衝撃波による鉱物，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.

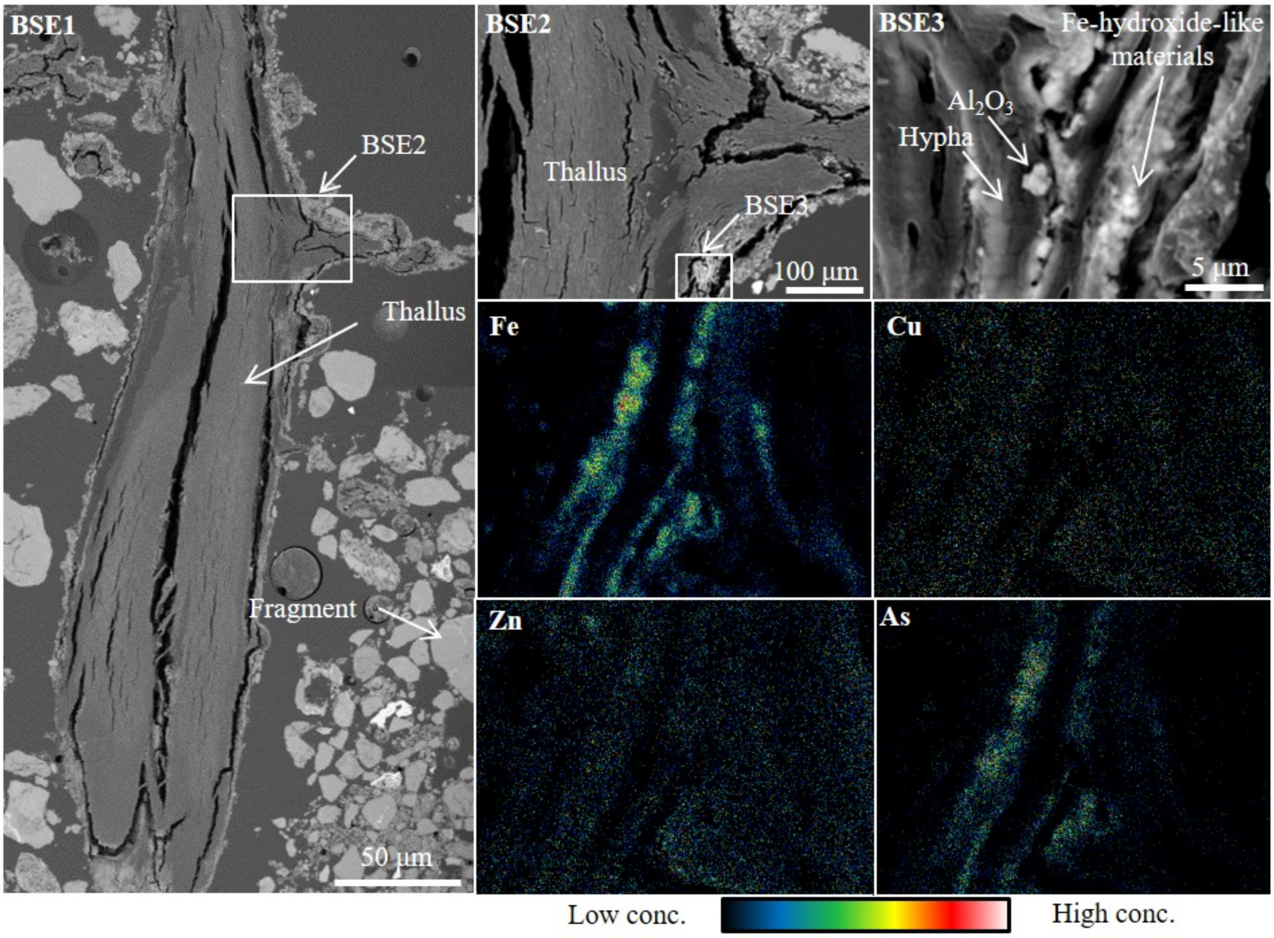
The slag that is a substratum of *S. exutum* consists primarily of willemite, fayalite, and/or magnetite and contains matte drops, which are mainly Cu-metals, -alloys, and -sulfides. The willemite and matte drops are ultimately converted to Fe-hydroxides during the weathering process. In addition to 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 $FeCl_3$, $Fe(NO_3)_3\cdot9H_2O$, 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.

[References]

Takashima, C. and Kano, A. (2008) Microbial processes forming daily lamination in a stromatolitic travertine. *Sedimentary Geology*, 208, 114-119.

Takashima, C., et al (2008) Laminated iron texture by iron-oxidizing bacteria in a calcite travertine. *Geomicrobiology Journal*, 25:3 193-202.

Tkashima, C.,et al (2011) Bacterial symbiosis forming laminated iron-rich deposits in Okuoku-hachikurou hot spring, Akita Prefecture, Japan. *Island Arc*, 20, 294-304.

Okumura, T., et al(2013) Processes forming daily lamination in a microbe-rich travertine under low flow condition at the Nagano-yu Hot Spring, Southwestern Japan. *Geomicrobiology Journal*, 30, 910-927.

Mizota, C. and Kusakabe, M. (1994) Spatial distribution of dD-d^{18}O values of surface and shallow groundwaters from Japan, south Korea and east Chian. *Geochemical Journal*, 28, 387-410.