

Exploring the hydrogen isotopic composition of deep-sea corals

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Despite the widespread use of hydrogen isotopic analyses in environmental investigations, no previously-published work has attempted to measure or utilize the hydrogen isotopic composition (δD) of deep-sea corals. Geographically widespread, forming annual growth rings, and having lifespans on the scale of hundreds of years, δD measurements of deep-sea coral skeletons have the potential to elucidate oceanographic parameters at well-resolved spatial and temporal resolutions.

We present a method for the determination of annually-resolved δD in gorgonin, a complex proteinaceous material making up the horny skeletal component of gorgonian corals. We address the issue of exchangeable hydrogen in gorgonin by controlling the isotopic composition of the exchangeable fraction of the total hydrogen pool using a heated batch equilibration technique. Coupled with seawater δD profiles, the δD of particulate organic matter (POM) filtered from seawater, and the δD of plankton trawl samples, we attempt to identify the relationships between trophic exchange, physical oceanographic parameters, and the δD of gorgonin from 3 species of live-collected coral.

Results include a 43-year record from a *Primnoa pacifica* colony collected from the Gulf of Alaska, three 10-year records from *Primnoa resedaeformis* colonies collected from the Labrador Sea, and a 40-year record from a *Keratoisis grayii* colony collected from southern Baffin Bay. Preliminary data show an unprecedented range of δD values in all three species, ranging from -40‰ to -110‰. Final results will determine the suitability of gorgonin δD as a potential marine environmental proxy by testing the reproducibility of δD values between adjacent colonies.

Keywords: Deep-sea, Coral, Hydrogen, Isotopes, Experimental, Geochemistry

段階的間隙水抽出による岩石間隙中の反応-輸送現象の不均質性の評価 Evaluation of heterogeneity of reaction-transport phenomenon in rock by sequential pore water extraction

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Heterogeneity of dissolution/precipitation and solute transport in rock pores has been drawing attention in recent years. This phenomenon has been often studied using numerical calculation, but direct analysis of pore water is important to know what is actually occurring in pores. However, most previous studies have analysed the composition of bulk pore solution and it is difficult to discuss the detail of reactive-transport behaviour in pores using the bulk composition. In the present study, an experimental technique to sequentially extract pore water by applying various gas pressures to wet sample was used. With this technique, pore water can be extracted for each pore radius, which provides information on the heterogeneity of reaction and transport in pores. In the experiment, pure water was first passed through a sandstone core to induce dissolution in pores (flow-through reaction), then pore water was extracted for each pore size and solute concentrations were measured. The result of the experiment showed that the concentrations of Na, Ca, Mg, and Si increased with decreasing pore radius and that the concentration increases of Ca, Mg, and Na were greater than that of Si. Qualitatively, this result can be explained by a numerical model of the advection and dissolution in a single tube for different pore radii. However, the observed concentration increases were significantly greater than the model calculation, and it seems possible to evaluate the extent of the mixing of solutions in narrow pore and large pore by comparing the model calculation and experimental result.

キーワード：間隙水、溶解、移流

Keywords: pore water, dissolution, advection

白亜紀の玄武岩質溶岩の風化は海底下で進行中？

ナノ鉱物解析と粘土鉱物同定による解明

Subseafloor weathering of cretaceous basaltic basement revealed by nanomineralogical and conventional clay characterizations

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海洋地殻上部に普遍的な玄武岩質溶岩は空隙率が高く、岩石と海水の反応により地球規模での元素循環に寄与している。しかし、形成後1000万年で空隙が二次鉱物により充填されるため、10 Ma以降の玄武岩基盤中で海水との反応が進行しているか不明である。本研究では、ナノスケールでの鉱物解析と従来の粘土鉱物同定法を組み合わせ、亀裂中で玄武岩と海水の風化過程で生成する粘土鉱物の有無と産状を明らかにすることを目的とする。

南太平洋環流域の形成年代84-120 Maの玄武岩基盤は、溶存酸素が浸透している厚さ約70 mの堆積物に覆われている。統合国際深海掘削計画第329次研究航海で取得された南太平洋環流域の基盤岩のコアのうち、異なる二次鉱物が亀裂を充填される深度102-121 mの3試料（U1365E7R-2は炭酸カルシウム鉱物、U1365E8R-4はセラドナイト、U1365E12R-2は酸化鉄鉱物）を対象とした。

亀裂中の粘土鉱物をコア試料の粉末から水ひで回収し、X線回折（XRD）パターンの解析を行った結果、どの試料からも $d_{001} = 1.5$ nmの回折ピークが得られ、エチレングリコール処理で1.7 nmに膨張した。粘土鉱物の(060)面の回折ピークの位置から、U1365E7R-2には三八面体スメクタイト、U1365E12R-2にはノントロナイト、U1365E8R-4は両者の混合があることがわかった。水ひ試料に対してエネルギー分散型X線分光装置（EDS）搭載の走査型電子顕微鏡（SEM）による化学組成の半定量分析を行った結果、XRD測定により同定されたノントロナイトと三八面体スメクタイトのサポナイトの組成が得られた。亀裂中でのスメクタイトの産状を明らかにするために、亀裂を含む玄武岩の薄片を作成し、SEM-EDSにより解析した。その結果、U1365E7R-2では炭酸カルシウム鉱物がサポナイトと隙間なく亀裂を充填しており、U1365E8R-4とU1365E12R-2の薄片中の粘土鉱物のFeが水ひ試料よりも過剰に存在することがわかった。

集束イオンビーム（FIB）加工によりU1365E12R-2の薄片中のFeが過剰に存在するノントロナイトの部位の超薄片を作成し、高分解能透過型電子顕微鏡（HR-TEM）で観察した結果、ノントロナイトとゲーサイトナノ粒子が鉱物共生するのを観察できた。薄片のSEM-EDS分析の結果から、粘土鉱物の鉄過剰分を補正して、亀裂中でのスメクタイトの産状を調べた結果、U1365E8R-4ではセラドナイトと玄武岩基質の境界部をノントロナイトとサポナイトが充填しているのに対し、U1365E12R-2では二次鉱物による空隙の充填率の低い亀裂中にノントロナイトが散在した。Feに富むノントロナイトほどKを多く含むことから、海水中に含まれるKを取り込みながら形成していることが示唆された。

基盤直上の堆積物中の間隙水の K^+ 濃度が深度方向に減少することから玄武岩基盤にKが現在でも吸収され、かつ堆積物を介して海水から供給される酸素で呼吸する微生物が亀裂中に生息することから、10 Ma以降の玄武岩基盤は現在も海水と反応して、地球規模での元素の挙動に影響を及ぼしている可能性が本研究により示された。

キーワード：ノントロナイト、海洋地殻、風化、FIB-TEM

Keywords: nontronite, oceanic crust, weathering, FIB-TEM

南アフリカ・バーバトン緑色岩帯ムーディーズ層群の3.2億年前の縞状鉄鉱層中の鉄鉱物に伴う有機物の地球化学的特徴と微細構造観察

Microstructure and geochemistry of organic matters associated with iron minerals in 3.2 Ga banded iron formations, Moodies Group, Barberton Green stone Belt, South Africa

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縞状鉄鉱層は鉄鉱物と珪酸塩鉱物の互層からなる化学堆積岩である。大酸化イベント以前の縞状鉄鉱層の形成プロセスについては未だ明らかになっていない。これを説明するために、以下の二つの仮説が提案されている。一つは既にシアノバクテリアが生息しており光合成で発生した遊離酸素により鉄が酸化されたとする説、もう一つは鉄酸化細菌による酸化が起こったとする説である。どちらの説も微生物活動が関与しており、岩石中に残された有機物の産状からそのプロセスを推定できる可能性がある。しかしながら鉄鉱層中の有機物含有量は一般的に低く、研究例が少ない。本研究では、約3.2億年前に形成された南アフリカ・バーバトン緑色岩帯ムーディーズ層群の浅海性縞状鉄鉱層を対象として、当時の海洋表層における微生物活動に制約を与えることを目的とした。試料採取はシェバ金鉱山坑道内で行い、主要鉄鉱物の種類と鉄含有量からMTタイプ（磁鉄鉱に富む砂岩、13–50 wt% Fe₂O₃）、SDタイプ（磁鉄鉱に乏しいシルト質砂岩、10–30 wt% Fe₂O₃）の2タイプに分類した。MTタイプは自形の磁鉄鉱や石英に富む層と黒雲母や緑泥石などの珪酸塩鉱物に富む層の互層から成る。SDタイプは主に菱鉄鉱や鉄苦灰石などの炭酸塩鉱物が卓越しており、粒径の大きい炭酸塩・石英に富む層と緑泥石や黒雲母に富む層の互層からなるSD-1、粒径の小さい石英、緑泥石、黒雲母からなり、葉理が不明瞭なSD-2に分類できる。

採取試料の有機炭素含有量は0.03–0.29wt%であった。代表的な試料の研磨片及び酸処理抽出試料を用いて、走査型電子顕微鏡による炭素質物質の観察を行った。観察された炭素質物質は大部分が直径20 μm程度の円形ないし楕円形に近い鱗片状の概形を示し、表面部分は皺を持つ薄膜状組織からなる様子がしばしば観察された。これら試料の有機炭素安定同位体比は–26～–28‰の値を示したことから、炭素質物質は微生物起源である可能性が考えられる。Javaux et al. (2010)は本研究と層序に近い泥岩中に微化石様構造を発見しており、楕円形で表面に皺のある構造は本研究の観察結果と一致するが、粒径分布(31–298 μm)は大きく異なる。また、酸処理抽出された炭素質物質のN/C比は0.002であり、変成度の近い他の太古代岩石中のケロジェンの値と整合的であった。この抽出試料の顕微ラマン分光分析結果から算出された炭素質物質が経験した変成温度は約500℃と、想定されるよりもやや高温であり、後の金鉱化作用に伴う流体が炭素質物質の構造に影響を及ぼした可能性がある。さらに、全試料において試料中の有機炭素含有量が増加するにつれて鉄含有量は減少する傾向がみられた。一方、炭酸塩炭素含有量と鉄含有量は正の相関を示した。SD-1試料の大部分は、炭酸塩炭素含有量と鉄含有量の比が菱鉄鉱中の炭素/鉄比よりも高い値を示した。またMTおよびSD-1試料の炭酸塩炭素の安定同位体比は約–4‰で、近隣鉱山の鉱化流体由来の炭酸塩炭素の値と整合的であった。このことからSD-1試料は流体沈殿による菱鉄鉱以外の炭酸塩鉱物が卓越していたことがわかった。

縞状鉄鉱層の有機物は鉄鉱物との反応で消費され、磁鉄鉱や菱鉄鉱を生成する可能性があるため(Perry et al., 1973, Kohler et al., 2013)、生物由来炭素からの炭酸塩鉱物の生成が予想される。しかしながら炭酸塩の

炭素安定同位体比から、MT試料の炭酸塩鉱物は流体由来と考えられる。またMT試料中の有機炭素含有量は0.03-0.26wt%と比較的高い値を示した。SD-2試料では有機炭素に富むが鉄に乏しく、炭酸塩炭素量が少ないため有機物の菱鉄鉱への変質は進まなかったと考えられる。このことから、生物由来有機物が続成・変成作用中に消費された量は少なく、本試料に見られる有機炭素量と鉄含有量との負の相関は初生の傾向である可能性が高い。Kohler et al. (2013)は縞状鉄鉱層に関与する微生物活動について、鉄酸化細菌は有機物と鉄を一定の比で沈殿させるのに比べ、シアノバクテリアは有機物をより多く沈殿させるという仮説を提唱した。この仮説を本研究結果に適用すると、炭素に富み鉄に乏しいSD-2試料はシアノバクテリア、炭素に乏しく鉄に富んだMT試料は鉄酸化細菌の活動を反映している可能性がある。以上のことから、ムーディーズ層群が形成された32億年前の沿岸部の海洋表層ではシアノバクテリアが繁茂し、遊離酸素に酸化された鉄に比べ有機物が多く沈殿したのに対して、遠洋域では海底熱水から供給された二価鉄を得て鉄酸化細菌が生息し、有機物に対し鉄を過剰に沈殿させることで縞状鉄鉱層が形成されたと考えられる。

キーワード：縞状鉄鉱層、バーバトン緑色岩帯、有機物

Keywords: Banded Iron Formations, Barberton Green stone Belt, organic matters

Depositional environment of graphite-bearing metasedimentary rocks and banded iron formations in >3.7 Ga Isua Supracrustal Belt, West Greenland

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Biogenic graphite in > 3.7 Ga metasedimentary rocks, Isua Supracrustal Belt (ISB), West Greenland, has been reported as the oldest remnants of life (Rosing, 1999; Ohtomo et al., 2014). However, ecosystem spreaded in the >3.7Ga ocean is still poorly understood. Depositional environments of metasedimentary rocks containing biogenic graphite and surrounding banded iron formations (BIFs) could give an insight into microbial activities in the >3.7Ga ocean. Graphite-rich schist reported by Ohtomo et al. (2014) contains rare earth element (REE) minerals such as monazite, zircon and xenotime. These REE minerals could have been derived by one or some of the following processes: detrital transport, precipitation from a seafloor hydrothermal fluid, generation during diagenesis and precipitation from a metamorphic fluid. Occurrence, geochemical composition and chronological information of the REE minerals might constrain their origin and provide information of depositional and/or alteration process of the graphite-rich schist. Here, we performed a geological survey in the west side of the ISB and investigated the petrographic and geochemical characteristics of sedimentary rocks to reconstruct the depositional environment. Chemical Th-U-total Pb Isochron Method (CHIME) was conducted on monazite to determine the age.

Samples collected in the whole west side of the ISB consist of alternate layers of magnetite-amphibole-chlorite-rich and quartz-rich layers. The samples were roughly divided into magnetite-rich type, which distributed at northeast to south, and silicate-rich type, mostly distributed at northwest, based on the dominant minerals. Bulk chemical compositions of the examined samples showed that magnetite-rich type are abundant in Fe, whereas silicate-type are rich in Mg. Magnetite-rich type primarily composed of Fe-rich amphibole, grunerite, whereas silicate-rich type contains more Mg or Ca-rich amphibole. Similarly, chemical compositions of chlorite in magnetite-rich type are Fe-rich, whereas that of silicate-rich type are Mg-rich. Amphibole and chlorite compositions in graphite-rich metasedimentary rocks are Mg-rich, which is similar to silicate-type BIF samples. The results suggest that Mg-rich characteristics of BIFs and graphite-rich metasedimentary rocks at north west, and Fe-rich characteristics of BIFs at north east to south are a primary signature. Ti and Al concentrations in BIFs and graphite-rich sedimentary rocks showed a positive correlation, indicating contribution of detrital components to them. Graphite-rich schist sample consisted of graphite-chlorite- and quartz-cummingtonite-dominated microlayers, containing high amounts of REE compared to samples showing low graphite content. The graphite-rich sample contained euhedral monazite, zircon and minor xenotime 2-10 μm in diameter, which were accumulated in graphite-chlorite microlayers and concordant with orientation of lamination, whereas most of the monazite in samples showing low graphite content were anhedral. CHIME age of the monazite in graphite-rich schist samples indicated $3630 \pm 91 \text{Ma}$, which ranges in the ages of prograde metamorphism and detrital zircon in previous report (Nutman et al., 2009). Considering monazite occurrence concordant with lamination of the graphite-rich schist, it is most likely that monazite was syngenetic with host rocks, probably derived from detritus and the age was modified during metamorphism, or crystallized during diagenesis to early metamorphism. Our results suggest that

BIFs and graphite-rich schist at north west of west side of the ISB deposited where clastic components such as Mg, Al, Ti and REE were supplemented at a relatively high rate, evoking that photosynthetic microorganisms might have been flourished in >3.7Ga shallow ocean.

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[2] Ohtomo *et al.* (2014) *Nature Geoscience*, **7**, 25–28.

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キーワード：イスア表成岩帯、希土類元素、モナズ石、グラファイト

Keywords: Isua Supracrustal Belt, rare earth element, monazite, graphite

Abiotic Nitrogen Fixation and Organic Synthesis by Photochemistry on Early Mars

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Detailed studies of Mars in recent years have provided many progress on understanding the possible view of environment on early Mars. With the fact that liquid water was present on early Mars, and the discovery of organic molecules as well as nitrogen-bearing compounds on Mars, there is possibility that life could have emerged on early Mars. Thus, it is important to understand the abiotic organic synthesis and nitrogen fixation process to evaluate the possible origin of life on Mars or other terrestrial planet. Previous studies suggested that organic matters can be produced by photochemistry. Total pressure of Martian atmosphere is lower than Earth. Thus, UV may penetrated down to the surface and can directly photolyze liquid water. This suggests that UV-induced photochemistry may have been more important. However, little is known about abiotic nitrogen fixation by UV light. This experimental study examines the nitrogen photochemistry at the surface of water. In the experiment, initial gas contains N_2O or N_2 with or without CO under the presence of liquid water. The starting condition may have existed on early Mars. The results showed that NH_3 , methylamine, glycine and other amino acids was produced from $N_2O + CO + H_2O$, whereas only trace amount of NH_3 was formed from $N_2 + CO + H_2O$. When gas phase do not contain CO, nitrate and nitrite were produced instead of NH_3 . A numerical model including 296 photochemical reactions was constructed, and can qualitatively explain the formation of NH_3 from N_2O . However, the concentration of NH_3 in the model is order of magnitude lower than the observed amount in the experiment, suggesting that current photochemical model still lack some possible reactions to generate NH_3 . The results provide important insights on chemical evolution theory that lead to the origin of life and the atmospheric evolution on Mars when the reaction pathway of NH_3 starting from N_2O and N_2 by UV light is confirmed.

Keywords: Mars, Nitrogen fixation, amino acid synthesis, UV

Distribution of Ammonium-Bearing Clay Minerals and their $\delta^{15}\text{N}$ values Occurred in Shallow-Seafloor Hydrothermal System in Kagoshima bay, Southern Kyushu, Japan.

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The seafloor hydrothermal fluids occurred in the arc and back-arc systems where are often covered with thick sediments contained organic matter are characterized by a high concentration of ammonium which is considered to originate from decomposition of the sedimentary organic matter. Under these conditions, ammonium cation can be fixed in interlayer space of 2:1 clay mineral during their formation associated with hydrothermal mineralization. However, the role of this process with respect to the nitrogen cycle around the Earth's surface has not been well understood until today. In this study, we measured ammonium concentrations and their isotopic ratios in the venting hydrothermal fluids and clay fraction in the hydrothermal altered sediments obtained from Kagoshima Bay, southern Kyushu, Japan.

The submarine volcano, Wakamiko, located in the submerged Aira Caldera, which formed during the late Pleistocene (ca. 29 ka) resulting from the huge eruption of the Ito pyroclastic flow, and about 200 m in water depth of depression area as well as it is filled with thick unconsolidated sediment layer up to 80 m. The hydrothermal activity of this area is associated with the Aira magmatism, and the emitting fluid has been characterized by a high ammonium concentration up to 17 mM, respectively.

All of samples were collected around vent expect for typical marine sediments of PC-4 site. Clay minerals were recovered as a clay size fraction ($2\ \mu\text{m}$) by hydraulic elutriation from the core sediments and then samples repeatedly treated by 30 % hydrogen peroxide solution and finally KOBBr-KCl solution to remove organic matter and exchangeable ammonium. After that clay fractions were measured by XRD for identification of clay minerals as well as their chemical composition were measured by EPMA. And NH group were detected by FT-IR. Nitrogen contents and their isotopic ratios were measured by EA/irMS. Total nitrogen (TN) contents and inorganic nitrogen (IN) contents were ranging from 0.03 to 0.28 $\mu\text{g/g}$ and from 0.002 to 0.01 $\mu\text{g/g}$, respectively. And $\delta^{15}\text{N}_{\text{TN}}$ and $\delta^{15}\text{N}_{\text{IN}}$ values were ranging from -6.2 to +4.6 ‰ (av. +0.3 ‰) and from -1.7 to +5.1 ‰ (av. +1.2 ‰), respectively. The $\delta^{15}\text{N}$ values of venting hydrothermal fluids and porefluids were ranging from -1.8 to +1.9 ‰ (av. -0.2 ‰) and from +2.4 to +2.9 ‰ (av. +2.7 ‰), respectively. Particularly, $\delta^{15}\text{N}_{\text{IN}}$ values can be divided two groups, relatively 15N-enriched and 15N-depleted. And those trends were consistent with the difference of $\delta^{15}\text{N}$ values between hydrothermal fluids and pore fluids. Further study, it is required that understanding of nitrogen fractionation between fluid and mineral in hydrothermal system through the synthesis of ammonium-smectite.

キーワード：海底熱水システム、窒素循環、2:1 粘土鉱物、アンモニウム、窒素同位体

Keywords: seafloor hydrothermal system, nitrogen cycle, 2:1 clay mineral, ammonium, nitrogen isotope

愛媛県西条市市之川鉱山における地球表層物質によるアンチモンの取り込み挙動

The uptake behavior of antimony with earth surface materials at Ichinokawa mine in Saijo city in Ehime prefecture

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アンチモン(Sb)は周期表第15属に属する元素であり、ヒ素(As)と化学的挙動が類似した元素である。SbはAsと同様に生物に対して毒性を有するため、地球表層環境における動態の理解が望まれている。地球表層で産出する二次鉱物(地球表層物質)の多くは細粒で産し、比表面積が大きく、化学反応性の高い準安定相で産することが知られている。有害金属に対して地球表層物質が有効な保持媒体と言われている(福土 2017)。代表的な地球表層物質として粘土鉱物(スメクタイト及びパーミキュライト等)、金属(水)酸化物(フェリヒドロライト、ゲーサイトなど)、炭酸塩鉱物(カルサイトやアラゴナイト)が挙げられる。地球表層物質によるAsの取り込み挙動は自然界の観察および室内実験により広範に検討されている。一方、Sbに関してはほとんど検討されていない。Sbの動態の解明あたっては、Sb濃度が高い地点を対象にするのが望ましい。本研究ではかつてSb鉱山として稼働していた愛媛県市之川鉱山坑道内に生成した鉄酸化物や炭酸塩鉱物によるSbの取り込み挙動を検討することを目的とした。

AFMによる炭酸塩鉱物の結晶成長・溶解現象のナノスケール解析

In situ AFM study on crystal growth and dissolution of calcite at a nano-level

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本研究では、環境変動指標鉱物の一つであり、わずかな温度変化や溶液濃度変化などでその溶解・結晶成長の様式を変化させると考えられている方解石について、より天然現象に近い温度条件と溶液濃度条件での溶解及び結晶成長過程を明らかにすることを目的とする。このため、原子間力顕微鏡(AFM)その場観察法を用いて、方解石の主要な平坦面(特異面)である{10-14}面と溶液間で起こる顕微的な溶解・結晶成長過程をリアルタイムで追跡し、その機構の解明と速度論的考察を深める。

本研究では、メキシコ-チワワ産の方解石を試料として実験を進めた。AFM実験開始直前にナイフで新たな(10-14)劈開面を露出させ、AFM試料台に固定した。炭酸カルシウム溶液については、あらかじめ作製した炭酸水素ナトリウム水溶液0.01Mと塩化カルシウム水溶液0.01Mの2つのストック溶液を用いて、水溶液中のカルシウムイオンと炭酸イオンの比が1:1になるように調整しながら目的の過(不)飽和溶液を作製した。過(不)飽和度は、プロログラムソフトPHREEQCにより計算した。AFM観察は、Digital Instruments社製のMultimode SPMユニットを搭載したNanoscope IIIで行った。溶解・結晶成長実験はBruker AXS社製のair/fluid heater/coolerを搭載した液中セルを用いてフロースルー法で行い、溶液をシリンジポンプで約10 ml/hの流速で流した。溶解・結晶成長実験での過(不)飽和度Sの範囲は-4.91から0.90で、また、純水中での溶解実験も行った。実験温度は25(±0.2)°Cで、温度制御はBio-HeaterとThermal Applications Controllerで行った。走査法はコンタクト・モードを用い、カンチレバーはSi₃N₄製、スキャナーは温度可変対応J-headを用いた。

溶解実験では、いずれの不飽和度でも4つのステップ(あるいは面)で囲まれた四角錐の形をしたエッチピットが形成された。ただし、不飽和度が高くなるにつれて、平行四辺形の一方の1組のステップ(あるいは面)の形状が湾曲する傾向にあった。また、ステップの後退速度に異方性が見られ、水平方向については、後退が速いステップはその速度の過飽和度依存性が高く、速度が遅いステップでは過飽和度依存性が低いことが分かった。一方、(10-14)面に垂直な方向に対する後退速度は前者よりかなり遅く、また、過飽和度依存も低くなることが分かった。

結晶成長実験でも、溶解実験同様4つのステップ(あるいは面)で囲まれた四角錐の形をしたスパイラル成長丘が形成された。この成長丘では稜線が明瞭に観察でき、上部は二層周期でうずを巻いていることが認められた。ちなみに、ステップ単層の高さは約3 Åであり、炭酸カルシウム1分子層の厚さに相当する。ステップあるいは面の前進速度については、水平方向については溶解時の後退速度よりも速いが、垂直方向については、溶解時の後退速度よりも遅い可能性がある。

キーワード：カルサイト、結晶成長、溶解、原子間力顕微鏡

Keywords: calcite, crystal growth, dissolution, AFM

Role of amorphous silica in forming calcium silicate hydrate for strength development of steel slag-dredged soil mixtures

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Dredged soils consists of minerals including clays, organic debris and seawater, and are excavated beneath ports to maintain the waterways. Partially they are landfilled due to its soft physical properties disabling its usage as construction materials. Indeed its characteristics differ greatly depending on the sampling areas due to the variation in its composition. Recently, it is discovered that mixing dredged soil with steel slag, that is also partially treated as waste produced as iron smelting process' s by-products, develops strength. This discovery may turn dumped fraction of both materials to resources by expanding their application into building materials for undersea constructions. Nonetheless, different combinations of a type of steel slag and dredged soil from various areas show gaps in the strength development even in under the identical mixing condition. The relationship between mixing condition and strength development is not yet clarified, making it difficult to be utilized for the above application.

Clarifying the hardening mechanism of the steel slag-dredged soil mixture will enable prediction of the strength with a particular combination of steel slag and dredged soil. In order to achieve it, clarifying the secondary mineral formation that contributes to hardening is essential. Previous studies suggest that the strength development is related to the pozzolanic reaction, which results in cementation by the formation of calcium silicate hydrates (C-S-H). Key factors in the pozzolanic reaction include the increase in pH of the pore water, and the supply of calcium and silica ions to pore water. Steel slag contains $\text{Ca}(\text{OH})_2$, which supplies calcium and increases pH of the mixture. Silica is said to be supplied from the dredged soils, but it is not clarified what is being the silica supply.

Focusing on the variation of dredged soil affecting the strength development, the objective of this study is to understand the effects of amorphous silica in dredged soils, which has faster dissolution rate compared to crystalline silica phases, to the early strength development of steel slag-dredged soil mixture.

In this study, dredged soils from various sampling locations (A, B, C and D) and steel slag from iron works 1 were mixed for the investigation. XRD analysis showed no significant difference between the mineralogical compositions of all the dredged soils. The unconfined compressive strength showed mixtures with soil A exhibits the highest strength, followed by those with B, C and D. Formation of C-S-H in mixture A was found to be denser than mixture D through scanning electron microscope, filling up pores in the mixture. In addition, the measurement of mixture' s pore water pH transition showed decreasing trend in pH from 12.5 in only mixtures A and B but not C and D from 1 day curing onward. This suggests stronger mixtures' (A and B) pore water' s pH were influenced by formed secondary minerals, such as C-S-H which expels H^+ when it forms, indicating that its formation was notably greater in stronger mixture. In our mixtures, the silica ion was most likely supplied from dredged soils. The silica concentration dissolved from diatom frustules were measured. Soils A and B showed higher dissolved silica concentration compared to C and D. Inorganic amorphous silica such as volcanic glass content is also discussed. From geochemical modelling which treats amorphous silica dissolution kinetically, it was clarified that stronger and weaker mixtures show significant difference in the volume of C-S-H forming. We suggest that the silica supply from amorphous silica in dredged soils may be the driving force for the pozzolanic reaction for early strength development.

キーワード：ポゾラン反応、浚渫土、製鋼スラグ、非晶質シリカ

Keywords: pozzolanic reaction, dredged soil, steel slag, Amorphous silica

Localization of magnetite from Fe-rich brucite induced by pH changes during serpentinization

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H₂-rich fluids from ultramafic-hosted hydrothermal vent is important for understanding generation of hydrocarbon and biosphere in deep sea floor. Key to the formation of hydrogen in such system is magnetite formed serpentinization reaction. Magnetite distribution in serpentinized peridotite is usually heterogeneous; randomly scattered, and/or localized at former olivine-grain boundaries. However, formation mechanism of magnetite segregation during serpentinization remain poorly understood.

In this study, hydrothermal experiment of olivine-H₂O system was conducted with varying initial solution pH from under conditions of 250 °C and vapor-saturated pressure of 3.98 MPa. In the autoclave, 1.0 g of olivine powder (Fo91; 38-75 μm) were set with solutions. Six solutions with varying initial solution pH at room temperature were used; pH at room temperature is 5.7, 6.8, 9.0, 10, 11, and 12. pH were adjusted by diluting NaOH solutions. The run time up to 63 days.

After the experiments, for solutions of initial pH = 5.7-9.0, pH increased to around 10. In contrast, for solutions of initial pH >10, the pH after experiments weren't changed. SEM observation revealed that Serpentine + Brucite + Magnetite were formed and no significant difference was not observed by changing pH of initial solution. Magnetite occurred with 5-10 μm, and seems that no localization of magnetite occur. After 63 days experiments, amount of serpentine and brucite, measured by thermogravimetry, were increased with increasing the pH of initial solutions. Amount of magnetite, which was measured by Alternating Gradient force Magnetometer, was increased with increased with increased with increasing initial pH up to 11. At initial pH = 12, the amount of magnetite after 63 days reaction was lower than that of initial pH = 11.

From EPMA analysis, the presence of ferric ion in serpentine and brucite were not observed. the iron content of the serpentine was almost similar with varying initial pH. In contrast, the iron content of the brucite roughly increased as pH was increased. The amount of products were almost proportional to reaction progress, indicating that reaction rates were approximately constant during the experiments. Mass balance calculation revealed that iron partitioning varies with pH; at initial pH = 6.8, the Fe partition ratio between brucite and magnetite was 3:7. With increasing the initial pH, the ratio gradually decreased to 6:4 at initial pH = 12.

Klein et al. (2013) suggests that magnetite was formed at >200 °C by breakdown of Fe-rich brucite formed at <200 °C. Our experiments revealed that Fe-rich brucite could be formed by reaction with alkaline solution (pH>11). This indicates that pH changes from alkaline to neutral could form magnetite from Fe-rich brucite. To test this hypothesis, further hydrothermal experiments were conducted. The solid samples, which reacted with initial pH = 12 for 27 days, was reacted with water for 14 days. As a result, two type of magnetite were observed; magnetite with 5-10 micro and magnetite with < 1 μm. The later magnetite was occur within brucite grains, which was not observed reaction with initial pH = 12 for 27 days.

Our experiments revealed that, by changing pH in solution from alkaline to neutral, magnetite were formed from Fe-rich brucite. Two stage process of magnetite formation were suggested; (1) low fluid-flux

serpentinization of olivine changes the fluid to alkaline to form serpentine and Fe-rich brucite. (2)
Reaction with fresh fluid which were transported via newly-formed cracks to form magnetite and hydrogen is generated.

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キーワード：蛇紋岩、磁鉄鉱、水熱実験、水素

Keywords: serpentine, magnetite, hydrothermal experiment, hydrogen

透過型電子顕微鏡 (TEM) と走査型透過X線顕微鏡(STXM)による地衣類 －溶岩界面の観察

Nano-scale observation of interface between lichen and basaltic lava by TEM and STXM

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はじめに: 火山噴火によって流出した溶岩は、次第に雨風による風化を受け、それに伴い様々な元素(e.g. Ca, Mg, Fe, Si, Al)が溶出する。これらのうちSi, Alは粘土鉱物として晶出し(Wilson, 2004), Ca, Mg, Feは粘土鉱物に吸着される。このようにして地表の肥沃化が進み、土壌が形成される(Kato et al., 2005)。近年、パイオニアプラントとして知られる地衣類が風化を促進している要因として指摘されている(Chen et al., 2000; Vingiani and Adamo, 2013; Jackson, 2015)。これまでの研究から、偏光顕微鏡や走査型電子顕微鏡(SEM)によって、ミクロレベルの細粒な生成物が地衣類－溶岩界面で複雑な組織を形成している様子が明らかになった

(Vingiani et al., 2013; Vasconcelos et al., 2015)。しかしながら、地衣類－溶岩相互作用メカニズムの解明には、それらの界面のナノスケール観察や化学状態解析が必須である。本研究では、透過型電子顕微鏡(TEM)、走査型透過X線顕微鏡(STXM)による地衣類－溶岩界面のナノスケール解析を行った。

実験方法: 伊豆大島の三原山で1986年に噴出した溶岩のうち地衣類が着生したものをを用いて実験を行った。地衣類－溶岩界面の厚片試料を作成した後、FIB(JEOL: JEM8530FIB)に供試し、地衣類－溶岩界面の透過電子顕微鏡(TEM)用試料および走査型透過X線顕微鏡(STXM)用試料を作成した。STXMは米国ローレンスバークレー研究所(LBNL)のAdvanced Light Source (BL 5.3.2.2), TEMは物質材料研究機構(NIMS)の電子顕微鏡(JEOL: JEM-2100F)をそれぞれ用いた。

結果と考察: 走査型透過電子顕微鏡法によるエネルギー分散型X線分析(STEM-EDX)および制限視野電子線回折(SAED)により、地衣類－溶岩界面の幅約2 μm の領域において特異的に、goethite (最大径約1.4 μm)、amorphous alumino-silicate (最大径約1.3 μm) および α -quartz (最大径約1 μm) が確認された。またSTEM-EDXの結果、amorphous alumino-silicateは主にSiとAlから構成され、少量のMg, Feと微量のKを含んでいた。これまでも、地衣類と岩石の界面には鉄酸化鉱物やアルミノケイ酸塩鉱物の生成が報告されており、これらは地衣類が分泌する有機物質と岩石の反応により生成する可能性が指摘されている(Adamo and Violante, 2000; Vingiani et al., 2013)。本研究で確認された地衣類 (*S. vesuvianum*) もフェノール類や脂肪酸を分泌することが知られ(Solberg, 1976; Szczygala and Olech, 1990)、これらの有機物質がgoethiteやamorphous alumino-silicateの生成に関与したと考えられる。一方、粉末X線回折の結果から溶岩中に α -quartzの存在は認められず、二次鉱物として α -quartzが生成することは考えにくい。したがって、 α -quartzは、風塵として地表に堆積した後に地衣類による被覆を受けたものと考えられる(Vingiani et al., 2013)。

キーワード：地衣類－岩石相互作用、TEM、STXM、ナノスケール

Keywords: lichen-rock interaction, TEM, STXM, nano-scale

モンゴル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 south Mongolia.

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The health risks associated with toxic chemicals in saline lake become environmental problems (Barber et al. 2009). In saline lakes, the dissolved matters are enriched in solutions because of the evaporation of lake water. The enrichments result in the formation of the contaminated lake water and salts deposits containing high levels of the toxic chemicals (Barber et al. 2009).

The toxic elements distribution between the sediments and lake water are essential for the understandings of the enrichment processes and the mobility of toxic species in surrounding environments. In present study, we investigated the distribution processes of arsenic and uranium by analyzing the lake waters, suspended matters and sediments in saline lakes (Olgoi, Boon Tsagaan and Orog lake) in south Mongolia.

The solid and liquid samples from the lake waters were separated by centrifugation. The solid phases were measured by XRD. Morgan and Tao extraction were conducted for solid phases and the extracts were analyzed by ICP-OES and ICP-MS. XRD profile shows that each sample has authigenic minerals, including calcite and Monohydrocalcite. The extraction experiment showed that arsenic and uranium are distributed into calcium carbonates rather than amorphous iron oxide.