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Characteristics and Significance of Rare Native Element Minerals and Intermetallic Compounds from the Garjoan Copper Deposit, Tibet

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Garjoan Au-Cu deposit is a typical skarn type ore deposit occurred in the northern margin of Bangonghu-Nujiang collision belt, between the Nanqiangtang Block to the north and Gangdese-Lhasa-Tengchong Block to the south. Previous work mainly focused on the research of ore deposit characteristics, diagenesis and ore-forming age, geochemistry of ore-bearing rock and so on, information about ore compositions and occurrence of ore-forming elements have been rarely provided. Through field investigation and systematic sampling, combined with the laboratory studies of microscope observation, scanning electron microscope, composition testing analysis of X-ray energy spectrum and electron probe spectrum, some rare native element minerals and intermetallic compounds, such as native ferrum, native bismuth with Os and Ni-Cr-Fe，Cu-Au，Cu-Zn, Au-Ag intermetallic compounds, have been found in the ores. Study of the native element minerals and intermetallic compounds is of important significance on the forming condition, environment and origin of resources of the ore deposit.

1 Geological Characteristics of Ore Deposit

Garjoan Au-Cu deposit occurs in the northern margin of Bangonghu-Nujiang collision zone. Ore formed in the Duoai Formation of lower Cretaceous which is composed of limestone, marble, volcanic breccia, tuff and hornfels. The ore-bearing strataum strikes north to south and dips to the north-northwest with a dipping angle of 15-85°.

Faults are the major geological structures in the ore deposit area. Northeast-southwest trending F_1 and F_2 faults are the ore control structures with multiple stage activity and the rest north-south trending faults were formed after the Au-Cu mineralization.

Widely distributed intrusive rocks of late Cretaceous Period occur as stocks, apophyse and dikes in the ore district with the main rock types of granite porphyry （$\gamma\pi_5^3$）, diorite-porphyrite ($\delta\mu_5^3$), quartzdiorite (δo_5^3), granodiorite （$\gamma\delta_5^3$）, granodiorite porphyry ($\gamma\delta\pi_5^3$) and aplite（Z_5^3）. Of the rock masses, the small sized stock, apophyse and dike of granite porphyry and quartz diorite porphyrite are closely associated with ore bodies and considered to be the ore controlling rocks. Zircon U-Pb dating of ore-bearing porphyries by LA-ICP-MS is 83.2±0.7Ma for granite porphyry, 87.1±0.4Ma for quartz diorite porphyrite respectively. Re-Os model age of molybdenite is 86.8~93.2Ma.

In the ore deposit area, there are 2 major ore bodies and 25 small ore bodies. They occur chiefly in the endocontact and exocontact zones of granite porphyry and marble, or in the fault belts developed in the country rocks. The 900 m long ore body I (average grade of Cu is 0.9%-1%) formed in the contact zone of igneous rock and country rock. It strikes towards northwest by west, dips to the north north east-northeast with dipping angle ranging from 32° to 71°. Its attitude is controlled by strataum and shaped as layer and pod. The lenticular ore body II is controlled by skarn of endocontact zone of rock mass. Wall rock alterations related to mineralization include garnetization, diopsidization, actinolitization, chloritization, silicification and marmorization.

2 Characteristics of Ore

Ores from the deposit exhibit massive structure, disseminated structure, taxitic structure and asterism structures. Ore textures include crystallization-related euhedral-hypidiomorphic texture, allotriomorphic texture;

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Table. 1 Energy Spectrum Chemical Components（*w*B%）and Crystal-chemical Formula of Native Element Minerals in Garjoan Cu-Au Deposit

Number of Samples	Minerals	Fe	Cu	Cr	Si	Bi	O	Co	S	Os	Total	Crystal-chemical Formula
G2051-135	Native	98.78		0.47				0.74			99.99	Fe
G2013-81	Ferrum	93.28			4.27		2.45				100	Fe
G2020-165.1	Native					92.86			2.18	4.95	99.99	Bi
G2020-184.7	Bismuth with Os	5.73				86.92				5.30	97.95	Bi
Z801-178m-(1)	Native		96.27				3.73				100	Cu
Z801-178m-(2)	Copper		97.28				2.72				100	Cu

Tested by: He Jiale and Gong Tingting （2012）

bioerosion structure, border ring texture, pseudomorph texture, stockwerke texture formed by metasomatism, lattice texture and emulsion texture formed by solid solution dissociation, spherulitic texture and framboidal texture formed by biodeposition; and colloidal structure formed by weathering.

The constituents of the ores are complex and the main metallic minerals include pyrite, chalcopyrite, bornite, molybdenite, chalcocite, native copper, blende, gelenite, native bismuth, bismuthinite, emplectite, tellurobismuthite, sulfur-containing tellurobismuthite, native gold, electrum, hessite, copper-gold iron, Zn-Cu intermetallic compound, native ferrum, magnetite, hematite, mushketovite, wustite, goethite, lepidocrocite, digenite and covellite.

3 Characteristics of Native Element Minerals and Intermetallic Compounds

The native element minerals in the ores include native gold, native silver, native ferrum, native bismuth and native copper. Intermetallic compounds includes silver and gold series minerals, grasberg mine, Zn-Cu intermetallic compounds and Fe-Cr-Ni intermetallic compounds. Some rare minerals are firstly found in Bannu metallogenic belt, and never reported in nature. The study of these minerals is of a great scientific significance.

3.1 Characteristics of Native Element Minerals

Native ferrum: Ferrum is an element with variable electrovalence, and its chemical properties are very agility. Usually, Ferrum is preserved in the form of oxide and sulfide. Native ferrum is a rare native element mineral in nature; it forms only on the condition of high pressure and extremely reductive environment. In Garjoan Au-Cu deposit, native ferrum occurs in the form of subhedral, xenomorphic granular (<5μm) and contains minor Cr and Ni. They are associated with skarn minerals such as garnet and diopside, and also associated with magnetite, rutile, native gold, chalcopyrite and bornite. The native ferrum observed is homogeneous and half hard with high reflectance and white and pale yellow reflected colors under microscope. With the help of Electron microprobe analysis of native ferrum shows that the content of Fe is very high, ranging from 93.28% to 98.78%, with minor Cr and Co (Table 1). Wustite has also been found in the ores by energy spectrum analysis with chemical components of Fe 74.27%, O 25.2%，Ti 0.53%. Experiment has showed that wustite is a chemical reaction product in the mantle boundary under high pressure condition and it is preserved by intergrowth with native ferrum in the diamond of Tanzania district, they are believe to form in lower mantle at depth of over 670 km.

Native bismuth: In Garjoan Au-Cu deposit, this sort of native mineral occurs in gangue minerals usually associated with native gold, hematite, blende, pyrite, chalcopyrite and quartz. Microscope and scanning electron microscope observation show that native bismuth is xenomorphic granular and heterogeneous, with bright white reflection color and high reflectivity. Its hardness is low and sometimes possesses polysynthetic twins. Analysis of energy spectrum reveals that native bismuth contains platinum family element-Os, and therefore, it belongs to Os-bearing native bismuth, which is a seldom seen native mineral and reflects the multiple source origin of ore deposit.

Native copper: Mainly formed in the gangue minerals with xenomorphic granular texture and lamellar structure. It is homogeneous with low hardness accompanying striation on the flaky surface. Native copper is often developed in the surface oxidation zone. Sustained decline of underground water table under the condition of drought, the secondary sulphides such as chalcocite and covellite are oxidized again, thus forming the native copper in the end.

3.2 Characteristics of Au-Ag Intermetallic Compounds

Gold and silver minerals in the ores mainly occur in magnetite, hematite, goethite, sulfide and sulfosalt

Table. 2 Electronic Probe Chemical Components（*w*B%）and Crystal-chemical Formula of Gold-Silver Minerals in Garjoan Cu-Au Deposit

Number of Samples	Minerals	Au	Ag	Fe	Cu	Cr	Te	Bi	Total	Relative Purity	Crystal-chemical Formula
G2020-165.1	Native Gold	93.81	0.08			2.15		0.68	96.72	970	Au
G2020-165.1	Native Gold with Silver	93.23	0.53	0.20	0.10	3.22		0.81	98.09	950	$Ag_{0.01}Au_{0.99}$
GPD01-M03		90.80	6.69	0.07		0.06	0.04	0.75	98.4	923	$Ag_{0.12}Au_{0.88}$
G-M08		90.13	10.25						100	950	$Ag_{0.01}Au_{0.99}$
G2020-184.7	Grasberg Mine with Ferrum	72.11	0.11	2.98	19.28	1.14		0.36	95.98	751	$(Fe_{0.14})Cu_{0.83}Au$

Tested by: Ren Kefa and Gong Tingting（2012）

Table. 3 Chemical Components（*w*B%）and Crystal-chemical Formula of Intermetallic Compounds in Garjoan Cu-Au Deposit

Number of Samples	Intermetallic Compound	Cu	Fe	Zn	Cr	Ni	Re	Total	Crystal-chemical Formula
G2051-135	Zn-Cu Intermetallic Compound	53.45	0.7	45.85				100.09	$Cu_{4.84}Zn_4$
		59.52		38.63		1.18		99.33	$Cu_{6.34}Zn_4$
		59.73		40.04				99.77	$Cu_{5.97}Zn_4$
		59.51		38.77		1.09		99.37	$Cu_{6.32}Zn_4$
		55.67		36.91			7.21	99.79	$Re_{0.27}Cu_{6.19}Zn_4$
Number of Samples	Intermetallic Compound	Cu	Fe	Zn	Cr	Ni	Re	Total	Crystal-chemical Formula
G2051-135	Fe-Cr-Ni Intermetallic Compound		73.33		14.64	12.03		100	$Ni_{0.78}Cr_{1.07}Fe_5$
			74.52		14.40	11.07		99.99	$Ni_{0.71}Cr_{1.06}Fe_5$
G2020-184.7			74.09		13.64	11.44		99.17	$Ni_{0.73}Cr_{0.98}Fe_5$

Tested by: He Jiale and Gong Tingting （2012）

minerals in the form of irregular microgranularity. The rest develops in the fissures of sulfide and quartz veins in the form of micro stringer. Native gold is homogeneous with low hardness and with striations on the surface, showing reflection color of golden yellow or pale yellow under microscope. The shape of native gold is usually irregular, characterized by angular, strip, round, lamellar and lentoid shapes. Its granularity is unequal-sized, mainly micro fine granule with the diameter of 3~20μm, most less than 10μm. The grain size of native silver occurred in the quartz veins of oxidizing zone is very fine. It is usually associated with quartz, chalcocite and zigueline in the form of lamellar, xenomorphic granule and round shape. Native silver in the ore shows heterogeneity and low hardness with bright white and cream yellow reflection colors under microscope.

Analysis of Au-Ag Intermetallic Compounds by scanning electron microscope energy spectrum and electron probe spectrum indicates that the purity of silver decreases as its content in the ore increases. The relative purity of silver is 988~533 and there is only a little impurity in ores (Table 2).

3.3 Characteristics of Intermetallic Compounds

Two rare intermetallic compounds have been found in the ores of Garjoan Au-Cu deposit, they are Zn-Cu intermetallic compounds and Fe-Cr-Ni intermetallic compounds.

①Zn-Cu intermetallic compounds occur in fissures of gangue minerals in form of xenomorphic granule by intergrowth with magnetite and native gold. Under microscope, it shows high reflectivity and light yellowish-white color, with grain size less than 5μm, similar to native gold under high magnification polarizing microscope. Scanning electron microscope analysis shows that Cu is 59.73%~53.45% and Zn is 45.85%~36.91%. Rare elements---Fe, Ni are also included and individual samples contain Re of 7.21%. The calculated average chemical formula is $Cu_{5.80}Zn_4$, skeleton symbol is Cu_6Zn_4, characteristic of α-phase Zn-Cu intermetallic compounds, similar to the Cu-Zn intermetallic compounds of Xifanping porphyry copper in Yanyuan Province and Sichuan Province. Three data points have been obtained by the analysis of electron microprobe, however, the granules of minerals are too small to get enough total compositions, so the results are for reference only (Table 3). Based on the ore types, mineral assemblage and ore fabrics, it is considered that the Zn-Cu intermetallic compounds are the product of skarn-oxide phase in hydrothermal mineralization period

②Fe-Cr-Ni intermetallic compounds form in gangue minerals, such as diopside, tremolite and quartz in the form of xenomorphic granule by intergrowth with magnetite, native gold, chalcopyrite and bornite. Under microscope, it shows high reflectivity and bright white color, with grain size less than 5μm. Scanning electron microscope analysis shows that Fe-Cr-Ni intermetallic compounds consist of Fe, Cr and Ni, Fe is 73.33% ~74.52%，Cr is 13.64%~14.64% and Ni is 11.07%

~12.03% (Table 3). The crystal chemical formula is $NiCrFe_8$, belonging to iron-rich Fe-Cr-Ni intermetallic compounds, which are never found and reported in nature. Fe-Cr-Ni intermetallic compounds (Chromium Iron Nickel ore) have been found in olivinite of chromite deposit in Luobusha district, Tibet.

4 Discussions

The forming conditions of these native minerals and intermetallic compounds are similar, at high temperature, high confining pressure and under strong reducing conditions, and mantle-core materials have participated in the mineralization process. Therefore, study of these minerals and intermetallic compounds plays an important role of determining the formation condition, material sources and origin of ore deposit. Meanwhile, Fe-Cr-Ni, Zn-Cu intermetallic compounds and native ferrum have been found in the skarn type deposit for the first time and many kinds of intermetallic compounds occur in the ophiolite of various plate conjunction zones in nature. The recognition and study of these intermetallic compounds and native minerals possess scientific significance for the research of mineralization background and structural setting of plate process and evolution.

Key words: native element minerals; intermetallic compounds; skarn; copper deposit; Garjoan; Tibet