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Sulfide assemblages in granulite xenoliths from Hannuoba Basalt, Hebei Province, China

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Abstract: Granulite xenoliths are important samples for understanding the forming and evolution of the crust. The granulite xenoliths enclosed in Cenozoic basalt of Hannuoba, Hebei Province, China, contain four types of sulfide assemblages: isolate rotundity enclosed sulfides, intergranular sulfides between minerals, secondary sulfide inclusions ranging in linear, and fissure-filling sulfides. Electron microprobe analysis shows that the components of sulfides are Ni-poor pyrrhotite with the molar ratios of (Ni+Co+Cu)/Fe less than 0.2. The molar ratios of (Fe+Cu+Co+Ni)/S are less than 0.875 of normal pyrrhotite, and are less than those of mantle xenoliths, reflecting a sulfur-saturated environment. Pyrrhotite in various occurrences contains some Au and Ag, with the averages of 0.19wt%-0.22wt% Au and 0.01wt%-0.02wt% Ag, showing the gold mineralization related to the granulitization of low crust. Ni, Co and Cu have a normal correlation with S in pyrrhotite, indicating that heavy metal elements have a same source similar to sulfur because of the degasification of upper mantle.

Key words: granulite: xenolith; sulfide inclusions; Hannuoba

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1 Introduction

Granulite xenoliths preserve much more information of the upper portion of crust/mantle boundary than Precambrian granulite, because they were rapidly brought to surface by Cenozoic basalt [1]. Based on the study of mineral chemistry and the forming conditions of granulite xenoliths in Southeastern China, J.H. Yu considered that granulites in this area were formed during Mesozoic [2]. Q.C. Fan *et al.* pointed out that the basic granulite of Hannuoba was formed by granulization of magnesium-ferrous rocks in lower crust during Mesozoic according to the zircon chronology and characteristics of REE of Hannuoba granulite [3]. Granulites contain a great many of CO_2 fluid inclusions, which are the important samples for studying low crust fluids [4-5]. Sulfides in granulite are also significant in understanding partial melting, metasomatism and mineralization in the boundary between mantle and crust, but they are not studied in detail. This paper reports the primary result of sulfide assemblage study in the basic granulite xenolith in Cenozoic basalt of Hannuoba, Hebei Province, China.

2 Characteristics of samples and the occurrence of sulfides

Granulite samples were collected from the Damaping of Zhangjiakou, Hebei Province. They were occasionally found in Cenozoic basalt, occurring as xenoliths. Two kinds of granulites were distinguished: 1) basic granulite, composed of hypersthene (30vol%), clinopyroxene (40vol%), and labradorfeldspar (30vol%, An=50mol%-56mol%); 2) ultra-basic granulite, composed of clinopyroxene (75vol%), orthopyroxene (20vol%), and plagioclase (<5vol%). According to the studies of Fan *et al.* [1, 3], basic granulite was formed at 900-1000°C and at the depth of 33-40 km during 120-124 Ma.

Different sulfide assemblages were found in clinopyroxene and intergranular with various mineral grains of the xenolith samples. They can be divided into four types: 1) immiscible sulfides in clinopyroxene occurring as isolate spherules (**figure 1**(a), (b)) with the sizes of 20-50 μm; 2) isolated grains among rock-forming minerals or in clinopyroxene with a size of 400 μm (figure 1 (c), (d)); 3) secondary sulfide in-

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clusions occurring as a string of beads in clinopyroxene (figure 1(e), (f)) with the sizes of 1-5 μm; 4) fissure-filling sulfides in the fractures of mineral grains **(figure 1(g), (h)) with the fracture lengths of 100-200 μm.**

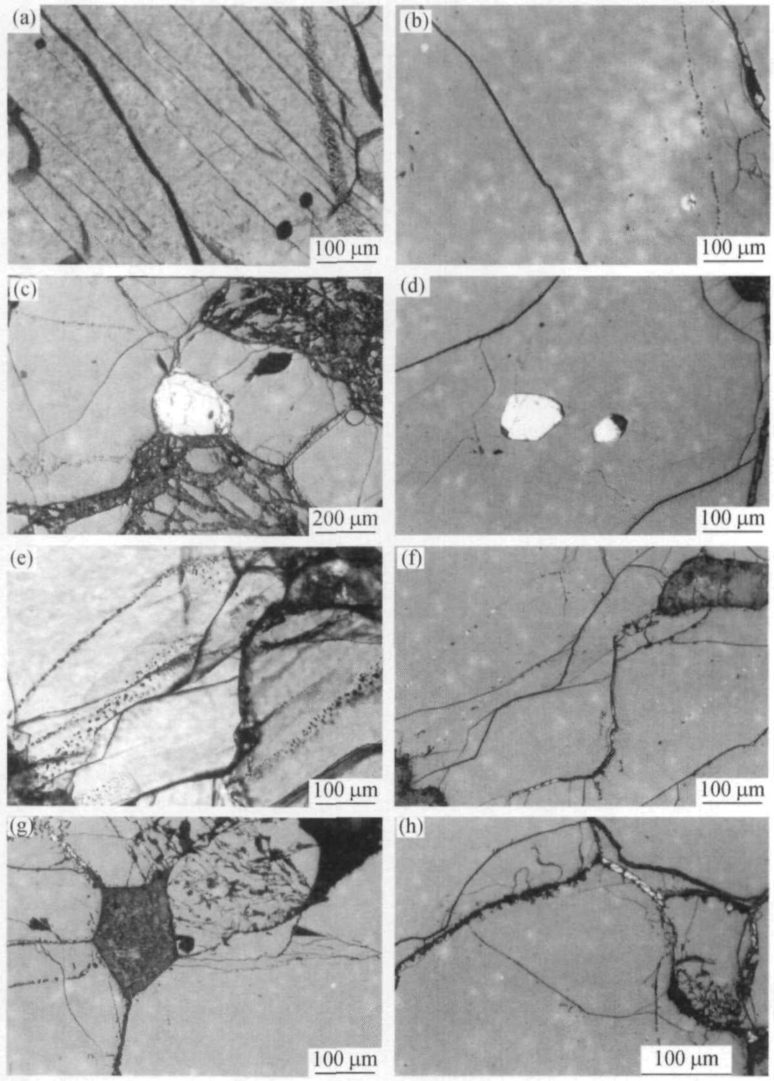

Figure 1 Occurrence of sulfides in the granulite. (a) Immiscible sulfides in clinopyroxene, occurring as isolate spherules, D08-1(4), polarizing microscope (-); (b) the same as (a), ore microscope (-); (c) sulfides between orthopyroxene and labrador-feldspar, D08-1(2), ore microscope (-); (d) isolated sulfide grains in clinopyroxene, D13-1(5), ore microscope (-); (e) secondary sulfide inclusions occurring as a string of beads in clinopyroxene, D13-1(7), polarizing microscope (-); (f) the same as (e), ore microscope (-); (g) filling sulfides along the tiny fractures of granulite, D08-1(3), ore microscope (-); (h) filling sulfides, D08-2(4), ore microscope (-).

Types 1 and 2 are primary and can be named as enclosed and intergranular, which were formed during the forming period of host minerals. Types 3 and 4 are secondary and may be named as array and fissure-filling, which were formed after the formation of host minerals.

3 Electron microprobe analysis of sulfides

The electron microprobe analysis of various sulfide assemblages was done at the Institute of Geology and Geophysics, Chinese Academy of Sciences and the results are listed in **table 1.** The characteristics of sulfide assemblages are as follows.

(1) Sulfide minerals in all samples are pyrrhotites with the molar ratios of metal elements to sulfur ((Fe+Cu+Co+Ni)/S) less than 1 **(table 2).** Immiscible sulfides and fissure-filling sulfides have a lower molar ratio of (Fe+Cu+Co+Ni)/S than the isolated grains and sulfide inclusions. The average molar ratios of (Fe+Cu+Co+Ni)/S decrease from sulfide inclusions (0.877), isolated grains (0.861), immiscible sulfides (0.844) to fissure-filling sulfides (0.836).

(2) The molar ratios of (Ni+Co+Cu)/Fe of sulfides are less than 0.2, so they are Ni-poor pyrrhotite. The average molar ratios of (Ni+Co+Cu)/Fe decrease from isolated grains (0.040), immiscible sulfides (0.035), fissure-filling sulfides (0.031) to sulfide inclusions (0.026).

(3) Sulfides in various assemblages contain 0.19wt%-0.22wt% Au and 0.01wt%-0.02wt% **Ag.**

Table 1 Analysis results of EPMA for sulfides in granulite xenoliths from Hannuoba basalt wt%

Element	D08-1(1) E	D08-1(2)a I	D08-1(2)b I	D08-1(3)a E	D08-1(3)b F	D08-1(5)a E	D08-1(5)b E	D08-1(5)c E	D08-1(6)
S	39.481	38.893	39.307	40.014	39.226	39.135	39.686	39.384	40.395
Fe	57.264	59.761	59.693	57.372	58.275	56.469	57.324	57.185	56.236
Co	0.311	0.239	0.284	0.258	0.235	0.281	0.241	0.303	0.249
Ni	1.316	0.933	1.162	1.112	1.002	0.818	1.186	1.256	1.477
Cu	0.080	0.162	0.235	0.512	0.000	1.611	0.008	0.000	0.011
Ag	0.057	0.015	0.000	0.000	0.000	0.021	0.024	0.012	0.014
Au	0.346	0.196	0.172	0.328	0.128	0.166	0.181	0.000	0.000
Total	98.860	100.200	100.850	99.600	98.866	98.502	98.650	98.140	98.380
Element	**D08-2(1) E**	**D08-2(2) F**	**D08-2(3) E**	**D08-2(4)3 F**	**D08-2(4)2 A**	**D13-1(3)1 A**	**D13-1(3)2 A**	**D13-1(5)1 E**	**D13-1(5)1b E**
S	40.503	40.280	38.649	40.147	38.954	38.236	37.047	40.348	40.339
Fe	55.959	57.252	58.421	55.646	55.648	55.734	54.293	54.911	55.100
Co	0.242	0.210	0.303	0.241	0.213	0.042	0.188	0.277	0.288
Ni	1.134	0.720	0.852	1.127	0.902	0.917	1.064	3.087	2.895
Cu	0.042	0.000	0.101	0.055	0.000	0.443	2.591	0.060	0.080
Ag	0.000	0.025	0.000	0.000	0.011	0.000	0.000	0.000	0.018
Au	0.332	0.146	0.284	0.297	0.002	0.180	0.266	0.103	0.196
Total	98.210	98.630	98.610	97.513	95.730	95.550	95.450	98.790	98.920
Element	**D13-1(5)2 E**	**D13-1(7)1 A**	**D13-1(7)2 A**	**D13-2(1)2 A**	**D13-2(2)1a E**	**D13-2(2)1b**	**D13-2(2)1c E**	**D13-2(4)1a E**	**D13-2(4)1b E**
S	40.168	37.884	32.336	35.966	38.680	39.646	40.265	40.754	39.745
Fe	54.790	57.695	51.027	53.173	57.019	56.605	57.299	55.143	54.827
Co	0.378	0.134	0.205	0.097	0.341	0.381	0.337	0.374	0.429
Ni	2.960	0.705	1.529	0.141	1.222	1.085	1.774	3.138	3.455
Cu	0.021	0.042	0.040	0.018	0.000	0.022	0.023	0.009	0.005
Ag	0.003	0.093	0.008	0.000	0.000	0.000	0.023	0.032	0.035
Au	0.168	0.290	0.276	0.323	0.117	0.489	0.127	0.136	0.226
Total	98.489	96.843	85.421	89.718	97.380	98.229	99.849	99.586	98.723

Note: 1) Analyzed at the Institute of Geology and Geophysics, Chinese Academy of Sciences; 2) Instrument: EPMA-1500 (SHIMADZU, JAPAN); 3) Laboratory conditions: ACC-20 keV, SC-10 nA; 4) Sulfides of D08-2(3) occur between orthopyroxene and labradorfeldspar, and others occur in clinopyroxene; 5) E—Enclosed, I—Intergranular, A—Array, F—Fissure-filling.

Table 2 Synthetic table of EPMA result from sulfide assemblages in granulite from Hannuoba wt%

Element	Enclosed sulfides (12)		Intergranular grains (6)		Array (6)		Fissure-filling sulfides (3)	
	Range	Average	Range	Average	Range	Average	Range	Average
S	40.75-38.68	39.81	40.35-38.650	39.62	38.95-32.340	36.74	40.28-39.23	39.88
Fe	57.37-54.83	56.56	59.76-54.790	57.11	57.70-51.030	54.60	58.28-55.65	57.06
Co	0.43-0.24	0.31	0.38-0.240	0.29	0.21-0.042	0.15	0.24-0.21	0.23
Ni	3.46-0.82	1.58	3.09-0.850	1.98	1.53-0.140	0.88	1.13-0.72	0.95
Cu	1.61-0.00	0.19	0.24-0.021	0.11	2.59-0.000	0.52	0.055-0.00	0.02
Ag	0.057-0.000	0.020	0.018-0.000	0.010	0.093-0.000	0.020	0.025-0.000	0.010
Au	0.49-0.00	0.20	0.28-0.103	0.19	0.32-0.002	0.22	0.30-0.13	0.19
(Ni+Co+Cu)/Fe	0.024-0.067	0.035	0.021-0.059	0.040	0.005-0.064	0.026	0.015-0.024	0.031
(Fe+Ni+Co+Cu)/S	0.812-0.868	0.844	0.828-0.900	0.861	0.836-0.936	0.877	0.810-0.870	0.836

Note: 1) Numbers in brackets are measured points; 2) (Ni+Co+Cu)/Fe and (Fe+Cu+Co+Ni) /S are the mole ratios.

4 Discussion

4.1 Comparison with sulfides in mantle xenoliths

Sulfide blebs in mantle xenoliths were observed in the 1980's and considered as the sulfide phases of fluid-melt inclusions [6]. The references of sulfide inclusion studies have been accumulated during last several decades [7-11]. Sulfides in xenoliths can provide the information relevant to understanding the processes such as mantle depletion and enrichment [9]. Detailed study on the paragenesis of sulfide minerals could be used together in the knowledge of silicate mineralogy to trace metasomatic events [10]. The origin of mantle sulfide minerals is related to the petrogenesis of the respective host rocks, and may control the platinum group elements (PGE) budget of mantle rocks [11]. In China, research papers are mainly focused on pyroxene megacryst [12] and lherzolite in Cenozoic basalt in East China [13-18]. Sulfide assemblages in mantle xenoliths can be divided into three kinds, that is, early sulfide grains (enclosed), sulfide-melt inclusions, and fissure-filling sulfides. Unlike those in granulite, sulfides in lherzolite are various minerals of Fe-Ni-Cu-S system, including MSS (monosulfide solid solution) with different ratios of Ni/Fe, pyrrhotite, pentlandite and chalcopyrite **(table 3).**

Table 3 Characteristics of sulfide assemblages in the mantle xenoliths from East China

District	Pyrrhotite		MSS		Pentlandite		Source
	Ni/Fe	(Ni+Fe)/S	Ni/Fe	(Ni+Fe)/S	Ni/Fe	(Ni+Fe)/S	
Changbaishang (44)	0.01-0.22	0.88-0.94	0.34-0.45	0.93-0.94	0.47-1.99	1.01-1.28	[17]
Hannuoba(14)	0.03-0.14	—	—	—	0.24-1.49	0.94-1.15	[14]
Liuhe, Jiangsu (34)	0.14-0.19	0.88-0.99	0.76-0.83	0.97-0.98	0.70-2.26	1.01-1.37	[16]
Xinchang,Zhejiang(15)	0.17	0.91	0.40-0.63	0.88-0.94	0.92-1.83	1.06-1.25	[15]
Qilin, Guangdong (56)	0.05-0.48	0.83-0.96	0.10-1.80	0.76-1.04	0.78-2.02	1.04-1.11	[11]
Hainan-Leizhou (36)	—	—	0.25-0.83	0.85-1.38	0.30-1.38	1.01-1.22	[18]

Note: 1) Ni/Fe and (Ni+Fe)/S are the mole ratios; 2) Numbers in brackets are measured points.

Compared with mantle lherzolite, sulfides in granulite xenoliths are Ni-poor. Although commonly occurring in the clinopyroxene of lherzolite and pyroxenite xenoliths, pyrrhotite in mantle xenoliths has higher molar ratios of Ni/Fe or (Ni+Co)/Fe than that in granulite. The molar ratios of (Fe+Ni)/S of pyrrhotite in mantle xenoliths range from 0.88 to 0.99, while that in granulite is less than 0.875 which is normal Fe/S of pyrrhotite Fe_7S_8, reflecting a sulfur-rich environment. Fan *et al.* believed that granulite xenoliths in Hannuoba were initially the accumulative rock of basaltic magma in early Cretaceous and had undergone the metamorphism of granulite facies within low crust [3]. Zajacz and Szabo concluded that metasomatism modified the cumulate xenoliths but did not affect the chemical composition of the sulfide inclusions based on the study of cumulate xenoliths from Nograd-Gomor Volcanic Field, north Hungary/south Slovakia [19]. Hence, primary sulfide assemblages (enclosed and array inclusions) may contain the information of the accumulative rock of basaltic magma in lower crust during Mesozoic, while secondary assemblages may contain the later events of metamorphism of granulite facies. Sulfur fugacity in low crust became high because of degasification, resulting in that Fe in clinopyroxene was combined with S to form pyrrhotite. With the increasing of sulfur degasification due to tectonics disturbance, filling sulfides in fracture have the lowest molar ratio of (Fe+Cu+Co+Ni)/S.

4.2 Trace elements in sulfides

Pyrrhotite in various assemblages of granulite from Hannuoba contains some Cu, Ni, Co, Au and Ag. Especially, the content of Au may be up to 0.20wt%, which is higher than that of pyrite in some vein gold deposits. Pyrite in Jiaojia gold deposit contains 0.06wt% of gold (8 data); pyrite and pyrrhotite in Sanshandao, 0.1 wt% (4 data) and 0; and pyrite in Wenyu-Dongchuang gold deposits, 0.14wt% (15 data). Colvine *et al.* believed that CO_2-rich fluids from the granulitization of low crust were the important source of gold-bearing ore-forming fluids [20], especially for greenstone belt gold deposits. Evidences from field geology, fluid inclusions and stable isotopes support this suggestion. That sulfides in granulite xenoliths are rich in gold provides significant information for the relationship between gold mineralization and granulization. In addition, Ni, Co and Cu in various occurrences of pyrrhotite have a positive correlation with S **(figure 2),** indicating that these metal elements might have derived from the same source as S. They entered into low crust during degasification in mantle.

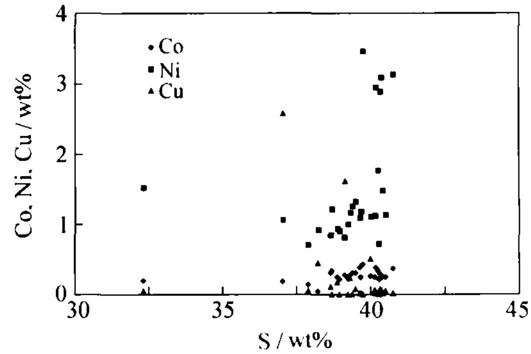

Figure 2 Correlation among Ni, Co, Cu and S.

5 Conclusions

(1) The granulite xenoliths enclosed in Cenozoic basalt of Hannuoba contain four types of sulfide assemblages: isolate enclosed sulfides, intergranular sulfides, secondary sulfide inclusions, and fissure-filling sulfides.

(2) Electron microprobe analysis shows that the components of sulfides are Ni-poor pyrrhotite, with the molar ratios of (Ni+Co+Cu)/Fe less than 0.2. The molar ratios of (Fe+Cu+Co+Ni)/S are less than 0.875 of normal pyrrhotite, and are less than those of mantle xenoliths (0.88-0.99), reflecting a sulfur-rich environment.

(3) Pyrrhotite in various occurrence contains some Au and Ag, with the averages of 0.19wt%-0.22wt% Au and 0.01wt%-0.02wt% Ag, showing gold mineralization related to the granulitization of low crust. Ni, Co and Cu have a normal correlation with S in pyrrhotite, so heavy metal elements may have a same source similar to sulfur because of the degasification of upper mantle.

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