Study of Earth and Planetary Matters by Thermoluminescence

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TL OF ORDINARY CHONDRITES: Induced TL (thermoluminescence), the response of a luminescent phosphor to a laboratory dose of radiation, reflects the mineralogy and structure of the phosphor, and provides valuable information on the metamorphic and thermal history of meteorites. Especially the sensitivity of the induced TL is used to determine petrologic subtype of unequilibrated ordinary chondrites [1]. Natural TL, the luminescence of a sample that has received no irradiation in the laboratory, reflects the thermal history of the mete-orite in space and on Earth. Natural TL data thus provide insights into such topics as the orbits of meteoroids, the effects of shock heating, and the terrestrial history of me-teorites [2]. Usually natural TL properties are applied to find paired fragments [3-5].

  We have measured TLs of 193 Yamato and 136 Asuka unequilibrated ordinary chondrites [6]. This time we measured induced and natural TL properties of thirty Yamato unequilibrated ordinary chondrites (LL3: 4, L3: 18, H3: 8) from Japanese Antarctic meteorite collection. Sampling positions of these chondrites were measured by GPS.

PAIRED FRAGMENTS: As reliable pairing approach, TL properties within large chondrites were analyzed, taking advantage of the fact that serial samples from these meteorites are known to be paired. Then a set of TL pairing criteria: 1) the natural TL peak height ratios, LT/HT, should be within 20%; 2) that ratios of raw natu-ral TL signal (LT) to induced TL signal (TL Sensitivity) should be within 50%; 3) the TL peak temperatures should be within 20℃ and peak widths within 10℃ was proposed [3].

    Above pairing criteria were applied to the 30 samples. Figure 1 shows how to search fragments satisfying the pairing criteria 1) and 2). We found 15 TL potential paired fragments. . They constructed one H3, three L3, and one LL3 groups.
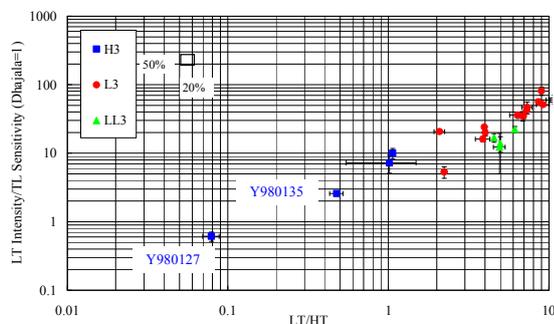

Fig.1. Ratio of LT to TL Sensitivity vs. LT/HT ratio to search fragments satisfying the pairing criteria 1) and 2).

PRIMITIVE ORDINARY CHONDRITES: Most of the chondrites had TL sensitivities over 0.1 (Dhajala=1), corresponding to petrologic subtype 3.5-3.9. Three chon-drites, Y980465 (H3), Y980576 (H3), and Y980320 (LL3) were revealed to be primitive ordinary chondrites, petrologic subtype 3.2, 3.3 and 3.4-3.5, respectively. They are not conflicted to olivine heterogeneity as shown in Fig.2. It is particularly significant in understanding the nature of primitive material in the solar system.
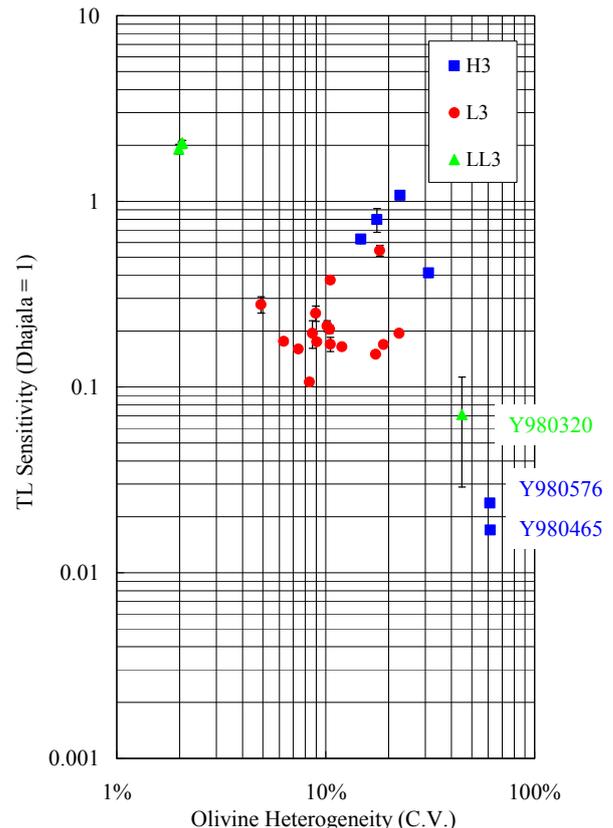

Fig.1. Dhajala-normalized TL sensitivity vs. olivine heterogeneity

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Measurement of Environmental Radioactivity and Heavy Metal in Seaweed Samples

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INTRODUCTION:
Sequential extraction has been proven to be a useful and practical technique for the speciation analysis of radionuclides in the soil and sediment samples [1-5]. We extracted ^{137}Cs and ^{129}I from surface soil samples after the Fukushima NPP accident to estimate impact of human activities.

EXPERIMENTS: The two soil samples of depths of 0−2.5cm were reduced by cone and quartering to approximately 10 g. Approximately 10 g of the samples were used in the sequential-extraction experiment. A solution/sample ratio of 5 (v/w) was used for extraction in each step (Fraction 1, 2, 3, 4, 5 and residue).
Fraction 1: Ultrapure water was added to the soil sample, and the sample was shaken for 24 h at room temperature. The sample was stored overnight. This fraction represents water-soluble species. The remaining solid on the filter paper was combined with the residue for the leaching in the next step.
Fraction 2: 1 M of NaAc was added to the residue from Fraction 1. The sample was shaken for 12 h at room temperature and stored overnight. This fraction represents exchangeable species.
Fraction 3: 1-M NaAc−HAc (pH 5) was added to the residue from Fraction 2, and the sample was shaken for 12 h at room temperature. This fraction represents carbonate-bound species.
Fraction 4: 0.04-M $NH_2OH \cdot HCl$ in 25% (v/v) HAc (pH 2) was added to the residue from the fraction and stirred in a hot-water bath at 80 °C for 4 h. This fraction represents species associated with solids via chemical-sorption mechanisms which can be released into the extraction solution with a weak reducing agent, and they mainly include species bound to Fe/Mn oxides.
Fraction 5: 30% H_2O_2 was added to the residue, in which

HNO_3 had already been added to adjust the final pH to 2, and the sample was agitated for 2 h at 85 °C. After the sample solution was cooled to room temperature, 1.8-M NH_4Ac in 11% HNO_3 (v/v) was added, and the extraction continued for 30 mins at room temperature. This fraction is associated with organic matter.
After extraction, each solution was separated from the soil residue by centrifugation at 2000 rpm for 5 mins. The solution was filtered through a filter paper with a pore size of 0.45 μm. After each fraction was stored into the U-8 vessel, ^{137}Cs was measured by gamma-ray spectrometry (Hokkaido University). I-129 was measured by AMS (Tokyo University).

RESULTS: The amount of ^{137}Cs leached into water (F1) from the Kanto-loam soil was below the detection limit. The rate of ^{137}Cs exchange from the two soil samples was less than 1%, with 50–60% of ^{137}Cs remaining in the residue. Approximately more than 90 % of ^{137}Cs was adsorbed on organic matter and the residue, while ^{129}I was mainly fixed by Fe-Mn oxidation and organically bound.

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CO5-3   Radiometric Dating for Paleoenvironmental Study of East Asia

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INTRODUCTION: Luminescence dating observes the natural accumulated radiation damage caused by radioisotopes such as U and Th as the form of glow after stimulation by heating or lightening. Thermally stimulated luminescence from calcite shows strong red emission [1]. However, calcites are less popular in thermoluminescence dating due to their variability in glow curves against temperatures and in alpha effectiveness [2,3].

To investigate luminescence characteristics of calcite, samples were artificially irradiated by alpha particles and gamma rays, and their luminescence intensities were calibrated against luminescence by x-ray, which is used to make a dose response curve to calculate equivalent accumulated doses. Stability of luminescence sites was also investigated by tracking the change in luminescence signals before and after the storage. For above mentioned experiments, calcite formed by precipitation through fluid circulation within ophiolite suits from Philippines was analysed. To test luminescence signals were reset at the time of calcite formation, luminescence from synthetic calcites were measured.

RESULT\<gamma vs x-ray\>: Glow curves of samples irradiated with gamma or x-rays show a common peak at 250°C (Fig. 1). However, peaks at lower temperature ranges are different; 80°C for x-ray but 140°C for gamma. Therefore, to omit the contribution of these low temperature peaks, samples are preheated at 200°C for 180 seconds. This process make a 250°C peak sift to 280°C. After the gamma ray irradiation of 134.2 Gy at the ^{60}Co gamma irradiation facility at Kyoto University Research Reactor, luminescence signals at the 280°C peak are calibrated by the dose response curve obtained by the x-ray irradiation. The calculated result was only 27% of the given gamma dose, indicating the different sample sensitivity against gamma and x-ray irradiations.

RESULT\<alpha vs x-ray\>: Alpha particles from ^{241}Am (5.4MeV) were irradiated to sample. First, number of alpha emission per unit area per a minute was estimated by the alpha track counting recorded on CR39 plastic sheet. Then luminescence intensity after alpha irradiation was calibrated against dose response curve formed by x-ray irradiation. Luminescence emission by alpha irradiation show peaks at temperature of ~280°C (note: after preheating at 200°C), same with x-ray or gamma-ray induced luminescence. As a result, the estimated dose was 76% of a given dose.

RESULT\<fading\>: For feldspar Infrared stimulated luminescence, fading of luminescence signal during the storage is a significant problem for its use in geochronology. To investigate the long-term stability of calcite luminescence, signals were measured before and after the storage and compared. Storage time was set as 24 hours. The results show no significant signal loss during the storage.

RESULT\<synthetic calcite\>: To make sure that luminescence is only caused by the exposure to radiation, luminescence measurement of newly synthetic calcite in the laboratory was carried out. Synthetic calcite shows a very small signal equivalent to ~10Gy at the temperature of 280°C. For very young samples, this value is not ignorable.

Summary: Calcite TL signal shows a potential to provide radiometric ages. When naturally accumulated dose is estimated as a comparison against x-ray induced luminescence, differential behavior between x-ray and naturally occurring radiations must be addressed. Emission of luminescence from 0-age sample suggests the importance of "background (non-radiation induced luminescence)" correction.

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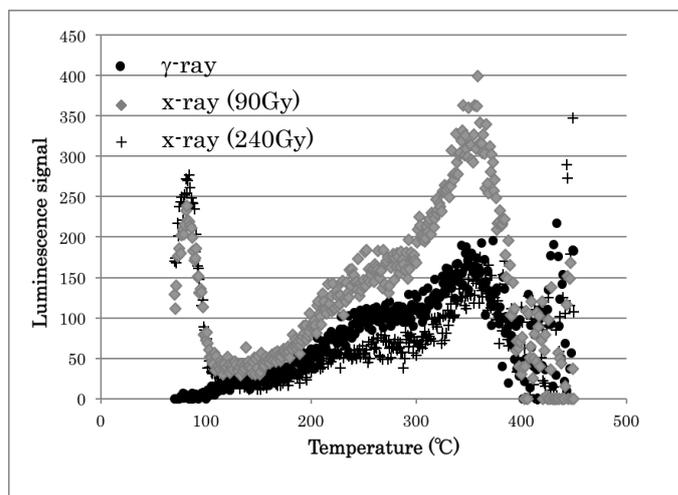[3] M. Gaft et al., Am. Mineral. **93** (2008) 158-167

Fig. 1 Luminescence glow curves after gamma or x-rays irradiations.

CO5-4   Behavior of Cesium during the Melting of Model Soil

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INTRODUCTION: After the 2011 Tōhoku earthquake and tsunami, contamination by the radioisotopes ^{134}Cs and ^{137}Cs released from the Fukushima Daiichi Nuclear Power Plant was spread widely in Fukushima Prefecture and the Kanto region of Japan. The contaminated property included land, houses, rubble, trees, agricultural crops, soil, and sewage sludge.

In this study, the stable isotope ^{133}Cs was added to model soil, and the concentrations and behaviors of ^{133}Cs were estimated in a pilot-scale melting of model soil, as is used to decontaminate soil. First, the ^{133}Cs concentrations in various melting residues of model soils were investigated using instrumental neutron activation analysis (INAA). Then, the decontamination of soils by melting was estimated from an analysis of ^{133}Cs and the composition of the model soils.

EXPERIMENTS: The model soil was an 85:15 mixture of decomposed granite soil and bentonite, to which an aqueous solution of Cs_2CO_3 was added. In addition, $Ca(OH)_2$ and Fe_2O_3 were added to control the basicity of the model soil, and $CaCl_2$ was added to control the Cl concentration.

Two model soils with different Cl concentrations were melted continuously for about 24 h at approximately 1773K. The melting fly ash and slag were sampled 4, 8, 18, and 22 h after the experiment started.

The Cs concentration in the samples was analyzed by INAA. The 50－100 mg of dried samples were packed into the double polyethylene bag and outside bag. Two samples were prepared per one kind of sample. Thermal neutron irradiation to the samples was carried out using by pneumatic transport pipe (Irradiation hole: Pn-2) at Kyoto University Research Reactor Institute. The irradiation time was 60 min, and after that, the samples were cooled down during 1 month. Radioactivated Cs in samples was analyzed by the germanium semiconductor detector with the 4096 channel peak analyzer. The measurement time was 7,200 sec. The energy with the highest peak, 795.8keV, was selected as the energy of Cs for gamma-ray spectrometry. The calculation of radioactivity of samples was carried out using by Fitz peaks (JF Computing Services). Cs concentration in each sample was determined by the comparison method using 25－50mg of the standard sample (NIST SRM 1633c: Coal fly ash, certified Cs level 9.36mg/kg [1]).

RESULTS: The Cs concentrations in the samples are shown in Table 1. The Cs in the model soil was concentrated in the melting fly ash after the melting treatment. The Cs concentration in the melting slag was 1/30 to 1/100 lower than that in the melting fly ash.

The Cs concentrations were lower in slag derived from the model soil having a higher Cl concentration. It was thought that chloride volatilization promoted the settlement of Cs in the melting fly ash. The boiling points of most Cs compounds range from 951 to 1568K, which is lower than the melting temperature used (1773K) [2], and there was little difference in the Cs concentration among the melting fly ash samples. Future laboratory-scale melting tests with mass balance estimation are needed.

Table 1. Cs concentration of some media on melting test

Item	Cs(mg/kg) INAA 795.8KeV
Melting fly ash 1-1	5278
Melting fly ash 1-2	6761
Melting fly ash 2-1	8465
Melting fly ash 2-2	9093
Melting fly ash 3-1	6788
Melting fly ash 3-2	6356
Melting fly ash 4-1	5851
Melting fly ash 4-2	5524
Slag 1-1	166.9
Slag 1-2	181.5
Slag 2-1	135.5
Slag 2-2	131.6
Slag 3-1	100.3
Slag 3-2	102.6
Slag 4-1	87.35
Slag 4-2	86.79
Model soil 1-1	1067
Model soil 1-2	1156
Model soil 2-1	1366
Model soil 2-2	1292
Model soil 3-1	1043
Model soil 3-2	1053
Model soil 4-1	1450
Model soil 4-2	1464

No.1-2: Model soil with low Cl conc.,
No.3-4: Model soil with high Cl conc.

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CO5-5   Foliar Uptake and Volatilization of Iodine Applied to a Leaf Surface in Small Drops

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INTRODUCTION: Foliar uptake of radionuclides is an important process that can be used to estimate their concentrations in plants. Iodine is an essential element for animals and it is well known that iodine is needed for the synthesis of thyroid hormones and iodine deficiency induces thyroid diseases. Radioiodine was the major radionuclide released from the Fukushima Daiichi Nuclear Power Plants after the accident in March 2011 because of its high fission yield and volatility. Therefore, the knowledge on the transfer of iodine necessitates estimating internal radiation exposure through agricultural food ingestion. In the present study, foliar uptake of iodine applied in small drops to a leaf surface and its volatilization from the leaf surface were determined by a laboratory experiment.

EXPERIMENTS: Orchard grass (*Dactylis glomerata* L.) was cultivated hydroponically in an artificial climate chamber (air temperature, 20°C; relative humidity, 70%; light intensity, 30 klx; light length, 12 h). After applying fifty 3 µL drops of NaI solution (200 mg I L^{-1}) on the leaf surface, the sample was closed in a transparent acrylic box. Air excluding iodine was ventilated at the flow rate of 18 L min^{-1} and volatile iodine released from the leaf surface was collected and divided into particulate, inorganic and organic iodine. Particulate iodine was collected with fluoropore AF07P filters (Sumitomo Electric, 47 mm ϕ). Inorganic gaseous iodine was collected with three cellulose filters (Whatman 41, 47 mm ϕ) impregnated with 1 M LiOH in a 10% glycerol water mixture[1] and organic iodine was collected with 6 activated carbon paper filters (STV-2465, Kynol, 47 mm ϕ). After cultivating 24 h in the box, the leaf sample was washed with a surfactant solution (0.1 % Triton X-100 at pH 9). The leaf and root samples were separated and dried at 50°C and pulverized with a stainless steel cutter/blender. Iodine in the plant samples was extracted with tetramethyl ammonium hydroxide. The concentration of iodine in the solution samples was measured with ICP-MS. The filter samples were sealed separately in a polyethylene bag, and analyzed by neutron activation analysis using the KUR reactor (Pn-3) at a thermal neutron flux rate of 4.9 × 10^{16} n m^{-2} s^{-1} for 150 s.

RESULTS: Table 1 shows the percentage distribution of iodine in the grass sample, which was separated into washing solution, leaf, and root, at 24 h after the application of small drops of a NaI solution to the leaf surface. The distribution of volatilized iodine fractions such as particulate, inorganic and organic iodine are also indicated in Table 1. The yields of applied iodine, that is, the sum of the amount in the washing solution, plant and volatile fractions, were 92 and 95%. The residue of iodine may have adsorbed on the surface in the box because the plant was kept in the closed box during the experiment. The volatile amount of iodine was only 0.1-0.2 % of the applied iodine which was in the inorganic fraction. It has been reported that the chemical forms of iodine collected as inorganic fraction were I_2, HI, HOI, and IO radicals. The percentage distribution of iodine in the washing solution, which was on the leaves, was about 5 %, whereas that inside the leaf was approximately 90%. This suggests that most of the iodide applied with small drops is immediately transferred from the leaf surface. However, the percentage distribution of iodine in the root was a negligibly small value, suggesting that the translocation of iodine from leaf to root was slow. More studies on foliar uptake and volatilization of iodine by applying iodine in aerosol and gaseous forms will be required.

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Table 1. Percentage distribution of iodine in washing solution, leaf, and root and in volatilized iodine fractions following the foliar application of small drops of a NaI solution

Sample No.	Plant （%）			Volatilization （%）			Yield （%）
	Washing solution	Leaf	Root	Particle	Inorganic gas	Organic gas	
OGLD_1d_a	7.4	84.4	0.2	—	0.2	—	92
OGLD_1d_b	4.5	90.3	0.2	—	0.1	—	95
Mean	5.9	87.3	0.2	—	0.2	—	94

CO5-6 Neutron Activation Analysis of Elemental Concentrations in Atmospheric Aerosols at Sakai,Osaka

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21 elements in atmospheric aerosols daily sampled at Osaka Prefecture University, Sakai, Osaka were analyzed by Neutron Activation Analysis. Average of concentrations in these elements were determined. Some of the elements have the effects from the non natural aerosols originated from industry or vehicle.

Samples

The atmospheric aerosols were daily sampled at Osaka Prefecture University, Sakai, Osaka. Table1 lists the sampling condition. The samples collected on January and February in 2007 were analyzed .

Table1 Sampling conditions of the aerosol particles.

Conditions	Description
Location	Osaka Prefecture University, Sakai Osaka
Period	24 hours
Filter	25mmΦ membrane (Advantec A100)
Particle Separation	Non-Separation(Total particle)

Neutron Activation Analysis

2 way of Neutron irradiation and measurement were done for each sample. One way is short irradiation for short lived activated element and the other is long irradiation for long lived activated element. Elements for each irradiation way are listed on Table2.

Table 2. Irradiation way and elements for each irradiation.

Irradiation Way	Elements
Short (120sec in PN1)	Al, Cl,Ca,Ti,V, Mn
Long(7200sec in PN2)	Na, K, Cr, Fe, Zn,As,Br,Rb,Mo,Sb,La, Ce,Sm,W

Result

Averages of each element are shown in Fig.1 and estimated concentrations of soil particle are shown together. These estimation have been carried out using concentration of Al and general rations of each element in soil. If the observation concentration is clearly higher than estimated soil particle concentration, for this element non natural effect, other than soil, is main contribution for the element. Rations (observation concentration to soil particle) are shown in Fig.2. The element for which non natural effect is high (ratios in Fig2 >10) are Cl(Sea Salt), Cr, Zn, As, Br, Mo, Sb, W.
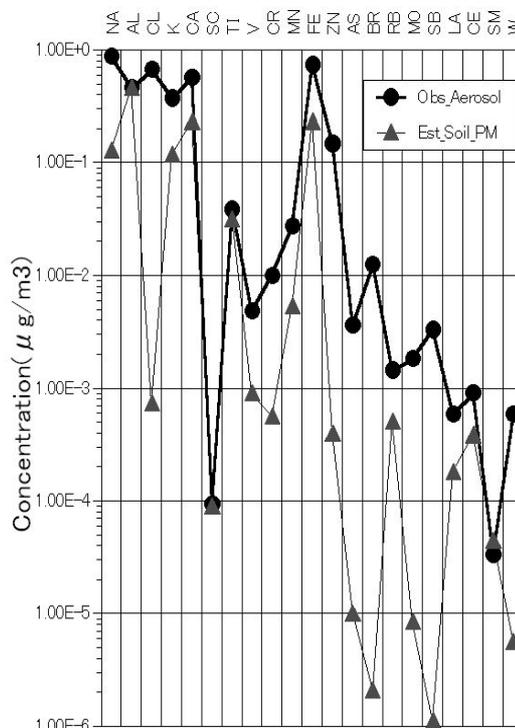

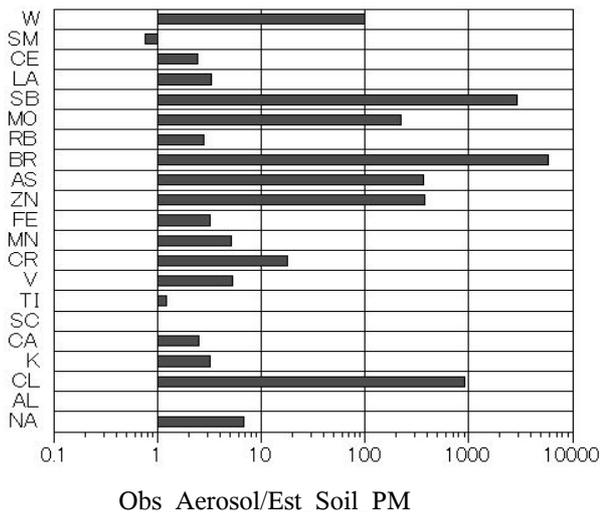Fig. 1. Average of each element(Obs_Aerosol) and estimated concentration of soil particle(Est_Soil_PM).

Obs_Aerosol/Est_Soil_PM

Fig. 2. Ratio of average concentratio (Obs_Aerosol) to estimated concentration of soil particle(Est_Soil_PM).

Evaluation of Hypoxia at Dredged Trenches in Tokyo Bay
by Determination of Fe and Mn in the Sediments

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INTRODUCTION: Hypoxia is water mass contained little dissolved oxygen (DO), which has influenced ecosystems and fisheries [1]. At the seabed in Tokyo Bay, large-scale dredging operations had been done in 1970s. In particular, the dredged trenches off Makuhari have the maximum area and depth. In dredged trenches strong hypoxia has been observed in summer, and the hypoxia has disappeared in winter. But the influence of dredged trenches on hypoxia is not revealed yet. Therefore, it is important to estimate the interannual variations of hypoxia by analyzing sediments.

To evaluate the sedimentary environment such as redox conditions, we have been studying the method using Fe and Mn, because their various chemical states on Eh-pH diagrams have become clear [2], and they are expected to take the chemical states corresponding to the redox conditions of seawater. We reported the concentrations of Fe and Mn in sediments from the Makuhari dredged trenches in summer [3]. In this study, sediment cores were collected in winter, and the concentrations of Fe and Mn were analyzed by instrumental neutron activation analysis (INAA).

EXPERIMENTS: The sediment samples were collected at two dredged trenches (water depth 24.7 m and 18.0 m) and reference site (non-dredged seabed, water depth 9.7 m) off Makuhari in Tokyo Bay on February 2012. Sediments were collected by a core sampler at each point. Water quality data were also obtained by a multichannel water quality meter and an oxidation-reduction potentiometer. All cores were cut in the vertical direction at 0.6 - 3.0 cm intervals after freezing. The divided samples were desalted by using an ultrasonic cleaner and a centrifuge, and then they were freeze-dried.

Approximately 30 mg of desalted and freeze-dried sediments were packed in double polyethylene film bags to perform INAA. All samples were irradiated at the pneumatic tube, Kyoto University Reactor (KUR). Two types of gamma-ray measurement were carried out corresponding to half-lives of elements. For analysis of Mn, samples were irradiated for 10 seconds at 1 MW, and then gamma-ray was measured for 600 seconds by Ge detector after 600 seconds cooling. Regarding Fe, samples were irradiated for 20 minutes at 1 MW or 4 minutes at 5 MW, and the measurement time of gamma-ray was for 9000 seconds after 3 weeks cooling.

RESULTS: The DO in the seawater at dredged trenches and reference site (non-dredged area) indicated the similar vertical distribution at each point. From the surface, the DO decreased gradually. At the bottom, the DO became 8 - 9 mg/L at every site. And hypoxia has not been observed in Tokyo Bay in the winter of 2012.

Figure 1 shows depth profiles of Fe and Mn in the sediments collected at both dredged and non-dredged area. At every site, concentrations of both elements were almost constant at the surface. On the other hand, we mentioned that concentrations of both elements decreased near the surface at dredged trenches in the summer of 2011 [3]. It is well-known fact that the concentrations of Fe and Mn in sediments increase when condition of seawater is oxi-dative. On the other hand, the concentrations decrease due to eluviations of Fe^{2+} and Mn^{2+} when condition of seawater is reductive like hypoxia. The results indicate that Fe^{2+} and Mn^{2+} were oxidized and precipitated under the oxic condition in the winter of 2012.
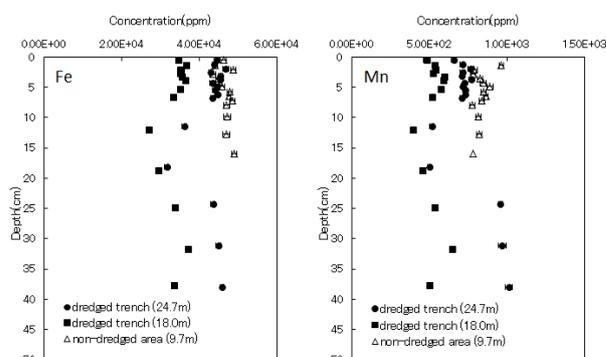

Fig. 1. Depth profiles of Fe (left) and Mn (right) in the sediments.

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CO5-8   **The Possibility of Radionuclide Detection in Atmospheric Precipitation**
far from Fukushima

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INTRODUCTION: The release of artificial radionuclides occurred into the atomosphere following Fukushima Daiichi Nuclear Power Station in March 2011. This accident caused the contamination of terrestrial and aquatic systems by radiocesium in the eastern Japan, mainly Kanto and Tohoku districts. Since the nuclear accident, many reports on the behavior of radionuclides in the environmental in these districts have been published. It is important to make a widespread investigation into the deposit of radioactive materials in Japan.

In this study, we monitored dry and wet deposition of ^{137}Cs in Sakai city in Kansai district, the western Japan to elucidate the possibility of radionuclide detection in atmospheric precipitation in Sakai city, Osaka far from Fukushima.

EXPERIMENTS: The monitoring started in December 2011 at the rooftop of Osaka Prefecture University located in Sakai City, Osaka. This monitoring site is approximately 700 km far from Fukushima Daiichi Nuclear Power Station.

A porcelain enamel bat (0.35 m × 0.45 m) is set for collection of each of dry and wet deposition. The former was collected for about 14-21 days, the latter was collected every rain events (>1mm). Dry deposition in the bat was rinsed with 100 mL of 0.6% nitric acid and distilled water. The liquid sample obtained was dried up using an electromagnetic induction heater and evaporation lamps followed by measuring radioactivity.

The amount of ^{137}Cs in the dry and wet deposition was measured using gamma-ray spectrometry with a Ge semiconductor detector (SEIKO EG and G Co., Ltd., Tokyo, Japan) coupled to a multi-channel analyzer (SEIKO EG and G Co., Ltd., Tokyo, Japan). The measurement time ranged from 1 hour to 10 days by trial and error.

RESULTS: Table 1 shows the ^{137}Cs activities of dry deposit during the monitoring period. The activities of ^{137}Cs are below 1 Bq in all the dry deposit samples as well as those of wet deposit (data not shown). In general, both dry and wet deposit of radioactive materials in the studied area was little detected during the monitoring

period. Ito reported that fallout of major concerning radionuclides ^{131}I, ^{134}Cs and ^{137}Cs in the area tested nearby the studied site was detected for one and half months after the nuclear accident, but that thereafter radioactivity concentration was under limit of detection [1]. The result obtained in our study was in agreement with those results reported. The risk of radionuclides from the Fukushima accident is probably very small in Sakai city.

The Fukushima Nuclear Accident is not brought to the end. Contamination of soil, water and air by radioactive materials potentially occurs following an expected incident. Moreover, there also is a possibility of the release of radionuclides from the nearby waste treatment station due to insufficient surveying of radiation measurement of wastes and/or improper treatment operation. It is important to continuously monitor the radiation and the presence of radionuclides with respect to risk of environment and human health.

Table 1 Radioactivities in dry deposit samples during test period

Collecting Duration	Radioactivity (Bq)
2011/12/23-2012/1/5	0.046
2012/1/6-23	0.016
2012/1/24-2/10	0.009
2012/2/11-/3/1	0
2012/3/2-3/21	0.004
2012/4/26-5/16	0.002
2012/5/17-6/3	0.003
2012/6/4-2012/6/22	0.002
2012/7/18-8/1	0.002
2012/9/12-10/5	0.005
2012/10/27-11/14	0.005
2012/11/15-12/4	0.006
2012/12/30-2012/1/20	0.008
2013/1/21-2/14	0.003

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CO5-9 Study on Thermal History of Rock Sample Based on Fission Track Dating Method

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INTRODUCTION: Fission track age dating was applied for the Tsukinuno bentonite mine to examine depositional ages of bentonite, and its relation with igneous rocks and tuffs which are distributed in surrounding area. The Tsukinuno bentonite deposit is located in central Yamagata Prefecture and high quality Tsukinuno bentonite is used in the foundry and civil engineering fields, and for cat-litter. The bentonite mainly hosted in mudstone is composed of 31 bentonite layers and each bentonite layer is assigned a number from the bottom to top (No.1 to No. 31). The bentonite is considered to have formed by diagenetic and low temperature hydrothermal alteration. Parent rocks of bentonite are generally considered to be tuffaceous rocks which contained abundant glass shards. However, based on chemical compositions including REE analysis, parent rocks of the Tsukinuno bentonite layers were considered to be genetically related to surrounding tuffs, volcanic rocks and granitic rocks [1]. The formation age was first reported by fission-track and K-Ar methods, but the ages vary from 13 to 21 Ma [2]. More recent microfossil and fission-track analysis of a few samples from mine tunnel gives ages from 9.1 and 9.6 Ma [1]. This inconsistency may be due to contamination by older detrital zircon or clay flakes.

EXPERIMENTS: Four bentonite layers (No.2, No.13 and No.29 and No.31) were collected from the Tsukinuno mine and tuffs (Ishikura tuff (IK-tuff)), volcanic rocks (Mazawagawa dacite (MZ-dacite)) and granitic rocks (Mitate Granite (MT-granite)) were collected from northeastern part of the Tsukinuno mine. Zircon grains were separated by conventional magnetic and heavy liquid separation techniques. Zircons were mounted in PFA Teflon, and then polished to reveal a complete internal surface. Zircons were etched in a NaOH-KOH eutectic melt at 225°C [3] for 24-32 hours. Samples were irradiated at pneumatic tube of graphite facility (Tc-pn) of Kyoto University Reactor (KUR). After irradiation, external detectors (mica) were etched in 46% HF at 25°C for 6-7 minutes (for mineral mounts) and for 20-50min (for NIST-SRM612). FT densities were measured at 1000× magnification with a dry objective. The zeta values used were 367.1±4.1 and ages were calculated using the Trackkey program [4].

RESULTS: Results are shown in Table 1. FT ages of bentonite layers were 10.4Ma, 9.6Ma, 9.5Ma and 9.6Ma, respectively. Almost analyses (except for No.31) passed χ^2 test at the 5% criterion [5]. This means that the variability in the track count data is limited to the inherent variability in radiometric decay process, and affect of detrital grains supplied from various parent rocks is relatively low. The obtained ages 10.4 - 9.6Ma probably indicate depositional ages of the bentonite layers. Tuff and igneous rocks collected at surrounding area of the mine show variable ages, 9.8Ma (IK-tuff), 9.2Ma (MZ-dacite) and 46.7Ma (MT-granite). IK-tuff and MZ-dacite are possibly correlated with bentonite layers. On the contrary, MT-granite (46.7Ma) show significantly older age, suggesting that the granite is not parent rock of the bentonite layers. K-Ar age of biotite of the MT-granite has been reported to be 9.5Ma [1]. The inconsistency between FT age (46.7Ma) and K-Ar biotite age (9.5Ma) is probably due to difference in thermal stability of each dating system. FT method is more stable for a certain type of hydrothermal alteration.

Table 1. Fission track analytical data.

Sample	No. Crys	ρ s (Ns)	ρ i (Ni)	Pχ^2 (%)	ρ d (Nd)	Age (1 σ)
No.31 Bentonite	23	3.514 (1395)	14.67 (5822)	1.4	2.174 (7178)	9.6 (0.3)
No.29 Bentonite	30	0.794 (711)	3.331 (2981)	99.5	2.174 (7164)	9.5 (0.4)
No.13 Bentonite	42	3.002 (1840)	10.57 (6482)	98.0	1.832 (7259)	9.6 (0.3)
No.2 Bentonite	30	1.615 (1187)	6.197 (4555)	94.7	2.174 (7171)	10.4 (0.4)
IK-tuff	34	1.827 (1498)	6.298 (5164)	49.1	1.832 (7259)	9.8 (0.3)
MZ-dacite	33	2.574 (1524)	9.417 (5575)	39.9	1.832 (7259)	9.2 (0.3)
MT-Granite	12	5.361 (1292)	3.855 (929)	28.0	1.832 (7259)	46.7 (2.1)

ρ=track density; N=total number of tracks counted; s for spontaneous, i for induced and d for dosimeter; P (χ²) =probability of obtaining χ² value for v degrees of freedom (where v=number of crystals-1) [5].

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CO5-10   Determination of Abundance of Rare Metal Elements in the Currently Forming Antimony Ore Deposits of Kagoshima Bay by INAA Techniques

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INTRODUCTION: To meet recent increased demand for rare metal elements as mineral resources, high sensitive multi-element analysis becomes more important as geochemical tools for mineral exploration. Instrumental neutron activation analysis (INAA) has the advantage of non-destructive analysis and is free from problems that concentrate of a specific element is often included in residue during acid dissolution. Previous studies have demonstrated that INAA enables rapid abundance determination for multi elements in ore samples collected from active seafloor hydrothermal fields that consist of variety of sulfide/sulfate/silicate minerals [1,2]. In order to extend the range of application of this technique, we started preliminary studies using hydrothermally altered sediment and antimony sulfide ore deposits.

EXPERIMENTS: Two groups of natural samples were provided for this study. One was antimony sulfide ore deposits collected by ROV/HyperDolphin, and the other was hydrothermal altered sediment collected by piston-corer within an active hydrothermal field in Wakamiko submarine crater in the Kagoshima Bay.
For analysis of long-lived nuclides (^{110m}Ag, ^{59}Fe, ^{203}Hg, ^{124}Sb, ^{65}Zn, ^{134}Cs) and mid-lived nuclides (^{76}As, ^{198}Au, ^{131}Ba), samples were irradiated at Pn-1 (thermal neutron flux = 3.86×10^{12} n/cm^2/sec at 1 MW) for 3 hours, and the gamma ray activity was measured for 3 hours after around 30 days cooling and for 50 minutes after 3-10 days cooling. For analysis of short-lived nuclides (^{66}Cu, ^{56}Mn, ^{115}In, ^{52}V, ^{83}Se), samples were irradiated at Pn-3 (thermal neutron flux = 4.86×10^{12} n/cm^2/sec at 1 MW) for 1 minute, and the gamma ray activity was measured for 5 minutes after 10-30 minutes cooling. Concentration of each element was calculated by comparison of gamma ray intensity between the sample and standard materials; Na for short-lived nuclides measurement and Co for mid- and long-lived nuclides measurement.

RESULTS: Indium (In), selenium (Se), vanadium (V), manganese (Mn), and gold (Au) were detected by NAA in addition to arsenic (As), antimony (Sb) and mercury (Hg), which have been previously reported anomalous condensation in this area. Concentrations of As, Sb and Au show obvious positive correlation in the sulfide ore deposits (Figs. 1 and 2, sample# 1363 ~1366). On the

other hand, correlation of As and Au relative to Sb in the hydrothermal altered sediments (Figs. 1 and 2, sample# P3 ~ P5) was not clear.

As, Sb and Hg are expected to precipitate directly from the hydrothermal fluid mostly as sulfide minerals, while hydrothermal alteration of sediments may be occurred relatively lower temperature condition, suggesting that remained As and Hg in the hydrothermal fluid continue to precipitate into the sediment layer and Sb and Au is already depleted in the fluid.

Relatively high concentration of Mn, V and In were observed in the sediment layer where hydrothermal alteration is not obvious. It may suggest those elements are precipitated from the bottom seawater containing hydrothermal components once emitted from the vents under suitable physicochemical condition.

As demonstrated above, INAA provided useful information for discussion on potential of mineral resources in a seafloor hydrothermal field.
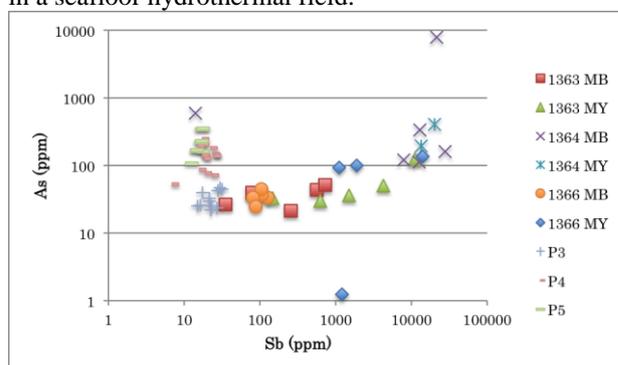

Fig. 1 Relation of Antimony and arsenic concentrations in the ore deposits (sample# 1363 ~ 1366) and hydrothermal altered sediment (sample# P3 ~ P5)
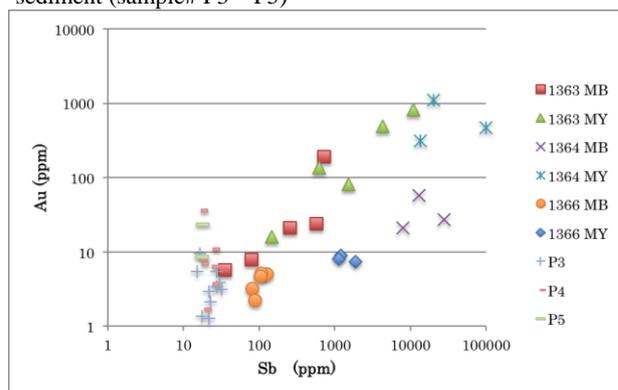

Fig. 2 Relation of Antimony and gold concentrations in the ore deposits (sample# 1363 ~ 1366) and hydrothermal altered sediment (sample# P3 ~ P5)

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CO5-11   Determination of Abundance of Rare Metal Elements in Seafloor Hydrothermal Ore Deposits by INAA Techniques-2: Determination of Indium Content

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INTRODUCTION: To meet recent increased demand for rare metal elements as mineral resources, high sensitive multi-element analysis becomes more important as geochemical tools for mineral exploration. Instrumental neutron activation analysis (INAA) has the advantage of non-destructive analysis and eliminates possible problems that concentrate of a specific element is often included in minerals poorly soluble during acid digestion. In order to extend the range of application of this technique, we have conducted preliminary studies using ore deposit samples collected from active seafloor hydrothermal fields. Here, we report evaluation for quantification of indium with INAA. Indium is included in ore deposits as a trace element which does not form a specific sulfide mineral. Indium content in ore deposits is usually ppm to sub-ppm order.

EXPERIMENTS: As demonstrated in previous studies [1,2], ^{115}In that is the dominant isotope of indium (natural isotopic abundance is 95.7%) has a large neutron cross section for a nuclear reaction to form ^{116m}In. Since a half life of ^{116m}In is 54.1 minute, we applied an analytical scheme designed for short-lived nuclides to the quantification. Samples were irradiated at Pn-3 (thermal neutron flux = 4.86×10^{12} n/cm^2/sec at 1 MW) for 2 minutes, and the gamma ray activity was measured for 5 minutes after 7-30 minutes cooling. Spectra of ^{66}Cu and ^{56}Mn were also quantified during the same analytical scheme. Content of each nuclide was calculated by comparison of gamma ray intensities between samples and standard materials which contains known content of Na and Mn.
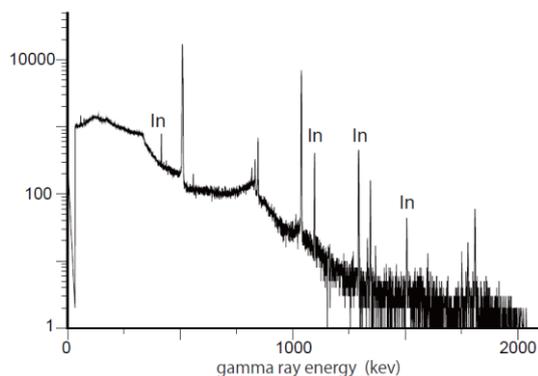

Fig. 1 A gamma ray spectrum of CCU-1d (the content of indium was reported as 7.0 ppm). The irradiation time was 120 seconds, cooling time was 1061 seconds, and measurement time was 300 seconds.

RESULTS: In order to evaluate analytical accuracy, we conducted a series of analyses for "Certified Reference Materials" provided by Natural Resource Canada [3]. Fig. 1 shows a gamma ray spectrum of CCU-1d which indium content was reported as 7.0 pppm. As shown in this figure, three dominant peaks of ^{116m}In (at 416.9 kev, 1097.3 kev and 1293.6 kev) were identified. For this sample, the peak area of ^{116m}In at 1097.3 kev was calculated with a relative statistical error of less than 5%. On the other hand, during analysis for WMS-1a which indicum content was reported as 0.2 ppm, it was difficult to obtain enough intensity of the spectrum of ^{116m}In under the same analytical scheme. From these results, we may estimate the lower limit of indium qunatification as an order of 1 ppm for sulfide ore deposit samples. This level is about one order small compared with ICP-MS analysis.

Table 1. Analytical results of Certified Reference Materials provided by Natural Resources Canada. Numbers enclosed in parantheses indicates informational values (for In), provisional values (for Mn and Cu of WMS-1a) and certified values (for Mn and Cu of CCU-1d).

	In (ppm)	Mn (ppm)	Cu (wt%)
CCU-1d	(7.0)	(99.4 ± 4.4)	(23.9 ± 0.3)
run 1	7.4 ± 0.3	84 ± 4	15.0 ± 0.1
run 2	6.5 ± 0.3	96 ± 5	14.9 ± 0.1
WMS-1a	(0.2)	(600 ± 70)	(1.40 ± 0.02)
run 1	0.21 ± 0.07	619 ± 6	0.92 ± 0.04
run 2	n.d.	430 ± 8	0.64 ± 0.02

Table 1 compiles results of the series of analyses for the Certified Reference Materials, CCU-1d and WMA-1a. Results of two runs agreed within a factor of about 1.5. Although this reproducibility was not so good, it would be enough for our original purpose to find anomalous enrichment of a specific element. In fact, we identified a few ore deposits showed anomalously high content of indium (from 20 to 200 ppm) among the samples collected from active seafloor hydrothermal fields in the Suiyo Seamount.

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^{40}Ar/^{39}Ar Age of Volcanic Tuffs in the Eastern Africa II

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INTRODUCTION: Direct radiometric dating of fossil bearing strata is technically difficult if they do not contain a mineral coeval with the sedimentation. Recent study indicates correlation of some mammals and human beings [1]. The study area has fossils of mammals, which seem to be associated with hominidae. In the previous studies, ^{40}Ar/^{39}Ar dating on the tuffs overlying immediately on the fossil bearing layer, was applied on mainly biotite, and they yielded ages of approximately 20Ma. However, some of the samples show quite disturbed age spectra, suggesting effects due to later alteration and/or weathering. Whole rock samples dated by K-Ar and most results distribute around 17 – 18 Ma. We separated the feldspars which seem to have less alteration under microscope.

EXPERIMENTS: Experimental procedure is the same as described as previous studies. Rock samples were crushed, and sieved in #25-50 mesh. After ultrasonic cleaning in distilled water, single mineral grains were handpicked. The minerals were irradiated in the KUR for 24 hours at 1 MW for ^{40}Ar/^{39}Ar age determination. The total neutron flux was monitored by 3gr hornblende age standard [2], [3], which was irradiated in the same sample holder. In the same batch, $CaSi_2$ and $KAlSi_3O_8$ salts were used for interfering isotope correction. A typical J-value was $(5.499 \pm 0.022) \times 10^{-3}$. In stepwise heating experiment, temperature of a mineral grain was measured using infrared thermometer whose spatial resolution is 0.3 mm in diameter with a precision of 5 degrees. Extracted argon isotopes were measured using the custom made mass spectrometer [4].

RESULTS: An example of age spectra of feldspars from stepwise heating experiments is shown in Fig. 1. The first three fractions in the lower temperatures suggest a possible excess component, but it could be ^{39}Ar recoil effect during irradiation. It was difficult to control the temperature above 700-800°C due to the abrupt change of emissivity, and the temperature was brought up to fusion in the last fraction. The change of emissivitiy is caused by the structural phase transition. However, the plateau-like age reasonably agree with the age of biotite in the previous results, giving a consistent age of the tuffs. On the
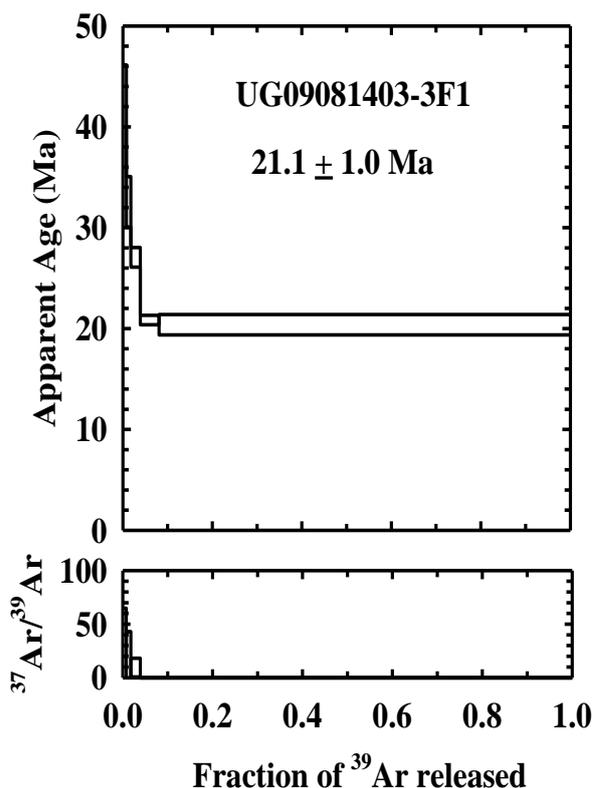

Fig. 1. ^{40}Ar/^{39}Ar age and ^{37}Ar/^{39}Ar ratio spectra of a feldspar from volcanic ash strata in Uganda. The ^{37}Ar/^{39}Ar ratio spectra suggest very low Ca and a homogeneous mineral phase at high temperature. The age and other plateau-like age spectra in biotite imply the age of volcanic activity is about 20 - 21 Ma.

other hand, ^{40}Ar/^{39}Ar age of whole rock samples are variable. Because of their various ages, whole rock samples may carry significant alteration.

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Geochemistry of Unbrecciated Diogenite, Yamato 002875

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INTRODUCTION: Howardite, eucrite and diogenite (HED meteorites) are the largest group of achondrite which are thought to have been derived from asteroid Vesta. Recently, the Dawn mission confirmed that the Vesta's surface is mineralogically and chemically similar to HED meteorites [1]. Depletions of siderophile elements in HED meteorites suggest that HED meteorites are products of differentiation [2]. Therefore, HED meteorites are important to elucidate the core formation of Vesta. Diogenite are mostly composed of orthopyroxene with such minor minerals as olivine, plagioclase and chromite. As almost all diogenites are brecciated, it is difficult to bring out their primitive chemical compositions. Some diogenites (e.g., Ellemeet and MIL 07001) were reported to contain foreign meteoritic components [e.g., 3]. From these materials, siderophile elements abundances may have been modified. A few unbrecciated diogenites have been found. As siderophile elements abundances for these unbrecciated diogenites were not affected by the incorporation of foreign materials, its chemical compositions give us the important information about the differentiation processes of Vesta. Yamato (Y) 002875 discovered by Japanese Antarctic Expedition Team was classified as an unbrecciated diogenite. This meteorite is nearly monomineralic diogenite composed of >99 % orthopyroxene. In this study, we determined elemental abundances for Y 002875 by using INAA and aimed to chemically characterize this meteorite in comparison with those for other diogenites.

EXPERIMENTS: Several chips of Y 002875 weighing 3.119 g were carefully ground in an agate mortars in order to obtain the representative chemical composition. In addition to this meteorite, we also analyzed Y 74013 and Y 74097, for which a total of 3.152 g and 3.100 g of chips were ground to powder in clean agate mortars. Powder samples of three diogenites were irradiated two times with different irradiation periods at KURRI. Both JB-1 and the Smithsonian Allende powder samples were used as reference standards.

RESULTS AND DISCUSSIONS: Our data for Y 74013 and Y 74097 are generally in good agreement with literature values [e.g., 4]. Our Cr and V values for Y 74013 and Y 74097 are consistent with the ranges for these elements of other diogenites, while literature values for these meteorites are higher. The differences of Cr and V abundances between our data and literature values are due to the heterogeneous distribution of chromite.

Based on mineralogy, petrology and bulk chemical compositions, Yamato diogenites are divided into two cate-

gories: Type A (Y 74013-type) and Type B (Y 74032-type). For pyroxene and chromite, mg number for Type A diogenites are higher than those for Type B diogenites. Plagioclase is present in Type A diogenites, but not in Type B diogenites. In bulk chemical compositions, Type B diogenites have higher incompatible elements abundances compared with Type A diogenites. An mg number and incompatible elements of Y 002875 are consistent with those for Y 74013 and Y 74097 and fall in the range of Type A diogenites. Thus, Y 002875 is chemically similar to Yamato Type A diogenites.

Figure 1 shows CI-normalized Ni/Co ratio and Ni abundances in diogenites. As shown in Fig. 1, there is no difference of Ni abundances and $(Ni/Co)_{CI}$ ratios between brecciated and unbrecciated diogenites. Being similar to the case for eucrites, Ni abundances and $(Ni/Co)_{CI}$ ratios systematically correlate among diogenites. We calculated Ni abundances and $(Ni/Co)_{CI}$ ratios of the mixture of the pristine diogenitic material and chondrite or FeNi-metal by changing mixing ratios of these two components. Calculations results are shown in Fig. 1. Apparently, contamination of chondritic material or FeNi-metal could explain systematically correlation between Ni abundances and $(Ni/Co)_{CI}$ ratios in diogenites. Even unbrecciated diogenites were affected by the contamination of foreign materials, suggesting that its incorporations were occurred before unbrecciated diogenites were crystallized.
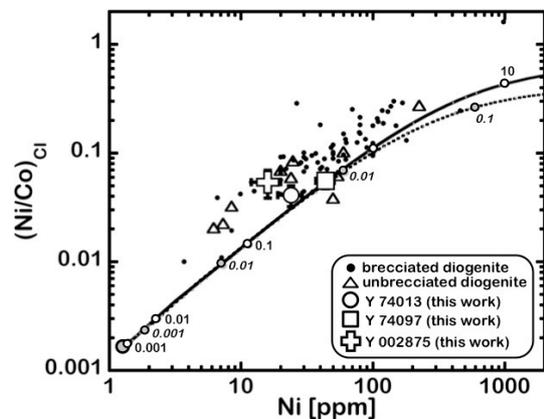

Fig 1. Ni abundances vs. $(Ni/Co)_{CI}$ ratios for diogenites. Solid and dash lines represent mixing line of the pristine diogenitic materials and FeNi-metal or chondritic clast, respectively. The numbers along these lines correspond to contributions in % of the FeNi-metal and chondritic clast.

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CO5-14

Comparison of RNAA Data with ICP-MS Data for Halogen in Sedimentary Rock Samples

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INTRODUCTION: Accurate and reliable data of halogen abundance have been rarely reported for terrestrial samples, such as crustal rock and mantle material, though halogens differ in volatility from element to element and their content and relative abundance are highly informative in discussing the petrogenesis of samples [1].

The shortage of accurate and reliable data of terrestrial rock samples is largely related to difficulties in determining trace amounts of halogens within these samples. To determine trace halogens in rock samples, either inductively coupled plasma mass spectrometry (ICP-MS) or neutron activation analysis (NAA) have commonly been utilized. Bromine and iodine are conventionally determined by ICP-MS after preconcentration of the elements using pyrohydrolysis of rock powder [2].

In this work, trace three halogens (Cl, Br and I) were determined by radiochemical NAA (RNAA) for nine sedimentary rocks. Our RNAA values are compared with the ICP-MS values for the nine sedimentary rock samples in order to evaluate the consistency of the two data sets. Since there was no chlorine data available from ICP-MS, only bromine and iodine data could be compared.

EXPERIMENTS: Trace amounts of Cl, Br and I in the nine sedimentary rocks were determined by RNAA. The RNAA procedure is described elsewhere [3].

RESULTS: Our RNAA values are compared with the ICP-MS values [2] for all nine sedimentary rocks in Table 1, where concentration ratios of ICP-MS values to RNAA values are given. These ratios are plotted in Fig. 1, where ratios for concentrations of bromine (Fig. 1a) and iodine (Fig. 1b) are compared separately. In calculating the mean ratio of bromine, a value for JCh-1 was ruled out using the outlier test under the 2σ-criterion. An uncertainty quoted for each ratio is simply the value calculated from two individual uncertainty values accompanied by RNAA and ICP-MS data. Please note here that the uncertainty of RNAA is a standard deviation (1σ) of three or four separately determined values, whereas the uncertainty of ICP-MS is a standard deviation of several (normally three) consecutive measurements of one solution sample. Although the two sets of data are fairly consistent between RNAA and ICP-MS, it can also be seen that the ICP-MS data are systematically lower than the RNAA data. In particular, ICP-MS data for bromine for three samples (JLs-1, JDo-1, and JSd-1) are lower than the corresponding RNAA data, even with the uncertainties being concerned. A similar situation can be seen for iodine in four samples (JLs-1, JDo-1, JSL-1, and JCh-1). However, the ICP-MS data for bromine and iodine are very consistent with the RNAA data for two samples (JLk-1 and JSd-3), where bromine and iodine contents are relatively high compared with those in the other seven samples. In the sample containing more than a few $mgkg^{-1}$ bromine and/or with more than 1000 μgkg^{-1} iodine, consistent data between RNAA and ICP-MS are likely to be obtained. Although inconsistency between RNAA data and ICP-MS data cannot necessarily be seen for a sample such as JSL-2 where bromine and iodine contents are relatively low, ICP-MS data of both bromine and iodine are evidently lower than RNAA data for the limestone sample (JLs-1), which consists mainly of calcium carbonate and is decomposed into refractory calcium oxide (having a high melting point of 2927 K) and carbon dioxide on heating.

Presumably, the quantitative collection of bromine and iodine cannot always have been achieved in the pyrohydrolysis procedure [2]. This suggests the limitation of the pyrohydrolysis procedure in the determination of halogens (at least bromine and iodine) by ICP-MS. It may be noted, however, that RNAA and ICP-MS data agree within 10% for both bromine and iodine, as shown by the mean values of individual ratios, and further that ICP-MS coupled with pyrohydrolysis can work well for such studies where only rough abundances of halogens are required. However, if accurate values of halogens are essential for the study, which corresponds to the analysis of reference samples, RNAA is the best choice of analytical procedure. There is also an advantage of choosing RNAA over ICP-MS when the sample mass used for analysis is limited and duplicate analyses are not possible or desirable, as is the case when analyzing extraterrestrial samples such as meteorites and lunar samples.

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Table 1. Ratios of ICP-MS values to RNAA values

Sample	ICP-MS/RNAA	
	Bromine	Iodine
JLk-1	1.02±0.08	1.03±0.07
JLs-1	0.65±0.1	0.82±0.1
JDo-1	0.85±0.08	0.90±0.09
JSL-1	0.89±0.14	0.80±0.08
JSL-2	0.90±0.16	1.04±0.13
JSd-1	0.89±0.06	0.95±0.09
JSd-2	1.04±0.07	1.09±0.11
JSd-3	1.07±0.13	1.00±0.08
JCh-1	2.22±1.54	0.84±0.10
Mean	0.92±0.19[a]	0.94±0.1

[a]A ratio for JCh-1 is ruled out (see text for details).

Fig.1 Concentration ratio of bromine (a) and iodine (b) between RNAA values and ICP-MS values.

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INTRODUCTION: Pigments include many kinds of heavy metal elements. It is famous that arsenic (As) was included in the hair of Napoleon Bonaparte because the paint on the wall tiles included it. It became clear by the analysis of INA [1]. When pigment includes toxic heavy metal elements, it becomes risk for human.

Many pigments named cadmium (Cd) are sold of not only the color of yellow but also red, orange and green. On the other hand, there are many same color pigments without claiming cadmium. Pigments were analyzed by INAA to study the concentration of Cd in them. At the same time, the pigments   were checked on the indications for relationship to health risk.

EXPERIMENTS: Samples were oil paints, acrylic paints, water paints and powder. Numbers of samples were 23, 5, 6 and 6, respectively. Each sample weight was measured and if it was necessary, some of them were dried under the infra-red lamp. Each of them was enclosed in a double polyethylene bag. The standard samples used were JA-2 and JR-2 of rock standard, and 10 ppm Cd and 50 ppm mercury of atomic absorption reagents were used applying to a filter paper. The samples were put in capsules with the standards and irradiated 5MW $\times$ 10 min or 1MW $\times$ 30 min at KUR. After cooling among 5 days, the capsules were opened, and then measured the gamma-rays of medium and long half life radionuclides.

RESULTS: The pigments named cadmium included Cd from approx. 4 ppm to 46%. Also the pigments named cadmium-red or -orange included not only Cd but also mercury; a few ten ppm. Other elements such as sodium, calcium, iron, cobalt, barium and chromium were detected in them from a few ppm to a few hundred ppm. All sorts of pigments included Cd when they were named cadmium; it does not depend on the pigment sorts except for color pencils.

Discussion: There was no information of the concentration of Cd included in the pigments. So, more than 40 samples were put in one capsule and irradiated. The concentration of Cd was high from a few percentage to a few ten percentage in many samples named cadmium, so it was considered that the neutrons were absorbed at many points and the results were not correct. So such the high Cd concentration samples were not suitable for INAA. On the other hand, the sample preparation was only dryness for INAA; undestroyed method. Except for Cd high concentration case, the INAA method is easy to analyze pigments which were organic and inorganic compounds mixture. In a near future, the samples are planned to analyze by a fluorescent X-ray method.

The indications on the pigments for health risk were as follows; 1. Not the all pigments including Cd had marks for health risk. 2. When the indications were on the pigments, there were a few marks. 3. These marks were shown little explanation. As these situations, users can not decide that the pigments are safe or not. It is considered that same marks will be necessary for all over the world and explanations of the marks will be necessary for safe use of pigments.

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Neutron Activation Analysis of Trace Mn in Iron Meteorites

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INTRODUCTION: Meteorites contain cosmogenic nuclides produced by a nuclear reaction with cosmic rays. Cosmogenic nuclides are useful for determination of exposure and terrestrial ages. In general, only radionuclides and noble gas stable-isotopes can be detected as cosmogenic nuclides. Although it is difficult to detect cosmogenic stable nuclides in stony meteorites, some cosmogenic stable nuclides could be detected in iron meteorites, which consist of mainly an iron–nickel alloy, since iron meteorites have little geochemical lithophile elements. Among such stable nuclides we focus on Mn.

Natural Mn is a monoisotopic (^{55}Mn) element. But iron meteorites have also a cosmogenic radioisotope, ^{53}Mn, which has longest half life among detectable cosmogenic radionuclides. One of practical methods for determination of ^{53}Mn is a preconcentration neutron activation analysis (preNAA) using ^{53}Mn(n, γ)^{54}Mn reaction. We suggested that ^{55}Mn content should be required for determination of ultra trace ^{53}Mn in iron meteorites by preNAA because of correction of ^{55}Mn(n, 2n)^{54}Mn. But accurate concentration in iron meteorites is rarely reported. Almost ^{53}Mn in iron meteorites is extrapolated to be comsogenic by ^{45}Sc contents [1]. If accurate ^{55}Mn concentration can be determined, ^{55}Mn-^{53}Mn system for exposure age will be also established. And estimation of original ^{55}Mn concentration is interesting for considering a differentiation of planets. Determination of ^{55}Mn in iron meteorites by NAA is well known to be interfered by ^{56}Fe(n, p)^{56}Mn reaction. Therefore, the removal of iron prior to irradiation or irradiation at a channel with high Cd ratio is required. Thus we tried to determine ^{55}Mn concentration in iron meteorites by preNAA using well thermalized neutrons.

EXPERIMENTS: Using radiotracers, a chemical procedure using an ion-exchange method was developed for separation of Mn from iron meteorites based on one by Fujimoto and Shimura [2]. After dissolution of a sample in 2 M HF, the HF solution was loaded on a cation exchange resin. Adsorbed Mn was eluted by 8M HCl, and then Mn in HCl - 2-propanol solution was purified by an anion exchange method. This procedure was applied to Japan steel standard samples and Gibeon iron meteorites followed by irradiation of separated Mn fraction for 4 hours at the thermal column pneumatic transport system (Tc-Pn) and for 1 hour at Pn-2 in Kyoto University Research Reactor (KUR). In addition, sensitivity of ^{55}Mn(n, g)^{56}Mn and contribution of ^{56}Fe(n, p)^{56}Mn at Tc-Pn in KUR and at PN-3 in the Japan Research Reactor-3 (JRR-3), Japan Atomic Energy Agency were evaluated by using Mn standard and Ti plate, respectively.

RESULTS: In Mn fraction irradiated for 1 h at Pn-2, no ^{59}Fe and ^{60}Co was observed. Our chemical procedure removed > 99.99% of Fe and Co and > 99.5% of Ni, Ir and Cr, and overall procedure blank of Mn was about 30 ng. Determined Mn concentration in steel standards (JSS003-5 and JSS001-5) and Gibeon meteorites are shown in Table 1. Low determination values in Run-1 were guessed to be caused by low chemical yield. In Run-2 a chemical yield was estimated to be 91% and determined concentrations on Mn in steel standards were consistent with certified values. It is concluded that down to 30 ppb of Mn can be determined by our method.

Sensitivities of Mn were 930 cps/mg and 2400 cps/mg for 4 h irradiation at Tc-Pn and 20 min irradiation at Pn-3, respectively. And contributions of (n, p) reaction were corresponding 16 ngMn/gFe and 97 ngMn/gFe for Tc-Pn and PN-3, respectively. Since Fe was sufficiently removed, contribution of ^{56}Fe(n, p) reaction was more than 150 times smaller than the present procedure blank. A detection limit of Mn by preNAA was 30 ppb, assuming that a half of induced ^{56}Mn is resulted by a blank. Even INAA using Tc-Pn can determine such concentration of Mn. Reducing a procedure blank is highly required for lower detection limit.

Table 1: Result of Mn content

Sample	Unit	NAA*			preNAA run1			run2			Certified Value		
JSS003-5	ppm	24.9	±	0.2	19.8	±	0.4	26.0	±	0.3	27	±	1
JSS001-5	ppb	36.1	±	2.2				27.5	±	2.2	30	±	10
Gibeon	ppb				273	±	9	415	±	7			

*Corrected for (n, p) reaction.

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CO5-17 Study on Sorption Behavior of Trace Elements in Sedimentary Rocks and Bentonite Using Sequential Extraction Method

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INTRODUCTION:

One of the major problems with nuclear power is the disposal of high-level radioactive waste (HLW). The accident at the Fukushima Daiichi Nuclear Power Plant has highlighted this issue.

Initially, HLW is highly radioactive, and takes about hundred thousand years to reach the same level of radioactivity as natural uranium ore. Geological disposal is used to isolate HLW for long time periods. Geological repositories contain a multi-barrier system of artificial barriers made of over-pack and cushioning bentonite clay, and natural barriers consisting of geological formations. Minor actinoid (MA) radionuclides, such as ^{237}Np, ^{243}Am and ^{247}Cm, which are produced by the neutron capture reaction of uranium, are present in HLW.

Although it is crucial to evaluate the behavior of MAs in the multi-barrier system over tens of thousands of years, MAs are very difficult to observe experimentally because they are extremely toxic and produced artificially in only limited quantities.

In this study, we have used the lanthanoids (Lns), Th and U as natural analogues for the MAs in order to determine the sorption behavior of the elements in flowing artificial groundwater with a sequential extraction method[1-2].

SAMPLES AND EXPERIMENTS:

The samples were collected from boreholes drilled by the Horonobe Underground Research Center of the Japan Atomic Energy Agency. The bentonite was purchased from Kunimine Industries Co., Ltd.

The trace elements (Lns, U and Th) were determined by neutron activation analysis (NAA) of the pulverized samples at the Kyoto University Research Reactor (KUR; Table 1). The artificial groundwater was produced by adding the Lns to natural groundwater.

The groundwater conditions were as follows: pH 8.0, temperature 18 °C, flow volume 5 L, flow rate 3 mL/min, Ln concentration 10 ppb.

Table 1. Irradiation conditions of KUR

Kyoto Univ.	Half times	Irrediation location	Output(MW)	Max thermal neutron flux (n/cm²/s)	Irradiation times
KUR	Long	PN-2	5	2.75×10^{13}	1hour
	Short	PN-3	1	4.68×10^{12}	40sec.

Sequential extraction was used to analyze the behavior of the elements in the samples. The extracted solution and the residue were analyzed by NAA and ICP-MS.

RESULTS:

Figure 1 shows the sequential extraction results. In step 2 (■) the Dy concentration increased compared with the blank. This suggests that Dy may co-precipitate with Mg. The results can be summarized as follows:

(1) natural analogue elements such as Dy may precipitate as hydroxides and co-precipitate with magnesium and ferric hydroxide;

(2) the light Lns (La-Eu, K_d: 0.97 (max)) adsorb to magnesium and ferric hydroxide more easily than the heavy Lns (Gd-Yb, K_d: 0.81 (minimum));

(3) heavy Lns adsorb to pyrite and organic matter more easily than the light Lns[3];

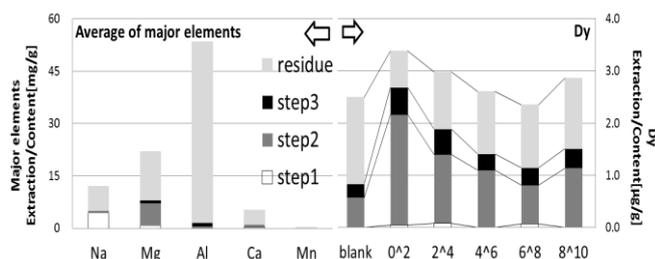(4) the natural analogue elements in bentonite, such as Dy, form sulfides following silicates; and

Fig. 1 Sequential extraction results for the major elements (left) and for Dy (right).

(5) bentonite and sedimentary rocks may delay the migration of MAs in groundwater to the surface, because the MAs may precipitate with Mg and Fe.

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CO5-18 Geochemical Mapping for the Upper Ara-river System Area, Saitama Prefecture by Neutron Activation Analysis (II)

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INTRODUCTION: Geochemical maps express areal distributions of chemical elements in the earth's land surface and give information about the chemical background in the natural environment to assess the artificial environmental changes [1, 2]. In this study, we report the geochemical mapping for the upper Ara-river system, Chichibu Mountain area, Saitama in 2012. Cosmo-Geochemistry Lab., Rissho University has been making up the geochemical maps since 2000.

EXPERIMENTS: We analyzed the stream sediments which had been collected as a sample representing the geochemical characters in each drainage basin. A sampling site 1 per 1 km^2 was selected in the area which a mountain ridge was surrounding and at 100m upper stream in the branch from the junction of main stream to avoid the contamination by floods. The stream sediment was sieved to 80 mesh (<180 µm) on site and the fine fraction was reserved for analysis. 47 elements in collected samples are analyzed by X-ray Fluorescence Analysis (XRF), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), Prompt Gamma-ray Analysis (PGA) and Instrumental Neutron Activation Analysis (INAA). INAA has great advantage for Au, As and Sb analyses compared with ICP-MS, because of their low ionization potential.

RESULTS: Japanese character Kanji "金" means gold (Au). Places around place name 金沢(Kanazawa), 金山(Kanayama), and 金崎(kanesaki) are possible Au-producing district. In 2012 year study area, there were 4 possible Au-producing districts (1223, 1224, 1225 and 1235) (Fig.1).
The geochemical maps of As and Sb indicate similar distribution of these elements and similar to Au. Table 1 shows the ana-

lytical results of Au, As and Sb for the above four districts samples by INAA. The results indicate only one district (1235) has high Au and As contents compared with those for another possible district samples, although the Sb contents is not so high. Sampling point of the sample 1235 is down stream from "Kanezaki." This suggest that place-name 金崎(Kanesaki) is Au producing district.
In 2011 study, the Au content in a sample was extremely high (22,560ppb), although As and Sb contents were normal [3]. In this study, the Au, As and Sb contents in the sample were analyzed again by INAA. The results for those elements of the sample in this study are just normal. High Au, As and Sb contents were not obtained. This suggest that the high Au content in 2011 study was artificial contamination for the sample. This sampling point is not Au producing district.

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Table 1. Au, As and Sb contents in samples 1223, 1224, 1225 and 1235

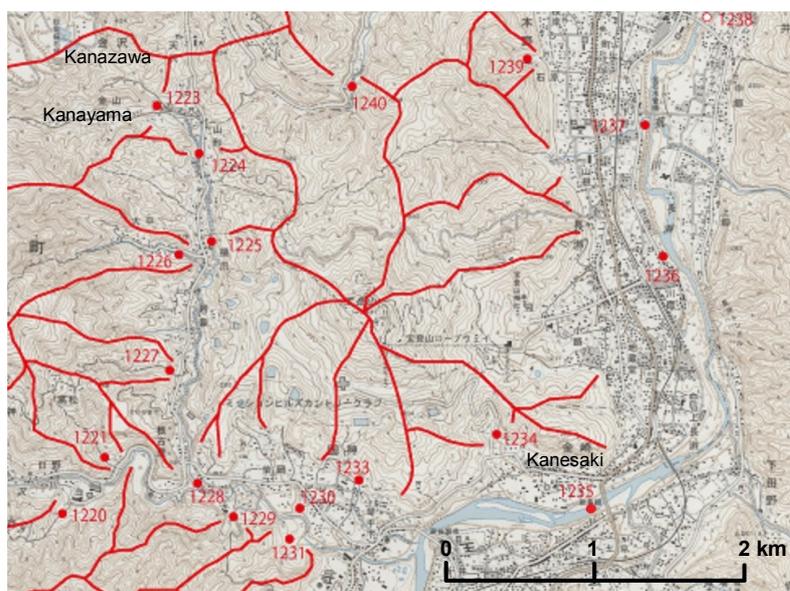| Sample name	Au ppb	As ppm	Sb ppm	Sampling point
1223	ND	7.4	0.1	Down stream from "Kanazawa" and "Kanayama"
1224	1.4	12.6	0.1	As above
1225	ND	3.0	ND	As above
1235	26.7	10.9	0.1	Down stream from "Kanesaki"

*ND: not detected

Fig. 1. Tophgraphic map showing sampling points
● Sampling point