Method Development and Evaluation of the infiTOF Time-of-Flight Mass Spectrometer for On-site Helium Isotopes Analysis

*Kirk Richard Jensen[1], Hirochika Sumino[2], Toshinobu Hondo[1,3], Michisato Toyoda[1]

1. Project Research Center for Fundamental Sciences, Graduate School of Science, Osaka University, Osaka, Japan, 2. Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Tokyo, Japan, 3. MS-Cheminformatics, LLC, Inabe-gun, Mie, Japan

Active volcanoes can cause devastating destruction, and as such, it would be desirable to be able to predict these disasters before their occurrence. One possibility involves measuring helium, which has two stable isotopes, ^{3}He and ^{4}He. The ratio of these two isotopes in geochemical reservoirs such as the atmosphere, ocean, crust, and mantle are different depending on the balance of primordial (relatively enriched in ^{3}He compared to the atmosphere) and radiogenic (predominantly ^{4}He) helium. The ^{3}He/^{4}He ratios of hot springs and groundwater around a volcano have values between magmatic (up to 1.1×10^{-5} or more) and crustal (less than 1×10^{-7}) helium isotope ratios, the latter resulting from dissolution of radiogenic helium into groundwater from crustal rocks. When magma becomes active, the ^{3}He/^{4}He ratios of nearby hot springs/groundwater may increase as the relative contribution of magmatic helium is expected to be higher. Such ^{3}He/^{4}He increases preceding volcanic eruptions have been reported for El Hierro Island, Canary (Padrón *et al.*, Geology, 41, 2013) and Ontake, Japan (Sano *et al.*, Scientific Reports, 5, 2014). The ^{3}He/^{4}He ratio of hot springs/groundwater around a volcano has great potential for monitoring magmatic activity. Currently, magnetic-sector mass spectrometry (MS) is used to measure ^{3}He/^{4}He, however, adequate mass resolution to discriminate ^{3}He from HD and a high-vacuum line to purify and separate helium from other gaseous species are required to measure ^{3}He/^{4}He ratios because helium concentration is generally quite low (1-100 ppmv in gas samples or 1-100 ppt in water samples). Moreover, ^{3}He accounts for only 0.1-10 ppm of total helium. For these reasons, helium isotope analysis is limited to a suitable laboratory, and on-site, real-time monitoring of ^{3}He/^{4}He around a volcano is almost impossible.

The "infiTOF" is a small, portable, time-of-flight (TOF) mass spectrometer capable of high mass resolution and high mass accuracy. The applicability of infiTOF for helium isotope monitoring was investigated by using software-based ion counting and a high-speed digitizer (commonly used in modern TOF instruments instead of a traditional time-digital-converter (TDC)), to measure extremely low-level signals. This configuration is advantageous compared to a TDC-based system because the averaged profile waveform can be used to monitor the overall spectrum, including high concentration ions. The concentration ratio of ^{3}He compared to ^{4}He in the expected sample is in the range of 10^{-6} to 10^{-8}, and because of this large difference, they can not be monitored together without saturating the detector. Therefore, ^{4}He^{2+} was measured as a quantitative reference for ^{4}He$^+$. The ^{3}He$^+$/^{4}He^{2+} ratio of a sample was measured using the infiTOF MS by counting ion peaks from each TOF trigger waveform. A ^{3}He standard was measured to verify the ^{3}He peak and measure mass accuracy, which was observed with an error of 4.30×10^{-5} Da. The ^{3}He$^+$/^{4}He^{2+} ratio was measured for three different helium gas cylinders by infiTOF. Mass accuracy for ^{4}He^{2+} and ^{3}He$^+$ was also determined for sample cylinders with errors of 3.00×10^{-8} Da and 2.25×10^{-4} Da respectively. All cylinders were also measured by magnetic sector MS at University of Tokyo using standard helium gas HESJ (Helium standard of Japan, Matsuda *et al.*, Geochem. J., 36, 2002). Using one cylinder as a secondary standard, the ^{3}He$^+$/^{4}He^{2+} ratios for the other cylinders were determined using infiTOF measurements, which were then compared to the magnetic sector MS measurements and found to be in agreement with less than 5% error. Mass drift was also investigated and found to be less than 50×10^{-6} Da over ten hours. Results indicate that this method is accurate, stable, and has enough

resolving power to differentiate helium isotopes, and may be a viable tool in future on-site analysis and prediction of volcanic activity.

Keywords: Helium Isotope, On-site Analysis, Volcanic Activity, Mass Spectrometry, Ion Counting, Time-of-Flight
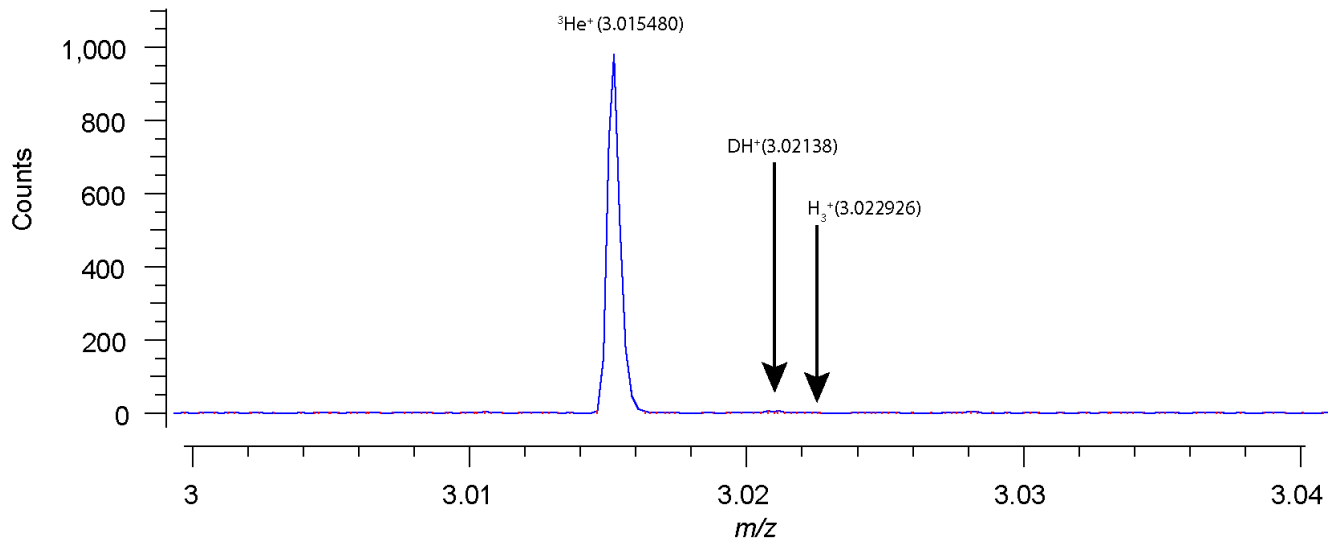
Oxide Production Mechanism in LA-ICPMS Revealed by Comprehensive Analysis of REE-Th-U Phosphates

*板野 敬太[1]、飯塚 毅[1]
*Keita Itano[1], Tsuyoshi Iizuka[1]

1. 東京大学大学院地球惑星科学専攻
1. Earth and Planetary Science, The University of Tokyo

Oxide production in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can cause spectral interferences precluding accurate determination of trace element abundances and isotopic ratios in geological samples. Previous studies revealed that the oxide production depends on many analytical parameters such as sample gas flow rate, plasma power and cone geometry. However, the understanding of what processes control the oxide production within ICP-MS is not enough. We investigated the mechanism of oxide production within ICP-MS by comprehensive analysis of synthetic and natural phosphates. Oxide production rates (MO^+/M^+) of 16 rare earth elements (REE), Th and U were determined at various sample gas flow rates. The response of MO^+/M^+ to gas flow change was quite different among the REE, depending on the oxide bond energy. The MO^+/M^+ of elements with low oxide bond energies were nearly constant over the range of studied sample gas flow rates, whereas those with high oxide bond energies increased with the gas flow rate from 0.85 to 1.00 L min^{-1}. Furthermore, the latter showed a linear correlation between Log (MO^+/M^+) and oxide bond energy where the slope is steeper at a higher gas flow rate. This linear correlation suggests that an equilibrium reaction between MO^+ and $M^+ + O$ within the plasma controls the observed MO^+/M^+ for strong-oxide forming elements, in which the steeper slope reflects a lower equilibrium temperature. This equilibrium reaction also explains the increase of MO^+ signals with the concomitant decrease of M^+ signals observed for these elements. In contrast, the independence of MO^+/M^+ on the gas flow rate observed for weak-oxide forming elements indicates that reactions within the boundary layer and/or interface region of ICPMS would rather control the MO^+/M^+. We found that the observed relation between Log(MO^+/M^+) and oxide bond energies can be well explained by oxide formation through collision of M^+ and metastable O followed by radiative decay of excited MO^+ to the ground state in the interface region. Our results demonstrate that the relative significance of these two independent oxide production processes change among the elements depending on the oxide bond energy and on analytical conditions controlling the plasma temperature.

キーワード：希土類元素、モナザイト、レーザーアブレーション、誘導結合プラズマ質量分析法
Keywords: rare earth element, monazite, laser ablation, ICP-MS

隕石の年代サイトメトリー解析に向けたマルチイオンカウンティング-ICP質量分析法の開発

Development of multiple ion counting- ICP-mass spectrometry for U-Pb Age cytometry on meteorite samples

*平田 岳史[1]、大林 秀行[1]、槇納 好岐[1]、折橋 裕二[2]
*Takafumi Hirata[1], Hideyuki Obayashi[1], Yoshiki Makino[1], Yuji Orihashi[2]

1. 東京大学大学院理学系研究科地殻化学実験施設、2. 東京大学地震研究所
1. Geochemical Research Center, The University of Tokyo, 2. Earthquake Research Institute, The University of Tokyo

Age distribution (age cytometry) is one of the most principal and versatile information to understand the geological events through the Earth's evolutional history. To take full advantage of the age cytometry, both the high analytical throughput and the better precision in the age determination is severely desired. Combination of laser ablation sampling technique and the high-sensitivity ICP-mass spectrometer (LA-ICPMS) enables us to measure precise U-Pb ages directly from the small area in the solid samples. Recently, we have developed an MC-ICPMS system equipped with multiple-ion counting using three Daly detectors (Obayashi et al., 2017). With the multiple-ion counting system, the analysis time for the U-Pb age determination could be dramatically shortened down to 1 - 5 sec, which was almost 1/4 - 1/10 levels over the conventional U-Pb age determinations using the single collector ICPMS instruments. This suggests that both the higher analytical throughput and the better precision in the Pb/U ratio measurements could be achieved. Moreover, with the Daly detectors, higher long-term gain stability can be obtained, obviating the risk of systematical error in the measured U-Pb isotope ratios. After the correction for the counting loss due to dead time, the Daly detector is capable to accept the signal intensities as high as 10^7 cps. This indicates that the overlap of the analysis range, between the Daly detector (10^0 –10^7 cps) and the Faraday detector (10^4 –10^{10} cps), would be at least two orders of magnitude, suggestive of easier cross calibration of the collector gain between the detectors. With the multiple ion counting using three Daly detectors, better precision and smaller contribution of the time-dependent changes in the gain and background counts could be achieved. We will discus the wide versatility of the present technique for the geochronology on the solar system evolution.

キーワード：年代サイトメトリー、マルチイオンカウンティング、レーザーアブレーション、ウラン―鉛年代測定法、デイリー検出器
Keywords: Age Cytometry, Multiple Ion Counting, Laser Ablation, U-Pb Dating, Daly Detector

地球内部・表層環境における硫黄同位体比変動の研究に向けた局所硫黄2同位体比分析手法開発

Development of in situ sulfur 2-isotope analysis technique for studies on sulfur isotope systematics of Earth's deep interior and surface environment

*牛久保 孝行[1]、清水 健二[1]
*Takayuki Ushikubo[1], Kenji Shimizu[1]

1. 海洋研究開発機構　高知コア研究所
1. Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology

Secondary Ion Mass Spectrometry with a multiple collector system (MC-SIMS) has capability to perform accurate in situ stable isotope analyses with sub-permil precision and analysis spot size of ˜10 μm in diameter [1]. In situ analysis technique with spatial resolution of micrometer range is useful to study multiple processes recorded within complex texture and to show primary signatures from metamorphosed samples. Sulfur isotope systematics of sediments and sedimentary/igneous rocks provides constraints on the biological activity, the evolution of Earth's atmosphere, and behaviors of volatile elements in the Earth's interior. Here, we present results of development of sulfur 2-isotope analyses ($^{34}S/^{32}S$) of pyrite, basaltic glass, and barite with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC. For all sulfur isotope test analyses, we used (1) a Cs^+ ion beam with a total impact energy of 20 kV, (2) a normal-incident electron gun for charge compensation, (3) the mass resolving power (MRP, M/DM) of ˜2200 for $^{32}S^-$ and ˜5000 for $^{34}S^-$, respectively, and (4) a secondary-ion accelerating voltage of 10 kV. Sulfur 2-isotope analyses of pyrite were performed with a 1 nA and 10 μm in diameter Cs^+ ion beam. The secondary ions ($^{32}S^-$ and $^{34}S^-$) were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate of $^{32}S^-$ was 1×10^9 cps. The UWPy-1 pyrite standard ($\delta^{34}S=16.04\pm0.18$‰)[2] was measured for test analyses. The reproducibility of spot-to-spot analyses was ±0.25‰ (2 SD, n=10). Based on the results of test analyses and the $^{32}S^-$ ion yield, we expect that the reproducibility of sulfur isotope analysis with a 50 pA and ˜3 μm in diameter primary beam will be better than ±1‰ (cf. [3]). We consider that in situ sulfur isotope analyses with larger (˜10 μm) and smaller (˜3 μm) primary beam conditions are suitable to measure $\delta^{34}S$ values of sedimentary pyrites and pyrite grains entrapped in igneous minerals. Sulfur 2-isotope analyses of basaltic glasses, EPR-G3 ([S]=1269 ppm) and FJ-G2 ([S]=1372 ppm) [4], were performed with a 1.5 nA and 10 μm in diameter Cs^+ ion beam. The secondary ions were detected with a Faraday cup detector for $^{32}S^-$ and an electron multiplier (EM) detector for $^{34}S^-$, simultaneously. A typical count rate of $^{32}S^-$ was 2.7×10^6 cps. Ten fragments of each basaltic glass were mounted in the same epoxy mount to examine homogeneity of sulfur isotope ratios. The reproducibility of sulfur 2-isotope measurements was ±0.52‰ (2 SD, n=20) for EPR-G3 and ±0.60‰ (2 SD, n=21) for FJ-G2, respectively, which are close to statistic errors based on intensities of secondary ions. This indicates that the reproducibility of the present analytical condition is ˜0.6‰ and sulfur isotope ratios of both basaltic glasses are homogeneous within analytical uncertainty. We plan (1) to perform sulfur isotope test analyses with higher intensity beam to achieve better analytical uncertainty by MC-SIMS, and (2) to determine sulfur isotope ratios relative to the VCDT value of these basaltic glasses by the fluorination method. We also plan to modify detector slits for sulfur 3-, and 4-isotope analysis with multiple collectors (cf. [2]). For sulfur 2-isotope test analyses of barite, we used a 1 nA and 10 μm in diameter Cs^+ ion beam and the secondary ions were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate

of $^{32}S^-$ was 2×10^8 cps. We could not determine analytical uncertainty because of absence of appropriate standard barite with homogeneous sulfur isotope ratio. Since the typical internal error of each analysis was ~0.2‰ (2σ), we expect to achieve analytical uncertainty of ~±0.3‰ for sulfur 2-isotope analyses of barite with an appropriate barite standard.

References:
[1] Kita N. T. et al. (2009) Chem. Geol. 264, 43-57.
[2] Ushikubo T. et al. (2014) Chem. Geol. 383, 86-99.
[3] Williford K. H. et al. (2011) GCA 75, 5686-5705.
[4] Shimizu K. et al. (2017) Geochem. J. (in press).

キーワード：硫黄同位体、二次イオン質量分析計、黄鉄鉱、メルト包有物
Keywords: Sulfur isotope, SIMS, pyrite, melt inclusion

磁場勾配による並進運動を用いた全固体粒子の分離と非破壊同定
Separation and non-destructive identification of diamagnetic paramagnetic particles using translational motion caused by magnetic field gradient in microgravity

*久好 圭治[1,2]、植田 千秋[1]、寺田 健太郎[1]
*Keiji Hisayoshi[1,2], Chiaki Uyeda[1], Kentaro Terada[1]

1. 大阪大学大学院理学研究科宇宙地球科学専攻、2. 大阪府立大手前高等学校
1. Dept. of Earth and Space Science, School of Science, Osaka University, 2. Otemae Senior High School of Osaka Prefecture

　一般に、微小重力空間に開放された固体粒子は，磁気的ポテンシャルによる並進運動を引き起こすが．その速度は粒子の質量に依存せず、物質固有の磁化率のみに依存する。このため得られた磁化率を文献値と対応することで、単一粒子で物質同定ができる[1][2]．これまでに私たちはmm～sub-mmサイズの反磁性鉱物について，上記の同定が可能であることを確認した．さらに揮発性固体である氷（H_2O）とドライアイス（CO_2）でも並進運動を観測した．今回，同じ原理により，磁化率の異なる複数の粒子の集団に関して，その分離，回収および同定を実現した[3].

　実験に必要な微小重力は,小型の落下ボックス（30×30×20cm）内に発生させた．落下距離は1.8mで，有効な微小重力継続時間は約0.5秒である．上記ｍｐボックス内に小型の磁気回路(B＜0.8T)，真空チャンバー（＜100Pa），照明器具およびハイスピードカメラを配置した．反磁性鉱物3種と常磁性鉱物2種からなる粒子の集団を，磁場勾配力が最大になる位置にセットし、微小重力空間に解放した．反磁性鉱物は磁場の外へ並進し，常磁性鉱物は磁石中心方向に並進した．これらの粒子は，それぞれの方向にセットした 2枚の回収板の上に，物質ごとに異なる粒子群として回収された(YouTube: Magnetic separation of general solid particles realised by a permanent magnet). また並進速度から，各試料の磁化率が求められ，それぞれ文献値と一致した．これにより分離が，仮定した原理に従って進行したことが確認された[3].

　これまで磁場による粒子の分離・抽出は，自発磁化を有する一部の物質に限られていたが，今回の実験によって，固体全体にこれが拡張できる展望が得られた．有機化学や生化学の分野では，精密分析に先立って有機分子の混合物を分子量ごとに分離する方法が，クロマトグラフィ技術として確立している．無機物質においてもこれと同様の技術が望まれるが，今回の磁気運動を取り入れることで，原理的には全ての固体物質でそれが実現する。地球化学では、異種粒子の混合試料を扱う場合が多いが，その分析の前処理過程として，今回の分離技術が利用できる。さらに無人探査機搭載のためのダスト分析装置にも応用可能である．このような装置は、小型で、しかも測定原理が単純であることが求められるが，磁気分離の原理はそれらの条件を満たしている.

References
[1] K. Hisayoshi, S. Kanou and C. Uyeda : Phys.:Conf. Ser., 156 (2009) 012021.
[2] C. Uyeda, K. Hisayoshi, and S. Kanou : Jpn. Phys. Soc. Jpn. 79 (2010) 064709.
[3] K. Hisayoshi, C. Uyeda and K. Terada : Scientific Reports,(Nature Pub) 6 (2016) 38431

キーワード：磁気分離、非破壊同定、微小重力、磁気並進運動、反磁性物質、常磁性物質
Keywords: magnetic separation, non-destructive identification, microgravity, magnetic translational motion, diamagnetic, paramagnetic
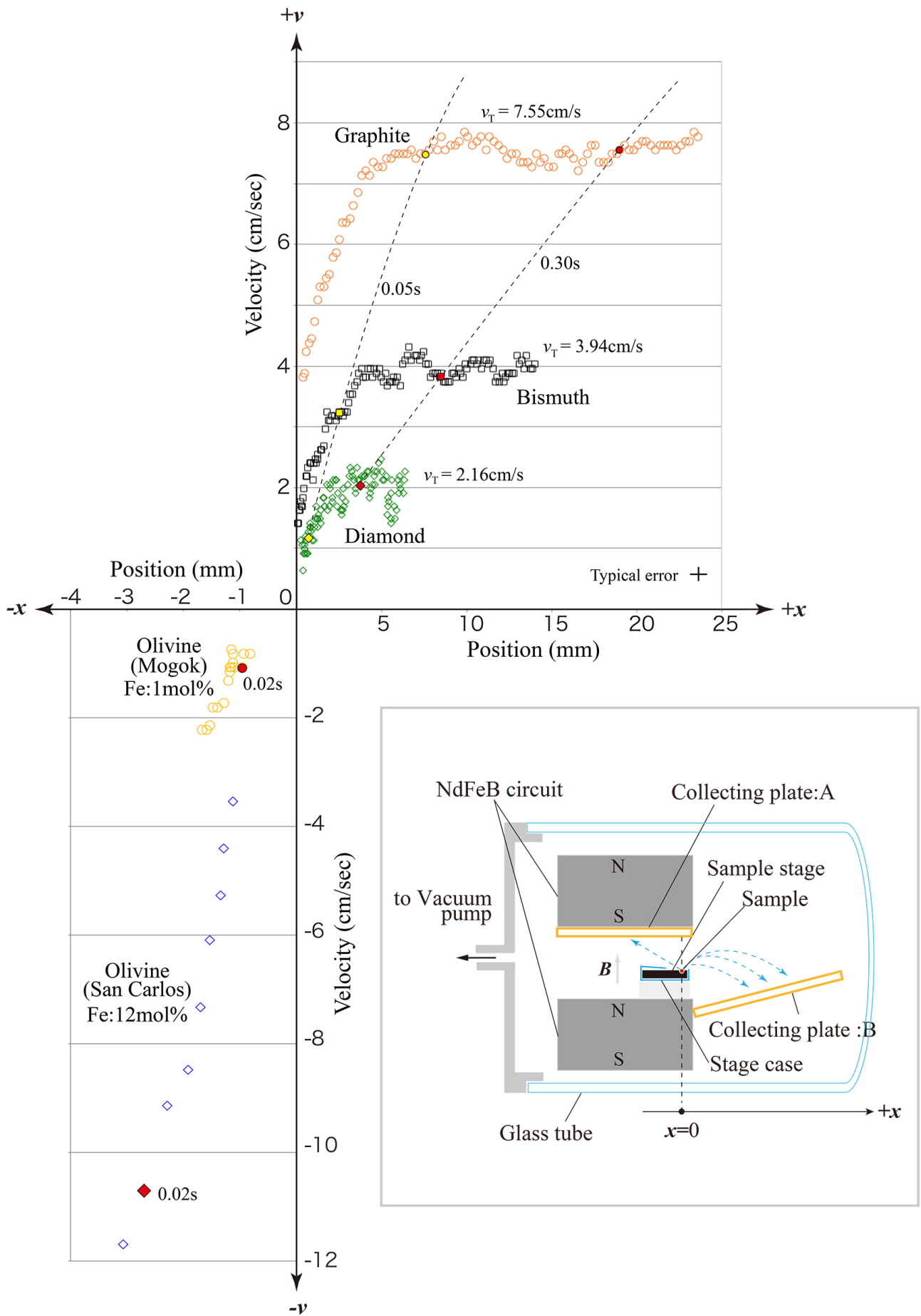
高温高圧下での鉄-ケイ酸塩-水系の中性子回折その場観察と地球進化過程への応用

In situ neutron diffraction of iron hydride under high pressure and temperature in Fe-silicate-water system: Implications for the Earth's evolution

*飯塚 理子[1]、八木 健彦[1]、後藤 弘匡[2]、奥地 拓生[3]、服部 高典[4]、佐野 亜沙美[4]

*Riko Iizuka-Oku[1], Takehiko Yagi[1], Hirotada Gotou[2], Takuo Okuchi[3], Takanori Hattori[4], Asami Sano-Furukawa[4]

1. 東京大学大学院理学系研究科地殻化学実験施設、2. 東京大学物性研究所、3. 岡山大学惑星物質研究所、4. 日本原子力研究開発機構J-PARCセンター
1. Geochemical Research Center, Graduate School of Science, The University of Tokyo, 2. The Institute for Solid State Physics, The University of Tokyo , 3. Institute for Planetary Materials, Okayama University, 4. J-PARC Center, Japan Atomic Energy Agency

　鉄を主成分とする地球中心核には、軽元素（S, Si, O, C, Hなど）が溶け込んでいると考えられており、どの軽元素がどの程度存在するのかという疑問に対して、これまで数多くの実験的研究がなされてきた。このうち有力候補の1つである水素は、X線回折などの従来の実験手法では検出できないこと、高圧下でしか有意に鉄に溶け込まず脱圧すると試料から抜けてしまうこと、などの実験上の制約から、その高温高圧下での振る舞いや鉄への固溶量についてよく分かっていなかった。そこで本研究では、水素を直接観察できる中性子回折法を用いて鉄-シリケイト-水系の高温高圧下その場観察を行い、含水鉱物が脱水してできる水と固体の鉄とが反応して、鉄水素化物が生成する様子をリアルタイムでとらえることに成功した。

　実験は、茨城県東海村の大強度陽子加速器施設（J-PARC）のパルス中性子源に建設された高温高圧ビームライン（PLANET）において、大型6軸プレス（圧姫）を用いて行った。地球形成初期に集積した物質をモデル化した出発試料（モル比が2:1:1の鉄ロッドとSiO_2と$Mg(OD)_2$(又はMgO) の混合粉末）に対して、高圧下約4 GPaで1000Kまで段階的に加熱を行いながら、高温高圧下での中性子回折測定を行った。

　結果として、水を含まない系では同時間で格子体積がほぼ不変であるのに対し、水を含む系では徐々に格子体積が膨張し飽和していくことが分かった。したがって、水を含む系では鉄が有意に水素を取り込み、鉄水素化物が生成したと考えられる。回収試料のSEM観察では、水を含む系にのみ、鉄ロッドと鉄に富むオリビンとの間にFeOの薄い層が確認され、含水鉱物から吐き出された水が鉄と酸化還元反応を起こしてFeOとFeH_xが生成したことが示された。本研究の結果から、高圧下で1000K程度の比較的低温でも水が存在すれば、固体の鉄にも水素が溶け込むことが明らかになった。このことから、原始地球では始源物質が集積していく初期段階で、水素はすでに鉄へと溶け込み始めていたと考えられる。すなわち、現在の地球核に含まれると考えられる軽元素の中でも、水素が地球進化過程の早期において他の軽元素に先駆けて固体鉄に溶け込んでいき、その後に核ーマントル分離や他の軽元素の溶融鉄への溶解が起きた可能性が高いことが示唆された。地球核の軽元素問題に向けた今後の展望として、これまで種々の実験が行われてきた純鉄とケイ酸塩の系だけではなく、水素化した鉄とケイ酸塩間での軽元素の分配を調べることが重要になると言えるだろう。

　発表では、本研究で開発したアンビルセルを用いた高圧高温中性子その場観察の紹介、および測定データの解析により得られた情報から地球のコアーマントル形成と水素の関わりについて考察する。

キーワード：水素、中性子回折、高温高圧下その場観察、コアーマントル形成
Keywords: Hydrogen, Neutron diffraction, In situ high pressure and high temperature observation, Core-mantle formation

A new statistical method to identify geochemical data structure

*岩森 光[1]、吉田 健太[1]、中村 仁美[1,2,3]、桑谷 立[1]、浜田 盛久[1]、原口 悟[1]、上木 賢太[4]

*Hikaru Iwamori[1], Kenta Yoshida[1], Hitomi Nakamura[1,2,3], Tatsu Kuwatani[1], Morihisa Hamada[1], Satoru Haraguchi[1], Kenta Ueki[4]

1. 海洋研究開発機構・地球内部物質循環研究分野、2. 東京工業大学・地球惑星科学専攻、3. 千葉工業大学・次世代海洋資源研究センター、4. 東京大学・地震研究所
1. Solid Earth Geochemistry, Japan Agency for Marine-Earth Science and Technology, 2. Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 3. Ocean Resources Research Center for Next Generation, Chiba Institute of Technology, 4. Earthquake Research Institute, The University of Tokyo

Identifying the data structure including trends and groups/clusters in geochemical problems is essential to discuss the origin of sources and processes from the observed variability of data. A rapidly increasing number and high dimensionality of recent geochemical data require efficient and accurate methods for capturing the data structure. For example, the two databases of GEOROC and PetDB contain ˜382,000 sets of data in total. Jenner and O'Neil [2012] provided analysis of 60 elements in 616 ocean floor basaltic glasses. The structure including trends and groups of these data cannot be identified by graphical methods (e.g., Harker diagrams and identifying trends/groups based on them). As will be demonstrated, even 2-dimensional data may be misinterpreted by graphical methods.
Here we propose a new multivariate statistical method that combines three conventional but powerful methods to capture the true structure of multivariate data [Iwamori et al., 2017, doi:10.1002/2016gc006663]; they are k-means cluster analysis (KCA), principal component analysis (PCA), and independent component analysis (ICA). The reasons for selecting the three methods are (i) KCA and PCA are probably the most fundamental yet powerful tools for multivariate analyses; (ii) ICA is not as common as PCA but is a unique tool for identifying hidden independent structures; and (iii) the three methods are newly found to be closely related and can be integrated to analyze the data effectively. In this study, we first describe the relationship of these three methods to elucidate the entire data structure based mainly on synthetic data. We apply this to a natural data set of isotopic compositions of basalts for which ICA has been performed. On the basis of the results, an effective combination of the methods is clarified, for which we provide an Excel program "KCA" at both doi:10.1002/2016gc006663 and http://dsap.jamstec.go.jp/ to allow readers to test and apply the program to individual problems.

キーワード：多変量統計解析、クラスタ分析、主成分分析、独立成分分析、地球化学データ
Keywords: multivariate statistical analysis, cluster analysis, principal component analysis, independent component analysis, geochemical data

イオン吸着型鉱床がレアアースの資源となる理由
Cause of Establishment of Ion Adsorption Ore for Rare Earth Resources

*山口 瑛子[1]、本多 翼、高橋 嘉夫[1]

*Yamaguchi Akiko[1], Tasuku Honda, Yoshio Takahashi[1]

1. 東京大学
1. University Of Tokyo

Introduction

Rare earth element (REE) is a set of chemical elements essential for high technology industries. Ion-adsorption deposits of REE are appropriate for industries, since REE in the deposits can be easily extracted without treatment of radioactive elements, uranium and thorium. Ion-adsorption deposits are formed by adsorption of REE on weathered granite. However, it is not clear the relationship between the degree of weathering and potential of the weathered granite as REE ion-adsorption deposit. In this study, abundances and extraction ratios of REE were systematically examined for weathered granite samples with different degrees of weathering, which should be related to the variation of secondary minerals formed in the granite. In addition, the interaction of REE with potential secondary minerals was also studied to clarify the characteristics of ion-adsorption deposit, which is likely unique as a resource of REE.

Methods

Weathered granite samples were collected from Hiroshima, Shimane, and Tottori Prefectures in Japan and also from various climate zones in Sri Lanka. Mineral and major element compositions were examined by X-ray Diffraction (XRD) and X-ray fluorescence (XRF), respectively. CIA, which represents the degree of weathering, is calculated using the results of XRF. To reveal extraction ratio of REE, decomposed solutions of REE were prepared by two methods and their REE were measured by ICP-MS. One was prepared by acid digestion, which gives total REE concentration. The other was obtained by extraction by ammonium chloride solution, which corresponds to extractable concentration. To reveal the relationship between REE and other cations, adsorption experiment was performed, by which K_d was calculated. REE was absorbed to vermiculite and ferrihydrite in three solutions; 0.10 M NaNO3 aq., 1.0 M NaNO3 aq., and 1.0 M NH4Cl aq. To reveal the comparison between REE and other elements, K-edge EXAFS of lanthanum (La), strontium (Sr), barium (Ba), potassium (K), rubidium (Rb), and cesium (Cs) were also performed after their adsorption on the adsorbents to identify their adsorption species.

Results & Discussion

The result of XRF analysis revealed that the ability of adsorption depends on the degree of weathering and can be highest in mildly weathered granite, or in granite of which CIA (Chemical Index of Alteration) is 65~75. Coulpled with the XRD results, it was found that the relationship of REE and clay minerals is very important for Ion-absorption deposit. These results suggest that the potential of ion-adsorption deposit depends on the climate controlling the degree of weathering.

K_d, which is calculated using the results of adsorption experiment, revealed that extraction ratio of REE adsorbed to ferrihydrite is low and extraction ratio of REE adsorbed to clay minerals is high. In the REE pattern of K_d, REE adsorbed to ferrihydrite shows tetrad effect, which shows the formation of REE inner-sphere complex. REE adsorbed to vermiculite, on the other hand, do not show tetrad effect, or REE outer-sphere complex. Thus, when REE form outer-sphere complex, the extraction ratio of REE becomes

high. Furthermore, K_d of REE and Sc are high. This is because they are trivalent and attracted electrostatically to a larger degree, which suggests that high charges of cations are important for ion-adsorption deposit. XAFS spectrum of the adsorbed mineral species similar to that of solution sample shows that the ion adsorbed to the mineral forms outer-sphere complex. The results revealed that the types of surface complex depend on the ionic size. Ions which are smaller than Ba^{2+} form outer-sphere complex, while ions larger than Ba^{2+} form inner-sphere complex. Thus, ions which can form ion-absorption deposit are smaller than Ba^{2+} and have high charges. Among the many hard ions, only REE meet the requirement to form the Ion-adsorption deposit.

キーワード：希土類元素、イオン吸着型鉱床、表面錯体、イオン半径、価数
Keywords: Rare Earth Elements, Ion Adsorption Deposit, Surface complex, Ionic size, Valence

分光学的手法およびバイオマーカー分析による石油根源岩の熟成度の多角的解析

Synthetic maturity evaluation of source rocks based on spectroscopic measurements and biomarker observations

渡邉 真央[1]、*鍵 裕之[1]、荻原 成騎[1]、纐纈 佑衣[3]、奥村 文章[2]、岩野 裕継[2]、早稲田 周[2]
Mao Watanabe[1], *Hiroyuki Kagi[1], Shigenori Ogihara[1], Yui Kouketsu[3], Fumiaki Okumura[2], Hirotsugu Iwano[2], Amane Waseda[2]

1. 東京大学大学院理学系研究科、2. 石油資源開発、3. 名古屋大学環境学研究科
1. Graduate School of Science, University of Tokyo, 2. JAPEX, 3. Graduate School of Environmental Studies, Nagoya University

Kerogens in petroleum source rocks transform to graphite with increasing maturity. Vitrinite reflectance (Ro) has been widely used to evaluate maturity of kerogens. Raman spectroscopy being applied as a geothermometer has a high spatial resolution compared with Ro measurement and is a nondestructive measurement. In this study, a new maturity indicator applicable to the wide range using Raman spectra, fluorescence spectra, biomarkers, etc. were developed.

Kerogens extracted from cuttings samples from two wells (Shin-Ayukawa AK-1 and MITI Yurioki-Chubu) were put into the resin and polished. Ro, Raman and fluorescence spectra were obtained on kerogens samples. There are two dolerite-intrusions in the depth range of 1500–2000 m in the Shin-Ayukawa well. Ro value reached to 3 %, the maximum value, beneath the intrusions. The intensity ratio of D1- and D2-bands to the fluorescence intensity at 1500 cm^{-1} (F), (D1+D2) / F showed the positive correlation with Ro values in the range of Ro = 0.2–3 % including immature kerogens which were difficult to evaluate only by Raman spectra. Kerogens affected by the short-term volcanic heat also showed the same correlation. The intensity of fluorescence spectra from Yurioki-Chubu decreased drastically in the ranges of Ro = 0.2 % to 0.4 %. Infrared absorption bands assignable to amides and ethers disappeared in the same range. These results indicate that the change of fluorescence intensity depends on the structure including oxygen and carbon atoms.

The bitumens extracted with an organic solvent were analyzed using GC-MS. CPI was almost 1 in a whole depth. Chain length of *n*-alkanes decreased by the volcanic heat. This result indicates that chain length of *n*-alkanes can be a maturity indicator for overmatured kerogens which were not investigated yet using biomarkers.

This study proposed a new indicator to evaluate the maturity in the wider range (Ro = 0.2-3 %) than the previous studies by combination of the several methods.

キーワード：炭質物、ケロジェン、石油根源岩、分光法、バイオマーカー
Keywords: carbonaceous materials, kerogens, source rocks, spectroscopy, biomarker
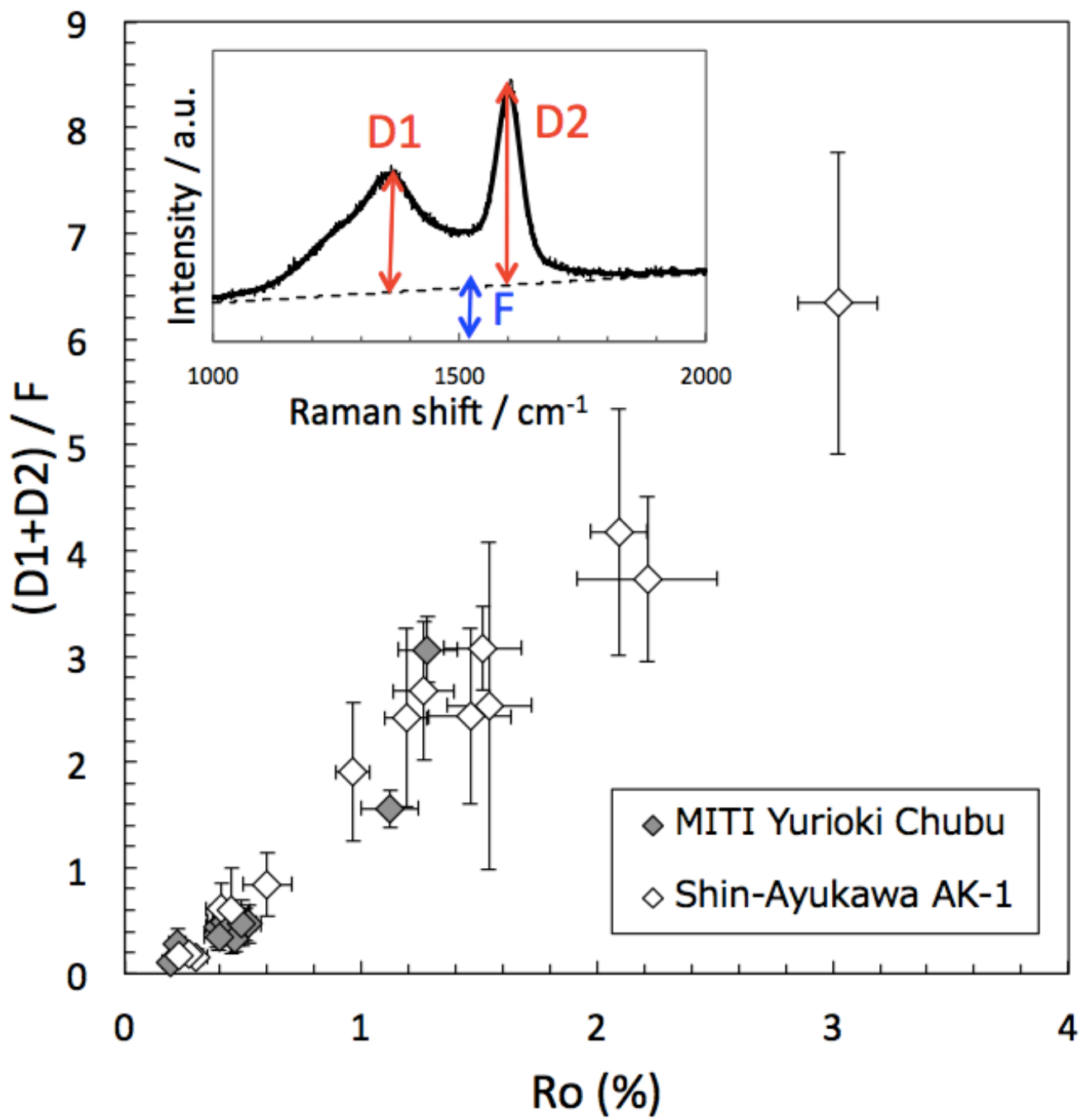
放射性炭素を用いた海洋生態系情報の取得
Acquisition of marine ecosystem information using radiocarbon

*宮入 陽介[1]、横山 祐典[1]
*Yosuke Miyairi[1], Yusuke Yokoyama[1]

1. 東京大学大気海洋研究所
1. Atmosphere and Ocean Research Institute, The University of Tokyo

　放射性炭素（[14]C）分析の応用は多岐にわたるが、その中で一番身近な利用は放射性炭素年代測定である。現在から約五万年前までの期間において、数十年程度の精度で年代測定ができる。その特徴を用いて、地球科学や考古学分野での応用が盛んに行われている。

　また、放射性炭素分析の応用として、今後発展が期待されるのが、海洋トレーサーとしての利用である。日本近海では、熱塩循環により、いわゆる古い海水が供給される親潮と新しい海水である黒潮系の海流が交わっている。一次生産者の[14]C濃度は海水のそれを反映しているため、[14]Cはそれらを捕食する魚類等の回遊履歴のユニークなトレーサーになることが期待される。しかしながら、[14]Cの分析は大がかりな加速器質量分析装置を利用する必要があるため、高額な測定コスト等も障害となり応用されてこなった。

　東京大学大気海洋研究所高解像度環境解析センターの加速器質量分析計（YSAMS）は、2010年度から導入計画を始め、2013年春に装置導入、2013年夏より定常測定を開始した。その後の現在までの3年間におよそ9000試料程度（標準試料及びテスト試料含む）の測定をこなしてきた。本装置は国内で初導入となるシングルステージ加速器質量分析計であり、同装置の特徴としては、 加速器質量分析計としては小型であること、加速電圧が250kvと低いため、絶縁ガス中に設置する必要がないなどの、従来機に比べた優位性があり、メンテナンス性も従来の大型の加速器質量分析計に比べて向上している。装置の設計測定精度も[14]C/[12]C比測定0.3%以下、[13]C/[12]C比測定0.3%以下と非常に高い。測定限界も[14]C/[12]C≦2.5×10^{-15}と従来機に比べ2倍程度高いものの十分な性能を有している。

　高精度測定、容易なメンテナンス性は、分析に試料数を必要するためにいままで十分に活用されてこなかった[14]Cの生態系解析等の分野への応用展開を切り開くものである。 本発表では同分析装置を用いた海洋生物の移動履歴の解明の研究例を紹介する。

キーワード：放射性炭素、海洋生態系、加速器質量分析
Keywords: radiocarbon, Marine ecosystem, Accelerator Mass Spectrometry

サンゴ骨格を用いた高時間分解能放射性炭素濃度測定による西太平洋海洋環境復元

Pacific Ocean current variations recorded as high-resolution bomb radiocarbon in the western Pacific corals

*平林 頌子[1,2]、横山 祐典[1,2]、鈴木 淳[3]、宮入 陽介[2]、阿瀬 貴博[2]
*Shoko Hirabayashi[1,2], Yusuke Yokoyama[1,2], Atsushi Suzuki[3], Yosuke Miyairi[2], Takahiro AZE[2]

1. 東京大学大学院理学系研究科、2. 東京大学大気海洋研究所、3. 産業技術総合研究所
1. Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 2. Atmosphere and Ocean Research Institute, The University of Tokyo, 3. Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST)

High-resolution measurements of radiocarbon (^{14}C) in corals can be used to reconstruct past variability in ocean conditions. However, the conventional ^{14}C measurement requires more than 10 mg of carbonate samples even for Accelerator Mass Spectrometry (AMS), which prevent us to establish a history of high-resolution seawater properties.

We established a new ^{14}C analytical method, which requires smaller amount of carbonates using AMS at the Atmosphere and Ocean Research Institute, The University of Tokyo. Using our new method, we report seasonal Δ^{14}C changes in coral from Ishigaki Island and compare with previously reported data from Palau and Guam. Our data clearly indicate a significant increase in Δ^{14}C from 1947 to 1998 related to atmospheric nuclear bomb testing. Additionally, the existence of three early Δ^{14}C spikes of nuclear bomb tests in 1950s was confirmed in the North Pacific western boundary current area. After 1976, variability in the Mindanao Dome region related to North Equatorial Current bifurcation latitude migration affected the Δ^{14}C difference between Palau and Guam, whereas difference between Ishigaki and Guam was not correlated with the bifurcation latitude. The Δ^{14}C difference between Ishigaki and Guam may be owing to mesoscale eddies in the Kuroshio area. On decadal scale, evidence suggests that stronger transport by the Kuroshio around the Luzon Strait resulted in less upwelling, which may be represented by a smaller Δ^{14}C difference between Ishigaki and Guam after 1976.

キーワード：放射性炭素、サンゴ骨格、西太平洋、北太平洋西岸境界流
Keywords: Radiocarbon, Corals, Western Pacific, north Pacific western boundary current

Geochemical implications of provenance and chemical weathering in the major river sediments of Myanmar and Thailand

*Hossain Zakir H. M.[1]、川幡 穂高[2]、Roser Barry[3]、三瓶 良和[3]、眞中 卓也[2]、大谷 壮矢[2]
*H. M. Zakir Hossain[1], Hodaka Kawahata[2], Barry P. Roser[3], Yoshikazu Sampei[3], Takuya Manaka[2], Souya Otani[2]

1. Jessore University of Science and Technology、2. 東京大学、3. 島根大学
1. Jessore University of Science and Technology, 2. The University of Tokyo, 3. Shimane University

The major rivers in Myanmar (Ayeyarwady and Sittaung rivers) and Thailand (Mekong and Chao Phraya rivers, and their tributaries) originating from the Himalaya-Tibetan orogenic belts, discharging into the Andaman Sea and South China Sea, respectively. The bulk major and trace element compositions, TOC (total organic carbon) and TN (total nitrogen) contents, and TOC/TN ratios of sediments have been used to constrain the provenance, chemical weathering intensities, and sources of organic matter. The UCC (Upper Continental Crust) normalized major and trace elements of the rivers sediments display a significant depletion of Na_2O, CaO, K_2O, Ba and Sr indicate destruction of feldspar during chemical weathering in the source area or in fluvial transportation. Enrichment of Zr, Th, Ce and Y relative to UCC demonstrate the potential influence of heavy minerals of specific size-grades. The results of different discriminant diagrams suggest that the Mekong and Chao Phraya river sediments are primarily derived from the felsic rocks, whereas the Ayeyarwady and Sittaung sediments are derived from the mixing of dominantly felsic rocks and lower mafic or ultramafic sources. The Th/Sc and Zr/Sc ratios imply that the investigated sediments are largely controlled by felsic rocks with composition close to rhyolite, UCC, I- and S-type granites. The CIA (Chemical Index of Alteration) and PIA (Plagioclase Index of Alteration) data reveals that the Ayeyarwady and Sittaung sediments experienced in low to moderate degrees of chemical weathering, while moderate to intense chemical weathering in the Mekong and Chao Phraya river basins. High TOC and TN contents in the finer sediments and comparatively low in the coarser ones represent a potential result of hydrodynamic sorting. However, TOC/TN ratios indicate that organic matter are derived typically from aquatic macrophyte and higher vascular plant to the river sediments.