

Experimental study on the interaction between peat, lignite and germanium-bearing solution at low temperature

QI Huawen^{1,2}, HU Ruizhong¹ & QI Liang¹

1. Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China;

2. Department of Earth Science, Nanjing University, Nanjing 210093, China

Correspondence should be addressed to Qi Huawen (email: qihuawen@sina.com)

Received December 30, 2003; revised December 24, 2004

Abstract The interaction between peat, lignite and germanium(Ge)-bearing solution with an initial Ge concentration of 5 mg/L was studied at 25 100 and at pH 2.96 12.08. The results show that the apparent transfer ratios of peat and lignite for Ge in the solution were positively correlated with temperature in acid environment (initial pH=2.96), and the ratios (up to 86.5%) of lignite were obviously higher than those (up to 58.5%) of peat, but the organic transfer ratios of lignite were lower than those of peat. The activation energy values for interaction between peat, lignite and Ge-bearing solution are 30.96 and 15.67 kJmol⁻¹, respectively. The strong acid (initial pH=2.96) and the strong alkaline (initial pH=12.08) environment contribute to the transfer of Ge in the solution. At 4 < pH < 10, the influences of pH on the interaction between peat and Ge-bearing solution are not significant, while weak acid environment (initial pH=6.38) conduces to the transfer of Ge into lignite. The interaction between peat, lignite and Ge-bearing solution are mainly attributable for the complexation of Ge with organic substrate. The experimental results from this study provide direct experimental evidence for the hydrothermal sedimentary genesis of abnormal enrichment of Ge in coal.

Keywords: low temperature, peat, lignite, Ge⁴⁺, complexation.

DOI: 10.1360/02yd0565

Since Goldschmidt discovered unexpectedly high concentration of Ge in coal in 1930^[1], many researchers have studied the characteristics of Ge-bearing coal, the existing form or mode of occurrence and the distribution characteristics of Ge in coal^[2-13], but little was known about the pathway and the physical-chemical conditions of Ge entering the coal^[7]. Although Ge exists mainly in the organic form in coal^[8,9], the organic Ge in natural water is stable and does not participate in the geochemical cycle of Ge^[14]. Along with the intensive studies on the geochemical behavior of Ge in the hydrothermal systems in middle ocean

ridges and the continental geothermal systems^[15-17], the solubility of tetrahedral GeO₂^[18-20], and the geochemical studies on several typical Ge-rich coal deposits, such as the Ge-coal deposit in Eastern Russia^[5], the Lincang Ge deposit and the Wulantuga Ge deposit^[6-13], more and more evidences have shown that the interaction between inorganic Ge rich hydrothermal solution and the coal seams is the main factor controlling the abnormal enrichment of Ge in coal, with the coupling effect of various metallogenic factors^[5,6,11,12]. The findings from the above-discovered superlarge Ge deposits have shown that Ge occurs

mainly in the lignite with low maturity. Therefore, the experimental studies on the interaction between peat, lignite and Ge-bearing solution are significant for revealing the mechanism of the abnormal enrichment of Ge, even the formation of independent Ge deposit in coal.

1 Experimental material and procedure

The peat and lignite samples were collected from Yunnan and Guizhou, and the sampling location, the $R_{0,max}$ and the elemental analysis results are listed in Table 1. Considering the solubility of tetrahedral GeO_2 in the solution varying from 0.6 to 9.9 mg/L at 25 °C [18], the initial Ge concentration (C_0) of the Ge-bearing solution was selected at 5 mg/L, closer to the natural geological condition. Market sold amorphous GeO_2 with purity of 99.99% was dissolved into rare HCl solution, then the solution was diluted until $C_0=5$ mg/L Ge was obtained from the diluents. The initial pH values (pH_0) of the prepared Ge-bearing solution were adjusted by adding rare NaOH solution, and were determined by pH-2C exact acidity meter (error <0.02). All the interactions were conducted in a constant temperature box and PTFE or Teflon vessels sealed with stainless steel cannulas.

0.5 g peat and lignite ground samples (meshed <63 μm) were put into PTFE vessels, to which 10 mL Ge-bearing solution was added, and then PTFE vessels were sealed with stainless steel cannula, and were put into a constant temperature box after the samples and the solutions were mixed well. After the samples and the solutions have been reacted at different temperatures with various durations, the vessels were taken out, and the residual solutions were filtrated and the residua of peat and lignite were washed for several times, then the filtrate and the lotion were switched into a 50 mL volumetric flask. The residual Ge concentrations in the solution were analyzed by ICP-MS using In as inner standard, and the analytical precision

is better than 5%. The apparent transfer ratios for Ge and the kinetic parameters were calculated.

2 Experimental results

2.1 Kinetic parameters

The pH values of the peat forming environment of the domical modern woody peat in Southeast Asia varies from 2 to 5 [21], thus the pH_0 of the Ge-bearing solution was selected to be 2.96. The results of the interaction between 10 mL Ge-bearing solution and 0.5 g peat or lignite, at $pH_0=2.96$, $T=25-100$ °C, and $C_0=5$ mg/L, show that the apparent transfer ratios (ATR) of peat and lignite for Ge in the solution are positively correlated with temperature; and the interaction durations are positively correlated with the reciprocal of the residual Ge concentration in the solution (Table 2, Figs. 1 and 2). Many studies have shown that Ge mainly exists in the organic component of coal [3,8,9]. Suppose that C, H, O, N and S occur in the organic form in the determined peat and lignite samples, the calculations of the organic transfer ratio (OTR) indicate that, the ATRs of lignite were higher than those of the peat, but their OTRs were lower than those of the peat and the diversity enhanced with the increase of temperature (Table 2). The results of various quantities of lignite in the solution, at $pH_0=2.96$, $T=75$ °C and $C_0=5$ mg/L with a duration of 60 h, indicate that the ATRs of lignite for Ge are positively correlated with its quantities (Table 2).

According to the classical kinetic theory, the interaction between Ge^{4+} and the organic substrate should be described by the following expression:

$$d[Ge^{4+}]/dt = -k \cdot [Ge^{4+}]^\alpha \cdot [OM]^\beta, \quad (1)$$

where k represents the rate constant of the reaction at a given temperature and α and β represent respectively the partial orders relative to Ge^{4+} and the organic substrate (OM). $[Ge^{4+}]$ represents the residual Ge^{4+} con-

Table 1 The elemental analysis results of the peat and lignite samples (%)

Sample No.	Location	$R_{0,max}$	Rank	N	C	S	H	O	Moisture	Ash	Total
SC-18	Weining County in Guizhou	0.26	Peat	0.54	21.75	0.20	2.11	7.36	6.00	57.58	95.54
ZT-20	Zhaotong County in Yunnan	0.37	Lignite	1.26	44.44	0.54	3.44	14.61	12.73	20.73	97.75

Table 2 The results of the interaction between 0.5 g peat, lignite and Ge-bearing solution at $\text{pH}_0=2.96$, $T=25-100$ and $C_0=5$ mg/L

$T/$	t/h	Peat			Lignite		
		C	ATR ^b (%)	OTR ^c / $\mu\text{g}\cdot\text{g}^{-1}$	C	ATR (%)	OTR/ $\mu\text{g}\cdot\text{g}^{-1}$
25	12	4.44	11.2	33.5	3.85	23.0	35.0
	24	4.26	14.9	44.5	3.55	29.0	44.1
	36	4.15	17.1	51.1	3.36	32.9	50.0
	48	3.85	23.0	68.8	3.28	34.5	52.5
	60	3.83	23.5	70.0	3.23	35.5	54.0
50	12	3.78	24.5	73.2	3.07	38.7	58.8
	24	3.47	30.6	91.5	2.66	47.3	71.9
	36	3.26	34.9	104	2.49	50.3	76.5
	48	3.05	39.0	117	2.40	52.0	79.1
	60	2.90	42.0	126	2.34	53.3	81.0
75	12	3.30	34.0	102	2.39	52.3	79.5
	24	2.83	43.5	130	1.82	63.7	96.9
	36	2.64	47.2	141	1.60	68.0	103
	48	2.51	49.8	149	1.40	72.0	109
	60	2.48	50.5	151	1.34	73.3	111
100	12	2.98	40.5	121	1.86	62.9	95.6
	24	2.64	47.2	141	1.17	76.7	117
	36	2.30	54.1	162	0.92	81.6	124
	48	2.26	54.9	164	0.84	83.3	127
	60	2.08	58.5	175	0.68	86.5	132
75	60	0.1g lignite + Ge-bearing solution			3.90	22.1	33.6
	60	0.2g lignite + Ge-bearing solution			3.24	35.3	53.7
	60	0.3g lignite + Ge-bearing solution			2.41	51.8	78.8

C , The residual Ge concentration in the solution (mg/L); $\text{ATR} = (C_0 - C)/C_0 \times 100\%$; $\text{OTR} = [(C_0 - C) \times 10] / [0.5 \times ((C + H + O + H + S)/\text{Total})]$.

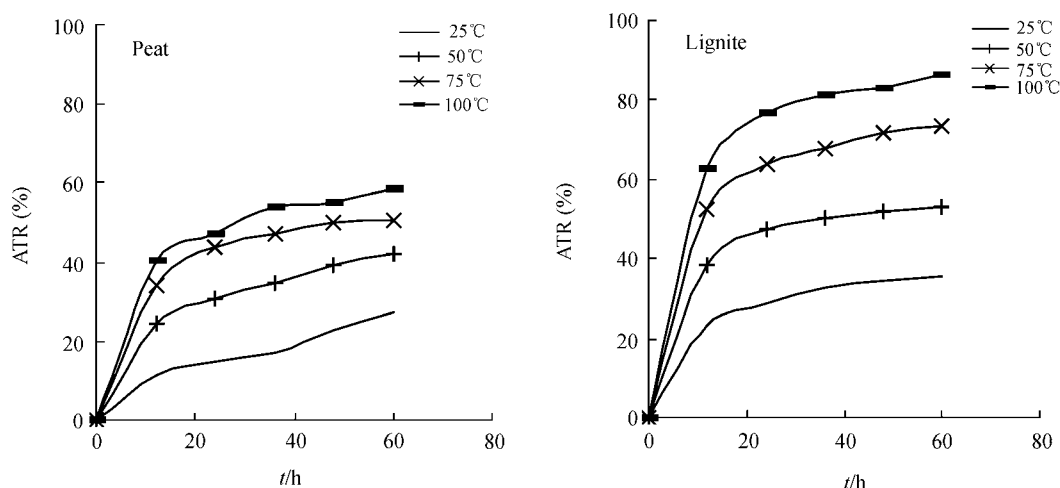


Fig. 1. The apparent transfer ratio (ATR) of the peat and lignite for Ge in the solution, as a function of duration, at $\text{pH}_0=2.96$, $C_0=5$ mg/L and $T=25-100$.

centration in the solution with various durations. [OM] represents the amounts of the organic substrate with various durations. The amount of organic substrate is abundant with respect to Ge^{4+} ions, and the consumption of organic substrate during the reaction can be neglected, so [OM] equals $[\text{OM}]_0$. The rate constant

can be

$$k_{\text{app}} = k \cdot [\text{OM}]_0^\beta \quad (2)$$

In this case, k_{app} is an apparent (or conditional) constant.

At a given temperature, the experimental results show a linear increase of the reciprocal of Ge^{4+} ions as a function of time for the four temperature values considered, indicating that the partial order (α) with regard to Ge^{4+} is equal to 2. After integration, eq. (1) can be rewritten as

$$1/[\text{Ge}^{4+}] - 1/[\text{Ge}^{4+}]_0 = k_{\text{app}} \cdot t, \quad (3)$$

where $[\text{Ge}^{4+}]_0$ represents the initial Ge^{4+} concentration in the solution. Eq. (3) shows that, the slope of linear equation of the reciprocal of $[\text{Ge}^{4+}]$ as a function of duration equals to the k_{app} of the reaction at a given reaction system and temperature (Fig. 2).

At constant temperature (75 in this case), the partial order β can be determined by the reaction with various amounts of the organic substrate. Eq. (2) can be transformed in the logarithmic way:

$$\log k_{\text{app}} = \beta \log[\text{OM}]_0 + \log k. \quad (4)$$

Equation (4) shows that $\log k_{\text{app}}$ is positively correlated with $\log[\text{OM}]_0$ and the slope equals the partial order β . The values of $\log k_{\text{app}}$ and $\log[\text{OM}]_0$ of different reactions with various amounts of organic substrate were calculated from eq. (3), and a value of 1.18 for β was calculated from these results. Considering the analytical error and β should be an integer, β was chosen to

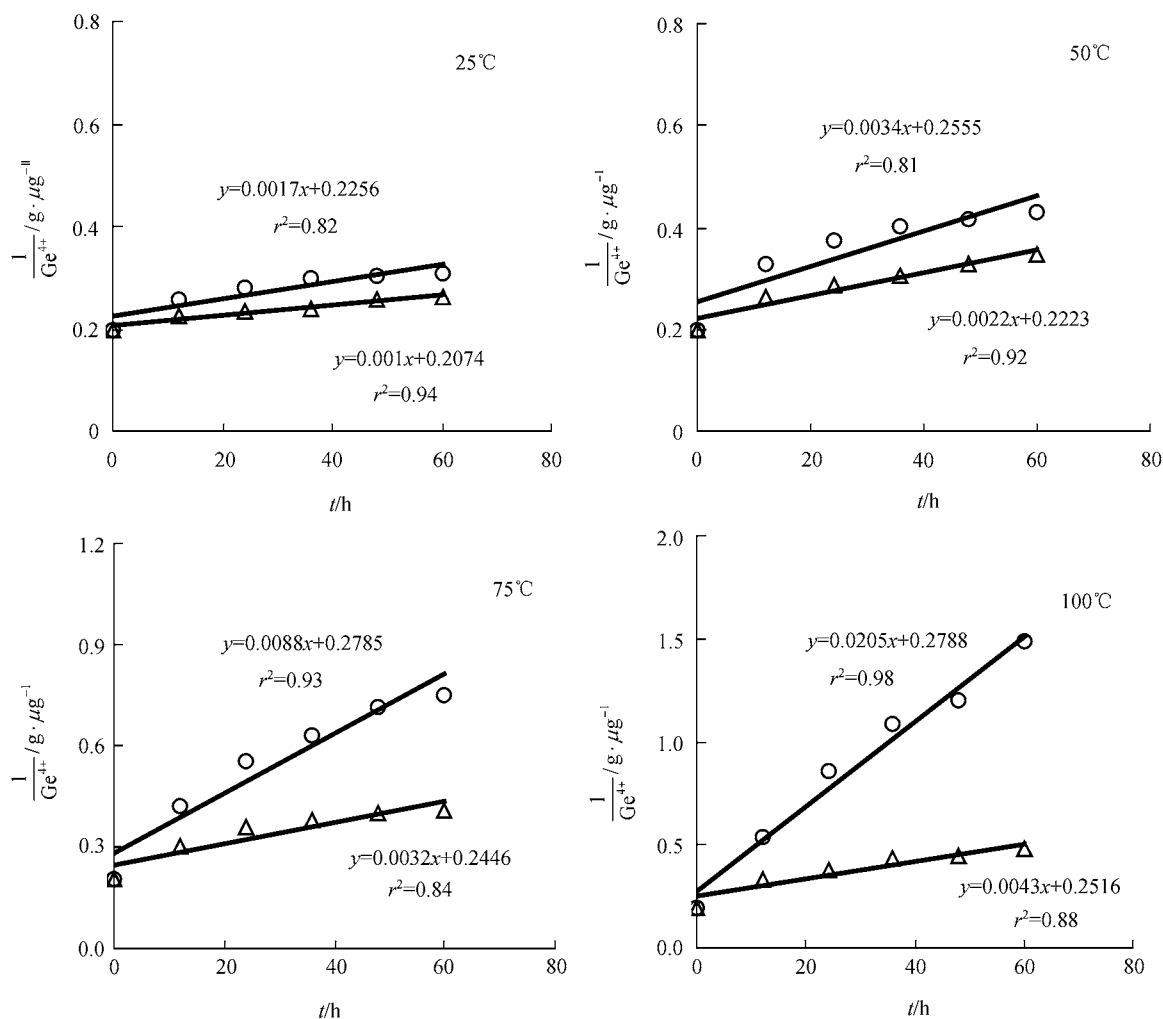


Fig. 2. The reciprocal of residual Ge concentration in the solution ($1/\text{Ge}^{4+}$), as a function of duration, at $\text{pH}_0=2.96$, $C_0=5$ mg/L and various temperatures. Blank cycles refer to lignite and blank triangle to peat.

be equal to 1.

According to the Arrhenius equation,

$$k_{\text{app}} = Ae^{-E/RT}, \quad (5)$$

where A is a constant, and $\ln A$ was selected to be another constant (C). Then, eq. (5) can be rewritten as

$$\ln k_{\text{app}} = C - E/(RT), \quad (6)$$

where E is the activation energy, R is the gas constant ($8.32 \text{ JK}^{-1} \text{ mol}^{-1}$), and T is the temperature (K). Eq. (6) shows that $\ln k_{\text{app}}$ is linearly correlated with $1/T$, and the slope in Fig. 3 equals $-E/R$. Then

$$E = -(\text{slope}) \cdot R. \quad (7)$$

The apparent rate constant (k_{app}) and the activation energy (E) of the interaction between peat or lignite and Ge^{4+} in the solution, with various temperatures, were calculated using the above methods, and the results are listed in Table 3.

2.2 pH and ATR of Ge in the Ge-bearing solution

At 75 °C, various initial pH values (pH_0) and a duration of 60 h, the results (Table 4 and Fig. 4) of the interactions of 0.5 g peat, lignite and 10 mL Ge-bearing solution ($C_0=5 \text{ mg/L Ge}$) show that strong acid ($\text{pH}_0=2.96$) and strong alkaline ($\text{pH}_0=12.08$) contribute to the transfer of Ge in the solution; at $4 < \text{pH} < 10$, the influences of pH on the interaction between peat and Ge-bearing solution are not significant, while weak acid ($\text{pH}_0=6.38$) conduces to the transfer of Ge into lignite.

3 Discussions

In order to explain the anomalously high amounts of some trace elements in black shale, peat, coal and petroleum, it is commonly thought that there are three kinds of mechanisms, biological processes, complexation and reduction, for the concentration of trace element, such as germanium, uranium, gold, zinc, etc., in organic substrate^[1].

Plants apparently absorb and concentrate Ge from both the air and the soil, but superfluous Ge will inhibit the growth of the plants and even produce poisonous effect^[3]. The distribution of Ge in coal is uneven whether in cross or longitudinal directions^[5, 7, 12], and there are only a few of coal seams containing relatively high Ge content^[7]. The concentrations of Ge show great diversities in coal which were derived from the same plants and grew in the same environment and the same era^[7]. The wall rock with high infiltration capacity favours the accumulation of Ge in coal^[2]. In addition, the distribution of Ge-rich coal seams was geologically controlled by fault zones^[5, 12, 13]. It is almost widely accepted that Ge in coal was not inherited from the coal forming plants, but introduced mainly from the surroundings in coal forming process and the later evolution^[3, 7].

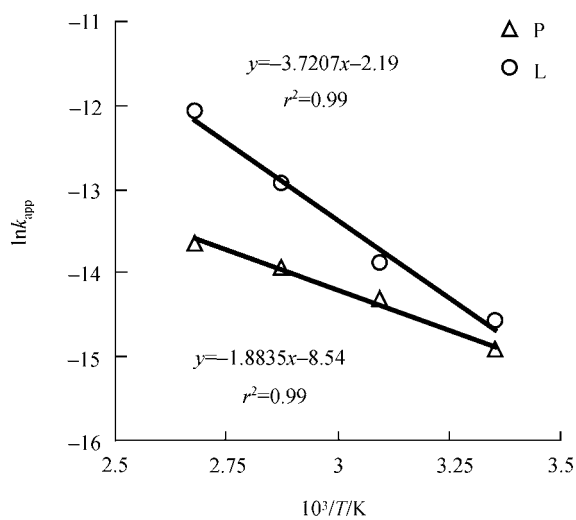
The reducing ability of the organic substrate is tightly associated with the standard potentials (E^0) of organic substrate and metallic ion redox or oxide couples^[4]. The Eh^0 of Ge^{4+} reduced to Ge (0.0V)^[22] is obviously lower than those of lignite and the other organic substrate (0.50–0.76 V)^[4], indicating that lignite, humic acid, etc. are incapable of reducing Ge^{4+} to Ge^0 at low temperature. Experimental studies on the reduction of Au^{3+} by lignite with low maturity or bitumen and kerogen^[23–25] have demonstrated the universality of the following mechanism: $[\text{MO}_{\text{red}}] + \text{M}^{n+} \rightarrow [\text{MO}_{\text{ox}}] + p\text{H}^+ + \text{M}^{(n-p)+}$, where $[\text{MO}_{\text{red}}]$ and $[\text{MO}_{\text{ox}}]$ represent the initial (redox) organic substrate and the final (oxide) organic substrate, respectively. That is to say, protons (H^+) were released during the process of reduction of metallic ion by organic substrate. The pH values of the solutions were apparently increased, after the interaction between 10 mL Ge-bearing solution and coal with various maturities at 25 °C^[1]. These facts further show that the interaction between Ge-bearing solution and organic substrate is not a process of reduction.

The mechanism during the interaction between

1) Qi Huawen, Continental hydrothermal sedimentation and the genesis of superlarge germanium deposit: A case study on the Lincang Ge deposit, Ph.D dissertation, Guiyang Institute of Geochemistry, Chinese Academy of Sciences, 2002.

Table 3 The kinetic parameters of the interaction between 0.5 g peat, lignite and Ge-bearing solution at $\text{pH}_0=2.96$, $C_0=5$ mg/L and $T=25-100$

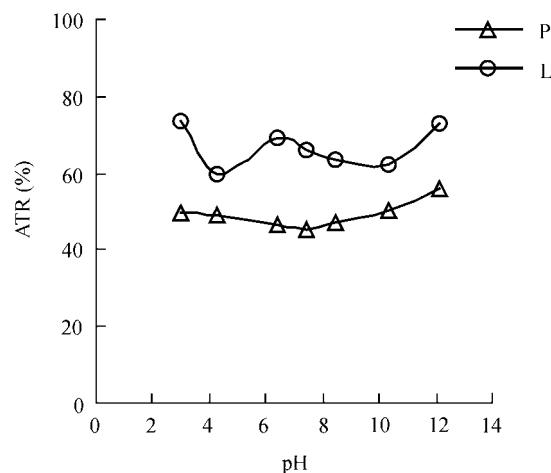
	k_{app}				E/kJmol^{-1}
	25	50	75	100	
Peat	$3.33 \times 10^{-7} \text{ t}^{-1}$	$6.11 \times 10^{-7} \text{ t}^{-1}$	$8.89 \times 10^{-7} \text{ t}^{-1}$	$11.9 \times 10^{-7} \text{ t}^{-1}$	30.96
Lignite	$4.72 \times 10^{-7} \text{ t}^{-1}$	$9.44 \times 10^{-7} \text{ t}^{-1}$	$24.44 \times 10^{-7} \text{ t}^{-1}$	$56.94 \times 10^{-7} \text{ t}^{-1}$	15.67

Fig. 3. $\ln k_{\text{app}}$ as a function of $1000/T$ at various temperatures (P, peat; L, lignite).Table 4 ATRs of peat and lignite for Ge at 75°C , $C_0=5$ mg/L, duration of 60 h and various pH_0

	pH_0	2.96	4.26	6.38	7.44	8.49	10.3	12.08
Peat	C	1.34	2.03	1.56	1.71	1.82	1.9	1.36
	ATR(%)	49.8	49.3	46.5	45.1	47.4	50.4	55.8
Lignite	C	2.51	2.54	2.68	2.75	2.63	2.48	2.21
	ATR(%)	73.3	59.5	68.9	65.9	63.6	62	72.9

Notes are the same as in Table 2.

peat, lignite and Ge-bearing solution is mainly the complexation of Ge by organic substrate, and Ge probably mainly formed complexes with the oxygen-bearing function groups. The main evidences are from: (1) many studies show that Ge is a typical organophile element and mainly incorporated in huminite or the macromolecular structure of vitrain, and no simple substance of Ge was discovered^[3,8,9]; (2) the experimental data available indicate that Ge^{4+} can form stable organic complexes with 6 oxygens in carboxylic acid and phenols, and Ge-O distance varies from 1.85 to 1.94 nm^[19,20]; and (3) the distribution of Ge and sulfur in the subvolcano thermally affected coal also indicates that the organic substrate in coal mainly “absorbed” Ge in the thermal fluid^[26].

Fig. 4. ATRs of peat and lignite for Ge as a function of initial pH at 75°C , $C_0=5$ mg/L and a duration of 60 h (P, peat; L, lignite).

4 Conclusions

The experimental results of the interaction between peat, lignite and Ge-bearing solution at temperature from 25 to 100°C , $C_0=5$ mg/L and various initial pH values show that the apparent transfer ratios of peat and lignite for Ge in the solution were positively correlated with temperature in acid environment (initial $\text{pH}=2.96$), and at the same conditions, the apparent transfer ratios (up to 86.5%) of the lignite were obviously higher than those (up to 58.5%) of the peat, while their organic transfer ratios for Ge were lower than those of the peat samples. The activation energy values for the interaction between peat, lignite and Ge-bearing solution are 30.96 and 15.67 kJmol^{-1} , respectively. This study also found that strong acid (initial $\text{pH}=2.96$) and strong alkaline (initial $\text{pH}=12.08$) environment favour the transfer of Ge in the solution; at $4 < \text{pH} < 10$, the influences of pH on the interaction between peat and Ge-bearing solution are not significant, while weak acid (initial $\text{pH}=6.38$) conduces to the transfer of Ge into lignite. The mechanisms of interaction between peat, lignite and Ge-bearing solution

are mainly the complexation of Ge with organic substrate. The above results provide direct experimental evidence for the hydrothermal sedimentary genesis of abnormal enrichment of Ge in coal, and are significant for revealing the mode of Ge in coal.

Acknowledgements The authors want to thank Prof. Hua Renmin of Department of Earth Science, Nanjing University and Profs. Feng Xinbin and Xiao Tangfu of the State Key Laboratory of Environment Geochemistry, Chinese Academy of Sciences for reviewing the manuscript and making valuable suggestions. This project was supported by the National Natural Science Foundation of China (Grant No. 40302018) and the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KZCX3-SW-125).

References

- Disnar, J. R., Sureau, J. F., Organic matter in ore genesis: Progress and perspectives, *Organic Geochemistry*, 1990, 16(1-3): 577 599. [\[DOI\]](#)
- Smimov, V. I., Deposit of germanium, *Ore Deposits of the USSR*, London: Pifman Publication, 1977, 455 462.
- Bernstein, L. R., Germanium geochemistry and mineralogy, *Geochemica et Cosmochemica Acta*, 1985, 49: 2409 2422. [\[DOI\]](#)
- Kulinenko, O. R., Relationship between germanium content and seam thickness in Paleozoic paralic coal basins of Ukraine, *International Geology Review*, 1977, 19(10): 1178 1182.
- Seredin, V. and Danilcheva, J., Coal-hosted Ge deposits of the Russian Far East (eds. Piestrzynski et al.), *Mineral Deposits at the Beginning of the 21st Century*, Lisse: Swets & Zeitlinger Publishers, 2001, 89 92.
- Hu Ruizhong, Bi Xianwu, Ye Zaojun et al., The genesis of Lincang germanium deposit A preliminary investigation, *Acta Mineralogica Sinica* (in Chinese with English abstract), 1996, 16(2): 97 102.
- Hu Ruizhong, Bi Xianwu, Su Wenchao et al., Some considerations on germanium mineralization in coal As exemplified by Lincang germanium deposit, *Acta Mineralogica Sinica* (in Chinese with English abstract), 1997, 17(4): 364 368.
- Zhang Shuling, Yin Jingshuang and Wang Shuying, Study on existent forms of germanium in coal, Bangmai Basin, Yunnan, *Acta Sedimentologica Sinica* (in Chinese With English abstract), 1988, 6(3): 29 41.
- Zhuang Hanping, Lu Jialan, Fu Jiamo et al., Germanium occurrence in Lincang superlarge deposit in Yunnan, China, *Science in China, Series D*, 1998, 41(supplement), 21 27.
- Lu Jialan, Zhuang Hanping, Fu Jiamo et al., Sedimentation, diagenesis, hydrothermal process and mineralization of germanium in the Lincang superlarge germanium deposit in Yunnan Province, China, *Geochimica* (in Chinese with English abstract), 2000, 29(1): 36 42.
- Qi Huawen, Hu Ruizhong, Su Wenchao et al., Genesis of carboniferous siliceous limestone in the Lincang germanium deposit and its relation with germanium mineralization, *Geochimica* (in Chinese with English abstract), 2002, 31(2): 161 168.
- Qi Huawen, Hu Ruizhong, Su Wenchao et al., Continental hydrothermal sedimentary siliceous rock and genesis of superlarge germanium (Ge) deposit hosted in coal : A study from the Lincang Ge deposit, Yunnan, China, *Science in China, Series D*, 2004, 47(11): 973 984.
- Wang Lanming, Introduction of the geological feature and exploration of Wulantuga germanium deposit in Xilingguole league, Inner Mongolia, *Geology of Inner Mongolia* (in Chinese with English abstract), 1999, 3: 16 20.
- Lewis, B. L., Froelich, P. N., Andreae, M. O., Methylgermanium in natural waters, *Nature*, 1985, 313(24): 303 305. [\[DOI\]](#)
- Murnane, R. J., Leslie, B. L., Hammond, D. E., Germanium geochemistry in the Southern California Borderlands, *Geochemica et Cosmochemica Acta*, 1989, 53: 2873 2882. [\[DOI\]](#)
- Mortlock, R. A., Froelich, P. N., Hydrothermal germanium over the Southern East Pacific Rise, *Science*, 1986, 231: 43 45.
- Arnorsson, S., Germanium in Icelandic geothermal systems, *Geochemica et Cosmochemica Acta*, 1984, 48: 2489 2502. [\[DOI\]](#)
- Pokrovski, G. S., Schott, J., Thermodynamic properties of aqueous Ge(IV) hydroxide complexes from 25 to 350 : Implications for behavior of germanium and the Ge/Si ratio in hydrothermal fluids, *Geochemica et Cosmochemica Acta*, 1998, 62: 1631 1642. [\[DOI\]](#)
- Pokrovski, G. S., Schott, J., Experimental study of the complexation of silicon and germanium with aqueous organic species: Implications for germanium and silicon transport and Ge/Si ratio in natural waters, *Geochemica et Cosmochemica Acta*, 1998, 62(21/22): 3414 3428.
- Pokrovski, G. S., Martin, F., Hazemann, J. L. et al., An X-ray adsorption fine structure spectroscopy study of germanium-organic ligand complexes in aqueous solution, *Chemical Geology*, 2000, 163: 151 165. [\[DOI\]](#)
- Peng Gelin, Zhang Zeyou, Wu Damao, The study status of correlation of peat with coal-forming environment, *Advance in Earth Sciences* (in Chinese with English abstract), 1999, 14(3): 247 255.
- Chang Wenbao, The concise analytical chemistry (in Chinese), Beijing: Peking University Press, 1981, 95.
- Gatellier, J. P., Disnar, J. R., Kinetics and mechanism of the reduction of Au() to Au(0) by sedimentary organic materials, *Organic Geochemistry*, 1990, 16(1-3): 631 640. [\[DOI\]](#)
- Liu Jinzhong, Fu Jiamo, Lu Jialan, Experimental study on the reduction of aqueous Au³⁺ by bitumen and kerogen, *Chinese Science Bulletin* (in Chinese), 1993, 38(23): 2169 2173.
- Hu Kai, Liu Yingjun, Jia Rongfen et al., Experimental study on mechanism Au concentrated by organic substance, *Science in China, series B* (in Chinese), 1993, 23(8): 880 888.
- Liu Jinzhong, Xu Yunqiu, Distribution of Ge, Ga, As, S in the subvolcano thermally affected coal, *Coal Geology & Exploration* (in Chinese with English abstract), 1992, 20(5): 27 32.