

マイクロ XAFS 法と FISH 法を組み合わせた新しいバイオミネラリゼーション観察手法の開発

Development of a new method to observe the biomineralization using FISH combined with micro-XAFS

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Ubiquitous presence of microbes in aquatic systems and their inherent ability of biomineralization make them extremely important agents in the geochemical cycling of inorganic elements. However, the detailed mechanisms in environments are largely unknown, because there are few adequate analytical techniques to observe in situ the biogenic reactions. Here, we report a novel technical approach to characterize specific biomineral associated with a target microbe on high spatial resolution. The technique was developed by combining directly in situ phylogenetic analysis, fluorescence in situ hybridization (FISH), with a synchrotron microprobe method, micro X-ray absorption fine structure spectroscopy (micro-XAFS), and was applied to iron deposition by iron-oxidizing bacteria (IOB). In situ visualization of microbes revealed that in natural iron mats, Betaproteobacteria dominated by IOB were dominantly localized within 10 micrometer of the surface. Furthermore, in situ chemical speciation by the synchrotron microprobe suggested that the Fe local structure at the IOB accumulating parts was dominantly composed of short-ordered Fe-O6 linkage, which is not observed in bulk iron mat samples. The present study demonstrated that coupled XAFS-FISH technique could provide direct information on specific biogenic reaction mediated by target microorganism.

キーワード: XAFS, バイオミネラル, FISH, マイクロ XAFS

Keywords: XAFS, biomineral, FISH, micro-XAFS

水酸化鉄およびマンガン酸化物への吸着における希土類元素安定同位体分別に関する実験的研究

An experimental study on stable isotopic fractionation of rare earth elements (REE) during the adsorption on iron and manganese hydroxides

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Regarding the isotopic fractionation during the adsorption, it has been clarified that heavier isotopes adsorb onto a solid phase for elements existing as cations in a solution, while elements existing as oxyanions in a solution adsorb lighter isotope fractionation onto a solid phase. However, our study on the stable isotope fractionation of Ce during adsorption on ferrihydrite and d-MnO₂ showed that the heavier isotopes remained in the liquid phase, though Ce should be dissolved as free cation under the experimental condition. This study, therefore, exhibits the results of stable isotopic fractionation of rare earth element (REE) during the adsorption experiment to discuss the cause of the isotopic fractionation among REE.

Lanthanum, Ce, Nd, and Sm chloride solutions were respectively added to both synthesized ferrihydrite and d-MnO₂, with the concentration of REE systematically changed. In all the systems, pH was adjusted to 5.00 (± 0.05) and shaken for 6 hours before the filtration. Stable isotope ratios in both liquid and solid phases were determined using MC-ICP-MS. REE-Cl₃ solutions used in the adsorption experiment were employed as standard solutions and the isotope ratio of each element was expressed in epsilon notation relative to the average standards, which is shown in the equation as follows: $\epsilon = (R_{sample}/R_{STD} - 1) \times 10^4$, where $R = {}^{139}\text{La}/{}^{138}\text{La}$, ${}^{142}\text{Ce}/{}^{140}\text{Ce}$, ${}^{145}\text{Nd}/{}^{143}\text{Nd}$, and ${}^{149}\text{Sm}/{}^{147}\text{Sm}$, respectively. For solid phase, K-edge EXAFS was measured at BL01B1 in SPring-8 to obtain the information of the coordination environment.

Though accurate determination of La isotope ratio was difficult due to the large difference in the isotopic abundance between ${}^{138}\text{La}$ and ${}^{139}\text{La}$, a broad trend obtained here suggested that the lighter isotope was partitioned into the solid phase. On the other hand, in Nd and Sm systems, results clearly show that lighter isotopes remain in the liquid phase, suggesting that physicochemical factors have been changed between Ce and Nd. According to the EXAFS analysis, split first shell (La-O bond) was observed for La-adsorption system, which suggests that the first coordination sphere is distorted in the system. Such distortion is also expected for Ce-adsorption system. On the other hand, split first shell was not observed for Nd and Sm systems. Thus, it is expected that the coordination environment, which can also cause the difference in their hydration numbers, affect the different isotope fractionations among REE.

Keywords: rare earth element, stable isotopic fractionation, XAFS

走査型透過軟 X 線顕微鏡を用いた地球惑星試料の微小領域有機化学 Organic chemistry within submicron regions of Earth and planetary materials using Scanning Transmission X-ray Microscopy

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Scanning Transmission X-ray Microscopy (STXM) は、サブミクロンの集光 X 線に対して、微小な試料を走査して、透過した X 線の強度を検出し軟 X 線吸収 (X-ray Absorption Near Edge Structure, XANES) スペクトルを測定することが可能な、化学状態分析に有力な手法である。STXM はローレンス・バークレー国立研究所の Advanced Light Source にある Polymer STXM ビームラインで利用することができる (Kilcoyne et al. 2003)。ポリマーの主成分である炭素、窒素、酸素などの K 吸収端をカバーする 250-800 eV の範囲に渡り、数十 nm サイズの軟 X 線を利用できる実験ステーションである。軟 X 線が十分に透過するように、試料はウルトラマイクロトームで約 100 nm の厚みに調製される。測定で得られた炭素、窒素、酸素の K 吸収端 XANES スペクトルには、有機物の化学結合に由来する微細構造が現れ、その強度から、元素組成分析に加えて化学状態の定量を行うことができる。

STXM では、微小試料の x, y 軸方向への精密微動や、試料に対するゾンプレーットの Z 軸位置を、干渉計で制御する。また、Order selection aperture (OSA) をゾンプレーットと試料との間に設置することで不要な 0 次回折光を遮光し、1 次回折光のみを通過させ、S/N 比を向上させている。試料を透過した X 線は光電子増倍管で検出され、次式により吸光度に変換される； $OD(\text{optical density}) = \ln(I_0/I)$ 。ここで、I は試料透過後の X 線強度、 I_0 は試料のない部分を透過した後の X 線の強度である。STXM 本体は、脱気・ヘリウム置換を施し、光子の吸収を抑え、チャンバー内を熱的に安定化し、干渉計のドリフトや装置の加熱を防ぐ。

STXM はもともと、90 年代初めにポリマー材料の分野で発展した分析法であるが、今日では宇宙・地球化学の幅広い分野でその威力を発揮している。たとえば、NASA による世界初の彗星塵サンプルリターン計画「STARDUST」では、2006 年に 81P/Wild 2 彗星の塵が地球へ持ち帰られ、彗星塵の初期分析の一環として種々の有機物分析が行われた際、彗星塵中のサブミクロン領域における炭素成分の識別と、それを構成する有機官能基の定性・相対定量に STXM が適用された (Sandford et al. 2006; Cody et al. 2008)。その他、生物地球化学分野では、海底熱水環境中の粒子性有機炭素における C と Fe の化学状態マッピング (Toner et al. 2009) や、38 億年以上前の縞状鉄鉱床に含まれる結晶性に乏しい炭素物質の STXM 分析 (Papineau et al. 2011) などの研究が行われている。さらに最近では、STXM を、集束イオンビーム (FIB)、透過電子顕微鏡 (TEM)、同位体顕微鏡と組み合わせることで、試料中で特に着目すべき微小領域の分子組成、同位体比、形態の関係を明らかにすることができるようになった (Yabuta et al. 2012, JPGU abstract)。また、STXM による角度走査ナノトモグラフィーを用いたポリマーの 3 次元元素マッピング法も開発されている (Hitchcock et al. 2008)。このように、高い空間分解能を備え、試料の抽出・分離などの前処理を不要とする局所分析技術は、自然界に存在する有機物の化学的不均一性・多様性を明らかにする上で非常に優れている点で、地球化学における STXM の要求は今後ますます高くなるものと思われる。

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キーワード: 走査型透過 X 線顕微鏡, X 線吸収端近傍構造, 軟 X 線, 有機物, 局所分析, 空間分解能

Keywords: Scanning Transmission X-ray Microscopy, X-ray Absorption Near Edge Structure, soft X-ray, organic matter, Advanced Light Source, high spatial resolution

J-PARC(MUSE) ミュオンビームを用いた軽元素の深度プロファイル分析 ?地球惑星 試料分析の実用化に向けて? Depth profile analysis of light elements using J-PARC MUSE

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負ミュオン (μ^- 粒子) は、電荷-1、質量が電子の約 200 倍の不安定素粒子である。近年、大強度陽子加速器施設 J-PARC MUSE(MUon Science Establishment) では、世界最高強度の Pulsed Muon Beam を生成する事に成功し、様々な分野への応用が期待されている (Miyake et al. 2009 ほか)。

ミュオンビーム分析の最大の特徴は、測定試料内で μ^- 粒子が重い電子として振る舞う事である。そのため、 μ^- 粒子は電子よりも原子核に近い軌道を周回し、結果として、EPMA のような電子プローブ分析に比べ、約 200 倍のエネルギーをもつ特性 X 線を発生する (例えば、 μ^- -C K 線=75keV、 μ^- -N K 線=102keV、 μ^- -O K 線=133keV)。このような高いエネルギーの X 線は、厚み数 mm のケイ酸塩の透過が可能であり、さらには cm オーダーの物質内部の化学組成の情報を得るポテンシャルを有する。

本研究では、J-PARC MLF 施設の負ミュオンビームを SiO₂, C(グラファイト), BN(窒化ボロン)、SiO₂ の 4 層 (各 1mm、計 4mm) からなる試料に照射した結果について報告する。 μ^- 粒子の運動量を 37.5MeV/c から 57.5MeV/c まで段階的に変化させ、発生する X 線を 2 台の Ge 半導体検出器でモニターしたところ、SiO₂ 越しに、B, C, N, O の有意なシグナルを随時検出することに成功した。従来の電子プローブ分析では、試料の自己吸収や検出器の入射窓による遮蔽効果により、Na よりも軽い元素の定性分析は困難とされてきたが、本結果は、軽元素の非破壊 3 次元定量分析への可能性を示すものである。今後、堆積岩中の有機物を含む層の位置の特定や、はやぶさ 2 が目指す C 型小惑星からのリターンサンプルの非破壊分析 (真空容器に封入したままでの測定、リターン試料内部の軽元素分布解析) への実用化が期待される。

キーワード: ミュオン, J-PARC, 特性 X 線, 非破壊分析, 深度プロファイル分析

Keywords: Muon, J-PARC, Characteristic X-ray, Non-destructive measurement, depth profile analysis

加速器質量分析装置による宇宙線生成核種を用いた地球表層プロセスの研究 Earth surface process study using in situ produced cosmogenic nuclides

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The in-situ terrestrial cosmogenic nuclides (TCN) are produced from the interactions with cosmic ray bombardments with terrestrial rocks. The TCN exposure history measurement method is undergoing major developments in the Earth Science field. This method can be applied to various geological problems including tectonics, coastal environments changes and climate changes. The method is employed in the geological studies of which time scale ranges from 10^2 to 10^7 years using currently established method (^3He , ^{10}Be , ^{21}Ne , ^{26}Al , and ^{36}Cl). Combining measurements of nuclides which have different half-lives is particularly useful to determine the history of the surface process and hence quartz grains have been widely used for this types of research since they contain both in-situ ^{10}Be and ^{26}Al . In this paper we present some examples using TCN to reveal past histories of earth surface processes.

キーワード: 宇宙線生成核種, 地形, 氷床, 浸食, 加速器質量分析装置, 年代測定

Keywords: cosmogenic nuclides, geomorphology, glacier, erosion, accelerator mass spectrometry, dating

化石の三次元像解析と微量元素・同位体分析：化学古生物学に向けて Chemopaleontology: 3D images and trace element and isotope analyses of fossils

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Earth is a unique planet, which is filled with a large variety and number of life. Recent active planetary expeditions and telescopic observations of extrasolar planets allow us to expect possibility of life in other planets. But, presence of metazoan distinguishes biosphere of the earth from others. Conventional paleontology is based on morphological comparison of fossils with modern biota. The methods are very useful to investigate ancient animals and plants with the same body forms and tissues of modern biota, and allow to successfully decoding biological evolution based on some fossils with well-preserved tissues since the Cambrian (e.g. Shu, 2008 Gondwana Research). However, it is well known that body forms of *trilobite* animals at the dawn of the Metazoa are very strange and are often out of our insight even for the Cambrian fauna (e.g. Gould, 1989) as well as for many biota in the Ediacaran (e.g. Hultgren et al., 2011, Science; Schiffbauer et al., 2011, GSA meeting). We need another tool to investigate fossils: 3D observations and chemical compositions of microfossils.

Recent X-ray micro-CT analyses of the microfossils provide new methods to observe the internal structures (e.g. Donoghue et al., 2006). Compared with microscopic and SEM observations of cutting planes of the microfossils, this technique has two advantages of *nondestructive* analyses on *any* cross-sections of internal structures. We started to observe three-dimensional structures of the Early Cambrian microfossils including embryo and larvae stage fossils and SSF, and Chengjiang fossils including an echinoderm, a fish, arthropods with/without eggs, a mollusk, and a brachiopod, South China with a Synchrotron X-ray micro-CT at SPring-8. The observations of microfossils reveal the internal structures of animal embryo fossils, which are partly covered with envelopes and contain, often shriveled, globules, larvae of cnidarians, which comprise an umbrella-like top and relatively small column at bottom, often with pentaradial symmetry, and a polyp or a sea anemone. Although preliminary, the three dimensional observation of an echinoderm, which possesses gill-like structures, shows a relict of an internal cavity. The synchrotron micro-CT technique provides convenient and effective observations of internal structures for microfossils with complicated, small internal structures and even for completely compressed fossils. In addition, the reconstructed 3D images are very helpful to determine the most effective crosscutting planes for geochemical analyses.

Recent drastic progress of paleontology of the earliest metazoan fossils provides many candidates for arthropods with their eggs, chordates with notochords, the oldest fishes with spines and gills, and putative animal embryos, calcite, aragonite and Ca-phosphate biomineralizing fauna, earliest animals with sexuality, quite high trophic levels and others. However, only morphological comparison with the modern equivalents is still insufficient to provide the evidence for the above. Another tools to obtain the evidence for evolution of biological functions are required. We would like to propose some geochemical possibilities such as Ca, Fe, Mo, N, C and Cu isotopes, and trace element accumulation in specific tissues.

キーワード: 化石古生物学, マイクロ CT, 三次元像, 微量元素分布, 同位体組成

Keywords: chemopaleontology, micro-CT, 3D images, trace element distribution, isotope composition

次世代高分解能 LA-ICP 質量分析法による地球化学研究の新展開 High Resolution Imaging Mass Spectrometry using Laser Ablation-ICPMS Technique : multifaced tool in Earth and Bioscienc

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As a result of its continuous development, LA-ICP-MS provides ever more precise elemental and isotopic data. Enhancements in elemental sensitivity achieved for ICP-MS, together with newly developed dual or triplicated-ion detection system (combination of multiplier ion counting and a charge integration-Faraday collectors), provides flexible multi-element determinations for both the trace- and major-elements in the samples. Moreover, fast-mass scanning protocol achieved by the ion deflector devices, equipped on a magnetic sector, have led to successive improvements in the precision of isotope ratio measurements. The ICP-MS technique is likely to become a method of choice for many geochemists because it is much more versatile and user friendly and efficient method for elemental and isotopic analyses of trace elements.

Many geologists and geochemists are increasingly interested in processes in rocks that operate at the microscopic scale such as zoning or metamorphic recrystallizations. These processes have implications for the larger scale behavior of the Earth and new technique for chemical and isotopic measurements at the um-scale need to be developed. The combination of laser ablation sample introduction technique and ICP-mass spectrometry (LA-ICPMS) has now become a fast and accurate method of in-situ trace-elements and isotopic analysis for solid geochemical and biochemical samples [1]. Laser ablation utilizing UV-light with a frequency-quintupled (213 nm) Nd:YAG laser, Ti:S femtosecond lasers equipped with THG devices (260 nm) or an ArF Excimer laser (193 nm) offers reduced elemental fractionation during ablation and better spatial resolution with a small ablation pit size, and is now the most widely used system for LA-ICP-MS. The progresses in the LA-ICPMS technique are well demonstrated in the precision and accuracy of the U-Pb age data for zircons. We are now trying to measure the U-Pb age data for zircons from smaller ablation pit sizes (2-5 um). For zircons with U contents of higher than 100 ug/g, we can measure U-Pb ages from zircons with the ablation pit size of smaller than 5 um. Moreover, 2-dimensional mapping (imaging mass spectrometry) for trace-elements can be made with a ablation pit size of 2 um. The resulting analytical-spatial resolution achieved in this study was better than 5um, and this is almost comparable to the conventional ion microprobe technique. It should be noted that the spatial resolution achieved by the LA-ICPMS technique can be improved by the new generation laser optics. In fact, ablation pit size of smaller than 1um could be achieved by the near field optics. Moreover, it should be noted that the laser ablation was made under the atmospheric pressure. This suggests that in-situ elemental and isotopic analyses can be made on a wet samples including cell or fluid samples (biochemical samples). With high-sensitivity ICP-MS instrument with new generation laser ablation technique, the LA-ICPMS technique has immediate potential as a reconnaissance method and given increasing improvement in instrumentation will in the future produce data comparable or even better quality to ion probes of nano-SIMS type.

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キーワード: 固体地球化学, 局所同位体分析, 質量分析, レーザー質量分析, イメージング

Keywords: Geochemistry, Cosmochemistry, Imaging mass spectrometry, Isotope chronology, Laser ablation technique, Plasma mass spectrometry

レーザーアブレーション ICP 質量分析法による第四紀ジルコン U-Pb 年代測定 U-Pb age determination for Quaternary zircons using a laser ablation-ICP-mass spectrometry

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Age data for the Quaternary zircons are very important to understand the time sequence of many interesting and scientifically valuable events in the past, such as origin and evolution of the life, climate changes as well as geological events including volcanic eruption and earthquakes. Among the various chronometers, fission-track (FT) and K-Ar (Ar/Ar) method of dating have been widely used to define the age of young rocks or minerals. Despite the obvious success in obtaining reliable age data, because of very long half-life of the spontaneous fission, the number of tracks found in minerals is not large enough to define the precise age data for the young samples. For the age data obtained by the K-Ar (Ar/Ar) systems, better time resolution (i.e., precision and reliability) could be achieved from single grain of K-bearing minerals such as biotite or sanidine. However, system closure for the K-Ar isotope systems could be lost through weathering of the biotite grains. Moreover, the sanidine grains are not ubiquitously presented in the rocks, and the practical utility of the sanidine K-Ar (Ar/Ar) dating method is severely restricted. Zircon geochronology is one of the principal dating tools available to geologists and its use has revolutionized our understanding of the evolution of continental crust or unveiled Archean history. Especially, the U-Pb chronology on zircons has been widely used to understand the timing of the geological events with high time resolution. This is because, (a) age data were intrinsically very accurate because the decay constants for both the ²³⁵U and ²³⁸U are well calibrated and established, (b) system closure can be evaluated by comparing the ²³⁸U-²⁰⁶Pb and ²³⁵U-²⁰⁷Pb ages (i.e., level of concordance) and (c) zircon contains high concentration U with almost very low Pb. In order to take full advantage of the zircon U-Pb chronology, we have developed a new analytical protocol to measure U-Pb age data for Quaternary zircons using a laser ablation-ICP-mass spectrometry.

In order to derive the precise and reliable U-Pb age data from young zircons, both the high elemental sensitivity of the ICPMS instrument and high transportation efficiency of the laser-induced sample aerosols from sample to the ICP ion source are essential. Moreover, evaluation and correction of the background signal especially on ²⁰⁷Pb is still key issue. We have applied the ABLATION BLANK protocol to obtain the true background signal of ²⁰⁷Pb using laser ablation of Pb-free samples. The resulting signal intensities of ²⁰⁶Pb and ²⁰⁷Pb obtained with the laser ablation (ablation blank) were systematically higher than the signal intensities obtained without laser ablation (gas blank). Moreover, signal intensities of ²⁰⁶Pb and ²⁰⁷Pb obtained by laser ablation of synthesized zircons were higher than those obtained with the ablation blank for high-purity Si wafer. This suggests that the release of the residual sample aerosols can be enhanced through the laser-induced shockwave on the zircon materials, and therefore, ablation blank must be measured on identical sample matrix or minerals. For the U-Pb age determinations for young zircons, isotope ratio measurements with high dynamic range over 5 orders of magnitude is highly desired. To overcome this, we have employed the suppressor technique on our ion counting devices, which enables us to measure isotope ratio with over 9 orders of magnitude. Using this technique, we can measure signal intensity of very small ²⁰⁷Pb signals together with very high intensity ²³⁸U signal from the optimum laser ablation conditions. We will demonstrate the resulting U-Pb age for young zircons of various ages ranging from 0.6 to over 2000 Ma. The U-Pb age data obtained in this study demonstrate clearly that the LA-ICPMS technique has a potential to become a significant tool for geological study using Quaternary zircons.

キーワード: ICP 質量分析法, レーザーアブレーション, U-Pb, 年代測定, ジルコン, 第四紀

Keywords: ICP-MS, laser ablation, U-Pb, dating, zircon, Quaternary

硝酸の自然同位体組成を指標に用いた窒素循環速度定量化手法の開発：人工トレーサー添加法との比較検証

Quantifying nitrate dynamics in hydrosphere using the natural stable isotopes as tracers

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硝酸 (NO_3^-) はアンモニアとともに自然環境中の固定態窒素の主要な存在形態であり、一次生産の制限因子となっていることも多い。水環境中における NO_3^- の多くは有機体窒素から硝化反応を経て再生した NO_3^- ($\text{NO}_3^-_{re}$) と考えられるが、それ以外に、大気からの沈着によってもたらされた NO_3^- ($\text{NO}_3^-_{atm}$) も存在する。

これまで水環境中の一次生産に伴う NO_3^- の同化速度 (F_{up}) は「 ^{15}N トレーサー培養」、すなわち、(1) (培養容器への) 試料採取、(2) 人工 $^{15}\text{NO}_3^-$ の添加、(3) 現場環境 (もしくは疑似現場環境) 下での培養、(4) 粒子状有機体窒素の回収と質量分析に基づく ^{15}N 移行速度の定量、という一連の煩雑な作業を経て定量化されてきた。またこうして得られた F_{up} データには、培養操作に伴う物理・化学環境変化とか、競合反応 (有機体窒素の再無機化反応など) の同時進行とか、同化された窒素の溶存態への流出といった点に関して、補正を加える必要がある。さらにこれで得られる F_{up} は特定水塊における特定時期の F_{up} でしかなく、対象とする湖沼 (or 海域) について年平均の F_{up} が必要となる場合には、深度毎や季節毎に F_{up} を定量する必要があり、さらに年平均の F_{up} の長期変化を定量する場合には、この一連の作業を毎年繰り返す必要がある。作業量や予算は多大になる一方で、信頼に足るデータを出すのは容易では無かった。

そこで本研究グループは、 NO_3^- の天然同位体組成である三酸素同位体組成 ($\Delta^{17}\text{O}$) に着目した。 $\Delta^{17}\text{O}$ 値は、 $\text{NO}_3^-_{re}$ と $\text{NO}_3^-_{atm}$ の間で値が大きく異なる上に、同化反応や脱窒反応を受けても変化しない。したがって NO_3^- の $\Delta^{17}\text{O}$ 値分布を実測するだけで、対象とする湖沼 (or 海域) 全体の NO_3^- に含まれる $\text{NO}_3^-_{re}$ と $\text{NO}_3^-_{atm}$ の混合比の定量化が実現し、これと対象とする湖沼 (or 海域) 全体に大気から供給される $\text{NO}_3^-_{atm}$ の沈着速度を組み合わせることで、対象とする湖沼 (or 海域) 全体の F_{up} が定量出来ることを、摩周湖における観測を例に実証した (Tsunogai et al., Biogeosciences, 8, 687-702, 2011)。さらに時期を変えて複数回観測を行うことで、観測インターバル間の F_{up} の時間変化を求めることが出来ることも明らかにした。

この新手法の汎用性と信頼性を検証するため、本研究グループでは、北海道の支笏湖と倶多楽湖において、従来法である ^{15}N トレーサー法との直接比較による検証実験を行った。本講演では、その結果について報告する。

キーワード: 硝酸, 大気沈着, 同化, 硝化, 窒素循環, 三酸素同位体

Keywords: nitrate, atmospheric deposition, assimilation, nitrification, nitrogen cycle, triple oxygen isotopes

超高感度希ガス質量分析技術の応用による希ガス・ハロゲン多元素同時分析が紐解くマントル内の水の起源

Ultrahigh-sensitive simultaneous determination of halogens and noble gases reveals the origin of water in the mantle

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Noble gas isotope ratios in various geochemical components in the Earth are significantly different, making them useful tracers to constrain origin of volatiles in the mantle. The development of noble gas mass spectrometry during the last decade has enabled us to detect less than 10000 noble gas atoms (e.g., [1]). Noble gases are generally concentrated in fluid/melt inclusions in mantle-derived minerals resulting from their high incompatibility and volatility. Noble gases in the inclusions can be extracted distinctively from mineral-hosted component by use of in vacuo crushing or laser microprobe. The great advantages of the latter are that it makes it possible to analyze an individual inclusion or small clusters of inclusions having the same origin and that it can be applied for the inclusion samples on which preceding non-destructive analyses, such as microthermometry and micro spectroscopy have been performed. Although this method remains quite challenging due to extremely low noble gas concentrations in a fluid inclusion, we have successfully applied the laser-microprobe to noble gas analysis of melt/mineral inclusions in olivine phenocrysts in kimberlites.

An extension of Ar-Ar and I-Xe dating methods enables us to simultaneously determine trace amounts of noble gases, halogens, K, Ca, Ba and U by use of ultrahigh-sensitive noble gas mass spectrometry on neutron-irradiated samples. This method has several advantages: (i) detection limits for halogens are two or three orders of magnitude lower than those of other conventional analytical methods, and (ii) several components of different origin can be distinguished based on their relationships with specific noble gas isotopes such as mantle-derived ³He and by using various noble gas extraction methods.

By using this method, we analyzed halogens and noble gases in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan in which relicts of slab-derived water are contained as hydrous mineral/fluid inclusions trapped at a depth ranging from 40 to 100 km [2, 3]. The striking similarities of the observed noble gas and halogen compositions with marine pore fluids challenge a popular concept, in which the water flux into the mantle wedge is only by hydrous minerals in altered oceanic crust and sediment (e.g., [4]). This is the first evidence of subduction of porefluid-derived water into the mantle wedge.

On the other hand, MORB-like ³He/⁴He and halogen ratios of olivines in lavas from the northern Izu-Ogasawara arc and a peridotite from the Horoman alpine-type peridotite complex in northern Japan indicate insignificant contribution to the mantle wedge of radiogenic ⁴He and porefluid-like halogens both observed in the subduction fluids in the Sanbagawa samples. This implies a relatively small amount of the pore water subduction fluids would be released from the Izu slab at a sub-arc depth resulting in further subduction to great depths in the mantle, resulting in the seawater-like heavy noble gas composition of the convecting mantle [5].

These results demonstrate that simultaneous determination of noble gases and halogens in mantle-derived rocks yields important information about the origin of slab-derived water-rich fluids and recycling of halogens and noble gases in the mantle.

[1] Sumino et al. (2001) J. Mass Spectrom. Soc. Jpn. 49, 61-68. [2] Sumino et al. (2010) Earth Planet. Sci. Lett. 294, 163-172. [3] Sumino et al. (2011) Mineral. Mag. 75, 1963. [4] Schmidt & Poli (1998) Earth Planet. Sci. Lett. 163, 361-379. [5] Holland & Ballentine (2006) Nature 441, 186-191.

キーワード: 希ガス, ハロゲン, 質量分析, マントル, 水, 沈み込み

Keywords: noble gas, halogen, mass spectrometry, mantle, water, subduction

高速デジタイザを用いた飛行時間型質量分析のイオンカウンティング法 Development of pulse counting system for TOF-MS with high-speed digitizer

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二次イオン質量分析法 (SIMS) は高い空間分解能と多元素を高感度に定量することが出来るため微小領域の同位体分析において重用されている。また、飛行時間型質量分析法 (TOF-MS) は、幅広い質量範囲のマスペクトルを1回のスペクトル取得イベントで取得でき、飛行距離を伸ばすだけで質量分解能を上げることができる。我々は高感度・高空間分解能・高質量分解能を目指し、一次イオンビームにより生成した二次中性粒子をフェムト秒レーザーによりポストイオン化する質量分析装置 (Laser Ionization MAss nanoScope: LIMAS, [1]) を開発している。LIMAS に用いられた質量分析計は MULTUM-II [2] と呼ばれる多重周回型質量分析計であり、質量分解能 10 万以上の性能を誇る。セクター型質量分析装置のような連続イオン化・イオン検出の方式と対照的に、TOF-MS は検出するイオンが m/z に従って1つのバケットとして検出器に到達する。つまりイオン検出の時間スケールが短く (ナノ秒程度)、マスペクトルを得るためには帯域が GHz 程度の高速オシロスコープが必要となる。また、TOF-SIMS は1回の一次イオンによるスパッタ (イオンのパルス幅 300 ns) で放出される二次イオンは連続ビームで放出される量の 1 万分の 1 程度であり、取得できる信号強度はこれに伴い微弱になる。微弱なアナログ入力信号をそのままデジタル値として取り込むと、信号以外のノイズも同時に集録してしまい、結果 S/N 比の低いデータとなる。微小な信号を定量的に扱うためには入射イオンに対してパルスカウント法を用いて検出するのが一般的である。

LIMAS のイオン検出システムは以下の構成となっている。イオンの入力信号を増幅する 2 段の MCP とプリアンプによって入射イオンの電気信号を増幅する。MCP にイオンが 1 個入射された時にアンプから出力されるパルスの半値幅は 3 ns で、高さは -58 mV 程度である。一方で、ノイズレベルの平均値は約 -6 mV でその変動は ± 7 mV (3%) なのでパルス出力とノイズを区別することができる。この出力信号は 1 秒間で最大 12.5 G サンプル集録可能な高速デジタイザ NI PXIe-5185 (以下 5185) を用いて集録している。集録は 2 枚の測定レンジが異なる 5185 を使い、分配器で出力信号を 2 つに分岐し、一枚はアナログ出力を収録、もう一枚でパルスカウントを行う。装置の各部位のタイミングはディレイジェネレータ (BNC model-575) を用いて管理している。

5185 に収録された波形データは各点が 8bit で表記された要素を持ち、1 kHz の基準トリガから指定した時間 (数マイクロ秒) 収録した配列である。取得した配列は 1/0 の配列にリアルタイムで解析される。解析のアルゴリズムは単純で、ある任意の連続した 3 点の中央値がその他の 2 点よりも低く、しかもその値が指定した閾値よりも小さい時にはその中央値の指標の値は 1、それ以外は 0 となる。このパルスカウント法の時間分解能はデジタイザのサンプリングレート (現在は 3 GS/s) と MCP の応答速度 (0.5 ns) に依存しており、現在の時間分解能は 2 ns 程度である。すなわち、この検出システムで検出できるイオンの量は、一定の繰返し周期のイオン入射の場合、1 から 5×10^8 cps であるが、統計的な入射周期ゆらぎのため数え落しが小さいのは 5×10^7 cps 程度までである。この最大カウント率は、TOF-MS のスペクトルデータの 1 マスピークあたりのカウントに換算する一回のスパッタ当たり 1.7 イオンである。そのため、それ以上の強度の質量信号は分配器で分岐したアナログ出力をもう一つの 5185 でデジタイズして測定している。

[1] 圀本ら (2011) 応用物理, 80, 979. [2] Okumura et al. (2005) Eur. J. Mass Spectrom., 11, 261.

キーワード: NI PXIe-5185, 高速デジタイザ, パルスカウント法, 飛行時間型質量分析法

Keywords: NI PXIe-5185, High-speed digitizer, Pulse counting, TOF-MS