



Petrogenesis of skarn in Shizhuyuan W-polymetallic deposit, southern Hunan, China: Constraints from petrology, mineralogy and geochemistry

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Received 10 April 2015; accepted 4 May 2016

Abstract: Skarn is the main altered rock type and is of great importance to mineralization and ore-prospecting in the Shizhuyuan area of Hunan province, China. Its features of petrography, mineralogy and geochemistry were studied systematically. The results show that the skarn mainly consists of garnet skarn, secondary wollastonite-garnet skarn, tremolite-clinzoisite skarn, and few wolframite garnet skarn, idocrase-garnet skarn and wollastonite skarn with granoblastic texture, granular sheet crystalloblastic texture, and massive structure, disseminated structure, mesh-vein structure, comb structure, and banded structure. And, it is mainly composed of garnet, fluorite, chlorite, hornblende, epidote, tremolite, plagioclase, biotite, muscovite, plagioclase, quartz, idocrase, and calcite and so on. The chemical components mainly include SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and CaO , and the trace elements and REEs consist of Li, Be, V, Co, Zn, Ga, Rb, Sr, Y, Ce, Nd, Pb and Bi, etc. And, the obvious fractionation exists between LREE and HREE, and it shows typical features of Nanling ore-forming granite for W–Sn polymetallic deposit. Skarn is derived from the sedimentary rock, such as limestone, mudstone, argillaceous rock, and few pelitic strips. It is affected by both Shetianqiao formation strata and Qianlishan granite during the diagenesis, indicating a strong reduction environment. The occurrence of skarn, whose mutation site is favorable to the mineralization enrichment, is closely related to the mineralization and prospecting.

Key words: skarn; petrogenesis; geochemistry; Shizhuyuan W-polymetallic deposit; southern Hunan

1 Introduction

The Shizhuyuan W–Sn–Mo–Bi polymetallic deposit in southern Hunan, China, is located in the Nanling middle section, about 15 km from the southeast of Chenzhou city, which is one of the most important W–Sn–Mo–Bi ore deposits in Dongpo ore field [1–3]. The ore deposit was discovered in 1957 and exploited in the early 1960s, with a history of more than 50 years. It is characterized by multiple kinds of minerals, large scale, abundant symbiotic components and complicated metallogenic conditions, especially for its huge metal reserves, sufficient ore source, perfect metallogenic

mechanism and unique metallogenic mode showing a very important position in south China [4–9]. The proven total metal reserves of W–Sn–Mo–Bi ore deposit are more than one million tons and it is a rare super-large scale tungsten polymetallic ore deposit in the world.

The Shizhuyuan W–Sn–Mo–Bi super-large polymetallic deposit is located in the central south China plate and the middle part of Qinhang suture zone, and just in the northern raised part of regional NNE Dongpo–Yuemei compound synclinal. The area has well-developed faults, consisting of meridional fault, NE-trending fault, NW-trending fault, EW-trending fracture and a large number of joints, and fractures [10,11]. And it is also located in the contact zone between the inside

Foundation item: Project (41202051) supported by the National Natural Science Foundation of China; Project (2015CX008) supported by the Innovation-driven Plan in Central South University, China; Project (2016JJ1022) supported by Hunan Provincial Natural Science Outstanding Youth Foundation of China; Project (CSUZC201601) supported by the Open-end Fund for the Valuable and Precision Instruments of Central South University, China; Project (2014T70886) supported by the Special Program of the Postdoctoral Science Foundation of China; Project (2012M521721) supported by China Postdoctoral Science Foundation; Project (XKRZ[2014]76) supported by the Platform of Scientific and Technological Innovation for Hunan Youth, China

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DOI: 10.1016/S1003-6326(16)64277-2

bend of Qianlishan granite and Devonian mud-banded limestone, with the largest length of 1200 m from north to south, the largest width of 600 m from east to west, and the thickness generally 200–300 m.

The Qianlishan complex granite of Yanshan epoch is closely related to the formation of skarn and W–Sn–Mo–Bi ore deposit, and the calcic skarn is the host rocks for polymetallic ore deposit [12,13]. Skarn is mainly composed of andradite–grossularite, diopside, hedenbergite, idocrase and wollastonite, and a small amount of amphibole group, epidote group, chlorite group, ilvaite and fluorite [10]. The W–Sn–Mo–Bi mineralization is closely correlated to garnet skarn and pyroxene skarn, and the skarnization, greisenization and fluoritization are the most correlative to metallogenesis, yet followed by potash feldspathization, plagioclase, tourmalinization and chloritization [14,15].

Because of its typical metallogenic characteristics and a huge amount of metal resources, a group of international and domestic academics have conducted a lot of theoretical and applied research, and accumulated an abundance of basic data and original materials, establishing good foundation for next research in depth. In general, the focus of the previous research is mainly the metallogenic mechanism, ore genesis, ore-forming conditions and metallogenic regularities, metallogenic model, prospecting prediction and the relevant petrology, mineralogy and geochemistry [1–3,5–7,9]. Admittedly, skarn, as the important hosting rock and main wall rock alteration, has a close connection with the mineralization of Shizhuyuan tungsten-polymetallic deposit, which reflected not only on the space relation, but also on the genetic relationship, and the skarn rock and its rock-forming mineral recorded a large amount of mineralization information. The research of skarn, by contrast, is particularly weak, specially the genesis, forming process and its relationship with mineralization, restricting on mineralization, deep ore prospecting are still worthy of further research. Undoubtedly, it is an effective way to use recorded information of skarn about diagenesis and mineralization to reveal and inverse the metallogenic mechanism and ore genesis, to further deepen the understanding the massive metal element enrichment mechanism [16–21]. So, in this work, some skarn samples from the latest development tunnel of Shizhuyuan deposit were collected, and a systematic study was carried out from aspects like petrology, mineralogy and geochemistry, just to provide new data and information for enriching the ore genesis and guiding the deep geological prospecting.

2 Samples and analytical methods

The skarn samples were collected from the fresh

rock, which was related closely to W–Sn–Mo–Bi polymetallic metallization. Firstly, the detailed field geological observation on the skarn was carried out, such as shape and occurrence, structure and construction, color and hue, and their relationship with tungsten polymetallic mineralization. Then, they were studied in detail and analyzed systematically, mainly consisting of microscopic petrology and mineralogy, major element geochemistry, trace element geochemistry, and rare earth element (REE) geochemistry. The petrological and mineralogical research was performed in the Key Laboratory of Metallogenic Prediction of Nonferrous Metals, Ministry of Education, Central South University, China. And, the geochemical analysis was carried out in the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

The samples for the trace element analysis were broken to less than 75 μm , and the analytical equipment was Axios PW4400 type X-ray fluorescence (XRF). The instrument for trace element analysis was Perkin Elmer ELANDRC-e type quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS), which was made by PerkinElmer in Canada. Argon was used as carrier and support gas in ICP-MS. The produced 7000 °C plasma by the high frequency oscillator can ionize the vast majority of elements, whose repeatability test relative standard deviation (RSD) is lower than 10%.

3 Petrology

In Shizhuyuan ore district, the skarn is dominant by garnet skarn, followed by wollastonite–garnet skarn, tremolite–clinozoisite skarn, containing wolframite garnet skarn, idocrase–garnet skarn and wollastonite skarn. Garnet is the important rock-forming minerals, and the color of skarn is affected by the content of garnet, showing red, brownness, amaranth, etc. The texture of skarn is mainly granoblastic texture and granular sheet crystalloblastic texture, with massive structure, disseminated structure, mesh-vein structure, comb structure, and banded structure (Fig. 1). Obviously, the mineralization is common in the skarn, such as W, Sn, Mo, Bi, and pyrite, chalcopyrite and rare metal.

The distribution of skarn near contact zone of magmatic rock is roughly north–south direction but tilts slightly to the east. About 1000 m from north to south and 800 m from east to west for the maximum width, it just looks like giant flat lens with a thickness of 50–500 m and a width of 150–300 m. The floor of skarn contacts with the top of the granite with a wavy interface. It is widely believed that the skarn is the product of contacting metasomatism between Qianlishan granite and the upper Devonian Shetianqiao formation carbonate [11].

4 Mineralogy

The main minerals of skarn are more than 20 kinds, consisting of garnet, fluorite, chlorite, hornblende, epidote, tremolite, plagioclase, biotite, muscovite, plagioclase, quartz, idocrase, calcite, clinozoisite, diopside, wollastonite, soapstone, sericite, scheelite, and some opaque minerals (Fig. 2), among which the garnet, idocrase, pyroxene, wollastonite, epidote, hornblende and fluorite comprise the main skarn rock-forming minerals. Specifically, the fluorite, called a “consistency mineral” to the Shizhuyuan W–Sn–Mo–Bi polymetallic deposit, appears at different metallogenic epoches and

different ore-forming stages with close relationship to W–Sn–Mo–Bi mineralization in genesis and is usually considered as one of the important ore indicators.

Garnet: Its content is 30%–78% and in the form of xenomorphic crystal, hypidiomorphic crystal or hypidiomorphic-xenomorphic crystal with 0.05–1.6 mm in size. Part of the garnet is characterized by clear zonary structure, and intragranular or intergranular fracture which is generally filled by calcite, chlorite, epidote, plagioclase and hornblende. And, the garnet is always replaced by chlorite, calcite, biotite and fluorite but coexists with idocrase, fluorite, wollastonite, plagioclase and scheelite.

Fluorite: Its content is 5%–20% and 0.025–1.6 mm

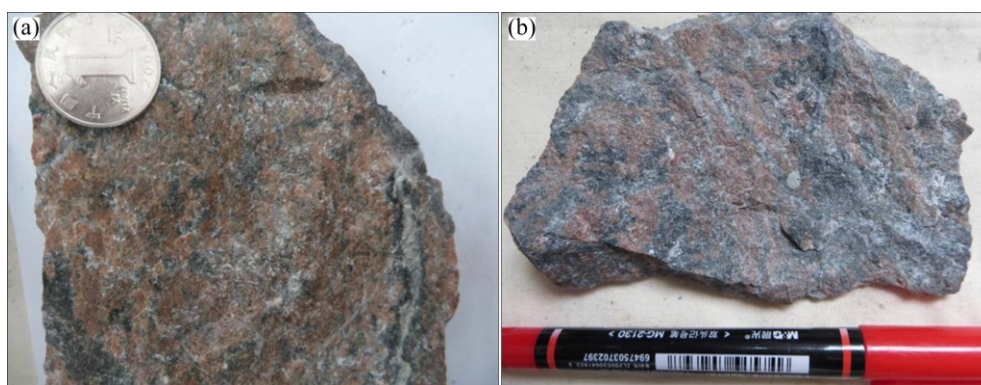


Fig. 1 Typical textures of skarn rock in Shizhuyuan W–Sn–Mo–Bi polymetallic deposit, Hunan, China: (a) Massive texture of skarn rock; (b) Disseminated texture of skarn rock

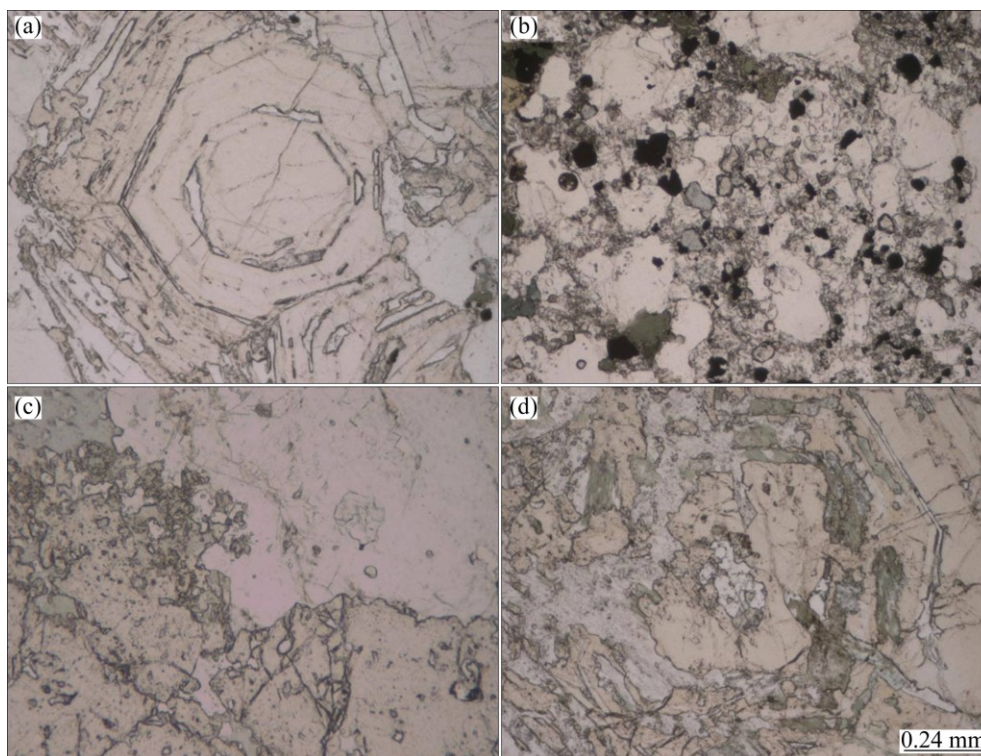


Fig. 2 Microstructures of skarn in Shizhuyuan W–Sn–Mo–Bi polymetallic deposit, Hunan, China: (a) Sample 470-1, scheelite garnet-bearing skarn, girdle texture; (b) Sample 470-1, scheelite garnet-bearing skarn, granoblastic texture; (c) Sample 490-2, garnet skarn, granoblastic texture; (d) Sample 514-2, garnet skarn, granoblastic texture

in size in the shape of xenomorphic crystal, irregular or granular crystal, coexisting with garnet, plagioclase, muscovite, hornblende, quartz, chlorite and sericite. Three groups of cleavage can be identified in fluorite that is always replaced along the garnet zonal texture.

Chlorite: It appears xenomorphic crystal with the shape of sheet, scaly, bunchy or radial assemblages with a content of 5%–15%, and is roughly less than 0.01 mm but few with 0.1–0.3 mm in size. Usually, the chlorite is closely associated with epidote, plagioclase, calcite and sericite, or fills in the intragranular or intergranular fracture of the garnet in the form of scale aggregate, or replaced the wollastonite particle in the form of irregular aggregate, or replaced the garnet partly.

Epidote: It is 4%–15% in content and is mainly in the form of xenomorphic crystal, granular or short column with a size of 0.05–0.7 mm, associating closely with hornblende, idocrase, sericite, plagioclase, fluorite, chlorite, garnet and some opaque minerals. Part of the epidote contains fine feldspar and fluorite, or constitutes vein aggregate with the plagioclase together.

Plagioclase: It is 5%–25% in content and in the form of xenomorphic crystal with the shape of granular or plate-like grain, which is characterized by visible polysynthetic twinning. The plagioclase generally constitutes vein aggregate, among which the crack is filled partly by muscovite, or appears argillization, sericitization and epidotization. The plagioclase always contains fine-grained chlorite and associates with hornblende and garnet.

Calcite: It is 3%–50% in content and is always xenomorphic crystal in the form of irregular or granular aggregate with a size of 0.01–1.0 mm. The calcite is usually filled in the intragranular or intergranular cracks of garnet, or associates with chlorite, or replaced garnet partly. And, the polysynthetic twinning and rhombic cleavage can be identified in coarse grained calcite. Yet, some calcites contain fine-grained diopside.

Wollastonite: It is mainly subhedral-xenomorphic crystal in the shape of granular, tabular or short columnar with a content of 25%–80% and is 0.07–1.0 mm in size. Most of the crystal surface appears chloritization, soapstone and fluoritization and associates with garnet.

Opaque mineral: It is mainly subhedral-xenomorphic crystal in the shape of irregular, granular or tabular and is 0.01–0.8 mm in size with a content of 1%–5%, and is characterized by the disseminated shape in the rock or occurs in the cleavage crack of muscovite. Occasionally, the suspected pyrite contains garnet.

Quartz: It is 1%–10% in content and is mainly xenomorphic crystal in the shape of granular or flake-like aggregate with the size of 0.1–1.0 mm, associating with fluorite and garnet. And, it usually contains fine-grained garnet.

Biotite: It is in the form of xenomorphic crystal and is less than 0.01 mm in size with a content of 5% approximately, associating frequently with chlorite.

Muscovite: It is roughly 35% in content and always appears in the form of subhedral-xenomorphic crystal but flake aggregation and is 0.05–0.2 mm in size. Yet, a part of muscovite, which is characterized by flake aggregation, associates with clinozoisite, showing directionally arranging or forming vein aggregation penetrating in the rock.

Sericite: It is mainly scale aggregate in xenomorphic crystal form with a size of less than 0.005 mm and a content of 15%, associating closely with chlorite frequently.

Hornblende: It is mainly granular or tabular in the form of xenomorphic crystal with a size of 0.05–0.4 mm and a content of 8%–20%, associating with plagioclase and idocrase, but is always replaced by fluorite showing an appearance of hollow-out form, and contains fluorite, plagioclase and fine-grained garnet, or forms graphic texture together with plagioclase.

Tremolite: It is about 5% in content and is mainly tabular aggregate and is in the form of xenomorphic crystal with a size of 1.0–2.0 mm, but is frequently replaced by muscovite and clinozoisite.

Clinozoisite: It has a content of about 25% and is mainly in the form of xenomorphic crystal and in the shape of graininess with a size of 0.015–0.05 mm, associating frequently with muscovite closely by the oriented arrangement, but forms vein aggregate partly with muscovite.

Diopside: It is mainly in the form of xenomorphic crystal and graininess, and is 0.04–0.2 mm in size with a content of 2%–19%, yet associates with chlorite and garnet. Two groups of nearly orthogonal cleavage can be identified in part of diopside.

5 Geochemistry

According to Tables 1 and 2, the major elements of skarn mainly consist of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and CaO , among which the SiO_2 content is dominant obviously, moreover, a small amount of Na_2O , K_2O , MnO , P_2O_5 and TiO_2 . Relatively speaking, the SiO_2 content is characterized by a large scope, ranging from 17.03% to 71.29%, with an average value of 30.82%, but most values are less than 30%, only a value of more than 70%. The content of Al_2O_3 is relatively uniform, ranging from 3.08% to 12.27% with an average value of 8.27%, and the content of Fe_2O_3 ranges from 0.85% to 14.17% (averaged, 5.95%). The contents of MgO and CaO are from 0.09% to 5.57% and from 0.802% to 43.62%, with the average values of 1.71% and 31.65%, respectively. And, the skarn is characterized by low content of Na_2O

Table 1 Major element (mass fraction, %) compositions of skarn in Shizhuyuan W-polymetallic deposit, Hunan, China

Sample No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	TiO ₂	LOI	Total
385–3	17.03	3.08	1.58	1.13	43.62	0.139	0.201	0.4791	0.0327	0.202	32.42	99.91
385–4	29.96	9.57	5.72	2.28	33.838	0.147	0.035	0.8358	0.0584	0.369	17.12	99.93
420–4	20.58	5.69	14.17	0.49	40.367	0.346	0.174	0.8144	0.0129	0.013	17.18	99.84
432–4	71.29	12.14	0.85	0.09	0.802	3.63	4.612	0.0225	0.0244	0.02	6.32	99.8
432–5	24.45	6.86	7.47	5.57	35.427	0.665	0.417	0.6383	0.0319	0.136	18.22	99.89
457–1	21.63	12.27	5.91	0.71	35.83	1.092	2.262	0.3716	0.0234	0.024	19.44	99.56
Min	17.03	3.08	0.85	0.09	0.802	0.139	0.035	0.0225	0.0129	0.013	6.32	99.56
Max	71.29	12.27	14.17	5.57	43.62	3.63	4.612	0.8358	0.0584	0.369	32.42	99.93
Average	30.82	8.27	5.95	1.71	31.65	1.0	1.28	0.53	0.03	0.13	18.45	99.82

Table 2 Nigel chemical parameters of skarn rock in Shizhuyuan W-polymetallic deposit, Hunan, China

Sample No.	Nigel parameter													
	<i>al</i>	<i>fm</i>	<i>c</i>	<i>alk</i>	<i>c/fm</i>	<i>si</i>	<i>ti</i>	<i>h</i>	<i>p</i>	<i>k</i>	<i>mg</i>	<i>o</i>	<i>t</i>	<i>qz</i>
385–3	3.48	6.3	89.72	0.5	14.25	32.69	0.29	0	0.03	0.49	0.51	0.36	–86.74	–69.33
385–4	11.17	16.67	71.83	0.33	4.31	59.36	0.55	0	0.05	0.14	0.4	0.51	–60.99	–41.95
420–4	5.67	20.43	73.14	0.75	3.58	34.8	0.02	0	0.01	0.25	0.06	0.88	–68.23	–68.22
432–4	46.86	5.19	5.63	42.32	1.08	466.96	0.1	0	0.07	0.46	0.17	0.81	–1.09	197.68
432–5	7.05	25.21	66.16	1.59	2.62	42.61	0.18	0	0.02	0.29	0.57	0.39	–60.7	–63.74
457–1	13.4	10.79	71.17	4.64	6.6	40.1	0.03	0	0.02	0.58	0.18	0.76	–62.4	–78.45

(0.139%–3.63%; average, 1.0%), K₂O (0.035%–4.612%; average, 1.28%), MnO (0.0225%–0.8358%; average, 0.53%), P₂O₅ (0.0129%–0.0584%; average, 0.03%) and TiO₂ (0.013%–0.369%; average, 0.13%). The value of LOI is characterized by a large variation, which ranges from 6.32% to 32.42% with an average value of 18.45%, showing a high value of LOI.

The content of Na₂O+K₂O ranges from 0.182% to 8.242%, with an average value of 2.287%. The sum of *w*(MgO) and *w*(CaO) is characterized by a large variation from 0.892% to 44.75%, but mostly more than 35%, with an average of 33.36%. The ratios of *w*(CaO)/*w*(MgO) show a large value, ranging from 6.36 to 82.38, with an average of 33.59. The ratio of *w*(Na₂O)/*w*(K₂O) is from 0.482 to 4.2, with an average value of 1.624.

The trace elements and REEs of skarn are composed of Li, Be, V, Co, Zn, Ga, Rb, Sr, Y, Ce, Nd, Pb and Bi, etc (Table 3). The content of $\sum \text{REE}$ ranges from 67.377×10^{-6} to 258.701×10^{-6} , with an average value of 163.176×10^{-6} . The contents of LREE and HREE range from 61.376×10^{-6} to 190.141×10^{-6} and 6.001×10^{-6} to 68.56×10^{-6} , respectively. Undoubtedly, it shows obvious fractionation between LREE and HREE, ranging from 2.773 to 14.705 (average, 7.604) for the value of *w*(LREE)/*w*(HREE). In addition, the values of *w*(LaN)/*w*(YbN), $\delta(\text{Eu})$ and $\delta(\text{Ce})$ range from 1.894 to 13.962 (averaged, 7.821), from 0.010 to 0.588 (averaged,

0.247), from 0.966 to 1.087 (averaged, 1.017), respectively. Obviously, the value of $\delta(\text{Eu})$ shows significant negative abnormality. Yet, according to the variation of $\delta(\text{Ce})$, it is characterized by the weak positive abnormality, whose mean value is greater than 1, in spite of two values less than 1.

6 Discussion

6.1 Evolution and formation mechanism

After long-term development and in-depth research, the diagenesis and mineralization theory of skarn have developed greatly, mainly consisting of magmatic hydrothermal type, magmatic origin type, regional metamorphic type and migmatization type [22]. The huge massive skarn, whose formation and origin have been well studied, is widespread along Qianlishan granite in southern Hunan, China. MAO et al [10] pointed out that the formation of massive skarn rock around the Qianlishan granite is difficult to be interpreted with the simple chemical composition diffusion, the maceration metasomatism and high-temperature hydrothermal diffusion along the fracture may be the major cause. After the formation of massive skarn, the extensive regressive alteration of native skarn along the contact zone of magmatic rock or tensile fracture and beside the late greisen veins led to the regressive alteration rock, also called the complex

Table 3 Trace element and REE compositions (mass fraction, 10^{-6}) of skarn in Shizhuyuan W-polymetallic deposit, Hunan, China

Element	Sample No.						Minimum	Maximum	Average
	385–3	385–4	420–4	432–4	432–5	457–1			
Li	24.9	62.6	19.9	17.4	29.6	63.2	17.4	63.2	36.3
Be	79	259	151	17	238	180	17	259	154
Sc	2.11	6.02	3.95	6.05	4.57	10.5	2.11	10.5	5.53
V	19.5	43.6	4.92	0.62	23.1	5.76	0.62	43.6	13
Cr	12.5	31.7	1.79	0.53	14.7	2.38	0.53	31.7	10.6
Co	11.5	70.5	53.9	157	30.8	11.9	11.5	157	55.9
Cu	9.57	16.73	6.02	7.29	3.32	42.7	3.32	42.7	14.3
Zn	196	321	57.2	16.2	160	104	16.2	321	142
Ga	7.42	18.1	23.6	28.3	23	31.6	7.42	31.6	22
Ge	2.66	3.57	13.3	2.49	6.08	8.74	2.49	13.3	6.14
As	17.1	27.3	18.3	15.8	29.6	13.9	13.9	29.6	20.3
Rb	44.4	1.32	73.4	715	34.7	733	1.32	733	267
Sr	344	79.9	45	11.6	60.2	70.1	11.6	344	101
Y	8.93	17.3	32.3	102	9.06	47	8.93	102	36.1
Zr	67.7	108	5.75	48.7	53.3	8.42	5.75	108	48.7
Nb	5.01	7.41	12.1	38.1	10.3	17.7	5.01	38.1	15.1
Mo	7.06	48.4	312	3.12	18.4	1870	3.12	1870	376
Ag	0.185	1.71	0.324	0.516	0.189	1.42	0.185	1.71	0.72
Cs	3.84	0.774	2.89	26.2	0.633	44.1	0.633	44.1	13.1
Ba	50.5	6.55	2.95	18.7	6.11	26	2.95	50.5	18.4
La	14.8	32.7	25.2	41.8	28.2	33.8	14.8	41.8	29.4
Ce	29.5	62.3	57.1	86.4	64.1	80.5	29.5	86.4	63.3
Pr	3.15	6.66	7.15	11	7.01	10.6	3.15	11	7.6
Nd	11.3	22.9	23.9	38.7	18.6	36.7	11.3	38.7	25.4
Sm	2.22	4.25	8.29	12.2	3.73	12.2	2.22	12.2	7.15
Eu	0.406	0.737	0.094	0.041	0.28	0.09	0.041	0.737	0.27
Gd	1.91	3.67	6.22	13.5	2.46	9.69	1.91	13.5	6.24
Tb	0.278	0.567	1.48	3.12	0.397	2.34	0.278	3.12	1.36
Dy	1.45	3.19	8.65	19.3	2.01	15	1.45	19.3	8.27
Ho	0.301	0.622	1.57	4.29	0.365	2.83	0.301	4.29	1.66
Er	0.929	1.75	4.72	12.4	1.17	8.68	0.929	12.4	4.94
Tm	0.131	0.28	0.916	1.94	0.2	1.63	0.131	1.94	0.85
Yb	0.872	1.68	6.48	12.3	1.48	12.8	0.872	12.8	5.94
Lu	0.13	0.237	0.864	1.71	0.209	1.73	0.13	1.73	0.81
Hf	1.81	2.53	0.329	3.82	1.32	0.507	0.329	3.82	1.72
W	117	1770	2310	901	375	4810	117	4810	1713
Tl	0.122	0.0462	0.255	3.59	0.127	2.89	0.0462	3.59	1.17
Pb	8.66	58.8	11.3	34.8	3.86	120	3.86	120	39.6
Bi	29.2	181	889	7.52	197	976	7.52	976	380
Th	3.99	7.55	4.89	23.3	4.83	9.53	3.99	23.3	9.02
U	1.72	4.53	14.5	26.1	20.7	25.6	1.72	26.1	15.5
$\sum \text{REE}$	67.377	141.543	152.634	258.701	130.211	228.59	67.377	258.701	163.176
w(LREE)	61.376	129.547	121.734	190.141	121.92	173.89	61.376	190.141	133.101
w(HREE)	6.001	11.996	30.9	68.56	8.291	54.7	6.001	68.56	30.075
w(LREE)/w(HREE)	10.228	10.799	3.940	2.773	14.705	3.179	2.773	14.705	7.604
w(LaN)/w(YbN)	12.174	13.962	2.789	2.438	13.667	1.894	1.894	13.962	7.821
$\delta(\text{Eu})$	0.588	0.557	0.038	0.010	0.266	0.024	0.010	0.588	0.247
$\delta(\text{Ce})$	1.008	0.978	1.028	0.966	1.087	1.035	0.966	1.087	1.017

skarn [10]. CHEN et al [15] thought that the skarn mainly experienced three stages: thermal contact metamorphism, hydrothermal metasomatism and regressive metamorphism, yet showing different geochemical behaviors for REE and other chemical elements in each evolutionary phase. CHENG et al [23] also thought that the formation of skarn went through three stages: the skarn stage, retrogressive metamorphic stage and sulphide stage, and the alkali metasomatic vein affected the evolution and mineralization of skarn and occurred in skarn stage and retrogressive metamorphic stage.

With regard to the classification of skarn, some disputes exist. WANG and ZHANG [14] pointed out that the endoskarn is extremely common, but MAO et al [10] thought that in Shizhuyuan area, the massive skarn is almost exoskarn. For a long time, the protolith restoration of metamorphic rock is considered as the important mean to reveal the genesis and features [24]. From the protolith restoration projection drawing of skarn (Fig. 3 [24]), the protolith consists of five thick argillite samples and only one sandstone sample, which suggests that the sedimentary rock is the primary protolith in Shizhuyuan area, such as the well-developed limestone and dolomite. For example, the upper Devonian Shetianqiao formation is dominated by limestone, but it is also rather common to contain high content of clay or mingle with more shale and shale stripe, such as argillaceous banded limestone, argillaceous limestone, muddy limestone interbedded with siltstone. The protolith is not only limestone, but also the mudstone, argillaceous rock, and even the pelitic strip. So, the result that the protolith of five out of six skarn rocks belongs to mudstone can be explained combining theory with practice, which is correlated to the lithology of hosting rock and its lithological association.

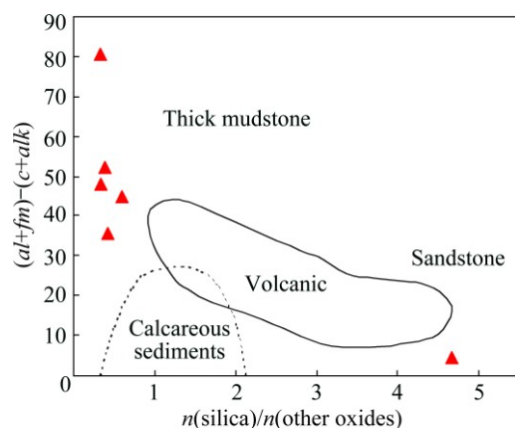


Fig. 3 Diagram of protolith restoration for skarn rock in Shizhuyuan tungsten-polymetallic deposit, Hunan, China [24] ($n(\text{silica})$ is total molecular number of silica, $n(\text{other oxides})$ is total molecular number of other oxides)

MAO et al [25] found that the manganoan skarn formed after the regressive alteration of calcareous skarn, which shows a close temporal and spatial relationship with greisen type tungsten polymetallic mineralization, and the manganoan content in manganoan-skarn mineral association and all kinds of manganese minerals increases gradually away from the contact zone. The massive skarn is the product of infiltration metasomatism and diffusive metasomatism along the contact zone by the hydrothermal solution of the granite, yet the fluorite developed widely can indicate its importance to the skarn formation [10].

According to the relation of SiO_2 and other major elements (Fig. 4), there exists a certain positive correlation between $w(\text{SiO}_2)$ and $w(\text{Al}_2\text{O}_3)$, $w(\text{MnO})$, $w(\text{MgO})$, $w(\text{Fe}_2\text{O}_3)$; however, the correlation between $w(\text{SiO}_2)$ and $w(\text{Na}_2\text{O})$, $w(\text{K}_2\text{O})$, $w(\text{Na}_2\text{O}+\text{K}_2\text{O})$ is not apparent. So, according to the content of major elements of skarn and their interrelations, the protolith of metamorphic rocks is characterized by the sedimentary rock on the whole but should be attributable to parametamorphic rock.

The average contents of ΣREE and Eu in Endoskarn of Shizhuyuan tungsten polymetallic deposit are 163.176×10^{-6} and 0.275, respectively, which are similar to the characteristics of rare earth elements of the typical hydrothermal metasomatic skarn ($w(\Sigma\text{REE}) = 121.01 \times 10^{-6}$, $\delta(\text{Eu}) = 0.92$) [22]. In addition, some other features also show similarity with hydrothermal metasomatic skarn, such as the less obvious Ce anomalies, apparent negative Eu anomaly and enrichment of light rare earth [22]. Overall, six skarn samples in this work show obvious Eu negative anomaly without exception, which is the important feature of ore-forming granite for Sn–W polymetallic deposit in Nanling mineralization belt, indicating that the skarn possibly inherited Eu negative anomaly characteristics from its protolith, yet there is almost not Ce anomaly for the skarn, which indicates no mixing of seawater possible in the fluid of skarn diagenesis [22].

However, the proposal or determination of magmatic skarn adds new content for the skarn metallogenic theory, and develops new research fields and directions, with great theoretical significance and practical significance, especially to broaden mind, expand prospecting scope and effect [26]. The mineralization of magmatic skarn was developed along with the injection and diagenesis of ore-bearing skarn magma, specifically the liquation, liquation–hydrothermal metasomatism and pneumatolytic hydrothermal pegmatite filling metasomatism [26]. The Shizhuyuan skarn primarily belongs to magmatic origin, whose scope is roughly uniform to mineralization zone, and before the skarn formation, the metallogenic element

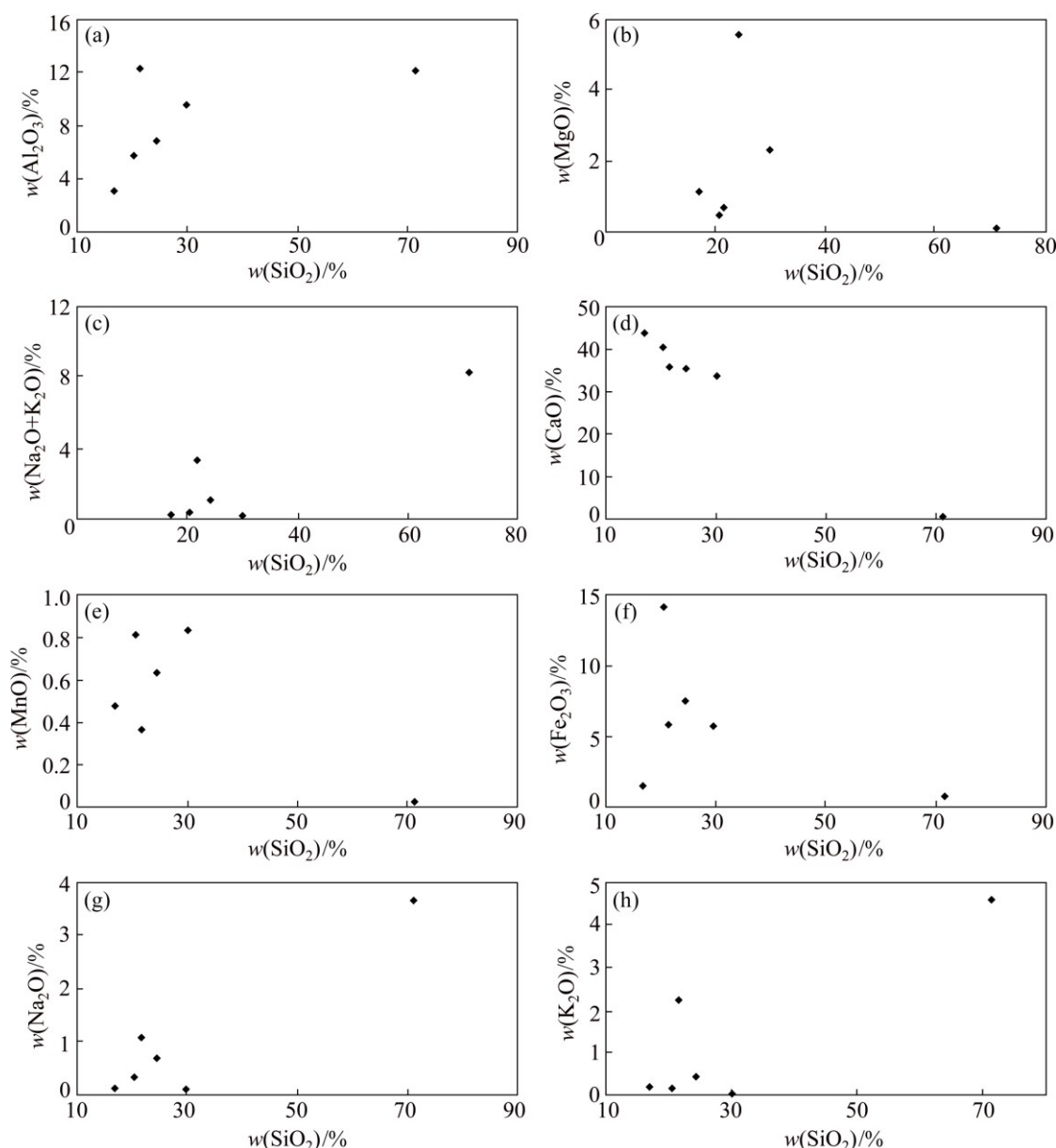


Fig. 4 Correlation diagrams of skarn composition in Shizhuyuan tungsten-polymetallic deposit, Hunan, China

had enriched rudimentary, but the postmagmatic mineralization (mainly greisenization and fluoritization) improved ore grade, increased deposit reserves and consequently led to the super-large deposit [11].

6.2 Indicator to metallogenic environment

Previously, it was widely believed that the contact zone or its nearby between the acid-intermediate intrusive bodies and carbonate stratum is the standard occurrence environment, which actually belongs to the single genesis point, the geological conditions of skarn forming can be even more comprehensive, including not only the contact metasomatism but also volcanic-subvolcanic pneumatolytic hydrothermal, migmatization, regional metamorphism and contact metamorphism [13].

Recently, QI et al [22] have also thought that the skarn and skarn deposit are generally characterized by polygenesis, besides the contact metasomatism, other geological processes usually exist, such as subvolcanism, regional metamorphism, contact thermal metamorphism, migmatization and hydrothermal sedimentary.

REE has been widely applied in the petrogenetic and metallogenic geochemical process tracer related magmatism [27]. According to the chondrite-normalized REE patterns of the Shizhuyuan skarn (Fig. 5 [27]), they all show a good consistency, exhibiting a gently right-dipping V-type curve with a severe depletion in Eu, but other rare earth elements do not show obvious loss characteristics. CHEN et al [15] found that the enrichment and distribution of REE in skarn rock are

affected by REE abundance of primary rocks, REE composition of hydrothermal fluid, containing capability to REE, among which the containing capability sometimes even plays an important role in determining REE redistribution.

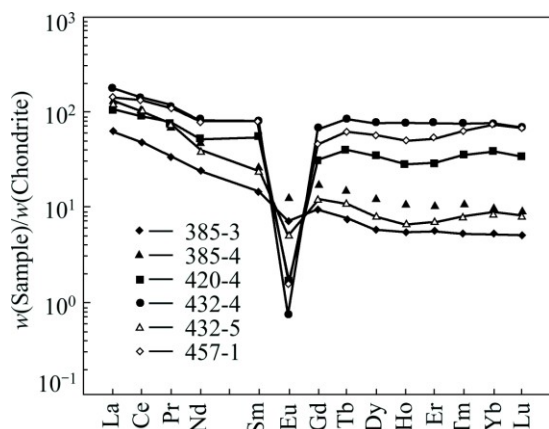


Fig. 5 Chondrite-normalized REE patterns of skarn rock in Shizhuyuan tungsten-polymetallic deposit, Hunan, China [27]

The REE distribution characteristics of skarn are closely related to the primary rock and the features of hydrothermal fluid. So, the well-developed huge massive skarn rock is affected synthetically by both Shetianqiao formation and Qianlishan granite, which would lead to an excellent inheritance to the features of hosting rock and intrusive body for skarn to some extent.

It is generally believed that in skarn system, some elements more often occur in highly reductive environment, such as Ca, Al, Ti and Mn, yet Fe is usually enriched in the strong oxidation environment. On the basis of the analysis result of major elements, the contents of both Al_2O_3 and CaO show a strong enrichment, but few Fe relatively, potentially indicating a strong reduction environment for skarn diagenesis.

6.3 Metallogenic prognosis and exploration direction

Undoubtedly, the skarn ore deposit, distributed all over the world, is of great importance because of its huge industrial value [28–32], being the main source of tungsten. China is one of the countries with the widest distribution and longest history of mining and metallurgy to skarn deposit in the world. And, the skarn deposit is the major type of the high-grade iron, copper, tungsten, tin and bismuth [33–36]. Generally, the formation of skarn deposit is restricted by the structure, magma, wall rock, physical and chemical conditions [37], especially the spatial zoning of intrusive rock can reflect fluid evolution, wall rock composition, temperature variation, oxidation–reduction environment, metallogenic depth, etc.

Usually, the skarn could be divided into metasomatism skarn and metamorphic skarn. And, based on the differences of wall rock and mineral association, the metasomatism skarn can be further divided into calcium skarn and magnesia skarn [38]. Then, MAO et al [10] thought that the mineral composition of calcium skarn consists of andradite–grossularite, diopside–hedenbergite and so on, whose wall rock is limestone, for example, globally the garnet of skarn Au–Mo deposit is the andradite–grossularite series and the pyroxene belongs to the diopside–hedenbergite series; however, the wall rock of magnesia skarn, whose mineral association usually consists of forsterite and other magnesite-rich mineral, is dolomite.

Current research shows that the characteristic of skarn is closely related to the mineralization type of ore deposit. ZHAO et al [38] pointed out that the mineralization is connected with the ratio of $w(\text{Mn})/w(\text{Fe})$ in pyroxene, which is usually less than 0.1 in the skarn Fe–Au deposit and skarn Cu–Mo deposit, yet the ratio of $w(\text{Mn})/w(\text{Fe})$ in diopside of skarn Mo deposit and skarn Pb–Zn deposit always ranges from 0.1 to 1, but it usually ranges from 0.1 to 0.3 for skarn tungsten deposit.

On the basis of the mineralization characteristics, the extensively developed huge massive skarn is not only the direct wall rock of ore body, but also the favorable location to the enrichment of tungsten polymetallic minerals. According to the spatial relations, the skarn locates in the contacting zone between Qianlishan granite and Devonian strata, with huge extended length and thickness (50–500 m) [10]. Therefore, as the main mineralization type, the skarn is one of the most direct and effective prospecting criteria. And, it should be also the main prospecting direction and basic ideas around the skarn. Undoubtedly, some particular contacting zones of Qianlishan granite and skarn deserve special attention, such as the depression of rock, harbor-shape contacting zone, where it is favorable to the precipitation and enrichment of metallic mineral, which are also verified in the exploration practice and will be the key areas and goals for the deep ore-prospecting in Shizhuyuan area in the future.

It is widely believed that the oxidation–deoxidation environment and pH value of ore-forming fluid in the process of the skarn formation play an important role in the formation of different skarn deposits. Generally, the relative high degree oxidation environment is more favorable to the formation of skarn Cu deposit, whose mineral association mainly consists of andradite, and a small amount of diopside, wollastonite, actinolite and epidote. Yet, in skarn Mo deposit, the hedenbergite is the most common calcium silicate minerals, along with a small amount of grossularite, wollastonite, hornblende

and fluorite, which shows relative reduction environment. And, the skarn Cu, Mo, Au, and Fe ore deposits are closely connected with calcium skarn.

Generally, the scope of the mineralization also has a guiding significance for prospecting prediction. ZHAO et al [38] pointed out that the skarn Pb–Zn deposit maybe occur in a great range from hundreds of meters to 1–2 km outside away from the contacting zone in the carbonate strata, and the crossing site of two groups of tectonic system has great controlling effects on mineralization. So, in Shizhuyuan area, the NNE-, NE-direction tectonic systems and secondary fractures restrict the occurrence of Sn and Pb–Zn ore. Although the Qianlishan intrusion rock is a small acidic composite intrusive rock, the particular location and internal contacting zone should be quite favorable to the mineralization.

7 Conclusions

1) The garnet skarn is dominated with granoblastic and granular sheet crystalloblastic texture, and mostly massive structure, but a few disseminated, mesh-vein, comb-shape and banded structures, whose rock-forming minerals are more than 20 kinds, mainly consist of garnet, idocrase, pyroxene, wollastonite, epidote, hornblende and fluorite, etc.

2) The major elements of skarn rock mainly consist of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and CaO , and the trace elements and REEs are composed of Li, Be, V, Co, Zn, Ga, Rb, Sr, Y, Ce, Nd, Pb, Bi, etc. The skarn rock is characterized by an obvious fractionation between LREE and HREE, significant Eu negative abnormality and weak positive Ce abnormality.

3) The skarn rock was mainly derived from sedimentary, like the well-developed limestone and dolomite, or argillaceous banded limestone, argillaceous limestone, muddy limestone interbedded with siltstone and even the pelitic strip, showing the features of parametamorphic rock and correlating to the lithology of hosting rock and their lithological association.

4) The huge massive skarn rock belongs to the common product of both Shetianqiao formation and Qianlishan granite, and it is possibly formed in a strong reduction environment for its diagenesis. The future geological prospecting should keep on closely combining with the skarn rock and intrusive body, especially the particular location of the contact zone.

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湘南柿竹园钨多金属矿床矽卡岩岩石成因： 岩石学、矿物学及地球化学约束

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摘 要：矽卡岩作为湖南柿竹园矿集区的主要蚀变岩石类型，对该区成矿作用以及找矿勘探具有十分重要的作用。为此，对矽卡岩的岩石学、矿物学以及地球化学特征进行了系统研究。结果表明，该矿集区的矽卡岩以石榴子石矽卡岩为主，其次为硅灰石石榴子石矽卡岩、透闪石斜黦帘石矽卡岩，少量含白钨石榴子石矽卡岩、符山石石榴子石矽卡岩以及硅灰石矽卡岩等。矽卡岩通常具有粒状变晶结构、粒状片状变晶结构，且表现为块状构造、浸染状构造、网脉状构造、梳状构造以及条带状构造等。岩石主要由石榴子石、萤石、绿泥石、角闪石、绿帘石、透闪石、斜长石、黑云母、白云母、斜长石、石英、符山石以及方解石等组成。矽卡岩的主量成分主要包括 SiO_2 、 Al_2O_3 、 Fe_2O_3 、 MgO 以及 CaO 等，微量以及稀土元素组成主要为 Li、Be、V、Co、Zn、Ga、Rb、Sr、Y、Ce、Nd、Pb 以及 Bi 等。轻、重稀土元素之间具有十分明显的分馏现象，且表现出南岭钨锡多金属矿床成矿花岗岩的典型特征。矽卡岩的主要原岩为沉积岩，包括灰岩、泥岩、泥质岩以及少量的泥质条带等，岩石成岩过程中主要受余田桥组地层以及千里山花岗岩体的共同影响，且为强烈的还原环境。矽卡岩岩石产状与成矿作用和找矿预测密切联系，岩石形态突变部位常常更加有利于矿化富集。

关键词：矽卡岩；岩石成因；地球化学；柿竹园钨多金属矿床；湘南地区

(Edited by Wei-ping CHEN)