

## Further Studies on the Adsorptive Behavior of Trace Elements onto the Sedimentary Grains in the Isolated Mountain Pond "Yasha-ga-Ike"

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### Abstract

In order to confirm directly the adsorptive behavior of the trace elements in the isolated undisturbed mountain pond "Yasha-ga-Ike" onto the sedimentary grains of chert by experimental techniques, both the surface rubbing-off and the nitric acid leach for the grain samples were carried out. In the former case, the grain sample was rubbed gently in an agate mortar by paste and the sieved fractions were analyzed by neutron activation in order to compare the element concentrations on and near the grain surface and the inner portion. In the latter case, the grain sample was leached with 8N nitric acid near the boiling point, and the leached amount was obtained either by ICPMS analysis of the leached solution or by taking the difference of the element concentrations of the particle, obtained by the neutron activation, before and after the leach.

The experimental results showed that (1) the concentration of element on and near the particle surface are clearly higher than that of the particle matrix and (2) the concentration of leached element is fairly close to that of adsorbed element over a wide range of particle diameter. These results are considered to give confirmative evidences of element adsorption on the surface of the particles. The concentration of adsorbed element can be obtained by subtracting the concentration of grain matrix, which is obtained by extrapolating the particle size to an infinitive, from the whole concentration of constituent element in the particle.

### 1. Introduction

A small pond named "Yasha-ga-Ike", with maximum depth of 7.5 m and about 40 are of water surface is located at an elevation of 1100 m near the ridge of mountain in Imajyo, Fukui Prefecture. The pond is supposed to be formed by landslide of the surrounding mountain of chert formation in the latter period of the diluvial epoch. The watershed of the pond is small and none of rivers flow in and out. The pond water is said to have never run dry, and a small Japanese diving beetle "Yasha-Gengoro" specially protected due to its

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rareness lives. The bottom of the central deep portion is covered with mud sediment and clastic grains of different sizes are found in the shallow place near the beach.

The researches on the pond water and the sedimentary grains have been carried out since 1998, and the properties of the pond water<sup>1)</sup>, the adsorptive properties of trace elements onto the grains<sup>2)</sup> and the concentrations of radioactive  $^{137}\text{Cs}$  and stable Cs in the pond water<sup>3)</sup> were reported. In the previous study on the adsorptive behavior of the elements<sup>2)</sup>, the analytical results by the neutron activation of the sedimentary grain samples indicated that the concentration of any constituent element of the grain matrix decreased with increase in particle size, and the adsorptive behavior of the elements onto the grains was postulated. The concentration of the adsorbed element was obtained by subtracting the concentration of grain matrix, which was estimated by extrapolating the grain size to an infinitive.

The chemical composition of the grain matrix, exclusive of the adsorbed constituent elements, was obtained by averaging the results of eight samples analyzed by the neutron activation method. The composition expressed by wt. % of main elements in oxide form are as follows:  $\text{Al}_2\text{O}_3$  3.21,  $\text{Fe}_2\text{O}_3$  1.45,  $\text{MgO}$  0.81,  $\text{K}_2\text{O}$  0.77,  $\text{TiO}_2$  0.14,  $\text{Na}_2\text{O}$  0.04,  $\text{MnO}$  0.02 and  $\text{BaO}$  0.01. The sum is 6.45 wt. % and the rest is considered to be mostly  $\text{SiO}_2$ . These values seem to coincide with the typical ones of the chert composition.

When trace elements are adsorbed on the grain surface, their concentrations on and near the surface are expected to be higher than those of the grain matrix. It is the purpose of the present study to ascertain this expectation directly by applying such two techniques as the surface rubbing-off and the nitric acid leach to the sieved particles and by comparing the element concentrations between the surface and the grain matrix.

## 2. Experimental Procedures

The samples of sedimentary grains were taken, and both the surface rubbing-off and the nitric acid leach techniques were applied to the sieved particle samples.

### 2.1 Measurements of Element Concentrations for the Grain Samples

Three samples of grains, named HB, IB and LB, were taken from the shallow place of about 50cm depth near the beach at different occasions from May 2000 to July 2001, where the water temperature was 19.0, 25.0 and 25.5 °C, respectively. The grain samples were dried and sorted by sieving into 11 fractions of diameters; 2 ~ 1mm, 1mm ~ 710  $\mu\text{m}$ , 710 ~ 500, 500 ~ 355, 355 ~ 250, 250 ~ 180, 180 ~ 125, 125 ~ 90, 90 ~ 63, 63 ~ 38 and < 38  $\mu\text{m}$ . 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 fraction of sorted grain samples, the neutron activation analysis was carried out. The samples of about 80 mg were irradiated for 20 sec and 60 min, respectively, by KURRI (Kyoto University Research Reactor), and the gamma spectrometry was applied. The concentrations of about 25 elements such as Na, K, Rb, Cs, Mg, Ba, Cr, Mn, Fe, Co, Al, Sc, La, Ce etc. were

determined.

## 2.2 The Grain Surface Rubbing-off and the Nitric Acid Leach of the Grain Samples

The grain surface rubbing-off and the nitric acid leach are applied to the sieved particles, and the concentrations of the element between the surface and the grain matrix are compared in order to confirm the adsorptive behavior.

In case of the surface rubbing-off in the previous study<sup>2)</sup>, the grains with wide range of diameter was rubbed-off and the sieving was done by one opening of 63  $\mu\text{m}$  only. Then the concentrations were compared between the larger particles and the smaller ones in order to know which side of the surface or the grain matrix is larger in the concentration. However, in the present study more elaborate work was carried out. Both the particles of HB1, which is a fraction having the size range of 2 ~ 1 mm of the sieved HB sample, and HB7 of 180 ~ 125  $\mu\text{m}$  are rubbed gently in an agate mortar by paste, respectively, and then sorted by sieving into fractions of diameter. The concentrations of elements in the sieved fractions are analyzed by neutron activation.

In case of the nitric acid leach, each fraction of sieved IB and LB samples was leached with 8N nitric acid for 3 hours near the boiling point. After the leach, the concentrations of elements in the residual particles were measured by neutron activation analysis, and the concentration leached was calculated as the difference between the concentrations before and after the leach. Also the concentration of elements in the acid solution after the leach was measured by ICP-MS, where the solution was diluted by 1000 times to obtain directly the leached amount of elements. The neutron activation analysis was not applied to the leached LB samples.

## 3. Experimental Results

### 3.1 Concentrations of Elements in the Grains

The concentrations of constituent elements for grain samples of HB, IB, and LB were obtained and the typical results for LB sample are plotted against the average diameter of the sieved particles in Fig. 1.

The concentration of the adsorbed element was obtained by subtracting the concentration of grain matrix, which was estimated by extrapolating the grain size to an infinitive<sup>2)</sup>, and the result for the LB sample is shown in Fig. 2.

Both of the concentrations of the constituent element and the adsorbed one decrease with increase in diameter, as reported in case of DB and GB samples in the previous report<sup>2)</sup>, and the difference of concentrations among three samples is not so large.

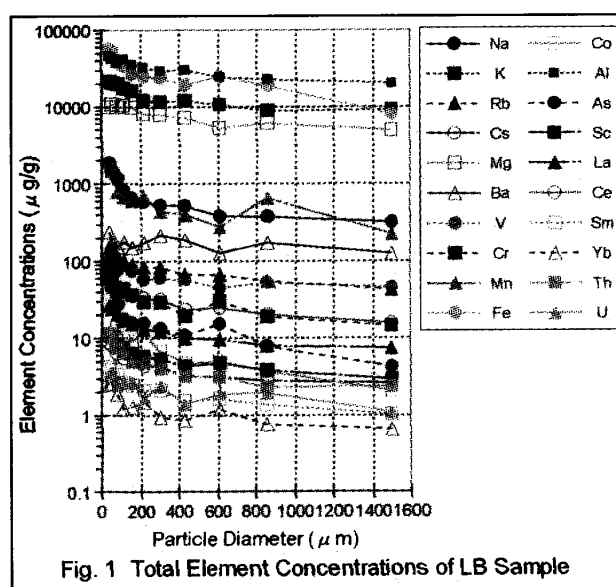


Fig. 1 Total Element Concentrations of LB Sample

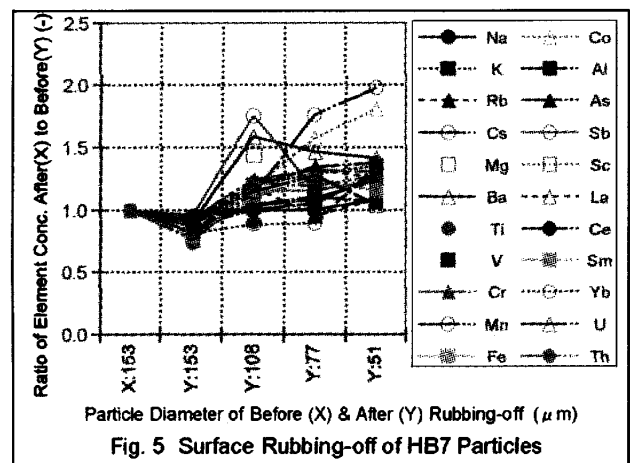
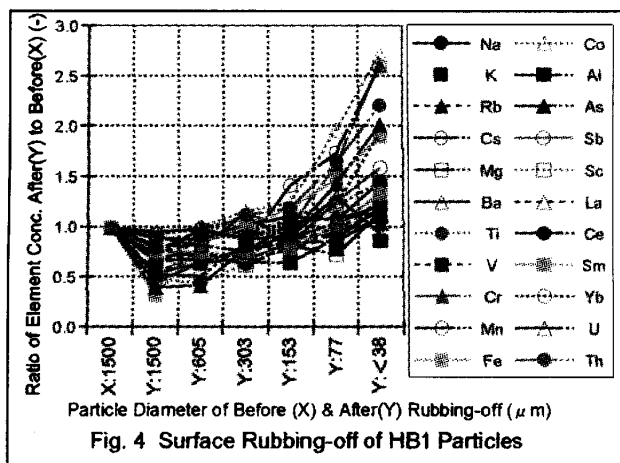
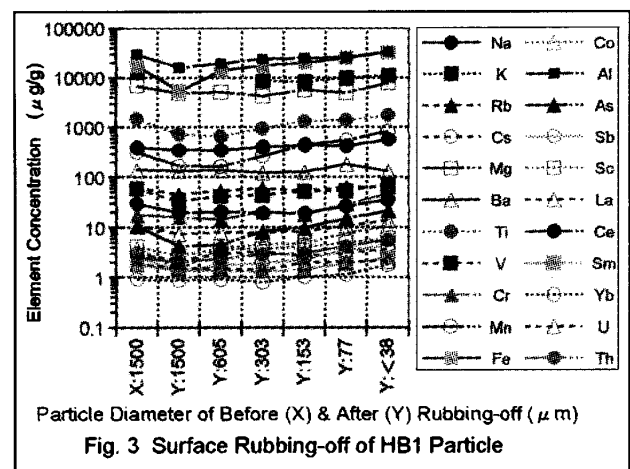
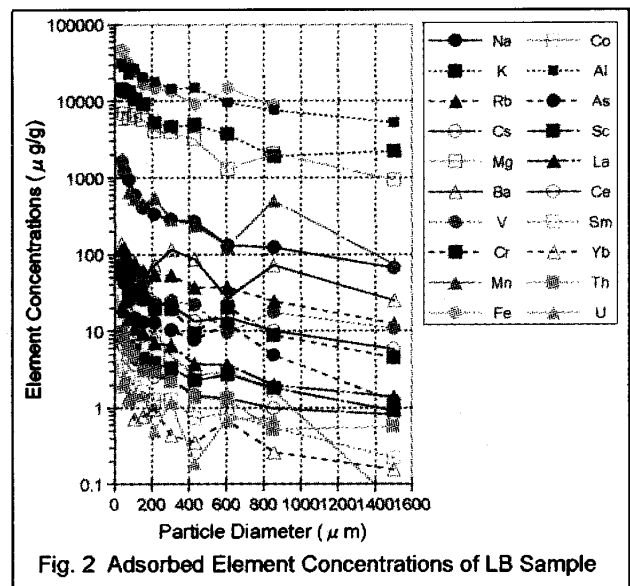
### 3.2 The Grain Surface Rubbing-off

After the surface rubbing-off of the particles of HB1 sample with 2 ~ 1 mm in diameter, the concentrations of elements were measured for the particle size ranges of 2 ~ 1mm, 710 ~ 500, 355 ~ 250, 180 ~ 125, 90 ~ 63 and < 38  $\mu\text{m}$ . The results are plotted against the average particle diameter in Fig. 3, where the figure shown after X (before the rubbing-off) or Y (after the rubbing-off) indicates the average diameter in  $\mu\text{m}$ . The same data are replotted in Fig. 4, where the ratio of the concentration

of the sieved particles after the rubbing to that of the original HB1 particles before the rubbing is plotted against the diameter. From these figures, it is seen that the concentration of any element in the residual particle, whose surface was rubbed-off and shown as Y:1500, is lower than that of both the original HB1 particle shown as X:1500 and the fine particles, which are derived from the near-surface and shown as Y:605, Y:303, Y:153, Y:77 and Y:< 38  $\mu\text{m}$ . Thus the concentration of any element on and near the particle surface was confirmed to be higher than that of the inner grain matrix.

The experimental result for the case of rubbing-off of the HB7 sample with 180 ~ 125  $\mu\text{m}$  in diameter is shown in Fig. 5.

The same conclusion as in the case of the HB1 particles is deduced, although the particle diameter of HB7 is smaller than HB1.



### 3.3 The Nitric Acid Leach

The concentrations of the element leached are determined by two means of the ICPMS and the neutron activation analysis for the IB sample and by the ICPMS for the LB sample, respectively.

Typical results of the nitric acid leach for the LB sample is shown in Fig. 6, where the leached amount of elements determined by ICPMS is plotted against the particle diameter. It is seen that the leached amount, expressed by  $\mu\text{g}$  leached per g particle, increases with decrease in particle diameter. The similar results were obtained for the IB sample.

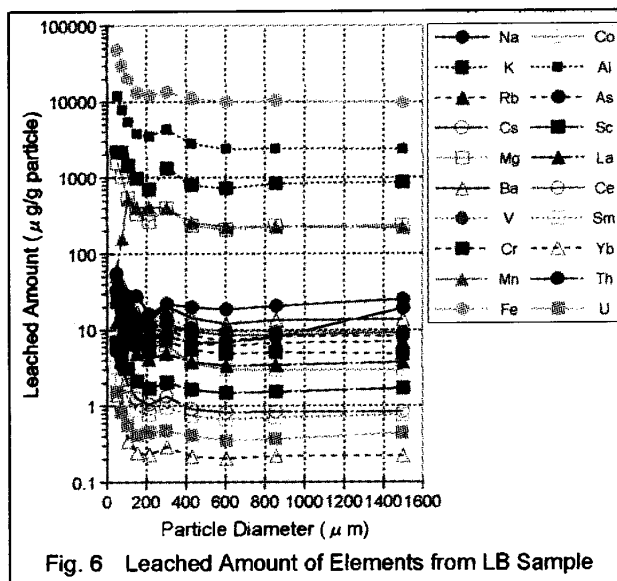


Fig. 6 Leached Amount of Elements from LB Sample

The behavior of the element by the nitric acid leach is shown in the following figures where each concentration of the constituent element in the whole particle before the leach, the element adsorbed, the element leached and the residual element after the leach are plotted against the average particle diameter. The element concentrations of the whole particle and the adsorbed for the LB sample were cited from Figs. 1 and 2, respectively.

For the LB sample, the behavior of such elements as Cs, Mn, Fe and La is shown in Figs. 7, 8, 9 and 10, respectively. In these figures, it is seen in general that the leached amount determined by the ICPMS decreases with increase in the particle diameter and the amount is fairly close to the concentrations adsorbed except the diameter range smaller

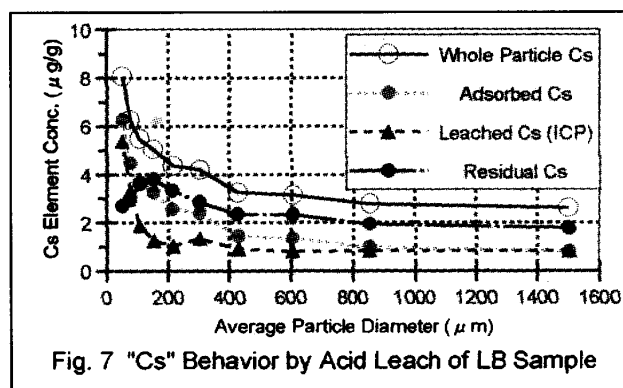


Fig. 7 "Cs" Behavior by Acid Leach of LB Sample

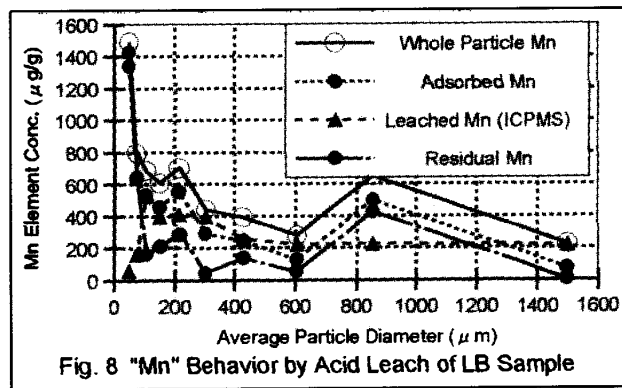


Fig. 8 "Mn" Behavior by Acid Leach of LB Sample

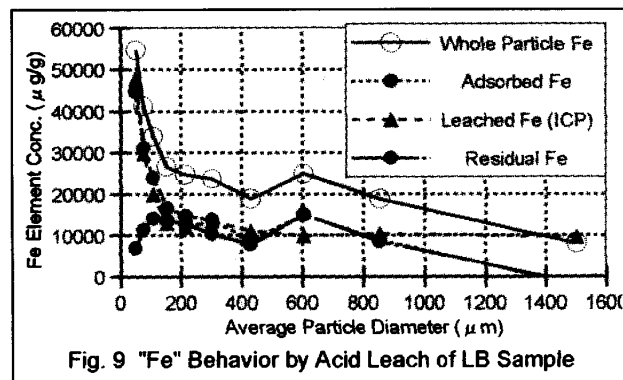


Fig. 9 "Fe" Behavior by Acid Leach of LB Sample

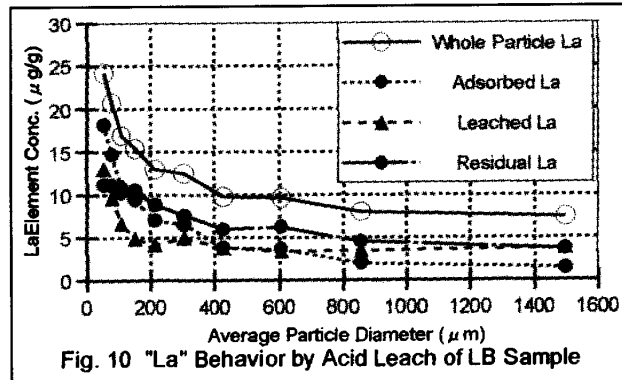
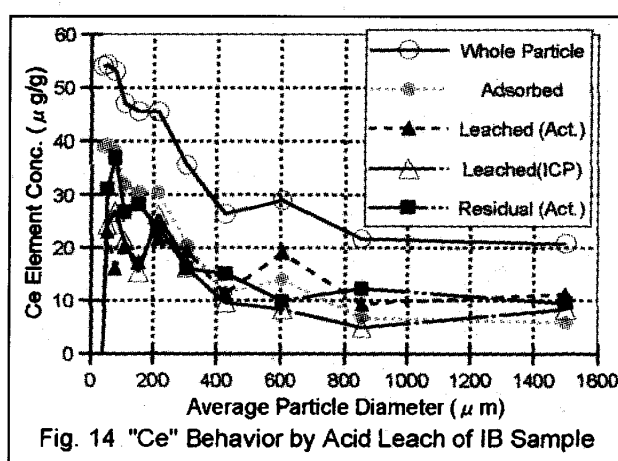
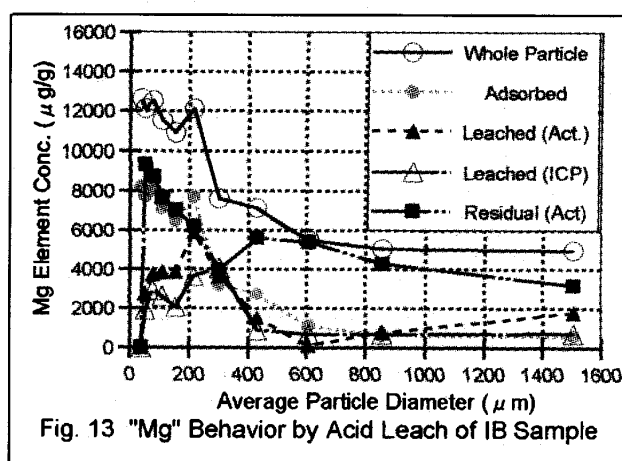
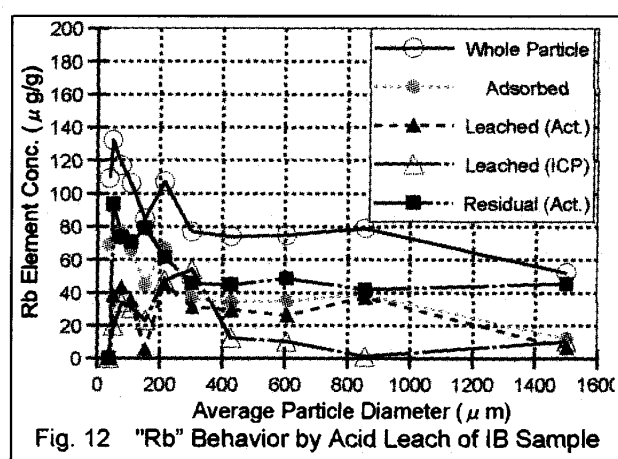
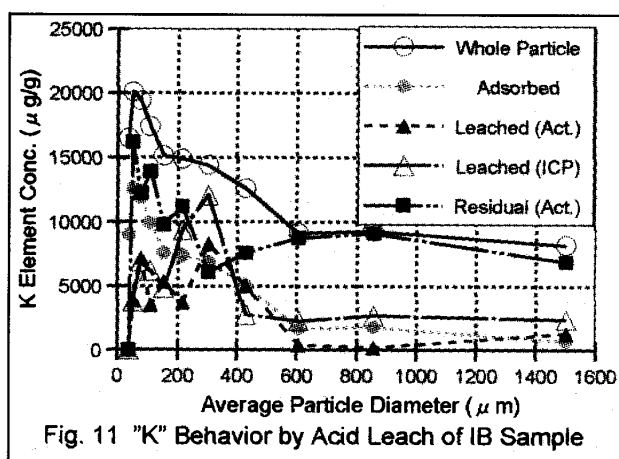


Fig. 10 "La" Behavior by Acid Leach of LB Sample

than about  $100\text{ }\mu\text{m}$ . This result indicates that the adsorbed elements were regarded to be dissolved by the acid leach. Furthermore, the concentration of the residual particle seems to be pretty uniform in the wide range of the diameter. It is to be noted that the residual particle concentration is very close to the grain matrix concentration that was used to subtract from the concentration of whole particle in order to obtain the adsorbed concentration shown in Fig. 3, where the value of the matrix concentration was chosen as 1.8 for Cs, 150 for Mn, 10000 for Fe and 6 for La in the unit of  $\mu\text{g/g}$ , respectively.

For the IB sample, the behavior of such elements as K, Rb, Mg and Ce are shown as the typical cases in Figs. 11, 12, 13 and 14, respectively. It is seen that the leached amounts determined by two means of the ICPMS and the neutron activation are regarded to agree pretty well each other. The leached concentrations are pretty close to the adsorbed concentrations, which suggests that the adsorbed elements are dissolved off by the acid



leach as in the case of the LB sample. It is also to be noted that the residual particle concentration is very close to the grain matrix concentration, whose value is 7500 for K, 40 for Rb, 4400 for Mg and 15 for Ce in the unit of  $\mu\text{g/g}$ , respectively.

#### 4. Discussions

In the previous work<sup>2)</sup>, the adsorptive behavior of elements was postulated from such experimental results as (1) the concentrations of the elements in the particles decreased

with the increase in diameter and (2) the element concentration of grain matrix was smaller than the grain surface portion. The experimental results obtained in this study showed that (1) the concentrations of elements on and near the particle surface are clearly higher than the concentration of the particle matrix and (2) the concentration of leached element is fairly close to that of the element, which was supposed to have adsorbed, over a wide range of particle diameter. These results are considered to give more direct evidences of element adsorption on the surface of particles. Furthermore, the fact that the nitric acid leach was necessary to strip off the adsorbed element indicates that the element is 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 elucidate in future.

Since the adsorptive behavior is thus confirmed, the concentration of the adsorbed element 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 of the particle. The matrix concentration is a constant among samples in principle, and the values of the concentrations chosen for the elements cited before are pretty close each other as shown in Table 1, although the samples were taken under different conditions of season and temperature.

Table 1 The concentrations of grain matrix of the samples

Grain sample	Element and the concentration( $\mu\text{g/g}$ )							
	K	Rb	Cs	Mg	Mn	Fe	La	Ce
IB	7500	40	3	4400	90	15000	7	15
LB	7000	30	1.8	4000	150	10000	6	10
Average*	6400	38	2.1	3900	150	10100	6	15

\* The average of eight sample including IB and LB.

Furthermore, the following result may give another evidence for the adsorptive behavior. The concentrations of several elements that showed lower concentrations of the adsorbed state are plotted in Fig. 15 against the reciprocal of the particle diameter which is proportional to the surface area. The linear relationship that intercepts the zero point of the co-ordinate axis is nearly established in this case, while it is not found in case of the whole element concentrations.

This result suggests that (1) the migration of elements from the water to the grains is based on the adsorption process rather than the mere diffusion process into the grain matrix, and (2) the concentration of adsorbed element is roughly proportional to

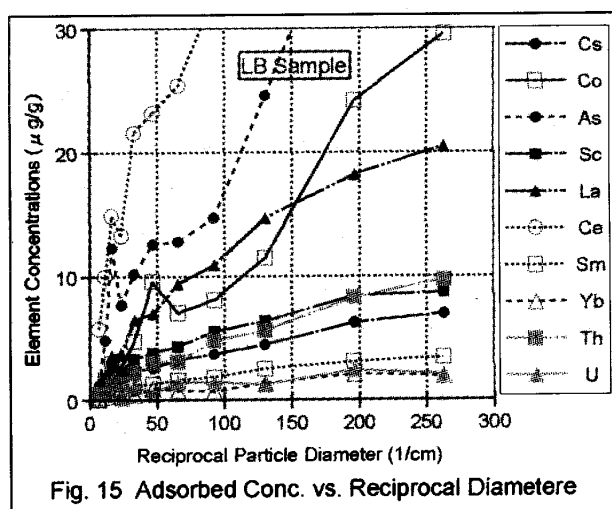


Fig. 15 Adsorbed Conc. vs. Reciprocal Diameters

the surface area of the particles.

## 5. Conclusions

In order to confirm directly the adsorptive behavior of the trace elements in the isolated undisturbed mountain pond "Yasha-ga-Ike" onto the sedimentary grains of chert by experimental techniques, both the surface rubbing-off and the nitric acid leach for the grain samples were introduced. In the former case, the sample was first rubbed gently in an agar mortar by paste and the sieved fractions were analyzed by neutron activation in order to compare the element concentrations on and near the grain surface and the inner portion. In the latter case, grain samples were leached with 8N nitric acid near the boiling point, and the leached amount were obtained either by ICPMS analysis of the leached solution or by taking the difference of the element concentrations of the particle, which were obtained by the neutron activation, before and after the leach.

The experimental results showed that (1) the concentrations of elements on and near the particle surface are clearly higher than the concentration of the particle matrix and (2) the concentration of leached element is fairly close to that of the element, which was supposed to have adsorbed, over a wide range of particle diameter. These results are considered to give confirmative evidences of element adsorption on the surface of the particles. Therefore, the concentration of adsorbed element can be obtained by subtracting the concentration of grain matrix, which is obtained by extrapolating the particle size to an infinitive, from the whole concentration of constituent element in the particle.

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## References

- 1) K. Iwamoto, T. Nishida, M. Kimura & K. Ando, *「On the Properties of Water in the Undisturbed Isolated Pond "Yasha-ga-Ike" (In Japanese)」*, Memoirs of Fukui University of Technology, 30, 271-278 (2000)
- 2) K. Iwamoto, M. Kimura, K. Ando, H. Moriyama, K. Kawamoto & J. Takada, *「On the Adsorptive Behavior of Trace Elements onto Sedimentary Grains in the Isolated Undisturbed Pond "Yasha-ga-Ike" Located at the Mountain」*, Memoirs of Fukui University of Technology, 31, 261-268 (2001)
- 3) K. Iwamoto, M. Kimura, K. Ando, H. Moriyama, K. Kawamoto, J. Takada & H. Amano, *「On the Concentrations of the Radioactive  $^{137}\text{Cs}$  and stable Cs in the water of the Isolated Undisturbed Mountain Pond "Yasha-ga-Ike"」*, Memoirs of Fukui University of Technology, 32, 255-260 (2002)

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