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Minor Elements in Japanese Coal (II)

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Abstract: The analytical data of ash content and nineteen trace elements of As, B, Ba, Co, Cr, Cu, Ga, Ge, Li, Mn, Mo, Ni, Pb, Sn, Sr, U, V, W and Zn in coals from twelve Japanese coal fields obtained in previous paper (TAKEDA, 1981) are statistically analysed.

The elements of As, Ge, Mo, U and W are concentrated in sub-bituminous and lignite coals 5 to 10 times larger than in bituminous coals. The high correlation coefficients for any two elements in coal are (1) ash-Cr, Cu, Ga, Mn, V (2) Ba–Sr (3) Cr–Ga, V (4) Ga–Li, V. The concentrations of the elements of As, B, Ge, Mo, U and W are high especially in sub-bituminous and lignite coals compared with earth's crust, and those of Co, Mn and Ni are generally low. Boron is apparently concentrated in coals deposited in waters with high salinity (more brackish or marine) or whose coal seam was closely associated with marine strata such as in Mino, Miike and Ube Coal Fields. Germanium is concentrated at the top and bottom of many coal seams. Organic and inorganic affinities are evaluated from the histogram of correlation coefficients of the elements with ash content in 34 bench sets. The elements of B, Ge, Mo and W have organic affinities and of Ba, Cr, Ga, Li, Mn, Pb, Sn, Sr, U and Zn have inorganic affinities. The affinities of Co, Mn and Ni are intermediate.

Introduction

The demand for coal as an energy source has increased during recent years due to the higher price of oil. Extensive research on the liquefaction and gasification of coal has been conducted. Thus, there is a renewed interest on the content of inorganic elements in coal because they are released into the atomosphere during the combustion and are the cause of serious environmental problems.

Trace elements in U. S. coals have been investigated intensively by GLUSKOTER *et al.* (1977) and RUCH *et al.* (1974). In Japanese coals the distribution of twenty one trace elements was described by one of the present authors using bench sets from twelve coal fields (TAKEDA, 1981). He also noted that the origin of trace elements in coal was mainly from mineral matters contained in coal. In the present work, we performed statistical analysis of a large amount of data in order to study the characteristics of occurrence and distribution of trace elements in Japanese coals.

The content of nineteen trace elements, namely As, B, Ba, Co, Cr, Cu, Ga, Ge, Li, Mn, Mo, Ni, Pb, Sn, Sr, U, V, W, Zn and ash content are discussed in this paper. Figure 1 shows the location of Mogami, Owari, Igu, Hiraga, Mino, Mikawa-Akatani, Sasebo, Kushiro, Sakito-Matsushima, Miike, Ube and Fukuoka Coal Fields where samples for this study were collected. Table 1 gives the number of bench sets (vertical segment of coal seam), coal samples, partings and rocks from each coal field which were used in this work. All samples were collected as bench sets which contained partings and foot and hanging wall. Analytical samples were obtained by cutting those bench sets in each 5 to 10 cm thick. The total number of bench sets and coals obtained from bench sets were 83 and 271, respectively, and total number of rocks and partings was 300.

Samples were dried in air and crushed and ground to 80 mesh, and further dried at

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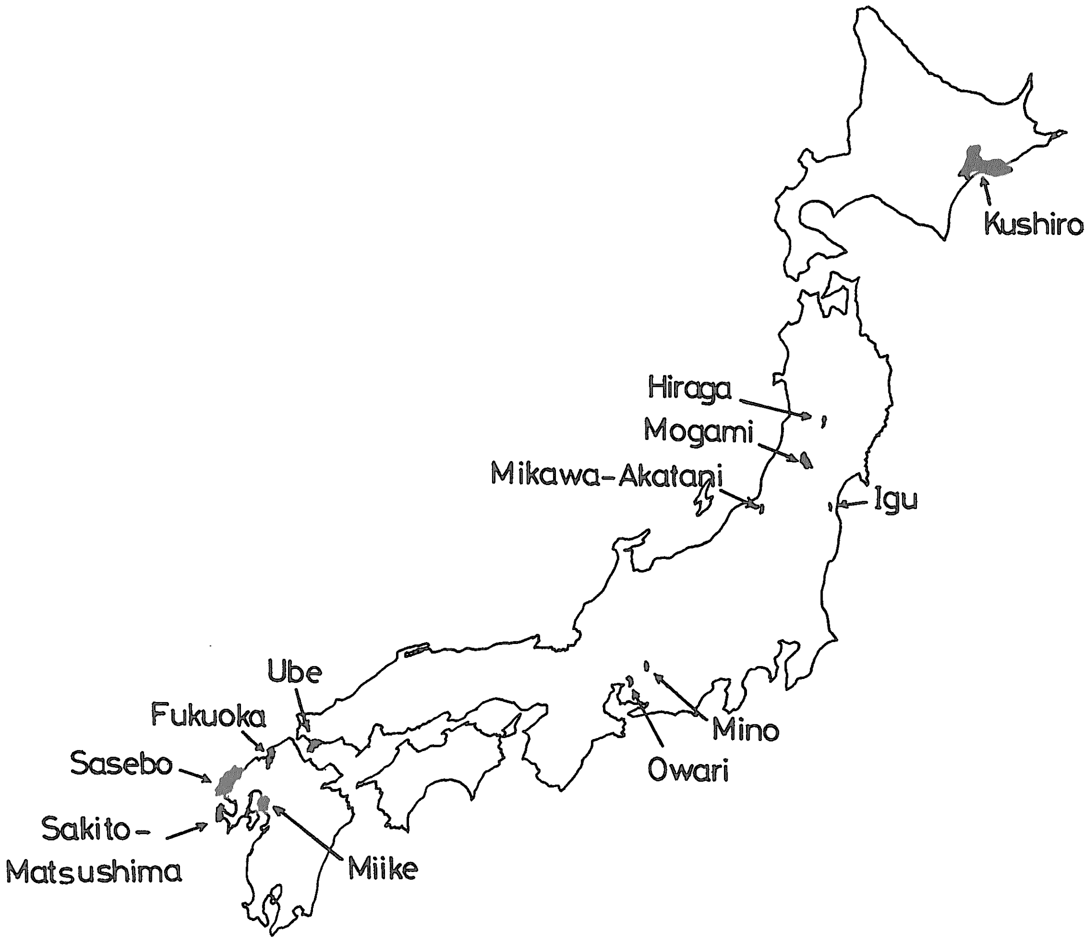

Fig. 1 Coal fields of Japan where samples in this study were collected.

Table 1 Number of bench sets, coals, rocks and partings collected from 12 coal fields.

Coalfield	bench set	coals	rocks, partings
Mogami	16	36	39
Owari	5	6	19
Igu	10	10	85
Hiraga	13	79	8
Mino	12	8	38
Mikawa-Akatani	17	9	91
Sasebo	2	12	4
Kushiro	3	45	10
Sakito-Matsushima	2	29	3
Miike	1	14	1
Ube	1	6	1
Fukuoka	1	17	1

105 °C for 2 hours before use. In case of coal samples, coal ash was used for chemical analysis, which were ashed below 500 °C gradually so that minor elements should not be lost. Chemical analysis of minor elements were made by DC arc optical emission spectrometry. Samples for emission spectroscopy were made by mixing coal ash and rock with equal amount of sodium chloride. Exposure and electric current were 120 seconds and 10 amperes to suppress matrix effects and improve reproducibility. Spectrometer used was JACO-Ebert type. Uranium was determined by fluorescence technique (MOCHIZUKI *et al.*, 1978).

Results and Discussion

Arithmetic and geometric means and stan-

Table 2 Arithmetic ($\bar{x}_a$) and geometric ($\bar{x}_g$) means and standard deviations (SD) of analytical data in each coal field.

	Mogami			Owari			Igu			Hiraga		
	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD
Ash*	14.62	12.67	7.20	20.00	17.64	8.66	22.81	21.77	6.02	15.02	14.09	5.73
As**	34	26	21	36	34	12	325	62	534	83	36	70
B	54	40	39	12	9	8	127	77	102	45	28	45
Ba	128	112	64	496	428	237	119	83	134	123	94	113
Co	5.0	3.8	4.9	5.2	4.4	2.9	11.6	8.2	9.1	7.0	4.4	6.7
Cr	15	13	7	20	18	9	23	22	6	15	14	5
Cu	19	14	14	15	13	6	42	26	42	25	17	24
Ga	5.0	3.2	5.4	8.3	5.7	5.3	11.0	7.6	6.6	4.2	3.4	2.6
Ge	27.6	3.7	66.9	28.7	7.2	39.1	19.9	14.8	13.9	6.3	2.9	10.3
Li	4.4	2.2	7.3	11.7	4.2	16.8	3.2	1.7	6.4	31.6	25.2	20.8
Mn	86	63	55	145	117	75	37	23	41	92	68	48
Mo	8.8	6.7	6.3	9.7	5.6	9.3	97.2	66.7	67.6	11.3	8.0	10.3
Ni	3.2	2.6	2.1	19.7	6.6	33.4	12.3	9.1	11.2	2.5	2.1	1.6
Pb	4.6	3.5	3.2	3.2	2.9	1.5	3.4	2.3	3.7	3.0	2.3	2.3
Sn	1.5	1.3	1.1	2.7	2.4	0.9	1.4	1.5	0.9	2.2	1.7	2.1
Sr	113	86	82	144	139	39	140	117	86	97	76	55
U	—	—	—	7.5	6.3	4.2	64.6	13.7	104	1.0	1.0	0.4
V	37	17	61	99	79	80	224	134	229	22	12	28
W	0.3	1.1	1.0	1.3	1.4	3.0	158	66	188	—	—	—
Zn	13	4	18	30	12	24	60	40	32	16	4	31

	Mino			Mikawa-Akatani			Sasebo			Kushiro		
	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD
Ash*	18.39	17.69	4.92	15.93	13.55	8.13	17.78	16.89	4.86	15.56	13.64	7.53
As**	42	11	47	24	10	19	29	5	71	5	2	9
B	221	212	59	47	23	42	81	52	65	53	25	59
Ba	111	80	95	307	132	400	365	245	356	573	495	299
Co	2.0	1.7	1.7	1.1	1.2	0.6	4.8	3.1	5.1	9.3	5.4	10.9
Cr	18	18	5	16	14	8	18	17	5	16	14	8
Cu	17	16	5	6	4	5	29	24	19	21	16	14
Ga	5.9	4.5	3.2	2.7	1.8	2.8	10.8	10.2	4.2	10.4	6.8	10.2
Ge	28.4	5.3	61.3	20.6	9.5	23.0	3.6	2.4	3.9	2.8	1.9	3.3
Li	1.4	1.3	3.6	3.6	1.7	8.4	29.6	21.8	20.9	7.2	3.2	10.1
Mn	120	114	35	65	38	59	78	68	32	56	44	35
Mo	33.3	13.9	38.4	107	78.2	79.1	6.9	3.7	7.4	3.7	2.0	5.0
Ni	6.0	4.6	4.1	1.1	1.2	0.6	8.6	8.0	3.4	7.9	5.6	7.0
Pb	2.0	2.2	1.3	7.0	3.1	8.7	7.2	4.3	8.2	13.2	7.4	16.7
Sn	1.1	1.1	0.3	0.6	1.1	0.7	2.5	1.8	2.5	1.6	1.4	1.2
Sr	271	259	77	132	69	134	360	244	382	220	163	177
U	5.0	4.3	2.7	70.7	27.4	114	1.1	1.1	0.3	1.3	1.2	0.7
V	57	36	40	51	25	51	97	64	69	71	20	81
W	187	45	183	16	10	17	—	—	—	—	—	—
Zn	32	23	13	13	3	21	24	11	19	33	21	25

* (%) ** (ppm)

Table 2 Continued

	Sakito-Matsushima			Miike			Ube			Fukuoka		
	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD	$\bar{x}_a$	$\bar{x}_g$	SD
Ash*	11.97	10.28	6.44	15.89	15.29	4.42	17.12	16.64	3.65	12.58	11.30	5.63
As**	16	4	50	6	2	10	3	2	7	5	2	10
B	98	58	80	124	76	103	204	193	66	50	36	32
Ba	178	106	225	900	799	301	524	299	487	157	119	107
Co	8.9	3.9	15.7	1.3	1.2	0.5	2.5	1.9	1.9	7.2	4.2	7.9
Cr	12	10	6	16	15	4	17	17	4	13	11	6
Cu	11	10	6	30	26	21	10	8	4	9	7	7
Ga	7.3	5.0	6.0	9.7	7.8	5.9	12.5	11.8	4.5	8.1	5.7	5.5
Ge	3.6	2.5	3.5	6.4	5.7	2.5	2.5	2.1	1.3	1.6	1.4	1.0
Li	10.3	4.4	14.5	206	154	138	28.0	27.1	7.0	12.5	9.9	7.7
Mn	5	3	6	95	91	28	327	255	212	115	74	127
Mo	5.0	3.0	5.4	1.1	1.1	0.3	1.5	1.4	0.5	2.1	1.7	1.3
Ni	21.2	116	26.2	19.6	10.6	22.2	3.8	3.3	2.0	4.3	3.1	3.8
Pb	5.2	3.5	5.9	8.9	4.9	9.9	4.5	3.8	2.0	3.4	3.0	1.6
Sn	2.3	1.6	3.1	2.6	2.0	1.8	1.3	1.3	0.5	0.9	1.0	0.2
Sr	193	164	108	822	780	225	131	108	80	51	29	41
U	1.2	1.2	0.4	1.2	1.1	0.8	1.0	1.0	0	1.0	1.0	0
V	69	30	58	98	48	81	53	49	15	120	41	172
W	—	—	—	—	—	—	—	—	—	—	—	—
Zn	17	12	10	114	90	72	7	4	8	1	1	2

dard deviation of the analytical results of the 271 coal samples from 12 coal fields are shown in Table 2. All data are based on the values in coal. Ash contents are shown in percentages (%) and other elements are as listed in parts per million (ppm). Geometric means are preferable especially in cases where extremely high values were obtained for comparison among samples because such high values are of less influence than arithmetic means.

In this paper, the data from coals whose ash content is more than 30 percent are excluded, though previous paper included coals of up to 80 percent ash. Zero is used when the content of trace element is less than detection limit.

The contents of trace elements can be classified into two groups of different degrees of coalification. One group is those in sub-bituminous and lignite coals and the other is the content in bituminous coals. The average values in two groups are listed in Table 3.

Table 3 The mean concentrations of the elements in sub-bituminous, lignite and bituminous coals (ppm).

	sub-bituminous and lignite coal	bituminous coal
As	80	10
B	61	81
Ba	149	437
Co	6.1	7.2
Cr	15	15
Cu	23	18
Ga	5.1	9.4
Ge	15.1	3.3
Li	18.9	34.4
Mn	89	72
Mo	23.5	3.7
Ni	4.1	11.7
Pb	3.6	8.4
Sn	1.8	1.9
Sr	117	268
U	12.9	1.2
V	46	82
W	22	–
Zn	20	32

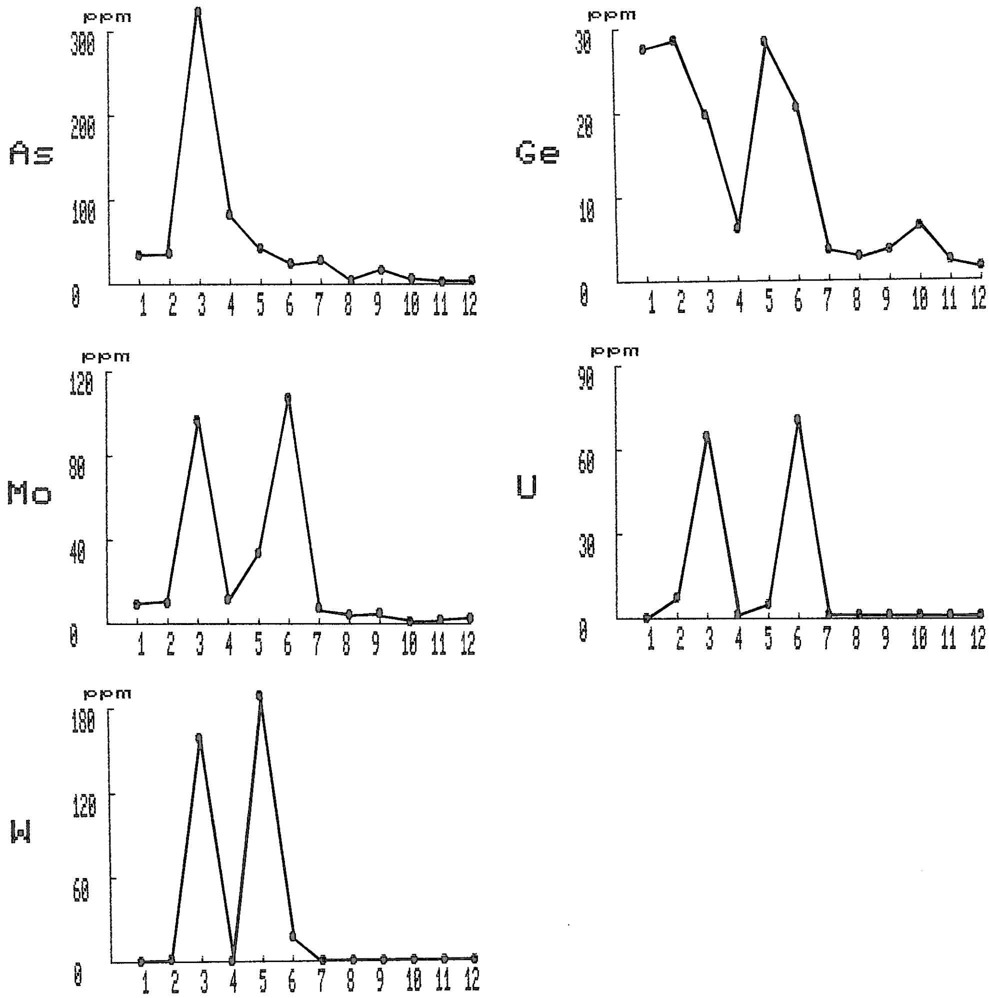

Fig. 2 The average contents of the elements of As, Ge, Mo, U and V in each coal field.
The numbers in abscissa means coal fields as follows, 1 Mogami, 2 Owari, 3 Igu, 4 Hiraga, 5 Mino, 6 Mikawa-Akatani, 7 Sasebo, 8 Kushiro, 9 Sakito-Matsushima, 10 Miike, 11 Ube, 12 Fukuoka.

For comparison of the distribution of trace elements among those coals, coals from twelve Japanese coal fields in this paper are divided into two groups tentatively; sub-bituminous and lignite coals obtained from Mogami, Owari, Igu, Hiraga and Mino Coal Fields and bituminous coals from Mikawa-Akatani, Sasebo, Kushiro, Sakito-Matsushima, Miike, Ube and Fukuoka Coal Fields. It is well-known that Japanese coals were formed during the Neogene are mainly sub-bituminous and lignite coals while those formed during the Paleogene are bituminous coals (Mita, 1960).

Table 3 shows that As, Ge, Mo, U and W concentrate in sub-bituminous and lignite coals. In fact, the contents of these elements in the sub-bituminous and lignite coals are 5–10 times larger than those in the bituminous coals. This result suggests that lowly-coalified sub-bituminous and lignite coals adsorb those elements more than highly-coalified bituminous coals. This is shown more clearly in Figure 2 which gives the average contents of As, Ge, Mo, U and W in each coal field. The age of coal formation becomes older from Mogami to Fukuoka Coal Fields as the number in abscissa increases. It is quite obvious that the contents

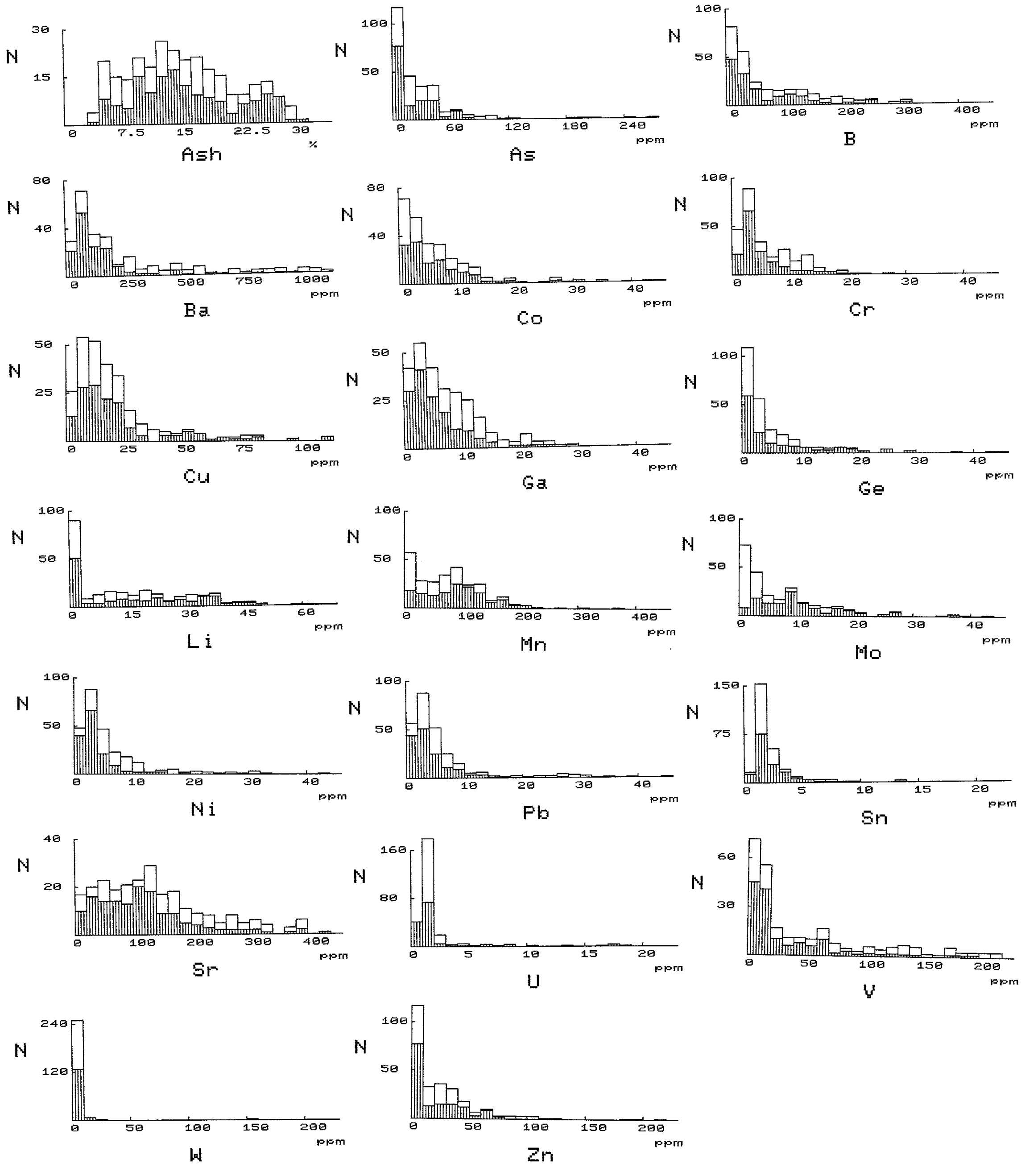

Fig. 3 Histograms of the contents of minor elements and ash in Japanese coal.
The data from subbituminous and lignite coal are plotted as vertically striped line, and those from bituminous coals as blank.

of the elements in coal fields 1 to 6 (subbituminous and lignite coals) are much higher than those in coal fields 7 to 12 (bituminous coals).

Histograms of the contents of trace elements and ash in Japanese coal are given in Figure 3. In appendix Figure 1 to 12 histograms for each coal field are shown in order to reveal

Table 4 Elements whose standard deviations (SD) are larger than average values (x) or less than one half of average values in each coal field.

	SD>x	SD<1/2 x
Mogami	Ge, Li, V, W, Zn	Cr
Owari	Ge, Li, Ni, W	As, Ba, Cr, Cu, Pb, Sn, Sr
Igu	As, Ba, Li, Mn, Pb, U, V, W	Cr
Hiraga	Ge, V, Zn	Cr, U
Mino	As, Ge, Li, Mo	B, Cr, Cu, Mn, Sn, Sr, Zn
Mikawa-Akatani	Ba, Ga, Ge, Li, Pb, Sn, Sr, U, Zn	
Sasebo	As, Co, Ge, Mo, Pb, Sr	Cr, Ga, Mn, Ni, U
Kushiro	As, B, Co, Ge, Li, Mo, Pb, V	
Sakito-Matsushima	As, Ba, Co, Li, Mn, Mo, Ni, Pb, Sn	U
Miike	As, Ni, Pb	Ba, Co, Cr, Ge, Mn, Mo, Sr
Ube	As	B, Cr, Cu, Ga, Li, Mo, Pb, Sn, V
Fukuoka	As, Co, Mn, V, Zn	Cr, Pb, Sn

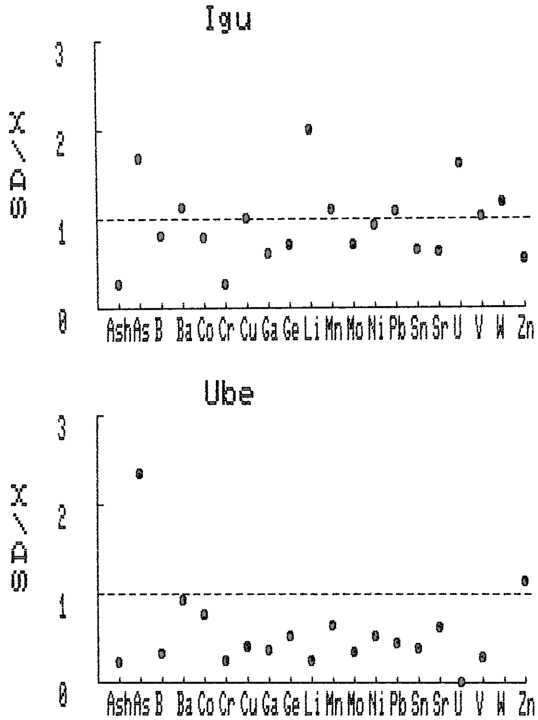

Fig. 4 The standard deviation divided by average (SD/x) for each element in Igu and Ube coal fields.

the characteristics of the distribution of trace elements in each coal field because the distributions in respective coal fields are much different.

Table 4 lists the elements which have relatively large ranges in concentration and standard deviation larger than average values and those that have narrow ranges and standard deviation less than one half of average values. From this table it is seen that many elements are distributed in a wide range and standard deviations are larger than average in the coal field of Igu, Mikawa-Akatani, Kushiro, and Sakito-Matsushima and many elements are distributed in a narrow range and standard deviations are smaller than one half of averages in Owari, Mino, Miike and Ube Coal Fields. In Figure 4 the standard deviation divided by average (SD/x) for each element in Igu coal field is compared with those in Ube coal field. Most of the values of SD/x in Ube coal field are smaller than 1, but the values in Igu Coal Field are relatively larger. On the whole, it is suggested that four elements, As, Ge, Li, and Pb have large ranges in concentration in most coal fields and chrominum has narrow range from these tables and histograms.

Table 5 reveals the elements that have high correlations in each coal field. In this paper "high correlation" is defined as larger than 0.8 when the number of samples are less than 10, and larger than 0.6 when the number is between 11 to 49, and larger than 0.5 when the number is larger than 50. Statistically, it is calculated in 99 percent confidence that one element correlates with the other if the correlation coefficient between them is more than 0.8 when number of samples is 7, and more that 0.5 when the number is 24.

From this table, high correlation which exist more than four coal fields is extracted as follows, (1) ash-Cr, Cu, Ga, Mn, V (2) Ba–Sr (3) Cr–Ga, V (4) Ga–Li, V. Most of these elements are thought to associated with minerals. Highest correlation coefficient in all coals (271 coal samples) of twelve coal fields

Table 5 Elements which have high correlation coefficients in each coal field.

Mogami	Ash–As,Ba,Mn,Pb As–Cu Ba–Mn,Sr Co–Cr Ge–W Mn–Pb
Owari	Ash–Cu,Ga,Mn As–Ge,Mo B–U Ba–Pb,Sr Co–V Cr–Li Cr–Sn
Igu	B–Sn,Sr Cr–Ge,Pb Ge–Pb Mo–W Ni–U,V,Zn Sn–Sr U–V
Hiraga	As–Ga,Sn Ba–Sr Co–Ni Ga–Sn
Mino	Ash–B,Cu,Mn,Sr B–Cu,Mn,Sr Cr–Ga,Mn,Sr,Zn Cu–Mn,Sr Ge–Li,Sn Li–Sn Mn–Sr
Mikawa-Akatani	As–B Ba–Mo,Sn,Zn Cr–Ga,Sn,V Cu–Sn,Zn Ga–Sn,V Mo–Pb,Sn,Zn Pb–U Sn–V,Zn
Sasebo	Ash–Cu,Li,Mn B–Cu Ba–Sr,Zn Co–Pb,V Ga–Li,U Li–U Mo–Sn Ni–Pb,V Pb–V Sr–Zn
Kushiro	Ash–Cr,Cu,Ga,Li,Mo,V Ba–Sr Cr–Cu,Ga,Li,Mo,V Cu–Ga,Li,Mo,V Ga–Ge,Li,Mo,U,V Li–Mo
Sakito-Matsushima	Ash–Cr,Cu,Ga,Li,V As–Mn Ba–Sr Co–Pb Cr–Cu,Ga,V Cu–Ga,V Ga–V Ge–Mo,V
Miike	Ash–As,Cr,Cu,Ga,Mn,Mo,Sr,V As–Cr,Mn,V Cr–Mn,Mo,V Cu–Mn Ga–Li,Mn,V Mn–Sr,V Ni–Pb,Sn
Ube	Ash–Pb,Co Ba–Ge,Mn,Sn,Sr Co–Ni Cr–Ga Ge–Mo,Sn,Sr Mn–Pb,Sn,Sr Mo–Sr Ni–Zn Sn–Sr
Fukuoka	Ash–Cr,Ga,V B–Co,Cu,Mn,Ni Ba–Co,Cu,Mn,Ni,Sr Co–Cr,Cu,Li,Mn,Ni Cr–Cu,Ge,Li,Pb,V Cu–Li,Mn,Mo,Ni Ga–Li Ge–Pb,V Li–Mn,Mo,Ni Mn–Ni Pb–V

are 0.70 for ash-Ga and Ba–Sr and 0.55 for Li–Sr and 0.49 for As–Mo and W–Mo.

Table 6 gives the elements whose contents are one order of magnitude larger or less than those in earth's crust, the clark values which is used in this paper are from TAYLOR (1964). It is obvious that elements of high concentration in coals are As, B, Ge, Mo, U and W. For example, in Igu Coal Field, enrichment factors of As, B, Ge, Mo, U and W are 232, 13, 65, 24 and 105. However, the concentration of these elements are high only in lignite and sub-bituminous coals of Mogami, Owari, Igu, Mino and Mikawa-Akatani in contrast to the very low concentration in bituminous coals of Sasebo, Kushiro, Sakito-Matsushima, Ube and Fukuoka. The elements whose contents in coals are low are Co, Mn and Ni and there is no difference in distribution of these elements among various coal fields.

Table 6 Elements whose contents are one order of magnitude larger or less than those in earth's crust.

	larger	less
Mogami	As, Ge	Mn, Ni
Owari	As, Ge	
Igu	As, B, Ge, Mo, U, W	Li, Mn
Hiraga	As	Mn, Ni
Mino	As, B, Ge, Mo, W	Co, Ni
Mikawa-Akatani	As, Ge, Mo, U, W	Co, Mn, Ni
Sasebo	As	Mn
Kushiro		Mn
Sakito-Matsushima		Mn
Miike	B, Li	Co, Mn
Ube	B	Co, Ni, Zn
Fukuoka		Cu, Ni, Zn

Table 7 The average concentration of boron in coal in each coal field.

	concentration (ppm)
Mogami	54
Owari	12
Igu	127
Hiraga	45
Mino	221
Mikawa-Akatani	47
Sasebo	81
Kushiro	53
Sakito-Matsushima	93
Miike	124
Ube	204
Fukuoka	50

It was reported that the concentration of boron indicates the paleosalinity of the environment of deposition (BOHOR and GLUSKOTER, 1973). The concentration of boron is thought to be higher in coals which were deposited in waters of higher salinity. Table 7 shows the concentration of boron in coals from various fields. In this table the concentrations of boron are relatively high in

Table 8 Averages of the contents of trace elements in rocks and partings in each coal field.

	As	B	Ba	Co	Cr	Cu	Ga	Ge	Li	Mn	Mo	Ni	Pb	Sn	Sr	U	V	W	Zn
Mogami	120	38	287	3	21	22	28	1	67	184	8	7	12	6	372	—	71	—	12
Owari	15	11	1400	17	53	58	14	2	68	391	2	18	13	8	511	10	193	—	19
Igu	109	27	239	20	21	20	21	5	10	99	30	13	8	6	284	11	117	16	85
Hiraga	280	46	239	28	14	67	19	2	159	399	13	7	8	7	378	1.0	56	—	8
Mino	93	51	395	23	50	66	20	1	37	453	5	14	13	4	1264	1.3	167	5	38
Mikawa-Akatani	36	11	590	9	8	9	8	1	38	310	8	5	17	2	297	16	115	2	91
Sasebo	50	86	450	36	65	113	43	3	78	388	3	38	8	8	370	4.7	288	—	4
Kushiro	40	37	825	7	24	88	42	4	54	215	7	25	8	7	685	3.0	242	—	10
Sakito-Matsushima	33	142	333	7	37	67	33	—	60	40	2	17	5	2	767	2.3	295	—	3
Miike	—	80	1800	5	10	40	50	—	60	500	2	20	5	5	600	1	8	—	1
Ube	—	230	500	5	10	51	100	2	150	200	6	20	30	5	1000	2	300	—	1
Fukuoka	—	100	300	4	7	7	50	5	30	100	4	5	35	4	—	2	20	—	1

Table 9 Elements whose contents in rocks and partings are larger than twice of those in coals or less than one half of those in coals.

	partings>2 x coals	partings< 1/2 x coals
Mogami	As,Ba,Ga,Li,Mn,Ni, Pb,Sn,Sr	Ge
Owari	Ba,Co,Cr,Cu,Li,Mn, Pb,Sn,Sr,V,Zn	As,Ge,Mo
Igu	Ba,Li,Mn,Pb,Sn,Sr,Zn	As,B,Cu,Ge, Mo,U,W
Hiraga	As,Co,Cu,Ga,Li,Mn, Ni,Pb,Sn,Sr,V,Zn	Ge
Mino	As,B,Ba,Co,Cr,Cu,Ga, Li,Mn,Ni,Pb,Sn,Sr, V, Zn	Ge,Mo,U,W
Mikawa-Akatani	Co,Ga,Li,Mn,Ni,Pb, Sn,Sr,V,Zn	B,Ge,Mo,U, W
Sasebo	Co,Cr,Cu,Ga,Li,Mn, Ni,Sn,U,V,Zn	Mo
Kushiro	As,Cu,Ga,Li,Mn,Ni, Sn,Sr,U,V	
Sakito-Matsushima	As,Cr,Cu,Ga,Li,Mn, Sr,V,Zn	Mo
Miike	Co,Ga,Mn	Li,V
Ube	Cu,Ga,Li,Mo,Ni,Pb, Sn,Sr,V,Zn	
Fukuoka	Ga,Ge,Li,Pb,Sn	V

coal fields of Mino, Miike and Ube, suggesting that the coals of these fields were deposited in waters with higher salinity (more brackish or more marine) than other coals.

In the samples of bench sets, vertical distributions of elements were investigated (distribution of each element in bench set, for example, from Hiraga coal field is shown in appendix Figure 13) and the content of elements in rocks and partings were compared with those in coals. Table 8 shows the concentrations of elements in rocks and partings in each coal field. In Table 9 the elements whose contents in rocks and partings are greater than twice of the content in coals or less than one half of that in coals are shown. In this table it is seen that As, Co, Ga, Li, Pb, Sn, Sr, V and Zn are concentrated in rocks and partings and B, Ge, Mo and W are concentrated in coals. For example, the distribution of boron in bench sets in Mogami, Mino and Kushiro Coal Fields are given in

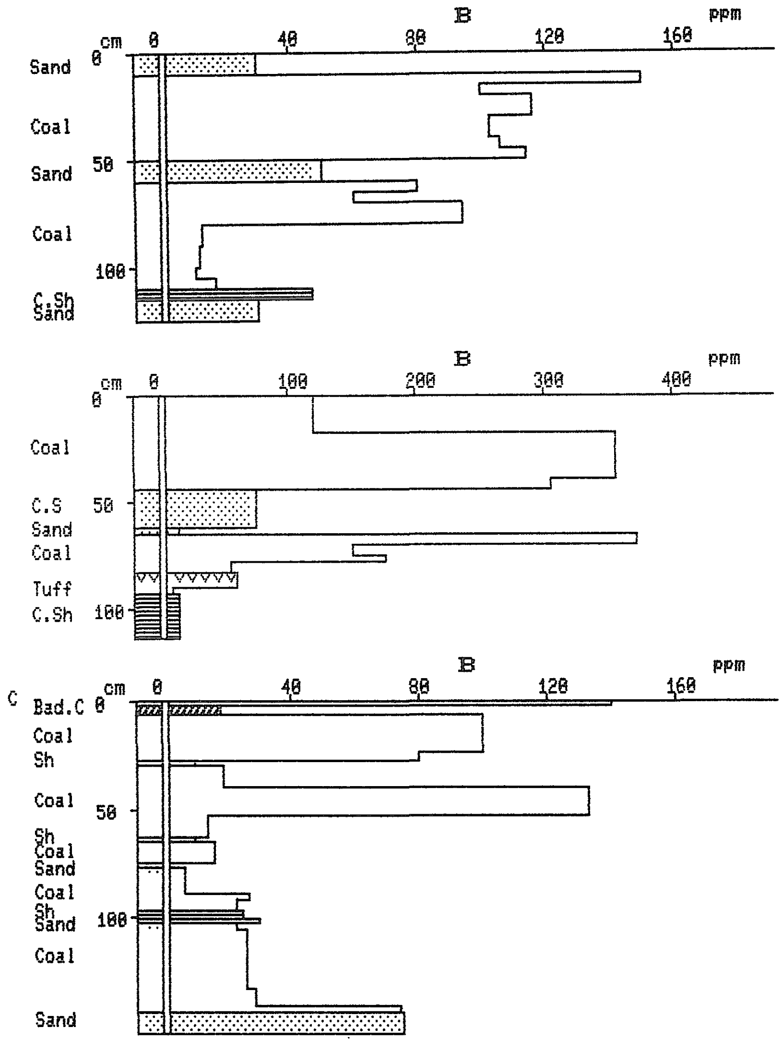

Fig. 5 Distributions of boron in bench sets from Mogami, Mino and Kushiro Coal Fields.
Bad.C; bad coal which is defined that ash content is more than 30%, Sh; shale, C.Sh; carbonaceous shale, C.Mud; carbonaceous mud, C.S.; carbonaceous sandstone, Sand; sandstone, C; coal.

Figure 5. These shows clearly that boron is concentrated in coal parts of the bench sets.

Germanium is not only concentrated in the coal parts, but also concentrated at the top and bottom of the coal seams. This is shown in Figure 6 for bench sets of Hiraga and Mino Coal fields. This suggested that germanium added to and adsorbed by coal beds after burial from neighboring rocks by circulating ground water.

Organic and inorganic affinities of the elements in coal were determined by using its washability which indicates whether the elements are concentrated in organic or inorganic parts of coal (Kuhn *et al.*, 1980). It is reported that the elements of B and Ge are associated largely with the organic part of coal while As, Cd and Zn are in the inorganic part. In the present paper, the correlation coefficient of each element with ash content is

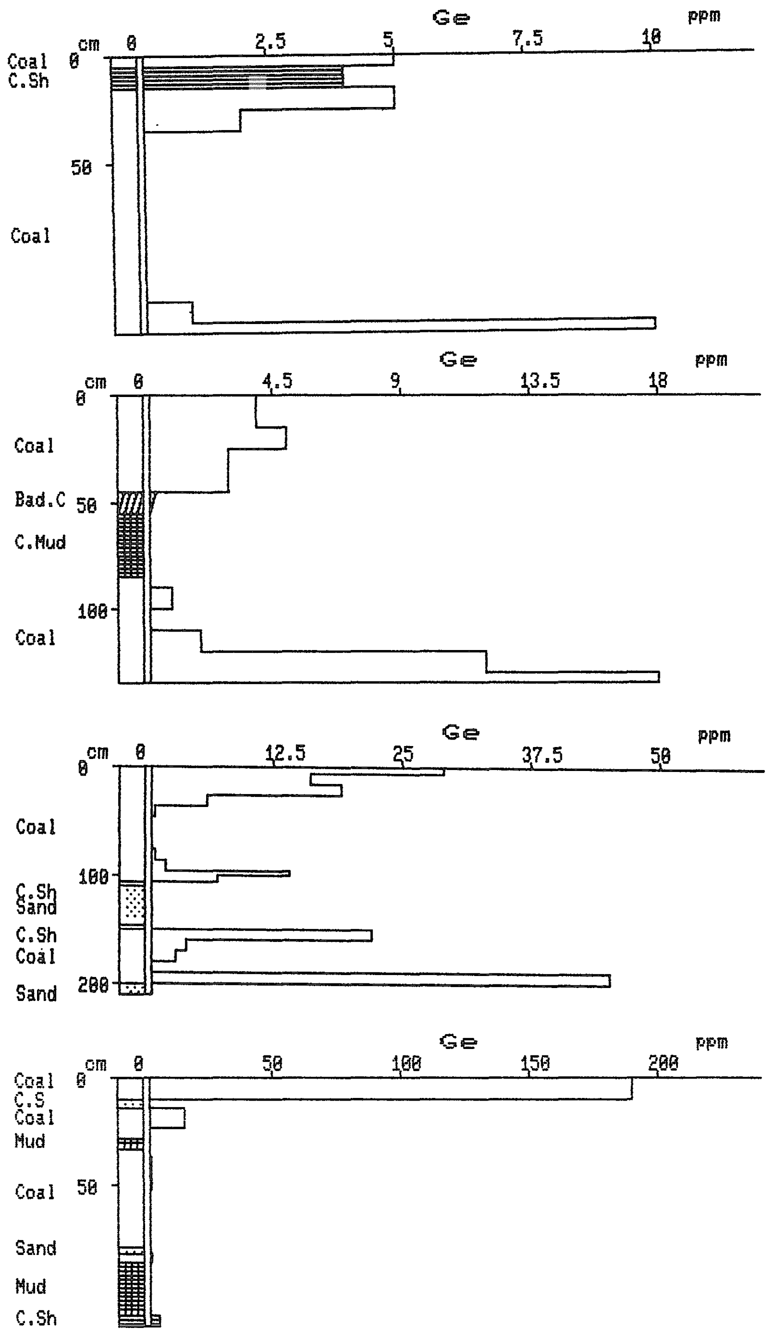

Fig. 6 Distributions of germanium in bench sets from Hiraga (top three) and Mino (bottom) Coal Fields.

calculated. The positive correlation is considered as the result of the association with the inorganic part, and the negative correlation as showing the high organic affinity. However, because of the difference of local environment of each coal field, the correlation coefficient calculated by using all coal fields' data has little significance as the indicator for organic or inorganic affinity of elements. Therefore, the correlation coefficient in each bench set is

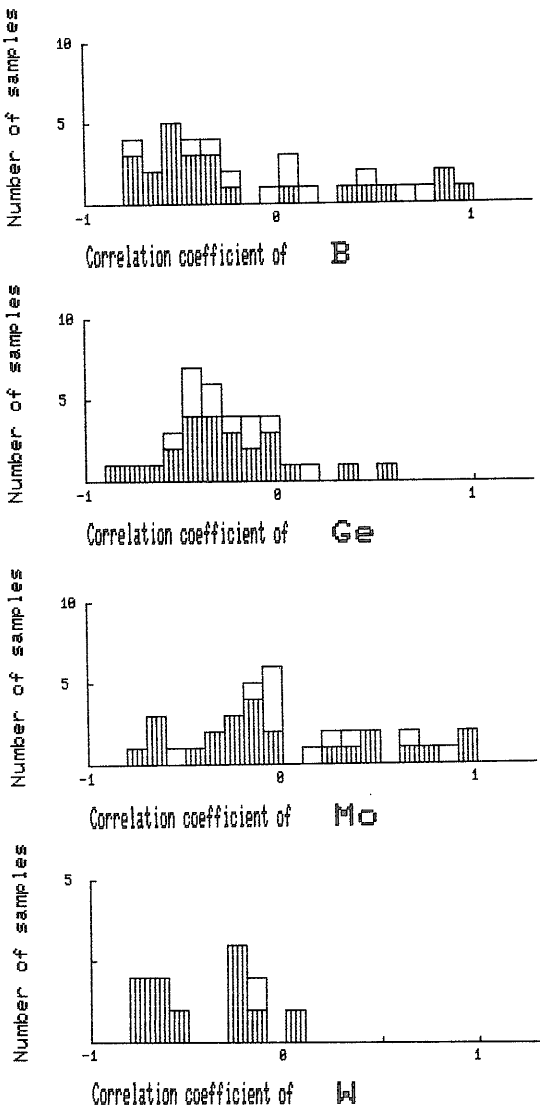

Fig. 7 Distributions of correlation coefficients of the elements of B, Ge, Mo and W in each bench set.

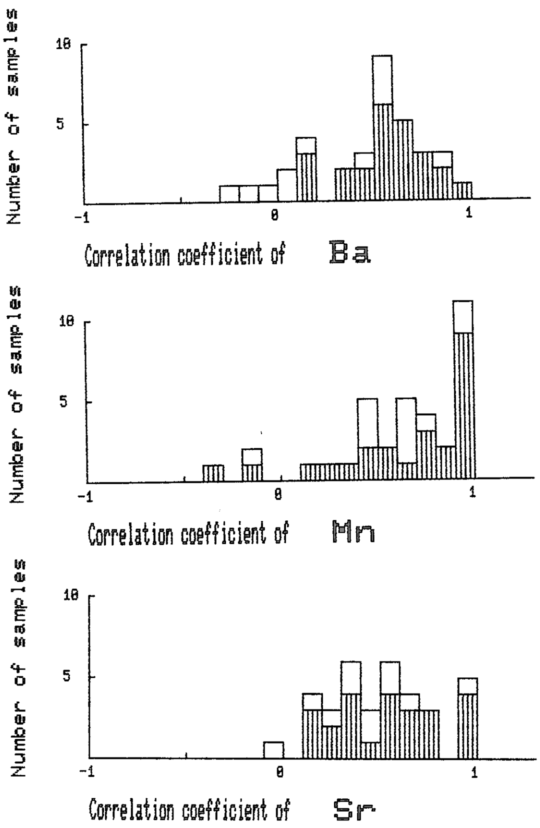

Fig. 8 Distributions of correlation coefficients of the elements of Ba, Mn and Sr in each bench set.

calculated from 34 bench sets are shown. In fact, in the histograms the correlation coefficient of each element differs from one bench set to another. Figure 7 shows the histograms of correlation coefficients for B, Ge, Mo, W. Apparently these elements are negatively correlated with ash contents and considered to be associated with the organic part in the coals. Figure 8 shows the positive correlation of Ba, Mn and Sr. The correlations of Ba, Cr, Cu, Ga, Li, Mn, Pb, Sn, Sr, U and Zn with ash content are positive. This means that these elements are associated with the inorganic part in the coals. In the histograms of the correlation coefficient for Co, Ni and V, the coefficients are distributed in wide range from negative to positive as shown in Figure 9 and the affinities of these elements are intermediate.

Acknowledgement

The authors would like to express their thanks to Dr. Y. Shimazaki for his careful reading of the manuscript.

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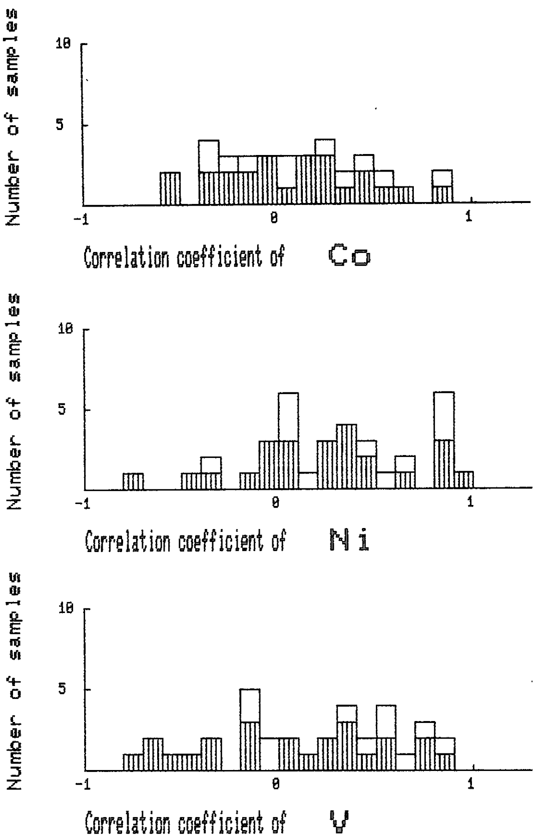

Fig. 9 Distributions of correlation coefficients of the elements of Co, Ni and V in each bench set.

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地 名 対 応 表

Mogami	最上	Owari	尾張	Igu	伊具
Hiraga	平鹿	Mino	美濃	Mikawa-Akatani	三川赤谷
Sasebo	佐世保	Kushiro	釧路	Sakito-Matsushima	崎戸松島
Miike	三池	Ube	宇部	Fukuoka	福岡

本邦における石炭中の微量成分に関する研究(III)

今井 登・安藤 厚・竹田栄蔵

要 旨

竹田(1981)により報告された本邦中の12地区の炭田から得られた石炭中のウラン・ヒ素・ホウ素・ゲルマニウム・銅・鉛・亜鉛，モリブデン等19元素と灰分の総計2万成分におよぶデータの統計的解析を行い，各炭田における微量元素の分布の特徴を明らかにした．

炭化度の低い亜炭・褐炭地区の炭田には As, Ge, Mo, U, W の元素が瀝青炭地区の 5-10 倍含まれて

いる．含有量のばらつきは As, Ge, Li, Pb が大きく，Cr が小さい．相関の高い元素は(1)灰分-Cr, Cu, Ga, Mn, V (2) Ba-Sr, (3) Cr-Ga, V (4) Ga-Li, V であり，これらは鉱物として石炭に混入したものと考えられる．

地殻の平均値と比較して As, B, Ge, Mo, U, W が石炭に 10 倍以上濃縮し，Co, Ni, Mn は地殻中の$^1/_{10}$以下の濃度である．ホウ素の濃度の高い美濃・三池等の炭田は他の炭田と比較して，石炭が堆積した時により高い塩度の水(汽水・海水)の影響を受けたと考えられる．

炭層中では石炭部分に濃縮する元素と挟みや上・下盤で高い濃度を示す元素がある．ゲルマニウムは炭層の上・下端や挟みの周辺で特徴的に高い値を示し，炭層に後生的に付加することを示唆する．各炭層ごとに灰分との相関をとった結果，有機物と親和力のある元素は B, Ge, Mo, W であり，無機物と親和力のある元素は Ba, Cr, Ga, Li, Mn, Pb, Sn, Sr, U, Zn であることがわかる．

(受付：1983年9月22日；受理：1984年6月1日)

APPENDIXS

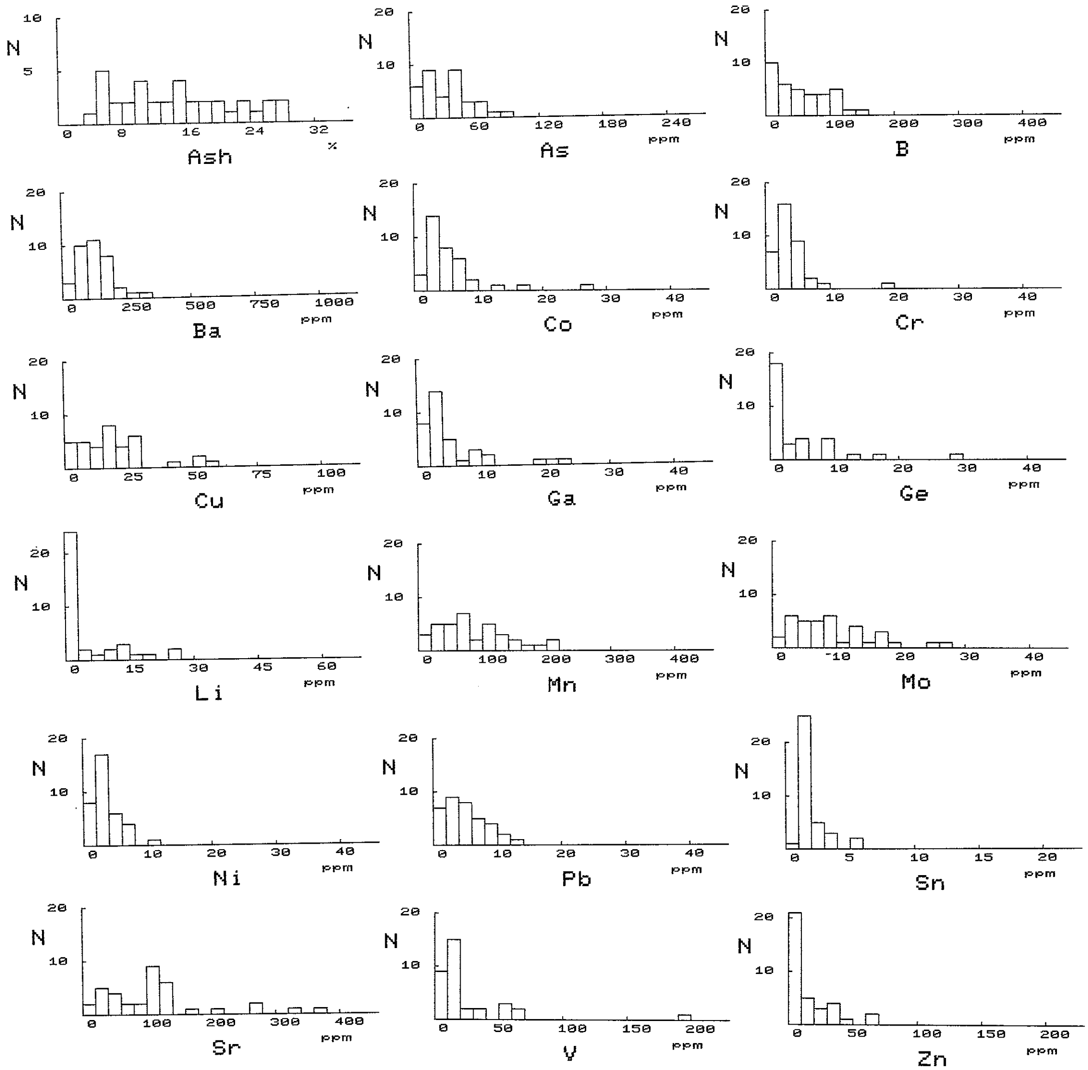

Fig. 1 Distributions of minor elements and ash content in Mogami Coal Field.

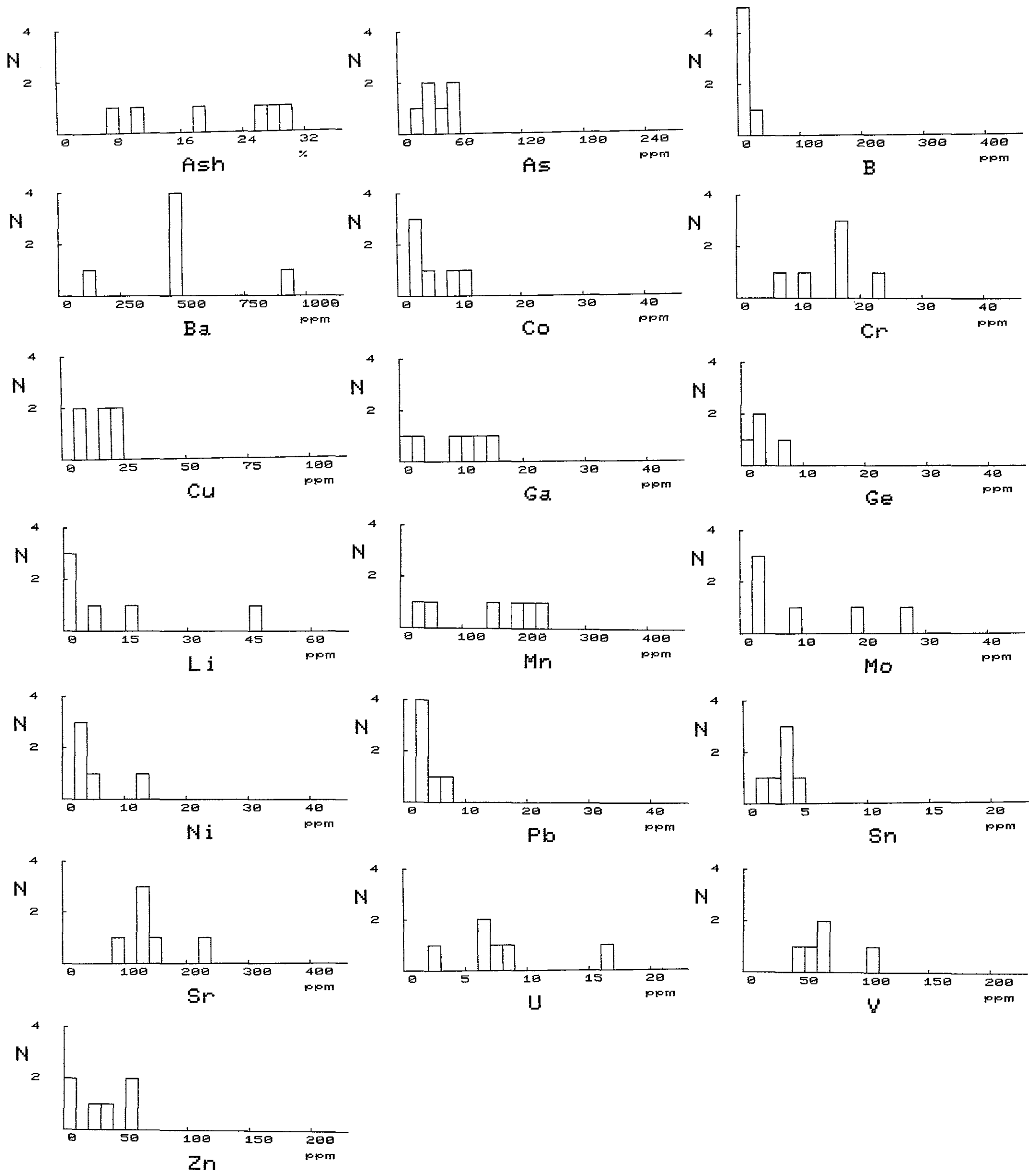

Fig. 2 Distributions of minor elements and ash content in Owari Coal Field.

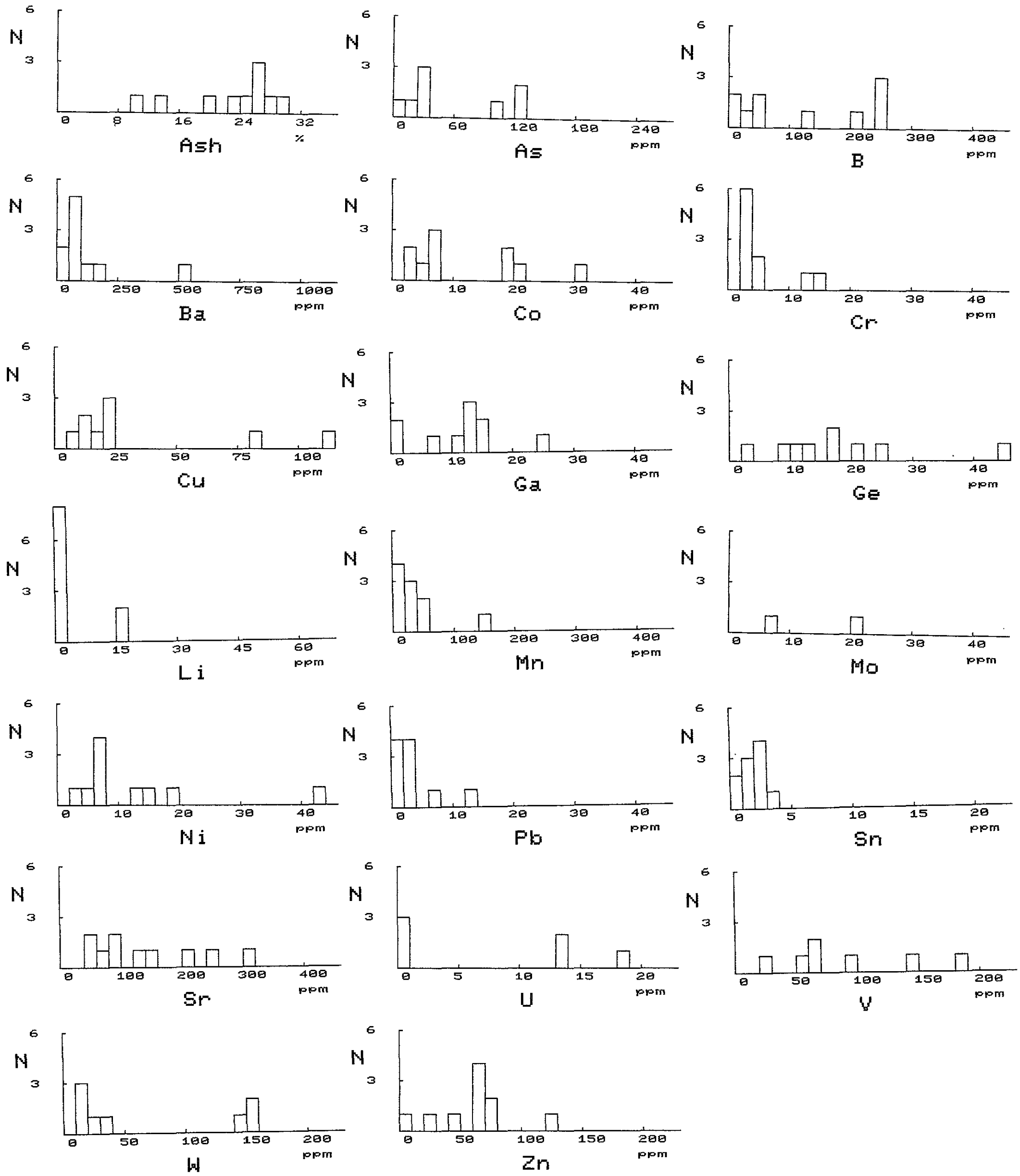

Fig. 3 Distributions of minor elements and ash content in Igu Coal Field.

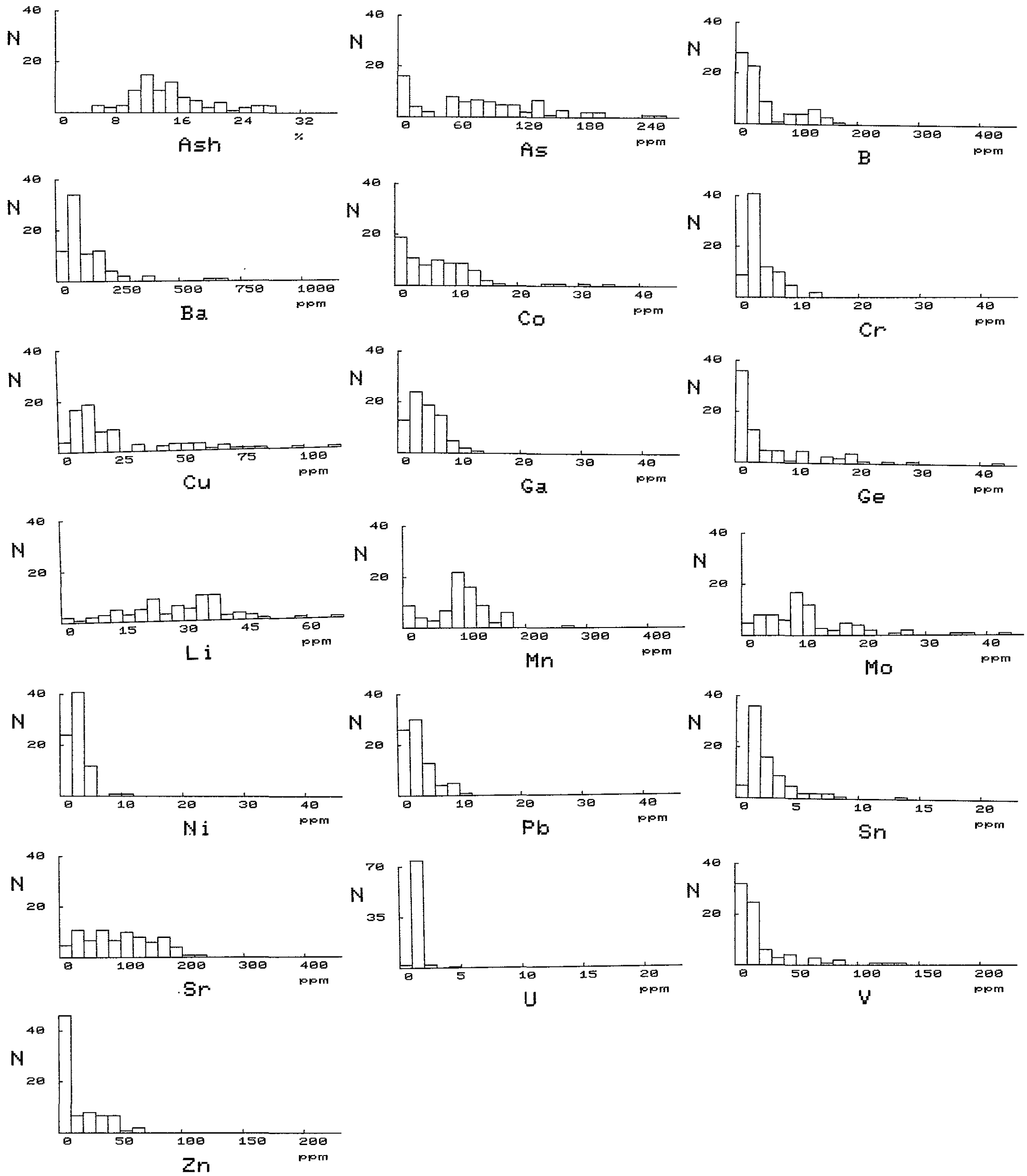

Fig. 4 Distributions of minor elements and ash content in Hiraga Coal Field.

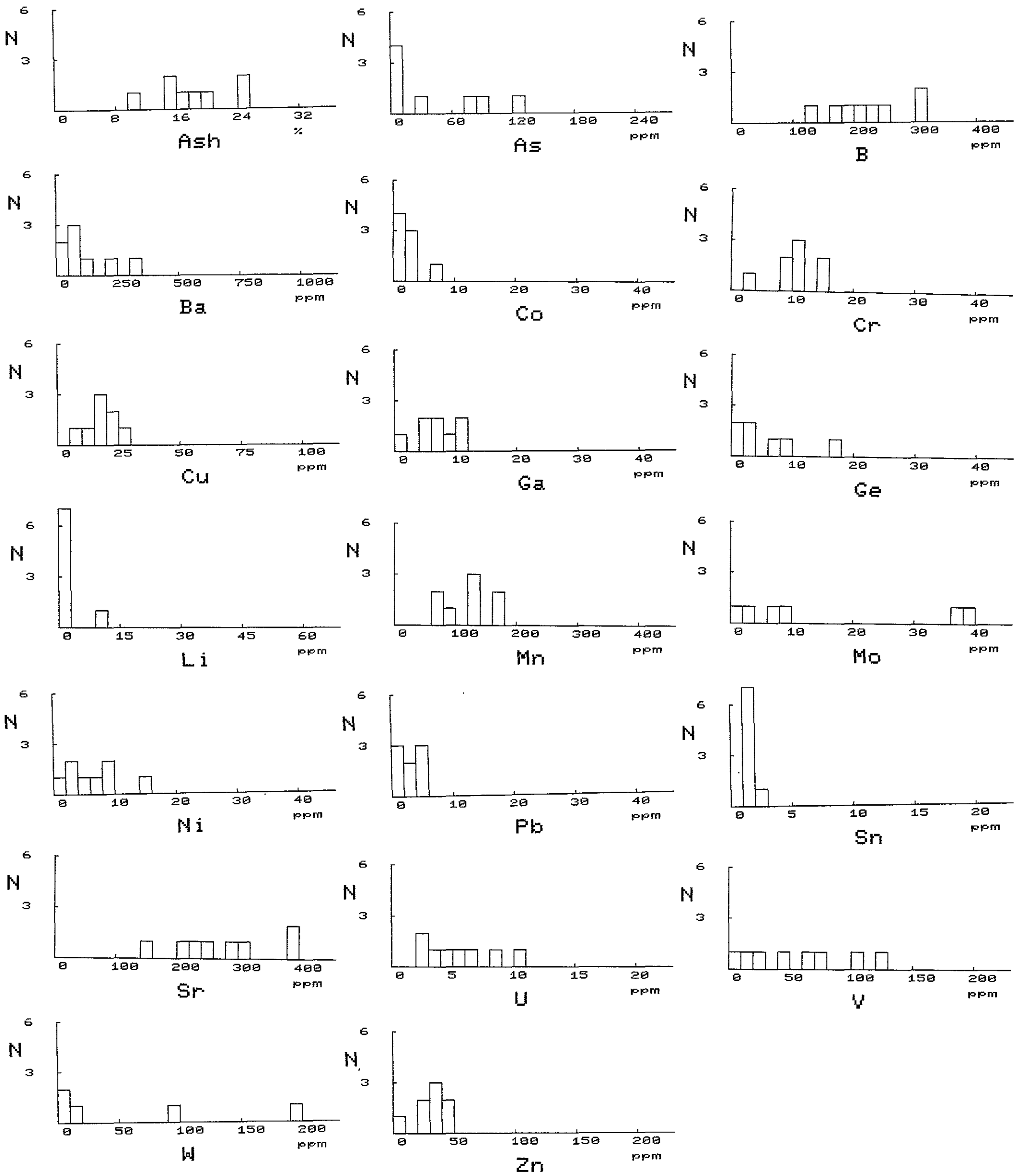

Fig. 5 Distributions of minor elements and ash content in Mino Coal Field.

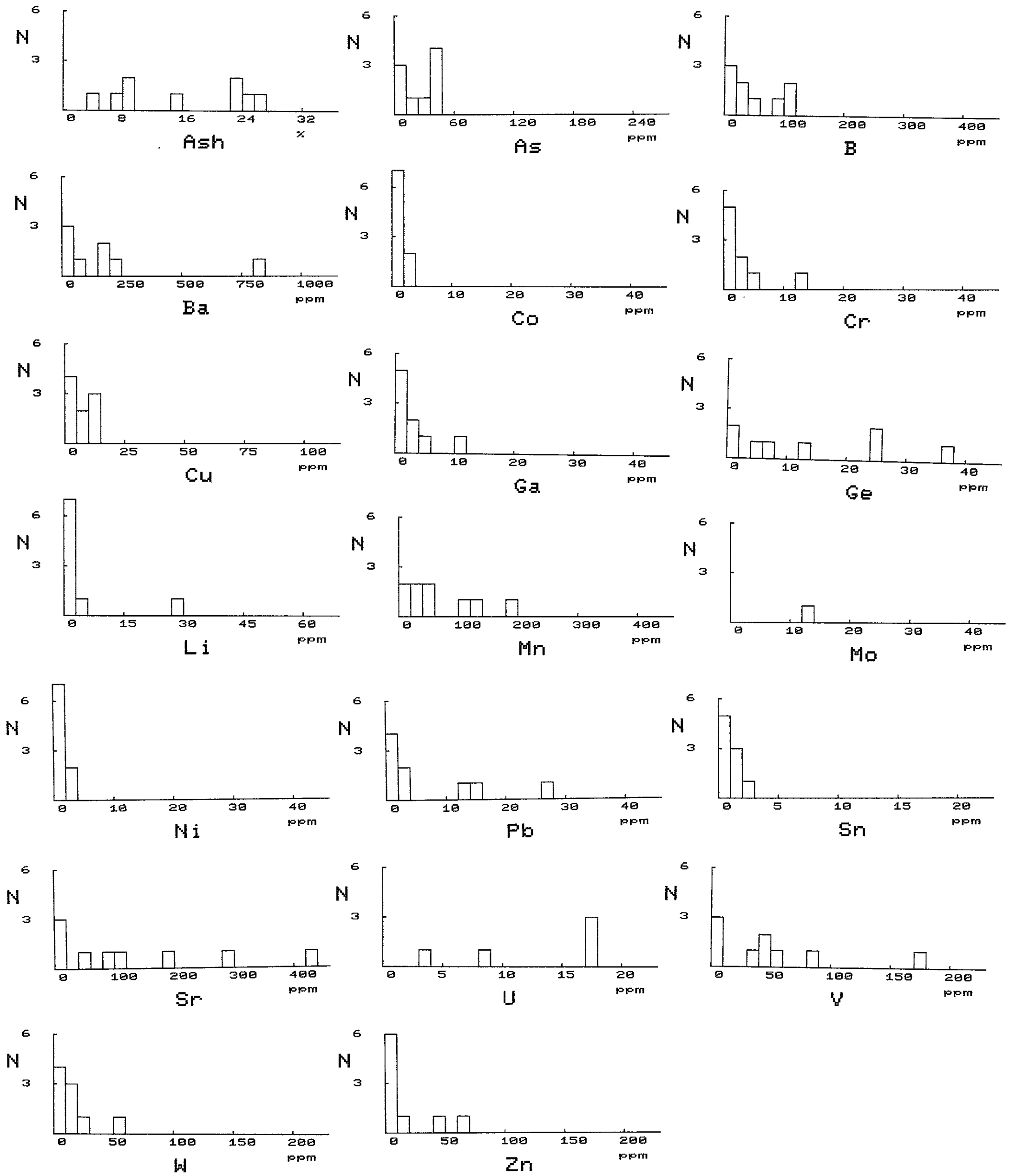

Fig. 6 Distributions of minor elements and ash content in Mikawa-Akatani Coal Field.

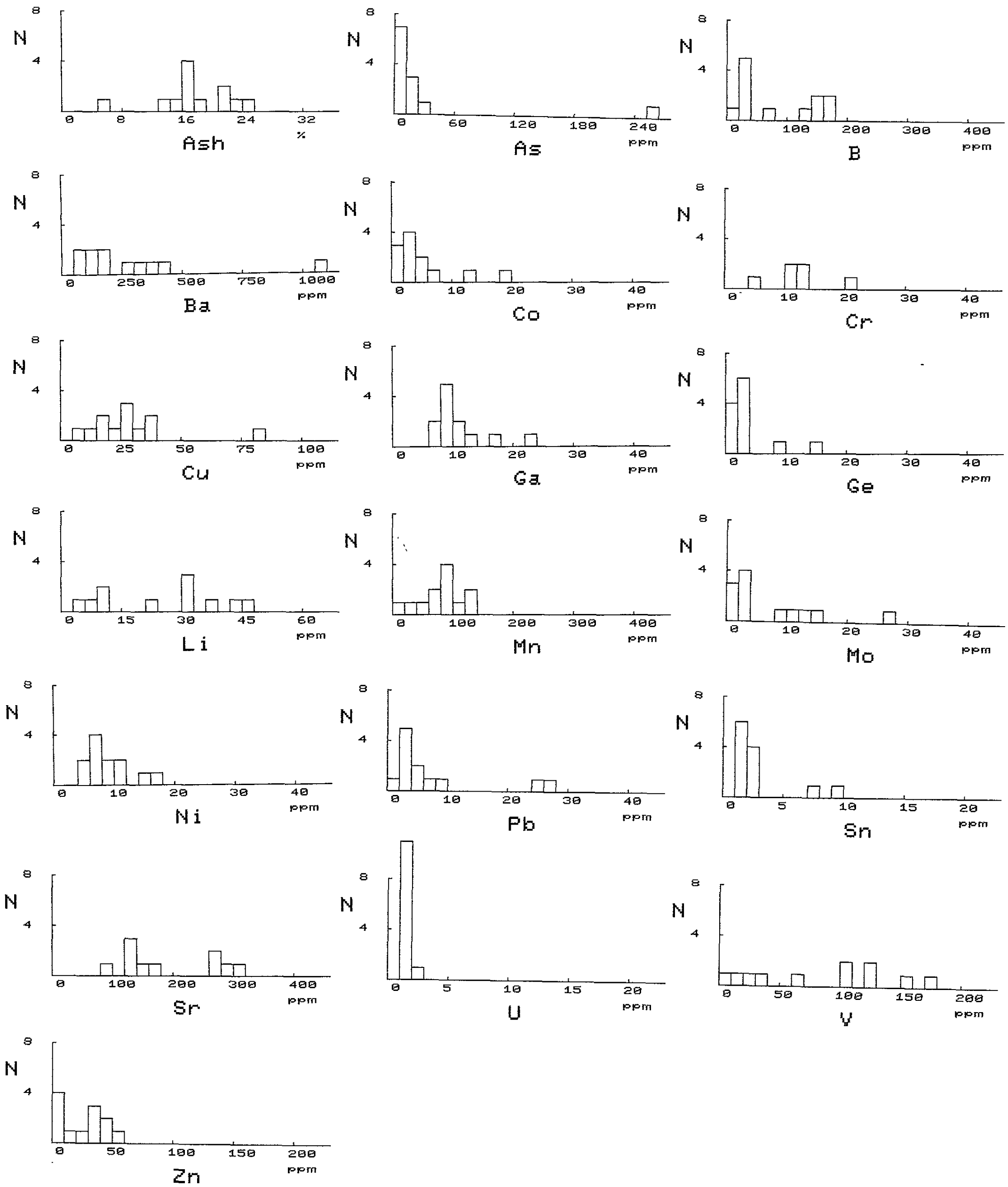

Fig. 7 Distributions of minor elements and ash content in Sasebo Coal Field.

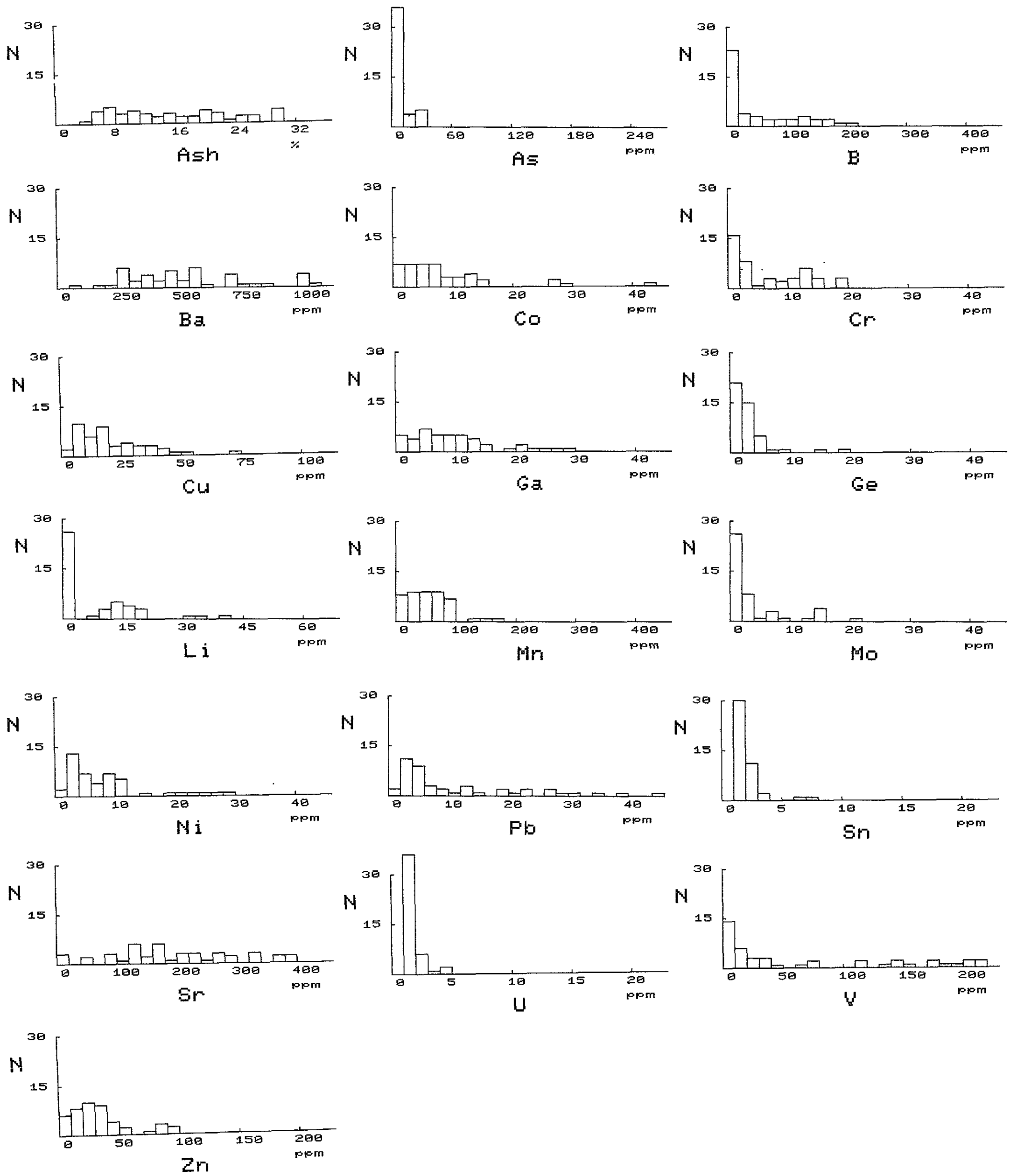

Fig. 8 Distributions of minor elements and ash content in Kushiro Coal Field.

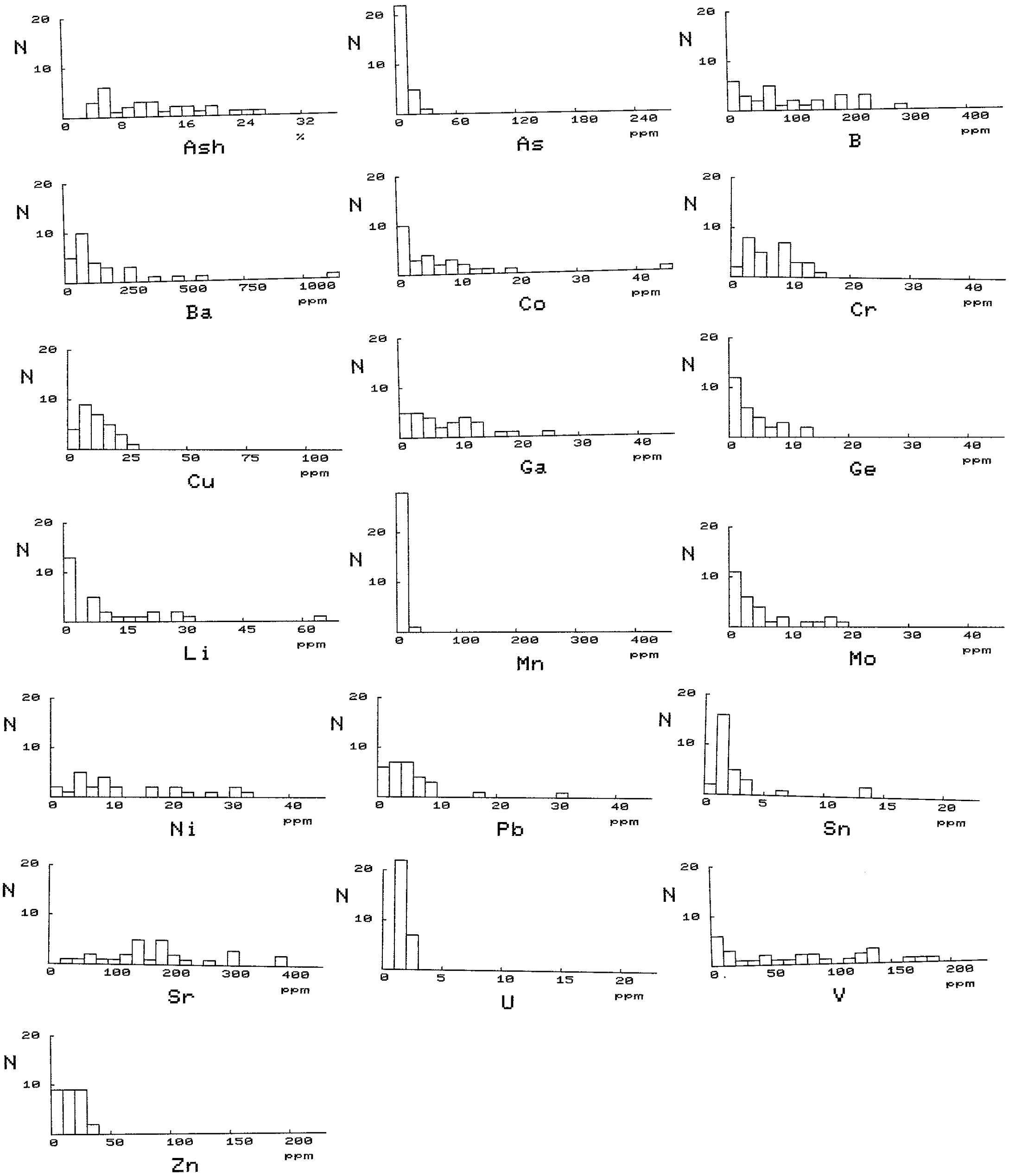

Fig. 9 Distributions of minor elements and ash content in Sakito-Matsushima Coal Field.

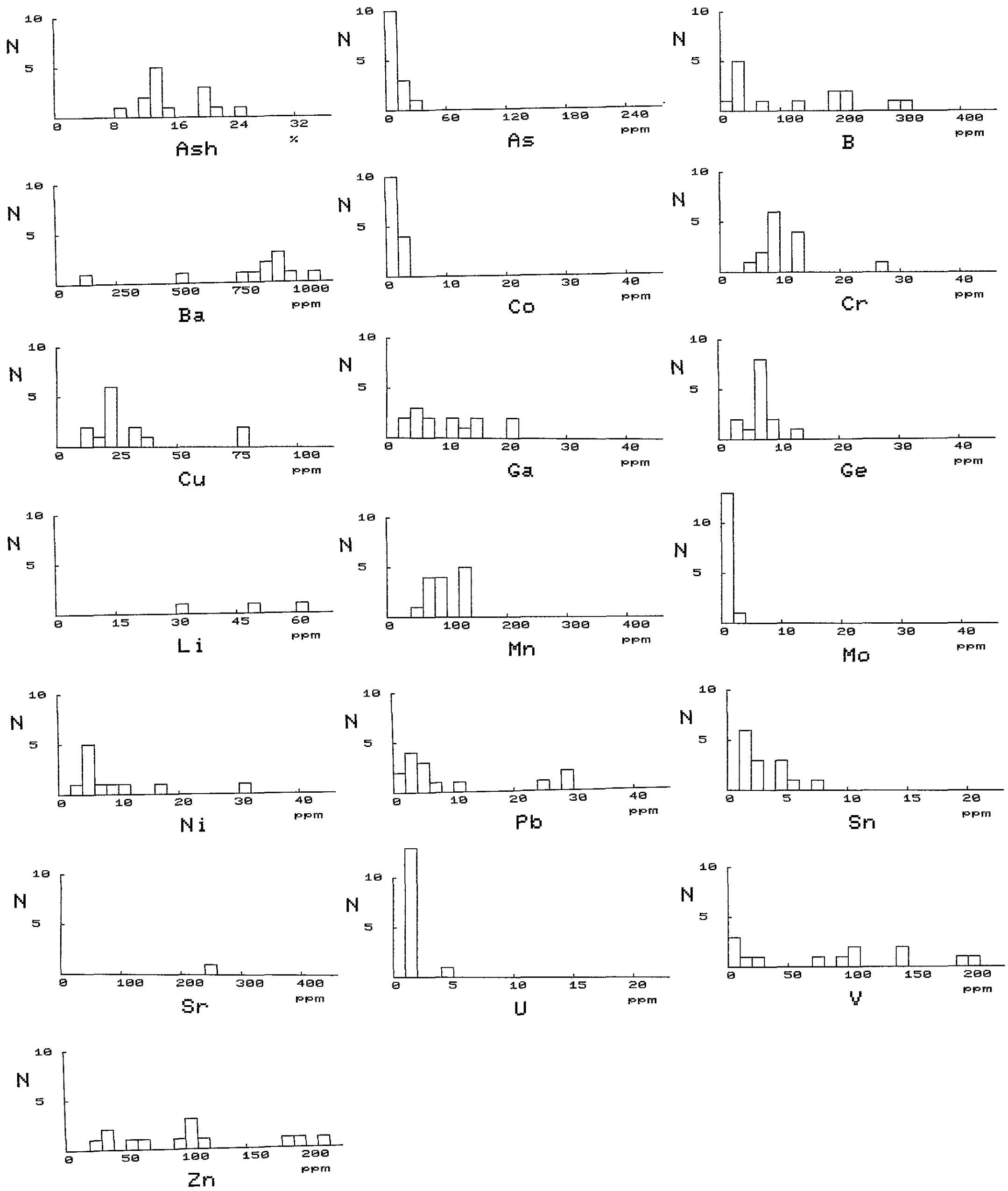

Fig. 10 Distributions of minor elements and ash content in Miike Coal Field.

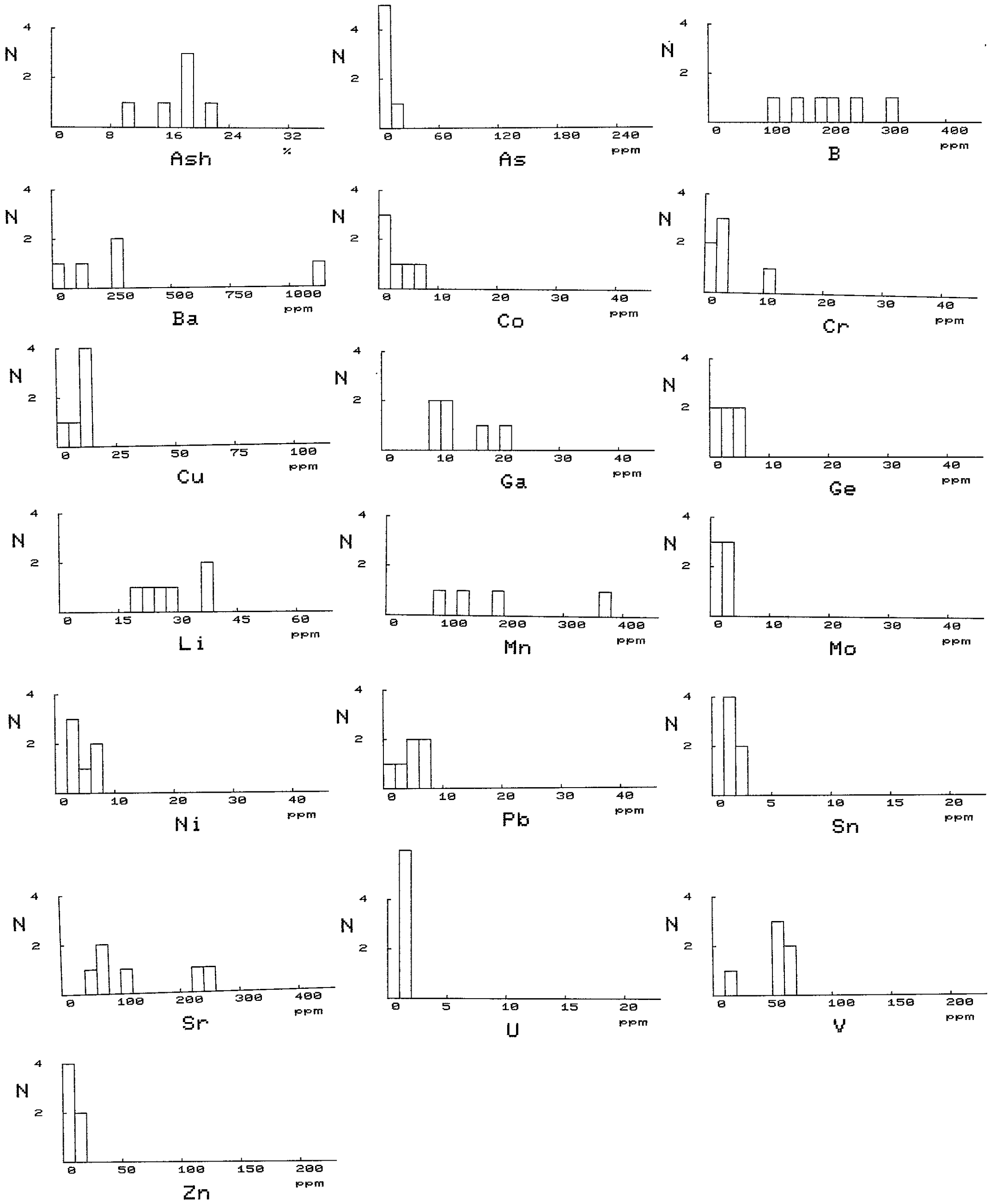

Fig. 11 Distributions of minor elements and ash content in Ube Coal Field.

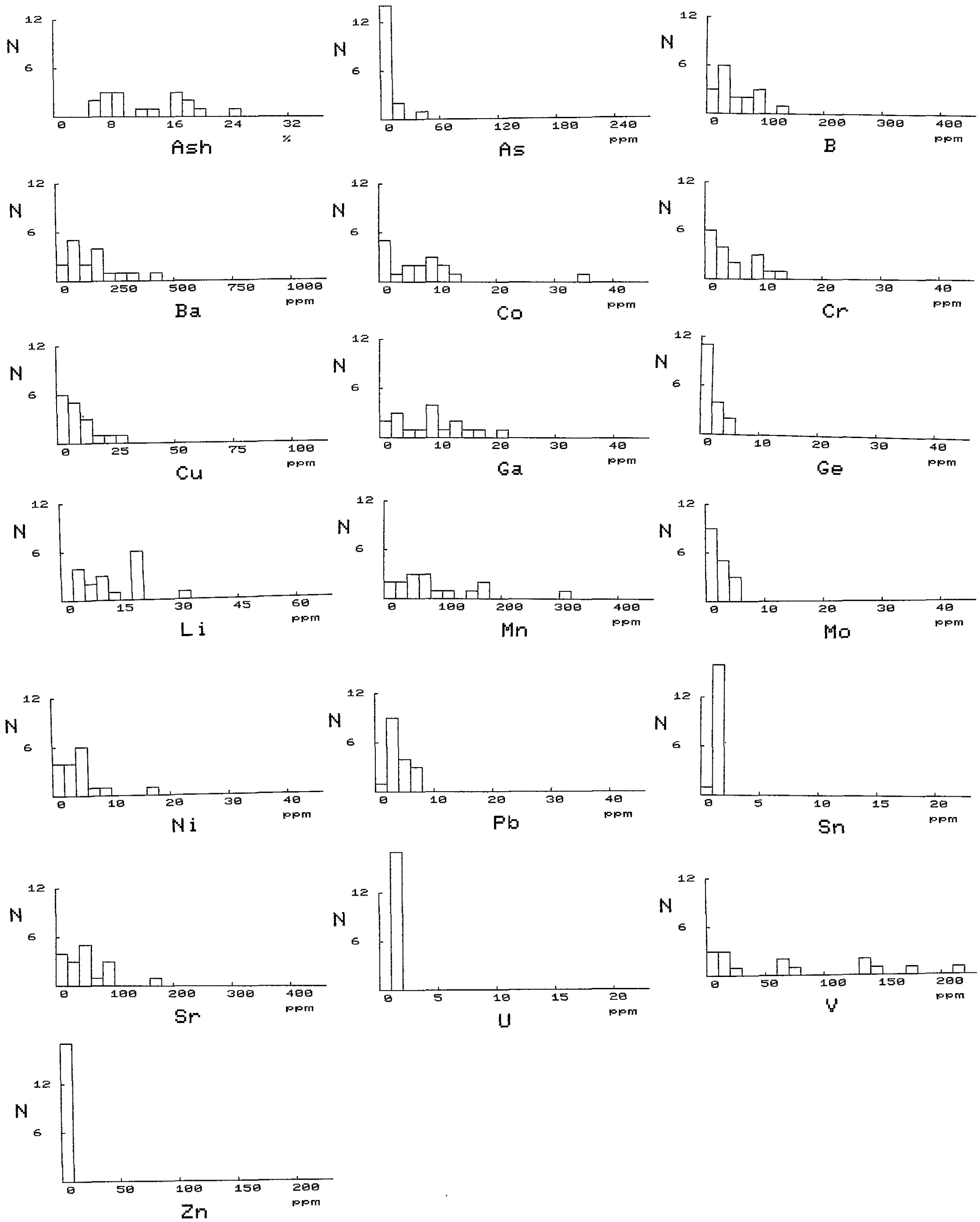

Fig. 12 Distributions of minor elements and ash content in Fukuoka Coal Field.

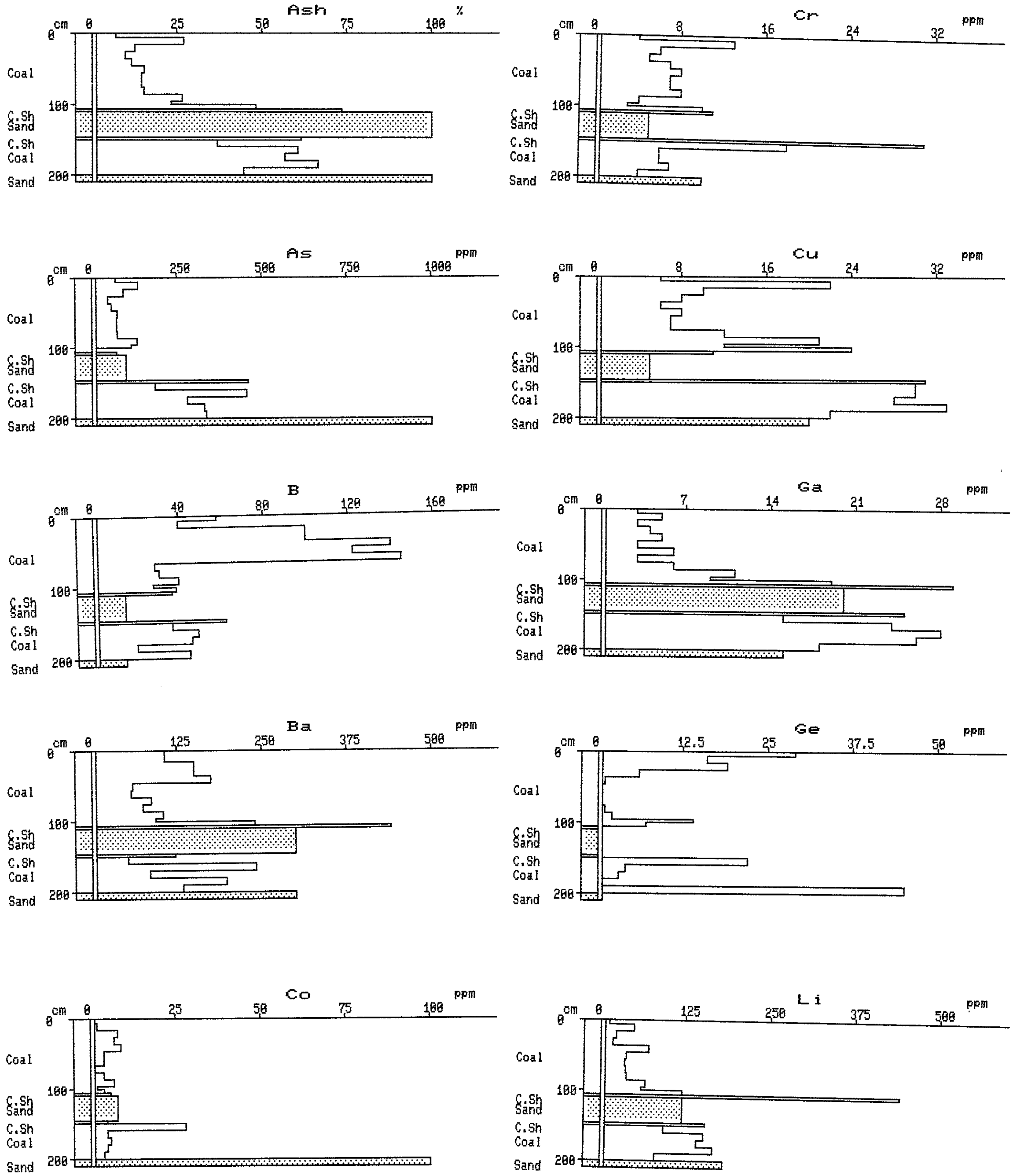

Fig. 13 Distributions of minor elements and ash in bench set from Hiraga Coal Field.

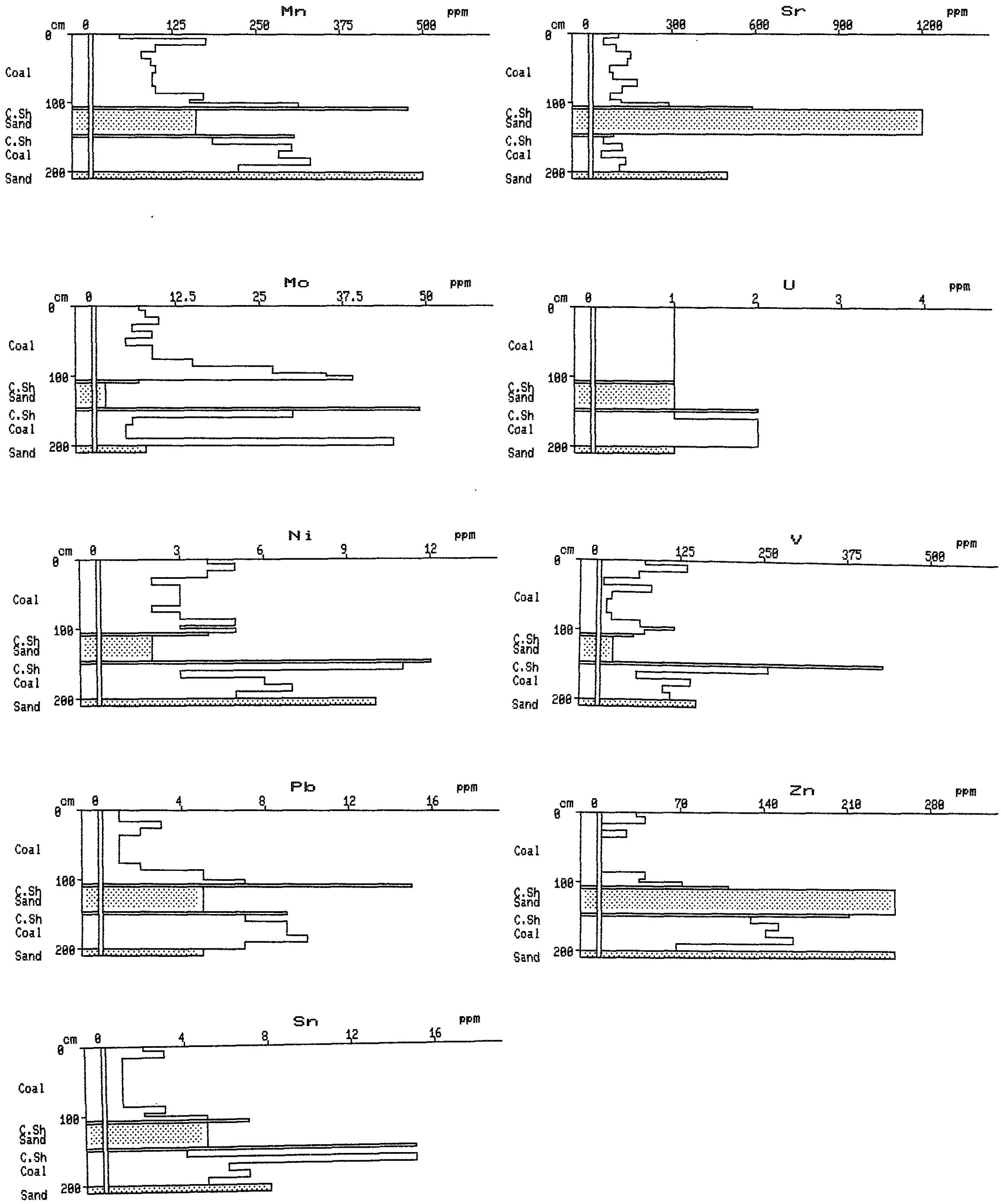

Fig. 13 Continued.