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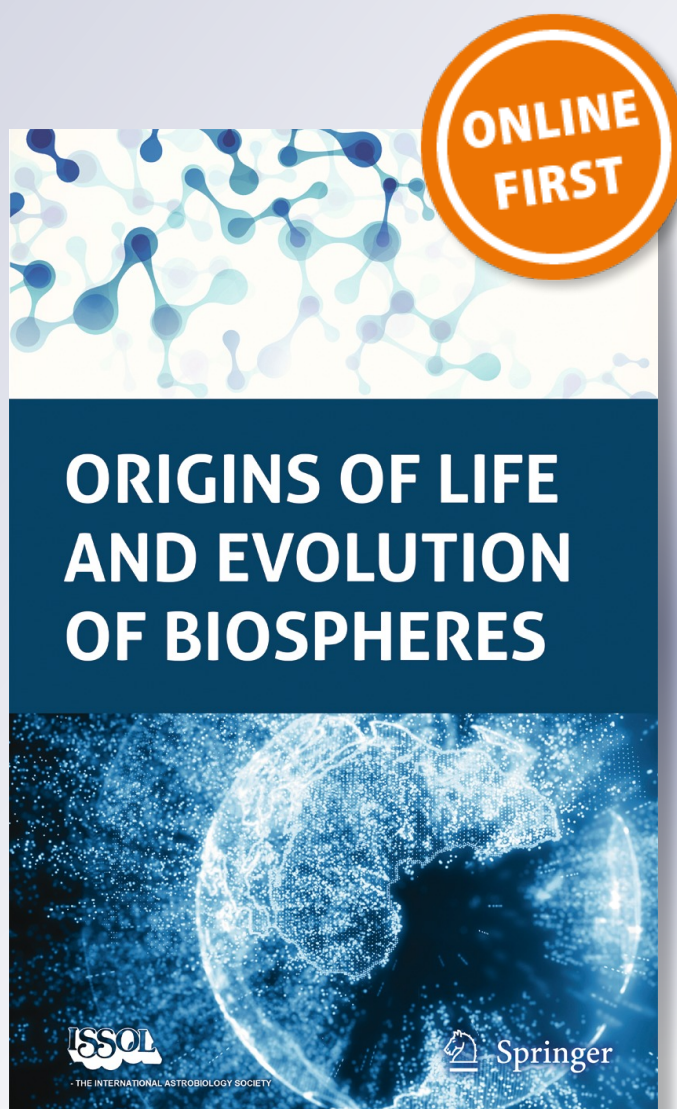
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# Thermodynamics, Disequilibrium, Evolution: Far-From-Equilibrium Geological and Chemical Considerations for Origin-Of-Life Research

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## Introduction

The 8th meeting of the NASA Astrobiology Institute's Thermodynamics, Disequilibrium, Evolution (TDE) Focus Group took place in November 2014 at the Earth-Life Science Institute, at the Tokyo Institute of Technology, Japan. The principal aim of this workshop was to discuss the conditions for early Earth conducive for the emergence of life, with particular regard to far-from-equilibrium geochemical systems and the thermodynamic and chemical phenomena that are driven into being by these disequilibria. The TDE focus group

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seeks to understand how disequilibria are generated in geological, chemical and biological systems, and how these disequilibria can lead to emergent phenomena, such as self-organization in bounded conditions eventuating in metabolism. Some planetary water-rock interfaces generate electrochemical disequilibria (e.g. electron, proton and/or ion gradients), and life itself is an out-of-equilibrium system that operates by harnessing such gradients across membranes. Disequilibrium in inorganic chemical systems also leads to the formation of a variety of patterns, structures, and dynamical systems. Understanding geochemical far-from-equilibrium systems and bounded self-organizing processes may be instructive in revealing some of the processes behind life's origin. In this workshop paper we will detail the outcomes of the 8th TDE meeting in Tokyo, summarizing the focus group's discussions regarding 1) the determination of some of the required conditions for generating geochemical disequilibria for life to originate on a wet, rocky world; 2) the spatial and temporal scales for the origin of life; 3) life's use of disequilibria and the relationship of life itself to self-organizing systems in an aqueous inorganic milieu; and 4) pathways forward for achieving the laboratory simulation of far-from-equilibrium systems concerning prebiotic chemical processes.

## **Generating Geochemical Disequilibria Responsible for the Origin of Life on a Wet and Rocky World**

We argue that life only emerges when and where particular planetary-scale conditions of chemical disequilibria are produced through the interactions of the atmosphere-hydrosphere complex with fresh mafic to ultramafic oceanic crust continually replenished by active partial melting of the mantle (Hess 1962, 1965). Earth of course still has such conditions; Venus may have harbored such conditions very early on; and there is evidence that Mars at least had surface water in the Noachian. For example, Martian shergottites display signs of aqueous interaction extending to the last few million years, and even now there are vestiges of a water table (Webster et al. 2014; Cockell 2014; Chatzitheodoridis et al. 2014). Sustained water-rock interaction may also occur on icy moons that host liquid water oceans in contact with a mafic silicate layer, thereby producing chemical disequilibria similar to those likely present on the early Earth (Vance et al. 2007; Hsu et al. 2015).

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As we continue to identify active liquid water environments in the Solar System, and as the diverse list of known exoplanets continues to grow, we can state some “ideal” factors from the astronomical point of view that would be most likely to give rise to such planetary-scale geological disequilibria. Liquid water (even beneath ice-covered moons) is the first requirement of life and habitability. The planetary body has to be large and radiogenic enough to sustain internal heat for timescales which would permit the development of a biochemistry, although tidal energy could play a part. Stellar radiation and electrical storms can assist in the generation of geochemical disequilibria through atmospheric production of oxidants (e.g.,  $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$ ) that might later react with hydrothermally-produced reductants. However, atmospheric chemistry is not strictly necessary to produce oxidants. On Jupiter’s icy moons, for example, bombardment of the ice shells by particles trapped on the giant planet’s magnetosphere can generate superficial  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{SO}_2$  that could be transferred into the subsurface ocean to serve a similar function (Hand et al. 2007). Even at the greater depths of these oceans, unstable nuclides could induce radiolysis of water, providing a source of highly reactive compounds (Draganić et al. 1991). All of these conditions can further be influenced by the dynamics of planet formation, as collisions of rocky/icy bodies affect the final spin, mass, and orbital distance of a planet (Wetherill 1985; Dones and Tremaine 1993; Ohtsuki and Ida 1998; Miguel and Brunini 2010).

Small bodies of the Solar System are considered to be the remnants of planetesimals from which the planets were formed. Because of their small sizes, most asteroids and comets are believed to have retained a record of the original composition of the Solar System’s protoplanetary disk, in an almost undifferentiated manner. Planetesimals may have been contributors of the water essential for life on Earth, and could also have been the source of carbon. Carbonaceous chondrite matter could have contributed a variety of complex organic molecules to planetary surfaces; for example, amino acids are abundant in meteorites and have recently been discovered in returned Stardust samples (Elsila et al. 2009). The organic compounds found in meteorites display great structural diversity, but also occasional chiral excesses have been found in the soluble fraction of meteoritic organic matter (Pizzarello and Cronin 2000). Against this, Dorn et al. (2011) show that these amino acids are compositionally different from typical earth biospheric distributions; for example, bearing considerable amounts of  $\beta$ -alanine, which is absent from coded proteins. Nevertheless, carbon from such sources would be processed and oxidized in the mantle and find its way to the surface again through volcanic activity in the form of  $\text{CO}_2$ .

The detailed information that we get from Solar System bodies is complemented with the stunning amount of data obtained from exoplanet observations. To date, close to 2000 exoplanets have been discovered and confirmed by different methods, and many more are expected to be found in the near future. With the *Kepler* planetary candidates, this number ascends to almost 5500. Even though statistical analysis of this sample shows that the vast majority are small planets (Neptune size and smaller (Howard et al. 2012; Fressin et al. 2013)), very small rocky planets ( $< 2$  Earth radii) are a challenge to observe. As of 2015, only ten planets of this huge exoplanet sample have been characterized as rocky bodies (Dressing et al. 2015; Berta-Thompson et al. 2015). However, even this small subpopulation of rocky worlds shows a remarkable diversity, ranging from “dense and hot” exoplanets close to their parent star, with planetary surface temperatures greater than 2000 K (e.g. Corot 7b (Barros et al. 2014; Haywood et al. 2014), Kepler 10b (Dumusque et al. 2014), 55 Cnc e (Gillon et al. 2012; Nelson et al. 2014) and the disintegrating planet Kepler-78b (Pepe et al. 2013; Howard et al. 2013)), to “less dense and cool” exoplanets with densities that make them prospective wet rocky worlds (such as GJ 1214b (Charbonneau et al. 2009) and HD97658b (Dragomir et al. 2013)).

The search for habitable exoplanets is for the moment related to the so-called Stellar Habitable Zone (HZ); that is, the range of distances from a star at which water can be liquid on the surface of the planet. The HZ can be tuned by greenhouse effects of the planetary atmosphere (Huang 1959; Kasting 1993; Underwood et al. 2003; Kaltenecker and Sasselov 2011) and also depends on the host star, not just for distance/temperature considerations but because stellar activity can greatly affect atmospheric composition. For example, there is the case of GJ 1214b and GJ1132b (Berta-Thompson et al. 2015) orbiting an M star, which would have sustained a very high level of UV and high-energy emissions over the planets' history, likely producing substantial surface and near-surface oxidants. In the last few decades, additional restrictions for a HZ have been added, e.g. considering the capability of a planet (or moon) to support carbon and water cycles and thus to bear stable water oceans, and, at the same time, considering the effects of albedo and runaway phenomena (Fogg 1992; Kasting 1990; Vladilo et al. 2013; Zsom et al. 2013). It is important to stress the concept that HZ corresponds to habitable conditions that can be detected remotely; the HZ definition is intentionally restricted to account only for the planets upon which possible extant life interacts with the atmosphere, even if indirectly. What we addressed in the TDE discussions, however, is a wider study of the general geological and disequilibrium conditions able to support the emergence of life. For example, it might be possible to drive the emergence of life (or, at least, proto-metabolism) on planets similar to the primordial Earth, but only deep underground, and this life might never evolve to produce an atmosphere noticeably out of equilibrium. It might also be possible for life to emerge beneath the surface of icy moons of outer giant planets, and could thus be challenging to detect.

Still, considering wet rocky Earth-like planets, once a planet is detected in the HZ of its host star, a first spectral analysis of the atmosphere would be necessary to understand its major composition and, in particular, disequilibria of atmospheric species that could serve as a biosignature (or, at least, a signature that a planet has conditions amenable to the emergence or presence of life). The use of the extent of chemical disequilibrium to study planetary habitability is one of the main active collaborations within the TDE Focus Group. Specifically, we aim to build a bridge between atmospheric studies of planetary habitability and the study of other geochemical disequilibria necessary for the emergence of life, so that we can assess the potential of similar emergence processes on exoplanets. The presence of easily detectable atmospheric species (e.g. CO<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O) is not an unequivocal sign of habitability or habitancy since they can be the result of geological, hydrological or photochemical activities. However, atmospheric data and modeling can give some sense of the degree of geochemical disequilibria that might be present on a wet rocky planet and allow us to make estimates regarding the processes at the seafloor. For that reason, new methods are being developed in order to measure the disequilibrium of planetary atmospheres and to link it with habitability (Simoncini et al. 2013; Simoncini et al. 2015; Krissansen-Totton et al. 2016).

An unambiguous sign of the widespread presence of life on Earth is the high degree of chemical disequilibrium associated with Earth's atmospheric composition (Lovelock 1965, 1975; Sagan et al. 1993; Line and Yung 2013). A particularly noticeable aspect of the atmosphere's disequilibrium is the coexistence of species at concentrations far from the expected thermodynamic equilibrium, as in the case of methane and molecular oxygen (Simoncini et al. 2013). On the early Earth when life emerged, and probably on any Earth-sized rocky planet at similar distance from its host star, the atmosphere and oceans may have been relatively oxidized compared to species emanating from hydrothermal systems. The surfaces of silicate-metal planets somewhat larger than Venus' mass (0.81 Earth masses) likely

become progressively more oxidized through a combination of metal sequestration in Fe-Ni cores, ferrous iron-disproportionation to ferric iron plus iron metal in the mantle during core growth, and the late arrival of volatile-rich and more oxidized planetesimals. This is confirmed for Earth by all modern geochemical observations of Hadean mineral compositions, as well as planet formation models (Wood et al. 1990, 2006; Wade and Wood 2005; Frost et al. 2008; Rubie et al. 2011; Trail et al. 2011, 2012). As far back as we can peer into Earth's formative stages, the mantle was close to its present oxygen fugacity (buffered at Fayalite-Magnetite-Quartz), and hence, gaseous species were dominated by CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, N<sub>2</sub> and minor concentrations of nitrogen oxides, many of which are electron acceptors rather than donors (Yung and McElroy 1979; Dasgupta and Hirschmann 2006; Martin et al. 2007; Hirschmann et al. 2009). Thus a planet-wide geochemical disequilibrium arises and is maintained for as long as this oxidized volatilesphere/environment remains in contact with reduced material coming from the interior of a planet, and would be enhanced if life were to make its presence felt through oxygenic photosynthesis.

One question, much disputed, is whether there was “dry land” at the time of life's origin on Earth, or at any time during the Hadean. It is certainly the case that small granitic masses dating to the Hadean have been discovered (Maas et al. 1992; Harrison et al. 2008). More recently, studies of Hf and Nd isotope distribution in the oldest rocks have shown that the basaltic-granitic dichotomy which distinguishes oceanic from continental crust has been around since ~4.45 Ga, although the volume of “continental” crust was significantly less (perhaps 2 % of present continental area, or about half the size of Australia) (Guitreau et al. 2014; Roth et al. 2013; Xing et al. 2014). However, whether “continental” crust represented “dry land” or not depends on the mean ocean depth. If the ocean depth was ~2 km (as it would be if the ocean volume was similar to its present value), there may well have been subaerial “low latitude Icelands”, as well as islands emerging above mantle plume heads (cf., Hawai'i, Samoa, Tahiti, Easter, Azores, Iceland, Canaries, Ascension, Galapagos, Cocos and the Ontong Java Plateau). However, the average ocean depth might have been a factor of two greater in the Hadean, the missing volume now lost to subduction of hydrated ocean floor and also through photodissociation (Bounama et al. 2001; Elkins-Tanton 2008; Genda 2016). Given such a *water world*, the lack of a silicate-weathering thermostat would likely render the climate extremely unstable, oscillating between freezing and perhaps 60 °C (Menou 2015; Cowan and Abbot 2014). This, combined with the planetary day lasting ~15 h, and a much closer Moon, would produce major continual storms, larger tides and thereby, perhaps rapid erosion of any islands puncturing the ocean surface (Denis et al. 2011).

In summary, the atmosphere of early Earth was likely relatively oxidized (containing CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, N<sub>2</sub> and minor NO) and it would have interacted with the hydrosphere to generate planet-wide disequilibria and geochemical gradients (Shock 1992, figure 17; Russell et al. 2013, figure 1). Some of these disequilibria might have been so extensive in the atmosphere as to be remotely detectable, rather than being evident only by in-situ studies. Life has pushed the atmosphere even further from equilibrium. In contrast to giant planets that may host Jupiter-like reducing atmospheres (containing molecular hydrogen, methane, ammonia, hydrogen cyanide, etc.), it is likely that silicate-metal terrestrial planets would instead contain electron acceptors in the atmosphere. Any surface oceans, upon equilibrating with the atmosphere, would also contain dissolved oxidants. Mixing would be rapid in such a water-world so that the reductants H<sub>2</sub> and CH<sub>4</sub> continually produced in, or leached from, the crust by serpentinization, would be juxtaposed against these oxidants at hot springs, especially through and across inorganic precipitate membranes. Such vectorial redox and proton gradients are

presumed by some to have driven the emergence of life (Russell and Hall 1997). Certainly, these gradients are comparable to the disequilibria that drive autotrophic life to this day. Similar geochemical gradients will exist until the planet runs to equilibrium or is swallowed by the planet's expanding and ever hotter Sun.

## Spatial and Temporal Scales for Life's Emergence

In the previous section, we discussed some of the relevant conditions for the generation of planetary disequilibria that could drive the emergence of life. Here, we summarize the TDE discussions regarding spatial and temporal scales for the emergence of a complex chemistry in a planetary body and then for life to emerge and evolve.

The timing of life's origin remains somewhat uncertain. It has long been debated whether the Late Heavy Bombardment (LHB) sterilized the planet around 3.8 billion years ago, thus putting the origin of life well after the LHB ceased, perhaps around 3.5 billion years ago (Maher and Stevenson 1988). However, it has been shown that the cooling time between even very large impacts (asteroids 300 km in diameter) could have been far shorter than the recurrence interval of individual large impacts (Abramov and Mojzsis 2009; Abramov et al. 2013). There is isotopic evidence for a hydrosphere on the Hadean Earth well before the LHB (Mojzsis et al. 2001; Wilde et al. 2001; Harrison 2009), and the oldest rocks of sedimentary origin date to about the time of the LHB (Rosing 1999; Nutman et al. 2009, 2010; Manning et al. 2006). It is unlikely that the early oceans – required for the emergence of life – were delivered by the LHB, as the amount of mass brought in by the LHB was less than about  $10^{-3}$  wt% of the Earth, which is too little to account for the hydrosphere (Genda 2016). Life could have emerged as soon as the hydrosphere formed and the relevant chemical and electrochemical disequilibria outlined above were established (e.g.,  $\text{CO}_2 \gg \text{NO}(\text{HNO}_3^-)$  vs.  $\text{H}_2 > \text{CH}_4$ , and pH 5.5 vs. pH 10.5), perhaps as long ago as 4.3 to 4.4 billion years. Based on the study of carbon isotopes in a 4.1 Ga zircon, Bell et al. (2015) propose that a terrestrial biosphere had emerged by 4.1 Ga. A biosphere certainly seems to have been in place by 3.8 billion years ago according to studies also involving carbon isotopes (Schidlowski 1988; Mojzsis et al. 1996; Rosing 1999; Ueno et al. 2002), and isotopes of iron (Dauphas et al. 2007), nitrogen (Papineau et al. 2005) and sulfur (Mojzsis et al. 2003; Papineau and Mojzsis 2006). Life's emergence may have been a geologically rapid process, perhaps taking place within a mere  $10^{20}$  ns or so – well within, for example, the duration of the Lost City hydrothermal vents according to Ludwig et al. (2011). Indeed, all dissipative structures in the Universe necessarily form quickly relative to their spatial scale, or else their potential initiating fluctuation subsides before the nonequilibrium phase transitions can be negotiated (Kramers 1940; Prigogine 1977). Here we refer to “emergence” of life, rather than “origin”, in order to better underline the fact that life is the last in a long line of emergent entropy generators beginning with the Big Bang. Each such generator is the mother of the next disequilibria converter spawned from a low entropy feed, and processing ever lower grades of “free energy” (Nitschke and Russell 2010; Russell et al. 2013).

The relative sophistication of chemical models in origins of life research compared to models of fluid mechanics used to simulate the types of environments often invoked for prebiotic processes (e.g., chemistry at fluid-solid interfaces, flow through porous geological materials, ocean circulation to provide material to the seafloor system) was noted at this meeting. Is this difference in sophistication justifiable, and can fluid mechanics be neglected in



this discussion? Let us consider fluid dynamics and the origins of life: Life almost certainly began associated with a fluid, most likely water, and it is thought that mineral surfaces (both external and internal, e.g., metal oxyhydroxides and sulfides) could have played key roles as concentrators, catalysts and even as nanoengines (e.g., a device that couples an endergonic reaction to a necessarily large exergonic reaction – a precursor to dual enzymes) for some of the earliest proto-metabolic reactions (Branscomb and Russell 2013). Regardless of the specific mechanism, fuel, oxidants, and relevant inorganic clusters, would need to be transported to the site, and in the far-from-equilibrium system of emergent life, heat and unreactive non-cooperative chemicals (e.g., ones without charge or propensity to aggregate) would be entrained in the effluent as waste. This is true whether the setting under discussion is the oceans, the atmosphere, hydrothermal systems, the porous medium of rock, or Darwin's original 'warm little pond'.

Without fluid flow, such as in a stagnant pool of water, chemicals can only mix by diffusion. This is a slow process with timescales for transport of the order of  $\tau_D = L^2/D$ , where  $L$  is the distance over which diffusion occurs and  $D$  is the molecular diffusivity of the chemical in the fluid. For example, the transport of a molecule of methane over a distance of 1 km in still water at 25 °C would take  $10^{13}$  s, or 300,000 years. This transport time could be reduced somewhat by the *motion* of the water confined in a pool or deep depression. However, typical speeds  $u$  of horizontal currents in the ocean are 0.01–1.0 m/s, although vertical speeds within a density-stratified ocean are much smaller, characteristically 0.0001 m/s. The timescale for the transport of a molecule from the atmosphere in a vertical current of seawater to a depth of 1 km would be  $\tau_C = L/u = 10^6$  s  $\sim$  1 year.

Present models often consider the simplified limit of a well-mixed environment (Ducluzeau et al. 2009; Sojo et al. 2016). In this case, the transport of molecules is assumed to be effectively instantaneous, so that the supply of a chemical is always in great excess of that required by a chemical or biological process. This assumption is valid only when the timescale for chemical or biological activity  $\tau_B$ , is much smaller than the timescale for transport  $\tau_D$  for diffusion or  $\tau_C$  for convection. According to this reasoning life could have therefore emerged on a timescale of 300,000 years for diffusive transport, or 1 year for convective transport, in a pool 1 km deep (cf. the Red Sea Brine Pools, Degens and Ross 2013) if it depended on small molecules like methane. For larger biological molecules, like RNA or DNA, the diffusivity is some three orders of magnitude less, and the timescales are correspondingly longer (though, it must be said that these molecules, requiring exergonic drives for their endergonic synthesis unless exceptional concentrations of their building blocks were somehow achieved, are likely produced only within the narrow confines of a cell (Wicken 1987; Kurland 2010). However, if the atmosphere and oceans were *not* well mixed, but stratified vertically and horizontally (as we may note both from images of Earth from space, and from images of the atmospheres of other planets in the Solar System), then, diffusive transport of chemicals alone is likely to be too slow to support life. The argument was made in this meeting that to drive a far-from-equilibrium system like life from pre-existing geochemical disequilibria, one needs a small "reactor site" in a flow-through setting: a place where there is a high ratio of catalyst surface area to reagent, where reactants are continually supplied and waste is continually removed, where mineral interfaces are present to facilitate reactions, and where some physical matrix and concentrator (within which complex chemistry can take place while maintaining these far-from-equilibrium conditions) is present (Russell et al. 2003, figure 27). This continual supply of reactants can be achieved by convection on larger length scales, and even with a strong convective supply of chemicals, gradients of concentration can exist within the local

environment and drive diffusive fluxes at smaller scales. The idea sometimes prevalent in origins of life research of a “soup” of well-mixed chemicals does not appear to meet these requirements (Lane et al. 2010).

We have thus established that life is likely to have begun in a small region of a larger sea or ocean, where chemicals could be readily exchanged with the neighboring environment and where there were the requisite disequilibria. But, supposing the ocean was stratified, where might such exchanges be found? Thermal and solutal differences (i.e., density gradients) are able to drive flows capable of disrupting and penetrating stably-stratified environments (Turner 1979; Cardoso and McHugh 2010). Strong currents supporting new life could have arisen from sources of heat or solutes. In an open stratified ocean, vertical currents driven by cooling are weak and would transfer chemicals from the atmosphere only rather slowly. This atmosphere-ocean transfer would be accelerated near putative continental margins where a cold current of fluid, laden with sediment particles rich in metals, phosphate and the required electron acceptors, can run downslope much faster and further than in an open ocean. However, if oxidized volatiles from the atmosphere were required only in low fluxes, then life-breeding regions could have developed near or at seafloor sources of solutes and reductants such as seafloor vents. Seafloor vents have several favorable characteristics, namely, providing a rich source of metal complexes as well as hydrogen and methane. Fluid flow also enhances the transport of these chemicals to neighboring regions, and toward a small steady supply of dissolved gases from the atmosphere. From this discussion, we postulate that life is most likely to have begun near continental slopes if atmospheric oxidants were essential for its emergence. Otherwise, being in close proximity to sea vents (where geochemical reactions take place within the crust and mantle of the Earth) produced the best reductants to nourish life – again, always assuming the availability of relatively high-potential electron acceptors from other sources.

After concluding that fluid dynamical systems are required for life to originate, we went on to consider how different the fluid mechanics of the Earth would be without life. Even solid Earth geology would be different without life, as would the nature of sedimentary deposits, even to the extent of microbially-mediated carbonate deposits initiating subduction and thereby plate tectonics (Bally and Snelson 1980). In this way CO<sub>2</sub> from the atmosphere is returned to the mantle – one sink for CO<sub>2</sub> – a “Gaian” control system that keeps the planet from overheating (Schwartzman and Lineweaver 2005; Sleep et al. 2012). Thus photosynthetic life increased the amount of carbonate in the subducting slab, facilitating the formation of future continental crust (Rosing et al. 2006; Höning et al. 2014). But it would be the atmosphere that would be most different in an Earth without life, both in temperature and in composition, so that atmospheric fluid dynamics would be utterly different. Photosynthetic life changed the concentration and distribution of CO<sub>2</sub> in the atmosphere and thereby the carbonate-silicate weathering cycle, which altered the equilibrium (i.e. the kinetics) of the process (Lenton and Watson 2004). One of the well-known effects of this transition is the Snowball Earth phenomenon (Hoffman and Schrag 2002).

## Life as a Self-Organizing System Driven by Disequilibria

Life is a bounded self-organizing system driven by appropriate and sustained disequilibria (e.g., Branscomb and Russell 2013), i.e. it is driven by the 2nd law of thermodynamics (Boltzmann's entropy law) and requires incessant regeneration. As Szent-Györgyi (1979)

articulated so long ago, life is all about the oxidation of hydrogen and electron transport; he maintained that, although dead tissue had a full complement of electrons, it was in a state in which no further exchange or flow of electrons could take place. Keeping in mind the necessary far-from-equilibrium state of living systems, and the particular kinds of disequilibria that life employs to keep metabolism going, the TDE Focus Group discussions at this meeting also aimed to arrive at a thermodynamically reasonable and logical explanation for how bioenergetics could have emerged from geological processes (Schoepp-Cothenet et al. 2013).

As with other entropy generators dissipating disequilibria in the universe, life is in the business of converting external disequilibria to lesser internal disequilibria. This concept has analogs in geological systems, for instance in hydrothermal vents where the disequilibria between ocean and vent solutions leads to the spontaneous formation of self-organized mineral chimney precipitates (Barge et al. 2012, 2015). To drive proto-metabolic reactions in seafloor settings on the Hadean Earth, the appropriate materials available would have included CHONPS plus Na, Cl, K, Se, Ca, Fe, Mn, Co, Ni, Zn, Mo and W (Goldschmidt 1937, 1952; Williams 1961, 1965; Wald 1962; Eck and Dayhoff 1968; Westheimer 1987; Schoepp-Cothenet et al. 2012); all either delivered through hydrothermal, volcanic/atmospheric, or serpentinization processes, or present in the relatively oxidizing oceans. Precipitation of oxyhydroxides, sulfides, clays, carbonates, and silicates in vent systems could have provided various mechanisms for catalyzing chemical reactions and concentrating and preserving reaction products. However, rather than discussing the specifics of mineral-catalyzed reactions in this TDE meeting, we focused on mechanisms by which the most highly endergonic or kinetically inhibited reactions (i.e., the reduction of  $\text{CO}_2$  and the possible oxidation of  $\text{CH}_4$ ) could be driven by geochemically-produced disequilibria, and how disequilibria might become coupled to one another to begin to approach a biological system (Ducluzeau et al. 2014).

Life is considerably more complex than mere catalysis or electron transfer. To couple disequilibria to perform useful work, cells use “molecular engine” enzymes to drive thermodynamically unfavorable reactions at the entries to metabolic pathways and cycles. These are exemplified in the biological membrane nanoengines of ATP-synthase and  $\text{H}^+$ -pyrophosphatase, which convert a trans-membrane proton gradient into concentrations of pyrophosphate very far from equilibrium in comparison to its hydrolysis products (Baltscheffsky 1971; Russell et al. 1994; Lane 2010; Branscomb and Russell 2013; Baltscheffsky and Persson 2014). This fundamental configuration of steep chemical gradients separated by a barrier, with a reduced interior and relatively oxidized exterior, has been proposed to be an echo of the geochemical situation of a hydrothermal vent where protons from the ancient ocean invaded the alkaline interior of a hydrothermal mound – in other words, an ambient proton motive force (Sojo et al. 2016, figure 1). Though it has not yet been demonstrated in the laboratory that a geochemical proton motive force can be harnessed to drive pyrophosphate formation, it is an intriguing possibility that might explain why life today pumps protons out of the cytoplasm, only to put them to work as the proton motive force (*pmf*), on their return to generate the pyrophosphate bond (e.g.,  $\text{PP}_i$  from  $\text{P}_i$ ) at *orders of magnitude* beyond its equilibrium value in bulk aqueous solution.

The redox gradients present between the oxidized ocean and the more reducing planetary interior could also have prefigured much of the drive for early metabolism. The terrestrial biosphere is clearly autotrophic, i.e., life generates its building blocks from inorganic carbon. At the base of the food chain organisms use hydrogen, released from water either geochemically or photosynthetically, to reduce carbon dioxide, so as to produce a small but ever-renewed stock of organic molecules (Goldschmidt 1952; Bernal 1960; Russell and Hall 1997).

One of the highly endergonic steps at life's emergence was the initial reduction of CO<sub>2</sub> to CO (Yamaguchi et al. 2014a, b). Whether this step was driven merely by the disequilibrium between CO<sub>2</sub> and H<sub>2</sub> (Martin et al. 2015; He et al. 2016), the proton motive force and pyrophosphate (Lane et al. 2010; Herschy et al. 2014), or through electron bifurcation, involving molybdenum as well as Brownian ratchet escapements (Chatterjee et al. 2006; Astumian 2007; Hoffmann 2012), is still disputed (Schoepp-Cothenet et al. 2012; Nitschke and Russell 2013; cf., Kaster et al. 2011). If the initial reduction of CO<sub>2</sub> by the first metabolism was driven by electron bifurcation – i.e., by the simultaneous transfer of one electron to a less exergonic acceptor and the other to a more exergonic acceptor – then, the reduction of CO<sub>2</sub> (the more energetically difficult reaction) would require mechanistic coupling to an even higher potential electron acceptor, for example NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and/or Fe<sup>III</sup> (Russell and Hall 1997; Ducluzeau et al. 2009). Reduction of CO<sub>2</sub> in a hydrothermal setting would require either mechanistic coupling to an even greater exergonic reaction, or coupling to a geochemical gradient acting across some kind of barrier.

A further dispute is how the intermediates in the acetyl coenzyme pathway (assumed to be among the first to originate (Fuchs 1989)) – namely, the formyl and methyl groups – were achieved as the entry to metabolism. Lane et al. (2010) have argued that CO was further reduced to these intermediates, whereas Russell et al. (2003, 2013) have suggested they were generated through the oxidation of hydrothermal methane. Determining which is the more likely scenario will require laboratory experimentation that realistically simulates the open and out-of-equilibrium flow-through system that was the seafloor setting of the early Earth, coupled with testing of various mineral catalysts that are likely to have precipitated in the mildly acidic, relatively oxidizing oceanic setting. Further experimentation will also be required to determine if/how it is possible for geochemical gradients (e.g., ambient *pmf*) acting across a mineral membrane to couple to the generation of disequilibrium of pyrophosphate with respect to phosphate, thus providing a mechanism for a “proto-pyrophosphatase” enzyme. Since its founding in 2010, the TDE Focus Group has promoted collaborations to develop detailed theoretical models for the emergence of redox enzymes and nanoengine disequilibrium converters to drive the first metabolism.

## Pathways Forward to Achieve Laboratory Simulations of Far-from-Equilibrium Prebiotic Processes

This consideration of the origin of life as a far-from-equilibrium process in a geological environment that sustained relevant gradients means that experimental efforts to reproduce prebiotic chemistry in the laboratory must take these conditions into account. Perhaps most importantly, any “prebiotic” system where disequilibria are harnessed must not be a closed system: it must have inputs and outputs that allow for the delivery of “useful” chemicals and ions and the removal of waste (the entropic output). The system furthermore needs a mechanism to generate, concentrate or filter useful substrates, whether this is a surface, membrane, or something else with some kind of selectivity (e.g., within an anionic interlayer gallery space in flexible hydrocalcites such as green rust (Arrhenius 2003; Hansen et al. 2001; Trolard and Bourrié 2012; Russell et al. 2013)). Non-invasive analytical techniques that can query such systems in real time, and that preferably prevent alteration of samples containing metastable minerals and intermediates, will also be required.

Only recently has the challenge been taken up through electrocatalysis. This involves analogies with fuel cell technologies, which employ electrons and protons in conditions just beyond those imposed by the stability field of water (Nakamura et al. 2010; Yamaguchi et al. 2014a, b; and see Narayanan et al. 2011). Electrochemical and fuel cell experiments attempt to characterize the ability of geochemical materials to drive redox reactions of interest, e.g., CO<sub>2</sub> reduction by Fe/Ni-sulfide minerals resembling the active sites of redox enzymes (Yamaguchi et al. 2014b; Herschy et al. 2014; Barge et al. 2014). Flow-through experiments involving possibly catalytic hydrothermal minerals produce simulated chimney structures (Mielke et al. 2011; Barge et al. 2015; McGlynn et al. 2012; Burcar et al. 2015; Batista et al. 2014; Herschy et al. 2014), thus providing the “inorganic membrane” separator that can focus and sustain the ambient chemical disequilibria. Electrochemical flow-through reactor designs to simulate seafloor systems would be useful in applying thermodynamic considerations to the attempted synthesis (oxidation) of highly endergonic intermediates from methane (such as formaldehyde) in C1 protometabolism through free-energy conversion by electron bifurcation by molybdenum species (Nitschke et al. 2013; Russell et al. 2014). The versatility of these types of experiments to different reaction systems allows for testing of any proposed ocean/hydrothermal fluid chemistries, including the putative environments of icy worlds, early Mars, or of exoplanets. Future studies of prebiotic chemistry in flow-through hydrothermal systems should continue to focus on temperature-dependent mineral formation and reactivity under a range of chemical conditions – but specifically in experimental setups that preserve the pH, redox and chemical gradients between the ocean and hydrothermal solutions.

Other considerations involve the physical scales relevant to the emergence of biological/prebiotic disequilibria coupling, as well as the emergence of feedbacks between reactions and organic/mineral interactions. Endergonic reactions in biological systems (e.g., coupling of proton gradients to pyrophosphate/ATP synthesis) only occur over very small scales, at the redox and proton disequilibria maintained across cell membranes ( $\leq 10$  nm thickness) (Mulkiđjanian et al. 2009). Experimental designs employing microfluidic technologies and microfluidic flow-through reactors would offer a significant advance to simulate reactions occurring at the nano-scale, and would also allow simulations of thermal-gradient-induced accumulation and replication of organics (Baaske et al. 2007; Kreysing et al. 2015). Although microfluidic fuel cells and microfluidic membrane reactors are well established for other purposes (Zhang et al. 2010; Choban et al. 2004; Kjeang et al. 2009), they are not yet well utilized by the astrobiology/origin of life community. Thus, there is a significant opportunity to develop microfluidic reactors, which combine chip-based technology with high-throughput analysis for exploring multiple simulated geological environments, their structures and reactivity. Pyrophosphate formation has never been accomplished via redox or proton gradients in prebiotic systems – only via substrate phosphorylation or extreme pH changes / heating – so success in this objective would constitute a major result for understanding prebiotic energetics. Development of a “nanoengine” of geologically realistic material – for example, a double layered iron oxyhydroxide as proposed by Russell et al. (2013) – and demonstrating coupling to an externally imposed gradient may only be possible at experimental scales approaching biological scales, i.e., nanometers. This scale is considered because of the requirement for Brownian impacts to produce instances of a reaction’s ‘backward’ (entropy-reducing) reaction (Branscomb and Russell 2013).

The synthesis of ever more complex organics in a flow-through chemical reactor may eventually begin to catalyze feedbacks between organics and mineral surfaces. Ligand-accelerated catalytic feedbacks can develop between mineral-organic surface interactions to

produce metal-organic complex intermediates (Jacobsen et al. 1988; Berrisford et al. 1995). For example, organics in iron sulfide chimney experiments affect the stoichiometry of the Fe/S minerals that precipitate (McGlynn et al. 2012), and can trap and stabilize Fe/S minerals such as greigite ( $\text{Fe}_3\text{S}_4$ ) (Rickard et al. 2001). Moreover, the incorporation of certain organic amines in Fe(Ni)S catalysts has been shown to increase their ability to reduce  $\text{CO}_2$  (Yamaguchi et al. 2014b). Recently it was shown that the catalytic iron sulfide phase mentioned above, greigite, which is structurally similar to the Fe(Ni)-S active site of the metalloenzyme that reduces  $\text{CO}_2$  (carbon monoxide dehydrogenase; CODH) (Nitschke et al. 2013), cannot only be synthesized at around 70 °C (White et al. 2015) but also at room temperature if it is precipitated in the presence of pyruvate or other  $\alpha$ -oxo acids (Wang et al. 2015). As the mineral precipitates at the hydrothermal/ocean interface are heterogeneous and contain any and all of these potential prebiotic catalysts at once, it is possible in this kind of flow-through reactor experiment to attempt to couple or combine seemingly separate chemical pathways. For example,  $\alpha$ -oxo acids may enhance redox activity of metal sulfides, while iron hydroxide and oxyhydroxides act as electron donors to generate ammonia from atmospherically-supplied nitrate. This could then react with  $\alpha$ -oxo acids to produce amino acids (with specific yields of particular chemical pathways varying from place to place, as the surrounding minerals preferentially accelerate certain pathways (Huber and Wächtershäuser 2003; Trolard and Bourrié 2012; Novikov and Copley 2013)). Experimental designs that preserve the far-from-equilibrium aspects of the system, combined with analytical techniques that favor real-time, in situ detection of metastable phases as reactions proceed, will be critical to this effort. It was for this reason that TDE Focus Group members discussed experimental collaborations that would involve considerations of analytical methods (e.g., laser spectroscopy) and using innovative experimental setups and technologies that are already designed to facilitate flow-through of reactants and electron/proton/ion gradients in other fields of science.

## Conclusions

While different models proposed for life's emergence were acknowledged and members agreed to disagree on these matters, there was a consensus built around the view that the supply or supplies of fuels, metals, phosphate and oxidants to embryonic life needed to be well-ordered, predictable and sustained until its birthing. It was also recognized that, overall, even the very beginnings of metabolism would have to generate entropy from low entropy aqueous feeds to satisfy the second law (Boltzmann 1886, Schrödinger, and see the Forward by Penrose to Schrödinger 1967). In other words, to be an entropy generator, emergent life itself needed to be low entropy, and thus a spatially-bounded open system. Whether the boundary was an internal mineral gallery, an inorganic or organic compartment, or within the confines of a pool or pond was left for another time. However, with these general pointers in mind, it was also agreed that a new experimental effort was called for on the issue now that mere mass action chemistry has been shown incapable of accounting for life's emergence (Lane et al. 2010) – and that these experiments would have to come to terms with the necessity of overcoming the many endergonic barriers along the pathways and cycles of metabolism and genetic guidance. After some discussion, agreement was also reached regarding preference for using “disequilibria” in place of energy when discussing details of the drive to life, while at the same time recognizing that the concept of “free energy” was so embedded in the discourse that it had to stand in as a sensible ‘colloquialism’ to

accommodate discussion. Seeing the issue in this light called for models that could satisfy the requirement for free energy conversion (second law), and not merely energy conservation (first law). As Elbert Branscomb argued in this meeting, “life is not a means of aggregating ‘building blocks’, but instead is concerned with developing nanoengines (not mere catalysts) that can couple thermodynamically opposed processes, in order to create one disequilibrium at the expense of dissipating another.”

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## References

- Abramov O, Mojzsis SJ (2009) Microbial habitability of the hadean earth during the late heavy bombardment. *Nature* 459:419–422
- Abramov O, Kring DA, Mojzsis SJ (2013) The impact environment of the hadean earth. *Chemie der Erde-Geochemistry* 73(3):227–248
- Arrhenius GO (2003) Crystals and life. *Helv Chim Acta* 86:1569–1586
- Astumian RD (2007) Adiabatic operation of a molecular machine. *Proc Natl Acad Sci* 104(50):19715–19718
- Baaske P, Weinert FM, Duhr S, Lemke KH, Russell MJ, Braun D (2007) Extreme accumulation of nucleotides in simulated hydrothermal pore systems. *Proc Natl Acad Sci U S A* 104:9346–9351
- Bally AW, Snelson S (1980) Realms of subsidence. in Miall, a. D., ed. *Facts and principles of world petroleum occurrence: Canadian Society of Petroleum Geologists Memoir* 6:9–94
- Baltscheffsky, H. (1971) Inorganic pyrophosphate and the origin and evolution of biological energy transformation (biological energy transformation origin and evolution, discussing inorganic pyrophosphates precursor to adenosine phosphates as energy carriers). In *Chemical Evolution and the Origin of Life*, edited by R. Buvet and C. Ponnampuruma, North-Holland Pub. Co., Amsterdam, pp 466–474
- Baltscheffsky H, Persson B (2014) On an early gene for membrane-integral inorganic pyrophosphatase in the genome of an apparently pre-LUCA extremophile, the archaeon *Candidatus Korarchaeum cryptofilum*. *J Mol Evol* 78:140–147
- Barge LM, Doloboff IJ, White LM, Russell MJ, Kanik I (2012) Characterization of iron-phosphate-silicate chemical garden structures. *Langmuir* 28:3714–3721
- Barge LM, Kee TP, Doloboff IJ, Hampton JM, Ismail M, Pourkashanian M, Zeytounian J, Baum MM, Moss JA, Lin CK, Kidd RD (2014) The fuel cell model of abiogenesis: a new approach to origin-of-life simulations. *Astrobiology* 14(3):254–270
- Barge LM, Cardoso SSS, Cartwright JHE, Cooper GJT, Cronin L, De Wit A, Doloboff IJ, Escobedo B, Goldstein RE, Haudin F, Jones DEH, Mackay AL, Maselko J, Pagano JJ, Pantaleone J, Russell MJ, Sainz-Diaz CI, Steinbock O, Stone DA, Tanimoto Y, Thomas NL (2015) From chemical gardens to Chemobionics. *Chem Rev* 115:8652–8703
- Barros SCC, Almenara JM, Deleuil M, Diaz RF, Csizmadia S, Cabrera J, Chaintreuil S, Cameron AC, Hatzes A, Haywood R, Lanza AF (2014) Revisiting the transits of CoRoT-7b at a lower activity level. *Astron Astrophys* 569:A74
- Batista BC, Cruz P, Steinbock O (2014) From hydrodynamic plumes to chemical gardens: the concentration-dependent onset of tube formation. *Langmuir* 30:9123–9129
- Bell EA, Boehnke P, Harrison TM, Mao WL (2015) Potentially biogenic carbon preserved in a 4.1 billion-year-old zircon. *Proc Natl Acad Sci* 112(47):14518–14521
- Bernal JD (1960) The problem of stages in biopoiesis. In: *Aspects of the origin of life*, edited by M. Pergamon Press, New York, Florkin, pp. 30–45

- Berrisford DJ, Bolm C, Sharpless KB (1995) Ligand-accelerated catalysis. *Angewandte Chemie International Edition in English* 34(10):1059–1070
- Berta-Thompson ZK, Irwin J, Charbonneau D, Newton ER, Dittmann JA, Astudillo-Defru N, Bonfils X, Gillon M, Jehin E, Stark AA, Stalder B (2015) A rocky planet transiting a nearby low-mass star. *Nature* 527(7577):204–207
- Boltzmann L (1886) Reprinted and translated in: theoretical physics and philosophical problems; selected writings (Vienna circle collection); chap. The second law of thermodynamics. Kluwer D. Reidel publishing Co., Dordrecht, Holland, p. 13–32, 1974
- Bounama C, Franck S, von Bloh W (2001) The fate of the Earth's ocean. *Hydrol Earth Syst Sci* 5:569–575
- Branscomb E, Russell MJ (2013) Turnstiles and bifurcators: the disequilibrium converting engines that put metabolism on the road. *Biochim Biophys Acta Bioenergetics* 1827:62–78
- Burcar BT, Barge LM, Trail D, Watson EB, Russell MJ, McGown LB (2015) RNA Oligomerization in Laboratory Analogues of Alkaline Hydrothermal Vent Systems. *Astrobiology* 15(7):509–522. doi:10.1089/ast.2014.1280
- Cardoso SSS, McHugh ST (2010) Turbulent plumes with heterogeneous chemical reaction on the surface of small buoyant droplets. *J Fluid Mech* 642:49–77
- Charbonneau D, Berta ZK, Irwin J, Burke CJ, Nutzman P, Buchhave LA, Lovis C, Bonfils X, Latham DW, Udry S, Murray-Clay RA (2009) A super-earth transiting a nearby low-mass star. *Nature* 462(7275):891–894
- Chatterjee MN, Kay ER, Leigh DA (2006) Beyond switches: ratcheting a particle energetically uphill with a compartmentalized molecular machine. *J Am Chem Soc* 128(12):4058–4073
- Chatzitheodoridis E, Haigh S, Lyon I (2014) A conspicuous clay ovoid in Nakhla: evidence for subsurface hydrothermal alteration on Mars with implications for astrobiology. *Astrobiology* 14(8):651–693
- Choban ER, Markoski LJ, Wiecekowski A, Kenis PAJ (2004) Microfluidic fuel cell based on laminar flow. *J Power Sources* 128(1):54–60
- Cockell CS (2014) Trajectories of Martian habitability. *Astrobiology* 14(2):182–203
- Cowan, N. B., Abbot, D. S. (2014) Water Cycling Between Ocean and Mantle: Super-Earths Need Not be Waterworlds. *arXiv preprint arXiv:1401.0720*.
- Dasgupta R, Hirschmann MM (2006) Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440(7084):659–662
- Dauphas N, Cates NL, Mojzsis SJ, Busigny V (2007) Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada. *Earth Planet Sci Lett* 254(3):358–376
- Degens ET, Ross DA (2013) Hot brines and recent heavy metal deposits in the Red Sea: a geochemical and geophysical account. Springer-Verlag
- Denis C, Rybicki KR, Schreider AA, Tomecka-Suchoň S, Varga P (2011) Length of the day and evolution of the Earth's core in the geological past. *Astronomische Nachrichten* 332:24–35
- Dones L, Tremaine S (1993) Why Does the Earth Spin Forward? *Science* 259(5093):350–354
- Dom ED, Neelson KH, Adami C (2011) Monomer abundance distribution patterns as a universal biosignature: examples from terrestrial and digital life. *J Mol Evol* 72(3):283–295
- Draganić IG, Bjergbakke E, Draganić ZD, Sehested K (1991) Decomposition of ocean waters by potassium-40 radiation 3800 Ma ago as a source of oxygen and oxidizing species. *Precambrian Res* 52(3–4):337–345
- Dragomir D, Matthews JM, Eastman JD, Cameron C, Howard AW, Guenther DB, Kuschnig R, Moffat AF, Rowe JF, Rucinski SM, Sasselov D (2013) MOST detects transits of HD 97658b, a warm, likely volatile-rich super-Earth. *Astrophys J Lett* 772(1):L2
- Dressing CD, Charbonneau D, Dumusque X, Gettel S, Pepe F, Cameron AC, Latham DW, Molinari E, Affer L, Bonomo AS, Buchhave LA (2015) The mass of Kepler-93b and the composition of terrestrial planets. *Astrophys J* 800(2):135
- Ducluzeau A-L, van Lis R, Duval S, Schoepp-Cothenet B, Russell MJ, Nitschke W (2009) Was nitric oxide the first strongly oxidizing terminal electron sink. *Trends Biochem Sci* 34:9–15
- Ducluzeau AL, Schoepp-Cothenet B, Baymann F, Russell MJ, Nitschke W (2014) Free energy conversion in the LUCA: quo vadis? *Biochim Biophys Acta Bioenergetics* 1837(7):982–988
- Dumusque X, Bonomo AS, Haywood RD, Malavolta L, Ségransan D, Buchhave LA, Cameron AC, Latham DW, Molinari E, Pepe F, Udry S (2014) The Kepler-10 planetary system revisited by HARPS-N: A hot rocky world and a solid Neptune-mass planet. *Astrophys J* 789(2):154
- Eck RV, Dayhoff MO (1968) Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences. *Science* 152:363–366
- Elkins-Tanton LT (2008) Linked magma ocean solidification and atmospheric growth for earth and Mars. *Earth Planet Sci Lett* 271:181–191
- Elsila JE, Glavin DP, Dworkin JP (2009) Cometary glycine detected in samples returned by stardust. *Meteorit Planet Sci* 44(9):1323–1330
- Fogg MJ (1992) An estimate of the prevalence of biocompatible and habitable planets. *J Br Interplanet Soc* 45(1):3–12



- Fressin F, Torres G, Charbonneau D, Bryson ST, Christiansen J, Dressing CD, Jenkins JM, Walkowicz LM, Batalha NM (2013) The false positive rate of Kepler and the occurrence of planets. *Astrophys J* 766(2):81
- Frost DJ, Mann U, Asahara Y, Rubie DC (2008) The redox state of the mantle during and just after core formation. *Philos Trans R Soc A* 366:4315–4337
- Fuchs, G. (1989) Alternative pathways of autotrophic CO<sub>2</sub> fixation. In *Autotrophic Bacteria*, edited by H.G. Schlegel and B. Bowen, Science Technology, Madison, pp 365–382.
- Genda H (2016) Origin of Earth's oceans: an assessment of the total amount, history and supply of water. *Geochem J* 50(1):27–42
- Gillon M, Demory BO, Benneke B, Valencia D, Deming D, Seager S, Lovis C, Mayor M, Pepe F, Queloz D, Ségransan D (2012) Improved precision on the radius of the nearby super-Earth 55 Cnc e. *Astron Astrophys* 539:A28
- Goldschmidt VM (1937) The principles of distribution of chemical elements in minerals and rocks. *J Chem Soc* 1937:655–673
- Goldschmidt VM (1952) Geochemical aspects of the origin of complex organic molecules on the earth, as precursors to life. *New Biology* 12:97–105
- Guitreau M, Blichert-Toft J, Mojzsis SJ, Roth AS, Bourdon B, Cates NL, Bleeker W (2014) Lu–Hf isotope systematics of the hadean–Eoarchean Acasta gneiss complex (northwest territories, Canada). *Geochim Cosmochim Acta* 135:251–269
- Hand K, Carlson RW, Chyba CF (2007) Energy, chemical disequilibrium, and geological constraints on Europa. *Astrobiology* 7(6):1006–1022
- Hansen HCB, Gulberg S, Erbs M, Koch CB (2001) Kinetics of nitrate reduction by green rusts: effects of interlayer anion and Fe(II): Fe(III) ratio. *Appl Clay Sci* 18:81–91
- Harrison TM (2009) The hadean crust: evidence from >4 Ga zircons. *Annu Rev Earth Planet Sci* 37:479–505
- Harrison TM, Schmitt AK, McCulloch MT, Lovera OM (2008) Early ( $\geq 4.5$  Ga) formation of terrestrial crust: Lu–Hf, d<sup>18</sup>O, and Ti thermometry results for hadean zircons. *Earth Planet Sci Lett* 268(3):476–486
- Haywood RD, Cameron AC, Queloz D, Barros SCC, Deleuil M, Fares R, Gillon M, Lanza AF, Lovis C, Moutou C, Pepe F (2014) Planets and stellar activity: hide and seek in the CoRoT-7 system. *Mon Not R Astron Soc* 443(3):2517–2531
- He Y, Li M, Perumal V, Feng X, Fang J, Xie J, Sievert SM, Wang F (2016) Genomic and enzymatic evidence for acetogenesis among multiple lineages of the archaeal phylum Bathyarchaeota widespread in marine sediments. *Nature Microbiology* 16035. doi:10.1038/NMICROBIOL.2016.35
- Herschy B, Whicher A, Camprubi E, Watson C, Dartnell L, Ward J, Evans JRG, Lane N (2014) An origin-of-life reactor to simulate alkaline hydrothermal vents. *J Mol Evol* 79:213–227. doi:10.1007/s00239-014-9658-4
- Hess HH (1962) History of ocean basins. In *Petrologic studies*, a. E. J. Engel et al., eds. Geological Society of America. N Y 4:599–620
- Hess HH (1965) Mid-oceanic ridges and tectonics of the sea-floor. *Submarine geology and geophysics, Colston Papers* 17:317–334
- Hirschmann MM, Tenner T, Aubaud C, Withers AC (2009) Dehydrationmelting of nominally anhydrous mantle: the primacy of partitioning. *Phys Earth Planet Int* 176:54–68
- Hoffman P, Schrag D (2002) The snowball earth hypothesis: testing the limits of global change. *Terra Nov.* 14:129–155
- Hoffmann PM (2012) *Life's ratchet: how molecular machines extract order from chaos*. Basic Books
- Höning D, Hansen-Goos H, Airo A, Spohn T (2014) Biotic vs. abiotic earth: a model for mantle hydration and continental coverage. *Planetary and Space Science* 98:5–13
- Howard AW, Marcy GW, Bryson ST, Jenkins JM, Rowe JF, Batalha NM, Borucki WJ, Koch DG, Dunham EW, Gautier TN III, Van Cleve J (2012) Planet occurrence within 0.25 AU of solar-type stars from Kepler. *Astrophys J Suppl Ser* 201(2):15
- Howard AW, Sanchis-Ojeda R, Marcy GW, Johnson JA, Winn JN, Isaacson H, Fischer DA, Fulton BJ, Sinukoff E, Fortney JJ (2013) A rocky composition for an earth-sized exoplanet. *Nature* 503(7476):381–384
- Hsu H-W, Postberg F, Sekine Y, Shibuya T, Kempf S, Horányi M, Juhász A, Altobelli N, Suzuki K, Masaki Y, Kuwatani T, Tachibana S, Sirono S, Moragas-Klostermeyer G, Srama R (2015) Ongoing hydrothermal activities within Enceladus. *Nature* 519:207–210. doi:10.1038/nature14262
- Huang SS (1959) Occurrence of life in the universe. *Am Sci* 47:397–402
- Huber C, Wächtershäuser G (2003) Primordial reductive amination revisited. *Tetrahedron Lett* 44(8):1695–1697
- Jacobsen EN, Marko I, Mungall WS, Schroeder G, Sharpless KB (1988) Asymmetric dihydroxylation via ligand-accelerated catalysis. *J Am Chem Soc* 110(6):1968–1970
- Kaltenegger L, Sasselov D (2011) Exploring the habitable zone for Kepler planetary candidates. *Astrophys J* 736: L25
- Kaster A-K, Moll J, Parey K, Thauer RK (2011) Coupling of ferredoxin and heterodisulfide reduction via electron bifurcation in hydrogenotrophic methanogenic archaea. *Proc Natl Acad Sci U S A* 108:2981–2986
- Kasting JF (1990) Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Orig. Life* 20: 199–231

- Kasting JF (1993) Earth's earliest atmosphere. *Science* 259:920–926
- Kjeang E, Djilali N, Sinton D (2009) Microfluidic fuel cells: a review. *J Power Sources* 186:353–369
- Kramers HA (1940) Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica* 7(4):284–304
- Kreysing M, Keil L, Lanzmich S, Braun D (2015) Heat flux across an open pore enables the continuous replication and selection of oligonucleotides towards increasing length. *Nat Chem* 7(3):203–208
- Krissansen-Totton J, Bergsman DS, Catling DC (2016) On detecting biospheres from thermodynamic disequilibrium in planetary atmospheres. *Astrobiology* 16(1):39–67 ArXiv:1503.08249v1 [astro-ph.EP]
- Kurland CG (2010) The RNA dreamtime. *BioEssays* 32(10):866–871
- Lane N (2010) Why are cells powered by proton gradients? *Nature* Ed 3:18
- Lane N, Allen JF, Martin W (2010) How did LUCA make a living? Chemiosmosis in the origin of life. *BioEssays* 32(4):271–280
- Lenton T, Watson A (2004) Biotic enhancement of weathering, atmospheric oxygen and carbon dioxide in the Neoproterozoic. *Geophys Res Lett* 31:5
- Line MR, Yung Y (2013) A systematic retrieval analysis of secondary eclipse spectra. III. Diagnosing chemical disequilibrium in planetary atmospheres. *Astrophys J* 779(1):3
- Lovelock JE (1965) A physical basis for life detection experiments. *Nature* 207:568–570
- Lovelock JE (1975) Thermodynamics and the recognition of alien biospheres. *Proc Roy Soc Lond B* 189:167–181
- Ludwig KA, Shen CC, Kelley DS, Cheng H, Edwards RL (2011) U–Th systematics and 230 Th ages of carbonate chimneys at the lost City hydrothermal field. *Geochim Cosmochim Acta* 75(7):1869–1888
- Maas R, Kinny PD, Williams I, Froude DO, Compston W (1992) The Earth's oldest known crust: a geochronological and geochemical study of 3900–4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia. *Geochim. Cosmochim. Acta* 56:1281–1300
- Maher KA, Stevenson DJ (1988) Impact frustration of the origin of life. *Nature* 331:612–614
- Manning CE, Mojzsis SJ, Harrison TM (2006) Geology, age and origin of supracrustal rocks at rosinAkilia, West Greenland. *Am J Sci* 306:303–366
- Martin RS, Mather TA, Pyle DM (2007) Volcanic emissions and the early earth atmosphere. *Geochim Cosmochim Acta* 71:3673–3685
- Martin, W. F., Neukirchen, S. & Sousa, F. L. (2015) Early Life. In *Microbial Evolution under Extreme Conditions*. Walter de Gruyter GmbH & Co KG pp. 171–184
- McGlynn SE, Kanik I, Russell MJ (2012) Modification of simulated hydrothermal iron sulfide chimneys by RNA and peptides. *Philos Trans R Soc Lond A: Phys Sci* 370:1–16
- Menou K (2015) Climate stability of habitable earth-like planets. *Earth Planet Sci Lett* 429:20–24
- Mielke RE, Robinson KJ, White LM, McGlynn SE, McEachern K, Bhartia R, Kanik I, Russell MJ (2011) Iron-sulfide-bearing chimneys as potential catalytic energy traps at life's emergence. *Astrobiology* 11:933–950
- Miguel Y, Brunini A (2010) Planet formation: statistics of spin rates and obliquities of extrasolar planets. *MNRAS* 406(3):1935–1943
- Mojzsis SJ, Arrhenius G, McKeegan KD, Harrison TM, Nutman AP, Friend CRL (1996) Evidence for life on earth before 3,800 million years ago. *Nature* 384(6604):55–59
- Mojzsis SJ, Harrison TM, Pidgeon RT (2001) Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago. *Nature* 409:178–181
- Mojzsis SJ, Coath CD, Greenwood JP, McKeegan KD, Harrison TM (2003) Mass-independent isotope effects in Archean (2.5 to 3.8 Ga) sedimentary sulfides determined by ion microprobe analysis. *Geochim Cosmochim Acta* 67(9):1635–1658
- Mulkidjanian AY, Galperin MY, Koonin EV (2009) Co-evolution of primordial membranes and membrane proteins. *Trends Biochem Sci* 34(4):206–215
- Nakamura R, Takashima T, Kato S, Takai K, Yamamoto M, Hashimoto K (2010) Electrical current generation across a black smoker chimney. *Angew Chem Int Ed* 49(42):7692–7694
- Narayanan SR, Haines B, Soler J, Valdez TI (2011) Electrochemical conversion of carbon dioxide to formate in alkaline polymer electrolyte membrane cells. *J Electrochem Soc* 158:A167–A173
- Nelson BE, Ford EB, Wright JT, Fischer DA, von Braun K, Howard AW, Payne MJ, Dindar S (2014) The 55 Cancri planetary system: fully self-consistent N-body constraints and a dynamical analysis. *Mon Not R Astron Soc* 441(1):442–451
- Nitschke W, Russell MJ (2010) Just like the universe the emergence of life had high enthalpy and low entropy beginnings. *Journal of Cosmology* 10:3200–3216
- Nitschke W, Russell MJ (2013) Beating the acetyl coenzyme-a pathway to the origin of life. *Phil. Trans. R. Soc. Lond. B. Biol. Sci.* 368:20120. doi:10.1098/rstb.2012.0258
- Nitschke W, McGlynn SE, Milner-White EJ, Russell MJ (2013) On the antiquity of metalloenzymes and their substrates in bioenergetics. *Biochim. Biophys. Acta, Bioenergetics* 1827:871–881
- Novikov Y, Copley SD (2013) Reactivity landscape of pyruvate under simulated hydrothermal vent conditions. *Proc Natl Acad Sci U S A* 110:13283–13288

- Nutman AP, Friend CRL, Paxton S (2009) Detrital zircon sedimentary provenance ages for the Eoarchaean Isua supracrustal belt southern West Greenland: juxtaposition of a ca. 3700 Ma juvenile arc assemblage against an older complex with 3920–3800 Ma components. *Precambrian Res* 172:212–233
- Nutman AP, Friend CR, Bennett VC, Wright D, Norman MD (2010) 3700 Ma pre-metamorphic dolomite formed by microbial mediation in the Isua supracrustal belt (W. Greenland): simple evidence for early life? *Precambrian Res* 183(4):725–737
- Ohtsuki K, Ida S (1998) Planetary rotation by accretion of planetesimals with nonuniform spatial distribution formed by the planet's gravitational perturbation. *Icarus* 131(2):393–420
- Papineau D, Mojzsis SJ (2006) Mass-independent fractionation of sulfur isotopes in sulfides from the pre-3770 Ma Isua Supracrustal Belt, West Greenland. *Geobiology* 4(4):227–238
- Papineau DMSJ, Mojzsis SJ, Karhu JA, Marty B (2005) Nitrogen isotopic composition of ammoniated phyllosilicates: case studies from Precambrian metamorphosed sedimentary rocks. *Chem Geol* 216(1):37–58
- Pepe F, Cameron AC, Latham DW, Molinari E, Udry S, Bonomo AS, Buchhave LA, Charbonneau D, Cosentino R, Dressing CD, Dumusque X (2013) An earth-sized planet with an earth-like density. *Nature* 503(7476):377–380
- Pizzarello S, Cronin JR (2000) Non-racemic amino acids in the Murray and Murchison meteorites. *Geochim Cosmochim Acta* 64(2):329–338
- Prigogine I (1977) *Self-Organization in Nonequilibrium Systems: From Dissipative Structures to Order through Fluctuations*, 1 edn. Wiley, New York
- Rickard D, Butler IB, Oldroyd A (2001) A novel iron sulphide mineral switch and its implications for Earth and planetary science. *Earth Planet Sci Lett* 189:85–91
- Rosing MT (1999)  $^{13}\text{C}$ -depleted carbon microparticles in >3700-Ma Sea-floor sedimentary rocks from West Greenland. *Science* 283:674–676
- Rosing MT, Bird DK, Sleep NH, Glassley W, Albarede F (2006) The rise of continents—an essay on the geologic consequences of photosynthesis. *Palaeogeogr Palaeoclimatol Palaeoecol* 232(2):99–113
- Roth AS, Bourdon B, Mojzsis SJ, Touboul M, Sprung P, Guitreau M, Blichert-Toft J (2013) Inherited  $^{142}\text{Nd}$  anomalies in Eoarchean protoliths. *Earth Planet Sci Lett* 361:50–57
- Rubie DC, Frost DJ, Mann U, Asahara Y, Nimmo F, Tsuno K, Kegler P, Holzheid A, Palme H (2011) Heterogeneous accretion, composition and core–mantle differentiation of the earth. *Earth Planet Sci Lett* 301(1):31–42
- Russell MJ, Hall AJ (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J Geol Soc Lond* 154:377–402
- Russell MJ, Daniel RM, Hall AJ, Sherringham J (1994) A hydrothermally precipitated catalytic iron sulphide membrane as a first step toward life. *J Mol Evol* 39:231–243
- Russell MJ, Hall AJ, Mellersh AR (2003) On the dissipation of thermal and chemical energies on the early earth: the onsets of hydrothermal convection, chemiosmosis, genetically regulated metabolism and oxygenic photosynthesis. In: "natural and laboratory-simulated thermal geochemical processes" R, Ikn edn. Kluwer Academic Publishers pp, Dordrecht, pp. 325–388
- Russell MJ, Nitschke W, Branscomb E (2013) The inevitable journey to being. *Phil Trans R Soc Lond B Biol Sci* 368:20120254. doi:10.1098/rstb.2012.0254
- Russell MJ, Barge LM, Bhartia R, Bocanegra D, Bracher PJ, Branscomb E, Kidd R, McGlynn SE, Meier DH, Nitschke W, Shibuya T, Vance S, White L, Kanik I (2014) The drive to life on wet and icy worlds. *Astrobiology* 14:308–343. doi:10.1089/ast.2013.1110
- Sagan C, Reid Thompson W, Carlson R, Gurnett D, Hord C (1993) A search for life on earth from the Galileo spacecraft. *Nature* 365:715–721
- Schidlowski M (1988) A 3800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* 333: 313–318
- Schoepp-Cothenet B, van Lis R, Philippot P, Magalon A, Russell MJ, Nitschke W (2012) The ineluctable requirement for the trans-iron elements molybdenum and/or tungsten in the origin of life. *Nat Sci Rep*, 2: 263. doi:10.1038/srep00263
- Schoepp-Cothenet B, van Lis R, Atteia A, Baymann F, Capowicz L, Ducluzeau AL, Duval S, ten Brink F, Russell MJ, Nitschke W (2013) On the universal core of bioenergetics. *Biochim Biophys Acta Bioenergetics* 1827(2):79–93
- Schrödinger, E. (1967) *What Is Life?* [With Forward by Penrose] Cambridge Univ Press.
- Schwartzman, D. and Lineweaver, C. (2005) Temperature, Biogenesis, and Biospheric Self-Organization. Chapter 16 in *Non-equilibrium Thermodynamics and the Production of Entropy*, Kleidon, A., and Lorenz, R. D. (Eds.). *Non-equilibrium thermodynamics and the production of entropy: life, earth, and beyond*. Springer Science & Business Media. 207–221.
- Shock EL (1992) Chemical environments of submarine hydrothermal systems. *Orig Life Evol Biosph* 22:67–107
- Simoncini E, Virgo N, Kleidon A (2013) Quantifying drivers of chemical disequilibrium: theory and application to methane in the Earth's atmosphere. *Earth System Dynamics* 4:1–15

- Simoncini, E., Grassi, T., Brucato, J. R. (2015) Disequilibrium in planetary atmospheres: a first calculation for Earth using KROME, submitted to OLEB.
- Sleep NH, Bird DK, Pope E (2012) Paleontology of Earth's mantle. *Annu Rev Earth Planet Sci* 40:277–300
- Sojo V, Herschy B, Whicher A, Camprubi E, Lane N (2016) The origin of life in alkaline hydrothermal vents. *Astrobiology* 16(2):181–197
- Szent-Györgyi A (1979) The living state and cancer, IN: Submolecular biology and cancer. In: *Ciba Foundation Symposium* 67. Excerpta Medica pp, New York, pp. 3–18
- Trail D, Watson EB, Tailby ND (2011) The oxidation state of hadean magmas and implications for early Earth's atmosphere. *Nature* 480:79–82
- Trail D, Watson EB, Tailby ND (2012) Ce and Eu anomalies in zircon as proxies for the oxidation state of magmas. *Geochim Cosmochim Acta* 97:70–87
- Trolard F, Bourrié G (2012) Fougerite a natural layered double hydroxide in gley soil: habitus, structure, and some properties. In: *Clay minerals in nature: their characterization, modification and application*, edited by M. Valaskova and G.S. Martynkova, InTech, Rijeka, Croatia, pp. 171–188
- Turner JS (1979) Buoyancy effects in fluids. Cambridge University Press
- Ueno Y, Yurimoto H, Yoshioka H, Komiya T, Maruyama S (2002) Ion microprobe analysis of graphite from ca. 3.8 Ga metasediments, Isua supracrustal belt, West Greenland: relationship between metamorphism and carbon isotopic composition. *Geochim Cosmochim Acta* 66(7):1257–1268
- Underwood DR, Jones BW, Sleep PN (2003) The evolution of habitable zones during stellar lifetimes and its implications on the search for extraterrestrial life. *Int J Astrobiol* 2:289
- Vance S, Harmmeijer J, Kimura J, Hussmann H, Demartin B, Brown JM (2007) Hydrothermal systems in small ocean planets. *Astrobiology* 7(6):987–1005
- Vladilo G, Murante G, Silva L, Provenzale A, Ferri G, Ragazzini G (2013) The habitable zone of earth-like planets with different levels of atmospheric pressure. *ApJ* 767(1):65
- Wade J, Wood BJ (2005) Core formation and the oxidation state of the Earth. *Earth Planet Sci Lett* 236(1-2):78–95
- Wald G (1962) Life in the second and third periods; or why phosphorous and Sulphur for high energy bonds? In: Kasha M, Pullman B (eds) *Horizons in biochemistry*. Academic Press, New York, pp. 127–141
- Wang W, Song Y, Wang X, Yang Y, Liu X (2015) Alpha-Oxo Acids Assisted Transformation of FeS to Fe<sub>3</sub>S<sub>4</sub> at Low Temperature: Implications for Abiotic, Biotic, and Prebiotic Mineralization. *Astrobiology* 15(12): 1043–1051
- Webster CR, Mahaffy PR, Atreya SK, Flesch GJ, Mischna MA, Meslin PY, Battalio M (2014) Mars methane detection and variability at gale crater. *Science* 1261713
- Westheimer FH (1987) Why nature chose phosphates. *Science* 235(4793):1173–1178
- Wetherill GW (1985) Asteroidal source of ordinary chondrites. *Meteoritics* 20:1–22
- White LM, Bhartia R, Stucky GD, Kanik I, Russell MJ (2015) Mackinawite and greigite in ancient alkaline hydrothermal chimneys: identifying potential key catalysts for emergent life. *Earth Planet Sci Lett* 430:105–114
- Wicken JS (1987) *Evolution, Thermodynamics and Information* Oxford University Press
- Wilde, S.A., Valley, J.W., Peck, W.H., and Graham, C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 gyr ago: *Nature*, v. 409, p. 175–178.
- Williams RJP (1961) Functions of chains of catalysts. *J Theor Biol* 1:1–13
- Williams RJP (1965) Electron migration in iron compounds. In: San Pietro A (ed) *Non-Heme iron proteins: role in energy conversion*, The Antioch Press. Yellow Springs, Ohio, pp. 7–22
- Wood BJ, Bryndzia LT, Johnson KE (1990) Mantle oxidation state and its relation to tectonic environment and fluid speciation. *Science* 248:337–345
- Wood BJ, Walter MJ, Wade J (2006) Accretion of the earth and segregation of its core. *Nature* 441:825–833
- Xing GF, Wang XL, Wan Y, Chen ZH, Jiang Y, Kitajima K, Ushikubo T, Gopon P (2014) Diversity in early crustal evolution: 4100 [emsp14] Ma zircons in the Cathaysia block of southern China. *Scientific Reports* 4
- Yamaguchi A, Inuzuka R, Takashima T, Hayashi T, Hashimoto K, Nakamura R (2014a) Regulating proton-coupled electron transfer for efficient water splitting by manganese oxides at neutral pH *Nature communications*:5
- Yamaguchi A, Yamamoto M, Takai K, Ishii T, Hashimoto K, Nakamura R (2014b) Electrochemical CO<sub>2</sub> reduction by Ni-containing iron sulfides: how is CO<sub>2</sub> electrochemically reduced at bisulfide-bearing deep-sea hydrothermal precipitates? *Electrochim Acta* 141(20):311–318. doi:10.1016/j.electacta.2014.07.078
- Yung YL, McElroy MB (1979) Fixation of nitrogen in the prebiotic atmosphere. *Science* 203:1002–1004
- Zhang C, Dehoff K, Hess N, Oostrom M, Wietsma TW, Valocchi AJ, Fouke BW, Werth CJ (2010) Pore-Scale Study of Transverse Mixing Induced CaCO<sub>3</sub> Precipitation and Permeability Reduction in a Model Subsurface Sedimentary System. *Environ Sci Technol* 44(20):7833–7838
- Zsom A, Seager S, De Wit J (2013) Toward the minimum inner edge distance of the habitable zone. *Astrophys J* 778:109