報　　文

546.791 : 543 : 553.94 (521.41)

On the Uranium in Coal-bearing Beds of Mikawa and Akatani Areas, Niigata Prefecture

By
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Abstract

(1) The uranium contents of 131 samples in Mikawa and Akatani areas were ranged from 2 to 450 ppm U_3O_8.

(2) Uranium is more concentrated in coaly shales or coaly mudstones, which have higher ash contents than in the good coal.

(3) In order to investigate the dependence of uranium contents upon the amounts of ash and organic matters which present in the coal samples, the contents of ash and uranium in each fraction of the samples, which was classified by different specific gravities, are determined.

(4) The uranium contents are not always proportional to the contents of organic materials.

(5) Minor elements such as vanadium, gallium, copper, molybdenum, chromium tungsten and nickel seem to be concerned with uranium.

Introduction

Lately the writers have reported on uranium in the coal of Ouchi coal field.

After that they have studied on the uranium in coal-bearing bed of Mikawa and Akatani areas, Niigata prefecture.

In this paper the writers describe on the distribution of uranium in coal-bearing bed, the correlation between the contents of uranium and organic materials, and the relation between uranium and other minor elements.

Geology

The Akatani fault which trends from Akatani station towards Igashima, influences the distribution of the Tertiary sediments on its opposite side.

On the east side of this fault, the mudstone bed belonging to the Nanatani stage and the Tsugawa formation which is the basal deposits in this area, gently slope to the west. Only the Tsugawa formation directly overlies granite on its west side.

Several radioactive anomalies are found at the basal parts of the Tsugawa formation on the west side of the Akatani fault, and they have been observed at two places : one is located about 2 km west of Mikawa hot spring and the other is found in the Kamiakatani colliery region.

The rock faces of the Tsugawa formation, especially the faces of the uraniferous horizons, vary in above two places.

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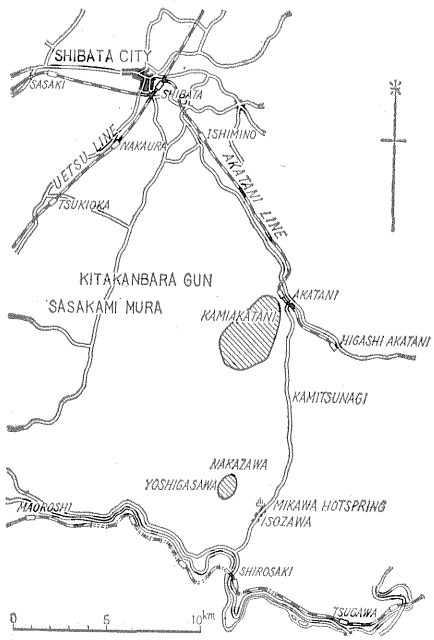


Fig. 1

In the region of Mikawa hot spring, the Tsugawa formation is divided into two members. The lower one consists mainly of conglomerate and sandstone which is accompanied with coaly mudstone or coal patch and often shows radioactive anomaly.

The upper member consists of brecciated tuff. No workable coal seam is deposited in this region.

At the Kamiakatani coal mine, Akatani coal-bearing bed, which consist of three members—coal-bearing sandstone, green sandstone and sandstone-conglomerate, is about 200 m in thickness as a whole. Coal-bearing sandstone, which is the lowest member of them, has workable thick coal seams. The shaly or sandy part of this member are often recognized as the uraniferous parts.

Sampling

As mentioned above, marked radioactivities in these areas have been observed at the coal-bearing bed which is lower layer of the Tsugawa formation.

The localities at which the samples were collected are given in fig. 2.

To observe in detail the vertical distributions of uranium in the coal-bearing bed, the samples were collected from every columnar section of about 5~10 cm in length of which the weathered surface was cut off.

But from the parts which are different apparently from each other in characteristics, the samples were collected in detail.

61 samples (four columns) at Mikawa area and 68 samples (seventeen columns)

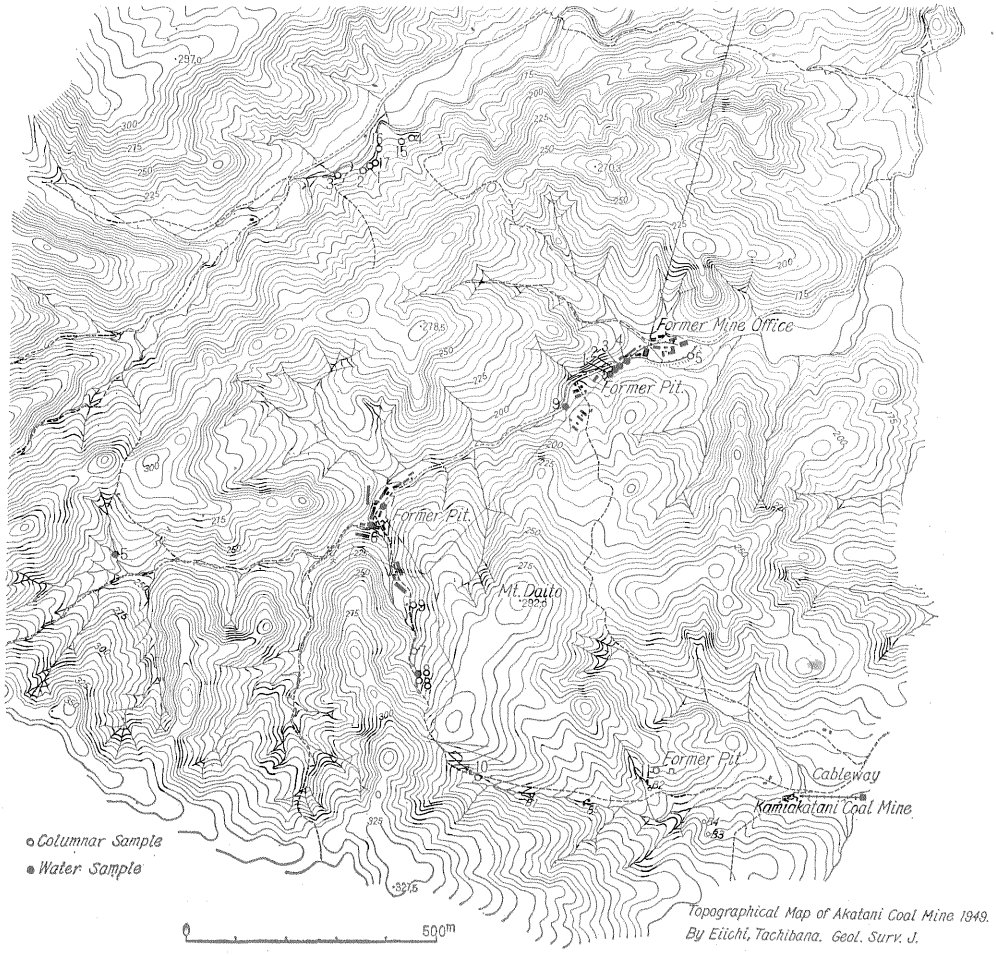


Fig. 2a Sampling map in Mikawa area (near Yoshigasawa)

at Akatani area were collected.

The diagrams of these columns are shown in fig. 3 with the analytical data.

Analytical Methods

The analytical methods used in this study are as follows :

Uranium : Uranium is analyzed by the solid fluorescence method.

Minor elements : Minor elements are analyzed by the method of semi-quantitative spectrochemical analysis, with D. C. arc excitation and silica-base comparison standards.

Ashing of coal have been carried out at the temperature lower than 500°C, so as to avoid the loss of elements by volatilization.

Analyses have been done under the following condition.

Spectrograph : Shimazu-QL 170 Littrow type quartz spectrograph.

Excitation : D. C. 220 V, 7 A. Anode excitation

Fig. 2b Sampling map in Akatani area

Exposure : 30sec

Arc gap : 2mm

Electrodes : Upper ; 6mm diameter graphite rod, and the end is 120° cone. (Hitachi Co., "Regular grade").

Lower ; 6mm diameter rod containing an axial crater 2 mm diameter, 8mm depth. (Hitachi Co., "Regular grade").

Spectral region : 2300～2980Å, 2900～5200Å

Slit width : 0.015mm

Plate : Sakura Process Plate

Developing : Developer designated by Sakura. 18°C, 3 min

The ash was ground and mixed in agate mortar with equal portion of chemically pure NaCl. The mixed samples were packed in graphite anode and arced under above conditions.

The spectral lines of each element were checked visually and the density values were shown with a sign such as ?, tr^-, tr, tr^+, 1^-, 1, 1^+, ……6^-, 6, 6^+, 6< and 6≪, in comparison with prepared density standards.

The contents of each element were determined semi-quantitatively by comparing above line density numbers with table 1.

Preparation of standard samples

To the weighed amounts of chemically pure NaCl, the various quantities of

each element (used chemically pure reagent) were added as the solution. The mixture was dried on water-bath and then in the air oven. After drying, it was transferred to agate mortar and ground with equal portion of chemically pure SiO_2.

The standard samples thus prepared were packed in graphite anode and arced under the same conditions as the unknown samples.

The correlations between the line density numbers and the contents of the elements were shown in table 1.

The uranium contents in coal-bearing bed

It is clearly recognized that the uranium is considerably concentrated in the samples which contain carbonaceous matters as shown in table 2 and fig. 3. These appearances are quitely the same as the results of Ouchi mine or of the previous studies which have been made on the sedimentary uranium deposits. The

Table 1. Correlation between line density numbers and contents of elements

Element	ppm / Analytical line	1	5	7.5	10	25	50	75	100	250	500	750	1000	2500	5000	7500	10000
Ag	3280.683 Å	tr$^+$	2$^+$	3$^+$	4$^+$	5	5$^+$	6$^-$	6	6$^+$	6<						
As	2349.84								?	?	tr$^-$	tr	tr$^+$	1$^+$	2	3$^-$	3
B	2497.733				?	tr$^-$	tr	tr$^+$	1$^-$	1$^+$	3$^+$	4$^-$	4	4$^+$	6	6<	6≪
Ba	4554.042	?	tr$^-$	tr	tr$^+$	1$^-$	2$^-$	3$^-$	3$^+$	4$^+$	5	5$^+$	6	6<	6≪		
Be	2348.610	?	tr$^-$	tr	tr$^+$	1$^-$	1	2$^-$	2	2$^+$	3	3$^+$					
Bi	3067.716				?	tr	1$^-$	1	1$^+$	2	3	4	4$^+$	5$^+$	6$^+$	6<	
Cd	3261.057						?	tr$^-$	tr	tr$^+$	1	1$^+$	2	3			
Co	3453.505		?	tr$^-$	tr	tr$^+$	1$^-$	1	2$^-$	3$^-$	3	3$^+$	4$^-$				
Cr	4254.346	tr$^-$	tr	tr$^+$	1$^-$	1$^+$	2$^+$	3$^+$	4$^-$	4$^+$	6	6$^+$	6<				
Cu	3247.540	tr	2$^-$	2	3$^-$	3	4$^-$	4$^+$	5	6$^-$	6	6$^+$	6<				
Ga	2943.637	?	tr$^-$	tr$^-$	tr	tr$^+$	1	1$^+$	2$^-$								
Ge	2651.178				?	tr$^-$	tr	tr$^+$	1$^-$	2	3$^-$	3	3$^+$				
Hg	2536.519				?	tr$^-$	tr	tr$^+$	1$^-$	1	1$^+$	1$^+$	1$^+$	1$^+$	2$^-$	2	2$^+$
In	4101.773	1$^-$	1	1$^+$	2$^-$	3	3$^+$	4	4$^+$	6$^+$	6≪						
Li	4602.863					?	tr$^-$	tr$^+$	1	1$^+$	2	2$^+$	3				
Mn	2794.817	?	tr	tr$^+$	1	1$^+$	2	3$^-$	3	3$^+$	4$^-$	4	4$^+$				
Mo	3170.347	?	tr$^-$	tr	tr$^+$	1$^-$	1	1$^+$	2$^-$	3$^-$	3$^+$	4$^-$	4$^+$	5$^-$			
Ni	3050.819				?	tr$^-$	tr	tr$^+$	1$^-$	2$^-$	3$^-$	3	3$^+$				
Pb	2833.069		?	tr$^-$	tr	tr$^+$	1$^-$	1	1$^+$	2	3$^-$	3	3$^+$	4			
Pt	3064.712						?	tr$^-$	tr	tr$^+$	1	1$^+$	2$^-$	3	3$^+$	4$^-$	4
Sb	2598.062							?	tr$^-$	tr	1$^-$	1	2$^-$	3	4$^-$	4	4$^+$
Sn	3034.121						?	tr$^-$	tr	tr$^+$	1	2	2$^+$	3	3$^+$		
Sr	4607.331	?	tr$^-$	tr	tr$^+$	1	1$^+$	2	2$^+$	3$^+$	5$^+$	6$^-$	6				
Ti	3361.263						?	tr$^-$	tr	1$^-$	1	2	3$^-$	4$^-$			
V	3183.982	tr$^-$	tr	tr$^+$	1$^-$	1$^+$	2	2$^+$	3$^-$	3$^+$	4$^-$						
W	2946.981						?	tr$^-$	tr	tr$^+$	1	2	2$^+$	3	4$^-$	4	4$^+$
Zn	4722.159										?	tr$^-$	tr	1	2	3$^+$	4
Zr	3391.975									?	tr$^-$	tr	tr$^+$	1$^-$			

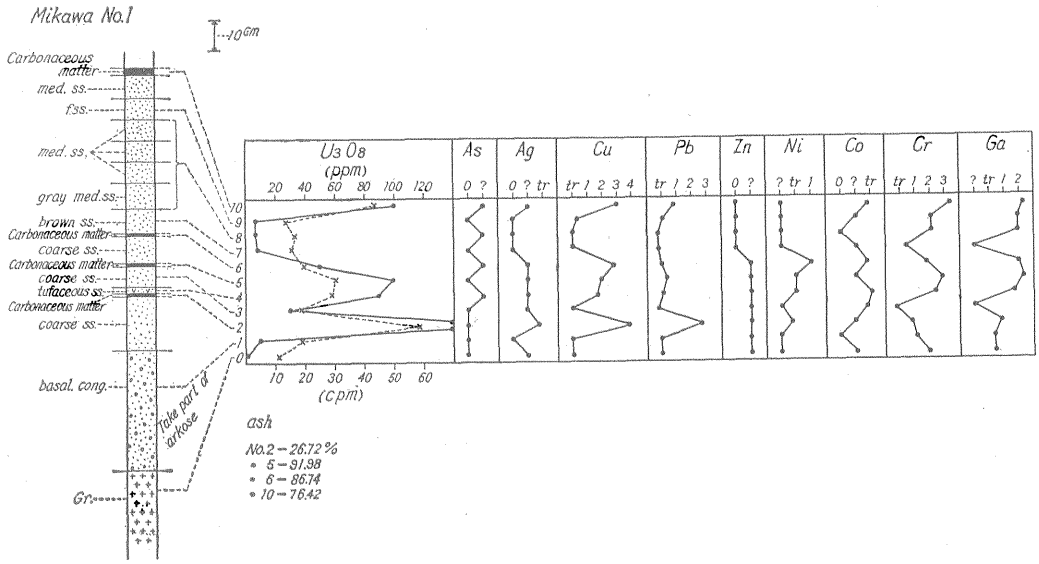
Table 2 Analytical data

Sample No.	Ash (%)	Count (cpm)	U_3O_8 (ppm) in ash	U_3O_8 (ppm) in original coal	Note
Mikawa					
1—0		10.9		2	Basal granite
1		19.6		10	
2	26.72	59.2	1,684	450	Carbonaceous matter in ss.
3		18.3		30	ss.
4		28.9		90	Tuffaceous ss.
5	91.98	31.0	108	100	Carbonaceous matter rich in ash (2~3cm)
6	86.74	19.0	88	50	〃
7		16.2		9	ss. (brown)
8		17.4		8	ss. (gray)
9		14.1		9	〃
10	76.42	44.2	131	100	Carbonaceous matter rich in ash
2—1		15.6		7	
2		19.6		10	Gray ss.
3		17.7		20	Brown fine ss.
4		17.7		20	Coarse ss.
5	90.10	23.4	89	80	Coaly mud.
6		19.3		10	Brown ss.
7		23.5		50	Yellowish brown ss.
8		14.0		10	Gray ss.
9		10.9		10	〃
10	93.01	18.1	22	20	Mud. contain slightly carbonaceous matter (2~3 cm)
11		13.4		3	Gray ss.
12	95.46	13.0	10	10	Mud. contain slightly carbonaceous matter (2~3 cm)
13		9.6		8	Gray ss.
14		14.4		10	〃
4—1		9.6		10	Matrix in basal conglom.
2		11.7		20	ss.
3	95.08	82.0	210	200	Mud. contains slightly carbonaceous matter
4		25.4		90	ss.
5		45.4		170	〃
6		4.5		10	Coarse ss.

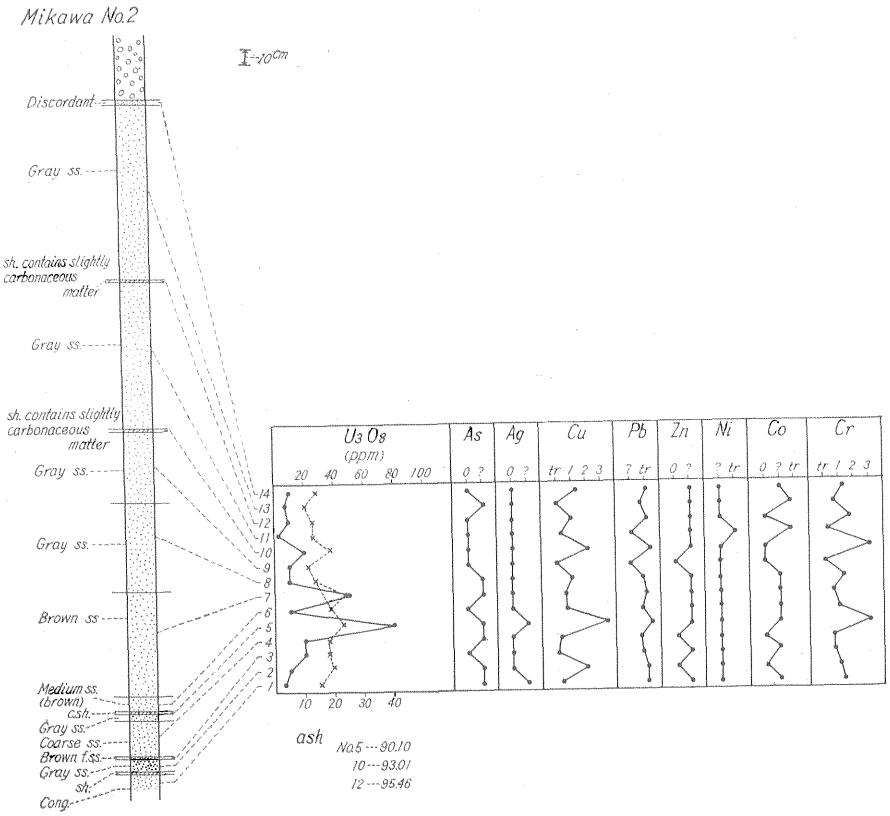
Sample No.	Ash (%)	Count (cpm)	U_3O_8 (ppm)		Note
			in ash	in original coal	
7		9.1		10	ss.
8		7.8		10	Coarse ss.
9	96.11	69.0	250	240	〃 (contains slightly carbonaceous matter)
10		22.1		50	Fine ss.
11	95.03	16.9	42	40	〃 (contains slightly carbonaceous matter)
12		5.2		3	Coarse ss.
13		2.4		3	ss.
14 a	93.47	6.6	9	8	Coaly mud, contains sand
14 b		14.4		40	〃
15	85.59	21.7	47	40	〃
16		5.0		3	Coarse ss.
17		2.7		2	ss.
18		6.9		3	〃
19		5.8		3	Matrix in conglom.
5—0		21.3		9	Granite
1		24.4		20	Matrix in basal conglom.
2		17.6		10	
3		19.2		20	ss.
4	96.17	81.7	384	370	Fine ss. contains slightly carbonaceous matter
5		29.1		90	ss.
6		23.6		40	ss.
7		18.2		20	Coarse ss.
8	24.55	46.4	530	130	Coal (0~5 cm)
9	91.00	71.0	154	140	Fine ss. contains carbonaceous matter
10		12.0		20	Fine ss.
11 a	89.20	28.7	45	40	
11 b	78.50	62.9	194	170	
12		40.0		50	Liparitic mud.
13		17.4		5	Coarse ss.
5—B		16.9		2	Weathered granite
Akatani					
1		11.2		10	Green ss.
2—1		9.9		2	Gray ss.

Sample No.	Ash (%)	Count (cpm)	U_3O_8 (ppm)		Note
			in ash	in original coal	
2		10.0		2	Granite
3		7.9		5	ss.
4		14.4		7	Green clay
5		19.9		50	Coarse ss.
3		25.6		8	Green ss.
4—1		3.3		4	Andesite
2		6.4		5	
3		9.0		7	
5	8.71	7.5	574	50	
7—1	84.58	10.5	7	6	Matrix in basal conglom. (contains slightly carbonaceous matter)
2	48.53	7.3	62	30	Coal
3		9.0		4	Conglom. (part of matrix)
4	81.06	13.6	12	10	Fine ss. contains slightly carbonaceous matter
5		14.5		4	Conglom. (part of matrix)
8—1	23.64	8.0	85	20	Coal
2	78.70	10.7	6	5	Coaly ss.
3		11.4		5	Green coarse ss.
4		32.4		20	〃
5	90.79	5.1	11	10	Green clay contains slightly carbonaceous matter
9—1	56.89	9.6		30	Coaly sh.
2		18.2	176	100	ss.
3	85.58	25.6	117	100	Coaly ss.
4	65.73	27.9	167	110	Coaly sh.
5	34.80	17.8	208	80	Coal
6	89.75	18.1	67	60	ss. contains a lens of coaly matter
7		6.8		10	Conglom. (part of matrix)
10		10.3		5	Granitic ss.
11—1		39.1		150	
2	75.45	5.9	53	40	Coal
12—1		7.6		5	Granitic ss.
2	86.62	11.2	23	20	Coaly sh.
3	89.76	11.9	11	10	〃
4	15.21	13.1	329	50	Coal

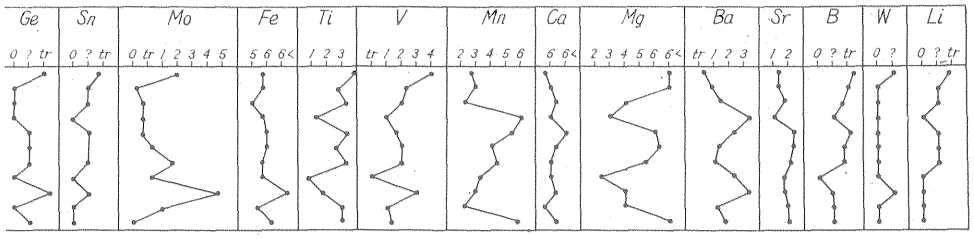
Sample No.	Ash (%)	Count (cpm)	U_3O_8 (ppm)		Note
			in ash	in original coal	
5	4.68	2.9	427	20	Coal. typical sample of a pit face
13—1		8.4		5	Conglom. (part of matrix)
2	7.55	2.0	40	3	Coal
3	9.14	9.5	109	10	〃
4		11.4		30	Green ss.
5		4.9		7	Green mud.
6		3.3		4	sh.
7		3.2		4	Coarse ss.
8		7.4		3	Granite
14—1	22.97	6.5	88	20	
2	82.16	21.6	110	90	
15—1		9.6		20	Andesitic ss.
2		9.9		9	〃
3		15.7		5	〃
4		7.8		5	Granitic conglom.
16—1		4.2		5	Surface soil
2		8.5		3	Granitic conglom.
3		5.0		5	Granitic ss.
4		7.6		5	Granitic conglom.
5		36.8		90	〃
6		27.5		60	〃
7		34.6		120	Fine ss.
8		14.5		20	Granitic conglom.
9		26.2		20	〃
17—1		8.0		2	Coarse ss. (reddish brown)
2		10.2		4	Coarse ss. (bluish green)
3		9.0		7	Medium ss.
4		9.5		7	
5		9.8		30	
6		11.8		20	
7		9.0		7	Conglom. (part of matrix)
8		7.2		3	
9		16.7		40	
10		22.1		20	
11		39.2		130	Bluish medium ss.


Mikawa No.1
10cm
Carbonaceous matter
med. ss.
f.ss.
med. ss.
gray med.ss.
brown ss.
Carbonaceous matter
coarse ss.
Carbonaceous matter
coarse ss.
tuffaceous ss.
Carbonaceous matter
coarse ss.
basal. cong.
Gr
Take part of arkose
U3O8 (ppm)
20 40 60 80 100 120
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
Ga
10 20 30 40 50 60
(cpm)
ash
No.2 — 26.72%
" 5 — 91.98
" 8 — 86.74
" 10 — 76.42

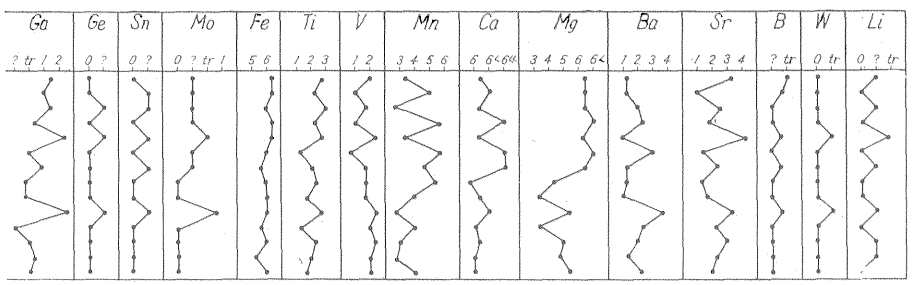
(a)

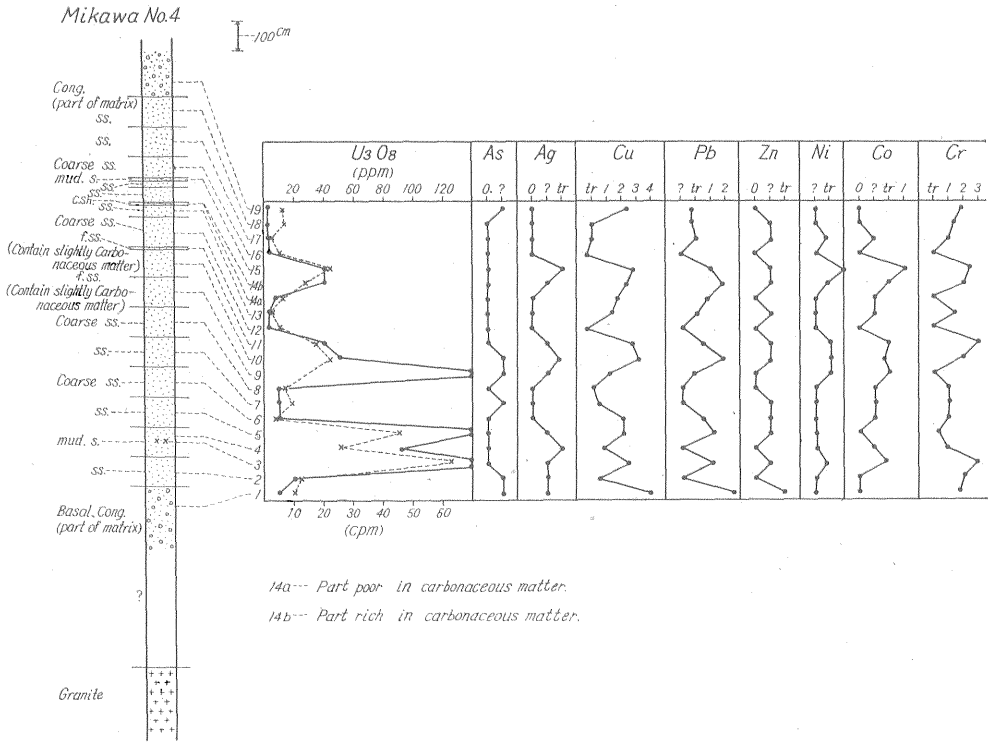

Mikawa No.2
10cm
Discordant
Gray ss.
sh. contains slightly carbonaceous matter
Gray ss.
sh. contains slightly carbonaceous matter
Gray ss.
Gray ss.
Brown ss
Medium ss. (brown)
c.sh.
Gray ss.
Coarse ss.
Brown f.ss.
Gray ss.
sh.
Cong.
U3O8 (ppm)
20 40 60 80 100
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
10 20 30 40
ash
No.5 --- 90.10
10 --- 93.01
12 --- 95.46

(b)


Ge
0 ? tr
Sn
0 ? tr
Mo
0 tr 1 2 3 4 5
Fe
5 6 6<
Ti
1 2 3
V
tr 1 2 3 4
Mn
2 3 4 5 6
Ca
6 6<
Mg
2 3 4 5 6 6<
Ba
tr 1 2 3
Sr
1 2
B
0 ? tr
W
0 ?
Li
0 ? tr


Tuff
Sandstone
Mudstone
Shale
Coal
Coaly mudstone
Coaly shale
Coaly sandstone
Tufaceous sandstone
Conglomerate
Granitic rock

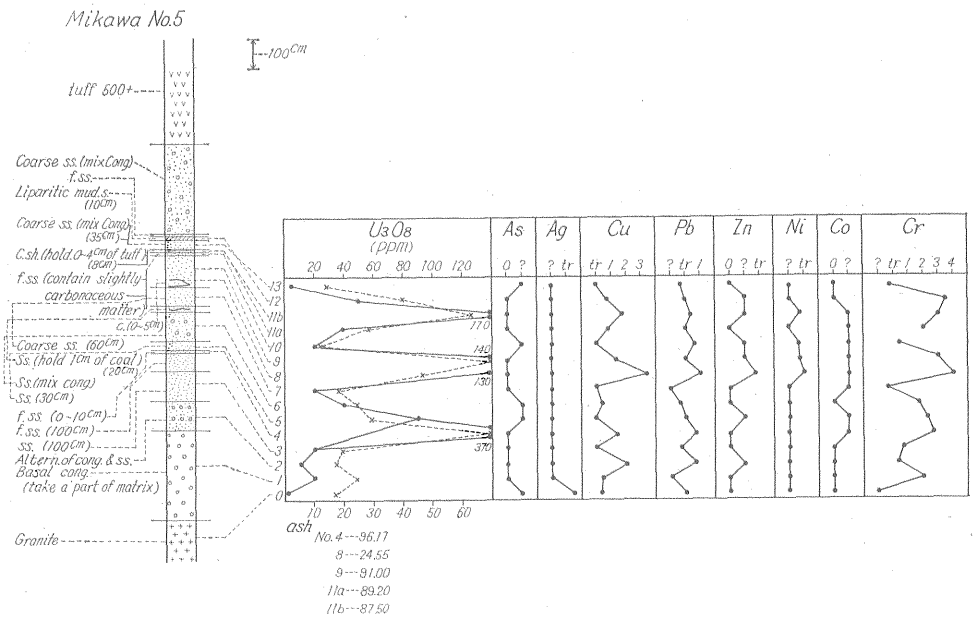

Ga
? tr 1 2
Ge
0 ?
Sn
0 ?
Mo
0 ? tr 1
Fe
5 6
Ti
1 2 3
V
1 2
Mn
3 4 5 6
Ca
6 6<6<
Mg
3 4 5 6 6<
Ba
1 2 3 4
Sr
1 2 3 4
B
? tr
W
0 tr
Li
0 ? tr



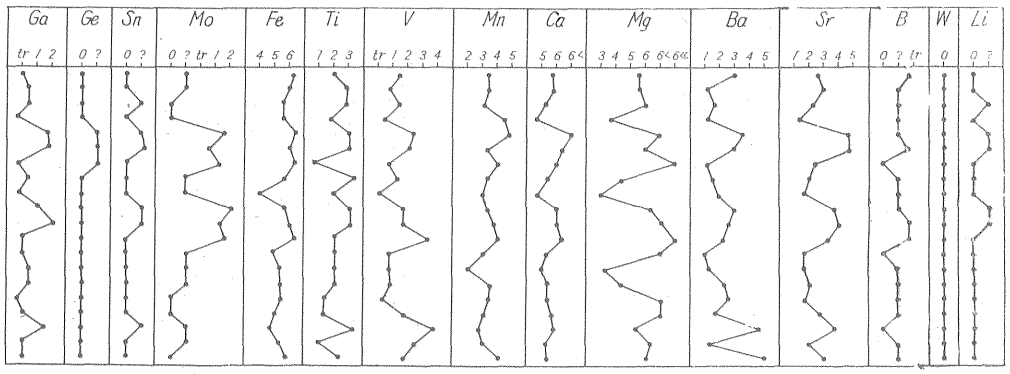
14a--- Part poor in carbonaceous matter.

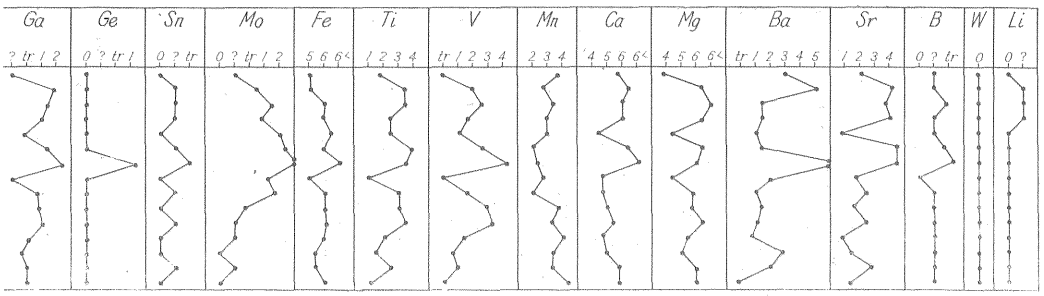
14b--- Part rich in carbonaceous matter.

(c)



(d)


Ga
tr / 2
Ge
0 ?
Sn
0 ?
Mo
0 ? tr / 2
Fe
4 5 6
Ti
1 2 3
V
tr / 2 3 4
Mn
2 3 4 5
Ca
5 6 6<
Mg
3 4 5 6 6< 6«
Ba
1 2 3 4 5
Sr
1 2 3 4 5
B
0 ? tr
W
0
Li
0 ?


Ga
? tr / 2
Ge
0 ? tr /
Sn
0 ? tr
Mo
0 ? tr / 2
Fe
5 6 6<
Ti
/ 2 3 4
V
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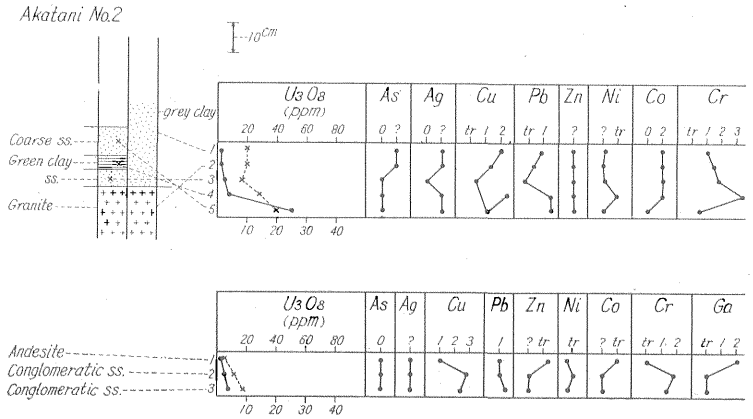
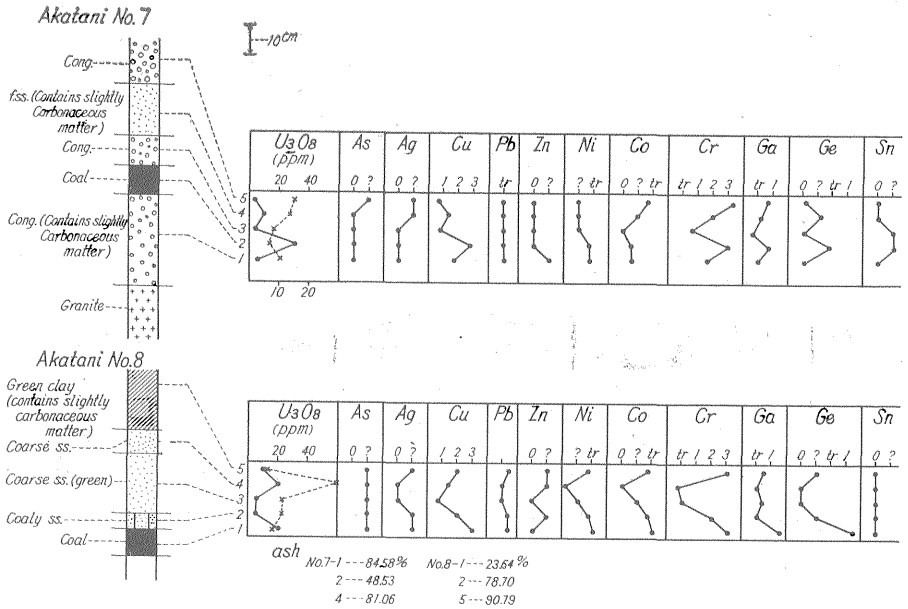
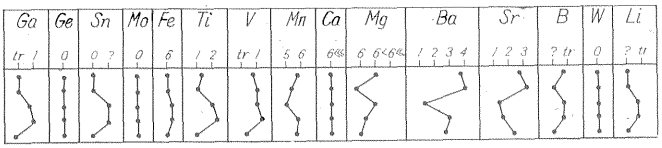
Mn
2 3 4
Ca
4 5 6 6<
Mg
4 5 6 6<
Ba
tr / 2 3 4 5
Sr
/ 2 3 4
B
0 ? tr
W
0
Li
0 ?

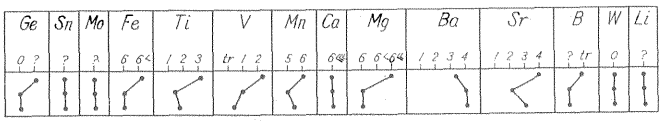

Akatani No.2
10cm
grey clay
Coarse ss.
Green clay
ss.
Granite
U3O8 (ppm)
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
Andesite
Conglomeratic ss.
Conglomeratic ss.
Ga

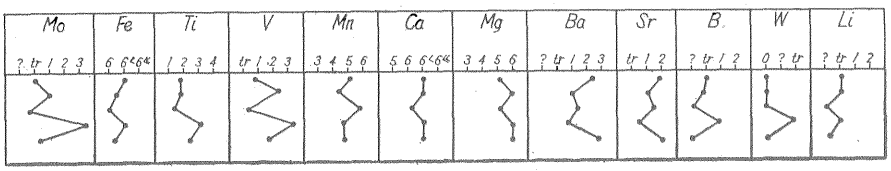
(e)

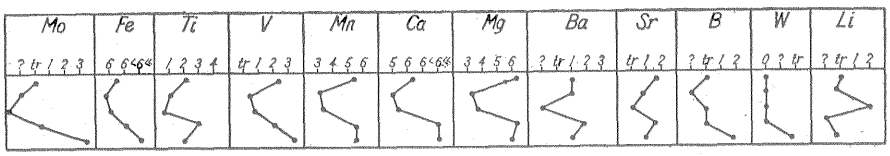

Akatani No.7
10cm
Cong.
f.ss. (Contains slightly Carbonaceous matter)
Cong.
Coal
Cong. (Contains slightly Carbonaceous matter)
Granite
U3O8 (ppm)
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
Ga
Ge
Sn
Akatani No.8
Green clay (contains slightly carbonaceous matter)
Coarse ss.
Coarse ss. (green)
Coaly ss.
Coal
ash
No.7-1 ---84.58%
2 ---48.53
4 ---81.06
No.8-1 ---23.64%
2 ---78.70
5 ---90.79

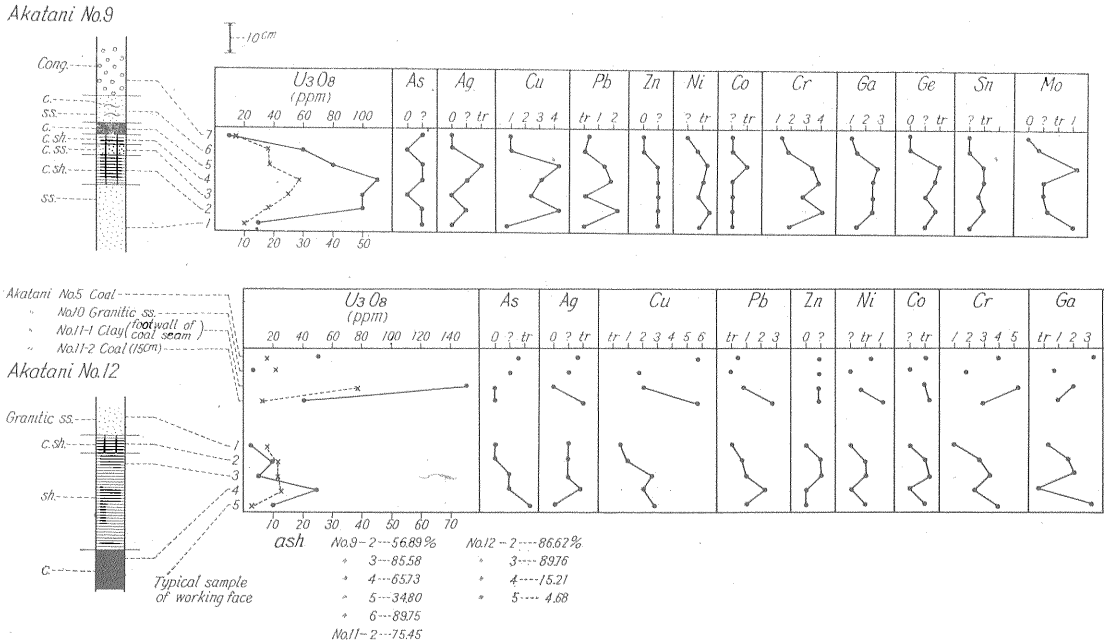
(f)


Ga Ge Sn Mo Fe Ti V Mn Ca Mg Ba Sr B W Li
tr / 0 0 ? 0 6 / 2 tr / 5 6 6 6 6<6 / 2 3 4 / 2 3 ? tr 0 ? tr

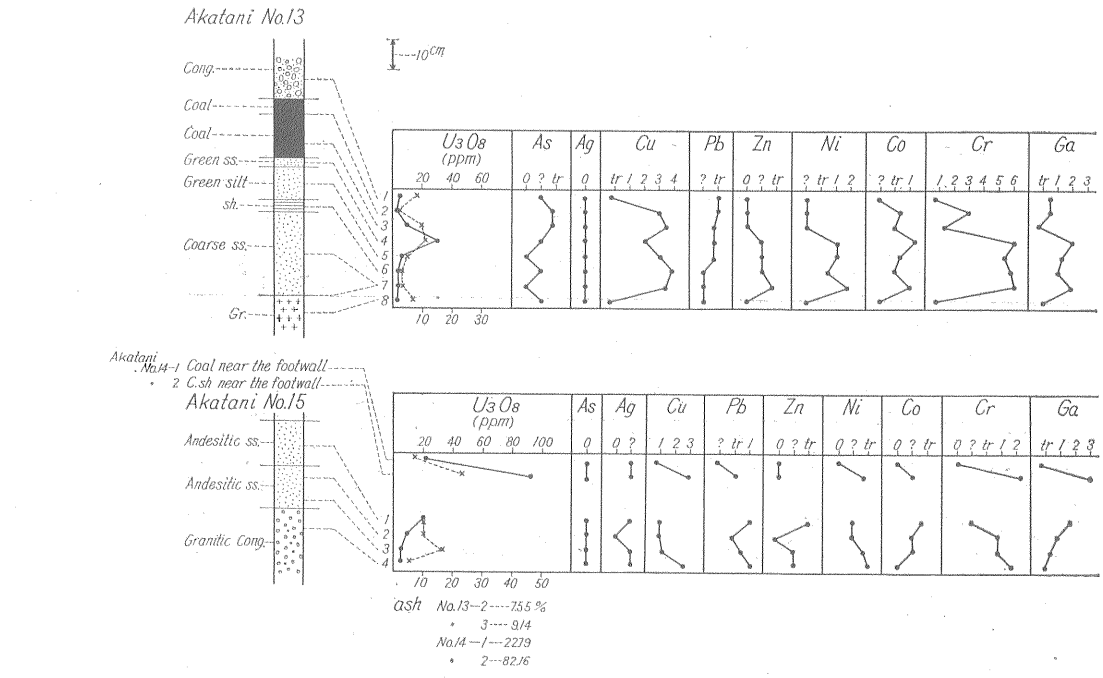

Ge Sn Mo Fe Ti V Mn Ca Mg Ba Sr B W Li
0 ? ? ? 6 6< / 2 3 tr / 2 5 6 6 6 6<6 / 2 3 4 / 2 3 4 ? tr 0 ?


Mo Fe Ti V Mn Ca Mg Ba Sr B W Li
? tr / 2 3 6 6<6 / 2 3 4 tr / 2 3 3 4 5 6 5 6 6<6 3 4 5 6 ? tr / 2 3 tr / 2 ? tr / ? 0 ? tr ? tr / ?

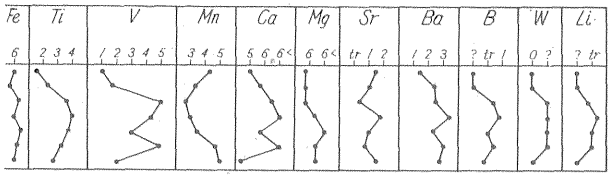

Mo Fe Ti V Mn Ca Mg Ba Sr B W Li
? tr / 2 3 6 6<6 / 2 3 4 tr / 2 3 3 4 5 6 5 6 6<6 3 4 5 6 ? tr / 2 3 tr / 2 ? tr / ? 0 ? tr ? tr / ?

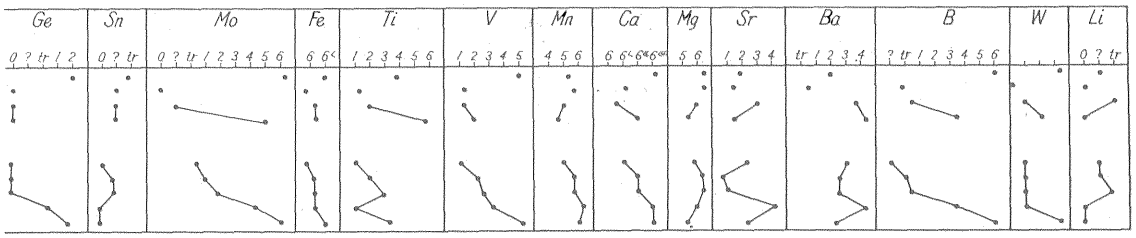

Akatani No.9
10cm
Cong.
c.
ss.
c.
c.sh.
c.ss.
c.sh.
ss.
U3O8 (ppm)
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
Ga
Ge
Sn
Mo
Akatani No.5 Coal
No.10 Granitic ss.
No.11-1 Clay (footwall of coal seam)
No.11-2 Coal (15cm)
Akatani No.12
Granitic ss.
c.sh.
sh.
c.
Typical sample of working face
ash
No.9-2---56.89%
3---85.58
4---65.73
5---34.80
6---89.75
No.11-2---75.45
No.12-2----86.62%
3----89.76
4----15.21
5---- 4.68

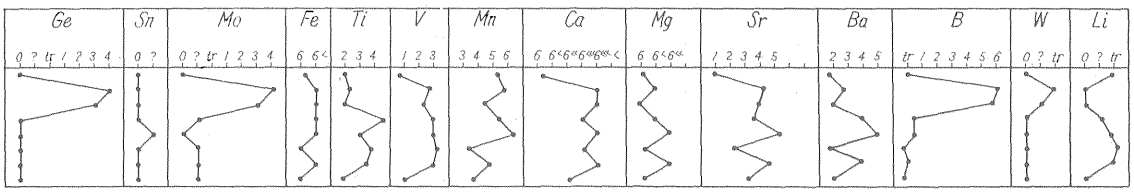
(g)

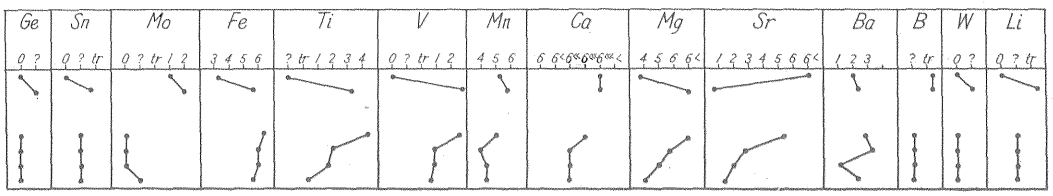

Akatani No.13
10cm
Cong.
Coal
Coal
Green ss.
Green silt
sh.
Coarse ss.
Gr.
U3O8 (ppm)
As
Ag
Cu
Pb
Zn
Ni
Co
Cr
Ga
Akatani
No.14-1 Coal near the footwall
2 C.sh near the footwall
Akatani No.15
Andesitic ss.
Andesitic ss.
Granitic Cong.
ash
No.13-2----75.5%
3---- 9.14
No.14-1---22.79
2---82.16

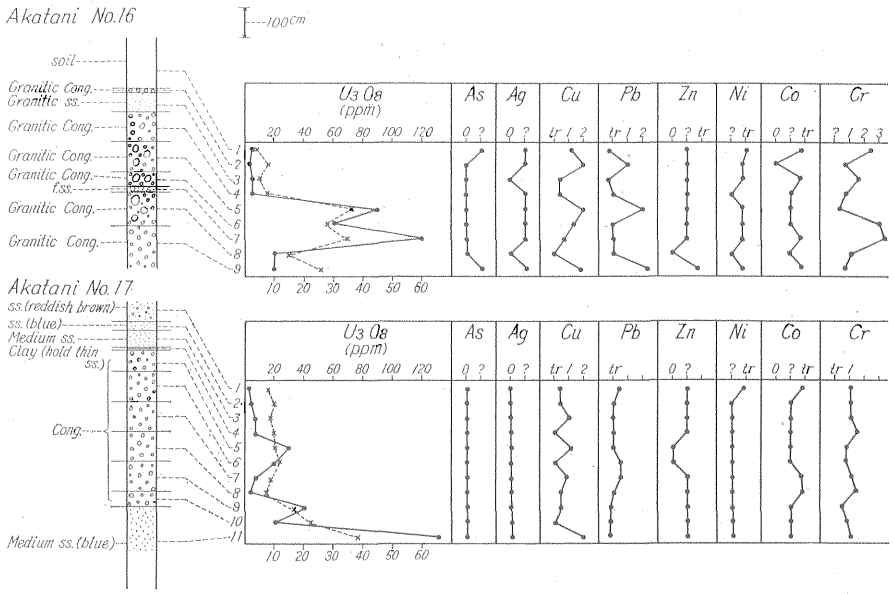
(h)


Fe
Ti
V
Mn
Ca
Mg
Sr
Ba
B
W
Li


Ge
Sn
Mo
Fe
Ti
V
Mn
Ca
Mg
Sr
Ba
B
W
Li


Ge
Sn
Mo
Fe
Ti
V
Mn
Ca
Mg
Sr
Ba
B
W
Li


Ge
Sn
Mo
Fe
Ti
V
Mn
Ca
Mg
Sr
Ba
B
W
Li



(i)

Fig. 3 Distribution of minor elements

Table 3 Average uranium contents of various rock types

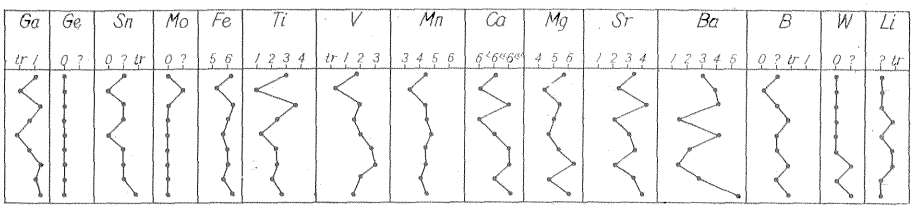
Rock types	Number of samples	Range (ppm)	Average (ppm)
Basal granitic rocks	5	2～9	3.6
Coarse sandstones	41	3～90	14.9
Medium sandstones	35	3～170	23.4
Fine sandstones	5	5～120	43.0
Shales or mudstones	6	4～50	12.1
Coaly shales or Coaly mudstones	26	5～370	85.1
Coals	10	3～450	83.3

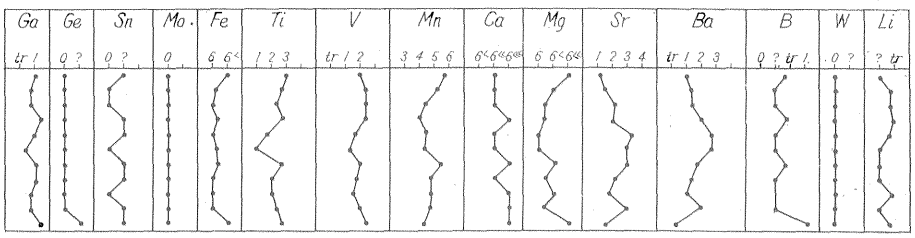
average contents of uranium in various rock types are given in table 2.

According to the table 3, the uranium contents of basal granitic rocks are very low. As for the contents of uranium in five samples, three were 0.2 ppm, one 3 ppm, and the other one 9 ppm U_3O_8.

In the sandstones, it seems that the smaller the particles are, the more average contents of uranium increase, but this case is caused by the influence of the very few samples which give extremely high amounts of uranium.

Many of such samples are contaminated by very small quantities of carbonaceous matter. It may be considered that the uranium contents of most sandstones in these areas are about from 15 to 20 ppm U_3O_8.





in coal-bearing bed (a~i)

In the shales or mudstones, which do not contain carbonaceous matter at all, the contents of uranium in six samples were 50 ppm in only one case and less than 10 ppm in the other five cases. And the average amount was 12 ppm U_3O_8.

It is clearly recognized that uranium is more enriched in coaly shales or coaly mudstones, which have higher ash content, than in the good coal.

In the coaly shales or coaly mudstones, the average content of uranium was 85 ppm U_3O_8, and in the coals 83 ppm U_3O_8.

The carbonaceous matters are closely concerned with the uranium enrichment but the relation is not always parallel.

Uranium Content in the Fraction of Different Specific Gravities

To observe the distributions of uranium in the fractions of different specific gravities, the contents of ash and uranium in each fraction which are classified into different specific gravities were determined.

The samples, all of which had passed a 20 mesh screen by the soft grinding in the porcelain mortar, were sieved to 20~60, −60 mesh fractions, and the fraction of 20~60 mesh was used for the specific gravity classification.

The classification was carried out by the float-sink in a liquid which is prepared for known specific gravity.

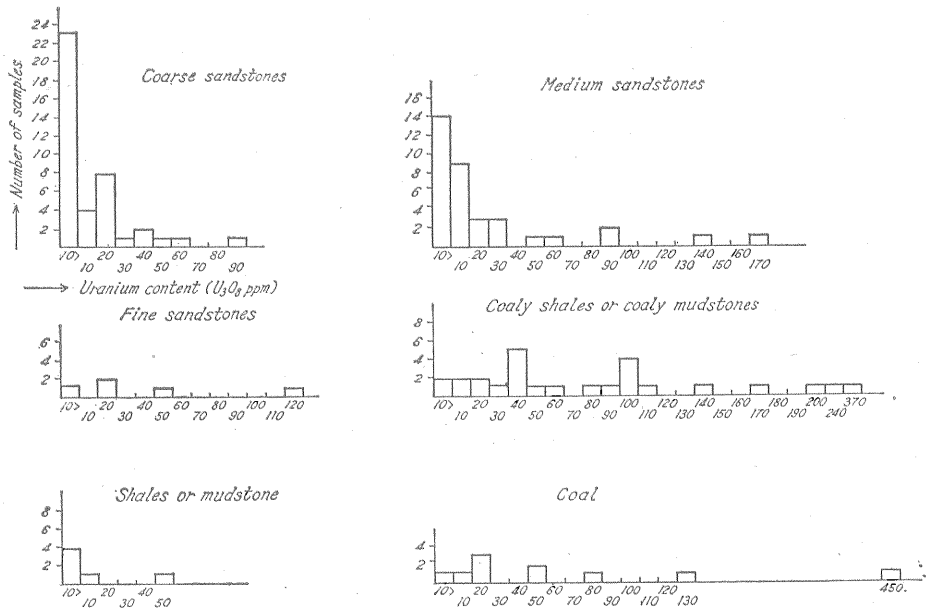


Fig. 4 Histogram of uranium content in various rocks

The liquids used were mixtures of each two components of toluene, carbon tetrachloride and bromoform. The specific gravity was classified to six fractions of <1.4, $1.4\sim1.5$, $1.5\sim1.6$, $1.6\sim1.7$, $1.7\sim1.8$ and >1.8.

The components of specific gravity of three samples were given in table 3, and the contents of ash and uranium in separated each fraction were given in table 4 and fig. 6.

The contents of uranium in the ash show extremely high amount in the fraction of the smaller specific gravity and this appears as if the uranium is concentrated specially in the part of organic matter.

But on the other hand, according to the equation of

$$U_1 = \frac{100\,U_2}{A}$$

here U_1 : % of U_3O_8 in ash

U_2 : % of U_3O_8 in original sample

A : % of ash

it is obvious that U_1 is inversely proportional to A, so that U_1 is only 1.25 times of U_2 when A is 80%, but it increases to 20 times by the decrease of A to 5 %. In this way, the value of uranium contents calculated by the ash base is so changeable widely by the ash contents of the samples that the discussion of uranium content in coal should be done with the contents in the original coal.

In the fig. 6, curve 1 shows the relations between the uranium contents in the original coal and the specific gravity. In sample 1 and sample 3, the uranium contents tend to increase slightly with the decrease of the specific gravity, but in

Table 4 Specific gravity and uranium contents

Specific gravity	Sample 1			Sample 2			Sample 3		
	Ash	U_3O_8		Ash	U_3O_8		Ash	U_3O_8	
		In ash	In original coal		In ash	In original coal		In ash	In original coal
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1.4—	6.53	0.107	0.007	5.92	0.160	0.009	8.83	0.234	0.021
1.4~1.5	20.75	0.024	0.005	18.43	0.079	0.016	20.16	0.063	0.013
1.5~1.6	32.98	0.009	0.003	31.06	0.074	0.024	32.60	0.033	0.011
1.6~1.7	43.84	0.007	0.003	41.55	0.054	0.023	42.95	0.025	0.011
1.7~1.8	52.76	0.004	0.002	52.34	0.025	0.015	60.33	0.018	0.011
1.8+	83.51	0.002	0.002	83.74	0.005	0.005	92.44	0.001	0.001

Table 5 Distribution of uranium in various specific gravity

Specific gravity	Sample 1			Sample 2			Sample 3		
	Component of s.g.	Amount of U_3O_8	Ratio for total U_3O_8	Component of s.g.	Amount of U_3O_8	Ratio for total U_3O_8	Component of s.g.	Amount of U_3O_8	Ratio for total U_3O_8
	(%)	(g)	(%)	(%)	(g)	(%)	(%)	(g)	(%)
1.4—	1.1	0.000077	3.6	3.5	0.000315	5.7	1.6	0.000336	19.6
1.4~1.5	0.7	0.000035	1.6	0.8	0.000128	2.3	0.8	0.000104	6.1
1.5~1.6	1.6	0.000048	2.2	0.6	0.000144	2.6	0.6	0.000066	3.9
1.6~1.7	4.7	0.000148	6.6	0.5	0.000115	2.1	0.5	0.000055	3.2
1.7~1.8	8.9	0.000178	8.3	0.7	0.000105	1.9	1.8	0.000198	11.6
1.8+	83.0	0.001660	77.6	93.9	0.004695	85.3	94.7	0.000947	55.5
Total	100.0	0.002146	99.9	100.0	0.005502	99.9	100.0	0.001706	99.9

sample 2 such tendency is not found at all, and the highest value of uranium is found in the fraction of the specific gravity ranging from 1.5 to 1.7. In the samples from Ouchi mine, it has been observed that the uranium contents in each fraction were nearly constant irrespective of specific gravity.

Generally speaking, the uranium contents in the fraction of each specific gravity is apt to increase slightly with the decrease of specific gravity, but it is not always so in every case.

Minor Elements in the Coal-bearing Bed

Detected frequency of minor elements

The analytical results of minor elements which were analyzed by spectrogra-

phic method are shown in fig. 3. The detected frequency of minor elements are shown in table 6.

Comparing these data with those of Ouchi mine, there have not been found great differences. But by observing those data in details, it may be mentioned that

(1) Both in the carbonaceous matters, and sedimentary rocks containing no carbonaceous matters at all, silver, beryllium and lithium were detected more frequently than in the case of Ouchi mine.

(2) Arsenic showed the result inversely as against the above elements.

(3) Antimony and cadmium were detected in the samples from Ouchi mine very rarely, but they were not detected at all in the samples from these areas.

(4) Zinc, cobalt and tin were detected slightly less frequently than in the case of Ouchi mine.

(5) Molybdenum and tungsten in the carbonaceous matters were detected more frequently than in the case of Ouchi mine, but in the sedimentary rocks,

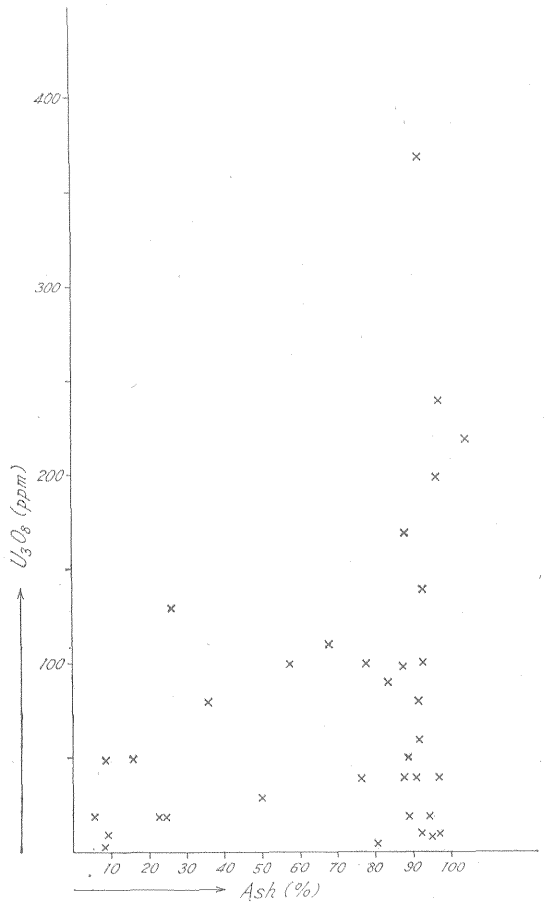
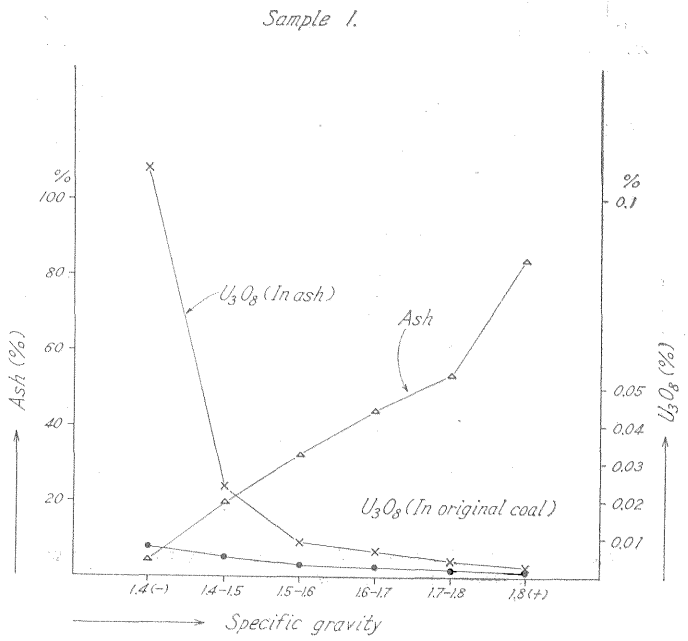
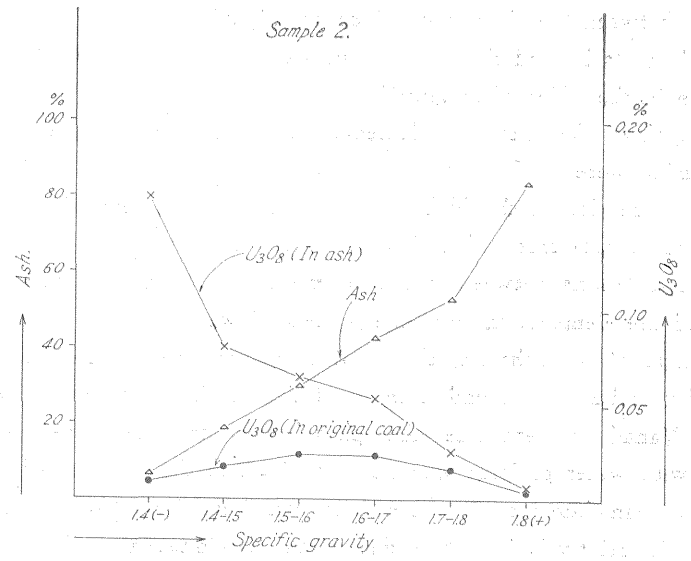


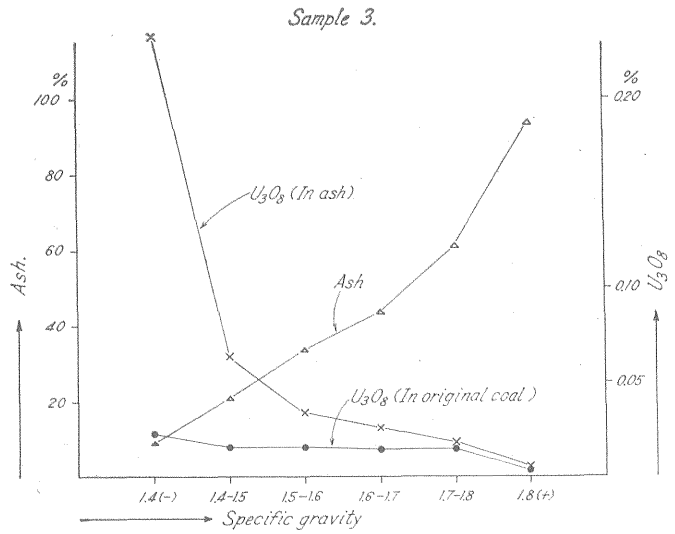
Fig. 5 Relationship between the contents of coal ash and uranium


Sample 1.
%
100
80
60
40
20
Ash (%)
U_3O_8 (In ash)
Ash
U_3O_8 (In original coal)
%
0.1
0.05
0.04
0.03
0.02
0.01
U_3O_8 (%)
1.4(−)
1.4–1.5
1.5–1.6
1.6–1.7
1.7–1.8
1.8(+)
Specific gravity

(a)


Sample 2.
%
100
80
60
40
20
Ash.
U_3O_8 (In ash)
Ash
U_3O_8 (In original coal)
%
0.20
0.10
0.05
U_3O_8
1.4(−)
1.4–1.5
1.5–1.6
1.6–1.7
1.7–1.8
1.8(+)
Specific gravity

(b)



(c)

Fig. 6 Relationship between the contents of coal ash and uranium in various specific gravity

they showed the contrary result.

Correlations between Minor Elements and Uranium

Correlation coefficients between the amounts of minor elements and uranium were calculated. Those are given in fig. 7.

The horizontal lines in the fig. 7, show the minimum value up to which the correlation between two factors could be considered.

The elements beyond the above value were Sn, V, Ga, Cu, Pb, Mo, Cr, Ti, W, Ni and Mn in the order of magnitude.

Among these elements, the elements which are in common with in the case of Ouchi mine were V, Ga, Cu, Mo, Cr, W and Ni.

On these results, it should be followed up with geochemical investigation by collecting more data from other deposits of this type.

The correlations between minor elements and uranium depend upon the behavior of the elements through the process of weathering.

According to Goldschmidt, the most important phenomenon during the weathering of vanadium compound is the oxidation of the vanadium to vanadate ion $(VO_4)^{3-}$. Vanadium pentoxide like phosphorous or arsenic pentoxide, readily combines with water to form vanadic acid which in the presence of suitable cations becomes vanadate ion. The trivalent vanadium ion, like trivalent iron or chromium, is relatively immobile due to the precipitation as the very sparingly soluble hydroxide even at rather low Ph values, while soluble vanadates are able to travel in the solution over a wide range of acidity or alkalinity. Vanadate ions

Table 6 Detected frequency of minor elements

Elements	Carbonaceous matter			Rock		
	Number of Sample	Detected sample	Frequency (%)	Number of sample	Detected samle	Frequency (%)
Ag	39	29	74	90	40	44
As	39	15	38	90	33	37
Sb	39	—	—	90	—	—
Cu	39	39	100	90	90	100
Pb	39	39	100	90	90	100
Cd	39	—	—	90	—	—
Zn	39	23	59	90	62	69
Ni	39	37	95	90	89	99
Co	39	32	82	90	61	68
Cr	39	38	97	90	90	100
Ga	39	39	100	90	90	100
Ge	39	26	67	90	5	6
Sn	39	28	72	90	41	46
Mo	39	39	100	90	44	49
Fe	39	39	100	90	90	100
V	39	37	95	90	90	100
Ti	39	39	100	90	90	100
Mn	39	39	100	90	90	100
Be	39	13	33	90	3	3
Ca	39	39	100	90	90	100
Mg	39	39	100	90	90	100
Ba	39	39	100	90	90	100
Sr	39	39	100	90	90	100
B	39	37	95	90	86	96
Al	39	39	100	90	90	100
W	39	21	54	90	6	7
Zr	39	2	5	90	1	1
Li	39	26	67	90	55	61
Te	39	4	10	90	1	1

resulting from weathering are therefore able to migrate with circulating solutions, either in soil or through porous rocks, until some chemical agent operates to precipitate some sparingly soluble vanadium compounds.

The factors causing the precipitation of less soluble vanadium compounds are as follows :

(1) Presence of reducing agents such as organic matter.

(2) Local concentration of cations of heavy metal such as Pb^{2+}, Zn^{2+}, Cu^{2+} which may form insoluble compounds with vanadate ion.

(3) A special case is the precipitation of vanadate ion in the presence of divalent uranyl cation $(UO_2)^{2+}$, in such minerals as carnotite or tynyamunite. Some authors consider carnotite and tynyamunite to be the secondary products

of re-oxidation of reduced vanadium-uranium compounds such as uranium-vanadium sulphide.

(4) Local precipitation of soluble vanadate ion, as well as of phosphate or arsenate ions, is frequently caused by hydroxides of aluminium or of ferric iron.

Among above four cases, the cases of (1) and (3) are caused by the reduced environments, therefore it may be considered that the precipitation of vanadium is greatly subjected to the redoxpotential during sedimentation.

The elements such as chromium, copper, molybdenum and nickel have been known as the elements which are apt to be concentrated under the reducing environments, and there are a number of data that these elements were enriched in coal or organic matter of forest soil.

Thus, the geochemical behavior of vanadium, chromium, lead, nickel etc. are very similar to uranium ; therefore, it should be probable that these elements are detected in parallel with uranium.

The geochemical relationship on the concentration of uranium and the other minor elements will be reserved for the later reports intending to collect more data.

Uranium in the Water

The stream water (partly pit water) was analyzed for uranium and other general components. The general components were analyzed by the method of JIS K 0101 (1960).

As for ground water, the suitable samples were not obtained.

According to table 7, uranium has been detected in all samples and its amounts were ranging from 0.1 to 5 ppm. The maximum value was found in

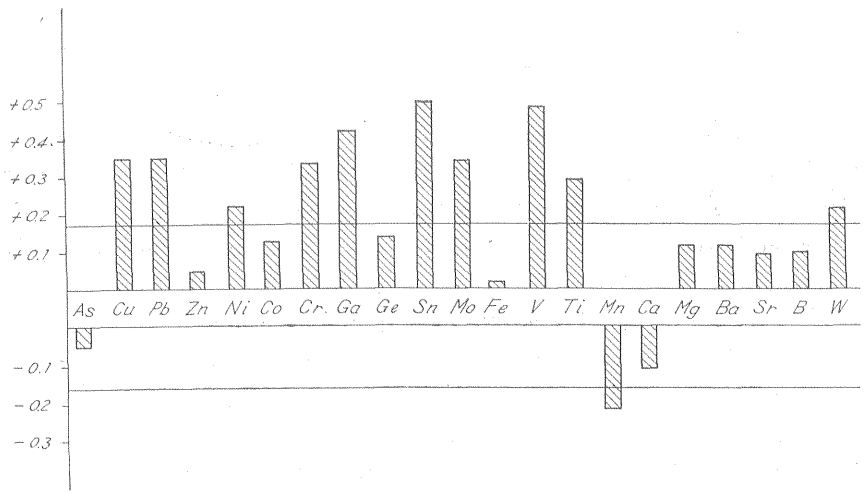


Fig. 7 Correlation coefficients between uranium and minor elements (131 samples)

the pit water from Kamiakatani mine.

No. 1～No. 3 were running out from the buried former pit. It is about 50 cm in width, 5 cm in depth and the speed of current was about 10cm per second.

From the exit of the pit to the distance of about 14～15m, there have been observed considerable precipitate of iron in the bottom of the trickle.

The uranium content of this precipitate was 51ppm U, and the iron content was 31.56% Fe.

It is probable that the iron was precipitated very gradually from water and also uranium was either co-precipitated with iron or adsorbed by iron hydroxide subsequently.

If the uranium was co-precipitated at the same time with iron, the ratio of uranium and iron in the precipitate and water should show approximately the same value. But in fact, these calculated values as follows :

in precipitated matter U/Fe=0.0051/31.56=0.00016

in water U/Fe=0.4/200=0.002.

Thus, the former value was less than one-tenth of the latter. From these results, it is considered that the uranium was adsorbed by iron hydroxide subsequently rather than it was co-precipitated with iron.

In any case, it would be worth to keep attention as the fact that the uranium concentration is occurring in recent times.

Chemical component of precipitated matter

Table 7 Data of water analysis

Sample No.	pH	RpH	HCO_3^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Na^+ (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Fe^{2+} (ppm)	P (ppm)	U ($\mu g/l$)	Note
Mikawa															
1	6.8	7.0	13.3	7.1	3.3	0.06	0.00	1.3	4.0	1.3	2.0	—	0.02	0.1	Stream water
2	7.0	7.2	18.3	7.9	4.9	0.00	0.00	1.0	5.5	1.8	2.1	—	0.02	0.2	〃
3	7.1	7.4	10.9	7.6	5.4	0.06	0.00	1.0	5.6	2.8	0.5	—	0.01	0.2	〃
Akatani															
1	6.4	6.6	100.6	10.7	13.0	0.10	1.14	1.1	8.8	27.0	3.5	0.20	0.01	0.4	Running out through the buried former pit
2	6.4	6.6	105.9	8.6	12.8	0.24	0.50	1.0	9.2	28.7	3.2	0.15	0.02	0.4	〃 The downstream of No. 1
3	6.6	6.8	95.7	8.5	11.8	0.00	0.14	1.0	8.4	25.9	3.3	0.12	0.02	0.4	〃
4	6.8	6.9	99.7	8.6	12.2	0.10	0.14	1.3	9.3	28.0	2.6	0.10	0.02	0.2	〃
5	6.9	7.0	13.3	7.4	3.1	0.00	0.00	0.7	4.4	5.4	1.3	—	0.02	0.1	Stream water
6	6.8	6.9	11.9	8.2	9.5	0.30	0.04	0.9	4.5	3.9	1.8	—	0.02	0.4	〃
7	6.0	6.3	11.9	8.3	9.9	0.12	0.00	0.8	4.5	4.3	1.2	—	0.02	0.2	〃
8	6.2	6.3	4.4	8.2	5.9	0.10	0.24	0.5	4.4	1.0	0.9	—	0.02	0.1	〃
9	6.5	6.6	2.8	7.6	4.0	0.00	0.14	0.4	3.8	0.8	0.5	—	0.02	0.1	Spring
10			25.2	7.0	3.3	0.00	0.20	0.9	4.6	5.5	1.2	0.15	0.01	5.0	Pit water of Akatani mine

Fe_2O_3	45.16% (31.56% Fe)
U_3O_8	0.006% (0.005% U)
CaO	1.43 %
MgO	0.41 %
P_2O_5	1.89 %
In soluble matter in HCl	19.88 %
Ig. loss	27.86 %
Minor elements	As, Ba, Cu, Mo, Pb, Sr, Ti, V (By spectrographic qualitative analysis)

Conclusion

Uranium in the coal-bearing bed is not always concentrated in the good coal, but rather enriched in the coaly shales or coaly mudstones which have higher ash contents.

The uranium contents of shales or mudstones which do not contain carbonaceous matter at all, were very low.

In the isolated pieces of coal, as well as thin coal seams occurring among sandstones or shales, there has not been observed marked enrichment of uranium.

From these results, it is considered that the carbonaceous matter has played the important roles in the uranium enrichment in the way of not only in adsorber but also of preparing and reserving the reducing environments which enable and accelerate the adsorption of uranium.

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新潟県三川・赤谷地区における夾炭層に伴なうウランについて

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要　旨

新潟県三川・赤谷地区における夾炭層に伴なうウランについて，その分布状況，比重組成とウラン含量との関係，ウランと他の微量成分との関係などについて検討を行ない概略次のような結果を得た。

(1) 夾炭層中におけるウラン含量は 2～450 ppm 平均 38 ppm であつた。(2) ウラン含量が特に高いのは良質の炭の部分よりもむしろ灰分の多い炭質頁岩または炭質泥岩である。(3) 試料中の有機物の量とウラン含量との間には定量的な関係は認められなかつた。(4) 炭質頁岩または岩質泥岩を比重分離してウランの分布を検討すると必ずしも低比重の部分に顕著な濃縮は認められない。(5) ウランと相関を示す微量成分としては V, Ga, Cu, Mo, Cr, W, Ni などがあげられる。