Continental hydrothermal sedimentary siliceous rock and genesis of superlarge germanium (Ge) deposit hosted in coal: A study from the Lincang Ge deposit, Yunnan, China

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Abstract There are abundant hydrothermal sedimentary structures and plant fragment fossils in the siliceous rocks from the Lincang Ge deposit. The major element compositions of these siliceous rocks are characterized by high content SiO_2, low TiO_2 and Al_2O_3 concentrations, and low Al/(Al+Fe+Mn) ratios (0.010 on average). The siliceous rocks are distinctly enriched in Ge, Sb, As, W, and secondly enriched in Cs, U, Mo and Tl. Their total REE content are generally less than 1μg/g, LREE relatively concentrated, and the values of Eu anomaly and Ce anomaly vary from 0.452 to 5.141 and 0.997 to 1.174, respectively. Their NAS-normalized REE patterns are plain or left-inclined. The Oxygen isotope compositions of these siliceous rocks are similar to those of the hydrothermal siliceous sinter. The above characteristics, as well as the geological setting of the deposit, indicate these siliceous rocks formed in continental hydrothermal environment. As the interlayer or cliff of the Ge-rich coal seams, siliceous rocks tightly contacted with ore-body, and the contents of Ge in siliceous rocks vary from 5.6 to 360 μg/g (78 μg/g on average). The Ge content increased in coal which close to the siliceous rocks. With the increase of Ge content, the typical trace element ratios (i.e., Ge/Ga, Nb/Ta and U/Th) and REE patterns of Ge-rich coal are more close to those of the siliceous rocks. The Ge concentrated in coal seams of the Lincang Ge deposit might be transported by the hydrothermal water, which demonstrated by the siliceous rocks, during the coal-forming processes.

Keywords: siliceous rock, continental hydrothermal sedimentation, superlarge Ge deposit, Lincang.

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The study on marine hydrothermal sedimentation tends to be perfect at present, and a suit of hydrothermal sedimentary distinguishing criterions (including structure, conformation, geochemistry, etc.) has been found[1—12]. While it is unsubstantial on the study of hydrothermal sedimentation in continental depositional environment, and little was known about the relation between continental hydrothermal sedimentation and metal mineralization. The Lincang Ge deposit, hosted in coal with independent commercially worthwhile value and a superlarge deposit scale, have been discovered recently in China[13]. As the typical deposit of dispersed element Ge mineralization, this deposit has been studied by some researchers after been found. The former studies mainly focused on the geological characteristics of the deposit, the organic geochemistry and the existent form or mode of Ge in coal[13—18]. These results have shown that Ge mainly exist in the form of organic complex[16,17], the characteristics of Ge-bearing coal, the distribution and existing form of Ge in the Lincang Ge deposit are similar to those of the Ge-bearing coal in other parts of the word[13]. It also show that the sources of Ge concentrated in coal are related to two-mica granites in the west region of the coal-bearing basin, but the pathway by which Ge entered the coal-forming basin or coal seams is still in controversy.

The Ge mineralization was not a simple, independent geological event in coal, the ore-bodies should genetically connected with the surrounding geological materials. Therefor, it is difficult to explain the particularity of Ge mineralization in coal of the Lincang Ge deposit, if only limited on the study of Ge-rich coal itself. Hu et al.[13] and Su et al.[15] have preliminarily studied the siliceous rock and regarded they are of hydrothermal origin. Abundant hydrothermal sedimentary structures and plant fragment fossils in the layered siliceous rocks have been found for the first time in further detailed research of this report, which not only provide the direct evidences of hydrothermal sedimentation, but also definitely define the time of hydrothermal activities. Based on the studies on the geological and geochemical characteristics of siliceous rock, the spatial distribution of Ge and the geochemical characteristics of Ge-bearing coal samples, the relation between siliceous rock and Ge mineralization was studied in this paper.

1 Geological setting of the Lincang Ge deposit

The Lincang Ge deposit, which include Dazhai Ge deposit and Zhongzhai Ge deposit, is located in the coal-bearing clastic rock Bangmai Basin with Ge-rich granites (ω_{Ge} = 3.9 μg/g) as the basement in the Lincang county, Western Yunnan Province (fig. 1)[13]. Strata in the basin consist of the Cenozoic Neogene Bangmai Group, and can be divided into three coal-bearing cycles (N_{1b}^2, N_{1b}^4 and N_{1b}^6) (fig. 2). At present, the proven Ge reserve of the Lincang Ge deposit is up to superlarge deposit scale with 860t Ge in Dazhai and at lest 200t Ge in Zhongzhai. Prospecting data show

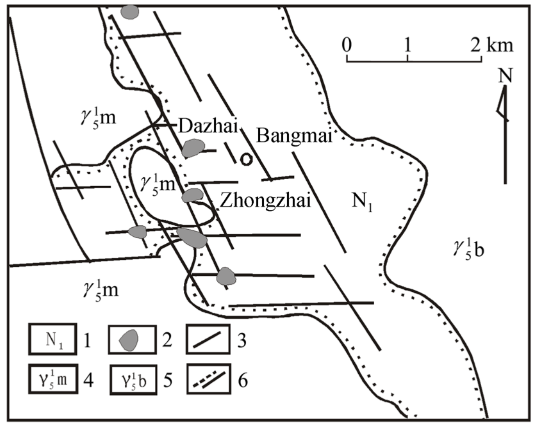

Fig. 1. The sketch geological map of the Bangmai Basin (modified after ref. [13]). 1, Neogene Strata; 2, Ge-rich sections of the coal seams; 3, syndepositional faults; 4, two-mica granite; 5, biotite granite; 6, unconformity interface.

the Ge in the Lincang Ge deposit is unevenly distributed no matter in vertical or horizontal direction of the coal seams, most industry-worthwhile value Ge mainly occurs in the lignite of the first coal-bearing cycle (N_{1b}^2) close to the basement granites. This cycle is mainly composed of conglomeratic coarse sandstone, fine sandstone, siltstone, coal seams, layered siliceous rocks and carboniferous siliceous limestone. There is no significantly Ge mineralization and a lack of siliceous rock in the coal seams of the upper two coal-bearing cycles (N_{1b}^4 and N_{1b}^6). In N_{1b}^2, the Ge ore-bodies are bedded, accordant with the strata, the coal seams generally are Ge ore-bodies. The spacial distribution of Ge-rich sections of the coal seams, the siliceous rocks and the syndepositional faults in the basement coincided with each other (fig. 1 and fig. 3). The Ge contents in these ore-bodies lie in a wide range from 20 to 2500 μg/g, 852 μg/g on average (51 samples).

2 Sample and method

The fresh siliceous rocks in the cliff and interlayer of the coal seams (Ge ore-body) in the first coal-bearing cycle (N_{1b}^2) of Zhongzhai were collected as the samples in this study. All samples were washed with distilled water, and were ground and passed through a 75 μm mesh sieve. After desiccation, their major element, trace element, rare earth element (REE) were analyzed in the Key Laboratory of Ore Deposit

Strata			Thickness /m	Steati-graphic column	Lithological characters	Ore deposit
Quaternary		Q	0—10		Eluvium, sliderock and alluvia	
Miocene	Bangmai Group	N_1b^8	0—21		Coarse sandstone	
		N_1b^7	19—81		Siltstone, argillaceous siltstone with abundant thin ferruginous zone	
		N_1b^6	11—346		Medium to fine conglomerate, fine sandstome, siltstone, coarse sand-stone with 3 to 8 interlayered coal seams with thickness up to 1 m, half dull-half	Coal
		N_1b^5	0—179		Low density diatomaceous siltstone with abundant ferruginous zone	Diatomite
		N_1b^4	44—263		Fine sandstone, siltstone, coarse sandstone with 6 to 17 interlayered coal seams with thickness up to 3 m, half bright coal. The second coal-bearing section.	Coal
		N_1b^3	7—95		Conglomerae with interbedded coarse sandstone	
		N_1b^2	19—364		Coarse sandstone, carboniferous siltstone, limestone, siliceousrocks with 8 to 14 interlayered coal seams with thickness up to 14 m thick half bright-bright coal. The first coal-bearing section.	Coal and germanium
		N_1b^1	20—686		Granitic clastic rock (giant grained conglomerate, conglomeratic coarse sandstone, coarse sandstone) with few interlayered fine sand-stone and siltstone	
Indosinian granite					Medium to coarse grained biotite, muscovite and two-mica granites with silicified zone and quartz vein in cracks	

Fig. 2. The sketch strata table of the Bangmai Basin (simplified after the data of No. 209 geological team, Yunnan Province).

Geochemistry, Chinese Academy of Sciences, and oxygen isotope analysis were made in the Institute of Ore Deposit Geology, Chinese Academy of Geosciences. The major element contents were determined by using the wet chemical method. The trace elements and REEs were analyzed by a Finnigan MAT ELEMENT high resolution ICP-MS with detection limit up to 10^{-9}. All analyses were calibrated with international rock reference materials (GBPG-1 and AMH-1) and parallel samples. The analytical precisions for different trace element are given in table 2, and for REEs are better than 5%. The oxygen isotope compositions were analyzed by using BrF_5 method, MAT 251 EM MS and SMOW international standard with analytical precision of 0.2‰.

3 Lithological characters of siliceous rock

The siliceous rocks are gray-black with solid massive, bedded or lentoid conformation, its thickness varies from 20—60 centimeters. They mainly unevenly distribute as interlayer or the cliff of the main ore-body of Zhongzhai Ge deposit. Microscopic studies show siliceous rock are grain-setting structure, and partial zonal or radial chalcedony filled structure, distinctly distinguishing from the sedimentary clastic quartz. The peripheral portions of the zonal structure consist of co-center laminated radial chalcedony with cruciform extinction in cross polarized light, while the medium portion consist of well shape or grained quartz. These characteristics are very similar to those of the mammillary structure named by Chen Xianpei

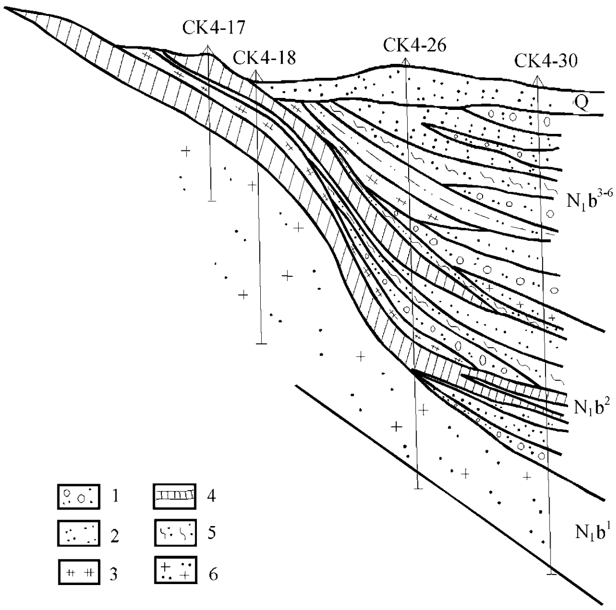

Fig. 3. No. 302-21 explorative cross-section of the Lincang Ge deposit (simplified after the data of No. 209 geological team, Yunnan Province). 1, Conglomerate; 2, siltstone; 3, siliceous rock; 4, coal seam; 5, mudstone; 6, ranitic clastic rock.

in upper Devonian hydrotheraml sedimentary siliceous rocks, Guangxi[9], and these structure can be regarded as the main lithological characteristics of hydrothermal sediments. Many carbonides and carbonaceous annuluses were found in the siliceous rocks from the Lincang Ge deposit. The carbonides were reciprocally filled with silicide. The radial and zebraic chalcedonies in the carbonaceous annuluses were intersectant at equal angle in line. The carbonaceous annuluses sometime were cut by the late vien. Abundant plant fragment fossils and a few pyrites have been found in the layered siliceous rocks. Pyrites generally are cubic with spherical or strawberry-like aggregation.

4 Geochemical character

4.1 Major element geochemistry

The siliceous rocks in the Lincang Ge deposit mainly consist of SiO_2, the SiO_2 contents vary from 84.31% to 97.60%, 92.77% on average, the secondary constituents are loss in ignition (carbonide in dominance), and the content of the other element are very low (table 1). Their major element compositions are similar to those of the typical marine hydrothermal siliceous rocks in the other part of the world. The Na_2O/K_2O ratios of most marine hydrothermal siliceous rocks are less than1, while the ratios of the siliceous rocks from the Lincang Ge deposit are higher than 1.

The Al/(Al+Fe+Mn) atomic ratios are an important indicator to evaluate the content of hydrothermal sedimentary components in various sediments, and the ratios decrease with the increase of the content of hydrothermal components. Low TiO_2 and Al_2O_3 content are the typical characters of the hydrothermal siliceous rocks. The Al/(Al+Fe +Mn) ratios of the sili-

Table 1 Major element composition of the siliceous rocks from the Lincang Ge deposit (%)

Sample No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Sum	Al/(Al+Fe+Mn)	Na/K
ZZ-19	84.31	0.01	0.01	1.00	0.20	0.06	0.11	0.20	0.12	0.02	0.08	13.31	99.43	0.008	6.00
ZZ-27	96.75	0.02	0.02	0.60	0.12	0.07	0.10	0.20	0.11	0.02	0.12	1.50	99.63	0.025	5.50
ZZ-38	97.60	0.01	0.03	0.86	0.10	0.07	0.10	0.40	0.11	0.01	0.11	0.26	99.66	0.028	11.0
ZZ-45	96.39	0.001	0.01	0.75	0.15	0.11	0.10	0.50	0.12	0.03	0.11	1.50	99.77	0.010	4.00
ZZ-57	89.83	0.001	0.01	0.54	0.10	0.07	0.10	0.20	0.11	0.04	0.15	8.70	99.85	0.014	2.75
ZZ-61	95.52	0.002	0.02	1.32	0.32	0.10	0.11	0.10	0.12	0.03	0.08	1.60	99.32	0.011	4.00
ZZ-74	95.60	0.02	0.01	0.39	0.10	0.06	0.10	0.10	0.11	0.04	0.07	3.20	99.80	0.018	2.75
ZZ-79	96.09	0.01	0.02	0.72	0.20	0.08	0.11	0.20	0.12	0.03	0.03	2.10	99.71	0.020	4.00
ZZ-81	89.06	0.001	0.02	0.70	4.70	0.20	0.11	0.70	0.11	0.02	0.15	4.06	99.83	0.004	5.50
ZZ-87	86.59	0.003	0.01	1.32	0.30	0.08	0.10	4.60	0.10	0.02	0.07	6.35	99.54	0.006	5.00
average	92.77	0.01	0.02	0.82	0.63	0.09	0.10	0.72	0.11	0.03	0.10	4.26	99.65	0.010	5.05
WQL[11]	95.30	0.04	0.41	1.03	0.58	0.03	0.19	0.68	0.06	0.08	0.25	1.06	99.71	0.153	0.75
YL[12]	98.46	0.006	0.01	0.46	0.14	0.05	0.001	0.26	0.05	0.005	0.02	0.20		0.011	10.0
Franciscan[1]	92.30	0.09	1.31	0.27	2.36	0.53	0.28	0.11	0.16	0.35	0.03			0.293	0.46
Shimanto[1]	87.87	0.05	1.09	0.52	2.52	1.08	0.86	1.05	0.35	0.24	0.12			0.209	1.46

WQL, YL, Franciscan and Shimanto: The average composition of marine hydrothermal cherts and associated rocks in the West Qinling, the Yangla copper deposit in West Yunnan, the Franciscan and Shimanto terranes, respectively; LOI: loss on ignition; Na/K: Na_2O/K_2O.

ceous rocks from the Lincang Ge deposit vary from 0.004 to 0.028, 0.010 on average, TiO_2 contents range from 0.001% to 0.02%, 0.01% on average, and Al_2O_3 contents vary from 0.01% to 0.03%, 0.02% on average. They are less than the Al/(Al+Fe+Mn) ratios, TiO_2 and Al_2O_3 contents of the typical marine hydrothermal siliceous rocks in the other part of the world, respectively (table 1). In the Triangle diagram of Al-Fe-Mn in different rocks, the siliceous rock samples fall into the hydrothermal field (fig. 4). So the major element compositional characters of the siliceous rocks from the Lincang Ge deposit indicate that the siliceous rocks in the area were hydrothermal sediments.

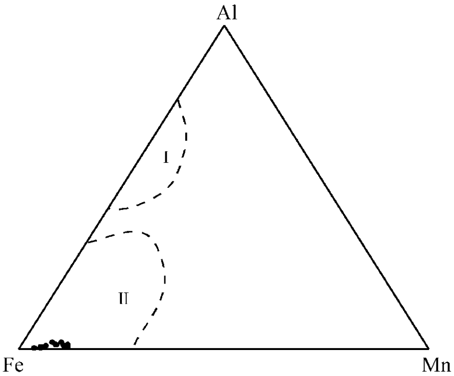

Fig. 4. Triangle diagram of Al-Fe-Mn in different rocks (based on refs. [1] and [11]). I, Biogenetic and non-hydrothermal sediments; II, hydrothermal sediments; ●, siliceous rock from the Lincang Ge deposit.

4.2 Trace element geochemistry

Hydrothermal sediments are relatively enriched in Cu, Ni and depleted in Co[4]. The high contents of Ba, As, Sb and B in sediments are the important evidence for hydrothermal sedimentation[5,6]. Results (table 2) show that the siliceous rocks from the Lincang Ge deposit are distinctively enriched in Ge, Sb, As and W, secondly enriched in Cs, U, Mo and Tl in various degree. The Co/Ni ratios of the siliceous rocks are less than 1, while U/Th ratios are greater than 1. In the U-Th diagram of various sediments, the siliceous rocks fall into hydrothermal field (fig. 5). In the triangle diagram of Fe-Mn-(Co+Ni+Cu)×10 in different

Table 2 Trace element composition of the siliceous rocks from the Lincang Ge deposit (μg/g)

	AP (%)	ZZ-19	ZZ-27	ZZ-38	ZZ-45	ZZ-57	ZZ-61	ZZ-79	ZZ-81	ZZ-87	Average	CV	F
Li	10	12	7.6	3.0	10	8.1	6.4	11	5.0	11	8.2	13	0.63
V	10	2.9	4.5	4.1	7.1	2.2	1.2	1.0	1.3	1.1	2.8	230	0.01
Cr	5	11.4	4.5	19.6	12.8	9.5	12.5	21	7.5	18.1	13.0	185	0.07
Co	10	1.8	4.5	1.8	2.6	1.6	2.2	1.5	4.9	1.6	2.5	29	0.09
Ni	10	6.0	4.5	4.8	7.3	4.4	7.6	5.4	6.2	5.1	5.7	105	0.05
Cu	3	9.4	4.5	7.7	11.6	9.1	8	7.7	8.5	8.7	8.4	75	0.11
Zn	2	7.2	7.7	3.2	2.97	8.0	2.54	4.43	6	3.29	5.0	80	0.06
Ga	3	0.88	0.58	0.77	0.57	1.06	0.35	0.42	0.39	0.39	0.6	18	0.03
Ge	10	360	25	22	25	160	29	43	5.6	34	78	1.6	48.86
As	10	35	4.7	10	2.9	5.8	5.0	14	4.1	17	11	1	11
Rb	2	3.49	2.55	1.95	2.47	5.4	2.5	2.57	1.61	2.21	2.8	32	0.09
Sr	6	5.8	3.7	2.2	4.1	5.9	4.5	5.2	5.9	nd	4.7	260	0.02
Y	5	0.80	0.17	0.39	0.21	0.68	0.16	0.14	0.20	0.26	0.33	20	0.02
Zr	5	1.66	1.31	1.56	1.75	4.9	0.77	0.6	0.21	0.71	1.5	100	0.01
Nb	3	18.6	6.5	27	3.7	19.3	5.0	6.4	0.31	1.02	9.8	11	0.89
Mo	3	1.68	1.02	1.55	1.56	1.40	1.29	1.82	1.25	2.76	1.6	1	1.59
Cd	10	0.07	0.06	0.04	0.04	0.09	0.08	0.05	0.04	0.09	0.1	0.098	0.67
Sn	10	1.2	2.1	0.9	1.1	1.9	2.2	1.0	1.2	1.8	1.5	2.5	0.60
Sb	2	17.0	4.50	10.8	1.83	28.1	1.57	6.6	1.79	1.69	8.2	0.2	41.04
Cs	2	6.19	4.18	2.47	6.0	5.6	6.9	5.7	3.76	3.32	4.9	1	4.90
Ba	3	70	44	14.8	42	390	40	67	60	210	104	250	0.42
Hf	10	0.12	0.02	0.04	0.05	0.13	0.01	0.01	0.03	0.05	0.05	3	0.02
Ta	10	0.03	0.02	0.01	0.01	0.05	0.01	0.01	0.01	0.01	0.02	1	0.02
W	10	29	3.7	9.8	6.3	17	2.9	2.6	6.3	7.6	9.5	1	9.5
Tl	5	0.66	0.07	0.27	0.05	1.34	0.15	0.66	0.05	0.61	0.43	0.36	11.9
Pb	4	1.25	0.99	0.81	0.75	1.43	0.66	1.08	0.68	1.02	0.96	8	0.12
Th	3	0.19	0.09	0.09	0.06	0.45	0.02	0.07	0.04	0.08	0.12	3.5	0.12
U	2	3.25	1.21	5.62	1.35	4.28	1.46	0.84	0.14	0.30	2.05	0.91	2.25

AP: Analytical precision; CV: the Clark values of the element after Taylor (1985)[19]; F: the element content relative to its Clark value (concentration coefficients).

sediments, the siliceous rock fall into the hydrothermal field close to the Fe-end member (fig. 6). The trace element composition and its characters also indicate that the siliceous rocks from the Lincang Ge deposit are hydrothermal sediments.

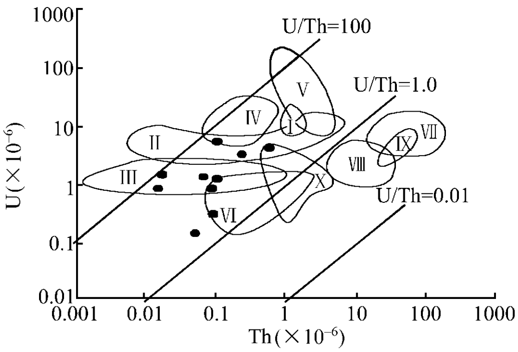

Fig. 5. U-Th diagram of various sediments (based on refs. [5] and [11]). I, TAG hydrothermal area; II,Galapagos spreading center deposits; III, amphitrite hydrothermal sediments; IV, Red Sea hot brine deposits; V, East Pacific Rise crest deposits; VI, Langban hydrothermal sediments; VII, ordinary manganese nodules; VIII, ordinary pelagic sediments; IX, laterites; X, fossil hydrothermal deposits (En Kafala ores); ●, siliceous rock from the Lincang Ge deposit.

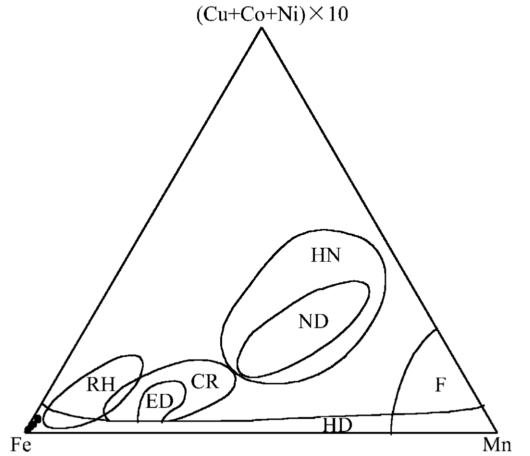

Fig. 6. Triangle diagram of Fe-Mn-(Cu+Co+Ni)×10 in defferent sediments (based on ref. [4]). HN, Hydrogenic sediments; ND, Hydrogenic concretion; ED, Eastern Pacific Hydrothermal metalliferous sediments; CR, hydrothermal Fe and Mn-crust sediments; HD, hydrothermal sediments; RH, Red Sea hydrothermal sediments; F, Francisan hydrothermal cherts; ●, siliceous rock from the Lincang Ge deposit.

4.3 REE geochemistry

REE composition and their characters are important indicators distinguishing hydrothermal sediments from Non-hydrothermal sediments[6]. Low total REE content and the left-inclined North American Shale-normalized REE patterns are the common characters of many hydrothermal cherts[1—12]. Results (table 3 and table 4) show that the total REE content of the siliceous rocks from the Lincang Ge deposit vary from 0.200 to 2.324 μg/g, usually less than 1 μg/g, LREE/HREE>1, the values of Eu anomaly (Eu/Eu*) and Ce anomaly (Ce/Ce*) vary from 0.452 to 5.141 and 0.997 to 1.174, respectively.

The North American Shale-normalized REE pat-

Table 3 The REE contents of the siliceous rocks from the Lincang Ge deposit (μg/g)

Sample No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ZZ-19	0.301	0.589	0.033	nd	0.061	0.006	0.064	0.013	0.068	0.021	0.067	0.014	0.079	0.014
	0.269	0.574	0.059	0.162	0.076	0.020	0.057	0.009	0.067	0.019	0.063	0.008	0.075	0.013
ZZ-27	0.144	0.253	nd	nd	0.017	0.004	0.014	0.005	0.024	0.002	0.021	0.002	0.013	0.003
	0.118	0.259	0.026	nd	0.033	0.010	0.021	0.003	0.020	0.004	0.015	0.001	0.013	0.003
ZZ-38	0.068	0.139	0.012	nd	0.013	0.005	0.013	0.004	0.021	0.005	0.017	0.003	0.027	0.006
	0.082	0.149	0.011	nd	0.017	0.004	0.018	0.002	0.022	0.005	0.015	0.002	0.032	0.006
ZZ-45	0.220	0.348	nd	nd	0.020	0.003	0.021	0.004	0.027	0.005	0.015	0.004	0.016	0.002
ZZ-57	0.566	1.242	0.096	nd	0.108	0.016	0.104	0.017	0.089	0.018	0.048	0.011	0.061	0.007
	0.544	1.394	0.141	0.406	0.114	0.024	0.101	0.015	0.087	0.021	0.047	0.009	0.059	0.011
ZZ-61	0.056	0.089	nd	nd	0.002	0.002	0.005	0.002	0.013	0.002	0.014	0.003	0.017	0.002
	0.032	0.073	0.006	nd	0.015	0.011	0.009	0.002	0.012	0.003	0.006	0.002	0.019	0.003
ZZ-79	0.167	0.275	nd	nd	0.032	0.003	0.013	0.003	0.018	0.004	0.013	0.003	0.015	0.002
	0.121	0.271	0.029	nd	0.025	0.013	0.020	0.004	0.023	0.004	0.009	0.001	0.015	0.002
ZZ-81	0.092	0.144	nd	nd	0.009	nd	0.007	0.001	0.014	0.005	0.021	0.004	0.016	0.002
	0.059	0.120	0.009	nd	0.013	0.016	0.015	0.003	0.019	0.005	0.018	0.002	0.019	0.004
ZZ-87	0.259	0.413	0.007	nd	0.003	0.013	0.025	0.005	0.046	0.006	0.020	0.004	0.025	0.006
	0.129	0.249	0.024	nd	0.022	0.035	0.027	0.006	0.034	0.006	0.012	0.004	0.025	0.003
ZZ-88	0.030	0.063	0.005	nd	0.009	0.010	0.004	0.002	0.011	0.003	0.013	0.001	0.018	0.003
Chondrite	0.34	0.91	0.121	0.64	0.195	0.073	0.26	0.047	0.3	0.078	0.2	0.032	0.22	0.034

nd: No detected; chondrite data after Wataki (1971) in ref. [20].

Table 4 The REE geochemical parameters of the siliceous rock from the Lincang Ge deposit

Sample No.	ΣREE	LREE	HREE	LREE/HREE	Eu/Eu*	Ce/Ce*	$(La/Yb)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$
ZZ-19	1.482	1.156	0.326	3.551	0.623	1.132	2.395	2.386	0.665
ZZ-27	0.633	0.551	0.082	6.722	1.032	0.978	6.520	3.005	1.139
ZZ-38	0.404	0.305	0.099	3.078	0.910	1.093	1.645	2.868	0.445
ZZ-45	0.810	0.716	0.094	7.615	0.452	1.000	8.897	6.309	1.111
ZZ-57	2.324	2.058	0.266	7.725	0.567	0.967	6.328	3.152	1.406
ZZ-61	0.233	0.176	0.057	3.083	2.599	1.111	1.582	2.969	0.329
ZZ-79	0.677	0.602	0.075	8.084	1.138	0.942	6.212	2.898	0.931
ZZ-81	0.362	0.285	0.078	3.677	4.487	1.129	2.792	3.936	0.532
ZZ-87	0.762	0.635	0.127	5.000	4.106	1.345	5.021	8.901	0.880
ZZ-88	0.200	0.145	0.055	2.635	5.141	1.147	1.078	1.912	0.188

The content of the no detected element are calculated using chondrite normalization, then the REE geochemical parameters were calculated. $Eu/Eu^*=[Eu_N(Sm_N \times Gd_N)]^{0.5}$, where N stands for chondrite normalization.

terns of the siliceous rocks from the Lincang Ge deposit are plain or left-inclined (fig. 7), basically similar to those of the typical marine hydrothermal siliceous rocks (chert). There is a lack of negative Ce anomaly, which usually appears in marine hydrothermal cherts[1—12], but a weak positive Ce anomaly in the North American Shale-normalized REE patterns of the siliceous rocks from the Lincang Ge deposit, this may be attributed to these siliceous rocks formed in the continental depositional environment. The available studies have shown that the average values of Ce anomaly (Ce/Ce*) of chert deposited near the spreading ridge and in an ocean-basin floor setting are 0.29 and 0.55, respectively, while the Ce anomaly is not distinctive or even positive (Ce/Ce*—0.90 to 1.30) in the chert deposited in continental margin regimes[7].

4.4 Oxygen isotope characters

The analyzed results of oxygen isotope composition of 11 siliceous rock samples from the Lincang Ge deposit (table 5) show that $\delta^{18}O_{SMOW}$ values vary from 10.9‰ to 15.7‰, 13.5‰ on average, distinguish from those of the volcanic genetic siliceous rocks (1.9‰—5.2‰, 3.3‰—12.4‰)[11] and biochemical

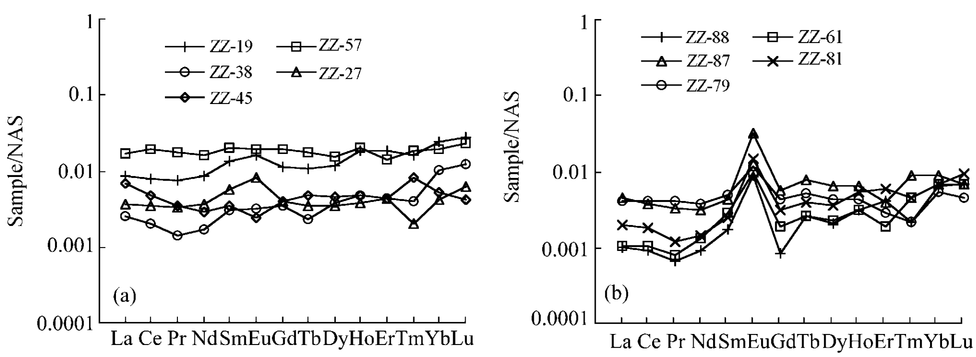

Fig. 7. The North American Shale-normalized REE patterns of the siliceous rocks from the Lincang Ge deposit.

Table 5 The oxygen isotope composition of the siliceous rocks from the Lincang Ge deposit

Rock	Sample No.	$\delta^{18}O_{SMOW}$‰	Rock	Sample No.	$\delta^{18}O_{SMOW}$‰
Siliceous rock	ZZ-19	13.9	Siliceous rock	ZZ-61	15.7
	ZZ-27	13.8		ZZ-74	12.6
	ZZ-38	13.6		ZZ-79	14.3
	ZZ-45	10.9		ZZ-81	13.3
	ZZ-57	13.3		ZZ-87	13.5
	ZZ-89	13.6		average	13.5

genetic siliceous rocks (21.6‰—26.7‰)[21], are close to those of hot-spring siliceous sinter (12.2‰—23.6‰)[22].

5 Siliceous rocks and Ge mineralization

5.1 The possibility of Ge being transported by hydrothermal water

Ge and silicon have identical outer electronic structure, very similar atomic and ionic radii, and exist in solution as similar hydroxyacids [$Ge(OH)_4$ and $Si(OH)_4$], Ge behaves as a heavy stable isotope tracer for Si in many low temperature geological processes. In most circumstances, the continental crustal rocks and minerals contain 1—2 μg/g Ge, display atomic Ge/Si ratios near 1×10^{-6}. Ge/Si ratios in clean rivers, in seawater, and in biogenic opal are about 10^{-6}, near to crustal value[23]. In hydrothermal fluids, the atomic Ge/Si ratio is much higher than that of rivers, oceans, and crustal rocks, both Ge concentration and Ge/Si ratios increase with temperature in most hydrothermal water[23—26]. For example, the Ge/Si ratios in hydrothermal fluids from black smoker vents on the East Pacific Rise very from 8×10^{-6} to 14×10^{-6}, much more greater than the ratio entering the ocean via rivers (0.54×10^{-6}) and being recycled in seawater (0.7×10^{-6})[24]. The ratio in Icelandic hydrothermal systems is up to 10^{-5}, and even 10^{-4}—10^{-3} in hot springs of the Massif Central, France[25]. Ge concentrations in seawater and river waters are 0.05 and 0.03 to 0.10 ng/g respectively. Ge is enriched in hydrothermal water and some ground waters relative to waters in rivers and seawater. Ge concentrations in geothermal waters in Japan are most frequently in the range of 1—15 ng/g but value as high as 40 ng/g are reported, in geothermal waters in Icelandic lie mostly in the range 2—30 ng/g[25], in the Lincang Ge deposit area vary from 3.5 to 44.1 ng/g[1)], there is an overall positive relation between the Ge content of the water and its temperature in hot spring waters in Iceland and the Lincang Ge deposit area[1)].

Kraynov (1965) found that highest Ge occurred in waters with one or more of the following characteristics: 1) high temperature, 2) high dissolved solids content and high alkalinity[27]. The absence of positive correlations between Ge concentrations and those of important inorganic ligands like Cl^-, HCO_3^-, H_2S, Na^+ suggests Ge does not form complexes with these ligands. The redox potential of most hydrothermal and surficial environments is too high to cause significant formation of divalent Ge species such as Ge^{2+}, $GeOH^+$ or $Ge(OH)_2$. As a result, tetravalent Ge (like Si) is present as hydroxide complexes in most natural fluids with the exception of seawater and organic-rich surficial waters[23]. The solubilities of the tetrahedral Ge oxide are positively correlated with the temperatures of the solution, and the distribution of Ge hydroxide species as a function of pH and temperature is similar to that of silicon hydroxide species. However, the significant differences between $Ge(OH)_4$(aq) and $Si(OH)_4$(aq) enthpaies of formation and heat capacities can lead to large variations with temperature of Ge/Si ratio in a solution in equilibrium with Ge-bearing silicates. For example, caculations show that the Ge/Si ratios in solutions in equilibrium with Ge-bearing wollastonite ($Ca(Si, Ge)O_3$) increases by an order of magnitude when temperature is raised from 25 to 500. This can be responsible for the high values of Ge/Si ratios measured in high temperature crustal fluids[23].

The above facts indicate that hydrothermal water can transport abundant Ge with sufficient supply of Ge from sources. The Ge contents in siliceous rocks from the Lincang Ge deposit vary from 5.6 to 360 μg/g, 78 μg/g on average and 49 times than crustal clark value (1.6 μg/g), implying that the hydrothermal water formed siliceous rocks indeed transported abundant Ge.

5.2 The spacial distribution of siliceous rocks and Ge ore-body

According to the variation of the cliff and bottom of the Ge ore-body, four typical cross-sections were

1) Zhang Lin, Han Yanrong, Yuan Qingbang，Ge source and geochemical characteristics of Ge deposit area in Lincang County, Yunnan Province, 1996.

selected to study the variation of Ge content in coal seams in N_{1b}^2 (fig. 8). In the cross-section (a) in Dazhai, the coal seams mainly consist of half bright-bright coal with a thickness about 10 m and sandstone as the cliff rock, without any interlayer. The Ge contents vary from 78 to 1800 μg/g, and Ge distinctly concentrated in the lower portion of the coal seams. In (b) cross-section in Zhongzhai, the coal seams contain 31 to 440 μg/g Ge with carboniferous siliceous limestone as the cliff rock and interlayered sandstone. Ge obviously concentrated in the upper and lower portion of the coal seams. As the interlayer or the cliff of the Ge-rich coal seams, the siliceous rocks tightly contacted with Ge ore-body in space. The Ge content increased in coal close to the siliceous rocks. In (c) cross-section in Zhongzhai, the Ge content in coal seams with siliceous rocks as the cliff rock and interlayered siliceous rocks and argillaceous rock vary from 1100 to 2500 μg/g. In (d) cross-section, the Ge contents of two coal samples close to the siliceous rocks are 1600 and 2100 μg/g, respectively. Prospecting data show the spacial distribution of Ge-rich sections in coal seams, syndepositional faults and siliceous rocks are accordant with each other (fig. 1 and fig. 3). These facts indicate that when the Ge (silicon) rich hydrothermal water entered the coal-forming basin, for its strong tendency toward accumulation in organic matters, Ge was adsorbed by the organic matter such as humic acids in coal and was transferred from the hydrothermal water into the coal seams. At the same time, for its low organic affinity, silicon was reserved and formed the indicator of hydrothermal sedimentation (the siliceous rocks).

5.3 Trace element and rare earth element

The previous studies show that the material sources of Ge in the coal seams of the Lincang Ge deposit are related to the two-mica granites in the west region of the Bangmai Basin, but the pathway by which Ge entered the coal-forming basin is still in

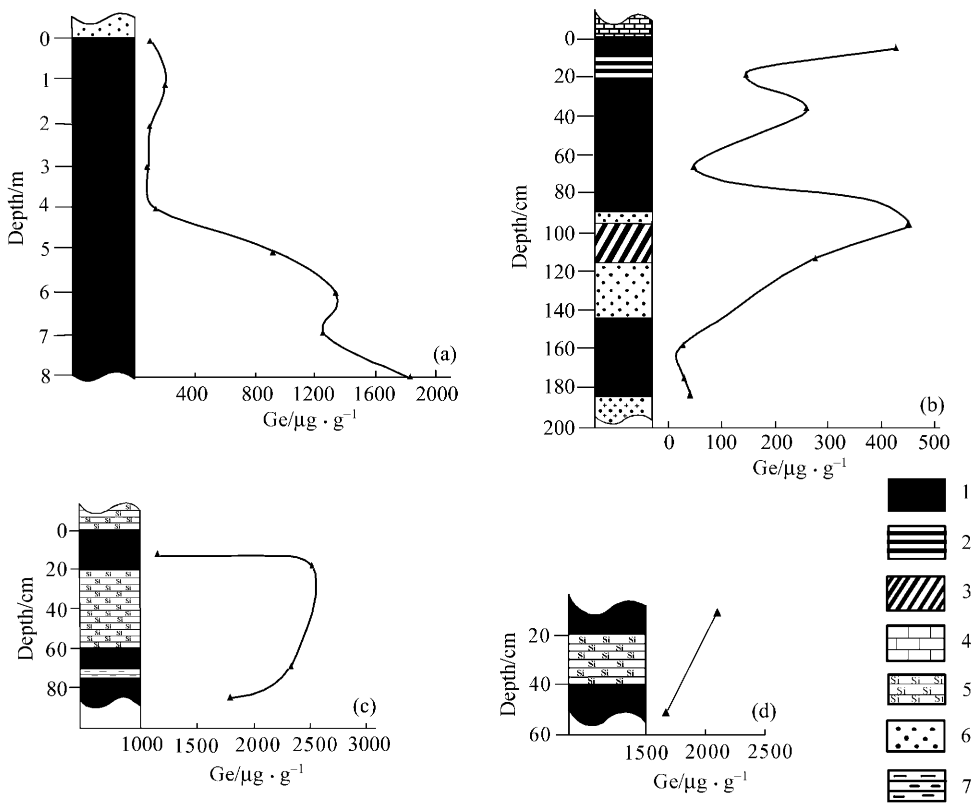

Fig. 8. The Ge content vs. depth diagram of coal sample from the main ore-bodies of the Lincang Ge deposit. 1, Coal; 2, thin-bedded coal; 3, oblique bedded coal; 4, carboniferous siliceous limestone; 5, siliceous rock; 6, sandstone; 7, argillite.

controversies, and the opinions can be summarized in three different genetic types: 1) the adsorption of coal-forming plants[16], 2) transportation of weathering products of granites[18], and 3) transportation of hydrothermal water[13]. Available data also show that too much Ge are poisonous to the growth of plant, and high grade plant could not adsorb abundant Ge[28]. The contributions of coal-forming plant to Ge mineralization in the Lincang Ge deposit are less than 4%[18]. Under about the same continental materials inputting backgrounds, the opinion of weathering of granites couldn't explain why Ge mineralization only existed in the first coal-forming cycle (N_{1b}^2) with hydrothermal genetic siliceous rocks, and no Ge mineralization in the two upper coal-forming cycles without hydrothermal sediments.

The trace element and REE compositions of different samples in different strata have been analyzed in this study. Results (table 6) show that compared to Ge-free coal samples in N_{1b}^4, with the increase of Ge content in coal,the characteristic trace element ratios (especially U/Th, Nb/Ta and Ga/Ge) of Ge-rich coal in N_{1b}^2 are close to those of the siliceous rock, while those ratios of Ge-free coal in N_{1b}^4 are close to those of the granitic clastic rock. Compared to non-hydrothermal sediments, the NAS-normalized REE patterns of hydrothermal sediments are characterized by the concentration of HREE. If Ge in coal seams from the Lincang Ge deposit was transported by hydrothermal water which formed siliceous rocks,the REE patterns of Ge-rich coal should be more and more close to those of the hydrothermal sediments (the siliceous rocks), with the increase of Ge content in coal or the degree of coal being influenced by hydrothermal water. Results (table 7) show that with the increase of Ge content in the coal from the Lincang germanim deposit,the LREE/HREE ratio gradually decreased, $(La/Yb)_N$ and $(Gd/Yb)_N$ ratios were more and more close to those of the siliceous rocks from Zhongzhai. The Chondrite-normalized REE patterns of low Ge (<100 μg/g) coal and Ge-free coal are similar to those of the two-mica granites in the basement, demonstrate that their REE mainly came from the basement two-mica granites. However, especially when Ge content is more than 1000 μg/g, the Chondrite-normalized REE patterns of Ge rich coal are more and more similar to those of the hydrothermal siliceous rocks in Zhongzhai (fig. 9). These facts imply that except the similar material sources with Ge-free coal and low germaniun coal, the Ge-rich coal was superimposed the other elements (including REE, Ge and other elements) transported by hydrothermal water.

Table 6 The average trace elemental ratios of different rocks in the Lincang Ge deposit

	Rock	Strata	Sample number	Ge content/μg • g^{-1}	Rb/Cs	Zr/Hf	Ba/Sr	U/Th	Nb/Ta	Ge/Ga
Dazhai	Ge-rich coal	N_{1b}^2	1	<100	0.74	1.98	1.65	10.2	8.04	73.5
			5	100—200	1.01	2.19	2.60	2.77	6.95	62.2
			6	200—1000	1.02	6.03	2.74	7.18	15.0	145
			6	1000—1500	1.18	5.38	2.41	18.68	51.4	314
			6	>1500	1.52	5.70	2.22	9.48	78.1	335
			average		1.17	4.66	2.44	9.65	37.6	211
Zhongzhai	Ge-rich coal	N_{1b}^2	8	<100	1.26	11.6	24.3	18.2	12.9	10.3
			8	100—1000	1.80	8.18	4.04	5.18	38.2	75.4
			7	1000—1500	1.37	14.1	3.12	7.76	182	261
			4	>1500	1.46	48.5	10.3	22.9	1530	645
			average		1.48	20.6	11.6	14.0	459	253
	Ge-free coal	N_{1b}^4	5		2.55	20.9	4.76	0.77	14.1	0.57
	Siliceous rock	N_{1b}^2	10		0.58	35.1	15.8	27.2	498	107
	Granitic clastic rock	N_{1b}^1	1		16.9	15.4	3.02	0.59	2.89	0.13
	Two-mica granite	Basement	3				5.08			1.70

Table 7 The average REE geochemical parameters of different rocks in the Lincang Ge deposit

Rock	Ge content (10^{-6})		ΣREE	LREE	HREE	LR/HR	Eu/Eu*	Ce/Ce*	$(La/Yb)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$
	Range	Ave.									
Ge-rich coal in Dazhai	<100	79	8.866	7.594	1.272	5.970	0.538	1.111	5.596	3.681	1.122
	100—200	130	18.52	15.98	2.539	6.294	0.394	1.079	6.910	3.047	1.612
	200—1000	490	28.74	23.27	5.469	4.254	0.435	1.049	5.037	2.515	1.262
	1000—1500	1300	48.49	36.53	11.96	3.054	0.285	1.133	2.065	2.002	0.876
	>1500	1600	30.05	19.96	10.09	1.978	0.248	1.064	1.245	1.876	0.594
Ge-rich coal in Zhongzhai	<100	45	29.16	25.21	3.955	6.373	0.389	1.152	5.465	2.473	1.461
	200—1000	340	25.45	21.33	4.120	5.177	0.379	1.032	4.836	2.261	1.412
	1000—2000	1400	19.16	13.39	3.462	3.748	0.347	1.086	2.385	2.043	0.827
	>2000	2400	18.22	14.43	3.785	3.813	0.335	1.095	2.672	2.243	0.777
Ge-free coal	<1	0.64	40.61	34.94	5.675	6.157	0.457	1.104	6.196	2.652	1.777
Siliceous rock		77	0.840	0.702	0.151	4.637	0.529	1.136	4.671	3.889	0.834
Granitic clastic rock		2.52	118.0	96.36	21.68	4.445	0.109	0.910	3.599	2.303	1.006
Two-mica granite		3.7	82.50	72.46	10.04	7.216	0.222	0.888	6.429	2.068	1.741

LR/HR=LREE/HREE; $Eu/Eu^*=[Eu_N(Sm_N \times Gd_N)]^{0.5}$, where N stands for chondrite normalization.

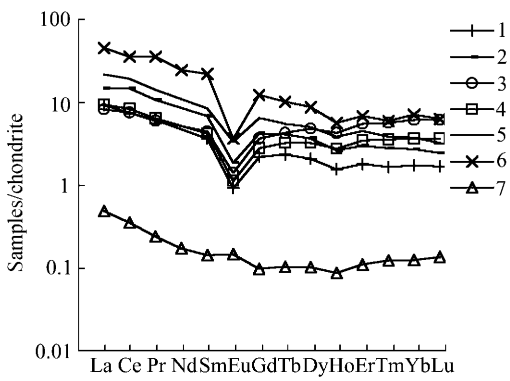

Fig. 9. The Chondrite-normalized REE patterns of different rock in the Zhongzhai Ge deposit. 1, Coal in N_{1b}^2 with Ge content less than10 μg/g; 2, coal in N_{1b}^2 with (10—100) μg/g Ge; 3, coal in N_{1b}^2 with (1000—2000) μg/g Ge; 4, coal in N_{1b}^2 with Ge content more than 2000 μg/g; 5, Ge-free coal in N_{1b}^4; 6, two-mica granite; 7, siliceous rock.

6 Discussions and conclusion

The following evidences can well explain the siliceous rocks from the Lincang Ge deposit were hydrothermal sediments: (1) Abundant hydrothermal sedimentary structures and plant frag fossil were found in the siliceous rocks, and the existing of plant fossil indicates the hydrothermal water activities and the coal-forming process happened basically in the same period. (2) The siliceous rock mainly consist of SiO_2 (92.77% on average), its Al/(Al+Fe+Mn) ratios vary from 0.004 to 0.028, 0.010 on average. The siliceous rock samples fall into the hydrothermal field in the triangle diagram of Al-Fe-Mn in different sediments. (3) The siliceous rocks are distinctively enriched in Ge, Sb, As, W, and secondly enriched in Cs, U, Mo and Tl, Co/Ni ratios are less than 1, and U/Th rations are more than 1. The siliceous rock samples fall into the hydrothermal field in the U-Th diagram and Fe-Mn-(Co+Ni+Cu)×10 triangle diagram. (4) The total REE contents of the siliceous rocks are very low, general less than 1 μg/g, their North American Shale-normalized REE patterns are plain or left-in- clined. (5) The $\delta^{18}O_{SMOW}$ values of the siliceous rocks vary from 10.9‰ to 15.7‰, 13.5‰ on average, close to those of the hot-spring siliceous sinter. As the interlayer or the cliff of the Ge-rich coal seams, the siliceous rocks tightly contacted with ore-body in space. The siliceous rocks contain 5.6 to 360 μg/g Ge, 78 μg/g on average. The Ge content rapidly increased in the coal close to the siliceous rocks. The characteristic trace element ratios and Chondrite-normalized REE patterns of Ge-rich coal are more and more similar to those of the siliceous rocks with the increase of Ge content in coal. The siliceous rocks can be regarded as the prospecting criteria of the Lincang Ge deposit.

It is summarized from the above discussions that the siliceous rocks from the Lincang Ge deposit were hydrothermal sediments, and the Ge in coal seams of the Lincang Ge deposit were mainly transported into the coal-forming basin by the hydrothermal waters which formed the siliceous rocks during the coal-forming processes.

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References

1. Yomamoto, K., Geochemical characteristics and depositional environments of cherts and associated rocks in the Franciscan and Shimanto terranes, Sedimentary Geology, 1987, 52(1/2): 65—108.[DOI]
2. Boatrom, K., Kraemer, T. and Gartner, S., Provenace and accumulation rates of opaline silica, Al, Fe, Ti, Mn, Ni, and Co in Pacific pelagic sediment, Chemical Geology, 1973, 11(1/2): 123—148.
3. Rona, P. A., Hydrothermal mineralization of oceanic ridges, Canadian Mineralogy, 1988, 26(3): 447—465.
4. Crerar, D. A., Namson, J., Chyi, M. S. et al., Manganiferous chert of the Franciscan assemblage: I. General geology ancient and modern analogues and implications for hydrothermal convection at oceanic spresding centers, Econ. Geol. , 1982, 77(3): 519—540.
5. Bostrom, K., Rydell, H. and Joensuu, O., Langbank An exhalative sedimentary deposit, Econ. Geol., 1979, 74: 10002—10011.
6. Marchig, V., Gundlach, H., Moller, P. et al., Some geological indicators for discrimination between diagenetic and hydrothermal matalliferous sediments, Marine Geology, 1982, 50(3): 241—256.[DOI]
7. Murray, R. W., Buchholtz, T., Jones, D. L. et al., Rare earth elements as indicators of different marine depositional environments in chert and shale, Geology, 1990, 18: 268—271.[DOI]
8. Song Tianrui, Ding Tiping, The trying application of silicon isotope of silication to analyzing edimentary facies, Chinese Science Bulletin (in Chinese), 1989, 34(18): 1408—1411
9. Tu Guangchi, Strata-bound Deposit in China (in Chinese) (Vol. 3), Beijing: Science Press, 1988, 196—197.
10. Zhang Qian, Zhang Baogui, Pan Jiayong et al., Characteristics and REE patterns of hydrothermal sedimentary siliceous rocks from Dajiangping pyrite deposit, Western Guandong, China, Chinese Science Bulletin (in Chinese), 1992, 17: 1588—1592.
11. Liu Jiajun, Zhen Minghua,Liu Jianming et al., The geological and geochemical characteristics of Cambrian chert and their sedimentary enviromental implication in western Qinling, Acta Petrologica Sinica (in Chinese), 1999, 15(1): 145—154.
12. Pan Jiayong, Zhang Qian, Ma Dongsheng, et al., Characteristics of siliceous rocks and its relation with mineralization in Yangla copper deposit, Western Yunnan, Science in China, Series D (in Chinese), 2001, 31(1): 10—16.
13. Hu Rui-zhong, Bi Xianwu, Ye Zaojun et al., The genesis of Lincang Ge deposit——A preliminary investigation, Acta Mineralogica Sinica (in Chinese), 1996, 16(2): 97—102.
14. Hu Ruizhong, Bi Xianwu, Su Wenchao et al., Ge-rich hydrothermal solution and abnormal enirchment of Ge in coal, Chinese Science Bulletin, 1999, 44(suppl.): 257—258.
15. Su Wenchao, Hu Ruizhong, Qi Huawen et al., Geochemistry of siliceous rocks and Ge mineralization of Lincang superlarge Ge deposit in Yunnan province, Chinese Science Bulletin, 1999, 44(suppl.): 156—157.
16. Zhang Shuling, Yin Jingshuang, Wang Shuying, Study on existent forms of Ge in coal, Bangmai Basin, Yunnan, Acta Sedimentologica Sinica (in Chinese), 1988, 6(3): 29—41.
17. Zhuang Hanping, Liu Jinzhong, Fu Jiamo et al., The existing form of Ge of Lincang supper-large Ge deposit, Science in China, Series D (in Chinese), 1998, 28(suppl.): 37—42.
18. Lu Jialan, Zhuang Hanping, Fu Jiamo et al., Sedimentation, diagenesis, hydrothermal process and mineralization of Ge in the Lincang superlarge Ge deposit in Yunnan Province, China, Geochimica (in Chinese), 2000, 29(1): 36—42.
19. Taylor, S. R. and McClennan, S. M., The Continental Crust: Its Composition and Evolution, Blackwell Scientific Publications, Oxford: 1985, 67.
20. Wang Zhonggang, Yu Xueyuan, Zhao Zhenhua et al., REE Geochemistry (in Chinese), Beijing: Science Press, 1989, 10—11.
21. Yao Linbo, Gao zhenmin, Yang Zhusen et al., Genesis of selenium-rich siliceous rocks in Yutangba selenium deposit, Hubei province, China, Science in China, Series D (in Chinese), 2002, 32(1): 54—63.
22. Clayton, R. N., High temperature isotope effects in the early solar system (eds. Vally et al.), Reviews in Mineralogy, Houston: Pergamon Press, 1986, 16: 129—139.
23. Pokrovski, G. S., Schottm J., Thermodynamic properties of aqueous Ge (IV) hydroxide complexes from 25 to 350℃: Implications for behavior of Ge and the Ge/Si ratio in hydrothermal fluids, Geochem. Cosmochem. Acta, 1998, 62: 1631—1642.[DOI]
24. Mortlock, R. A., Froelich, P. N., Feely, R. A. et al., Silica and Ge in Pacific Ocean hydrothermal vents and plums, Earth and Planetary Science Letters, 1993, 119: 379—386.[DOI]
25. Arnorsson, S., Ge in Icelandic geochermal systems, Geochem. Cosmochem. Acta, 1984, 48: 2489—2502.[DOI]
26. Murnane, R. J., Leslie, B. L. and Hammond, D. E., Ge geochemistry in the Southern California Borderlands, Geochem. Cosmochem. Acta, 1989, 53: 2873—2882.[DOI]
27. Kraynov, S. R., Geochemistry of fluorine, tungsten and germanium in nitrogeneous thermal waters of crystalline rocks, Geochem. Int., 1965, 2: 1001—1011.
28. Bernstein, L. R., Ge geochemistry and mineralogy, Geochemica et Cosmochemica Acta, 1985, 49: 2409—2422.[DOI]