

## Skarns and Genesis of the Huanggang Fe-Sn Deposit, Inner Mongolia, China

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**Abstract:** The skarns and genesis were studied of the Huanggang Fe-Sn deposit and the nearby Sumugou Zn-Pb deposit in Inner Mongolia, China. In the Huanggang mine, Nos. 1 to 4 Fe ore bodies are arranged along a calcareous horizon from proximal to distal in this order to a granite intrusion named Luotuochangliang, while Sn ore body is situated near another granite intrusion named 204. According to the distance from the granitic intrusions, mineral assemblages in skarns are systematically changed. Garnet is the most predominant skarn mineral throughout the deposit. Hastingsitic amphiboles, however, predominate in the proximal skarns. Fluorite is common in the proximal skarns, while instead calcite is common in the distal skarns. Chlorite is characteristically present only in No. 3 ore body, and chlorite geothermometry gives near 300°C for the mineralization of later stage.

When garnet crystal shows zonal structure, isotropic andraditic garnet occupies the core, and is surrounded with anisotropic less-andraditic garnet. The presence of white skarn along the boundary between main skarns and host sedimentary rocks confirms relatively reducing environment prevailing as a whole in the studied area. However, the compositional relation between coexisting garnet and clinopyroxene demonstrates that relatively oxidizing condition was achieved for garnet skarn and magnetite ore in the distal, Nos. 2 to 4 Fe ore bodies and Sumugou deposit, compared to that for garnet skarn in the proximal, No. 1 and Sn ore bodies. Preliminary study on the tin content of garnets in the studied area revealed a certain degree of contribution brought from granitic intrusives since the early stage of skarn formation, irrespective of proximal or distal.

Oxygen isotope study on garnet, magnetite, quartz and skarn calcite, as well as hydrogen isotope study on hastingitic amphibole, demonstrates mainly meteoric water origin for the skarn- and ore-forming solutions. The occurrence of Sn, W, Mo and F minerals indicates that those elements were mainly supplied to the deposit later than the formation of skarns and iron ores, overlapping to them. These constraints allow to delineate the formation model of the deposit as follows (Fig. 10): At the time of late Jurassic to early Cretaceous, felsic activity occurred in this region as a part of Yanshanian magmatism, and formed granitic intrusions as well as thick volcanic piles on the surface. The circulation of meteoric water was provoked by the heat brought by the intrusions. By this circulation, much amount of iron was extracted from andesites of the Dashizhai Formation, and precipitated as skarns and magnetite ores along calcareous horizons near the bottom of the Huanggangliang Formation. Subsequently, volatile-rich fluids with Sn, W and Mo were expelled from the solidifying granitic magmas, and precipitated these metals in the pre-existing skarns and ores.

### 1. Introduction

The Linxi district is situated near the southwestern end of the Da Hinggan Mountains, and its geological features and related mineralizations are discussed by many previous workers (e.g. Zhao et al., 1997) and in the papers in this special issue (e.g. Sun and Akiyama, 2001; Wang, J-B. et al., 2001). This district includes some important tin-producing mineral deposits such as the Huanggang, Dajing and Anle (Ishiyama et al., 2001).

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The Huanggang Fe-Sn skarn deposit is one of the important, large-size mineral deposits in North China. The deposit is characterized by the occurrence of tin, which is so far known as rare in North China. As a part of the research project, "The establishment of a genetic model of metal mineralization in the Linxi district, Inner Mongolia, China", carried out by Chinese Academy of Sciences (CAS) and Japanese International Cooperation Agency (JICA), the present authors have done field observation, sampling and laboratory works on the Huanggang deposit since 1998, with some considerations about the genesis of the deposit. The Sumugou base-metal skarn deposit, situated about several kilometers northeast of the Sn Ore Body of the Huanggang mine, has also been studied for comparison, and the results on this deposit are also included in this paper.

The Huanggang deposit is located at about 50 km west of Linxi Town (Fig. 1). The Huanggang mine, operated at present by Inner Mongolia Huanggang Mining Co., Ltd., has started in 1993 the exploitation of iron and tin ores at Skarn No. II and No. III zones, respectively. Those names of skarn zones were given at the stage of

preliminary exploration by No. 3 Geological Team of Inner Mongolia since 1977 to 1983. At present, although the exploitation of tin ore is dormant, one thousand tons

of iron crude ore with the grade of about 39 wt% Fe are produced per day from open pits located at Skarn No. II zone. In the present study, Nos. 1 to 4 Fe ore bodies (O.B., hereafter) at Skarn No. II zone and Sn O.B. at Skarn No. III zone in the mine were investigated, along with the Sumugou base-metal skarn deposit. The name of the deposits and mine is often referred as Huanggangliang instead of Huanggang in literatures, but they refer the same deposits and mine.

**2. General Geology**

Many reports have so far been published as to the general geology of the studied area by previous workers. Among those, Inner Mongolia No. 3 Geologic Team (1992) gives the most detailed information about the general geology of the area, which is shown as in Figure 2. The following is a brief summary of general geology around the Huanggang and Sumugou deposits based on previous reports and the present study.

The studied area is occupied by Permian strata, named the Qingfengshan, Dashizhai, Huanggangliang and Linxi Formations from lower to upper, striking NE and dipping NW. They are mainly composed of clastic sediments, like shale and sandstone. Some shales and sandstones are tuffaceous in part. Minor conglomerate beds are also intercalated in the strata. The upper Dashizhai Formation is rather exceptional, and mainly composed of thick

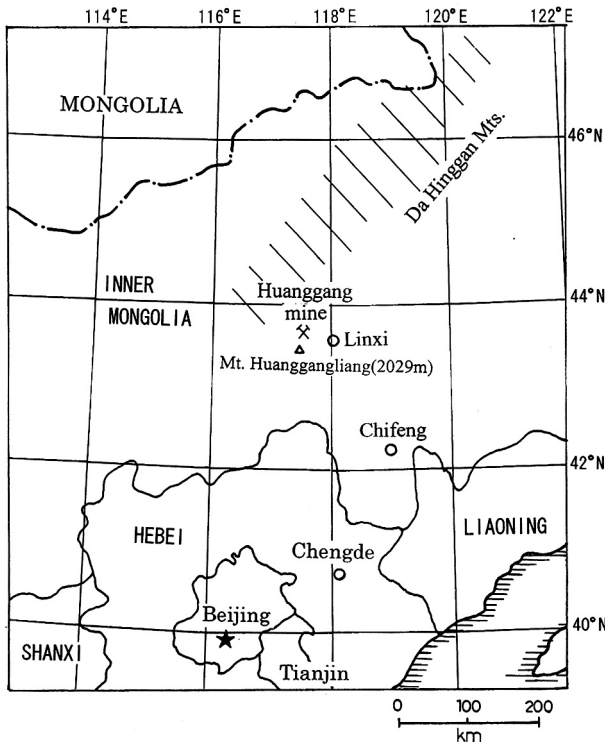


Fig. 1 Index map of the Huanggang mine.

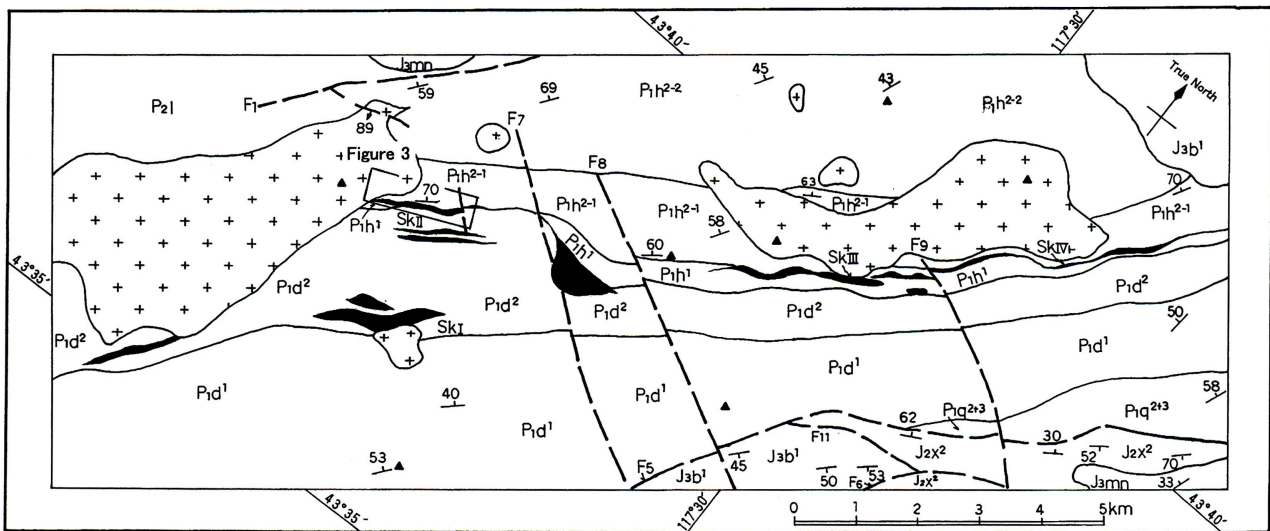


Fig. 2 Geological map of the Huanggang mining area (slightly modified from a map given by Inner Mongolia Geologic Team, 1992). Cross symbol means Yanshanian granitic rocks. Broken lines denote faults. Skarn zones are shown in black. Sk I to Sk IV mean Skarn No. I zone to Skarn No. IV zone, following the nomenclature of Inner Mongolia No. 3 Geologic Team (1992). Solid triangle shows a mountain peak. The strata are, from lower to upper, Lower Permian middle to upper Qingfengshan Formation ( $P_{1q}^{2+3}$ ), lower Dashizhai Formation ( $P_{1d}^1$ ), upper Dashizhai Formation ( $P_{1d}^2$ ), lower Huanggangliang Formation ( $P_{1h}^1$ ), upper Huanggangliang Formation ( $P_{1h}^{2-1}$  and  $P_{1h}^{2-2}$ ) and Upper Permian Linxi Formation ( $P_{2l}$ ). They are covered by Middle Jurassic upper Xinmin Formation ( $J_{2x}^2$ ), Upper Jurassic Manitu Formation ( $J_{3mn}$ ) and lower Baiyingaolao Formation ( $J_{3b}^1$ ).

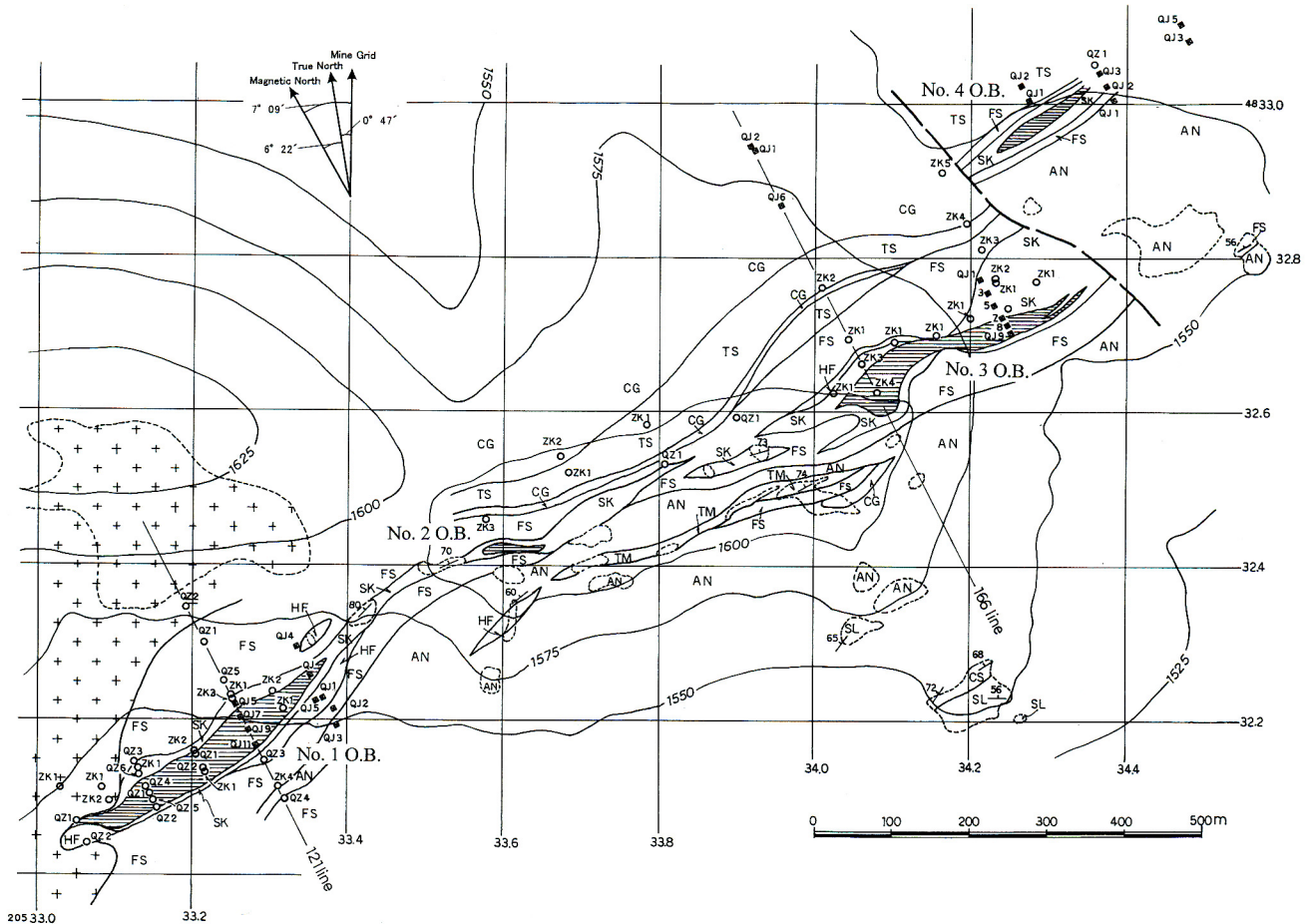


Fig. 3 Geological map around the Nos. 1 to 4 Fe O.B. in the Huanggang mine (compiled from the data of the mine).

Outcrops are shown by broken line. Cross symbol means the Luotuochangliang granite mass. The pattern with thick horizontal lines denotes Nos. 1 to 4 Fe O.B. No. 4 Fe O.B. is displaced northwestwards by a fault. Contour lines show the height above sea level of 1525m to 1625m with 25m interval. Abbreviation of rock units, approximately from lower to upper: SL spotted shale, CS pebble-bearing tuffaceous sandstone, AN andesite, FS tuffaceous siltstone, TM tuff, HF mica-bearing hornfels, SK skarn, CG tuffaceous conglomerate and TS tuffaceous sandstone. Open circle and square with cross show the sites for long and short drillings, respectively.

andesite lavas with pillow structure in some parts. The Xinmin, Manitu and Baiyingaolao Formations of Jurassic age consist mainly of andesitic tuff breccia and sandstone, unconformably covering the Permian strata.

Two Yanshanian granitic intrusives and some much smaller ones are exposed in the area (Fig. 2). The western intrusive is called as the Luotuochangliang granite, and the central-east one as the 204 granite. They are highly differentiated and fine-grained granites. Close space and age relations between the Yanshanian granitic activity and Jurassic volcanic activity suggest that the latter is the effusive equivalent of the former (Zhang, 1997).

### 3. Outline of the Deposit

Many skarn zones are distributed with NE-SW direction in the studied area of 10 to 15 km by 0.5 to 2 km

(Fig. 2). The two skarn zones of the Huanggang Fe-Sn deposit, Skarn Nos. II and III zones, are arranged along calcareous horizons situated just above the lower limit of the Huanggangliang Formation. The Sumugou Zn(-Pb-Cu) skarn deposit, once operated by local people as a small-scale mine, is situated at about ten kilometers northeast extension of Skarn No. III zone, just outside of the right-hand side limit of Figure 2.

Figure 3 shows a geological map of Skarn No. II zone of about 2 km in length and a few to 100 m in width. Four iron ore bodies, called as Nos. 1 to 4 Fe O.B. from southwest to northeast, occur as a chain of discrete magnetite-bearing lenses in this skarn zone. They are exploited by open-pit mining. Sn O.B. of the mine occurs in Skarn No. III zone, located at about several kilometers northeast of No. 4 Fe O.B., as a skarn lens cut by cassiterite-bearing quartz-feldspar veins. This ore body had

been exploited by an open pit of 60 × 20 m. The Sumugou deposit is also a skarn lens with massive magnetite aggregates and dissemination of base-metal sulfides such as sphalerite and galena.

As stated above, these deposits are situated along certain calcareous horizons near the bottom of the Huanggangliang Formation, making a straight line with NE direction. In Skarn No. II zone, however, neither limestone beds nor remnant limestone blocks in skarns could be observed during the present study. On the contrary, a limestone quarry is operated in Skarn No. III zone, several hundreds meters southeast of Sn O.B. A small limestone quarry is also present at the upper part of the Sumugou deposit, clearly showing that the deposit is derived from the limestone bed.

Close spatial association of these deposits with Yanshanian felsic igneous activity is also worthy of mentioning. As shown in Figure 3, the southwestern end of No. 1 Fe O.B. in Skarn No. II zone contacts with the Luotuochangliang granite mass. Sn O.B. skarns are cut by many pegmatitic to aplitic dikes as well as cassiterite-bearing quartz-feldspar veins. The 204 granite mass is closely situated at northwest of this ore body (Fig. 2). At the northwest side of the Sumugou deposit, there occurs a thick pile of Jurassic volcanic rocks. A part of this mass appears at the northern corner of Figure 2. A magma chamber is supposed to have been present beneath the Sumugou area, which supplied the volcanic pile.

#### 4. Analytical Procedures

Chemical composition of minerals was determined using an electron probe micro-analyzer, Shimadzu EPMA-1500, installed in Research Center for Mineral Resources Exploration (RCMRE), CAS. Conventional ZAF corrections were applied with factors and programs supplied by Shimadzu. Tin content of garnets was determined using an ICP-MS, Finnigan MAT Elements, installed in RCMRE. About 40 mg of hand-picked, powdered garnet specimen was dissolved by hydrofluoric acid and nitric acid in a Teflon bomb for one week at 160°C.

Oxygen isotopic composition of garnet, magnetite and quartz, and carbon and oxygen isotopic composition of calcite, were determined with Finnigan MAT Delta S mass spectrometer of RCMRE. Oxygen in silicate and oxide samples was extracted by the BrF<sub>5</sub> technique. About 10 to 20 mg of pulverized samples were placed in nickel reaction tubes, and were reacted with BrF<sub>5</sub> at 550 to 600°C. Generated oxygen was reacted with heated carbon rod to obtain CO<sub>2</sub> gas for the mass spectrometer. About 20 mg of powdered calcites were decomposed by 100 % phosphoric acid at 25°C to obtain CO<sub>2</sub> gas. All carbon and oxygen data are given in terms

of a  $\delta$  expression in permil relative to V-PDB for <sup>13</sup>C/<sup>12</sup>C and V-SMOW for <sup>18</sup>O/<sup>16</sup>O ratios. The analytical uncertainty is ±0.2 ‰ or better.

Sulfur isotopic composition of sulfide minerals was determined also with Finnigan MAT Delta S mass spectrometer. Hand-picked sulfide separates of 10 to 20 mg were baked with CuO of 60 to 120 mg under vacuum, to produce SO<sub>2</sub> gas for mass spectrometry. Sphalerite was baked at 1000°C for 30 minutes, while other sulfides were at 1100°C for 15 minutes. The resulting  $\delta^{34}\text{S}$  values are given as permil relative to CDT. The analytical uncertainty is ±0.2 ‰ or better.

Hydrogen isotopic composition of OH in amphiboles was determined with Finnigan MAT 252 mass spectrometer installed in RCMRE. Amphibole separates of 100 to 200 mg were heated at 200°C under vacuum to eliminate adsorbed moisture, and then their structural waters were extracted by step-by-step heating for about 30 minutes upto 1200°C. The waters released were reduced to H<sub>2</sub> by reaction with uranium metal heated at 650°C, for the D/H ratio measurement. Isotopic composition is expressed in the  $\delta$  notation in permil relative to V-SMOW. The analytical uncertainty is ±2 ‰ or better.

#### 5. Skarns and Skarn Minerals

In the studied area, metallic minerals are exclusively impregnated in skarns, and it is obvious that the study of skarns and skarn minerals is essential to obtain the information on genetical conditions of the deposits.

Mainly based on the field observation, observation under the microscope, and electron probe microanalysis, it was clarified that skarn lenses of Nos. 1 to 4 Fe O.B., Sn O.B. and Sumugou ore deposit, consist of various kinds of skarns, and that each skarn lens has a certain characteristic skarn mineral assemblage. Table 1 lists up the mineral assemblages and chemical composition of minerals in some representative specimens from each ore body. The following is a summary of skarn mineral assemblages and detailed chemical feature of some main skarn minerals.

##### 5.1. Skarn mineral assemblages

A common feature of skarns through Nos. 1–4 Fe O.B., Sn O.B. and Sumugou ore deposit, is the presence of so-called white skarn. The skarn consists mainly of plagioclase and clinopyroxene, and was sometimes called as banded skarn in previous works due to its banding structure derived from original sedimentary structures. The occurrence of this skarn is confirmed in all skarn lenses studied, along the boundary between main skarn body and surrounding host aluminous rocks like shale, sandstone and tuff. The presence of this skarn suggests relatively reducing environments for the skarn formation.

Table 1 List of mineral assemblages and chemical composition of minerals in the Huanggang and Sumugou skarns.

Sample No.	Type	Cpx	Garnet	Amphibole	Plagioclase	Epidote	Ves	Chl	Apt	Sph	Cle	Flr	Qtz	Remarks
<b>No. 1 Ore Body</b>														
WL880606	Garnet skarn	X	Ad62-78(6)	Hast(5), Fehbl(1)										
WL880607	Amph skarn			Hast(9), Feact(5)				X	X				X	Zircon
WL880608	Garnet skarn		Ad64-76(6)	Hast(4), Feparg(1)				X	X				X	Al-bg, Sph
WL880610	White skarn	Hd69-72(5)		Hast(3)	XX			X	X					
WL880611	White skarn	Hd72-73(2)	Ad56(2)	Hast(2)	An39-40(2)	Ps25-29(2)							X	Gar with Pyrralspite mol.
WL880616	Amph & Gar sk	Hd80(2)	Ad18-60(5)	Hast(1), Feparg(1)						X				Gar with Pyrralspite mol.
WL880617	Amph skarn			Hast(7), Feparg(1), Feedn(1), Feact(2)		Ps32-33(2)							X	
WL880618	Amph skarn			Hast(3), Feedn(3), Feact(3)		Ps31(1)		X					X	Zircon, Ce-Allanite(2)
WL880619	Amph skarn			Hast(1), Feedn(1), Feact(2)										
WL880702	Magnetite ore			Feedn(3), Feact(4)										
WL980601	White skarn	Hd81-87(5)		X	An4(2)			X	X					
<b>No. 2 Ore Body</b>														
WL880704	White skarn	Hd73-86(4)				Ps28(2)		X		X			X	Zircon, K-feldspar(2)
WL880705	White skarn	Hd69-76(4)	Ad23-25(2)	X	XX	Ps30(2)							X	Gar with Pyrralspite mol.
WL880706	Magnetite ore	Hd2(2)	Ad75-92(4)	Fehbl(1), Feact(1)									X	Cassiterite, Silician Magnetite(3)
WL880708	Garnet skarn	Hd4-7(5)	Ad61-69(4)	Fehbl(1)	X					X				
WL880709	Magnetite ore			Feact(3)				X					X	Tourmaline, Silician Magnetite(2)
WL081911	Garnet skarn		Ad62-77(6)	Hast(2), Feedn(1)					X					
<b>No. 3 Ore Body</b>														
WL881003	Gar-Ves sk		Ad68-73(4)					X(2)	X(4)		X			Mgchl(4)
WL881006	Magnetite ore		Ad48-89(4)					X	X(4)	X(2)	X		X	Mgchl(2)Fechl(2), Al-bg, Sph
WL881103	Garnet skarn	Hd5-21(2)	Ad40-43(2)					X	X	X	X		X	
WL881104	Garnet skarn		Ad53-79(6)					X	X	XX	X		X	Mgchl(2)Fechl(2)
WL881106	White skarn	Hd71-73(2)	Ad21-47(2)		X	Ps19-30(2)							X	
WL881108	Garnet skarn	X	Ad60-80(4)					X(4)	X	X	X		X	Mgchl(3)Fechl(1)
WL881110	Garnet skarn		Ad49-76(4)					X(2)	X	X	X		X	Mgchl(1)Fechl(1)
WL881111	Garnet skarn		Ad55-79(4)			Ps30(2)		X(2)	X	X	X		X	Mgchl(2)
WL881112	Skrarnized hf	Hd57-70(4)			XX			X(2)	X				X	Fechl(2), Scapolite(3)
WL881114	White skarn	Hd66-67(3)			An27(2)			X(2)					X	
WL881116	Garnet skarn		Ad47-90(8)					X(4)	X	X	X		X	Mgchl(3)Fechl(1)
WL881117	Garnet skarn		Ad47-76(5)			Ps24-29(2)		X(2)	X	X	X		X	Mgchl(2)
WL881123	Garnet skarn	X	Ad74-80(2)		X			X		X	X			
<b>No. 4 Ore Body</b>														
WL880905	White skarn	Hd33-73(4)			An33-36(4)								X	
WL880907	Magnetite ore	Hd3-4(2)	Ad67-96(4)											
WL880908	Garnet skarn	Hd2-11(3)	Ad20-70(3)							X	X			
WL880910	Magnetite ore	Hd5-14(2)	Ad63-71(2)					X(2)						
WL880911	Magnetite ore	Hd5(2)	Ad62-77(6)										X	
WL880913	Garnet skarn		Ad65-78(4)										X	
WL880914	Garnet skarn		Ad61-75(4)										X	
WL880916	White skarn	Hd41-43(2)			An23(2)						X		X	Wollastonite(2), K-feldspar(1), Prehnite Lievrite(3)
WL082505	Lievrite skarn			Fehbl(1), Feact(2)							X			
<b>Tin Ore Body</b>														
WL880302A	Garnet skarn	Hd72-75(3)	Ad32-37(3)					X(2)		X			X	Tourmaline(1), Gar with Pyrralspite mol.
WL880303A	White skarn	Hd79-84(5)		Hast(1), Feedn(1)	An87-96(2)					X	X	X	X	
WL880303B	White skarn	Hd75-78(4)	Ad34-47(5)		An14-20(3)			X		X			X	Allanite
WL880407	Magnetite ore		Ad73-99(6)	Hast(4)	An2(2)								X	Cassiterite, Silician Magnetite(2)
WL880409	Magnetite ore				An1-3(2)								X	Cassiterite
<b>Sumugou Deposit</b>														
WY880211	Garnet skarn	Hd3-8(4)	Ad73-81(4)					X(2)			X			
WY880212	Garnet skarn	Hd3-18(4)	Ad75-98(4)					X(2)			X			
WY880213	Garnet skarn	Hd3-7(5)	Ad68-75(6)					X(1)			X			
WY880216	Ves Skarn	Hd3-5(5)						XX(3)			X			
WY880218	Garnet skarn	X	Ad91-99(4)	Feact(3)					X	X	X			Axinite(4)
WY880220	Garnet skarn	Hd3-4(3)	Ad71-77(4)					X(2)	X	X	X			Fechl(4)
WL980801-3	Garnet skarn	Hd4-10(4)	Ad80-99(5)	Fehbl(2), Feact(1)							X			

X: present, XX: abundant. Numbers in parenthesis are those of points for EPMA analysis. Abbreviations are: sk for skarn, and hf for hornfels. Abbreviations of mineral names and their chemical compositions are as follows.

Cpx: clinopyroxene.....consists mainly of hedenbergite (Hd)  $\text{CaFeSi}_2\text{O}_6$  – diopside  $\text{CaMgSi}_2\text{O}_6$  series solid solution.

Gar: garnet.....consists mainly of andradite (Ad)  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$  – grossularite  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  series solid solution. Some garnets contain certain amounts of pyrralspite molecule (Mg, Fe, Mn) $_3\text{Al}_2\text{Si}_3\text{O}_{12}$ .

Amph: amphibole.....consists of so-called calcic amphibole, but complicated solid solution exists. In the studied skarns, the following species are recognized so far.

Hast: hastingsite..... $6.5 > \text{Si} > 5.5$ ,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) < 0.5$ ,  $\text{Al}^{\text{VI}} < \text{Fe}^{3+}$ ,  $(\text{Na} + \text{K})_{\text{A}} > 0.5$

Feparg: ferropargasite..... $6.5 > \text{Si} > 5.5$ ,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) < 0.5$ ,  $\text{Al}^{\text{VI}} > \text{Fe}^{3+}$ ,  $(\text{Na} + \text{K})_{\text{A}} > 0.5$

Feedn: ferro-edenite..... $\text{Si} > 6.5$ ,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) < 0.5$ ,  $(\text{Na} + \text{K})_{\text{A}} > 0.5$

Fehbl: ferrohornblende..... $7.5 > \text{Si} > 6.5$ ,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) < 0.5$ ,  $(\text{Na} + \text{K})_{\text{A}} < 0.5$

Feact: ferro-actinolite..... $8.0 > \text{Si} > 7.5$ ,  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) < 0.5$ ,  $(\text{Na} + \text{K})_{\text{A}} < 0.5$

Plagioclase.....consists mainly of anorthite (An)  $\text{CaAl}_2\text{Si}_2\text{O}_8$  – albite  $\text{NaAlSi}_3\text{O}_8$  series solid solution.

Epidote.....consists mainly of pistacite (Ps)  $\text{Ca}_2\text{Fe}_3\text{Si}_3\text{O}_{12}(\text{OH})$  – clinozoisite  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$  series solid solution. Occurrence of allanite is also confirmed.

Chl: chlorite.....consists mainly of clinochlore (Mgchl)  $\text{Mg}_5\text{AlSi}_3\text{AlO}_{10}(\text{OH})_8$  – chamosite (daphnite) (Fechl)  $\text{Fe}_5\text{AlSi}_3\text{AlO}_{10}(\text{OH})_8$  series solid solution.

Ves: vesuvianite, Apt: apatite, Sph: sphene, Cle: calcite, Flr: fluorite and Qtz: quartz.

Because, when skarn is formed more oxidizing conditions, epidote skarn is expected to form instead of white (plagioclase-clinopyroxene) skarn (Shimazaki, 1980).

Except for the presence of white skarn, skarn lenses in the studied area have characteristically different skarn mineral assemblages from each other. In the following sections, remarkable skarn mineral assemblages in each ore body will be summarized.

**5.1.1. No. 1 Fe O.B.:** This ore body contacts with the Luotuochangliang granite mass at its southwestern end, and seems to have formed at the most proximal position to the igneous activity among others. The most remarkable feature of this skarn lens is the abundant occurrence of amphibole skarn (Table 1) near the center of skarn lens. Not only in the amphibole skarn, amphibole minerals are widely observed in the skarns of this lens almost without exception. As will be stated later in detail, most abundant amphibole in the skarn is hastingsite (–ferropargasite) to ferro-edenite in composition. Garnet skarn is common, and predominant in some parts surrounding the amphibole skarn. Clinopyroxene is occasionally a main constituent of skarns. Epidote, sphene and apatite are present in some skarns. Analyzed sphene shows relatively high content of  $Al_2O_3$  up to 5.3 wt%. Zircon and Ce-allanite are also recognized in this skarn zone. Ce-allanite gives pleochroic halo to surrounding amphiboles (Fig. 4-a).

Much amount of fluorite is recognized in interstitial space in skarns, sometimes associated with scheelite and molybdenite. On the contrary, calcite, known as a common interstitial mineral in usual calcic skarns, is very scarce to almost lacking in this skarn lens (Table 1).

**5.1.2. No. 2 Fe O.B.:** Garnet skarn predominates (Table 1). Amphiboles are present but their composition and occurrence are quite different from the main phases of No. 1 O.B. They belong mostly to ferrohornblende to ferro-actinolite series in composition, and seem to be retrograde products from clinopyroxene in this ore body. Clinopyroxene, epidote, sphene and apatite are present. Zircon and tourmaline is rarely recognized.

Similar to No. 1 O.B., fluorite is present and calcite is almost lacking. The presence of cassiterite is confirmed in this skarn lens closely associated with magnetite (Table 1). Small amount of sphalerite is also recognized.

**5.1.3. No. 3 Fe O.B.:** Garnet skarn predominates (Table

1). The skarn is often brecciated and cemented by magnetite aggregates. Clinopyroxene is present in some garnet skarn, but amphibole is completely lacking in this skarn lens. In addition to epidote, sphene and apatite, recognized are vesuvianite, scapolite (marialite molecule-rich) and prehnite, demonstrating plenty, primary and retrograde, Ca-bearing minerals present in the lens. Analyzed sphene has relatively high  $Al_2O_3$  contents up to 5.2 wt%.

Differing from the above two ore bodies, fluorite is lacking in this skarn lens. Instead, much amounts of calcite and quartz with chlorite are recognized interstitially among skarn minerals (Fig. 4-d). The condition for retrograde stage seems much different from those for Nos. 1 and 2 O.B. Although Inner Mongolia No. 3 Geologic Team (1992) reported some Sn ores with up to 0.12 wt % Sn present in the ore body, no cassiterite, scheelite and molybdenite have so far been confirmed in this No. 3 and following No. 4 O.B.

**5.1.4. No. 4 O.B.:** Similar to the skarns in No. 3 O.B., garnet skarn predominates (Table 1). In general, amphibole, epidote and apatite are very scarce or almost lacking. Vesuvianite, sphene and prehnite are sometimes observed. Similar to No. 3 O.B., no fluorite occurs, and calcite and quartz are common as interstitial minerals. However, differing from the No. 3 O.B., chlorite is lacking here.

At central part of the south wall of the open pit, an exceptional occurrence of amphibole, fluorite, quartz and lievrite is observed. The amphibole is ferrohornblende to ferro-actinolite in composition. The lievrite has much amounts of MnO up to 5.6 wt %. These minerals aggregate as a small mass in garnet skarn. Small amount of chalcopyrite is also associated with this mass. This may represent channel of the fluid coming from a little different source during the retrograde process.

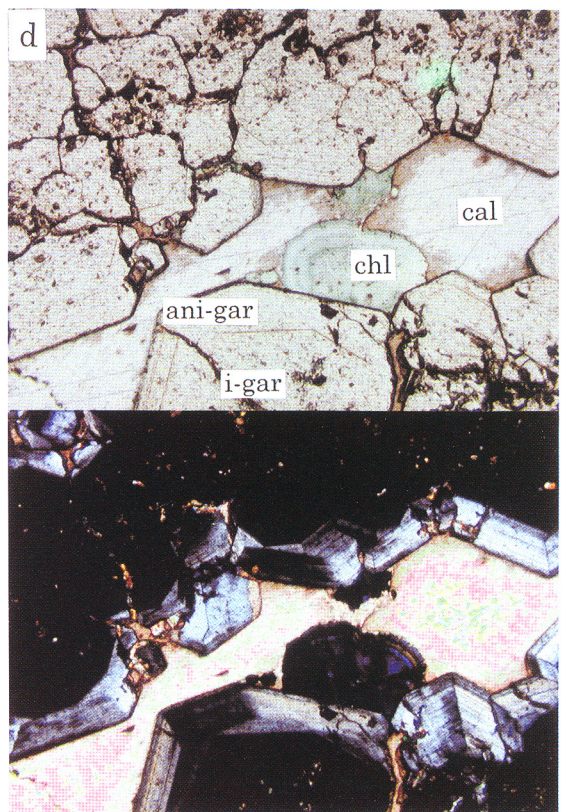
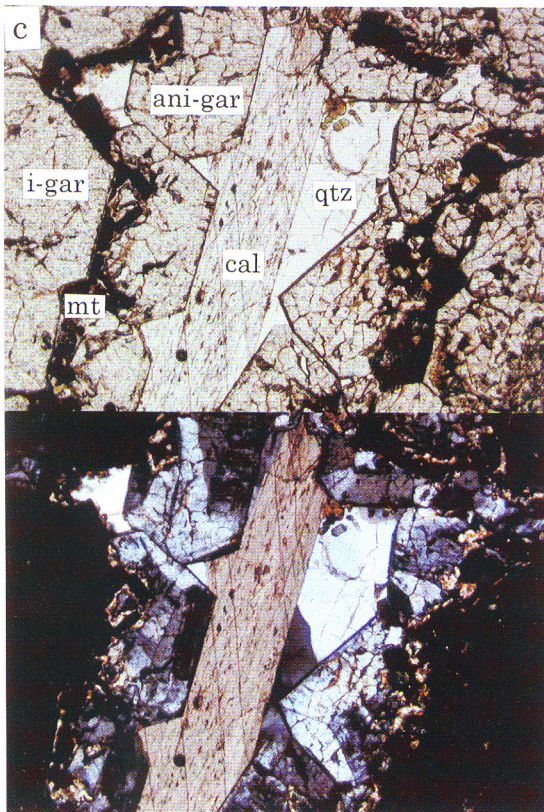
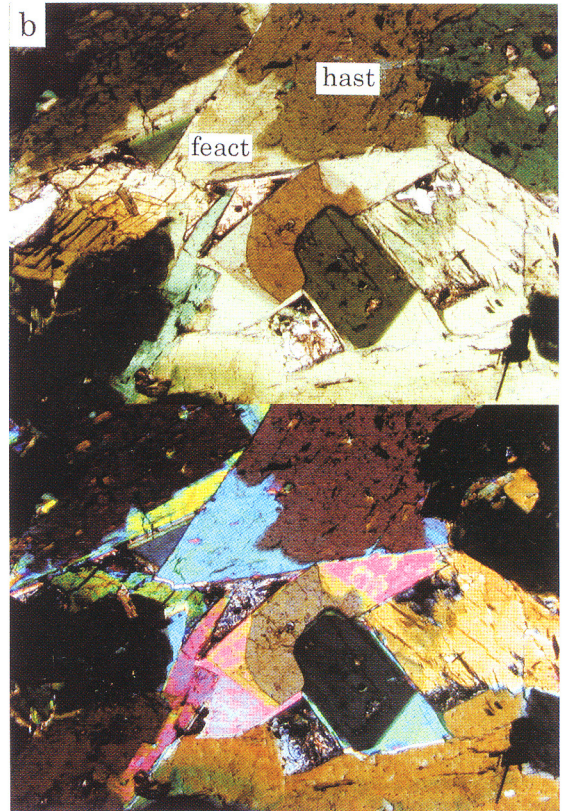
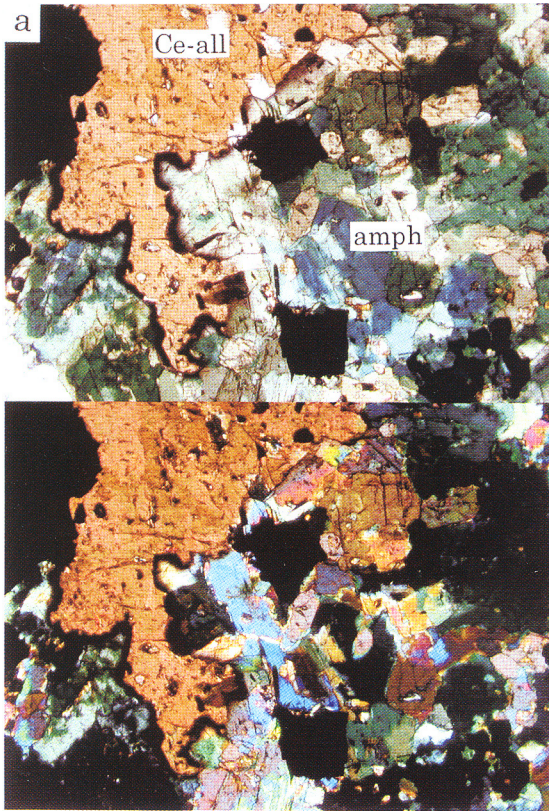
**5.1.5. Sn O.B.:** The feature of skarns in this ore body is similar to that of No. 1 O.B. Although garnet skarn predominates in the skarn lens, some amounts of amphiboles are often observed (Table 1). They belong to hastingsite to ferro-edenite series. Clinopyroxene is common in garnet skarn and magnetite ore. Epidote, vesuvianite, sphene, apatite, zircon, allanite and tourmaline are observed.

Similar to No. 1 O.B., fluorite commonly occurs in interstitial space among skarn minerals. Instead, neither calcite nor chlorite is observed. The presence of cassi-

Fig. 4 Microphotographs of some skarn minerals in the Huanggang deposit.

- WL880618, No. 1 O.B. Ce-allanite (Ce-all) in an amphibole (amph) skarn, giving pleochroic halo to the surrounding minerals.
- WL880607, No. 1 O.B. Hastingsite crystals (hast) overgrown by ferro-actinolite (feact) of the same crystallographic orientation.
- WL081912, No. 2 O.B. Isotropic garnet (i-gar) overgrown by relatively Fe-poor anisotropic garnet (ani-gar) with magnetite seam (mt) near the boundary. Interstitial calcite (cal) and quartz (qtz) present.
- WL881116, No. 3 O.B. Occurrence of interstitial calcite (cal) and chlorite (chl) in a garnet skarn. Garnet crystals with isotropic core (i-gar) and anisotropic rim (ani-gar).

In each set of photographs, a to d, the top shows one polar, and the bottom crossed polars. The width of photographs is approximately 1.6 mm.



terite is confirmed in skarns besides its abundant occurrence in quartz-feldspar veins. These features explicitly indicate much contributions from granitic intrusion. Similar to No. 1 O.B., proximal position of this skarn lens to granite, the 204 mass, guarantees the supply of materials from it.

One feature worthy of mentioning is the relation between skarns and cassiterite-bearing quartz-feldspar veins. The latter always cut the former with, almost without exception, dark green-colored reaction rim of a few millimeters to a few centimeters width. This reaction rim usually consists of hastingsitic to ferro-edenitic amphiboles, fluorite, plagioclase, magnetite and cassiterite. The presence of this reaction rim demonstrates that the Sn vein mineralization occurred later than the main skarn formation.

**5.1.6. Sumugou Ore Deposit:** In this skarn lens, garnet skarn also predominates. Clinopyroxene and vesuvianite are commonly found. Vesuvianite-rich skarn is also present (Table 1). Amphiboles of ferrohornblende to ferro-actinolite series are recognized as the retrograde products from clinopyroxene. Prehnite and apatite are present in small amounts. Rare occurrence of axinite ( $Fe > Mn$ ) is also confirmed.

Calcite is almost always recognized as an interstitial mineral in skarns, but no fluorite occurs. Chlorite rarely occurs with calcite. Dissemination of sphalerite is commonly observed in skarns. Generally speaking, the features observed in the Sumugou deposit could be cited as typical ones for common base-metal skarn deposits derived from limestone. However, some features, such as the lack of manganese concentration, frequent occurrence of vesuvianite, and lack of epidote in the retrograde stage, are different from the features typical for Zn-Pb skarns in the world as given by Einaudi et al. (1981).

As will be shown later in a diagram, andradite-rich garnets and hedenbergite-poor clinopyroxenes are remarkable in this skarn deposit (Table 1). This feature could be interpreted as the indication of relatively oxidizing condition for this skarn zone.

## 5.2. Amphiboles

As stated above, two kinds of amphiboles, Al-rich hastingsite (–ferropargasite) to ferro-edenite series and Al-poor ferrohornblende to ferro-actinolite series, occur in the studied skarns. In general, the latter series occurs commonly in calcic skarns as a primary phase or as a retrograde product from clinopyroxene. However, the occurrence of former series is rare in usual calcic skarns. In particular, it is worth noting that it occurs as the main skarn phase in No. 1 O.B.

About 40 analyses have been done by electron probe micro-analyzer for about 10 specimens from No. 1 O.B. After the classification and nomenclature proposed by

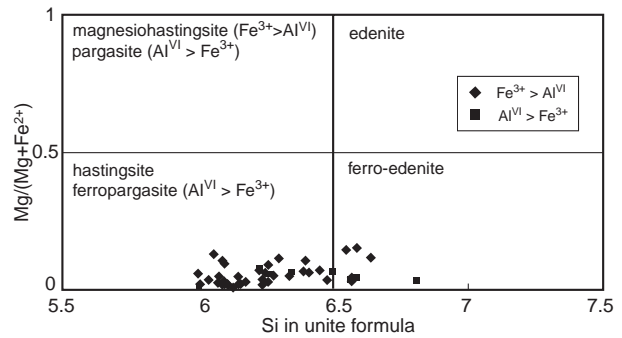


Fig. 5 Chemical composition of Al-rich amphiboles from the Huanggang No. 1 O.B.

Leake et al. (1997), the composition of these amphiboles is plotted in a part of calcic amphiboles pigeon box (Fig. 5). They are silica-poor (usually Si = 6.0 to 6.5 in a formula unit; some extend to more than 6.5, corresponding to the region for ferro-edenite), very Fe-rich and Mg-poor ( $Mg/(Mg + Fe^{2+}) = 0.2$  to 0.0), and K-rich ( $K = 0.4$  to 0.5 in a formula unit). According to the analytical results by Dr. Y. Yamaguchi of Shinshu University (pers. comm., 2000), they are rich in chlorine with approximate average of 2.5 wt%. On the contrary, in spite of the abundant occurrence of fluorite in interstitial space among these amphiboles, fluorine contents are low as mostly around 0.2 wt%. The substitution of Si by Al, Mg by Fe, and Na by K, all smaller-sized ions by larger-sized ions, is supposed to provide preferable site for relatively large-sized Cl instead F and OH (Y. Yamaguchi, pers. comm., 2000).

Under the microscope, these amphiboles with unusual compositions are strongly pleochroic, dark greenish blue to dark brown. As shown in Figure 4-b, these Al-rich amphiboles are often overgrown by Al-poor ferrohornblende to ferro-actinolite series amphiboles of the same crystallographic orientation with sharp boundary. These Al-poor amphiboles are poor in chlorine and fluorine with approximate averages of 0.3 and 0.2 wt%, respectively (Y. Yamaguchi, pers. comm., 2000).

The occurrence of this kind of Al-rich amphiboles as a main phase of skarns, has been reported by Shimazaki (1982) from the Yoshioka mine, Japan. In this mining area, no limestone occurs, then hastingsite-clinopyroxene skarn is concluded to have been derived from black shale by the supply of calcium and iron from hydrothermal fluids. Zhao et al. (1980, 1983) reported the occurrence of similar amphiboles from skarns associated with iron ore deposits in southwestern Fujian, China, and concluded that they are derived from diabase-diorites by metasomatism. These interpretations seem to be also applicable to the Huanggang No. 1 O.B. As stated above, near Nos. 1 to 4 O.B., neither limestone bed nor remnant limestone mass in skarns is so far known. Certain parts of skarns,

including main parts of No. 1 O.B., were probably derived from calcareous shale and sandstone, not from pure limestone bed.

### 5.3. Garnets

The following is a brief summary of the occurrence and chemical composition of garnets (Table 1). They belong to andradite to grossular series. The range of solid solution extends widely from 18 to 96 mole% of andradite in the Huanggang skarns. On the contrary, the garnet in the Sumugou deposit shows a limited range of iron-rich composition from 68 to 99 mole % of andradite (Table 1).

**5.3.1. Pyralspite molecules:** Solid solution towards pyralspite series, which is common in some reduced-type Sn-W skarns (e.g., Shimazaki, 1977; Sato, 1980; Dobson, 1982), has been recognized in some garnets from Nos. 1 and 2, and Sn O.B. (Table 1). Those garnets have negligible amount of pyrope molecule, but almandine plus spessartine molecules up to 12 mole %. Some of those garnets are light orange in color under the microscope. Although Shimazaki (1977) emphasized that grossular-rich garnet could contain certain amounts of pyralspite molecules, the above garnets from the Huanggang deposit have 30 to 60 mole% of andradite, supporting the conclusion by Newberry (1983) that the garnet with up to 75 mole% andradite can contain significant pyralspite component. As summarized by Newberry (1998), this effect is most likely due to the low calcium activities characteristic of proximal occurrences of skarns to intrusives.

**5.3.2. Zoning:** At the central, main parts of No. 3 O.B., coarse-grained garnet aggregate hosts massive magnetite ore. As mentioned above, brecciated garnet skarn is often cemented by massive magnetite. Garnet in these occurrences generally shows a strong zoning, that is, optically isotropic core is surrounded by optically anisotropic rim (Fig. 4-c and 4-d). This relation is also occasionally observed in Nos. 2 and 4 O.B. Chemical composition of the core mostly ranges 71–90 mole% andradite, while that of the rim 47–69 mole% andradite (Fig. 6). This abrupt decrease of iron contents seems to correspond to the beginning of magnetite precipitation. Indeed, magnetite seams could be recognized between the isotropic core garnet and anisotropic rim garnet in some specimens (Fig. 4-c). However at present, it is difficult to predict whether this compositional gap caused the magnetite precipitation, or the former resulted from the latter.

**5.3.3. Sn content:** Since classical works on stannian andradites (McIver and Mihalik, 1975; Dobson, 1982), it is well known that garnets in certain skarns could contain

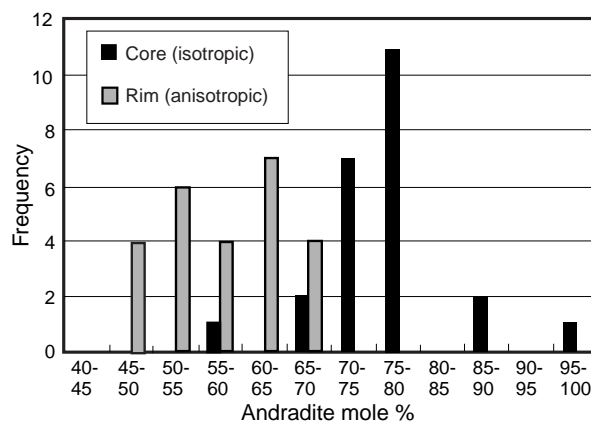


Fig. 6 Histogram of core and rim garnets compositions from Nos. 3 and 4 O.B.

considerable amounts of tin. In order to evaluate how much contribution came from granitic intrusions to the formation of skarns, tin content of garnets in the studied area was determined using ICP-MS. The results are shown in Table 2 together with those from representative Japanese skarns determined for comparison. The Damogutu magnetite skarn deposit is situated about 40 km east northeast of the Huanggang mine. The tin content of garnets from the studied area is as high as several hundreds to several thousands ppm.

In Table 2, Japanese skarn deposits are divided into two groups shown as (IL) and (MT). The former deposits are associated with felsic activities of ilmenite-series, and the latter with those of magnetite-series (Ishihara, 1977). Some typical Japanese skarn deposits in Table 2 are characterized by Shimazaki (1980), particularly in terms of their oxidation conditions. Those from deposits associated with ilmenite-series activities show high tin contents from a few hundreds ppm to more than 1 wt% Sn. On the contrary, those from deposits associated with magnetite-series activities have low tin contents, less than 20 ppm.

The genesis of the Kamioka deposits, the largest Zn-Pb skarn deposits so far known in Japan, is somewhat controversial. Although Shimazaki (1980) classified them to the group associated with ilmenite-series, they are here included in the group with magnetite-series, based on the classification given by Ishihara (1981). Irrespective of the nature of associated igneous activity, it is also plausible that the tin content of garnet from the deposits is low, because they are formed by hydrothermal solutions of meteoric water origin (Shimazaki and Kusakabe, 1990). Some examples, however, such as the Kamaishi and Sannotake deposits, are confirmed to have formed by solutions of magmatic water origin (Morishita and Matsuhisa, 1983; Kato, 1999), and the tin content of garnets from these deposits is clearly low as shown in Table 2.

Table 2 Sn contents of garnets from the Huanggang area and from Japanese skarns.

The Huanggang Area		
Specimen No.	Ore Body	Sn (ppm)
WL880608(B)	No. 1	473
WL880621	No. 1	1760
WL081912	No. 2	969
WL881108	No. 3	2120
WL881115	No. 3	1400
WL081913	No. 3	1400
WL880911	No. 4	1040, 1030
HSCOISOT-8	No. 4	1080
WL082609-G	Sn	1060
WL082609-B	Sn	626, 359
WL980801-3	Sumugou	5600
WL082314	Sumugou	1140
HS081505	Damogutu	3630

Japanese Skarns (IL)		
Specimen No.	Mine	Sn (ppm)
M18871	Hoei	231
M19098	Hoei	219
20441	Hoei	58, 41
HS73031804	Kiura	1400
HS73031527	Obira	490
20099	Obira	456
HS74031604	Toroku	11300
HS76112203	Kiwada	213
M18923	Fujigatani	252, 560
20113	Jinmu-Mihara	6180
HSSP	Sanpo	5370
HS77070904	Date-Nagai	989

Japanese Skarns (MT)		
Specimen No.	Mine	Sn (ppm)
HS74101307	Sannotake	14, 16
HSKB	Kawaba	11
HS95072703	Kamioka	4.5
HS74110604	Kamaishi	2.7
HS74110622	Kamaishi	12
HS72110710	Kamaishi	4.5

Two values in a column of one specimen show results of duplicated measurement. As to the locality of garnets, see text. Japanese skarns (IL) and (MT) mean skarns associated with ilmenite-series and magnetite-series felsic activities, respectively.

These facts demonstrate that the tin content of garnets could reflect the nature of igneous activities genetically related to the deposits. In the Huanggang mining area, the contribution from granitic masses could be confirmed during the main stage of skarn formation, regardless of the distance from the masses. It is worthy to note that not only the Huanggang deposit but also the Sumugou and Damogutu deposits show high tin contents of garnets, manifesting cognate magmas relating to the formation of these deposits.

#### 5.4. Clinopyroxenes

Clinopyroxene is also a main, ubiquitous constituent of various skarns, and its chemical composition ranges

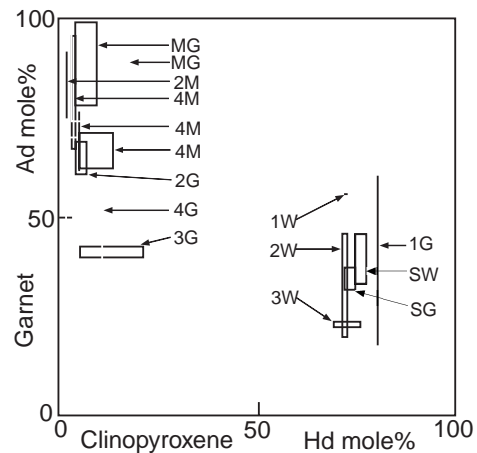


Fig. 7 Chemical compositions of coexisting garnet and clinopyroxene in the Huanggang and Sumugou deposits. Abbreviations: Ad andradite and Hd hedenbergite. Two letters attached each compositional field are as follows: the first letters 1 to 4, S and M mean Nos. 1 to 4 O.B., Sn O.B. and Sumugou deposit, respectively; the last letters G, M and W mean garnet skarn, magnetite ore and white skarn, respectively.

from 2 to 87 hedenbergite mole% in the Huanggang skarns. On the contrary, clinopyroxene from the Sumugou skarns is remarkably diopsidic, and has a limited composition of 3–18 hedenbergite mole% (Table 1). As stated above, together with the fact that the garnet in this deposit is rich in andradite molecules, the feature indicates relatively high oxidation condition during the Sumugou skarn formation.

#### 5.5. Garnet and clinopyroxene

These two minerals are abundant in the studied skarns, and they commonly coexist in skarns and magnetite ores. Chemical compositions of both coexisting minerals were determined for some cases (Table 1), and are illustrated in Figure 7. They are clearly divided into two groups, diopsidic clinopyroxene group and hedenbergitic clinopyroxene group. The former group includes garnets with a wider compositional range up to 99 mole% andradite, and constitutes garnet skarns and magnetite ores in Nos. 2 to 4 O.B. and the Sumugou deposit. The latter group constitutes garnet skarns in No. 1 O.B. and Sn O.B., and some white skarns. This relation demonstrates relatively oxidizing conditions for the main skarns and magnetite ores in the distal Nos. 2 to 4 O.B. and the Sumugou deposit, whereas relatively reducing formation conditions for the proximal skarns, such as those in No. 1 and Sn O.B., and for some white skarns contacting to host sedimentary rocks.

#### 5.6. Chlorites

Chlorite is an essentially Ca-free mineral, and generally

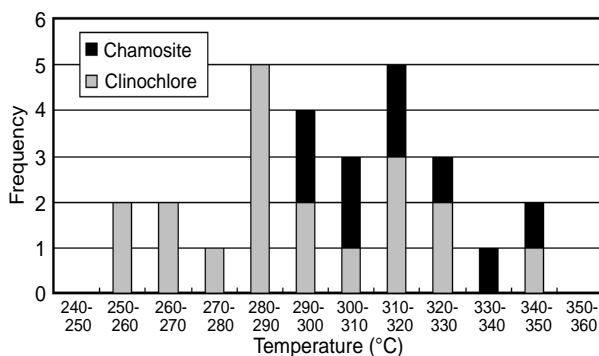


Fig. 8 Histogram of calculated formation temperature of chlorites from the Huanggang No. 3 O.B. based on the equation by Jowett (1991). Iron-chlorite, chamosite, tends to give relatively higher temperatures compared with those for magnesium-chlorite, clinocllore.

not common in usual calcic skarns. As stated above, however, skarns in No. 3 O.B. solely contain much amounts of interstitial chlorite (Fig. 4-d). During the retrograde stage, partial pressure of  $\text{CO}_2$  increased much in this ore body, though the reason is not clear at present, and decomposed the pre-existing skarn minerals. The extracted calcium was combined with  $\text{CO}_2$  as calcite, and Ca-free hydrous mineral, such as chlorite, was precipitated through this alteration.

Using chemical composition of natural chlorites, several geothermometers have been proposed by previous workers. Here an empirical equation proposed by Jowett (1991) is adopted in the present study, and formation temperature of chlorites was estimated and shown in Figure 8 as a histogram. The 28 analyses for nine specimens (Table 1) give the range from 253 to 348°C with the average of just 300°C, although there is a tendency that Fe-rich chlorites, chamosites, often give relatively higher temperatures, while Mg-rich, clinocllore, give lower temperatures even in the same specimens (Fig. 8). The temperature 300°C could be taken as that for the retrograde alteration stage.

## 6. Ore Minerals

Only magnetite is the iron ore mineral so far exploited in the Huanggang deposit. Magnetite is mainly precipitated with, or a little later than, skarn silicates. It usually hematitized more or less along the grain boundary. Small amounts Ti, Al, Mg, Mn and Ca, are sometimes detected by electron probe micro-analysis, but magnetite in the studied area is in general pure in composition.

Only the exception is the occurrence of silician magnetites from No. 2 and Sn O.B. (Table 1). This mineral was first reported by Shiga (1988, 1989) from the Kamaishi mine, Japan, and later its wide occurrence in nature

was established by Shimazaki (1998). The silician magnetites from No. 2 and Sn O.B. contain 5 to 13 %  $\text{Fe}_2\text{SiO}_4$  molecule. The presence of silician magnetite is a common feature of magnetite skarns in the world (Shimazaki, 1998), and the Huanggang deposit is not the exception.

As mentioned previously, scheelite and molybdenite are often observed in No. 1 O.B., although they are so far not recovered. These two minerals are found as interstitial minerals with fluorite among amphibole and/or garnet crystals. This occurrence strongly demonstrates that the W and Mo mineralization is later than the main stage of skarn formation. The similar relation is recognized for the Sn mineralization as discussed below.

Cassiterite was exploited from cassiterite-bearing quartz-feldspar veins in Sn O.B., although the exploitation is stopped at present. As described previously, the cassiterite-bearing veins cut skarns with reaction zone, and clearly show that Sn mineralization is later than the main stage of skarn formation. These features will give a great constraint to the genetic model of mineralization in this area.

Many researchers (e.g. Tao et al., 1983; Inner Mongolia No. 3 Geologic Team, 1992; Yang and Bao, 1997) mentioned the occurrence of a phase with composition of  $\text{H}_2\text{SnO}_3$ . Field and laboratory survey by the present authors, however, failed to confirm whether this phase is really present or not in the Huanggang deposit.

Some sulfide minerals like arsenopyrite, pyrite, sphalerite and chalcocopyrite, are only sparsely recognized in Nos. 1 – 4 O.B. and Sn O.B., except for molybdenite, which is frequently observed in interstices of skarns in No. 1 O.B. On the contrary, in the Sumugou deposit, large amounts of sulfide minerals, mainly sphalerite and galena, are present, and were exploited in the past. Loellingite associated with arsenopyrite, and molybdenite are recognized in the deposit, besides pyrite and chalcocopyrite.

## 7. Formation Age of the Deposits

Although the deposits in the studied area are all thought to have genetical relations to Yanshanian igneous activities, the formation age of the deposits have not yet been fully established. Hastingsite – ferropargasite – ferroedenite series amphiboles occurring in No. 1 O.B. contain certain amounts of potassium, 1.5 – 2.5 wt%  $\text{K}_2\text{O}$ , and are suitable for K/Ar age determination. Three separates of those amphiboles from skarns were sent to Geochron, Co., USA, and their K/Ar ages were determined. Obtained three results are shown in Table 3, and identical to each other in the error range, giving  $130 \pm 3$  Ma. The value is close but not completely identical with the result, 140 and 154 Ma, given by Tao et al. (1983) for amphiboles from the Huanggang deposit. However, these data confirm that the Huanggang deposit was formed at the time of latest

Jurassic to early Cretaceous with genetical relation to Yanshanian igneous activities.

## 8. Stable Isotope Data

In order to understand the genesis of ore-forming fluids, stable isotopic data are indispensable. In the present research, so far obtained are the data on oxygen isotopic compositions of garnet, magnetite and quartz, carbon and oxygen isotopic compositions of calcite, sulfur isotopic compositions of molybdenite, arsenopyrite, chalcopyrite, galena and sphalerite, and hydrogen isotopic compositions of hydroxyl in amphiboles. The following is a brief summary of the data and interpretation based on them.

### 8.1. Oxygen isotopes of garnet, magnetite and quartz

Oxygen isotopic compositions of garnet and magnetite in skarns and ores, and of interstitial quartz among skarn minerals, were determined (Table 4). Garnet has

Table 3 The results of K-Ar dating on hastingsite-series amphiboles from No. 1 O.B.

Sample No.	Av. K (%)	Av. rad. <sup>40</sup> Ar (ppm)	Age (Ma)
WL880607	1.395	0.01302	130 ± 3
WL880608(A)	1.332	0.01257	131 ± 3
WL880617	1.314	0.01234	130 ± 3

Constants used are :  $\lambda_{\beta} = 4.962 \times 10^{-10}$ /year,  $(\lambda_{\epsilon} + \lambda_{\epsilon'}) = 0.581 \times 10^{-10}$ /year,  $^{40}\text{K}/\text{K} = 1.193 \times 10^{-4}$  g/g.

isotopic compositions of  $-2.2$  to  $+3.9$  ‰. No systematic variation is recognized among the proximal to distal ore bodies. A relatively high temperature, such as  $400^{\circ}\text{C}$ , could be assumed for the formation temperature of studied garnets. Using this temperature and empirical and experimental fractionation data given by Bottinga and Javoy (1975), Taylor and O'Neil (1977), and Matthews et al. (1983), the fractionation between garnet and water could be estimated as about one permil. The calculated isotopic values for water coexisting with these garnets at  $400^{\circ}\text{C}$  are given as about  $-3$  to  $+3$  ‰ (Table 4).

Oxygen isotopic values for magnetite were determined as  $-2.3$  to  $+0.7$  ‰ (Table 4). The fractionation factor given by Becker and Clayton (1976) gives the oxygen isotopic values of coexisting water as about 0 to  $+3$  ‰ at  $400^{\circ}\text{C}$ .

Quartz shows two different isotopic values; one is nearly  $+2$ , and the other is  $+9$  to  $+10$  ‰ (Table 4). Assuming  $300^{\circ}\text{C}$  as the temperature for retrograde stage, the isotopic values of water precipitating these interstitial quartz are calculated with the fractionation factor by Matsuhisa et al. (1979) as about  $+2$  to  $+3$  ‰ for No. 1 and Sn O.B., and about  $-5$  ‰ for No. 3 O.B.

The data above confirm that the fluids prevailed at the skarn and ore stage as well as retrograde stage have oxygen isotopic values near zero permil. In the distal ore bodies like No. 3 O.B., the fluid with  $-5$  ‰ prevailed at the

Table 4 Oxygen isotopic compositions (V-SMOW) of garnet, magnetite and quartz. Oxygen isotopic composition of fluids coexisting with these minerals is also given.

Specimen No.	Sample Locality	Mineral	Remarks	$\delta^{18}\text{O}$ ‰	$\delta^{18}\text{O}$ (H <sub>2</sub> O) ‰
WL880608(B)	No. 1 O.B.	Garnet	Reddish brown, massive garnet zone in amphibole skarn	-2.2	-3.2
WL081912	No. 2 O.B.	Garnet	Brownish yellow, coarse-grained bands in magnetite ore	2.4	1.4
WL881108	No. 3 O.B.	Garnet	Brownish yellow, coarse-grained garnet skarn	1.9	0.9
WL881115	No. 3 O.B.	Garnet	Euhedral large crystals with brown color in garnet skarn	2.0	1.0
WL081913	No. 3 O.B.	Garnet	Reddish brown, massive garnet brec and cemented by magnetite	-0.6	-1.6
WL880911	No. 4 O.B.	Garnet	Pale yellow, coarse-grained garnet bands with magnetite bands	1.1	0.1
HSCOISOT-8	No. 4 O.B.	Garnet	Brownish yellow, coarse-grained garnet skarn	1.1	0.1
WL082609-G	Sn O.B.	Garnet	Dark green, coarse-grained, euhedral crystal part in garnet skarn	3.8	2.8
WL082609-B	Sn O.B.	Garnet	Brownish yellow, fine-grained massive part in the same skarn above	3.8	2.8
WL980801-3	Sumugou Dep.	Garnet	Brownish green garnet skarn contacting with limestone	3.9	2.9
WL082314	Sumugou Dep.	Garnet	Reddish brown, massive garnet skarn	3.6	2.6
WL081801	No. 1 O.B.	Magnetite	Small massive aggregate in hastingsite skarn	-2.3	0.4
WL081908	No. 2 O.B.	Magnetite	Massive magnetite ore	-0.8	1.9
WL081917	No. 3 O.B.	Magnetite	Aggregate in garnet skarn with a druse filled by calcite	-2.3	0.4
WL082004	No. 4 O.B.	Magnetite	Fine bands in garnet skarn	-1.0	1.7
WL082608	Sn O.B.	Magnetite	Massive magnetite ore with garnet and fluorite crystals	0.7	3.4
WL082614	Sn O.B.	Magnetite	Massive magnetite ore with fluorite crystals	-1.0	1.7
WL082313	Sumugou Dep.	Magnetite	Magnetite bands in garnet skarn	0.2	2.9
HSOISOT-1	No. 1 O.B.	Quartz	Massive aggregate filling a druse in hastingsite skarn	9.4	2.5
WL081915	No. 3 O.B.	Quartz	Small euhedral crystals in a druse in altered garnet skarn	2.3	-4.6
WL082501	No. 3 O.B.	Quartz	Small euhedral crystals in a druse in garnet-magnetite skarn	2.0	-4.9
WL082606	Sn O.B.	Quartz	Milky gray massive aggregate in cassiterite-bg qtz-feld vein	9.8	2.9
WL082613	Sn O.B.	Quartz	Small euhedral crystals in a druse in fluorite-feld vein	9.3	2.4

Abbreviations: bg bearing, brec brecciated, feld feldspar, qtz quartz.

$\delta^{18}\text{O}$  (H<sub>2</sub>O) values are calculated assuming the precipitation temperatures of garnet and magnetite as  $400^{\circ}\text{C}$  and of quartz as  $300^{\circ}\text{C}$ .

retrograde stage. Similar results are obtained through isotopic study on interstitial calcites as given below. The fluids with such near zero to negative isotopic values are exclusively meteoric in origin. Meteoric water circulation brought oxygen-shifted water with variable degrees ( $\delta^{18}\text{O} = -3$  to  $+3$  ‰) to the site of skarn and ore deposition at the main stage, and then less oxygen-shifted water ( $\delta^{18}\text{O} = -5$ ‰) came directly to certain precipitation sites at the later stage due to decrease of circulation temperatures and coating of fluid channel walls by light oxygen. As mentioned above, however, skarn garnets in the studied area contain some amounts of Sn. Taking this into consideration, not completely rejected is the possibility that the fluid with near zero permil oxygen isotope values was originated from the mixing of meteoric water with magmatic water.

Feng (1992) gave  $\delta^{18}\text{O}$  values for magnetites from the Huanggang deposit as  $-0.4$  to  $+4.6$  ‰. If the formation temperature for those magnetites could be assumed as  $400^\circ\text{C}$ , these values give approximately  $+2$  to  $+7$  ‰ for the coexisting solutions (Becker and Clayton, 1976). Yang and Bao (1997) gave  $\delta^{18}\text{O}$  values of  $+4.4$  to  $+9.8$  ‰ for the solutions responsible for the formation of quartz and magnetite in the Huanggang deposit. These heavy values are rather inconsistent with the present results, though the reason is not clear at present.

## 8.2. Carbon and oxygen isotopes of calcite

In general, calcite is commonly observed as an interstitial mineral in calcic skarns. Calcite of this occurrence is called "skarn calcite", and is useful to obtain the information about carbon and oxygen isotopic nature of the fluids prevailed during later stages of skarn mineralization (Shimazaki et al., 1986). In order to apply this method to the Huanggang and Sumugou deposits, about 40 specimens of skarn calcites and limestone calcites were analyzed for carbon and oxygen isotopic compositions. The results are listed in Table 5, and shown in Figure 9. As

Table 5 Carbon and oxygen isotopic compositions of skarn calcite in the Huanggang and Sumugou deposits, and of limestones. Oxygen isotopic composition of coexisting fluids is also given for skarn calcites assuming the precipitation temperature as  $300^\circ\text{C}$ .

Sample No.	Sample Locality	$\delta^{13}\text{C}$ ‰ (V-PDB)	$\delta^{18}\text{O}$ ‰ (V-SMOW)	Average $\delta^{13}\text{C}$ ‰	Average $\delta^{18}\text{O}$ ‰	$\delta^{18}\text{O}(\text{H}_2\text{O})$ ( $300^\circ\text{C}$ ) ‰
HSCOISOT-1	No. 1 O.B.	-11.1	-1.5			
HSCOISOT-2	ibid	-12.0	5.5	-11.5	2.3	-3.3
HSCOISOT-3	ibid	-11.7	2.1			
WL081906	ibid	-11.3	3.1			
HSCOISOT-4	No. 2 O.B.	-12.6	1.7	-12.6	1.7	-3.9
HSCOISOT-5*	ibid	(-12.9	11.2)			
WL881109	No. 3 O.B.	-13.1	0.6			
WL881118	ibid	-12.6	2.9			
WL881124	ibid	-12.8	0.8			
WL881104	ibid	-12.4	-2.4			
WL881111	ibid	-12.5	-0.4	-12.3	0.7	-4.9
WL881126	ibid	-11.5	3.0			
HSCOISOT-6	ibid	-10.8	4.1			
WL081916	ibid	-13.8	-5.5			
WL081917	ibid	-10.9	-1.6			
WL082501	ibid	-12.0	5.6			
WL880908*	No. 4 O.B.	(-15.5	18.7)			
HSCOISOT-7	ibid	-8.5	-0.5			
WL082001	ibid	-11.4	-0.6			
WL082002	ibid	-11.6	0.2	-10.8	-0.4	-6.0
WL082504	ibid	-10.0	-2.1			
ibid	ibid	-11.8	1.3			
HSCOISOT-8	ibid	-11.8	-0.7			
HSCOISOT-9	Sn O.B.	-9.8	8.5	-9.8	8.9	3.3
HSCOISOT-10	ibid	-9.8	9.3			
WY880214	Sumugou Deposit	-2.9	8.9			
WY880217	ibid	-8.8	8.8			
WY880224	ibid	-9.8	9.6			
WY880225	ibid	-3.2	8.1	-6.9	9.1	3.5
WY880227	ibid	-8.5	9.4			
WL082311	ibid	-5.8	9.3			
WL082314	ibid	-6.2	9.4			
WL082315	ibid	-9.7	9.3			
WL880402**	Ls Quarry near Sn O.B.	3.0	17.7			
ibid**	ibid	2.1	16.5			
WL880404**	ibid	1.6	17.4	2.8	16.8	
WL082621**	ibid	3.9	16.1			
WL082305**	Sumugou Ls Quarry	3.2	16.5			

\*Apparently exceptional values and omitted from average calculations. \*\*Limestone (Ls).

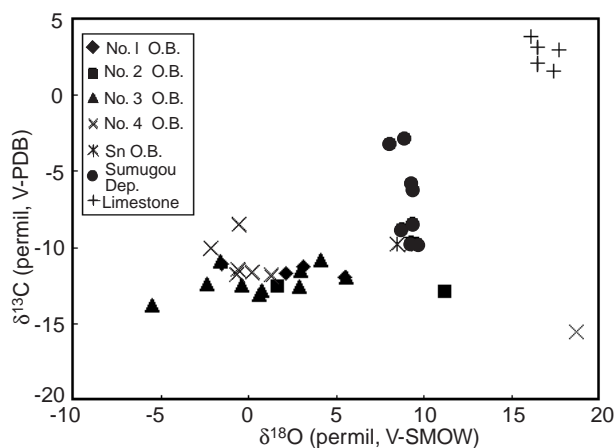


Fig. 9  $\delta^{13}\text{C}$  vs  $\delta^{18}\text{O}$  values of skarn calcites and limestones.

Table 6 Sulfur isotopic composition of sulfides from the Huanggang and Sumugou deposits.

Sample No.	Sample Locality	Mineral	Remarks	$\delta^{34}\text{S}$ (CDT) ‰
HSSISOT-2	No. 1 O.B.	Molybdenite	Euhedral crystal in druse	4.5
HSSISOT-3	ibid	ibid	ibid	2.3
HSSISOT-4	ibid	ibid	ibid	2.3
WL082403	No. 2 O.B.	Arsenopyrite	Euhedral crystal aggregate	-1.0
WL082006	No. 4 O.B.	Chalcopyrite	Massive aggregate	-0.9
WL082306	Sumugou Deposit	Galena	Massive vein in marble	0.1
WL082309	ibid	ibid	ibid	-2.0
WL082310	ibid	Sphalerite	Massive aggregate	0.0
WL082315	ibid	ibid	Dissemination in calcite aggregate	0.6

described in early pages, skarn calcite is abundant in Nos. 3 and 4 O.B. and in Sumugou deposit, but very scarce in Nos. 1 and 2 O.B. and Sn O.B. With this reason, only limited numbers of specimens were available from the latter group ore bodies.

Calcites from the limestone occurring along the mineralized horizon, that is, near the bottom of the Huanggangliang Formation, give  $\delta^{18}\text{O}$  values of 16.1–17.7 ‰ and  $\delta^{13}\text{C}$  values of 1.6–3.9 ‰ (Table 5). Although highly variable, the oxygen isotopic composition of majority of Permian carbonate rocks drops in the range of 22 to 27 ‰ (Veizer and Hoefs, 1976). The oxygen isotope values in the studied limestones are a little light compared with these values. However, the reason is not clear at present. It may have been caused from isotopic alterations by hydrothermal fluids with meteoric water contribution, as has recently been reported by Morishita (1999). The carbon values seem to be normal as Permian carbonate rocks.

Calcites from Sn O.B. and the Sumugou deposit, have relatively constant  $\delta^{18}\text{O}$  values of +8.1 to +9.6 ‰, while those from Nos. 1–4 O.B. have values ranging widely from -5.5 to +5.6 ‰, even excluding two exceptional values of +11.2 and +18.7 ‰ (Table 5). Using the fractionation factor given by O'Neil et al. (1969) at 300°C, averaged  $\delta^{18}\text{O}$  values of fluids at the retrograde stage are calculated as -3.3 ‰ for No. 1 O.B., -3.9 for No. 2 O.B., -4.9 for No. 3 O.B., -6.0 for No. 4 O.B., +3.3 for Sn O.B. and +3.5 for the Sumugou deposit (Table 5). As mentioned above, these light values indicate the origin of fluids as mainly meteoric. From Nos. 1 to 4 O.B., that is, proximal to distal, meteoric water predominance increases in this order.

Carbon isotopic values for skarn calcites are considerably low, ranging from -2.9 to -13.8 ‰ (Table 5). Among those, the data for the Sumugou deposit are most variable from -2.9 to -9.8 ‰ (Fig. 9) with the average of -6.9 ‰. Carbon with large, negative  $\delta^{13}\text{C}$  values could undoubtedly be supplied from organic matter in surrounding sedimentary rocks, while probable reservoir for that with some positive values is limestone associating with the deposit. Carbon isotopic val-

ues for skarn calcites in the Sumugou deposit are possibly determined with the mixing of these two factors.

On the contrary, skarn calcites from Nos. 1–4 and Sn O.B. show a strong concentration of  $\delta^{13}\text{C}$  values at around -10 to -13 ‰. Averaged  $\delta^{13}\text{C}$  values are -11.5 ‰ for No. 1 O.B., -12.6 for No. 2 O.B., -12.3 for No. 3 O.B., -10.8 for No. 4 O.B. and -9.8 for Sn O.B. (Table 5). These values demonstrate the source of carbon in the fluids is mostly organic material in the host sedimentary rocks.

### 8.3. Sulfur isotope

Sulfide minerals are sparsely present in the Huanggang deposit, except for molybdenite in No. 1 O.B. Thus only limited numbers of specimens were provided for sulfur isotope works, that is, three molybdenites from No. 1 O.B., one arsenopyrite from No. 2 O.B., one chalcopyrite from No. 4 O.B., and two galenas and sphalerites each from the Sumugou deposit. Obtained  $\delta^{34}\text{S}$  values range from -2.0 to +4.5 ‰ (Table 6).

The value close to zero is commonly encountered in the previous studies on hydrothermal deposits in the Linxi district. For example, Feng (1992) gave isotopic values of seven sphalerites from the Huanggang deposit as -4.3 to +1.1 ‰ with the average of -0.3 ‰, and those of chalcopyrite, galena, sphalerite, pyrite and arsenopyrite, total 43 specimens, from the Dajing deposit as -5.1 to +3.4 ‰ with the average of +0.4 ‰. Chu and Liu (1999) analyzed more than 20 specimens of pyrite, sphalerite, chalcopyrite and galena from the Dajing deposit, and reported that their sulfur isotopic compositions range -1.8 to +3.8 ‰ with the average of nearly zero permil.

Considering the oxidation condition and fractionation factors between minerals and hydrogen sulfides, it could be concluded that  $\delta^{34}\text{S}$  value of total dissolved sulfur in the solutions is close to zero permil. The source of sulfur is not obvious at present. However, it may be difficult to suppose that highly differentiated ilmenite-series granitoids like the Luotuochangliang and 204 bodies could supply the sulfur with  $\delta^{34}\text{S}$  of nearly zero permil (Sasaki and Ishihara, 1979), although Ishihara

et al. (2000) pointed out that little systematic variation exists between the nature of granitoids and sulfur isotope composition of associated deposits in Northeast China. One possible source is thick andesite lavas in the Dashizhai Formation widely present underneath the mineralized horizon.

#### 8.4. Hydrogen isotope

Hydrogen isotopic compositions for OH in amphiboles from No. 1 O.B. were determined. Used are two amphibole separates, which are the same as those provided for K/Ar age determination, and the results give  $-183$  and  $-185$  ‰. Considering that those amphiboles are very Fe-rich and Mg-poor, and have some amounts of Al (0.2 to 0.5 Al in a formula unit) in octahedral crite, the water precipitated them is estimated to have had  $\delta D$  value of about  $-120$  ‰ (Suzuoki and Epstein, 1976; Graham et al., 1984; Y. Kuroda, pers. comm., 2000). The water with this  $\delta D$  value is hard to be pure magmatic (Taylor, 1997), and probably of meteoric in origin. This result is consistent with those obtained from oxygen isotope study given above.

Wang, L.-J. et al. (2001) have reported a value of  $-106$  ‰ for the inclusion water released at  $500^{\circ}\text{C}$  from quartz in cassiterite-bearing feldspar-quartz vein at Sn O.B. The value indicates participation of meteoric water, at least if not all, to the fluid for Sn mineralization. Previous workers also reported similar  $\delta D$  values for hydrothermal solutions which prevailed at the time of Yanshanian mineralization in this district, e.g.,  $-108$  to  $-140$  ‰ for inclusion waters in quartz from the Dajing deposit (Ai and Feng, 1993; Chu and Liu, 1999). Those workers also suggest the meteoric water origin of the Dajing deposit.

### 9. Genetic Model for the Formation of Deposits

Based on the data given above, the following constraints are given to the genetic model for the formation of deposit in the Huanggang mine. That is, the fluids of main skarn stage are probably oxygen-shifted meteoric water, and of later stage mineralization are also mostly of meteoric water origin. The predominance of meteoric water in the later stage increases with the distance from granitic intrusions. In addition, granite-related elements such as Sn, W, Mo and F are supplied to the deposit at rather later stage of mineralization overlapping to the main stage skarns.

The Huanggang deposit is essentially iron deposit. Besides ore magnetite, a huge amount of iron is precipitated as skarn silicates. Thus the source of iron must be considerably large geologic unit(s). Highly differentiated granitic masses seem hardly to be the source of such huge amount of iron. In fact, previous researchers, e.g.

Li and Duan (1988), and Inner Mongolia No. 3 Geologic Team (1992), thought that thick andesite lavas in the Dashizhai Formation could be the source bed for iron supplied to the Huanggang deposit. The latter reported that the maximum iron content of andesites reaches to 10.7 wt%, while iron contents of hydrothermally altered andesites decrease to 1.6 wt%.

Any data obtained in the present study do not contradict this. As stated above, oxygen isotope data indicate that the fluid for the main skarn and ore stages is mainly of meteoric water origin. High chlorine content of amphibole skarn in No. 1 O.B. suggests that such fluid is rich in chlorine. The presence of transparent daughter mineral(s) in fluid inclusions in garnet, reported by Wang, L.-J. et al. (2001), confirms the highly saline nature of the fluid for the main skarn stage. These lines of evidences support the hypothesis of extraction and transportation of iron by the heated meteoric water circulation.

Bearing those constraints and possibility of the Dashizhai Formation as an iron source in mind, the genetic model could be drawn as shown in Figure 10. At the time of late Jurassic to early Cretaceous, Yanshanian granitic magma intruded to this area, and made the Luotuochangliang and 204 masses. A mass not cropped out at the present erosion surface may also be present underneath the Sumugou deposit area as a magma chamber which supplied so-called Jurassic volcanic rocks. Due to these intrusion activities, the thermal structure of the area was much disturbed, and heated groundwater began circulation following the newly established thermal structure. This circulation extracted much amount of iron from the Dashizhai andesite lavas, and precipitated it along the upper calcareous horizon making skarn minerals and magnetite.

The circulating fluid at this stage is rich in chlorine as stated above. Although the origin of chlorine is not obvious at present, but it possibly came also from the Dashizhai formation. The presence of chlorine is favorable to the transportation of iron as chloride complex. The importance of chlorine in hydrothermal fluid has been argued in the geneses of ore deposits associated with granitic intrusion, since the classical work by Holland (1972) repeatedly to the present, such as by Ishihara and Imai (2000), and Imai (2001).

The presence of considerable amount of tin in garnets in the studied area confirms a certain degree of participation of magmatic fluids to the circulating system of meteoric water. As the solidification of granitic magmas proceeded gradually, volatile-rich fluid was concentrated, and finally expelled from the magmas subsequent to the completion of solidification. The elements such as Sn, W, Mo and F were transported by the fluid, and precipitated at the site where pre-existing skarns provided favorable condition for precipitation.

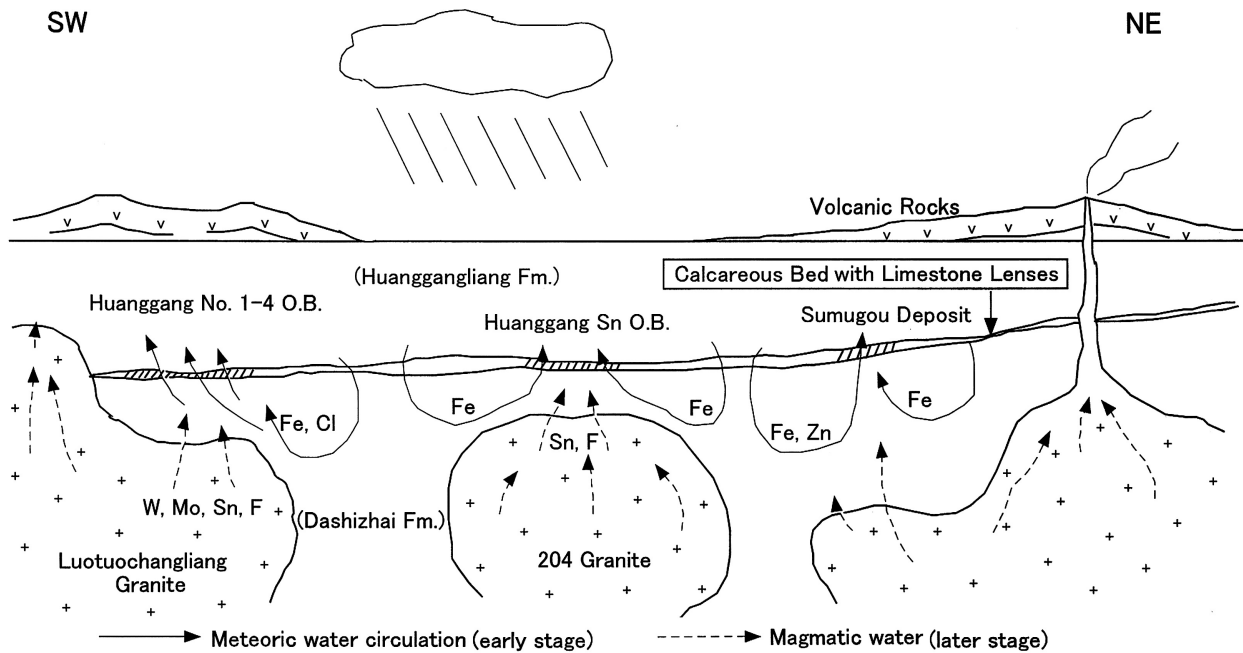


Fig. 10 Schematic cross section showing the genetic model of the formation of mineral deposits at the time of Yanshanian igneous activity. The horizontal distance of the figure is about 20 km, but vertically not in scale.

Although a small amount of molybdenite is recognized, the contribution of fluid from granitic intrusion seem to be much less in the Sumugou deposit. Generally speaking, the mineral assemblages and metal commodity in the deposit have a common feature as usual base-metal skarn deposits in the world. They can typically be formed by the circulation of meteoric water, as exemplified by the Kamioka Zn-Pb skarn deposits in Japan (Shimazaki and Kusakabe, 1990). High tin content, however, of garnets from this deposit certifies a certain degree of contribution to the deposit from a hidden granitic intrusion.

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