

U020-01

会場:304

時間:5月23日 09:00-09:15

モリブデンおよびタングステンの水溶解性に及ぼす酸化還元環境の影響 Influence of redox condition on the solubilities of Mo and W

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It is well known that concentrations of trace elements in sea water are primarily correlated with their concentrations in serum levels in animals. This fact suggests that the availability of each trace element from the environment is an important factor whether the element is essential or not for biota. Thus, the chemistry deciding the concentrations of trace elements in sea water can be basic information on the understanding of the history of essential elements in biota. From this point of view, a twin element, Mo and W, is of great interest, since (i) Mo is an essential element but W is toxic to almost all biota at present, but (ii) some hyperthermophilic archaea appear to be W dependent. These facts suggest that W could be more abundant in primordial ocean or in hydrothermal water. To approach this matter, we think that it is primarily important to compare the chemistries controlling the solubilities of Mo and W in the present seawater and primordial marine environment where primitive life evolved.

Solubilities of trace elements in sea water are often controlled by adsorption reactions on solid phases in contact to the aqueous phase. Based on our laboratory experiments and analyses of natural samples in terms of their concentrations and speciation by X-ray absorption spectroscopy (XAS), we found that the solubilities of W and Mo in oxic seawater at present are controlled by their surface complexes on Fe hydroxides, outer sphere complex or inner sphere complex. The former is more soluble than the latter, since the latter has direct chemical bonding to the oxide surface. The formation of inner-sphere complex, in turn, is related to the acidity of the oxyanions such as molybdate and tungstate ions. Thus, it was revealed that the concentrations of oxyanions including Mo, W, As, and Se in sea water are primarily controlled by the acidity of the oxyanions.

On the other hand, solubilities of Mo and W in possible primordial marine environment that can be rich in sulfide were discussed based on the adsorption reactions of Mo and W on sulfide minerals (pyrite and pyrrhotite) and analyses of sediment core samples collected near the hydrothermal vent systems in the Izena Cauldron, Okinawa Trough. The core sample was particularly selected since the sulfide minerals were formed at 20 cm depth, but not at the surface within the core. The analyses of the samples at various depths from the core enable us to compare the Mo and W solubilities and reactions controlling the concentrations. As a result, formation of sulfidic species of Mo was confirmed at the 20 cm depth, but not at the surface for Mo. Although W species cannot be determined by XAS, formation of sulfidic species of W was not found in the sediment samples which were incubated under reducing condition in laboratory, where a small amount of Mo was in the sulfide form. This result suggests that the solubilities of Mo and W in "sulfide world", or the environment where primitive life evolved, can be controlled by their affinities to sulfur.

キーワード: モリブデン, タングステン, 海水, 溶解性, スペシエーション

U020-02

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砂岩の水飽和率と反応表面積との関係

Relationship between water saturation and reactive surface area of sandstone

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鉱物の溶解・沈殿や鉱物への溶存物質の吸着は、水と鉱物の接触面で起こる。水と鉱物の接触（反応）面積を見積もることは、岩石内部の反応や物質輸送を定量的に扱う上で非常に重要である。従来の岩石-水反応に関する研究では、間隙を完全に水で飽和させた岩石に水を流し、その際に生じる溶解の速度や反応表面積を評価した例が多い。しかし、地球表層環境では、岩石内部の間隙は必ずしも完全に水で満たされてはおらず、水と空気が混在した状態にある。このような不飽和な状態下では、部分的に水と接触していない鉱物が存在するため、その反応表面積は飽和状態とは異なる値になると予想される。しかし、水飽和率の変化が岩石の反応表面積に及ぼす影響を定量的に評価した研究はほとんど見当たらない。

そこで本研究では、様々な水飽和率の下で溶解実験を行い、水飽和率の変化に伴う反応表面積の変化を調べた。試料には、フランス産フォンテーヌブロー砂岩（間隙率：7.4%、間隙径：1-10 μm 、鉱物組成：ほぼ100%石英）を用いた。水飽和率を0%、50%、100%に調節した砂岩コア試料（直径35mm、高さ10mm）に対して定水位法にて水を流し、各水飽和率において試料を透過した溶液中のSi濃度（モリブデンブルー法）、および流量を測定した。これらの値を、完全飽和時の値で割ることにより、相対反応表面積（完全飽和時の反応表面積に対する相対値）を算出した。その結果、水飽和率が減少するに従って反応表面積も減少し、初期水飽和率が0%（透水後水飽和率39%）のとき相対反応表面積は約50%程度にまで減少した。

水飽和率の変化に伴う反応表面積の変化幅は鉱物組成や間隙構造によって異なる可能性があるが、本研究の結果は、地球表層の岩石-水反応を定量的に扱う上で、水飽和率の影響の評価は重要であることを示している。

キーワード: 反応表面積, 水 岩石相互作用, 浸透流, 水飽和率, 砂岩

Keywords: reactive surface area, water-rock interaction, water flow, water saturation, sandstone

U020-03

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岩石の風化に対する水飽和率の影響 ~ 流紋岩の例 ~ Effect of water saturation on weathering of a rock: an example of rhyolite

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岩石の風化は、溶解・沈殿等の反応と移流・拡散等による元素移動の結果として進行する。地下水面より上では、岩石の間隙中には空気と水が存在し、不飽和な状態になる。本研究では、神津島の多孔質流紋岩を対象として、水飽和率の変化が反応速度や元素移動にどのような影響を及ぼすかを調べた。

真空含浸により間隙を完全に水で飽和させた流紋岩コアを用いて、透水実験および透過拡散実験を行い、飽和状態における透水係数と、岩石間隙中の溶存 Si の有効拡散係数を測定した。また、同様の実験を乾燥試料を用いて行い、不飽和状態の透水係数と有効拡散係数を測定した。その結果、不飽和透水係数は飽和透水係数の約 0.08 倍、不飽和拡散係数は飽和拡散係数の約 0.4 倍となり、特に透水係数の変化幅が大きかった。透水係数や拡散係数が水飽和率によって変化するものは、流路の屈曲度、連結度、サイズ、本数等が間隙中の空気の割合によって変化するためと考えられる。

流紋岩の風化速度 (Si の溶解速度) を飽和状態と不飽和状態とで比較するために、透水実験・拡散実験で求めた値と、別途測定した流紋岩の単位反応面積当たりの溶解速度を用いて、反応・輸送方程式による風化速度の数値計算を行った。その結果、飽和状態の風化速度は $7\text{E-}18 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$ 、不飽和状態の風化速度は $9\text{E-}19 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$ という値が得られた (岩石の大きさ 50 cm の場合)。神津島の流紋岩については、風化年数の異なる流紋岩の化学組成の比較から、天然の風化速度として約 $6\text{E-}19 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$ が得られている。天然の風化速度と数値計算結果とを比較すると、不飽和状態における計算値がより天然の値と近いことが分かる。このことは、天然の風化速度を正確に予測する上で、水飽和率の影響の評価が重要であるということを示している。

U020-04

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表面錯体構造の比較による鉄マンガン酸化物への吸着に伴うモリブデンの同位体分別機構の解明

Mechanisms of adsorptive isotopic fractionation of Mo on ferromanganese oxides based on the systematics of its surface c

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Molybdenum (Mo) shows large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which affects isotopic composition of Mo in modern oxic seawater. Due to this fractionation process, isotopic ratio of Mo in marine environment is expected to be used as a paleocean redox proxy. The aim of this study is to reveal the fractionation mechanisms of Mo isotopes during adsorption on natural ferromanganese oxides. We investigated surface complex structures of Mo on various Fe/Mn (oxyhydr)oxides, key factors for isotopic fractionation, and compared them with previously-reported isotopic fractionations.

Adsorption experiments were conducted using synthetic amorphous ferrihydrite and *delta*-MnO₂, and crystalline goethite and hematite as adsorbents. Solutions were adjusted to pH 8 and I = 0.70 M (NaNO₃). The structures of adsorbed species were investigated by conventional fluorescence XAFS method. Measurements for Mo K-edge EXAFS were performed at BL01B1 in SPring-8, and those for Mo L₃-edge were at BL-9A in Photon Factory.

Our XAFS analyses revealed that Mo forms a *Td* outer-sphere complex on ferrihydrite and distorted *Oh* inner-sphere complexes on *delta*-MnO₂ (Kashiwabara et al., 2009). In addition, Mo forms inner-sphere complexes on crystalline goethite and hematite: *Td* edge-sharing (46%) and *Oh* double corner-sharing (54%) for goethite; *Td* double corner-sharing (14%) and *Oh* edge-sharing (86%) for hematite. These structural information showed the excellent correlation with the degree of isotopic fractionation during adsorption reaction of Mo reported in previous studies: the proportion of *Oh* species or their magnitude of distortion in Mo surface complexes become larger in the order of ferrihydrite < goethite < hematite < *delta*-MnO₂, a trend identical to the degree of isotopic fractionation (Goldberg et al., 2009). Based on the comparison with previous reports for Mo surface species on various oxides such as MgO, Al₂O₃, and TiO₂, chemical factors that affect Mo surface complex structures were also discussed. The hydrolysis constant of cation in oxides, log K_{OH}, (or the acidity of the oxide surfaces, PZC) is well correlated with the mode of attachment (inner- or outer-sphere) of Mo surface complexes. Furthermore, the symmetric change in Mo species from *Td* to *Oh* is suggested to be driven by the formation of inner-sphere complexes on specific sites of the oxide surfaces.

References

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Goldberg et al., (2009) *Geochim. Cosmochim. Acta*, **73**, 6502-6516.

Keywords: molybdenum, isotopic fractionation, surface complex structure, ferromanganese oxides

U020-05

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時間:5月23日 10:00-10:15

セリウム安定同位体分別に関する実験的研究 Experimental study on cerium isotopic fractionation

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Cerium (Ce) anomaly that appears in rare earth element (REE) pattern is a tool to estimate paleoredox condition and has been used for many studies. Discussion in previous studies, however, has been limited to qualitative based on a REE pattern. In addition, the formation process of Ce anomaly is not fully understood. This study, therefore, aims to provide fundamental information on the redox condition in paleoenvironment by Ce stable isotope ratio related to the redox-sensitive property of Ce. If fractionations of Ce stable isotope respond differently to various geochemical processes such as (i) oxidative scavenging on Mn oxide, (ii) precipitation as CeO₂ or Ce(OH)₄, and (iii) adsorption of Ce³⁺ without oxidation, it is possible that Ce stable isotope ratio can give much information on redox condition in paleoenvironment. It is expected that the coupling of the Ce stable isotope ratio and Ce anomaly can be a unique paleoredox tracer.

In this study, a laboratory experiment under equilibrium condition was conducted. Cerium(III) chloride solution was added to manganese oxide and iron hydroxide, respectively, with various Ce concentration. In both systems, pH was adjusted to 5.00 (±0.05) and shaken for 6 hours before the filtration using 0.2 micrometer membrane filter. In addition, precipitation of Ce was obtained by bubbling of O₂ gas in the same CeCl₃ solution. Stable isotope ratios of Ce in both liquid and solid phases were determined using a MC-ICP-MS at Kochi Institute for Core Sample Research. The isotope ratios are expressed in standard epsilon notation relative to the average standards, which is shown in an equation as follows; $\epsilon^{142}\text{Ce} = [({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{sample}}/({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{CeCl}_3} - 1] \times 10000$. For solid phase sample, Ce L_{III}-edge XANES was measured at BL-12C in Photon Factory, and Ce K-edge EXAFS was measured at BL01B1 in SPring-8.

Mean isotopic fractionation factors between liquid and solid phases (a_{Lq-So}) of the systems of (i) adsorption on manganese oxide (ii) adsorption on iron hydroxide, and (iii) spontaneous precipitation of Ce were 1.000411 (±0.000079), 1.000145 (±0.000022), and 1.000196 (±0.000031), respectively. In this case, Ce adsorbed onto Mn oxides was oxidized to tetravalent, while that on Fe hydroxide remains trivalent. In addition, XANES spectrum of the spontaneous precipitation of Ce clearly showed that Ce was tetravalent. These facts indicate that isotopic fractionation of Ce between liquid and solid phases becomes larger as the redox condition becomes oxic in the order of adsorption without oxidation, Ce(IV) precipitation, and oxidative adsorption. Thus, it is suggested that the combination of Ce stable isotope ratio and Ce anomaly which respond differently to various redox conditions can be a useful tracer to discuss the change of redox condition of paleocean.

キーワード: セリウム, 安定同位体, XAFS

Keywords: Cerium, Stable isotope, XAFS

U020-06

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時間:5月23日 10:15-10:30

極低酸素条件下における溶存 Fe (II) の酸化 速度、機構とその適用 Ferrous iron oxidation under very low O₂ conditions: Rates, mechanisms and application

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Although there have been numerous studies on Fe(II) oxidation kinetics, few have paid attention to the kinetics under very low O₂ conditions. The importance of Fe(II) oxidation under very low O₂ conditions has been recognized recently; Fe(II) oxidation kinetics has been shown to be applied to the Fe(II)/Fe(III) compositions of paleosols, ancient soils formed by weathering, which can give a quantitative pattern of atmospheric oxygen increase during the Paleoproterozoic (from < 10⁻⁶ atm to > 10⁻³ atm of partial pressure of atmospheric oxygen, pO₂). The effects of pO₂ on Fe(II) oxidation rate was investigated to establish Fe(II) oxidation rate-pO₂ relationship under very low O₂ conditions. All oxidation experiments were carried out in a glove box by introducing Ar gas under conditions of 10⁻³ - 10⁻⁵ atm of pO₂ and 7.57 - 8.12 of pH at room temperature. Because of very low concentrations of Fe(II) (down to ~ 0.1 ppb), new methods were developed to measure Fe(II) concentrations. The dominant species related to oxidation in the pH range examined is suggested to be Fe(OH)₂. The rate law changes from $d[\text{Fe}^{2+}]/dt = -k'_{0-high} [\text{Fe(II)}][\text{OH}^-]^{2.0} [\text{O}_2]^{1.0}$ to $-k'_{0-low} [\text{Fe(II)}][\text{OH}^-]^{2.0} [\text{O}_2]^{0.5}$ (k'_0 , the rate constant; [O₂], the concentration of dissolved oxygen) at 0.2 - 0.005 and < 0.005 atm of pO₂, respectively. The former rate law is explained by well-known mechanisms of the four-step reactions. The latter law is established for the first time, where the Fe(II) oxidation rate is faster than that predicted by the classical rate law. To explain the mechanisms, it is suggested that reactions where oxygen produces radicals and hydrogen peroxide play a critical role in addition to the four-step reactions. Such a reaction occurs due to dilute nature of the solutions of ~ 5 - 0.5 ppb of [O₂] and ~ 10 - 0.1 ppb of [Fe(II)], and therefore, will have impact on red-ox chemistry in very dilute solutions. Application of this new oxidation rate law to Fe(II)/Fe(III) ratios of paleosols gives a new quantitative pattern of atmospheric oxygen evolution between 2.5 and 2.0 Ga; atmospheric oxygen evolved rapidly from very low O₂ levels (pO₂ < 10⁻⁶ atm) to ~ 10⁻⁶ atm of pO₂ at ~ 2.45 Ga and then gradually increased to 10⁻³ atm of pO₂ at 2.0 Ga. Although the constraints set by geological records such as mass independent fractionation of sulfur (i.e., < 10⁻⁶ atm prior to ~ 2.45 Ga, > 10⁻⁶ atm at 2.32 Ga and > 10⁻³ atm at < 2.0 Ga) were not used for the calculations, the atmospheric oxygen evolution model proposed here is consistent with these constraints.

キーワード: Fe(II) 酸化速度, 低酸素, 風化, 大気酸素進化

Keywords: Fe(II) oxidation rate, low oxygen, weathering, atmospheric oxygen evolution

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U020-07

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資源地質学の現状と将来 Perspectives on resource geology

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Here I present several examples of my current researches on resource geology. One is a research on a new type of submarine mineral deposit that may potentially produce huge amounts of rare-earth resource. Last September, a "rare-earth shock" accompanied the announcement that China would reduce its exports of rare-earth elements to the West. The newly-discovered mineral deposit may break such a concern about a deficient supply of rare-earth resource to the world in the future. Secondly, I discuss about a genesis of Besshi-type Cu deposits in the Sambagawa metamorphic belt in Japan. The Besshi-type Cu deposits are strata-bound volcanogenic massive sulfide deposits that were the ancient counterparts of modern Cu-rich seafloor massive sulfide deposits and were formed/preserved as products of environmental changes of the Earth's surface. Finally, I present a new concept on origins of hydrothermal deposits in the Japanese island arc. These hydrothermal deposits in the island arc crust may have been directly formed from slab-derived fluids in the deep crust.

U020-08

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熱水環境下における鉄酸化物のトランスフォーメーションメカニズム Mechanisms of Iron Oxide Transformations in Hydrothermal Systems

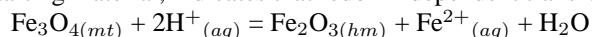
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Coexistence of magnetite and hematite is observed in various hydrothermal systems (e.g., banded iron formations (BIF), seafloor hydrothermal systems, volcanogenic massive sulfide (VMS) deposits, iron oxide copper gold ore (IOCG) deposits). They have often been used to constrain the redox potential of fluids, assuming that the redox equilibrium is attained among all minerals and aqueous species. However, as temperature decreases, disequilibrium mineral assemblages may occur due to the slow kinetics of reaction involving the minerals and fluids. In this study, we conducted a series of experiments in which hematite or magnetite was reacted with an acidic solution under H₂-rich hydrothermal conditions (T = 100-250 degree C, P of hydrogen = 0.05-5 MPa) to investigate the kinetics of redox and redox-independent transformations between hematite and magnetite, and the mechanisms of iron oxide transformation under hydrothermal conditions.

The formation of euhedral crystals of hematite in 150 and 200 degree C experiments, in which magnetite was used as the starting material, indicates that redox-independent transformation of magnetite to hematite occurred within 24 hours:



The chemical composition of the experimental solutions was controlled by the redox-independent transformation between magnetite and hematite throughout the experiments. While solution compositions were controlled by the redox-independent transformation in the first 3 days in a 250 degree C experiment, reductive dissolution of magnetite became important after 5 days and affected the solution chemistry. At 100 degree C, the presence of maghemite was indicated in the first 7 days. Based on these results, equilibrium constants of redox-independent transformation between magnetite and hematite and those of redox-independent transformation between magnetite and maghemite were calculated. Our results suggest that the redox transformation of hematite to magnetite occurs in the following steps: (1) reductive dissolution of hematite to Fe²⁺(aq) and (2) non-redox transformation of hematite and Fe²⁺(aq) to magnetite.

We propose that transformation mechanisms observed in the experimental study are applicable to various natural systems involving low-temperature hydrothermal solutions. For example, coexistence of magnetite and hematite is commonly observed in typical oxide-type BIFs. Many geochemical and mineralogical studies (e.g., Hoashi et al., 2009) suggested that hematite is a primary mineral in the BIFs, and that magnetite is a transformation product of primary hematite. Our study showed that redox-independent transformation of hematite to magnetite is a plausible process in the BIFs, by a reaction between primary hematite and Fe²⁺-rich hydrothermal fluids during early diagenesis. An important implication in considering the origin of magnetite in BIFs is that magnetite was likely formed under the conditions where the system was far from redox equilibrium. Therefore, the presence of magnetite in BIFs cannot be used to constrain the atmospheric or oceanic oxygen levels during the deposition of BIFs.

Reference

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キーワード: hydrothermal system, iron oxide, redox reaction, banded iron formation, hematite, magnetite
Keywords: hydrothermal system, iron oxide, redox reaction, banded iron formation, hematite, magnetite

U020-09

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ヘマタイトナノ粒子の還元的溶解に与える粒径・形態・凝集状態の影響 Influence of size, morphology and aggregation state on reductive dissolution of hematite nanoparticles

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Nanoscale iron (oxyhydr)oxide minerals are omnipresent in natural environments and initial studies have found their size can influence chemical reactivity, e.g., dissolution kinetics. Their dissolution behavior is important because it influences the bioavailability of nutrients for plant growth and the migration of pollutant metals and organic compounds. In natural environments, reductive dissolution is the most important dissolution mechanism (Sulzberger et. al. 1989). Madden and Hochella (2005) reported the oxidation of Mn²⁺ catalyzed by hematite nanoparticles depended upon nanoparticle size. These results suggest that other redox reactions occurring on hematite surfaces may be size-dependent as well. In this study, we have investigated the size dependence of the reductive dissolution of hematite with ascorbic acid using two types of nanoparticles with average diameters of 7 nm and 30 nm.

Hematite nanoparticles were synthesized by forced hydrolysis of ferric nitrate and characterized with powder XRD, TEM, and BET surface area measurements. Reductive dissolution experiments were carried out in continuously stirred Teflon beakers at 302 K in the absence of light under approximately 1 atm nitrogen gas. Aqueous [Fe(II)] was measured by the ferrozine assay. The evolution of crystal morphology by reductive dissolution was examined by high resolution TEM (HRTEM). In addition, electron tomography technique was employed to understand the real three-dimensional structure of individual particles and aggregates. This technique allows us to reconstruct 3D images from a series of TEM images taken from an area of interest. HRTEM revealed that the 7 nm hematite crystals are pseudo-hexagonal plates and the 30 nm hematite crystals are rhombohedral. Hematite nanoparticles of both sizes have defective surfaces. The two types of dissolution rates, initial rate and steady state rate, were determined and compared after surface areanormalization. The surface area-normalized initial rates of reductive dissolution are more than 2 times greater in 7 nm hematite. However, no significant size dependence is observed for steady state rates. TEM observation of individual crystals and aggregates of partially-dissolved hematite reveal that dissolution initiates from surface defects or sharp edges on crystals. Also, aggregation state changes as the dissolution progresses. This study directly shows the importance of surface roughness, defects, crystal morphology and aggregation states on dissolution rates.

キーワード: ヘマタイト, 溶解速度, 粒径, 結晶形態, 凝集状態, 透過電子顕微鏡

Keywords: Hematite, dissolution kinetics, particle size, crystal morphology, aggregation state, transmission electron microscopy

U020-10

会場:304

時間:5月23日 11:40-11:55

北海道幌延地域における堆積岩中のヨウ素の化学形態および $^{129}\text{I}/^{127}\text{I}$ 比分析 Iodine speciation and $^{129}\text{I}/^{127}\text{I}$ ratios in sedimentary rocks in Horonobe, Hokkaido

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Introduction

Iodine-129 is one of the most problematic radionuclides, which is produced by nuclear related activities such as nuclear power generation and nuclear fuel reprocessing, because of its long half-life (15.7 million years) and high mobility. To investigate behavior of iodine in sedimentary rocks is important to evaluate the effectiveness of the natural barrier for nuclear waste repositories. In Horonobe area, iodine rich brine exists in deep underground. The region is underlain mainly by Neogene to Quaternary marine sedimentary rocks, the Wakkanai Formation (Wk Fm), and the overlying Koetoi Formation (Kt Fm): siliceous and diatomaceous shale. We determined iodine distribution, speciation, and isotope ratio ($^{129}\text{I}/^{127}\text{I}$), to investigate long-term migration of iodine in diatomaceous and siliceous shale.

Experiment

All core and groundwater samples were collected by at JAEA Horonobe underground research center. Iodine concentrations in groundwater samples were determined by ICP-MS. For core samples iodine was separated by pyrohydrolysis or alkaline extraction (using Tetramethyl ammonium hydroxide) and determined by ICP-MS. Iodine species in groundwater were separately detected by high performance liquid chromatography (HPLC)-ICP-MS, using anion exchange column and size exclusion column for separation of IO_3^- and I^- , and organic and inorganic iodine, respectively. Iodine species in core samples were determined by iodine K-edge XANES (SPring-8 BL01B1). Thin sections of core samples were prepared, and iodine mapping were obtained by micro-XRF analysis (SPring-8 BL37XU). $^{129}\text{I}/^{127}\text{I}$ ratios in groundwater and core samples were measured by accelerator mass spectrometry (MALT, Univ. of Tokyo).

Results and discussion

Concentration of iodine in groundwater varied widely and was much higher than that of seawater with high correlation with that of chlorine ($R^2 = 0.90$). Iodine in core samples decreased near the boundary between Wk and Kt Fm. Iodine existed as I^- in groundwater, while that in shale was a mixture of organic and inorganic I. Iodine mapping showed that iodine accumulated to micro region (< 30 micron). Iodine isotope ratios ($^{129}\text{I}/^{127}\text{I}$) were higher in siliceous shale compared with that of groundwater. According to these results, migration of iodine in this area can be expected as follows; 1) iodine accumulated as organic iodine in siliceous sediment, 2) iodine was released from layers deeper than Wk Fm during diagenetic process where I^- was dissolved into iodine-rich groundwater, 3) iodine-rich groundwater was distributed to Wk and Kt Fm due to the compaction of the layers, 4) both iodine and chlorine were diluted by freshwater from the surface.

It was suggested that I^- is released to the ground water during the maturation of organic matter. Dissociated I^- can move toward the surface because of the upward water flow driven by compaction. Thus, iodine rich brine is created by integration of iodine released from underlying formation. Because of high mobility of I^- , released I^- remains in solution phase, and concentration of the iodine in solution has increased during sedimentation history.

キーワード: ヨウ素, X線吸収端近傍構造, HPLC-ICP-MS, ヨウ素同位体比

Keywords: Iodine, XANES, HPLC-ICP-MS, Iodine isotope ratio

U020-11

会場:304

時間:5月23日 11:55-12:10

オマーン高アルカリ泉における二次鉱物生成がヨウ素の移行挙動に与える影響 The effect of secondary mineral formation for the migration behavior of iodine at hyperalkaline springs in Oman

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In Japanese transuranic (TRU) waste disposal facilities, ¹²⁹I is the most important key nuclide for the long-term safety assessment. Thus, the distribution coefficients (K_d values) of I to natural minerals are important factor in the safety assessment. However, the degradation of cement materials in the repositories can produce high pH pore fluid which can affect the anion transport behaviour. Therefore, it should be necessary to understand the behaviour of anions such as I⁻ under the hyperalkaline conditions.

This study examined the naturally-occurring hyperalkaline conditions near the springs in Oman as natural analogue for the interaction between cement pore fluid and natural Mg-HCO₃⁻ river water. The generated natural hyperalkaline spring water (pH>11) from the partly serpentinized peridotite in the Oman ophiolite is characterized as hyperalkaline, reducing, low-Mg, Si and HCO₃⁻, and high-Ca while the river water where the alkaline spring, is moderately alkaline, oxidizing, high-Mg and HCO₃⁻. The mixing of these spring and river water resulted in the formation of secondary minerals, forming river terrace with height of more than 10 meters. The present aim of this paper is to examine the conditions of secondary mineral formation and the anion uptake capacity of these mineral phases generated. The long-term stability of this sorption behaviour in this system was also investigated.

Water and precipitate samples were collected at various distances from the spring vent to identify the effect of mixing ratios between spring and river water on mineral composition and water-mineral distribution coefficient of various anions. On-site synthesis was also carried out to support these data quantitatively. Furthermore, samples of deposits were collected from the river terrace at different height which corresponds approximately to the depositional age in order to find out the alteration of minerals and possible anion desorption.

The results of the mineralogical and chemical characterization of the collected samples confirmed that the formation of secondary mineral was dominated by aragonite at the mixing points of the spring and surface water, due to high Mg content of the latter. Hydrotalcite like compound (Mg-Al hydroxides) was also detected as accessory minerals since the hyperalkaline springs contain relatively rich in Al.

During the formation of the minerals at the mixing points, HCO₃⁻ in the river water was fixed as carbonate minerals in aragonite and calcite phases while H₃SiO₄⁻ in the river water was dominantly fixed into the interlayers and surfaces of HTlc. Iodine in spring and river water was mainly fixed in aragonite. XRD quantitative analysis by Rietveld method indicated K_d values of iodine increase proportionally to the aragonite content in the precipitate samples. Consequently, in terms of short-term assessment, particularly for I⁻, uptake by secondary minerals can be expected at hyperalkaline conditions as observed at Oman hyperalkaline springs.

キーワード: 炭酸塩鉱物, ヨウ素, アラゴナイト, カルサイト, ハイドロタルサイト, ナチュラルアナログ研究

Keywords: calcium carbonate, iodine, aragonite, calcite, hydrotalcite, natural analogue study

U020-12

会場:304

時間:5月23日 12:10-12:35

オマーンの高アルカリ環境に生息する魚類の形態・生理・生態 Morphology, physiology, and ecology of the fish inhabiting highly alkaline environments in Oman

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オマーンオフィオライトからはpH11-12の高アルカリ温泉が湧出している。多くの温泉水は周囲の河川水と混ざり合い、複雑なアルカリ環境を作り出しているが、そこに魚類が観察される。高アルカリ環境に生息する魚類については、pH9.6-10.0で、 Na_2CO_3 と NaHCO_3 を主成分とするトロナが形成されるケニアのマガディ湖のティラピア (*Alcolapia grahami*) [1] や富栄養化の影響により一部でpH10.5に達することもあるイギリスの淡水湖スラプトン・レイのパーチ (*Perca fluviatilis*) およびパイク (*Esox lucius*) [2] に関する報告などがあるが、研究例は少なく、オマーンの高アルカリ環境に生息する魚類に関する報告は皆無である。しかも、オマーンの高アルカリ環境には、源泉のpHが11を超える点や源泉の周辺に多量の CaCO_3 塩が形成される点などの特徴があり、このような環境に対する魚類の適応機構に興味を持たれる。私たちは、日本学術振興会・科学研究補助金(基盤研究(B))の支援を受けた研究プロジェクト「オマーンに湧出する高アルカリ泉から学ぶアルカリ環境の地球・生物資源科学」(研究代表者:北大・佐藤努博士)に参加し、2009年12月および2010年12月にオマーンのBat'h, Faydh, Fizh, Hiltiを訪れ、高アルカリ環境に生息する魚類について調査・実験を行った。また、採集した魚類の形態や組織構築を解析し、高アルカリ環境に対する魚類の生存戦略について考察した。

調査の結果、高アルカリ泉の周辺には、3種の魚類 [*Garra barreimiae*, *Cyprinion microphthalmum*, アラビアメダカ (*Aphanius dispar*)] が生息し、特に*G. barreimiae*と*C. microphthalmum*の生息数が多いことが判明した。これらの魚は、アルカリ温泉水だけのプールには見られず、河川水、あるいは温泉水が河川水と混ざり合う水域のpHが高くない場所を選んで生息しているように観察された。*G. barreimiae*を用いて、アルカリ温泉水と河川水の混合水に対する生存能力を調べてみたところ、70%アルカリ水では魚は生存したが、80%アルカリ水では24時間以内にすべて死亡した。しかしながら、70%アルカリ水で24時間生存した魚は80%アルカリ水に移しても、80%以上の個体が12時間以上生き残った。この結果は、*G. barreimiae*が24時間以内に80%アルカリ水への適応能を獲得したことを示唆している。また、*G. barreimiae*を入れたアルカリ混合水のpHが、魚を入れていない混合水のpHよりも、より速く低下したことから、魚が、呼吸、粘液、あるいは尿などの排泄物により、個体周辺の水のpHを下げる可能性が示唆された。*G. barreimiae*の形態と組織を解析した結果、皮膚の表皮、および主要な浸透圧調節器官である鰓に粘液細胞が認められた。また、透過型電子顕微鏡による観察では、魚の海水適応時に働くと思われるタイプの塩類細胞が鰓に認められた。

本講演では、両生類など他の生物についても紹介する予定です。日本地球惑星科学連合の会員の方々から、ご意見・ご指摘を頂けましたら幸いです。

キーワード: オマーン, 高アルカリ環境, 魚, 動物

Keywords: Oman, highly alkaline environment, fish, animals

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U020-13

会場:304

時間:5月23日 14:15-14:40

53年目の新セントラル・ドグマ A new Central dogma for life in the Universe after 1958

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地球惑星合同大会において生命?水?鉱物?大気相互作用(以前は生命?水?鉱物相互作用)セッションができて、10年以上経つ。相互作用の典型としての多くの研究が、セッション設立時から発表されてきた。また、地質学、岩石学、鉱物学、無機・有機化学、古生物学、微生物生態学が、同じ土俵で議論するという場も、「ハレ」から「ケ」となりつつある。その先鞭をつけた本セッションは、ユニオンセッションに進化した。

各論での議論は深みを増したことはまちがいない。しかし、いまだ議論の展開軸はねじれの位置にある場合も多い。生命?水?鉱物?大気相互作用を議論する上での一つの絶対的な座標軸として、エネルギー論から見た生命活動、生命?地質相互作用という考え方がある。この座標軸は、地球のいかなる環境であれ、いかなるスケールであれ、宇宙であれ、共通して適用できるものであり、1958年にフランス・クリックによって提唱されたセントラル・ドグマを超える、宇宙共通原理としての生命?地質相互作用の中心原理と言える。本家たるエヴェレット・ショックや宇宙生物学者トリ・ホエラーが言わないので、自分で言うしかないが、これは「新セントラル・ドグマ」と呼ぶべきものである。

キーワード: 生命存在条件, セントラルドグマ, エネルギー論

Keywords: habitability, central dogma, energy mass balance

U020-14

会場:304

時間:5月23日 14:40-14:55

深海底に生息する化学合成微生物の群集遺伝学的構造解明へのアプローチ A new approach for clarifying the population genetic structure of chemoautotrophic bacteria in deep-sea hydrothermal field

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深海底熱水環境には、硫酸酸化や水素酸化などを行う化学合成微生物が支える独特な生態系が存在する。世界中の深海底熱水環境において Epsilonproteobacteria 綱に属する化学合成微生物が普遍的に優占して生息していることが明らかとなってきた。本分類群は胃潰瘍や胃癌、腸炎等の原因となる *Helicobacter pylori* や *Campylobacter jejuni* といった病原性微生物を含むことで知られている。これら病原性 Epsilonproteobacteria の群集遺伝学的構造は、突然変異や水平伝播の頻度が極めて高く特徴的だが、深海性のものに関しては研究例がない。そこで本研究では、深海性 Epsilonproteobacteria の群集遺伝学的構造を MLSA 法によって明らかにすることを目的とした。

有人・無人潜水艇により、西太平洋・インド洋など世界各地の深海底熱水活動域において採取された試料を希釈培養した後、限界希釈法に供し単離を行った。複数のハウスキーピング遺伝子の塩基配列をもとに、系統樹作成および突然変異や組換え頻度等を算出し、群集遺伝学的構造を決定する要因を調査した。

系統樹作成の結果、類似性の高い 16S rRNA 遺伝子配列を持つ分離株内で、その由来する地域ごとにクレードが形成される傾向が見られた。このことから、深海底熱水環境に生息する化学合成微生物群集では、多くの微生物群集で観察される地理的な混合が起こっていないことが示唆された。本発表では、微生物の生物地理についての所見を示しつつ、深海性 Epsilonproteobacteria の群集構造やゲノムレベルの多様性を生み出す原動力について議論したい。

U020-15

会場:304

時間:5月23日 14:55-15:20

西部北太平洋亜寒帯域の生物生産を支える鉄分の供給過程 Iron supply processes which support biological production in the western subarctic Pacific

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Iron is an essential nutrient and plays an important role in the control of phytoplankton growth. Atmospheric dust has been thought to be the most important source of iron, supporting annual biological production in the Western Subarctic Pacific (WSP). We argue here for another source of iron to the WSP. Multi-year (2003-2008) time series observations along the A-line provided information on the temporal variability of the dissolved iron (diss-Fe) concentration in the Oyashio region of the western subarctic Pacific and the data indicate that an annual cycle of surface diss-Fe occurs every year. Diss-Fe was supplied into the surface water in this region every winter and supports the spring phytoplankton bloom after development of the thermocline. The diss-Fe concentration was drawn down during the phytoplankton bloom period, and was depleted in summer in some water masses. Then diss-Fe increased from autumn to winter with the increasing depth of the surface mixed layer. The high diss-Fe concentrations in the surface layer in winter were controlled by mesoscale oceanic intrinsic processes, such as vertical winter mixing and horizontal Fe-rich intermediate water transport. Difference in magnitude of the winter mixing processes among different water masses caused the heterogeneous distribution of diss-Fe concentration in the surface layer. Moreover, the vertical section profiles along a cross-Oyashio transect showed the occurrence of Fe-rich intermediate water, and upward transport of materials from the intermediate water to the surface layer via winter mixing processes are important mechanisms to explain the high winter surface diss-Fe concentrations. Additionally, the substantially higher diss-Fe/NO₃ ratio in the winter surface layer in this studied area than the other HNLC region indicating that the winter surface water in the Oyashio and the Oyashio-Kuroshio transition zone has a high potential to stimulate phytoplankton growth.

キーワード: 海洋, 鉄, 生物生産, 供給過程, 植物プランクトン

Keywords: ocean, iron, supply processes, phytoplankton

U020-16

会場:304

時間:5月23日 15:20-15:35

サンゴ骨格と無機合成アラゴナイト結晶の比較 Comparison of crystallographic texture coral skeleton with synthesized aragonite

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Coral skeletons are constituted of aragonite (CaCO_3). Aragonite is a metastable phase compared to calcite under the coral growing environment. The growth process of aragonite has been interested for long years but not been revealed clearly, although it should be greatly important for the reconstructing paleoclimate using variation of the trace elements and isotope in coral skeletons.

Organic matters play important role in biomineralization, and sometimes control the growth texture of minerals. For example, the nacre of the shell is composed of layered aragonite platelets shaped hexagonal and the crystallographic c-axis normal to the plane of platelets. It is well known that organic matrix sheets between the platelets control the formation of mineral texture in nacre. However aragonite crystals in coral skeletons formed by biomineralization show needle-like shape and elongate along the c-axis.

In this study, we compared mineral textures of the synthetic of aragonite with natural coral skeleton in order to consider the biomineralization process of coral skeleton growth.

Synthetic aragonite was prepared by precipitating from quasi-seawater without organic matrix at 25 degrees C. Observation was made by using a scanning microscope and a transmission electron microscope.

Keywords: coral skeleton, aragonite

U020-17

会場:304

時間:5月23日 15:35-15:50

含水炭酸カルシウム鉱物の変質速度と溶解度に及ぼすマグネシウムイオンの影響 Effects of magnesium ion on alteration rate and solubility of hydrated calcium carbonate

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INTRODUCTION

Calcium carbonates are abundant in nature. There are six distinct calcium carbonate species. Anhydrous polymorphs are calcite, aragonite, and vaterite, and hydrated forms are monohydrocalcite (monohydrate), ikate (hexahydrate), and amorphous calcium carbonate. Although calcite is most stable among these six phases, solutions containing Mg^{2+} , SO_4^{2-} , and organic matter, such as sea waters and brines have been known to inhibit the formation of calcite [1]. Monohydrocalcite have been found in saline and alkaline lakes and sea water environment [2]. Monohydrocalcite is metastable unlike anhydrous calcium carbonates and transformed to aragonite in aqueous solutions [3]. However there have been few studies that examine the metastability of monohydrocalcite quantitatively. In the present study, effects of magnesium ion on the alteration rate of monohydrocalcite to aragonite and on the solubility of monohydrocalcite have been examined in the laboratory experiments.

METHODS

Monohydrocalcite was synthesized by mixing solutions containing 60 mM $CaCl_2$ and 6, 30, 45, 60, and 120 mM $MgCl_2$ ($[Mg]/[Ca]$ ratio was 0.1 to 2), where Na_2CO_3 was added to yield a 80 mM CO_3^{2-} solution. The resulting suspension was collected every several hours and filtered through a 0.22 μ m membrane. Total alkalinity of filtered solutions were evaluated by acid titration and the total concentrations of Ca^{2+} and Mg^{2+} were measured with inductive coupled plasma optical emission spectrometry (ICP-OES, SII SPS7700). The filtered solid were air-dried, and analyzed by X-ray diffraction (XRD, Rigaku RINT2000). The amounts of monohydrocalcite and aragonite contained in the resulting solid were evaluated by the external standard method [4]. Solubility products of monohydrocalcite were calculated by Geochemist's Workbench [5] based on total alkalinity, total concentrations of cations, and pH.

RESULT AND DISCUSSION

Monohydrocalcite formed when mother solution contained Mg^{2+} of 30, 45, 60, and 120 mM. XRD analyses revealed that aragonite was formed 78-98, 101-126, 79-106, and 101-126 hours after beginning of the experiments of 30, 45, 60, and 120 mM of Mg^{2+} , respectively. After aragonite was formed, the peak intensity of monohydrocalcite decreased with time, while that of aragonite increased with time. Alkalinity, Mg^{2+} , and pH of the solution gradually decreased with time. Ca^{2+} increased with time until XRD peak intensity of monohydrocalcite completely disappeared. After monohydrocalcite disappeared, Ca^{2+} slightly decreased. The increment of Ca^{2+} resulted in decrement of alkalinity, because the concentrations of dissolved components must be determined by a solubility product of solid phase. The calculated solubility products of monohydrocalcite were constant in the series of Mg^{2+} concentrations, but different among experimental conditions. The solubility products of monohydrocalcite may be affected by the concentration of Mg^{2+} in solution. However, our result suggests the induction time of transformation of monohydrocalcite to aragonite were not affected macroscopically by Mg^{2+} contents in mother solutions.

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キーワード: 炭酸カルシウム鉱物, 準安定相, 変質速度, 溶解度

Keywords: calcium carbonate, metastable, alteration rate, solubility

U020-18

会場:304

時間:5月23日 15:50-16:05

インドネシアジャワ島中央部に発達する縞状トラバーチンの生命地球化学 Biogeochemistry of laminated travertines in Central Java, Indonesia

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Travertines are calcite or aragonite precipitates from hot-spring water containing a sufficient amount of calcium and carbon dioxide. Most of travertines show sub-mm order laminations that were formed by daily microbial activities. Two previous studies have suggested different processes in terms of responsible microbe for lamina formation; cyanobacteria that can grow and trap detritus on the travertine surface in the daytime and heterotrophic bacteria that can quickly degrade organic matter from cyanobacteria on the travertine surface in the daytime. The former model was consistent to some calcite travertines (e.g. Takashima and Kano, 2008) and an aragonite precipitates on microbial mat (Okumura et al. 2010), while the latter model was confined to one aragonite travertine (Okumura et al. 2011). Here, we study a huge travertine mound in Indonesia to consider the applicability of these processes for the diverse laminated texture of the travertines.

Pancuran Pitu is one of the hot springs that occur around Mt. Slamet, an active stratovolcano in Central Java, Indonesia. Here, a huge travertine mound was formed along the water passage flowing on the mountain surface, which is 180 m long, 60 m wide and 70 m relative elevation. The water temperature was 51°C at the vent, 45 to 35°C at the mid stream, and decreased to 29°C at the downstream. pH increased from 6.2 to 8.3, and Ca²⁺ concentration decreased toward the downstream (273 to 100 ppm) with respect to CO₂-degassing and CaCO₃ precipitation. The other chemical components were constant throughout the water passage. The mineralogy of the travertines was mainly aragonite throughout the mound, which likely reflects high Mg/Ca molar ratio (1.6 to 3.8) in water. Three types of travertine were observed in the mound; (1) brown hard travertine at the upper stream, (2) light yellow friable travertine with green microbial mats at the midstream, and (3) light yellow crystalline hard travertine at the downstream cascade. All types of travertines have sub-mm order lamination, however irregularity in the lamina thickness was recognized only in the brown hard travertine formed near the vent where the water had the highest temperature and iron concentration. The lamination of the brown travertine was unlikely formed by the daily cycle. Light yellow crystalline travertine was formed only under high flow condition as in the cascade, while friable travertine with green microbial mat was formed under low flow condition. The microbial abundance in the friable mat increased with decreased water flow and temperature. Observation using fluorescence microscope revealed that distribution of phototrophs along the lamination was only recognized in the friable travertine with microbial mat, but not in the other types of travertines, in which some other microbes were responsible for the lamination.

The difference in depositional conditions, such as temperature and water flow, resulted in different types of laminations that were likely formed by different microbial processes. Understanding such variations provide some useful information for interpretation of the ancient stromatolites.

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キーワード: トラバーチン, 縞組織, アラゴナイト, インドネシア中央部

Keywords: travertine, lamination, aragonite, Central Java

U020-19

会場:304

時間:5月23日 16:30-16:55

全球凍結による動物多細胞化の誘発 Animal multicellularity induced by the snowball Earth

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新元古宙後期は気候激変と動物進化の時期である。この2つの事件は強い因果関係で結ばれているのか、あるいは全くの無関係であるのかは解らない。しかし、生物進化が与えられた環境的試練を乗り越えることで次の局面へと前進するのであれば、因果関係が存在したと考えるべきであろう。近年の新元古宙に関する地球科学的研究の進歩は目覚ましく、この問題についての議論が可能になった。

現時点で最も広く受け入れられているのは酸素濃度の増加が動物の進化を促したというものだ。マリノアン全球凍結時に蓄積した栄養に富む海水が、全球凍結後(635 Ma)に爆発的な光合成を誘発し、高まった酸素がコラーゲンの分泌と動物の呼吸に有利に働いたとされる。確かにこの仮説は約550 Ma頃に起きた左右相称動物の進化には良く合いそうだ。しかし、海洋の著しい酸化は全球凍結から5千万年後の585 Maであり、より原始的な動物はそのほかに昔に出現していたのである。

原始的な海綿・刺胞動物も元古宙の気候激変期に進化している。これらの進化を理解するには、全球凍結後に必然的に起こった海洋の層状化を考えれば良い。全球凍結後の海洋が富栄養であり生産性が高かったという点では異論は無いが、Sr同位体のデータを考慮すると、栄養のソースは熱水性のものではなく、大陸風化起源のものであろう。すなわち、水柱を攪拌する湧昇水は弱く、海洋は比重の軽い融氷水により層状化された。表層海水で大量に生産された有機物は酸化還元インターフェースでもある比重勾配で蓄積し、動物に食料を提供した。想定される進化の場合は、現在の深海サンゴ礁と良く似ている。また、この仮説は原始的動物グループが濾過栄養であることと符号する(Kano et al., in press)。進化のキーワードは酸素ではなくエサであったのではない。

最も原始的な多細胞動物である海綿動物は襟鞭毛虫から進化したようだ。この原生動物は鞭毛細胞に形態的に類似しているだけでなく、細胞接着を司るタンパク質合成のための遺伝子を持っており、多細胞化に前適応していたといえる(King et al., 2008)。さらに興味深いのは海綿動物に共生する微生物群集である。海綿の細胞連結組織には極めて特有の微生物が共生しており、驚くべき事に、その構成が系統と地理的分布が異なる海綿で共通している。すなわち、これらは海綿動物が出現した当時から、独自に進化してきたという仮説が提唱されている(Hentschel et al., 2002)。海綿特化微生物の重要な構成グループには、非酸素発生型光合成細菌であるChloroflexiグループや硫酸還元デルタプロテオバクテリアが含まれる。これらは、酸化還元インターフェースをすみかとする。全球凍結後の海洋に集積した有機物を食べるために集まった襟鞭毛虫が、貧酸素の環境で泳ぐのをやめ多細胞化するときに、そこに住んでいた微生物が取り込まれたのではないだろうか。

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Kano, A. et al. (in press) The evolution of animal multicellularity stimulated by dissolved organic carbon in early Ediacaran ocean: DOXAM hypothesis. *Island Arc*.

キーワード: 新元古宙, 海綿動物, 海洋層状化

Keywords: Neoproterozoic, Sponges, Ocean stratification

U020-20

会場:304

時間:5月23日 16:55-17:10

先カンブリア紀のストロマトライト形成における酸素発生型光合成の役割 Role(s) of oxygenic photosynthesis in Precambrian stromatolite formation

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ストロマトライトは生命-水-鋳物相互作用で形成された微生物起源の堆積構造物であり、特に先カンブリア紀においては炭酸塩堆積物の多くを構成している。ストロマトライトの形成には微生物の代謝による鋳物形成が重要であり、堆積物捕集や鋳物核形成場提供といった作用は副次的である。微生物代謝の中でも、特に始生代に誕生したと考えられている酸素発生型光合成は CaCO_3 を沈殿させることが知られており、またそれは光と DIC (溶存無機炭素) が利用可能な幅広い環境で起きることから、ストロマトライトの形成に重要な役割を持っていたと期待される。しかしながら、現世海成ストロマトライトを用いた研究では、光合成によって沈殿した CaCO_3 は呼吸によって溶解されるために、ストロマトライト形成に果たす役割は極めて小さいと考えられた (Reid et al. 2000, Nature 406, 989-992)。またシミュレーションに基づく研究により、先カンブリア紀のような高 DIC 環境では光合成は CaCO_3 沈殿にほとんど影響しないことが示唆された (Arp et al. 2001, Science 292, 1701-1704; Aloisi 2008, GCA 72, 6037-6060)。しかしこれらは間接的な観察結果に基づく予測であり、実測によって検証する必要がある。

そこで本研究では、ストロマトライト表面近傍の $\text{pH} \cdot \text{O}_2 \cdot \text{CO}_2 \cdot \text{Ca}^{2+} \cdot \text{CO}_3^{2-}$ プロファイルを微小電極によって測定し、実際に光合成がストロマトライト形成に与える影響について検討した。まずストロマトライトが発達する自然環境において測定を行ったところ、光合成による CaCO_3 の活発な沈殿が認められた。一方、呼吸は周囲の炭酸化学に対する影響が光合成に比べて非常に小さく、検出可能なレベルの溶解は起こらなかった。次に DIC を人工的に変えて測定を行ったところ、高 DIC 条件 (最高で約 300mM) でも光合成による活発な沈殿が認められた。これは周囲の CaCO_3 過飽和度が十分高ければ、光合成の影響が小さくても沈殿を誘発しうることを示している。

以上の結果から、酸素発生型光合成は先カンブリア紀においてもストロマトライトの形成に重要な役割を果たしていた可能性が高いと考えられる。

キーワード: ストロマトライト, 光合成, シアノバクテリア, 微小電極

Keywords: stromatolite, photosynthesis, cyanobacteria, microelectrode

U020-21

会場:304

時間:5月23日 17:10-17:25

海洋衝突生成有機分子の衝突進化過程

Impact chemical evolution processes for biomolecules formed by oceanic impacts

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地球上の生物有機物の起源は、隕石飛来説の外的要因か何らかのエネルギーで無機炭素源から地球上で生成する地球内要因がある。後者で衝突エネルギーを重要視する立場からは、後期重爆期などの隕石衝突が激しい時に複数回の衝突が起きると無機炭素から生成した単純有機分子がその後どう化学進化するかを検討し、起き得るプロセスを特定化する必要がある。本発表では最も単純なアミノ酸（グリシン）が、当時の海水中で隕石衝突を受けた時の化学進化を知る目的で実験的検討を行ったので、その途中経過であるが、発表する。実験では13Cでマークされたグリシンを使用し、液体クロマトグラフ及び質量分析計で生成物の分析を行った。衝突回収実験はステンレス密閉容器中で行った。天然オリビン粉末にグリシン水溶液を浸透させ、容器試料空間中には空気が存在する条件で衝撃波を試料に与え、得られた試料は、水溶液部分は容器を液体窒素で冷却した状態で採取し分析を行った。また、固体部分は液体部分を採取後、乾燥させた後に分析を行った。グリシンの分解生成物と同時に、新しく生成したのも見つかった。この結果を踏まえ、後期重爆期の様な衝突が激しい場合には、有機分子は生成と同時に分解を起こす。このようなことから単純に簡単な有機分子が生成するプロセスの一方通行だけでなく、複雑な多岐に渡るプロセスがあると考えられる。今回の実験条件は、限られたものであるが、恐らく一度の衝突でも空間的なエネルギー不均質性が生じるので、このことも考慮する必要がある。

キーワード: 生物有機分子, 衝突エネルギー, 化学進化, アミノ酸, 後期重爆期

Keywords: Biomolecules, Impact energy, Chemical evolution, Amino acids, Late heavy bombardment

U020-22

会場:304

時間:5月23日 17:25-17:40

3.2 billion years ago Geochemical signatures pointing to an oxygenated shallow ocean 3.2 billion years ago

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Timing of the emergence of oxygenic photoautotrophs (e.g., cyanobacteria) is critical to understanding the evolution of life and the earth's surface environments. Yet, no palaeontological or biochemical signature in rocks has provided unequivocal evidence for the emergence of cyanobacteria in the Archean era. Recently, Javaux et al. (2010) discovered large, well-preserved microfossils, which are possibly the remnants of eukaryotes, from sedimentary rocks of the Moodies Group, South Africa (-3.2 Gyr). Since the emergence of eukaryotes likely requires molecular oxygen, cyanobacteria is expected to have been evolved before 3.2 Gyr if the microfossils are indeed the remnants of eukaryotes. Therefore, the objective of this study was to find geochemical signatures for the emergence of cyanobacteria in a shallow ocean environment from the same stratigraphic unit as that Javaux et al. found the microfossils.

We collected 26 sample of the Moodies Group both from outcrops and underground mining sites (e.g., Sheba gold mine) in the Barberton Greenstone Belt, South Africa. Sedimentary rock samples from the Sheba mine were divided into Magnetite-Rich Shale (MRS) group and Banded Chert (BC) group. Samples in the MRS group contain quartz, magnetite, hematite, chlorite, biotite, and chromite. While fine-grained hematite (less than 5 micro meter in diameter) is interpreted as a primary mineral in the rock, large-grained (more than 100 micro meter in diameter) magnetite is interpreted as a secondary mineral transformed from hematite during diagenesis. All chromites observed in the MRS group is euhedral and overgrown by magnetite. The boundary between chromite and magnetite is sharp. These characteristics of the chromites in the MRS group indicate that they were syn-genetically formed during diagenesis. On the other hand, samples in the BC group contain quartz, siderite, chlorite, biotite, and chromite. Chromites in the BC group are included in silicate minerals (e.g., chlorite and biotite), and often unehedral crystals.

Chemical compositions of the bulk samples in the MRS group showed that U/Th ratios have a negative correlation with both Cr/Ti and Fe_{tot}/Ti ratios. This correlation is very difficult to explain if minerals containing these elements were detrital in origin, because while U is enriched in a felsic rock, Cr is enriched in a mafic rock. Furthermore, the changes in the U/Th and Cr/Ti require the oxidation of U and Cr to decouple geochemical behaviors of U relative to Th and Cr relative to Ti. Correlations of Fe_{tot}/Ti ratios with U/Th and Cr/Ti ratios indicate that dissolved Cr and U species (e.g., CrO_4^{2-} and UO_2^{2+}) in ocean were adsorbed onto the surface of ferric (hydr)oxides during the formation of iron-rich sediments. These results suggest that a part of shallow ocean was oxygenated -3.2 Gyr, containing oxidized Cr and U species, and that ferric (hydr)oxides were precipitated due to the oxidation of dissolved ferrous iron by molecular oxygen. Therefore, our findings imply that oxygenic photoautotrophs flourished in the photic zone of the 3.2 Gyr ocean.

Keywords: South Africa, hematite, magnetite, chromite

U020-23

会場:304

時間:5月23日 17:40-17:55

カナダ・Lumby Lake 地域に産する 30 億年前堆積岩の地質学的・地質学的研究 Geological and geochemical study of Archean sedimentary rocks of the 3.0 Ga Lumby Lake Group, Canada

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Ecosystems at ca. 3.0 Ga on the Earth's surface environments are not well understood. In particular, it is uncertain (1) whether phototrophic microorganisms were active and (2) where methanogens and methanotrophs were active. In order to answer those questions, we have conducted geological survey of sedimentary rocks of the Lumby Lake Group, located in the Atikokan area, Ontario, Canada.

Ultramafic-mafic volcanic rocks, including pillow and massive lavas and hyaloclastite were dominant in the area. In the studied area, marine sedimentary rocks, including banded iron formations (BIFs), were also observed. Black shales were spatially associated with the BIFs making alternate layer.

Petrographical and geochemical analyses were performed on the BIFs and black shales. The BIFs were composed of alternating magnetite-rich and silica-rich layers. Apatite was found in magnetite-rich zone. This support that a primary phase before magnetite was hematite (or goethite) because phosphates are easily adsorbed on Fe-(hydro) oxides. The black shales contain 0.1 to 4.3 wt% of total organic carbon and 0.0 to 24.9 wt% of Ssulfide. The carbon isotope compositions of organic carbon in the black shales showed a bimodal distribution: -47 to -38 per mil (studied area A) and -27 to -20 per mil (studied area C). The carbon isotope compositions of the black shales is negatively correlated with Ssulfide contents. The lighter values suggest the activity of methanogens and methanotrophs while the heavier values suggest the activity of photoautotrophic primary producer. Methanogens could have been active in this anoxic part of ocean water.

These shales also contain two types of pyrite: fine-grained layered type and nodular type. Layered deposition of pyrites indicates that these pyrites were formed syngenetically with other matrix materials. On the other hand, the nodular pyrites were composed of aggregates of pyrite and other sulfides (e.g., chalcopyrite, sphalerite and pyrrhotite), indicating that they were precipitated from later hydrothermal fluids. Therefore, alterations of the sedimentary rocks by submarine hydrothermal activities was widely recognized in the area.

REEs concentrations in the BIFs were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS). BIFs in the all studied area contain insignificant or positive Ce anomalies. This trend in Ce anomalies indicates that the BIFs would have formed in low oxygen condition. On the other hand, studied area A contains significant positive Eu anomalies which contrast with studied area C having insignificant Eu anomalies. This suggests that submarine hydrothermal activities in the studied area A was more larger than studied area C. In particular, methanogens activities were constrained in very reducing bottom water environments where hydrogen from hydrothermal fluids was available.

キーワード: 海底熱水活動, メタン生成菌, 光合成微生物, 希土類元素

Keywords: submarine hydrothermal activity, methanogens, phototrophic microorganisms, REEs

U020-24

会場:304

時間:5月23日 17:55-18:10

四国中西部の北部秩父帯の古生代玄武岩類から発見されたフィラメント状微生物化石

Filamentous microbial fossils from Paleozoic metabasalts of Northern Chichibu Belt in western and central Shikoku, Japan

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地球史における地下微生物圏の解明は、生命の進化や多様性、地球表層の物質循環、さらには火星などの地球型惑星における生命の存否を検討する上で極めて重要である。最近、演者らは日本列島の付加体に含まれるの中・古生代の玄武岩から多数の地殻内微生物化石およびそれらの生痕化石を発見した(たとえば、榊原ほか, 2009; 菅原ほか, 2009; 榊原ほか, 2010; 菅原ほか, 2010 など)。本研究では、それらのうち、四国中西部の北部秩父帯の変玄武岩類から発見されたフィラメント状微生物化石について、形態記載、生息時期ならびに付加体における再結晶プロセスについて検討した。

フィラメント状微生物化石は、愛媛県大洲市および愛媛県久万高原町の北部秩父帯における石炭紀中期～ペルム紀後期に形成されたと考えられる海山起源の玄武岩類から発見された。これら玄武岩類は主にかんらん玄武岩である。主要な変成鉱物はぶどう石、パンペリー石、緑れん石、緑泥石、白色雲母、チタナイト、方解石、赤鉄鉱、アルバイトおよび石英で、その変成条件はぶどう石-パンペリー石相に相当する。

地殻内微生物化石は、インターサタル組織を示す玄武岩の結晶粒間を充填する方解石もしくはパンペリー石中に見出される。それらは、長さ約 0.2~0.5 mm、直径 5~10 μm のフィラメント状の形態を呈し、直線状もしくは湾曲状で斜長石、単斜輝石およびチタン鉄鉱から内部に向かって成長している。その長さは一般に 50~200 μm 程度で、幅は 5~20 μm 程度である。このフィラメント状微生物化石は、玄武岩の石基もしくは発泡孔を埋める方解石中に産する。それは主に Fe に富む緑泥石からなり、核部に少量の Fe 鉱物を含む。このフィラメント状微生物化石も方解石や石英が埋める石基中に産する。それはフェンジャイトによって主に構成され、核部に少量の Fe 鉱物を含む。方解石内部のものは、厚さ数 μm の細粒パンペリー石集合体によって取り囲まれている。

試料の方解石の炭素・酸素同位体比を測定した。測定は、高知大学の海洋コア総合研究センターの安定同位体比質量分析計 IsoPrimo を用いて行った。緑色岩類中の方解石脈およびプールの ¹³CPDB は -2.49~+0.67 ‰ で、¹⁸OPDB は -11.3~-9.62 ‰ であった。

今回、北部秩父帯の変玄武岩から発見されたフィラメント状の微生物化石は、ドイツのデボン紀枕状溶岩の発泡孔から発見されたもの (Peckmann et al., 2008;) に酷似している。フィラメントは、変成鉱物組み合わせおよびそれらの化学組成に基づくと、北部秩父帯の広域変成作用を受けて再結晶していると考えられる。

以上のデータに基づくと、フィラメント状微生物化石はプレート内火成作用によって形成された海山起源の玄武岩形成後(ペルム紀後期?)からジュラ紀前期の付加体形成までの間のある時期に海底下の地殻内で生息し、その後、これら海山が沈み込んだ際に北部秩父帯の変成作用を受け、再結晶したと推定される。

キーワード: 四国中西部, 付加体, 北部秩父帯, 古生代, 玄武岩, フィラメント状微生物化石

Keywords: western and central Shikoku, accretionary complex, Northern Chichibu Belt, Paleozoic, basalt, filamentous microbial fossil