Origin of seleniferous cherts in Yutangba Se deposit, southwest Enshi, Hubei Province

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Abstract At the top of the Lower Permian Maokou Formation limestones are developed carbonaceous cherts ($P_{lm}{}^{3}$), which constitute the dominant seleniferous layer of the Yutangba Se deposit. The cherts contain as much Se as 1646×10^{-6} on average. In addition, they are rich in organic carbon, Al_2O_3, Si_2O, but poor in S. In addition to Se, as well as Mo, Cd, V, and Co, etc are also highly enriched in the cherts. The chert samples are characterized by low ΣREE, slight LREE enrichment, relatively heavy Si isotope enrichment, and insignificant variations in δ^{30}Si value within the range of 1.1‰—1.2‰. Generally, it can be judged from the major element, trace element and REE data and the Si isotopic characteristics that the Yutangba seleniferous cherts were formed in the shallow sea to semi-deep sea anoxic environments and their formation is controlled chiefly by bio-chemical processes.

Keywords: Yutangba, seleniferous chert, REE, trace element, Si isotope.

The Early Permian is a period of the most extensive sea transgression during the Late Paleozoic in South China, and accompanying this event of sea transgression a suite of bedded cherts deposited in various parts of South China. The bedded cherts are distributed largely in the Gufeng Formation or the Dangchong Formation consisting dominantly of cherts overlying the Lower Permian Maokou Stage. Moreover, in the upper part of the Maokou Formation consisting mainly of carbonate rocks are also recognized bedded cherts in minor amounts[1,2]. There has been no unity in thinking about the origin of this suite of cherts. There are three major hypotheses, i.e. biogenetic origin[1—3], hydrothermally sedimentary origin[4], and upwelling oceanic currrent origin[5].

In the carbonaceous cherts at the top of the Lower Permian Maokou Formation limestones at Yutangba, Shuanghe Town, Enshi, Hubei Province, the element Se is so abnormally enriched as to have formed an independent Se deposit[6]. Since the discovery of this deposit, great efforts have been devoted to research on its geology and geological setting[6,7], but no systematic geochemical evidence has been found for its origin. The seleniferous cherts are the main ore type of the Yutangba Se deposit. The present paper is focused on the origin of the seleniferous cherts in terms of their petrochemical composition, REE and trace element characteristics and Si, O isotopic composition, in conjunction with the tectonic background of sedimentation and the features of the rocks in an attempt to shed much more light on the origin of the Yutangba Se deposit.

1 Geology

Geotectonically this mining district is located in the northeastern sector of the Upper Yangtze Platform of the Yangtze Paraplatform. The mining district lies in the middle part of the N-W flank of the Shuanghe syncline, with the synclinal axis extending NEE, and is developed gently in waveform. The Triassic Daye Formation limestones are developed in the core and the Permian strata on both flanks. The strata strike NEE and dip SSE with a dipping angle of 40°—70°. Fault structures are less developed and are generally SSE-dipping uniclinal structures (fig. 1). The strata exposed in the mining district are the Lower Permian Maokou Formation, the Upper Permian Wujiaping and Dalong formations and the Lower Triassic Daye Formation[7]. The Yutangba seleniferous layer consists of the Lower Permian Maokou Formation carbonaceous cherts, in pseudo-conformable contact with the Maokou Formation limestones and in parallel unconformable contact with the overlying Wujiaping Formation. Lithologically the Yutangba seleniferous layer can be divided into three parts and their characteristics are listed in table 1.

Table 1 The description of the seleniferous strata in the Yutangba Se deposit

System	Series	Formation	Member	Code	Lithological character
Permian	upper	Wujiaping	coal-bearing	P_{2w}^{1}	top: black siliceous nodule with carbonaceous mudstone; middle: grey thin-medium-layered detritus fine-grained sandstone, argillaceous siltstone interbedded with black carbonaceous shales and coal seams; lower: light grey pyrite- and oolite-bearing clayey rocks; bottom: lime mudstone or thin-layered pyrite; 6.8—13.4 m in thickness
	lower	Maokou	carbonaceous chert (seleniferous layer)	P_{1m}^{3-3}	black carbonaceous shales, horizontal bedding well developed, exhibiting laminated structure, with impregnated pyrite, 2.4—5.50m in thickness
				P_{1m}^{3-2}	black thin-layered carbonaceous cherts interbedded with siliceous carbonaceous shales; lower part: they both occur alternatively; middle-upper parts: inerbedded with miner argillaceous dolocrimite lenses; bottom: 0.65 m-thick black thin-layered carbonaceous chert interbedded with 2—70 cm-thick 2—3 layers of mineralized sparolitic coal, laminated structure and micro-waved horizontal bedding well developed, with impregnated pyrite, *Ammonoidea*, *Radiolaria*; 5.22—8.97 m in thickness
				P_{1m}^{3-1}	black thin-layered carbonaceous cherts interbedded with minor siliceous carbonaceous shale; top: both occurring alternatively; lower part: interbedded with minor dolomicrite lenses, with micro-waved horizontal bedding and laminated structure, containing impregnated pyrite, *Ammonoidea and Brachiopoda*, 2.26—6.30 m in thickness
			limestone	P_{1m}^{2}	grey, dark grey thick-layered chert-bearing nodular limestones and bio-detritus limestones, >200 m in thickness

Selenium is enriched mainly in the upper part of the lower member and the lower part of the middle member. It occurs mainly in the form of lenses and its attitude is consistent with the wall rocks. The average grade of orebodies is 0.13% and the proven reserves are estimated at 50 t.

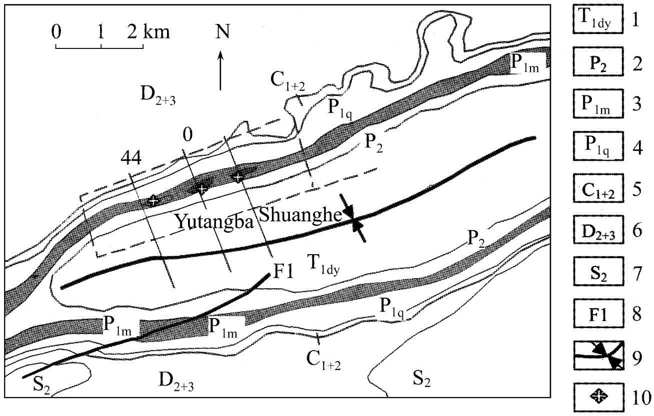

Fig. 1. Geological sketch map of the Yutangba Se deposit (after Wang Hongfa[7]). 1, Lower Triassic (Daye Formation); 2, Upper Permian; 3, Lower Permian (Maokou Formation); 4, Lower Permian (Qixia Formation); 5, Middle-Lower Carboniferous; 6, Middle-Upper Devonian; 7, Middle Silurian; 8, fault; 9, synclinal axis; 10, sample locality.

2 Petrological characteristics of the seleniferous layer

The seleniferous layer is generally a suite of black thin-layered carbonaceous cherts and the cherts are the typical bedded cherts with horizontal bedding and laminated structure. In the lower (P_{1m}^{3-1}) and middle (P_{1m}^{3-2}) members are the rhythmic layers being composed of carbonaceous cherts and siliceous shales, and in the upper member (P_{1m}^{3-3}) are Si-bearing carbonaceous shales. In the middle member are better developed micro-fine rhythmic layers and in the lower member are developed several layers of mineralized semi-dark sapropelitic coal, generally high in carbon. The cherts in the rhythmic layers are generally 3—11 cm in thickness and the shales are 2—8 cm in thickness. The cherts exhibit massive, laminated structures and amorphous and organic textures. The shales exhibit laminated structures. The cherts are composed dominantly of amorphous quartz, chalcedony, carbon and hydromica, accounting for 97% of the total, and other minerals include pyrite, pyrrhotite, selenium minerals (chalcomenite, klockmannite, krutaite, native selenium), apatite, xenotime and so on[8].

The seleniferous layer is characterized by well developed horizontal bedding and laminated bedding, reflecting an anoxic or oxygen-poor marine-facies sedimentary environment. Relatively high carbon contents indicate that biological activities were involved in the formation of the seleniferous layer.

3 Experimental methods

Relatively pure chert samples were collected from the lower and middle parts of the seleniferous layer and their weathering surface was moved. After removal of contamination with distilled water, the samples were finely ground to 200 meshes and dried for use. The prepared samples were used as starting specimens for analysis in the next step. The major elements were analyzed chemically and the trace elements and REE were analyzed by ICP-MS. An ELEMENT

Type high-resolution ICP-MS made by Finnigan MAT Company was employed in the analyses, with the ICP power, 1.2 Kw, sample gas, 0.65 $Lmin^{-1}$, resolution power, 300, samples per peak, 10, and scanning manner, jumping peak. Si and O isotope analyses were conducted on an MAT 251 EM mass spectrometer. First, the contaminated organic carbon was removed by burning at high temperature and then the SiF_4 and BrF_4 methods were used to pretreat the samples. The international standards used are NBS-28 and SMOW, respectively. The analytical precision of NBS-28 was ±0.1%, and that of SMOW was ±0.2%.

4 Geochemical characteristics of the seleniferous cherts

4.1 Petrochemical characteristics

The Yutangba carbonaceous cherts contain mainly SiO_2, C_{org} (organic carbon) and Al_2O_3, which account for 95.97% of the total. SiO_2 is 88.72%, C_{org}, 6.02%, Al_2O_3, 1.23%, Mn<0.001%, Fe, 0.32%, and S, 0.35% on average, with K content being higher than that of Na because of the occurrence of illite in the samples. In addition, the contents of Ca and Mg are not high (table 2). Sampling analysis shows that P contents are less than 1%.

As compared with the Gufeng Formation cherts contemporaneously deposited in other parts of South China[2,4], the Yutangba cherts are obviously enriched in Se, C_{org}, but slightly depleted in Si, Al, Ca , Mg, and remarkably depleted in Fe, Mn and Ti, with K_2O/Na_2O being relatively high.

Table 2 Chemical composition of the Yutangba seleniferous cherts (%)

Sample No.	99-0	99-2	99-9	99-13	99-14	
Sample locality	orebody No.5	Orebody No.5	Orebody No.5	Orebody No.5	Orebody No.5	average
Stratigraphic position	P_{1m}^{3-1}	P_{1m}^{3-1}	P_{1m}^{3-2}	P_{1m}^{3-2}	P_{1m}^{3-2}	
SiO_2	89.80	85.03	89.44	88.61	90.70	88.72
TiO_2	0.059	0.11	0.078	0.054	0.06	0.07
Al_2O_3	1.07	1.84	0.88	1.38	0.99	1.23
Fe_2O_3 a)	0.29	0.44	0.27	0.40	0.20	0.32
MnO	<0.001	<0.001	<0.001	<0.001	<0.001	—
MgO	0.15	0.12	0.14	0.1	0.073	0.12
CaO	0.21	0.023	0.15	0.025	0.044	0.09
Na_2O	0.044	0.055	0.027	0.032	0.032	0.04
K_2O	0.22	0.3	0.19	0.25	0.16	0.22
C_{org}	5.23	7.66	5.68	6.18	5.37	6.02
S	0.38	0.54	0.28	0.41	0.13	0.35
Se ($\times 10^{-6}$)	1646	2582	621	1285	415	1646
LOI b)	6.83	11.09	7.75	9.25	7.19	8.42
Total	98.67	99.01	98.93	100.10	99.45	99.23

a) The value of Fe_2O_3 represents that of total iron (including Fe^{2+} and Fe^{3+}). b) The value of LOI (loss on ignition) includes Se, S, C_{org} and H_2O. Analyst: Ling Hongwen of the Institute of Geochemistry, Chinese Academy of Sciences.

Listed in table 3 are the average ratios of MnO/TiO_2, Fe_2O_3/FeO, SiO_2/MgO, SiO_2/MgO, SiO_2/Al_2O_3, $SiO_2/(K_2O+Na_2O)$ and Al/(Al+Fe+Mn). According to table 2, we have made the correlation diagrams of SiO_2-Al_2O_3, SiO_2-MgO, SiO_2-(K_2O+Na_2O) (the other data from Wang Dong'an[12]) and SiO_2-TFe (figs. 2—5).

Table 3 Comparison of the chemical compositions of cherts of different origins

Genetic type	MnO/TiO_2	Fe_2O_3/FeO	SiO_2/MgO	SiO_2/Al_2O_3	$SiO_2/(K_2O+Na_2O)$	$Al/(Al+Fe+Mn)$
Biochemically sedimentary[a)]	2.3	4.4	346	107	235	
Volcano-sedimentary[a)]	0.24	0.46	69.5	13.7	36	
Hydrothermally sedimentary[b)]	1.44		68	23	82	0.109
Yutangba chert	<0.01		814.9	77.52	355.69	0.74

a) Data from Wang Dongan[12]. b) Data from Xia Bangdong[4].

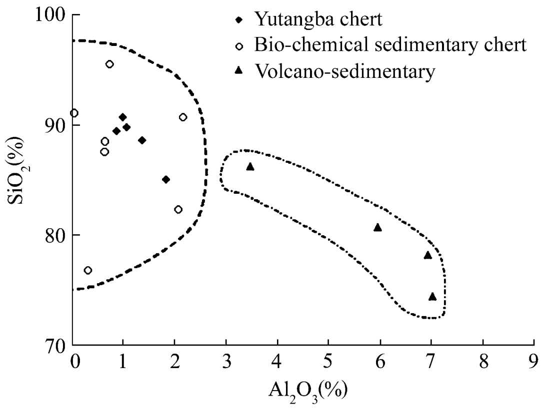

Fig. 2. SiO_2-Al_2O_3 correlation diagram of cherts.

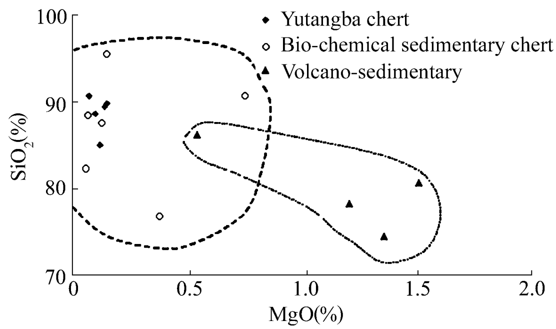

Fig. 3. SiO_2-MgO correlation diagram of cherts.

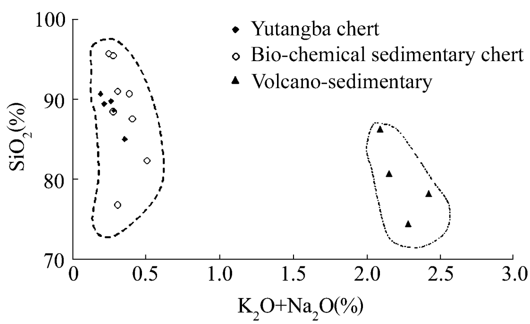

Fig. 4. SiO_2-(K_2O + Na_2O) correlation diagram of cherts.

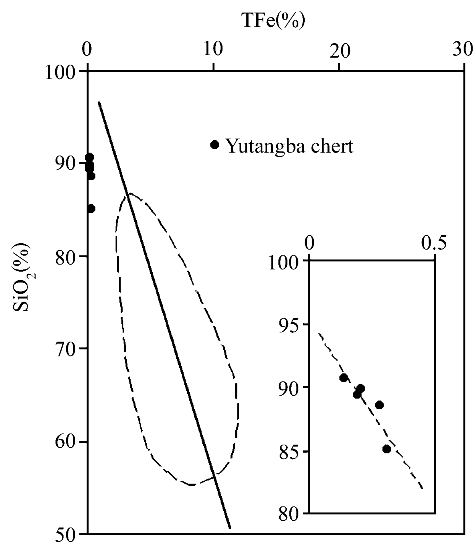

Fig. 5. SiO_2-TFe correlation diagram of seleniferous cherts. The regression line was calculated by way of least square in terms of the data from the samples collected from Mino geological block. In the area defined by the dashed line are non-hydrothermal sediments beyond cherts. The original map after Adachi [10].

The enrichment of Fe and Mn in marine sediments is related to the involvement of hot water, and that of Al is related to terrigenous materials. The Al/(Al+Fe+Mn) ratio can be used as an indicator to identify whether hydrothermal components are involved in sedimentation and this ratio tends to increase with decreasing hydrothermal sediment. In normal marine sediments the ratio of Al/(Al+Fe+Mn) is about 0.6, much smaller than that of sediments related to hydrothermal processes[9]. As pointed out by Adachi, this ratio varied from 0.01 (pure hydrothermal sediments) to 0.6 (pure pelagic biogenetic sediments)[10]. Al/(Al+Fe+Mn) ratios in the cherts of this area are relatively high, averaging 0.74. So it can be ruled out that the Yutangba cherts are of hydrothermal sedimentation origin, and instead they should be of normal bio-chemical sedimentation origin with the involvement of some terrigenous materials.

The ratios of SiO_2/MgO, SiO_2/Al_2O_3, and $SiO_2/(K_2O+Na_2O)$ in the cherts of this area are close to those of bio-chemically sedimentary cherts (table 3). As can be seen in the corresponding SiO_2-Al_2O_3, SiO_2-MgO and SiO_2-(K_2O+Na_2O) diagrams, the data points of the Yutangba cherts all fall within the field of bio-chemically sedimentary cherts.

The relationship between SiO_2 and TFe (total iron) contents of cherts is an indicator to discriminate cherts of hydrothermal sedimentation origin from those of non-hydrothermal sedimentation origin. As is shown in the SiO_2-TFe diagram, non-hydrothermal sedimentary cherts all show a good negative correlation and the data points are below the regression line near the origin. But hydrothermal sedimentary cherts show no correlation and their data points are all plotted above the regression line, at the terminal near the origin. The Yutangba cherts all fall within the field of non-hydrothermal sedimentary cherts and the data points show good negative correlations (fig. 7).

Many scholars consider that Mn is an indicator element derived from the ocean, and MnO/TiO_2 ratio can be used to determine the distance of sediments from the continent[11]. The cherts of this area are low in Mn contents, implying that the Yutangba cherts were formed in a sedimentary environment closer to the continent.

From the above analysis, we can come to the conclusion that the Yutangba cherts belong to the normal bio-chemical sediments and they were formed in an environment closer to the continent.

4.2 Trace elements

As compared with the Clarke value (Vinogradov, 1962), the relatively abundant elements include Se, Mo, Cd, V, Co, Sb, U, Cr, Ni, and Tl. The other elements are relatively poor or depleted (table 4). The Yutangba seleniferous cherts are characterized by an element association of Se, Mo, Cd, V, Co, Sb, U, Cr, and Ni, with Se being abnormally enriched (table 2). In addition, the average values of Mo and V are 143×10^{-6} and 939×10^{-6}, respectively, 130 and 10 times the Clarke values, coming up to the industrial requirements.

The ratios V/(V+Ni), V/Cr and U/Th are the relatively reliable geochemical indices to identify paleo-redox phase. Jones conducted geochemical studies of the paleo-redox phase of Late Jurassic sediments in northwestern Europe and considered that $U/Th > 1.25$ and $V/Cr > 4.25$ are indicative of a suboxic or anoxic environment[13]. Wignal thought that $V/(V+Ni) > 0.83$ would be indicative of an anoxic environment[14]. In the Yutangba cherts V/(V+Ni) ratios range from 0.908 to 0.918, U/Th ratios vary between 7.47 and 22.1, averaging 15.7, and V/Cr ratios are within the range of 3.66—5.26, indicating that the cherts were formed in an anoxic environment. Moreover, Se, Mo and V are all bio-active elements and they are highly enriched, indicating that biological activities were involved in the formation of the Yutangba cherts.

Table 4 Trace element composition of the Yutangba seleniferous cherts ($\times 10^{-6}$)

Element	99-0	99-2	99-9	99-13	99-14	Element	99-0	99-2	99-9	99-13	99-14
Li	5.03	5.49	5.02	3.32	2.51	Nb	2.42	1.46	1.39	1.50	1.19
TiO_2(%)	0.033	0.051	0.033	0.052	0.031	Mo	160	99.7	82.7	200	175
V	1043	1218	931	888	616	Cd	12.2	3.33	2.15	1.68	0.794
Cr	262	235	254	232	117	Sn	0.407		0.011	0.336	0.002
Co	194	66.1	109	211	223	Sb	6.77	2.53	2.18	2.91	3.60
Ni	105	116	90.6	79.6	56.1	Cs	0.405	0.543	0.351	0.445	0.371
Cu	38.3	46.0	26.6	15.0	11.2	Ba	28	32.2	24.6	36.1	33.5
Zn	82.0	27.4	7.91	13.3	2.61	Hf	0.445	0.546	0.500	0.546	0.391
Ga	1.06	1.51	0.731	1.52	0.82	Ta	0.208	0.145	0.159	0.203	0.298
Ge	1.80	2.09	0.917	1.49	0.414	Tl	1.73	1.07	0.901	1.32	1.13
Rb	8.14	11.67	7.32	9.69	6.06	Pb	2.81	2.31	1.87	1.72	1.76
Sr	42.0	15.2	35.3	19.4	32.7	Th	0.625	0.847	0.583	0.882	0.554
Y	13.9	4.56	9.47	4.53	3.49	U	13.8	8.51	13	6.59	9.08
Zr	17.6	16.7	17.9	17.6	14.9						

Analyst: Qi Liang of the Institute of Geochemistry, Chinese Academy of Sciences.

4.3 REE

REE analyses of the Yutangba cherts are listed in table 5.

Table 5 The REE composition of the Yutangba seleniferous cherts ($\times 10^{-6}$)

REE	99-0	99-2	99-9	99-13	99-14	REE	99-0	99-2	99-9	99-13	99-14
La	4.907	2.872	3.803	3.185	2.478	Yb	0.854	0.365	0.697	0.32	0.313
Ce	5.105	3.286	3.778	3.311	2.879	Lu	0.121	0.053	0.099	0.053	0.041
Pr	0.944	0.619	0.868	0.611	0.483	Y	13.859	4.564	9.473	4.525	3.492
Nd	3.665	2.564	3.303	2.19	1.866	ΣREE	20.236	12.498	16.846	11.845	9.991
Sm	0.882	0.629	0.777	0.521	0.485	LREE	15.689	10.093	12.680	9.908	8.268
Eu	0.186	0.123	0.151	0.09	0.077	HREE	4.547	2.405	4.166	1.937	1.723
Gd	0.96	0.621	0.979	0.508	0.42	δEu	0.887	0.864	0.760	0.768	0.749
Tb	0.178	0.106	0.182	0.075	0.074	δCe	0.517	0.537	0.453	0.517	0.573
Dy	1.107	0.677	1.051	0.438	0.382	(La/Yb)N	0.557	0.762	0.529	0.964	0.767
Ho	0.278	0.129	0.253	0.112	0.097	(La/Sm)N	0.991	0.813	0.872	1.089	0.910
Er	0.926	0.392	0.794	0.382	0.352	(Gd/Yb)N	0.670	1.014	0.837	0.946	0.800
Tm	0.123	0.062	0.111	0.049	0.044	LR/HR	3.450	4.197	3.044	5.115	4.799

Analyst: Qi Liang of the Institute of Geochemistry, Chinese Academy of Sciences.

The Yutangba seleniferous ores are low in ΣREE and are characterized by indistinctive fractionation between HREE and LREE, slight LREE enrichment, moderate negative Ce anomaly, and weak negative Eu anomaly. As the HREE are much easier than the LREE to dissolve and migrate in seawater and organic matter is highly capable of adsorbing REE, especially the HREE, the Yutangba cherts are relatively enriched in LREE.

The typical marine hydrothermal sediments are characterized by low Σ REE, HREE enrichment, and remarkable negative Ce anomaly. The North American shale-normalized REE distribution patterns in the Yutangba cherts are represented by almost horizontal and slightly left inclined curves (fig. 6). Having systematically studied the metallic deposits of hydrothermal origin and hydrogenetic metallic deposits of non-hydrothermal origin throughout the world, Fleet thought that the former is characterized by low ΣREE, negative Ce anomaly and a tendency to be enriched in HREE while the latter by high ΣREE, positive Ce anomaly and HREE depletion. But the above features show a continuous variation between the two types of metallic deposits, i.e. as can be seen in the North American shale-normalized distribution patterns, Ce anomaly tends to become less remarkable with decreasing proportion of hydrothermal sediments and the REE curves change from left-inclined to horizontal[15]. At a glance of fig. 6 we can see clearly that the process of formation of the Yutangba cherts seems not to have been affected by hydrothermal activities, but is characterized by normal biochemical deposition.

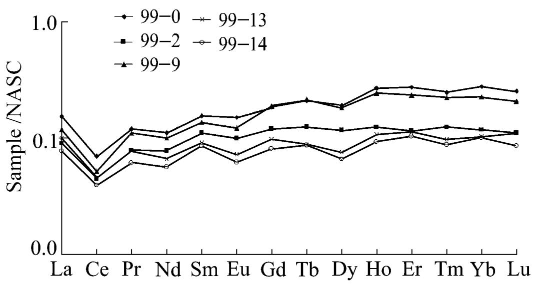

Fig. 6. The REE distribution patterns in the Yutangba seleniferous cherts.

4.4 Si and O isotopes

Samples were selected from different parts of the seleniferous layer of No. 5 orebody for Si and O isotopic analysis. Vein-1 represents well crystallized quartz which occurs as druses in cavities developed in member I (P_{1m}^{3-1}). This kind of quartz was formed during the post-diagenetic tectonic process. 99-a, sh-45 and sh-48 are fresh samples, vein-1 occurs in the stratigraphic position where 99-a is located, and sample sh-52 has been weathered to some extent because of being close to the surface. The results of the measurement are listed in table 6.

Table 6 Si, O isotopic composition of the Yutangba seleniferous cherts

Sample No.	Name	Sample locality	$\delta^{30}Si_{-NBS-28}$(‰)	$\delta^{18}O_{-SMOW}$(‰)
Vein-1	quartz	P_{1m}^{3-1}	0.0	26.7
99-a	carbonaceous chert	P_{1m}^{3-1}	1.2	24.7
sh-45	carbonaceous siliceous shale	P_{1m}^{3-2}	1.2	21.3
sh-48	carbonaceous chert	P_{1m}^{3-2}	1.1	21.6
sh-52	carbonaceous siliceous shale	P_{1m}^{3-1}	0.0	17.3

As can be seen from table 6, the δ^{30}Si values of all the samples are larger than, or equal to, zero, and their δ^{18}O values vary between 17.3‰ and 26.7‰. As for fresh Se ore samples, the δ^{30}Si values of either cherts or siliceous shales show a little change, ranging from 1.1‰ to 1.2‰, indicating that the Yutangba chert samples are enriched in relatively heavy Si isotope. The δ^{30}Si values of tectonogenic quartz and the samples affected by weathering and leaching are equal to zero, indicating no isotope fractionation.

Silicon which stemmed from different sources possesses different isotopic compositions. For instance, hot water-sourced cherts have relatively low δ^{30}Si values, ranging from −1.5‰ to 0.8‰, and cherts of metasomatic origin have relatively high δ^{30}Si values, varying between 2.4‰ and 3.4‰[16,17]. Pelagic radiolarian cherts usually have relatively low δ^{30}Si values, and neritic or bathyal radiolarian cherts are always characterized by relatively high δ^{30}Si values[18]. Studies of cherts of different ages in China have shown that their δ^{30}Si values fall mainly within the two ranges, i.e. from 0.1‰ to −0.5‰, in consistence with the ranges of δ^{30}Si values for pelagic radiolarian cherts, for the most part of hydrothermal deposition origin, and from 0.3‰ to 0.5‰, in consistence with the ranges of δ^{30}Si values for neritic and bathyal cherts, which is always associated with carbonate rocks and their δ^{30}Si values range from 0.3‰ to 1.3‰, showing the characteristics of shallow sea-facies rocks[19]. The Yutangba cherts have relatively high positive δ^{30}Si values, whose δ^{30}Si values are within the ranges for the neritic and bathyal cherts (fig. 7), showing significant differences from Sedex cherts.

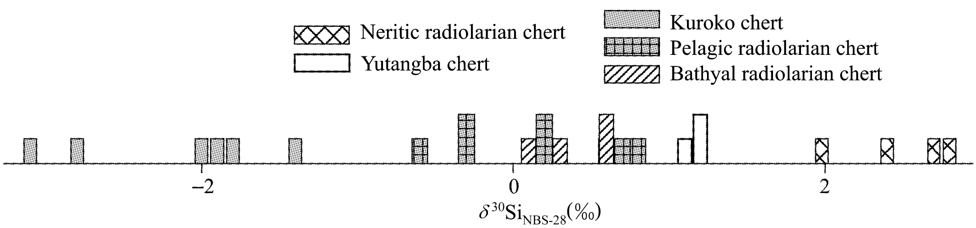

Fig. 7. Comparison of the Si isotopic compositions of the Yutangba cherts and other genetic types of cherts (the other data from Ding Tiping[19]).

The δ^{30}Si values of fresh Se ore samples from Yutangba vary between 21.6‰ and 26.7‰. According to Yang Yuqing, the δ^{18}O values of the Gufeng Formation cherts of bio-chemical origin are within the range of 20.9‰—26.4‰ and their δ^{30}Si values, 1.1‰—1.6‰[2]. The Si, O isotopic composition of the Yutangba Se ores is generally consistent with the results obtained by Yang Yuqing.

The effects of dynamic isotope fractionation caused by biological activities would lead to the enrichment of heavier isotopes in the cherts, as evidenced by positive δ^{30}Si values. Si isotope studies provide further evidence for the previous viewpoint, i.e. the Yutangba seleniferous cherts are of neritic to bathyal bio-sedimentation origin.

5 Discussion

5.1 Stratigraphic division of the Yutangba seleniferous cherts

The stratigraphic division of the Maokou Formation cherts has been well documented by previous researchers. This suite of cherts is called the Dangchong Formation in Hunan Province, the

Mingshan Layer in Jiangxi Province, the Gufeng Formation in central Guangxi, and the Luojia Formation or the Yanzhijie Formation in Hubei Province. Stratigraphically, this suite of cherts appears frequently between the Longtan Formation and the Qixia Formation and these rocks vary greatly both in lithology and in thickness when they extend to the areas along the middle-lower Yangtze region. As a result, the cherts are named diversely. Feng Zengzhao et al. divided them into three types, i.e. the Maokou Formation consisting dominantly of limestones, the Gufeng For mation consisting principally of cherts, and the Yanqiao Formation making up of detrital rocks[1]. According to this scheme of classification, the cherts at the top of the Yutangba-Maokou Formation are assigned to the Maokou Formation.

We consider that the key problem is the contact relationship between this suite of cherts and the Maokou Formation limestones. It was traditionally held that they were of continuous sedimentation in conformable contact with each other. So the cherts are designated to the contemporaneous heteropical sedimentation of the Maokou Formation limestones[20]. More recent evidence indicates that both are in disconformable contact with each other. The evidence is the discovery of terrigenous detrital rocks at the bottom of the Gufeng Formation at Jianshi and Huangyan, western Hubei, further indicating that there is a gap of sedimentation between the Gufeng Formation and the Maokou Formation[21]. Therefore, we think that it is better to designate this suite of cherts as an isolated stratigraphic unit to the Gufeng Formation. It is the scarce distribution of the Gufeng Formation and frequent transformation into limestones that it is generally called the Maokou Formation[22]. Comparative studies of global sea level change during the Permian period indicate that during the Late Guadalupian (corresponding to the late Early Permian), the drop of sea level exerted a great influence on the paleo-geographical framework of South China. Most of the strata were exposed on the Earth surface and were thus subjected to weathering denudation, resulting in the lack of the top of the Lower Maokou Formation and the accumulation of 0—50 m-thick residual sediments[23]. The sedimentary characteristics of the Yutangba cherts also reflected a process in which water body became from shallow to deep. In the lower member are the thin-bedded cherts (the thickness is greater than that in the middle part), in the middle member are the thin-bedded cherts alternating with shales, at the bottom are the sapropelitic coal measures (stone coal measures), at the top are developed minor dolomicrite lenses, and in the upper member are the carbonaceous siliceous shales.

5.2 Sedimentary environment of the Yutangba seleniferous cherts

The Permian period witnessed frequent, intensive tectonic activities of the South China continental plate, which were generally predominated by intraplate rifting and descending and ascending processes[24]. Under the action of intraplate rifting, a number of rift-like deep-water basins were formed in the different parts of the continental plate. It is the Lower Permian bedded cherts (the Gufeng Formation) that were just formed in these rift-like deep water basins. During the Early Permian Maokou stage this area was designated to the sedimentation area of the Lichuan-

Jiujiang neritic-facies carbonate rock platform[1]. It is considered that the bedded cherts of the Maokou Formation (just like the Yutangba cherts) were formed in the platform basins[2] or fault basins[25] developed on the carbonate rock platform in response to tectonic extension.

The above geochemical evidence lends strong support to the conclusion that the Yutangba Se deposit was formed in a bathyal to neritic anoxic environment. Due to the difference in sedimentary environments, the cherts deposited in this area are significantly different from those (the Gufeng Foramtion) developed in the rift-like deep water basins. The former is characterized by a small sedimentary thickness, only ranging from 10 to 20 m or so, with low P, Mn contents and high C contents, and occurrence of stone coal measures. The stone coal is a kind of high-grade metamorphosed sapropelitic coal, which contains abundant super-microscopic fossils and bacterial and algal fossils. The main coal-forming precursors are lower organisms (plankton and benthonic micro-plant populations dominated by algae), and marine facies stone coal is usually formed in the reducing environment along the shallow sea slope[26]. The occurrence of stone coal in the Yutangba cherts indicates that the cherts were deposited in a shallow sea environment.

5.3 Sources of Se and Si and the mechanism of their enrichment

In normal cases the rivers are the main sources of Se and Si. Another important source of Se is meteoric water. During the Permian period volcanic activities were common in southern China and its vicinities. For example, in the Sichuan-Yunnan-Guizhou-Guangxi areas there occurred extensive basalt effusion during the Late Maokou stage and in a number of areas along the middle-lower Yangtze region there were developed tuffaceous sediments. In the Gufeng Formation chert interbeds there have been found numerous argillized pyroclastic rocks and lavas[4]. So, extensive basalt effusion and limited volcanic and hydrothermal activities provided large quantities of Se and Si. The stratigraphic and lithological characters and paleontological fossil species in the north marginal area and central-south area of the Lower Permian Yangtze platform can be well compared with those in western Qinghai, paleo-Tethysian sea of western Yunnan and the paleo-Pacific Ocean, indicating that the rift basins in the north marginal area and central-south area linked with the paleo-Tethysian sea and the paleo-Pacific Ocean. These extra amounts of Se and Si would be transported by the horizontally moving oceanic currents to the loci of sedimentation.

Evidence developed from the investigations of modern oceans has confirmed that the euphoric zone or the oxic zone is usually within the expand of 0—100 m, the suboxic zone is in the expand of 100—200 m, and the anoxic layer (below the O_2/H_2S interface) is below 200 m. In the euphoric zone the dissolved Se is dominated by Se (VI), and with increasing depth the reduced organic Se (the dissolved peptide is seleniferous amino acid, for instance, the condensates of Se methionine and Se cystine) increases rapidly, but Se (VI) tends to decrease progressively[27]. Studies on the Se circulation in seas and oceans have shown that selenium is a bio-active element and turns into instable organic state by way of bio-fixation (reduction of oxidized selenium species). In surface waters (oxic layer or eupholic layer) marine organic matter can absorb selenium and make it turn into organic particulates. After organic bodies die, they will be decomposed in the deep-water area and selenium will be a survivor. The dissolved selenium is transported by upwelling ocean currents to the surface water area and will be combined with organisms, starting its recycling again. Metabolism of Se by marine living organisms maintains selenium balance in the whole sea. The cycling of Se after it is incorporated into sediments under the action of organic matter is a very slow process and the most majority of Se fixed by organic matter will survive and only a minor portion of it will be transported to sediments[28,29].

So, the circulation of Se in the sea is controlled chiefly by biological activities. The following preconditions must be satisfied before a regional abnormally seleniferous layer is formed: (i) sufficient supply of Se and destruction of the original dynamic balance; (ii) anoxic environment leading to reproduction and accumulation of numerous biotic communities; (iii) a unique sedimentary environment—relatively stagnant shallow sea basins where there is no upwelling ocean currents blocking recycling of selenium in sediments.

The total amount of Se in seas and oceans is estimated at 2.2×10^5 kT and the contents of Se erupted from hydrothermal solutions at the mid-ocean ridges are 15—103 nmol/kg, and the average content of Se in the mid-ocean ridge basalts (MORB) is 0.2×10^6[28]. Basalt effusion could provide abundant ore-forming materials for Se mineralization.

The cycle of Si in the sea is controlled by similar factors. Its enrichment and precipitation are controlled dominantly by siliceous planktons (diatomea, radiolaria, sponge, etc.). That is to say, biogenetic siliceous fossils (remains) are the principal source of siliceous materials for the formation of cherts. The silicon derived from hydrothermal activities and sea-floor volcanic eruption is a supplementary source [10]. It is hard to distinguish correctly hydrothermal cherts from biogenetic ones merely on the basis of whether there are contained radiolarian fossils or not because radiolarian fossils are widely spread both in shallow-sea sediments and in pelagic sediments, though dominantly in the latter. Ecological evidence of micro-fossils is based on the precise identification of the types of fossils. Owing to their old ages and variations during the post diagenesis, it is difficult to identify correctly the types of fossils. So the various lines of petrochemical and geochemical evidence appear more reliable, which would be a bit easier to obtain.

From the following pieces of evidence it can be confirmed that the Yutangba cherts are of biochemical deposition origin. (i) As for their chemical composition, the cherts in the region studied are dominated by SiO_2, C_{org} (organic carbon) and A_2lO_3, with relatively low Mn contents and relatively high Al/(Al+Fe+Mn) ratios (averaging 0.74), showing significant differences from hydrothermal cherts. On the SiO_2-A_2lO_3, SiO_2-MgO, SiO_2-(K_2O+Na_2O) diagrams the Yutangba cherts fall within the field of cherts of biochemical deposition origin, belonging to normal biochemical deposits. (ii) The cherts are high in organic carbon, up to 6.02% on average. In addition, bio-active elements such as Se, Mo and V are of high enrichment, indicating that the bio-activities are very obvious. (iii) V/(V+Ni) ratios in the cherts range from 0.908 to 0.918, U/Th ratios from 7.47 to 22.1 with an average of 15.7, and V/Cr ratios from 3.66 to 526, implicating that the formation of cherts seems to be related to the anaerobic environment created as a result of large-scale accumulation of living organisms. (iv) The cherts are relatively low in ΣREE and show no sign of remarkable LREE/HREE fractionation, with the LREE being slightly enriched. Moreover, they possess moderate negative Ce and weak negative Eu anomalies. The North American Shale-normalized REE distribution patterns of the cherts are represented by the nearly horizontal curves, quite different from those of hydrothermal cherts. (v) The $\delta^{30}Si_{NBS\text{-}28}$ values of the cherts are positive, within the range of 1.1‰—1.2‰, intermediate between those of neritic and bathyal radiolarian cherts, while those of hydrothermal cherts are generally negative, indicating that the $\delta^{30}Si$ values of the Yutangba cherts are generally controlled by normal biochemical processes.

To sum up, we have come to the following conclusions in regard to the mechanism of formation of the Yutangba Se-rich cherts. The Dongwu movement occurring in the late Early Permian led to the gentle uplift of the crust in the region studied. Owing to the difference in extent of crustal uplifting the relatively closed and stagnant anaerobic conditions were created in the basin. Moreover, the effusion of Emeishan basalts in southwest China was accompanied with limited sea-floor hydrothermal activities and volcanic eruption. These distal-source magmas and hydrothermal activities brought about large quantities of Si and Se. Under such circumstances the original normally cycling mechanism would necessarily be destroyed and the dynamic balance would be broken, thus leading to vast reproduction of siliceous planktons (mainly plankton plants) to consume the excess Se and Si. Meanwhile, these organisms would die rapidly and be precipitated on the sea floor to form Se-rich carbonaceous cherts.

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