CO5-1 Evaluation of Radioactive Cesium Behavior in Natsui River Basin, Fukushima

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INTRODUCTION:

Most of radioactive cesium (^{137}Cs) released by the nuclear accident in 2011 remains in the basin soil, but a part of it has flowed out into the water environment and accumulate in the bottom sediment or moves to further downstream such as bay and sea. For example, in Dam Lake, it was confirmed that about 90% of the ^{137}Cs which have been flowed from its watershed is accumulated$^{1)}$. It is concerned that ^{137}Cs remaining in various places such as lake bottom sediments we have an impact on our life through elderution phenomena and bioaccumulation.

In this study, on-site sampling and analysis of samples obtained there were conducted at the Natsui River Basin in Fukushima for the purpose of estimating and predicting ^{137}Cs concentration and its dynamics in the dam lake. We focus on the particle origin (originated from internal production and derived from river SS) in the dam lake, and report the findings obtained on the ^{137}Cs concentration and its dynamics.

SURVEY and EXPERIMENT METHODS:

The area surveyed in this study is the Natsui river basin (750km^2) in Fukushima, and lake water was collected especially at the Kodama dam located in the middle stream, the Kodama river water that flow into the Kodama dam and the Natsui river water as main stream. At the Kodama dam, bottom sediment and surface water were collected at a point 40m (water depth 55m) upstream from the dam body, and also river water was collected at Kodama and Natsui river. At each site, 1-5 tons of environmental water was locally concentrated by a pore size of 38-250 μm sieves. The recovered particles and sediment samples were brought back to the laboratory and have been freeze-dried. The amount of particles recovered in this survey (on-site concentration) was 50-400 mg dry weight per each point.

For environmental water (30-100L), solid-liquid separation was first carried out by 1μm pore size of GFF. The residue on the GFF was used as a suspended sample, and ^{137}Cs in the filtrate (30 L) was selectively concentrated with Empore$^{\text{TM}}$ Rad-disc made by 3M Inc. ^{137}Cs was analyzed by Ge semiconductor detector (mainly GX 4018, Canberra), CN ratio of particles was analyzed CN coder (NC-22F, Sumitomo Chemical), stable carbon isotope ratio of particles, δ^{13}C, was analyzed by mass spectrometer (DELTA V Advantage).

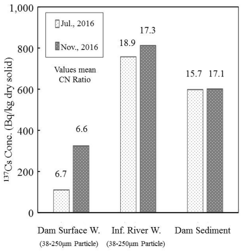
RESULTS and DISCUSSIONS:

Fig.1 shows the ^{137}Cs concentrations of 38-250μm particles at Kodama dam and Kodama river, and the dam sediment in the July and November 2016. The CN ratios of them are also shown in the figure. Particles on the surface water of the dam were estimated to be derived from internal production (*i.e.*, plankton) based on their particle size and CN ratio. ^{137}Cs concentrations of particles in surface water at the dam were 3-6 times lower than those of the inflowing Kodama river. This fact means that the suspended ^{137}Cs concentration assumed to be derived from internal production tends to be lower than that derived from outside river. The ^{137}Cs concentration of the dam sediment was also slightly lower than the SS of the inflowing river, then it was speculated that it was also influenced by particles originating from internal production also from the CN ratio. The ratio, which is corresponding to BCF, of the ^{137}Cs concentration in the planktonic and dissolved matter at the surface water was estimated as 1.3-3.6 (×10^5 L / kg).

Fig.2 shows the analytical results of distribution coefficient K_d and δ^{13}C of the SS in Kodama dam surface water and Natsui river water. The K_d was indicated the value obtained by dividing the suspended ^{137}Cs (Bq/kg-SS) by the dissolved ^{137}Cs (Bq/L). In many cases at normal stage conditions especially, the K_d value of dam surface water tended to be smaller than that of river water.

As the results, focusing on the difference of particle origin by δC, seasonal fluctuation was confirmed in dam surface water, unlike river water. Because seasonal variation of δ13C in phytoplankton has been reported$^{2)}$, it was indicating that SS of dam surface water was affected by internal production. Since BCF of plankton was lower than the K_d value of river water, it was suggested that the K_d value is reduced due to the influence of internal production.

From the results of this study, it was found that the dam lake at the flood stage condition was greatly influenced by the inflowing river. On the other hand, at the normal stage conditions the influence of the origin due to the internal production was larger than that by inflowing of river water, then the influence have been also reflected in dam sediment.



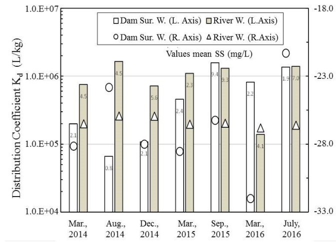


Fig.1: ^{137}Cs concentration of suspended matter in Kodama dam lake and its influent river (Left figure above)
Fig.2: Partition coefficients and stable carbon isotope ratios of dam surface water and Natsui river water (Right figure above)

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CO5-2

Size Distribution of Bromine in the Atmospheric Aerosols

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Bromine which is a halogen atom with symbol Br and atomic number 35 naturally exist mainly in the sea water(65mg/L) and industrially used mainly as a organic compounds used for fire-resistant sheet. These consumed compounds are finally burned in the incinerator and exhausted as a gaseous matter. Gaseous bromine can be easily changed to the atmospheric aerosols with its high boiling point (332K). Because of its poison properties the concentration levels and size distribution of bromine in the atmospheric aerosols must be investigated. Here we show the result of observations in bromine in the atmospheric aerosols at Sakai, 2012. Also we show the size distribution of Chlorine as a same halogen atoms to compare the differences of properties owing to the boiling point (239K Cl).

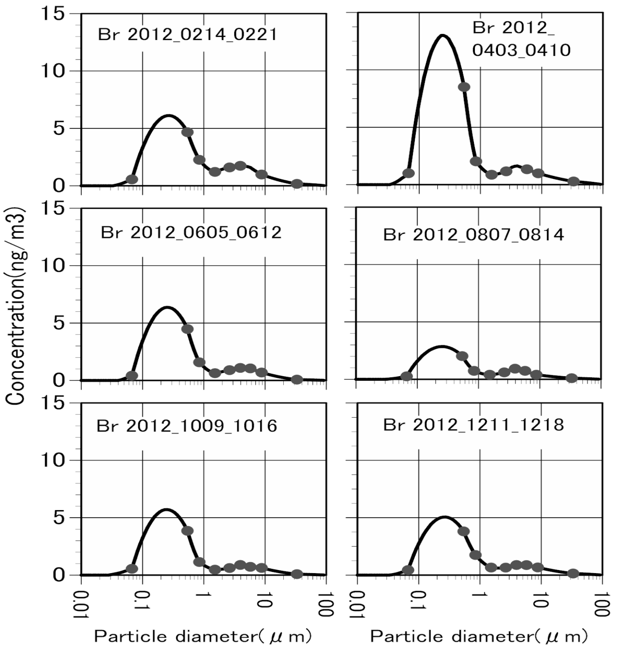

Fig. 1 Size distribution of Bromine observed at Saka,2012

The atmospheric aerosols were collected on 6 periods (Feb.12-14, Apr.03-10, Jun.05-12, Aug.07-14, Oct.09-16, Dec.11-18) in 2012. The aerosols were collected on an polyethylene sheet attached with 9satages by the rages (>11μm,7.0-11.0μm, 4.7-7.0μm,3.3-4.7μm, 2.1-3.3μm, 1.1-2.1μm, 0.65-1.1μm, 0.43-0.65μm, <0.43μm) using Andersen Sampler. Bromine and Chlorine in these samples were analyzed by Neutron Activation Analysis using Kyoto University Reactor.

We have got the size distribution profile of Bromine which have high concentration in fine (<1μm) particles that were products from gaseous bromine and short coarse (>1μm) concentrations mainly come from sea salt particle (Fig.1). The peaks in fine range can be found around 0.2μm and concentration is changed from 1.2 to 4.3(ng/m^3). Peaks in fine range for Chlorine can be found as a smaller than that in coarse range except winter period (1211-1218)(Fig.2).

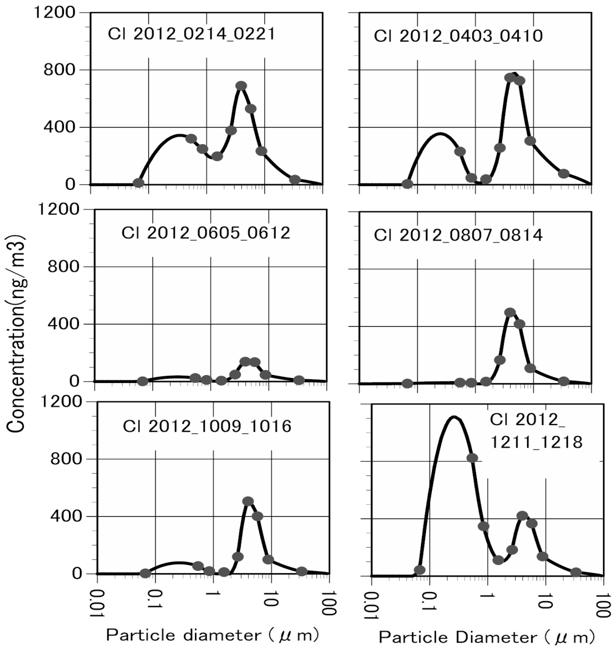

Fig. 2 Size distribution of Bromine observed at Saka,2012

Concentrations in coarse(C) and fine (F) ranges and ratio to Na are listed on Table1. Ratios to Na in the coarse for both of Bromine and Chlorine are small for that of sea salt, extremely lowest in summer (0807-0814). This decrease suggest the halogen loss by the temperature effect.

Table1 Concentrations of Bromine and Chlorine in coarse range(C,>2.1μm) and fine range (F <2.1μm), ration to Sodium(Br/Na,Cl/Na) in coarse range (Br/Na=6.2x10^{-3}, Cl/Na=1.8 in sea water)

	Concentration(ng/m^3)				Ratio to Na in coarse range	
	Br		Cl			
Period in 2012	C	F	C	F	Br x10^{-3}	Cl
0214-0221	1.1	2.9	250	170	6.8	1.5
0403-0410	1.1	4.3	290	44	3.8	0.99
0605-0612	0.57	2.0	42	11	5.0	0.47
0807-0814	0.49	1.2	110	18	2.8	0.58
1009-1016	0.46	2.4	91	20	3.2	0.64
1211-1218	0.6	2.1	140	230	5.9	1.3

CO5-3 Characteristics of Synthetic Calcite Thermoluminescence by Gamma and Beta Irradiation

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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. When thermoluminescence characteristics of calcites are examined using natural occurring calcite, their response to the various radiations depends on minor chemistry (Fe, Mg, Mn and Sr). In this study, calcites with controlled impurity concentrations were synthesized and analyzed to evaluate relationship between mul-tiple impurity concentration and thermolumines-cence properties quantitatively, together with natu-ral calcites.

EXPERIMENTS: Calcite were synthesized from so-dium carbonate (>99.8wt%) and calcium chloride (>95 wt%). Iron (II) chloride (>99.0-102.0 wt%), magnesium chloride (>98.0wt%), and manganese chloride (>99.0- wt%) were added at different levels to produce calcites with different amount of impurity. Chemical composition of resultant calcite were measured by LA-ICP-MS. Gamma irradiation was carried out at the ^{60}Co gamma irradiation facility at Kyoto University Research Reactor. Alpha and beta ray irradiations were carried out with disc-type ^{241}Am and ^{90}Sr source, respectively. Given doses by Gamma and beta irradiation were estimated by quartz irradiated together with synthesized calcite. A given dose by alpha irradiation was estimated by alpha track counting. Then luminescence emission from cal-cite was measured by the luminescence reader MOSL-22, and dose was estimated by the external x-ray source, whose dose rate is calibrated as 0.1 Gy/sec with quartz. This measured dose on calcite was compared to the given dose on quartz, and the ratio (calcite/quartz) was calculated for each irradiation (gamma, beta). Results on alpha irradiation will be reported later.

RESULTS: Calcite/quart ratios in dose estimate by luminescence were different among samples. Gamma and beta efficiencies are 0.115-0.398 and 0.122-0.481, respectively, and it indicates that equivalent doses of calcite samples were underestimated with X-ray calibrated using quartz. The gamma and beta efficiencies may be inversely proportional to Mg+Mn+Fe and (Mg+Mn+Fe)/Fe, respectively(Fig1&2). These may be caused by differences in the common substitution elements of calcite and quartz, as well as the interactions between medium with different atomic numbers and various radiation energies. The contribution of photoelectric effect increases with increasing impurity (Mg, Mn and Fe) concentration for radiation of 0.059MeV (tungsten target X-ray), thus gamma efficiency may decrease with increasing total impurity concentrations (Mg+Mn+Fe). Beta efficiencies must be considered together with the CL emission. Fe, which works as quencher in CL, may keep radiation energy from beta ray instead of transmitting to activator, thus accumulated dose of calcite may increase with increasing Fe concentration; therefore, beta efficiency may depend on (Mg+Mn+Fe)/Fe.

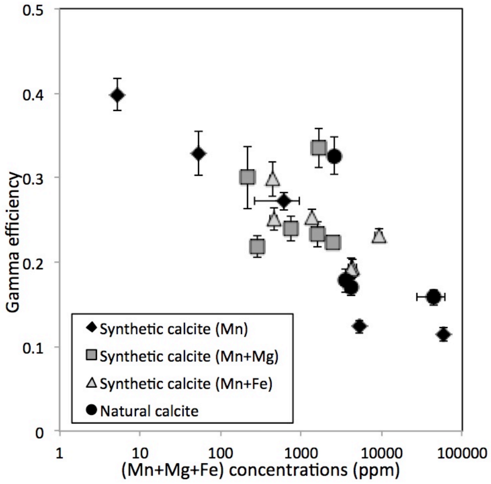

Fig. 1. Gamma efficiency as a function of (Mg+Mn+Fe).

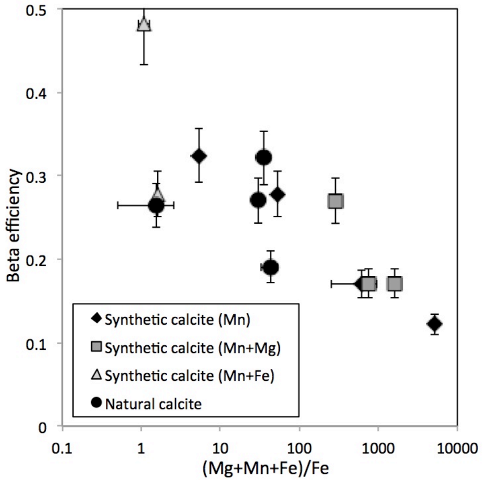

Fig. 2. Beta efficiency as a function of (Mg+Mn+Fe)/Fe.

CO5-4 Application of Neutron Activation Analysis to Micro Gram Scale of Solid Samples

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INTRODUCTION: Instrumental neutron activation analysis (INAA) is often used in cosmochemistry, where meteorites are the objects for INAA. Chondritic meteorites (chondrites) and iron meteorites contain relatively high contents of Co and Ir compared with those in the earth crust. As Co and Ir have high sensitivity in INAA, they can be good markers for the identification of such extraterrestrial materials. In NAA of chondrites, a few tens mg of specimen is commonly used. For such a case, a few hundred μg kg^{-1} of Ir and a few hundred mg kg^{-1} of Co can be reliably determined. When an extremely small size (e.g., micro gram) of samples such as micrometeorites recovered on the Earth surface and tiny particles returned from extraterrestrial asteroids are to be analyzed by INAA, the conventional INAA procedure used for a few tens mg is not suitable. For such tiny samples, neutron irradiation with high neutron flux and long irradiation time (namely, high neutron dose) is required. Recently we have presented the INAA procedure for micro gram scale of solid samples [1]. In this report, one typical example for the application of the proposed procedure is shown with limited scientific discussion.

RESULTS: Instrumental NAA results of the magnetic spherule are summarized in Table 1, where elemental concentrations are also given.

Table 1 Elemental contents in magnetic spherule analyzed by INAA in this study

	Content	Concentration
Sm	< 0.4 pg	< 0.06 mg kg^{-1}
La	< 1.6 pg	< 0.24 mg kg^{-1}
Sc	< 1.8 pg	< 0.27 mg kg^{-1}
Fe	3.90 ± 0.05 μg	601 ± 8 g kg^{-1}
Na	0.406 ± 0.008 ng	62.5 ± 1.3 mg kg^{-1}
Co	20.4 ± 0.2 ng	3140 ± 40 mg kg^{-1}
Cr	1.06 ± 0.06 ng	164 ± 9 mg kg^{-1}
Ni	328 ± 4 ng	50 ± 1 g kg^{-1}
Au	0.59 ± 0.05 pg	0.091 ± 0.007 mg kg^{-1}
Zn	< 0.98 ng	< 0.1 g kg^{-1}
Ir	16.3 ± 0.4 pg	2.51 ± 0.06 mg kg^{-1}

The magnetic spherule analyzed is characterized by high concentrations of iron (601 g kg^{-1}) and nickel (50 g kg^{-1}). These two elements comprise 65% of the bulk mass. Its Ir concentration (2.51 mg kg^{-1}) also is extremely high compared with terrestrial samples. Apparently, this spherule is extraterrestrial in origin. Such spherules are called cosmic spherules and often picked up from the deep sea sediment [2].

Elemental abundances of this spherule are illustrated in Fig. 1, where abundances are normalized to CI chondrite values [3]. Data for the other magnetic spherules from our previous work [4] are also indicated for comparison. Based on the elemental composition, magnetic spherules can be classified into two groups: one group have high CI-normalized abundances of Ir, Co, Ni and Fe (siderophile elements), and low abundances of Cr and Sc (lithophile elements), whereas another group have unfractionated CI-normalized abundances of both siderophile and lithophile elements. The magnetic spherule analyzed in this study apparently belongs to the former group. There has not been reported for Sc values for this group. It now becomes obvious that Sc is even lower than Cr in their CI-normalized abundances.

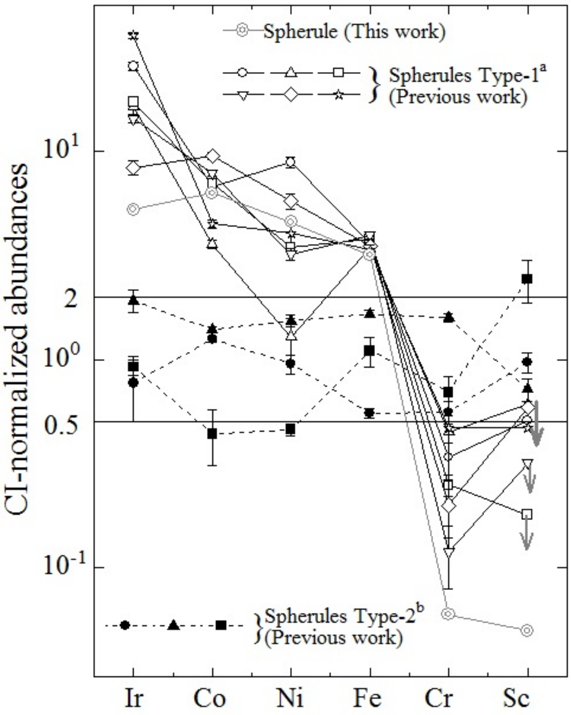

Fig. 1 CI-normalized abundances of Ir, Co, Ni, Fe, Cr and Sc in cosmic spherules

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CO5-5 Characteristics of a Hydroxide by Reaction of M_xO_y and $H_zT_{2-z}O$

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INTRODUCTION: Oxides like MgO and CaO react with water (H_2O) very easily and hydroxides such as $Mg(OH)_2$, and $Ca(OH)_2$ are formed. The reaction (e.g. hydration) between the oxide and water is very quick, the reaction also happens in the air. For that, CaO is used as a desiccant. The oxide will be able to be reacted with tritium water, easily. Tritium is a radioisotope and has been increasing by the nuclear testing and utility of nuclear power. In Japan, the accident of Fukushima the 1st atomic power station had released many kinds of radioisotopes and we are still removing the material with radioisotopes and there are some radioisotopes that the removal is difficult. Tritium is one of them. Tritium was a radioisotope of hydrogen. The characteristics of tritium are almost the same as hydrogen. In water, tritium water behaves almost similar to water. The boiling temperature and the decomposition of the electrolysis of tritium water are slightly different from those of water. If the extreme care should not be taken to remove tritium, it is very difficult to remove tritium water from water by the boiling temperature and decomposition of the electrolysis. We investigate that the hydroxide prefers tritium ion to proton, or proton to tritium ion, when the hydroxide is formed from the oxide and water including tritium water [1].

EXPERIMENTS: We used MgO (light) to be on the market. Since CaO reacts with water very easily, it was very difficult to prepare the treatment. $Ca(OH)_2$ can react CO_2 or carbonic acid, easily, and OH and OT of calcium hydrate removed to water again. We did not use CaO. For the reaction of MgO and tritium in water, we prepare the glass bottles with 10 cm^3 of water including tritium water and 1, 1.5 or 2g of MgO. The bottles were left for 1 to 24 h. On the other hand, glass bottles were stirred by the shaker for 1 to 24 h. After our purpose time, suspension was filtered by 0.45 or 0.2 μm of a disposable filter. For the measurement of concentration of tritium, 0.1 cm^3 of supernatant was mixed by 20 cm^3 of the liquid scintillator. The mixture solution was measured by a scintillation detector (Packard, Liquid Scintillation Analyzer).

RESULTS: Figure 1 shows the removal of tritium from water including tritium water by MgO to the variation of time. In the case of Fig. 1 (a), the bottles were not shaken but left on the table. In the reaction with MgO, tritium would be caught to $Mg(OH)_2$ formed. The concentration of tritium was smaller than the initial water. For leaving on the table, the surface of MgO reacts with water and $Mg(OH)_2$ would hardly removes from the surface. In Fig. 1 (a), the reaction of MgO and water would be quick and the removal might be high. The removal would be stable or decreasing after 5 h. MgO would not react with water on the surface. When the bottles were stirred (Fig.1, b), the removal shows slightly negative slope to the time. After the reaction, the concentration of tritium would increase in supernatant, because MgO preferred the reaction of proton to that of tritium and H_2O would decrease slightly in supernatant. Most MgO reacts with water (H_2O) and $Mg(OH)_2$ is formed. MgO is a cubic structure and $Mg(OH)_2$ is a hexagonal structure. $Mg(OH)_2$ would be removed from MgO surface because the particles were collided by the stirring. Water would be contacted with a fresh surface of MgO. In Fig. (b), the removal is almost around zero within 5 h after shaking. We can not find out the selection of tritium or proton of MgO. The removal would be negative, gradually in a long shaking time. In both Fig. 1 (a) and (b), the equilibrium reaction would not be achieved. We would investing the difference between Fig. 1 (a) and (b).

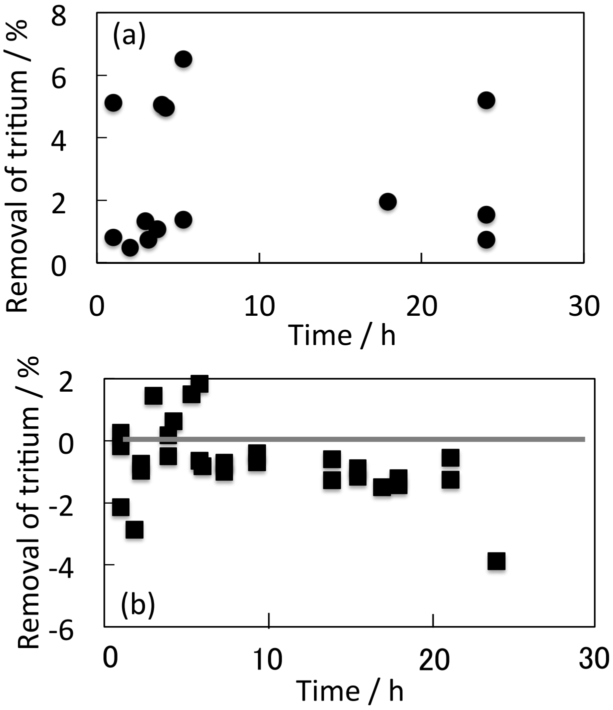

Fig. 1 Removal of tritium to the variation of time when the bottles were left (a), and the bottles were shaken (b). The gray line in (b) shows zero. The removal (%) was calculated by $R=(C_0-C)/C_0 \bullet W \bullet 100$, where R is removal, C_0 is the count of the initial water including tritium water, C is the count of supernatant after the contact with MgO and W is the weight of MgO.

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CO5-6 Chemical Variations of Miller Range 091010 (CV) Collected in the Ice at Miller Range, Antarctica

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INTRODUCTION: Most of meteorites are currently collected from cold and hot deserts. As these meteorites may have resided on the Earth's surface, they have experienced variable degree of terrestrial weathering. Terrestrial weathering obscures petrographic and chemical features, leading to misclassification and misunderstanding of geochemistry and cosmochemistry of these meteorites. In addition, misinterpretations probably result from sampling effect [1]. A large data set for carbonaceous chondrites was obtained by using 250-350 mg of sample [2]. It was reported that this amount of sample is not enough to obtain representative chemical compositions [1]. Therefore, we examine how sampling problem affect chemical classification by using Miller Range (MIL) 091010 (CV) which was collected in the ice at Miller Range, Antarctica.

EXPERIMENTS: Five different aliquots were taken from MIL 091010. These five samples were analyzed by INAA and IPAA at the Kyoto University Research Reactor Institute. For INAA, samples were irradiated two times with different irradiation periods which are adjusted for the half lives of the nuclides usable for determining elemental abundances. For IPAA, electrons are accelerated by the linear accelerator to 20 MeV, with an electron current of 120 μA. The samples were irradiated for 30 hrs. For comparative method, JB-1 was used as reference standard.

RESULTS AND DISCUSSION: Twenty nine elements could be determined by using INAA and IPAA. Sodium, Mg, K, Ca, Sc, Ti, Cr, Mn, Co and Ni were determined by both INAA and IPAA. Our data obtained by these two methods are in excellent agreement with each other. Heterogeneity of chemical compositions is significantly higher (less than 10% for Mg, Cr, Mn and Fe; more than 20% for other elements) than the previous study [2]. Carbonaceous chondrites are grouped into main eight groups (CI, CM, CO, CV, CK, CR, CH and CB) and C-ungrouped derived from diverse asteroids according to petrological, mineralogical, chemical and oxygen isotopic features. This meteorite was grouped into CV based on petrological and mineralogical studies [3]. It has been shown by Goodrich and Delaney [4] that carbonaceous chondrites can be easily distinguished from each other in Fe/Mn and Fe/Mg ratios. Figure 1 compared Fe/Mn and Fe/Mg ratios of carbonaceous chondrites. As seen in Fig. 1, our five samples have Fe/Mn and Fe/Mg ratios similar to those for CV and CK chondrites. It was reported that there are no clearly resolvable difference between CV and CK chondrites [5]. Carbonaceous chondrites can be also distinguished from each group based on volatile elements abundances relative to refractory elements abundances. Figure 2 shows Al/Mn and Zn/Mn ratios of our five samples. Most samples do not fall in the ranges of CV and CK chondrites. It was observed that variations of Al/Mn ratios among the five samples are significantly higher than those of Zn/Mn ratios. The sample mass of about 0.6 g is not large enough to obtain the representative chemical compositions. Aluminum is cosmochemically grouped into refractory elements, while Mn is grouped into moderately volatile elements. In CV chondrites, a major host phase for Al is considered to be Ca-Al-rich inclusion (CAI). Therefore, observed large variations of Al/Zn ratio are attributed to the heterogeneously distribution of CAIs. The two samples (11,04 and 11,07) have higher refractory element abundances than those for the other three samples.

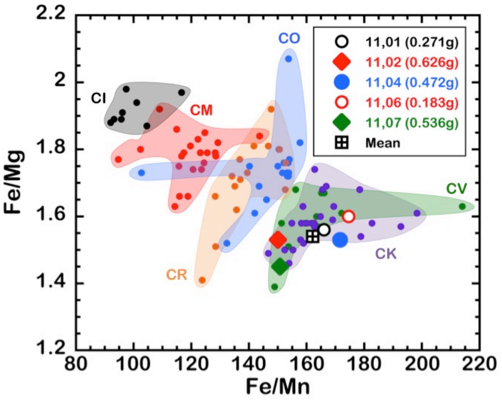

Figure 1. Fe/Mn vs. Fe/Mg diagrams for carbonaceous chondrites.

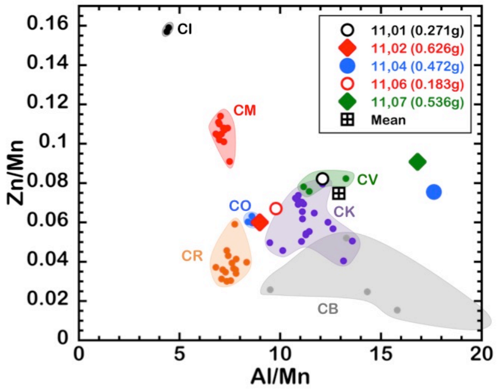

Figure 2. Al/Mn vs. Zn/Mn diagrams for carbonaceous chondrites.

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