

## Experimental study on chemical nature of fluids in komatiite-hosted hydrothermal system on the early Earth

\*Hisahiro Ueda<sup>1</sup>, Takazo Shibuya<sup>2</sup>, Yusuke Sawaki<sup>3</sup>, Masafumi Saitoh<sup>2</sup>, Ken Takai<sup>2</sup>, Shigenori Maruyama<sup>4</sup>

1. Tokyo Institute of Technology, 2. Japan Agency for Marine–Earth Science and Technology, 3. The University of Tokyo, 4. Earth-Life Science Institute

H<sub>2</sub>-rich hydrothermal fluids generated through the serpentinization of ultramafic rocks would have driven prebiotic chemical evolution and the development of biotic energy metabolisms (e.g., Amend and McCollom 2009; Shibuya et al., 2016). Hydrothermal systems on Early Earth could be different from modern equivalents, for example in terms of CO<sub>2</sub> content and pH value in parent seawater. Previous works demonstrated that carbonate formation during the serpentinization of olivine under CO<sub>2</sub>-rich conditions and ferrous iron incorporation into the carbonate minerals suppress H<sub>2</sub> generation in fluids (Jones et al., 2010; Klein and McCollom, 2013; Neubeck et al., 2014). Some experiments recently were performed in komatiite-CO<sub>2</sub>-H<sub>2</sub>O systems (Lazar et al. 2012; Hao and Li 2015), but H<sub>2</sub> generation in fluids was not the objective in these experiments. Therefore, the potential for hydrogen generation through the serpentinization of komatiites over a wide temperature range has not yet been experimentally evaluated under CO<sub>2</sub>-rich conditions.

To understand the chemical nature of hydrothermal fluids in the komatiite-hosted seafloor hydrothermal system in the Hadean, we conducted hydrothermal serpentinization experiments involving synthetic komatiite and a CO<sub>2</sub>-rich acidic NaCl fluid (pH = 4.9 at 25 °C) at 100, 250, 300, and 350 °C, 500 bars. H<sub>2</sub> concentrations in fluids increase as the temperature is raised, and the maximum H<sub>2</sub> concentration at 350 °C was 2.9 mmol/kg. During the experiments, the total carbonic acid concentrations ( $\Sigma$ CO<sub>2</sub>) in fluids decreased from starting values, which is consistent with the carbonate mineral formation in the serpentinized/carbonated komatiites. Precipitated carbonate minerals at 100, 250, 300, and 350 °C were ankerite/magnesite, dolomite, dolomite/calcite, and calcite, respectively. These carbonate mineral formation are thermodynamically consistent with Mg/Ca ratios in fluids. Ferrous iron contents in the carbonate minerals decrease with increasing temperature. The negative correlation between ferrous iron content in carbonate mineral and H<sub>2</sub> concentration in fluid suggests that the incorporation of ferrous iron into the carbonate mineral likely limited iron oxidation and consequent H<sub>2</sub> generation in the fluid. Fluid H<sub>2</sub> concentrations in the experiments at 350 °C are almost same as that of Kairei hydrothermal field (Central Indian Ridge) (Takai et al., 2004; Gallant and Von Damm, 2006; Kumagai et al., 2008; Nakamura et al., 2009), where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. Even under CO<sub>2</sub>-rich conditions, the high-temperature serpentinization of komatiite would provide H<sub>2</sub>-rich hydrothermal environments that were necessary for the emergence and early evolution of life. In contrast, as considering that carbonate mineral becomes more stable and involve more ferrous iron with decreasing temperature, H<sub>2</sub>-rich fluids may not have been generated by serpentinization at temperatures below 300 °C in komatiite-hosted hydrothermal systems on the Hadean Earth.

Chemical compositions of fluids have another implication for the Early Earth. The precipitated carbonate species strongly influenced Mg concentration in the hydrothermal fluid. At 350 °C, Mg-poor calcite is stable and Mg concentration is at most 1.2 mmol/kg. On the other hand, Mg-rich carbonate minerals such as magnesite and dolomite are stable below 300 °C, and Mg concentrations are at least 10 times higher than that at 350 °C. Therefore, in contrast to modern seafloor hydrothermal systems (e.g., Alt, 1995), the reactions between komatiite and CO<sub>2</sub>-rich seawater at temperature range 100-300 °C could have been the source of Mg for the Hadean ocean.

Keywords: komatiite, CO<sub>2</sub>-rich condition, early Earth, hydrothermal alteration, serpentinization, experiment

## Short peptides formed under Enceladus hydrothermal condition

\*Wataru Takahagi<sup>1,2,3</sup>, Kaito Seo<sup>1,3,4</sup>, Takazo Shibuya<sup>1</sup>, Kosuke Fujishima<sup>3,5</sup>, Yoshinori Takano<sup>1</sup>, Masafumi Saitoh<sup>1</sup>, Masaru Tomita<sup>3,4</sup>, Ken Takai<sup>1</sup>

1. Japan Agency for Earth-Marine Science and Technology, 2. Systems Biology Program, Graduate School of Media and Governance, Keio University, 3. Institute for Advanced Biosciences, Keio University, 4. Department of Environment and Information Studies, Keio University, 5. Earth-Life Science Institute, Tokyo Institute of Technology

Enceladus is one the sixth largest moon of the moons of Saturn, and it has been known to harbor interior ocean beneath the icy crust. , which hold important factors necessary for life such as organic compounds, liquid water, and high temperature condition. The mass spectrometry data and the presence of nanometer sized silica particles obtained by *Cassini* spacecraft indicates the presence of salty, and most likely alkaline ocean containing various simple organic compounds. While geochemical and other radiation related processes for the *in situ* production of organics remain elusive, thermally unaltered carbonaceous chondrites, consisting the main body of Enceladus are known to be enriched with organic matters such as simple amino acids. potentially including the Therefore we Enceladus alkaline seawater, we hypothesized that an ongoing chemical evolution and polymerization of amino acids coupled with water-rock interaction under simulated Enceladus hydrothermal condition. Serpentinization coupled may contribute to dehydration may lead to condensation of surface localized amino acids leading to peptide formation. Short peptide is significant important for primitive life in terms of initial chemical evolution In order to test this hypothesis, we have developed the Enceladus hydrothermal reactor based on the chemical constraints obtained through previous experimental and theoretical studies. We have added six different abiotically available L-amino acids (Gly, Ala, Asp, Glu, Ser, Val) that are and introduced a thermal fluctuation system simulating the periodic tidal heating of the interior chondritic core. The pH monitoring and H<sub>2</sub> and CO<sub>2</sub> Gas Chromatography (GC) data clearly indicated the occurrence of serpentinization / carbonation reaction. Organic compounds data estimated by Orbitrap Fusion suggest the interaction between amino acids, aqueous alteration reaction and thermal cycling processes for the role of abiotic peptide formation under alkaline hydrothermal condition. Here, we discuss the interaction between aqueous alteration reactions and thermal cycling processes for the role of abiotic peptide formation under the Enceladus hydrothermal condition.

Keywords: Enceladus, Amino acid, Peptide synthesis, Hydrothermal reactor

# Geo-electrochemical CO production: Implications for the autotrophic origin of life

\*Norio Kitadai<sup>1</sup>

1. Earth-Life Science Institute, Tokyo Institute of Technology

Hydrothermal activities on the primitive Earth were considered to be much greater than the present level, and hydrothermally produced geo-electrochemical potential may have facilitated CO<sub>2</sub> reduction and the formation of organic compounds that preceded the origin of life. To test the possibility, we examined electrochemical CO<sub>2</sub> reduction on low-crystalline sulfides of various metals (Ag, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, W, or Zn) in the simulated ancient seawater. Results showed that CdS and Ag<sub>2</sub>S have excellent catalytic efficiency for the CO<sub>2</sub> reduction to CO, together with the H<sub>2</sub> evolution. At potentials below -1.0 V (versus the standard hydrogen electrode), the CO production on CdS and Ag<sub>2</sub>S accounted for around 40 and 30 % of the total electric current, respectively. The threshold potential could be readily generated in the H<sub>2</sub>-rich, high-temperature and alkaline hydrothermal vents that were probably widespread over the early ocean floor. The electrochemical production of CO, a crucial energy and carbon sources for abiotic and biotic organic synthesis, could have been a key initial step of the prebiotic CO<sub>2</sub> fixation in the early ocean hydrothermal systems, and provided the materials for the origin and early evolution of life.

# Reconstruction of Water Quality from Adsorbed Heavy Elements in Sediment: Surface Complexation Modeling of Trace Uranyl Adsorption on Iron Oxide

\*Yui Kobayashi<sup>1</sup>, Tomoki Ushiyama, Keisuke Fukushi<sup>2</sup>, Aya Sakaguchi<sup>3</sup>, Noriko Hasebe<sup>2</sup>

1. School of Natural System, College of Science and Engineering, Kanazawa University, 2. Institute of Nature & Environmental Technology, Kanazawa University, 3. Faculty of Pure and Applied Science

Since the birth of the earth, the earth's surface environment has undergone various changes. How the nature of water on the earth (water quality) has been responded to the environmental changes is essential to understand the origin and evolution of life. Also, the understanding of the changes of water quality that had been occurred in planets which possess water is essential to evaluate the possibility of existence of life. The most important and fundamental parameter that indicates the chemical nature of water is pH. It controls the chemical behavior of elements in water via dissolution, precipitation and complexation, and dominates the transfers of energy and substance through water. In geology, the past water quality is reconstructed from proxies left in sediments and fossils (geological records) at the time, but there is no versatile proxy of pH at the moment.

Natural water contains various trace elements. These trace elements adsorb to mineral surface depending on water condition such as pH. Therefore it is possible to consider that trace elements adsorbed on mineral record the information about the water quality during the adsorption. Thermodynamic adsorption model called "surface complexation modeling (SCM)" can theoretically predict the adsorption behavior of trace elements as a function of water quality. Application of SCM inversely is capable to predict the water quality from adsorption behavior of trace elements. The goal of the present study is to develop the methodology for the reconstruction of water quality using SCM from the trace elements information of sediments.

One of heavy elements contained in relatively high concentration in natural water is uranium (U). U thermodynamically exists as a hexavalent valence U(VI) under the condition that the oxygen partial pressure is approximately  $10^{-50}$  atm or higher. U(VI) possesses relatively high solubility and therefore high mobility, but U(VI) has the nature for strongly adsorbing on iron oxide. U(VI) adsorption on iron oxide is frequently observed in nature. For example, previous study reported that U(VI) concentration of the sediments core from the continental ancient lake (Lake Hovsgol) varies with age. It is pointed out that the fluctuating U concentration may be explained by adsorption and desorption processes on iron oxide.

In this study, we conducted the adsorption experiments of trace amounts of uranium with iron oxide at laboratory and tried to parameterize the adsorption behavior using SCM from the obtained experimental results. Then we attempted to reconstruct the paleo water quality of Lake Hovsgol using the constructed surface complex modeling.

Keywords: adsorption, trace heavy element, iron oxide

# EXPERIMENTAL STUDY ON MANGANESE OXIDE FORMATION: INTERPRETATION OF MANGANESE OXIDE ON GALE CRATER AND OXIDIZING ENVIRONMENT ON EARLY MARS.

\*Natsumi Noda<sup>1</sup>, Shoko Imamura<sup>1</sup>, Yasuhito Sekine<sup>1</sup>, Soichiro Uesugi<sup>1</sup>, Minako Kurisu<sup>1</sup>, Chihiro Miyamoto<sup>1</sup>, Haruhisa Tabata<sup>1</sup>, Yoshio Takahashi<sup>1</sup>, Takashi Murakami<sup>1</sup>

1. Department of Earth and Planetary Science, The University of Tokyo

The Curiosity rover has found Mn enrichments within sandstones in the Kimberley region of the Gale crater on Mars [1]. These enrichments were detected within fracture-filling materials, *i.e.*, veins, crosscutting the surrounding sandstones, implying that Mn was once concentrated in subsurface fluids and then precipitated within ancient aquifers [1]. The chemical composition analysis for the Mn-rich materials also show that the abundance of Mn is coupled with those of transition trace metals, particularly Ni and Zn; meanwhile, Si, Ca, Cl and/or S are inversely correlated or not correlated with Mn [1]. This indicates that Mn exists as oxides in the fracture-filling materials, rather than silicate, carbonate, or chloride [1]. Since oxidation of Mn requires high levels of redox potential [2], the findings of Mn oxides indicate a possible coexistence of a highly oxidizing atmosphere and wet conditions on early Mars [1]. However, the  $pO_2$  level at the time of deposition of Mn oxides remains poorly constrained. In the present study, we conducted laboratory experiments in order to constrain the  $pO_2$  level at the time of deposition of the Mn oxides based on the elemental pattern of coprecipitation of Mn oxides. In the experiments, we synthesized  $MnO_2$ ,  $Mn_3O_4$ , and  $Mn(OH)_2$  from solutions of dissolved Mn, Ni, Zn, and Cr using different oxidants, such as  $KMnO_4$  [8] or  $H_2O_2$  [9]. After the reactions, filtered solutions and solid precipitates were collected. The recovered solid precipitates were analyzed with X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD). In addition, concentrations of dissolved Mn, Cr, Ni, and Zn in the remnant solution samples were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). We found that only formation of  $MnO_2$  can explain the enrichments of Mn together with Ni and Zn, which is consistent with the pattern of trace metal enrichments of the Mn oxides in the Gale crater. On the other hand, formations of  $Mn_3O_4$  or  $Mn(OH)_2$  cannot account for the observations. Given that precipitation of  $MnO_2$  requires a high level of  $O_2$  ( $>0.01$  bar), our results strongly suggest the presence of an  $O_2$ -rich atmosphere on early Mars at the time when groundwater was active within the Gale crater. These results, in turn, imply effective formation of  $O_2$  via  $H_2O$  photolysis and/or ineffective loss of  $O_2$  due to limited amounts of reductants on early Mars.

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Keywords: Early Mars, Planetary environment, Atmospheric evolution

# Cycles and escape of water on Earth and Mars: implications from hydrogen isotopic compositions

\*Hiroyuki Kurokawa<sup>1</sup>, Tomohiro Usui<sup>1</sup>, Julien Foriel<sup>1</sup>

1. Earth-Life Science Institute, Tokyo Institute of Technology

The presence of water influences the tectonics and mantle convection and therefore changes the chemical reactions occurring on planetary surfaces, the volatile cycles among different reservoirs, and the thermal evolution of planets. Because Earth is the only planet known to be sustaining oceans through its history and Mars probably lost the liquid water that once existed on its surface, comparative planetology of these planets would help us to understand the sustainability of water on terrestrial planets.

As hydrogen isotope (D/H) compositions vary among different sources of water and fractionate through planetary processes, the origins and evolution of water can be constrained by D/H data. The D/H ratios of the terrestrial water and the primitive Martian water are nearly identical, suggesting their common origins (Usui et al. 2012). The D/H ratios of surficial water on present-day Mars are  $\sim 6$  times higher than the primitive value, suggesting significant water loss through its history (Villanueva et al. 2015).

By combining theoretical models of cycles of water among different reservoirs with D/H data, we constrained the cycles and escape of water on Earth and Mars. The small difference in D/H ratios of the oceans and mantle of Earth can be understood as resulting from a balance between the fractionation due to the ingassing and outgassing processes, suggesting an efficient water cycle (Kurokawa et al. in prep). On the other hand, the D/H ratios of different water reservoirs on Mars are likely to be quite inhomogeneous (Usui et al. 2015), suggesting the less efficient, limited cycles of water at least from  $\sim 4$  Ga to present (Kurokawa et al. 2016). An increase in the D/H ratios of the terrestrial oceans from Archean to present (Pope et al. 2012) is likely to be a signature of the evolution toward a steady state, rather than that of the water loss (Kurokawa et al. in prep). In contrast, our study demonstrated that water loss from Mars before  $\sim 4$  Ga was more significant than during the rest of its history. Our model suggested that a significant fraction of paleo-oceans is stored as ground ice on present-day Mars (Kurokawa et al. 2014).

The fates of Earth and Mars probably diverged very early ( $\sim 4$  Ga) in their evolutions.

Keywords: Earth, Mars, Isotopes, Water cycle, Atmospheric escape

## What is “habitable”?: Toward development of aqua planetology

\*Yasuhito Sekine<sup>1</sup>, Keisuke Fukushi<sup>2</sup>, Takazo Shibuya<sup>3</sup>, Hidenori Genda<sup>4</sup>, Tomohiro Usui<sup>4</sup>

1. Department of Earth and Planetary Science, University of Tokyo, 2. Institute of Nature and Environmental Technology, Kanazawa University, 3. JAMSTEC, 4. ELSI, Tokyo Institute of Technology

Earth is an aqua planet that holds liquid water on the surface and can support life. On Earth, liquid water has played many essential roles in the biogeochemical cycles and interior evolution, which make our planet to have been habitable during its history. For instance, liquid water causes chemical weathering of lands, which in turn provides nutrients to life and can stabilize climate through the carbon cycle. The presence of water in the interior can also affect mantle convection in association with plate tectonics and continuous degassing. On the other hand, recent theoretical studies of planetary science suggest a possibility that the amount of water on Earth might have been determined stochastically in the planetary formation process. If Earth had possessed greater or less amounts of water on the surface, some of the essential roles that water plays on current Earth would not have worked effectively.

How was the amount of water on Earth determined? How would the biogeochemical cycles have changed if Earth had possessed different amounts of water? To answer these fundamental questions, it is required research at the interactions of geology, geochemistry, biosphere science, planetary science, and solar system exploration. Near-future spacecraft missions for volatile-rich asteroids, Mars, and icy satellites will provide unique observational constraints on water activity on planetary bodies with various amounts of water. Using the observational data, theory based on experiments and modeling could reconstruct water and geochemical cycles occurred on these bodies. Revealing cycles and fixation of water occurred within volatile-rich asteroids are key to determine the amounts of water delivered to Earth during its formation. Knowledge on geochemical cycles on early Mars and icy satellites will also allow to predict possible ecosystems and biomarkers occurred there, which are important for searching for life in future missions. This paper discusses a strategy how to develop the new fields of research, termed “aqua planetology”, at the interdisciplinary interactions. Aqua planetology aims at understanding the roles of liquid water on planetary bodies and tries to make a new definition of habitability on Earth and beyond.

Keywords: aqua planet, terrestrial planet, geochemical cycles



# Compound- and position-specific carbon isotopic study of hydrocarbons from serpentinite-hosted hot spring in Hakuba Happo, Japan

\*Konomi Suda<sup>1</sup>, Alexis Gilbert<sup>2</sup>, Keita Yamada<sup>3</sup>, Naohiro Yoshida<sup>2,3</sup>, Yuichiro Ueno<sup>2,4,1</sup>

1. Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2. Earth-Life Science Institute (WPI-ELSI), Tokyo Institute of Technology, 3. Department of Chemical Science and Engineering, Tokyo Institute of Technology, 4. Department of Earth and Planetary Sciences, Tokyo Institute of Technology

Olivine is one of the major constituent minerals of various meteorites (Rubin, 1997). During serpentinization process of ultramafic rocks, water in contact with olivine is reduced to form molecular hydrogen (H<sub>2</sub>) (e.g., McCollom and Bach, 2009). The highly reduced (H<sub>2</sub>-rich) condition created by serpentinization is thermodynamically favorable for abiotic organic synthesis. Elevated concentrations of CH<sub>4</sub> and higher hydrocarbon gases have been observed in serpentinite-hosted systems, regardless of continental or seafloor setting (e.g., Charlou et al., 2002; Proskurowski et al., 2008; Etiope et al., 2011; Szponar et al., 2013). Abiotic synthesis has been invoked to account for the carbon isotopic distribution among low-molecular weight hydrocarbons (e.g., Proskurowski et al., 2008). However, uncertainties still remain regarding specific abiotic production mechanisms for serpentinite-hosted systems. In this study, we report a new geochemical study of hydrocarbon gases (methane, ethane, propane, butane, pentane) from the borehole well at the on-land hot spring associated with serpentinization in Hakuba Happo, Japan. We have conducted position-specific as well as compound-specific stable carbon isotopic analyses of hydrocarbons.

The gas samples were collected from Hakuba Happo hot spring that lies on an serpentinized ultramafic rock body. Highly-alkaline hot spring water with temperature of around 50°C mainly contains N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> gases (Homma and Tsukahara, 2008; Suda et al., 2014). The concentrations of C<sub>1</sub> to C<sub>5</sub> hydrocarbons were determined by Gas Chromatography. A compound-specific carbon isotope measurement for C<sub>1</sub>-C<sub>5</sub> hydrocarbons was performed by GC-C-IRMS coupled with an on-line pre-concentration system. A position-specific <sup>13</sup>C composition in propane molecule (C<sub>3</sub>H<sub>8</sub>) was measured using the GC-Py-GC-C-IRMS (Gilbert et al., 2016) coupled with an on-line pre-concentration system. The straight chain alkanes (*n*-alkanes) for the Happo sample show an isotopic depletion in <sup>13</sup>C with increasing carbon number ( $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \dots$ ). This <sup>13</sup>C depletion trend is very similar to those of some seafloor serpentinite-hosted hydrothermal systems (Proskurowski et al., 2008; Charlou et al., 2010), and undisputed abiogenic origin for the Murchison meteorite (Yuen et al., 1984). The observed isotopic trend can be explained by a simple polymerization model developed in this study. Our model assumes that, for any particular alkane, (i) all of the subsequently added carbon atoms that are bonded to the growing carbon chain have the same isotopic composition, and (ii) those are depleted in <sup>13</sup>C with respect to the first carbon atom that initiates the carbon chain. The fit of this model suggests that *n*-alkanes for the Happo sample can be formed via polymerization from single-carbon compound (potentially methane) with a constant kinetic isotopic fractionation of  $-8.9 \pm 1.0\%$ . To understand the type of polymerization mechanism, we next focus on the position-specific carbon isotopic compositions of hydrocarbons. For the first time, we applied a new method, namely position-specific <sup>13</sup>C analysis of propane, to a natural sample derived from a serpentinite-hosted system. The difference of  $\delta^{13}\text{C}$  values between terminal and central carbon atom positions of propane molecule for the Happo sample was  $-1.2 \pm 0.9\%$ . We show the important potential of the position-specific <sup>13</sup>C analysis to identify different polymerization mechanisms that can not be discriminated by compound-specific isotopic analysis.

Keywords: serpentinite, hydrocarbon, position-specific isotope analysis, stable carbon isotope

## Serpentinization and habitability in the Enceladus' subsurface ocean

\*Takazo Shibuya<sup>1</sup>, Yasuhito Sekine<sup>2</sup>, Ken Takai<sup>1</sup>

1. Japan Agency for Marine-Earth Science and Technology, 2. The University of Tokyo

Saturn's moon, Enceladus, is presently discharging water-vapor plume from its south pole. The discovery of silica nanoparticles in the plume strongly suggested the presence of ongoing hydrothermal activities at the bottom of the subsurface ocean (Hsu et al., 2015). In this work, to estimate the composition of hydrothermal fluids, we conducted thermodynamic modeling of chondrite-seawater reactions at 100 to 300 degrees C and 100 bars with four representative initial seawater compositions; pH = 5.6-13.2 and DIC = 70-320 mmolal (Marion et al., 2012; Postberg et al., 2009; Hsu et al., 2015; Sekine et al., 2015; Glein et al., 2015).

The results show that the chondritic core is serpentinized by the interaction with seawater, generating chemically-varied hydrothermal fluid in all cases. Although SiO<sub>2</sub> concentration in the hydrothermal fluid partially depends on the initial seawater composition, it generally increases with increasing temperature of chondrite-seawater reactions. However, the SiO<sub>2</sub> concentration in hydrothermal fluids even at 300 degrees C does not exceed the solubility of silica in seawater in the cases with seawater pH values higher than 9.0 because NaHSiO<sub>3</sub>(aq) increases with increasing pH when Na is the primary cation in seawater (e.g., silica solubility is 1.8 mmolal at pH = 8.5 and 216 mmolal at pH = 10.5). Therefore, pH of seawater is estimated to be less than 9.0 to keep the silica-saturated seawater by subseafloor hydrothermal activities. Taking into account the observation of Na<sub>2</sub>CO<sub>2</sub> in the plume (Postberg et al., 2009), the most reasonable pH of Enceladus' seawater would be fall within the range between 8.5 and 9.0.

Molecular hydrogen (H<sub>2</sub>) concentration in the hydrothermal fluid also changes with the initial seawater composition and the temperature of chondrite-seawater reactions. Based on the modeling of the mixing between seawater and hydrothermal fluid, we calculated the Gibbs free energies of hydrogenotrophic methanogenesis and acetogenesis in the mixing zone at the seafloor. As a result, it was revealed that these redox reactions are endergonic under all assumed conditions. Especially, H<sub>2</sub> concentration in hydrothermal fluid exceeds 50 mmolal at 300 degrees C, which can generate relatively high energies comparable to those of O<sub>2</sub>-respiring microbial metabolic reactions (e.g., aerobic sulfide oxidation and hydrogen oxidation) in terrestrial seafloor hydrothermal systems. The results suggest that these hydrogen-based redox reactions can assure the energetic habitability of potential living forms in the hydrothermal systems within Enceladus.

Keywords: Enceladus, hydrothermal system, serpentinization, habitability

# Experimental investigations on hydrothermal reactions within large icy satellites and Martian crustal rocks using a 130-MPa hydrothermal autoclave

\*Shuya Tan<sup>1</sup>, Yasuhito Sekine<sup>1</sup>

1. Department of Earth and Planetary Science, Graduate School of Science, the University of Tokyo

Geochemical cycles of carbon (C) and sulfur (S) within interior oceans on icy satellites are key to understand the chemical evolution of the oceans and potential habitability (Gaido et al., 1999). Knowledge on geochemical cycles of C and S on early Mars is also critical for its chemical and climate evolution of the surface environment (Halevy et al., 2007). In the geochemical cycles on these bodies, oxidizing C- and S-bearing species, CO<sub>2</sub> and SO<sub>2</sub>, could have been reduced to CH<sub>4</sub> and H<sub>2</sub>S, respectively, by reactions with H<sub>2</sub> under hydrothermal conditions at water-rock interfaces. For instance, CH<sub>4</sub> in Titan's atmosphere could have been generated through high-temperature water-rock interactions in its interior during the formation and early evolution (Atreya et al., 2006). On Europa, H<sub>2</sub>SO<sub>4</sub> and CO<sub>2</sub> on the surface might have been transported into the subsurface ocean and could have reduced in the interface between the ocean and rock components, which, in turn, may control redox state of the oceans and availability of metabolic energy for microbial life (e.g. Zolotov and Shock, 2004; Vance et al., 2016). On Mars, CH<sub>4</sub> could have been produced through hydrothermal reactions within deep crustal rocks, which may explain the detection of a trace amount of CH<sub>4</sub> on Mars (Webster et al., 2015).

Despite the importance of hydrothermal reactions of CO<sub>2</sub> and SO<sub>2</sub>, kinetics of these reactions under the conditions corresponding to the interiors of icy satellites and Mars' crustal rocks are poorly constrained. This is because the previous experimental studies have mainly focused on the reactions in hydrothermal systems on Earth, where pressure typically reaches at ~30–50 MPa (e.g. McCollom et al., 2001). On the other hand, hydrothermal reactions within icy satellites and Mars' crustal rocks are proposed to occur at higher pressures (e.g., > 100 MPa) (Vance et al., 2016). In fact, recent experimental studies suggested the presence of pressure dependence on reaction products of the hydrothermal reactions (Lazar et al., 2015). However, both kinetics and reaction mechanisms remains unclear because they have used closed-system hydrothermal autoclaves, which is incapable of tracing time variations of dissolved species during the experiments.

In the present study, we have developed a 130-MPa hydrothermal apparatus that allows to perform on-line sampling using a flexible gold reaction cell, based on the experimental apparatus for investigations of Earth's hydrothermal systems (e.g., McCollom and Seewald, 2003, Shibuya et al., 2013). During the experiments on hydrothermal reactions of CO<sub>2</sub> and SO<sub>2</sub>, we measure time variations of dissolved gas species. Based on the results, we discuss the reaction mechanisms and implications for the aqueous environments on icy satellites and early Mars.

Keywords: hydrothermal reaction, geochemical cycle, icy satellite, mars

# Terrestrial Planet Formation: Delivery of Water to Mercury and Venus

\*Petryk Sofia Lykawka<sup>1</sup>, Takashi Ito<sup>2</sup>

1. Astronomy Group, School of Interdisciplinary Social and Human Sciences, Kindai University, 2. National Astronomical Observatory of Japan

The formation of the four terrestrial planets of the solar system is one of the most fundamental problems in the planetary sciences. However, the delivery of water and other volatiles to Mercury and Venus during their formation remains poorly understood. Indeed, although previous works have focused on the delivery of such substances to Earth based on N-body simulations, to our knowledge no similar studies have discussed the same delivery to the other terrestrial planets in the context of formation of the other terrestrial planets.

We investigated terrestrial planet formation by performing N-body simulation runs using hundreds of embryos and thousands of disk planetesimals representing a primordial protoplanetary disk. To investigate the formation and the delivery of water to Mercury and Venus, these simulations considered an inner region of the disk (the Mercury region) and disks with and without mass enhancements beyond the ice line location in the disk.

Although Venus and Earth analogs (considering both orbits and masses) successfully formed in the majority of the runs, Mercury analogs were obtained in lesser runs. We found that our Mercury analogs acquired most of their final masses from embryos/planetesimals initially located between the disk inner edge and  $\sim 1-1.5$  au within 10 Myr, while the remaining mass came from a wider region up to  $\sim 3$  au at later times. Although the ice line was negligible in the formation of planets located in the Mercury region, it enriched all terrestrial planets with water. Indeed, Mercury and Venus analogs showed a wide range of water mass fractions at the end of terrestrial planet formation. In particular, the region beyond  $\sim 1-1.5$  au would have the potential to source Mercury with water and possibly other volatiles during a late veneer period of accretion.

Keywords: planet formation, water, terrestrial planets, Mercury, solar system, Venus

## Formation condition of oceans under hydrogen-rich atmospheres

\*Keiko Hamano<sup>1</sup>, Hidenori Genda<sup>1</sup>, Yutaka Abe<sup>2</sup>, Masanori Onishi<sup>3</sup>

1. Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, 2. Department of Earth and Planetary Science, University of Tokyo, 3. Graduate school of natural science and technology, Okayama University

The formation of oceans requires thermodynamic conditions allowing the presence of liquid water on planetary surface. Such conditions have been explored under CO<sub>2</sub>-H<sub>2</sub>O atmospheres, while early atmospheres may contain some amount of H<sub>2</sub>. Pierrehumbert and Gaidos (2011) showed that collision induced absorption of tens bar of H<sub>2</sub> atmospheres can keep a surface temperature above 280 K beyond a habitable zone.

Adding hydrogen to a steam atmosphere increases atmospheric scale height. Given that a partial pressure of water vapor at the surface is equal to its saturation pressure, a column mass of water vapor would increase. This means that a larger amount of water is required to keep a sufficient partial pressure for ocean formation.

In this study, we investigate atmospheric structure of an H<sub>2</sub>-H<sub>2</sub>O atmosphere using a 1D radiative-convective equilibrium model. We present a relation among incident stellar flux, partial pressure of hydrogen, and a total mass of surface water, which is required for an ocean to form.

Keywords: Reducing atmospheres, Formation of oceans, Early surface environment, Habitable zone

# ABEL Bombardment as the trigger to initiate plate tectonics of Earth: From stagnant lid to plate tectonics

\*Shigenori Maruyama<sup>1</sup>

1. Earth-Life Science Institute, Tokyo Institute of Technology

Here, we address the long-standing question of when and how plate tectonics began on the Earth. Augmented by both the records of Earth-Moon geology and the asteroid belt, we theorize that the onset of plate tectonics was during the Middle Hadean (between 4.37-4.20 Ga) triggered by ABEL Bombardment which delivered oceanic and atmospheric components to a completely dry reductive Earth system (originally comprised of enstatite chondrite-like materials). Through the accretion of volatiles, shock metamorphism proceeded with vaporization of both CI chondrite and supracrustal rocks at the bombardment sites, as well as significant recrystallization under wet conditions, causing considerable eclogitization in the primordial continents; the primordial continents were composed of an upper (~ 21 km thick) anorthosite-enriched, felsic crust, and even thicker (~ 50 km) KREEP lower crust. Eclogitization must have yielded a powerful slab-pull force to initiate plate tectonics in the Middle Hadean. Another important factor is the extent of the bombardment. Through the formation of Pacific-Ocean-size impact craters by 1,000 km-diameter impactors, the operation of rigid-plate (stagnant-lid) tectonics since the Early Hadean was destroyed, and oceanic lithosphere was generated resulting in bi-modal lithosphere on the Earth which drove plate tectonics. Considering the importance of the ABEL Bombardment event which initiated plate tectonics including the appearance of ocean and atmosphere, we propose that the Hadean Eon be subdivided into three periods; (1) Early Hadean (4.57-4.37 Ga), (2) Middle Hadean (4.37-4.20 Ga), and (3) Late Hadean (4.20-4.00 Ga).

Keywords: ABEL Bombardment, secondary accretion of volatiles, initiation of plate tectonics, eclogitization