

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 KOB₂-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 NH₄⁺ 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 increased 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.

References

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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.