初期地球のコマチアイト熱水系における流体の化学的性質に関する実験的研究
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.

キーワード：komatiite、CO2-rich condition、early Earth、hydrothermal alteration、serpentinization、experiment
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.

キーワード：エンセラダス、アミノ酸、ペプチド合成、熱水反応実験
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.

堆積物中の吸着重元素分布を利用した水質復元：鉄酸化物による微量ウラン吸着の表面錯体モデリング

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

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地球誕生以来, 地球表層環境はさまざまな変化を遂げてきた. 地球上の生命にとって水は必須であり, 環境変化に伴って地球上の水の性質(つまり水質)がどのように応答したかを理解することは生命の起源や進化を理解する上で必須である. また地球以外の天体のおける生命存在の可能性を評価する上でも, その天体で生じた水質変遷の理解は必須であろう. 水の化学的性質を示す最も重要かつ基本的なパラメータはpHである. pH は水中における元素の化学的挙動(溶解・沈殿・錯形成)をコントロールし, 水を介したエネルギーと物質の移動を支配する. 地質学では過去の水質を当時の堆積物や化石(地質記録)に残された何らかの代替指標(プロキシ)を読み解くことにより復元するが, 汎用的に利用できるpH のプロキシは現在のところない.

天然水にはさまざまな微量元素が含まれる. 微量元素はpHをはじめとする水質条件に依存し鉱物表面に吸着する性質がある. したがって鉱物に吸着した微量元素には, 吸着当時の水質情報が保存されていると考えることができる. 「表面錯体モデリング」と呼ばれる熱力学的吸着モデルは, 水質条件の関数として重元素の吸着挙動を理論的に予測することができる. 表面錯体モデリングを逆方向に適用すると, 微量元素の吸着挙動から水質を予測できる可能性がある. 本研究は堆積物に残された微量元素情報から表面錯体モデリングを用いて, 吸着時の水質を復元する手法を構築することを目的としている.

天然水に比較的高濃度に含まれる重元素にウラン(U)があげられる. Uは熱力学的には酸素分圧がおおよそ10^{-50}気圧以上の条件で6価の価数を持つU(VI)として存在する. U(VI)は溶解度が高く移動性が高いが, 鉄酸化物に強く吸着する性質がある. U(VI)の鉄酸化物への吸着は自然界では頻繁に認められている. 例えば, 大陸内部古代湖フブスグル湖の湖底堆積物コア中ではU濃度は年代によって変動することが確認されているが, 変動するU濃度は鉄酸化物への吸着・脱離過程により説明される可能性が指摘されている.

本研究では, 自然界に近い水質条件で鉄酸化物による微量Uの室内吸着実験を行い, その実験結果を表面錯体モデリングによりモデル化した. 構築した表面錯体モデリングにより, 古代湖堆積物のU分布を利用した古水質復元を試みた.

キーワード：吸着、微量重元素、鉄酸化物
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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キーワード：初期火星、惑星環境、大気進化

Keywords: Early Mars, Planetary environment, Atmospheric evolution

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.

キーワード：地球、火星、同位体、水循環、大気散逸
Keywords: Earth, Mars, Isotopes, Water cycle, Atmospheric escape