety of mixed polar solvents; below 170 K these solvents become so viscous that diffusion limits effectively stop chemistry from happening, a limit that would not apply to the liquids in Table 5.

Thus the origin of life in such circumstances would be slower and more dependent on the presence of endogenous catalysts. However, maintenance of life after that would be no harder to imagine than maintenance on Earth. It is notable that the "rate of living" of terrestrial organisms is not usually dependent on ambient temperature; the natural rate of growth of bacteria in the Antarctic seas and in black smoker volcanic vents is determined by competition for nutrients, not on how fast their chemistry can run.

Life and the chemistry of water

Traditionally, it has been assumed that liquids other than water are fundamentally unsuitable for the complex catalysis that is essential for biochemistry; the hydrogen bonding potential and high dielectric constant of water (or water/ammonia) were believed to be essential for enzymes to work. However, this is not so. It is certainly true that terrestrial biochemistry relies on an aqueous environment (Saenger, 1987); it would be odd if, having evolved in that environment, it did not use it. However, even terrestrial enzymology can operate in a variety of non-aqueous solvents, and even completely apolar solvents

TABLE 5. COMPARATIVE RATES OF DIFFUSION-LIMITED REACTION RATES IN DIFFERENT LIQUIDS AT THEIR FREEZING POINTS

Liquid	Freezing point (K)	Viscosity at freezing point ($M\eta$)	Relative diffusion-limited reaction rate
Water	273.16	317	1
Water/ammonia[a]	200	200	0.86
Methane	90.7	102.8	0.76
Nitrogen	63.2	152	0.35
Hydrogen	13.96	13.2	0.91

Physical data are from Arkharov *et al.* (1982).
[a]Values are speculative, as the properties of the mixture depend on the proportions of the components.

such as benzene, diphenyl ether, or straight-chain hydrocarbons from heptane through hexadecane (Carrea *et al.,* 1995; Cabral, 2001; Klibanov, 2001), demonstrating that complex, catalytic chemistry can be built in completely anhydrous, apolar solvent systems. Around 20% of the human gene complement is integral membrane proteins that probably require the relatively apolar environment of the cell membrane to function at all (Lander *et al.,* 2001). There is no reason to suppose that other macromolecular chemistry could not be similarly flexible.

AN ILLUSTRATION—SILICON LIFE

Why silicon?

One problem with considering life in extremely cold environments, which is not addressed above, is that nearly all compounds dissolve very poorly in liquids at cryogenic temperatures. One of the advantages of water as a solvent is that it can dissolve a wide variety of small molecules at high concentration—selective condensation of these into polymers provides the basis for life. Apolar solvents such as hydrocarbons also can dissolve many uncharged molecules, but solubility declines with temperature, and one might expect that at 70 K almost nothing will dissolve in any solvent. A series of studies by Dabrowska and co-workers indicated that this is so (Dabrowska, 1984, 1991, 1996; Szczepaniec-Cieciak and Krzeczkowska, 1998; Magdalena *et al.,* 2001)—solubility in liquid nitrogen (presumed to be an apolar solvent) is generally low, and declines logarithmically with increasing molecular

weight. Thus methane, acetylene, and other atmospheric components are likely to be soluble in any liquid methane/ethane present on Titan or liquid nitrogen present on Triton (alkynes have chemical similarities with dinitrogen, but this does not appear to bias their solubility unduly), but the more complex molecules essential for life could be extremely insoluble.

Possible exceptions are the silanols, the silicon-containing analogues of alcohols (Lickiss, 1995, 2001). Silanols have surprising solubility properties, with diisobutylsilane diol being soluble in water and hexane, for example (P. Lickiss, personal communication), and some hindered silane triols are similarly soluble in a variety of liquids (Murugavel *et al.,* 1995). Their solubility is in part mediated by forming molecular assemblages in solution, such as the complexes formed by diisopropylsilane diol and a cyclic tetrahydroxy silicone (Unno *et al.,* 2000), and the discoic liquid crystals formed by diisobutyltetrahydroxysiloxane (Compound I in Fig. 8) (Bunning *et al.,* 1982), which suggests that its unusual solubility properties are the result of unusual solution processes and, hence, thermodynamics.

Could this extend to cryogenic liquids such as liquid methane or nitrogen? Preliminary measurements of the solubility of a small number of silanols in liquid nitrogen suggest that it may (Fig. 8). This is, of course, neither a definitive measurement of silanol solubility in liquid nitrogen nor a demonstration that other molecules are not equally soluble. However, if these measurements are upheld by future experimentation, they suggest that silanols could dissolve in liquid nitrogen at concentrations sufficient to be the precursors of life. And unlike other molecules that
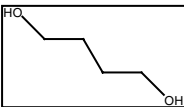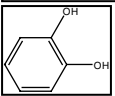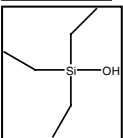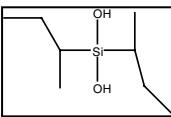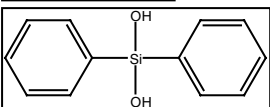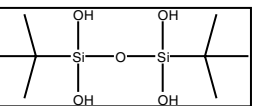
FIG. 8. Solubility of selected compounds in boiling liquid nitrogen. Diamonds represent data generated by Dabrowska (1984, 1991, 1996), Szczepaniec-Cieciak and Krzeczkowska (1998), and Magdalena *et al.* (2001). Squares represent data generated by the author. Bars shown for materials that have higher boiling points than water − 2 SD error limits. Triangles represent data generated by the author for compounds that have similar boiling points to water. In the experimental protocol, solids and liquids were added to 100–200 ml of boiling liquid nitrogen and stirred for 15–20 min. Potential solutions were filtered through unsupported cellulose filter paper into preweighed new glass tubes, where the nitrogen was allowed to boil off. For materials solid at room temperature, the tubes were warmed to 40°C for 10 min and then 50°C for 20 min to drive off condensed moisture, and then allowed to re-equilibrate with atmospheric moisture at room temperature. The amount of material was determined by three weight measurements before adding nitrogen and three after for each tube. Each measurement represents the average of five tubes, normalized to blank tubes with no solute. For materials liquid at room temperature, essentially the same process was followed, but tubes were only heated to 30°C for 1 min after evaporation of nitrogen, and any remaining condensation was removed manually. Measurements for volatiles are thus inherently more unreliable than measurements for solids, and have not been assigned error bars. Values for tetrahydroxydisiloxane have been replicated using both protocols. BP, boiling point; DMF, dimethylformamide; DMSO, dimethyl sulfoxide.
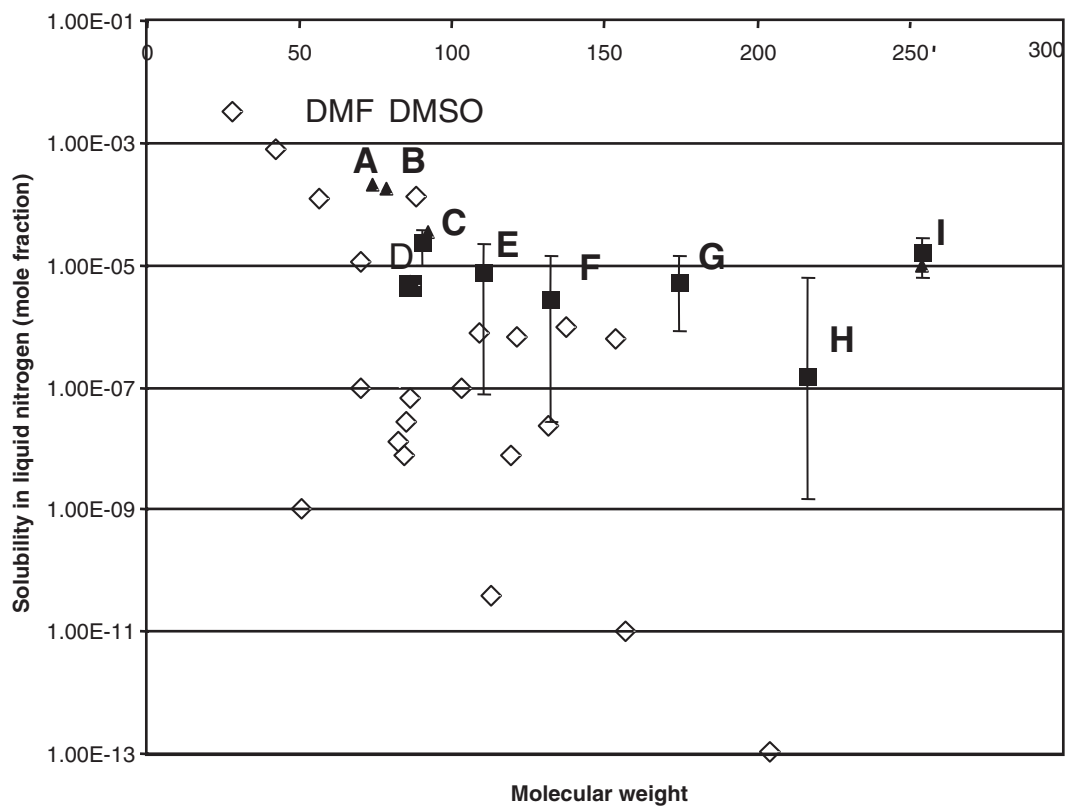
are soluble in liquid nitrogen, silanols are relatively large, complex, and capable of rapid condensation chemistry to yield complex polymers.

A second reason for "why silicon" is that silicon compounds are often more chemically reactive than analogous carbon compounds. This is a liability for terrestrial biochemistry, but for metabolism in colder environments the stability of the carbon-heteroatom bond to thermal chemistry is not needed, and greater lability means that less catalytic efficiency is needed to allow some chemistry to happen.

The greater reactivity of silicon compounds derives from three features of its chemistry (Brook, 2000). First, it is more electropositive, and so most bonds with non-metals are more strongly polarized and thus more liable to electrophilic and nucleophilic attack (the Si-O bond is particularly labile in this respect). Second, some common Si-X bonds are weaker than equivalent C-X bonds, and so require less thermal energy to break for any given reaction mechanism. Thirdly, silicon has energetically accessible *d*-orbitals, which enables higher coordination numbers for silicon not energetically accessible to carbon. These enable low-energy reaction pathways for some reactions, notably hydrolysis and ammonolysis, which carbon can only attain via a free radical, ion, or unstable "transition state" intermediate. For example, silicon tetrachloride is hydrolyzed almost instantly in water, where carbon tetrachloride, which is also thermodynamically unstable to hydrolysis, is stable for years in the presence of water. Reaction of both silane and methane with oxygen is clearly exothermic. Methane, however, may be mixed with oxygen at 200°C without reacting, whereas silane spontaneously combusts in air at 0°C. This is an advantage in ultracold conditions, where a more rapid spontaneous rate of reaction could overcome the non-catalyzed barrier to biochemistry discussed above.

Thus from a kinetic standpoint silicon chemistry, and specifically the chemistry of the silanols, could be a more attractive candidate than carbon for the base chemistry of "life" in extremely cold liquids (specifically in liquid nitrogen, as this is the liquid in which solubility measurements have been carried out, although liquid methane/ethane would be expected to have similar properties). But can silicon chemistry fulfill the structural requirements of a biochemistry?

Why not silicon?

Pace (2001) followed convention in dismissing silicon as the core element in another potential biochemistry because (1) silicon forms stable bonds with only a very limited number of other elements (unlike carbon), (2) silicon polymers are monotonous, (3) silicon cannot form stable double and triple bonds, which limits its ability to capture and delocalize electronic energy, and (4) silicon chemistry is not stable in an aqueous environment.

Chemical "monotony" is a side issue. Silicon can form stable polymers with an Si-Si (silanes), Si-C, or Si-O (silicones) "backbone." All are used in an industrial context, but silicones are by far the most common by mass, and probably by chemical diversity. Clearly, most of these polymers are monotonous. However, so are most industrial carbon polymers. Many biological molecules such as DNA were originally thought to be monotonous polymers, but we now understand that by varying the monomer type and sequence, enormous flexibility can be generated. Monotony is necessary for function in an industrial plastic, but is not required by the chemistry: There is no reason why a high-molecular-weight silane or siloxane should not have a highly diverse, highly structured set of side chains, analogous to proteins, nucleic acids, or carbohydrates. Block copolymers, made in large amounts industrially, are a step in the direction of non-monotonous silicon-containing polymers.

Silicon's supposed limited chemistry is also largely a myth, believed true in the 1960s when xenobiology was being established but now outmoded by further chemical research. Silicon forms stable covalent bonds with itself, carbon, germanium, nitrogen, phosphorus, oxygen, sulfur, and the halogens, as well as with many metals (Walsh, 1981; Muller *et al.,* 1998). Silicon can form stable tetra-, penta-, and hexa-coordinate compounds with N, C, and O bonds, with or without overall charge on the molecule. This demonstrates as great a flexibility of coordination as carbon can command. There is an immense diversity of structures that can and have been assembled from such chemistry, including ring systems (Hengge and Janoschek, 1995), highly polarized systems, systems where rapid, reversible chemistry occurs (Sharma and Pannell, 1995), where hydrogen bonding stabilization and powerful steric effects modulate the properties of

the molecule. Ring structures that are direct analogues of sugars are well known in silicone chemistry. Cage systems such as the silsesquioxanes provide for complex "core" structures, which may be decorated with other groups that are orientated precisely in space (Harrison, 1997; Feher, 2000). The siloxenes—polymeric structures formed from calcium silicide and of the general formula $Si_6H_6O_3$—are made of cyclosilane rings with attached -OH groups (DettlaffWeglikowska *et al.,* 1997), whose monomeric units have an obvious structural analogy with the hexose carbohydrates and whose linked ring structures have structural and electronic similarities to the porphyrin units of heme and chlorophyll.

Energy metabolism is a particular concern here. Many critical biological processes capture and transform electronic energy as chemical energy. Carbon atoms with sp^2 hybridization are important in this because of their ability to delocalize charge over a large structure. Silicon's sp^2 structure is energetically disfavored over sp^3. However, sp^3 silicon can delocalize electrons via s-orbital overlap to a degree that carbon cannot, to the extent that polysilanes (the silicon equivalent of polythenes) are semiconducting (Tokito and Okazaki, 1998; West, 2001). Electron delocalization could therefore occur readily in appropriate silicon compounds, and light-activated electronic effects (the base, in our biochemistry, of photosynthesis) also occur (Fujino, 1987). "Layered silanes" synthesized from calcium silicide, of the general formula $(SiH)_n$ have a layered structure very similar to graphite, and are electroluminescent (Dahn *et al.,* 1993).

Not all redox biochemistry relies on sp^2 carbon for electron delocalization: The iron sulfur redox enzymes delocalize single electrons over a cubic lattice of iron and sulfur atoms, where the function of the surrounding protein is to protect those clusters from the surrounding milieu, not to confer carbon-mediated electronic properties (Cammack, 1992). There is no reason to suppose that silicon chemistry could not find different "solutions" to the same problem, using silicon's ability to change from IV through V to VI coordination, to complex metal ions in silicates, *etc.*

In terms of chemical flexibility and functionality, therefore, silicon can match carbon, albeit not using the same chemistry to achieve the same goal. The key is to look for functional analogues, rather than structural analogues of known chemistry.

Pace (2001), however, dismissed silicon as a key element in a biochemistry because of the water/ammonia lability of much of the silicon chemistry touched on above. Clearly direct replacement of carbon with silicon in terrestrial biochemicals would produce molecules that would be almost immediately hydrolyzed in water, and, in the case of many silanes and siloxenes, are spontaneously inflammable at 0°C. Of course, much of terrestrial biochemistry is unstable to "dirty" water as well, as anyone who has tried to isolate RNA can attest, and some is so water-sensitive that it cannot be isolated outside its native biological context. Examples include allene oxide intermediates in lipid oxidation (Brash *et al.,* 1988) and the catalytic core of enzymes such as nitrogenase (Orme-Johnson, 1985). But in general C-X bonds are more stable to aqueous attack than Si-X ones. For example, C-H bonds are stable to hydrolysis under conditions more extreme than those experienced by any living system, while Si-H bonds are readily hydrolyzed in a matter of a few hours to Si-OH under mammalian physiological conditions (see, *e.g.,* Tacke and Linoh, 1989). If silicon were to be used as the basis of terrestrial life, that life might have to restrict its chemistry substantially or use an unreasonable amount of energy to protect its core molecules from degradation.

As a barrier to using silicon for living systems, however, this is only a problem if we assume that strongly protonating solvents (water, ammonia, hydrogen sulfide, and sulfuric acid in a cosmological context) are the solvent base. Oceans of cold, non-protonating fluids, and specifically liquid nitrogen, would be more favorable for silicon life. In such environments, the inherently greater reactivity of silicon-based chemicals could be an advantage, enabling "living" processes to occur at greater than geological speeds at the relatively lower temperatures where such fluids are stable. Such fluids could also include liquid methane, ethane, neon, or argon.

In terrestrial biochemistry a common energy currency is "proticity" (Mitchell, 1976), the generation of concentration gradients of solvated protons and coupling of the dissipation of those gradients to chemical synthesis. The protic gradient has been coupled primarily to the synthesis of polyphosphates, which are then used to synthesize a host of other special carbon chemistries that have been used by terrestrial biochemistry, reflecting the need for unstable as well

as stable chemistry. Proticity is far from the only type of energy currency in a cell ("substrate-level" phosphorylation generates all of a fermenting yeast's ATP, without recourse to the electron transport chain), but is uniquely suitable as an energy currency in an aqueous environment, as solvated protons are stable and highly mobile (Gierer and Wirtz, 1949), and the chemical potential in a coupled concentration and electric field gradient can be coupled readily to many processes.

Protons are not stable in most liquids, and so another energy currency is needed if we are to avoid water as a solvent. Silicon chemistry can oblige. Double-bonded silicon systems are known and can be isolated. However, they are relatively unstable compared with carbon ones (West, 2002). The cold-silicon functional equivalent of ATP might be the silicon structural analogue of ethene. The "solution" that evolution has found to allow highly unstable biochemical systems to exist in carbon chemistry is to protect them in the cores of complex macromolecular assemblies; if silicon double bond systems were valuable, they could also be generated using similar mechanisms. Interestingly, an early way to generate silicon-carbon double bonds was by ultraviolet photolysis on an ultracold matrix (West, 2002), not unlike the surface of Triton or Pluto.

Another aspect of terrestrial bioenergetics is charge separation chemistry. Light energy is used to separate charge in water and generate oxygen and "reducing equivalents" (hydrogen associated with a carrier molecule). Charge is separated in oxidative phosphorylation to generate proton gradients much larger than single molecules. How can this charge redistribution occur in cryogenic, non-polar liquids? The simplest answer is that such charge separation occurs intramolecularly, as it does in the initial photon capture events in terrestrial photosynthesis. Polysilanes are photoconductors (Fujino, 1987) due to the ability of light to separate charge within the molecules. Charge separation in a protonating solvent is not the only way to capture photon energy in chemical form.

When discussing the structural specification for life above, the requirement for structural elements as unimportant in constraining the chemistry of life was dismissed. This may seem cavalier. However, many chemistries can form complex and flexible multimolecular and polymeric assemblies. The ability of silicon to form

stable silica and silicones is obvious, and silica is used even in terrestrial biochemistry as a structural element in diatoms and plants. Silane polyols (which solubility issues would suggest are potential components of a silicon-based biochemistry) can also form flexible, macromolecular assemblies in the form of sheets, strings, tubes, and other forms, similar to those formed by lipid bilayers in carbon biochemistry (Lickiss *et al.*, 1991, 1993; Unno *et al.*, 2000). The limited evidence available suggests that silicon chemistry could be as flexible as carbon chemistry when required to define the boundaries of non-rigid domains.

So the "builders specification" requirement for life does not rule out silicon as a base element in place of carbon; its chemical and structural flexibility *in non-aqueous environments* can provide analogues to all the functions of terrestrial biochemistry.

GENERATING SILICON COMPOUNDS IN NON-AQUEOUS ENVIRONMENTS

For silicon life to be plausible, there must be a mechanism for generating silicon compounds other than silica in a liquid environment. Non-aqueous liquids provide the environment in which silanes and silanols could be generated.

In our hypothetical nitrogen ocean, the thermodynamically disfavored reaction

$$SiO_2 + 2H_2 \rightarrow SiH_2(OH)_2$$
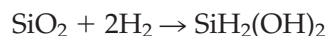
could occur if the volatile products were separated from the involatile starting materials and deposited in the liquid nitrogen phase by geysers before they decayed through back reaction with ices. Geysers could occur on any world with a surface liquid and a radioactively warmed rocky core [see Lorenz (2002) for the specific treatment of a potential geothermal mechanism for the geysers on Triton]. Hydrogen would be generated through the olivine/serpentine reaction:

$$Mg_nFe(II)_mSiO_4 + xH_2O \rightarrow Mg_aFe(II)_bSi_2O_5$$
$$+ Mg(OH)_2 + Fe_3O_4 + zH_2 \uparrow$$
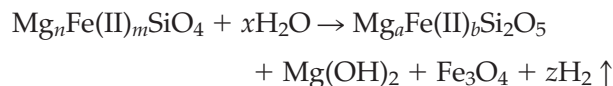
The reaction is almost certainly responsible for outgassed hydrogen in terrestrial ocean floor vents, and is also responsible for substantial re-

duction of carbon to methane and other organic molecules. It is presumed that the same chemistry resulted in the limited CO in Triton's crust today (Rothery, 1992).

This chemistry happens slowly and inefficiently in liquid water, and rather faster in gas phase (McCollom and Seewald, 2001), but is strongly catalyzed by awaruite (a natural nickel/iron alloy), which is abundant in meteorites today (Connolly *et al.,* 2001; Nakamura *et al.,* 2001; Campbell *et al.,* 2002) and likely to have been similarly abundant in the early Solar System.

Serpentization is usually written as a reaction releasing gaseous hydrogen as above, and this certainly occurs, but would be better described as a reaction that generates activated reducing equivalents ([H] in biochemical terminology), which can react in a number of ways. One of the most common oxidized species available in olivine is silicate, so we would expect the reaction

$$Si—O—Si \xrightarrow{2[H]} Si—O—H \ H—Si$$

$$\Delta G \sim -75 \ kJ/mol$$
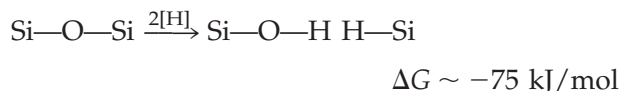
to occur. In an aqueous environment, the silane would be hydrolyzed back to the silanol, which would then condense to a silicate; silica would have played a catalytic role in the generation of molecular hydrogen. On Triton, however, any volatile silane or silanol could be delivered to the colder overlying regions of the planet before hydrolysis, resulting in a complex mix of partially reduced silanes and siloxanes. The same thermodynamics drive the commercial production of silicon metal and (volatile) CO_2, silicon carbide, and (volatile) CO from silica and carbon, and of (volatile) alkyl silicon chlorides from silicon in the "direct process" (Patai and Rappoport, 1989), through removal of the volatile product as it is formed. The local decrease in free energy is overcome by coupling to the macroscopic entropy increase in the system as a whole; the geyser would be slightly cooler than it would otherwise have been.

Once formed, silanols condense to siloxanes fairly readily. They do not immediately or inevitably condense. Even under terrestrial temperatures, many silanols and silane diols may be purchased as stable, pure chemicals. One silane triol is sold commercially, and dimethylsilanediol

can be readily prepared in the lab, though its propensity to condense to polydimethylsiloxane means that it is rarely sold pure. So silanols have the inherent potential to polymerize to complex macromolecules, with many Si-OH, Si-H, and other groups on them, but will not always do so.

ORGANOSILANES IN ASTRONOMICAL CONTEXT

The premise that reaction of water or ammonia, rock, and organics can generate organosilanes might seem too implausible to countenance no matter what the liquid system and physical arrangement. A common objection to the idea of silicon-based life is that silicon is effectively only found in silica; because of the strength of the silicon-oxygen bond and the abundance of oxygen, any silicon chemistry will inevitably be the chemistry of rocks. Although this is rather like saying that carbon is not a suitable basis for life because stoichiometry means that all the Universe's carbon will be methane, there is some truth to this argument; on Earth nearly all naturally occurring silicon chemistry is silicate chemistry. But this is terracentric thinking. In environments other than the thermodynamically equilibrium chemistry of the Earth's surface, silicon compounds other than silica are being found with increasing frequency.

The silicon-oxygen bond is a strong one, stronger than most silicon-atom bonds, although not so as to necessarily dominate silicon's chemistry (Table 6). The reason silica dominates the chemistry of silicon in the dense, mesothermal conditions of the Earth has as much to do with kinetics as thermodynamics. Silicon-containing chemicals are more reactive than their carbon counterparts, so any mixture of silicon- and oxygen-containing compounds in dense systems tends to equilibrate rapidly to a mixture that includes a substantial

TABLE 6.   BOND STRENGTHS OF SILICON AND CARBON BONDS IN SELECTED CONTEXTS (KJ/MOL)

X	C	Si
H	385	378
O	380–385	452–535
N	334	418

Data are for the strength of the bond [C or Si]-X. The exact bond energy depends on the substituents on the C or Si. Data are from Patai and Rappoport (1989).

proportion of SiO$_2$. As silica is far less reactive than nearly all other non-metal oxides and highly insoluble in water, the silicon is then trapped in this state. Silicone polymers are similarly protected—they contain Si-O-Si linkages that, in smaller molecules, would be readily hydrolyzed. But in a large hydrophobic polymer they are effectively stabilized by their kinetic inaccessibility.

However, to extrapolate from this to the Universe as a whole requires that the Universe is at chemical equilibrium, which is clearly not so. Three types of disequilibrium could be considered that could lead to silane synthesis, and subsequent silane or silanol chemistry. The first is environments where even stronger reductants than silicon are available to abstract oxygen from silica—the use of carbon at elevated temperatures to produce elemental silicon on an industrial scale shows that this is practical. The second is where macroscopic physical processes prevent chemical equilibrium from being established. The third is when the system has not had time to come to equilibrium.

All have occurred. Even in the highly oxidized environment of the Earth's crust, silicon carbide can be found as a *bona fide* mineral (Leung *et al.,* 1990), where it may be the result of metamorphic reprocessing of silicate under highly reducing conditions (Mathez *et al.,* 1995). Silicon carbide is also a widely distributed component of carbon-rich grains in carbonaceous chondrites (Bernatowicz *et al.,* 2003), as is silicon nitride (Pillinger, 1992). This is surprising because the isotope ratios in the same grains suggest that they were formed in oxygen-rich regions of supernova remnants, where SiC would be thermodynamically unlikely (Travaglio *et al.,* 1997), though the grains themselves contain very little oxygen (Hoppe *et al.,* 1996). How the silicon and the oxygen became separated is still unknown (Ebel and Grossman, 2001).

Silanes may also be common in some stellar environments. They would not be detected in stellar material analyzed under terrestrial conditions because the free oxygen in Earth's atmosphere would oxidize them. However, ice/silicate grains exposed to ultraviolet light (Blanco *et al.,* 1999) or to 1 MeV protons (Nuth and Moore, 1988) in a hydrogen atmosphere readily form silane groups, which have a characteristic 4.6 μm infrared absorbance. The Si-H groups in this material are air stable at room temperature for 72 h, suggesting that they are not part of SiH$_4$ molecules (which

are rapidly oxidized under these conditions). Their exact chemical nature has not yet been determined, but may be related to the layered silanes or siloxenes.

The same 4.6 μm absorbance has been observed in comets and the protostellar disc W33A (Blanco *et al.,* 1999). Silanes could be formed in these environments by the effects of stellar wind on reduced grains, or of condensation of shock-vaporized silicon atoms in hydrogen-rich domains. If the 4.6 μm absorbance in W33A is due primarily to silicon-hydrogen bonds (something that is still disputed), then it would suggest that between [1/250]1–4 and 1/40 of all infrared-visible silicon atoms in the entire protostellar disc have a hydrogen atom directly bonded to them. If this were all SiH$_4$ (and we can be reasonably sure that it is not), it would be a mass of silane of the same order of magnitude as the mass of the Moon.

Other silicon-containing molecules have been detected in circumstellar shells—the gas streaming outwards from evolved stars—including SiO, SiNC and SiCN, SiS, SiN, SiH$_4$, and SiC$_n$ ($n = 1$–4). A variety of other structures have been formed in supersonic jets under laboratory conditions that mimic circumstellar shells (McCarthy *et al.,* 2003).

Lastly, organosilicon compounds can be synthesized naturally even under terrestrial surface conditions. Zbik *et al.* (2000) have demonstrated the presence of organosilicon compounds in the irghizites (impact glasses) in the Zhamanshin meteorite impact crater. They show that ions characteristic of polyorganosiloxanes (C$_3$H$_9$Si, C$_5$H$_{15}$OSi$_2$, C$_7$H$_{15}$O$_2$Si$_3$, *etc.*) can be detected in the bubbles on the surface of the glasses. Similar ions are not found in the tektites from Australian strewn fields (impact glasses that are millions of years old). The amount of organosilane signature ions detected at the mouth of the crater was substantially less than that in the base. Zbik *et al.* (2000) postulated that these represent compounds that form during condensation of the hot vapor created by the impact and captured in the relatively dry environment of the glass particles. The parallel of this process and the proposed mechanism by which silanes and silanols could be deposited in cryogenic environments is clear.

So silicon chemistry has the flexibility and capacity to support a "biochemistry," and does occur frequently on an astronomical scale to produce a diversity of compounds. Could this lead

to the more complex, self-propagating chemistry that might initiate life?

A PATH TO SILICON LIFE?

None of this chemistry is relevant if there is no plausible path by which life based on silicon/silicone chemistry could arise. This is especially true at the low temperatures involved—the rate of reactions other than diffusion-limited reactions, and other than those energized by external events such as photolysis, will be geologically slow on the surface of moons such as Titan and Triton.

It would be presumptuous to argue from some general properties of silicon and cosmically observed silicon compounds to a specific biochemistry. The path illuminated by Russell and Hall (1997) suggests that critical elements of such biochemistry would be:

- a free energy source that the preferred biochemistry can use, which cannot be "short-circuited" by geochemical processes
- demonstration that the proposed biochemistry is catalytic in that transformation
- demonstration that the proposed energy source chemistry also generates more catalyst, thus leading to a positive feedback loop

Abundant chemical free energy is delivered to the surface of all the cold, reduced planets of the Solar System by the solar radiation photolysis of methane into hydrogen and reduced hydrocarbons, and ultimately to polymeric "kerogen." The hydrogen escapes into space. Acetylene is an example of such a source of chemical free energy, and has been suggested as a base for "prebiotic" carbon chemistry on Titan (Abbas and Schulze-Makuch, 2002). Acetylene is known to be present on the surface of Triton and in the atmosphere of Titan. There is a strong thermodynamic drive to react this with the hydrogen proposed to be generated from the olivine/serpentine reactions, or with water or ammonia known to be present in ices:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad \Delta G = -241 \text{ kJ/mol}$$

$$H_2C_2 + H_2O \rightarrow CO + CH_4 \qquad \Delta G = -179 \text{ kJ/mol}$$

$$H_2C_2 + NH_3 \rightarrow HCN + CH_4 \qquad \Delta G = -142 \text{ kJ/mol}$$

[Data for thermodynamic calculations were taken from Yaws (1999). ΔG is calculated for 70 K, where data are available on ΔS terms. Where specific data for silane and silanol ΔG (formation) are not available, best estimates have been calculated from bond energies as per Patai and Rappaport (1989).] The reaction rate for this in the absence of efficient catalysis is vanishingly small, yet methane is abundant in the atmosphere of Titan, and present at modest levels in that of Triton. There is no consistent explanation for this (as any free methane should be photolysed by solar ultraviolet back to acetylene); possible reasons are an unexpectedly large reservoir of methane on the surface or some sort of biochemistry. The idea that the methane in the atmosphere of Titan is biological in origin was first put forward by Fortes (2000), though it is not a widely accepted explanation for why this geologically unstable compound continues to exist in significant amounts in the moon's atmosphere.

Acetylene hydration reactions are industrially catalyzed by the Lewis and Bronsted acid groups present on silica supports (Wilson and Clark, 2000). Usually multiple silanol groups are necessary for catalysis, and complexation with copper or other electron-deficient metal ions accelerates reactions substantially (Meier and Marsella, 1993; Izumi, 1997), though non-metallic acid catalysts are known (Tsuchimoto *et al.,* 2000). In the addition of alkynes to aryl- or alkenylsilanols and silane diols, the presence of the silanol group is essential for efficient catalysis, and two silanol groups are substantially more efficient than one (Fujii *et al.,* 2002). Thus silanol groups in any context could catalyze this chemistry, and more complex silanols, providing more specific Si-OH groups would be expected to catalyze more efficiently.

Further reactions of the sort

$$H_4C_2 + H_2O \rightarrow CH_2O + CH_4 \qquad \Delta G = \sim 0 \text{ KJ/mol}$$

would also be catalyzed by this chemistry, and provide further reducing equivalents to generate more silanols from silicate to perpetuate the cycle.

It should be noted that the catalysts need not be highly specific or efficient to start with. There is a perceived qualitative difference between industrial, bulk-phase catalysts and biological catalysts, with the former relying on interaction of reactants with a few atoms fortuitously arranged on the surface of the molecule, the latter on in-

teractions with many atoms arranged in a very complex, three-dimensional shape. However, intermediate catalysts can also exist. Proteins such as serum albumin, which have not been selected for catalytic properties, nevertheless can weakly catalyze some reactions (Hollfelder *et al.,* 1996; Riva *et al.,* 1998; Kirby *et al.,* 2000), and known enzymes can catalyze reactions quite unrelated to their "normal" function (O'Brien and Herschlag, 1999). Local "pockets" in the protein, although not highly specific for one substrate, can provide a favorable environment for a specific type of chemistry. Clearly, if that chemistry were generating more catalyst, then those variants with "pockets" that more effectively performed that catalysis would be produced in larger amounts. The road from undifferentiated silicone oligomers to discrete molecules catalyzing different reactions is complex but unbroken. How this chemistry leaps to being *coded* chemistry, as required by the specification for life at the start, is as much a mystery for silicon life as for carbon life.

Life is not just chemistry—it is chemistry that dissipates energy and is organized. The energy source and sink need to be an inherently self-organizing homogeneous system (Prigogine, 1974; Nicholis and Prigogine, 1977), spatially separated (Morowitz, 1974), or both. The physical structure outlined above provides for spatial separation of energy source and sink, the Prigogine basis for self-organizing systems. The overall schema is shown in Fig. 9. The net reaction chemistry (ignoring exact stoichiometry) is

$$CH_4 + H_2O + NH_3 \rightarrow HCN + CO + H_2$$
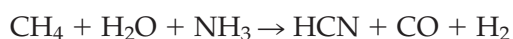
with some methane being recycled and complex, multifunctional silanols playing a central catalytic role.

SILICON LIFE IN OUR SOLAR SYSTEM

The discussion above centers on liquid environments in general, and draws on a variety of solar system chemistries and examples. The estimates of the frequencies of liquids at different distances from a star assume a power law average density of planet-sized bodies. In our Solar System we have a known, specific distribution, and so can be more specific. Titan and Triton could be suitable abodes for a silicon-based biochemistry.

Titan is the most obvious, and has been widely cited as a potential home for "life." In this context the possibility that extensive lakes of liquid methane/ethane exist on the surface of Titan allow a surface-based (and hence photosynthesizing) biochemistry to arise on this moon.

Triton is the other possibility, as liquid nitrogen may exist there. Whether the liquid nitrogen is only the effect of solar heating on a solid nitrogen crust (Soderblom *et al.,* 1990) or whether it is more permanent is not known—the latter is physically possible, as a methane/nitrogen ice would float on "pure" liquid nitrogen, and give surface spectra like those observed on this moon. However, the existence of geologically stable liquid on Triton itself is still very speculative.

A NOTE ON OTHER FLUIDS

Throughout this discussion, "fluid" has been equated with "liquid." Very dense gases near their critical point [near-critical solvents or supercritical fluids (SCFs)] could also provide the dense, mobile environment in which macromolecular "solution" chemistry could occur. Supercritical carbon dioxide is well known for its industrial application as a solvent that can dissolve many materials insoluble in other, liquid solvent systems (Cygnarowicz and Seider, 1991), including a variety of complex biochemicals such as steroids, nitrogenous bases, and lipids (see, *e.g.,* Cheng *et al.,* 2002). If solubility is a barrier to biochemistry in cryogenic solvents, it surely will not be in SCFs. Indeed one might imagine that the opposite is the case, and that SCFs are such good solvents that nothing like a cell membrane or a protein cytoskeleton could form. This need not be so, although again the only data available are for supercritical CO_2. While many polymers swell in supercritical CO_2 (Chang *et al.,* 1998), only a few polymers are actually soluble in it (Rindfleisch *et al.,* 1996; Luna-Barcenas *et al.,* 1998; Stenjy *et al.,* 1998; Behles and DeSimone, 2001); polydimethylsiloxanes are among them (Liu and Kiran, 1999, and referencs therein). Silicones can act as surfactants in supercritical CO_2, and both small-molecule compounds (Beckman and Smith, 1990; Beckman *et al.,* 1991) and polymers (DeSimone and Keiper, 2001) can form micelles with water in this solvent.

The issue for an SCF chemistry has more to do with how stable such an environment might be,
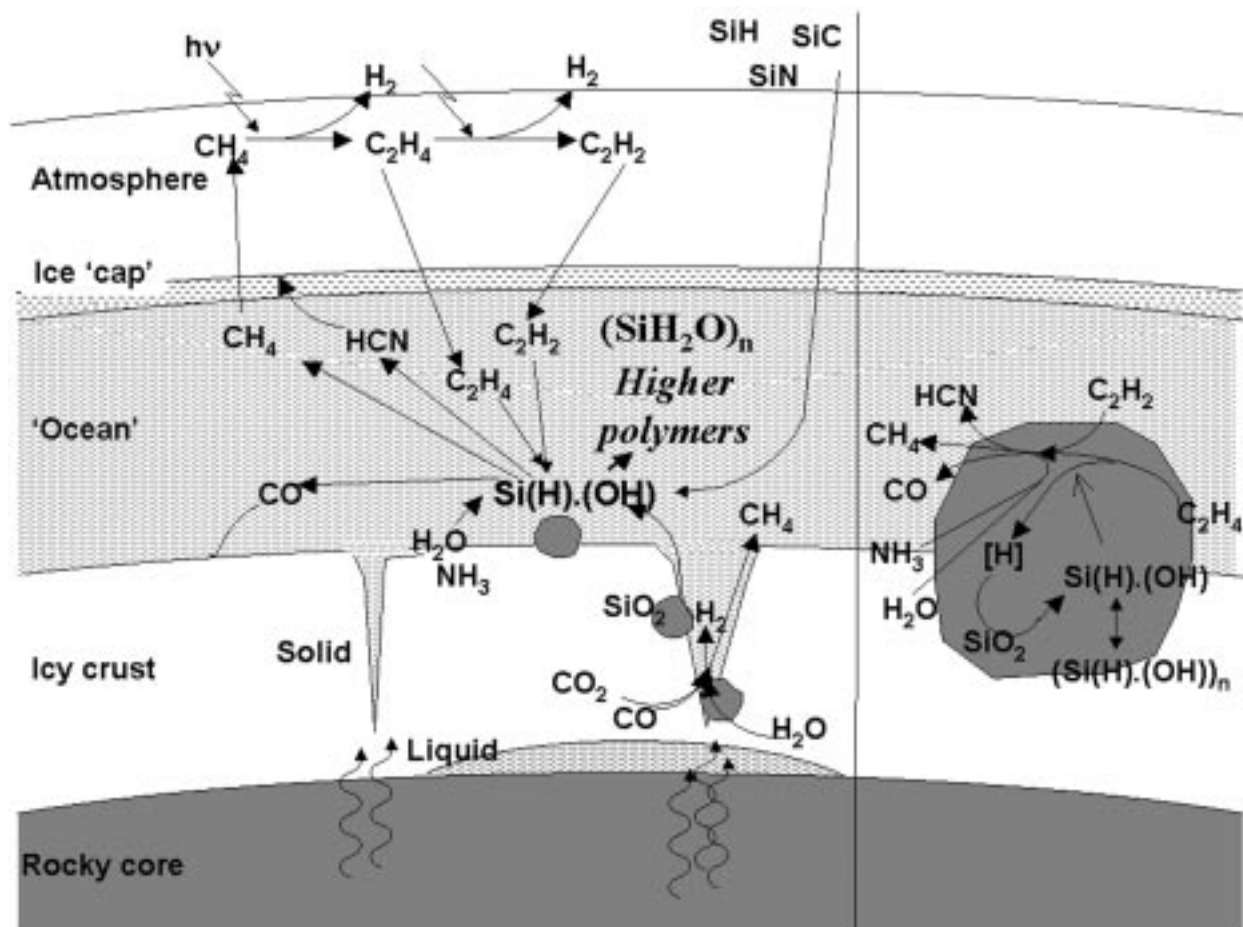
FIG. 9. Entirely hypothetical arrangement of chemistry through which a silane/silanol biochemistry could be initiated in a liquid nitrogen environment. Left-hand side: Overall geochemistry postulated. Crustal CO, CO_2, water, and/or ammonia react with silica in a serpentization-type reaction to generate methane, hydrogen (as gas or as nascent hydrogen reducing equivalents), and silanols/silanes. The exact chemistry of the silicon volatiles is not specified here. Silanols and silanes are transported to the ocean by geyser-like action, driven by radiogenic heat. Silanols, silanes, and their polymeric precursors can also be delivered by primary accretion of stellar dust. Methane is photolysed by solar ultraviolet, solar wind protons, and other high-energy radiation to unsaturated hydrocarbons and hydrogen, which escapes to space. At the ocean floor (as shown) or the ocean surface, depending on relative densities and stirring regimes, silanols catalyze the hydrolysis/ammonolysis of unsaturated hydrocarbons to methane (which largely escapes to the atmosphere or returns to a frozen "crust" over the ocean), hydrogen cyanide, and carbon monoxide. **Right-hand side:** Illustration of how surplus reducing equivalents could provide a feedback mechanism for generating further catalytic silanols on the surface of silica grains.

as all these solubility properties alter dramatically with relatively small changes in pressure (unlike those of a liquid) as well as temperature. Could the complex chemistry of life survive an environment where a slight change in pressure or temperature could cause a radical change in the physical properties of the environment (Clement, 1964)?

T7   Table 7 lists the critical temperatures and pressures for some of the volatiles listed above as potential liquids, together with carbon dioxide. For most compounds, the pressure requirement seems to point to bodies that would be so large their "surface" temperatures would be substantially higher than the critical value, and so the fluid would behave more like a conventional gas and be incapable of dissolving large molecules. The most promising candidate might be Neptune. However, the condensation of methane, ammonia hydrosulphide, and other chemicals into droplets in the troposphere shows that here conventional liquids form rather than SCFs (Gautier

TABLE 7.   CRITICAL TEMPERATURE AND PRESSURE FOR COSMICALLY COMMON VOLATILES

Liquid	Critical temperature (K)	Critical pressure (atmospheres)
Ammonia	405.6	111.5
Argon	150.9	48.5
Carbon dioxide	304.5	72.9
Ethane	305.2	48.2
Hydrogen	33.26	12.8
Methane	190.9	45.8
Neon	44.4	26.3
Nitrogen	126.1	33.5
Water	647.4	218

and Conrath, 1995). Models of deeper structure suggest that this partition between conventional liquid and gas is maintained down to a solid "ice" surface at 2,500 K (Guillot, 1999).

CONCLUSION

This paper illustrates an approach, rather than characterizing a certainty. None of the arguments above proves that anything as exotic as a silicon chemistry-based life using liquid nitrogen or liquid methane as a solvent system actually exists. But some understanding of silicon chemistry suggests that apolar solvent/silicon chemistry-based life is not as implausible as a biochemist might believe, and that environments where it could exist may be quite common. More generally, there may be many environments where the physical and chemical nature of a liquid allows complex, patterned, self-sustaining chemistry, which we would recognize as life, but which is structurally quite different from the CHON life with which we are familiar. Consequently, looking for the equivalent of sugars or nucleic acids, or even just for complex molecules dissolved in water, would not lead to their discovery. However, they could in principle be functionally similar; complex macromolecules could be built in a programmed way to capture matter and energy in order to replicate the program that directed their own synthesis.

This should inform searches for extraterrestrial living systems, which should look for a self-sustaining ability to perturb a local environment from thermodynamic chemical equilibrium into complex, patterned, non-equilibrium chemistry, rather than for narrower measures of terrestrial CHON biochemical output. The nature of the local chemical and energetic environment will constrain the sort of chemistry we look for, but the adaptability of life on Earth suggests that we should not be excessively constrained. I hope that this work will stimulate more extensive models of the occurrence or otherwise of liquids on other planets, and the chemistry that we should look for in those environments.

ABBREVIATIONS

CHON, carbon, hydrogen, oxygen, and nitrogen; HZ, habitable zone; SCF, supercritical fluid.

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