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journal or publication title	Proceedings, International Symposium of the Kanazawa University 22st-Century COE Program
volume	1
page range	229-234
year	2003-03-16
URL	http://hdl.handle.net/2297/6401

Proceedings: International Symposium of the Kanazawa University 21st-Century COE Program Vol. 1 (2003)
Edited by Naoto KAMATA

Reflectance and Carbon Isotopes of Kerogen in Lower Cambrian Black Shales of Zunyi and Zhangjiajie, Southwest China: Indicators to the Source of Au-Ag-PGE

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ABSTRACT In the Lower Cambrian black shales of south China developed a metal-rich bed with large amounts of Au, Ag and platinum group elements (NME) and many other metals such as Ni, Mo, As, Ba and Se. The concentrations of NME are much higher in Zunyi of Guizhou province (PGE+Au, 1 138 $\times 10^{-9}$; Ag, 91 775 $\times 10^{-9}$) than that in Zhangjiajie of Hunan province (PGE+Au, 605 $\times 10^{-9}$; Ag, 18 534 $\times 10^{-9}$). The R^{o}_{mean} data are of 2.550 and 2.393 for the metal-rich bed and black shale in Zhangjiajie and the equivalent data are of 3.054 and 3.272 in Zunyi. The $\delta^{13}C$ (PDB, ‰) values are of –31.008～-31.181 (±0.2) for kerogen from Zhangjiajie and –31.723～-33.854 (±0.2) from Zunyi. Correspondently, the Proterozoic and Cambrian ultramafic magmatism in Guizhou province is much more developed than that in Hunan province. This might be of significance to indicate that the NME in the black shales were originally from ultramafic magma or the igneous rocks.
KEY WORDS: reflectance and carbon isotopes of kerogen, black shale, noble metal elements, Lower Cambrian, Guizhou-Hunan provinces, China.

I Introduction

In more than 10 provinces of south China exists Lower Cambrian black rock series(Fig.1). The bottom of the series sporadically contains thin beds and lenses carrying large amounts of Ni, Mo and less amounts of As, Se, U, Ba, Cu, Pb, Zn, V, P, Au, Ag and platinum group elements (NME). These metal-rich beds are scattered through a northeast-east trending region extending for about 1 600 km from Yunnan in the west to Zhejiang in the east.The abnormally enrichment of these elements in the Lower Cambrian black shales of south China has been reported by Fan et al.[1,2], Zhang et al.[3], Chen et al.[4], Coveney et al. [5-7], Li S et al.1)[8-12], Gao et al.[13,14] and Li Y et al [15-17], Liang et al. [18], Ding et al. [19], Wu et al. [20-22] and Zeng[23].

With regard of the source of Au-Ag-PGE in the black shale, several models have been put forward. According to element parageneses and Ir anomaly, Fan [1] and Fan et al[2] pointed out that platinum group elements, Ni and Co might be of extraterrestrial origin, and other elements

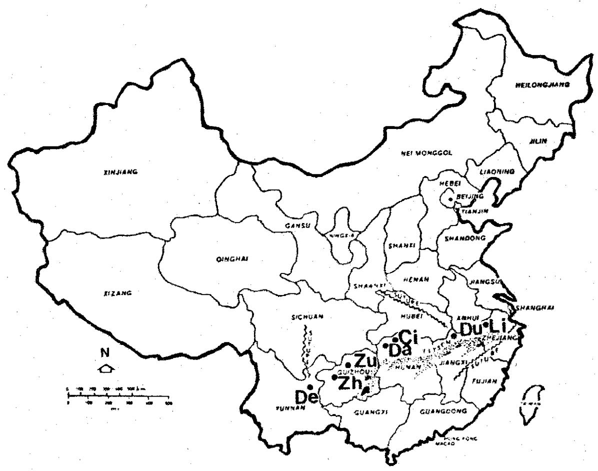

Fig. 1 Locations of Lower Cambrian NME-bearing black rock series. De, Dezhe; Zh, Zhijin; Zu, Zunyi; Da, Zhangjiajie(Dayong); Ci, Cili; Du, Duchang; Li, Lizhe. Dotted area: Flysch terrene; Irregular black: Ophiolites. After Coveney et al. [5]

such as Zn, Mo, Ba, U, Cd, Se and Tl might be related with sea floor hot spring. Based on the linear distribution of metal-rich bed in south China, Coveney et al. [5-7] thought that the enrichment of the metals might be the result of syngenetic precipitation of metals from sea floor hot spring related with deep-seated fractures. Based on some laboratory experiments, Chen (1995, personal communication) put forth a supergene-leaching model for the element enrichment. On the basis of the REE study of the metal-rich bed and the REE models of marine sediments, we once discussed the hydrothermal sediment characteristics of the metal-rich bed [8]. We also reported the discovery of hydrothermal chert in the black rock series [9]. Our further studies of the NME ratios, relations, distribution patterns disclosed that the NME in the black shales were not directly from extraterrestrial materials. Our studies of NME abundance, NME partition patterns and the distribution of ultramafic igneous rocks disclosed that the NME were not enriched by normal syngenetic sedimentation but might be related to ultramafic rocks. In addition, Mao's Re-Os dating on molybdenum-nickel ore samples from the Huangjiawan mine, Zunyi district, defines an age of 541±16

1) Li S, *Geochemistry of Au-Ag-PGE in Lower Cambrian black rock series of Hunan and Guizhou Provinces*, Post-Ph. D. Dissertation, Institute of Geochemistry, Chinese Academy of Sciences, 1994 (in Chinese with English Abstract; kept in Beijing State Library)

Huangjiawan mine, Zunyi district, defines an age of 541±16 Ma [24], and our Re-Os isochronal dating on 6 molybdenum-nickel ore samples from Zhongnan of Guizhou province, and Ganziping and Sancha of Hunan province defines an age of 542(±11) Ma, which is in agreement with the stratigraphical age of the black shale host [12]. Synthesizing all these results, the authors thought that the ultramafic and mafic igneous rocks were the main source of the NME and that the enrichment of the NME was mainly by hydrothermal process [10-12].

As we have already known that within the black rock series exist a large quantity of organic materials mainly composed of kerogen, and the values of their reflectance and isotope might be affected by the mineralization and the related geological activities which were obviously different in Zhangjiajie and Zunyi areas, these values might be useful in the study of the origin of the mineralization in the black rock series. To further disclose the nature of the major event leading to the mineralization of Au, Ag, PGE, and many other metals, the present study is fulfilled of the reflectance and carbon isotopes of kerogen.

II Geological background

Palaeogeographically, the region with black rock series in Cambrian period belongs to the Yangtze plate margin (Fig.1). The region was tectonically metastable with polycycle magmatism and a series of NE directed deep-seated faults which had been acting since Proterozoic. By comparing the magmatic and tectonic intensity in Guizhou Province and Hunan Province, it is found that the magmatism was much stronger in Guizhou than that in Hunan.

The Lower Cambrian NME-rich black rock series is well developed in the regions near Zhangjiajie city in northwest Hunan province and Zunyi city in north Guizhou province. The series consists of five lithological members. The stratigraphical sequence of the series is recognized to contain the following lithological members, in the order from upper to lower: carbonaceous illite shale (30-40 m), carbonaceous-argillaceous chert (upper chert, 0-18 m), metal-rich shale bed with calcite dominated and apatite dominated nodules (0.2-1 m), argillaceous phosphorite (0.1-0.8 m), carbonaceous and argillaceous chert (lower chert, 0-1.0 m).

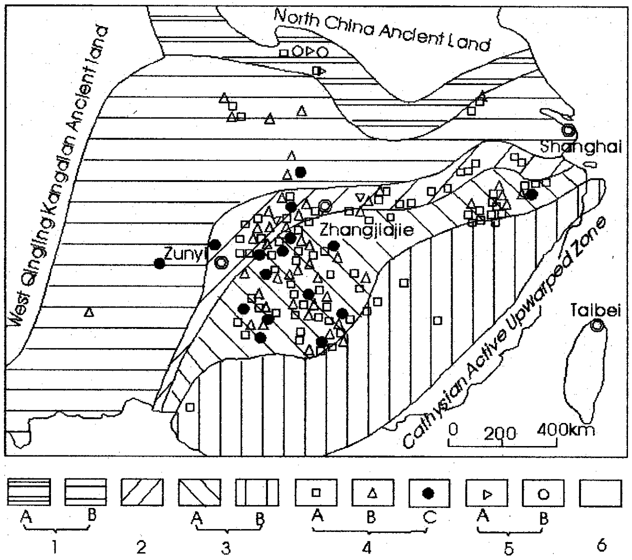

Fig.2 Locations of Lower Cambrian bone coal, vanadium & poly-element (Ni-Mo-As-Au-PGE and many others) deposits and biographical divisions.[1] 1, N. China type: a, N. China division; b, Yangtze division; 2, Transitional division; 3, SE China type: a, Jiangnan division; b, Zhujiang division; 4, Hetang period: a, bone coal; b, vanadium; c, poly-elements; 5, Xingji period: a, vanadium; b, poly-elements; 6, Ancient land

The evolution and mineralization of the black rock series can be divided into four periods: syngenetic, diagenetic, catagenetic and hypergenetic periods. The syngenetic period is the most important for NME mineralization. The orther periods, however, are responsible for further enrichment of NME.

The analyses of Au, Ag, PGE reveals that the NME are highly concentrated in the metal-rich beds (TABLE 1). A correlation between Zunyi and Zhangjiajie shows that the abundance of NME in the metal-rich beds in Zunyi is much higher than that in Zhangjiajie (TABLE 2).

TABLE 1 Analyses of noble metal elements in the black rock series (10^{-9})

Lithology	Number of analyses	Os	Ru	Rh	Ir	Pt	Pd	Au	Ag
Metal-rich Bed	8	51-190	3-40	2-16	1-43	45-580	92-500	70-349	10200-97600
Illite shale	8	bdl-21	bdl-92	bdl-6	bdl-3	4-180	bdl-100	5.57-50	450-4200
Chert	2	bdl	bdl-1	bdl	bdl- 3	2-4	bdl- 6	1.87-2.4	140-431
Phosphorite	1	2	2	bdl	2	6	bdl	13.7	1320

Note: bdl means below detection level (< 1×10^{-9} ,calculated in 0.5×10^{-9}). After Li S [11]

TABLE 2 Correlation of NME in the metal-rich beds between Zunyi and Zhangjiajie

Region (Number of analyses)	Os	Ru	Rh	Ir	Pt	Pd	Au	Ag	ΣPGE
Zunyi (4)	150	16	13	11	368	370	210	91775	928
Zhangjiajie (4)	88	6	6	2	173	186	144	18534	461

Unit of the measurements: 10^{-9}. After Li S [11]

III Reflectance of kerogen

A Sample description, analytical methods and results

Totally 12 black shale samples were collected from two systematic sections in Ganziping near Zhangjiajie city and Tianeshan near Zunyi city. Separation experiments displayed that the organic materials in the rock samples are predominantly kerogen and resolvable organic materials occupy only a small part. Kerogen, the main organic material in the black rock series, shows as micro-grains of anisotropic bitumen under microscope distributed mostly along the micro-fractures in the black shales. It is the product of diagenesis without large-scale transference during its formation somewhat similar with the sulfide-calcite veinlets in forming time.

The reflectance of kerogen or solid bitumen (R_b) is measured by micro-photometer in the National Key Laboratory of Organic Geochemistry in Guangzhou. The samples are prepared to be polished sections of bulk rocks and polished sections of kerogen. In view of the anisotropic nature of the kerogen, 12-40 (generally 25-30) data are measured for each polished section. The standard deviations are between 0.08-0.68 and generally 0.3-0.4. The results of R_b for both the polished sections of bulk rock and kerogen are very close (TABLE 3).

B Paleogeotemperature

The calculation of paleogeotemperature was made on the basis of vitrinite reflectance. Vitrinite is a kind of gel formed by biochemical degradation and gelatification of the lignin of vascular plant. In some marine and carbonate strata, especially the strata formed before Devonian when vascular plants appeared, there are few, even no vitrinite. In this case vitrinite reflectance is obtained from conversion of bitumen reflectance. For calculating paleogeotemperature, the mean values of bitumen reflectance ($R_{b,\ mean}$) are conversed into those of vitrinite (R^o) (TABLE 3) by means of equation $R^o = 0.668\ R_b + 0.346$ [25]. TABLE 4 shows the differences of R^o values between Zhangjiajie and Zunyi.

Due to the anisotropic characteristics of the bitumen, the R^o values for same bed varies within quite large range. The maximum value is the only one that can reflect the real thermal evolution of the bitumen, whereas the mean value, as a comprehensive value of different measuring spots, can be utilized to weaken the effect of those accidental errors, which is an important supplement to the maximum. It is noticed that the maximum and mean values of R^o for the metal-rich shale and thin-/thick-bedded shale show no prominent and regular variation, but the values for both the metal-rich shale and thin-/thick-bedded shale in Zunyi are prominently higher than those in Zhangjiajie (TABLE 4).

During Paleozoic Era, the region with the black shales was basically marine sedimentary basin and during the Mesozoic it's continental basin. Erosion of the region started from Cenozoic. In such a background, the heating time of the black shales is supposed to be 500 Ma. Plotting the R^o_{mean} data of Table 2 on Karwell diagram [25] with 500 Ma line being extrapolated by the authors, the geotemperature the black shale gone through is about 81—85℃ in Zhangjiajie and 95—101℃ in Zunyi. Plotting the R^o_{max} data of Table 2 on Karwell diagram with 500 Ma line being extrapolated by the authors, the geotemperature the black shale gone through is about 83 — 86 ℃ in Zhangjiajie and 90—95 ℃ in Zunyi.

Hood et al. [26] constructed a LOM-T_{max}-T_{eff} ternary diagram, where LOM is the index of thermal maturity of organic matter, T_{eff} is effective time and T_{max} is maximum geotemperature. With this diagram, conversing vitrinite reflectance (R^o_{mean}) into LOM and supposing T_{eff} to be 500 Ma, the T_{max} is measured to be about 170 ℃ in Zhangjiajie and 200 ℃ in Zunyi(Fig.3).

IV Carbon isotope

Representative samples of kerogen were analyzed in the National Key Laboratory of Organic Geochemistry in Guangzhou for carbon isotopes, among of which 3 were from Zhangjiajie and 4 from Zunyi. The results are listed in TABLE 5.

It is noticed from TABLE 5 that the $\delta^{13}C$ (PDB, ‰) values are much higher for kerogen from Zhangjiajie than those from Zunyi. The average of $\delta^{13}C$ for kerogen from Zhangjiajie amounts to -31.119 (3) whereas that from Zunyi amounts to -32.792 (4).

According to Degens [27], the $\delta^{13}C$ values for both petroleum and organic carbon of different geologic times decrease with the times become older, the $\delta^{13}C$ of organic carbon in Cambrian-Ordovician sediments are greater than -29 (PDB, ‰). It is prominent that the $\delta^{13}C$ values of

TABLE.3 Reflectance of organic materials in the black shales

Sample No.	Lithology	Bitumen reflectance measured (R_b, %)			Vitrinite reflectance converted (R°, %)	Nature of sample
		$R_{b, max}$	$R_{b, min}$	$R_{b, mean}$		
DG06	Metal-rich shale	4.073	2.427	3.055	2.387	Bulk rock
DG07	Metal-rich shale	5.682	3.667	4.707	3.491	Bulk rock
DG08	Thin-bedded shale	4.685	2.983	3.836	2.909	Bulk rock
DG09	Thick-bedded shale	2.084	1.052	1.435	1.305	Bulk rock
DG10	Thick-bedded shale	5.079	3.786	4.596	3.416	Bulk rock
D(O)	Metal-rich shale	3.193	2.160	2.718	2.162	Kerogen
DG08	Thin-bedded shale	5.980	3.664	4.757	3.524	Kerogen
DG09+10	Thick bedded shale	3.387	2.289	2.771	2.229	Kerogen
ZT04	P-nodule-metal-rich shale	5.825	4.494	5.133	3.775	Bulk rock
ZT05	P-nodule-metal-rich shale	5.829	3.796	4.577	3.404	Bulk rock
ZT06	Thick bedded shale	5.503	4.150	4.751	3.346	Bulk rock
ZT09	Thick bedded shale	5.623	4.030	4.710	3.493	Bulk rock
ZT11	Thick bedded shale	5.479	4.014	4.757	3.520	Bulk rock
Z(O)	P-nodule-metal-rich shale	5.188	3.759	4.500	3.352	Kerogen
ZT06+09	Thick bedded shale	4.687	2.570	3.593	2.746	Kerogen
ZT11	Thick bedded shale	5.341	3.415	4.357	3.256	Kerogen
DP01	Catagenetic anthraxolite	5.758	4.155	4.974	3.669	Kerogen

Note: The samples with DG, DP and D(o) as the first two letters of the numbers are from Zhangjiajie and those with ZT and Z(o) are from Zunyi. Measurer: Shen Jiagui.

TABLE 4 Differences of R° values between Zhangjiajie and Zunyi

Location	lithology	R^o_{max} (%)	R^o_{min} (%)	R^o_{mean} (%)	LOM_{mean}	Statistic number
Zhangjiajie	Metal-rich shale	3.510	2.446	2.550	15.8	8
	Thin- and thick-bedded shale	3.687	1.946	2.393	15.3	16
Zunyi	P-nodule-metal-rich shale	4.025	0.959	3.054	17.6	12
	Thick-bedded shale	4.089	2.532	3.272	17.9	10

Note: The data of LOM are measured from the LOM-R° diagram of Hood et al. (1975)

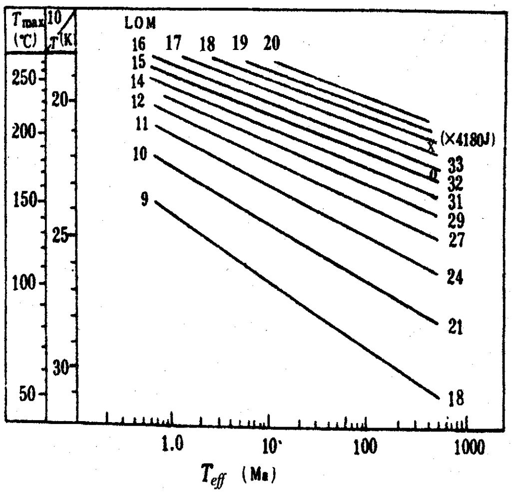

Fig. 3 LOM-T_{max}-T_{eff} ternary diagram. [26] Lines 17,18,19,20 are extrapolated by the authors; O—Plots of the data from Zhangjiajie; X—Plots of data from Zunyi

kerogen in Cambrian shales from both Zhangjiajie and Zunyi are all less than Degens' statistic values of the same times. According to Shen et al. [27], temperature, maturity and carbon isotope are closely related to each other, the increasing of temperature will lead to the increasing of maturity and the decreasing of $\delta^{13}C$. The relatively low values of $\delta^{13}C$ for the organic matters in Zhangjiajie and Zunyi means that the maturity of the organic matters here is higher than that Degens summarized. To the organic matters of the same times, temperature is no doubt the main controller of the maturity. This means that the black shales in Zhangjiajie and Zunyi have gone through relatively higher temperature during their evolution than those Degens summarized, and that compared with that in Zhangjiajie, the temperature in Zunyi was higher. This result corresponds with what we get from the study of kerogen reflectance.

TABLE 5 Carbon isotopes of kerogen

Sample No.	Lithology	Location	$\delta^{13}C$(PDB, ‰)
D(O)	Metal-rich shale (mixture)	Ganziping and Sancha, Zhangjiajie	-31.008±0.2
DG08	Thin-bedded shale	Ganziping, Zhangjiajie	-31.167±0.2
DG09+10	Thick bedded shale	Ganziping, Zhangjiajie	-31.181±0.2
ZT(O)	P-nodule-metal-rich shale (mixture)	Tianeshan, Zunyi	-31.723±0.2
ZT04	P-nodule-metal-rich shale	Tianeshan, Zunyi	-33.854±0.2
ZT06+09	Thick bedded shale	Tianeshan, Zunyi	-31.844±0.2
ZT11	Thick bedded shale	Tianeshan, Zunyi	-33.708±0.2

Measurer: Shen Jiagui.

V Discussion

Some discoveries of significance were made from detailed studies of the geochemical data related with the Lower Cambrian black shales in Zunyi and Zhangjiajie. Both the reflectance and carbon isotope of the kerogen in the black shales show systematic differences between the two regions. Based on the R^o and $\delta^{13}C$ values, it is worked out that the peak geotemperature the black shales suffered in Zunyi is higher than that in Zhangjiajie.

In our previous study[10,11,14], we have already mentioned that the NME mineralization intensity in Zunyi is stronger than that in Zhangjiajie. This result is correspondent with the R^o and $\delta^{13}C$ values, namely, stronger NME mineralization intensity correspond with lower $\delta^{13}C$, higher R^o and peak geotemperature in Zunyi, and weaker NME mineralization intensity correspond with higher $\delta^{13}C$, lower R^o and peak geotemperature in Zhangjiajie (TABLE 6).

Murowchick et al. [28] published their result of sulfur isotopic study of pyrite nodules from Tianeshan of Zunyi and Daping of Zhangjiajie. The $\delta^{34}S$ value changes greatly from the core to the rim of the pyrite ranging between -25‰—22‰ in Zunyi and -4‰—-28‰ in Zhangjiajie. The difference in sulfur isotopes between Zunyi and Zhangjiajie is clear. Although the sulfur isotopic data in both the two regions all change in a large range, the data in Zunyi are of "positive and negative mixture type", whereas the data in Zhangjiajie are of "light sulfur type". Looking into the $\delta^{34}S$ data in a single grain of pyrite, we find that these data vary rhythmically from the core to the rim and the rhythm number amounts up to 2.5-6 in the pyrite from Zunyi whereas the rhythm number amounts up to only 0-1.5. The rhythm number is related directly with measuring spots. There are 17 measuring spots within 600 μm in the pyrite from Zunyi and there are only 5 spots within 500 μm in the pyrite from Zhangjiajie. Even though, frequent change in the formation medium of pyrite from Zunyi should also not be ignored.

TABLE. 6 Correlation of geochemical data between Zunyi and Zhangjiajie regions

Region	**Organic matter maturity (R^o)**	**Peak geotemperature (℃)**		**$\delta^{13}C_{PDB}$ of kerogen**	**Rhythm number of $\delta^{34}S_{CDT}$ in pyrite***	**PGE+ Au ($\times10^{-9}$)**
		Karweil method	Hood method			
Zunyi	3.196 (8)	81-85	170	-32.792 (4)	2.5-6 (3)	1138 (4)
Zhangjiajie	2.445 (9)	95-101	200	-31.119 (3)	0-1.5 (4)	605 (4)

Note: The data in brackets are the analysis numbers. * Calculated from Murowchick et al. (1994).

Our previous studies show that the magmatic intrusion during pre-Cambrian to Cambrian was stronger and frequenter and ultramafic igneous rocks are more developed around Zunyi than around Zhangjiajie. Relating these facts with the higher concentration of NME in Zunyi than in Zhangjiajie, we think that the NME are from buried ultramafic igneous rocks. The development of hydrothermal chert under and on the metal-rich bed and the hydrothermal characteristics of the metal-rich bed show that hydrothermal fluid was the transference medium of the metals including NME from ultramafic rocks to the black shales. Combined with our present study we think that the lower $\delta^{13}C$, higher R^o and peak geotemperature in Zunyi are the result of stronger and frequenter magmatic intrusion and related hydrothermal activity. Conversely, the R^o and $\delta^{13}C$ data supply further evidences to the magmafic source of the NME in the black shales of Zunyi and Zhangjiajie.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 49873013, 40073012), the National Key Project for Basic Research (G1998040800) and China Geological Survey (199910200264, 2001020223023). Helping in the study from Professors Liu Dehan, Shen Jiagui, Chen Nansheng, Fan Delian, Zhang Aiyun and Academicians Tu Guangchi and Ouyang ziyuan are sincerely acknowledged.

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