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PIXE Analysis on Desorption of Elements from Coastal Sediments

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Coastal sedimental elements were desorbed with ultrapure water, artificial seawater, 0.2M $(NH_4)_2C_2O_4$, 1M CH_3COONH_4, 0.01M EDTA•2Na, 1N HCl and 6N HCl, independently. Fluid volume to sediment weight ratio was 28ml/g for batch systems. Extraction by 10 minutes stirring per day were done for 8 to 16 days. 56 μl of extracted fluid was dropped on Kimfoil to make a target. Beam bombardment was done with a cyclotron using a 4.5 MeV proton energy. For a typical sample, the maximum concentration of Fe seen in the samples was obtained by extraction with 6NHCl (7.6mg/g). In comparison, the concentration of Fe observed after extraction with ultrapure water, artificial seawater, and 1M ammonium acetate were essentially zero. However, the amounts seen with 0.01M EDTA • 2Na and 0.2M ammonium oxalate were high as 18% and 9.5% of the 6N HCl value, respectively. About the extraction with EDTA having most excellent characteristics of chelate agent, alkali earth elements, Mg^{2+} and Ca^{2+} were detected in almost all samples because they form ionic bonding chelates. Desorption rates of transition metal elements which form coordinate bonding chelates were observed to be proportional to the stability constant except for Mn^{2+} and Cu^{2+} anomalies.

1. Introduction

At present it is internationally expected for Japan to achieve some responsibility and to play an important role for protection of the environment with a global scale. We have to respond to the international expection by displaying leadership in environmental problems, such as the application of charged particle beams to elemental analysis of environmental pollutants. The environments in the neighboring seas and the coasts around our country have seriously become worse, even though attempts are being made to recover the natural marine environment by improving the clarification capacity with an artificial seashore, partially constructed. It is important to find the adsorption-desorption kinetics of elements in coastal sediments, as a means to estimate the behavior of pollutants,

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especially the heavy metal elements. For the purpose of the assessment, it may be effective to make clear the behaviors of elements with coastal sediments by the use of the several kinds of the chemical extracting solutions.

This paper describes the result of attempts to obtain information on the adsorption/desorption kinetics of elements in coastal sediments. The extraction method uses independently the following seven kinds of extracting solution; ultrapure water, artificial seawater, 1M ammonium acetate, 0.2M ammonium oxalate, 0.01M EDTA • 2Na aqueous solutions, and 1N and 6N hydrochloric acids adopted by Fukui et al.[1,2]

It is very important to analyze the cause of turbidity and to discover the origin of the adsorbed matters[3,4] on the coastal sediments for learning the adsorption/desorption characteristics of the elements[1,5,6].

The reason why the extraction procedures were attempted as the pretreatment for PIXE analysis will hereinafter be described. It may be expected that ultrapure water and artificial seawater desorb the seawater-soluble matters adsorbed on the surfaces or porous porosities of coastal sediments. Fukui[2] reported that ammonium ions in aqueous solution could more readily desorb trace metals adsorbed by the ion-exchange mechanism than by the sodium ion abundant in seawater. In these studies, (1) both ammonium salts of acetate (1M) and oxalate (0.2M) were used in order to obtain information on desorption kinetics under readily exchangeable and suboxic conditions, respectively; (2) EDTA • 2Na (0.01M) was used for examining the possible formation of chelate compounds with the heavy metals; and (3) HCl (1N and 6N) was used for investigating metal desorption destroying a part of mineral lattices in the solution.

Why PIXE? PIXE analysis has the following three outstanding characteristics for the assessment of the environmental pollution. (1) Multielements can be determined simultaneously without destroying the samples; (2) it needs only trace amounts; and (3) a valuable sample, involving great time, effort and expense in chemical extraction, can be analyzed by repeated procedure at various sensitivities. In brief, chemical extraction plus PIXE is predicted to be very useful for work in the marine environment.

2. Experimental

2.1 Sample and pretreatment

At five points in the Osaka Bay Shore, near South of Sensyu, Osaka Prefecture (Fig. 1), ten samples of deposits from the surface mud layer and the 20cm deep layer were collected[3] and used in this experiment. The samples were dehydrated by centrifuging (≦5800 rpm, 10min) for three days after the samples were collected, then dried for 64 hours in a thermostat kept at 75℃. The samples thus obtained were sieved into four stages with 16, 24 and 32 mesh screens as shown in Table 1. External characteristics of samples after dehydration, dry-

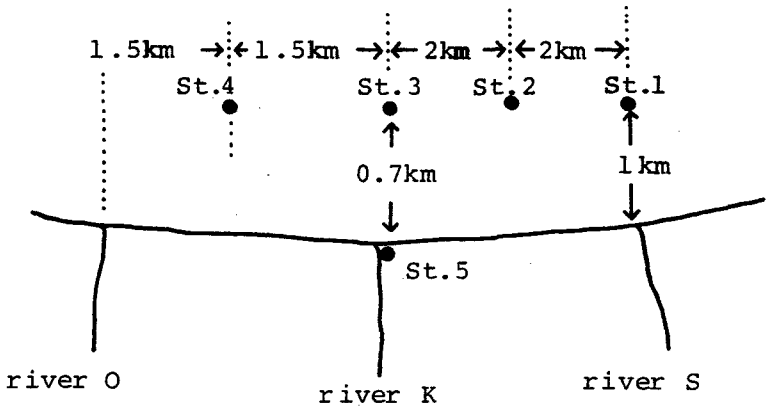

Fig. 1 Schematic map of the sampling stations

Table 1 Characteristics of analytical sieve fractions

Stage	Mesh	Diameter (mm)	Diameter of sieving (μm)
1	>Mesh 16	d>0.590	1000
2	Mesh 16~Mesh 24	0.590>d>0.350	710
3	Mesh 24~Mesh 32	0.350>d>0.290	500
4	Mesh 32 >	0.290>d	

Table 2 External characteristics of samples

Collecting sites	Geographical position	Characteristics
St. 1 Surface layer*	Dredging near Sano river	Mud, sand
20cm deep layer*		Shoulder and sand
St. 2 Surface layer	Aperture	Many shoulders
20cm deep layer		Pebble
St. 3 Surface layer	Dredging near Kashii river	Bottom sediment
20cm deep layer		Mud, sand
St. 4 Surface layer	Tarui, Aperture (Sennan City)	Bottom sediment
20cm deep layer		Mud
St. 5 Surface layer	Okadaura near kashii river	Bottom sediment, shoulder
20cm deep layer		Sand

* Surface layer: Collecting mud from surface to 2cm depth

**20cm deep layer: Collecting 2～3cm bottom mud obtained by inserting a pipe to 23～24cm depth of bottom of the sea

Table 3 Particle size distribution of deposition

Collecting sites	Pebble + Shoulder	Rate of sieve fraction (%)			
		Stg. 1	Stg. 2	Stg. 3	Stg. 4
St. 1 Surface layer	20.58%	24.03	8.57	13.81	33.01
20cm deep layer	25.05%	28.45	6.97	14.29	25.23
St. 2 Surface layer	37.90%	28.28	6.44	8.38	18.99
20cm deep layer	25.51%	38.50	5.65	8.94	21.44
St. 3 Surface layer	0%	0.82	1.01	3.00	95.17
20cm deep layer	0%	11.18	3.75	4.03	81.04
St. 4 Surface layer	5.50%	33.43	7.32	8.35	45.40
20cm deep layer	17.98%	24.48	9.60	9.84	38.10
St. 5 Surface layer	0%	6.87	1.75	5.00	86.38
20cm deep layer	0%	0.23	0.60	4.76	94.41

ing and sieving are shown in Table 2. Table 3 represents a distribution of the grain size of deposits, indicating the distribution of the whole containing the pebbles and the shells which have been removed before sieving.

2.2 Chemical extraction procedures

The stage 4 sample was most finely sieved. Each sample consisting of 1g at this stage was used in this extraction procedure. In the desorption test of the surface mud layer of the station 2 and 4, 0.5g of each sample was ground to powder in an agate mortar and was used for the extractions. Table 4 represents the constitution of extracting solution. A flow chart of the desorption test is shown in Fig. 2. To each sample of 1g or 0.5g, extracting solutions of 27.85 or 13.9ml were added in volumetric flasks of 100 or 50ml, respectively. In the desorption tests using ultrapure water and artificial seawater as extracting solution, samples were shaken occasionally for 10min per day during 15 and 16 days, respectively. In the desorption tests using 1M ammonium acetate, 0.2M ammonium oxalate, 0.01M EDTA • 2Na, and 1N and 6N hydrochloric acids, samples were extracted during eight and four days, respectively with the same shaking condition as that described above. It was considered that the extraction condition was nearly the same, although a shaking period differed somewhat with the kind of extracting solution. The liquids obtained by extraction with occasional shaking were filtered with a membrane filter (TM-2, pore size 0.45 μm, cellulose nitrate 47mm diameter) by the use of a Witt type filtering flask to which a stainless filter support screen was attached, *in vacuo*. The extracts from ultrapure water, artificial seawater, 1M ammonium acetate and 1N hydrochloric acid were filtered by the suction method mentioned above. In order to prevent the corrosi on by strong acid, the filtrations of the extracts from 0.2M $(NH_4)_2C_2O_4$, 0.01M EDTA • 2Na and 6N HCl were carried out by the use of a polycarbonate support screen instead of the stainless support screen. Each filtration time of 27ml of

extract was about 3min, devided into two protions, where it took about 30s per filtration. Analytical data of the extracts from 1M ammonium acetate and 1N ydrochloric acid which were first filtered must be checked against the contamination arising from the stainless support mesh screen, which is readily corroded by acids.

Table 4 Preparation method of extracting solution

Extracting solution	Preparation method
Ultrapure water	Distilled water → ion exchange column → Millipore filter
Artificial seawater	*Pure water → Lyman and Fleming method
1M Ammonium acetate	*Pure water → 1M CH_3COONH_4 dissolved
0.2M Ammonium oxalate	*Pure water → 0.2M $(NH_4)_2C_2O_4 \cdot H_2O$ dissolved
0.01M EDTA • 2Na	*Pure water → 0.01M $C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$ dissolved
1N Hydrochloric acid	*Pure water → Diluted Ultrapure HCl (40%) to 3.59%
6N Hydrochloric acid	Ultrapure water → Diluted ultrapure HCl (40%) to 19.93%

*Pure water was obtained by treating distilled water through ion exchange

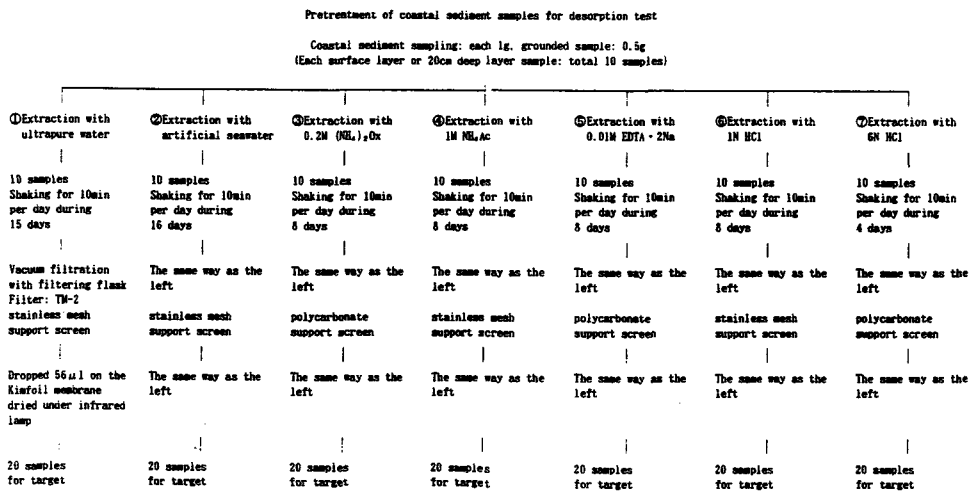

Fig. 2 Pretreatment of coastal sediment samples for desorption test

2.3 PIXE analysis

PIXE target samples were analyzed by the PIXE analysis system in the cyclotron room at the Faculty of Science, Osaka University. A block diagram of the PIXE analysis system is shown in Fig. 3. Beam bombardment was done using 5MeV protons of the cyclotron, degraded to about 4.5MeV with a Kapton foil beam smoother (2.5mg/cm^2). The beam cross section diameter at the target

position was defined to 8mm by double graphite collimators. Beam current was about 1nA and cumulative charge was about 600nC. Characteristic X-rays from samples were measured with a Si(Li) detector (effective area: 28.3mm^2, FWHM: 160eV at 5.9keV) with a pierced Lumilar "funny" filter in front of the Be window. The angle between the sample plane and the beam direction was 45°. The distance between the sample plane and the Be window of Si(Li) detector was 5cm, and the angle between the detector head and the beam direction was 135°.

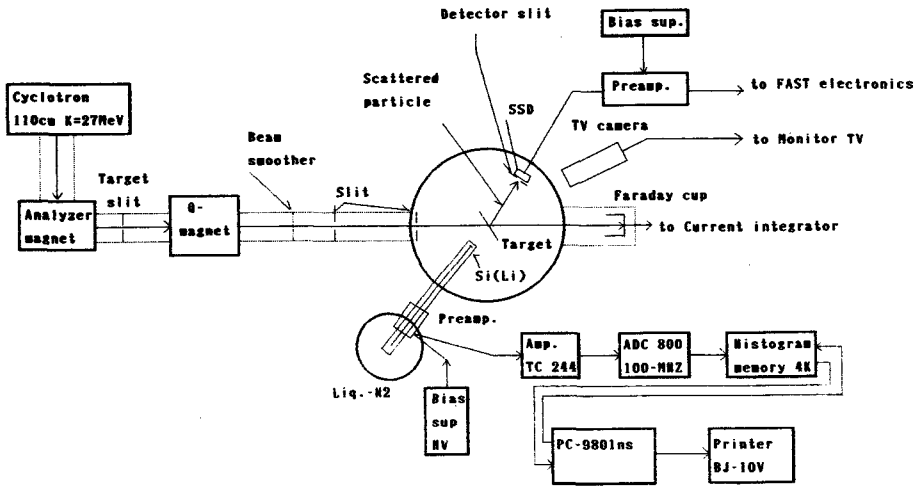

Fig. 3 Block diagram of PIXE+FAST system

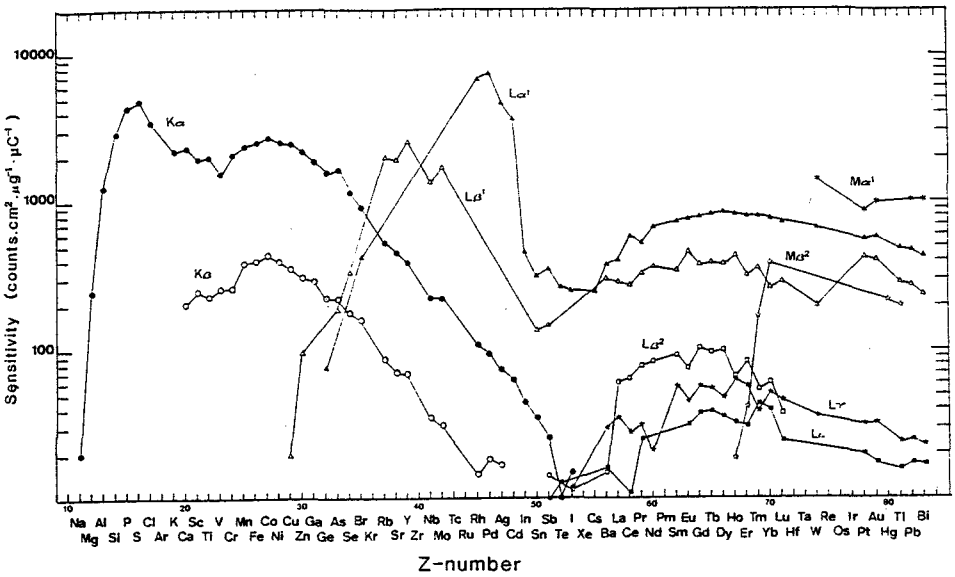

Fig. 4 Sensitivity curves of the PIXE system

As references, standard samples for PIXE of Micromatter Co. were used. Sensitivity curves of the system are shown in Fig. 4. Spectrum analysis was done by using a personal computer based commercial MCA software, and the quantitative determination of elements was undertaken by calculating X-ray self absorption corrections.

2.4 NAA analysis

Part of the samples made as described in 2.2, two sets of samples of St.1 surface mud layer and 20cm deep layer were assayed by NAA to assure analytical results and increase the numbers of determined elements. Each sample portion on target Kimfoil membranes was scissored out and was seeled into a small polyethylene bag. These bags were put into a polypropylene capsule together with NBS standard river sediment and bovine lever references. This capsule was neutron irradiated in the F ring (thermal neutron flux: 1.4×10^{12}n • cm^{-2} • sec^{-1}) of the reactor of Rikkyo University for 6 hours. A gamma-ray measurement was done tow times, for 4,000 and 40,000s with the γ-ray emmitting nuclide analysis system consisted of a shield box (10cm thick lead, 5mm thick copper lining, 5mm thick opaque acrylic lining, volume: $320\times320\times420mm^3$) and a coaxial n-type pure Ge detector (relative efficiency: 30%) of Research Institute for Advanced Science and Technology, University of Osaka Prefecture. Neutron flux was confirmed with an NBS river sediment standard sample, and found to be equal to the nominal value. Spectral analysis was done by using a personal computer based commercial MCA software for nuclide analysis.

3. Analytical results and discussion

The PIXE analytical results of St.1 surface and 20cm deep layer samples are listed in Table 5 as a typical example for main elements, together with the results of extracting liquid blanks. 21 elements, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Hg and Pb were determined. Seven elements, Si, S, Cl, K, Ca, Fe and Zn, were determined for all kinds of extracted samples. The NAA results corresponding to them are listed in Table 6. From the results, the following eight facts were found.

1) Hydroxides of Ca, Mg, and K were released from silicates in sediments by hydrolysis[8]. They were extracted with ultrapure water in the order, Ca>K>Mg (Ca:47-726μg/g, K:17-134, Mg:not detected), and with artificial seawater in the order, Mg>Ca>K (Mg:350-2090μg/g, Ca: 94-1087, K:4-540).

2) By 0.2M $(NH_4)_2Ox$, K^+ was extracted much (K:99-417μg/g) in the form of $K_2C_2O_4$, while Ca^{2+} was scarcely detected because it precipitated as CaC_2O_4. S was extracted fairly much (S:142-2360μg/g) in the forms of SO_4^{2-}/S^{2-} through some reactions with $CaSO_4$ and FeS. Ti^{4+} ion was extracted much (Ti:205-342μg/g) in the form of $[Tio(C_2O_4)_2(H_2O)]^{2-}$. V^{5+} is desorbed as VO_2^+ by the exchange with

Table 5—1 Analytical results of PIXE Content (unit: $\mu g/g$ sediment or $\mu g/27.85ml$ extracting blank)

Sample	Elements																				
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr
ultrapure water blank	ND	ND	405	ND	ND	27.5	ND	21.5	310	ND	ND	ND	22	ND	ND	17	ND	ND	ND	ND	ND
artificial seawater blank	ND	ND	333	ND	ND	318	ND	32.5	460	ND	ND	ND	26	ND	ND	11	ND	ND	ND	ND	ND
0.2M $(NH_4)_2Ox$ blank	ND	ND	633	ND	ND	ND	2.5	34.5	468	1.5	ND	ND	23	ND	ND	9.3	ND	ND	ND	ND	ND
1M NH_4Ac blank	ND	ND	343	ND	ND	ND	3.5	18.8	222	ND	ND	ND	19	ND	ND	7.3	ND	ND	ND	ND	ND
0.01M EDTA・2Na blank	ND	ND	300	ND	ND	39.3	5.0	9.75	173	14	ND	ND	17	ND	ND	5.3	ND	ND	ND	ND	ND
1N HCl blank	ND	ND	633	ND	ND	201	33.8	32.8	152	16	ND	ND	21	ND	ND	18	ND	1.3	ND	82	ND
6N HCl blank	ND	ND	64.8	ND	ND	7.0	7.25	67.8	131	8.5	ND	ND	17	ND	ND	17	ND	ND	ND	500	ND
St.1 sf ultrapure water	ND	ND	107	ND	71	3400	110	400	ND	ND	ND	ND	23	ND	ND	ND	ND	ND	ND	ND	ND
St.1 sf artificial seawater	680	ND	ND	ND	81	2140	97.5	463	18.0	ND	ND	2.8	51	0.5	ND	1.5	ND	ND	ND	40	ND
St.1 sf 0.2M $(NH_4)_2Ox$	ND	ND	550	ND	2360	2030	308	5.3	710	9.8	7	48	740	ND	ND	29	ND	ND	ND	ND	ND
St.1 sf 1M NH_4Ac	310	ND	ND	ND	88	2680	125	3230	11.8	ND	ND	29	16	ND	ND	ND	ND	ND	ND	ND	ND
St.1 sf 0.01M EDTA・2Na	29	ND	613	ND	343	2470	202	2600	715	ND	ND	79	1390	ND	8.5	48	ND	ND	ND	ND	ND
St.1 sf 1N HCl	ND	190	147	ND	465	10100	68.8	938	ND	ND	ND	ND	3850	ND	ND	ND	ND	2.5	ND	ND	ND
St.1 sf 6N HCl	ND	780	64	35	273	17000	475	1990	490	ND	ND	95	7600	ND	ND	ND	22	ND	79	320	13
St.1 20cm ultrapure water	ND	ND	137	ND	10	3080	28	283	16	8	ND	ND	19	ND	ND	ND	ND	ND	ND	17	ND
St.1 20cm artificial seawater	350	22	31	1.3	33	953	13	127	16	ND	ND	ND	17	1.3	.25	1.0	ND	ND	ND	13	ND
St.1 20cm 0.2M $(NH_4)_2Ox$	780	ND	483	ND	370	2500	293	57	673	55	ND	1.8	36	.25	ND	17	ND	ND	ND	ND	ND
St.1 20cm 1M NH_4Ac	150	ND	73	ND	273	2050	335	4530	6	ND	ND	ND	19	2.8	ND	ND	ND	ND	ND	ND	8.0
St.1 20cm 0.01M EDTA・2Na	110	ND	620	ND	26	1800	98	5600	630	ND	ND	16	595	.75	3.3	19	ND	ND	ND	7.5	25
St.1 20cm 1N HCl	ND	103	173	ND	598	17800	390	3200	21	ND	ND	38	5730	ND	ND	ND	ND	ND	ND	ND	ND
St.1 20cm 6N HCl	1750	308	148	ND	400	18900	388	3800	558	ND	ND	61	6950	ND	1.0	49	60	ND	ND	343	33
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr

Table 5−2 Analytical results of PIXE

Content (unit: $\mu g/g$ sediment or $\mu g/27.85ml$ extracting blank)

Sample	Elements																				
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr
St.2 sf ultrapure water	ND	ND	115	ND	433	4330	70.3	748	ND	ND	ND	ND	6	ND	ND	1.8	ND	ND	ND	18.5	ND
St.2 sf artificial seawater	568	ND	ND	ND	2270	9580	200	315	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND	ND	ND
St.2 sf 0.2M $(NH_4)_2Ox$	14.8	ND	403	ND	345	3230	420	49.3	685	ND	ND	12.3	683	ND	ND	33	ND	ND	ND	24.3	ND
St.2 sf 1M NH_4Ac	470	ND	83	ND	233	3730	94.5	5130	21	ND	ND	21	ND	1.5	1.3	.75	ND	ND	ND	ND	ND
St.2 sf 0.01M EDTA・2Na	60.5	ND	573	ND	470	3900	348	4530	658	ND	ND	30.5	733	.25	2.0	3.3	ND	ND	ND	19.8	11
St.2 sf 1N HCl	ND	249	ND	88.8	535	10100	43.3	1650	ND	ND	ND	ND	3180	ND	ND	ND	ND	ND	ND	ND	ND
St.2 sf 6N HCl	1930	420	135	ND	418	17800	60.3	2630	580	ND	ND	19.8	5900	ND	ND	ND	6.8	ND	16	285	ND
St.2 20cm ultrapure water	ND	ND	ND	ND	1970	2850	17.3	258	ND	ND	ND	ND	16.3	ND	ND	ND	ND	ND	ND	ND	ND
St.2 20cm artificial seawater	1430	ND	ND	ND	3300	31800	380	898	ND	ND	ND	2.5	3.5	ND	ND	1.0	ND	ND	ND	418	110
St.2 20cm 0.2M $(NH_4)_2Ox$	ND	ND	538	ND	142	1000	140	12.5	703	34	ND	ND	298	ND	ND	22	ND	.75	ND	ND	ND
St.2 20cm 1M NH_4Ac	153	ND	73.5	ND	213	1930	433	5100	12.3	2.5	ND	10	17.8	ND	ND	ND	ND	ND	ND	3.3	ND
St.2 20cm 0.01M EDTA・2Na	ND	ND	448	ND	69.5	1790	118	5350	433	ND	2.5	12.5	625	ND	2.0	18	ND	ND	4.5	1	24
St.2 20cm 1N HCl	ND	168	14.3	ND	530	8500	313	1830	ND	ND	ND	40	3550	ND	ND	ND	ND	ND	25	ND	ND
St.2 20cm 6N HCl	1490	265	166	ND	1850	13600	161	2680	525	ND	ND	28.3	5480	ND	ND	20	94	ND	ND	308	19
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr
St.3 sf ultrapure water	ND	ND	91	ND	161	3800	81.8	101	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
St.3 sf artificial seawater	2090	ND	155	ND	2730	32500	540	1120	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	450	156
St.3 sf 0.2M $(NH_4)_2Ox$	588	ND	568	ND	328	2650	300	49.3	808	ND	ND	7.3	758	ND	ND	15	ND	ND	ND	ND	ND
St.3 sf 1M NH_4Ac	200	143	ND	ND	247	1680	247	715	15	ND	ND	11.3	19	ND	ND	ND	ND	ND	ND	7.5	ND
St.3 sf 0.01M EDTA・2Na	229	ND	520	ND	4.0	1930	179	710	618	ND	ND	23.8	1910	1.8	ND	24	ND	ND	ND	6.8	ND
St.3 sf 1N HCl	ND	528	75.5	ND	184	8350	93.3	390	ND	ND	ND	68.8	4080	ND	ND	ND	ND	ND	24	ND	ND
St.3 sf 6N HCl	ND	863	142	ND	73.3	7250	68.0	510	793	ND	ND	33.0	4730	ND	8.0	42	ND	ND	ND	270	ND
St.3 20cm ultrapure water	ND	ND	78.3	ND	255	1830	118	72	ND	ND	ND	ND	15.3	ND	ND	ND	ND	ND	ND	ND	ND
St.3 20cm artificial seawater	1230	ND	5450	ND	3380	32800	283	855	ND	ND	ND	ND	13.5	ND	ND	ND	ND	ND	ND	ND	ND
St.3 20cm 0.2M $(NH_4)_2Ox$	515	ND	540	ND	222	2220	253	53.5	775	ND	ND	21.3	142	ND	ND	21	ND	ND	ND	11	ND
St.3 20cm 1M NH_4Ac	170	ND	81.0	ND	146	1690	226	543	8.75	ND	ND	ND	19.5	ND	ND	7.3	ND	ND	ND	11	8.5
St.3 20cm 0.01M EDTA・2Na	410	62.5	690	ND	128	2040	208	733	728	ND	ND	26.5	2410	ND	4.5	41	ND	ND	ND	4.5	5.5
St.3 20cm 1N HCl	305	232	250	72	273	6950	89.8	298	ND	9.8	ND	61.5	3300	ND	ND	ND	ND	ND	ND	ND	ND
St.3 20cm 6N HCl	2160	325	149	ND	300	13300	24	360	583	ND	ND	42.3	5400	ND	ND	34	ND	ND	42	298	ND
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr

Table 5−3 Analytical results of PIXE Content (unit: μg/g sediment or μg/27.85ml extracting blank)

Sample	Elements																				
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr
St.4 sf ultrapure water	ND	ND	116	ND	120	3480	64	608	ND	ND	ND	ND	7.3	ND	ND	ND	ND	ND	ND	ND	ND
St.4 sf artificial seawater	618	68.8	34	ND	358	3150	25.5	470	ND	ND	ND	ND	20.3	ND	ND	2.3	ND	ND	ND	ND	ND
St.4 sf 0.2M $(NH_4)_2Ox$	515	ND	418	ND	303	3400	268	278	703	ND	ND	ND	61.8	ND	ND	17	ND	ND	ND	17.5	ND
St.4 sf 1M NH_4Ac	338	ND	83	ND	465	2680	59	2800	ND	ND	ND	ND	11.0	ND	ND	4.8	ND	ND	ND	11	ND
St.4 sf 0.01M EDTA・2Na	152	ND	610	ND	99.5	2130	228	2160	620	ND	ND	28.5	1540	2.3	ND	30	9.8	ND	3.5	2.3	ND
St.4 sf 1N HCl	575	240	202	ND	458	9880	83	1140	ND	ND	ND	79.3	3850	ND	ND	26	ND	ND	ND	ND	14
St.4 sf 6N HCl	ND	755	20	ND	2530	18500	408	1630	445	ND	ND	74.3	7330	ND	ND	48	ND	5.3	ND	360	ND
St.4 20cm ultrapure water	ND	ND	158	ND	2880	4200	134	228	8.3	ND	ND	ND	20	ND	ND	ND	ND	ND	ND	ND	ND
St.4 20cm artificial seawater	ND	30	27.3	ND	413	3200	147	165	ND	ND	ND	ND	17.8	ND	ND	ND	ND	ND	ND	45	14
St.4 20cm 0.2M $(NH_4)_2Ox$	373	ND	525	ND	318	2400	318	53.3	738	ND	ND	25.3	320	1.3	ND	15	ND	ND	ND	ND	ND
St.4 20cm 1M NH_4Ac	325	ND	56.5	ND	253	1990	55	2800	3.0	ND	ND	ND	14.8	ND	ND	ND	ND	ND	ND	ND	ND
St.4 20cm 0.01M EDTA・2Na	223	ND	643	ND	111	1580	137	2380	658	ND	ND	32.5	1580	1.3	ND	ND	ND	ND	ND	6.5	ND
St.4 20cm 1N HCl	ND	338	320	ND	980	16800	76.5	1720	52.8	ND	ND	79.8	6700	2.5	ND	39	ND	ND	ND	76	6.8
St.4 20cm 6N HCl	1840	236	179	ND	222	14300	268	1100	610	ND	ND	45.8	5080	ND	ND	5.8	ND	ND	ND	320	ND
	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr
St.5 sf ultrapure water	ND	ND	91	ND	503	3830	102	533	ND	ND	ND	ND	40	ND	ND	ND	ND	ND	ND	ND	ND
St.5 sf artificial seawater	2040	ND	ND	ND	1570	6930	500	853	ND	ND	ND	5.3	6.75	1.3	ND	ND	ND	ND	ND	149	ND
St.5 sf 0.2M $(NH_4)_2Ox$	710	ND	485	ND	275	2550	323	50.5	810	ND	ND	ND	174	ND	ND	22	ND	ND	ND	17	ND
St.5 sf 1M NH_4Ac	236	ND	47.8	ND	121	2440	214	893	8.5	ND	ND	2.8	16.3	ND	ND	3.0	ND	ND	ND	13	ND
St.5 sf 0.01M EDTA・2Na	393	72.3	590	ND	12	2700	283	1330	748	ND	ND	20.3	2650	ND	4.3	27	ND	ND	9.5	6.5	ND
St.5 sf 1N HCl	ND	325	73.5	ND	410	7700	59.8	483	ND	ND	ND	ND	3430	ND	2.3	23	ND	ND	ND	ND	ND
St.5 sf 6N HCl	1780	1680	117	ND	473	9250	214	925	558	ND	ND	13.5	5950	ND	ND	43	ND	ND	ND	330	ND
St.5 20cm ultrapure water	ND	ND	51.3	ND	338	2160	96	68.8	ND	ND	ND	ND	27.5	ND	ND	ND	ND	ND	ND	ND	ND
St.5 20cm artificial seawater	ND	ND	44.5	ND	18.0	57.0	4.0	31.8	15.5	ND	ND	ND	16.8	ND	ND	ND	ND	ND	ND	ND	ND
St.5 20cm 0.2M $(NH_4)_2Ox$	217	ND	490	ND	184	1400	102	20.5	695	43.8	ND	2.75	570	ND	ND	18	ND	ND	ND	.5	ND
St.5 20cm 1M NH_4Ac	167	ND	37.8	ND	145	1330	95.3	132	10.3	ND	ND	ND	14.3	ND	ND	3.0	ND	ND	ND	4.0	ND
St.5 20cm 0.01M EDTA・2Na	98.3	171	448	ND	368	2230	2.0	280	715	ND	ND	ND	1660	ND	4.5	33	ND	ND	ND	11.3	ND
St.5 20cm 1N HCl	ND	211	308	ND	57.3	5100	109	109	22.3	ND	ND	ND	2110	ND	ND	8.0	ND	ND	ND	48.8	ND
St.5 20cm 6N HCl	ND	197	385	ND	498	4400	66	140	855	ND	ND	7.8	2750	ND	13	31	ND	ND	ND	218	ND
		Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Hg	As	Pb	Br	Sr

Table 6 Analytical results of NAA

Content (unit: $\mu g/g$ sediment or $\mu g/27.85ml$ extracting blank)

Sample	Elements																					
	Na	K	Sc	Cr	Mn	Fe	Co	Zn	Br	Ag	Cd	Sn	Cs	Ba	La	Sm	Eu	Lu	Hf	Ta	Pa	Yb
ultrapure water blank	39	ND	.06	ND	ND	ND	ND	ND	49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	.68
artificial seawater blank	140000	1150	ND	ND	ND	ND	ND	ND	13200	ND	ND	ND	ND	ND	ND	ND	ND	120	ND	ND	ND	ND
0.2M $(NH_4)_2Ox$ blank	77	ND	.01	ND	ND	ND	ND	ND	34	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1M NH_4Ac blank	47	ND	ND	ND	ND	ND	ND	ND	40	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
0.01M EDTA・2Na blank	3400	ND	ND	ND	ND	ND	ND	ND	8300	ND	ND	ND	ND	ND	5.5	2.9	ND	ND	ND	ND	ND	ND
1N HCl blank	64	ND	ND	6.6	ND	ND	42	ND	1300	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6N HCl blank	50	ND	ND	ND	ND	ND	ND	ND	8330	ND	ND	ND	ND	ND	ND	ND	24	160	ND	ND	ND	ND
St.1 sf ultrapure water	3200	ND	ND	ND	ND	ND	ND	ND	340	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
St.1 sf artificial seawater	220000	6000	ND	ND	ND	ND	11	ND	17100	6.2	ND	550	ND	5990	ND	ND	ND	ND	4.9	5.3	ND	ND
St.1 sf 0.2M $(NH_4)_2Ox$	5300	ND	.11	1.1	ND	ND	1.7	ND	356	ND	2.8	ND	ND	ND	ND	.12	ND	ND	ND	.84	ND	ND
St.1 sf 1M NH_4Ac	3400	ND	.01	1.9	4.7	140	1.4	17	323	.71	ND	360	.30	5650	ND	ND	.02	ND	1.2	ND	ND	ND
St.1 sf 0.01M EDTA・2Na	11000	ND	ND	22	ND	2870	2.9	57	326	10	ND	300	ND	164	1.4	1.1	.13	ND	ND	4.1	.52	.69
St.1 sf 1N HCl	3400	490	.22	21	156	10300	5.7	91	1510	ND	ND	ND	ND	ND	4.5	2.4	.27	ND	ND	3.4	ND	.23
St.1 sf 6N HCl	3400	ND	.33	12	165	12100	7.0	3090	8300	ND	ND	ND	1.1	ND	5.5	2.9	.22	ND	4.3	ND	.35	ND
St.1 20cm ultrapure water	2500	ND	ND	2.8	ND	ND	8.6	ND	260	ND	ND	ND	ND	5800	ND	ND	ND	ND	ND	ND	ND	ND
St.1 20cm artificial seawater	124000	2900	ND	5.6	ND	ND	5.2	ND	20900	ND	ND	ND	ND	ND	ND	ND	11	ND	ND	ND	ND	ND
St.1 20cm 0.2M $(NH_4)_2Ox$	2900	ND	.13	5.0	5.1	3400	24	25	368	.68	ND	230	ND	4500	4.4	ND	ND	38	ND	1.4	.40	.54
St.1 20cm 1M NH_4Ac	2600	ND	.07	ND	ND	ND	ND	19	384	2.2	ND	450	ND	3500	ND	.13	ND	ND	ND	ND	ND	ND
St.1 20cm 0.01M EDTA・2Na	9600	ND	.17	ND	ND	810	1.2	32	243	ND	ND	160	ND	ND	1.2	.87	ND	170	86	ND	ND	ND
St.1 20cm 1N HCl	3200	ND	.48	ND	143	9600	7.9	110	1580	ND	ND	ND	ND	ND	5.2	2.6	.07	ND	ND	7.0	.50	1.2
St.1 20cm 6N HCl	2700	ND	.44	7.8	167	11000	8.1	84	8100	ND	ND	ND	1.8	7300	4.8	2.5	.16	.11	ND	7.5	8.9	ND
	Na	K	Sc	Cr	Mn	Fe	Co	Zn	Br	Ag	Cd	Sn	Cs	Ba	La	Sm	Eu	Lu	Hf	Ta	Pa	Yb

NH_4^+ and forms complex anion, $[VO_2(C_2O_4)_2]^{3-}$ with oxalate ion (V:8-53 μg/g). Mn^{2+} is desorbed by the exchange with NH_4^+, but Mn was not detected or detected with low concentrations (Mn:2-48 μg/g) because the stability of the nonionic complex $[Mn(C_2O_4)(H_2O)_4]^0$ is low. As for Fe, the portion adsorbed as Fe^{3+} is desorbed as very stable complex anion $[Fe(C_2O_4)_3]^{3-}$. Fe was detected at a fairly high concentration (Fe:13-735 μg/g). As for Zn, desorbed Zn^{2+} by the exchange with NH_4^+ forms the stable complex anion $[Zn(C_2O_4)_2]^{2-}$. Zn was detected in almost all samples (Zn:6-24 μg/g).

3) By 1M NH_4Ac with an ion-exchange function of NH_4^+ ion, Mg^{2+}, K^+ and Ca^{2+} were extracted from clay minerals in the order, Ca>Mg>K (Ca:113-5110 μg/g, Mg:150-470, K:51-429).

4) Desorption behavior with 0.01M EDTA・2Na is as follows. EDTA makes ionic chelates with alkali earth metal elements. Mg^{2+} and Ca^{2+} were detected in almost all samples. Among them, the desorbed amounts and rates of Ca with EDTA are especially high. This is because when *edta*$^{4-}$ ions as doner ions arranged around a metal ion, the size of Ca^{2+} ion (1.18Å, $e^2/r=3.4$) is suitable for making a chelate compound having maximum stability (stability•constant, $\log K_1=10.6$). The size of Mg^{2+} ion is smaller than Ca^{2+} ion ($e^2/r=4.9$), nevertheless the desorbed amounts and rates of Mg are smaller than Ca[7] by more than one order. This is because chelate compounds having lower stability constants ($\log K_1=8.7$, etc.)[9] than those of Ca were formed.

On the other hand, among transition metal elements, the detected elements in this experiment, Ti, V, Mn, Fe, Cu, and Zn, form coordinate bonding chelates with EDTA. Except V among them, generally the desorption rates of these elements were proportional to the stability constants of chelates. About the sediment samples collected at St.1 surface and St.1 20cm depth, desorption amounts and rates with 0.01M EDTA・2Na and the stability constants of chelates are shown in Table 7. According to this table, the order of the desorption rate of transition metal elements are

$Mn^{2+}>Ti^{4+}>Zn^{2+}>Fe^{3+}>Cu^{2+}$ (St.1 surface)

$Ti^{4+}>Zn^{2+}>Fe^{3+}$ (St.1 20cm depth).

The desorption tendency was in accordance with the order of the stability constants, $Cu^{2+}>Ti^{4+}>Zn^{2+}\geqq Fe^{3+}>Mn^{2+}$, except for Mn^{2+} and Cu^{2+} ions. These Mn^{2+} and Cu^{2+} anomalies show that a greater part of Mn is in inorganic forms and a greater part of Cu is in organic forms as reported before by Matsuda et al[3]. The existing modes of chemical forms of these elements coincide with the report by Sugimura et al[6].

5) In 6N HCl extracting liquid, Al and Fe which are thought to be mineral components were detected with the highest concentrations among all extracting liquids tested. For a typical sample, the maximum concentration of Fe seen in the samples was obtained by extraction with 6N HCl(7.6 mg/g). In comparison, the

Table 7 Desorption with 0.01M EDTA and the stability constants of chelates

Sample \ Element		Mg^{2+}	Ca^{2+}	Ti^{4+}	Mn^{2+}	Fe^{2+}	Cu^{2+}	Zn^{2+}
*Conc. (μg/g)	St. 1 sf	27700	12700	3990	488	39900	959	608
	St. 1 20cm	≦8300	33800	5320	<480	63200	≦200	378
St. 1 surface	Desorption (μg/g)	29	2590	542	79	1373	8.5	42.7
	Desorption (%)	0.105	2.04	13.6	16.2	3.44	0.886	7.02
St. 1 20cm	Desorption (μg/g)	110	5590	457	16	578	3.3	13.7
	Desorption (%)	≧1.3	16.5	8.59	>3.3	0.915	≧1.7	3.62
Stability constant, $\log K_1$ of metal-EDTA chelates[9]		8.7	10.6	17.5	14.5	15.2	18.8	15.9

* ≦ and < show the values of the estimated limits because the elements were not detected.

Fe concentration observed after extraction with ultrapure water, artificial seawater, and 1M ammonium acetate were essentially zero. However, the amounts seen with 0.01M EDTA • 2Na and 0.2M ammonium oxalate were as high as 18% and 9.5% of the 6N HCl value, respectively. Hg and Pb were extracted which were not desorbed by any other extracting liquids. In 1N HCl, mineral components were generally less desorbed than 6N HCl, as expected.

6) As for St.1 surface and 20cm deep layers, elements detected by both PIXE and NAA methods had general tendencies that were similar to each other. However, the NAA values were greater than the PIXE values. It is thought that the main reason for these discrepancies is the evaporation loss of volatile matter in vacuum and during proton bombardments in vacuum.

7) With most elements, excepting a few elements (especially as seen in St.1 case Ca with each extracting liquid), desorption amounts tended to be greater in surface layer than in the 20cm deep layer.

8) From the NAA results, light rare earth elements, La, Sm and Eu, were extracted with chelate agent EDTA, 1N HCl and 6N HCl regularly, and the order of the desorpted concentrations were EDTA<IN HCl<6N HCl.

In summary, these techniques, chemical extraction plus PIXE, are shown to be very useful to understand adsorption/desorption behavior in environmental conditions. The accumulation of the experimental data obtained by continuation of the study should clarify the effects of seashore through the formation of a fundamental base of the study of marine science.

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