A geochemical study of the peat and soft-brown coal from the Zhenan basin, Western Yunnan, China

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ABSTRACT Little is known about the geochemistry of peat and soft-brown coal. The analytical chemical data of forty eight samples have been obtained for the peat and soft-brown coal in the Zhenan basin, western Yunnan.

Injection of continental detritus into the swamp is favourable for the degradation of plant remains and the formation of humic acid. The oxide compositions of the ash of the peat and soft-brown coal and their distribution-types have indicated that the continental detritus come from two kinds of parent rocks.

The Al_2O_3 and SiO_2 have a positive correlation with humic acid (Hmz), showing that the organic matter is advantageous to the formation of aluminosilicate mineral (mainly kaolinite, authigenic organic clay minerals).

The TiO_2 enrichment is mainly related to mineral materials. The Ge content in the peat and soft-brown coal ranges from $0.2 \sim 2.6 \times 10^{-6}$, and it is mainly bound to those minerals with Al_2O_3 and organic matters. The Ga content is from $2.3 \sim 19.1 \times 10^{-6}$, and it is associated with minerals that are MgO-bearing aluminosilicate minerals. The uranium ($0.3 \sim 4.9 \times 10^{-6}$) is mainly bound in the Ca-and Mg-bearing minerals. They are not enriched and not related to organic matter.

KEY WORDS peat soft-brown coal geochemistry

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1 Introduction

More recently, research on peat and soft-brown coal has been on the increase (Dickinson and Pugh, 1974; Van Geel, 1978; Teichmuller and Durand, 1983; Styon and Bustin, 1983; Jin and Qin, 1989; Cohen and Raymond et al., 1989; Rollins and Cohen et al., 1990.)[1~7], nevertheless, an adequate study has not been done on peat and soft-brown coal geochemistry so for (Shotyk and Nesbitt et al., 1990; Kumari, 1990; Shotyk and Wayne, 1992.)[8~10], and existing geochemical data of peat and soft-brown coal is poor; hence a fair degree of geochemical uncertainty exists. Knowing the geochemical characteristics of peat and soft-brown coal is important, not only for its utilization but also for understanding the theory of coal geology.

2 Geological setting and samples

2.1 Zhenan Basin and sediments

The Zhenan basin is a small intermountain fault basin. It formed in the Cenozoic era and its formation resulted from the collision of the India plate with the Sino-Korean plate. The Zhenan basin extents NNW-SSE (Fig. 1), and its length is about 9km and the width is from 0.9 to 2.5km (Zhong, 1991)[11].

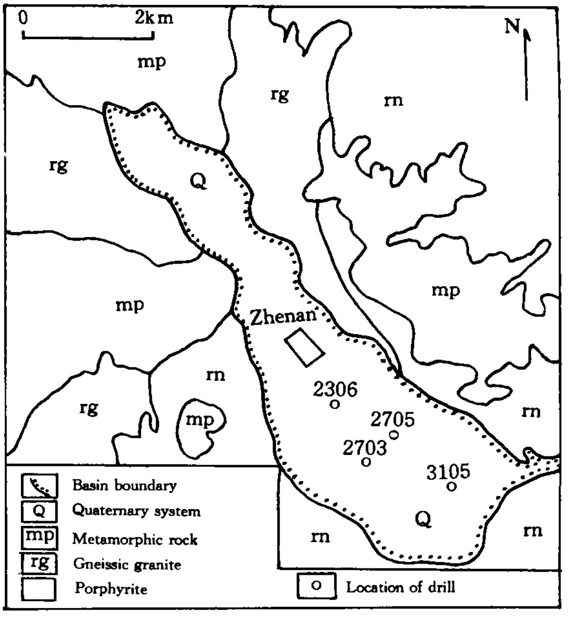

Fig. 1 Simplified geologic map of the Zhenan basin showing the location of the study drill holes

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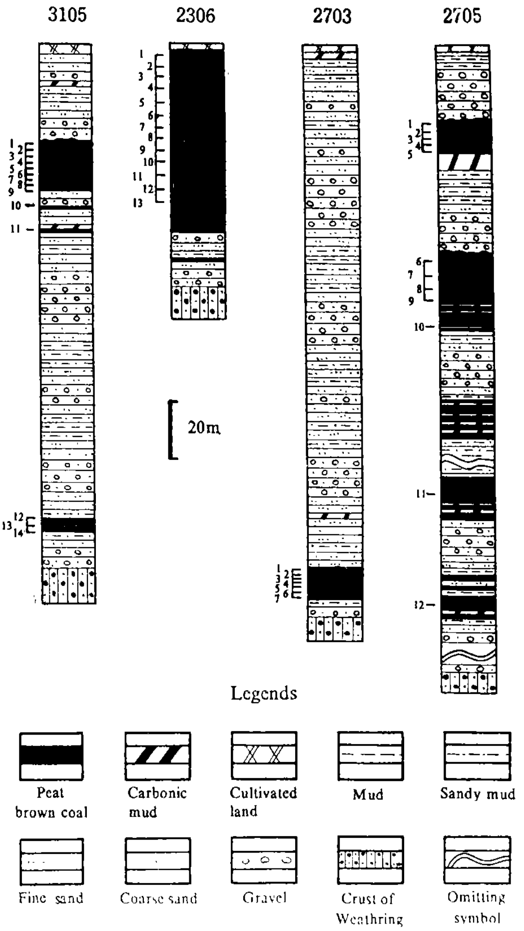

Fig. 2　Lithological logs of the studied drill holes and the position of collected samples

The basement of the Zhenan basin consists mainly of Mesozoic granite and Palaeozoic schist, on which were deposited the loose and semi-consolida-tion sediments of the Quaternary and Late Tertiary period. The sediment in thickenss is from 200 to 300 meters. The compositions of the sediments are mainly gravel, sand, mud, peat and soft-brown coal (Fig. 2). The gravels can often be seen in outcrops and drill holes, amounting to more than 25% of total sediments.

2.2　Peat and soft-brown coal

Most widespread in the Zhenan basin are peat and soft-brown coal that are formed mainly from herbs and woody plants. The peat is loose or poorly consolidated. The color of freshly exposed peat is yellowish brown to reddish brown. The peat has relatively abundant plant remains. The soft-brown coal, petrologically and chemically distinguishable from the peat, has become consolidated in a certain degree, having a dark orange color when freshly exposed and greyish black upon weathering (oxidation). Rarely are plant remains preserved in the soft-brown coal. All the technological and elemental analysis data are summarized in Table 1.

3　Analytical methods and results

The 46 samples used in this study were collected from 2306, 2703, 2705 and 3105 drill holes (figure 2) and the other two samples were collected from a peat outcrop. The analysis of the samples was accomplished by the laboratory of coal-exploration company of Yunnan Province. The major elements were analysed with the wet chemical technique. Ge, Ga, and U were determined by x-ray fluorescence. The results are given in Table 2.

Table 1　Technological and elemental analysis results from the peat and soft-brown coal in the Zhenan basin, western Yunnan

Types	Aad (%)	Wt (%)	Cdaf (%)	Hdaf (%)	Odaf (%)	Ndaf (%)	Sdaf (%)
Peat	15.11~54.98 28.37	65.59~405.58 93.35	56.26~65.00 61.71	5.10~7.02 5.61	27.75~38.97 32.21	0.98~1.76 1.24	0.13~0.29 0.23
Soft brown coal	8.92~48.95 27.91	30.61~65.00 51.36	65.00~68.25 66.60	5.12~6.49 5.61	22.65~33.37 26.13	0.87~1.54 1.22	0.18~0.25 0.21

Aad= ash, water free; Wt= total water; Cdaf= carbon, dry and ash free; Hdaf= hydrogen, dry and ash free; Odaf= oxygen, dry and ash free; Ndaf= nitrogen, dry and ash free; Sdaf= sulfur, dry and ash free.

Table 2 Geochemical data for the 48 samples of the peat and soft-brown coal in the Zhenan basin, western Yunnan

Sample	Aad (%)	Hmz (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	TiO_2 (%)	Ge ($\times10^{-6}$)	Ga ($\times10^{-6}$)	U ($\times10^{-6}$)
2705-1	34.29	76.04	58.41	10.42	20.59	2.57	1.55	1.39	0.6	7.3	0.9
2705-2	26.71	82.69	60.08	8.46	21.71	2.08	1.46	1.28	0.7	9.1	0.9
2705-3	31.71	86.65	58.03	10.66	21.22	2.81	1.47	1.26	0.9	7.6	0.9
2705-4	28.16	82.00	63.52	5.44	21.65	1.77	1.58	1.26	0.5	6.8	1.2
2705-5	25.56	75.00	62.58	5.01	21.98	1.58	1.26	1.39	0.5	5.8	1.0
2705-6	21.85	65.54	66.75	3.29	20.58	1.36	1.44	1.46	0.6	6.3	1.2
2705-7	22.42	63.13	67.12	3.15	21.96	1.80	1.45	1.44	0.5	6.2	1.2
2705-8	21.34	73.34	64.47	3.94	23.01	1.54	1.44	1.38	0.8	6.9	1.2
2705-9	23.91	73.98	64.36	4.12	22.88	1.72	1.54	1.37	0.7	5.8	1.1
2705-10	29.52	71.95	54.48	3.07	23.52	0.88	1.29	1.42	0.7	8.5	1.0
2705-11	23.99	68.05	67.46	4.65	22.06	1.30	1.41	1.44	0.5	6.7	1.2
2705-12	34.38	62.43	64.85	6.53	20.78	1.39	1.55	1.36	0.6	9.3	0.9
3105-1	29.30	71.34	67.68	4.26	20.84	2.78	2.16	1.48	0.5	8.9	2.9
3105-2	35.33	72.99	65.53	2.98	22.82	1.55	1.94	1.38	0.2	11.9	1.2
3105-3	22.91	66.51	66.50	3.04	22.12	1.77	1.98	1.46	0.6	10.7	2.3
3105-4	31.13	80.18	66.93	2.38	22.46	1.29	1.86	1.51	0.2	10.5	1.6
3105-5	22.94	70.19	64.64	2.11	22.10	1.22	1.56	1.49	0.8	10.9	1.7
3105-6	34.95	78.69	65.95	2.33	23.36	1.11	1.65	1.54	0.6	12.5	1.3
3105-7	29.86	80.67	65.89	1.75	22.22	1.42	1.51	1.48	0.4	9.8	2.1
3105-8	30.54	81.73	64.79	2.12	22.90	1.83	1.93	1.44	0.5	10.80	1.8
3105-9	31.08	86.34	58.34	2.56	26.11	2.73	2.00	1.29	0.7	10.5	2.6
3105-10	39.78	50.85	60.42	3.00	23.66	3.24	2.29	1.04	0.9	11.6	1.4
3105-11	21.35	44.25	56.92	4.56	19.84	6.27	2.28	1.16	2.6	5.8	2.6
3105-12	25.32	58.67	70.69	4.71	10.50	6.04	1.74	1.16	0.5	5.3	3.3
3105-13	15.11	47.27	57.78	7.44	15.52	9.92	2.90	1.30	0.4	3.4	4.9
3105-14	19.04	45.81	57.48	6.03	19.79	6.16	2.06	1.14	0.8	6.1	1.8
2306-1	54.98	74.26	59.06	3.98	27.36	0.43	1.12	1.23	1.7	19.1	2.7
2306-2	35.87	69.92	60.86	5.80	24.30	1.11	1.36	1.39	1.2	8.8	4.2
2306-3	45.52	74.00	63.92	5.60	21.53	0.96	1.40	1.38	0.4	11.5	0.3
2306-4	23.30	63.23	63.28	8.36	18.14	1.88	1.58	1.60	0.3	5.5	0.9
2306-5	39.21	68.62	65.34	5.13	20.19	0.96	1.48	1.44	0.9	9.4	1.9
2306-6	39.73	75.32	65.77	5.00	21.61	0.68	1.34	1.40	0.8	10.0	1.9
2306-7	43.04	66.39	67.72	4.44	21.54	0.45	1.32	1.37	0.4	10.4	0.7
2306-8	33.30	61.90	64.60	4.38	18.52	0.45	1.27	1.16	0.3	8.4	1.5
2306-9	33,95	70.38	63.96	5.23	19.27	0.70	1.08	1.43	0.7	8.9	2.1
2306-10	29.43	72.35	60.58	5.08	20.54	0.77	1.37	1.48	0.5	7.4	2.1
2306-11	32.05	69.41	65.20	4.70	25.91	0.64	1.52	1.11	0.4	9.4	4.6
2306-12	30.97	79.18	65.20	4.90	20.72	0.86	1.30	1.48	0.2	7.1	2.5
2306-13	37.55	65.54	62.58	5.08	20.34	0.84	1.28	1.49	0.8	9.5	2.6
2703-1	34.04	49.46	63.32	5.34	20.42	1.78	1.26	1.49	0.9	11.8	2.4
2703-2	31.57	60.32	61.43	4.07	23.10	1.18	1.23	1.66	0.7	12.0	2.1
2703-3	25.50	57.26	59.87	5.04	23.28	1.73	1.44	1.82	0.9	9.9	3.4
2703-4	33.27	77.01	63.74	3.53	24.98	1.02	1.22	1.30	0.8	9.8	1.1
2703-5	35.26	77.23	63.52	6.37	20.47	1.70	1.70	1.32	0.9	10.8	1.0
2703-6	27.67	73.39	61.26	4.98	24.80	1.54	1.54	1.18	0.9	10.9	0.7
2703-7	16.10	73.00	57.27	5.63	26.44	1.20	1.37	1.48	1.0	7.5	0.9
E-1	35.54	77.15	67.98	4.97	20.92	0.99	1.28	1.40	0.9	2.3	0.8
E-2	20.72	70.46	66.90	4.07	21.66	0.98	1.52	1.39	0.8	6.1	2.6

Aad- ash, water free; Hmz- humic acid, dry and ash free; Oxides except P_2O_5, As_2O_3 and SO_2

Table 3 Test results of the Aad, Hmz, Ge, Ga, U and oxides of the peat and soft- brown coal from the Zhenan basin

		Aad	Hmz	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	Ge	Ga	U
	X test	1	1	0	0	0	0	0	1	1	1	1
ND	K test	1	0	0	0	0	0	0	1	1	1	1
	r_1, r_2 test	1	0	1	0	0	0	1	1	1	1	1
	X test	/	/	0	1	0	0	0	/	/	/	1
LND	K test	/	0	0	1	0	0	0	/	/	/	1
	r_1, r_2 test	/	0	1	1	0	0	0	/	/	/	1

1= Obey, 0= Not obey, /= Not tested, ND= Normal distributions, LND= Lognormal distributions

4 Discussion

4.1 The distribution features and experiment significances of Aad, Hmz, Ge, Ga, U, and oxides

The distribution types of Aad, Hmz, Ge, Ga, U and oxides have been tested with 3 testing methods. The results are in Table 3.

Table 3 indicates that the Aad, TiO_2, Ge, Ga, and U are normally distributed, and the Fe_2O_3 is lognormally distributed, and the Al_2O_3, Hmz, CaO, MgO and SiO_2 are neither distributed normally nor lognormally.

According to our consideration, the Aad normal distribution suggests that this peat-forming environment was relatively stable. From this, we can recognize that although the Zhenan basin was located in tectonic-mobil region and influenced by tectonic movements during the peat-forming process (gravel, sand, mud, peat and soft-brown coal occur alternately and frequently), the overall background of the basin changed only infrequently. The lack of a distribution fit for the Hmz may be related to the communities and characteristics of the peat-forming plants and types of deposition. If the peat is rich in allochthonous plant remains, especially oxidized plant remaines, the amount of Hmz would be less. The normal distributions of TiO_2, Ge, Ga and U indicate that these elements and TiO_2 in the parent rocks are relatively uniform. The lack of distribution fits for SO_2, Al_2O_3, CaO and MgO may show that these oxides in the parent rocks (granite and schist) were not uniform. When the ditritus comes mainly from the granite, the SiO_2 content will be higher than if the ditritus comes from the schist; this makes the SiO_2 distribution bimodal. It is necessary to point out that some of the SiO_2 and Al_2O_3 is formed in cliagenesis. This can be fully proved by observing the thin or block sections under microscopy. We can observe a large number of clay minerals often filling in the remained cell oval.

4.2 Factor analysis

In order to obtain a clear picture of the relationship between the variables, the analytical data were subjected to factor analysis. This is a very useful technique for sorting variables (i. e. the individual elements) into groups, the purpose being to reduce the original 11 components to a smaller number of varibles (factors), each comprising elements vary in a smaller way to one another. The calculation has shown that when we select the first 6 major components (Table 3), the percent of communal factors variance distribution is over 85%, so we think that the first 6 major factors contain much more of information than the other variables. This relatively small number of new variables can then be handled and visualised more easily than the large number of original variables, thereby make 6 main components to obtain varimax rotated factor matrix (Table 4).

4.2.1 Factor 1 (Aad, Ga)

Factor 1 has strong positive loadings for Aad and Ga. This shows that the Ga has some genetic relationship with Aad.

Goldschmidt (1944) gave 0.4% as the maximum Ga content in coal ash (the Ga abundance is 18×10^{-6} in earth crust). It is evident that the Ga content in the coal reported by Goldschmidt is much higher than the Ga crustal aboundance, and other vesearchers have discovered that the Ga is chiefly enriched in the vitric component. The investigation of the peat and soft-brown coal in the Zhenan basin led to the conclution that the Ga is obviously bound to mineral components (in Table 4, the Ga has a strong positive loading with Aad), and that the mineral components seem to be aluminosilicates. This conclusion supports Bouska′s (1981) opinion that the Ga is mainly contained in the aluminosilicate minerals and is opposite to that of Otte (1953)[12,13]. Of course, from Table 1, we know that the Ga in the peat and soft-brown coal has not been enriched, and its content is near to the crustal abundance. It is certain that, in coalification, the organic material (mainly humic and fulsic acid) can absorb gallium from the groundwater or other mineral material surrounding the peat, brown coal or coal; if not, the maximum Ga amount in some coal would not be so high.

4. 2. 2 **Factor** 2 (**TiO_2, SiO_2, Hmz**)

Table 4 has shown that Factor 2 has relatively strong positive loadings for TiO_2 and SiO_2 and a weak positive loading for Al_2O_3 and Hmz. The above phenomenons tell us that the TiO_2 has some relationship with SiO_2, Al_2O_3 and Hmz.

Table 4 Varimax rotated factor matrix for a 6- factor model explaining 85% of the total variables

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Aad	0.9730	-0.1105	-0.1253	-0.0505	0.0107	0.1447
Hmz	0.1104	0.1172	-0.0202	0.1181	-0.1962	0.9598
SiO_2	0.1419	0.3467	0.5513	-0.6747	-0.2404	0.2066
Fe_2O_3	-0.0476	-0.0597	-0.9852	-0.0599	-0.1361	0.0389
Al_2O_3	0.2847	0.0678	0.1923	0.8610	-0.1801	0.3218
CaO	-0.5432	-0.5402	-0.0260	-0.1658	0.4803	-0.4049
MgO	-0.4177	-0.6071	0.2971	-0.0260	0.5828	-0.1893
TiO_2	-0.1077	0.9727	0.1179	0.1652	0.0332	-0.0034
Ge	0.0177	-0.9320	-0.0827	0.3139	0.0748	-0.1419
Ga	0.8799	-0.0582	0.3613	0.3026	-0.0009	-0.0180
U	0.0689	0.0051	0.0596	-0.0248	0.9824	-0.1643

Some researchers (Jones and Miller, 1939) found that the vitrain from Northumberland England contained an extraordinary amount (7.0%~24.3%) of TiO_2 in coal ash, when there was a small content of ash matter[14]. Reynolds reported 9.2%~15.0% TiO_2 (in ash) with 1.6 to 1.9% ash content from the Peacock seam. Other researchers also discovered that the TiO_2 content in coal was higher than that of other common rocks (on the average, 1.39% TiO_2 in granite and 0.2% in shales, with the Ti abundance in the crust being $6\,400\times10^{-6}$). Table 3 gives the average TiO_2 content in the peat and soft-brown coal is 1.39%. There for, we can make the conclusion that the Ti is evidently enriched in some coals and not enriched in the peat and soft-brown coal in the Zhenan basin. The cause of the Ti enrichment seems to be related to organic matter. This tendency has not been found in the peat and soft-brown coal in the Zhenan basin (Factor 2 only has weak loading for TiO_2 and Hmz, but a strong positive loading with SiO_2). These phenomena suggest that the enrichment of TiO_2 in coal occurs mainly in coalification and not in peatification.

4. 2. 3 **Factor** 3 (**SiO_2, MgO, Al_2O_3, Ga**)

Factor 3 shows relatively strong positive loadings for SiO_2, MgO, Al_2O_3 and Ga.

The phenomenon above tells us that the Ga is genetically related to the minerals with SiO_2, MgO and Al_2O_3. Goldschmidt thought the Ga^{3+} had relatively tight relationship with Al^{3+} and, the Ga^{3+} was mainly bound in Al-bearing minerals. We think that the Ga is probably bound in the MgO-bearing alumosilicates, which seems to be montmorillonite. It is possible that the Ga is absorbed by the gel of MgO, Al_2O_3 and SiO_2.

There are many reports which tell us that Ga is often enriched in coal. Goldschmidt (1944) reported 0.4% as the maximum Ga content in coal ash. Otte (1953) determined 0.1% Ga in ash from the coal of the Katharina seam (Ruhr Basin). Generally speaking, the Ga content in coal or brown cool ranges from a few tens to a few hundreds $\times 10^{-6}$. Bouska et al. thought that the Ga was associated rather with the clayey rock than with the coal itself. Consistent with their conclusion is our result of the present study.

4.2.4 **Factor** 4 (**Al_2O_3, Ge**)

In Table 4, Factor 4 has relatively positive loadings for Al_2O_3 and Ge. The studies of germanium in coal started long ago, and in 1930, Goldschmidt discovered that coal ash contains a major amount of germanium. Since then, many researchers have given their attention to the economic value of gernamium in coal. Goldshmidt (1930) determined the maximum concentration in coal ash to be 1.1% and gave 0.05% Ge in coal ash as mean value (for the data available to him at that time). Nevertheless, the Ge amount in the crust is only $4\sim7\times10^{-6}$. On comparing the Ge values reported by Goldschmidt with the Ge crustal value, the Ge in coal was enriched 1 600~2 800 times. Germanium is generally believed to have accumulated in the coal. Most investigators believe that germanium is chiefly bound to organic and not inorganic components and its concentration is related to the absorption capacity of the coal matter (Bouska, 1981). Nevertheless, opposite to common opinion, in the peat and soft-brown coal from the Zhenan basin, the Ge enrichment is not evident and is almost always lower than that of the crust. In Table 4, the Ge has a considerably weak positive correlation with Hmz, so it is difficult to believe that the Ge in the peat and soft-brown coal has any relationship with organic matter. The fact also reveals that the enrichment of germanium in coal occurs mainly in the process from peat to bitumin coal and is related to the absorption by organic matter of the germanium by way of complexing and /or chelation.

4.2.5 **Factor** 5 (**U, CaO, MgO**)

Factor 5 has relatively strong positive loading for U, CaO and MgO and weak negative loading for U and Hmz. This phenomenon indicates that the uranium is chiefly bound to minerals with CaO and MgO, and its genesis is not closely tied to organic matters.

Moore (1954) found that coal possesses a high absorption capacity for uranium[15]. Hoffmann (1943) recorded the U content in peat as 1×10^{-6}, as 3.3×10^{-6} in brown coal, and as 3.72×10^{-6} in bituminous coal, and he proposed a model that the U content increases with increasing coal rank[16], but many investigators thought that those values had been surpassed in many cases. Nevertheless, it has been widely accepted that uranium is enriched in coal organic matter. Many recent studies have proved that the genesis of a large number of uranium ores are, more or less, related to organic material. The absorption properties of organic material (e.g., humic acid and fulvic acid) are favourable for the enrichment of uranium.

In the Zhenan basin, nevertheless, U enrichment is not so evident, and the U content in the peat and soft-brown coal varies from 0.3 to 12.3 $\times10^{-6}$, and averages 2.18×10^{-6} (1.7×10^{-6} U in the crust and 3.5×10^{-6} U in the granite). From Table 4, we see that in Factor 5 there is weak negative loading for U and Hmz, which shows that the organic matter in the peat and soft-brown coal have evidently not absorbed uranium, and their uranium content in the Zhenan basin is even lower than that of granite ($2.13\sim24.58\times10^{-6}$) in the Zhenan basin. This leads to an opposite result to the common view. In contrast, the uranium is mainly bound to the inorganic components, especially those with CaO and MgO. These inorganic components are assumed to be some clay minerals (e.g., montmorillenite). The studies of the relationship between uranium, minerals and organic matter suggest that the U enrichment in the coal might occur during coalification (mainly from peat to bituminous coal).

4.2.6 **Factor** 6 (**Hmz, Al_2O_3, SiO_2, Aad**)

Factor 6 has positive loading for Hmz, Al_2O_3, SiO_2 and Aad, and a weak negative loading for the other variables (CaO, MgO, etcetera). This tendency suggests that the Hmz has some connection with Aad, Al_2O_3 and SiO_2.

As we know, humic acid is formed by means of bacterial degradation of plant remains. The influencing factors to bacterial degradation are mainly the availability of fresh water and oxygen, which is capable of reducing swamp acidity and is favourable for bacterial activity. The amount of Aad could indirectly reveal the availability of fresh water and oxygen when peat is forming, because mineral material (Aad) is carried into the swamp by running water. The running water also brings oxygen into the swamp. This phenomenon shows that the more mineral material present in the deposit, the more the humic acid. The positive correlation between Hmz and SiO_2 and Al_2O_3 is displayed through the clay minerals, mainly kaolinite. Using microscopy we can see that the cell cavity remaining is often filled with clay minerals. This phenomenon also shows that the humic acid is beneficial to the formation of clay mineral, which results mainly from the absorption of humic acid of the SiO_2 and Al_2O_3 gels.

5 Conclusion

The drilling projects and widespread outcrops in the Zhenan basin offer the best opportunity to examine the samples of the peat and soft-brown coal. From our 48 samples we can make conclusions as summarized below:

(1) The oxide percentages and their distribution types suggest that the mineral components in the peat and soft-brown coal in the Zhenan basin do not come from one kind, but the two kinds of parent rocks (granite and schist),

(2) Injection of ditritus is favorable for the degradation of plant remains and the conversion of plant remains to humic acid,

(3) The possitive correlation between Aad and humic acid indicates that inorganic material is beneficial to the formation of "organic clay", and this can be used to interpret why there are a great number of small clay particles in the microscope cell cavities remaining in huminites,

(4) The TiO_2 in the peat and soft-brown coal is not evidently enriched, and is bound mainly to the mineral components. A positive correlation between TiO_2 and organic matters (Hmz) is not evident,

(5) The Ge in the peat and soft-brown coal is contained chiefly in the mineral components with Al_2O_3 and has a weak positive correlation with organic matter (humic acid),

(6) The Ga in the peat and soft-brown coal is also bound mainly to the mineral components where montmorillonite appears to be the main carrier, and

(7) The U is combined mainly in minerals with CaO and MgO.

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