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西藏多龙矿集区铁格隆南超大型 Cu(Au、Ag)矿床 硫锡砷铜矿研究及其地质意义 *

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摘要 铁格隆南矿床位于班公湖-怒江成矿带西段多龙矿集区, 是青藏高原发现的首例具有典型高硫型浅成低温热液矿化特征的超大型 Cu(Au、Ag)矿床。笔者通过对该矿床进行系统的矿相学研究, 结合电子探针显微分析, 首次在该矿床发现了硫锡砷铜矿, 虽然其总量不多, 但其与不同矿物组合特征可反演其形成时的物化条件, 对矿床成因类型判别具有一定指示意义。该矿床中的硫锡砷铜矿多为粒径约 10 μm 的不规则细粒, 无内反射, 均质性, 与硫砷铜矿、砷黝铜矿等 Cu-As-S 体系矿物伴生产出时呈乳黄色-淡黄色, 与斑铜矿、黄铁矿、蓝辉铜矿等 Cu-Fe-S 体系矿物伴生产出时呈乳褐色-浅褐色。根据矿物之间的交代关系发现, 硫锡砷铜矿形成于黄铁矿、斑铜矿、砷黝铜矿、硫砷铜矿之后, 蓝辉铜矿、铜蓝之前。电子探针分析显示, 硫锡砷铜矿的基本成分包括 Cu、As、V、S、Sn、Sb, 普遍含有少量 Fe、Ge、Zn, 部分样品中含少量 W、Au、Ag, 以 S 原子数为 32 为基础, 计算得出其分子式为 $\text{Cu}_{23.71\sim26.92}\text{V}_{1.43\sim2.10}(\text{As}_{2.55\sim5.86}, \text{Sb}_{0\sim0.63})_{3.15\sim5.95}(\text{Sn}_{0\sim2.6}, \text{Ge}_{0\sim0.7})_{0.01\sim2.60}(\text{Fe}_{0\sim2.4}, \text{Zn}_{0\sim0.24})_{0\sim2.4}\text{S}_{32}$, 其中, 存在 $\text{Sb}^{5+}\leftrightarrow\text{As}^{5+}$ 和 $\text{Sn}^{4+}\leftrightarrow\text{Ge}^{4+}$ 、 $(\text{As}, \text{Sb})^{4+}+\text{Cu}^{+}\leftrightarrow(\text{Sn}, \text{Ge})^{4+}+(\text{Fe}, \text{Zn}, \text{Cu})^{2+}$ 以及 $\text{V}^{5+}\leftrightarrow\text{V}^{4+}+\text{Cu}^{+}$ 等复杂的元素耦合置换。结合矿石矿物组合及蚀变组合分析指出, 酸性或略偏中性的、中低温高硫化态环境是促使硫锡砷铜矿生成的关键控制因素。

关键词 地质学; 硫锡砷铜矿; Cu-As-S 体系矿物; Cu-Fe-S 体系矿物; 高硫化浅成低温热液矿化; 班公湖-怒江成矿带; 西藏

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A study of colusite from Tiegelongnan superlarge Cu (Au, Ag) deposit and its geological significance

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Abstract

Tiegelongnan deposit, located in the Duolong ore district in the western part of Bangong Co-Nujiang metallogenic belt, is the first large-sized Cu (Au, Ag) deposit with typical features of high-sulfidation epithermal mineralization. Through the study of the systematic metallogeny, combined with the electron microprobe analysis, colusite was found in the deposit for the first time. Although its total amount is not much, it can be used to reflect the condition of materialization and, to some extent, to be indicative of the types of genesis. Colusite is an ir-

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regular fine particle with a diameter of about $10\mu\text{m}$, and has the characteristics of no internal reflection and homogeneity. Associated with Cu-As-S series minerals, such as enargite and tennantite, colusite is milky yellow-pale yellow; when it occurs with Cu-Fe-S series minerals, such as bornite, pyrite and digenite, it is milky brown-light brown. According to the intergenerational relationship between minerals, colusite is formed after Py, Bn, En, Ten and before Dg, Cv. The results of electron microprobe analysis show that the basic components of colusite include Cu, As, V, S, Sn and Sb, with a small amount of Fe, Ge and Zn. Besides, some samples contain a small amount of W, Au and Ag. On the basis of 32 sulfur atoms per formula unit, the general formula of colusite in the Tiegelongnan deposit is $\text{Cu}_{23.71-26.92}\text{V}_{1.43-2.10}(\text{As}_{2.55-5.86}, \text{Sb}_{0-0.63})_{3.15-5.95}(\text{Sn}_{0-2.6}, \text{Ge}_{0-0.7})_{0.01-2.60}(\text{Fe}_{0-2.4}, \text{Zn}_{0-0.24})_{0-2.4832}$, in which there are complex mechanism of coupled substitutions such as $\text{Sb}^{5+} \leftrightarrow \text{As}^{5+}$ and $\text{Sn}^{4+} \leftrightarrow \text{Ge}^{4+}$, $(\text{As}, \text{Sb})^{5+} + \text{Cu}^+ \leftrightarrow (\text{Sn}, \text{Ge})^{4+} + (\text{Fe}, \text{Zn}, \text{Cu})^{2+}$, as well as $\text{V}^{5+} \leftrightarrow \text{V}^{4+} + \text{Cu}^+$. Combined with ore mineral assemblages and alteration analysis, it is pointed out that the acidic or slightly neutral, neutral, medium and low temperature and high sulfuric acid environment constitute the key controlling factors of colusite formation.

Key words: geology, colusite, Cu-As-S series minerals, Cu-Fe-S series minerals, high-sulfidation epithermal mineralization, Bangong Co.-Nujiang metallogenic belt, Tibet

硫锡砷铜矿(Colusite)是一种稀少罕见、成分复杂的Cu-V硫盐矿物,基本成分包括Cu、As、V、S、Sn、Sb等元素,国际新矿物命名委员会批准的标准分子式为 $\text{Cu}_{26}\text{V}_2(\text{As}, \text{Sn}, \text{Sb})_6\text{S}_{32}$ (Orlandi et al., 1981)。国外对其研究较为深入(Landon et al., 1933; Nelson, 1939; Kovalenker et al., 1984; Spiridonov et al., 1984; 1992; 2003; Cvetković et al., 1999, 2013; Spry et al., 1994; Wagner et al., 2005; Makovicky, 2006; Repstock et al., 2015),而国内对其研究则较薄弱,仅刘文元(2015)对紫金山矿床产出的硫锡砷铜矿进行了较为详细的阐述,其次是在一些矿相学研究教程中有简单介绍,并称之为锡黝铜矿(徐国风,1986;尚浚等,2008;卢静文等,2010)。

铁格隆南Cu(Au,Ag)矿床是青藏高原发现的首例具有典型高硫化型浅成低温热液矿化特征的超大型矿床(唐菊兴等,2014a; 2014b; 2016; 杨超等,2014; 方向等,2015; 李光明等,2015),截至2015年底,探获铜资源量(332+333,含少量334)超过1100万t@0.53%,伴生金超过120t@ 0.08×10^{-6} ,伴生银超过2500t@ 1.80×10^{-6} 。目前,学者们对于该矿床的地质特征(唐菊兴等,2014a; 2016; 杨超等,2014; 李光明等,2015; 杨欢欢等,2016)、成岩成矿时代(方向等,2015; Lin et al., 2016; 2017)、岩体地球化学特征(王勤,2015)、矿石矿物学(王艺云等,2018)、成矿物质来源(Lin et al., 2016; 王艺云等,2017)及勘查模型(唐菊兴等,2016)等方面进行了较为详细的研究,而对矿床具有特殊指示意义的稀少罕见矿物方面的研究却尚未谈及。笔者通过对铁格隆南矿床进行系统

矿相学研究,并结合电子探针显微分析,首次在该矿床发现了硫锡砷铜矿,虽然其总量不多,但其与不同矿物组合特征可反演其形成时的物化条件,对矿床成因类型判别具有指示意义(Wagner et al., 2005; 刘文元, 2015; Liu et al., 2016),同时,也可为进一步深入研究该类矿物提供基础研究资料。

1 硫锡砷铜矿(Colusite)的起源、分类及产出

硫锡砷铜矿(Colusite)是二十世纪初才识别出来的一个新矿物,Murdoch(1916)将其命名为古铜色硫砷铜矿,Landon等(1933)通过对美国蒙大纳州Butte地区的Leonard和Mountain View矿区的部分样品进行分析才首次对其光学特征及化学成分组成进行公开阐述;后来的研究者又根据硫锡砷铜矿的晶体格架及其化学成分组成,进一步划分出几种与之相关的矿物相(表1):①以Sn为主的端员矿物——硫钒锡铜矿(Nekrasovite)(Kovalenker et al., 1984);②以Sb为主的端员矿物——硫锑锡铜矿(Stibiocolusite)(Spiridonov et al., 1984);③以Ge为主的端员矿物——硫钒锗铜矿(Germanocolusite)(Spiridonov, 1992);④以As为主的端员矿物——硫锡砷铜矿(Colusite)(Spry et al., 1994)。Anisimova等(2002)在硫钒锡铜矿中发现Zn含量异常高,推断自然界中可能存有以Zn为主的硫锡砷铜矿族矿物;此外,硫锡砷铜矿族矿物可能还包含有含Mo的Maikanite(暂无中文名)和以W为主的Ovambioite(暂无中文名)(Spiridonov, 2003)。如今一般所说的

硫锡砷铜矿泛指以As为主的硫锡砷铜矿族矿物(Colusite-group minerals)(Mandaron, 1992; Spry et al., 1994; 刘文元, 2015)。与硫锡砷铜矿族矿物相关的矿物相还包括有硫锗铜矿(Germainte)(Tettenhorst et al., 1984)、硫锗铁铜矿(Renierite)(Bernsein, 1986)和硫砷锡铁铜矿(Vinciennite)(Spiridonov et al., 1994),详细分类汇总见表1。

硫锡砷铜矿族矿物在不同类型的热液矿床中均有产出,在浅成低温热型矿床中广泛分布,如美国蒙大纳州的Gies矿床(Spry et al., 1994)、保加利亚的Chelopech矿床(Kovalenker et al., 1984; Spiridonov et al., 1994)、菲律宾的Lepanto矿床(Hedenquist et al., 1998)、中国福建省的紫金山矿床(刘文元, 2015; Liu et al., 2016)、智利Cordilleran矿床(Bendezu et al., 2009)、希腊东北部的Pefka矿床(Repstock et al., 2015);在部分有浅成低温热液矿化叠加的斑岩型Cu矿、Cu-Mo矿床及与斑岩有关的脉状矿床中也有产出,如美国亚利桑那州的Campbell矿(Harris et al., 1984)、塞尔维亚东部的Bor矿(Cvetković et al., 1999, 2013)、保加利亚的Medet矿床(Strashimirov et al., 2002)、内蒙古的Oyu Tolgoi矿床(Khashgerel et al., 2006);分布于火山岩型块状硫化物矿床中的硫锡砷铜矿族矿物普遍含锗,如俄罗斯乌拉尔河南部的Gray矿床(Pshenichnyy et al., 1975)、加拿大魁北克的Bousquet矿床(Touringy et al., 1993)、澳大利亚昆士兰州北部的Waterloo矿床(Wagner et al., 2005)。此外,在碳酸盐岩型矿床中也偶见含锗、含钨的硫锡砷铜矿,如纳米比亚的Khusib Spring矿床(Melcher et al., 2006)。

通常情况下,硫锡砷铜矿族矿物产出微量,与大多数硫化物(如黄铁矿、斑铜矿、黄铜矿、闪锌矿、方铅矿)和硫盐矿物(如硫砷铜矿、块硫砷铜矿、硫钒铜矿、硫锡铁铜矿、黝铜矿、砷黝铜矿)以及碲化物(如碲银矿)共伴生产出(Spry et al., 1994; Wagner et al., 2005)。

2 铁格隆南矿区概况

铁格隆南矿区位于多龙矿集区中北部,出露地层简单,主要为中下侏罗统色哇组($J_{1-2}s$)长石石英砂岩、岩屑砂岩和下白垩统美日切错组(K_1m)斑状英安岩和安山岩,矿区西北部发育少量上渐新统康托组(E_3k)-上白垩统阿布山组($K_2a?$)紫红色砂砾岩、含砂砾岩以及矿区中部沿沟谷分布的第四系残坡积物(图1)。其中,色哇组是矿区主要含矿围岩,蚀变强烈,长石、岩屑多被明矾石、高岭石、地开石、绢云母等交代。美日切错组与下伏色哇组及铜(金)矿体呈角度不整合接触,该套岩浆岩均较新鲜,未见明显大规模蚀变。

矿区岩浆活动较强烈,喷出岩主要为白垩纪美日切错组斑状英安岩和安山岩,侵入岩以花岗闪长斑岩、石英闪长玢岩为主,二者均未出露地表。其中,花岗闪长斑岩呈岩枝状侵位于矿区中部,是矿区的主要侵入岩和成矿斑岩体。石英闪长玢岩以小岩枝状侵位于矿区的南部,也是矿区重要的成矿斑岩。

由于矿区地质研究程度不高,矿床构造等因素被地表地层及火山岩覆盖,目前仅从前人的基础地质调查工作中推断出矿区内地层主要为1组北西向 F_8 断层和1组北东向 F_{10} 断层(段志明等, 2013)(图1)。

表1 硫锡砷铜矿族矿物的通用分子式及其相关矿物相(据Wagner et al., 2005)

Table 1 Generalized formula of colosite-group minerals and of related phases (after Wagner et al., 2005)

矿物名称	通用分子式	参考文献
硫锡砷铜矿族矿物	硫锡砷铜矿 Colusite $Cu_{26}V_2(As,Sn,Sb)_6S_{32}$	Orlandi et al., 1981
	硫钒锡铜矿 Nekrasovite $Cu_{26}V_2Sn_6S_{32}$	Kovalenker et al., 1984
	硫钒锗铜矿 Germanocolusite $Cu_{26}V_2(Ge,As)_6S_{32}$	Spiridonov et al., 1992
	硫锑锡铜矿 Stibiocolusite $Cu_{26}V_2(Sb,Sn,As)_6S_{32}$	Spiridonov et al., 1994
	Maikainite $Cu_{20}(Fe,Cu)_6Mo_2Ge_6S_{32}$	Spiridonov, 2003
相关矿物相	Ovamboite $Cu_{20}(Fe,Cu,Zn)_6W_2Ge_6S_{32}$	Spiridonov, 2003
	硫锗铜矿 Germainte $Cu_{26}Fe_4Ge_4S_{32}$	Tettenhorst et al., 1984
	硫锗铁铜矿 Renierite $Cu_{20}(Zn_{2-x}Cu_x)(Ge_{4-x}As_x)Fe_8S_{32}$	Bernsein, 1986
	硫砷锡铁铜矿 Vinciennite $Cu_{22}Sn_2As_2Fe_8S_{32}$	Spiridonov et al., 1994

注:0<x<2;矿物的中文名称据何明跃, 2007。

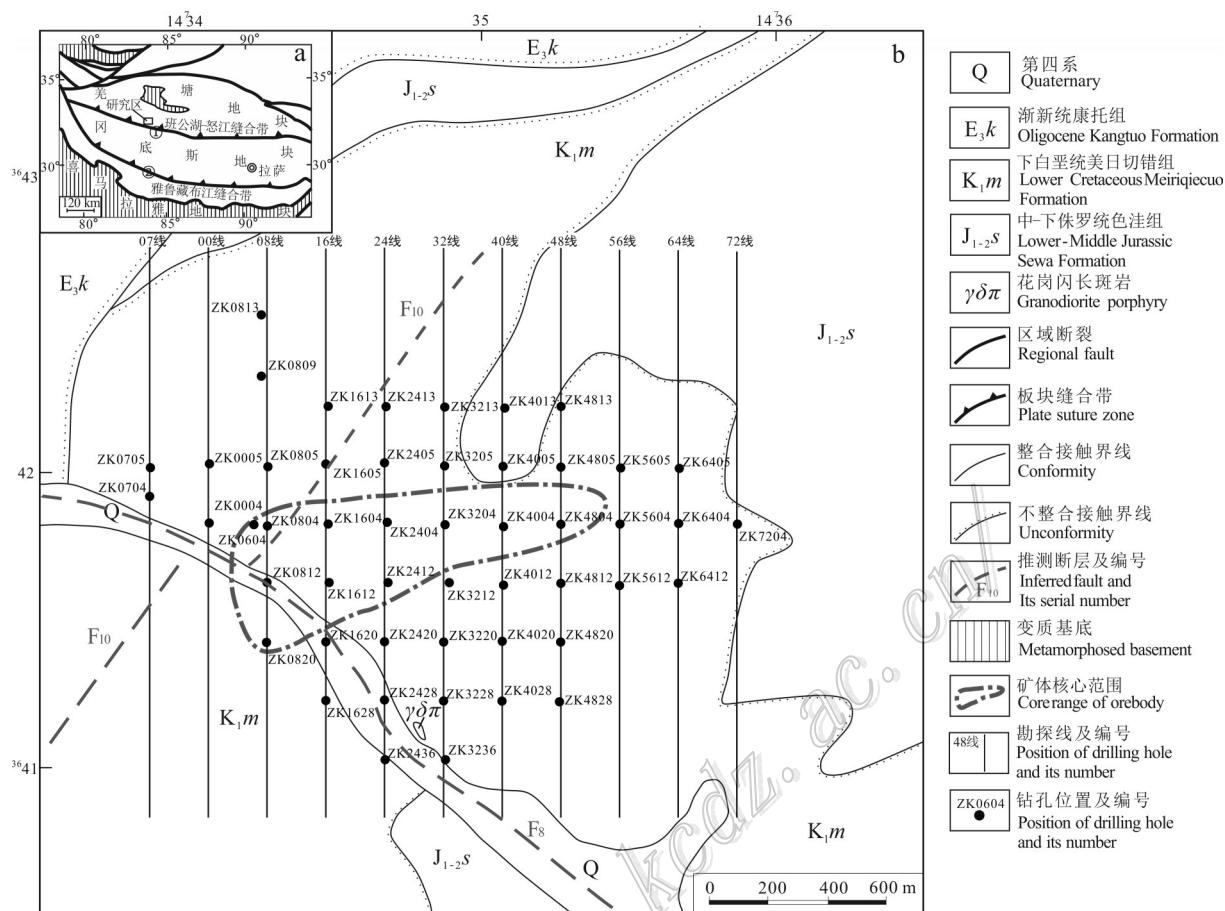


图1 青藏高原构造单元划分(a,据潘桂堂等,2004)和西藏铁格隆南矿床地质图(b,据王勤,2015)

Fig. 1 Simplified geological map of tectonic outline of the Tibetan Plateau (a, modified after Pan et al., 2004) and map of Tiegelongnan ore deposit, Tibet (b, modified after Wang, 2015)

根据已施工的49个钻孔及化学取样分析结果,铁格隆南矿区共圈定6个Cu(Au、Ag)矿体,包括1个主矿体(I号)和5个次要矿体(II、III、IV、V、VI号)。I号主矿体主要产于7号~56号勘探线之间,总体呈北东向展布,北东向长约1.8 km,北西向宽约1.4 km,向下延伸最厚可达960 m,向南东向缓倾斜,整体呈“倒钟状”(图2)。矿体产状基本与侵入体花岗闪长斑岩的产状一致,指示矿体具有明显受侵入体控制的特征(杨超,2015)。矿化类型有高硫型浅成低温热液矿化和斑岩型矿化2种。其中,斑岩型矿化以发育细脉浸染状铜矿石为特征,包括(细脉)浸染状黄铁矿、黄铜矿、斑铜矿,细脉状的石英-黄铁矿、石英-黄铜矿和少量的石英-黄铁矿-辉钼矿等(图3a~g);高硫化型浅成低温热液矿化以铜蓝-蓝辉铜矿为代表的Cu-S体系和以硫砷铜矿-砷黝铜矿为代表的Cu-As-S体系的(细)脉状、角砾状矿石为特征。

(图3h,i)。总的来说,与Lepanto、紫金山等著名浅成低温热液矿床不同的是,铁格隆南矿床高硫化型浅成低温热液型矿化与斑岩型矿化并没有空间上的分离,而是前者叠覆于后者之上。

矿区蚀变发育,且具有明显的蚀变分带,从深部到浅部,分别为钾硅酸盐化带、绢英岩化带、高级泥化带和青磐岩化带(图4)。钾硅酸盐化蚀变主要发育在矿床深部24号~48号勘探线之间侵位的斑岩体及其附近的黑云母化角岩化砂岩中,主要由黑云母化组成,有少量钾长石化。绢英岩化蚀变是铁格隆南矿床分布最广泛的蚀变类型,被后期泥化蚀变叠加,其自身又强烈叠加于早期钾硅酸盐化之上,主要由绢云母、硅化、黄铁矿化组成。高级泥化分布于矿床中上部,以发育大量宽大脉状、团块状明矾石+高岭石为典型特征,其次为浸染状、(细)脉状高岭石/地开石、明矾石、叶腊石及少量水铝石、重晶石等。根据

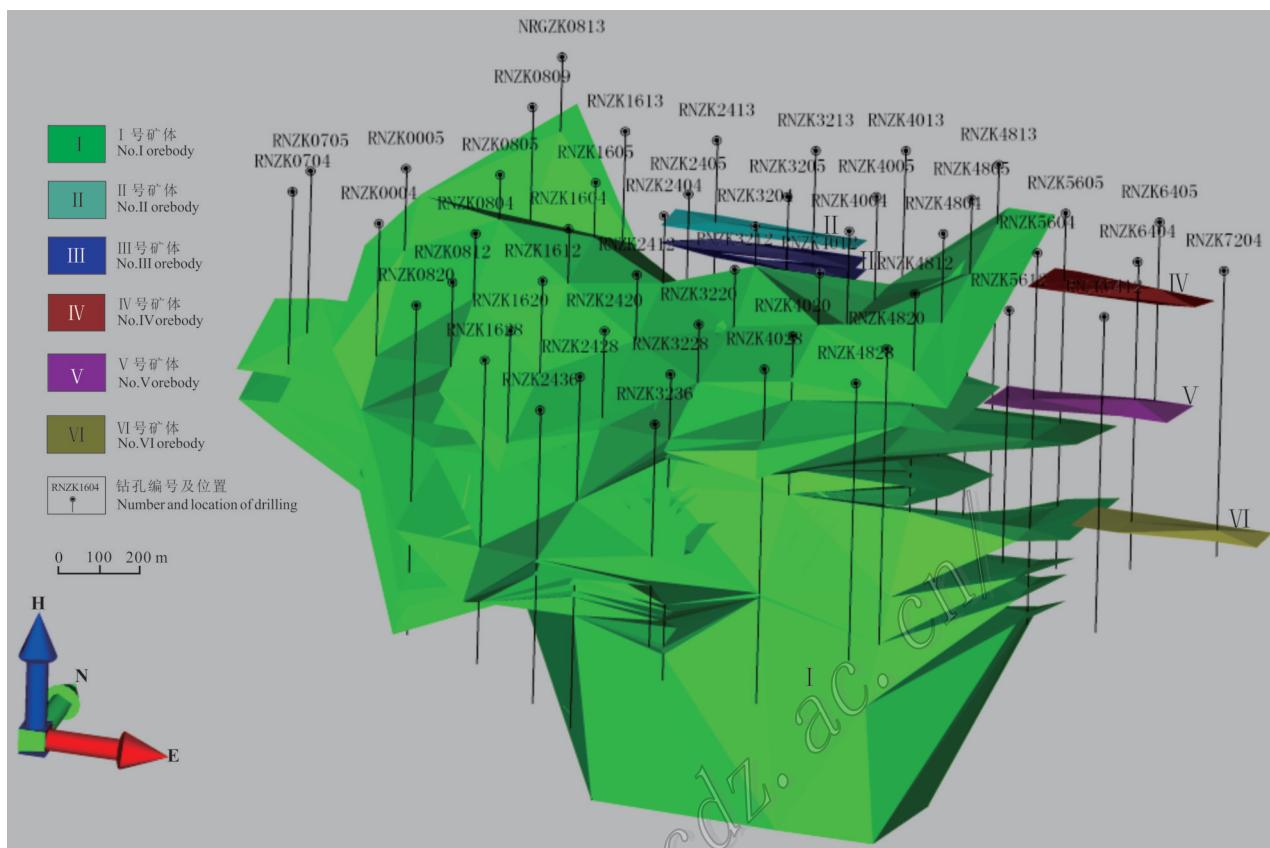


图2 铁格隆南矿床矿体三维模型(据唐楠,2017)

Fig. 2 The three-dimensional model of orebody for the Tiegelongnan deposit(after Tang, 2017)

明矾石、叶腊石、地开石、高岭石等典型高级泥化蚀变矿物的集中分布位置,可进一步细分为是石英-叶腊石-绢云母亚带、石英-明矾石-地开石-高岭石化亚带和石英-高岭石-褐铁矿-赤铁矿亚带(图4)。青磐岩化蚀变主要发育在围岩中,仅在斑岩体边部局部地段可见,常叠加在绢英岩化之上,局部与弱绢英岩化和弱泥化蚀变伴生。总体来看,高级泥化带与高硫型浅成低温热液成矿关系最为密切,青磐岩化带、绢英岩化带及钾硅酸盐化带与斑岩型矿化密切相关。

3 样品采集与分析方法

以铁格隆南矿床Ⅰ号主矿体中心部钻孔的铜矿化岩矿芯为重点研究对象,进行系统采样,取样间距约100 m,局部矿化典型的有加密取样,具体采样位置见图4。送至中国科学院广州地球化学研究所磨制成厚度为60 μm的光薄片,进行矿相学观察及电子探针显微分析。

矿相学观察:将采集的矿石样品磨制成光薄片

和光块,使用Leica DP4500型偏光显微镜进行镜下观察、描述和照相,识别不同矿石的矿物组成及其组构特征。

电子探针显微分析:在偏光显微镜下详细观察矿石样品中主要矿物组成及组构关系后,选择具有代表性的矿石样品进行包括二次电子成像、背散射图像观察、能谱扫描定性分析等测试,并在此基础上对部分样品进行了电子探针波谱定量分析。本项测试分析工作在福州大学紫金矿业学院电子探针实验室完成,测试分析过程按照国家微束分析标准执行。所使用的仪器为JXA-8230电子探针分析仪,测试条件为:加速电压20 keV,电流20 nA,电子束斑直径5 μm,收集时间20 s,所有被测元素使用天然硫化物和金属国家标样进行校正,分析精度优于2%。

4 研究结果

4.1 矿相学特征

详细的矿相显微观察发现,铁格隆南矿床中硫

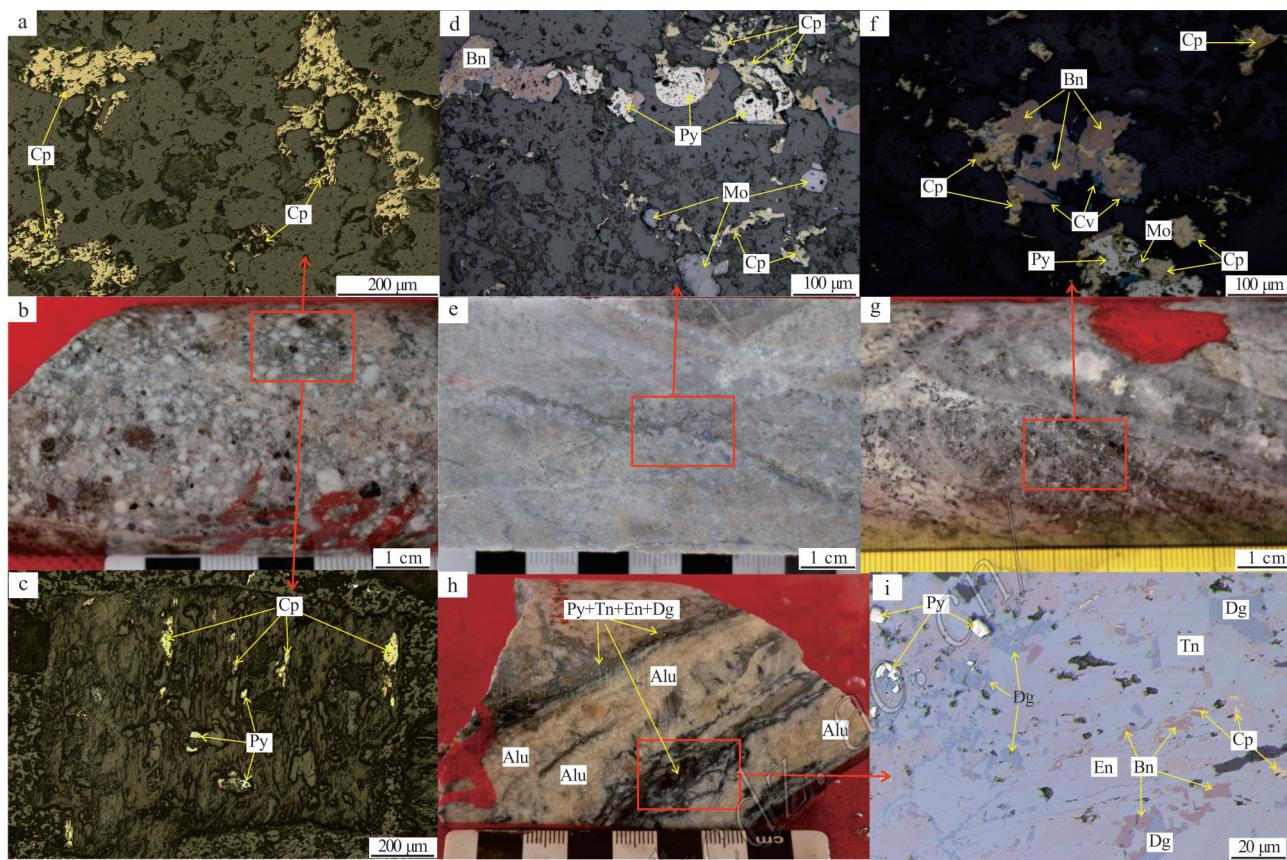


图3 铁格隆南矿床典型矿化及矿物组成(红色方框代表显微现象的大致位置)

a~c. RNZK4004-993 m, 蚀变花岗闪长斑岩中浸染状黄铁矿+黄铜矿, 图a、c分别为基质及斑晶中的黄铜矿(+黄铁矿)矿化;

d~e. RNZK4004-1026.8 m, 蚀变长石英砂岩中黄铁矿+黄铜矿+斑铜矿+辉钼矿脉; f、g. RNZK1604-671.48 m, 蚀变长石

石英砂岩中细脉浸染状黄铁矿+黄铜矿+斑铜矿+铜蓝矿化; h、i. RNZK0804-189.99 m, 蚀变长石石英砂岩中

黄铁矿+砷黝铜矿+硫砷铜矿+蓝辉铜矿+明矾石脉

Alu—明矾石; Bn—斑铜矿; Cp—黄铜矿; Cv—铜蓝; Dg—蓝辉铜矿; En—硫砷铜矿; Mo—辉钼矿; Py—黄铁矿; Tn—砷黝铜矿

Fig. 3 The typical mineralization and mineral assemblages in the Tiegelongnan deposit

(The red box represents the approximate position of the microscopic phenomenon)

a~c. RNZK4004-993 m, disseminated pyrite+chalcopyrite in the altered granodiorite porphyry, and Fig. a and Fig. c indicating mineralization

of chalcopyrite (+pyrite) in matrix and phenocryst, respectively; d~e. RNZK4004-1026.8 m, pyrite+chalcopyrite+bornite+molybdenite

vein in the altered feldspar-quartz-sandstone; f, g. RNZK1604-671.48 m, pyrite+chalcopyrite+bornite+covellite mineralization

in the altered feldspar-quartz-sandstone; h, i. RNZK0804-189.99 m, pyrite+tenantite+enargite+digenite+alunite vein

Alu—Alunite; Bn—Bornite; Cp—Chalcopyrite; Cv—Covellite; Dg—Digenite;

En—Enargite; Mo—Molybdenite; Py—Pyrite; Tn—Tennantite

锡砷铜矿多呈不规则粒状,粒径集中在10 μm左右,少数可达50~60 μm,具无多色性、无内反射、显均质性特征。与不同矿物伴生产出时,其反射色不同。与大量硫砷铜矿、砷黝铜矿等Cu-As-S体系矿物伴生产出时,呈乳黄色-淡黄色(图5a~d);与大量斑铜矿、黄铁矿、蓝辉铜矿等Cu-Fe-S体系矿物伴生产出时,呈乳褐色-浅褐色(图5e~i)。结合硫锡砷铜矿与不同矿物的相互交代关系(图5a~i),可推断出铁格

隆南矿床矿物的大致生成顺序为:黄铁矿→黄铜矿、斑铜矿→砷黝铜矿→硫砷铜矿→硫锡砷铜矿、方铅矿→蓝辉铜矿→铜蓝。

4.2 化学成分特征

对铁格隆南矿床的37个硫锡砷铜矿颗粒进行了电子探针测试分析,详细结果见表2。分析表明,硫锡砷铜矿的基本成分包括Cu、As、V、S、Sn、Sb,普遍含有少量Fe、Ge、Zn,少数样品中含少量W、Au、

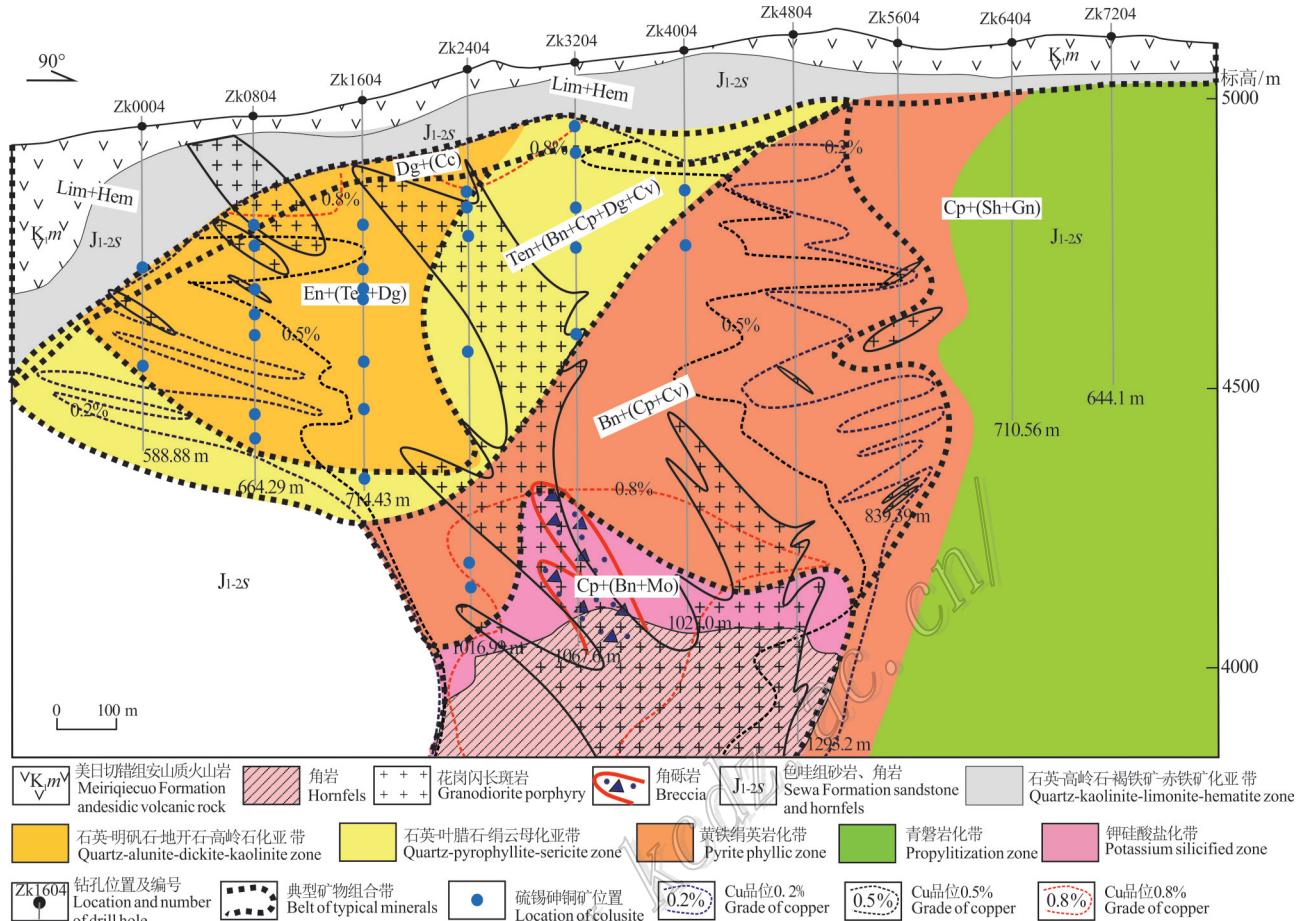


图4 铁格隆南矿床矿相学研究取样位置及硫锡砷铜矿大致分布图

Alu—明矾石; Bn—斑铜矿; Cc—辉铜矿; Cp—黄铜矿; Cv—铜蓝; Dg—蓝辉铜矿; En—硫砷铜矿; Gn—方铅矿; Hem—赤铁矿; Lim—褐铁矿; Mo—辉钼矿; Py—黄铁矿; Sh—闪锌矿; Ten—砷黝铜矿

Fig. 4 The sampling location of the metallogenetic study and the general distribution of colusite in the Tigelongnan deposit

Alu—Alunite; Bn—Bornite; Cc—Chalcocite; Cp—Chalcopyrite; Cv—Covellite; Dg—Digenite; En—Enargite; Gn—Galena; Hem—Hematite; Lim—Limonite; Mo—Molybdenite; Py—Pyrite; Sh—Shalerite; Ten—Tennantite

Ag,大多也低于检测限,其他元素(如Te、Mo、Se、Re、Bi、Pb、Co、Ni等)则普遍低于检测限。 $w(\text{Cu})$ 介于46.91%~51.4%, $w(\text{As})$ 、 $w(\text{V})$ 、 $w(\text{Sn})$ 和 $w(\text{Sb})$ 分别为5.59%~13.99%、1.89%~3.34%、0~9.02%、0.01%~2.28%。各硫锡砷铜矿颗粒中 $w(\text{Zn})$ 总体很低,颗粒之间的含量变化不大。但是,各颗粒中Fe元素含量变化较显著,当其与大量Cu-Fe-S体系矿物紧密伴生时,其中, $w(\text{Fe})$ 和 $w(\text{Ge})$ 总体相对较高(平均含量分别为0.53%、0.21%,且个别 $w(\text{Fe})$ 、 $w(\text{Ge})$ 达1.12%、1.53%);而当与大量Cu-As-S体系矿物紧密伴生时,Fe和Ge含量总体相对偏低(平均分别为0.23%、0.11%)。这可能也是硫锡砷铜矿与不同矿物紧密伴生时,其反射色不同的原因。

5 讨 论

以S原子个数32为基础,计算得出硫锡砷铜矿的分子式为 $\text{Cu}_{23.71\sim26.92}\text{V}_{1.43\sim2.10}(\text{As}_{2.55\sim5.86}, \text{Sb}_{0\sim0.63})_{3.15\sim5.95}(\text{Sn}_{0\sim2.6}, \text{Ge}_{0\sim0.7})_{0.01\sim2.60}(\text{Fe}_{0\sim2.4}, \text{Zn}_{0\sim0.24})_{0\sim2.4}\text{S}_{32}$ 。整理发现,(As+Sb)与(Sn+Ge)呈显著负相关(图6),说明这2组元素至少存在一组元素耦合置换机理,如 $(\text{As}, \text{Sb})^{5+} \rightleftharpoons (\text{Sn}, \text{Ge})^{4+} + \text{Cu}^+$ (Spry et al., 1994)或 $\text{Sb}^{5+} \rightleftharpoons \text{As}^{5+}$ 和 $\text{Sn}^{4+} \rightleftharpoons \text{Ge}^{4+}$ (Wagner et al., 2005);V与(As+Sb)或(Sn+Ge)之间没有明确的相关性,说明它们之间不太可能会发生耦合置换;Cu与其他任何元素之间都没有明显的相关性,由此反应出硫锡砷铜

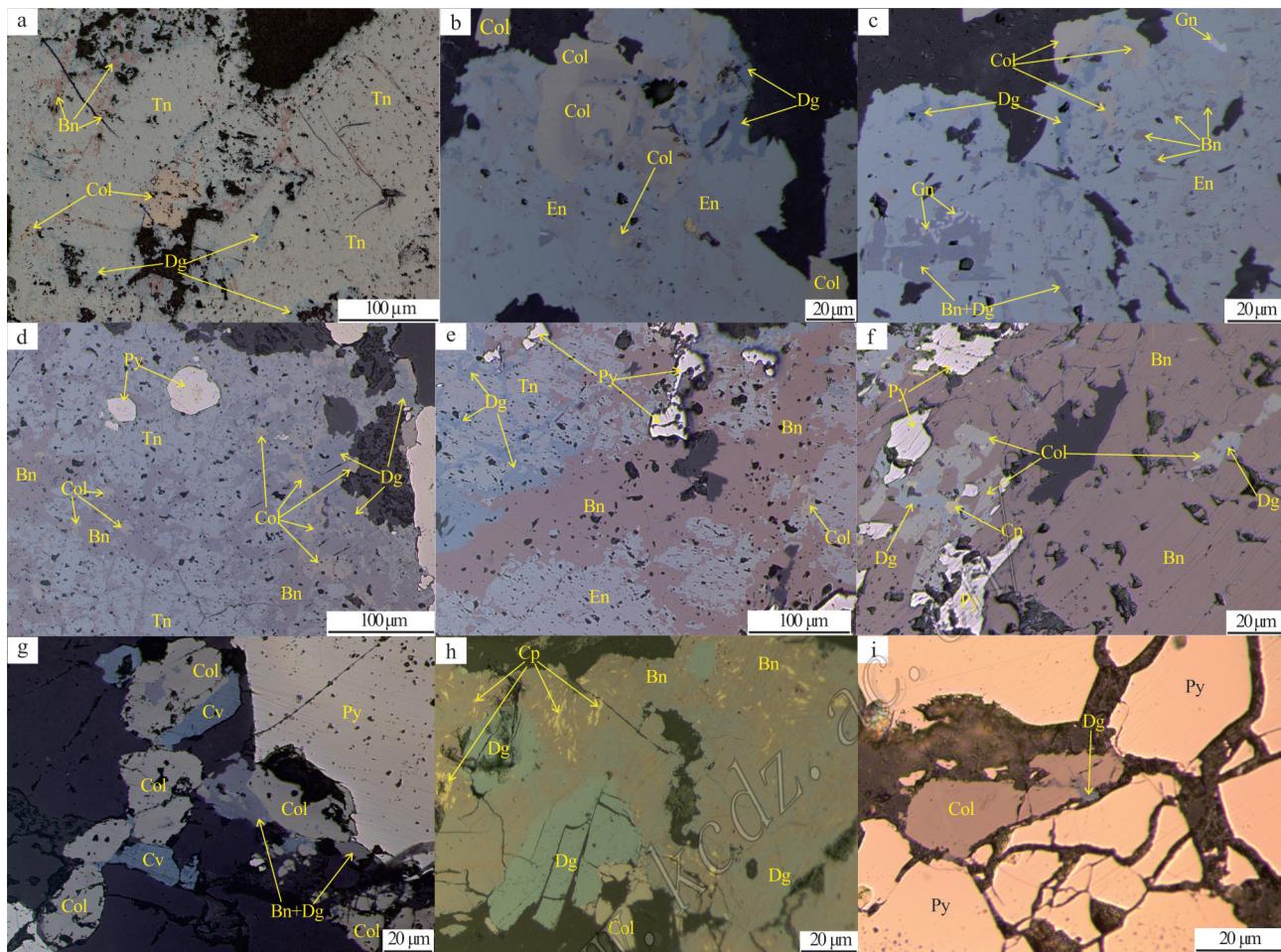


图5 铁格隆南矿床中硫锡砷铜矿的产出特征

a. RNZK0004-585.49 m, 斑铜矿被交代成残余结构, 砷黝铜矿被硫锡砷铜矿和蓝辉铜矿交代;b. RNZK0804-568.4 m 硫砷铜矿被硫锡砷铜矿、蓝辉铜矿交代;c. RNZK0804-312.6 m 硫砷铜矿被硫锡砷铜矿、方铅矿、蓝辉铜矿交代;d. RNZK2404-644.5 m, 斑铜矿被砷黝铜矿、蓝辉铜矿交代, 砷黝铜矿被硫锡砷铜矿、蓝辉铜矿交代, 黄铁矿形成最早, 被所有矿物交代;e. RNZK1605-639.09 m, 黄铁矿被斑铜矿交代, 斑铜矿被硫砷铜矿、砷黝铜矿、硫锡砷铜矿交代, 蓝辉铜矿交代砷黝铜矿;f. RNZK3204-592.98 m, 硫锡砷铜矿交代斑铜矿、黄铜矿, 被蓝辉铜矿交代;g. RNZK0804-682.95 m, 斑铜矿交代黄铁矿, 被硫锡砷铜矿、蓝辉铜矿、铜蓝交代;h. RNZK4004-552.7 m, 黄铜矿呈叶片状出溶于斑铜矿中, 蓝辉铜矿、硫锡砷铜矿交代黄铜矿;i. RNZK1604-458.2 m, 硫锡砷铜矿交代黄铁矿, 被蓝辉铜矿交代, 通过上述交代关系, 可大致得出铁格隆南的矿物生成顺序:

黄铁矿→黄铜矿、斑铜矿→砷黝铜矿→硫砷铜矿→硫锡砷铜矿、方铅矿→蓝辉铜矿→铜蓝

Bn—斑铜矿; Col—硫锡砷铜矿; Cp—黄铜矿; Cv—铜蓝; Dg—蓝辉铜矿; En—硫砷铜矿; Py—黄铁矿; Tn—砷黝铜矿

Fig. 5 The characteristics of colusite at Tiegelongnan deposit

a. RNZK0004-585.49 m, bornite composed of residual worm-like, and tennantite replaced by colusite and digenite; b. RNZK0804-568.4 m, enargite replaced by colusite and digenite; c. RNZK0804-312.6 m, enargite replaced by colusite, galena and digenite; d. RNZK2404-644.5 m, bornite replaced by tennantite, which was replaced by colusite and digenite , and the pyrite formed earliest; e. RNZK1605-639.09 m, bornite replaced by enargite, which was replaced by colusite and digenite , and the pyrite formed earliest; f. RNZK3204-592.98 m, chalcopyrite and bornite replaced by colusite, which was replaced by digenite; g. RNZK0804-682.95 m, pyrite replaced by bornite,which was replaced by colusite, digenite and covellite; h. RNZK4004-552.7 m, chalcopyrite assuming leaf-like dissolved in bornite, and digenite, colusite replacing chalcopyrite; i. RNZK1604- 458.2 m, colusite replacing pyrite and replaced by digenite. Through the above-mentioned metaphysical relationship, it is possible to draw the order of mineral formation in ferrisgate: pyrite → bornite, chalcopyrite → tennantite → enargite → colusite, galena → digenite → covellite

Bn—Bornite; Cp—Chalcopyrite; Cv—Covellite; Dg—Digenite; En—Enargite; Gn—Galena;

Mo—Molybdenite; Py—Pyrite; Tn—Tennantite

表2 铁格隆南矿床中硫锡砷铜矿的电子探针分析结果
Table 2 EPMA results of colusite in Tiegelongnan deposit

序号	样品编号	w(B)/%												
		Cu	As	Sb	V	Sn	Ge	Fe	Zn	S	Au	Ag	W	总和
1	RNZK1604-270.33	50.06	13.08	0.24	3.08	0	0.22	0.99	0.01	32.41	0.05	0.03	0	100.17
2	RNZK1604-270.33	50.66	13.21	0.23	3.27	0.01	0.48	0.29	0.05	32.08	0.06	0.02	0	100.36
3	RNZK1604-458	49.93	9.60	0.86	3.21	3.87	0.03	0.70	0.04	31.55	0	0	0	99.79
4	RNZK1604-458	49.44	8.14	1.32	2.96	5.64	0.12	0.92	0.02	30.72	0	0	0	99.28
5	RNZK1604-458	49.64	7.92	1.62	3.02	6.46	0.05	0.78	0.04	30.58	0	0.04	0	100.15
6	RNZK1612-694.64	48.69	10.22	0.03	2.17	5.44	0.01	0.43	0	31.43	0	0	0	98.42
7	RNZK2405-244.64	49.43	13.83	0.30	3.12	0.03	0	0.55	0.03	33.46	0	0	0.03	100.78
8	RNZK2405-539.5	47.98	11.25	0.08	2.75	0.02	1.53	1.04	0	31.05	0	0.01	0.46	96.17
9	RNZK2405-539.5	47.29	11.67	1.05	2.50	1.21	0.13	1.12	0	31.81	0	0.02	0.08	96.88
10	RNZK2405-539.5	48.70	12.15	0.36	2.17	0.19	0.5	0.18	0	32.20	0	0	0	96.45
11	RNZK2404-850.94	48.34	13.99	0.35	2.26	0.28	0.13	0.11	0	32.64	0.02	0.01	0	98.13
12	RNZK2404-903.67	49.24	10.57	0.23	2.22	4.63	0.05	0.44	0	30.91	0	0.05	0	98.34
13	RNZK3204-592.98	47.78	10.88	0.78	2.06	3.11	0.12	0.52	0	31.50	0	0.02	0.12	96.89
14	RNZK3204-592.98	47.89	10.88	1.33	2.34	1.21	0.15	0.44	0.05	31.97	0	0.04	0.02	96.32
15	RNZK3204-592.98	48.68	12.40	0.76	2.33	0.42	0.08	0.42	0	32.77	0.04	0.03	0	97.93
16	RNZK0804-295.69	50.05	9.03	0.51	2.10	5.81	0	0.09	0.01	30.72	0.01	0	0.03	98.36
17	RNZK0804-513.7	48.65	10.92	0.46	2.32	3.36	0	0.43	0	31.96	0	0	0.02	98.12
18	RNZK0804-513.7	47.35	12.20	0.23	2.61	2.23	0.02	0.13	0.05	31.23	0	0	0.03	96.08
19	RNZK0804-568.4	48.03	9.38	1.66	2.27	3.24	0.07	0.12	0.03	31.60	0	0	0	96.40
20	RNZK0804-568.4	48.77	10.08	1.27	2.33	2.99	0.10	0.09	0	31.66	0	0.01	0	97.30
21	RNZK0804-568.4	49.58	7.45	1.53	1.89	6.95	0.06	0.40	0.13	30.61	0.02	0	0.17	98.79
22	RNZK0804-568.4	50.41	12.57	0.67	2.22	3.22	0	0.67	0.24	30.80	0	0	0	100.80
23	RNZK0804-682.95	48.03	12.89	0.25	2.27	1.51	0.04	0	0	32.40	0	0	0	97.39
24	RNZK0804-682.95	50.45	8.75	0.20	2.17	5.95	0	0.22	0.01	30.20	0	0	0	97.95
25	RNZK0004-585.49	50.09	11.14	0.28	2.37	2.08	0.03	0.53	0.32	31.42	0	0.01	0.03	98.3
26	RNZK0004-585.49	49.82	8.49	0.15	2.78	5.47	0	0.19	0.32	31.28	0	0	0.04	98.54
27	RNZK0004-585.49	49.54	8.18	0.29	3.13	5.12	0	0.05	0.31	31.20	0	0.02	0	97.84
28	RNZK0004-585.49	49.76	8.72	0.32	3.09	4.48	0	0.12	0.07	31.17	0	0.03	0	97.76
29	RNZK0004-585.49	50.15	13.89	0.12	3.11	0.43	0.07	0.08	0.05	32.90	0	0	0.06	100.86
30	RNZK1604-149	47.43	12.25	0.44	2.99	1.61	0.04	0.09	0.08	32.07	0	0	0	97.00
31	RNZK1604-149	46.91	12.03	0.50	2.97	1.59	0.04	0.13	0	31.88	0	0.03	0	96.08
32	RNZK1604-270.33	51.40	13.26	0.22	3.34	0.04	0.52	0.03	0.04	31.91	0.03	0.01	0.03	100.83
33	RNZK1604-270.33	49.35	12.97	0.17	2.81	0.14	0.22	0.19	0.02	32.92	0	0.04	0	98.83
34	RNZK1605-712	51.02	8.54	0.01	3.09	6.10	0.09	0.26	0	31.31	0	0.01	0.04	100.47
35	RNZK2412-494	50.25	12.02	0.29	3.05	0.02	0.47	0.44	0.04	32.21	0	0.02	0.05	98.86
36	RNZK2412-494	50.73	13.17	0.41	3.04	0.04	0.33	0.47	0.49	31.94	0	0	0	100.62
37	RNZK2405-284.3	48.79	7.44	2.28	2.94	5.11	0.16	0.29	0.03	30.41	0	0	0.32	97.77

注:“0”代表低于检测下限;1~18号为与Cu-Fe-S体系矿物紧密伴生的硫锡砷铜矿测点;19~37号为与Cu-As-S体系矿物紧密伴生的硫锡砷铜矿测点。

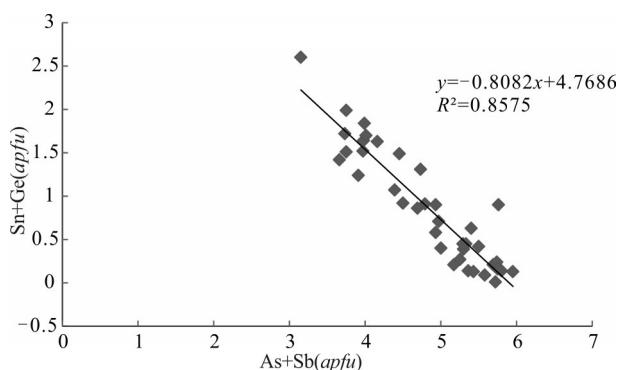


图 6 硫锡砷铜矿的(As+Sb)与(Sn+Ge)相关性投图

Fig. 6 The plot of (As+Sb) versus (Sn+Ge) for colusite

矿晶体架构中元素的置换机理非常复杂。

对硫锡砷铜矿进行背散射图采集显示,这类硫锡砷铜矿至少有2个世代,第Ⅱ世代穿插、交代第Ⅰ

世代(图7)。对其进行电子探针扫面分析发现,这2个世代中Fe含量总体很低,Cu、V含量分布均匀;但是第Ⅱ世代中的Ge、As含量较第Ⅰ世代更高,而第Ⅱ世代中的Sn、Sb含量则明显较第Ⅰ世代更低(图7),这印证了铁格隆南矿床中的硫锡砷铜矿中很可能存在 $Sb^{5+} \leftrightarrow As^{5+}$ 和 $Sn^{4+} \leftrightarrow Ge^{4+}$ 类元素耦合置换(Wagner et al.,2005)。

硫锡砷铜矿的晶体架构已基本建立完善(Spry et al.,1994; Wagner et al.,2005; Makovicky, 2006),主要是由似闪锌矿架构中共同晶角连接起来的 CuS_4 和 AsS_4 四面体构成,且各晶胞中总存在有空位(所谓空位即晶体中某结点上的原子空缺了)。Wagner等(2005)通过研究全球各典型矿床中硫锡砷铜矿的化学成分指出,每摩尔硫锡砷铜矿分子式中的空位介于约-2.0~2.5 mol;其中,空位为负值时,暗示硫锡砷

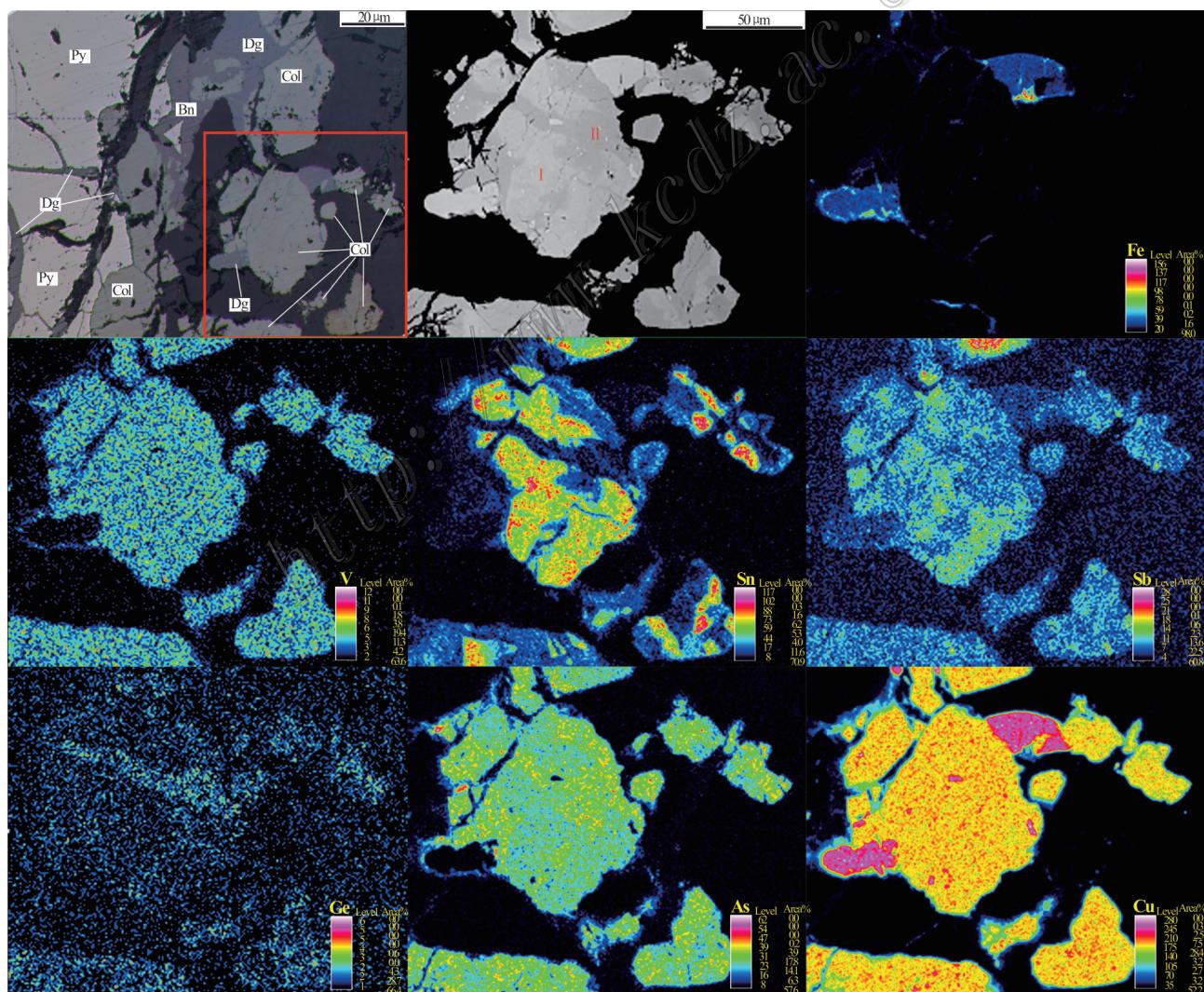


图 7 硫锡砷铜矿电子探针面扫分析(红色方框代表面扫区域)

Bn—斑铜矿; Col—硫锡砷铜矿; Dg—蓝辉铜矿; Py—黄铁矿

Fig. 7 EPMA mapping of colusite (the red block represents the sweeping area)

Bn—Bornite; Col—Colusite; Dg—Dignite; Py—Pyrite

铜矿中可能还存在有其他金属元素参与元素的耦合置换,如 $(As, Sb)^{5+} + Cu^+ \rightleftharpoons (Sn, Ge)^{4+} + (Fe, Zn, Cu)^{2+}$ 以及 $V^{5+} \rightleftharpoons V^{4+} + Cu^+$;同时,每摩尔分子式中的空位与 $(Cu + Fe + Zn)$ 、 $(As + Sb)$ 与 $(Sn + Ge)$ 呈显著负相关,进而推导出硫锡砷铜矿的分子式为 $Cu_{24+x-y-z}V^{5+}_{2-z}V^{4+}_z(As, Sb)^{5+}_{6-x+y}(Sn, Ge)^{4+}_{x+y}(Fe, Zn, Cu)^{2+}_yS_{32}$ ($0 \leq x \leq 2$, $0 \leq y \leq 6-x$, $0 \leq z \leq 2$)。由此看来,铁格隆南矿床中的硫锡砷铜矿与Wagner等(2005)所推导出的分子式基本吻合,其中必然也存在上述这一系列元素耦合置换。

前人研究发现,硫锡砷铜矿与含有大量Cu-As-S体系矿物(硫砷铜矿、砷黝铜矿)的浅成低温热液矿床关系最为密切(Kesler et al., 1984; Spry et al., 1994);在一些含锡矿物(黄锡矿、锌黄锡矿、硫锡铁铜矿、硫砷锡铁铜矿等)大量产出的热液矿床中则常见硫钒锡铜矿产出(Hannington et al., 1999; Carvalho et al., 1999);在黝铜矿或其他含锑矿物大量产出的热液矿床中则往往有硫锑锡铜矿产出(Spiridonov et al., 1994)。本次硫锡砷铜矿的电子探针分析结果显示,其Ge含量普遍很低,仅一个样品中 $w(Ge)$ 达1.53%,说明铁格隆南矿床中很可能不存在以Ge为主的硫锡砷铜矿族矿物(硫钒锗铜矿Germanoclusite),因而将电子探针数据投入Sn-Sb-As三员图解(图8),结果显示研究样品全部落入硫锡砷铜矿(Colusite)区,这与铁格隆南矿床无其他大量含锡、含锑、含锗矿物产出的现象一致。

铁格隆南矿床具有明显的蚀变分带特征(图3),矿床上部主要为与高硫化型浅成低温热液成矿有关的高级泥化蚀变,指示为强酸性、中低温环境;中部泥化带为与浅成低温热液型矿化向斑岩型矿化的过渡带;而矿床下部主要为与斑岩型矿化有关的绢英岩化叠加钾硅酸盐化蚀变,指示为偏中性、高温环境(杨超,2015)。在斑岩成矿系统中,从深部往浅部体现为斑岩型矿化向高硫浅成低温热液型矿化过渡,这是一个温度降低,但总体硫化态上升的过程,其中矿物组合特征反应了硫化态的转变—— $5CuFeS_2$ (黄铜矿)+ $S_2 = Cu_5FeS_4$ (斑铜矿)+ $4FeS_2$ (黄铁矿)、 $0.67Cu_{12}As_4S_{13}$ (砷黝铜矿)+ $S_2 = 2.67Cu_3AsS_4$ (硫砷铜矿)、 $Cu_{1.8}S$ (蓝辉铜矿)+ $0.4S_2 = 1.8CuS$ (铜蓝)(Einaudi et al., 2003)(图9)。铁格隆南矿床中硫锡砷铜矿附近或多或少都有斑铜矿、Cu-As-S体系矿物或直接

产于其中(图5),而在Cu-As-S体系矿物减少至消失、黄铜矿增多至大量产出的深部环境,硫锡砷铜矿的量也随之减少并消失,由此说明强酸性-酸性、中低温、高硫化环境可能是硫锡砷铜矿生成的关键控制因素,这也许是甲玛、驱龙、帮铺、雄村等有大量黄铜矿产出的大型超大型斑岩铜多金属矿床中未报道有硫锡砷铜矿产出的重要原因之一。

系统的矿相显微观察发现,铁格隆南矿床I号主矿体中与硫锡砷铜矿紧密伴生的矿物由浅至深变化较大:在矿体中上部,与硫锡砷铜矿紧密伴生的矿物以硫砷铜矿为主,其次为斑铜矿、蓝辉铜矿、黄铁矿,少量砷黝铜矿、铜蓝;在矿体中下部,与之紧密伴生的矿物以斑铜矿为主,其次为黄铁矿、砷黝铜矿、硫砷铜矿、蓝辉铜矿、铜蓝;越往深部,随着Cu-As-S体系矿物的消失,黄铜矿含量增多至大量产出,硫锡砷铜矿随之逐渐消失,这指示了一个高硫化浅成低温热液型矿化向中-低硫化斑岩型矿化过渡的过程。

6 结 论

(1) 矿相显微观察发现,硫锡砷铜矿多为粒径约 $10 \mu m$ 的不规则细粒,呈乳黄色-淡黄色、乳褐色-浅褐色,无多色性、无内反射、显均质性,形成于黄铁

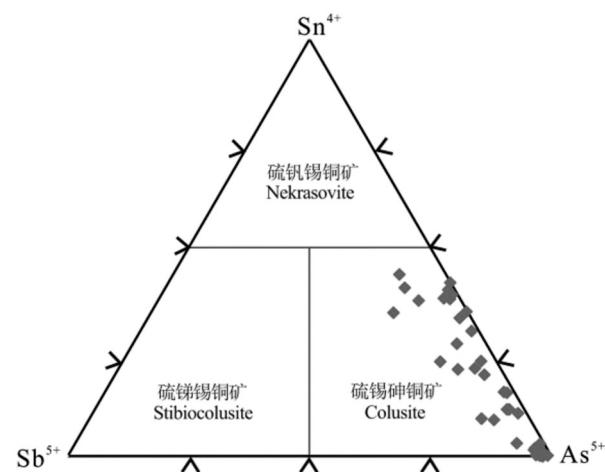


图8 硫锡砷铜矿的Sn-Sb-As三元图解

(底图据Repstock et al., 2015)

Fig. 8 Chemical variation of volusite in a ternary Sn-Sb-As plot (base map after Repstock et al., 2015)

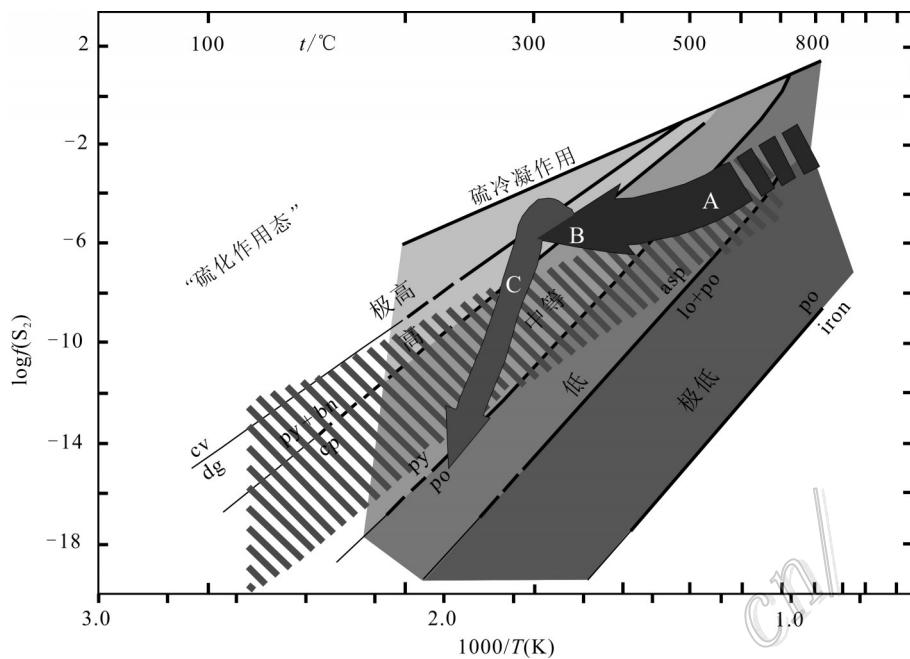


图9 热液流体硫化态分类 $\log(f(S_2))$ - $1000/T$ 图解(Einaudi et al., 2003)

A-B-C代表斑岩型矿化到高硫化型矿化,再到中硫化型和低硫化型碱金属矿物的演化

asp—毒砂;bn—斑铜矿;cp—黄铜矿;cv—铜蓝;dg—蓝辉铜矿;lo—斜方砷铁矿;po—磁黄铁矿;py—黄铁矿

Fig. 9 $\log(f(S_2))$ - $1000/T$ diagram defining the relative sulfidation state of hydrothermal fluids (after Einaudi et al., 2003)

A-B-C—the evolution of metallic minerals of the deposit passing through porphyry mineralization, high sulphidation mineralization, mild sulphidation mineralization and low sulphidation mineralization in sequence

asp—Arsenopyrite; bn—Bornite; cp—Chalcopyrite; cv—Covellite; dg—Digenite; lo—Loellingite; po—Pyrrhotite; py—Pyrite

矿、斑铜矿、硫砷铜矿、砷黝铜矿之后,蓝辉铜矿、铜蓝之前。

(2) 电子探针分析显示,硫锡砷铜矿的基本成分包括Cu、As、V、S、Sn、Sb,普遍含有少量Fe、Ge、Zn,部分样品中含少量W、Au、Ag,在Sn-Sb-As三员图解中全部落入硫锡砷铜矿(Colusite)区,其中存在 $Sb^{5+} \leftrightarrow As^{5+}$ 和 $Sn^{4+} \leftrightarrow Ge^{4+}$ 、 $(As, Sb)^{5+} + Cu^+ \leftrightarrow (Sn, Ge)^{4+} + (Fe, Zn, Cu)^{2+}$ 以及 $V^{5+} \leftrightarrow V^{4+} + Cu^+$ 等复杂的元素耦合置换。

(3) 根据矿石矿物组合及蚀变组合分析得出,酸性或略偏中性的、中低温高硫化态环境是促使硫锡砷铜矿形成的关键控制因素。因此,硫锡砷铜矿可用于反演其形成时的物理、化学环境;同时,对矿床成因类型判别具有一定的指导作用。

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