

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

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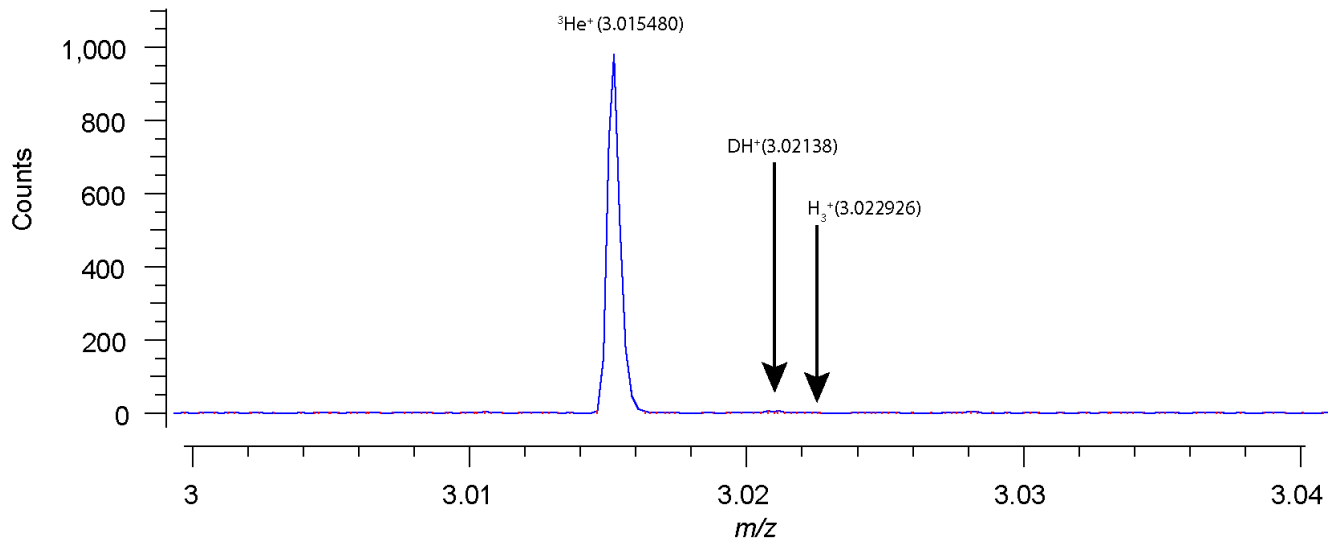
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Active volcanoes can cause devastating destruction, and as such, it would be desirable to be able to predict these disasters before their occurrence. One possibility involves measuring helium, which has two stable isotopes, ³He and ⁴He. The ratio of 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 ³He compared to the atmosphere) and radiogenic (predominantly ⁴He) helium. The ³He/⁴He 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 ³He/⁴He ratios of nearby hot springs/groundwater may increase as the relative contribution of magmatic helium is expected to be higher. Such ³He/⁴He 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 ³He/⁴He 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 ³He/⁴He, however, adequate mass resolution to discriminate ³He from HD and a high-vacuum line to purify and separate helium from other gaseous species are required to measure ³He/⁴He ratios because helium concentration is generally quite low (1-100 ppmv in gas samples or 1-100 ppt in water samples). Moreover, ³He 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 ³He/⁴He 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 ³He compared to ⁴He 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, ⁴He²⁺ was measured as a quantitative reference for ⁴He⁺. The ³He⁺/⁴He²⁺ ratio of a sample was measured using the infiTOF MS by counting ion peaks from each TOF trigger waveform. A ³He standard was measured to verify the ³He peak and measure mass accuracy, which was observed with an error of 4.30×10^{-5} Da. The ³He⁺/⁴He²⁺ ratio was measured for three different helium gas cylinders by infiTOF. Mass accuracy for ⁴He²⁺ and ³He⁺ 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 ³He⁺/⁴He²⁺ 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

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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.

Keywords: rare earth element, monazite, laser ablation, ICP-MS

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

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Age distribution (age cytometry) is one of the most principal and versatile information to understand the geological events through the Earth's evolutionary 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 discuss the wide versatility of the present technique for the geochronology on the solar system evolution.

Keywords: Age Cytometry, Multiple Ion Counting, Laser Ablation, U-Pb Dating, Daly Detector

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

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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 $\sim 10 \mu\text{m}$ 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 ($^{34}\text{S}/^{32}\text{S}$) 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 $^{32}\text{S}^-$ and ~ 5000 for $^{34}\text{S}^-$, respectively, and (4) a secondary-ion accelerating voltage of 10 kV. Sulfur 2-isotope analyses of pyrite were performed with a 1 nA and $10 \mu\text{m}$ in diameter Cs^+ ion beam. The secondary ions ($^{32}\text{S}^-$ and $^{34}\text{S}^-$) were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate of $^{32}\text{S}^-$ was 1×10^9 cps. The UWPY-1 pyrite standard ($\delta^{34}\text{S} = 16.04 \pm 0.18\%$) [2] was measured for test analyses. The reproducibility of spot-to-spot analyses was $\pm 0.25\%$ (2 SD, $n=10$). Based on the results of test analyses and the $^{32}\text{S}^-$ ion yield, we expect that the reproducibility of sulfur isotope analysis with a 50 pA and $\sim 3 \mu\text{m}$ in diameter primary beam will be better than $\pm 1\%$ (cf. [3]). We consider that in situ sulfur isotope analyses with larger ($\sim 10 \mu\text{m}$) and smaller ($\sim 3 \mu\text{m}$) primary beam conditions are suitable to measure $\delta^{34}\text{S}$ 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 $10 \mu\text{m}$ in diameter Cs^+ ion beam. The secondary ions were detected with a Faraday cup detector for $^{32}\text{S}^-$ and an electron multiplier (EM) detector for $^{34}\text{S}^-$, simultaneously. A typical count rate of $^{32}\text{S}^-$ 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 $\pm 0.52\%$ (2 SD, $n=20$) for EPR-G3 and $\pm 0.60\%$ (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 $\sim 0.6\%$ 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 $10 \mu\text{m}$ in diameter Cs^+ ion beam and the secondary ions were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate of $^{32}\text{S}^-$ 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 $\sim 0.2\%$ (2σ), we expect to achieve analytical uncertainty of $\sim \pm 0.3\%$ for sulfur 2-isotope analyses of barite with an appropriate barite standard.

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Keywords: Sulfur isotope, SIMS, pyrite, melt inclusion

Separation and non-destructive identification of diamagnetic paramagnetic particles using translational motion caused by magnetic field gradient in microgravity

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We previously developed a new magnetization measurement method using field-induced translational motion in microgravity space, and proposed a material identification based on this translation [1][2]. Solid particles released in a dilute space cause translational motion in the magnetic field due to its magnetic potential. Since this motion derives from a field-induced body force, its acceleration \mathbf{a} uniquely depends on the magnetic susceptibility assigned to the material; \mathbf{a} is independent of the mass of the particle. Therefore, by comparing the obtained magnetic susceptibility with its published value, it is possible to identify the material of a single particle without destructing it. We have confirmed that the magnetic susceptibility obtained by the translational motion of the sample agree with the published value for various diamagnetic particles having the size of mm ~ sub-mm. Magnetic susceptibility was also obtained from translational motion in volatile solids, namely H₂O and CO₂. Based on the principle, ensemble of diamagnetic particles and paramagnetic particles with different susceptibilities were simultaneously released from a certain position in the magnetic field. As a result, we were able to separate, collect and identify the particles by the variance of particle velocity [3].

Microgravity was generated using a short drop shaft. The length of the shaft is 1.8 m. The effective microgravity duration is about 0.5 seconds. The device for observing the translation was set in a box of 30 × 30 × 20 cm. The device consists of a small NdFeB magnetic circuit (B < 0.8 T), vacuum chamber, lighting, battery and high speed camera. The inner pressure of vacuum chamber was reduced to ~100 Pa to eliminate the effect of air resistance.

An ensemble of heterogeneous particles was set at a position located in an area of monotonically decreasing field. The particles were composed of three diamagnetic materials and two paramagnetic materials were released in the microgravity space at the maximum value in the magnetic field gradient. Diamagnetic materials minerals translated out of the magnetic field, paramagnetic minerals translated in the magnet center direction. Particles were supplemented as different groups on a collection plate coated with two silicon greases set in both directions (YouTube: Magnetic separation of general solid particles realised by a permanent magnet). In addition, the magnetic susceptibility of each sample was found from the velocity of translational motion, which agreed with the published value, respectively [3].

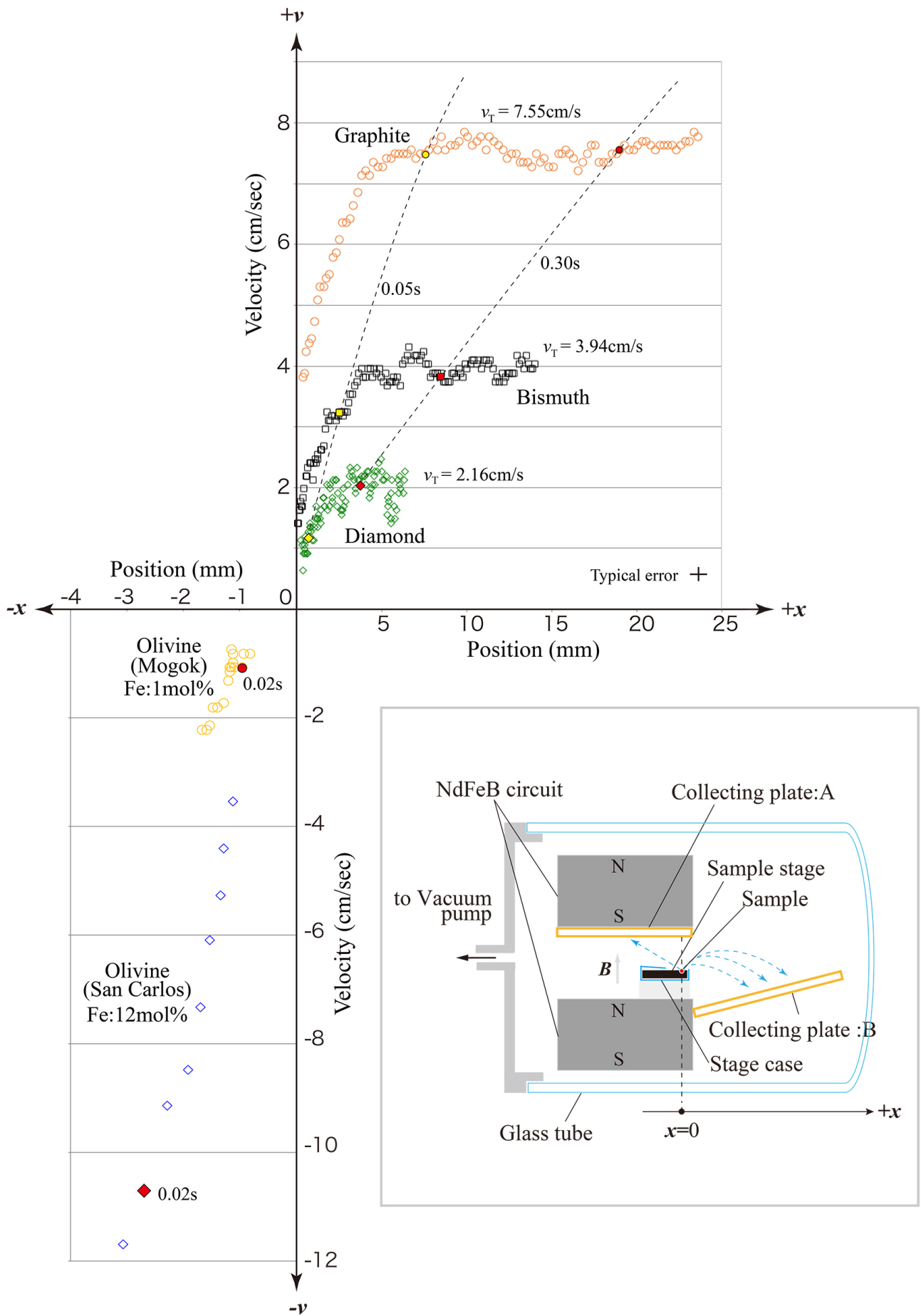
So far, field-induced separation and extraction of solid is recognized in materials that bear spontaneous magnetization. The present results strongly indicate that the separation can be expanded to general solids using a hand magnet. The potential of this method as an analytical technique is comparable to that of chromatography separation because the extraction of new solid phases from a heterogeneous particle ensemble will lead to important discoveries about inorganic materials.

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Keywords: magnetic separation, non-destructive identification, microgravity, magnetic translational motion, diamagnetic, paramagnetic



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

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Hydrogen is the most abundant element in the solar system and considered to be one of the promising candidates of the light element in the Earth's core. However, the amount of hydrogen dissolved in the core and its process are still unknown because hydrogen cannot be detected by X-ray and it easily escapes from iron by the release of pressure. In this study, we have conducted high-pressure and high-temperature *in-situ* neutron diffraction experiments on the iron-hydrous mineral system using high-pressure "PLANET" beamline at J-PARC. We observed that the water which is released from hydrous mineral at about 4 GPa reacts with iron and they form both iron oxide and iron hydride. The obtained iron hydride remained stable after further increase in temperature. This formation of iron hydride occurred below 1000K, at the temperatures where no materials melted. This suggests the possibility that hydrogen had preferentially dissolved into iron before any other light elements have dissolved in the very early stage of Earth's evolution.

Keywords: Hydrogen, Neutron diffraction, In situ high pressure and high temperature observation, Core-mantle formation

A new statistical method to identify geochemical data structure

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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.

Keywords: multivariate statistical analysis, cluster analysis, principal component analysis, independent component analysis, geochemical data

Cause of Establishment of Ion Adsorption Ore for Rare Earth Resources

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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 adsorbed 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. Coupled with the XRD results, it was found that the relationship of REE and clay minerals is very important for ion-adsorption 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-adsorption 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.

Keywords: Rare Earth Elements, Ion Adsorption Deposit, Surface complex, Ionic size, Valence

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

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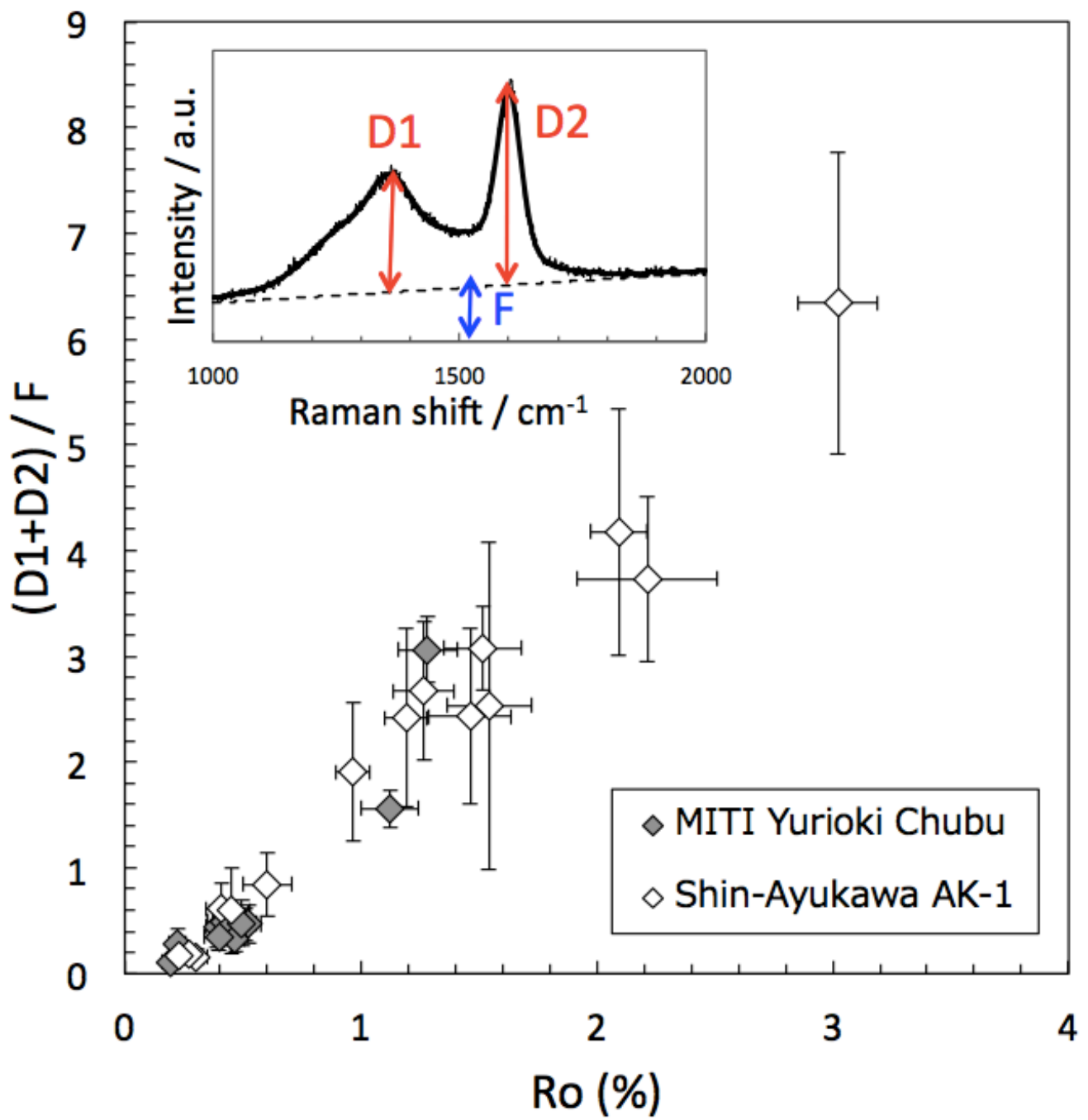
Kerogens in petroleum source rocks transform to graphite with increasing maturity. Vitrinite reflectance (Ro) has been widely used to evaluate maturity of kerogens. Raman spectroscopy being applied as a geothermometer has a high spatial resolution compared with Ro measurement and is a nondestructive 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.

Keywords: carbonaceous materials, kerogens, source rocks, spectroscopy, biomarker



Acquisition of marine ecosystem information using radiocarbon

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Radiocarbon concentration of DIC in sea water changes greatly depending on location. .Therefore, ¹⁴C will be a unique tracer of marine ecosystem.However, as ¹⁴ C measurement is difficult, such applications have not been attempted until now. There was one of the innovations in accelerator mass spectrometry. It is development of single stage AMS.Since insulating gas is not required, single stage AMS is easy to maintain.For the analysis of marine ecosystems, it requires analysis of a lot of samples.Single stage AMS that is easy to maintain is ideal for this application.In this presentation, We will present research on marine ecosystem analysis using Single stage AMS.

Keywords: radiocarbon, Marine ecosystem, Accelerator Mass Spectrometry

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

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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 $\Delta^{14}\text{C}$ changes in coral from Ishigaki Island and compare with previously reported data from Palau and Guam. Our data clearly indicate a significant increase in $\Delta^{14}\text{C}$ from 1947 to 1998 related to atmospheric nuclear bomb testing. Additionally, the existence of three early $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ difference between Palau and Guam, whereas difference between Ishigaki and Guam was not correlated with the bifurcation latitude. The $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ difference between Ishigaki and Guam after 1976.

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

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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.

Keywords: geochemistry, provenance and weathering, organic matter, river sediments, Myanmar, Thailand

Distribution and speciation of copper in seawater of East China Sea and its surrounding areas

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I. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life-supporting systems, and is present in many enzymes and proteins. However, at high concentrations in seawater, Cu^{2+} is known to be toxic to marine microorganism. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of Cu^{2+} and reduce its toxicity. As a result, at the eutrophic surface waters, more than 99% of Cu are complexed with organic ligands. Hence, in this study, we determined the total dissolved Cu concentrations, Cu speciation parameters and Cu^{2+} concentrations at 15 stations in the East China Sea and its surrounding areas.

II. Sampling and Methods

Seawater samples were collected using acid-cleaned, Teflon-coated X-type Niskin samplers mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) onboard R/V Shinsei Maru during KS-15-6 cruise (June-July 2015) and R/V Hakuho Maru during KH-15-3 cruise (October 2015). The samples were collected in low-density polyethylene bottles through a 0.2 μm -pore size filter. Samples for total Cu analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for CLE/CSV analysis, was frozen at -18°C immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV with salicylaldoxime (SA) as the competing ligand (Campos and van den Berg, 1994).

Samples used for total dissolved Cu were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. Frozen samples for Cu speciation analysis were allowed to thaw for 24 hours at 4°C , and then placed at room temperature for 4-8 hours. 10mL of sample, borate buffer, and a known concentration of Cu were added into two sets of 10 Teflon vials, left for at least 2 hours to allow the natural ligands to equilibrate with the added Cu, and the competing ligand, SA, was then added into the solution. The vials were then left to equilibrate overnight before analysis. 5 μM SA and 1 μM SA were used as the competing ligand for each of the two titrations, respectively.

III. Results and Discussion

The highest concentration of total dissolved Cu was found at the surface (10m) of Stn.05, where $[\text{Cu}] = 4.65\text{nM}$ and the lowest concentration was at Stn.13 ($[\text{Cu}] = 0.47\text{ nM}$ at 100m). Surface waters at Stn.03, Stn.04 and Stn.05 have relatively low salinities when compared to those of other stations, and this can be attributed to the freshwater discharge from Yangtze River, which is likely a major source of copper into the East China Sea (Koshikawa et al., 2007; Abe et al., 2003). Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand, L_1 , ranged from 0.63 nM to 6.11 nM, with an average log K value of around 14, whereas for the weaker ligand, L_2 , the concentrations were in the range of 4 nM to 27 nM, with an average log K value of around 12.3. Cu^{2+} concentrations remain constant at all stations ($\sim 10^{-14}\text{ M}$) despite the large fluctuations in total Cu concentrations. The large ligand pool had probably buffered against changes in Cu concentration in seawater.

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Keywords: Copper, Speciation, East China Sea

The Translocation and Remediation of Thallium and Chromium by River System after Pollution

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Heavy metal pollution of water system has been and still is the most serious environmental in most country especially development country. In 2013, the West river and He river system have accidentally polluted by large amount of wastewater containing high amount of thallium and chromium. Right after the accident, we collected and analyzed more than 2000 water samples around the accident site and downstream of the river to access the scope of the pollution. We also collected and analyzed many sediment samples from river bed to evaluate the translocating of those heavy metal. In this report, we first discussed the analytical techniques and sample preparation methods for the analysis. Furthermore, we correlated the determined content of Tl and Cr from those collected water samples with the distance of sample collecting sites from the pollution source site, and discussed the spatial migration. We also correlated the the Tl and Cr content with the collection time of those water samples and discussed the translocation on time base. At last, by comparing the data from water and sediment samples, we further discussed the translocating rate (in both time and quantity scale) of these two pollution metals between different matrix. Those results will provide significant impact and insight on studying spontaneous remediation, and the translocation/absorption of pollution by large river.

Keywords: Thallium and chromium, River pollution, Remediation, Dynamic translocation

Towards high-precision Pb-Pb dating of extra-terrestrial materials by MC-ICPMS

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Knowledge of the timescales of condensation of the first solids from the solar nebula, accretion, differentiation and metamorphism of asteroids is essential to decode the early evolution of our solar system. Considering the possible overall time spans from molecular cloud to planetary systems of ~10 Ma, and much shorter timescales of individual events, a high-precision age determination (error ± 0.1 Ma) is required. The U-Pb system offers such high-precision chronometer because of having two decay chains. In this study, we have evaluated the precision and accuracy of Pb isotope analysis by multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS). The MC-ICPMS has advantages in simple usage and high analytical throughput compared with TIMS which is the conventional method to measure Pb isotope ratio. We applied two independent mass-bias correction methods for Pb isotope ratio measurements of synthetic Pb solution: external-normalization by doping Tl standard and internal-normalization by adding ^{202}Pb - ^{205}Pb double spike. We found that there is no remarkable difference in the analytical accuracy between the two methods. We also found that a precision of 0.01% can be achieved for isotope analysis of ~100 pg of Pb.

Taking another view of high precision and accuracy Pb dating, removal of non-radiogenic Pb is important before isotopic analysis and this can be achieved by acid leaching. For establishing a robust leaching method, it is important to understand what minerals and elements are eluted in multiple leaching steps. This has been investigated by combining SEM imaging of acid-washed samples and chemical analysis of leachates.

Keywords: the early solar system, Pb-Pb dating, ICPMS

High-precision multipoint radiocarbon dating and reconstruction of the eruption history of the Mt. Fuji during the last 8,000 years using sediment cores obtained from the Fuji Five Lakes

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Mt. Fuji is an active volcano, located at the plate boundary of the Philippine Sea plate, the Eurasia plate and the North American plate, with the continuous activity characterized by basaltic magma from about 100,000 years ago. Drilling on land has been conducted repeatedly to reconstruct the eruption history through the stratigraphy of the volcanic product. However, there are only a few studies on lake sediments of the Fuji Five Lakes, especially Lakes Motosu and Sai and the sedimentary environment is less understood. Here we present the sedimentary stratigraphy using X-ray fluorescence core-scanner analysis in Lake Motosu and Sai, combined with the high-resolved radiocarbon dates of bulk sediments (109 samples) and plant fossils (20 samples) using accelerator mass spectrometry to reconstruct the eruption history of Mt. Fuji.

The radiocarbon dates of bulk sediments and plant fossils indicates the continuous sedimentary environment during the last 8000 year. A high-resolved age model was constructed in Lake Motosu and the validity of the age model was evaluated by Kawagodaira Pumice (3149 ± 12 cal yBP ;Tani et al., 2013). The number of scoria layers in cores was more than previous works on land, suggesting that the analysis of lake sediments could detect small eruptions. Moreover, the analysis of organic matter properties (total organic carbon, total nitrogen, total sulfur content and C / N ratio) indicates the change in supply of organic matters from the lake catchment. We concluded that the analysis of the lake sediments near the volcano is useful for clarifying the history of volcanic eruption, as well as paleoclimate change.

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Keywords: Mt. Fuji, Radiocarbon dating, Eruptive history, Age model