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

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H_2-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_2 content and pH value in parent seawater. Previous works demonstrated that carbonate formation during the serpentinization of olivine under CO_2-rich conditions and ferrous iron incorporation into the carbonate minerals suppress H_2 generation in fluids (Jones et al., 2010; Klein and McCollom, 2013; Neubeck et al., 2014). Some experiments recently were performed in komatiite-CO_2-H_2O systems (Lazar et al. 2012; Hao and Li 2015), but H_2 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_2-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_2-rich acidic NaCl fluid (pH = 4.9 at 25 ˚C) at 100, 250, 300, and 350 ˚C, 500 bars. H_2 concentrations in fluids increase as the temperature is raised, and the maximum H_2 concentration at 350 ˚C was 2.9 mmol/kg. During the experiments, the total carbonic acid concentrations (ΣCO_2) 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_2 concentration in fluid suggests that the incorporation of ferrous iron into the carbonate mineral likely limited iron oxidation and consequent H_2 generation in the fluid. Fluid H_2 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_2-rich conditions, the high-temperature serpentinization of komatiite would provide H_2-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_2-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_2-rich seawater at temperature range 100-300 ˚C could have been the source of Mg for the Hadean ocean.

Keywords: komatiite, CO2-rich condition, early Earth, hydrothermal alteration, serpentinization, experiment

Short peptides formed under Enceladus hydrothermal condition

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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_2 and CO_2 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

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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_2 reduction and the formation of organic compounds that preceded the origin of life. To test the possibility, we examined electrochemical CO_2 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_2S have excellent catalytic efficiency for the CO_2 reduction to CO, together with the H_2 evolution. At potentials below -1.0 V (versus the standard hydrogen electrode), the CO production on CdS and Ag_2S accounted for around 40 and 30 % of the total electric current, respectively. The threshold potential could be readily generated in the H_2-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_2 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

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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: INTERPRETAION OF MANGANESE OXIDE ON GALE CRATER AND OXIDIZING ENVIRONMENT ON EARLY MARS.

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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

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

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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 ~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 ~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 ~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 (~4 Ga) in their evolutions.

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