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雪峰弧形构造带中段典型金锑矿床成矿流体对比研究

周超¹, 孙骥¹, 郭爱民¹, 贾朋远¹, 陆文¹, 魏含涛², 郭鼎³, 蔡毅¹

(1. 湖南省地质调查院,湖南长沙 410116;2. 自然资源部成矿作用与资源评价重点实验室,北京 100037;
3. 河南工业职业技术学院,河南南阳 473000)

提要:古台山矿床和龙王江矿床是雪峰弧形构造带中段颇具代表性的石英脉型金锑矿床。古台山金锑矿床位于白马山复式岩体的外接触带,而龙王江金锑矿床则距离白马山岩体较远。本文从流体包裹体和氢氧同位素研究入手,讨论了成矿流体的特征、来源及其与成矿的关系。流体包裹体岩相学观察和显微测温表明,古台山矿床成矿期石英中包裹体以气液水两相包裹体和CO₂-H₂O三相包裹体为主,均一温度集中在199~298°C,盐度集中在2.07%~11.46%NaCl_{eqv};龙王江矿床成矿期石英中包裹体以气液水两相包裹体为主,均一温度集中在164~238°C,盐度集中在1.40%~8.41%NaCl_{eqv}。氢氧同位素研究表明,古台山矿床成矿流体来源主要为岩浆水和变质水的混合流体;龙王江矿床成矿流体主要来源于变质水。根据流体包裹体岩相学观察,结合显微测温,认为流体不混溶是导致古台山矿区矿质沉淀的主要机制;而龙王江矿区矿质沉淀很可能是温度和(或)压力的变化,或大气降水的加入(混合)所导致。

关 键 词:流体包裹体;流体不混溶;古台山金锑矿床;龙王江金锑矿床;雪峰弧形构造带;矿产勘查工程

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A comparative study of the ore-forming fluids of the typical gold-antimony deposits along Middle Xuefeng arc structure belt

ZHOU Chao¹, SUN Ji¹, GUO Aimin¹, JIA Pengyuan¹, LU Wen¹, WEI Hantao², GUO Ding³, CAI Yi¹

(1. Hunan Institute of Geology Survey, Changsha 410116, Hunan, China; 2. Key Laboratory of Mineralization and Resource Evaluation, Ministry of Natural Resources, Beijing 100037, China; 3. Henan Polytechnic Institute, Nanyang 473000, Henan, China)

Abstract: The Gutaishan and Longwangjiang quartz vein type gold-antimony deposits, located in Xinhua and Xupu County, respectively, are two representative ones in the middle of Xuefeng arc structure belt. The Gutaishan gold-antimony deposit occurs in the external contact zone of Baimashan composite granite mass, while Longwangjiang gold-antimony deposit is far from Baimashan composite granite mass. Based on the study of fluid inclusions and hydrogen and oxygen isotopic geochemistry, this paper discusses the characteristics and origin of ore-forming fluids so as to provide an insight into the ore genesis. Petrographic observation and microthermometric measurements of fluid inclusions show that ore-forming stage quartz veins in the Gutaishan

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作者简介:周超,男,1989年生,硕士,工程师,主要从事矿产勘查及矿床学研究;E-mail: zhouchao_1106@163.com。

gold–antimony deposit mainly contain liquid–vapor two–phase aqueous inclusions and $\text{CO}_2\text{–H}_2\text{O}$ three–phase inclusions. The homogeneous temperature and salinity of primary fluid inclusions are in the range of 199~298°C and 2.07~11.46% NaCl_{eqv} . The ore-forming stage quartz veins of the Longwangjiang gold–antimony deposit mainly contain liquid–vapor two–phase aqueous inclusions, with the homogeneous temperature from 164°C to 238°C and salinity from 1.40% NaCl_{eqv} to 8.41% NaCl_{eqv} . Hydrogen and oxygen isotopic geochemistry shows that the ore-forming fluids of the Gutaishan gold–antimony deposit was composed of the mixture of magmatic water and metamorphic water, and the Longwangjiang gold–antimony deposit was mainly derived from metamorphic water. Based on geological and fluid inclusion characteristics, it is suggested that fluid immiscibility may have been the main mechanism for metal precipitation in the Gutaishan gold–antimony deposit. The mechanism of the ore-forming process in the Longwangjiang deposit was probably caused by the change of temperature and/or pressure, or the addition (mixing) of metamorphic water.

Key words: fluid inclusions; fluid immiscibility; Gutaishan gold–antimony deposit; Longwangjiang gold–antimony deposit; Xuefeng arc structure belt; mineral exploration engineering

About the first author: ZHOU Chao, male, born in 1989, master, engineer, majors in mineral exploration and study of mineral deposits; E-mail: zhouchao_1106@163.com.

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1 引言

雪峰弧形构造带地处江南造山带的西南段(黄汲清, 1960), 属扬子—华夏地块所夹持的线状构造隆起带(图1a)。隆起带自新元古代以来, 先后经历了俯冲碰撞、陆陆碰撞造山, 以及板内造山作用; 奠定了区域极为复杂的地质过程, 成矿地质背景得天独厚, 成矿条件极其优越。多期多阶段多机制造山作用过程导致前寒武系广泛变质变形, 并发生了构造–岩浆–金(锑)成矿作用, 湖南省内90%以上的金矿床(点)均产于该造山带内的前寒武系浅变质岩系中(俗称湖南省“金腰带”)。

雪峰弧形构造带中段现已发现包括大坪、铲子坪、古台山、龙王江、大新、金山等众多金(锑)矿床(图1b), 为湖南重要的黄金生产基地(彭建堂和戴塔根, 1998)。区内金(锑)矿床大致可以分为两类, 一类为产于白马山复式岩体外接触带及附近, 在空间上与岩体关系密切, 以古台山、铲子坪、大坪为代表; 一类为远离白马山岩体外接触带, 以龙王江、黄溪口为代表。区内金(锑)矿床成矿作用与岩浆活动的关系存在争议, 可以概括为: ①金(锑)成矿与岩浆活动无成因联系, 成矿物质主要来源于地层, 成矿流体主要为变质流体(谌锡霖等, 1983; 肖启明

和李典奎, 1984; 邹同熙, 1988; 文国璋等, 1993; Fan et al., 2004); ②金(锑)成矿作用与岩浆作用有关, 岩浆作用为金(锑)矿化提供了岩浆热液、成矿物质或热源条件(李智明, 1993; 陶琰等, 2001; 彭建堂等, 2002; 李华芹等, 2008; 李伟等, 2016; Li et al., 2018)。本文选取代表性矿床古台山金锑矿床和龙王江金锑矿床为研究对象, 通过对矿床地质特征、流体包裹体和氢、氧同位素对比研究, 分析了各典型矿床成矿流体的性质、来源及其与成矿的关系, 旨在探讨矿床成因与岩浆活动的关系。

2 区域地质背景

雪峰弧形构造带中段大地构造位置处于扬子地块与华夏地块的过渡部位(图1a)。区域出露地层主要为新元古界青白口系板溪群(高涧群), 次为南华系、震旦系、寒武—奥陶系、侏罗—白垩系等。其中青白口系冷家溪群、板溪群和富含火山物质的南华系长安组是区内重要的赋矿层位, 主要由一套浅变质砂砾岩、板岩、凝灰岩组成, 局部含基性、中酸性火山岩和炭质板岩; 其Au、Sb含量为上部大陆地壳平均值的几倍至几十倍(王甫仁等, 1993; 鲍振襄等, 1999; 马东升等, 2002)。古生代至中生代地层主要由泥质页岩、砂岩、粉砂岩、灰岩、白云岩等

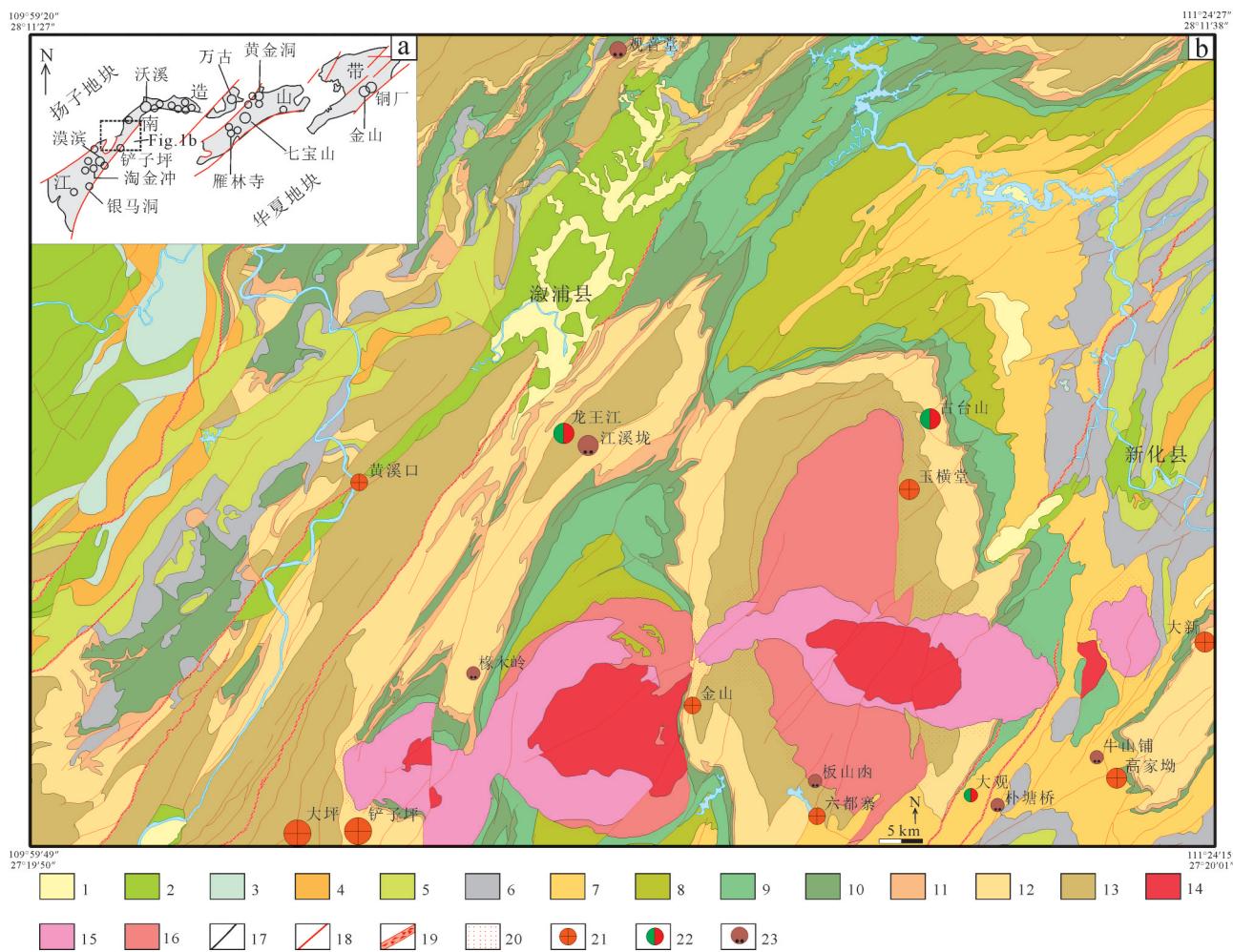


图1 雪峰弧形构造带中段大地构造略图(a)、雪峰弧形构造带中段区域地质简图(b)

1—第四系—古近系; 2—白垩系; 3—侏罗系; 4—三叠系; 5—二叠系; 6—石炭系; 7—泥盆系; 8—志留系; 9—奥陶系; 10—寒武系; 11—震旦系; 12—南华系; 13—青白口系; 14—侏罗纪花岗岩; 15—三叠纪花岗岩; 16—志留纪花岗岩; 17—地质界线; 18—断裂; 19—韧性剪切带; 20—角岩化变; 21—金矿床(点); 22—金锑矿床(点); 23—锑矿床(点)

Fig. 1 Sketch map showing tectonic units of the middle of Xuefeng arc structure belt (a) and simplified geological map of the middle of Xuefeng arc structure belt (b)

1—Quaternary-Palaeogene; 2—Cretaceous; 3—Jurassic; 4—Triassic; 5—Permian; 6—Carboniferous; 7—Devonian; 8—Silurian; 9—Ordovician; 10—Cambrian; 11—Sinian; 12—Nanhua system; 13—Qingbaikou system; 14—Jurassic granite; 15—Triassic granite; 16—Silurian granite; 17—Geological boundary; 18—Fracture; 19—Ductile shear zone; 20—Hornfels alteration; 21—Au deposit; 22—Au-Sb deposit; 23—Sb deposit

海相、陆相及海-陆过渡相沉积岩组成。

研究区经历了多期次构造事件,断裂、褶皱构造发育,主体为NE~NNE走向。大型断裂构造主要是怀化—沅陵、溆浦—靖州、通道—安化、城步—新化等四条主干断裂。其中怀化—沅陵、溆浦—靖州断裂为倾向SE的逆断裂;通道—安化、城步—新化断裂主要表现为倾向NW的逆断裂,组成区域背冲构造样式(梁新权等,1999; Wang et al., 2005; 柏道远等,2014)。

区内岩浆活动强烈,出露白马山复式花岗岩体,由加里东期二长花岗岩—花岗闪长岩岩基及侵入其中的印支期黑云母花岗闪长岩、燕山早期花岗闪长岩岩株、二云母花岗岩岩株和一些小规模的基性—酸性脉岩群组成(曹有金等,2014)。年代学数据显示,白马山岩体的形成年龄集中于422~411 Ma(Chu et al., 2012; 王高,2013; 杨俊等,2015)和227~194 Ma(陈卫锋等,2007; 罗志高等,2010; Chu et al., 2012; 李国亮等,2014; 杨俊等,2015; 张义平等,2015)。

3 矿床地质特征

3.1 古台山金锑矿床

矿区出露的地层主要有青白口系板溪群五强溪组、南华系长安组、富禄组和洪江组,其中,五强溪组和长安组是矿区的主要赋矿地层(图2)。区内

断裂构造比较发育,按其走向可分为北西、北东、近东西和近南北向四组,其中近南北向和北西向断裂为矿区的控矿构造。矿区距白马山复式花岗岩体约2 km,处于岩体的外带中—低温热液活动区。

金(锑)矿体呈脉状产出(图3),严格受走向338°~25°、倾向东、倾角48°~62°的剪切性裂隙控制,

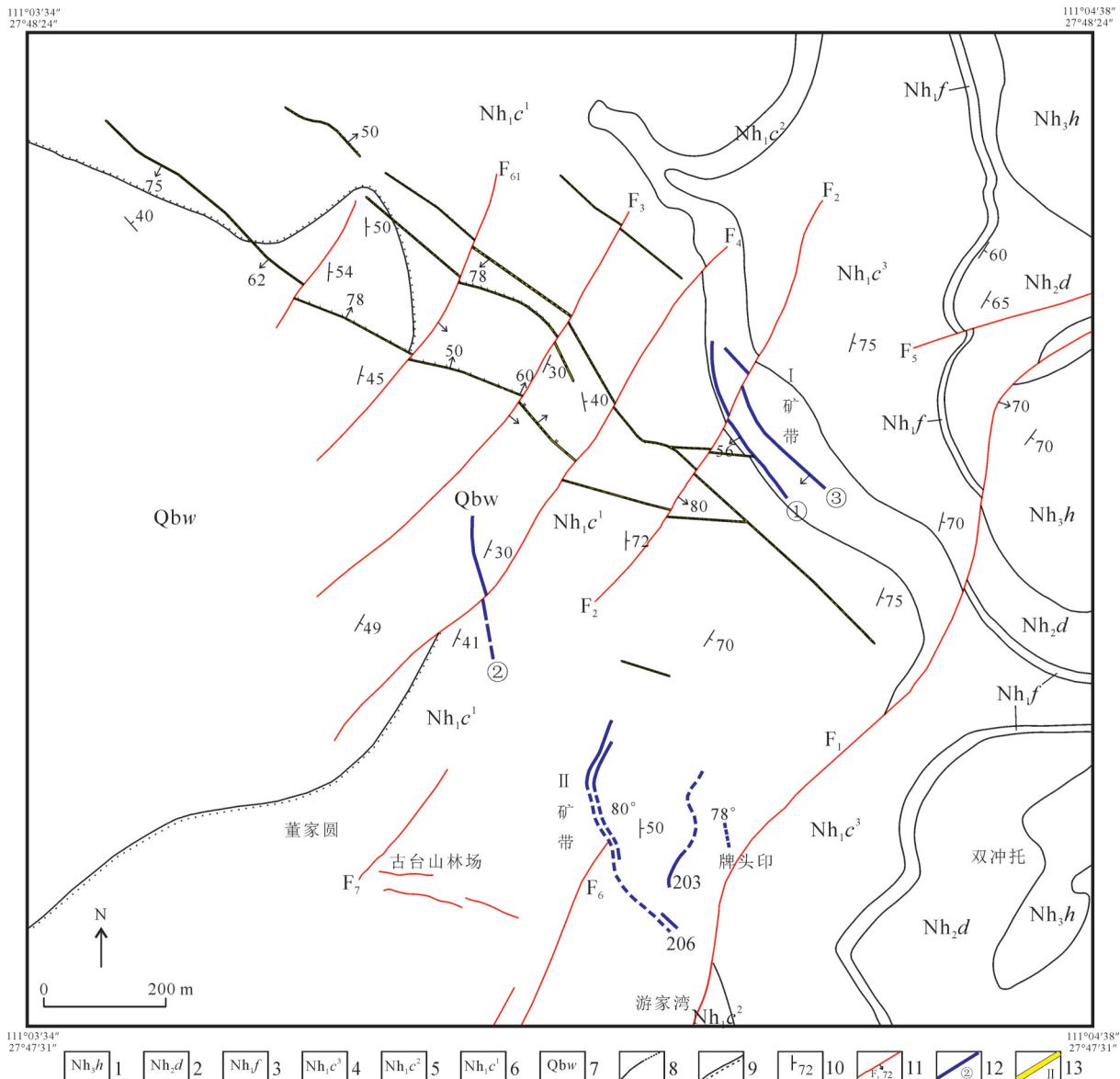


图2 古台山金锑矿床矿区地质图

1—洪江组;2—大塘坡组;3—富禄组;4—长安组第三段;5—长安组第二段;6—长安组第一段;7—板溪群五强溪组;8—地质界线;9—不整合地质界线;10—地层产状;11—实测、推测断层及产状;12—矿脉及编号;13—矿化破碎带及编号

Fig.2 Geological map of the Gutaishan Au-Sb ore district

1—Hongjiang Formation; 2—Datangpo Formation; 3—Fulu Formation; 4—First member of Changan Formation; 5—Second member of Changan Formation; 6—Third member of Changan Formation; 7—Wuqiangxi Formation of the Banxi Group; 8—Geological boundary; 9—Unconformity geological boundary; 10—Formation attitude; 11—Measured or inferred fault and attitude; 12—Vein and its serial number; 13—Mineralized fracture zone and its serial number

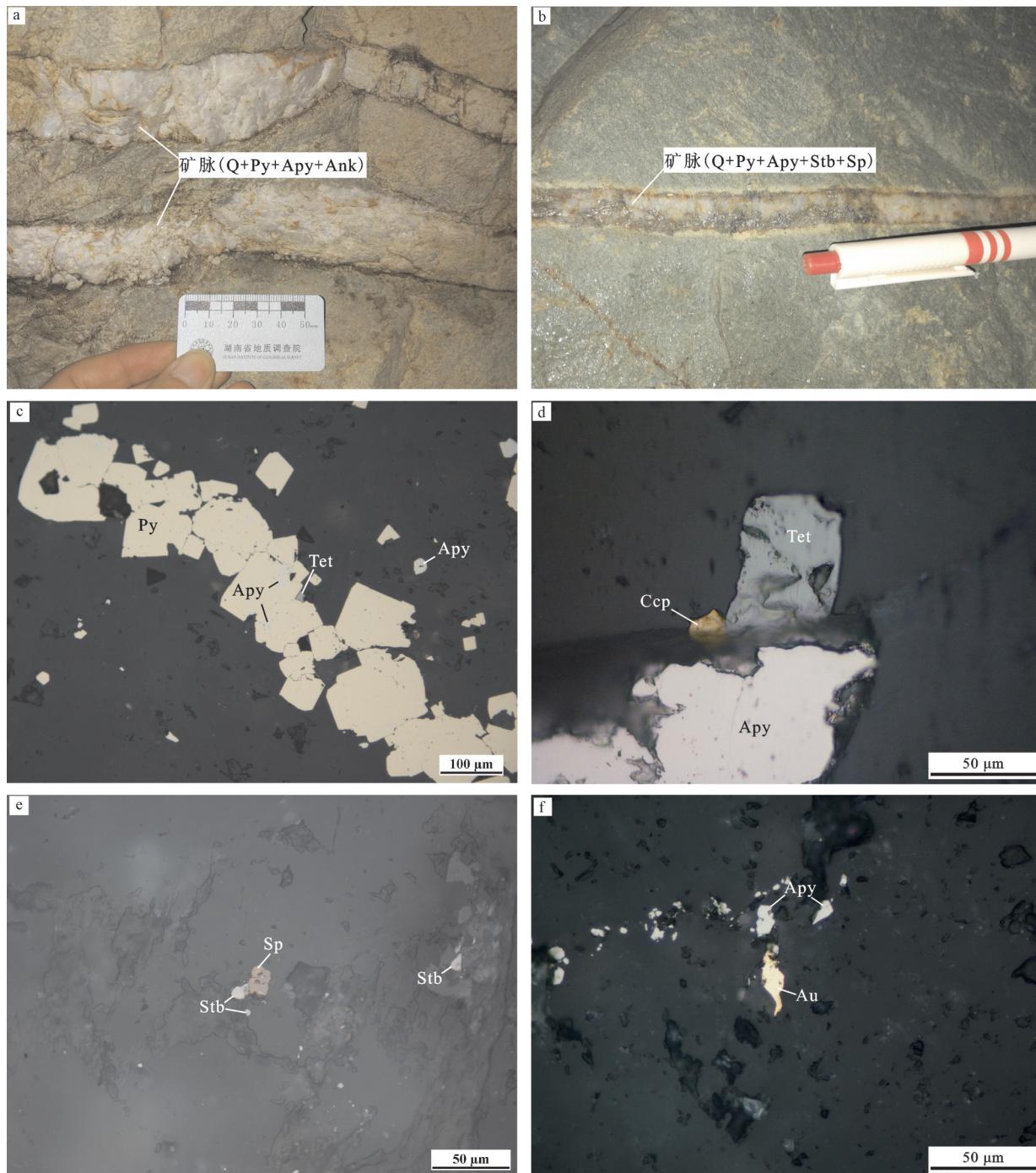


图3 古台山金锑矿床矿脉和矿石镜下照片

a、b—含矿石英脉;c—他形一半自形粒状黄铁矿、毒砂沿裂隙呈脉状分布;d—半自形毒砂与他形黄铜矿、黝铜矿共生;e—他形辉锑矿交代闪锌矿;f—他形自然金产于毒砂边缘;Q—石英;Py—黄铁矿;Apy—毒砂;Ank—铁白云石;Stb—辉锑矿;Sp—闪锌矿;Tet—黝铜矿;Ccp—黄铜矿;Au—自然金

Fig. 3 Ore vein and microscopic photos of ores from the Gutaishan Au-Sb deposit

a, b—Ore bearing quartz veins; c—Anhedral–subhedral arsenopyrite and pyrite filling along the fissure; d—Subhedral arsenopyrite, anhedral chalcopyrite and xenomorphic tetrahedrite; e—Sphalerite replaced by anhedral stibnite; f—Native gold along the edge of the arsenopyrite. Q—Quartz; Py—Pyrite; Apy—Arsenopyrite; Ank—Ankerite; Stb—Stibnite; Sp—Sphalerite; Tet—Tetrahedrite; Ccp—Chalcopyrite; Au—Native gold

相互平行展布,产状稳定,沿走向、倾向具小幅度波状起伏,裂隙面平整光滑。矿脉界面清晰、呈突变关系;每一矿脉一般都由1~5条宽仅0.1~5 cm的含矿石英细脉、复脉组成,细脉间可见雁行侧列现象或简单的燕尾式分支,分支后迅速尖灭;自然金往往赋存在石英脉中或两侧强黄铁矿化的蚀变带中。

矿石矿物组成较为简单,矿石矿物主要有辉锑矿、白钨矿、自然金,其次有黄铁矿、方铅矿、闪锌矿、毒砂和锑华(图3);脉石矿物主要有石英、方解石、白云石、绢云母、白云母和重晶石等。根据矿物共生组合及脉石矿物种类,又可将本区矿石划分为石英-自然金型、石英-自然金-硫化物型和石英-自然金-辉锑矿型矿石3类。矿石结构主要有晶质粗粒—细粒结构、他形粒状结构、不等粒变晶结构,碎裂结构和泥质结构。矿石的构造主要有块状构造、浸染状构造、角砾状构造、细脉状构造和蜂窝状构造。

矿床围岩蚀变广泛发育,蚀变类型包括硅化、毒砂化、黄铁矿化、碳酸盐化、绢云母化和绿泥石化等。其中硅化、毒砂化、黄铁矿化与金锑矿化关系密切。根据矿物组合、结构构造及脉体相互穿插关系可将成矿过程划分为4个阶段:石英-铁白云石阶段、石英-硫化物阶段、石英-自然金-硫化物-碳酸盐阶段和石英阶段(李伟等,2016)。

3.2 龙王江金锑矿床

矿区出露地层为青白口系高涧群岩门寨组。岩门寨组即为矿区的赋矿地层(图4)。矿区位于区域性褶皱龙鼻桥—陶金坪复式背斜中部,邱家湾背斜的北西翼。区域性大断裂洞头坪断裂(F1)、黑土坡断裂(F2)位于龙鼻桥—陶金坪复式背斜的两翼,对区内金锑矿床控制作用明显。金锑矿床就位于F1、F2所挟持的复式背斜近轴部之次级背斜两翼,矿脉(体)受其次级断裂控制,突出表现了构造控矿的主导作用。矿区未见岩浆岩出露。在矿区东南约20 km的葛竹坪—小沙江一带大面积出露白司马山花岗岩体。

矿区已知金(锑)矿脉10条(编号1~9),各矿脉大致平行展布,间距8~90 m。具工业价值的矿脉有1、2、2-1、3、6、7号。矿脉总体走向约30°,地表延伸150~1700 m,倾向南东,倾角27°~87°,总体具上缓下陡趋势,上部一般42°~46°,下部达55°~60°,沿倾

斜方向波状起伏明显(图5)。

矿石矿物组成较为简单,矿石矿物主要有辉锑矿、毒砂、黄铁矿、自然金、黝铜矿、方铅矿、闪锌矿,少量锑华、黄锑华、褐铁矿等(图5);脉石矿物主要为石英,次为白云石、方解石、绢云母、绿泥石。矿石类型以石英脉型矿石为主,其次为蚀变板岩型矿石和构造角砾岩型。石英脉型矿石,充填于断裂裂隙中,与围岩界线清楚;矿物组成主要由石英构成,其次为辉锑矿、黄铁矿和少量毒砂,部分含有少量自然金。蚀变板岩型矿石分布于断裂带两侧,与围岩呈渐变过渡关系。蚀变矿物主要为浸染状的黄铁矿、毒砂及少量粒状石英、绢云母、绿泥石等。构造角砾岩型矿石分布于构造破碎带中,由构造角砾和石英等胶结物组成。矿石的结构主要为半自形—他形柱粒状结构、细粒状结构和不等粒他形柱状结构,其次为碎裂结构、交代溶蚀结构等。矿石的构造主要为块状构造、脉状、斑块状和细脉浸染状构造,其次还有角砾状和条带状构造。

矿床围岩蚀变广泛发育,主要蚀变类型有黄铁矿化、毒砂化和硅化,其次为绿泥石化、碳酸盐化和绢云母化等,其中与金锑矿化关系紧密的主要原因是毒砂化、黄铁矿化、硅化和绢云母化等。根据矿物共生组合与元素的地球化学特点,成矿作用从早到晚划分为热液期和表生期,其中热液期又可划分为3个成矿作用阶段:石英-硫化物阶段、石英-自然金-辉锑矿阶段和石英-绿泥石阶段。

4 流体包裹体地球化学

4.1 样品的采集及分析方法

本文中用于流体包裹体测试分析的地质样品均为与金锑矿化共生的石英,其中古台山金锑矿床的地质样品采自V2号矿脉坑道内,龙王江金锑矿床的地质样品采自2号矿脉坑道内。测试工作是在中国地质大学(武汉)地质过程与矿产资源国家重点实验室流体包裹体分室完成的,测试仪器为Linkam THMS600型冷热台。其技术参数为:铂电阻传感器,控制稳定温度为±0.01°C,温度显示最低为0.01°C,测温范围为-196~600°C,样品轴向移动16 mm,光孔直径1.3 mm,加热/冷冻速率为0.01~130°C/min。相对于标准物质误差在400°C时为±2°C,-22°C时为±0.1°C。在加热/冷冻过程中控制温度速率一般为

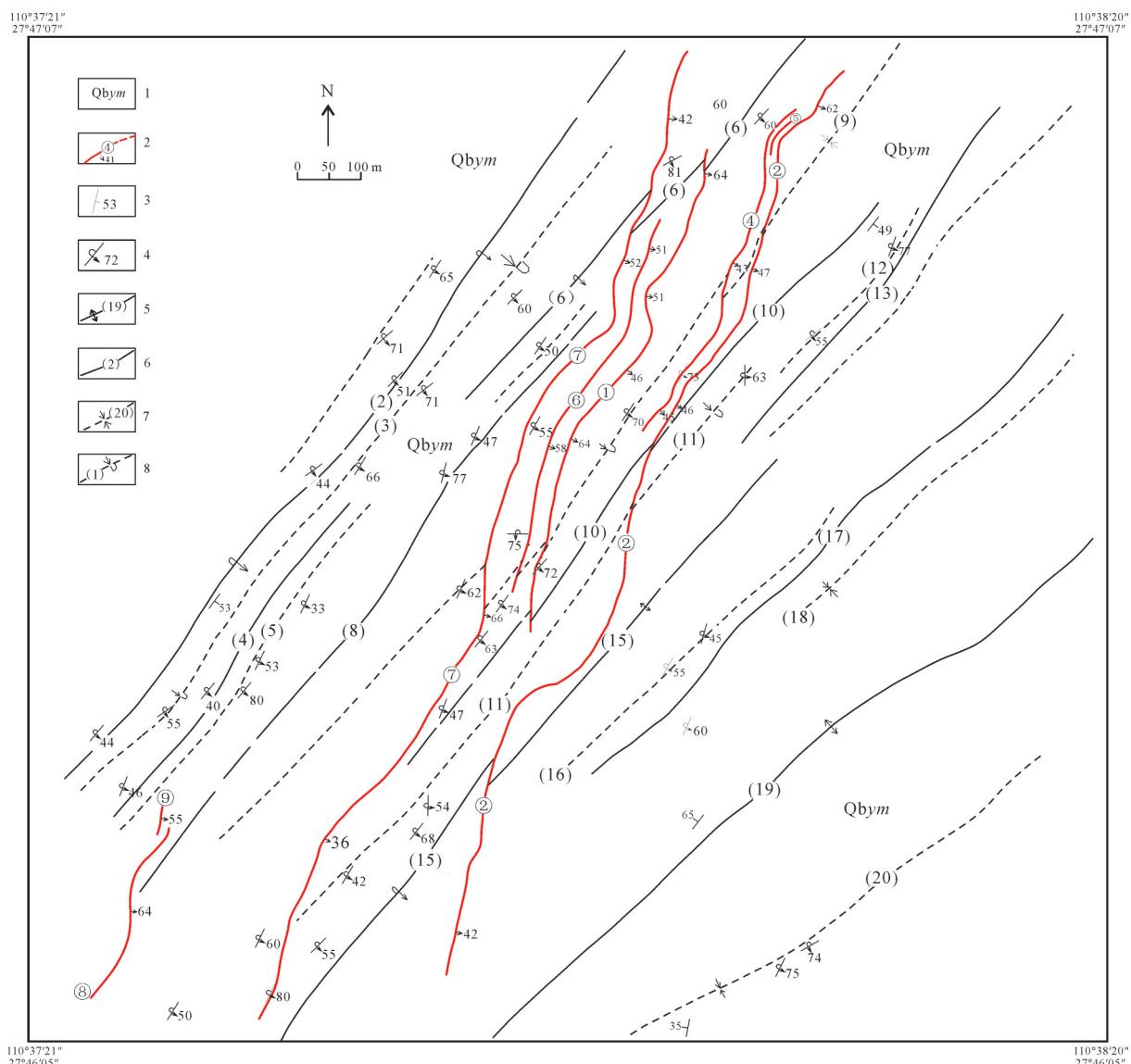


图4 龙王江金锑矿床矿区地质图

1—高涧群岩门寨组;2—实推测矿脉及编号、产状;3—岩层产状;4—倒转岩层产状;5—背斜及编号;6—倒转背斜及编号;7—向斜及编号;
8—倒转向斜及编号

Fig.4 Geological map of the Longwangjiang Au-Sb ore district

1—Yanmenzhai Formation of the Gaojian Group; 2—Vein and its serial number and attitude; 3—Formation attitude; 4—Inversion strata and attitude; 5—Anticline and its serial number; 6—Overturned anticline and its serial number; 7—Syncline and its serial number; 8—Overturned syncline and its serial number

10°C/min, 在相变点附近小于1°C/min。

4.2 包裹体岩相学特征

古台山矿床包裹体显微岩相学观察显示,石英中流体包裹体主要为原生包裹体,少量定向分布的次生包裹体。室温(25°C)条件下,原生包裹体以气液水两相包裹体为主,其次为CO₂-H₂O三相包裹体和纯液相水包裹体,少量纯气相包裹体,偶见纯CO₂

包裹体。包裹体大小不一,最小者不到1μm,最大者可达40μm,大多为3~25μm。包裹体通常呈星散状或孤立状随机分布;形态多样,主要有椭圆形、不规则多边形、长条形、三角形、长方形、负晶形、长条形、不规则状等。本文分析研究对象均为原生包裹体。各主要类型包裹体特征简要描述如下:

气液水两相包裹体:室温(25°C)下由液相水和

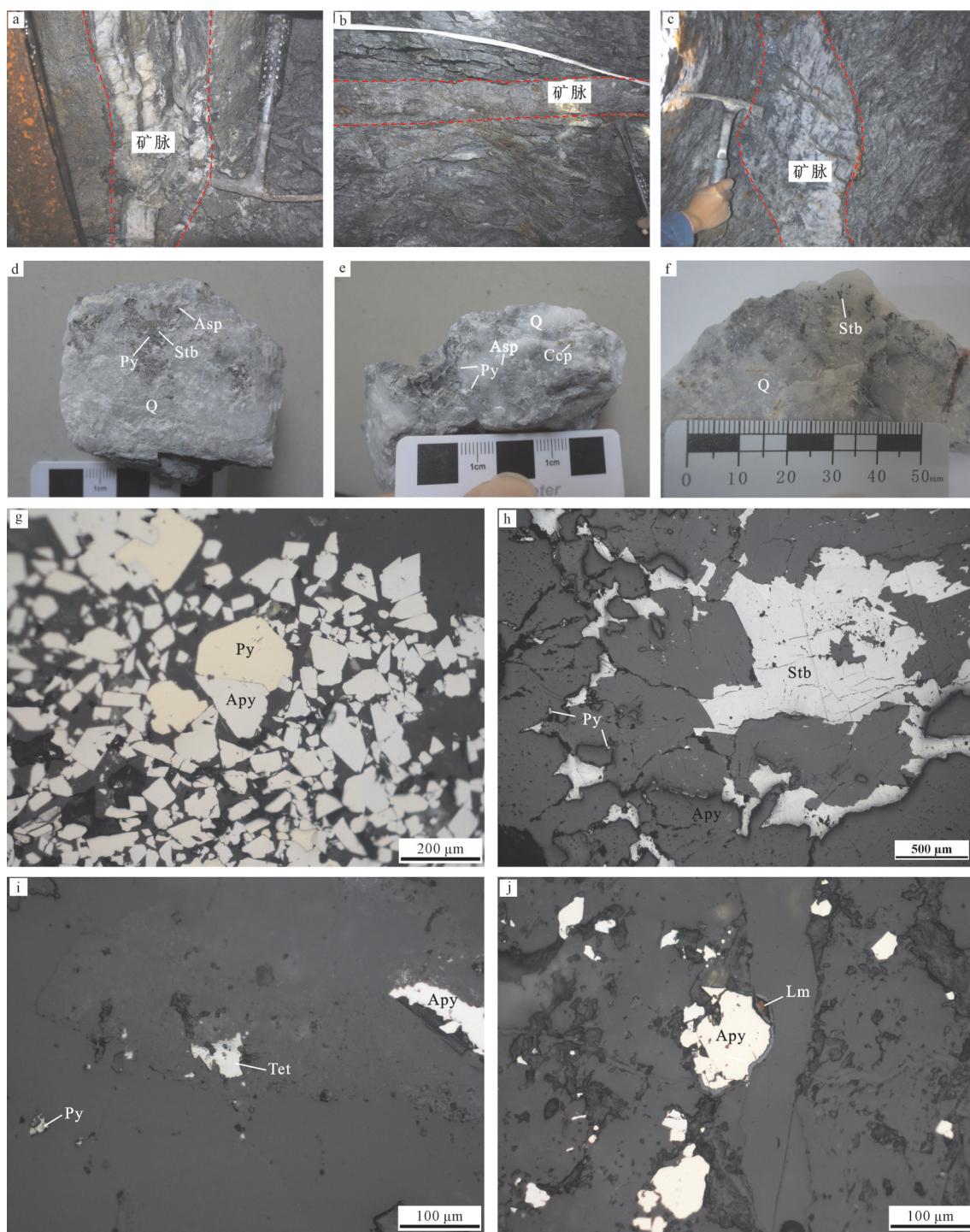


图5 龙王江金锑矿床矿脉及矿石组构照片

a, b, c—含矿石英脉；d, e, f—含矿石英，矿石中可见辉锑矿、毒砂、黄铁矿和黄铜矿等矿物共生；g—他形一半自形毒砂、黄铁矿共生；h—辉锑矿呈半自形—他形粒状结构；i—黝铜矿呈他形粒状结构；j—他形褐铁矿交代毒砂。Q—石英；Py—黄铁矿；Apy—毒砂；Stb—辉锑矿；Ccp—黄铜矿；Tet—黝铜矿；Lm—褐铁矿

Fig. 5 Ore vein and photos of ore fabric from the Longwangjiang Au-Sb deposit

a, b, c—Ore bearing quartz veins; d, e, f—Ore containing stibnite, arsenopyrite, pyrite and chalcopyrite; g—Coexistence of anhedral–subhedral arsenopyrite and pyrite; h—Anhedral–subhedral stibnite; i—Anhedral tetrahedrite; j—Arsenopyrite replaced by anhedral limonite. Q—Quartz; Py—Pyrite; Apy—Arsenopyrite; Stb—Stibnite; Ccp—Chalcopyrite; Tet—Tetrahedrite; Lm—Limonite

气相水两相组成(图6a、b、d、e、f),约占包裹体总数的80%,大小主要介于5~20 μm,气相分数主要集中于5%~35%,形态多呈椭圆形、长条形、负晶形、圆形、多边形及不规则状,加热均一至液相。

$\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体:室温(25°C)条件下表现为两相或三相($\text{L}_{\text{co}_2} + \text{L}_{\text{H}_2\text{O}} \pm \text{V}_{\text{co}_2}$),其中两相的包裹体降温后一般出现三相(图6b、c)。包裹体中 CO_2 相($\text{L}_{\text{co}_2} + \text{V}_{\text{co}_2}$)所占比例变化于15%~85%,差别较大。该类包裹体多呈椭圆形、长条形和不规则状,少量呈负晶形或三角形,大小5~25 μm,个别较大,可达40 μm。

纯液相水包裹体:室温(25°C)下包裹体为单一的液相水(图6d、f),约占包裹体总数的5%,一般较原生包裹体要小,大小主要介于1~10 μm,形态多呈椭圆形及不规则状。

纯气相包裹体:室温(25°C)下包裹体为单一的气相水(图6e、f),该类包裹体较少,大小一般1~10 μm,多呈椭圆形、长条形或不规则状。

纯 CO_2 包裹体:室温(25°C)下,包裹体表现为两相($\text{L}_{\text{co}_2} + \text{V}_{\text{co}_2}$)或单一的液相 CO_2 (图11b)。单一相降温出现气相 CO_2 。该类包裹体多呈椭圆形、长条形、不规则状或负晶形,大小一般5~15 μm。

龙王江金锑矿床包裹体显微岩相学观察显示,石英中流体包裹体主要为原生包裹体,少量次生包裹体。室温(25°C)条件下,原生包裹体以气液水两相包裹体为主,其次为纯液相水包裹体,偶见纯气相包裹体,通常呈星散状或孤立状随机分布;包裹体大小不一,最小者小于1 μm,最大者约50 μm,大多为2~25 μm;包裹体形态多样,主要有椭圆形、长条形、长方形、三角形、负晶形、长条形、多边形、不规则状等。次生包裹体常沿裂隙呈线性排列,其形态多为长条形或椭圆形。各主要类型包裹体特征简要描述如下:

气液水两相包裹体:室温(25°C)下由液相水和气相水两相组成(图7a、b、c、d),约占包裹体总数的90%,大小主要介于5~25 μm,气相分数主要集中于5%~35%,形态多呈椭圆形、长条形、负晶形、圆形、多边形及不规则状,加热均一至液相。

纯液相水包裹体:室温(25°C)下包裹体中只有液相水(图7c),约占包裹体总数的5%,一般较气液水两相包裹体要小,大小主要介于2~8 μm,形态多

呈椭圆形及不规则状。

4.3 均一温度和盐度

对古台山金锑矿床于金锑矿化共生的石英测温表明,气液水两相包裹体均一温度为198.9~298.3°C,平均233.3°C(图8)。测得冰点温度范围-7.8~-1.2°C,平均-3.7°C;根据冰点温度,利用Potter et al. (1978)提出的盐度公式计算盐度为2.07%~11.46% NaCl_{eqv} ,平均5.93% NaCl_{eqv} ; $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体均一温度为236.1~282.4°C,平均259.4°C。测得 CO_2 笼合物熔化温度为7.2~8.9°C,平均8.2°C;根据 CO_2 笼合物熔化温度,利用Collins(1979)提出的盐度公式获得盐度为2.22%~5.41% NaCl_{eqv} ,平均3.48% NaCl_{eqv} (表1)。

对龙王江金锑矿床矿化阶段共生的石英中原生包裹体测温表明,气液水两相包裹体均一温度为163.9~237.6°C,平均196.5°C。测得冰点温度为-5.4~-0.8°C,平均-3.39°C;根据冰点温度换算成盐度为1.40~8.41% NaCl_{eqv} ,平均5.49% NaCl_{eqv} (图9,表1)。

4.4 流体的密度和压力

气液水两相包裹体密度根据刘斌和段光贤(1987)提出的密度式计算, $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体密度利用Shepherd(1985)的相图进行估算。计算得出古台山金锑矿床成矿阶段气液水两相包裹体密度为0.78~0.91 g/cm³, $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体密度为0.79~0.90 g/cm³;龙王江气液水两相包裹体密度变化范围0.84~0.95 g/cm³,平均0.91 g/cm³(表2)。

古台山金锑矿床成矿流体富含 CO_2 ,流体可以近似看成 $\text{CO}_2\text{-H}_2\text{O-NaCl}$ 体系,包裹体的捕获压力利用Flincor软件(Brown, 1989; Brown and Lamb, 1989)计算。计算得出包裹体捕获压力分别为98.0~193.2 Mpa,平均135.5 Mpa。结果详见表2。

龙王江金锑矿床成矿流体压力依据 $\text{NaCl-H}_2\text{O}$ 溶液包裹体压力公式(邵洁涟和梅建明,1986)计算,得出矿床成矿压力范围11.40~21.56 MPa,平均16.85 Ma。结果详见表2。

4.5 成矿流体的成分

古台山金锑矿床激光拉曼分析结果表明,包裹体液相成分主要为 H_2O ,气相成分主要为 H_2O 、 CO_2 及少量 CH_4 和 N_2 (李伟等,2016)。由包裹体测温数据可知不同阶段包裹体中 CO_2 三相包裹体的固相融

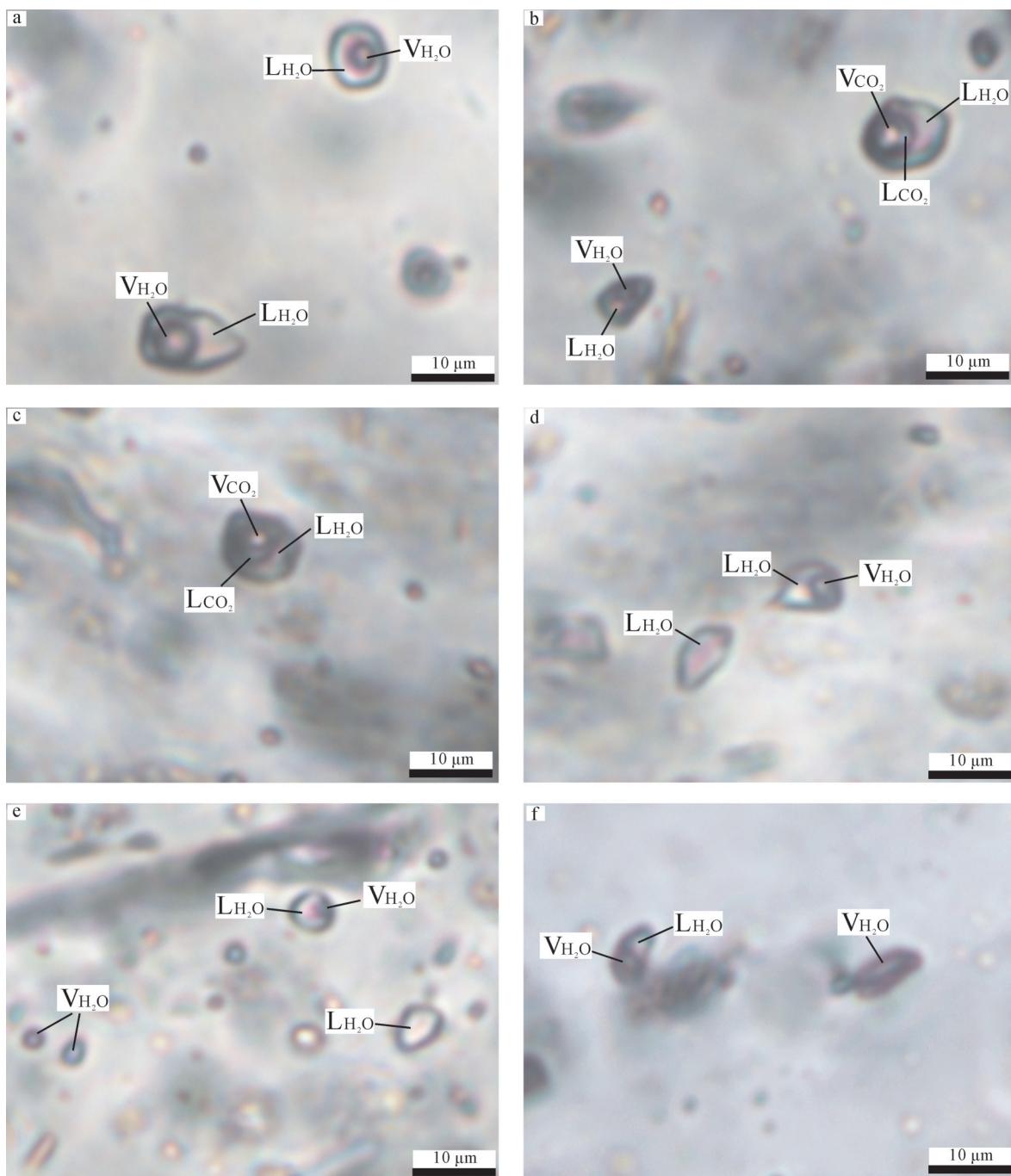


图6 古台山金锑矿床流体包裹体显微照片

a—气液水两相包裹体;b—气液水两相包裹体和CO₂-H₂O三相包裹体;c—CO₂-H₂O三相包裹体;d—气液水两相包裹体和纯液相水包裹体;
e—气液水两相包裹体、纯液相包裹体和纯气相包裹体;f—气液水包裹体和纯气相包裹体

Fig. 6 Microphotographs of fluid inclusions in quartz from the Gutaishan gold-antimony deposit

a—Liquid-vapor two-phase aqueous inclusions; b—Coexistence of liquid-vapor two-phase aqueous inclusions and CO₂-H₂O three-phase inclusions; c—CO₂-H₂O three-phase inclusions; d—Coexistence of liquid-vapor two-phase aqueous inclusions and monophase liquid inclusions; e—Coexistence of liquid-vapor two-phase aqueous inclusions with monophase liquid inclusions and vapor aqueous inclusions; f—Coexistence of liquid-vapor two-phase aqueous inclusions and vapor aqueous inclusions

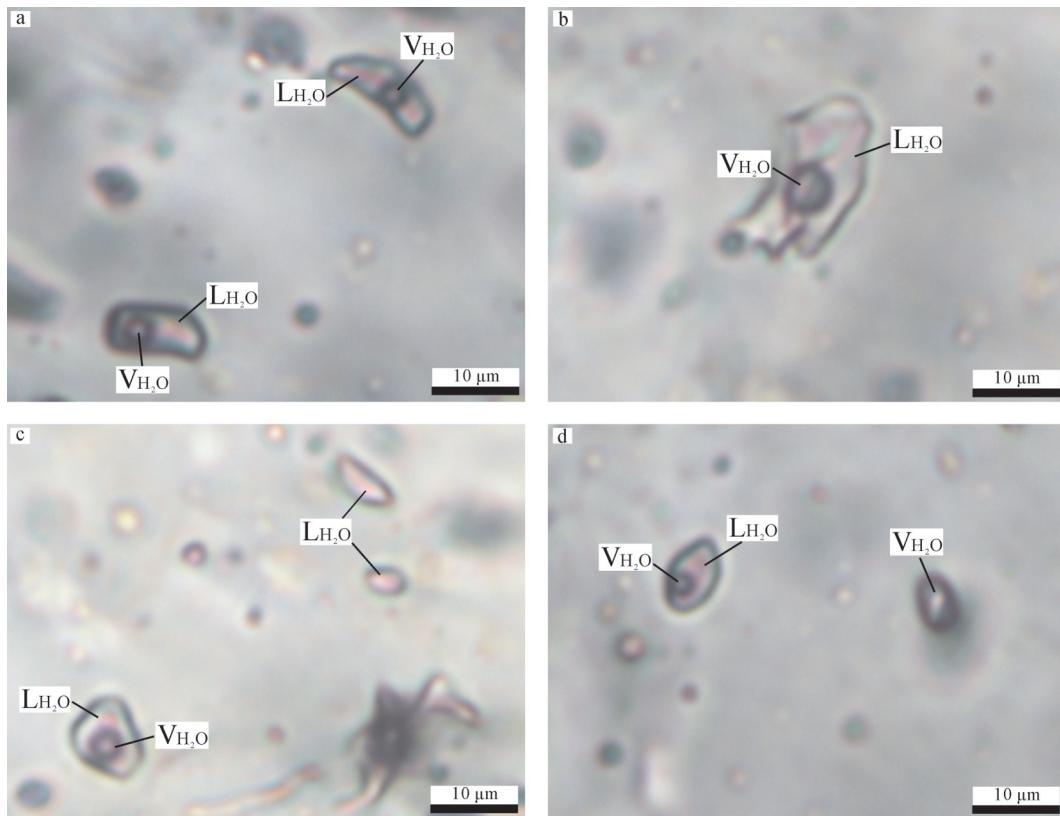


图7 龙王江金锑矿床流体包裹体岩显微照片

a、b—气液水两相包裹体; c—气液水两相包裹体与纯液相水包裹体共生; d—气液水两相包裹体与纯气相包裹体共生

Fig. 7 Microphotographs of fluid inclusions in quartz from the Longwangjiang gold-antimony deposit

a,b—Liquid-vapor two-phase aqueous inclusions; c—Coexistence of liquid-vapor two-phase aqueous inclusions and monophase liquid inclusions;
d—Coexistence of liquid-vapor two-phase aqueous inclusions and vapor aqueous inclusions

化温度低于纯CO₂包裹体的冰点(-56.5°C),表明气相成分中含一定量的CH₄、N₂等组分,这也与激光拉曼测定出包裹体中含有CH₄、N₂等组分相吻合。

龙王江金锑矿床矿物包裹体分析结果表明,成

矿溶液成分液相以Na⁺、K⁺、Cl⁻(F⁻)、SO₄²⁻为主,气相成分除H₂O外,以CO₂、N₂、CO为主,H₂、CH₄亦有较高含量。在离子中Ca²⁺、Na⁺占优势,可以确定含矿溶液以富碱金属为特征,成矿阶段的CO₂含量

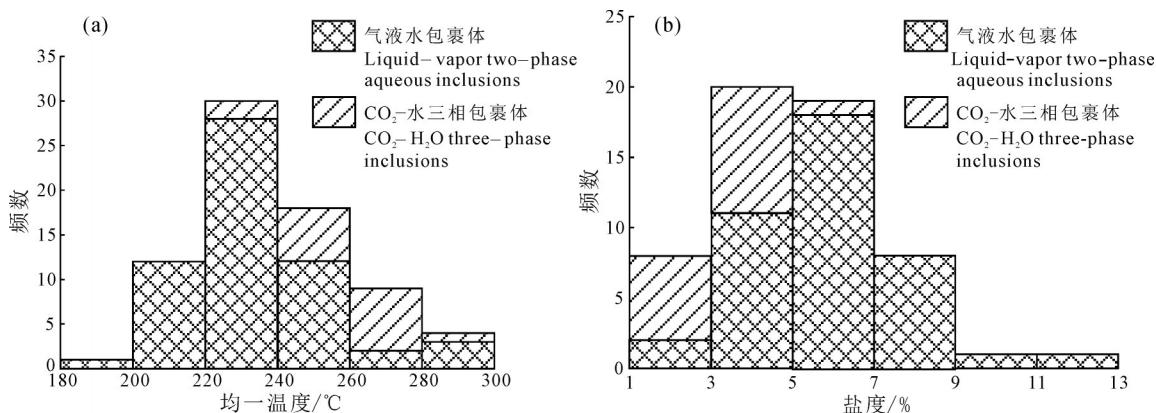


图8 古台山金锑矿床流体包裹体均一温度和盐度频率直方图

Fig. 8 Histogram showing homogenization temperatures (a) and salinities (b) of fluid inclusions from the Gutaishan gold-antimony deposit

Table 1 Homogenization temperature and salinity date of fluid inclusions from the Gutaishan and the Longwagnjiang gold–antimony deposit

矿床名称	包裹体类型	T_{m, CO_2} /°C	$T_{m, \text{NaCl}}$ /°C	T_{h, CO_2} /°C	$T_{m, \text{ice}}$ /°C	$T_{h, \text{tot}}$ /°C	盐度 NaCl _{eqv} /‰
		范围(测定数)	均值	范围(测定数)	均值	范围(测定数)	
古台山	气液水两相包裹体	-7.8~1.3(41)	-1.3(41)	-7.8~1.3(41)	-3.7	198.9~298.3(58)	233.3 2.07~11.46(41) 5.93
	CO ₂ -H ₂ O三相包裹体	236.1~282.4(16)	22.2	236.1~282.4(16)	259.4	2.2~5.33(14)	3.43
龙王江	纯CO ₂ 包裹体	18.2(1)	18.2	164~238(61)	196.5	1.40~8.41(40)	5.49

注： T_{m, CO_2} —CO₂固相熔化温度； $T_{m, \text{NaCl}}$ —CO₂笼合物融化温度； T_{h, CO_2} —CO₂部分均一温度； $T_{m, \text{ice}}$ —冰点温度； $T_{h, \text{tot}}$ —完全均一温度。

表2 古台山金锑矿床和龙王江金锑矿床流体包裹体密度和压力和结果

Table 2 Density and pressure date of fluid inclusions from the Gutaishan and the Longwagnjiang gold–antimony deposit

矿床	包裹体类型	密度/(g/cm ³)		压力/MPa	
		范围(测定数)	均值	范围(测定数)	均值
古台山	气液水两相包裹体	0.78~0.91(41)	0.87		
	CO ₂ -H ₂ O三相包裹体	0.79~0.90(14)	0.84	98.0~193.2/14	135.5
龙王江	气液水两相包裹体	0.84~0.95(40)	0.91	11.40~21.56(40)	16.85

表3 古台山金锑矿床氢、氧同位素组成

Table 3 Hydrogen and oxygen isotopic compositions from the Gutaishan gold–antimony deposit

样品号	$\delta^{18}\text{O}_{\text{V-SMOW}}/\text{\textperthousand}$	$\delta\text{D}_{\text{V-SMOW}}/\text{\textperthousand}$	$\delta^{18}\text{O}_{\text{H}_2\text{O}}/\text{\textperthousand}$	资料来源
GTS-1	14.4	-52.00	4.80	
GTS-2	16.1	-57.00	6.50	
GTS-3	17	-47.00	7.40	本文
GTS-4	16.7	-48.00	7.10	
GTS-5	13.8	-63.00	4.20	
GTS-6	14.8	-59.00	5.20	
GTS-119	16.8	-71.00	8.30	
GTS-126	15.6	-61.00	4.50	
GTS-156	16.9	-66.00	8.10	
GTS-109	15.9	-63.00	7.10	
GTS-114	16.5	-52.00	7.00	
GTS-137	16.4	-66.00	6.20	
GTS-160	16.3	-72.00	7.40	李伟等, 2016
GTS-107	17.6	-78.00	8.10	
GTS-113	16.7	-60.00	7.60	
GTS-115	17.1	-76.00	8.00	
GTS-135	17.3	-49.00	6.90	
GTS-139	17.2	-70.00	7.80	
GTS-143	17.9	-69.00	7.10	
GTS-147	16.2	-60.00	5.60	

高,反映出具有高含量的CO₂组分的矿化剂对金的富集和成矿起了很大作用。成金阶段SO₄²⁻含量较高,这与含金矿石中出现较多的硫(砷)化物吻合。由此看出,成矿流体属于一种富CO₂的NaCl-H₂O体系(鲍肖和陈放,1996)。

5 氢氧同位素研究

5.1 样品的采集及分析方法

用于氢、氧同位素测试的样品为古台山金锑矿区金矿化共生的石英,均采自坑道内的V2号脉。首先将石英样品逐级破碎至40~60目,过筛后在双目镜下挑选出纯度大于98%的单矿物样品,然后将其研磨至200目以下,以供实验室测试分析。

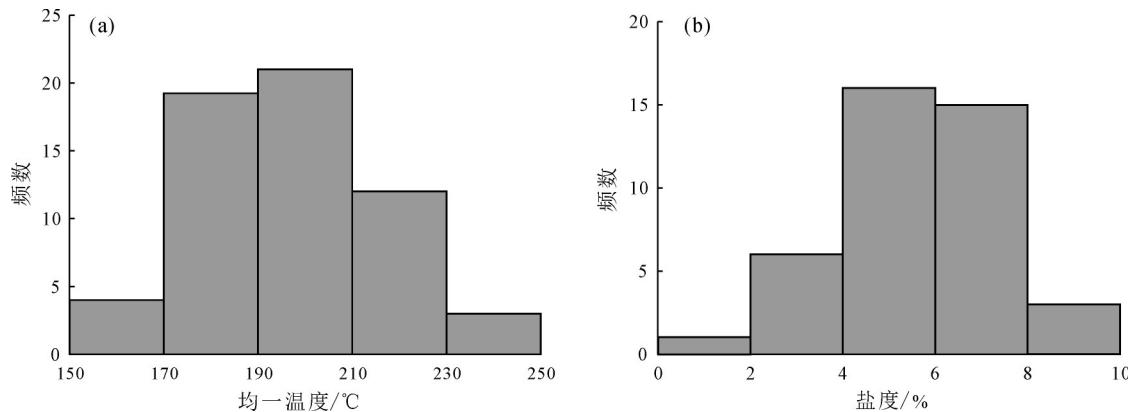


图9 龙王江金锑矿床流体包裹体均一温度和盐度频数直方图

Fig. 9 Histogram showing homogenization temperatures (a) and salinities (b) of fluid inclusions from the Longwangjiang gold-sulfide deposit

测试工作是在澳石分析检测(广州)有限公司完成的。H同位素测定所用仪器为Thermo-Finnigan Delta^{plus} XP连续气流同位素质谱仪,测试方法:称取约2 mg样品装入5 mm×3.5 mm的银舟中,于100°C除气1 h,然后转入与高温热解炉相连的自动进样器。样品在石墨坩埚中于还原条件下燃烧(1450°C),析出的H₂O转化为H₂,再通过PORAPLOT-Q气相色谱柱把H₂分离出来,然后采用Thermo-Finnigan同位素比值质谱仪(型号Delta^{plus} XP)进行测定同位素比值²H/H,数据基于V-SMOW国际标准水样标准化,报δD值或δH(‰),典型的测试精密度为SD<3‰。O同位素测试仪器为Finnigan MAT252稳定同位素比质谱仪,按照Clayton and Mayeda(1963)所描述的BrF₅提取氧的流程、采用Finnigan MAT252稳定同位素比质谱仪测定氧同位素。称取约5 mg样品与BrF₅于550~600°C条件下进行氧化还原反应12 h以上,收集析出的氧,经过高温的石墨棒转化为CO₂,然后采用“Finnigan MAT252稳定同位素比值质谱仪”测定氧同位素比值¹⁸O/¹⁶O,数据基于V-SMOW国际标准水样标准化,报为δ¹⁸O值(‰),典型的测试精密度为SD<0.3‰。

5.2 氢氧同位素特征

为了更好研究矿区成矿流体的来源,笔者在古台山金锑矿区采集6件与金矿化共生的石英进行氢、氧同位素测试。结果显示,古台山金锑矿床δ¹⁸O_{矿物}变化范围13.8‰~16.7‰,δD_{V-SMOW}变化范围-63‰~-52‰(表3);根据流体包裹体显微测温的平

均温度236.8°C,采用石英-水氧同位素分馏方程1000lnα_{石英-水}=3.38×106/T²-3.4(Clayton et al., 1972)获得δ¹⁸O_{H₂O}‰变化范围4.2‰~7.4‰。在δ¹⁸O-δD同位素关系图上(图10),样品大多数落在了原生岩浆水和变质水范围,远离大气降水,暗示成矿流体可能主要为变质水和岩浆水的混合流体。

鲍肖和陈放(1996)获得龙王江矿区矿石石英的δ¹⁸O值平均为16.02‰(3件),与地层的δ¹⁸O值16.37‰极为相近,一定程度上说明石英中的流体和地层流体具有同源性,且求得的δ¹⁸O_{H₂O}‰的均值为9.63‰,说明成矿流体具有变质流体氧同位素的组成特点。氢、氧同位素研究资料显示,矿区石英δ¹⁸O同位素为16.10‰~18.30‰,可计算出矿区对应成矿流体的氧同位素组成为4.62‰~9.21‰,石英中流体包裹体的δD为-55‰~-18‰(顾然,2015)。在δ¹⁸O_{H₂O}-δD关系图上,发现大多数投影点落在变质水范围内(图10)。另外,陈方楠(2015)在对龙王江矿床成矿期石英进行流体包裹体研究时,发现存在有CO₂-H₂O三相包裹体。流体包裹体成分分析也表明,包裹体气相成分除H₂O以外主,其CO₂含量较高(鲍肖和陈放,1996;鲍振襄,1996;陈方楠,2015),显示出变质水的特点。这与氢、氧同位素研究指示龙王江金锑矿床成矿流体来源主要为变质水相符。

6 讨论

6.1 成矿流体的性质

古台山金锑矿床成矿期与金共生的石英流体

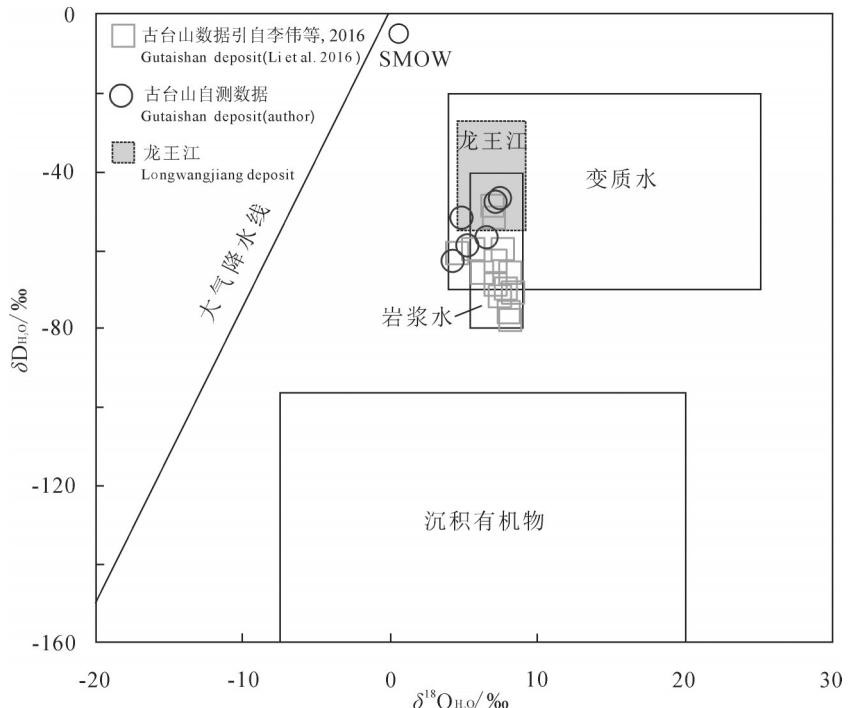


图10 古台山金锑矿床和龙王江金锑矿床成矿流体 $\delta^{18}\text{O}-\delta\text{D}$ 同位素关系图(底图据Sheppard, 1986; Goldfarb et al., 2004修改)
Fig. 10 Plot of $\delta^{18}\text{O}-\delta\text{D}$ for ore-forming fluids in the Gutaishan and the Longwangjiang gold-antimony deposit (modified after Sheppard, 1986; Goldfarb et al., 2004)

包裹体研究显示,气液水两相包裹体和CO₂-H₂O三相包裹体完全均一温度分别为198.9~298.3°C(平均233.3°C)和236.1~282.4°C(平均259.4°C),相应的盐度为2.07%~11.46%NaCl_{eqv}(平均5.93%NaCl_{eqv})和2.2%~5.33%NaCl_{eqv}(平均3.43%NaCl_{eqv})。结果显示,气液水两相包裹体盐度较CO₂-H₂O三相包裹体盐度高,这可能是因流体中含一定量的CO₂成分,导致测定的冰点值偏低(Hedenquist and Henley, 1985)。根据偏低的冰点值,按NaCl-H₂O体系计算出的盐度则高于实际值。显微测温结果表明,成矿期流体具中温、低盐度的特征。激光拉曼分析结果表明,包裹体液相成分主要为H₂O,气相成分主要为H₂O、CO₂及少量CH₄和N₂。综合认为,古台山金锑矿床成矿期流体总体属中温、低盐度的CO₂-NaCl-H₂O体系。

龙王江金锑矿床成矿期与金锑共生的石英流体包裹体研究显示,气液水两相包裹体完全均一温度为163.9~237.6°C(平均196.5°C),相应的盐度为1.40%~8.41%NaCl_{eqv}(平均5.49%NaCl_{eqv}),表明成矿期流体具中低温、低盐度的特征。包裹体群体分析结果表明,成矿溶液成分液相以Na⁺、K⁺、Cl⁻

(F⁻)、SO₄²⁻为主,气相成分除H₂O外,以CO₂、N₂、CO为主,含少量的H₂、CH₄。本次包裹体岩相学观察未发现CO₂-H₂O三相包裹体,说明龙王江金锑矿床成矿流体中CO₂含量较古台山金锑矿床要低。综合认为,龙王江金锑矿床成矿期流体总体属中低温、低盐度、富CO₂的NaCl-H₂O体系。

6.2 成矿流体的来源

古台山金锑矿床成矿流体的H-O同位素组成, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ 变化范围4.2‰~7.4‰, $\delta\text{D}_{\text{H}_2\text{O}}$ 变化范围-63‰~-52‰;在 $\delta^{18}\text{O}-\delta\text{D}$ 同位素关系图上,样品大多数落在了原生岩浆水和变质水范围,暗示成矿流体主要为岩浆水和变质水的混合流体。C-O同位素研究资料显示,铁白云石 $\delta^{13}\text{C}_{\text{V-PDB}}$ 分布范围为-10.3‰~-8.6‰, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ 分布范围6.55‰~8.05‰(李伟等, 2016)。暗示成矿流体中的碳属于与岩浆有关的深源碳(-9‰~-3‰, Taylor and McLennan, 1985),很可能来源于岩浆的CO₂去气作用; $\delta^{18}\text{O}$ 则分布在岩浆水(5.5‰~10.0‰; Hoefs, 2009)和变质水的范围。据Li et al. (2018)对古台山金锑矿床与金矿化共生的白云母进行Ar-Ar同位素定年,获得成矿年龄为223.6±5.3 Ma,与白马山岩体成岩时代(223~204

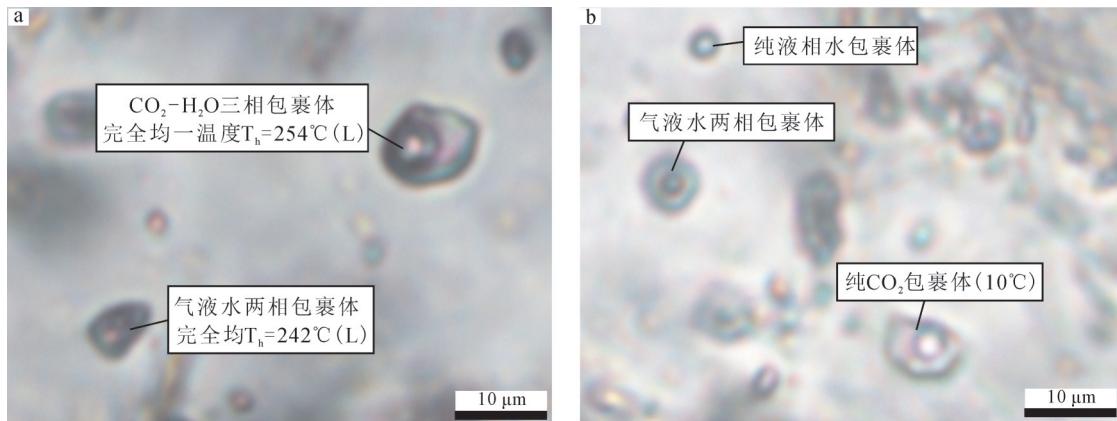


图11 古台山矿床不混溶包裹体群镜下特征

a— $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体与气液水两相包裹体在同一视域下共存,且两者完全均一温度相近;b—纯 CO_2 包裹体与气液水两相包裹体、纯液相水包裹体在同一视域下共存

Fig.11 Microscopic characteristics of immiscible inclusion groups from the Gutaishan gold-antimony deposit

a—Coexistence of $\text{CO}_2\text{-H}_2\text{O}$ three-phase inclusions and liquid-vapor two-phase aqueous inclusions, and two kinds of fluid inclusions have similar homogenization temperatures; b—Coexistence of pure CO_2 inclusions with liquid-vapor two-phase aqueous inclusions and vapor aqueous inclusions

Ma)相当,表明矿床形成于印支期,与白马山岩体密切相关。白马山岩体很可能为古台山金锑矿床的形成提供了岩浆流体,这也与位于白马山岩体周边的大坪金矿床和铲子坪金矿床的研究结果一致(骆学全,1993;李华芹等,2008;曹有金等,2014;曹亮等,2015a,b;马小双,2016)。综合认为,古台山金锑矿床成矿流体主要为岩浆水和变质水的混合流体。

龙王江金锑矿床H-O同位素研究资料显示,成矿流体的 $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ 组成为 $4.62\text{\textperthousand} \sim <9.21\text{\textperthousand}$, $\delta\text{D}_{\text{H}_2\text{O}}$ 为 $-55\text{\textperthousand} \sim -18\text{\textperthousand}$,主体显示出变质水的特征,不排除有部分大气降水的加入。包裹体成分分析显示,成矿流体中富含 CO_2 成分,具变质流体的特征。综合认为,龙王江金锑矿床成矿流体主要来源于变质水。

6.3 金的沉淀机制

前人研究表明,流体不混溶(沸腾)作用、水-岩反映、温度或(和)压力的变化及流体的混合作用等是导致成矿流体中金属沉淀的主要机制,广泛发生于国内外的许多矿床中(Gustafson and Hunt, 1975; Rodder, 1984; 华仁民, 1994; 张文淮等, 1996; 张德会, 1997; Hedenquist et al., 1998; 李福春等, 1999; Gu et al., 2003; Calagari, 2004; 刘军等, 2012; 周超等, 2014; 门兰静等, 2018)。

古台山金锑矿床成矿期石英中广泛发育流体不混溶作用,来自流体包裹体特征方面的证据有:

①成矿期与金矿化共生的石英中气液水两相包裹

体、纯液相包裹体与 $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体、纯 CO_2 包裹体在同一视域下密切共生(图11a,b);② $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体中 CO_2 相($\text{L}_{\text{co}_2} + \text{V}_{\text{co}_2}$)所占比例变化于15%~85%,差别较大;③ $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体完全均一方式各异,即均一成液相 H_2O 和均一成液相 CO_2 ,且均一温度相近;④气液水两相包裹体与 $\text{CO}_2\text{-H}_2\text{O}$ 三相包裹体完全均一温度相近(图11a,b)。

综上证据说明这些流体包裹体是从非均匀流体中捕获的,表明古台山金锑矿床成矿流体经历了不混溶作用(卢焕章等, 2004)。研究表明, CO_2 流体与Au成矿有着非常密切的联系。由于Au和 H_2S 之间的化学键相对于Au和 CO_2 之间的化学键较强,因此,Au在富含 CO_2 的成矿溶液中多以 $\text{Au}(\text{HS})_2^-$ 络合物形式迁移。 $\text{Au}(\text{HS})_2^-$ 络合物在溶液中的溶解度与pH值关系密切,当 $\text{Au}(\text{HS})_2^-$ 溶解度最大时,溶液pH值近中性(沈阳等, 2010; 章永梅, 2012)。成矿过程中, CO_2 作为一种弱酸对成矿流体的pH值调节起到很大的作用,它的大量存在提高了Au在流体中的溶解度并使其维持还原硫的络合作用进行迁移(Phillips and Evans, 2004; 卢焕章, 2008)。当成矿流体发生 $\text{H}_2\text{O}-\text{CO}_2$ 不混溶时,大量 CO_2 从成矿流体中溢出,致使成矿溶液的 CO_2 逸度(f_{co_2})和 O_2 逸度(f_{o_2})降低,pH值升高(李保华等, 2011)。同时伴随温度的下降,Au在成矿溶液中的溶解度急剧下降,从而快速沉淀富集成矿。

龙王江金锑矿床流体包裹体显微岩相学观察,未发现不混溶包裹体群的存在,暗示流体不混溶作用导致Au、Sb沉淀的可能性较小。龙王江金锑矿床位于区域性脆韧性剪切带上,成矿严格受剪切带控制,Au、Sb的沉淀机制可以简述为:前寒武纪,新元古代形成的冷家溪群弧后盆地火山-沉积碎屑岩和板溪群(高涧群)裂谷碎屑岩,造就了Au、Sb成矿元素的初始富集;区域变质作用阶段,区内地层变质脱水形成的含Au、Sb元素变质流体,运移过程中不断淋滤地层中的成矿元素;并以络合物形式沿区域脆-韧性剪切带上升至浅部,由于温度和压力的变化,或大气降水的加入,导致Au、Sb的大量沉淀,在脆-韧性构造层次形成龙王江金锑矿床。

7 结 论

(1)古台山金锑矿床成矿期石英中流体包裹体以气液水两相包裹体和CO₂-H₂O三相包裹体为主。流体包裹体显微测温和成分分析表明,流体富含CO₂,并有一定量的CH₄和N₂,成矿流体属于中温、低盐度的CO₂-NaCl-H₂O体系。

(2)龙王江金锑矿床成矿期石英中流体包裹体以气液水两相包裹体为主。流体包裹体显微测温和成分分析表明,流体含一定量的CO₂,成矿流体属于中低温、低盐度、富CO₂的NaCl-H₂O体系。

(3)氢氧同位素研究表明,古台山金锑矿床成矿流体来源主要为岩浆水和变质水的混合流体。龙王江金锑矿床成矿流体主要来源于变质水。

(4)流体包裹体岩相学观察和显微测温表明,古台山金锑矿床成矿期流体发生了不混溶作用,认为流体不混溶是导致古台山矿区矿质沉淀的主要机制;龙王江金锑矿床成矿流体不混溶作用不明显,矿质沉淀很可能是温度和(或)压力的变化,或大气降水的加入(混合)所导致。

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