On the Adsorptive Behavior of Trace Elements onto Sedimentary Grains in the Isolated Undisturbed Pond "Yasha-ga-Ike" Located at the Mountain

K. Iwamoto[1], M. Kimura[1], K. Ando[1], H. Moriyama[2],
K. Kawamoto[2] and J. Takada[2]

Abstract

From the isolated undisturbed pond "Yasha-ga-Ike" located at an elevation of 1099m in Fukui Pref., sedimentary grain samples were taken and sieved into fractions of different sizes. The concentration of consituent elements of the samples was analysed by neutron activation method in order to elucidate the behavior of the elements of the grains that have been under water for a very long time. The constituent elements of sedimentary grains were found not to leach into the water, but the trace elements in the water have been adsorbed onto the grain surface contrariwise. The concentration of any element in the grains decreased with the increase in particle diameter, and then the concentration of the adsorbed element on the particles was obtained by subtracting the concentration of grain matrix, which was estimated by extrapolating the grain size to an infinitive, from the observed concentration of any size. The concentration of any element adsorbed depends largely upon the kind of element and increased with the decrease in the particle diameter.

1. Introduction

A small pond named "Yasha-ga-Ike", with maximum depth of 7.5m and about 40are of water surface is located at an elevation of 1099m near the ridgeline 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" speciallly protected due to its rareness lives. Thus the "Yasha-ga-Ike" is regarded as an isolated undisturbed non-volcanic pond. As to the sediments of the pond, mud covers the central deep location, and clastic grains of different sizes are found in the shallow place near the beach. The grains were also found at the flat beach where is covered with water and snow in winter. The outline of the pond is given in Fig. 1, where the locations and dates of grain samplings are included.

It is interesting to search the nature of the isolated pond especially from viewpoint of the relationship between the sediments and the water environ-

[1] Department of Applied Physics and Chemistry, Fukui University of Technology
[2] Research Reactor Institute, Kyoto University

ment, since the grains has been kept under water during a very long time. The research on the sedimentary grain and the pond water has been carried out since 1998[1),2),3)], and such properties of the water as pH, electrical conductivity and oxidation-reduction potential are reported in the previous report[1)]. It is the purpose of this study to elucidate whether the conctituent elements of the grains have leached into the water or the trace elements in the pond water have adsorbed onto the surface of the grains contrariwise. Thus, in this study, the sedimentary grains sampled from both the pond and beach were dried, sieved into different sizes, and neutron-activated in order to analyze the concentration of trace constituent elements of the grains. The behavior of the elements are discussed in relation to the size of the grains.

2. Experimental Procedures

(1) Sampling and treatment of sedimentary grains

From the shallow place of about 50cm depth near the beach, where sedimentary grains are present, the grain samples with a diameter of < 2 mm were taken by scooping up at the sites of AX, BX, DX and GX as shown in Fig. 1. The grain samples are also taken from the beach at BY site where is covered with water and snow in winter time. The following treatments were applied to the grain samples, as shown in Fig. 2. Most of the grain samples taken from the pond were dried and sieved. Furthermore, since the element concentration of grains holding the existing state in the pond as much as possible is required, the grains were first sieved in the pond water and dried (hereafter, noted as wet sieving) in order to compare with the case of dry and sieved (dry sieving). The grains taken at AX and BX sites in the pond and at BY site in the beach, which were named as AB, BB and BY bulk samples, respectively, were dried and sieved into three classes of particle diameters; 1mm ~ 250μm, 250 ~ 63μm and < 63μm. At the BX site, wet sieving using pond water was done to obtain grain samples (noted as BW) with three classes of diameters; 1mm ~ 250μm, 250

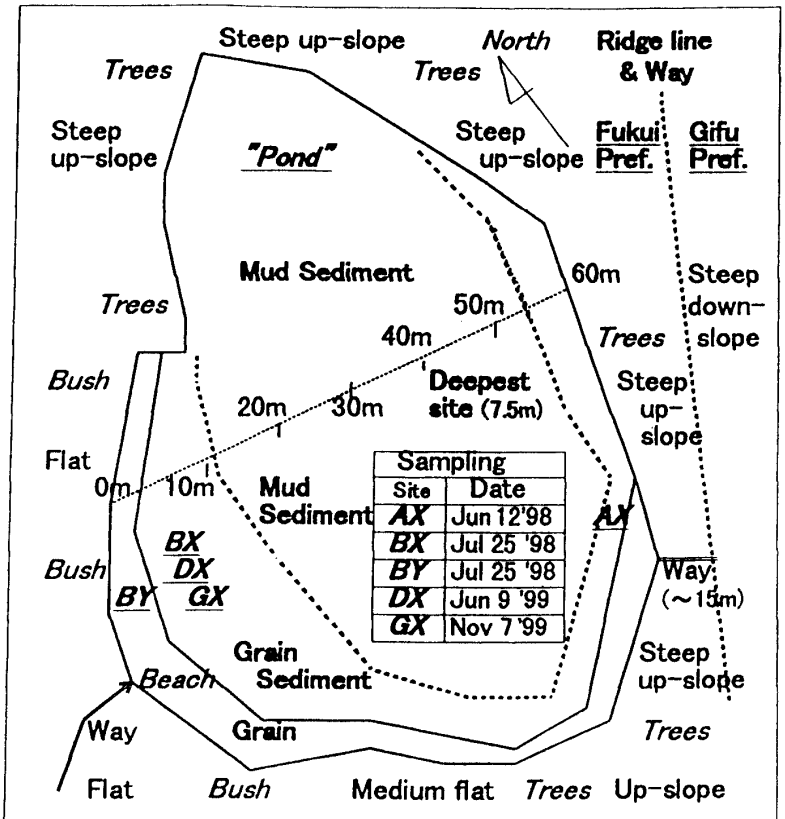

Fig. 1 The Pond "Yasha-ga-Ike" and Grain Sampling Sites: BX,DX,GX in Pond and BY in Beach

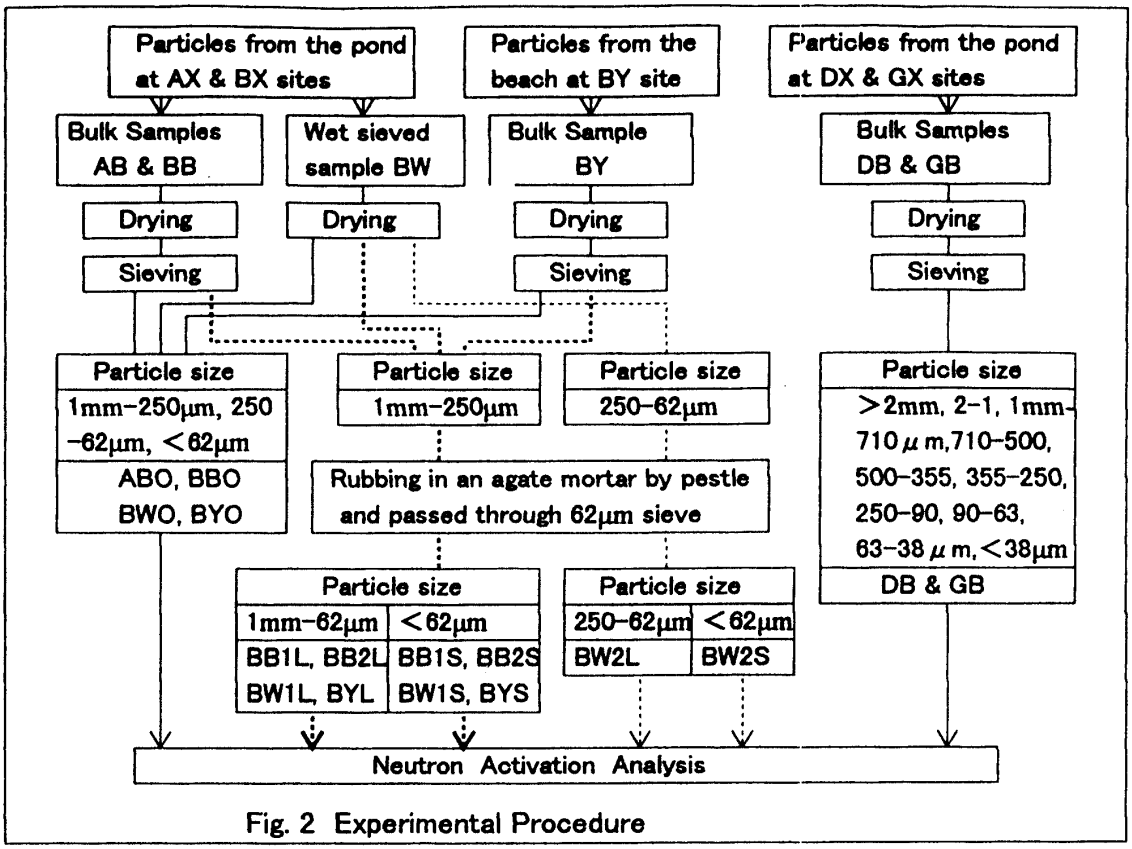

Fig. 2 Experimental Procedure

~ 63μm and < 63μm.

The comparison of the concentration of elements in the outer surface of the grain with that of the grain matrix is expected to produce an evidence on whether the elements leached out of the grain into the water or the elements in the water adsorbd onto the surface contrariwise. Therefore, the grains with size of 1mm ~ 250μm (noted as BB1O, BB2O, BW1O, BYO) and 250 ~ 62μm (notd as BW2O) sieved from BB, BW and BY samples were further rubbed gently in the agate mortar by pestle to take off the outer surface as much as possible and then passed through 63μm sieve. The grains obtained after the rubbing-off operation were noted as BB1L, BB2L, BW1L, BYL and BW2L for the larger size of > 63μm and BB1S, BB2S, BW1S, BYS and BW2S for < 63μm.

Furthermore, in order to elucidate the dependence of element concentration upon grain size more confirmly, the grains from the pond at DX and GX sites were dried and sorted into 11 fractions of diameters; 2 ~ 1mm, 1mm ~ 20μm, 710 ~ 500μm, 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 samples described above, 50 ~ 100mg were weighed and sealed in the polyethylene sheet triply for neutron activation analysis in order to determine the element concentrations.

(2) Neutron Activation Analysis

Sample grains were irradiated by KURRI (Kyoto University Research Reactor). The short term (20sec) irradiation was done by using neumatic tube of Pn-3 and the long term (60min) by Pn-2. After the irradiations, gamma spectrometry was both applied to the short-term irradiated samples right after the irradiation and after one-day cooling, and to the long term samples after one week and one month cooling, respectively. The gamma counting data were analyzed and the concentra- tions of such 25 elements as Na, K, Rb, Cs, Mg, Ba, Ti, V, Cr, Mn, Fe, Co, Zn, Al, As, Sb, Sc, La, Ce, Sm, Eu, Yb, Hf, U, and Th were obtained for each sample.

3. Results and Discussion

(1) Grain samples taken at AX, BX and BY sites

For the grain samples of AB, BB and BY, the relation between the element concentration and particle size is shown in Fig. 3. The concentration depends largely on the kind of element and Al, K, Fe and Mg show pretty high values in concentration, followed by Ti, Na, Ba, Mn and so on. Since all of the conctituent elements were not analyzed by the neutron activation method, a chemical analysis is to be done in future. However, it is to be noted that the concentrations of all elements increase with the decrease in particle-diameter

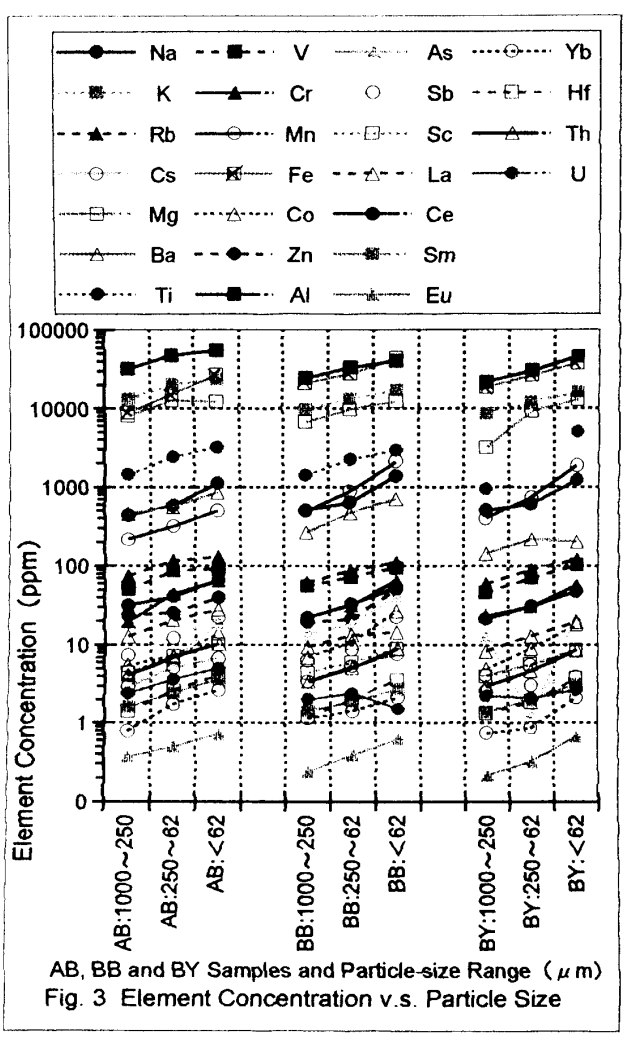

Fig. 3 Element Concentration v.s. Particle Size

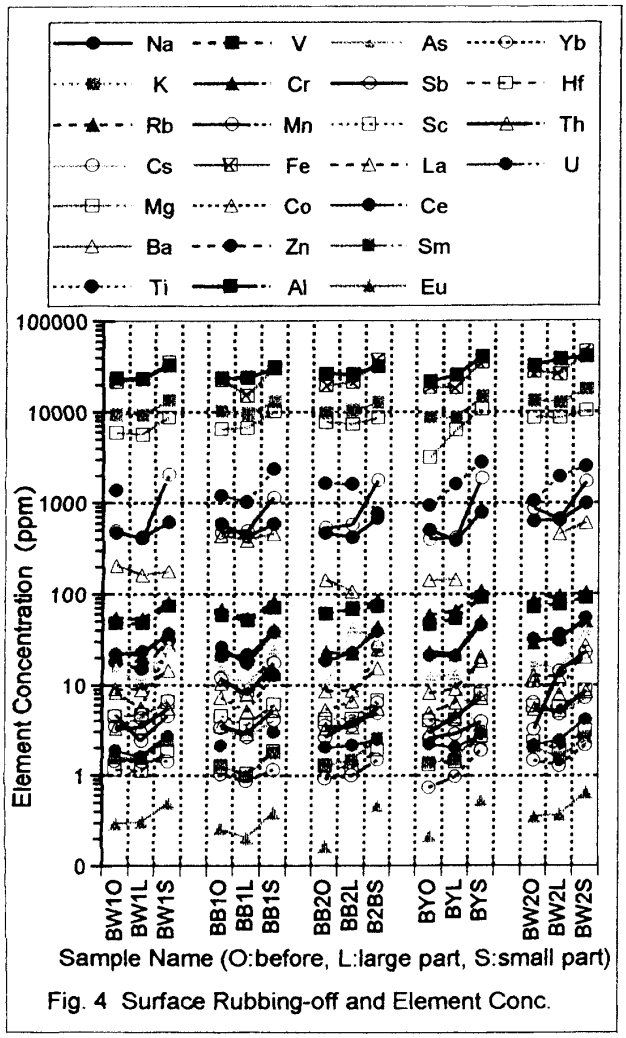

Fig. 4 Surface Rubbing-off and Element Conc.

range for all samples.

The results of the surface rubbing- off for the grains BW, BB and BY are given in Fig. 4. In case of the samples BW1O, BB1O, BB2O and BYO with diameter range of 1mm ~ 250μm, the elements concentrations of the large particles BW1L, BB1L, BB2L and BYL that were obtained after the rubbing and have the size range of 1mm ~ 63μm are smaller than the stripped-off portion of BW1S, BB1S, BB2S and BYS with < 63μm. The concentrations of grains before the rubbing are just between those of the large particles and the stripped-off portion. The same results were obtained for the grains BW2O with the small size range of 50 ~ 62μm.

The results of element concentra- tions for the dry sieved samples of BB1 and BB2 and of the wet sieved one of BW are compared in Fig. 5, which suggests that the sieving method dose not affect the element analysis. Thus the dry sieving method was mostly adopted in this study.

These results described above suggest that the constituent elements of sedimentary grains do not leach into the water, but the trace elements in the water are adsorbed onto the surface of grains contrariwise.

(2) Grain samples taken at DX and GX sites

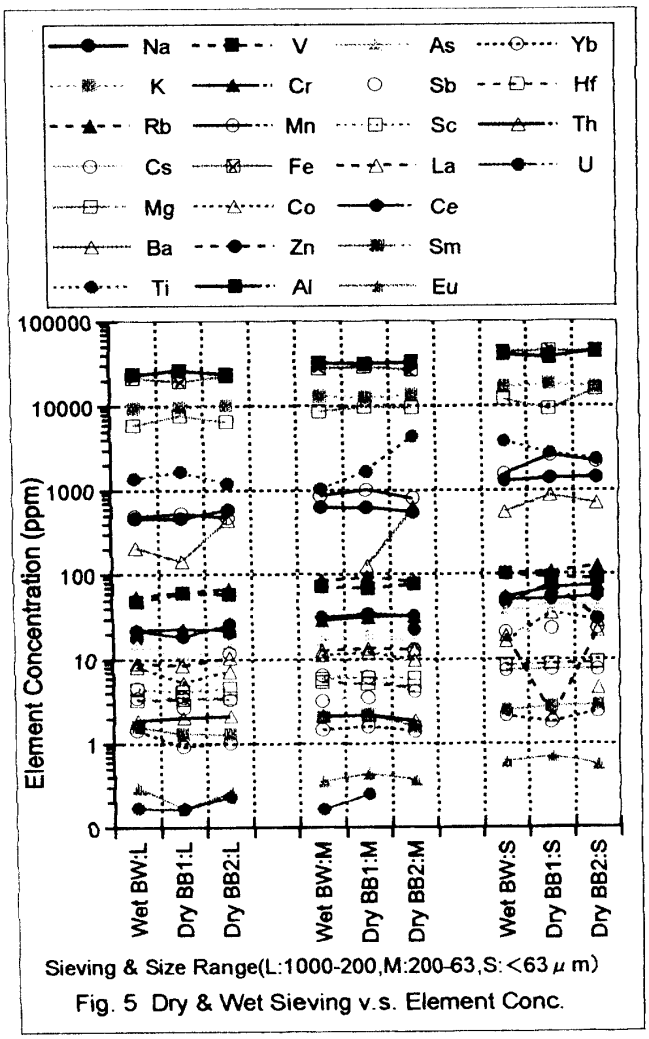

Fig. 5 Dry & Wet Sieving v.s. Element Conc.

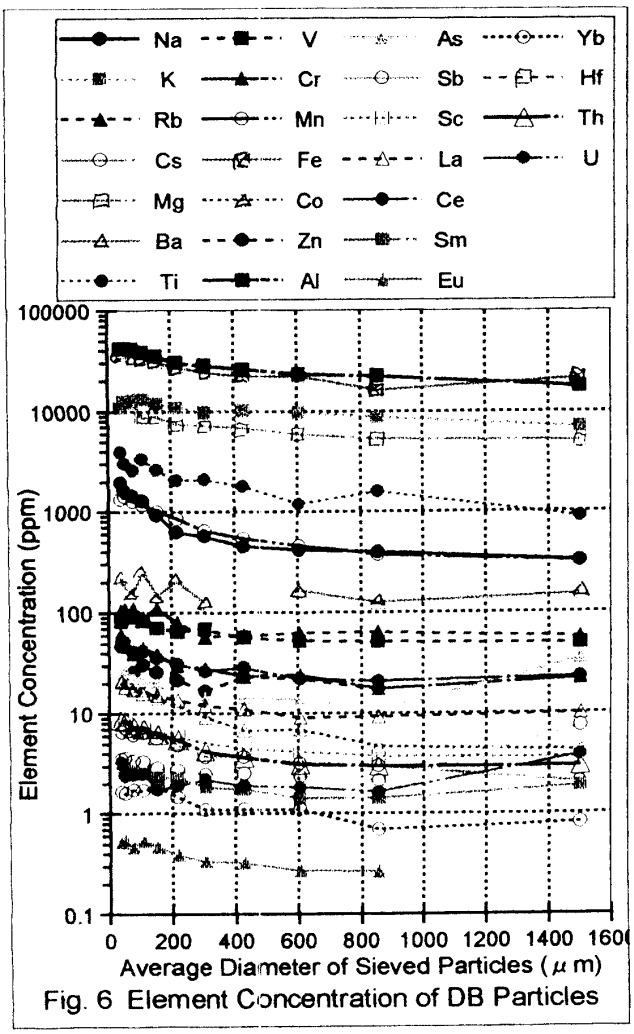

Fig. 6 Element Concentration of DB Particles

The grain samples of DB and GB taken at DX and BX sites, respectively, were dried and sorted into 11 particle-size ranges of 2 ~ 1mm, 1mm ~ 710μm, 710 ~ 500μm, 500 ~ 355, 355 ~ 250, 250 ~ 180, 180 ~ 125, 125 ~ 90, 90 ~ 63, 63 ~ 38 and < 38μm. In Fig. 6, the concentrations of the elements for the sample of DB are plotted by logarithmic scale against the particle diameter, expressed by an arithmetric mean of the sieve-size range. Similar plots by ordinary scale for typical elements are given in Fig. 7 and the dependence of the concentration upon the diameter is more clearly seen. It is to be noted that the concentrations change largely with the kind of elements and also the concentrations of all the elements are obviously decreasing with particle diameter. As in the case of the samples of AB, BB and BY described in the previous clause, the concentrations of such elements as Al, K, Fe and Mg show pretty high values, folowed by Ti, Na, Ba, Mn and so on.

The results for the sample of GB shown in Fig. 8 also indicate the same tendency.

These results described above support definitely the view that the trace elements in the water are adsorbed onto the surface of grains. The concentrations of trace elements existing in the pond water are studied apart from this study by ICP-MS analysis method and it is observed that the concentration of the trace elements in the pond is so small to be expressed by ppb units such as Na:1200, K:400, Mg:250, Mn:85, Fe:22, Al:3.6 etc.

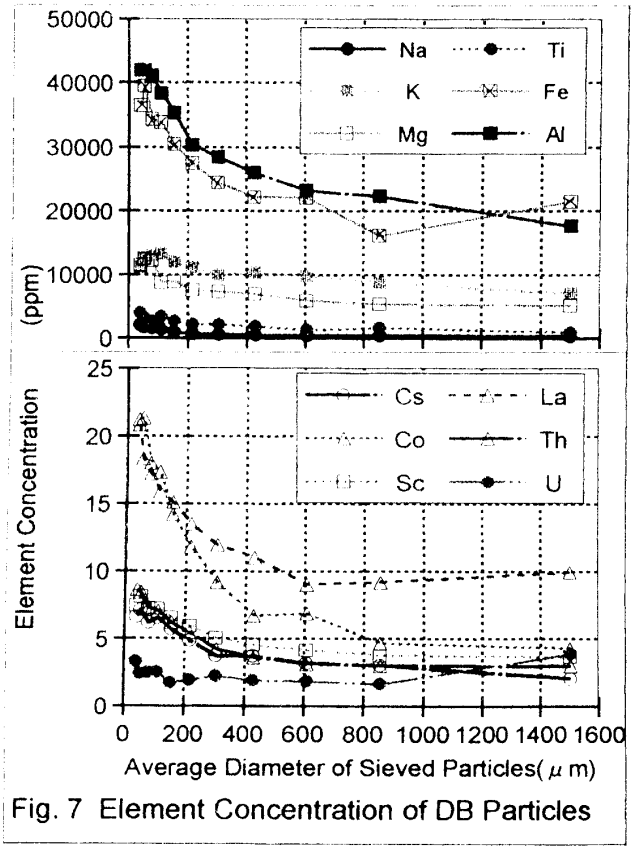

Fig. 7 Element Concentration of DB Particles

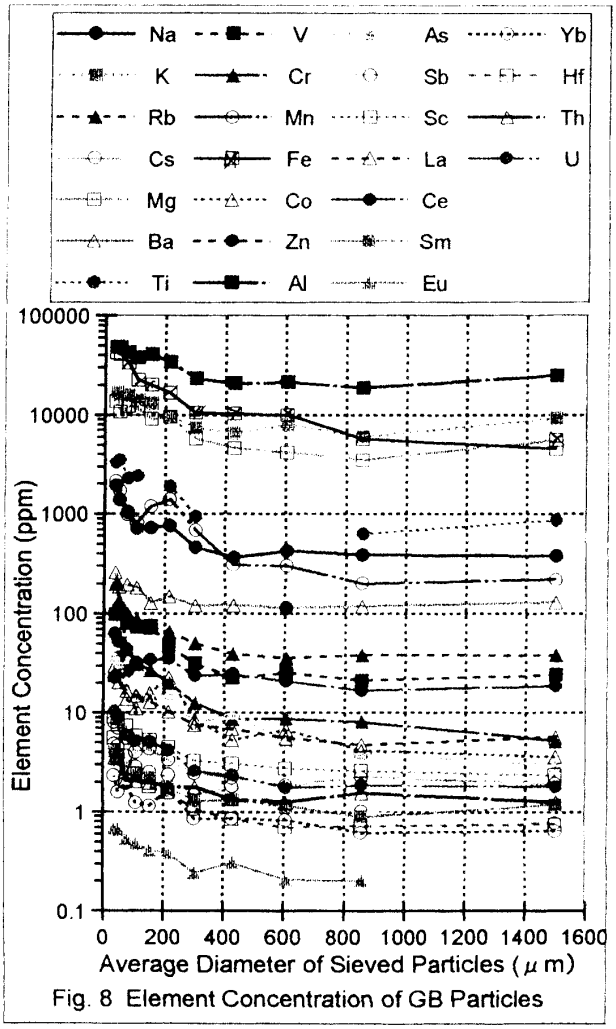

Fig. 8 Element Concentration of GB Particles

(3) Derivation of the concentration of adsorbed elements on the particle

Since the concentration of any element of the particles decreases with the increase in particle diameter and that of infinite size corresponds to that of constitutent element of the particle matrix, the difference of concentrations between the particles of different sizes and the matrix itself is regarded as the concentration of the adsorbed element on the particles. The concentration of particles with infinite size can be estimated by an extrapolation of diameter to infinitive from such plot of the concentration against particle size as Fig. 6. The absorbed concentration of elements obtained from Fig. 6 are shown in Figs. 9 and 10 for all the elements. From this figure it is seen that the concentrations of the adsorbed elements decrease with increase in particle size.

Since it was made clear that the adsorbed amounts of elements onto the particles can be determined by the method described above, it is intended in future to make the analyses of the grains from mineralogical approach including the chemical analysis and furthermore to study the distribution behavior of the trace elements between the grain and the water by carrying out the analysis of the element concentration of the water by ICP-MS method[3].

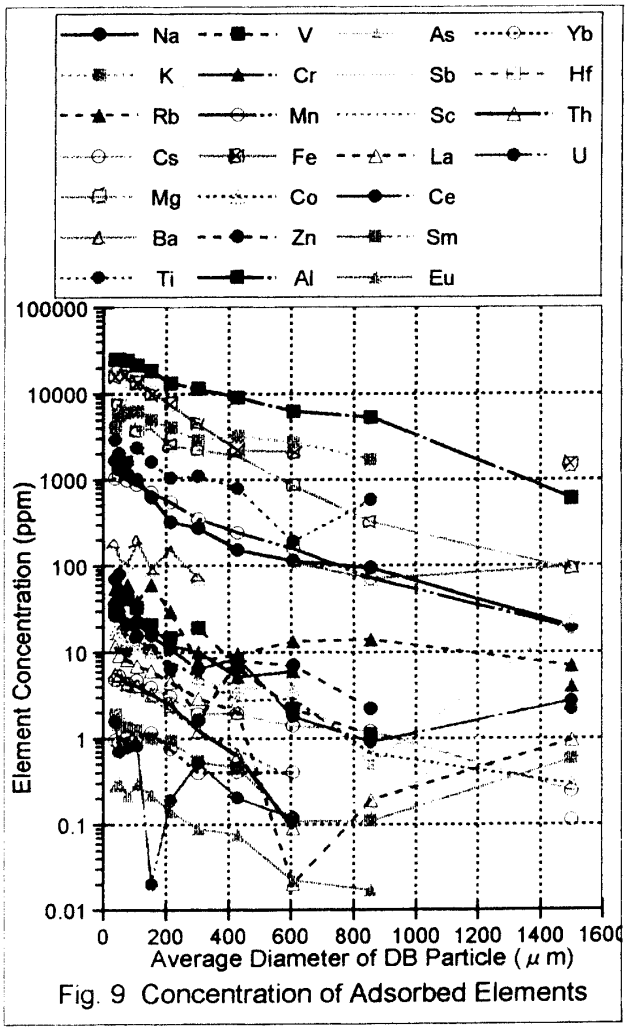

Fig. 9 Concentration of Adsorbed Elements

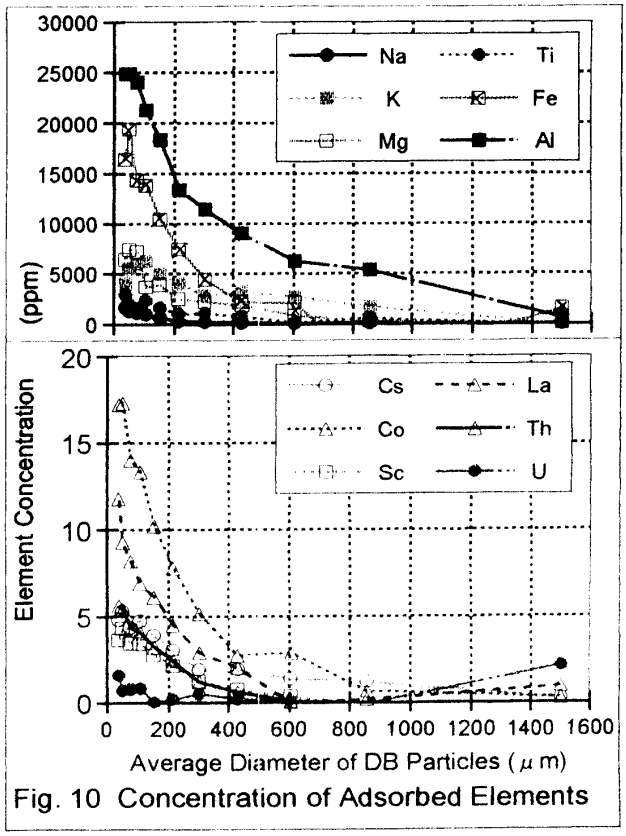

Fig. 10 Concentration of Adsorbed Elements

4. Conclusion

From the isolated undisturbed pond "Yasha-ga-Ike", sedimentary grain samples were taken and sieved into fractions of different sizes, and the concentration of consituent elements of the samples were analysed by neutron activation method. The following results were obtained.

(1) The method of grains sieving, wet or dry, does not affect the element analysis, and the dry method was adopted.

(2) The constituent elements of sedimentary grains, which have been under water for a very long time, have not leached into the water, but the trace elements in the water are adsorbed onto the surface of grains contrariwise.

(3) The concentration of any element in the grains decreases with the increase in particle diameter.

(4) The concentration of the adsorbed element on the particles can be obtained by subtracting the element concentration of grain matrix, which is estimated by extrapolating the grain size to an infinitive, from the observed concentration of any size.

(5) The concentration of any element adsorbd depends largely upon the kind of element and increases with the decrease in particle diameter.

Acknowledgment

The work of neutron activation analysis has been carried out under the Visiting Rsearcher's Program of the Research Reactor Institute, Kyoto University.

Reference

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, T. Nishida, M. Kimura, H. Moriyama, J. Takada , K. Kawamoto, M. Matsushita and H. Amano 「*Research on the water environment of an Isolatd Undisturbd Pond Located at the Ridge of Mountain (2) Preliminary Studies of Sediments (in Japanese)*」 1A206, 1999Meeting of Society of Environmental Science, Japan (Nov. 1999)

3) K. Iwamoto, M. Kimura, K. Ando, H. Moriyama, J. Takada , K. Kawamoto, M. Matsushita and H. Amano; 「*Research on the water environment of an Isolatd Undisturbd Pond Located at the Ridge of Mountain (3) The Partition of Elements between Water and Sedimentary Particles (in Japanese)*」 2A01, 2000 Meeting of Society of Environmental Science, Japan, (Sept. 2000)

(Received November 30, 2000)