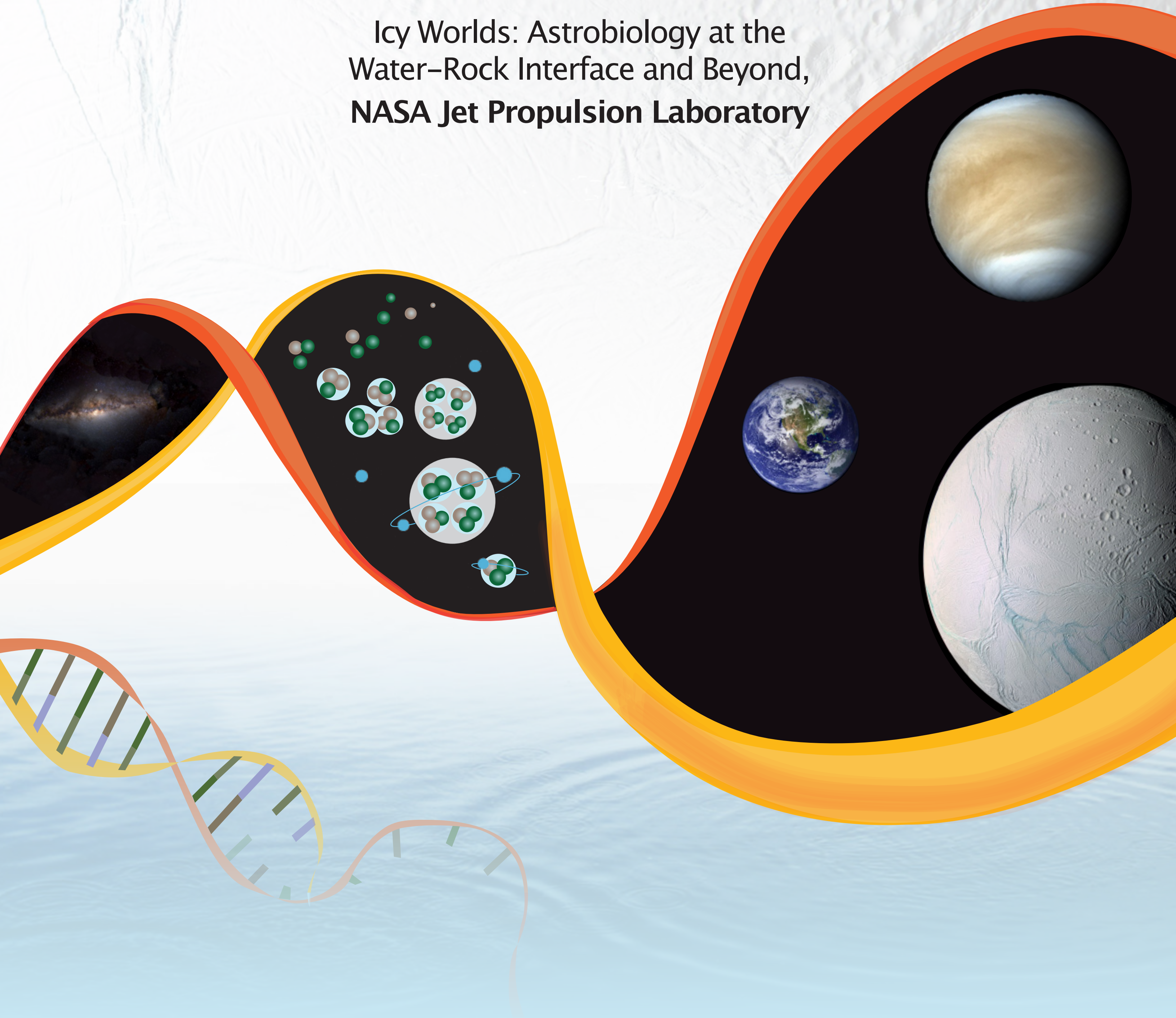
National Aeronautics and Space Administration

NASA Astrobiology Institute
2016 Annual Science Report
Team Report:

Icy Worlds: Astrobiology at the
Water-Rock Interface and Beyond,
NASA Jet Propulsion Laboratory



Icy Worlds: Astrobiology at the Water-Rock Interface and Beyond

Lead Institution:
NASA Jet Propulsion Laboratory

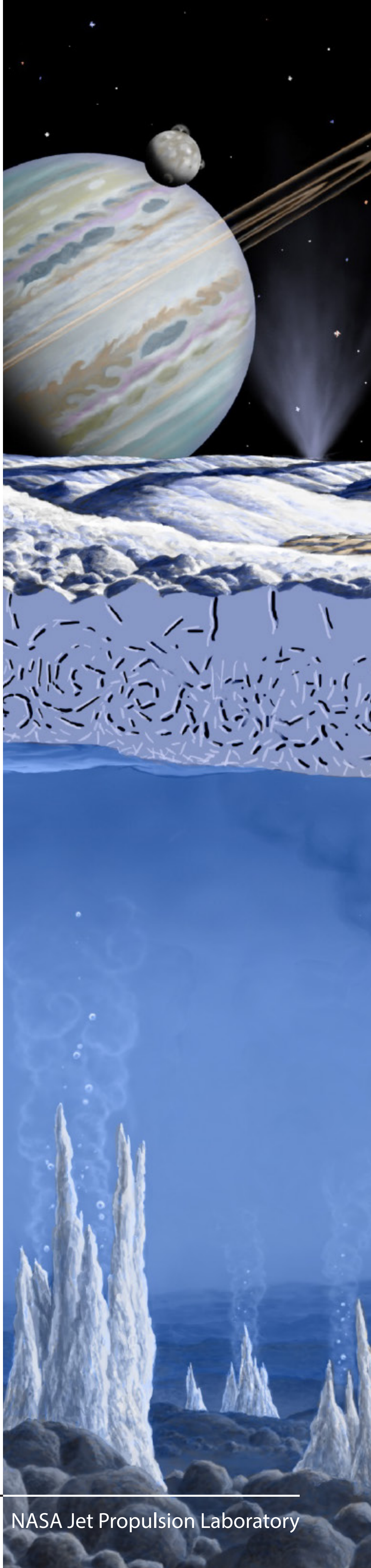
Principal Investigator:
Isik Kanik

Team Overview

Astrobiology at water-rock interfaces found on icy bodies (e.g., Europa, Enceladus and Ganymede) in our Solar System (and beyond) is the unifying theme for the proposed research. In this interdisciplinary research, our Team (The Icy Worlds: Astrobiology at the Water-Rock Interface and Beyond) conducts a highly synergistic combination of experimental, theoretical, and field-based lines of inquiry focused on answering a single compelling question in astrobiology: How can geochemical disequilibria drive the emergence of metabolism and ultimately generate observable signatures on icy worlds? Our Team's primary goal is to answer one of the most fundamental questions in all of astrobiology: What geological and hydrologic factors drive chemical disequilibria at water-rock interfaces on Earth and other worlds? Our research encompasses four investigations (INV's):

- What geological and hydrologic factors drive chemical disequilibria at water-rock interfaces on Earth and other worlds?
- Do geoelectrochemical gradients in hydrothermal chimney systems drive prebiotic redox chemistry towards an emergence of metabolism?
- How, where, and for how long might disequilibria exist in icy worlds, and what does that imply in terms of habitability?
- What can observable surface chemical signatures tell us about the habitability of subsurface oceans?

Team Website: https://icyworlds.jpl.nasa.gov



2016 Executive Summary

In INV 1, we continued to work on hydrothermal serpentinization experiments. We have shown that there was likely an ample nitrate and/or nitrite source in the Hadean ocean to produce sufficient ammonium to aminate carboxylic acids to amino acids in green rust. We formulated what we call the denitrifying methanotrophic acetogenic pathway, a putative pathway that still results in the target molecule for life's beginning, viz., acetate (Fig. 1). We also have shown that this alternative methanotrophic pathway is thermodynamically plausible. We also look into water/mineral interactions to explain the generation of organic molecules, suggesting that green rust comprising a portion of the membrane can be the facilitator of protobiotic reactions. In order to understand how geochemical disequilibria can be converted and drive this type of metabolism, INV 1 researchers teamed up with the members of the University of Illinois Team (NAI-CAN 6: Towards Universal Biology) to explain how "energy coupling" of enzyme-catalyzed biochemical reactions really works.

In year 2, INV 2 has focused on understanding amino acid synthesis and organic/phosphorus retention in hydrothermal minerals on early Earth; electrochemical characterization of simulated hydrothermal systems; and organic-mineral feedback toward emergent metabolism in these systems. The synthesis of amino acids catalyzed by hydrothermal metal sulfides and hydroxides, has been investigated along with the effect of the type of mineral catalyst, the hydrothermal pH/redox gradients, and temperature on the yield (Fig. 2). Results thus far indicate that the amount of reduced vs. oxidized iron in seafloor minerals has a dramatic effect on the rate and concentration of amino acid that is produced, and that synthesis is most efficient near the inside of the chimney. We also studied simulated hydrothermal iron oxyhydroxides and found that they are efficient absorbers of phosphorus species as well as amino acids. However, the presence of phosphorus in the mineral surfaces affects the amount and type of the amino acid(s) that can be simultaneously adsorbed. We also have been working on the development of new methods to characterize redox processes at prebiotic vent systems, and on how the addition of organics changes the structure and growth of hydrothermal chimneys. We have developed custom methods of growing simulated hydrothermal metal sulfide chimneys around electrodes in anoxic systems for *in situ* electrochemical studies to test how organic/mineral feedback can emerge in these systems.

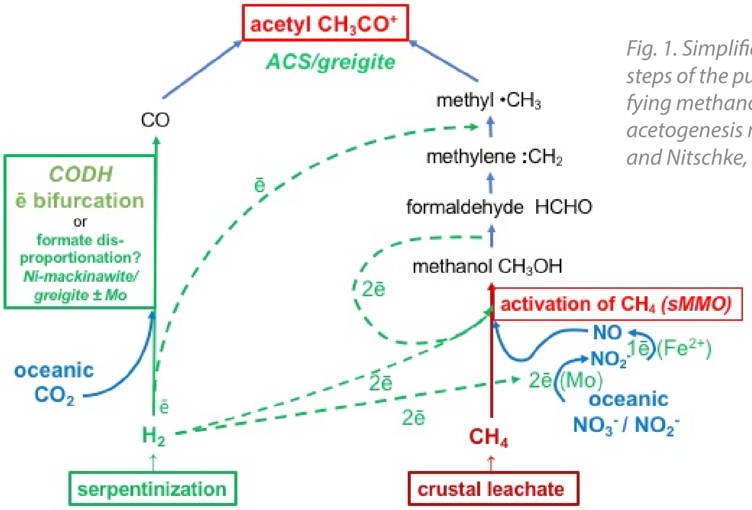


Fig. 1. Simplified reaction steps of the putative denitrifying methanotrophic acetogenesis model (Russell and Nitschke, 2017).

INV 3 focuses on the habitability of icy worlds in the Solar System and beyond. We developed a revolutionary new way to compute thermodynamic properties of fluids under icy satellite pressure and temperatures. The computational framework for fitting thermodynamic data uses b-splines in combination with regularization techniques more typical in geophysics (Brown, in prep). Self-consistent Gibbs-energy based equations of state (EOS) from sound speed, density and heat capacity are yielding unprecedented precision and breadth in P and T needed for modeling conditions in ocean worlds. INV 3 researchers carried out a series of experiments to investigate the phase stability and properties of salty solutions and ices. These studies suggest that salts regulate the transport properties of high pressure ices, but this depends strongly on pressure that varies from relatively small and low-density worlds (e.g., Callisto) to larger hypothetical habitable icy exoplanets (Fig. 3). We published a detailed analysis of the evolution of the Europa system, providing the first computations of the coupled fluxes of hydrogen and oxygen into its ocean. We also developed a simple analytical model to address previously unconsidered ice-ocean interactions in Europa and other satellites. We have continued to develop the interior structure model first conceived for testing hypotheses about the influence of ocean salinity on water-rock interactions and ice dynamics on Ganymede. Co-I Goodman has developed a COMSOL based model describing non-Newtonian viscous relaxation of topography at the ice-water interfaces of icy worlds. This model demonstrates that irregularities at the base of the ice shell flow away in decades to centuries, and predicts that the interface surface should be extremely flat on local scales.

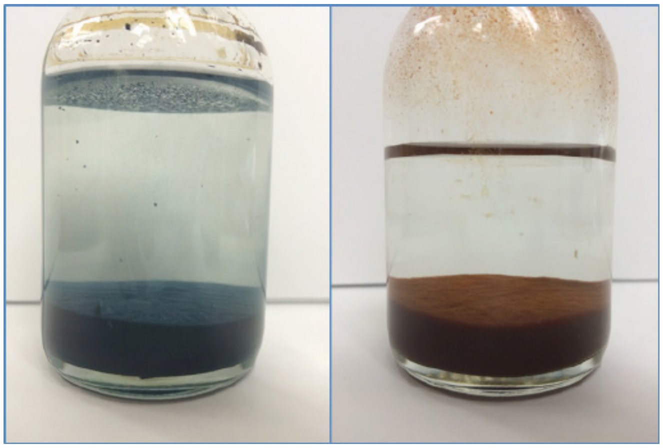


Fig. 2. Reduced (L) and oxidized (R) iron hydroxides freshly precipitated from simulated early Earth seawater and alkaline hydrothermal fluid. These minerals form catalysts that can drive amino acid formation at certain iron oxidation states.

As a part of INV 4 activities in Year 2, we conducted experiments focused on freezing solutions of sodium, magnesium, sulfate and chloride – four commonly suggested major components of Europa's Ocean. We studied frozen chloride-salt brines and sodium-ammonium-chloride-carbonate brines. The chloride salt study involved frozen saturated salt solutions, prepared at temperatures, pressures and radiation conditions (UV) that simulated conditions on the surface of Europa and other airless bodies. Hydration states of various chloride salts as a function of temperature were determined using Raman spectroscopy. Near IR reflectance spectra of identically prepared samples were measured to provide reference spectra of the experimentally identified hydrated salts. Our investigation into freezing of sodium-ammonium-chloride-carbonate brines was conducted in analogy to our initial Europa study, but focused on Ceres. Observations of the Dawn spacecraft have indicated that the bright spots contain large amounts of NH_4Cl or NH_4HCO_3. It has been suggested that these materials originate from freezing of brines originating from a subsurface reservoir. Our study sought to investigate the chemistry of frozen brines containing the ions required to form these minerals.

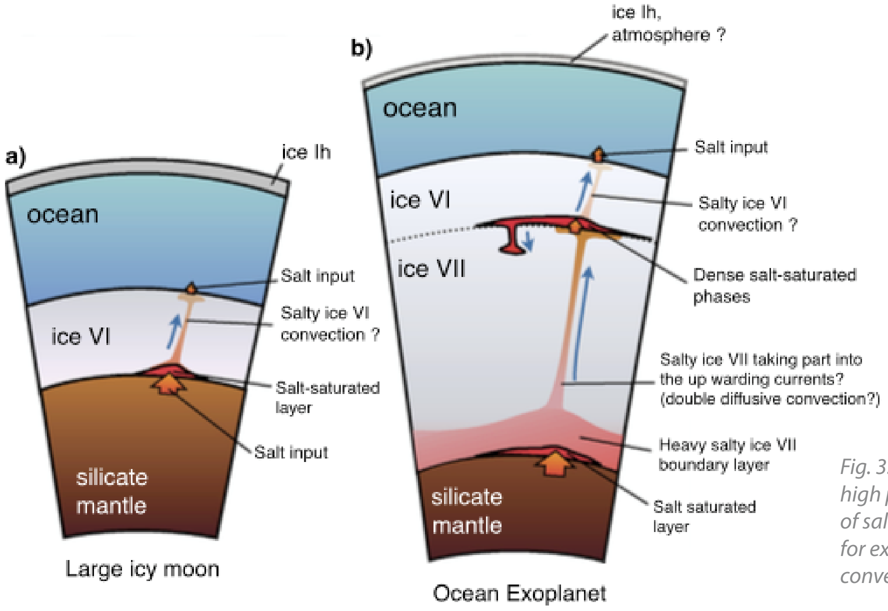


Fig. 3. Experiments reveal the incorporation of ions into high pressure ices. The extent and effect of partitioning of salts into the crystal structure is pressure dependent, for example making ice VI less dense and thus more convective, but densifying ice VII at high pressures.

Project Reports

INV 1 - Geochemical Reactor: Energy Production at Water-Rock Interfaces

INV 1 will aim to answer the Key Question: What geological and hydrologic factors drive chemical disequilibria at water-rock interfaces on Earth and other worlds? In this investigation, we examine water-rock interactions in the lab and in the field, to characterize the geochemical gradients that could be present at water-rock interfaces on Earth and other worlds, taking into account different ocean and crustal chemistries, and to inform INV 2.

Although we have reduced carbon dioxide to formate in a matter of minutes in hydrothermal water/rock (serpentinization) experiments, neither methane nor any organic molecules were produced in the 72 hours of the runs. Yet we know that the eight-electron reduction of NO_3^- to ammonium takes place in less than 200 minutes as green rust oxidizes. Thus at least that other vital element of life, nitrogen, could be fed through reduction directly to the hydrothermal mound forming at a submarine alkaline vent. As support for this nitrogen supply, we have shown that there was likely an ample nitrate and/or nitrite source in the Hadean ocean to produce sufficient ammonium to aminate carboxylic acids to amino acids in green rust (Wong et al., 2017).

However, the failure to reduce CO_2 or HCO_3- to organic molecules beyond formate has forced us to rethink how the first pathway to carbon fixation was channeled and negotiated (Russell and Beckett, 2017). Thus, we formulated what we call the denitrifying methanotrophic acetogenic pathway, a putative pathway that still results in the target molecule for life's beginning, viz., acetate (Russell and Nitschke, 2017). Shibuya et al. (2016) have shown that this alternative methanotrophic pathway is thermodynamically plausible.

Up until now, the most puzzling of all missing links has been that between putative aqueous geochemical/mineralogical interactions at a submarine alkaline vent and the first cell. We have certainly felt uneasy about the formulations of Russell and Martin (2007) that assumed a protocell enveloped in transition metal sulfides as being the first common ancestor. Now we look to these other water/mineral interactions to explain the generation of organic molecules, suggesting that green rust comprising a portion of the membrane can be the facilitator of protobiotic reactions (Russell and Nitschke, 2017). Indeed, we hypothesize that such a ready-made highly-structured mineral vehicle provided – as a memoryful sensor – an entity with the potential to evolve partway toward the Last Universal Common Ancestor (LUCA). Our candidate 'launch' vehicle is a screw-dislocated helicoidal green rust (GR), a double layer hydroxide that grew implosively in a spiral producing successive, though connected, nano-galleries that could accept and react with intercalated anions (Russell and Beckett, 2017) (Fig. 4). At the margins of an alkaline hydrothermal submarine mound, we envision these green rusts contributing to the bafflements that held the bulks of exhaling alkaline hydrothermal fluid and the carbonic ocean at bay. Nitrate and nitrite from the ocean intercalated the GR galleries where they were rapidly reduced to ammonium as the ferrous iron components were oxidized, as shown to be plausible and demonstrated with collaborators (Flores, Barge et al. 2016; Shibuya et al., 2016; Wong et al., 2017)

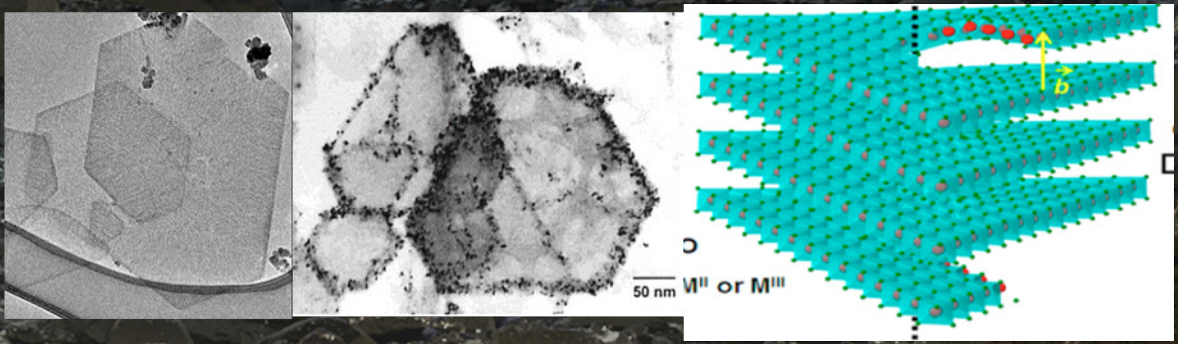


Fig. 4. A natural screw-dislocated helicoidal green rust (left); green rust with adsorbed UO_2 clusters mimicking how phosphate protects the conformation of green rust through redox changes (center); a model of a screw dislocated double layer hydroxide (right).

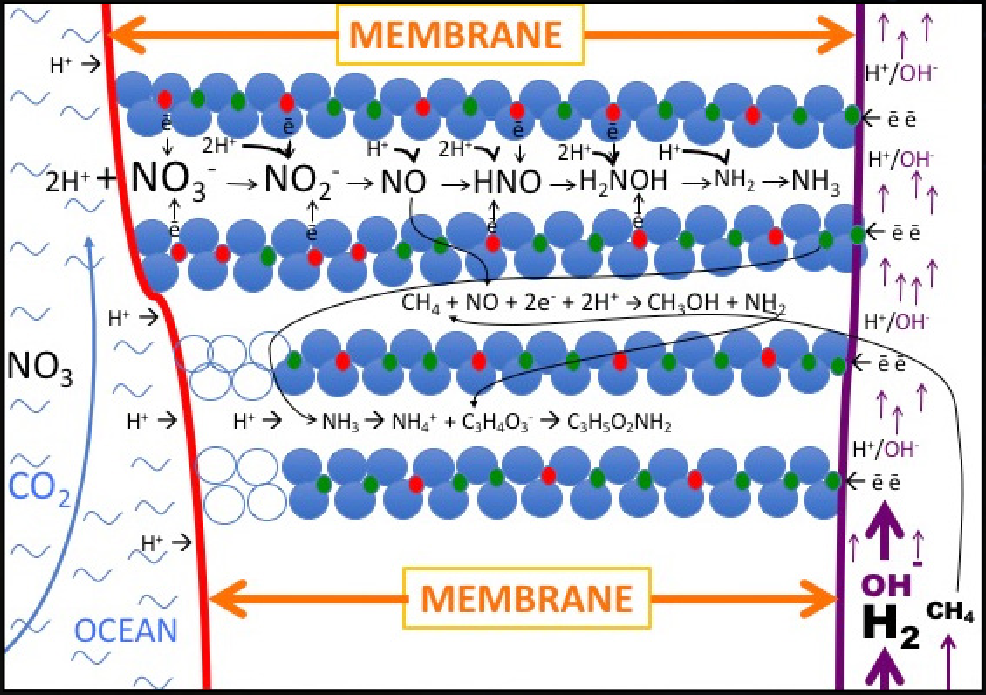


Fig. 5. Model of green rust as a ready-made difunctional enzyme precursor operating across the inorganic membrane to reduce nitrate to aminogen or ammonium between the 'brucite' galleries. At the same time, methane would be converted to a methyl group by NO – a yet to be tested hypothesis. The inorganic membrane, represented in this case by green rust, separates the alkaline hydrothermal solution on the right, from ocean water on the left.

(Fig. 4). In these conditions and at the same time hydrothermal methane may have been converted to a methyl group (Russell and Nitschke, 2017) and electrons derived from hydrothermal hydrogen at contiguous mackinawite [Fe(Ni)S] were conducted along the iron layers to augment the re-reduction of GR and reduce CO_2 to CO and/or formate involving an H-bond network in the interstices of green rust as argued with collaborators (Duval et al., 2016). These protobiotic reactions organized themselves through interactions within this helicoidal GR– a 'multi-functional-protoenzyme' – acted to produce acetate and higher carboxylic acids. The path taken – the one of least resistance – was via denitrifying methanotrophic acetogenesis, terminating at succinate and glyoxylate (Russell and Nitschke, 2017).

In our conception of how information evolved in parallel to proto-metabolism, the oscillating Fe^{2+} and Fe^{3+} sites in GR acted as zeros and ones whereby reactions were sensed from one twin layer to the immediately adjacent layers 'beneath' and 'above', producing feedback and feedforward control processes. Aminations of carboxylic acids to amino acids (Flores, Barge et al. 2016) and condensations of product within the confined galleries followed, which produced peptide nests. These nests could sequester the inorganic elements in protoenzymes in a division of labor, while at the same time generating and exuding enough excess peptide as amyloid to have induced the splitting or division of GR, thus providing the first peptidic membranes encapsulating the newly informed off-spring.

In parallel to this work and in order to understand how geochemical disequilibria can be converted and drive this type of metabolism we are collaborating with the NAI CAN6 University of Illinois Team "Towards Universal Biology". Together we have written what a referee has termed "an impressive *tour de force* through some fundamental aspects of bioenergetics…which clarifies, in a detailed, pedagogically beautiful way, how 'energy coupling' of enzyme-catalyzed biochemical reactions really works. The manuscript (Branscomb, Biancalani, Goldenfeld and Russell, 2017) is a unique, very valuable contribution at the border between physics and biochemistry."

INV 2 - From Geochemistry to Biochemistry

INV 2 focuses on experimentally simulating and characterizing the geological disequilibria and catalytic minerals that may drive the origin of life in hydrothermal systems. For the past year, INV 2 has focused on understanding amino acid synthesis and organic/phosphorus retention in hydrothermal minerals on early Earth; electrochemical characterization of simulated hydrothermal systems; and organic-mineral feedback toward emergent metabolism in these systems.

The synthesis of amino acids catalyzed by hydrothermal metal sulfides and hydroxides is significant for the alkaline hydrothermal origin of life model since it is proposed that green rust can reduce nitrate/nitrite to ammonia, aminating pyruvate to form alanine within the chimney membranes. Our student, Erika Flores' work over the past two years has looked into the conditions required to synthesize amino acids in simulated hydrothermal systems. In particular, she has investigated the effect of the type of mineral catalyst, the hydrothermal pH/redox gradients, and temperature on the yield. Results thus far indicate that the amount of reduced vs. oxidized iron in seafloor minerals has a dramatic effect on the rate and concentration of amino acid that is produced, and that synthesis is most efficient at alkaline pH (i.e., near the inside of the chimney). This project is complementary to our other student's (Yeghegis Abedian) work, which investigates how phosphorus (e.g. phosphate or phosphite dissolved in the early Earth ocean) concentrates and reacts within these hydrothermal minerals. Her experiments have found that simulated hydrothermal iron oxyhydroxides are efficient adsorbers of phosphorus species as well as amino acids. However, the presence of phosphorus in the mineral surfaces affects the amount and type of the amino acid(s) that can be simultaneously adsorbed. Instrumental to this effort has been our work with Co-I Marc Baum's group at Oak Crest, who advised on mineral synthesis and characterization, and Dave VanderVelde at Caltech, who has developed custom analysis methods for organics and phosphorus using Liquid Nuclear Magnetic Resonance spectroscopy (a challenge in such iron-rich experiments).

Meanwhile, students Ryan Cameron and Ninos Hermis are working on the development of new methods to characterize redox processes at prebiotic vent systems. New custom methods of growing simulated hydrothermal metal sulfide chimneys around electrodes in anoxic systems for *in situ* electrochemical studies were developed to test how organic/mineral feedback can emerge in these systems. One exciting preliminary result from Ryan's and Arden's work is the finding that adding certain organics to simulated chimneys not only causes feedback with mineral structure and growth but also changes the electrical activity of the inorganic membranes. For these dynamic far from equilibrium systems, *in situ* non-invasive analysis is essential, and so we are working with Pablo Sobron from the SETI Institute Team to do spectroscopic analysis of hydrothermal metastable minerals and redox processes.

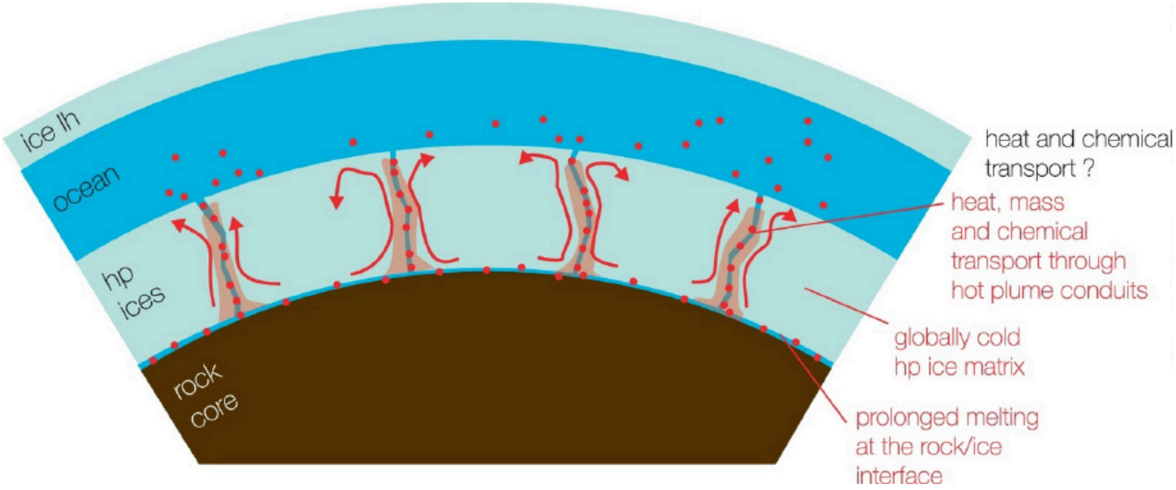


Fig. 6. Two-phase convection in high-pressure ices should allow hydrothermal fluids to move from the seafloor to the overlying ocean. Our Team will continue this work, including considering the as-yet-unaccounted-for role of salts.

INV 3 - Planetary Disequilibria: Characterizing Ocean Worlds and Implications for Habitability

INV 3 looks at how, where, and for how long might disequilibria exist in icy worlds, and what that may imply in terms of habitability. A major interest for this work is how ocean composition affects habitability.

In year 2, we conducted a comprehensive analysis of the evolution of the Europa system, providing the first computations of the coupled fluxes of hydrogen and oxygen into its ocean (Vance et al. 2016). The work compares global redox of the Europa and Earth systems. The high fluxes of oxidants and reductants mean that Europa might have produced complex multicellular life. Similar analyses can be produced for other ocean worlds. The paper describes high fluxes of hydrogen in Enceladus and Ceres. The corresponding fluxes of oxidants require further consideration.

We also developed an analytical model to describe previously unconsidered ice-ocean interactions in Europa and other satellites (Zhu et al., submitted).
We continued our work to develop the interior structure model first conceived for testing hypotheses about the influence of ocean salinity on water-rock interactions and ice dynamics on Ganymede. (Vance et al. 2014). The model, the first to include effects of salinity on ice dynamics, is now optimized to run in only a few seconds and so is suitable for stepping through time. While work continues on providing robust thermodynamics of relevant solutions, Vance has adopted available solution thermodynamics for seawater and ammonia. The model includes switching functions that streamline execution for different ocean compositions and different ocean worlds.

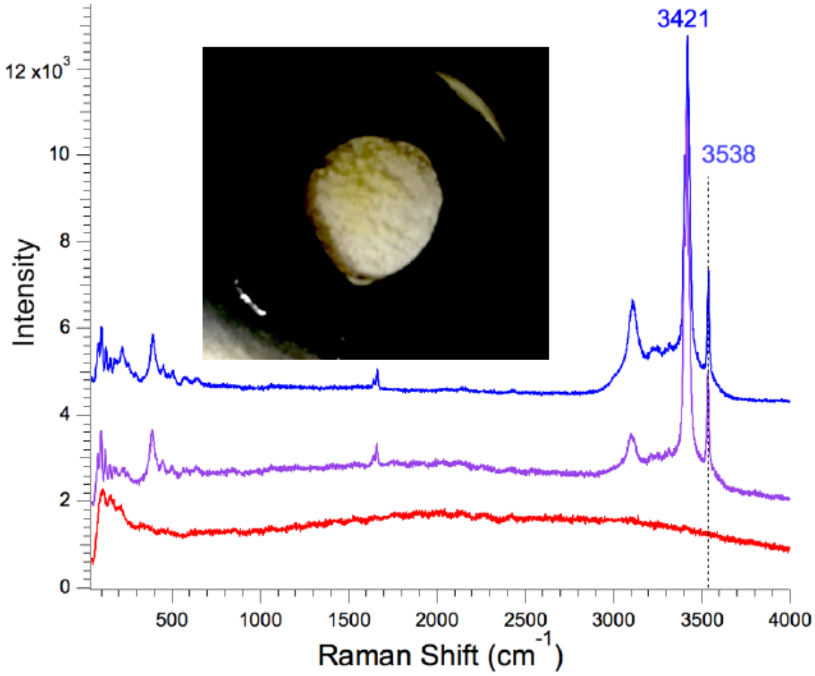


Fig. 7. Raman spectra of powdered frozen saturated NaCl brine at 153 K. The inset shows a photograph of the sample after 5 hours of irradiation with a Kr lamp. The blue spectrum was taken prior to irradiation while the purple and red spectra were taken post irradiation of the white and yellow regions, respectively.

Icy Worlds Team Co-I Goodman has developed a COMSOL model describing non-Newtonian viscous relaxation of topography at the ice-water interfaces of icy worlds. This model demonstrates that irregularities at the base of the ice shell flow away in decades to centuries, and predicts that the interface surface should be extremely flat on local scales. On global scales, however, temperature variation with latitude could lead to thickness variations of a few km. This model confirms previous theoretical work (Nimmo et al, 2003 DOI:10.1016/j.icarus.2003.08.002), is easily modified to allow for rapid hypothesis testing, and provides melting/freezing rate information needed for models of Europa's ocean circulation.

In addition, Goodman has developed simple mathematical models describing the erosion of ice-basal topography by water flow via the "ice pump" (Lewis and Perkin, 1986) effect. This flow can be driven by tidal action (completed work) or buoyancy forces (in progress). For the tidally-driven ice pump, the rate of topographic flattening depends very strongly on tidal amplitude: it is probably less important than ice flow (described above) unless Europa's tides are in a resonant state (Tyler, 2008, DOI:10.1038/nature07571).

New laboratory facilities for ocean worlds that will enable us to measure sound speeds with a high precision of a part in 10,000 in materials at pressures exceeding those at the bottom of Ganymede's H_2O layer, as high as 1.2 GPa or 12,000 atmospheres, and temperatures from 180 K to 420 K, have been set up. We are leveraging the new data with previously published values at higher pressures to construct broadly applicable thermodynamic frameworks applicable to broader pressures and temperatures in oceanic exoplanets.

Co-I Sotin's team completed work which determines how melting in high-pressure ices influences the composition and thermal evolution of Ganymede (Kalousova et al. 2015). The team's work shows that high pressure ices are warm and that fluids move freely from the lower icy layer to the upper icy layer over millions of years (Fig. 6).

We also developed a revolutionary new way to compute thermodynamic properties of fluids under icy satellite pressure and temperatures. The computational framework for fitting thermodynamic data uses b-splines in combination with regularization techniques more typical in geophysics (Brown, in prep). Self-consistent Gibbs-energy based equations of state (EOS) from sound speed, density and heat capacity are yielding unprecedented precision and breadth in P and T needed for modeling conditions in ocean worlds.

Team Members

Jan Amend
Laura Barge
Rory Barnes
Marc Baum
Rohit Bhartia
Bruce Bills
Elbert Branscomb
J. Michael Brown
Mathieu Choukroun
Lance Christensen
Geoffrey Collins
Steven Desch
Giuseppe Etiope
Nigel Goldenfeld
Jason Goodman
Robert Hodyss
Jennifer Jackson
Paul Johnson
Jeffrey Kargel
Terence Kee
Jun Kimura
Giles Marion
Jose Marques
Victoria Meadows
Kenneth Nealson
Robert Pappalardo
Michael Russell
Takazo Shibuya
Christophe Sotin
Shino Suzuki
Ken Takai
Steve Vance
David VanderVelde
Peter Willis

Icy Worlds: 2016 Publications

Barge L.M., Branscomb E., Brucato J.R., Cardoso S.S., Cartwright J.H., Danielache S.O., Galante D., Kee T.P., Miguel Y., Mojzsis S., Robinson K.J., Russell M.J., Simoncini E., Sobron P. (2016). Thermodynamics, Disequilibrium, Evolution: Far-From-Equilibrium Geological and Chemical Considerations for Origin-Of-Life Research. *Origins of Life and Evolution of Biospheres*. DOI: 10.1007/s11084-016-9508-z

Barge L.M., Cardoso S.S.S., Cartwright J.H.E., Doloboff I.J., Flores E., Macías-Sánchez E., Sainz-Díaz C.I., Sobrón P. (2016). Self-Assembling Iron Oxyhydroxide / Oxide Tubular Structures: Laboratory-Grown and Field Examples from Rio Tinto. *Proceedings of the Royal Society A*. DOI: 10.1098/rspa.2016.0466

Choblet, G., Tobie, G., Sotin, C., Kalousova, K., and Grasset, O. (2017). Heat transport in the high-pressure ice mantle of large icy moons. Icarus, 285, p252. DOI: 10.1016/j.icarus.2016.12.002

De Sanctis, M. C., Raponi, A., Ammannito, Ciarniello, E., M., Toplis, M. J., McSween, H. Y., Castillo-Rogez, J. C., Ehlmann, B. L., Carrozzo, F. G., Marchi, S., Tosi, F., Zambon, F., Capaccioni, F., Capria, M. T., Fonte, S., Formisano, M., Frigeri, A., Giardino, M., Longobardo, A., Magni, G., Palomba, E., McFadden, L. A., Pieters, C. M., Jaumann, R., Schenk, P., Mugnuolo, R., Raymond, C. A., Russell, C. T. (2016). Bright carbonate deposits as evidence of aqueous alteration on (1) Ceres. *Nature* 536, 54–57. DOI: 10.1038/nature18290*

Duval, S., Santini, J.M., Lemaire, D., Chaspoul, F., Russell, M.J., Grimaldi, S., Nitschke, W., Schoepp-Cothenet, B. (2016). The H-bond network surrounding the pyranopterins modulates redox cooperativity in the molybdenum-bisPGD cofactor in arsenite oxidase. *Biochimica Biophysica Acta*, *Bioenergetics*, 1857, 1353–1362 DOI: 10.1016/j.bbabio.2016.05.003

Romero-Wolf, A., Schroeder, D.M., Ries, P., Bills, B.G., Naudet, C., Scott, B.R., Treuhaft, R., and Vance, S. (2016). Prospects of passive radio detection of a subsurface ocean on Europa with a lander. *Planetary and Space Science*, 129, 118-121. DOI: 10.1016/j.pss.2016.06.010*

Shibuya T., Russell, M.J., Takai K. (2016). Free energy distribution and hydrothermal mineral precipitation in Hadean submarine alkaline vent systems: Importance of iron redox reactions under anoxic conditions. *Geochimica et Cosmochimica Acta*, 175, 1-19. DOI: 10.1016/j.gca.2015.11.021

Steinbock, O., Cartwright, J.H.E., Barge, L.M. (2016). The Fertile Physics of Chemical Gardens. *Physics Today*, 69(3), 44, DOI: 10.1063/PT.3.3108. (Featured on cover of March 2016 issue).

Vance, S., Hand, K., and Pappalardo, R. (2016). Geophysical controls of chemical disequilibria in Europa. *Geophysical Research Letters*, 43, 4871-4879. DOI: 10.1002/2016GL068547

Vu, T.H., Hodyss, R., Choukroun, M., and Johnson, P.V. (2016). Chemistry of Frozen Sodium-Magnesium-Sulfate-Chloride Brines: Implications for Surface Expression of Europa's Ocean Composition. *The Astrophysical Journal Letters*, 816(2), L26, DOI: 10.3847/2041-8205/816/2/L26

*acknowledges support from NASA but not explicitly NAI