

Examination of anomalous fading for foraminifera luminescence dating

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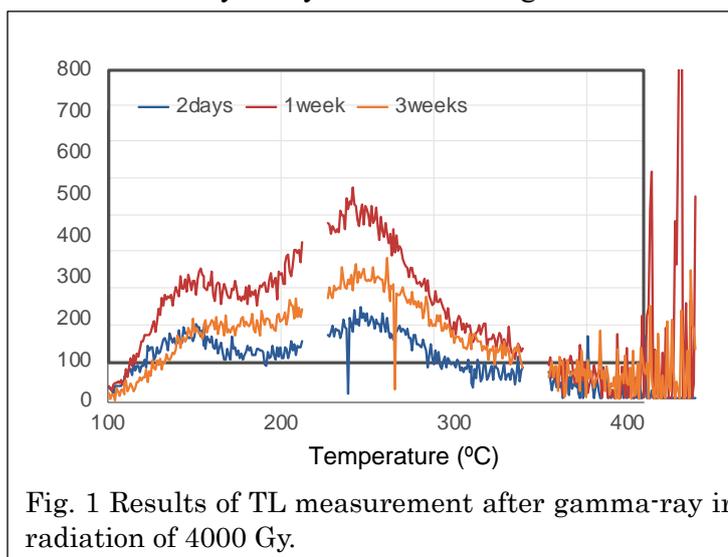
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INTRODUCTION: Luminescence dating observes the natural accumulated radiation damage caused by radioisotopes such as U and Th as a form of glow after stimulation by heating or lighting. Typically, quartz and feldspar are target minerals for thermoluminescence (TL) dating; however, carbonate minerals, although less frequently studied, have also been investigated in TL dating. Foraminifera, some species of which have carbonate shells, are found in marine sediments and are age index fossils [1]. Foraminifera fossils have often been dated by the ¹⁴C dating method. Given that TL dating has a potential, in principle, to measure older samples than the ¹⁴C method, we tested the feasibility of TL dating applied to foraminifera by examining the stability of luminescence sites formed by different radiation sources.

EXPERIMENTS: The carbonate rich ooze, whose main component is foraminifera, collected from the western tropical Pacific during IODP Expedition 363 was treated with hydrogen peroxide, rinsed with distilled water, and dried at 60°C. X-ray diffraction (XRD: Rigaku Ultima IV) identified the mineral type as calcite. This study exposed foraminifera rich samples to α (Am²⁴¹), β (Sr⁹⁰), and γ (Co⁶⁰) sources, and thermoluminescence was measured immediately or after storage in darkness for a period of time to study the luminescence fading behavior. The γ -ray exposure was carried out at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, and 4000 Gy was given to the sample. For α and β exposures, a single disc was repeatedly irradiated and measured, whereas for γ -ray exposures, multiple discs were used and each disc was measured only once. TL was measured in Kanazawa University for a temperature range of 100-450°C after a preheating at 80°C for 10 seconds. IRC-65L and R-60 filters were used. An X-rays unit (Varian, VF-50JW) is installed in the luminescence reader and characteristics of luminescence by X-ray are also investigated.

RESULTS: The luminescence signal measured in this experiment was limited to a few dozen to several hundred counts. There was no significant signal decay after α , β , and γ irradiation over several weeks (Fig. 1), while X-ray irradiated sample showed notable signal reduction within about a week. Therefore, foraminifera calcite has the potential to store luminescence from natural radiation. However, the luminescence signal intensity is weak, and only a long irradiated sample (old sample) would be dated.



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High-pressure transformations of olivine under high differential stress

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INTRODUCTION: Phase equilibria studies have demonstrated that $(\text{Mg, Fe})_2\text{SiO}_4$ olivine transforms into a spinelloid structure (wadsleyite) and then into a spinel structure (ringwoodite) with increasing pressure. Based on the characterization of planar defects in wadsleyite and ringwoodite found in meteorites, shear-promoted mechanisms were proposed for the high-pressure transformations between the olivine polymorphs [1]. The transformation models also predicted the possible occurrence of an intermediate phase with a new spinelloid structure. This phase has recently been discovered as a new mineral poirierite in shocked meteorites [2]. In this study, we have performed high-pressure transformation experiments on olivine to constrain the formation conditions of poirierite.

EXPERIMENTS: A natural $(\text{Mg}_{0.91}, \text{Fe}_{0.09})_2\text{SiO}_4$ olivine crystal was crushed into a powder with a heterogeneous grain size of less than 100 μm to generate non-hydrostatic stress among the olivine grains in high-pressure experiments. The powder was kept at 12–16 GPa and 900 °C for 120 minutes by using a Kawai-type high-pressure apparatus. The product phases in the recovered samples were first characterized using a micro-area X-ray diffractometer (XRD) at KURNS. The portions at the reaction boundaries were extracted and processed into ultrathin sections by using a focused ion beam apparatus, and then examined using a transmission electron microscope (TEM).

RESULTS AND DISCUSSION: The olivine grains partially transformed at their grain boundaries in all the experiments. XRD patterns show that the product phases are wadsleyite, wadsleyite+ringwoodite, and ringwoodite at 12, 14, and 16 GPa, respectively (Table 1). These phases occur as euhedral and subhedral crystals with grain sizes of 0.5–1.5 μm under TEM (Fig. 2). Most of the ringwoodite grains exhibit stacking faults on $\{110\}$. Their electron diffraction (ED) patterns show weak extra ED spots other than ringwoodite, corresponding to the poirierite structure (Fig. 2). The ED patterns also show that both phases have a topotaxial relationship: $(001)_{\text{Poi}}//\{001\}_{\text{Rw}}$ and $(100)_{\text{Poi}}//\{110\}_{\text{Rw}}$. Some of the wadsleyite grains exhibit stacking faults on the (010) plane, but no extra electron diffraction spots. The relict olivine grains have high dislocation densities of $1.4\text{--}2.1 \times 10^9 / \text{cm}^2$, corresponding to a differential stress of 0.5–0.6 GPa according to an olivine piezometer [3]. These microstructural and crystallographic results suggest that nanoscale poirierite lamellae are only metastably formed from ringwoodite grains above 14 GPa, when high differential stresses are applied at relatively low temperatures.

Table 1. μXRD and TEM results

Run No.	P (GPa)	T (°C)	Duration (min.)	Major products	Superlattice reflections (Rw/Wad)	Dislocation density (relict olivine) ($1/\text{cm}^2$)
OE-02	16	900	120	Rw	Common	1.4×10^9
OE-03	14	900	120	Rw>Wad	Rare	2.1×10^9
OE-04	12	900	120	Wad	No	1.6×10^9

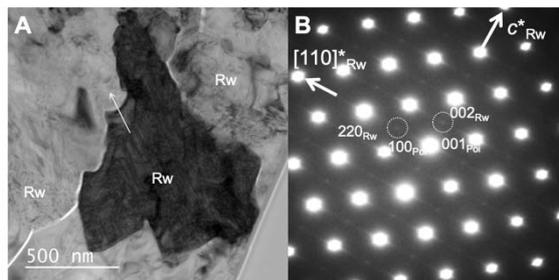


Fig. 1. Transmission electron micrograph (A) and electron diffraction pattern (B) of a ringwoodite (Rw) grain with intergrown poirierite (Poi) in the olivine sample kept at 14 GPa. The arrow in (A) indicates the direction of the stacking faults.

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NAA and Ar-Ar dating for small-sized extraterrestrial samples

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INTRODUCTION: Minor element abundances and Ar-Ar ages of extraterrestrial materials are one of the important information to elucidate the origin and evolution history of the solar system materials. We have developed and applied the combination analytical method that enables us to carry out gamma-ray measurements and Ar-Ar dating for the same individual samples of sub-milligram mass (e.g., Projects #R3007, R3038, and R3127).

EXPERIMENTS: In this project, we have conducted irradiation experiments under two different conditions in Oct 2023 and Jan 2024. The first one is a short-duration irradiation (1MW × 24 hours) for young (~300 Ma) samples with smaller amounts of radiogenic ⁴⁰Ar. We irradiated terrestrial minerals as analytical standards; Madagascar orthoclase [1] and Japanese wollastonite were used for the K and Ca corrections, respectively. The Allende CV chondrite (provided by Smithsonian museum [2]), the Murchison CM chondrite, and the Tagish Lake ungrouped-carbonaceous chondrite powdered samples were used as our laboratory standards. Plagioclase mineral separates from eucrites (Agoult, HaH262, Y-792510, Y-792769, Y980319, Y980433, and Y983366) were also irradiated. The second irradiation was conducted under our nominal condition (1MW × 47 hours + 5MW × 6 hours). In the 2nd experiment, the Asuka 12325 shergottite (a bulk sample and a shock-vein separate) and the Holbrook L/LL chondrite (a bulk and plagioclase separate) samples were irradiated in addition to the standard mineral and meteorite samples as used in the 1st one.

Each of the samples was placed in a conical dimple (φ1, depth ~ 0.5 mm) of a sapphire disk (φ5.5, 1.5 mm thick), and covered with a sapphire disk (φ5.5, 0.3 mm thick). Each of the sapphire container was wrapped with pure aluminum foil. These Al-wrapped containers were stacked and sealed in the capsules for the Hydro irradiation.

The 1st-irradiated samples were recovered from the irradiation Al capsule in Dec 2023, and a portion of the samples were transported to Kyushu University for noble gas analyses. The noble gas analyses were carried out in Jan-Feb 2024. The 2nd-irradiated samples were recovered and transported in Feb 2024. The gamma-ray measurement was done for the meteorite standards and the Holbrook samples. Noble gas analyses will be conducted in Apr 2024.

RESULTS: We have obtained noble gas data from the eucrite plagioclase separates irradiated in the 1st experiment. The ³⁹Ar/⁴⁰Ar ratios for the samples give Ar-Ar ages consistent with our previous measurements and previous reports (e.g., [3]). The analytical uncertainties on the Ar isotopic ratios of the 1st experiment samples are reasonably small. Therefore, we can choose an appropriate irradiation condition for extraterrestrial samples with various ages ranging from 300 Ma (e.g., shergottites) to 4.6 Ga (e.g., eucrites and chondrites). We are currently calculating precise Ar-Ar ages and preparing a paper in conjunction with the data we have obtained in the series of our experiments at KUR. The NAA data and Ar-Ar age for the Holbrook chondrite will also be obtained and compiled for another publication, along with the data obtained by Dr. Sekimoto.

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Gallium concentration of GSJ rock samples

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INTRODUCTION: Geological reference materials are used as a terrestrial standard in various studies. The Geological Society of Japan issues rock reference materials, which are mainly composed of igneous and sedimentary rocks that were collected throughout Japan. Although these are standard reference materials, not all elemental concentrations have been certified within them. Gallium (Ga) is one element that has not been certified in all reference materials. Although Ga is a metal, it exists in the crust at high concentrations at 18 ppm [1]. Since the advent of Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) and the development of high precision isotope measurements for low concentrated elements, Ga has been recently studied extensively, in terrestrial [2, 3], lunar [4] and meteorites [5]. Currently, there are 14 rock standards that do not have a certified value. In this study, we measured the Ga concentration in GSJ rock reference samples that do not have a certified Ga concentration value as well as those that do have for confirmation.

EXPERIMENTS: Samples used in this study were JA-1a (Andesite), JB-2a (Basalt), JB-3a (Basalt), JB-1b (Basalt), JF-1(Feldspar), JG-1(Granodiorite), JGb-1(Gabbro), JSy-1(Syenite). 0.1 g of rock samples were measured and dissolved in a HNO₃ and HF solution and heated at 100°C for 1 week. The samples were then dried down and redissolved in HCl. The Ga concentration was measured by Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS) at Kyoto University.

RESULTS: Out of the samples measured for their Ga concentration in this study, JB-1b, JB-2a and JB-3a do not have certified values. Their Ga concentrations were JB-1b: 20.3 ppm (n = 2), JB-2a: 20.3 ppm (n = 2) and JB-3a: 22.9 ppm (n = 2). For samples that have a known value, their values were JA-1a: 27 ppm (n = 1), JF-1: 31 ppm (n = 1), JG-1: 31 ppm (n = 1), JGb-1: 24.2 ppm (n = 2), JSy-1: 37ppm (n = 1). These values were all up to 1.7 times enriched compared to literature values [6] suggesting that further measurement of multiple batches of the samples is needed.

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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 the evolving Philippine Sea Plate for the period immediately before and after subduction initiation at ~52 Ma to form the Izu-Bonin-Mariana arc is prerequisite to understand cause of subduction initiation. Understanding of nature and origin of overriding and subducting plates is especially important because plate density is a key parameter controlling subduction initiation based on numerical modelling. There is increasing evidence that multiple geological events related to changing stress fields took place in and around Philippine Sea plate about the time of subduction initiation at ~52 Ma [1,2]. To understand tectonics during the period of subduction initiation, it is important to understand the pattern and tempo of these geological events, particularly the duration and extent of seafloor spreading in the Mesozoic arc terrane (Daito Ridge Group). This year we focused on the intersection of the WPB spreading center and the Kyushu-Palau Ridge, which is a remnant of ancient Izu-Bonin-Mariana arc, to understand tectonic relationship between the West Philippine Basin (WPB) and the Izu-Bonin-Mariana arc. This remains one of the key issues to reconstruct tectonics at subduction initiation of the Philippine Sea Plate.

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 180 – 250 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: 5 samples from the western escarpment of the Kyushu-Palau Ridge have been dated by the laser-heating $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique. These basaltic samples show age range between 32.0 and 33.0 Ma. The strike of the escarpment is at high angle to the remnant spreading center of the WPB, probably formed as fault along the boundary between the KPR and the WPB in association with spreading of the WPB. Ages of basaltic lava blocks from this escarpment provide constraint on the age of formation of this escarpment, i.e., the escarpment must have formed after these volcanics. This means that the escarpment probably formed after 32 Ma, which implies that the intersection between the spreading center and the Kyushu-Palau Ridge occurred after this age.

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Experimental evaluation of shock-induced reactions of carbonate minerals: Implications for understanding environmental change by planetary impacts

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INTRODUCTION:

Planetary impacts by asteroids and comets can dramatically alter the state of the planetary surface due to their high energy density. Carbonate minerals are the main reservoirs of carbon species (e.g., CO₂ and C) on the Earth's surface, and have significant effects on the carbon cycle and atmospheric circulation in the Earth. To model planetary impacts and evaluate impact-induced environmental changes, we need to understand the shock behavior of carbonate minerals under extreme conditions induced by the impact process. In this study, shock-compression recovery experiments were performed on several carbonate minerals to experimentally simulate planetary impacts. After shock compression, the recovered samples were investigated by X-ray diffraction (XRD) measurement for crystal phase identification and by transmission electron microscopy (TEM) for microstructural observation in order to evaluate the shock metamorphism and shock-induced reactions of carbonate minerals.

EXPERIMENTS:

Shock recovery experiments were performed using a single-stage propellant gun at the National Institute for Materials Science, Japan [1]. The peak shock pressure was estimated by the impedance mismatch method [2]. After the experiments, shocked sample were subjected to XRD analysis for the phase identification, using a Rigaku Ultima IV diffractometer with CuK α radiation driven at 40 mA and 40 kV, which is installed at the Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS). In addition, the shocked sample was subjected to TEM and scanning transmission electron microscopy (STEM) analyses. Several 150 nm thick sections for TEM and STEM analysis were prepared using focused ion beam (FIB) instruments FEI Quanta3D200i installed at KURNS, and HITACHI SMI4050 installed at the Japan Agency for Marine Earth Science and Technology (JAMSTEC). TEM and STEM observations of the ultrathin sections were performed using a transmission electron microscope (JEOL JEM– ARM200F) at JAMSTEC, operating at an accelerating voltage of 200 kV.

RESULTS:

We have successfully performed shock recovery experiments on three types of carbonate minerals: calcite CaCO₃, dolomite CaMg(CO₃)₂, and siderite FeCO₃. Each sample was subjected to the shock pressure of 35, 40, and 45 GPa, respectively. The result of XRD measurements showed the presence of MgO, FeO and Fe₃O₄ as decomposition products of dolomite and siderite in shock induced reactions. The decomposition reaction of dolomite and siderite occurs at shock pressures above ~40 GPa due to the high temperature and high pressure caused by shock compression. Based on these results, we first focused on dolomite and tried to observe the shock deformation microstructure by TEM. The TEM observation revealed a bubbled microstructure as a trace of the decomposition reaction of dolomite: CaMg(CO₃)₂ \rightarrow MgO + CaCO₃ + CO₂ (Figure 1). Selected area electron diffraction (SAED) results of this structure showed the presence of MgO (inset in Figure 1). In future work, we will try to clarify the dominant shock response of other carbonates at each shock pressure. Our goal is to establish the shock metamorphic indicator of carbonate minerals through the study of other recovered samples.

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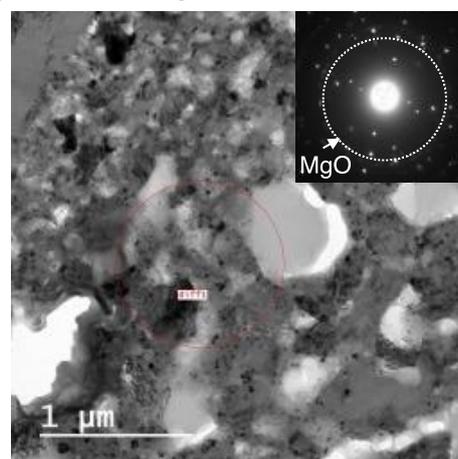


Fig. 1. TEM image of recovered dolomite shocked at 40 GPa. Inset: SAED pattern obtained from the area diff 1.

Determination of Abundance of Rare Metal Elements in Seafloor Hydrothermal Ore Deposits by INAA Techniques-10: Determination of Barium in Sulfide-sulfate Ore

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INTRODUCTION: Instrumental neutron activation analysis (INAA) has several advantages for geochemical tools to provide useful information for mineral exploration. For example, INAA enables highly sensitive multi element analysis without geochemical pretreatment. We have conducted studies using mineralized samples collected from seafloor hydrothermal deposits, with a view to extend the range of application of this technique. Barite (BaSO_4 as chemical formula) is one of gangue minerals of seafloor hydrothermal ore deposits and Ba content in sulfide-sulfate ore widely varies from a few hundred ppm to more than 50 wt%. Since barite is useful for chronological studies, we focus on determination of Ba content in this report.

EXPERIMENTS: 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 (3~10 minutes). Barium content was determined using the peak at 165.85 keV of Ba-139 ($t_{1/2}=1.38$ hours). 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 20 minutes, and the gamma ray activity was measured for 15 minutes after adequate cooling time (~30 hours). Barium content was determined using the peak at 496.26 keV of Ba-131 ($t_{1/2}=11.8$ days).

RESULTS: In the case that Ba content is less than 1000 ppm (=0.1 wt%), determination by Ba-139 was inaccurate because of high background level. Determination by Ba-131 is applicable for sulfide-sulfate ore with Ba content around a hundred ppm. Figure 1 shows the result of comparison between Ba content determined by Ba-131 and that determined by Ba-139. The latter content was systematically lower than the former content, although scatter of data is not so significant. Further study based on a cross check with other analytical techniques is necessary.

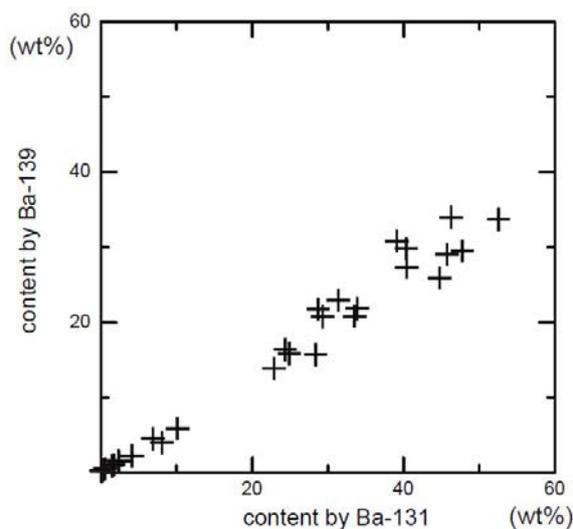


Fig. 1. Comparison between Ba content determined by Ba-131 and Ba content determined by Ba-139

Yearly Change in Concentration of Soil Particles in the Atmospheric Aerosols at Sakai

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The soil particles in the atmospheric aerosols which are main constituents in the atmospheric coarse particles have made a yearly decreasing change in the concentration of the coarse particles observed at Sakai (Fig.1). The decrease trend in the soil particles have been estimated from the result of concentration change in Al,Ca, which are the main elements in the soil particles. We found the difference of the increase (decrease) trend in the Al,Ca concentration by the coarse particle size ranges ($>11\mu\text{m}$, $7.0-11\mu\text{m}$, $4.7-7.0\mu\text{m}$, $3.3-4.7\mu\text{m}$, $2.1-3.3\mu\text{m}$). The most largest particle size range ($>11\mu\text{m}$,) has the biggest decrease rate, meaning the contribution from local soil effect has decrease trend. By the way, in the smallest particle size range($3.3-4.7\mu\text{m}$, $2.1-3.3\mu\text{m}$), Ca has bigger decrease trend than other particle size range ($7.0-11\mu\text{m}$, $4.7-7.0\mu\text{m}$,) contrast to Al decrease trend that does not show explicit difference between the ranges ($7.0-11\mu\text{m}$, $4.7-7.0\mu\text{m}$, $3.3-4.7\mu\text{m}$, $2.1-3.3\mu\text{m}$). This result shows the characteristic change in element on the China land particle(,Kosa Particle) which effect the smaller soil particle($3.3-4.7\mu\text{m}$, $2.1-3.3\mu\text{m}$)[1] because of its easy transportation in the long distance. This characteristic change in the constituents elements in which Al and Ca are main constituents , might make the decrease trend of ratio of Ca to Al (Ca/Al)(Fig.2).

METHODS: Aerosol samples have been collected by the Andersen sampler which can collect the atmospheric aerosols by 9 particle size ranges ($>11\mu\text{m}$, $7.0-11\mu\text{m}$, $4.7-7.0\mu\text{m}$, $3.3-4.7\mu\text{m}$, $2.1-3.3\mu\text{m}$, $1.1-2.1\mu\text{m}$, $0.65-1.1\mu\text{m}$, $0.43-0.65\mu\text{m}$, $<0.43\mu\text{m}$) at Sakai,Osaka since 1994. The atmospheric aerosols are collected on polyethylene sheet($80\text{ mm}\phi$) attached to the dishes in the each particle size. The elements in the particles of some samples were analyzed by the neutron activation analysis using Kyoto Nuclear Reactor.

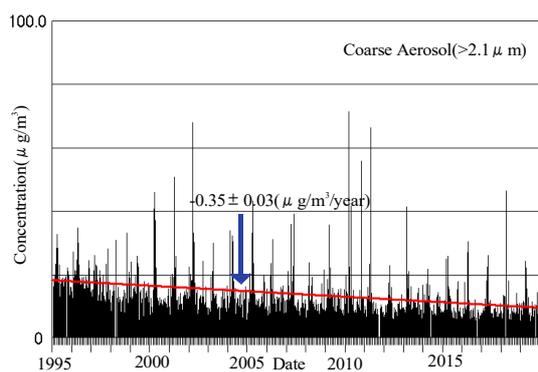


Fig.1 Yearly change in coarse particle concentration at Sakai since 1994

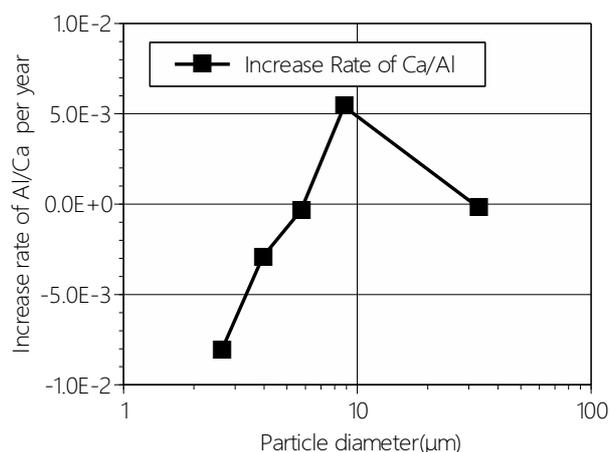


Fig.2 Increase rate of Ca/Al by the particle size range in the coarse atmospheric aerosols

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Absorption of alkali metal ions by white radish sprouts (V)

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INTRODUCTION: According to a consumer awareness survey on agricultural, forestry, and fisheries products produced in the disaster area conducted by the Consumer Affairs Agency in January 2024; Of those who answered that they "care" or "somewhat care" about the country of food production when shopping, 9.3% said "I want to buy food that does not contain radioactive materials." even though it has been about 13 years since the Fukushima Daiichi Power Plant accident occurred [1]. Therefore, in order to prevent damage by rumors it is necessary separating radioactive cesium from the soil.

Our previous reports have shown that adding the stable cesium to contaminated soil and growing plants can remove radioactive cesium from the soil [2, 3]. However, addition of excess amount of stable cesium caused an obstacle to growth of plant [4]. Therefore, in the present work, effects of alkali metal ions on plant growth were investigated using white radish sprouts.

EXPERIMENTS: Hydroponic cultivation of white radish sprouts was carried out by adding various concentrations of cesium or the congener element rubidium ion. Cultivation was also carried out in soil (andosol and vermiculite) that had been simulated decontaminated using cesium or rubidium, and determination of trace elements in leaves and stems was performed by INAA. Soil washed with water after simulated decontamination was also studied. 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.

RESULTS: The results of soil cultivation experiments are described here. In the cultivation experiment after simulated decontamination, andosol or vermiculite was immersed in 0.01 mol/L CsNO₃ or RbNO₃ and then either left unwashed or washed once or three times with water. No growth disorder was observed in the white radish sprouts grown in each soil. As a result of our separate experiments, 0.014 or 0.14 mol/L of Rb⁺ and Cs⁺ showed a decontamination rate of about 40% for andosol, and that of 10 to 15% for vermiculite. The Cs⁺ and Rb⁺ contained in leaves and stems of radish sprouts grown in andosol were 2 to 10 times higher than those grown in vermiculite. Concentration of both ions decreased as the number of washings increased. Generally, Cs ions are easily adsorbed by vermiculite. However, no difference in the uptake rate between Cs⁺ and Rb⁺ was observed because Cs⁺ was washed before being adsorbed to the adsorption sites of vermiculite. A tendency for K⁺ concentration in the stems of radish sprouts grown in the andosol used for simulated decontamination with Cs to decrease was observed, suggesting that absorption of K⁺ was inhibited. However, no effect was observed on the appearance of growth. No significant changes were also observed in the concentrations of other trace elements.

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Basic Research on Trace Elemental Analysis of Airborne Particulate Matters in an Environment by INAA & IBA

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INTRODUCTION: To discuss the elemental distribution of airborne particulate matter (APM) in environments with large variability, it is necessary to accumulate a large amount of measurement data. This requires sufficient time and a large number of samples. In order to efficiently perform a large number of measurements and analyses, we believe it is important to use both ion beam and reactor-based analytical methods in parallel. Tokyo City University Atomic Energy Research Laboratory (TCU-AERL) operated the Musashi reactor until 1989 and conducted research using neutrons, including instrumental neutron activation analysis (INAA). Although currently in the decommissioning phase, the facility is still in operation for RI-based experiments. In 2018, a 1.7 MV Pelletron Tandem Accelerator (TCU-Tandem) was installed and began research using IBA [1], including particle-induced X-ray emission (PIXE) [2] and ion beam induced ion luminescence (IBIL) analysis [3-4]. In this study, APM samples were analyzed for trace elements by instrumental neutron activation analysis and ion beam analysis using a tandem accelerator.

EXPERIMENTS: A high-capacity air sampler (Shibata Scientific Technology LTD: AD-VAN-TEC, QR-100 (collection efficiency: 99.99% for 0.3 μm particles)) was used, with an intake flow rate of 700 L min^{-1} . The radioactivity of the collected filters was measured with a high-purity germanium (HP-Ge) semiconductor detector, and some of the filters were stored for INAA. Irradiation was performed at the research reactor KUR at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, and four machine times were conducted from October to February in FY2023. Irradiation conditions are shown in Table 1.

RESULTS: Several samples of stocked airborne dust were measured. In addition, PIXE and IBIL analysis is being conducted at TCU-Tandem. Figure 1 shows an example of a typical IBIL spectrum. It shows IBIL measurements of compounds containing various forms of Eu, where luminescence is easily observed. Different chemical bonding states have different energy levels, and light originating from transitions between different energy levels was identified.

Table 1. Irradiation conditions

Irradiation			Operating power	Thermal neutron flux
date	time	position		
2023/10/11	60 min	Pn-2	1 MW	5.5×10^{12} n/cm ² /sec
2023/12/6	60 min	Pn-2		5.5×10^{12} n/cm ² /sec
2024/2/7	60 min	Pn-2		5.5×10^{12} n/cm ² /sec
2024/2/14	30 sec	Pn-3		4.7×10^{12} n/cm ² /sec

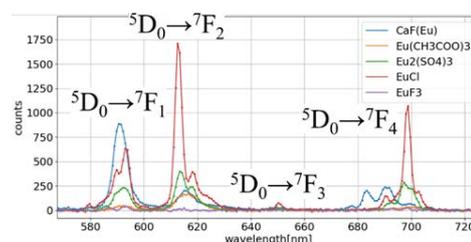


Fig. 1. Examples of IBIL spectra of Eu

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Model Improvement for the Transport of Cs in Soil on Forest Slopes

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INTRODUCTION: In this study, the estimation model for the transport of radioactive Cs in the forest slope, which was developed in the previous study [1] to evaluate the distribution of radioactive Cs concentrations in soil and changes over time in air doses in forests resulting from the Fukushima Daiichi Nuclear Power Plant accident, is first improved to be more realistic by examining the physical meanings of the parameter values used in the model. Furthermore, we will measure the distribution of radioactive Cs in forest soil in the slope direction in Kawauchi-village, Fukushima Prefecture, to examine the validity of the simulation results using the improved model by comparing them with the measured values, which was not done in the previous study.

MODEL IMPROVEMENT: As an improvement of the model, the previous study assumed that the flow rate in the forest soil becomes constant after a certain distance from the top of the slope. In this study, the maximum value of the flow rate was determined from the saturated hydraulic conductivity and the hydraulic head gradient, and the flow rate was improved to be constant after reaching that value. The values of the saturated hydraulic conductivity and the depth of the slope through which water flows were adjusted so that the simulation results were close to the measured concentration of radioactive Cs in the soil of a wooded area in Mariyama district of Kawauchi Village, Fukushima Prefecture as shown in Fig. 1. The estimated saturated hydraulic conductivity value of 5×10^{-3} cm/sec and the soil depth of 5 cm on the slope through which water flows are considered to be reasonable values for a forest in this area.

MODEL VALIDATION: The improved model was validated using measured data in 2018 and 2023 in Modo Area, Kawauchi Village, Fukushima Prefecture, and estimated values for the concentration of radioactive Cs in rice fields, which is estimated from the cumulative amount of radioactive Cs discharged after the Fukushima Daiichi Nuclear Power Plant accident, were close to the measured values in both years. In the measured data, there were cases where the concentration increased or decreased between 2018 and 2023, even at the same lower end, depending on the slope, and it was difficult to match the simulation results of the secular change of concentration to the measured values for all slopes.

RESULTS: In the improvement of the model for estimating the amount of radioactive Cs in forests in the direction of slope, the slope inclination and saturated hydraulic conductivity of soil were assumed to be constant over the entire area of the slope in this study. However, in order to reproduce the actual measured values of soil radioactive Cs concentrations on the slopes in the Modo area in the simulation, it was considered necessary to consider the case where these values vary from place to place.

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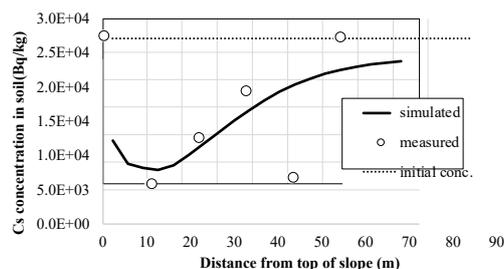


Fig. 1. Fitting of parameters by comparison with measured data.

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

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INTRODUCTION: Radiometric dating is a valuable tool for unveiling the formation and evolution process of planetary material. The K-Ar and ^{40}Ar - ^{39}Ar methods are invaluable in determining the timing of heating events on planetesimals and asteroids (e.g. Swindle et al. (2014) [1]). The ^{40}Ar - ^{39}Ar dating method with laser heating technique is suitable for tiny samples (e.g. Kelley, 1995[2] and Hyodo, 2008 [3]). To obtain ^{40}Ar - ^{39}Ar dates of the extraterrestrial material using the facility in KURNS, we have continued developing a ^{40}Ar - ^{39}Ar dating system, which includes laser-heating gas extraction and gas purification lines. The system was initially designed by Dr. R. Okazaki (Kyushu University) and has been developed for several years. Previous progress reports have de-scribed details and the schematic diagram of the system (Nos. 31126, R2079, R3121, R4068).

EXPERIMENTS: In FY2023, we continued assembling the gas extraction and purification system (Fig. 1). We baked out the gas extraction and gas purification lines to attain ultra-high vacuum conditions. We also degassed the SORB-AC pump. Separately, we commissioned the Nd-YAG laser.

RESULTS: After the bakeout of gas extraction and gas purification lines, vacuum pressure in the vacuum plumbing lines reached 1×10^{-6} Pa at a vacuum gage on the top of the turbomolecular pump and 4×10^{-4} Pa at a vacuum gage in the purification line under pumping. The vacuum quality is insufficient for ^{40}Ar - ^{39}Ar dating in KURNS, so we need more bakeout treatments. We tried to test-run the Nd-YAG laser, but we couldn't confirm the presence of laser output. It is necessary to reexamine the condition of Nd-YAG laser equipment and its usage procedure.

The next step in this development is to install a charcoal trap on a gas purification line, install a quadrupole mass spectrometer, and make an electrical connection for a noble pump.

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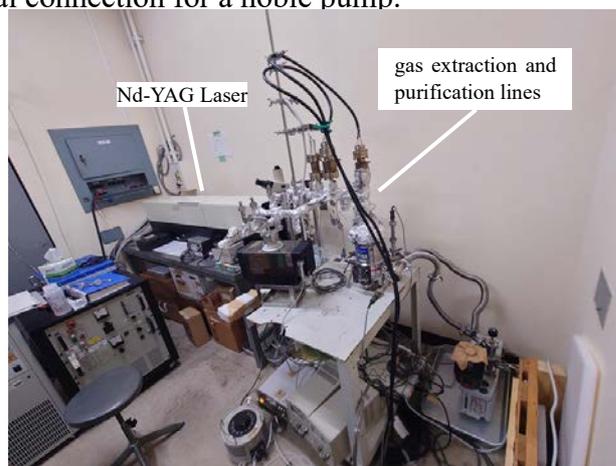


Fig. 1. Overview of the ^{40}Ar - ^{39}Ar dating system. The layout of the equipment was changed in FY2023.

An Evaluation of Three Halogens (Cl, Br, and I) Data from a GSJ Geochemical Reference Materials by RNAA

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INTRODUCTION: Among the five halogens, F, Cl, Br, and I are present in the environment as stable elements. Halogens are highly mobile, volatile, and incompatible elements in a range of geochemical processes. Due to their chemical characteristics, these elements have been widely used to trace the water cycle in subduction zones, understand the mechanism of magma degassing, and evaluate the recycling of solid earth materials in the crust and mantle. Despite the importance of halogens in geochemical processes, the determination of halogens in geological samples is scarce. The reason for this is the difficulty in determining these elements due to their volatility and low concentrations in geological samples. In this study, a total of 12 GSJ geochemical reference materials (JA-1, JB-2a, JB-3a, JF-2, JG-3, JGb-1, JH-1, JP-1, JR-3, JCp-1, Jct-1, and JSO-1) were analyzed by using RNAA. This will contribute to establishing certified or recommended values of these halogens for these materials and to expanding the utility of these materials for the determination of halogens.

EXPERIMENTS: The analytical procedure of RNAA is described in Sekimoto and Ebihara [1]. GSJ reference materials were weighed into plastic vials and an appropriate amount of each halogen standard solution dropped on a filter paper was sealed in polyethylene as halogen reference samples. Both of these were irradiated for 10 min at the Kyoto University Research Reactor Institute. Known amounts of three halogens and Mn carriers were added into a Ni crucible with the irradiated reference materials and then were fused in NaOH. The fuse cake was digested in water, and a hydroxide precipitate was removed from the supernatant, which contained the halogens. After acidification of the supernatant, iodine was precipitated as PdI₂, and Cl and Br were precipitated as a mixture of AgCl and AgBr precipitates. These precipitates were subjected to the measurement of ¹²⁸I, ³⁸Cl, and ⁸²Br. The chemical yields of the three halogens during radiochemical separation were determined using the reactivation method.

RESULTS: The mean values for the chemical yields were 72% for Cl, 58% for Br, and 67% for I in this study. Our three halogen contents were compared with the literature values obtained using NAA, IC, ID-MS, ICP-MS, and NI-NGMS. Our RNAA data for the three halogens are in agreement with literature values using NAA, ID-MS, and IC. Almost all of our RNAA data are higher than the NI-NGMS [2] and ICP-MS [3] data. In NI-NGMS, the sample is irradiated with a high dose of neutrons, and the noble gas nuclides produced through beta-decay of the neutron capture halogen nuclides are extracted by stepwise heating, it is likely that the lower values produced by NI-NGMS can be explained by the loss of noble gases during the procedure. In the ICP-MS procedure with pyrohydrolysis, a sample mixed with V₂O₅ is placed into a quartz tube and heated. The evaporated Br and I are collected in a trap solution containing tetramethylammonium hydroxide. As mentioned by Sekimoto and Ebihara [1], the quantitative collection of Br and I cannot always be achieved by the pyrohydrolysis for some solid samples. Thus, our higher Br and I values can be explained by the fact that the quantitative collection of Br and I cannot be achieved in the ICP-MS procedure combined with pyrohydrolysis.

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Halogen and noble gas characteristics of Archean ultramafic rocks from the Isua Supracrustal Belt in southwestern Greenland

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INTRODUCTION: Since some of the halogens (fluorine, chlorine, bromine, and iodine) are converted to corresponding noble gas isotopes by neutron irradiation and detection limits for noble gas isotopes by mass spectrometry are low (down to ten thousand atoms), they can be analyzed with high sensitivity by using neutron irradiation and noble gas mass spectrometry [1]. We investigated the halogen and noble gas geochemistry of ultramafic rocks from the Isua Supracrustal Belt (ISB) in southwestern Greenland. Water plays a crucial role in recycling volatiles on Earth through the subduction of oceanic/crustal plates, but the composition of mantle volatiles and their modification processes remain largely unknown. In this study, noble gas and halogen analyses were performed on Archean ultramafic rocks from ISB to constrain the volatile element evolution of the mantle. The ISB is an arch-like supracrustal package about 30 km long and 4 km wide, subdivided into two terranes, southern (3.8 Ga, where Ga = billion years ago) and northern (3.7 Ga). The 3.7 Ga terrane contains ultramafic bodies, including dunite (olivine-dominated peridotite) lenses A and B [2]. Both have different and complex metamorphic histories, such as hydration and dehydration (e.g., [3]). The origin of the dunite has been proposed as either residual peridotite of mantle melting [2] or as olivine cumulate formed from basaltic melt intruding the crust [4]. The Lens A dunite samples are likely composed of primary olivines, except for grain boundaries. Valuable information from this period may be preserved within the fluid/melt inclusions in the olivines.

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 ultra-high-vacuum, noble gas extraction, purification, and separation line. Noble gases were extracted from the samples by heating up to 1800°C, purified with hot Ti-Zr getters, separated into each noble gas with temperature-controlled cold traps, and then determined their isotope compositions with a noble gas mass spectrometer [1]. The thermal and fast neutron flux was estimated from the production of ³⁹Ar and ³⁸Ar from ³⁹K and ³⁷Cl in the Hb3gr hornblende standard, in which K and Cl contents have been determined.

RESULTS: The noble gas composition of fluid/melt inclusions in the peridotites reflects the contribution of noble gases from a radiogenic (crust-like) component. Two models can be proposed to explain the crustal noble gas signatures: (1) slab-derived fluid/melt penetrated and was trapped in the dunite, and (2) crustal fluid was trapped in the dunitites during the metamorphism of the ISB. If (1) is correct, it suggests the possibility that the mantle experienced substantial contributions from radiogenic components in fluids/melt derived from partial melting of the slab.

Halogen compositions of the Lens A dunitites are consistent with (1) since the halogen composition cannot be explained without the contribution of a slab-derived subduction component. The results of this study suggest the possibility that the recycling of volatile components into the mantle beneath ancient subduction zones was more active than it is today, indicating an essential process for modifying volatile components in the mantle during this period [5].

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Improvement of Determination Method of Uranium-Containing Particles as Close-In Fallout from A-Bomb Using Fission-Track Analysis

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INTRODUCTION: The fission track analysis technique combined with heavy-liquid separation developed in the previous work demonstrated to be effective in detecting particles containing a high concentration of uranium in soil samples [1]. This method can detect the presence of uranium particles by detecting a cluster of fission tracks. The soil particle sample in which many clusters were detected in the previous work was observed using SEM/EDX, and particles containing several percent uranium were found. Since the concentrations of uranium of particles derived from the atomic bomb would be much higher, these particles are thought to be natural soil particles containing high concentrations of uranium. It is necessary to distinguish between natural and atomic bomb-derived uranium particles to extract the latter particles in a soil sample. Uranium particles derived from the atomic bomb have a higher ^{235}U content than natural soil particles, so particles of the same size generate more than thousand times tracks in the fission track analysis. Therefore, it might be possible to distinguish between natural particles and atomic bomb-derived uranium particles by reducing neutron irradiation fluence in the fission track analysis.

EXPERIMENTS: A part of soil sample collected in Hiroshima was mixed with sodium polytungstate (SPT) solution adjusted to 3.0 g/cm^3 and centrifuged at 3000 rpm for 10 minutes to separate particles of higher relative density particles. The separated particles were collected on a PTFE filter and attached to a track detector. Particles and the detector were irradiated by about $3 \times 10^{13} \text{ n/cm}^2$ of thermal neutrons using the pneumatic irradiation facility (TC-Pn) at Kyoto University Research Reactor. After the irradiation, the track detectors were etched and observed by optical microscope.

RESULTS: The number of tracks generated by one particle under the above irradiation conditions is estimated to be about ten thousand by assuming that the uranium particles derived from the atomic bomb have a diameter of $2.5 \mu\text{m}$, uranium concentration of 100% (^{235}U isotope ratio of 80%), and a specific gravity of 19 g/cm^3 . On the other hand, even if natural uranium-rich soil particles are assumed to have a diameter of $10 \mu\text{m}$, a concentration of natural uranium of 10%, and a specific gravity of 3 g/cm^2 , the number of generated tracks is expected to be less than one. Those mean only the uranium particles derived from the atomic bomb will be detected as clusters of tracks.

An example of the detected cluster is shown in figure 1. The cluster has several thousand tracks, and the particle generating this cluster is thought to be originated from the atomic bomb. However, no particles containing high concentrations of uranium could be found using SEM. Since the particle size estimated by the number of tracks is few μm which is less than position resolution of the SEM system applied in this work, it is considered difficult to detect.



Fig. 1 The cluster of fission track generated by neutron irradiation using TC-Pn of KUR.

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Concentration of ^{137}Cs in litter in *Quercus serrata* and *Cryptomeria japonica* forests

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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 [1–7]. 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. 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. We directly measured root distribution of *Cryptomeria japonica* [3], indicating that mature it is not effective to absorb radiocesium by the root uptake due to the distribution of the fine root [3, 5]. The radiocesium is higher in Konara than in *Cryptomeria japonica* [1]. *Quercus serrata* with shallow roots and lateral distribution is more likely to absorb radiocesium than *Cryptomeria japonica*.

Focusing on litter, from which radiocesium is more easily leached than mineral soil, the distribution of radiocesium in litter in *Quercus serrata* and *Cryptomeria japonica* forest in a 1m x 1m area was investigated. We measured the concentration of radioactive cesium in litter layer, and then we re-considered most severe absorption concentration of it.

EXPERIMENTS: Litters were collected at the Koriyama, Fukushima. The sampling sites were forest in *Quercus serrata* and *Cryptomeria japonica*. The collected the samples in the field were transported to the laboratory and stored it in the dark for 12 years. The ^{137}Cs in the litter was determined by gamma-ray spectrometry (HPGe). The concentration of ^{137}Cs was corrected on March 12, 2011.

RESULTS: ^{137}Cs in litter were from 1.3×10^4 Bq/kg to 1.7×10^4 Bq/kg (av: $(1.6 \pm 0.1) \times 10^4$ Bq/kg, $n=10$) in *Quercus serrata* area and from 1.6×10^4 Bq/kg to 3.2×10^4 Bq/kg (av: $(2.2 \pm 0.5) \times 10^4$ Bq/kg, $n=10$) in *Cryptomeria japonica* area. The average transfer factors of stable Cs estimated for the sapwood region ($9.59 \pm 2.56 \times 10^{-3}$ for *Quercus serrata* and $8.34 \pm 2.55 \times 10^{-4}$ for *Cryptomeria japonica* [1]). Therefore, even under the condition that all fine roots are in the litter layer, utmost ^{137}Cs in the xylem for *Quercus serrata* and *Cryptomeria japonica* would be 150Bq/kg and 18 Bq/kg, respectively. However, such concentration of it in the xylem for *Quercus serrata* are not found in the area. Currently, it is considered as follows: 1) the leaching rate of radioactive cesium in litter is not so high, and 2) the fine roots of *Quercus serrata* are also located deeper in the soil and are not easily leached into the soil water. Therefore, even if we take the most conservative conditions into account, the amount of ^{137}Cs in xylem will not increase.

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Identification of Products in Traces of "Black Rain" on the Gold Folding Screen (made of Western gold leaf)

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INTRODUCTION: In 2022, the gold folding screen (Western gold leaf: copper alloy foil containing zinc) with traces of the "Black Rain" was discovered in a private house in Hiroshima City. As a result of analyzing the traces with an optical microscope and an electron microscope, it was found that Cu, the main component of the gold leaf, was dissolved by S and N, which are elements thought to constitute the "Black Rain". Consequently, we aimed to identify the products containing Cu, S, and N by X-ray diffractometry (XRD). Furthermore, we attempted to verify the products obtained from the corrosion simulation experiment of a model gold screen using sulfuric acid containing S and nitric acid containing N.

EXPERIMENTS: Three gold folding screen pieces with black traces (Sample ID: No.3, No.6, No.8), a control piece (No.2), and products obtained from corrosion simulation experiments were analyzed using a fully automated X-ray diffractometer (Rigaku SmartLab Cu K α source, tube voltage 40 kV, tube current 200 mA, micro-incident optics, scan speed 0.5°/min). In simulated experiments, aqueous solution at pH 1 is dropped onto a model gold screen "RSY-001" (Western gold leaf) and exposed indoors for several days to months.

RESULTS: Analysis of the black traces of No. 3 shown in Fig. 1 revealed copper sulfate pentahydrate (presumed) as indicated by the arrow in Fig. 2, but no copper nitrate compounds were detected. No copper nitrate compounds were not detected in No.6 and No.8. This is presumably due to the amount of traces and the presence or absence of crystallinity. That is, copper sulfate hydrate is detected due to its crystalline nature, but copper nitrate compounds are not detected due to their tidal nature[1]. The experimental results showed that the copper sulphate hydrate was a crystalline product and the copper nitrate compound (presumed) was a liquid product. The ageing products have not been analyzed. In conclusion, no copper nitrate compounds were detected in the "Black Rain" traces on the gold screen, but copper sulfate hydrates were estimated to be mixed in the traces. This suggests the possibility that sulfuric acid was mixed in the "Black Rain".

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ACKNOWLEDGMENTS: We are grateful to the staff of the Hiroshima Peace Memorial Museum, especially the curatorial staff and the donor for permission to cut the gold folding screen. We thank Rekiseisha Co., Ltd. for a model gold screen and Prof. Takuo Okuchi of our institute for his guidance in XRD analysis.

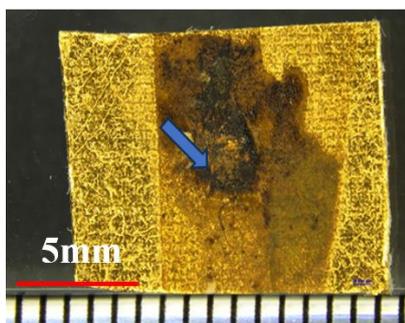


Fig.1 "Black Rain" trace of No.3 cut from the gold folding screen.

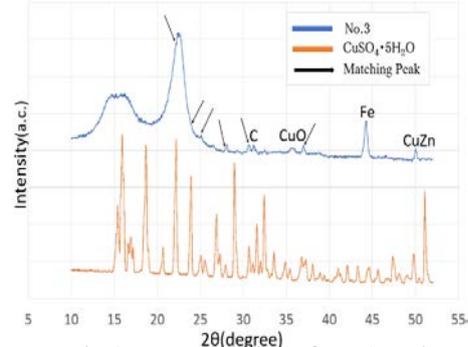


Fig.2 XRD profiles of No.3 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.