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Discriminating geochemical anomalies by geological-geochemical method: A case study on Nagan section of E'dong area in Wuxu ore field in Guangxi Province, China

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The Edong Pb-Zn-Sb ore district is an important mineralized anomaly area in the Wuxu ore field, Guangxi province China. The secondary halo method was used to locate blind Pb-Zn-Sb ore bodies in the Edong district. A strong single Zn secondary anomaly was found across the F3 fault zone in the Edong ore district. Alteration features and trace element concentration of country rock along the F3 fault and the ore veins in the Edong mineralized district were compared to discriminate if the Zn secondary anomaly was caused by mineralization or not. The F3 fault zone did not underwent alteration as those associated with Pb-Zn-Sb ore veins. The country rocks across the F3 fault zone is characterized by strong Zn anomaly without Pb anomaly and the country rocks surrounding ore veins, on the other hand, have anomalies of Pb and Zn. Based on the above difference between the F3 fault zone and Pb-Zn-Sb veins in alteration features and geochemical anomaly of element association, together with the geochemical characteristics of galena, sphalerite, and stibnite during weathering, it is concluded that the strong single Zn anomaly around the F3 fault zone does not caused by mineralization, but rather by the absorption of zinc sulfate by clay mineral in the F3 fault zone. Our conclusion has been testified by drill hole. This work provides a clue for discriminating if a geochemical anomaly is caused by mineralization or not and is therefore very important for supervising ore exploration.

Key words: Geochemical anomaly detection; geochemical features of ore forming elements; Wuxu ore field; Guangxi

INTRODUCTION

Geochemical prospecting is an effective and widely used method for precious metals and nonferrous metals prospecting, it features economical, fast and simple and so on[1]. The results of the geochemical analysis are usually massive amounts of analytical data and a variety of geochemical anomalies. Anomaly recognition is the basis of anomaly evaluation[2][3].How to find the anomalies corresponding to the ore body among the large amount of geochemical anomalies is the key to geochemical exploration[4]. For decades, geotechnical prospecting engineers have been working to solve this problem, and have proposed a geological prospecting method; cross section method at the anomaly center[5]; multi-method comprehensive study[6]; determine whether the mine is caused by anomaly by analyzing the relevant ore-forming elements ratio and zoning[7][8]; estimate the geochemical anomaly from geology, structure, terrain, mineral elements and other aspects[9]; some researchers analyze geochemical anomalies through elemental geochemical migration behavior, but are mainly limited to volatile elements such as mercury[10]. In this paper, the geological significance of geochemical anomalies in the E'dong Pb-Zn-Sb ore district, Wuxu ore field is analyzed by means of mineralization element anomaly combination, mineralization element endogenous and supergene geochemical behavior and anomaly area alteration. This work provides a new method and idea for the effective identification of anomaly.

GEOLOGICAL CHARACTERISTICS OF WUXU OREFIELD AND E'DONG DEPOSIT

Wuxu orefield is located in the southern section of the Dumeng polymetallic metallogenic belt (Fig. 1 a) in Guangxi China, which is an important ore deposit area of Danchi metallogenic belt. There are Devonian Naxing Formation, Luo Fu Formation, Durian River Group, Wuzhishan Formation, and some Carboniferous and Middle Triassic in the exposed strata of this region. The ore-hosting rock bodies are mainly standard group of mudstone and malm sandstone of the Middle Devonian, followed by Luofu group of mud limestone and charcoal limestone. The deposits are mainly in the form of veins in the stratigraphic fracture zone, which is a medium-low temperature hydrothermal deposit [11]. The composition of mineral elements is complex, mainly Pb, Zn, Sb, Ag, mineralization alteration is weak, mainly sericite, silicification, pyrite mineralization and carbonation. The main deposits of Wuxu orefield are located in the west of the anticline, and the eastern mineralization is weak. The mineralization element combination of Wuxu orefield has obvious zoning (Fig. 1b), that is, the central part on the plane has a combination of Pb, Zn, Sb, Ag, the surrounding of Hg and As.

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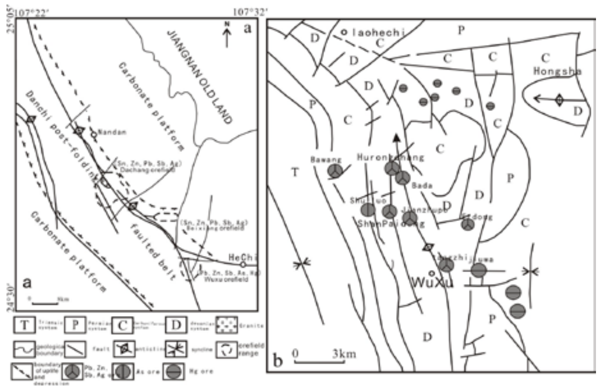

Fig.1. Simplified geological map of the Danchi ore belt (a) and the Wuxu ore field (b)

E'dong Pb, Zn, Sb mineralization anomalies are located at the east of Wuxu orefield (Fig. 1b), with Pb and Zn mineralized small veins, two 20 to 40 cm thick Pb and Zn veins at depths of more than 180 meters of drill hole (ZK02) are found, veins move towards SN, tend to west. The Nagan ore block is located in the north of the E'dong mineralized anomaly area, and the exposed strata are mainly the mudstone and malm sandstone of the Middle Devonian Donggangling Formation (D2d) and the Late Devonian Liujiang group (D3l). A near-SN F3 fracture (Fig. 2a) is developed along Nagan ore block, sporadic gossan are seen along the F3 fault which is considered to be an important potential area for ore prospecting.

SAMPLES AND ANALYTICAL METHODS

Sporadic exposed gossan are seen along F3 fault, with possible development of mineralization deep down, Hechi Yuanhe Mining Co., Ltd. made a secondary halo scouring on the F3 fault zone surface to analyze the deep prospect of F3 fracture prospecting. The sampling profile of the geochemical scanning surface is perpendicular to the F3 fracture (Fig. 2a), the distance between the sampling lines is about 100 meters, about 20 meters between the samples, main collecting B layer soil. The original halo samples are located in the F3 fault zone and are collected along the vertical F3 fault. The trace element composition of the sample was completed at the analysis and test centre of Guilin Institute of Mineral Geology. Ag and Sn were analyzed by WSP-1 spectroscopy, the analysis error is less than 2%; Cu, Pb, Zn, As, W and Sb were analyzed by ICP-MS, and the analysis error is less than 3% (Table 1).

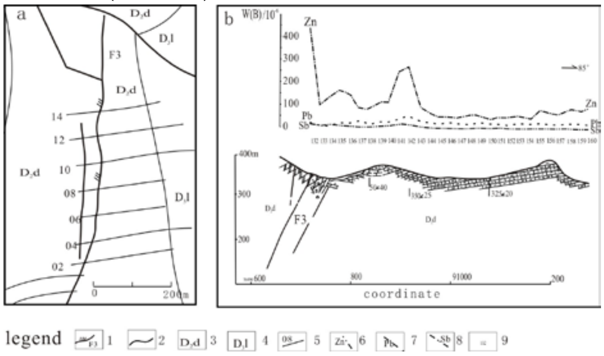

Fig.2. Simplified geological map of the Nagan mineralized spot (a) and ore forming anomalies along the profile number 8 line (b) (1. F3 Fault；2. Fault；3. Middle Devonian；4. Late Devonian；5. Geochemical scanning line；6. Zinc anomaly line；7. Lead anomaly line；8. Antimony anomaly line；9. Geochemical sampling number)

Table 1. Trace element contents of primary and secondary halos across the F3 fault

No.\Sec-halos	Pb	Zn	Sb	Cu	As	No.\Sec-halos	Pb	Zn	Sb	Cu	As
132	20.1	439	14.9			147	20.1	45.9	4.98		
133	8.12	91.4	8.21			148	16.9	60.4	4.12		
134	9.43	136	13.4			149	25.8	60.3	7.46		
135	20.1	165	8.98			150	20.9	41.2	4.23		
136	20.4	150	7.41			151	19.7	53.2	8.99		
137	31.2	81.3	3.46			152	14.9	49.2	5.34		
138	14.1	86.2	5.12			153	24.8	57.4	4.98		
139	27.1	116	6.12			154	19.7	37.2	5.11		
140	25.4	115	9.98			155	25.1	84.1	6.22		
141	35.2	260	15.8			156	19.2	69.4	7.41		
142	53.3	273	17.2			157	20.4	66.3	4.87		
143	30.1	96	9.21			158	25.3	89.2	5.96		
144	24.4	68.1	6.41			159	24.2	79.9	3.97		
145	20.3	51.2	5.41			160	20.1	95.8	4.97		
146	24.9	50.1	6.13								
No.\Pri-halos	Pb	Zn	Sb	Cu	As	No.\Pri-halos	Pb	Zn	Sb	Cu	As
GP3	26.7	84.7	5.92	78.7	58.9	Ng-06	11.6	670	13.7	323	80.7
GP4	25.6	131	8.31	131	19.5	Ng-05	17.4	3600	27.0	206	156
GP7	16.3	716	4.98	114	127	Ng-04	17.8	277	7.82	281	31.2
GP10	13.2	678	26	42.1	155	Ng-03	21.1	1100	4.6	111	228
GP11	9.5	1900	5.25	928	87.5	Ng-01	21.2	3500	8.8	201	308
Ng03-01	10.7	880	14.4	166	88.3						

CHARACTERISTICS OF GEOCHEMICAL ANOMALY IN NAGAN MINERALIZED BLOCK

The microelement analysis results of the secondary halo and primary halo are shown in Fig. 1 and Fig. 2b. From Fig. 2b, it is known that there is a high Zn anomaly near F3 fault zone in the Nagan ore block (Fig. 2b). Primary halo analysis showed that zinc content in the primary halo in F3 fault zone is particularly high, up to 3600ppm, almost reached the industrial grade of zinc ore; Pb and Sb content is not high, even lower than the average of this area (mean: Pb: 44.9ppm, Sb: 5.5ppm, 638 sample mean values). The main mineralization elements are Zn, Pb, Sb, Ag in Wuxu orefield, while only Zn anomaly in F3 fault, with a lack of Pb and Sb. So, is the Nagan ore Zn anomaly in the F3 fault zone of Nagan ore block an ore-caused anomaly? Has deep mineralization occurred in F3 fault zone?

Geochemical anomaly plays a key role in ore prospecting [4], in the evaluation of geochemical anomaly, it is necessary to consider the anomaly intensity changes, but not be limited to high intensity anomaly. This is mainly because there are many complex factors that affect the intensity of anomaly, including the impact of mineralization, and the role of post-epigenetic effects. Therefore, geochemical anomaly evaluation should not only consider the intensity, but also the mineralization characteristics, the element combination of mineralization of the mining area or the mineralization point, the geochemical behavior of the element under hydrothermal action, and the geochemical behavior of the element under hypergenesis.

Hydrothermal deposit is the formation of deposits from the hydrothermal large-scale precipitation of ore-forming elements due to materialized environment changes[12-16]. After the precipitation of ore-forming elements, the residual ore-forming fluids will continue to migrate upward, and chemical reactions with rocks occurs while rising, forming an ore-forming element anomaly and alteration belt much larger than the orebody at the top[16-20]. If the F3 fault is formed by mineralization (zinc has almost reached the boundary grade), the relevant mineralization alteration and the relevant element combination should be seen. Therefore, through the alteration feature analysis of F3 fault zone, comparison of ore-forming elements combination anomaly in the vertical F3 fault and at the mineralized anomaly point, we can identify whether it is an ore-generated anomaly.

(1) Characteristics of anomaly belt alteration and its geological significance

The deposit in this area is a low-temperature hydrothermal deposit, with major alteration of carbonate, sericite, silicification and pyrite [21]. Therefore, if mineralization occurs at deep F3 fault, the top should develop some low-temperature alteration combination.

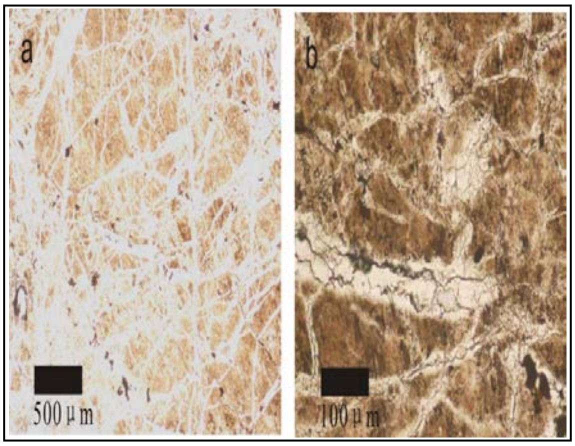

Fig.3. Microscopic photos showing the alteration characteristics of the argillaceous siltstone in the F3 fault zone

We performed a microscopic observation of the F3 fault zone samples, and found non-directional arrangement (Fig. 3a) in argillaceous siltstone and directional aligned veins of quartz and limonite (Fig. 3b), with no low-temperature alteration mineral combinations. The veins of quartz are very clean with no sulfide, with limonite formed by leaching. The veins of quartz and the mineralization alteration are completely different, hence it is reasonable to conclude that the quartz are not related to mineralization and are more likely to be side secreted products. The alteration mineral characteristics of argillaceous siltstone in F3 fault zone do not support that mineralization occurred deep in F3 fault zone.

(2) Characteristics of Ore-forming Primary Halo Elements Combination in E'dong Mineralized Area

The deposits with the same ore-forming role also have a similar ore-forming elements combination [13]. The mineralization of Pb and Zn in the E'dong mineralized anomaly zone has the development of Pb and Zn mineralization in ZK02 drill hole at about 2 km south of Nagan ore block. The geochemical behavior of Pb and Zn in hydrothermal fluids is similar and migrates mainly in the form of chlorine complexes in hydrothermal fluids [22,23]. Thus, if F3 anomaly is an ore-caused anomaly, theoretically the primary halo should form Pb-Zn anomaly instead of single-zinc anomaly. In order to analyze the characteristics of E'dong mineralization halo anomaly, we analyzed the composition of 21 core-like trace elements in the upper and lower plate rocks of Nagan ore block drill hole ZK02 lead-zinc mineralization (Table 2). The results show that the contents of Pb and Zn in the rocks of the upper and lower plates of the mineralization veins are relatively high, which is consistent with the theoretical analysis.

Table 2. Trace element content of roof and floor rocks surrounding ore vein in the Edong mineralized area

Nb.	Pb	Zn	Ag	W	Sn	As	Sb
ZK02-1	64.4	380	0.03	1.2	2.9	262	14.6
ZK02-2	50.3	138	0.03	1.1	2.6	31.9	13.3
ZK02-3	69.2	62.1	0.07	1.0	1.9	23.6	3.62
ZK02-4	11.6	23.8	0.09	1.2	1.1	72.9	1.01
ZK02-5	99.3	155	0.07	1.3	3.7	45.8	1.63
ZK02-6	25.9	41.1	0.07	1.0	1.0	1.8	0.42
ZK02-7	219	479	0.04	1.3	2.9	11.2	0.73
ZK02-8	240	329	0.06	1.0	3.1	58.3	3.01
ZK02-9	28.3	32.6	0.06	1.2	2.5	126	5.21
ZK02-10	52.2	72	0.04	1.0	2.3	9.9	1.44
H1	24.3	125	0.05		4.0	46.4	7.33
H2	2000	1100	2.28		4.1	89.5	13.7
H3	44.5	124	0.09		4.1	130	10.9
H4	32.3	65.1	0.10		4.3	32.2	10.6
H5	130	199	0.26		3.6	34.9	103
H6	40.6	144	0.11		4.4	51.9	9.23
H7	49.6	110	0.08		4.3	32.5	42.6
H8	576	257	0.19		4.3	42.3	257
H9	2000	872	0.76		3.5	58.7	1865
H10	433	501	1.10		3.9	60.5	236

(Analysis unit: test report of Guilin Analysis and Test Center of Nonferrous Metals. Test results: ωB/10-6)

To compare the anomaly combination characteristics of the primary halo elements in drill hole ZK02 and F3 fault in the E'dong mineralized area, we used SPSS software to study and compare the two groups of ore-forming elements model (Fig. 4), and found that the correlation between lead and zinc in F3 fault zone was very poor, almost 0 (0.0454).

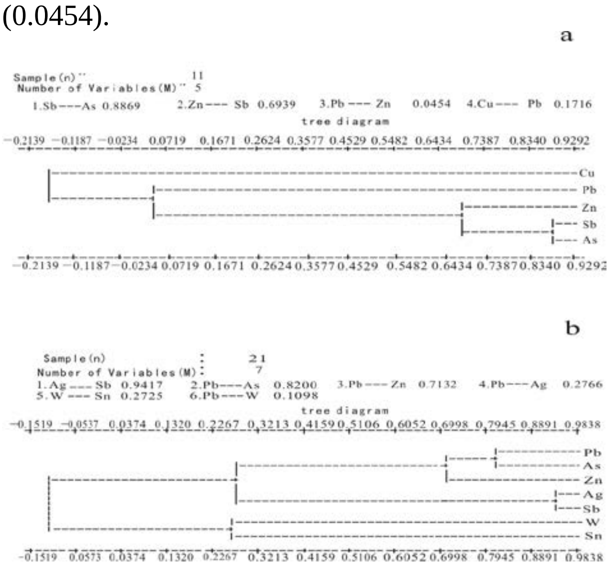

Fig. 4. Cluster diagrams of the rock samples from the F3 fault zone (a) and drill hole surrounding the ore veins in the E'dong mineralized area (b)

The correlation analysis of ore-forming elements in the primary halo of drill hole shows that the mineralization of the Nagan orefield will form Pb-Zn anomaly instead of single-Zn anomaly. Wuxu orefield has mainly Pb-Zn-Sb-Ag mineralization, with no single Zn mineralization. The analysis of massive geological data (analysis report of ore field reserves) of Wuxu orefield shows a combination of Pb, Zn and As. Only single-Zn anomalies are around F3, and lack of anomalies formed by Pb, As or other elements, hence it is not an ore-caused anomaly.

(3) Analysis of single zinc and high anomaly formation in F3 fault zone

The obvious difference among the alteration characteristics of F3 fault zone, single-Zn anomaly in the secondary and primary halo and ore-forming primary halo elements combination in Wuxu orefield and E'dong mineralized area indicates that the single-Zn anomaly in Nagan ore block is not an ore-induced anomaly, so how did it form?

E'dong area is an old mine with a certain history of mining, and in the past there had been indigenous refinery near the F3 fault zone. During the process of indigenous mineralization, the above elements will be polluted on the surrounding surface. The elements of Zn, Pb, Sb and other elements are different in the geochemical environment under the geochemical environment (Liu Yingjun et al., 1980). Zn, Pb, Sb mineralization in the mining area are mainly in the forms of galena, sphalerite and refractory antimony ore. To understand why there is such a high single-zinc anomaly along the F3 fault zone, firstwe need to understand the main ore minerals: the geochemical behavior of sphalerite, galena and stibnite under supergene conditions.

Galena is stable in the surface conditions than the sphalerite, and it will form $PbSO_4$ that is insoluble in water in oxidation. $PbSO_4$ has poor activity and is difficult to migrate, when encountered carbonate rock, it further forms lead carbonate (cerusite), and cerusite is more stable and easy to dissolve in water. Therefore, lead is not easy to migrate in the surface conditions. Sphalerite has very low oxidation potential and is very susceptible to weathering, especially when there are other sulfides. Sphalerite is more easily oxidized and the oxidation reaction is as follows: $ZnS+2O_2 \rightarrow ZnSO_4$ [24]. Zinc is highly active in the geochemical environment of the earth and is susceptible to oxidation and migration with surface water. Clay minerals have a certain adsorption of zinc sulfate[24], broken rocks in the crushed zone are more easily weathered to form clay mineral zone. When the zinc sulfate-containing fluid goes through the broken zone, it is easy to be adsorbed by clay minerals, and zinc enrichment can occur in the crushing zone. Stibnite forms valentinite when being oxidized, stibnite and other valentinite-containing complex sulfur minerals have very low solubility in the surface fluid, and are not easy to migrate under supergene conditions [24].

It can be seen from the above analysis that the activity of Zn under supergene conditions is strong, Pb and Sb are inert, while clay minerals have strong adsorption effect on zinc sulfate. F3 fault zone is relatively broken, easier to occur leaching and weathering at the surface conditions, forming clay mineral enrichment zone. Since this area is a Zn, Pb and Sb mineralization area, and the indigenous soil refining near F3 fault zone in the past will pollute the surrounding strata. The Zn, Pb, Sb and other elements in the polluted surrounding surface will undergo differential migration at the late supergene conditions, enriching Zn in the relative development of clay mineral fissure zone and forming high single-Zn anomaly.

To sum up, we think that the single-Zn anomaly in F3 fault is not an ore-caused anomaly, but formed in the late supergene conditions from absorption, and the deep F3 fault zone does not have great mineralization potential.

Although we carried out a comprehensive analysis, it is suggested that the Zn anomaly in F3 is not an ore-caused anomaly and the potential of deep prospecting is not great, but the technical staff of the production unit think it necessary to carry out engineering verification considering such a high zinc anomaly developed in the tectonic broken zone of mining area. Hechi Yuanhe Mining Co., Ltd worked on F3 in November 2013 to verify the hole depth of 345.5 m, penetrated the F3 fault zone and found no mineralization alteration, which further confirmed that our anomaly evaluation is correct. This further shows that in-depth understanding of the geology and geochemical characteristics of deposits can be more effective in identifying geochemical anomalies, providing a successful example for future identification of anomalies.

CONCLUSION

(1) The high-zinc anomaly in the F3 fault zone of Nagan ore block, E'dong mineralized area, Wuxu orefield is not an ore-caused anomaly, but formed through when the contaminated zinc in the surface is melted and migrated under supergene conditions in indigenous smelting or by being adsorbed by clay or limonite in the F3 fault zone.

(2) Geochemical anomalies are not necessarily ore-caused anomalies, in the analysis of geochemical significance of geochemical exploration, it is necessary to understand the combination and alteration characteristics of ore-forming elements, but also to understand the geochemical behavior of different mineral elements in the supergene environment.

(3) An in-depth understanding of the geology and geochemical characteristics of deposits can be more effective in identifying geochemical anomalies, providing guidance for ore prospecting.

Our conclusion is based on the special area along the F3 fault zone in which clay minerals are well developed. More attention should be paid to geochemical behavior of sulfide minerals such as galena, sphalerite, pyrite, stibnite etc. during weathering in the future work. To comprehensively realize the role of clay minerals in the formation of secondary halo anomaly, the absorption of clay mineral for Pb, Zn, Sb, Ag and Au should be detailed studied in the future.

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REFERENCES

1. Ch. B. Wu, Y. W. Qiu, *Geology and Exploration*, **3**, 49 (1985).
2. P. Gong, Zh. D. Ma, *Earth Science-Journal of China University of Geosciences*, **38**, S1, 113 (2013).
3. S.G. Zhou, K.F. Zhou, Y. Cui, J.L. Wang, J.L. Ding, *Journal of Geochemical Exploration*, **154**, 171 (2015).
4. A.M. Gonbadi, S.H. Tabatabaei, E.J.M. Carranza, *Journal of Geochemical Exploration*, **157**, 81 (2015).
5. X.Ch. Zhu, *Geology and Exploration*, **8**, 58(1980).
6. Y.J. Wang, F. Chen, *Geology and Exploration*, **6**, 22 (1965).
7. H. Li, G.Y. Zhang, B. Yu, D.L. Li, *Earth Science Frontiers*, **17**(1), 287 (2010).
8. D.L. Wan, *Geology and Exploration*, **1**, 45 (1990).
9. G.A. Lyu, Q.Q. Liu, *Geology and Exploration*, **9**, 53 (1987).
10. G.K. Hu, J.J. Tian, W.M. Lai, *Geology and Exploration*, **12**, 55(1980).
11. J.M. Cai, X.H. Xu, B.H. Li, *Journal of Chengdu Institute of Technology*, **22**(1), 69 (1995).
12. J.W. Hedenquist, J.B. Lowenstern, *Nature*, **370**, 519 (1994).
13. H. Y. Liang, P. Xia, X. Z. Wang, J. P. Cheng, Z. H. Zhao, C.Q. Liu, *Ore Geology Reviews*, **31**, 304 (2007).

14. T. Baker, E. V. Achterberg, C.G. Ryan, *Geology*, **32**, 117 (2004).
15. W.C. Su, C.A. Heinrich, T. Pettke, X.C. Zhang, R Z. Hu, B. Xia, *Economic Geology*, **104**, 73 (2009).
16. Y.J. Chen, *Earth Science Frontiers*, **17**(2), 27 (2010).
17. H.Y. Liang, W.D. Sun, W.C. Sun, *Economic Geolog*y, **104**, 587 (2009）.
18. W.D. Sun, H.Y. Liang, M.X. Ling, *Geochimica et Cosmochimica Acta*, **103**, 263 (2013).
19. M.J. Kalczynski, A.E. Gates, *Ore Geology Reviews*, **61**, 226 (2014).
20. J. Mick, R.M. Tosdal , T. Bissig, CM. Chamberlain, K.A. Simpson, *Economic Geology*, **109**, 891 (2014).
21. L. Chen, W.T. Huang, J. Wu, J. Zhang, H.Y. Liang; Sh.P. Lin, Y.Q. Zou, *Geochimica*, **11**,546 (2015).
22. Z. Zajacz，W.E. Halter，T. Pettke, M. Guillong, *Geochimica et Cosmochimica Acta*, **72**(8), 2169 (2008).
23. X. Chen, J.J. Liu, D.H. Zhang, Y.L. Tao, *Geological Journal of China Universities*, **20**(3), 388 (2014).
24. Y.J. Liu, L.M. Cao, Zh.L. Li, H.N. Wang, T.Q. Chu, J.R. Zhang, *Geochemistry of element* [M]. Beijing: Science Press, 1984: 518.