ELSI 4th international symposium

"Three experiments in biological origins: early Earth, Venus and Mars"

- Abstracts for oral presentaions -

Introductory day (Tue 12th)	
14:00 - 14:15	**Kei Hirose, George Helffrich (ELSI, Japan)** Welcome and Introduction
14:15 - 15:00	**Shigeru Ida (ELSI, Japan)** Introduction to day 1 topics: Planet formation and volatile delivery to terrestrial planets (p. 3)
15:00 - 15:45	**Dave Stevenson (Caltech, USA)** Introduction to day 2 topics: The Nature of Planets (p. 4)
15:45 - 16:30	**Norm Sleep (Stanford, USA)** Introduction to day 3 topics: Disequilibria and the requirements for (successful) pre-biotic chemistry (p. 5)
16:30 - 16:35	Instructions to poster presenters
16:35 - 18:30	*Coffee and poster viewing*
19:00 – 20:30	Public lecture: *"Does water define a planet's habitability?"* **Victoria Meadows (University of Washington/NASA Astrobiology Institute)** **Tomohiro Usui (Tokyo Tech)**
Day 1 (Wed 13th) - The Formation of Venus, Earth and Mars	
09:00 - 09:40	**Colette Salyk (Vassar College, USA)** Chemistry in terrestrial planet forming regions of protoplanetary disks (p. 6)
09:40 - 10:20	**Hal Levison (SwRI, USA)** The Formation of Terrestrial Planets from the Direct Accretion of Pebbles (p. 7)
10:20 - 10:50	*Coffee*
10:50 - 11:30	**Francis Albarede (ENS Lyon, France)** Volatility scale, gravitational escape, and abundance of water and volatiles in the Moon and Earth (p. 8)
11:30 - 12:00	**Q&A and discussion** Discussion leaders: Shigeru Ida
12:00 - 13:30	*Lunch*
13:30 - 14:10	**Bernard Marty (CRPG Nancy, France)** Origins and timing of volatile elements on Earth and Mars in view of the results of the Rosetta mission (p. 10)
14:10 - 14:50	**Hidenori Genda (ELSI, Japan)** Giant impacts and early evolution of terrestrial planets (p. 11)
14:50 - 15:20	*Coffee*
15:20 - 16:00	**Kosuke Kurosawa (Chiba Tech, Japan)** An atmospheric response against from impact bombardments on Earth and Venus: The role of impact ejecta (p. 12)
16:00 - 16:40	**Patrick McGovern (LPI, USA)** The Martian Crustal Dichotomy: an Ancient and Fundamental Feature (p. 13)
16:40 - 17:10	**Q&A and discussion** Discussion leaders: Steve Mojzsis
17:10 - 18:30	*Poster viewing*

Day 2 (Thu 14th) - Planets as Integrated Systems	
09:00 - 09:40	**Victoria Meadows (U Washington, USA)** Exoplanets: A New Era of Comparative Planetology (p. 14)
09:40 - 10:20	**Yuk Yung (Caltech, USA)** Chemistry of the Atmospheres of Planets and Exoplanets (p. 15)
10:20 - 10:50	*Coffee*
10:50 - 11:30	**Caroline Dorn (U Bern, Switzerland)** Interiors of low-mass exoplanets: what can we learn from observations? (p. 16)
11:30 - 12:00	**Q&A and discussion** Discussion leaders: Dave Stevenson
12:00 - 13:30	*Lunch*
13:30 - 14:10	**David Catling (U Washington, USA)** Planetary atmospheres, biospheres, and chemical disequilibrium (p. 17)
14:10 - 14:50	**Axel Kleidon (MPI Jena, Germany)** What can thermodynamics tell us about the functioning of the Earth system, its habitability, and its evolution? (p. 18)
14:50 - 15:20	*Coffee*
15:20 - 16:00	**Roger Buick (U Washington, USA)** Evolution of Earth's biogeochemical nitrogen cycle: an example of an integrated system influencing planetary habitability (p. 19)
16:00 - 17:15	**Q&A and discussion**
17:15 - 18:30	*Poster viewing*

FROM 19:00 — SYMPOSIUM BANQUET HELD IN ELSI-1 BUILDING, 2ND FLOOR

Day 3 (Fri 15th) - Starting Conditions and Requirements for Prebiotic Chemistry	
09:00 - 09:40	**Steve Vance (JPL, USA)** Atmosphere disequilibration in different planetary contexts (p. 20)
09:40 - 10:20	**Yuichiro Ueno (ELSI, Japan)** Disequilibrium of prebiotic atmosphere: C-H-O systems and role of water (p. 21)
10:20 - 10:50	*Coffee*
10:50 - 11:30	**Everett Shock (ASU, USA)** Geologic Sources of Chemical Disequilibria on Terrestrial Planets (p. 22)
11:30 - 12:00	**Q&A and discussion** Discussion leaders: Jim Cleaves
12:00 - 13:30	*Lunch*
13:30 - 14:10	**Wolfgang Nitschke (IMM/BIP, France)** From thermodynamic disequilibria in alkaline hydrothermal vents to dissipative structures giving birth to life (p. 23)
14:10 - 14:50	**Ken Takai (JAMSTEC, Japan)** Prebiotic chemistry for energy and central metabolisms in early ocean of Earth (and Mars) (p. 24)
14:50 - 15:20	*Coffee*
15:20 - 18:00	**Wrapup discussion "Why?"** Discussion leaders: Eric Smith & Steve Mojzsis

Day 0 – Introductory day

Planet formation and volatile delivery to terrestrial planets

Shigeru Ida (ELSI/Titech)

Observations show rich diversity and surprisingly high occurrence rate of exoplanetary systems. It is also expected that earth-size planets commonly exist in habitable zones of exoplanetary systems, in which liquid water can exist on planetary surface. However, protoplanetary disks where planets are formed have too low gas density for H2O ice grains to condense in the habitable zones; the icy grains can condense in outer colder disk regions. Note that other important elements for life, C and N, condense in further colder regions. Thus, for planets in habitable zones to indeed harbor life, H2O, C and N must be delivered to the planets from outer disk regions by some mechanism. I will discuss scattering of icy planetesimals (1-100 km size bodies) by giant planets, orbital migration of icy planets due to planet-disk gravitational interactions, and orbital migration of pebbles (1-100 cm size bodies) due to gas drag, as possible mechanisms to deliver H2O, C and N.

The Nature of Planets

Dave Stevenson (Caltech)

Our own solar system has diverse planets but exoplanetary observations have taught us that the richness of planets is far greater than our local sample. This should not surprise us since the nature of a planet depends on how it was built and the materials available, and there is surely no single, universal story of planet formation even though there is universality of the general principles of physics and chemistry. Chance (the stochastic nature of the process) also matters. Planets have interacting components: We must not think of the atmosphere (or ocean) as being isolated from the interior. Can we figure out the planet by looking at the atmosphere? It may be possible; to some extent this is what we do locally. It is a major challenge of exoplanetary studies. But at this early stage in our understanding of exoplanets, we have at most four things to work with: Location (orbit of the planet and nature of the central star together with its cosmochemical make-up, e.g. metallicity), planet mass (often from Doppler, but greatly augmented by TTV), planet radius (from transit), and (in a few cases) something about the nature of the atmosphere or clouds. Location is important and has often been emphasized because of the concept of a "habitable zone" (though I will argue that this concept is partly anthropocentric and possibly unimaginative). Certainly, overall composition matters, but also the oxygen fugacity (crucial in understanding the speciation of carbon, for example). Mass and radius have enabled us to recognize some compositional systematics, though in many cases it is ambiguous because capture of a hydrogen atmosphere substantially contributes to the radius but not the mass. This is testament to timing (in our solar system, the terrestrial planets approached their final masses after the nebula had departed). Other kinds of information (e.g., magnetic fields, existence of exomoons or rings, direct imaging, detailed spectroscopy) will eventually help.

Disequilibria and the requirements for (successful) pre-biotic chemistry

Norm Sleep (Stanford)

Life gathers energy and materials from its environment, reproduces with some fidelity, and then disperses. There is expectation that tracks of early energy sources exist in extant life. Threshold theory provides a relevant testable framework. Nascent life competes with nonlife. An organism became quite abundant once it passed a threshold in gathering, reproduction, and dispersal. There is likely a clean origin of life and a clean bottleneck associated with major biological innovations. With regard to geology, the presence of various rock types, circulating hydrous fluids, solar radiation, asteroid impacts, and the hydrologic cycle make disequilibria inevitable on Mars, Ceres, and the early Earth. In all cases, one must vet putative prebiotic environments, as life as greatly modified the crust and even the mantle of the Earth. One approach is to work backward from energy sources for extant life. Carbon dioxide and dihydrogen and carbon monoxide are chemical sources. Extant life harvests photoelectric currents. Other energy sources do not have uses by extant organisms. Osmotrophic life might live from chemical (including pH) gradients. Life might benefit from turning olivine into serpentine. Life likely evolved anoxygenic photosynthesis by 4.1 Ga before much geological record. It is thus helpful to work forward from conditions after the moon-forming impact. Seeding terrestrial life from Mars or Ceres is more testable than origin on the Earth because the geological record persists.

Day 1 - The Formation of Venus, Earth and Mars

Chemistry in terrestrial planet forming regions of protoplanetary disks

Collete Salyk (Vassar College, USA)

In this talk, I will present an astronomer's perspective on our current understanding of disk chemistry in terrestrial planet-forming regions, focussing on the protoplanetary disk phase, which encompasses the first few Myr of planet formation. I'll begin by discussing the challenges associated with these observations, followed by a description of the cutting-edge techniques that allow us to overcome some of these challenges. Then, I will focus on a few observational results (and works in progress) most relevant for terrestrial planet diversity. In particular, I will discuss observations of bulk molecular chemistry in terrestrial planet forming regions, evidence for the condensation sequence, and attempts to constrain rates of radial mixing.

The Formation of Terrestrial Planets from the Direct Accretion of Pebbles

Hal Levison (SWRI-Boulder)

Building the terrestrial planets has been a challenge for planet formation models. In particular, classical theories have been unable to reproduce the small mass of Mars and instead predict that a planet near 1.5 AU should roughly be the same mass as the Earth (Chambers 2001, Icarus 152,205). Recently, a new model, known as 'viscously stirred pebble accretion' (VSPA), has been developed that can explain the formation of the gas giants (Levison+ 2015, Nature, 524, 322). This model envisions that the cores of the giant planets formed from 100 to 1000 km bodies that directly accreted a population of pebbles (Lambrechts & Johansen 2012, A&A 544, A32) - centimeter- to meter-sized objects that slowly grew in the protoplanetary disk. Here, I review the development of terrestrial planet models and describe a new set of calculations (Levison+ 2015, PNAS 112, 14180) that apply VSPA to the terrestrial planet region. I will show that these VSPA can reproduce the basic structure of the inner Solar System, including a small Mars and a low-mass asteroid belt. In particular, for an initial population of planetesimals with sizes similar to those of the main belt asteroids, VSPA becomes inefficient beyond ~1.5 AU. As a result, Mars's growth is stunted and nothing large in the asteroid belt can accumulate.

Volatility scale, gravitational escape, and abundance of water and volatiles in the Moon and Earth

Francis Albarède (ENS-Lyon)

Because the balance of melting and vaporization during impact biases estimates of how much late veneer was added to the Earth, currently estimated at 0.5 percent from PGE abundances in the terrestrial mantle, the amount of volatile-rich material added to the Earth by late accretion is underestimated by up to a factor of eight. Increasing the proportion of late veneer to two percent to account for the overlooked segregation metallic fraction of impactors to the terrestrial core, could bring the amount of water in the mantle well above 1000 ppm and make the age of the Giant Lunar Impact calculated using the priciples outled by Jacobson et al. (Nature Geosciences 2014) as early as 30 My after the formation of the formation of the Solar System.

In a series of landmark papers, Hauri and Saal (Nature and Science, 2008-2013) presented data on water concentrations measured in melt inclusions in olivine from the volcaniclastic 'orange' and 'green' glasses that compare with contents in terrestrial MORB. A number of moderately volatile elements such as F, Cl, and S have been outgassed from lunar basalts, but this observation is not in itself evidence that water was present in the first place. So far no conclusive evidence has been found that other types of lunar basalts had ever contained such high water contents. Whether high water contents reflect the processes associated with volcaniclastic glass emission rather than being an indication that the lunar mantle is wet is therefore a valid question. Comparing elemental abundances in the Moon and the Earth requires one to address the relative importance of gravitational loss and intrinsic volatility, which is the topic of the present talk. Gravitational loss should strongly fractionate elements with comparable chemical properties and different atomic masses, typically halogens and alkali elements, among themselves, which is not what current compositional models of the Moon show. The proto-lunar disk lacked hydrogen, which makes significant hydrodynamic entrainment unlikely. Given the very fast accretion of the Moon, Jean's loss from the exobase, which Ward (ApJ 2012) places at several thousands of kilomers above the lunar disk equatorial plane must have remained a minor phenomenon. The pattern based on Albarede et al.'s (MAPS, 2014) bond-energy scale is smooth pattern for both the Moon and the Earth. What makes the latter scale useful is the possibility of inter/extrapolating the abundance of a particular element from those of neighboring elements. This plot predicts that the abundance of water in the Moon is in the sub-ppm to the ppm range, which is confirmed by the actual H_2O/Ce ratios measured in non pyroclastic glasses by Chen et al. (EPSL, 2015). The observed level of depletion of moderately volatile elements in the Moon with respect to BSE such a F and Rb (1/10), Zn and I (1/100), makes the nearly terrestrial H abundance postulated for the Moon unlikely. The lingering puzzle is why Earth and Moon received such different volatile endowments. Embedded in this question are the modes and extent of late veneer delivery and the age of the lunar impact.

Origins and timing of volatile elements on earth and Mars in view of the results of the Rosetta mission

Bernard Marty (U. Lorraine/CNRS-Nancy)

Recent measurements of the volatile composition of the coma of Comet 67P/Churyumov-Gerasimenko (hereafter 67P) allow constraints to be set on the origin of volatile elements (water, carbon, nitrogen, noble gases) on Mars and Earth. Analyses by the ROSINA mass spectrometry system onboard the Rosetta spacecraft indicate that 67P ice has a D/H ratio three times that of the ocean value and contains significant amounts of N2, CO, CO2, and importantly, argon. From mass balance calculations, and provided that 67P is representative of the cometary ice reservoir, we conclude that the contribution of cometary volatiles to the Earth's inventory was minor for water (≤ 1%), carbon (≤ 1%), and nitrogen species (a few % at most). However, cometary contributions to the terrestrial atmosphere may have been significant for the noble gases. They could have taken place towards the end of the main building stages of the Earth, after the Moon-forming impact and during either a late veneer episode or, more probably, the Terrestrial Late Heavy Bombardment around 4.0-3.8 billion years (Ga) ago. Contributions from the outer solar system via cometary bodies could account for the dichotomy of the noble gas isotope compositions, in particular xenon, between the mantle and the atmosphere. A mass balance based on 36Ar and organics suggests that the amount of prebiotic material delivered by comets could have been quite considerable – equivalent to the present-day mass of the biosphere. On Mars, several of the isotopic signatures of surface volatiles (notably the high D/H ratios) are clearly indicative of atmospheric escape processes. Nevertheless, we suggest that cometary contributions after the major atmospheric escape events, e.g., during a Martian Late Heavy Bombardment towards the end of the Noachian era, could account for the Martian elemental C/N/36Ar ratios, solar-like krypton isotope composition and high 15N/14N ratios.

Giant impacts and early evolution of terrestrial planets

Hidenori Genda (ELSI-Titech)

There are wide varieties of physical and chemical states among terrestrial planets in our solar system, such as their sizes, orbits, spin states (also the presence of a moon), the amount and composition of atmosphere, the presence of ocean and life etc. How have these varieties been built? Here we focus on the formation stage of the terrestrial planets. This is because very energetic events occur during the planet formation, such as the collisions among planetesimals and protoplanets. Especially, several tens of Mars-sized protoplanets collide with each other to form the terrestrial planets during the last stage of the terrestrial planet formation. This stage is called the giant impact stage. Such energetic collisions should have a great influence on the various features of the terrestrial planets. For example, giant impacts are responsible for the creation of the Moon and the Martian satellites, and planets with extremely large cores such as Mercury. Giant impacts also affect volatile budget in terrestrial planets, and lead to magma oceans. Cooling of a magma ocean and escape of water vapor results in a difference in water content on Earth and Venus. Even in extrasolar planetary systems, giant impact events are thought to be common.

Recently, tens of warm debris disks around extra-solar-type (FGK) young stars have been observed. These warm debris disks are estimated to be located roughly 1 AU to several AU from the central stars, which corresponds to the terrestrial planet region in the solar system. Based on their stellar ages and locations of the debris disks, the relation between these warm debris disks and giant impact events has recently been discussed.

An atmospheric response against from impact bombardments on Earth and Venus: The role of impact ejecta

Kosuke Kurosawa (U. Chiba)

The fate of surface water on Venus is one of the most curious problems in comparative planetology. The mechanism responsible for causing a water deficit on the Venusian surface must be explored to understand the origin of the significant difference in the surface environment between Earth and Venus. Here I would like to propose a new concept to explain water removal on a steam-covered proto Venus, referred to as "impact-driven planetary desiccation". Since water vapour is photochemically unstable, a steam atmosphere dissociates into hydrogen and oxygen. Then, hydrogen escapes easily into space through hydrodynamic escape. The focus is on the intense impact bombardment during the period of late accretion as generators of a significant amount of reducing agent. The fine-grained ejecta remove the residual oxygen, the counter part of escaped hydrogen, via the oxidation of iron-bearing rocks in a hot atmosphere. Thus, hypervelocity impacts cause net desiccation of the planetary surface. I constructed a stochastic cratering model using a Monte Carlo approach to investigate the cumulative mass of nonoxidized, ejected rocks during the period. Next, an upper limit on the total amount of removed water was calculated using the stoichiometric limit of the oxidation of basaltic rocks. It is shown that a thick steam atmosphere with a mass equivalent to that of the terrestrial oceans would be removed. The cumulative mass of rocky ejecta released into the atmosphere reaches 1 wt% of the host planet, which is 10000 times of the current mass of the Earth's atmosphere. This process does not work efficiently on a ocean-covered proto Earth because the oxidation of impact ejecta would not proceed during its flight. These results suggest that the form of surface water (i.e., ocean versus a steam atmosphere) is an important factor in determining the fate of surface water against to the impact bombardment.

The Martian Crustal Dichotomy: an Ancient and Fundamental Feature

Patrick McGovern (LPI Houston)

The hemispheric dichotomy is a fundamental feature of Mars, expressed by a physiographic and geologic divide between the heavily cratered southern highlands and the relatively smooth plains of the northern lowlands. Joint analysis of gravity and topography data indicates that the dichotomy is rooted in crustal thickness variations, with the crust of the southern highlands thicker than that of the northern lowlands. The observed high density of impact craters and basins in the southern highlands establishes that the crust there formed by the Early Noachian, the oldest characterized epoch of Martian history. While images of the northern lowlands show few impacts, signifying a young surface, laser altimetry reveals a population of buried impact structures spanning a large range of sizes, in numbers that establish northern basement formation as also by the Early Noachian. Thus, the crustal dichotomy is the most ancient preserved structural feature of Mars, and is superposed by still "ancient" but younger impact basins and volcanic provinces. Dichotomy formation mechanisms can be grouped into endogenic (internal) and exogenic (external) categories. Endogenic mechanisms invoke flow of the Martian mantle to deform an initially uniform-thickness crust: for example, overturn of a crystallizing magma ocean or a degree-1 solid-state convection cell might thicken the crust over a singular large downwelling in the south. Alternatively, abundant melting over a degree-1 upwelling could drive volcanic crustal thickening in the south. Exogenic mechanisms produce the dichotomy by removal of material in the north by one or more impacts. The most successful exogenic hypothesis invokes formation of an elliptical Borealis basin via a single oblique impact, creating a basin outline consistent with the observed expression of the dichotomy boundary while avoiding excessive heating and melting that would tend to diminish the crustal thickness variations.

Day 2 - Planets as Integrated Systems

Exoplanets: A New Era of Comparative Planetology

Victoria Meadows (U. Washington)

We now know of over 2000 planets orbiting other stars, and several thousand additional planetary candidates. These discoveries are revolutionizing our understanding of planet formation and evolution, while providing targets for the search for life beyond the Solar System. Exoplanets display a larger diversity of planetary types than those seen in our Solar System – including terrestrials larger than Earth, and low-density, low-mass objects. They are also found in planetary system architectures very different from our own, even for stars similar to our Sun. Solar System and exoplanet studies can be mutually beneficial: known Solar System planetary processes can inform our understanding of exoplanets, while the diversity and broader perspective that exoplanets bring improves our overall understanding of planetary science, with application to Solar System planets. Exoplanets challenge us to consider the outcome of a planet's evolution as an interplay between planet, star, and planetary system - for different planetary compositions, planetary system architectures and host star type. This broader - yet integrated - view is especially relevant to studies of factors that affect planetary habitability. In particular, while M dwarfs are the most likely habitable planet hosts in the Galaxy, the habitability of planets orbiting them will be influenced not only by radiative, but also gravitational effects. In advance of observations to characterize potentially habitable exoplanets, we will discuss how Solar System planets inform the search for life elsewhere, and how we are using the rich heritage of planetary science models to explore the potential diversity of exoplanet environments and star-planet interactions. This research helps us identify the factors and processes that lead to, maintain or preclude habitability - and further illuminates Earth's unique position in our Solar System as the only planet to support a surface biosphere.

Chemistry of the Atmospheres of Planets and Exoplanets

Yuk Yung (Caltech)

We now understand the chemistry of planetary atmospheres in our Solar System ranging from the primitive atmospheres of the giant planets to the highly evolved atmospheres of terrestrial planets and small bodies. Our understanding can be distilled into three important ideas: (1) The stability of planetary atmospheres against escape of their constituents to space, (2) the role of equilibrium chemistry in determining the partitioning of chemical species, and (3) the role of disequilibrium chemistry, which produces drastic departures from equilibrium chemistry. To these three ideas we must also add a fourth: the role of biochemistry at Earth's surface, which makes its atmospheric chemistry unique in the cosmochemical environment. Only in the Earth's atmosphere do strong reducing and oxidizing species coexist to such a degree. Life provides a means for using solar energy to drive chemical reactions that would otherwise not occur; it represents a kind of photochemistry that is special to Earth, at least within the Solar System. It remains to be seen how many worlds like Earth there are beyond the Solar System, especially as we are now exploring the exoplanets using Kepler, TESS, HST, Spitzer, soon to be launched missions such as JWST and WFIRST, and ground-based telescopes. The atmospheres of the Solar System provide a benchmark for studying exoplanets, which in turn serve to test and extend our current understanding of planetary atmospheres. Ultimately, we may be able to answer these profound questions: Are we alone in the universe? What makes a planet habitable? How does life originate? And what is the destiny for life on our own planet?

Interiors of low-mass exoplanets: what can we learn from observations?

Caroline Dorn (U. Bern)

In recent years, the efforts in detecting small mass exoplanets below 10 Earth masses have yielded a diversity of candidates. One key question is whether these exoplanets are Earth-like in terms of structure and dynamics. If plate tectonics, as on Earth, is required to form life is a matter of debate. But since the only planet where life has been identified is distinct from other terrestrial planets by plate tectonics, it is crucial to understand both the possible structures and dynamics of exoplanets in order to determine their habitability. Of course, other types of planets may be able to harbor life.

In order to determine the range of probable interior structures for an exoplanet of general composition, we perform a full probabilistic analysis that formally accounts for data and model uncertainties. Our model assumes a possible four layer structure of iron core, silicate mantle, water ice layer and an atmosphere of H, He, C, and O. Layer thicknesses and compositions of mantle and atmosphere are conditioned to planetary data.

We discuss the application of this method to five exoplanets for which not only mass and radius are known as constraints but also additional abundance proxies. Theoretical studies and empirical evidences from Solar System objects strengthen the possibility that the relative refractory element composition of a planet is directly correlated to its host star composition, namely the ratios of Fe, Mg, and Si. Constrained structural parameters are differently sensitive to our assumptions on these planet bulk ratios. Our ability to constrain interior structure highly depends on data and data uncertainties.

The main focus of this talk is the characterization of exoplanets in terms of interior structure. Dependencies of the tectonic regime (plate tectonics or stagnant lid) are reviewed. To determine the tectonic regime of an exoplanet will be extremely difficult due to severe limitations on constraining key parameters that influence dynamics.

Planetary atmospheres, biospheres, and chemical disequilibrium

David Catling (U. Washington)

The most interesting question about exoplanets is whether any of them are inhabited. Apart from noble gases, Earth's atmosphere is biologically cycled, which has led to the idea of detecting life on exoplanets from atmospheric absorption spectra. Earth's atmosphere is anomalous because major (N2, O2) and minor gases (e.g., CO2, CH4, and N2O) are biogenic; the atmosphere also has much chemical disequilibrium [1]. Of course, all planetary atmospheres are in disequilibrium to some extent because of free energy from insolation, internal heat, or tidal heat. So, whether a biosphere can be inferred from disequilibrium is a question of degree. Certainly, when quantified as the Gibbs energy of an observed atmosphere minus that of all gases reacted to equilibrium, Earth's atmosphere-ocean system has ~20 to 2 million times larger disequilibrium than that of other Solar System atmospheres [2]. But the issue is subtle. First, planetary atmospheres evolve in composition and so must change their disequilibrium with time. Second, the type of biosphere should affect whether there is significant disequilibrium or not. Photosynthesis generates significant disequilibrium whereas simpler chemosynthetic biospheres probably favor atmospheres close to thermodynamic chemical equilibrium. Third, under certain circumstance, untapped chemical disequilibrium in an atmosphere indicates no biosphere rather than life, i.e., a "free lunch" that no one is eating. The presence of relatively abundant CO on Mars is an example. Fourth, several metrics could quantify disequilibrium but they're yet to be fully explored and their comparative merits need evaluation.

[1] Lovelock, J. E. (1975) Thermodynamics and the recognition of alien biospheres. Proc. R. Soc. Lon. B189, 167-181. [2] Krissansen-Totton, J., Bergsman, D. S., Catling, D. C. (2016) On detecting biospheres from chemical thermodynamic disequilibrium in planetary atmospheres, Astrobiology, in press.

What can thermodynamics tell us about the functioning of the Earth system, its habitability, and its evolution?

Axel Kleidon (MPI-Jena)

I present a thermodynamic view of the whole Earth system with the aim to describe the fundamental constraints on its dynamics and magnitudes of processes, its evolution, and to evaluate the role of life in the system. The starting point forms the Carnot limit, which follows directly from the first and second law of thermodynamics. It limits how much of the radiative heating can be converted into mechanical work that drives planetary motion. When this limit is combined with energy balances, it yields a maximum power limit, because a greater heat flux results in a lower temperature difference. When this maximum power limit is applied to present-day conditions, it predicts the spatial and temporal variation of the surface energy balance partitioning as well as its sensitivity to change very well. We can then infer rates of mass cycling from this limit and thus infer magnitude of hydrologic and geochemical cycling. Motion provides the means to exchange the moistened air from places where water evaporates with drier air from where it condenses and it replaces products with reactants where chemical reactions take place. It thus forms an essential process to maintain geochemical cycling in a state of thermodynamic disequilibrium. This mass exchange provides essential resources to and removes waste products of the metabolic reactions of life. We thus have a planetary description from the radiative forcing to motion and mass cycling to biotic activity that places a particular emphasis on transport limitations of biogeochemical transformations that follow from thermodynamic constraints, which can, however, be altered by changing the radiative properties of the planetary system. I discuss how this view of the thermodynamic Earth system can serve as a template to understand other planetary environments, link it to its habitability, and describe how it may help us to better understand planetary evolution.

Evolution of Earth's biogeochemical nitrogen cycle: an example of an integrated system influencing planetary habitability

Roger Buick (U. Washington)

Nitrogen is a major nutrient for all terrestrial life, occurring in catalytic proteins, informational nucleic acids and energetic ATP. Life's distribution, abundance and evolution is thus dependent on the bio-availability of this essential element, but conversely life's evolution has modified the distribution, speciation and abundance of nitrogen. The biogeochemical cycling of nitrogen therefore shows a co-evolutionary relationship with Earth's biosphere and as a result, the nitrogen cycle has changed markedly through time. In the Hadean and Eoarchean, abiotic fixation would have accounted for a very small flux of bio-available nitrogen from the atmosphere, severely limiting the size and diversity of the primordial biosphere. However, efficient biology fixation using Mo-nitrogenase was established by 3.2 Ga in the Mesoarchean, leading to large biomass deposition in marine settings and (possibly) depletion of nitrogen from the atmosphere as a result of enhanced organic burial. During the late Neoarchean in conjunction with the first whiffs of biogenic oxygen to the atmosphere, aerobic nitrogen cycling was temporarily initiated, marked by positive fractionations of nitrogen isotopes indicating active denitrification sending nitrogen gas back to the atmosphere. The Paleoproterozoic "Great Oxidation Event" and subsequent "oxygen overshoot" during the Lomagundi carbon isotopic excursion marked widespread aerobic cycling with vigorous denitrification. Towards the end of the Paleoproterozoic and through the Mesoproterozoic, expanded euxinic (sulfidic) conditions in the oceans during the "boring billion" years of environmental stasis caused spatial perturbations in the nitrogen cycle, with aerobic cycling near-shore but anaerobic fixation-dominated cycling offshore. As sulfide strips dissolved copper from seawater, thus removing the key cofactor for the critical enzyme in the last step of denitrification, a nitrous oxide greenhouse may have been operative at this time. It is not clear when the nitrogen cycling attained its modern fully aerobic aspect, but it may have been as late as the Devonian when the deep oceans may have finally become permanently oxidized. So, the temporal changes in Earth's nitrogen cycle illustrate the reciprocal co-evolution of the planetary physical and biological environment, modulated in particular by the redox state of the oceans and atmosphere.

Day 3 - Starting Conditions and Requirements for Prebiotic Chemistry

Atmosphere disequilibration in different planetary contexts

Steve Vance (JPL-Caltech, EON)

I will discuss the planetary atmosphere as a chemical interface essential for life, and consider whether the icy surface of Jupiter’s moon Europa may perform a similar role to that of Earth’s atmosphere. Radiolysis of Europa’s surface ice produces oxidants at rates that may be compared with those of the Earth system. The high flux of oxidants to Europa's ocean is only useful to life if the rocky interior provides a reliable source of reductants and minerals to keep the engine of life running. I describe models for hydrothermal activity on Europa that suggest that-rock alteration in Europa causes hydrogen fluxes only slightly smaller than Earth's. Europa's ocean may have become reducing for a brief epoch, after a thermal-orbital resonance following accretion, creating an environment that may have favored an independent origin of life. The range of estimated oxidant flux to Europa's ocean is comparable to estimated hydrogen fluxes.

Disequilibrium of prebiotic atmosphere: C-H-O systems and role of water

Yuichiro Ueno (ELSI/Titech)

Redox disequilibrium of Hadean atmosphere is a key to enable the emergence of life on Earth. Simple organic compounds can be synthesized by photochemistry that can initiate prebiotic synthesis of complex organic molecules. In contrast to the other possible sources like Miller-Urey-type lightning and delivery of organics by extraterrestrial impact, UV-driven photochemistry could ceaselessly supply organics everywhere on the surface of the Earth, thus has a potential to sustain further network of reactions in the ocean. Also, photolysis of H2O likely produce redox gradient or disequilibrium at the surface of the ocean or lake. In order to predict the photochemical production qualitatively and quantitatively, we have conducted a series of laboratory experiments of C-H-O system. The results show that the speciation of synthesized compounds may be sensitive to the amount of water. Their production rate depend largely on redox state of the system and actinic flux particularly shorter than 200 nm. These results suggest that not only atmospheric composition but also hydrosphere and its redox state should be the key to control the fate of organic molecules supplied from early atmosphere into hydrosphere.

Geologic Sources of Chemical Disequilibria on Terrestrial Planets

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Processes that combine chemical constituents that are far from equilibrium with each other generate disequilibria. Planetary habitability reflects the supply of oxidation-reduction (redox) disequilibria provided by planetary processes. Volcanism and active tectonics, as well as surface weathering and transport are among the geologic processes on terrestrial planets that generate redox disequilibria. On Earth, mantle convection, subduction, and an active hydrosphere augment the opportunities for the emergence of redox disequilibria that can support microbial ecosystems. At high temperatures and pressures abiotic reactions rates can be fast enough for rapid re-equilibration. Redox reactions have substantial activation energies and are among the first reactions to depart from equilibrium upon cooling, which stifles the dissipation of chemical energy, and opens the door for catalysis. Lifeforms emerge as adaptive catalytic systems challenged at first with beating abiotic catalysts, and ultimately with partitioning the supply of redox disequilibria. Exploration has revealed microbial ecosystems supported by the dissipation of geologically generated redox disequilibria in hydrothermal systems, in deeply buried sediments, and wherever rocks formed at high temperatures and pressures can be chemically weathered. That exploration is unlikely to be complete.

From thermodynamic disequilibria in alkaline hydrothermal vents to dissipative structures giving birth to life

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Life fundamentally is a thermodynamic far-from-equilibrium phenomenon. Combining the analysis of the free-energy-converting mechanisms in extant life ("top-down approach") and the survey of the types of strong thermodynamic disequilibria likely available on the early Earth ("bottom-up approach") points towards alkaline hydrothermal vents as promising hypothetical locales for life's origin. The two major types of thermodynamic disequilibria operating in extant life, that is, redox and pH gradients, are inherent features of these vents. The cascade of order-generating mechanisms from the cosmological level to the nanoscale eventually yielding the dissipative structures generating life in the alkaline hydrothermal vent scenario will be briefly reviewed. The phenomena frustrating thermodynamic equilibration of the redox and pH gradients in alkaline hydrothermal vents will be detailed and likely archetypal free-energy-converting reactions ("engines") inferred from their descendants in extant life. The inorganic metal catalysts playing crucial roles in such reactions in modern life will be used as guides for deducing initial chemical/mineralogical conditions of the alkaline hydrothermal vent setting during life's putative origin. Resulting ramifications for the likelihood of life originating on Earth's sister planets in the solar system will be discussed.

Prebiotic chemistry for energy and central metabolisms in early ocean of Earth (and Mars)

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It has been widely believed that the most ancient ancestral prokaryotes in the Earth would have originated from deep-sea hydrothermal environments. Thus, it also seems the most likely that preceded prebiotic chemical evolution and birth of living forms would have taken place in same or similar hatchery places, deep-sea hydrothermal environments. The building blocks of prebiotic chemistry would be derived from extraterrestrial sources (meteorites and cosmic particles) and/or terrestrial sources (atmospheric generation and crustal hydrothermal circulations) and are mainly CO2, C1-C3 organic acids and hydrocarbons, and NOx and ammonia in the deep-sea hydrothermal environments. How was the living forms created from these very simple building blocks? The key would be directional autocatalytic metabolisms and driven by abiotic energy sources and catalysts. I would like to introduce our scenario that the directional autocatalytic metabolisms would have introduced monotheistic generation of living forms in the Earth and our experimental approaches to this scenario. This scenario could be common in the early Earth, Mars and even Venus due to their similar formation mechanisms.