

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

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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

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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

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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 seafloor 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

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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

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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

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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

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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