The Distribution Behavior of Stable and Radioactive Cs between the Clastic Grains and Water in the Isolated Undisturbed Mountain Pond

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The concentrations of stable Cs and radioactive fallout ^{137}Cs were determined for the clastic grain of the isolated undisturbed pond "Yasha-ga-Ike", located at an elevation of 1100m near the ridge of mountain in Fukui Pref. The concentrations of both cesiums varied with particle size and increased with a decrease in diameter. Using the concentration data for the pond water, the in-situ distribution coefficient Kd defined by the ratio of the element concentration adsorbed on the particle to that of the water was obtained both for the stable Cs of eight samples, taken at different times from June 1999 to October 2001, and the radioactive^{137}Cs of four samples. The values of Kd increased with a decrease in particle diameter and ranged from about 10 to 1000m^3/kg, and the Kd for the stable Cs were slightly larger than those of ^{137}Cs. The results suggest that the adsorption of the stable Cs was established before the fallout of the ^{137}Cs, and the isotopic exchange between both cesiums has been proceeding from the water to the adsorbed layer and the grain matrix.

1. Introduction

The distribution coefficient, which is defined as partitioning of a solute between a solid and liquid phase, is used in various models which describe the migration and transport phenomena of radionuclides in environment and is one of the important parameters for environment safety assessment of nuclear waste disposal. The data of the coefficients are obtained mostly through in-vitro batch or column experiment using radioactive tracer and less through in-situ measurement in the environment[1)-5)]. As to the behavior of caesium in the environment, the migration and sorption in the lake or river have been studied only on the radioactive caesium derived mostly from the weapon-testings and Chernobyl accident[6)-10)], and the studies on both radioactive and stable caesiums are found in the transfer and accumulation in such plant ecosystem as the soil-plant and/or fungus-animal pathway[11)-12)]. Thus the studies for obtaining the distribution coefficients of both caesiums from a natural appropriate environment are few. This study concerns the simultaneous measurement of in-situ distribution coefficients of both radioactive ^{137}Cs and stable Cs between clastic grains and pond water in the small isolated undisturbed pond named "Yasha-ga-Ike", where the partitioning equilibrium in the pond was regarded to be attained in a long period.

The researches on the water and the grains of this pond have been carried out as in the following. The samples of grains and pond water were taken near the beach and the concentrations of elements were analyzed by the neutron activation and the ICP-MS method, respectively. The concentration of any constituent element of the grain was found to decrease with increase in particle size, and the adsorptive behavior of trace elements onto the grains was postulated[13)] and then confirmed[14)]. The concentrations of radioactive ^{137}Cs from the global fallout of the weapon testings in the sixties and stable Cs in the pond water were determined, as will be referred later[15)]. It is the purpose of the present study to elucidate the distribution behavior of radioactive ^{137}Cs and stable Cs between the clastic grains and water, and the in-situ distribution coefficients of both

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cesiums between the grains and the pond water were obtained and compared.

2. Experimental Procedures

2.1. Small Isolated Undisturbed Pond "Yasha-ga-Ike"

The pond "Yasha-ga-Ike", with maximum depth of 7.5m and about 40are of water surface is located at an elevation of 1100m near the ridge of mountain in Fukui Pref. The pond is supposed to be formed by landslide of the surrounding mountain of chert formation in the latter period of the diluvial epoch.   Three sides of the pond is surrounded by steep slopes except one side covered with bush.   The watershed of the pond is small and none of rivers flow in and out.   The pond water is usually clear having the turbidity of about 2mg/l at deepest point except the rainy day and is said to have never run dry.   A small Japanese diving beetle "Yasha-Gengoro" specially protected due to its rareness lives in the water.   Thus this pond is regarded as an isolated undisturbed non-volcanic pond, and it is supposed that all the fallouts from the sky have been accumulated.   The outline of the pond is shown in Fig. 1, in which a bold line indicates the countour of water surface, a thin line the beach, a dotted line the portion of mud sediments and a bold double dotted line the ridge line deviding Fukui Pref. and Gifu Pref.   As to the sediments of the pond, mud covers the central deep location, and clastic grains of chert with different sizes are found both at the shallow place in the pond and the flat beach which is covered with water and snow in winter time.

As described in the following, the samples of amber-colored clastic grains and pond water were taken, and the concentrations of stable Cs and radioactive ^{137}Cs were determined by the neutron activation, the ICP-MS or the

Fig. 1   The pond "Yasha-ga-Ike"

gamma spectrometry.   Both the grain surface rubbing-off and the nitric acid leach techniques were applied to the grain samples to confirm the adsorptive behavior of both cesiums.   After determining the adsorbed amounts of them, the distribution coefficients between the grains and the pond water were obtained.
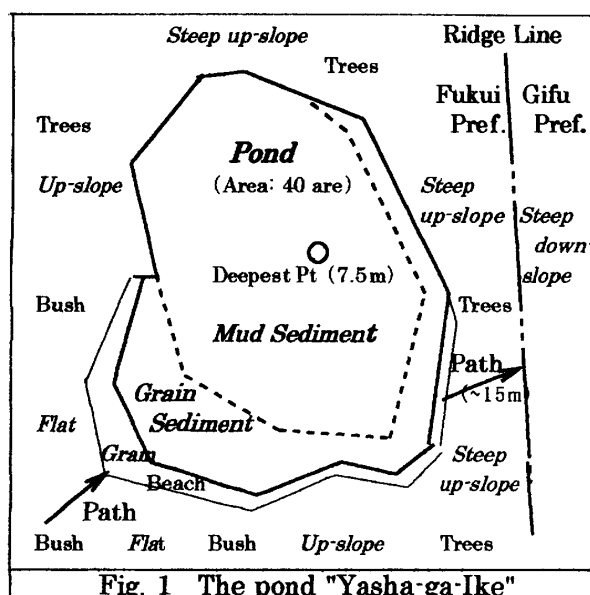
2.2. Measurements of Stable and Radioactive Cs Concentrations for the Grain and Water Samples

Seven samples of grains and pond water from the shallow place of about 50cm depth near the beach and one grain sample from the beach were taken at different times from June 1999 to October 2001 as given in Table 1, where the temperature of water varied from 12.5 to 25.5 ℃.   The grain samples were dried and sorted into 11 fractions of diameters; 2-1mm, 1mm-710μm, 710-500, 500-355, 355-250, 250-180, 180-125, 125-90, 90-63, 63-38 and < 38μm.   The sieves were chosen so as to meet the ratio of the opening dimension of any screen to that of the next smaller screen is square root of two.   For each fractions of sorted grain samples, neutron activation analysis and ^{137}Cs radioactivity measurement were carried out.   The samples of about 80 mg were irradiated for 20 sec and 60 min under thermal neutron flux of 2.3x10^{23} and 2.8x10^{13} n/cm$^2\cdot$s, respectively, by KURRI (Kyoto University Research Reactor) and the gamma spectrometry was applied in

order to obtain the concent-
rations of about 25 elements
such as Na, K, Rb, Cs, Mg,
Ba, Cr, Mn, Fe, Co, Al, Sc,
La, Ce etc., although only
the Cs is referred in this
study. The gamma-ray
spectrometry by a Ge(Li)
detector was applied to each
particle sample of about 60g
contained in thepolystylene
vessel with6cm diameter by
2cm high, and the concent-
tration of ^{137}Cs was mea-
sured.

Table 1   The Grains and Water Samples and Notations

Exp No.	Sampling Date	Water Temp.(℃)	For Stable Cs		For ^{137}Cs	
			Grain	Water	Grain	Water
D	June 9, '99	18.0	DB	DW	DB*	DW*
F	Oct. 16, '99	15.0	FB	FW	FB*	
G	Nov. 07,'99	12.5	GB	GW	GB*	GW*
H	May 23,'00	19.0	HB	HW	HB*	
I	July 17,'00	25.0	IB, IY	IW	IB*	IW*
J	Oct. 14,'00	15.5	JB	JW		
K	May 20,'01	20.0	KB	KW		
L	July 23,'01	25.5	LB	LW	LB*	LW*
N	Oct. 13,'01	14.0	NB	NW	NB*	
Note : IY sample was taken from the beach.						

The decay corrections for the samples were made as to February 2000, when the
measurement of DB sample was done.

For the water samples, the concentrations of stable Cs was measrued by the ICP-MS,
and the radioactive ^{137}Cs collected in-situ at the pond by pumping the water to the packed
column of acrylic fibre adsorbent, impregnated with copper hexacyanocobalt ferrate[16], was
analyzed by the gamma-ray spectrometry, as described in the previous report[15].

2.3. The Grain Surface Rubbing-off and the Nitric Acid Leach of the Grain Samples

When the cesium element is adsorbed on the grain surface, the concentration of cesium
on and near the surface is expected to be higher than that of the grain matrix.   To
ascertain this expectation directly, the following two methods of the surface rubbing-off and
the nitric acid leach are applied to the sieved particles.   In case of the surface rubbing-off
technique, the particles of HB1 and FB1 samples
with size range of 2-1 mm in diameter are
rubbed gently by using agate mortar and pestle
and then sieved.   The concentrations of stable
Cs and ^{137}Cs in the sieved particles are analyzed
by the neutron activation and the gamma
spectrometry, respectively, and compared.   In
case of the nitric acid leach, the sieved particle
samples of IB and LB that have finished the
measurement of ^{137}Cs radioactivity are leached
with 8N nitric acid near the boiling point for 3
hours.   After the leach, the concentrations of
stable Cs and ^{137}Cs in the residual particles were
measured and the concentration leached was
obtained as the difference between the
concentrations before and after the leach. Also
the concentration of stable Cs in the acid
solution after the leach is measured by the
ICP-MS, where the solution was diluted by 1000
times, to obtain directly the concentration
leached.

Fig 2   The concentrations of Stable Cs
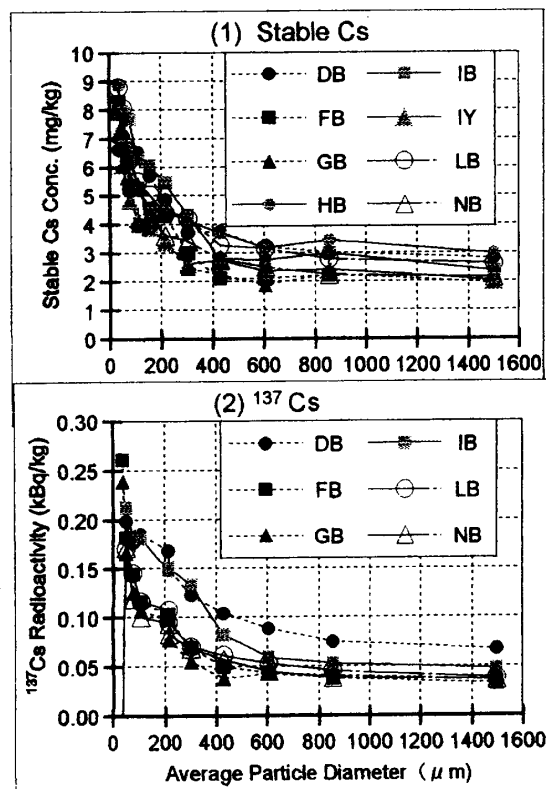and ^{137}Cs in the Grain Samples

3. Experimental Results

3.1. Concentrations of Stable Cs and Radioactive ^{137}Cs in the Grains

The concentrations of stable Cs for the eight grain samples of DB, FB, GB, HB, IB, IY, LB and NB are plotted against the average diameter of the sieved particles in Fig. 2(1) and those of ^{137}Cs for the six samples of DB*, FB*, GB*, IB*, LB* and NB* in Fig.2(2). It is seen that the concentrations of both stable Cs and ^{137}Cs decrease with increase in diameter, as reported for many stable elements in cases of DB and GB samples in the previous report[15], and that the difference of concentrations among samples is not so large.

The concentration of stable Cs or ^{137}Cs in the grain matrix was obtained by extrapolating the grain size to an infinitive. The concentration of stable Cs is 2.4mg/kg for DB, 1.5 for FB, 1.3 for GB, 2.4 for HB, 2.0 for IB, 1.5 for IY, 2.0 for LB and 1.5 for NB, and that of ^{137}Cs is 0.080kBq/kg for DB*, 0.030 for FB*, 0.025 for GB*, 0.035 for IB*, 0.025 LB* and 0.025 for NB*, respectively.

3.2. The Grain Surface Rubbing-off and the Nitric Acid Leach of the Grain Samples

(1) The Grain Surface Rubbing-off

After the surface rubbing-off of the particles of HB1 and FB1 samples with 2-1 mm in diameter, the concentrations of stable Cs and ^{137}Cs were measured for the particles size ranges of 2-1mm, 710-500, 355-250, 180-125 and 90-63 μm. The results are shown in Fig. 3, where the

Fig. 3 The Results of Surface Rubbing-off

ratio of the concentration of the residual particles after the rubbing to that of the original HB1 or FB1 particles, denoted as X:1500, is plotted against the diameter in order to make the effect of the rubbing clear. It is seen that the concentration of the residual particle, whose surface was rubbed-off and shown by Y:1500, are lower than those of the fine particles which are derived mostly from the near-surface and shown as Y:605, Y:303, Y:153 and Y:77 corresponding to the size range. Thus the concentration on and near the particle surface was confirmed to be higher than that of the inner grain matrix.

(2) The Nitric Acid Leach

After the nitric acid leach, the concentrations of stable Cs both in the residual particles and the leached solution and those of radioactive ^{137}Cs in the residual particles were measured, and the results for the sample LB are shown in Fig. 4. In this figure, such concentrations as the whole cesium in the particle before the leach, the adsorbed cesium, the leached cesium and the residual cesium after the leach are plotted against the average particle diameter. The concentration of the adsorbed cesium was calculated by subtracting the concentration of grain matrix from the whole concentration. The concentration of the leached cesium was determined by the analysis of the leached solution by the ICP-MS and that of ^{137}Cs by taking the difference of gamma radio-activities of the particles before and after the leach. The similar results were obtained for the sample IB .
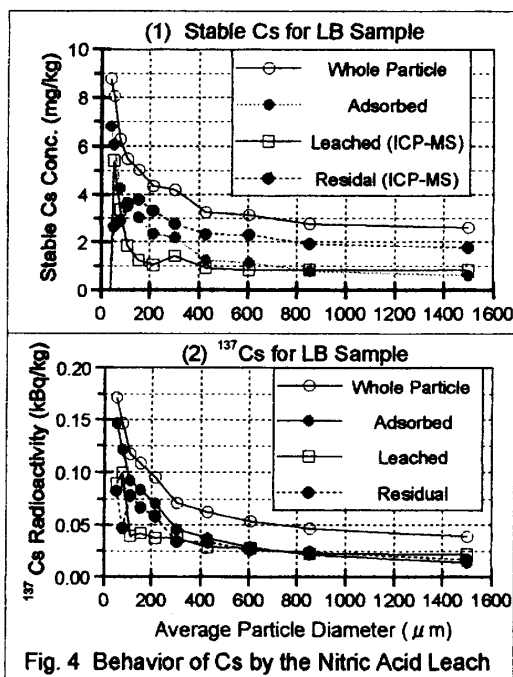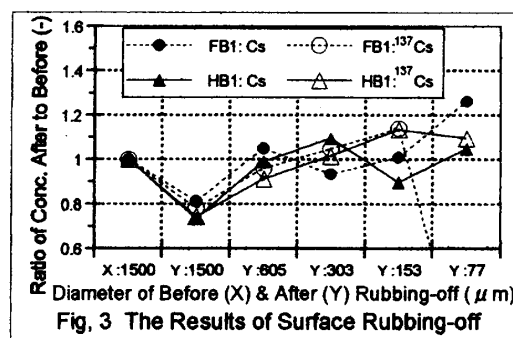

Fig. 4 Behavior of Cs by the Nitric Acid Leach

The followings results were obtained from the nitric acid leach: (1) The leached concentrations of stable Cs and ^{137}Cs decreased with increase in particle diameter and they are fairly close to the adsorbed concentrations over a wide range of the particle diameter.

(2) The residual concentrations after the leach show fairly uniform values of about 2.1mg/kg for stable Cs and 0.025kBq/kg for ^{137}Cs for the sample IB and 2.0mg/kg and 0.025kBq/kg for the sample LB, respectively, except the values for smaller diameters. These values are pretty close to the particle matrix concentrations, which are obtained as 2.0mg/kg for stable Cs and 0.035kBq/kg for ^{137}Cs for the sample IB and 2.0mg/kg and 0.025kBq/kg for the sample LB, respectively.

4. Discussions

4.1. Adsorptive Behavior of Cs onto the Grains

In the previous study[14], both techniques of the surface rubbing-off and the nitric acid leach described befoe were applied to the grain samples and the adsorptive behavior of non-radioactive trace elements was confirmed. The experimental results obtained in this study showed that (1) the concentrations of both stable Cs and ^{137}Cs on and near the particle surface are clearly higher than that of the particle matrix and (2) the concentrations of leached stable Cs or ^{137}Cs are fairly close to that of each cesium which was supposed to have adsorbed over a wide range of particle diameter. These results are considered to give more direct evidences of adsorption on the surface of particles rather than such mechanism as the diffusion into the grain. Furthermore, the fact that the nitric acid leach was necessary to strip off the adsorbed Cs from the grain indicates that the adsorbed Cs on the grain are so tightly adhered to the surface. It is to be pointed out here that the chemical adsorptive behavior of the elements on the grain is still remained to be eleucidated in future.

Since the adsorptive behavior is thus confirmed, the concentration of the adsorbed cesium can be obtained by subtracting the concentration of grain matrix, which is estimated by extrapolating the particle size to an infinitive, from the whole concentration. The matrix concentration is a constant among samples in principle, but the concentrations estimated varied from 1.3 to 2.4 mg/kg for the stable Cs and 0.025 to 0.060 kBq/kg for the ^{137}Cs as described before, and the average values are about 2.0 mg/kg for the stable Cs and about 0.03 kBq/kg for [137]Cs. All the data of the adsorbed concentrations are shown in Fig. 5 for stable Cs of eight samples and for ^{137}Cs of six samples. It is to be noted in this figure that the adsorbed concentrations of both stable Cs and ^{137}Cs are pretty close among samples although they were taken under different conditions of season and temperature as given in Table 1. The adsorbed concentrations for the IY sample seem to be slightly smaller than those of IB sample. This
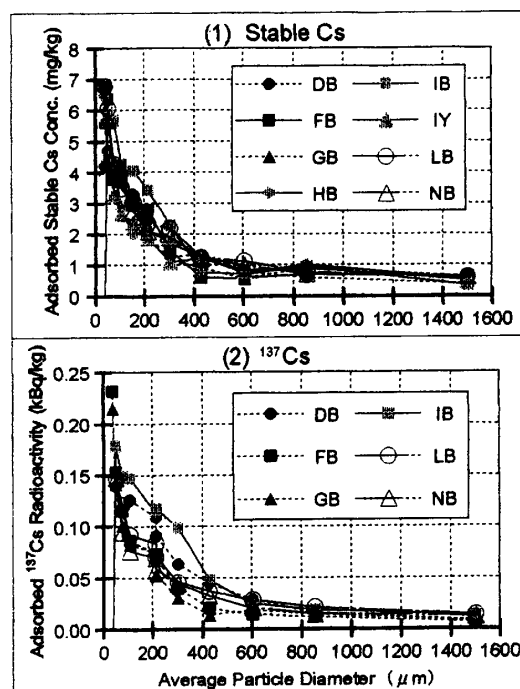

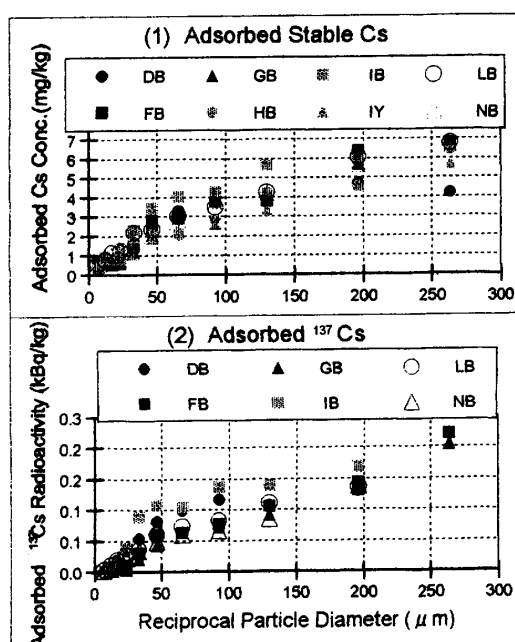Fig. 5 The Concentrations of Adsorbed Stable Cs and ^{137}Cs in the Grain Samples

Fig. 6 Plots of Cs Conc. against Reciprocal of Particle Diameter

may come from the fact that the IY sample was taken from the beach where is covered with water only in the winter time.

Furthermore, when the concentrations of stable Cs and ^{137}Cs are plotted against the reciprocal of the particle diameter, the linear relationship that intercepts the zero point of the co-ordinate axis is not found in case of the whole cesium concentrations, but found in case of the adsorbed cesium concentrations as shown in Fig. 6. This result suggests that the migration of cesium from the water to the grains is based on the adsorption rather than the mere diffusion into the grain matrix, and the concentration of adsorbed cesium is roughly proportional to the surface area of the particles.

4.2. In-situ Distribution Coefficients of Stable Cs and ^{137}Cs

Since the concentrations of stable Cs and ^{137}Cs adsorbed on the particles are obtained and their concentrations in the pond water were already reported as quoted in Table 2[15], the distribution coefficient Kd defined by the ratio of the element concentration adsorbed on the particle to that of pond water is obtainable. The in-situ distribution coefficients of

Table 2 Concentrations of Stable Cs and Radioactive ^{137}Cs in the Water Samples[15]
(Concentration unit is mg/m^3 for stable Cs and Bq/m^3 for ^{137}Cs)

Sample	D	F	G	H	I	J	K	L	N
Stable Cs	0.0050	0.0089	0.0055	0.0122	0.0147	0.0108	0.0110	0.018	0.013
Rad. ^{137}Cs	0.23	-	0.27	-	0.85	-	0.84	-	-

stable Cs for the samples DB, FB, GB, HB, IB, IY, LB and NB and of radioactive ^{137}Cs for the samples DB, GB, IB and LB are plotted against the particle diameter in Fig. 7. It is seen for both cases of stable Cs and radioactive ^{137}Cs that (1) the Kd depends largely on particle diameter and increases with the decrease in diameter, (2) the change of Kd among samples is small, although the samples were taken at different conditions, (3) the Kd of ^{137}Cs seems to be slightly smaller than that of stable Cs and (4) the values of Kd ranged from about 20 to 1200m^3/kg for stable Cs and about 15 to 1000m^3/kg for ^{137}Cs. The Kd seems to depend largely on the concentration in the water, since the adsorbed concentrations do not differ largely among samples as seen in Fig. 5.

4.3. Comparison of Distribution Coefficients of Stable Cs and ^{137}Cs

The in-situ distribution coefficients of stable Cs and radioactive ^{137}Cs are compared in Fig. 8 for the samples of DB, GB, IB and LB, respectively. The in-situ Kds for the radioactive ^{137}Cs (shown with *) seem to be slightly smaller than those for the stable Cs. In order to elucidate until what degreee the radioactive ^{137}Cs migrated into the

Fig. 7 In-situ Distribution Coefficient Kd of Stable Cs and ^{137}Cs

grain during these about forty years after the nuclear weapon testings in the atmosphere, it is interesting to compare the ratios of ^{137}Cs to stable Cs concentration in the whole particle, in the adsorbed layer and in the grain matrix. The variations of the ratios with particle
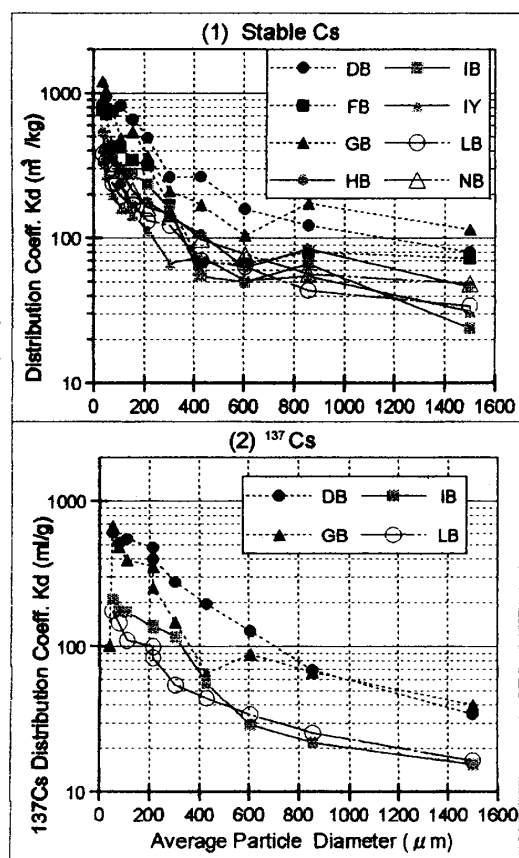
diameter are shown in
Fig. 9 for the whole
particle and the ad-
sorbed layer. The
ratios seem to decrease
slightly with increase
in diameter, and the
degree of the decrease
is larger in case of the
adsorbed. The average
values of the ratios,
ignoring the effect of
diameter dependence,
for the whole particle,

Fig 8 Comparisson of Kd between Stable Cs and ^{137}C (shown with*)

the adsorbed layer and
the grain matrix are
compared among the
samples in Fig. 10. It
is seen that the ratio
of the adsorbed layer
is larger than that of
the matrix, and the
average values of the
ratios for all the

Fig. 9 Ratio of ^{137}Cs to Stable Cs Concentration in the Whole
Particle and the Adsorbed Layer

samples are 23 for the whole particle, 26 for the adsorbed layer and 19 MBq/kg for the
grain matrix. This result may be explained in the following way: the adsorption of stable
Cs was held before the deposition of the ^{137}Cs and
the isotopic exchange between ^{137}Cs and stable Cs
has been proceeding from the water to the ad-
sorbed layer preferably and to the matrix partially
during these forty years. Furthermore, the ratio
for the pond water was 47MBq/kg and is twice of
the particle, which suggests that the isotopic
exchange between the stable Cs and radioactive
^{137}Cs is still proceeding.

5. Conclusions

Fig. 10 Comparison of the Concentration
of Stable Cs and ^{137}Cs in the Whole
Particle and the Adsorbed Layer

The concentrations of stable Cs and radioactive
fallout ^{137}Cs were determined for the clastic grains of chert in the isolated undisturbed
mountain pond "Yasha-ga-Ike", located at the ele va- tion of 1100m near the ridge of
mountain in Fukui Pref. The concentration of each cesium was found to decrease with
increase in the particle size. After confirming their adsorptive behavior by surface
rubbing-off and nitric acid leach techniques, their adsorbed concenrations on the grain were
determined by subtracting the con- centration of grain matrix. These concentrations
increased with decrease in particle size and the variation among samples was small. The
in-situ distribution coefficients Kd between the particles and the pond water were obtained
for the stable Cs of eight samples and for ^{137}Cs of four samples The followings were
elucidated: (1) The values of Kd depend largely on particles diameter and increase with the
decrease in diameter from about 10 to 100m^3/kg, (2) the Kd depends less on the kind of the
samples, (3) the Kd of ^{137}Cs seems to be slightly smaller than that of stable Cs. It was
considered that the adsorption of stable Cs was held before the deposition of fallout ^{137}Cs
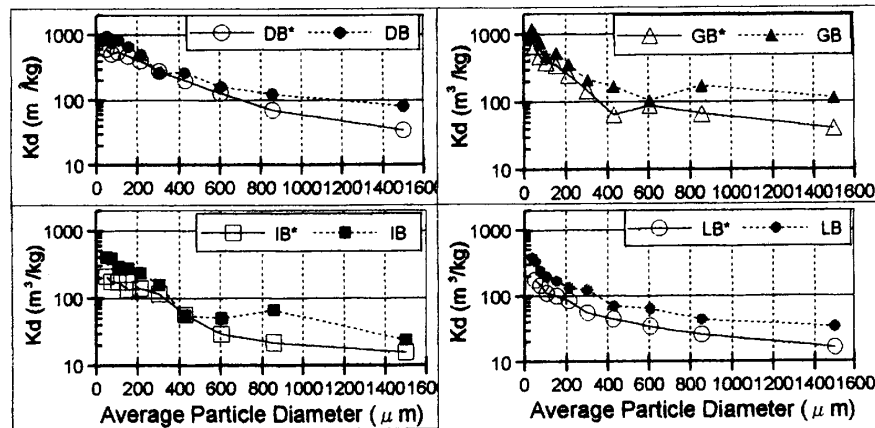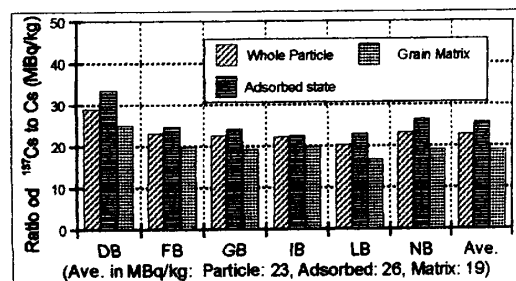
and the isotopic exchange between each cesium has been proceeding from the water to the adsorbed layer and the matrix.

Acknowledgment

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