RELATIONSHIPS BETWEEN MAJOR INORGANIC ELEMENTS AND MINERALS IN COALS FROM THE ASHIBETSU DISTRICT, ISHIKARI COAL FIELD, JAPAN

Tatsuo Kimura
Energy Resources Department
National Institute for Resources and Environment
16-3 Onogawa, Tsukuba-shi, 305 Japan

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INTRODUCTION

Information from both mineralogical and elemental analyses of coal is important for coal utilization technologies such as combustion, gasification, liquefaction, and coking, as well as for environmental considerations. The analyses have often been carried out separately. However, a combination of both analyses would bring more fruitful results than separate analyses concerning the nature of the mineral matter in coal. Two methods of coal sample collection for both analyses are available: collection of various kinds of coal samples on rank from different locations and collection of coal samples from different coal seams at the same location. The former method provides a wide range of information on coal mineral phases and elements and the latter provides precise specification of coal mineralogical and elemental characteristics. The goal of this study was to explore the relationships between major inorganic elements and mineral phases in coals by analyzing samples from different coal seams in the Ashibetsu district, Ishikari coal field, Japan. The geochemical implications of mineral abundances were previously reported (1-3).

ANALYTICAL PROCEDURES

Coal samples were hand picked along vertical transects from near roof to near floor at seven coal pit faces of six coal seams. Coal samples containing less than 40% ash were selected. Minerals were identified by X-ray diffraction analysis of the low-temperture ashes (LTA) obtained by ashing powdered coal samples in an oxygen plasma reactor. The major inorganic element (Si, Al, K, Ti, Na, Mg, Ca, Fe, Sr, P, F, and Cl) and total sulfur contents were determined by X-ray fluorescence analysis.

RESULTS AND DISCUSSION

Kaolinite and quartz are the most dominant silicate minerals in coals from the Ashibetsu district (Table 1), and were found from the very lowest ash to the highest ash coals. The silicate minerals, plagioclase, illite, illite/smectite (I/S) mixed-layer clay minerals, smectite and K-smectite were also found, but chlorite is very rare. Calcite and ankerite are the most dominant carbonate minerals. They occur as cleat and fracture fillings (3). Carbonates also occurred as siderite, dolomite (Fe-dolomite) and aragonite. Siderite and dolomite are syngenetic minerals which occur as aggregates of fine nodules (3). Pyrite was abundant in only one coal seam and marcasite was very rare. The low abundance of pyrite suggests that most of these coal seams were formed under fresh water environments. Gypsum, which was identified as bassanite or anhydrite in the LTA, and other five iron sulfate minerals occur in some coal samples as a result of weathering of pyrite. Apatite was present in more than 60% of the coal samples, and was sometimes accompanied by goyazite. Some coal samples contained boemite.

The high correlation coefficients between all pairings of ash, Si, Al, K, Ti, and Na (Table 2) indicates that these five elements are associated with silicate minerals. The correlation coefficient between Si and ash contents is the highest because Si is contained in quartz and all aluminosilicate minerals in the coal samples. Most of the Al is associated with aluminosilicate minerals, although a minor fraction is also associated with goyazite and boehmite.

The ash and K contents (Fig. 1) of the coal samples containing K-bearing clay minerals (illite, K-smectite, and/or I/S mixed-layer clay minerals) were closely correlated, indicating that K is contained as an interlayer cation in these clay minerals. The Al and Ti contents (Fig. 2) were closely correlated (correlation coefficient 0.83). Ti is thought to substitute for Al in clay minerals and the maximum amount of Ti substituted for Al was 12.5%. Several studies (4-7) have already pointed out that the correlation coefficients between any pair of ash, Si, Al, K, and Ti are high and that these elements are associated with silicate minerals in coal. However, the mineral species associated with these elements have not previously been determined.

Relatively high correlation coefficients for Na with ash, Si, Al, K, and Ti suggest that the Na content reflects the existence of Na-bearing minerals such as plagioclase, smectite, and I/S mixed-layer clay minerals. The weight ratio of Na to ash is higher for the coal samples containing two or three Na-bearing minerals than for those containing one Na-bearing mineral.

Fig. 3 shows ash versus Mg. The Mg and ash contents of the coal samples containing Mg-bearing clay minerals (illite, I/S mixed-layer clay minerals, smectite, K-smectite, and/or chlorite) were closely related.

The frequencies of mineral occurrences in the coal samples (see Table 1)

suggests that Mg is primarily associated with carbonate minerals and to a lesser extent associated with Mg-bearing clay minerals (Fig. 3). Most of the Ca exists in calcite and ankerite, although some occurs in apatite, dolomite and plagioclase. The great abundance of ankerite resulted in a comparatively high correlation coefficient (0.63) between Ca and Mg. Most of the coal samples contained less than 1.5% Ca and less than 0.2% Mg (Fig. 4).

The average Ca, Mg and Fe contents in the coal samples containing only calcite and ankerite as the Ca-, Mg-, and/or Fe-bearing minerals are 0.895% (29 samples), 0.097% (45 samples), and 0.290% (43 samples) respectively. Both the Ca and Mg contents of these coal samples are estimated to be approximately the same as those in recent plants (8). However, the Fe content is higher in these coal samples than those in recent plants and approximately the same as those in recent peats (8). This result implies that Ca, Mg and Fe in both calcite and ankerite could originate from the organic materials of plants and peats.

The coal samples have been classified based on their Mg and Fe contents into three groups (Fig. 5): (1) samples plotting along the Fe-axis (solid circles), (2) samples distributed diagonally from the origin (diamonds) and (3) samples containing moderately increasing Fe content with increasing Mg content (open circles). Fe in the first group is mostly associated with pyrite. Siderite and ankerite were the Fe-bearing carbonate minerals in the second group with the exception of one coal sample, which contained dolomite instead of ankerite. Ankerite was the only Fe-bearing carbonate mineral found in coal samples from the third group. The slope of the Fe to Mg weight ratio of samples from the third group almost matched that in ankerite. The difference between the slopes of the second and third groups is due to the presence of siderite in the third group, proving that the siderite in the coal samples is Mg-bearing siderite.

Fe occurs both in carbonate minerals (ankerite and siderite) and Fe in pyrite, marcasite and iron sulfate minerals. The high correlation of Fe with S is caused by several samples which contained higher amounts of pyrite and iron sulfate minerals.

A substantial number of the coal samples were rich in both P and Sr (Fig. 6). P occurs as apatite and goyazite but Sr occurs only as goyazite. As P and Sr show a high correlation coefficient (0.92), these two phosphate minerals are thought to be of similar origin. A similar correlation between P and Sr was reported for Eastern Tennessee coals (4).

No close correlation between F and P was observed. Since the P content as goyazite is evaluated by Sr content, the P content as apatite can be evaluated by subtracting the P content as goyazite from the total P content. The relationship between P content as apatite and F content (Fig. 7) has a straight line, indicating that fluorapatite is present. Apatite is thought to exist mostly as fluorapatite since most of the coal samples contain enough F to form fluorapatite. The remainder of the F is believed to be organically bound.

The Cl content in the coal samples was less than 0.04%. Fig.8 shows Na versus Cl. Both inorganic and organic Cl appear to exist although the total Cl content is low. The correlation coefficients of Cl for Na, the other silicate related elements and ash are relatively high, suggesting that a certain amount of inorganic Cl is included in the coal samples. The correlation coefficient between Na and Cl increased with increasing Na-bearing clay mineral (smectite and/or I/S mixed-layer clay mineral) content, suggesting that inorganic Cl was incorporated into the coal seams by these clay minerals. Since the minimum Cl content was around 0.01% as the Na content approaches 0 (Fig. 8), at least up to about 0.01% of the Cl appears to be organically bound.

CONCLUSIONS

The major inorganic elements studied in the coal samples from the Ashibetsu district have been classified with respect to mineral sources. Si, Al, K, Ti and Na are associated with silicate minerals. K occurs as an interlayer cation in clay minerals. Mg is mostly associated with carbonate minerals and partly with clay minerals. Most of the Ca exists as calcite and ankerite, although part of the Ca exists as apatite. Fe was primarily found in carbonate minerals and pyrite. A minor fraction of the Al was associated with goyazite and boehmite. P occurs as fluorapatite and goyazite and Sr also occurs as goyazite. F exists not only as fluorapatite, but also appears to be organically bound. Cl also appears to exist in both inorganic and organic forms. Inorganic Cl is thought to be incorporated into the coal seams by clay minerals.

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Table 1 Frequency of mineral occurrence in coal samples containing less than 40% ash.

Coal seam	-600 m L					-695 m L		Total
	Torakawa	Torashita -sanshaku	No.10	Upper No.8	No.8	Torashita -nishaku	No.8	
Thickness (cm)	165	156	105	366	71	115	452	
Number of samples	10	6	9	12	8	9	20	74
Silicates								
Quartz	10	5	8	10	8	8	14	63
Plagioclase	9	0	1	0	1	0	1	12
Kaolinite	10	6	9	12	8	9	19	73
Illite	1	0	0	4	2	1	1	9
Illite/smectite mixed -layer clay minerals	5	0	0	4	2	1	1	13
Smectite	5	0	1	0	0	0	0	6
K-smectite	6	0	2	0	0	0	0	8
Chlorite	0	0	0	0	0	1	0	1
Carbonates								
Calcite	9	6	9	3	8	8	19	62
Aragonite	0	0	0	0	3	0	0	3
Ankerite	6	3	9	6	7	3	19	53
Siderite	2	2	0	2	3	1	5	15
Dolomite	0	0	0	3	0	0	0	3
Sulfides								
Pyrite	0	6	2	1	0	4	5	18
Marcasite	0	1	0	0	0	0	0	1
Sulfates								
Gypsum	0	6	2	0	0	0	1	9
Melanterite	0	1	0	0	0	0	1	2
Szomolnokite	0	0	0	0	0	0	1	1
Conquinbite	0	0	0	0	0	0	1	1
Roemerite	0	0	0	0	0	0	1	1
Hydronium jarosite	0	0	0	0	0	0	1	1
Phosphates								
Apatite	8	1	5	8	5	6	13	46
Goyatzite	2	0	0	5	3	3	4	17
Boehmite	1	0	0	1	5	5	12	24

Table 2 Correlation coefficients for coal samples containing less than 40% ash.

	Si	Al	K	Ti	Na	Mg	Fe	Ca	Sr	P	Cl	F	S
Ash	0.96	0.72	0.75	0.64	0.61	0.31	0.08	0.25	0.15	0.25	0.49	0.01	0.08
Si		0.61	0.72	0.57	0.58	0.25	0.09	0.18	0.03	0.11	0.49	0.02	0.05
Al			0.77	0.83	0.58	0.05	0.09	0.11	0.43	0.50	0.38	0.15	0.04
K				0.68	0.62	0.16	0.12	0.05	0.08	0.20	0.45	0.07	0.13
Ti					0.48	0.00	0.00	0.07	0.24	0.41	0.38	0.18	0.07
Na						0.16	0.13	0.03	0.12	0.22	0.66	0.26	0.13
Mg							0.26	0.63	0.15	0.13	0.11	-0.23	0.17
Fe								0.11	0.19	0.15	0.20	-0.17	0.81
Ca									0.09	0.17	0.12	-0.17	0.02
Sr										0.92	0.18	0.22	0.11
P											0.28	0.29	0.07
Cl												0.42	0.24
F													-0.17

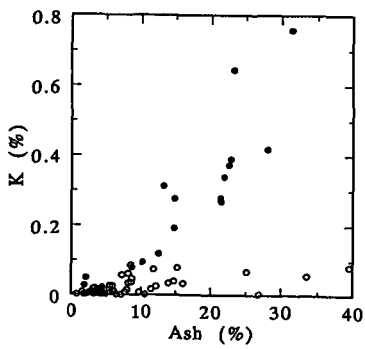

Fig. 1 Relationship between ash and K contents. Solid circle=coal samples containing K-bearing clay minerals.

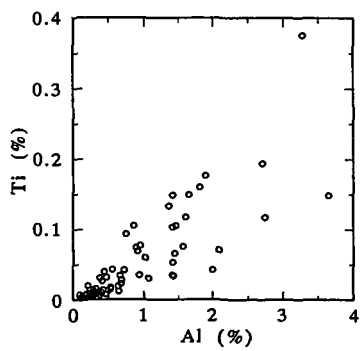

Fig. 2 Relationship between Al and Ti contents.

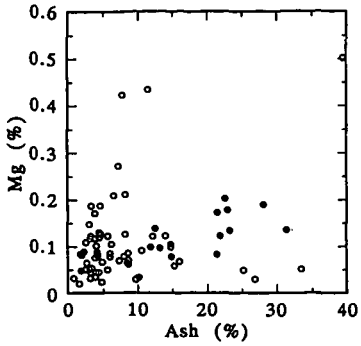

Fig. 3 Relationship between ash and Mg contents. Solid circle=coal samples containing Mg-bearing clay minerals.

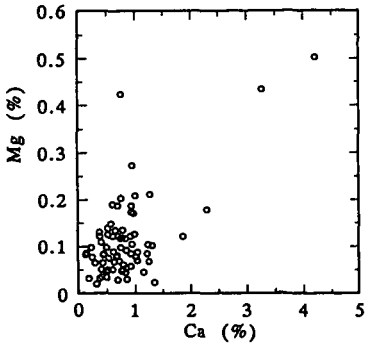

Fig. 4 Relationship between Ca and Mg contents.

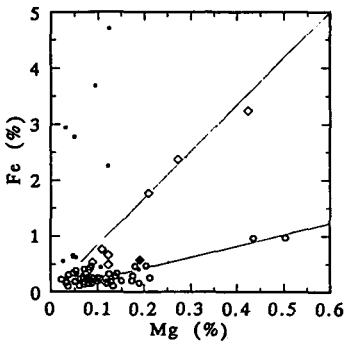

Fig. 5 Relationship between Mg and Fe contents. Solid circle, diamond, solid diamond, open circle=coal samples containing pyrite, both siderire and ankerite, both siderite and dolomite, and ankerite, respectively.

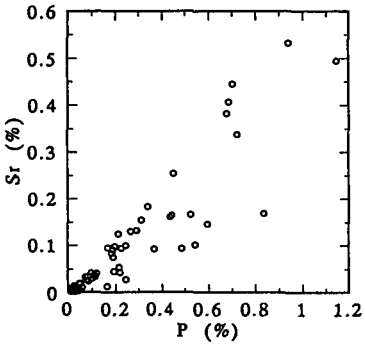

Fig. 6 Relationship between P and Sr contents.

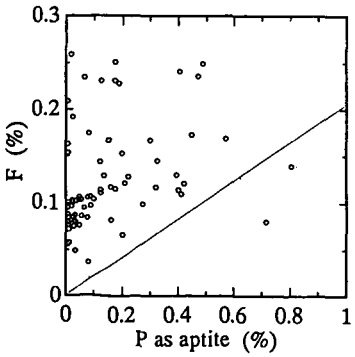

Fig. 7 Relationship between P content as apatite and F content. Solid line =F/P weight ratio of fluoroapatite.

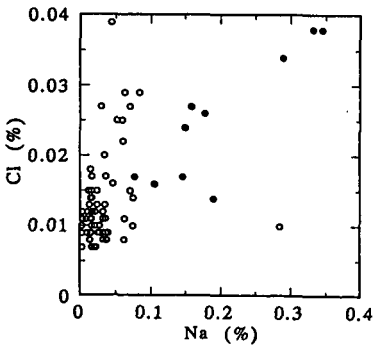

Fig. 8 Relationship between Na and Cl contents. Solid circle=coal samples relatively rich in Na-bearing clay minerals.