

CO5-1 Trace elements, halogen, and Ar-Ar/I-Xe analyses of the Hayabusa2 returned samples

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INTRODUCTION: The spacecraft Hayabusa2 brought back the surface and sub-surface materials from the C-type near-Earth asteroid (162173) Ryugu [1]. The Ryugu samples were allocated to the volatile sub-team, which is one of the Hayabusa2 initial analysis sub-teams [2]. As part of the volatile team's studies, we conducted combination analyses of the neutron-irradiated Ryugu samples to determine the abundances of minor/trace elements by Instrumental Neutron Activation Analysis (INAA), Ar-Ar and I-Xe ages, and the halogen abundances. Prior to the neutron-irradiation, Fourier-Transform Infrared (FT-IR) spectroscopy, Field-Emission Scanning Electron Microscope (FE-SEM) observation, and Secondary Ion Mass Spectrometry (SIMS) analysis were carried out [3]. Measurements of the native volatile compositions such as noble gas and nitrogen isotopes were also carried out using different grains of the Ryugu samples [4, 5]. These analytical results provided important information about the evolution history of the primitive bodies in the early solar system.

EXPERIMENTS: In advance of the Hayabusa2 sample analyses, the rehearsal was conducted in July 2021 using meteorite samples (Allende, Murchison, Bjurböle, and Shallowater) and our standard samples (JB-1, BHVO-2, DTS-2b, MMhb1, orthoclase, and wollastonite). For short-lived nuclide measurements, NaCl and CaCO₃ standards were also prepared. Each of the samples was encapsulated in diamond dishes sealed with polyester tape. The samples in the diamond dishes were first subjected to the Pn3 irradiation for gamma ray measurements of short-lived nuclide measurement (project #: R3038, PI: N.S.). Prior to the Hydro irradiation, the polyester tapes were removed from the diamond dishes. Each of the diamond dishes was wrapped with pure aluminum foil and encapsulated in the Hydro irradiation capsules for long-live nuclide measurement and conversion of halogens and potassium to noble gases (project #: R3127, PI: Y.N.M.).

In June 2021, the Hayabusa2 samples (typically 0.8 mm-sized individual grains) were allocated to the volatile sub-team. Each of them was pressed onto pure Cu disks and pelletized. The pelletized samples were studied by the FT-IR, FE-SEM, and SIMS analyses prior to the INAA and noble gas analyses. After the SIMS analysis, each of the pelletized samples was removed from the Cu disks to collect in the diamond disk containers. Each of

the samples in the diamond container was measured for short-lived nuclides (project #: R3038, PI: N.S.), and then subjected to the Hydro irradiation (project #: R3121, PI: N.I.). As in the rehearsal, the meteorite samples and the standard samples were also analyzed in the same way as the Hayabusa2 samples.

REUSLTS and DISCUSSION: In the rehearsal, short-lived nuclides (²⁴Na, ²⁷Mg, ²⁸Al, ³⁸Cl, ⁴⁹Ca, ⁵¹Ti, ⁵²V and ⁵⁶Mn) were determined for Allende and Murchison samples by gamma-ray measurements. Noble gas isotopes were measured for the mineral standard samples. These results of the rehearsal confirmed the validity of our measurement procedures.

The Hayabusa2 samples were irradiated in the Hydro irradiation term of Oct. 2021. One month later, the irradiated samples were removed from the irradiation capsule, and it was found that the irradiation capsule had been flooded by reactor cooling water during the irradiation. The Al foils that wrapped the sample-containing disks became gray, cloudy and hardened (Fig. 1). The samples were carefully recovered from the disks, and long-lived nuclides (⁴⁶Sc, ⁵¹Cr, ⁵⁸Co, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ⁷⁵Se, ¹⁵²Eu and ¹⁹²Ir) were measured.

After the gamma ray measurements, only small amounts of the samples were transferred to Kyushu Univ., enough to ensure that no radioactivity was detected. The effects of alteration due to the exposure to water are being evaluated based on the noble gas compositions of the standard and meteorite samples.



Fig. 1. Recovered diamond dishes after the Hydro irradiation.

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CO5-2 Track observation in muscovite irradiated by ^{252}Cf and ^{241}Am sources

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INTRODUCTION: Uranium or thorium emit alpha particles and U,Th/He or U/Pb datings is applied to geological samples. When parent atoms emit alpha particles, these parent atoms recoil in accordance with the law of momentum conservation and leave disordered parts in crystal structure. When chemically etched, these disordered parts are selectively dissolved and leave tracks, which are known as alpha recoil tracks (ARTs), on the etched surface of geological samples (Fleischer, 2003). Compared to the fission tracks, which are formed by the travel of ionized particles with more energy than recoiling, ARTs are expected to be small and thus less commonly used in Geology. To establish ART dating, knowledge on their appearance under particular sample treatment and observation equipment is necessary. Here in this study, we tried to create artificial ARTs by ^{252}Cf (Hashimoto et al., 1989) and ^{241}Am sources.

EXPERIMENT: Mica samples with clear cleavage is used as an ART recorder. Uranium and thorium concentrations of the mica are measured by the LA-ICPMS beforehand, and the results was under the detection limit. However, when etched with 48% HF for 2h at 32°C, two types of tracks are observed (Figure 1). One is the size of about 10µm in diameter and deep, the others show variety of size and shallow, almost invisible. Therefore mica sheets were first annealed at 600°C for 5 hours then irradiated under the vacuum by ^{252}Cf and ^{241}Am sources at the Cf facility, KUR.

RESULTS: Because ^{252}Cf sources (200MBq and 1MBq were available) are rather strong and accompany by spontaneous fission, the resultant irradiated mica had so many fission tracks and they made the observation of ART difficult. When the cover of 200MBq ^{252}Cf source was tested as a irradiation source, the strength of activity was fine, but the distribution was heterogeneous, again not suitable for experiment. When ^{241}Am source (around 200kBq) was tested, the number of tracks on the mica surface was increased against time (Figure 2), and indicate that ^{241}Am source is capable of giving artificial ART on crystals. Hereafter, after investigating the registration efficiency on the mica sheet, we will irradiate other minerals to see shape and registration efficiency of ART therein. Then we plan to apply ART dating to un-

known geological samples.

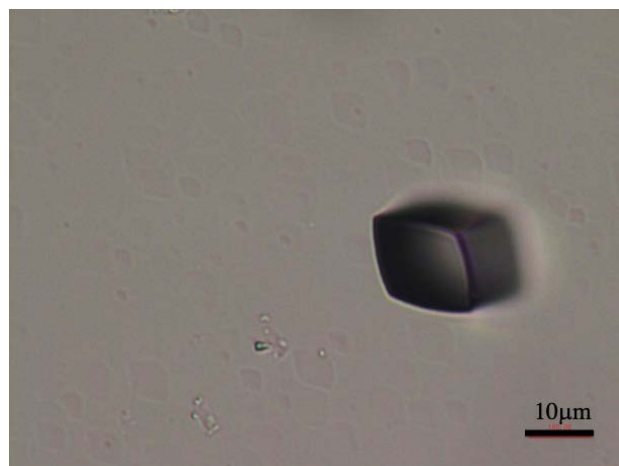


Fig. 1. Microscopy photo of mica after etching without annealing nor artificial irradiation.

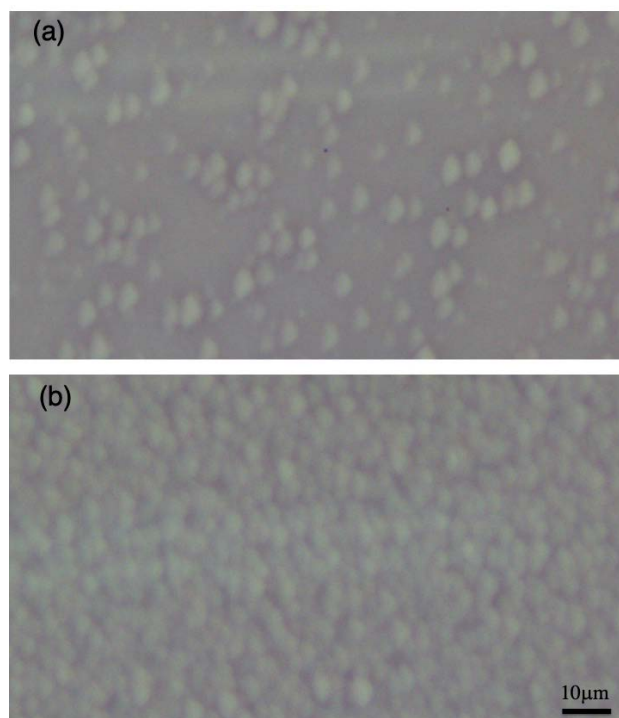


Fig. 2. Phase contrast microscopy photo of mica after annealing, irradiation and etching. (a) after 12h irradiation. (b) after one week irradiation

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CO5-3 Volcanic and Tectonic History of Philippine Sea Plate (South of Japan) Revealed by $^{40}\text{Ar}/^{39}\text{Ar}$ Dating Technique

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INTRODUCTION:

Robust tectonic reconstruction of Philippine Sea Plate evolution for the period immediately before and after subduction initiation at ~52 Ma along the western Pacific margin is prerequisite to understand cause of subduction initiation and test competing hypotheses for subduction initiation such as spontaneous or induced nucleation (e.g., Stern, 2004). Since gravitational instability between the neighboring plates is thought to be a critical factor for subduction initiation (e.g., Leng and Gurnis 2015), it is important to understand the age, origin and crustal structure of the overriding plate.

In this study we have investigated magmatism in the oldest part of the Philippine Sea Plate to 1) reveal for the first time the age and origin of Kita-Daito Basin and the intervening Daito Ridge Group; 2) understand origin of Eocene magmatism widely distributed in and around the Daito Ridge Group. The outcome of these studies will assist in understanding the time sequence of magmatic and tectonic events which took place within a relatively short period around 45-52 Ma, i.e., during and after subduction initiation along the Pacific margin.

EXPERIMENTS: Ages of the igneous rocks were determined using the $^{40}\text{Ar}/^{39}\text{Ar}$ dating facility at the Geological Survey of Japan/AIST. 10-15 mg of phenocryst-free groundmass, crushed and sieved to 250 – 500 μm in size, was analyzed using a stepwise heating procedure. The samples were treated in 6N HCl for 30 minutes at 95°C with stirring to remove any alteration products (clays and carbonates) present in interstitial spaces. After this treatment, samples were examined under a microscope. Sample irradiation was done either at the Kyoto University Reactor (KUR). The neutron irradiation was performed for 10 h at the hydro-irradiation port under 1 MW operation, where thermal and fast neutron fluxes are 1.6×10^{13} and 7.8×10^{12} n/cm² s, respectively, or for 2 h under 5 MW operation, where thermal and fast neutron fluxes are 8.15×10^{13} and 3.93×10^{13} n/cm² s respectively. Argon isotopes were measured in a peak-jumping mode on an IsotopX NGX noble gas mass spectrometer fitted with a Hamamatsu Photonics R4146 secondary electron multiplier.

RESULTS: 9 samples have been dated by the laser-heating $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique. Andesitic rocks from the basin floor of the Kita-Daito Basin show age range between 41.04 and 46.11 Ma. Andesites and basalts from the Northern Philippine Sea Seamounts gave age range between 42.10 and 46.29 Ma. Dioritic samples from the KPR–Daito Ridge intersection were dated on biotite separates by stepwise heating analysis. For the sample 6K1438R11, duplicate analyses gave consistent plateau ages of 48.1 ± 0.4 Ma and 47.66 ± 0.14 Ma. Porphyritic andesite from the southeastern part of the Oki-Daito Ridge returned slightly disturbed age spectrum with increasing ages with increasing laser output (i.e., temperature). 13 steps at higher temperature steps give indistinguishable ages with a weighted average of 109.30 ± 0.20 Ma.

SUMMARY:

1) Eocene andesitic magmatism (Northern Philippine Sea volcanics) has been discovered in and around the Kita-Daito Basin. $^{40}\text{Ar}/^{39}\text{Ar}$ and zircon U-Pb dating results of these igneous rocks indicate that the andesitic rocks formed mainly between 45 and 42 Ma.

2) The results of this study strongly imply that the Kita-Daito Basin postdate subduction initiation of the western margin of the Pacific Plate to form Izu-Bonin-Mariana arc.

3)

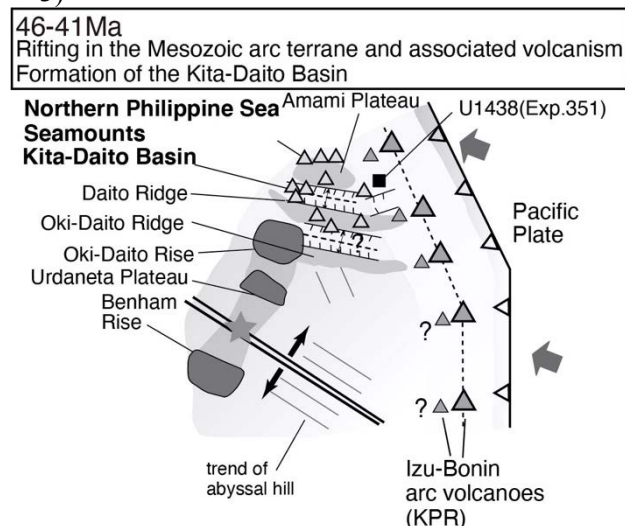


Fig. 1. Schematic tectonic history for the northern part of the Philippine Sea Plate (Ishizuka et al., 2022).

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CO5-4 Determination of Mercury content using INAA

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INTRODUCTION: Mercury is cosmochemically classified as a highly volatile element based on its condensation temperature, meaning that Hg is supposed to have condensed at a relatively low temperature from the hot solar nebular gas in the early solar system [1]. Elemental abundance of Hg can potentially be used as cosmo-thermometers. Geochemically, Hg is classified as a chalcophile element. Mercury provides us information about the mantle-core differentiation including core formation [e.g., 2]. There is a paucity of accurate Hg values in cosmochemical and geochemical samples due to the potential loss of Hg during analysis. It has been known that sample is easily contaminated with Hg in analytical laboratories, which could explain the extremely large variations of observed in meteorite samples [3]. Among the analytical procedure, INAA is suitable for the determination of Hg due to the non-destructive method. In INAA, two isotopes (¹⁹⁷Hg and ²⁰³Hg) were usually used. The 77.4 keV peak of ¹⁹⁷Hg could not be detected by INAA. Although the 279.2 keV peak of ²⁰³Hg could be detected, there is possibility of spectral interferences from Se and Ta. In this study, Hg abundances of environmental samples with having different Hg/Se ratios were determined by INAA, and the accuracy of the obtained values was evaluated.

EXPERIMENTS: JSAC 0601-2 (plastic), JSAC 0602-2 (plastic) and NIES No.5 (human hair), No.9 (sargasso) and No.13 (human hair) was used in this study. Mercury abundances for the four reference standard materials (JSAC 0601-2, 0602-2, NIES No.5 and NIES No.13) were reported as certified value, while reference value was reported for NIES No. 9. These samples weighing 20 – 40 mg were sealed in high pure polyethylene bag. Single element standard solutions for atomic absorption analysis were used for Se and Ta to confirm spectral interferences from these two elements. These standard samples were prepared by dropping known concentration solution of these elements on the three sheets of filter papers. Samples were irradiated for 1 h at the pn-2 of KURRI, whose thermal and fast neutron fluxes are 5.6×10^{12} and $1.2 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$, respectively. After irradiation, samples were measured for gamma-rays several times with different cooling intervals.

RESULTS : The 279 keV peaks for all samples were detected. As the ⁷⁵Se and ¹⁸²Ta peaks interfere with the ²⁰³Hg peak at 279.2 keV and correction must be performed. The ¹⁸²Ta peaks for all samples analyzed in this study could not be detected. In this study, we estimated the ratio of the intensity of the gamma-ray peak of 264.7 keV to the 279.5 keV peak using a standard sample for Se. This ratio was applied to the 264.7 keV peak of the sam-

ple, and the intensity of the gamma-ray peak of 279.5 keV of ⁷⁵Se was subtracted from the those of 279.2 keV peak of ²⁰³Hg. The 264.7 keV peak of ⁷⁵Se could not be detected in JSAC 0601-2 (plastic), JSAC 0602-2 (plastic), and No.9 (sargasso), and the correction of spectral interference from Se was not made. For other elements, Se abundances were calculated by using a reference sample for Se, and the correction was performed. Among the samples analyzed in this study, JSAC 6020-2 has the highest Hg content, and the degrees of spectral interferences from ⁷⁵Se and ¹⁸²Ta were negligible. Thus, this sample was used as a reference standard for the determination of Hg. Analytical results were shown in Table 1, where certified values for Hg and Se are shown for comparison. Our Se values for NIES No. 5 and No. 13 are in good agreement with certified values. Our Hg value for JSAC 0601-2 was consistent with the certified value. However, differences in Hg values between our data and certified value were observed for the other three samples (NIES No. 5, No. 9, and No. 13). For NIES No. 9, no gamma-ray peaks for Se and Ta could be detected, and a correction was not performed. Our value was about eight times higher than the certified value. Contributions of spectral interferences from Se were about 5-6% for NIES No. 5 and 6-8% for NIES No. 13. Our values for NIES No. 5 and No. 13 were 25% and 13% higher than certified values, respectively. Although it is recommended that the minimum sample weight for NIES No. 5, No. 9, and No. 13 are 200, 400, and 120 mg, sample weights for these samples were 20 to 40 mg in this study. Differences between our data and certified values may be explained by sample heterogeneity. We need to confirm whether there is heterogeneity at the level of several ten mg of the sample by analyzing these samples with different weights.

Table 1. Analytical result for the four reference standard materials.

Reference material	Hg (ppm)		Se (ppm)	
	This work	Certified value	This work	Certified value
JSAC 0601-2 Plastic	1.30±0.05	1.3±0.1	n.d.	
NIES No.5 Human hair	5.49±0.17	4.4±0.4	1.50±0.16	1.4
NIES No.13 Human hair	4.97±0.13	4.4±0.4	1.84±0.10	1.79±0.17
NIES No.9 Sargasso	0.324±0.030	0.04	n.d.	

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CO5-5 Basic research on the trace elements analysis of airborne dust in the environment by INAA & PIXE

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INTRODUCTION: Compared to a few decades ago, when air pollution was a serious social problem, environmental standards are now properly defined and rarely cause negative influence on the human body. On the other hand, since the distribution of substances in the environment is known to have a large degree of variation, it is important to continuously sample and analyze the dynamics of elements over a long period of time.

The Atomic Energy Research Laboratory of Tokyo City University (TCU-AERL) operated the Musashi reactor until 1989 and has been conducting research using neutrons, including instrumental neutron activation analysis (INAA). Although now it is in the decommissioning phase, the facility is still in operation as a facility for conducting experiments using RI. In 2018, a 1.7 MV Pelletron tandem accelerator (TCU-Tandem) was installed to conduct trace element analysis using Particle Induced X-ray Emission (PIXE) [1]. As it becomes increasingly difficult to conduct experiments using research reactors, the advancement of analytical methods using accelerator ion beams is considered to be an effective. With the development of accelerator neutron sources also progressing, the realization of accelerator-based neutron activation analysis methods is also being considered.

We believe that the idea of combining ion beam analysis and neutron activation analysis may be effective as an analytical method for environmental samples that require analysis of a large number of samples in a short period of time.

In this study, we measured airborne dusts sampled at the TCU-AERL, where sampling has been ongoing since 2002 [2]. During the years since 2011, we have been studying the decay of radiocesium (Cs-137) and changes in its chemical form using another analytical method [3, 4].

EXPERIMENTS: We use a high volume air sampler (Shibata Scientific Technology LTD., HV-1000F, filter: ADVANTEC, QR-100 (collection efficiency: 99.99% for 0.3 μm particles)) with an inhalation flow rate of 700 L min^{-1} . The radioactivity of the filter that has collected dust is measured by a high-purity germanium semiconductor detector, and a part of the filter was stored for neutron activation analysis.

Irradiation was performed at the research reactor KUR at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, between the July and August with four machine times in FY2021. The irradiation conditions are shown in Table 1. The measurement of radioactivity of short half-life nuclides was carried out using the HP-Ge semiconductor detector of the hot laboratory of KUR.

And long and medium-lived nuclides, after cooling for one or two weeks, transported to the TCU-AERL, and was measured by a HP-Ge semiconductor detector. JLK-1 was used as a comparative standard substance.

Table 1. Irradiation conditions.

Irradiation			Operating power	Thermal neutron flux
date	time	position		
2021/7/6	60 min	Pn-2	1 MW	5.5×10^{12} n/cm ² /sec
2021/7/27	30 sec	Pn-3		4.7×10^{12} n/cm ² /sec
2021/8/3	60 min	Pn-2		5.5×10^{12} n/cm ² /sec
2021/8/24	30 sec	Pn-3		4.7×10^{12} n/cm ² /sec

RESULTS: In FY2021, 24 samples sampled between 2014 and 2019 were measured. We plan to organize the data together with the results of past measurements. In addition, PIXE analysis is being conducted at TCU-Tandem. Fig. 1 shows an example of the results of PIXE analysis for mainly light elements in vacuum. In addition, we are now adjusting the beamline for PIXE measurement in air in order to measure more samples efficiently.

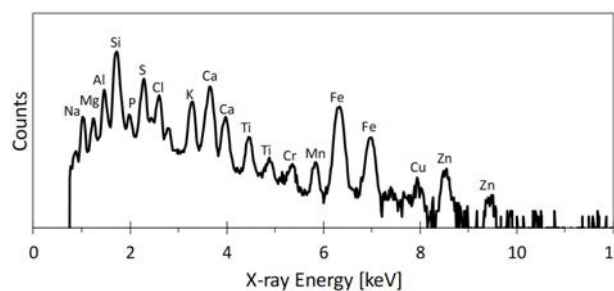


Fig. 1. An example of PIXE Spectra measured by PIXE beam line of TCU-Tandem.



Fig. 2. In-air PIXE analysis system at TCU-Tandem.

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CO5-6 Long term change in soil elements of the atmospheric coarse particle observed at Sakai,Osaka

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Atmospheric aerosols, which are particles suspended in the atmosphere, have a particle size of 0.001 to 100 μm (radius when spherical) and have various chemical compositions. The particle size and chemical composition vary depending on where and how it was made. The fine particles of which particle size is smaller than 2 μm are almost made from the combustion process and through some chemical reactions of gaseous matters. Coarse particles of which size are larger than 2 μm are almost naturally derived particles such as soil particles and sea salt particles and particles made by physical fracture. Fine particles that enter the respiratory tract can affect the health. For the indirect effect of coarse particle, cloud formation and solar scattering, coarse particles contribute to the some factors on which a climate changes. Consequently, coarse particles do not have much direct health effects, but they can have a greater impact on humankind by their effecting on the climate.

Our observations of the aerosols at Sakai show that the change in atmospheric aerosol concentration observed in Sakai City since 1995 has been decreased for both fine and coarse particles. The decreasing tendency of fine particles was caused by the decrease of particles derived from anthropogenic sources due to environmental measures, but the decreasing tendency of coarse particles is unlikely to decrease due to environmental measures, and it is due to changes in the natural environment including land use. Coarse particles are greatly influenced by soil particles which are affected by soil particles from a wide area as well as around the observation point and also affected by areas more than 2000 km away, such as yellow sand particles from China land. We will evaluate how much the effect is near the observation point or far away (from China land). In this

report, we focus on the concentration change in aluminum (Al) and calcium (Ca), which are the main components of soil particles that occupy the main part of coarse particles, and have estimated the factors that cause the reduction of coarse particles.

We have collected the coarse particle (> 2 μm) in 5 particle size ranges (>11, 7.0-11, 4.7-7.0, 3.3-4.7, 2.1-3.3 μm) using Andersen sampler and analyzed the elemental composition concentration in each particle size range by neutron activation analysis. From the results of Al and Ca concentrations, we found the following.

1) The concentration of coarse particles have decreased (1995-2020) and also the main components Al and Ca tended to decrease. (Fig.1)

2) However, there was no clear decrease in the concentrations of Al and Ca in the particle size range with the largest particle size (> 11 μm), in which range the influence of the vicinity was large, but the concentrations of Al and Ca in the particle size range below this range have clear decrease trend.

From the above, we have concluded that the ratio of Al and Ca to silicon (Si), which is the main component of soil in the neighboring soil particles, might changed (Si cannot be analyzed by neutron activation analysis). This change in composition might be caused by the effect of changes in the properties of soil particles from the surrounding area. Because the concentration of coarse particles in March and April is not clearly decreasing compared to other periods, this shows that the influence of soil particles from mainly China land, which has a large impact during this period, has not decreased much. From this results, we have estimated that the influence of soil from the surrounding area might be changed by the land use and changes in rolled up soil particles due to changes in traffic volume.

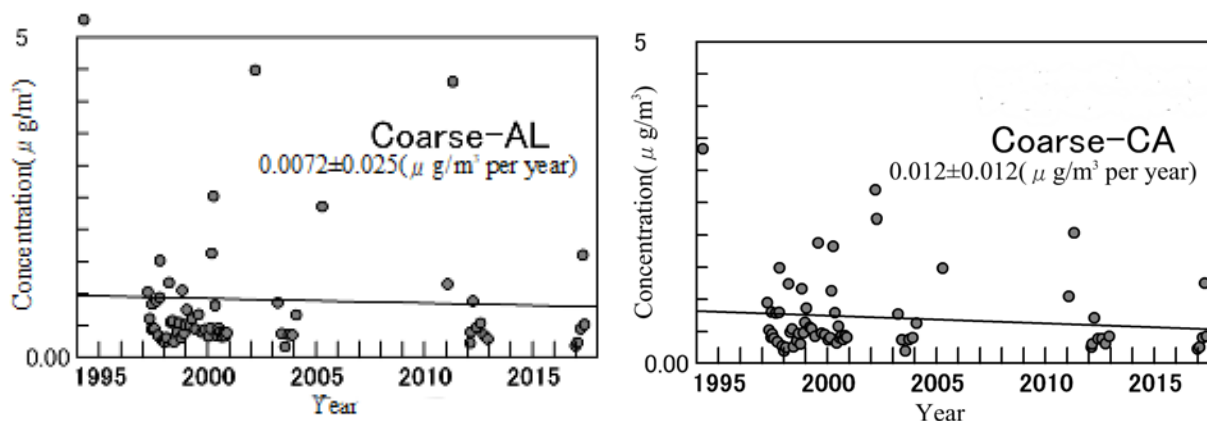


Fig.1 Long term (1995-2020) change in concentration of Al and Ca in the atmospheric coarse particle (>2 μm).

CO5-7 Eoarchean gneisses and their thermal histories

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INTRODUCTION: The Canadian Shield has the oldest rocks; Acasta gneiss in the Northwest territory, and orthogneiss in the Saglek Block in the Labrador; both showing U-Pb age of c.a. 4.0 Ga [1]. We have already reported ⁴⁰Ar/³⁹Ar age results on zircons and potassic minerals [2]. Acasta gneiss results are consistent among all the minerals, giving 1.9-2.0 Ga ages of Wopmay orogen, whereas only Labrador zircon showed ages older than 4.0 Ga. Recent study [3] indicated that the part of Greenland possibly belonged to Rae Province which recorded c.a. 1.9 Ga event. These results suggest that the Labrador zircon somehow might have preserved the 4.0 Ga age. Zircon does not contain potassium, but it normally has many little inclusions. The age might originate from these inclusions with some potassium. We analyzed the gas release pattern of the Labrador and Acasta zircons, and compared the diffusion characteristics of the zircons.

EXPERIMENTS: Rock samples were sieved in #25-100 mesh. After ultrasonic cleaning in distilled water, single mineral grains were separated by handpicking. The mineral grains were irradiated using the hydraulic facility of KUR for 47 hours at 1 MW, and subsequently 6 hours at 5MW. The total neutron flux was monitored by 3gr hornblende age standard [4], irradiated in the same sample holder. In the same batch, CaSi₂ and KAlSi₃O₈ salts were used for interfering isotope correction. A typical J-value was $(1.183 \pm 0.090) \times 10^{-2}$. In stepwise heating experiment, the minerals were heated under defocused laser beam, and temperature of sub-millimeter grains was measured using infrared thermometer of which spatial resolution is 0.3 mm in diameter with a precision of 5 degrees. A feedback circuit for relatively long time-lag heating control is used not to overshoot the programmed temperature. Zircon has relatively high melting point, and a near-infrared laser was used for final fusion. Argon isotopes were measured using a mass spectrometer with mass resolution of approximately 400, allowing to separate hydrocarbon from ³⁹Ar and other argon isotopes.

RESULTS AND DISCUSSIONS: An example of argon release pattern of step heating results from a Labrador zircon grain is illustrated in Fig.1. The ⁴⁰Ar fraction at the highest temperature over 1400 degrees has a small error, giving a ⁴⁰Ar/³⁹Ar ratio of Eoarchean age (> 4.0 Ga). The

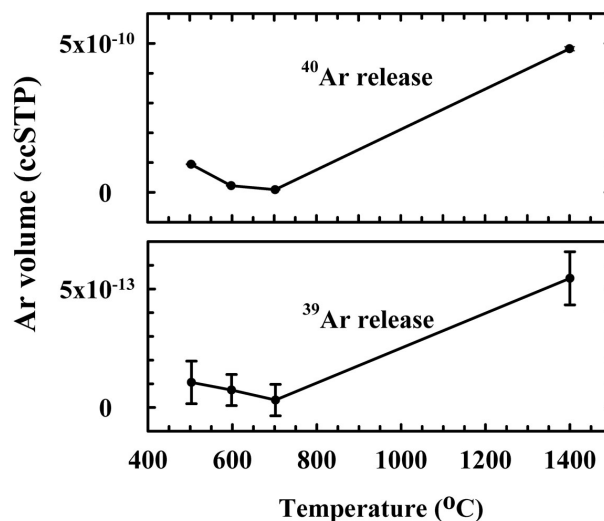


Fig. 1. ⁴⁰Ar/³⁹Ar release pattern during step heating of a Labrador zircon grain. The experimental error in ⁴⁰Ar analyses is very small while ³⁹Ar error is moderately large due to its small amount. The highest temperature step gave older than 4.0 Ga.

K-Ar and ⁴⁰Ar/³⁹Ar ages in Labrador area generally show c.a. 1.9 Ga. The results from Acasta gneiss showed that ⁴⁰Ar/³⁹Ar step ages of zircons are close to the and the U-Pb age of apatite (c.a. 1.9 Ga) [5]. Comparison of these results suggests that potassium carrier in the Labrador zircon did not experience the 1.9 Ga overprint event. In argon geochronology, presence of excess argon cannot be excluded in metamorphic rocks. In this case, the very high extraction temperature may play a key role to distinguish between the nearly-true age and excess age. The Labrador hornblende and biotite data do not suggest excess ages, and Wopmay orogen seems to have overprinted the Acasta zircon as well as hornblende and biotite. If we assume excess argon only in the Labrador zircon, we need to assume a special conditions to create excess argon only in the zircon at very high temperature. This may be clarified in view from P-T condition analyses in metamorphic petrology.

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CO5-8 Absorption of alkali metal ions by white radish sprouts (III)

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INTRODUCTION: Previously, we reported that the absorption of radioactive cesium ions from contaminated soil into rice plants increased by adding stable cesium ions to irrigation water and that the possibility that the cesium ions added were replaced with radioactive cesium ions in soil [1, 2]. However, we also noted addition of excess amount of stable cesium caused an obstacle to growth of rice plant [3].

Therefore, in the present study, we examined the removal of radioactive cesium from soil through chemical treatment with various kinds of alkali ion solutions. At first, two types of soil, kuroboku soil (Andsols) and vermiculite were contaminated artificially to understand the distribution and behavior of radioactive cesium in soil and to provide insights into removal methods. Second, the effect of decontamination with alkaline ions on the growth of plants was investigated. In investigation of the behavior of trace elements in white radish sprouts, simulated decontamination with alkaline ions was performed on the soil containing no radioactive cesium and examined.

EXPERIMENTS: ¹³⁷Cs removal from soil A sample (30 g) of commercially obtained vermiculite or kuroboku soil was placed in a metal mesh, immersed in 300 mL of aq. ¹³⁷Cs (116 Bq) solution for one day, then removed from the solution and dried. After that, 100 mL of 0.140 mol/L KCl, RbCl or CsCl solution were added to a beaker containing the contaminated soil and the mixture was stirred. After stirring, the beaker of soil and solution was allowed to stand for 10 minutes, then, each soil was washed with pure water once or twice. The same treatments were applied to soil that was not contaminated with radioactive cesium.

Materials and Method The dried each soil mentioned above was placed in a plastic pot, wetted with pure water and 1.0 g of radish sprouts seeds were sown on it. After germination, Hyponex diluted 2000 times was added as liquid fertilizer. After that, they were cultivated for 14 days while giving only pure water as appropriate. White radish sprouts cultivated in soil without radioactive cesium were subjected to INAA.

INAA The samples in polyethylene capsules were irradiated in Pn-3 for 90 seconds and in Pn-2 for 4 hours, for short and long irradiation, respectively. As comparative standards, the certified NIST Standard Reference Material 1577b Bovine Liver as well as elemental

standard for Cs was used. The γ -ray spectroscopic measurements with an HPGe detector were performed repeatedly for the short-irradiated samples: the first measurements for 120 – 900 seconds after decay time of 5 - 15 minutes and the second one for 250 - 1200 seconds after 60 - 150 minutes. The long-irradiated samples were measured for 1 - 24 hours after an adequate cooling time (15 - 60 days).

RESULTS: When KCl solution was used as a decontamination agent, no growth disorder of white radish sprouts was observed. When a CsCl solution was used as a decontamination agent, radish sprouts cultivated in kuroboku soil that had not been washed with pure water after decontamination showed significant growth disorders. On the other hand, the growth disorder of radish sprouts cultivated with vermiculite was not so remarkable. This indicates that cesium ions are retained in kuroboku soil in a form that is easily absorbed by plants. When the RbCl solution was used as the decontamination agent, a slight growth disorder was observed for kuroboku soil that were not washed with pure water.

The decontamination effect estimated from the radioactive cesium absorbed by white radish sprouts was hardly observed in the KCl solution. As same as our previous report, the CsCl solution was able to remove some radioactive cesium from both kuroboku soil and vermiculite. On the other hand, although the RbCl solution had a low effect of removing cesium in vermiculite, a remarkable decontamination effect could be observed on kuroboku soil.

The concentration of trace elements in radish sprouts cultivated in soil after decontamination with RbCl is described. Even when cultivated in soil washed with pure water after decontamination treatment, the concentration of rubidium ions absorbed by radish sprouts was high. However, no abnormality was found in the concentrations of essential elements such as potassium and manganese. Just as there was no apparent growth disorder. Considering that the actual field soil is a mixture of kuroboku soil and clay minerals, it is necessary to consider the use of Rb ions, which are highly effective in decontaminating kuroboku soil.

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CO5-9 SEM-EDS analysis of fine particles produced from model debris, (U,Zr)O₂, by laser ablation for decommissioning of Fukushima Daiichi Nuclear Power Plant

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INTRODUCTION: Recently, first preliminary removal of the fuel debris remaining in Fukushima Daiichi Nuclear Power Plant (1F) is just trying to be started. In the removal, however, fine particles containing alpha emitters such as ²³⁵U and ²³⁹Pu are concerned to be generated in cutting the debris. We are therefore developing a novel real-time detection method of the scattered fine particles using Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) which can measure the particle size and can identify chemical composition and contained isotopes for each particle floated in carrier gas. At present, we are fabricating an enlargement and condensation apparatus to increase the detection sensitivity of ATOFMS by enlarging non-measurable tiny particles with ATOFMS to measurable-sized ones. The present study aims at evaluating influence of the enlargement and condensation of fine particles to detection sensitivity of ATOFMS by its surface observation. Here we carried out SEM-EDS measurement of modeled fine particles containing ²³⁸U without condensation.

EXPERIMENTS: Fine particles were prepared from (U,Zr)O₂ pellets as well as a ZrO₂ one by laser ablation. The pellets had different U/Zr ratios. Laser power was 20-30 kW. In a closed chamber, the pellet was irradiated by the laser. The generated fine particles were swept out of the chamber by carrier gas of dried air and were collected on a carbon tape in an impactor connected with a thin tubing. SEM-EDS measurement of the collected samples was carried out after the transportation of these to KURRI. Energy of bombarded electrons was 10 kV or 15 kV. SEM images and X-ray spectra of the samples were taken for a few tens of fine particles found on the carbon tapes.

RESULTS: In Fig. 1, a SEM image of the fine particles from the ZrO₂ pellets were demonstrated as an example. Many of tiny particles with a diameter of less than one micrometer and a few of larger particles were observed. We also analyzed the fine particle by EDS. An example is the particle in Fig. 1, in which analyzed point is depicted by a cross symbol. In Fig. 2, observed spectrum is showed. Characteristic X-rays of C, O, Y, and Zr are seen. Zr and O peaks from ZrO₂ are clearly observed. Because the commercially available ZrO₂ pellets used contains 8mol% Y₂O₃, the x-ray of Y is also detected. C is from the carbon tape as a support. For other fine particle samples prepared from (U,Zr)O₂, results are under analysis.

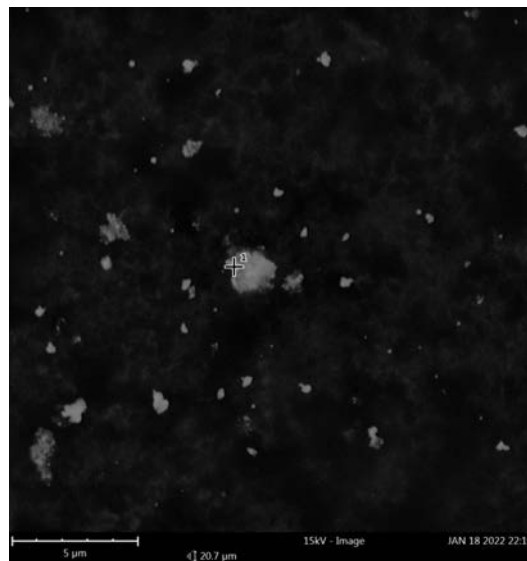


Fig. 1. SEM image of fine particles prepared from ZrO₂ pellet by laser ablation.

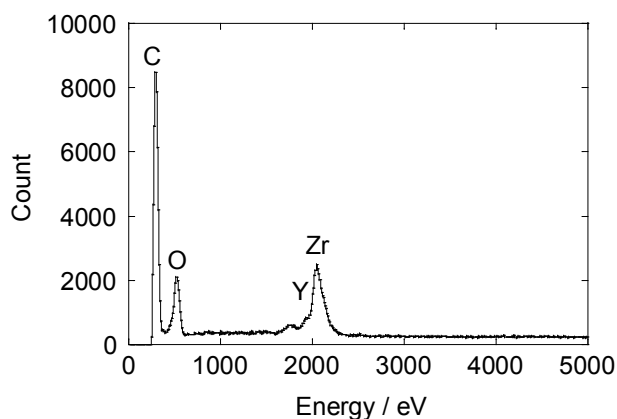


Fig. 2. EDS spectrum of fine particles prepared from ZrO₂ pellet by laser ablation.

CO5-10 ^{40}Ar - ^{39}Ar Dating of Extraterrestrial Materials in KURNS

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INTRODUCTION: Radiometric dating is useful tool for unveiling formation and evolution process of planetary material. ^{40}Ar - ^{39}Ar method is invaluable to date the timing of heating events on planetesimals and asteroids (e.g. Swindle et al. (2014) [1]). Especially, ^{40}Ar - ^{39}Ar dating method with laser heating technique is suitable for small amount sample (e.g. Kelley, 1995 [2] and Hyodo, 2008 [3]).

For example, tiny material returned from asteroid 25143 Itokawa is dated using laser heating ^{40}Ar - ^{39}Ar dating method by Park et al. (2015) [4] and Jourdan et al. (2017) [5]. These ages indicate the timing of catastrophic events which occurred on Itokawa's precursor body. Combining the ^{40}Ar - ^{39}Ar ages and other chronological data, Terada et al. (2018) [6] overviewed the time evolution of the Itokawa asteroid. Successor to earlier works, ^{40}Ar - ^{39}Ar dating of material that recovered from asteroid 162173 Ryugu and other extraterrestrial materials have been carried out using KUR (project #R3007, PI: RO, [7]).

To implement of dating of extraterrestrial material by ^{40}Ar - ^{39}Ar method, we will develop a system which includes laser-heating gas extraction and gas purification line in KURNS (Fig. 1).

EXPERIMENTS: Dr. R. Okazaki of Kyushu University designed the system. A continuous Nd-YAG laser (~60 W) extract gas from neutron irradiated sample. The extracted gas is purified using a SORB-AC getter pump in purification part. After the purification of extracted gas, argon isotope ratios in the gases are analyzed by using an on-line connected quadrupole mass spectrometer. Alternatively, purified gases are encapsulated into metal gas trap, and are transported to laboratories of noble gas analysis (e.g. Kyushu University). Then, argon isotope of the gas is analyzed using a high sensitivity mass spectrometer. Whole of the extraction and purification parts will be evacuated by an oil rotary pump, two turbo molecular pumps and an ion pump to ultra-high vacuum condition.

RESULTS: We have continued assembling of the gas extraction and purification system in KURNS in FY2021. We could evacuate the extraction and purification parts using oil rotary pump. Unfortunately, the construction work was not finished due to influence of epidemic prevention of COVID-19. We are going to continue setting the system up during FY2022.

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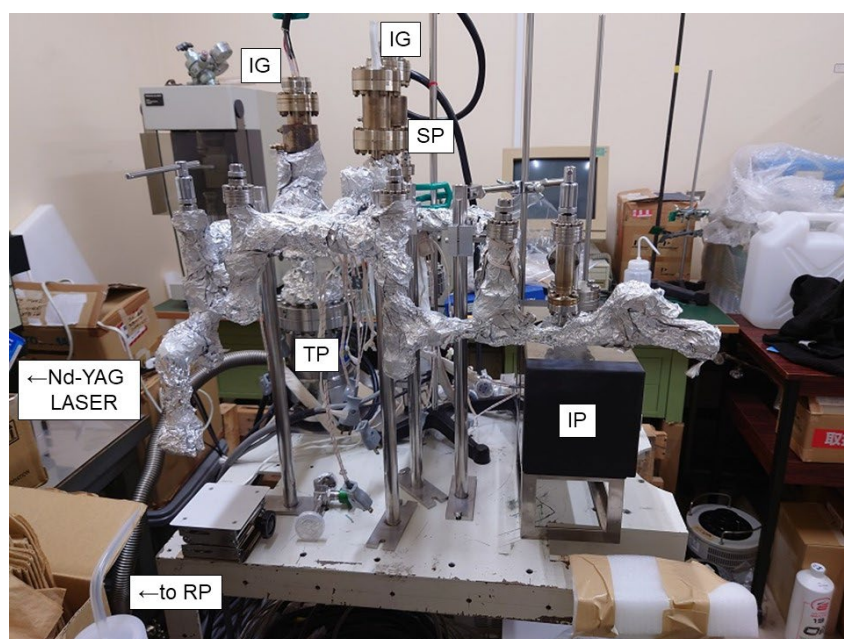


Fig. 1. View of gas extraction and purification line at KURNS. RP, TP, IP, SP and IG respectively denotes oil rotary pump, turbo molecular pump, ion pump, SORB-AC getter pump and ion gauge.

CO5-11 Ar-Ar and I-Xe Dating for Meteorites and the Hayabusa2 Returned Samples

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INTRODUCTION: Extra-terrestrial materials, such as meteorites, micrometeorites, and samples collected by asteroid/planet explorations, provide a variety of information for understanding the origin and evolution of the solar system. In particular, age determination gives us direct knowledge about thermal histories as well as timing of the events occurred in solar nebular and on the parent bodies. Ar-Ar and I-Xe ages usually, but not always, correspond to aqueous alteration and/or thermal events due to metamorphism/meteoroid impacts suffered on the parent body, and the parent body formation, respectively [e.g., 1, 2]. Despite of their importance, Ar-Ar and I-Xe dating is performed at limited laboratories because they require technique involving neutron irradiation and isotope measurements of the radioactive materials. In order to conduct Ar-Ar and I-Xe dating for extra-terrestrial samples, we attempt to establish the analytical protocol and apparatus. A system for gas extraction, purification, and measurements is being constructed at KURNS.

EXPERIMENTS: (i) Hayabusa2, a mission operated by the Japan Aerospace Exploration Agency (JAXA), returned samples from the C-type near Earth asteroid (162173) Ryugu. Small grain samples (typically 0.8 mm in size) were distributed to us (PI. R. Okazaki) for Ar-Ar and I-Xe dating. Prior to analyses of the Hayabusa2 samples, advanced experiments were performed. One of the experiments were conducted in July 2021. Two meteorites (Allende and Murchison) and terrestrial rocks and minerals were subjected to hydro irradiation as standard and interference-monitor samples. Individual samples were put in a hole of the diamond dish, which were wrapped with Al foil and stored in a Hydro irradiation capsule. In October 2021, returned Ryugu samples set on diamond dishes were irradiated (R3038; R3007) [3].

(ii) In Ar-Ar and I-Xe dating, isotope measurements of Ar and Xe for samples after neutron irradiation are necessary. For quicker and easier operation of Ar-Ar dating, we are constructing an apparatus for gas extraction, purification, and Ar isotope analyses. It needs ultra-high vacuum state and is composed of an Nd-YAG laser, a SORB-AC getter, vacuum gauges, and vacuum pumps (a mass spectrometer has not connected yet). Gases are extracted from samples by laser heating. Extracted gases are purified by the getter. And then, gases are planned to be (a) measured on-site with a quadrupole mass spectrometer (QMS) and/or (b) stored in bottles and measured with a high sensitivity sector-type mass spectrometer at Kyushu University. Va-

lidity of QMS was reported for K-Ar dating [e.g., 4-6]. In situ Ar-Ar dating using the laser heating and Ar measurements by a QMS at KURNS can avoid transportation of irradiated samples. We are examining the sensitivity, background level and availability of the QMS at the Univ. of Tokyo.

RESULTS: (i) The samples were first studied for short lived nuclides by Dr. Shirai and co-investigators. Then, the samples were irradiated, cooled, isolated from the dishes and transported to Kyushu University to measure noble gases (including Ar and Xe) with the sector-type mass spectrometer. The results are being analyzed in detail.

(ii) Most of the line components were assembled and evacuated at KURNS. The heating examination for the laser has not been done. The QMS that is planned to be connected to the line at KURNS was installed into the ultra-high vacuum system at the Univ. of Tokyo (Fig. 1) for performance tests. Because the amounts of Ar released from irradiated samples are generally small, low background conditions are required. To examine analytical procedures and to determine the sensitivity and the precision of isotopic ratios, quantitative amounts of air, $\leq 7 \times 10^{-6}$ cm³STP for ⁴⁰Ar, were introduced into the QMS. Suitable sample amounts and heating temperature steps will be discussed based on the results from these experiments.

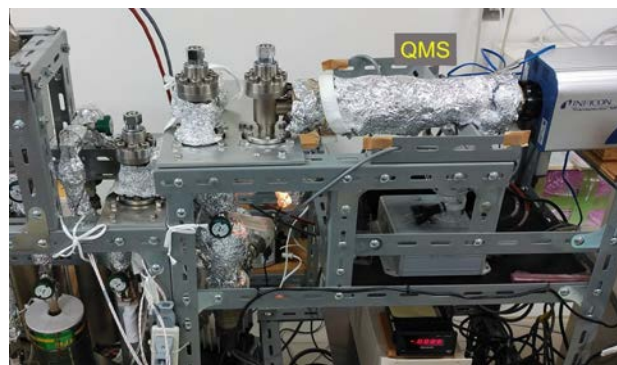


Fig. 1. The QMS is connected to the ultra-high vacuum line.

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CO5-12 Neutron Activation Analysis of cosmo- and geo-chemical samples

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INTRODUCTION: Halogen elements are a group of the elements belonging to group 17 in a periodic table of the elements, consisting of fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) as stable elements. Geochemically, halogens behave with relatively high volatility and incompatibility with silicates. Therefore, halogens are relatively abundant in several reservoirs in the outer layer of the earth such as sea water, oceanic sediments and crustal materials. Cosmochemically, halogens are grouped into moderately volatile (for F and Cl) and highly volatile elements (for Br and I). However, their behavior in the early solar system is not well understood even at present. A major reason for making difficult in understanding the cosmochemical behavior of halogens is the lack of reliable data of halogen contents in bulk meteorite samples. A main goal of this study is to obtain reliable halogen content data for chondritic meteorites, especially carbonaceous chondrites for better understanding of the halogen behavior when our solar system formed. Before reaching this goal, we determined halogen contents in geochemical reference samples to establish the analytical procedure applicable to meteorite samples. Contents of the three halogens were determined by radiochemical neutron activation analysis (RNAA).

EXPERIMENTS: Two geochemical reference samples of about 200 to 300 mg each in clean plastic vials and reference standard samples of the three halogens were irradiated with neutrons for 10 min with a thermal neutron flux of $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in the Pn-3 irradiation tube. After the irradiation, the samples were subjected to radiochemical separation of the three halogens. The radiochemical procedure used was essentially the same as previously described ([1], [2]) and are briefly summarized in the following. Each meteorite specimen was alkaline-fused with sodium hydroxide. The resulting fusion cake was disaggregated with water and the supernatant fractions was recovered by centrifugation. After neutralizing with nitric acid, I was precipitated as palladium iodide, which was immediately measured for a 423 keV gamma-ray emitted by ¹²⁸I whose half life is 27 min. From the supernatant, silver chloride and silver bromide precipitates were recovered by adding silver nitrate solution. Gamma-rays of ³⁸Cl (half-life: 30 min) and ⁸²Br (half-life: 35 h) were measured just after the measurement of ¹²⁸I and on the following days, respectively. After completion of all gamma-ray measurements, the palla-

dium iodide and silver chloride-bromide mixture precipitates were reactivated for determining chemical yields.

RESULTS: Some preliminary results are summarized in Table 1. Errors quoted are uncertainties due to counting statistics (one standard deviation) in gamma spectrometry.

Table 1 Analytical results (in $\mu\text{g/g}$) of three halogens.

sample	Cl		Br		I	
AGV-2	76.5	± 3.2	0.085	± 0.006	0.023	± 0.005
<i>lit. 1</i>	72.5	± 2.7	0.101	± 0.007	0.197	± 0.038
BCR-2	100	± 2.2	0.121	± 0.009	0.048	± 0.018
<i>lit. 1</i>	112	± 1	0.144	± 0.008	0.082	± 0.022
BHVO-2	97	± 3.4	0.253	± 0.017	0.081	± 0.008
<i>lit. 1</i>	104	± 4	0.240	± 0.013	0.307	± 0.050
GSP-2	336	± 14	0.067	± 0.010	0.011	± 0.007
<i>lit. 1</i>	363	± 29	0.117	± 0.020	0.075	± 0.018
GSR-1	126	± 4	0.120	± 0.024	0.012	± 0.005
<i>lit. 2</i>	116	± 10	0.58	± 0.07		
GSR-2	38.9	± 3.6	0.021	± 0.013	0.011	± 0.005
<i>lit. 2</i>	49.1	± 5.6	0.17	± 0.01	0.004	± 0.003
GSR-5	37.2	± 1.5	0.238	± 0.014	0.249	± 0.014
<i>lit. 2</i>	49.7	± 5.4	0.51	± 0.02	0.14	± 0.01
GSD-7a	43.4	± 7.1	0.813	± 0.045	0.471	± 0.016
<i>lit. 2</i>	39.0	± 6.5	1.05	± 0.11	0.38	± 0.04
GSD-11	320	± 12	1.41	± 0.05	2.56	± 0.08
<i>lit. 2</i>	276	± 13	1.88	± 0.10	1.86	± 0.10
JR-3	139	± 9	0.549	± 0.023	0.469	± 0.023
<i>lit. 3</i>	134	± 12	0.577	± 0.045	0.482	± 0.037

lit. 1: [3], *lit. 2:* [4], *lit. 3:* [2] ("*lit.*" denotes literature)

Data in *lit. 1* and *lit. 3* were obtained by RNAA using the same analytical procedure as used in this study. Data of *lit. 3* were obtained by ICP-MS. In Comparison with literature values, the following features can be seen; (i) (for Cl) literature data and our data are all consistent, (ii) (for Br) all data of *lit. 2* are systematically lower than ours, (iii) (for I) all data of *lit. 1* are systematically higher than ours, while some of *lit. 2* are lower than ours, (iv) (for three halogens) data of *lit. 3* and ours are consistent. We have repeatedly analyzed reference samples including those listed in Table 1 to critically evaluate the literature values. Outcomes will be submitted to scientific journals in near future.

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CO5-13 Collisional histories of the LL chondrite parent body revealed by $^{40}\text{Ar}/^{39}\text{Ar}$ dating

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INTRODUCTION: A collisional event is a fundamental process of evolving and disrupting asteroidal bodies in the solar system. Because collisions induce shock metamorphism in meteorites, we can reveal a history of asteroidal evolution/destruction by examining shocked meteorites. Ordinary chondrites, the most abundant meteorites reported, record complex collisional histories on their parent bodies, particularly in the “early” solar system. Although LL chondrites are less investigated than H and L chondrites, certain authors suggested that LL chondrite parent body(ies) underwent a shock event before 4.5 Ga and a major shock event at 4.2 Ga [e.g., 1,2].

For discussions on such collisional histories, $^{40}\text{Ar}/^{39}\text{Ar}$ ages have been commonly adopted to examine collisional ages. The high diffusion rate of Ar leads to loss of radiometric Ar during shock heating [e.g., 3]. On the other hand, some shock events are accompanied by postshock heating so weak (e.g., Fritz et al., 2017; Gillet & El Goresy, 2013; Sharp & Decarli, 2006; Stöckler et al., 1991, 2018) that a resetting of $^{40}\text{Ar}/^{39}\text{Ar}$ ages is not always attained, and resistance against resetting depends on shock textures [e.g., 4]. Moreover, certain meteorites may have experienced multiple shock events, and possibly aliquots from the same meteorites having different petrological textures yield distinct $^{40}\text{Ar}/^{39}\text{Ar}$ ages. Therefore, when we conduct $^{40}\text{Ar}/^{39}\text{Ar}$ chronological analysis to determine collisional ages, we should carefully observe shock textures and use the same aliquot for $^{40}\text{Ar}/^{39}\text{Ar}$ analysis. However, the number of such chronological–petrological studies is still limited [e.g., 5], and relations between shock ages and collisional events are unclear, except for a major shock event at 0.5 Ga on the L chondrite parent body. To explain such collisional histories, including a time transition of impact scales, we require a chronological–petrological study of multiple meteorites. In this study, we focused on an LL chondrite and performed $^{40}\text{Ar}/^{39}\text{Ar}$ chronological–petrological analyses of an LL 6 brecciated chondrite to delineate the collisional history of the LL chondrite parent body.

EXPERIMENTS: The samples of 5-50 mg each and standards for neutron fluence were wrapped with aluminum foil and put in aluminum capsules of $\phi 10$ mm x

30 mm. The capsules were irradiated with neutrons in KUR. After the irradiation, the samples were sent to the University of Tokyo. The samples were loaded into an ultrahigh-vacuum, noble gas extraction, purification, and separation line. Argon was extracted from the samples by heating up to 1800°C, purified with hot titanium-zirconium getters, separated into each noble gas with temperature-controlled cold traps, and then determined their isotope compositions with a noble gas mass spectrometer [6,7]. The fast neutron flux was estimated as $(1.0\text{--}1.2) \times 10^{18}$ neutrons cm^{-2} , from the production of ^{39}Ar from ^{39}K in the Hb3gr hornblende standard in which K contents have been determined by [8].

RESULTS: Petrological observations revealed that NWA 2139 experienced at least five impact events, including at least two brecciation events, and two shock-induced heating events inducing silicate darkening and healing cracks, and one weak shock event inducing thin shock veins. $^{40}\text{Ar}/^{39}\text{Ar}$ analysis demonstrated that four aliquots of NWA 2139 provided a mini-plateau age of 4.17 ± 0.10 Ga in high-temperature fractions. One aliquot shows a partial degassing event at <3.9 Ga. The heating event at 4.17 ± 0.10 Ga induced the recrystallization of the thick veins and healing cracks in NWA 2139, which is the major heating event on the LL chondrite parent body, as reported in other LL chondrites [e.g., 1,2]. Silicate darkening, thick shock vein formation, and two brecciations occurred before the major heating event at 4.17 ± 0.10 Ga, whereas the thin shock vein formed after the heating event. The LL parent body might have been broken up by 1.7 Ga, based on studies of probably from 4.2 to 3.8–3.9 Ga. No brecciation occurred after 4.2 Ga, and many other LL chondrites, including NWA 2139, did not experience a strong shock event within 1.5–1.7 Ga reported for Itokawa particles and the Chelyabinsk meteorite. Moreover, the heating event at 4.2 Ga is a common event in multiple LL chondrites.

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CO5-14 Application of the Single Comparator Method to Photon Activation Analysis at KURNS

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INTRODUCTION: Instrumental photon activation analysis (IPAA) is multielemental and nondestructive analytical method like instrumental neutron activation analysis (INAA). Comparative method is generally used for determination of elemental contents in IPAA. In INAA, k_0 method, which was developed based on a single comparator method, as well as comparative method is used. A single comparator method and k_0 method can determine all elemental contents by using only single element comparator. But there are no reports on determination by the single comparator method in IPAA as far as we know. So, we have applied single comparator method to IPAA at the Research Center for Electron Photon Science (ELPH), Tohoku University using photoreaction yield ratios obtained by Oura et al.[1] at ELPH. Since neutron spectrum is unique to each irradiation position in a reactor, its correction is essential in k_0 -INAA. However, energy spectrum of the bremsstrahlung from any electron accelerator should be nearly identical for the same acceleration energy of the electrons and the same converter material. There must be no need to correct the energy spectrum as for the k_0 -INAA. That is, the yield ratios by Oura et al. should be also used to perform IPAA in any institution. In this study, the single comparator method was performed on various reference standard samples at the electron accelerator at the Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS) other than ELPH.

EXPERIMENTS: Several geochemical and environmental reference samples, which were same as those analyzed at ELPH, in an Al foil container were irradiated with stainless steel (SUS) foil fluence monitors by bremsstrahlung with $E_0 = 33.3$ MeV from an electron LINAC at KURNS under air-cooling for 6 hours. The bremsstrahlung was produced by a Pt converter (2-mm thick x 2 pieces). After irradiation, samples were transferred to a new Al foil container. Then, γ -rays in samples were measured by a Ge detector calibrated with ^{152}Eu and ^{182}Ta sources. Samples were placed at approximately 10-20 cm from the Ge detector to reduce true coincidence.

The determination calculation was performed using the single comparator method. In this study, Ni was used as the comparator, and the elemental mass fraction was calculated using Equation (1),

$$C = \frac{M_x \times r_{Ni}}{M_{Ni} \times r_x} \times \frac{A_x}{A_{Ni}/w_{Ni}} \times \frac{\sigma_{Ni}}{\sigma_x} \times \frac{1 - e^{-\lambda_x t}}{1 - e^{-\lambda_{Ni} t}} \div W \quad (1)$$

where C is the elemental mass fraction, A is the induced radioactivity at the end of the irradiation period, W is the sample mass, w is mass of an element, M is the atomic

weight, r is the isotopic abundance, σ is the reaction yield, λ is the decay constant, and t is the irradiation time. The suffixes 'x' and 'Ni' express the parameter for the sample and Ni monitor, respectively. The reaction yield ratios (σ_x/σ_{Ni}) were taken from Oura et al.[1] The specific activity of ^{57}Ni (A_{Ni}/w_{Ni}) at the position of each sample position was calculated using an interpolation of ^{57}Ni activities in SUS foils using a function determined by the least squares method.

RESULTS: Ratios of determination values to literature values (certified or recommended values) for determined elements are shown in Fig.1 with analytical results obtained at ELPH, where yield ratios used in the single comparator method were determined at. Determination values obtained at ELPH expressed by open symbols were consistent with literature values within $\pm 10\%$ for almost elements, and some results were within $\pm 20\%$. The results obtained at KURNS expressed by closed symbols, which is a different facility from the one where reaction yield ratios were determined, were also consistent with literature values like the result at ELPH. It is concluded that the single comparator method using reaction yield ratios obtained with the LINAC at ELPH [1] can generally be applied to IPAA using any accelerators.

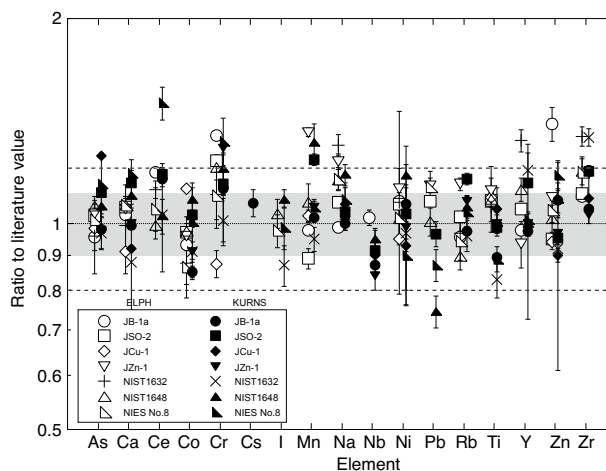


Fig. 1. Comparison between mass fractions determined in 7 kinds of reference samples and their literature values. The irradiation energy was $E_0 = 33.3$ MeV. The shaded area and dotted lines express the range of $\pm 10\%$ of the literature value and $\pm 20\%$ of the literature value, respectively.

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CO5-15 Distribution of radiocesium in forestry area in Fukushima

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INTRODUCTION: Vast forest was markedly contaminated by radioactive plums containing radiocesium in the wide range of the eastern part of Japan in 2011 [1–4]. As forests have an important role in preventing landslides and maintaining the ecological and hydrological system, the destructive forest should be avoided and an appropriately managed tree-felling should be conducted. It is necessary to know the environmental dynamics of radiocesium in forest to keep the forestry vividly.

In our previous field study [1], most of the radiocesium in the tree rings was directly absorbed by the atmospheric direct uptake via the bark and leaves rather than by roots. The chemical form of radiocesium on the leaves and bark would have been a mixture of water-soluble and insoluble forms. Another our previous study [2] demonstrated that the effluence rate of radiocesium (¹³⁷Cs) obtained from dissolved assay experiments on the trunks of *Cryptomeria japonica*, indicating that the radiocesium in the trees was mainly water-soluble.

As radiocesium in tree may be absorbed from the roots in the future, it is important to know how much dissolved radiocesium is released from the soil. In this study, sequential-extraction experiment of radiocesium was attempted to the surface soil 10 years after the accident, and compare the distribution ratio of the radiocesium in the soils: 2 years after the accident and 10 years after the accident.

EXPERIMENTS:

We extracted ¹³⁷Cs from the surface soil sample from the Fukushima. The soil of depths of 0–2.5 cm was well mixed and the samples were used in the sequential-extraction experiment [4]. A ratio of solution to sample of 5 (v/w) was used for extraction in each step. After each fraction was stored into a U-8 vessel, ¹³⁷Cs was measured by gamma-ray spectrometry.

Furthermore, we measured radiocesium in tree ring of *Cryptomeria japonica* in the Fukushima. Detailed pre-treatment of the tree-ring and measurement of the radiocesium in the samples are described by our previous study[1].

RESULTS: As shown in Fig. 1, the sequentially chemical fractionations of ¹³⁷Cs in the soil indicate that most part of ¹³⁷Cs were insoluble 2 years after the accident.

After 10 years later from the accident, ¹³⁷Cs was strongly fixed in the mineral of the soil, ¹³⁷Cs in the water soluble fraction and ion exchange fraction decreased (Fig. 2).



Fig. 1 Distribution of ¹³⁷Cs in the surface soil collected at the Fukushima [4].

*1: ultrapure water, F: 1 M of NaAc, F: 1-M NaAc-HAc (pH 5), 4: 0.04-M NH₂OH · HCl in 25 % (v/v) HAc (pH 2), 5: 30 % H₂O₂ (with HNO₃, pH 2), 1.8-M NH₄Ac in 11 % HNO₃(v/v), 6: Residual

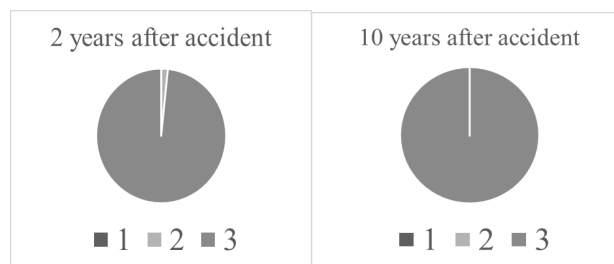


Fig. 2 Distribution of ¹³⁷Cs in the surface soil collected at the Fukushima.

*1: ultrapure water, 2: 1 M of NaAc, 3: Residual

Furthermore, concentrations of the tree ring were less than 50Bq/kg collected in 2014. We compared that the concentration of the tree ring at the same sampling site, the concentration of radiocesium did not increase from 2012 to 2014. We concluded that the radiocesium was not absorbed from the root effectively.

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CO5-16 Determination of Abundance of Rare Metal Elements in Seafloor Hydrothermal Ore Deposits by INAA Techniques-8: Cross check with ICP-QMS analysis (2)

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INTRODUCTION: Instrumental neutron activation analysis (INAA) has several advantages for geochemical tools to provide useful information for mineral exploration. INAA enables highly sensitive multi-element analysis without geochemical pretreatment. We have conducted studies using mineralized samples collected from seafloor hydrothermal fields, with a view to extend the range of application of this technique. Here we report a result of cross check with inductively coupled plasma quadrupole mass spectrometry (ICP-QMS analysis).

EXPERIMENTS: Sulfide deposit and metalliferous sediment collected from an active seafloor hydrothermal field in a seamount in Izu-Bonin Arc were provided for cross check analysis. In total 29 samples were selected to examine analytical accuracy in wide range of concentrations, and aliquots for INAA and ICP-QMS analysis were split from the same powdered sample.

INAA analysis was conducted by two runs. For short life nuclides, powdered samples of 10-20 mg were irradiated at Pn-3 (thermal neutron flux = 4.68×10^{12} n/cm²/sec) for 30 seconds, and the gamma ray activity was measured for 3 minutes after adequate cooling time (3~15 minutes). For long life nuclides, powdered samples of 10-20 mg were irradiated at Pn-2 (thermal neutron flux = 5.50×10^{12} n/cm²/sec) for 30 minutes, and the gamma ray activity was measured for 15 minutes after adequate cooling time (~30 hours).

ICP-QMS analysis followed the procedure reported in the previous study [1]. Powdered samples of ca. 50 mg were dissolved by HNO₃-HClO₄-HF digestion in Teflon PFA screw-cap beakers, then heated overnight on a hot plate at 110 °C. The digested samples were progressively evaporated at 110 °C for more than 12 h, 130 °C for 3 h and 160 °C until dryness. The residue was dissolved in 5 mL Milli-Q de-ionized water combined with 4 mL HNO₃ and 1 mL HCl, then further diluted to 1:100 by mass (total dilution factor ca. 20,000) before introduction into the ICP-QMS (Agilent 7500ce).

RESULTS: Content of nine elements (Al, Mn, Cu, Zn, Ba, Na, As, Sb and Au) determined by INAA is plotted against that by ICP-QMS analysis (Fig. 1). Contents determined by two analytical techniques basically well agreed, except for the case that determination of some specific elements was difficult due to extremely low content. Disagreement in Ba content for Ba-rich ore sample is caused by incomplete dissolution during the chemical treatment for ICP-QMS analysis [1]. Accuracy of INAA was confirmed for determination of metal elements in adequate content ranges such as Zn (>1%), Cu (>1000 ppm), As (>100ppm), Sb (>100ppm) and Au (>1 ppm). Determination of Al in low contents below 1000 ppm showed rather poor accuracy by INAA probably due to short irradiation time to inhibit back ground.

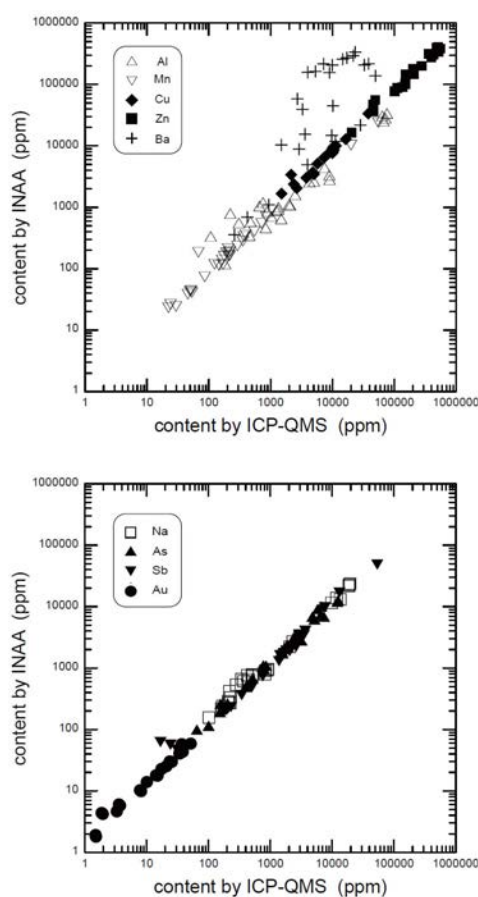


Fig. 1. Result of cross check analyses between ICP-QMS and INAA for sulfide deposit and metalliferous sediment (Upper: short lived nuclides, Lower: long lived nuclides). Note that both axes are in logarithm scale.

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CO5-17 Neutron activation analysis of carbonate reference materials: coral (JCp-1) and giant clam (JCt-1)

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INTRODUCTION: Geochemists are often interested in the abundance of halogen elements in geochemical materials such as crustal rocks, mantle materials, and meteorite samples, because halogens play an important role in investigating the petrogenesis of such materials and assist in tracing their origins and/or precursor materials [1-3]. In our previous work, radiochemical neutron activation analysis (RNAA) was refined to accurately determine even trace amounts of halogens (chlorine, bromine, and iodine) in sedimentary rock reference samples [4]. Subsequently, U.S. Geological Survey (USGS) geochemical reference materials were subjected to RNAA, and the data obtained were compared with literature data [5]. The two kinds of carbonate reference materials investigated here, JCp-1 (Coral) and JCt-1 (Giant Clam), are prepared by the Geological Survey of Japan/National Institute of Advanced Industrial Science and Technology (GSJ/AIST), and the concentrations of many major and a few trace elements in these materials have been determined [6-8]. Data about the halogen contents in these materials is expected to significantly contribute to a better understanding of the chemistry of seawater and the marine environment, since halogens (especially iodine) are known to be extremely useful in investigating the geochemical circulation of terrestrial materials [9]. However, to our knowledge, there is not much data on the halogen contents of these carbonate materials.

The present study aims to use RNAA and instrumental NAA (INAA) to determine trace amounts of three halogens in JCp-1 and JCt-1, together with other elements. Based on the halogen data, the differences between the two carbonate reference materials is investigated.

RESULTS: To probe the utility of the halogen data in interpreting geochemical formations, we have compared the halogen contents in these two carbonate materials with those in nine sedimentary rock materials (RNAA was used to determine the halogen content in all cases [4]). The ratios for I/Cl and Br/Cl in all these materials were calculated and are shown in Fig 1. Here, the sedimentary rocks are classified into two groups (the rocks in seawater and those in inland water). The ratios corresponding to sedimentary rocks in seawater (denoted by closed triangles) tend to be lower than the ratios for the sedimentary rocks in inland water (closed circles). This can be attributed to the fact that sedimentary rocks in

seawater are affected to a greater extent by the high chlorine content in seawater. Since the two carbonate materials, coral and clam, are both found in seawater, it is reasonable that JCp-1 and JCt-1 exhibit lower ratios than the four sedimentary rocks in inland water. The ratio of I/Cl for JCt-1 is lower than those for the five sedimentary rocks in seawater, as well as lower than that for JCp-1 by more than one order of magnitude, suggesting that iodine may have been fractionated from Br during the process of formation of JCt-1.

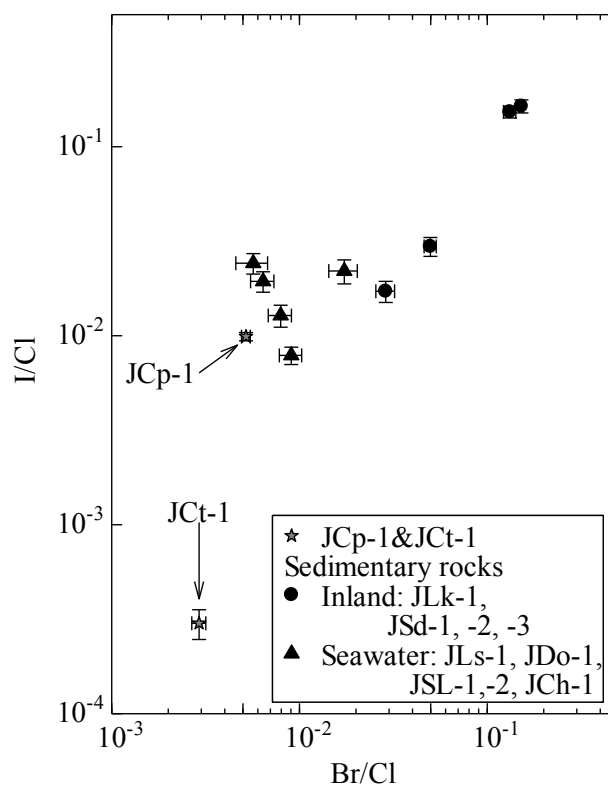


Fig. 1 I/Cl vs. Br/Cl ratios for JCp-1, JCt-1 and sedimentary rocks.

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