鉄酸化バクテリアが生成するナノ酸化鉄とその生物地球化学的意義

Nano-sized biogenic iron oxides produced by neutrophilic Fe-oxidizing bacteria and its implications for biogeochemical cycling

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Neutrophilic microaerophilic Fe-oxidizing bacteria (NMFeOB) are thought to play a significant role in global biogeochemical cycling of Fe and associated elements. They are commonly found at redox boundaries in both of freshwater and marine iron-rich environments, and produce extracellular iron biominerals that interact with various elements. However, ecophysiology of NMFeOB is still poorly understood due to the difficulty of cultivation. Recently, *Ferriphaselus amnicola* strain OYT1 and *Ferriphaselus* sp. strain R-1, which produce a unique twisted-ribbon-like extracellular iron biomineral structure called a stalk, have been reported (Krepski et al., 2012; Kato et al., 2014). The present study demonstrates the strains OYT1 and R-1 also produce extracellular nano-sized biogenic iron oxides (nanoBIOS), which are morphologically distinct from stalks. Energy dispersive X-ray spectroscopy indicates that the nanoBIOS contain P, as well as the stalks. Given the chemical and morphological characteristics, nanoBIOS may contribute to P, Fe and other metal transport in the environment as a vector. Furthermore, the first genome sequencing of stalk-forming NMFeOB was performed in the present study. Comparative genomics propose potential genes involved in the formation of stalks and nanoBIOS, which are similar to genes involved in extracellular polysaccharide production, and potential genes in iron oxidation, which have been previously suggested as key iron oxidation genes in other NMFeOB. These genes can be used as marker genes for detection of NMFeOB producing iron biominerals. Overall, the detailed microscopy and first genomic analysis of the freshwater stalk-forming NMFeOB provide novel insight into the ecophysiology and biomineralization of enigmatic NMFeOB.

キーワード：鉄酸化バクテリア、ナノ酸化鉄、生物地球化学的循環
Keywords: Fe-oxidizing bacteria, Nano-sized iron oxides, Biogeochemical cycling

シアノバクテリアの細胞外高分子がストロマトライト・スロンボライト形成を規制する

Cyanobacterial extracellular polymeric substances (EPS) control stromatolite and thrombolite formations

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ストロマトライトとスロンボライトは，微生物岩の主要構成要素である．ストロマトライトは主に中～新原生代に多産するが，古生代前期になるとストロマトライトは衰退し，スロンボライトが多産するようになる．当初，このような微生物岩の遷移は，多細胞動植物の進化に伴う生物擾乱の結果であると考えられていたが，スロンボライトの多くは初生的構造であることが近年明らかとなってきている．それゆえ，古生代前期に起きた微生物岩遷移の原因について，再検討を行う必要がある．しかしながら，ストロマトライト・スロンボライトとも現世環境ではほとんど形成されておらず，しかも両者が同一環境で見られる場所は知られていなかったため，詳細な検討は困難であった．そのような中，ストロマトライトとスロンボライトが同一環境で形成されている場所が，岡山県高梁市のトゥファ（淡水性炭酸塩堆積物）堆積場から発見された．そこで本研究では，この試料を用いて微生物岩組織の形成要因について検討を行った．
ストロマトライトおよびスロンボライト形成場において，水化学組成に大きな違いはなく，また微小電極測定の結果から両者とも光合成誘導$CaCO_3$沈殿によって形成されていることが明らかとなった．共焦点レーザー走査顕微鏡観察やDNA解析の結果からは，ストロマトライトに生息するシアノバクテリアが主に*Phormidium* sp.であり，それらの細胞外高分子は酸性官能基を持つために結晶核形成場となり，その結果としてストロマトライト組織を形成していることが示された．一方，スロンボライトに生息するシアノバクテリアは主に*Leptolyngbya* sp.であり，それらの細胞外高分子は酸性官能基を持たないために結晶核形成場とはならず，その結果としてスロンボライト組織を形成していることが示された．これらの結果は，微生物岩組織の形成において細胞外高分子の化学的性質が極めて重要であることを示している．
この結果をそのまま過去に当てはめるならば，酸性官能基を含まない細胞外高分子鞘を持ったシアノバクテリアが古生代前期に進化したという仮説が立てられる．その妥当性については，今後の検討が必要である．

鉱物表面におけるアミノ酸重合挙動の定量的評価：アモルファスシリカーリシンーグリシン系を例として
Lysine polymerization on amorphous silica: A thermodynamic evaluation

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When, where and how did life on the Earth originate? To resolve that fundamental question, one must first ascertain the reactivity of biomolecules, and the response of reactivity to changing environmental conditions such as pH, temperature, dissolved composition, and mineral surfaces. Amino acids are building blocks of proteins, which are fundamental to life. Therefore, the polymerization behavior of amino acids has been a topic of many experimental and theoretical works (Shock, 1992).
This study focuses on thermodynamic effects of minerals on amino acid polymerization. To date, widely various oxide minerals and clays has been examined for their roles in this reaction (Cleaves et al., 2012). Results have demonstrated their positive influences with regard to reaction rate, peptide length, and the amounts of polymers synthesized. However, reported experiments have mostly emphasized catalytic properties of minerals. Consequently, in most cases, experiments have been terminated before polymerization reaches its steady state. It remains unclear whether minerals promote polymerization in thermodynamics as well as kinetics.
To examine the thermodynamic effects, we have evaluated adsorption behaviors of amino acids and peptides on minerals by using extended triple layer model (ETLM; Sverjensky and Fukushi, 2006). Obtained adsorption parameters are used, by combining thermodynamic parameters for amino acids and peptides in aqueous solution, to predict amino acid/peptide equilibria on mineral surfaces. In this presentation, we will present our findings for a lysine/amorphous silica system.

キーワード：吸着、リシン、シリカ
Keywords: Adsorption, Lysine, Silica

二価鉄を含む古海洋表層において生成する有機物の光化学実験

A role of ferruginous ocean in photochemical synthesis of organic compounds

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Photochemistry is important for the origin of life and the early earth’s environment. Previous photochemical experiments suggest that the reaction initiated by UV in CO-rich atmosphere can produce simple organic compounds mainly formaldehyde and methanol (Bar-Nun and Chang, 1983). The amount and speciation of organic molecules are known to depend on the redox state of the atmosphere. The reducing ocean containing ferrous iron may also control the redox state of the ocean-atmosphere system, though the role of ferruginous ocean for abiotic UV synthesis is poorly understood. We have conducted photochemical experiments simulating the reducing atmosphere and Fe(II)-bearing ocean. The results of our experiment suggest that formate, acetate, propionate, and normal alkanes are synthesized under CO-atmosphere. When irradiating UV under the presence of Fe(II)-bearing water, the production rate of formate is about three times faster than the simple CO-H_2O system without ferrous iron. Furthermore, formate is formed even when the gas phase is pure CO_2 when liquid-phase contains Fe(II). These results suggest that the production rate and speciation of organic matter depends on the availability of H_2O as well as total redox state of the whole atmosphere and ocean system. Based on the results, we have modeled the reaction pathway and estimate the flux of each organic compounds supplied to early ocean.

キーワード：生命起源
Keywords: origin of life

微生物由来の水酸化鉄へのセレンおよびセシウムの吸着：無機水酸化鉄との吸着特性の比較
Selenium and cesium adsorption onto biogenic iron oxyhydroxides:Comparison with inorganic iron oxyhydroxides

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Iron(Fe) oxyhydroxides are considered to be important sorbents of trace elements in surface environment. This widely view mainly extends from many laboratory studies using inorganic Fe oxyhydroxides. However, most of the natural Fe oxyhydroxides are referred to as biogenic Fe oxyhydroxides(BIOS) which are complex mixtures with various organic matters. The presence of organic matters in BIOS can cause unique adsorption behaviors of trace elements for BIOS, but they have not been characterized well. This study aims to reveal adsorption characteristics of trace elements onto BIOS.
Biogenic Fe oxyhydroxides were collected from Sambe hot-spring in Shimane prefecture. The samples consist of very fine particles of two-line ferrihydrite, coexisting with biogenic organic matters including stalks, extracellular polysaccharides, and bacterial cells. We have conducted adsorption experiments of selenium(Se) and cesium(Cs) on BIOS and synthesized ferrihydrite in a batch system. Our experiments revealed significant differences in Se and Cs adsorption between BIOS and inorganic Fe oxyhydroxides in a wide range of pH, even though they have similar Fe mineralogy. In the case of positively-charged Cs, BIOS showed larger adsorption than inorganic Fe oxyhydroxides. In contrast, negatively-charged Se showed smaller adsorption on BIOS compared with that on inorganic Fe oxyhydroxides. Especially, the decrease of Se adsorption on BIOS compared to inorganic Fe oxyhydroxides was more significant in Se(VI) than in Se(IV), corresponding to their formation of different surface complexes. We consider that the unique adsorption behaviors of Cs and Se on BIOS and their difference with inorganic Fe oxyhydroxides can be explained by the electrostatic effect caused by the coexisting biogenic organic matters in BIOS.

キーワード：水酸化鉄、微生物、吸着挙動
Keywords: iron oxyhydroxides, bacteria, adsorption behavior

風化花崗岩がレアアースのイオン吸着型鉱床になる上で必要な条件
Limiting factor for weathered granitic rocks to be ion adsorption ore

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Main rock of ion adsorption type deposit which is important as rare earth element (REE) resource is weathered granite, from which we can extract REE readily using aqueous solution such as ammonium chloride or ammonium sulfate solution, because REE can be extracted from weathered granite by ion exchange reaction. Previous studies of the ion adsorption type REE deposit has been carried out mainly using weathered granite found in the Southeast Asia, but there are few studies on the weathered granite present in Japan in terms of the REE deposit. In addition, there are no studies which clarify the relationship between REE chemical state and extraction properties in the weathered granite at molecular level. Therefore, the aim of this study is (i) to clarify the relationship between the extraction characteristic of REE in the weathered granite and its chemical state at the molecular level using XAFS method and molecular orbital calculation and (ii) to study the dependence of extraction rate of REE on the degree of weathering of the granitic rocks. In this study, we analyzed granite or weathered granite samples collected in Hiroshima, Shimane, and Tottori in Japan, Sri-Lanka, and Myanmar. The collection of the samples from various sites are strongly needed to cover granitic rocks having various degrees of weathering. Initially, the mineral and major element compositions were examined by XRD and X-ray fluorescence (XRF) analyses. After the analysis, local chemical state of Y, one of REE, was determined using bulk XAFS and μ-XRF-XAFS method at SPring-8 and KEK-PF, scanning electron microscopy (SEM), and molecular orbital calculation. As a result, it was suggested that REE in the samples with high CIA can be readily extracted and the REE chemical state suggested by Y K-edge EXAFS is outer-sphere complex adsorbed weakly in the weathered granite. The μ-XRF-XAFS and SEM analyses showed that REE was mainly adsorbed on phyllosilicates such as halloysite and weathered biotite. On the other hand, the extraction ratio of REE in the samples with low CIA are low and its REE chemical state is inner-sphere complex, or REE incorporated possibly into primary minerals or phosphate. The ratio of outer-sphere complex among total REE determined by the fitting of EXAFS spectra in k space is positively correlated with that of REE extraction ratio. In addition, weathered granite with higher REE extraction ratio exhibits larger negative Ce anomaly, suggesting that REE with negative anomaly in aqueous phase was adsorbed to the granitic rocks, which finally induces the correlation between the degree of negative Ce anomaly and REE extraction ratio. Thus, it is suggested that the degree of negative Ce anomaly is one of the characteristics of ion adsorption type REE deposit. However, strongly weathered granite samples with CIA values higher than 85 do not show high REE extraction ratio. Mineralogy of the samples is dominated by kaolinite and gibbsite, which suggests that the fraction of REE adsorbed on clay minerals is minimal for the strongly weathered granites compared with intermediately weathered granitic rocks with CIA value around 70. Thus, we can conclude that medium weathering characterized by the presence of vermiculate/smectite with CIA value around 70 is an important limiting factor to establish the sample as an REE ion adsorption ore.

土壌中における有機ヒ素化合物の吸着挙動
－有機物の影響－

Adsorption behavior of organoarsenic compounds in soils
- Influence of organic matters -

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Anthropogenic originated organoarsenic compounds such as diphenylarsinic acid (DPAA) are a water pollution source as well as naturally occurring inorganic ones. For example, DPAA polluted well water caused serious health problems in Kamisu, Japan. However, their adsorption behavior in soils is still well unknown. In general, the adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. In soils, organic matters (OMs) affect adsorption behavior of trace metals on minerals. Thus, it is important to understand the adsorption mechanism of the arsenic compounds with taking account of influence of OMs to predict future fate of them in environment. In this study, we conducted adsorption experiments for several soils which have different contents of Fe/Al-(oxyhydr)oxides and OMs, and adsorption amounts and structures were analyzed by ICP-MS and As K-edge XAFS measurements. The same experiments and analysis were conducted with OM extracted soils to understand the influence of OMs. The As K-edge EXAFS spectra for arsenic compounds adsorbed on soil samples were well fitted with corresponding EXAFS spectra As adsorbed on Fe- and Al-(oxyhydr)oxides. The fact indicates that these arsenic compounds adsorbed on these minerals mainly. The adsorption ratios for Fe- and Al-(oxyhydr)oxides were estimated by the fitting, and the deviation of the ratio from the Fe/Al content was larger with increasing the OM content in soils. In addition, in most cases, the adsorption amounts of arsenic compounds increased by removing OMs. Thus, it is considered that the OMs prevent arsenic compounds from being adsorbed on minerals by covering their surface. However, even though OMs were removed from soils, the adsorption ratios were still not always reflected Fe/Al content ratio by removing OMs depending on the arsenic compounds. This fact indicates that the affinity of arsenic compounds for Fe/Al-(oxyhydr)oxides is different.

キーワード：有機ヒ素化合物、吸着、土壌、X線吸収微細構造
Keywords: organoarsenic compound, adsorption, soil, XAFS

埋没深度数cmから数百mまでの南海トラフの泥質堆積物の微細組織の変化
Change processes of microfabrics in the Nankai Trough muddy sediments from several centimeters through several hundreds meters in burial depths

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【はじめに】
数百 mにおよぶ埋没圧密では，堆積物の力学特性に異方性が生じることが知られる（Bennett. et al., 1991）．特に南海トラフのような付加体の発達する場所では，付加変形前に埋没圧密による変形が生じ，堆積物粒子が強い配向性を持つとされる（Kawamura and Ogawa, 2004）．これは，デコルマンなどのすべり面発達に大きく影響すると考えられ，南海付加体の変形プロセスを考えるうえで，重要な知見となる．このように，付加変形前の変形，すなわち埋没圧密変形は，南海付加体の変形プロセスを考えるうえで，重要な要因である．圧密を生じさせる堆積物，すなわち含水未固結試料の粒子配向性を電子顕微鏡や光学顕微鏡で観察する場合，試料を乾燥させる必要があり，乾燥には収縮が伴う．これにより粒子配向性などの微細組織の初生構造が破壊されてしまう．しかし，凍結乾燥法・樹脂包埋法を用いることで，収縮を伴わずに試料の観察が可能となる（滝沢ほか, 1995）．
本研究では，凍結乾燥法により特殊処理した南海トラフの泥質堆積物のオリジナルな微細組織観察を行い，埋没深度数百mまでの微細組織の変化について詳細に報告し，その変化過程を考察する．
【研究試料】
本研究では，1）表層20cmの不撹乱堆積物として泥質堆積物である3K1345C-1, C-2, C-3, C-4, 3K1346C-1を，2）埋没深度数百mの堆積物としてExpedition 333 C0018Aを用いた．
1）3K1345C-1, C-2, C-3, C-4, 3K1346C-1は，水深おおよそ2500～3000 mでMBARI corerによって南海トラフの陸側斜面から採取されたコア長約20 cmの堆積物である．本研究でコア試料の物性値を測定し，微細組織観察を行った．
2）C0018Aは，Hydroric pisoton corerによって掘削されたコア長314.15 mの南海トラフの海底堆積物である．C0018AはUnit IA, IBに分かれており，0～190 mbsfのUnit IAは頻繁に火山灰層が挟在する半遠洋性泥層と6枚の海底地すべり堆積層（MTD層）からなるのに対し，Unit IBは砂質タービダイト層で構成される．本研究では，C0018Aの物性値は船上データを用いた．
【結果】
半遠洋性泥層とMTD層とで，特徴的な微細組織がSEMにより観察された．
半遠洋性泥層の微細組織は，F-F接触のClay flakeの水平配列によって特徴づけられる．それに対して，MTD層は，1～5ミクロンのregular aggregationや，20ミクロン以上のirregular aggregationによって特徴的づけられ，独立したClay flakeがほとんど観察されない．

キーワード：微細組織、南海トラフ、海底地すべり堆積物
Keywords: Microfabric, Nankai trough, Mass transport deposits

熊野灘南海トラフにおける海底堆積物中のヒ素の化学形態と間隙水への溶出過程
Chemical forms of arsenic in marine sediments and dissolution mechanisms into porewater of Kumano Basin, Nankai Trough

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The purpose of this study is to clarify the accumulation process of arsenic and the behavior during an early stage of diagenesis in modern marine sediments.

The cored sediments and porewaters at Sites C0002 and C0022, Nankai Trough. At the Site C0002 (0-1050mbsf), sediments at <800mbsf was composed of forearc basin sedimentary rock (terrestrial sediment) and the lower part was of accretionary prism.

In the Site C0002, total arsenic concentrations of sediments increased at 0-330mbsf with depth. The highest concentration was recorded at 330mbf (13ppm). Then, the concentration decreased, and became constant about 5ppm below 500mbsf. Total arsenic concentration was higher in forearc basin sedimentary rocks than the underlying accretionary prism sediments. It suggest that the primary arsenic was mostly derived from subareal region via detrital fragments.

The result of BCR sequential extraction analysis showed that about 40% of As in the sediment was fixed in insoluble phases, i.e., structure of sulfide and/or silicate minerals. Arsenic in insoluble phase was >80% in the sediment at 1000mbsf, implying that the arsenic was fixed in authigenic pyrite in the deep part of the sediment column.

The ratio of dissolved arsenic arsenic $_{\text{(porewater)}}$ to Total arsenic of the sediment was especially high at those depth. Thus, the arsenic dissolution was promoted at those depth. Similar high dissolved arsenic ratio was shown at 100-200mbsf, Site C0022, suggesting the same mechanisms to release arsenic in the sediment at these depth.

Speciation of arsenic-being phases in the adsorbed fractions onto sediment particles were analyzed by HPLC and analyzed by ICP-MS/MS. Arsenate, arsenite, MAA, and AsB were only detected from the sediments at C0002, C0022. Total concentration of these arsenic compounds was 60% of total arsenic of the sediment, and most of them were arsenate and arsenite. It indicate that over half of total arsenic in the sediment was adsorbed as inorganic arsenic onto the mineral surface. The concentration of arsenite increased below 100mbsf, suggesting that the arsenate was reduced below this depth. The MAA was not large compared to the total arsenic, however, it is important to evaluate the contribution of microbiological activity to the arsenic cycle in the marine sediments. As mentioned above, arsenic fixed in the sediments releases into the porewater at 100-200mbsf. Decomposition of organic matters are extensive in 0-150mbsf evidenced by increasing concentration of NH_4^+ of porewater and Br^- (accumulate in red algae). Thus, MAA would be a product of decomposition of organic arsenic compounds, such as arsenosugar contained in algae.

Below 200mbsf, increasing pH controlled arsenic dissolution. The average of pH was 7.79 in 0-200mbsf, then graduate increased below this depth. It’s peak was about 7.98 at 400mbsf. Surface potential of iron oxyhydroxides/oxides changes at pH=7.9. Negatively changed arsenic (mainly arsenate) was intensely released into the solution at pH>7.9. Observation of this study showed that the small change of pH considerably controls the dissolved arsenic in porewater.

This study demonstrates the importance of input of subareal detrital materials for the arsenic cycle in the crust through hydrosphere and microbiological activity to change the arsenic phases in the marine sediments at the very early stage of diagenesis.

キーワード：ヒ素、IODP、porewater
Keywords: arsenic, IODP, porewater

高アルカリ条件下における酸化マグネシウムによる亜セレン酸の取り込み
Selenite sorption on magneaium oxide under the highly alkaline conditions

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石炭火力発電所における脱硫過程で発生する排水に工業排水基準(100ppb)を超えるセレンが含まれるケースが報告されている(電力中央研究所, 2005). 溶液は排煙を高率的に溶かし込む為, アルカリ性に保たれている. セレンは溶液中で主にセレン酸($H_xSeO_4^{2-x}$, Se(Ⅵ))又は亜セレン酸($H_ySeO_3^{2-y}$, Se(Ⅳ))として存在し, 陰イオンを形成する. 脱硫過程で発生する廃液中においてセレンの多くは亜セレン酸として存在している(電力中央研究所, 2005). その為, アルカリ条件下における亜セレン酸の効率的な除去が望まれている.

酸化マグネシウム(MgO)は地表環境で準安定相であり, 水溶液中でブルーサイト($Mg(OH)_2$)に変質する(矢部 他, 2011). また, MgOが変質した$Mg(OH)_2$は高い反応性を持ち,溶液中の陰イオンに対して有効な除去能力を持つとされている(Liu et al., 2011). 本研究では, 低濃度条件における収着挙動の理解する為, 本研究では酸化マグネシウムによる溶液中での低濃度における亜セレン酸の取り込み挙動とそのメカニズム検討した.

本研究ではMgO試料としてクニミネ工業製:M511を使用した(以降M511試料). また, M511試料をNaCl0.01Mに調整した溶液で60時間反応させ, 凍結乾燥したものを$Mg(OH)_2$試料(以降Brucite試料)とした. 試料は其々, BET法にて比表面積を測定し, XRDにて鉱物相の同定を行った.

バッチ収着実験はNaCl0.01M, 初期亜セレン酸濃度2μM(160μM)に調整した混合溶液50mlに対して固液比2g/Lとなるように固体を添加し行った. 懸濁液が入ったポリ容器は大気にオープンとし, 25℃又は10℃に保たれたインキュベーター内のマグネティックスターラーで0.5-60時間反応させた. 各反応時間でpH測定後,固液分離し, 液相は濃硝酸を添加した. 固相はイオン交換水で数回洗浄し, 凍結乾燥した. 液相はICP-OESにてMg濃度を測定し, ICP-MSにてSe濃度を測定した.固相はXRDにて鉱物相の同定を行った. 測定したpHやCa,Mg,Se濃度より各種のスペシエーション分析と関連鉱物の飽和指数をGeochemist’s Workbench(GWB,1998)で計算した.

XRDパターンよりM511試料は24時間で完全に$Mg(OH)_2$に変質した. 懸濁液のpHは両試料共に,30分の時点で11程度の高い値を示し, 時間経過に伴い減少した. M511試料とM511試料より作成したBrucite試料との間にはSe(Ⅳ)の収着能に対し, 大きな差が認められた. 160μg/LであったSe(Ⅳ)濃度は, M511試料では数μg/L程度までSe(Ⅳ)濃度が低減したのに対し, Brucite試料ではM511試料より全ての実験期間を通し高い値を示し, 最大で58μg/Lまでしか低減しなかった. この収着能の違いはM511試料とBrucite試料のSe(Ⅳ)の収着メカニズムの違いに起因すると考えられる.

安定なBrucite試料では$Mg(OH)_2$の高いpH_{IEP}により, 表面水酸基とSe(Ⅳ)とで表面錯体生成をし, Se(Ⅳ)を表面に2次元的に吸着すると考えられる. 一方, 準安定相であるM511試料ではMgOが溶解し, $Mg(OH)_2$へと変質する. Brucite試料と同様に生成した$Mg(OH)_2$にSe(Ⅳ)が吸着するが, その後$Mg(OH)_2$の結晶成長が生じ, その結晶内にSe(Ⅳ)を3次元的に保持すると考えられる.

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キーワード：亜セレン酸、酸化マグネシウム、準安定相、水酸化マグネシウム、アルカリ条件
Keywords: Selenite, Magnesium Oxide, Metastable Phase, Magnesium Hydroxide, Alkaline Conditions

土壌鉱物における鉛の吸着挙動と表面化学種分布の全水質条件に対応した予測モデル
Predictive model for Pb(II) adsorption on soil minerals (oxides and low crystalline aluminum silicate) consistent with spectroscopic evidence

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Mobility of Pb(II) in surface condition is governed by the adsorption processes on soil minerals such as iron oxides and low crystalline aluminum silicates. It has been documented that the adsorption effectiveness and the surface complex structures of Pb(II) sensitively varies with the solution conditions such as pH, ionic strength, Pb(II) loadings and electrolyte anion types. Present study aims to construct the quantitative model for Pb(II) on the soil minerals, which can predict the adsorption effectiveness and surface complex structures under any solution conditions by means of extended triple layer model (ETLM).

The Pb(II) adsorption data on goethite, ferrihydrite, quartz and low crystalline aluminum silicate (LCAS) were analyzed with ETLM to retrieve the surface complextion reactions and these equilibrium constants. The adsorption data on goethite, ferrihydrite and quartz come from previous studies. Those on LCAS were measured in present study under wide range of pH, ionic strength and Pb(II) loadings in $NaNO_3$ and NaCl solutions. All adsorption data can be reasonably regressed by ETLM with the assumptions of inner-sphere bidentate complexation and inner-sphere monodentate ternary complexation with electrolyte anions, which are consistent with the previously reported spectroscopic evidences. The predictions of surface speciation under wide range of solution conditions by ETLM revealed that the inner-sphere bidentate complex is predominant species at neutral to high pH conditions. The inner-sphere monodentate ternary complex becomes important at low pH, high surface Pb(II) coverage and high electrolyte concentrations, of which behavior is consistent with the spectroscopic evidences.

The comparisons of the obtained adsorption constants on goethite, ferrihydrite and quartz exhibited good linear relationships between the reciprocals of dielectric constants of solids and adsorption constants. The linear relationships enable the predictions of the adsorption constants of all oxides based on Born solvation theory. The adsorption constants of LCAS are comparable to those of goethite. The comparisons of the adsorption constants of soil minerals suggest that the ferrihdyrite, goethite and LCAS are three most important sorbents for Pb(II). Ferrihydrite and goethite are ferric oxides which are unstable in reducing conditions while LCAS is insensitive to the redox changes. The present study also implies that adsorption of Pb(II) in subsurface soil conditions may be governed by LCAS.

キーワード：土壌鉱物、表面錯体モデリング、鉛、酸化物、低結晶性アルミニウムケイ酸塩
Keywords: soil minerals, surface coplexation modeling, Pb(II), oxides, low crystalline aluminum silicate

衝撃波のよる鉱物，水，生体分子の相互作用: 隕石衝突下のオリビンとアミノ酸水溶液の反応による粒子形状変化
Interactions among mineral, water and biomolecule by shock wave: morphological changes of olivine grains reacted with amino acid solutions by impact process

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Early oceans on Earth might have contained a certain amount of biomolecules such as amino acids, and were subjected to meteorite impacts, especially during the late heavy bombardment. When hypervelocity meteorites impact to oceans on Earth, some minerals contained in meteorite may react with solutes in oceans under high pressure and temperature conditions and subsequent pressure release processes induced by impact process. We performed shock recovery experiments to simulate shock reactions of marine meteorite impacts among olivine as meteorite components, water and biomolecules as oceanic components. Olivine is one of the most typical minerals in ordinary chondrites that represent about 90% of flying meteorites to Earth. In the present study, we investigate reactions between olivine and amino acids in water during impact process. We present the results of changes of olivine grains. We conducted shock recovery experiments by using a propellant gun at National Institute for Materials Science. Shock recovery experiments were performed that a metal flyer as projectile accelerated by a propellant gun impacted to the metal sample container after sealed with two screws as targets. Amino acid solutions (130 μl) were set with olivine powders (200 mg) and air gap in the sample room in sample containers. Impact velocities measured by using the magnetoflyer method were about 0.9 km/s. Shock pressure was calculated with the measured impact velocity using the impedance match method. After experiments, experimental products were collected from holes drilled on the impact surfaces of the recovered containers. Recovered solid samples were analyzed using X-ray powder diffraction method (XRD), scanning electron microscopy (SEM), electron probe microanalyser (EPMA), and transmission electron microscopy (TEM) with energy dispersive X-ray spectrometry (EDX). The analytical results on the shocked sample of water-amino acid-olivine mixtures demonstrated the metallic material, shocked olivine grain affected by water and carbon rich material like spike as experimental products. Analytical result of EPMA indicated the metallic material derived from stainless 304 of sample container, and a detectable decreasing deviation in the atomic ratio of Mg/Si in shocked olivine relative to that of the starting olivine. The shocked olivine was shown the traces of water molecule impacting on surface by TEM observation. The results of TEM observation and EDX analysis indicated the carbon rich material derived from amino acids. The present study suggests the water-amino acid-olivine system under shock reaction is able to interact with each other. Especially, organic compounds related to origin of life in early ocean might transform to solid state by meteorite impacts. Hence, it is necessary to consider the phase change of initial materials on pre-biotic experiments simulated natural condition.

キーワード：隕石衝突、かんらん石、アミノ酸
Keywords: Meteorite impact, Olivine, Amino acid

新潟県上越市上部中新統のメタン湧水炭酸塩岩中の吸着ガス分析
Experimental study of adsorbed methane in a methane-seep carbonate from the upper Miocene in Joetsu City, Niigata Prefecture

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海底から主にメタンを含む流体が湧き出すメタン湧水は，天然ガスの主成分かつ強力な温室効果ガスであるメタンの主要な放出の場であることから着目されてきた．メタン湧水ではメタン酸化古細菌と硫酸還元菌の共同体によりメタンが嫌気的に酸化され，生成する重炭酸イオンからメタン由来の炭酸塩鉱物が沈殿する．地質時代のメタン湧水も，地層中に保存された炭酸塩岩のメタンに由来する低い炭素安定同位体比や，嫌気的メタン酸化に関与する微生物のバイオマーカーから認定でき，過去のメタンの生成と移動，放出の直接の証拠として重要である．メタンは堆積物浅部での微生物または深部での熱による有機物の分解により生成し，それらはメタンの炭素安定同位体比などで識別される．過去の湧水中のメタンが微生物起源か熱分解起源かを明らかにできれば，過去の湧水の起源深度や湧出経路が推定できるほか，石油や天然ガスの生成時期の理解にもつながると考えられる．しかしながら，その起源を直接推定する方法は確立されていない．堆積物中の自生炭酸塩岩は周囲の炭化水素ガスを吸着することが報告されており（Ijiri et al., 2009），もし同様に地層中のメタン湧水炭酸塩岩がそれを沈殿させた過去の湧水中のメタンを吸着していれば，その同位体比などを測定することで起源を推定できる可能性がある．そこで本研究では，過去の湧水中のメタンの起源を推定するため，メタン湧水炭酸塩岩からの吸着ガスの抽出および炭素安定同位体比（$\delta^{13}C$）の分析を試みた．分析には新潟県上越市の上部中新統能生谷層より採取した炭酸塩岩を用いた．この炭酸塩岩は暗灰色のミクライト質アラゴナイトを基質とし，明色の針状アラゴナイト結晶で縁取られた多数の空隙を持つ．ミクライト部も空隙中の針状アラゴナイト部も低い$\delta^{13}C$値（-42.6～-15.4‰ vs. PDB）を示し，また前者には嫌気的メタン酸化古細菌のバイオマーカーであるペンタメチルイコサン（PMI），クロセタンが含まれ，炭酸塩岩がメタン湧水で沈殿したことを示している．吸着ガスは炭酸塩粉末をリン酸で溶解させることで放出させ，GC-IRMSに導入して濃度と炭素同位体比の分析を行った．分析を行ったすべての試料からメタンを抽出することができ，その$\delta^{13}C$値は-60.7～-40.0‰と幅広い値を示した．$\delta^{13}C$値より，抽出されたメタンには微生物起源メタンと熱分解起源メタンが様々な比率で混合したもの，あるいはメタン酸化に伴う分別により同位体比の高くなった微生物起源メタンが含まれていることが示唆される．メタンと炭酸塩の炭素同位体比は弱い正の相関を示し，例外はあるものの空隙を縁取る針状アラゴナイト部の方がメタン・炭酸塩の$\delta^{13}C$値ともにミクライト部より低い傾向が見られた．このことから炭酸塩沈殿時に周囲の湧水中のメタンが捕獲されており，炭酸塩の各組織の沈殿場の条件（堆積物中または空隙中）とそれらに供給・捕獲されたメタンの起源やフラックスとが関連している可能性がある．ただし，メタンが炭酸塩沈殿後や埋没過程で吸着された可能性もあるため，今後炭酸塩中のガスがどのように存在しているのか明らかにし，メタンが炭酸塩に捕獲・吸着された過程を検討していく必要がある．

キーワード：メタン湧水、炭酸塩、中新世、上越市、吸着ガス
Keywords: Methane seep, Carbonate, Miocene, Joetsu City, Adsorbed gas

水熱反応実験における玄武岩の組成変化と液相溶存元素の挙動
Hydrothermal experiments between basalt and H_2O at 130°C and 230°C

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Water-rock interaction occurs during weathering on ground surface, hydrothermal alteration around hot spring on continental crust, and reaction in oceanic crust. Many hydrothermal experiments have been conducted to examine the rock alteration and/or chemical composition of solution under various reaction temperature conditions, but most of them were focused on compositional variation after reactions between seawater and rock samples. In this study, as a primary, pure water was reacted as solvent with basalts samples under 130°C and 230°C conditions to understand the temporal evolution of composition of the basalts and solution under simple reaction in different temperature conditions.

In the experiments at 230°C, many kind of elements were dissolved in the solvent from basalts after reactions. Especially, concentrations of SiO_2 and Na_2O decreased by their dissolutions, on the other hand, Fe_2O_3 and MgO increased by their insolubility, relatively. The run products at 230°C experiments changed their compositions from starting materials more greatly than those at 130°C. In such run products, coarse grains(>200μm) were more outstanding at 230°C experiments, on the other hand, fine grains(<200μm) were kept leaving after long-term experiments at 130°C. It is suggested that groundmass as glass components and fine crystals dissolved precedingly at 230°C during reactions.

Solubility in the solvent showed different temporal variations every element. However, they can be classified into three major patterns. First, concentration of element increased primary and then decreased (pattern I). Secondly, concentration increased primary, decreased secondly, and then increased again (pattern II). Thirdly, concentrations repeated increasing and then decreasing twice (pattern III). Decreasing of elemental concentrations shows its precipitation by saturation after dissolution of starting material. Concentration increasing after decreasing suggests that the precipitated materials dissolved again under unsaturated situation by over precipitation. In the experiments at 130°C, behavior of Fe, Mg and Al, which are classified into pattern I, suggest immediate precipitation unless redissolution after reactions. In contrast, behavior of Si, Na, K, Ca, and Nb, pattern II, suggest that such elements redissolve it easily by the situation of the solution changing even if they were precipitated by oversaturation. Such elemental behaviors in solution are consistent with temporal variations of compositions of solid materials modified after basalt samples: increasing Fe and Mg, decreasing SiO_2, progressively. On the other hand, experiments at 230°C showed immediate precipitations of Fe, Na, K and Nb (pattern I) and re-precipitations of Si, Mg, Ca, and Al after redissolution(pattern III). It is expected that the degree of dissolution and variation of elements in the solution depend on temperature. And then, such factors changed basalt compositions variously detailed in different run products, caused by difference of elemental precipitation or dissolution during reactions.

キーワード：水熱反応実験、玄武岩、変質作用
Keywords: Hydrothermal experiments, Basalt , Alteration

重金属汚染環境における地衣－基盤相互作用
Lichen-substratum interactions in severe environment polluted by heavy metals

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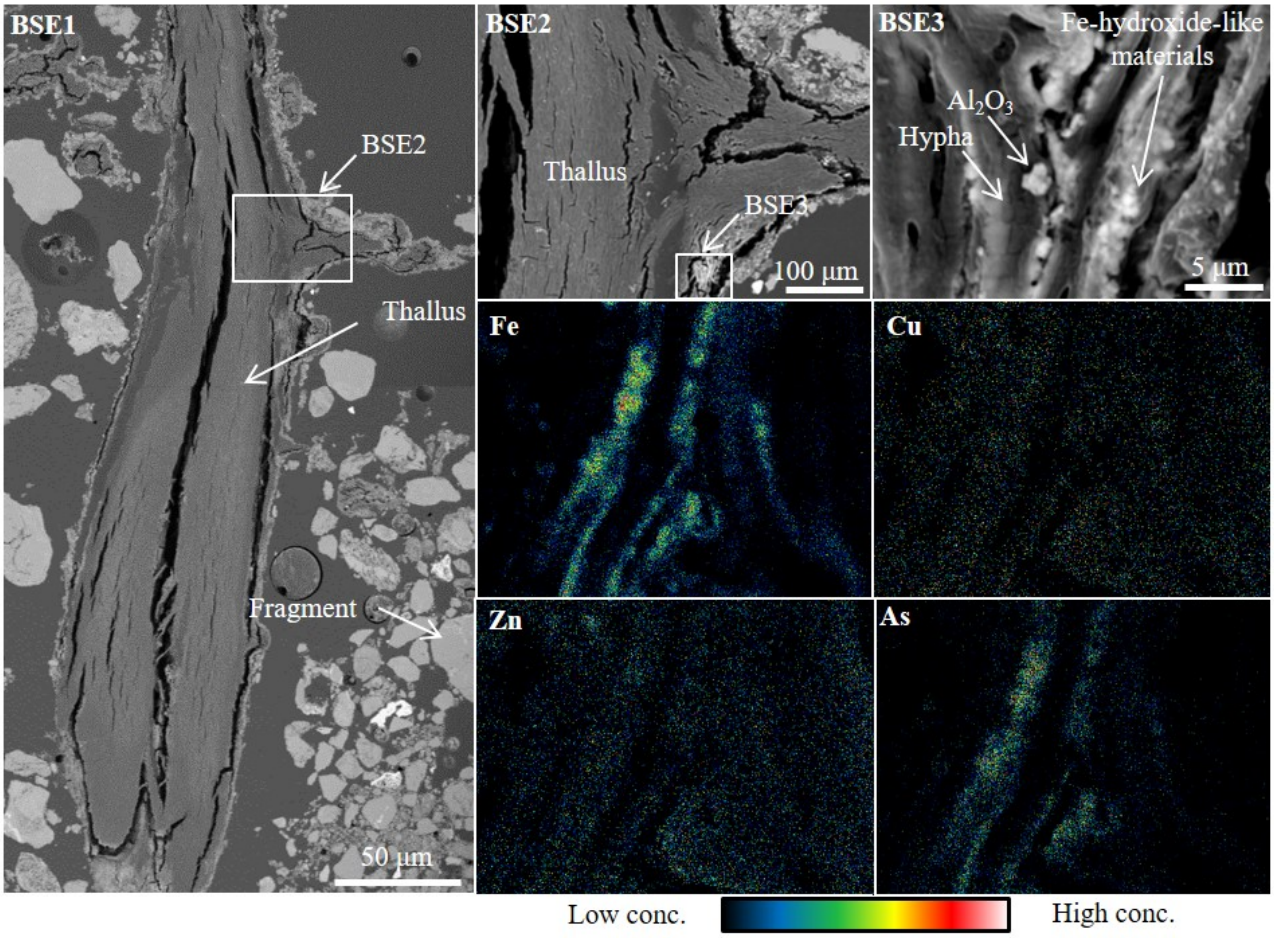
Heavy metal pollution is a worldwide problem. The use of native organisms for assessment and monitoring of polluted sites is an approach that could contribute to a reduction on costs and secondary environmental impacts. Because several fruticose lichens occur even in areas highly polluted by heavy metals, lichens may meet the requirements. Therefore, interactions between lichens and substrata is an important key to determine the behavior of heavy metals in surface environment polluted by heavy metals.
Although, no studies have investigated interactions of fruticose lichens and the corresponding substrata comprehensively from the aspect of biogeochemical behavior of heavy metals. Therefore, several fruticose lichens, including *Stereocaulon exutum* and several *Cladonia* Spp., from contaminated abandoned mine sites and the corresponding substrata were investigated (1) to determine the behavior of heavy metals during the weathering of slag mediated by *S. exutum*, (2) to determine the distribution of the heavy metals in the thalli of *S. exutum*, and (3) to determine the correlations between the heavy metal concentrations of lichens and those of the corresponding substrata.
The slag that is a substratum of *S. exutum* consists primarily of willemite, fayalite, and/or magnetite and contains matte drops, which are mainly Cu-metals, -alloys, and -sulfides. The willemite and matte drops are ultimately converted to Fe-hydroxides during the weathering process. In addition to abiotic weathering, the heavy metals are dissolved during the biotic weathering by substances from the lichen and hyphal penetration. The dissolved heavy metals are absorbed into the lichen thalli. Absorbed Cu and Zn are distributed within the cells of hyphae, whereas Fe and As are distributed on the surface of hyphae. Fe-hydroxide-like materials are occur on the surface of hyphae (Fig).
Based on previous studies, cations in thalli are distributed into four fractions, e.g. the intercellular and surface, ion exchange site, intercellular, and residual fractions. Although the form of the ions was not identified in this study, the distribution of elements in the hyphal cells may indicated the possible absorption of ions into the cytoplasm through ion exchange sites from external solutions. For the Fe and As concentrated on the surface of hyphae as Fe-hydroxide-like materials, this distribution could be explained by elemental precipitation or the formation of compounds on the hyphae.
The concentrations of Cu, Zn, As, and Pb of *Cladonia* Spp. thalli were positively correlated with those of the corresponding substrata. Distribution maps of the average heavy metal concentrations of the lichens and the corresponding substrata were made to determine the practical applications of the lichens as a biomarker. The maps for the distribution of Cu, Zn, and As in the lichens had very similar distributions to those of the corresponding substrata at the scale of all study sites in southwest Japan. Therefore, a large-scale analysis of lichens with many samples successfully detected the distribution of heavy metal pollution of soil.
In conclusion, *C.ladonia* Spp. lichens can be used in practical applications for biomonitoring and assessment of heavy metal pollution of soil. Because lichen is a pioneer organism in polluted areas by heavy metals worldwide, the investigation of interactions between lichens and substrata could

contribute to determine the elemental cycle between biosphere and lithosphere during natural recovery process of polluted areas.

キーワード：廃止鉱山、スラグの風化、樹状地衣、重金属吸収、環境指標生物
Keywords: abandoned mine site, weathering of slag, fruticose lichen, absorption of heavy metals, biomarker



Back-scattered electron images and elemental maps of the medulla inside the cortex of thallus (Sueoka *et al*., 2015).

pH 2-4における水酸化鉄(III)生成の反応速度
Reaction rate of ferric hydroxide formation at pH 2-4

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Iron hydroxides widely exist in the Earth’s environment, and their formation processes, adsorption properties, and transport behavior have been attracting great attention. Dissolved Fe^{3+} reacts with water and transforms to ferric hydroxide ($Fe(OH)_3$) as time passes. We focused on the early process of ferric hydroxides formation and evaluated the reaction rate constants and activation energies under a wide range of solution conditions (pH 2-4, initial Fe concentration 5-300 ppm, temperature 5-55 °C, and dissolved anion species Cl^-, NO_3^-, SO_4^{2-}). Aqueous solutions containing ferric ions were prepared by dissolving one of the following $FeCl_3$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Fe_2(SO_4)_3 \cdot nH_2O$ in pure water. As dissolved ferric ions change to ferric hydroxide, the pH of the solution gradually decreases. The time variation of pH was monitored under the constant temperature, and the rate constant k was determined by converting the pH change to the change in the concentration of dissolved ferric species (assumed to be a 1st order reaction as with Grundl and Delwiche, 1993) using a geochemical code PHREEQC (Parkhurst and Appelo, 1999). Comparison of the k values of ferric hydroxide formation at pH 2-3 under the presence of the different anion species revealed that the k values for Cl^- and NO_3^- were almost the same and that for SO_4^{2-} was approximately one half to one fourth of the values for Cl^- and NO_3^-. Despite the dependence of the rate constants on the anion species, activation energies were almost the same between Cl^-, NO_3^-, and SO_4^{2-} (~120 kJ/mol). In the experiment using $FeCl_3$ solution, the k value increased as the initial pH increased from 2 to 4. On the basis of the pH dependence of k at 25 °C, an equation to predict k for various pH was obtained.

キーワード：水酸化鉄、反応速度
Keywords: Ferric hydroxide, Reaction rate

南モンゴルの塩湖におけるヒ素とウランの固液分配挙動
Distribution of arsenic and uranium between lake waters and sediments in saline lakes in Southern Mongolia.

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近年塩湖環境における有害化学種に関連した健康被害が問題となっている(Barber et al. 2009)。塩湖では水分の蒸発に伴い溶存成分の濃縮が生じ、高濃度の有害化学種を含む湖水や塩の沈殿物が生成する。
塩湖における化学堆積物と湖水間の微量有害元素の分配は、塩湖環境における有害元素の蓄積過程や移動性の理解にとって必須であると考えられるが、これまであまり検討されていない。本研究はモンゴル南部の塩湖（オルゴイ湖、ブンツァガーン湖、オログ湖）を対象とし、湖水、懸濁粒子、堆積物の詳細な化学的・鉱物学的な分析から、塩湖環境における有害微量元素（特にヒ素とウラン）の固液分配挙動に関する知見を得ることを目的とした。

Barber, L.M., Peterson, R.K.D., Montagne, C., Inskeep, W.P., Schleier III, J.J. (2009) A dietary risk assessment for indigenous consumption of natural salt deposits in the Darhad Valley, northern Mongolia. Human and Ecological Risk Assessment, 15 (5), pp. 907-922.

キーワード：塩湖、モンゴル、ヒ素、ウラン
Keywords: Saline lakes, mongolia, arsenic, uranium

鹿児島県塩浸温泉にみられる縞状堆積物の形成過程
Laminated textures of deposits in Shiohitari hot spring, Kagoshima Prefecture

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Fe-rich deposits and travertine (carbonate-rich deposits) are precipitated from hot springs containing amount of minerals. Some of these deposits have laminated textures and origins of laminated textures are explained by several papers. In terms of Fe-rich deposits, metabolism of iron-oxidizing bacteria and symbiosis of cyanobacteria and iron-oxidizing bacteria forms laminated textures (Takashima et al., 2008; Takashima et al., 2011). On the other hand, lamination of travertine are contributed by photosynthetic bacteria showing daily cycle (Takashima and Kano,, 2008; Okumura et al., 2013). This study focuses on laminated deposits in Shiohitari hot spring. Shiohitari hot spring is located at Kirishima city, Kagoshima Prefecture and emit naturally without artificial effects. This is registered in Kirishima Geopark.

The hot spring deposit occur along10-m-long flow path. The water from the vent first flows about 2 m on a narrow (30 cm) and gentle passage and then widely on a steep slope on the travertine dome. Below the dome, the water flows into Amafuri River. Unconsolidated Fe-rich deposit is precipitated at the vent is, and in the lower part, travertine covered by green colored biofilm is. Both deposits have laminated texture.

This water is 51.2 degree celsius, neutral pH and microaerobic. The water is rich in Ca^{2+}, Na^{+} and Cl^{-}, and poor in Mg^{2+} and SO_4^{2-}. To the downstream, the water temperature decreases, pH increase, and conversely alkalinity and Ca^{2+} concentration decrease. This is consisted with travertine deposition. Because an oxygen isotopic ratio of the water (-6.8 per mill) is similar to that of surface and shallow groundwater in southern Kyushu area (-7~-6 per mill; Mizota and Kusakabe, 1997), the origin of water may be fresh water. A carbon isotopic ratio of the water is -6.8 per mill which is similar in that of magmatic gases.

Mineralogy of the Fe-rich deposits in Shiohitari hot spring is ferrihydrite and exhibit micron order laminations which alternate with a dense part and a not dense part. The dense part is composed of dendritic structure ferrihydrite. In addition, meshwork atructure like organic matter is observed from specimens treated with citric acid. This possibly shows that precipitation of ferrihydrite is induced by bacterial metabolism.

The travertine in Shiohitari hot spring is mainly composed of aragonite forming dumbbell-shape and spherical crystals. Between crystals, organic matter like EPS is observed. The lamination of the travertine is likely formed by photosynthetic bacteria same as other travertine.

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