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Mineral

Daughter minerals in fluid inclusions of garnet and diopside from Tongguanshan Copper Deposit by SEM/EDS and LRM

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Abstract: Tongguanshan copper deposit of Tongling large ore belt is one of the typical skarn copper deposits. Based on careful observation under microscope many daughter minerals including transparent ones and opaque ones have been distinguished in the fluid inclusions of garnet and diopside. The results of SEM/EDS (scanning electron microscope/energy dispersive spectrometer) and LRM (laser Raman microprobe) analysis show that these daughter minerals in garnet are sylvite, halite, sphalerite, chalcopyrite and carbonate. Sylvite daughter mineral is very popular in garnet and diopside. The existence of so much sylvite daughter mineral and other daughter minerals in the fluid inclusions indicates that the ore-forming fluid is of supper-high salinity and high potassium concentration. High potassium concentration in the fluid inclusions agrees with K-rich mesotype-acid rock and K-silicate alteration that occurred widely in this area. The daughter mineral assemblage in garnet and diopside is similar to the mineral assemblage of ore-forming stage that followed skarn stage.

Key words: Tongguanshan copper deposits; skarn; fluid inclusion; daughter mineral; potassium-rich fluid

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1 Introduction

Tongguanshan copper deposit, located in Tongling of Anhui Province, China, is a famous skarn deposit in the middle-low reaches of Yangtze River Fe-Cu metallogenic belt. Many researches have been made for Tongguanshan copper deposit, including petrology, tectonics, ore geology and sources of ore materials and ore-forming fluids [1, 2]. That ore-forming fluids associated with Yanshanian magmatic activity are characterized by high salinity has been mentioned in many references [3-6]. Daughter minerals can be usually found in garnet and diopside from skarn deposits. High salinity fluid inclusions containing daughter minerals are usually seen in the skarn minerals in Tongguanshan copper deposit. Halite, sylvite and sulfide daughter minerals were found based on fluid inclusion petrography and heating test [5], but no paper about SEM/EDS (scanning electron microscope/energy dispersive spectrometer) and LRM (laser raman microprobe) on daughter minerals has been reported, including the types of carbonates and sulfides. SEM/EDS and LRM techniques are widely used for studying daughter minerals recently [7-10]. SEM/EDS is not only used for analyzing the shapes of daughter minerals in fluid inclusions, but also for analyzing the solid composition of daughter minerals. In addition to analyzing vapor and liquid composition in fluid inclusions, LRM is also good at analyzing the composition of daughter minerals without destroying them especially for carbonates, sulfides and silicates. This paper focused on the study of daughter minerals in garnet and diopside including their types, mineralogical chemical composition and their implication to genesis.

2 Geological outline

Tongguanshan Copper Deposit plays an important role in the middle-low reaches of Yangtze River Fe-Cu metallogenic belt in China. The deposit occurs in the contact zone between Yanshanian quartz diorite intrusion and Carboniferous-Permian carbonate rocks, which is situated at the northwestern wing of Tongguanshan anticline. The ore bodies occur mainly as bedded-like and lensoid shape, but as abnormal shape at the top and the bottom of it. The upper part of the ore body occurs in the contact zone between quartz diorite intrusion and carbonates of Carboniferous

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Huanglong formation, with typical skarn mineral assemblage [11]. The intrusions which associated with ore-forming emplaced polygenically, occurring as small stock and distributed along the northeastern direction. The rock types include quartz monzodiorite, granodiorite and quartz diorite, with the characteristics of high-alkali, high-potassium, silicon-rich and low iron and magnesium [12]. The main metallic mineral assemblage includes magnetite, pyrite, pyrrhotite, chalcopyrite, sphalerite and galena, and gangue minerals are dominated by garnet, diopside, quartz, calcite and chlorite. Garnet and diopside are main skarn minerals, which were formed by the activity of early ore-forming fluids.

3 General characteristics of fluid inclusions

Great many of fluid inclusions in garnet and diopside can be seen under microscope. The sizes of fluid inclusions are from 1 to 20 μm, some up to 50 μm, and the shapes include negative-crystal, elongated-sphere, lentiform and irregularity. The fluid inclusions can be divided into three types: (1) two phase aqueous fluid inclusions (**figure 1**(d)); (2) multi-phase fluid inclusions containing one or more daughter minerals which may be transparent or opaque (figure 1 (a)-(c)). The transparent daughter minerals have the shapes of cube, round-cube, rhombi or rod shaped, while the opaque ones have the shapes of tetrahedron, cube and irregularity; (3) pure liquid inclusions without bubbles. Fluid inclusions in diopside are larger than those in garnet, and usually contain daughter minerals, but they were not analyzed by SEM/EDS because of small mineral sizes. However, carbonates were found in fluid inclusions of diopside by using LRM. The homogenization temperatures of fluid inclusions in garnet are very high and range from 580 to 885°C, and the homogenization process are complicated with various melting temperatures of daughter minerals (usually from 240 to 350°C). However, some daughter minerals are not melted even above 800°C, they are preliminarily identified as carbonates.

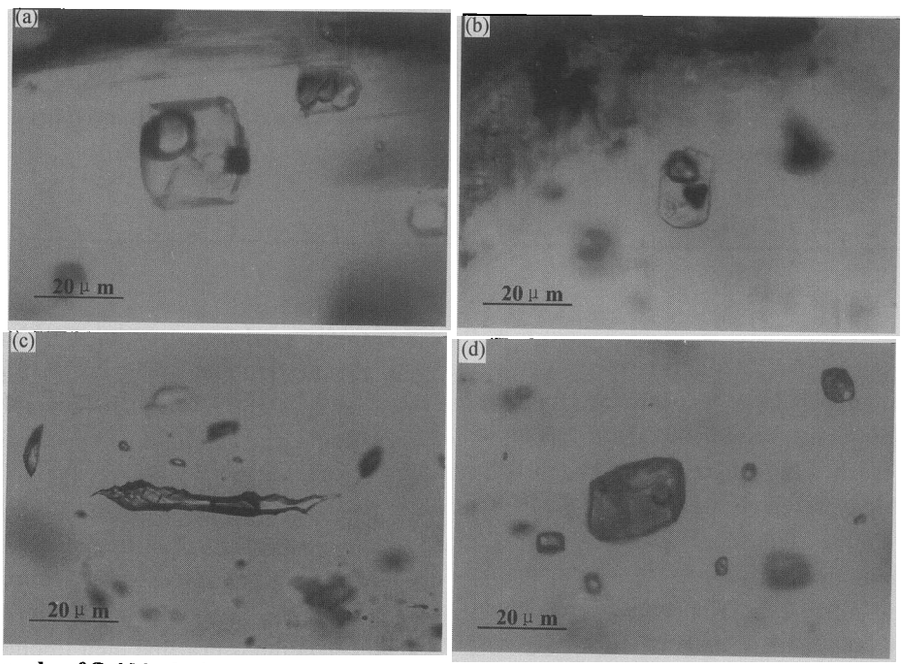

Figure 1 Photographs of fluid inclusions under microscope: (a) fluid inclusion containing several daughter minerals in diopside; (b) fluid inclusion containing transparent and opaque daughter minerals in diopside; (c) fluid inclusion containing cubic daughter minerals in garnet; (d) two phase aqueous fluid inclusions with no daughter minerals in garnet.

4 SEM/EDS and LRM analysis for daughter minerals in fluid inclusions

Daughter minerals in the fluid inclusions of garnet were carefully studied by using SEM/EDS. First, the fresh garnet samples were crashed into small pieces, then fixed them onto the glass plate (having the flat surfaces up) and to be spray coated with carbon. The interval from crashing samples to spreading carbon was several hours. There are a lot of inclusions in the prepared samples when observing under SEM (**figure 2**(e)). Most inclusions contain one or more daughter minerals. Some daughter minerals were dissolved partly (figure 2 (c)) during sample preparation. The EDS analysis shows that those dissoluble daughter minerals are sylvite, which have irregular, rod-shaped or round-cube shapes. Their EDS spectrograms show high K and Cl contents and K/Cl is about 1/1 (atom ratio), excepting the composition of host minerals (**figure 3** (e)). Some small daughter minerals with tet-

rahedral shapes were proved to be sphalerite (figures 2(b) and 3(f)). Chalcopyrite (figures 2(a) and 3(b)) and halite were also found in the fluid inclusions by using SEM/EDS. Some daughter minerals with rhombus shapes were detected to be rich in Fe or Ca. They are presumed to be siderite and calcite (figures 3(c) and (d)), because C and O can not be analysed by the equipment in this study. Some acicular daughter minerals can not be determined owing to their tiny size or locating too deep. Further study will be done for these daughter minerals.

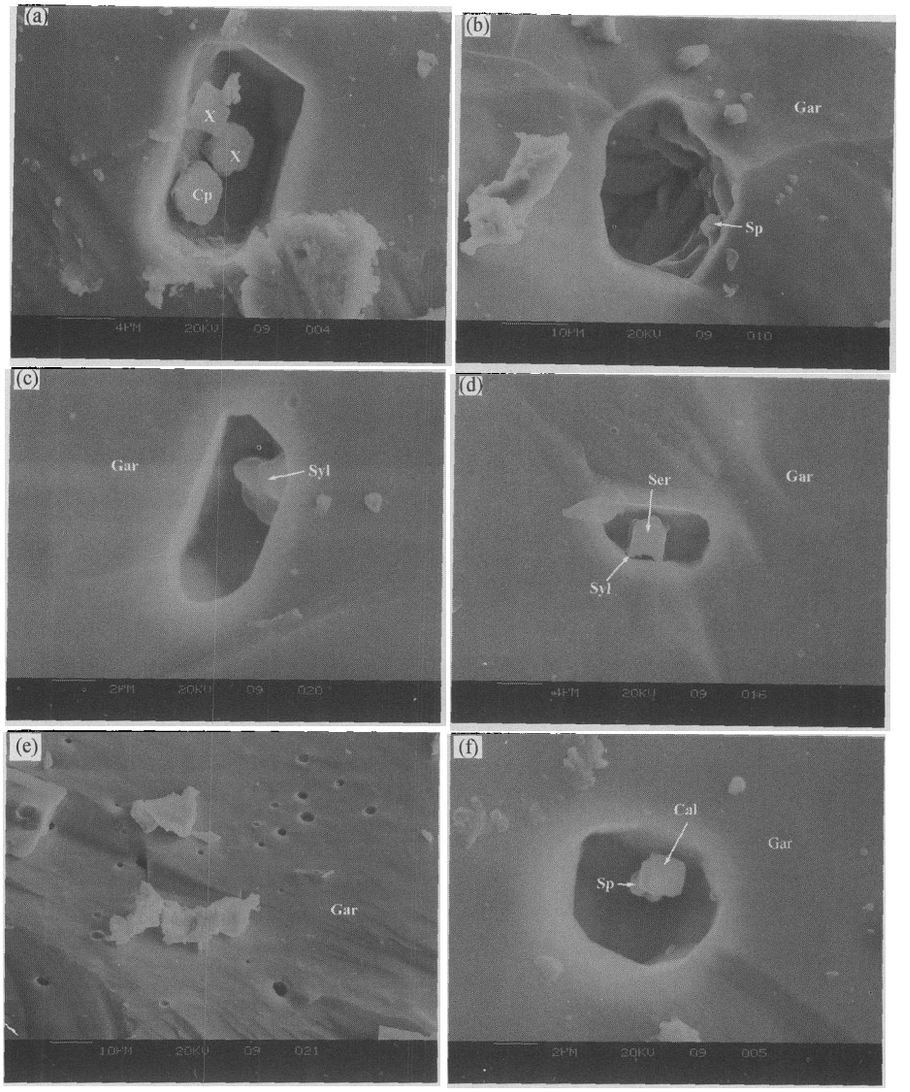

Figure 2 SEM photographs of fluid inclusions with daughter minerals in garnet: (a) fluid inclusion containing several daughter minerals; (b) fluid inclusion containing sphalerite daughter mineral; (c) partly dissolved sylvite daughter mineral; (d) siderite and sylvite daughter minerals in fluid inclusion; (e) a group of fluid inclusions with daughter minerals; (f) calcite and sphalerite daughter minerals in fluid inclusion. Cp—chalcopyrite; Sp—sphalerite; Syl—sylvite; Ser—siderite; Cal—calcite; Gar—garnet; X—unidentified.

LRM was also performed for fluid inclusions in garnet and diopside. The measurements were performed in the Institute of Mineral Resources, Chinese Academy of Geological Science, some of the spectrograms are shown in **figure 4**. The results suggest that the vapor phase and liquid phase of the fluid inclusions be dominated by H_2O. CO_2 and CH_4 were not detected in this study. Except the host mineral peaks, the spectrograms of some transparent daughter minerals with rhombi shapes in garnet and diopside have the peaks at 1087 and 716 cm^{-1} and that suggested the existing of calcite daughter mineral (comparing with the normative calcite spectrogram from Renishaw Mineral and Inorganic Materials Database).

5 Conclusions

(1) Fluid inclusions in garnet and diopside from Tongguanshan Copper Deposit were dramatically developed, especially high salinity fluid inclusions containing daughter minerals. Sylvite, halite, carbonates, sphalerite and calcopyrite were found in fluid inclusions by using SEM/EDS and LRM analysis. The

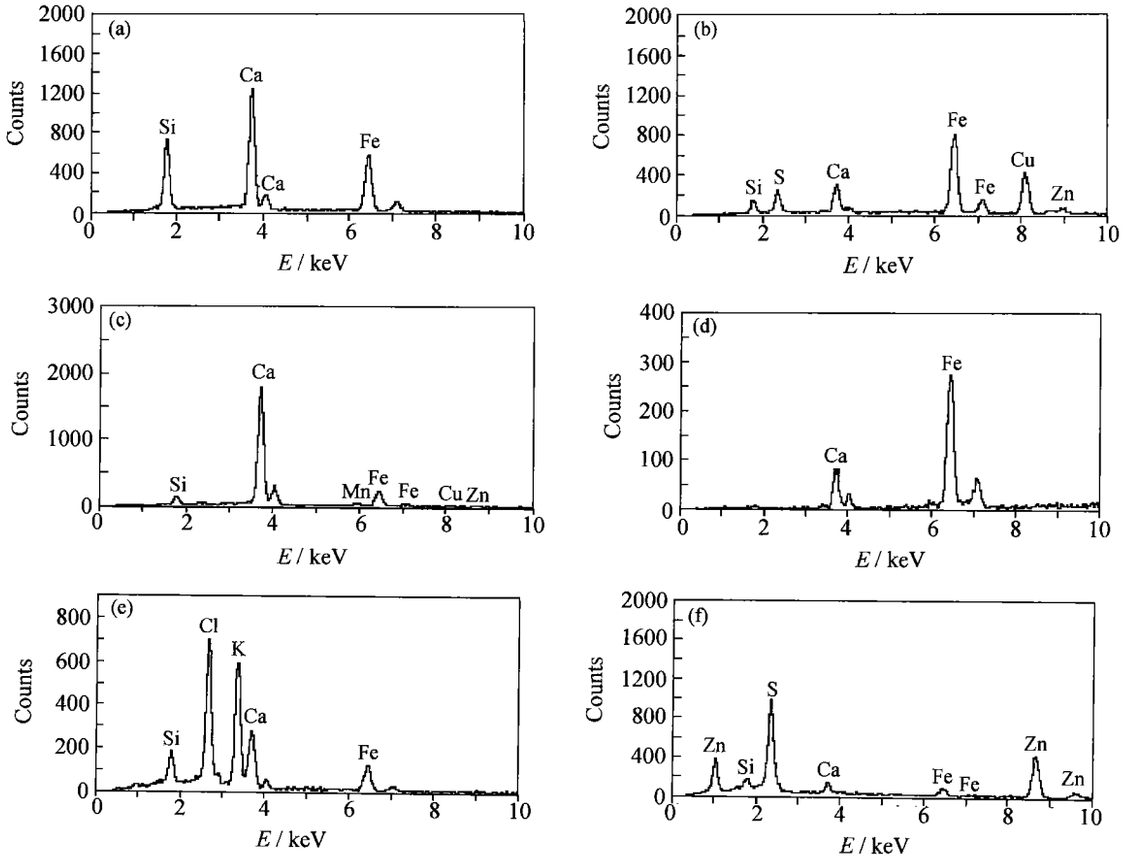

Figure 3 EDS diagrams of daughter minerals and host mineral: (a) host mineral (garnet); (b) chalcopyrite; (c) calcite; (d) Siderite; (e) sylvite; (f) sphalerite (the main components of host mineral are Ca, Si and Fe).

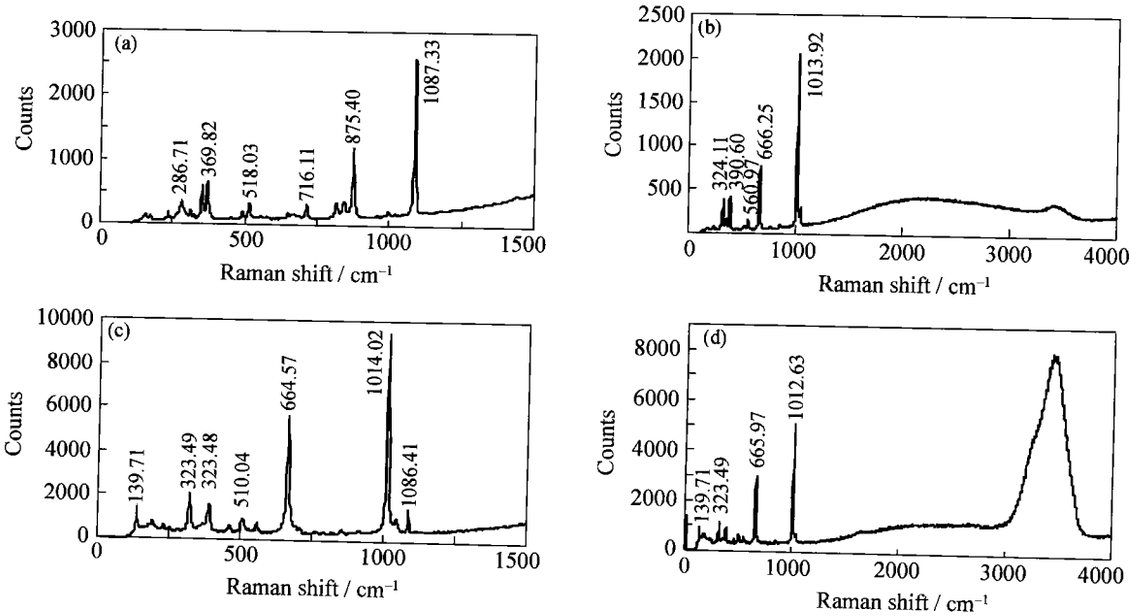

Figure 4 LRM spectrograms of fluid inclusions: (a) carbonate daughter mineral in fluid inclusion of diopside; (b) brine phase in the fluid inclusion of garnet; (c) carbonate daughter mineral in the fluid inclusion of garnet; (d) vapor phase in the fluid inclusion of garnet.

daughter mineral assemblages are similar to the mineral assemblage of later mineralization stages after skarn stage.

(2) The homogenization temperatures of high salinity inclusions are from 580 to 885°C and the salinity estimated according to the melting temperature of halite is from 37.8wt% to 44.9wt% NaCleq. High temperature and high salinity are the typical characteristics of magmatic fluid. The complicated homogenization process during heating suggested that

the ore-forming fluids related to skarns were particular.

(3) A great deal of sylvite daughter mineral in fluid inclusions suggests that ore-forming fluids were rich in potassium. K-rich fluid is in agreement with Yanshanian high-potassium, alkali-rich intrusion and potassic alteration wildly occurring in this area and indicates that ore-forming fluids were associated with Yanshanian magmatism.

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