

太行山南段洪山沟铜金矿床白云母和绿泥石特征及其找矿意义

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摘要: 洪山沟斑岩型铜金矿床是洪山多金属成矿区的典型矿床, 位于华北克拉通中部南缘山前断隆武安凹陷区, 矿体主要赋存于洪山正长斑岩体内。矿化中心及外围白云母和绿泥石十分发育。为探讨洪山沟铜金矿床白云母和绿泥石的成岩成矿意义, 运用电子探针(EPMA)、激光剥蚀电感耦合等离子体质谱(LA-ICP-MS)分析了矿床中不同产状和成矿阶段的白云母和绿泥石。结果显示, 矿区内绿泥石根据其分布特征可分为3类: 与金属矿物共(伴)生的绿泥石(Chl-1)、由角闪石蚀变而成的绿泥石(Chl-2)及由黑云母蚀变而成的绿泥石(Chl-3)。3种绿泥石均为Fe绿泥石, 指示形成于还原环境, 其结构中存在Fe对Mg的置换以及Si对Al^{IV}的置换, 表明绿泥石的形成受富Fe、Mg的成矿流体影响, 由地质温度计计算出的绿泥石形成温度在112~272℃之间, 属于中-低温热液蚀变范围。LA-ICP-MS结果显示完全蚀变的绿泥石更富Cu、S、Rb、Zn、Ti、Ga、V、Co、Ni、Sn; 白云母主要有原生白云母(Ms-1)与次生白云母(Ms-2)两类, 分别属于普通白云母和多硅白云母。与矿化密切相关的白云母具高Si、Fe、低Al的特征, LA-ICP-MS结果显示还原环境下形成的白云母, 氧化环境下形成的白云母更富V、W, 暗示流体后期有大气降水的混入。综合本文研究成果认为, 洪山沟铜金矿床成矿流体早期呈酸性, 后期有大气降水的混入并逐渐向中性转变, 铜金矿化成矿环境为近中性-还原的中-低温环境, 成矿流体富Fe、Mg, 贫Si。

关键词: 白云母; 绿泥石; 电子探针; 洪山沟铜金矿床; 华北克拉通

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Characteristics of muscovite and chlorite in Hongshangou copper-gold deposit and its prospecting significance

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Abstract: The Hongshangou porphyry copper-gold deposit is a typical deposit in the Hongshan polymetallic metallogenic area. It is located in the Wu'an depression of Shanxi fault uplift in the southern margin of the central North China Craton. The ore body mainly occurs in the Hongshan syenite porphyry. Muscovite and chlorite are well developed in the mineralization center and periphery. In order to discuss the diagenesis and mineralization significance of muscovite and chlorite in Hongshangou copper-gold deposit, electron probe microanalysis (EPMA) was used to analyze muscovite and chlorite in different occurrences and metallogenic stages of the deposit. The results show that the distribution characteristics of chlorite in the mining area can be divided into three categories: chlorite associated with metal minerals (Chl-1), chlorite altered from hornblende (Chl-2) and chlorite altered from biotite (Chl-3). The three chlorites are all Fe chlorites, indicating that they were formed in a reducing environment. The replacement of Fe to Mg and the replacement of Si to Al^{IV} in the structure indicate that the formation of chlorites is affected by Fe- and Mg-rich ore-forming fluids. The formation temperature of chlorite calculated by geological thermometer is between 112~272°C, which belongs to the range of medium-low temperature hydrothermal alteration, LA-ICP-MS results show that the completely altered chlorite is richer in Cu, Sn, Rb, Zn, Ti, U, Sr, V, Co, Ni and Sn. Muscovite mainly includes primary muscovite (Ms-1) and secondary muscovite (Ms-2), which belong to ordinary muscovite and polysilicic muscovite respectively. The muscovite closely related to mineralization has the characteristics of high Si, Fe and low Al, LA-ICP-MS results show that the muscovite formed in the reducing environment is richer in V and W than the muscovite formed in the oxidizing environment, suggesting the mixing of meteoric water in the later stage of the fluid. Based on the research results of this paper, the ore-forming fluid of Hongshangou copper-gold deposit is acidic in the early stage and gradually changes to neutral in the later stage. The ore-forming environment of copper-gold deposit is near neutral and reduced medium-low temperature environment. The ore-forming fluid is rich in Fe, Mg and poor in Si.

Key words: muscovite; chlorite; electron probe microanalysis; Hongshangou porphyry copper-gold deposit; North China Craton

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绿泥石为含水层状铁-镁-铝硅酸盐矿物,形成于高-中-低变质作用、成岩作用和热液蚀变作用等各种地质环境中(Wiewióra and Weiss, 1990; Zane and Weiss, 1998; Li *et al.*, 2022),在自然界中广泛分布,与铜、金、铀等多金属矿床成矿作用密切相关(张展适等, 2007; 王小雨等, 2014; Basori *et al.*, 2022; Feng *et al.*, 2022; 曾淑明等, 2023)。不同成因的绿泥石的成分有较大差异,通过分析其化学成分能够反演形成时所处环境的物理化学条件。Cathelineau (1988)在分析绿泥石的成分和温度之间的关系时发现绿泥石中的 Al^{IV} 含量与其形成时温度存在正相关性,由此提出绿泥石固溶体温度计。近年来,国内外学者对绿泥石的形成环境、机制与温度进行了大量研究,探讨绿泥石与多金属矿床矿化之间的关系并取得大量成果(赵友东等, 2016; Xiao *et al.*, 2018; Wu *et al.*, 2019; Zhang *et al.*, 2020)。

白云母是具有二八面体的层状硅酸盐矿物,在斑岩型矿床、矽卡岩型矿床等矿床中广泛发育,是热液作用过程的产物(Keppler, 1993; Černý *et al.*, 2003; 马万伟等, 2020)。白云母由于其结构的特殊性会发生类质同象替换,包括 Tschermark 替换($\text{Al}^{\text{IV}} \Leftrightarrow \text{Si} = \text{Al}^{\text{VI}} \Leftrightarrow \text{Fe} + \text{Mg}$)及层间 $\text{Na}^+ + \text{Ca}^{2+} \Leftrightarrow \text{K}^+$ 替换(Thompson *et al.*, 2009),其种类、结构特征以及矿物地球化学特征可以指示流体演化程度及过程(Neiva, 2013; Laakso *et al.*, 2016; Schirra *et al.*, 2022; 付建刚等, 2023; 楚翔凯等, 2023),因此,通过研究白云母化学成分及结构有助于了解各类型矿床的成矿流体演化与成矿过程(Tischendorf *et al.*, 1997; Li *et al.*, 2015; Legros *et al.*, 2018; Yin *et al.*, 2019; 王葆华等, 2021)。

太行山南段是我国东部重要的金属成矿区,构造上位于大兴安岭-太行山构造岩浆带南段(权瑞等, 2016)。中生代大规模构造-岩浆活动到燕山期造山过程中的大规模岩浆活动使区内形成一系列碱性-钙碱性侵入岩,为形成金属矿床提供了条件(翟明国等, 2005; 吴福元等, 2008; 张海东等, 2014; 息朝庄等, 2021)。受印支期古西伯利亚板块向南俯冲、古扬子板块向北仰冲与燕山期太平洋板块向西俯冲的影响,我国东部处于强拉应力区,导致区内断裂与褶皱均发育,西部北北东向紫山-鼓山大断裂以及北东向褶皱为区内主要容矿构造(刘昕曜, 2016)。该区地层剖面较为完整,依次为太古宇下赞皇群,中元古界长城系,古生界寒武系、奥陶系、石炭系、二叠系,中生界三叠系、白垩系,新生界古近系及第四系(刘昕曜, 2016)。前人研究表明,洪山岩体分3次岩浆活动:第1次为火山喷发活动,形成一套粗面质火山岩系;第2次为岩浆侵入,主要形成辉石(角闪)正长岩系列;第3次为钙碱性系列岩石大规模侵入,形成以浅色正长岩为主的洪山岩体的主体。洪山沟铜矿化的发生应与正长斑岩侵位后的岩浆热液活动有关(李玉成等, 2016; 李随民等, 2022)。

斑岩型矿床是产于岩浆弧与陆缘弧环境、成因上与中酸性浅成-超浅成侵入岩密切相关的一类岩浆-热液矿床,流体演化一直是斑岩型矿床研究的热点问题(陈静等, 2007; 侯增谦等, 2007; Richards *et al.*, 2012; Richards, 2015; Hou *et al.*, 2015; Mernagh *et al.*, 2020)。随着研究手段不断发展,对流体演化的研究逐渐精细化,通过流体包裹体、硫化物成分分析等手段对流体演化过程已有较为清晰的认知(Chang *et al.*, 2018; Wang *et al.*, 2018; Yang *et al.*, 2022; Adegoke *et al.*, 2022),普遍认为斑岩型矿床成矿流体具高温、高氧逸度、高盐度的特征,通常含有水蒸气、二氧化碳等挥发性物质(Pak *et al.*, 2004; 李进文等, 2006)。然而,部分研究表明,斑岩型成矿流体的特征存在显著差异,例如一些矿床的成矿流体在初期可能表现为低氧逸度和还原性(Sillitoe, 1972, 2010)。流体性质对矿床规模具有重要控制作用,初期低氧逸度、还原性流体通常形成规模较小的矿床。因此,流体特征及其演化过程对矿床的形成起着决定性作用。蚀变矿物作为成矿流体与围岩相互作用的直接产物,其类型和组合特征对揭示成矿环境和流体演化具有重要意义。绿泥石和白云母是斑岩型矿床中常见的蚀变矿物,其化

学成分和结构特征能够有效反映成矿流体的物理化学条件。例如,绿泥石的成分变化可指示成矿温度及流体性质,而白云母中Si、Al的置换关系则能够反映流体的pH值、氧逸度及水岩反应过程。通过研究这些蚀变矿物的类型及其地质意义,能够深入揭示成矿流体的演化路径及其对铜金成矿的控制作用。

洪山沟铜矿位于邯郸市永年区西侧洪山岩体北部,受洪山古火山机构与紫山-鼓山断裂控制,矿体主要分布于洪山沟正长斑岩内。目前,洪山沟铜金矿床的地质特征(常浩等, 2020)、成岩成矿时代(权瑞等, 2016; 李随民等, 2022)、成岩成矿作用(权瑞等, 2016; 白富生, 2022)、岩浆演化(张波等, 2020)等方面研究成果较多,但洪山沟铜金矿床蚀变矿物类型及其组合分带特征尚未厘清,成矿环境以及流体演化也缺乏详细研究。因此,本文基于野外地质调查,利用电子显微镜观察、电子探针化学分析(EPMA)、激光剥蚀电感耦合等离子体质谱(LA-ICP-MS)对洪山沟铜金矿床中绿泥石和白云母的类型、组分、形成温度、环境及其形成机制进行了系统研究,以期查明与绿泥石和白云母有关的各成矿阶段成矿流体的性质,约束洪山沟铜金矿床成矿流体的演化特征及铜金沉淀的物理化学环境。

1 区域地质背景

洪山多金属成矿区位于华北板块中部太行山南段,大地构造位置属于山西断隆太行山拱断束中的武安凹断束东部,东邻太行山断裂带(图1)(史志伟等, 2020; 崔晓亮等, 2022)。区域地层为一套以海相沉积为主的盖层岩系。区域内中生代燕山期岩浆活动强烈,分布广泛。岩浆岩主要有武安岩体、矿山岩体及洪山杂岩体(Xu, 2001; 王春光等, 2011; 息朝庄等, 2021)。其中武安岩体以闪长岩为主,矿山岩体以闪长岩、二长岩为主,洪山杂岩体中心侵入为正长岩(尹明等, 2014; 息朝庄等, 2021),向南、北两侧分别为晶屑凝灰岩、凝灰熔岩、黑云辉石粗面岩、黑云辉石粗面斑岩及黑云正长辉石岩、黑云辉石正长岩等。该区构造活动强烈,断裂及褶皱具明显中生代滨太平洋域构造特征,褶皱构造为新城-武安向斜和鼓山背斜,断裂为邯郸大断裂与紫衫-鼓山大断裂,均为北北东向断裂(许文良等, 1990a, 1990b; 耿国建等, 2023; 杨长青等, 2023),紫山-鼓山断裂及其一级构造为本区重要的导矿构造,许多金矿

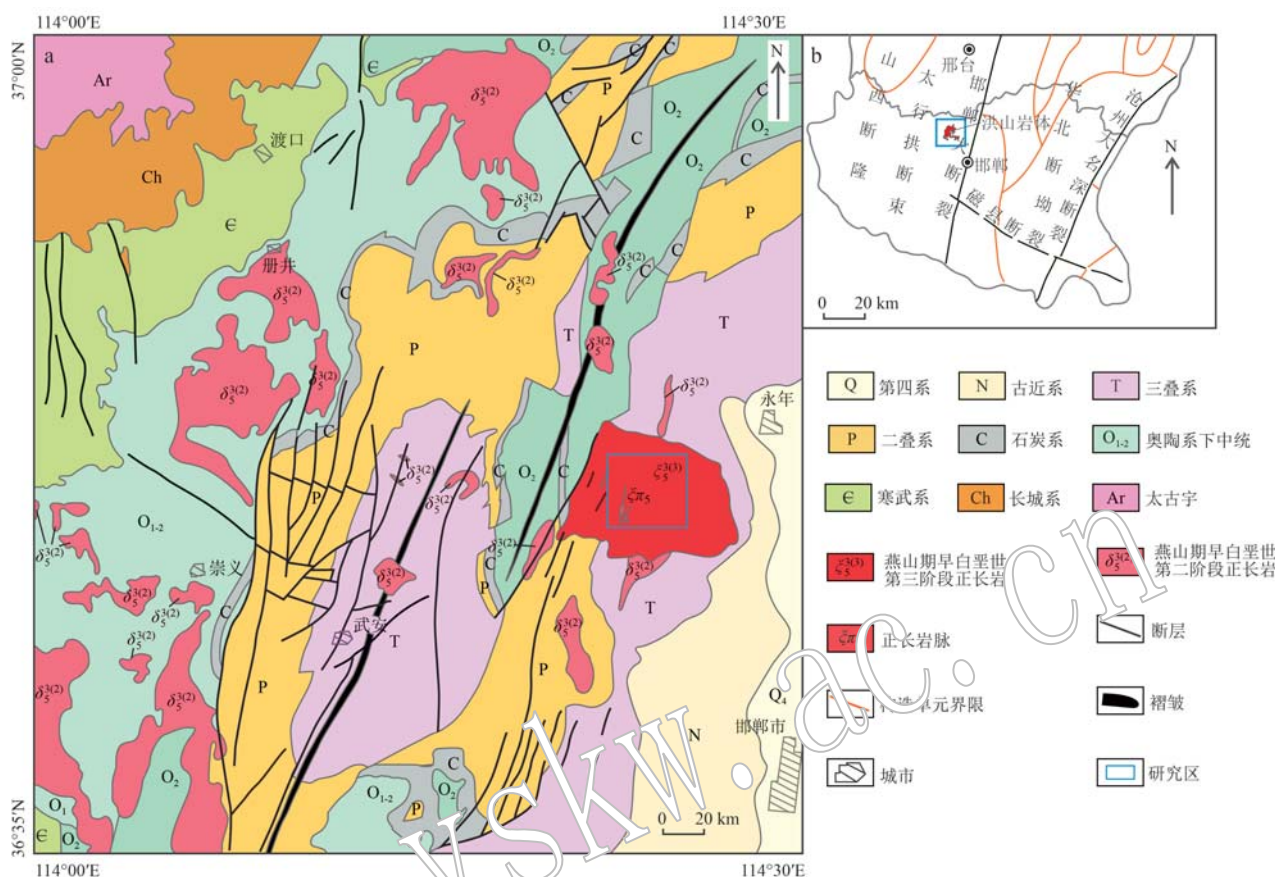


图1 洪山岩体与其周围区域地质图(a)及大地构造位置图(b)(据刘昕耀, 2016 修改)

Fig. 1 Geological map of Hongshan rock mass and its surrounding area (a) and geotectonic location map (b) (modified from Liu Xinyao, 2016)

化点沿该断裂带分布。

区域矿产较丰富,以煤、铁矿种为主,金、铜多金属矿(化)点分布于洪山岩体及其周边,主要有营里、娄里、泉上金矿点以及洪山沟、里三窑、娄里金矿等。

2 矿床地质特征

洪山沟斑岩型铜金矿床位于邯郸市洪山岩体北部,分布于邯郸大断裂与紫山-鼓山大断裂之间的北北东向构造岩浆岩带内(图2)(常浩等, 2020)。

洪山岩体主要由碱性正长岩类组成,岩体与围岩之间呈侵入关系。锆石 U-Pb 年龄显示洪山岩体形成于早白垩世(周凌等, 2005; 权瑞等, 2016),可分为喷出相-超浅成侵入相、侵入相两种岩相。喷出相主要分布在岩体的南北两侧边部,呈近东西向带状分布,岩石类型主要为凝灰岩、粗安玢岩、粗面岩、黑云辉石粗面岩和辉石-粗面岩等中性及中偏碱性

岩浆岩;侵入相主要为霓辉正长岩和正长岩。

洪山沟铜金矿床的矿体主要赋存于含铜正长斑岩内,斑岩体矿化明显,主要为浸染状及细脉浸染状。矿石类型为斑岩型铜矿石,矿石矿物以黄铜矿为主,蓝辉铜矿次之,脉石矿物有条纹长石、霓辉石、石英、黑云母、绢云母、角闪石、霓石或方解石等。矿石结构为他形粒状结构、充填交代结构以及反应边结构,构造主要呈浸染状及细脉浸染状(刘昕耀, 2016)。矿床按期次可分为:①霓辉石-硫化物阶段,主要矿物为霓辉石、黄铁矿、黄铜矿;②浸染状硫化物阶段,为主成矿阶段,黄铁矿、黄铜矿等硫化物呈浸染状分布在含铜正长斑岩中,与霓辉石、磁铁矿共生;③石英-黄铁矿阶段,主要矿物为石英和黄铁矿,二者常呈细脉产出。围岩蚀变主要为绢云母化、绿泥石化、钾化、硅化及黑云母化等。矿体中心以硅化及钾化为主,外围以绢云母化及绿泥石化为主。铜矿化与硫化物及硅化密切相关(姚士新等, 1993; 常浩等, 2020)。

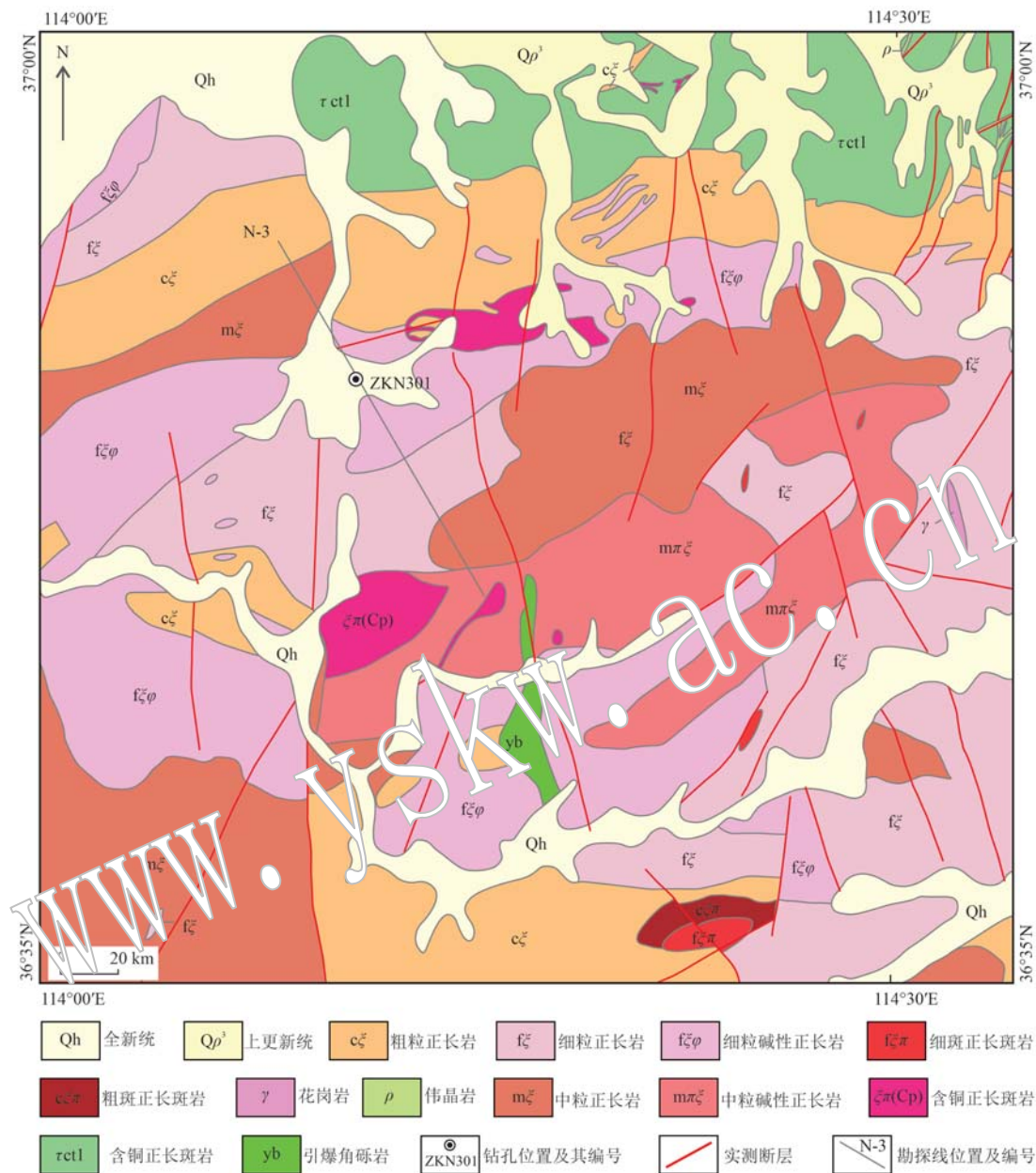


图 2 洪山沟矿区地质图(据常浩等, 2017 修改)

Fig. 2 Geological map of Hongshangou mining area (modified from Chang Hao *et al.*, 2017)

3 蚀变矿物岩相学特征

3.1 绿泥石类型及分布特征

绿泥石是洪山沟铜金矿床中重要的热液蚀变矿物,在洪山沟铜金矿床的矿体与岩体中广泛分布,尤其在矿体发育部位发育。通过室内镜下鉴定,根据绿泥石蚀变类型及分布特征,将洪山沟铜金矿床中绿泥石分为:① 与金属矿物共生的完全蚀变型绿泥

石(Chl-1),是矿区内绿泥石的主要发育类型,绿泥石在单偏光下呈灰绿色-绿色,与金属矿物和长石共生,为流体交代暗色矿物形成(图 3a、3b、3c);② 角闪石蚀变型的绿泥石(Chl-2),发育程度次于 Chl-1,绿泥石呈细小鳞片状,单偏光镜下呈绿色,为流体不完全交代角闪石形成,与角闪石共生(图 3d、3e);③ 黑云母蚀变型绿泥石(Chl-3),在矿区内不发育。绿泥石为细小鳞片状,单偏光下为墨绿色,为流体不完全交代黑云母形成,与黑云母共生(图 3f)。

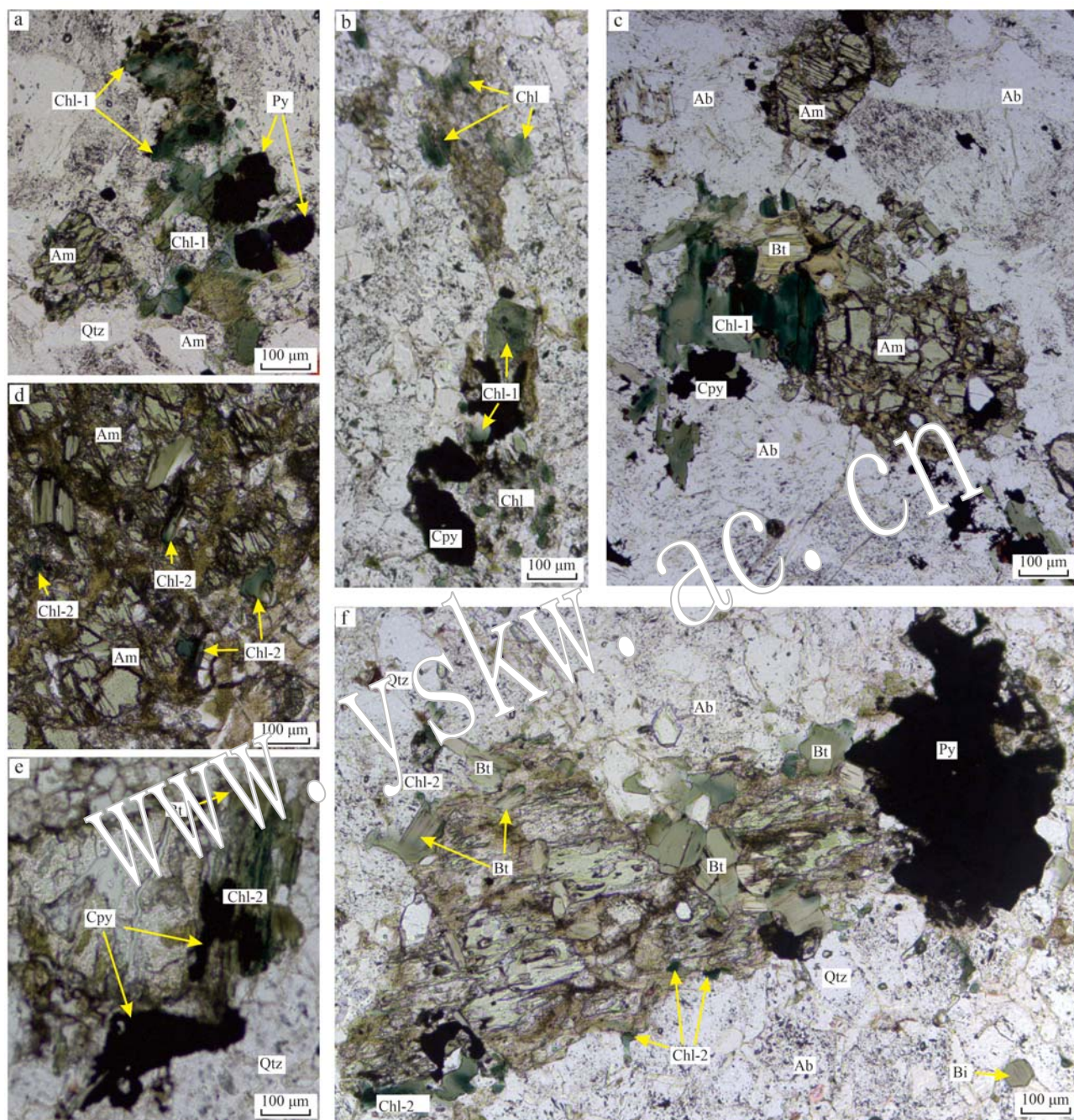


图3 绿泥石电子显微镜单偏光照片

Fig. 3 Typical microphotographs (plane-polarized light) of chlorite

a—Chl-1, 绿泥石完全交代暗色矿物, 与角闪石、长石、石英、黄铜矿共生; b—Chl-1, 绿泥石完全交代暗色矿物, 可见不完全交代角闪石骸晶, 与角闪石、长石、石英、黄铜矿共生; c—Chl-1, 绿泥石完全交代暗色矿物, 可见不完全交代黑云母骸晶, 与角闪石、黑云母、长石、石英、黄铜矿共生; d—Chl-2, 颗粒较小, 与角闪石共生; e—Chl-2, 角闪石部分蚀变为绿泥石, 与黑云母、黄铜矿共生; f—Chl-3, 黑云母部分蚀变为绿泥石, 与黑云母、黄铁矿共生; Ab—钠长石; Am—角闪石; Bt—黑云母; Chl—绿泥石; Cpy—黄铜矿; Py—黄铁矿; Qtz—石英

a—Chl-1, chlorite completely metasomatism dark minerals, and coexists with amphibole, feldspar, quartz, and chalcopyrite; b—Chl-1, chlorite completely metasomatism dark minerals, visible incomplete metasomatism amphibole skeleton crystal, and amphibole, feldspar, quartz, chalcopyrite symbiosis; c—Chl-1, chlorite completely metasomatism dark minerals, visible incomplete metasomatism biotite crystal, and hornblende, biotite, feldspar, quartz, chalcopyrite symbiosis; d—Chl-2, small particles, symbiotic with hornblende; e—Chl-2, hornblende is partially altered into chlorite, which is symbiotic with biotite and chalcopyrite; f—Chl-3, biotite partially altered into chlorite, coexisting with biotite and pyrite; Ab—albite; Am—hornblende; Bt—biotite; Chl—chlorite; Cpy—chalcopyrite; Py—pyrite; Qtz—quartz

3.2 白云母的类型及分布特征

热液白云母是洪山沟铜金矿床中另一广泛发育的蚀变矿物,白云母的成因及成分差异可指示洪山沟铜金矿床成矿流体的演化过程。白云母岩相学特征及电子探针结果可以判定白云母成因。原生白云母一般呈自形-半自形,矿物颗粒粗大,端面清晰,不与其他矿物呈反应关系,不含包裹体等,而次生白云母则相反,通过镜下白云母形态将洪山沟铜金矿床中的白云母分为原生白云母(Ms-1)与次生白云母(Ms-2)。

根据其矿物组合将原生与次生白云母进一步详细划分。原生白云母:①与长石共生的片状白云母 Ms-1.1,干涉色主要为蓝色,呈集合体或片状在长石边缘产出(图 4a、4b);②与方解石共生的片状白云母 Ms-1.2,干涉色为紫色、橙色,呈片状与碳酸盐矿物伴生(图 4c、4d)。次生白云母:①与长石共生的细小鳞片状白云母 Ms-2.1,干涉色为橙黄色、蓝色,颗粒较细,叠加于长石之上(图 4e、4f);②与长石、黄铜矿共生的片状白云母 Ms-2.2,较为发育,干涉色多为蓝色、橙红色;颗粒较细,叠加于长石之上,与黄铜矿共生(图 4g);③与方解石、黄铜矿共生的鳞片状-片状白云母 Ms-2.3,干涉色为绿色、蓝色以及紫色,与方解石共生,呈片状或鳞片状,与黄铜矿、黄铁矿共生(图 4h、4i)。

4 测试方法

本次研究针对绿泥石、白云母采用电子探针(EPMA)、激光剥蚀电感耦合等离子体质谱(LA-ICP-MS)分析其主微量元素变化。

绿泥石、白云母的 EPMA 分析在中国地质科学院矿产资源研究所电子探针实验室完成,电子探针测试仪器为日本岛津公司的 EPMA-8320,加速电压 15 kV;电流 20 nA;束斑直径 5 μm ;校正 ZAF;温度 25 $^{\circ}\text{C}$;湿度 55%~60%。

绿泥石、白云母的主微量元素分析在河北省战略性关键矿产资源重点实验室完成,实验仪器采用搭载 Laurin Technic S155 样品池和 GeoStar μGISTM 软件的澳大利亚 RESolution-LR 型 ArF 准分子激光剥蚀系统,质谱仪为美国赛默飞 iCAP RQ 型等离子体质谱仪,按照其标准操作规程,采用的激光束斑大小为 50 μm ,能量密度为 3 J/cm²,频率为 8 Hz,氦气为载气。元素含量采用 NIST610 作外标,²⁹Si 为内标

元素进行校正,实验测得数据采用 ICPMSDataCal 软件进行同位素比值及元素含量的计算。

5 绿泥石化学成分特征

由于本次研究的绿泥石颗粒比较细小且与其他矿物形成伴生关系,化学成分极易受混染,影响电子探针结果(Inoue, 1995),经前人研究证明绿泥石的($\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO}$)含量<0.5%表明分析过程中未发生其他矿物的混染(Hillier, 1993; Zang and Fyfe, 1995),经人工筛查后确认洪山沟铜多金属矿床 3 种绿泥石样品的($\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO}$)含量均小于 0.5%,测试结果有效。各类型绿泥石化学成分含量详见表 1,其中电子探针数据显示样品中 SiO_2 的含量在 26.41%~34.41%之间, Al_2O_3 的含量在 8.24%~13.16%之间,差别较小;FeO 含量在 25.53%~35.67%之间,MgO 含量在 10.58%~18.08%之间,差别较大;此外,Chl-1、Chl-2、Chl-3 中 FeO 平均含量分别为 30.00%、25.34%、25.73%,MgO 平均含量分别为 13.51%、17.42%、13.59%,说明绿泥石随成矿流体演化发生离子置换。

绿泥石 LA-ICP-MS 分析结果详见表 2,根据 LA-ICP-MS 结果,绿泥石 Li、Sn、Ga、Sc、Ti、V、Cr、Co、Ni、Cu、Zn、As、Rb、Sr 等元素的含量为 $0.01\times 10^{-6}\sim 1800\times 10^{-6}$,Nb、Y、La、Nd 等低于检出限。相较于未完全蚀变的绿泥石,完全蚀变的绿泥石具有更高的 Cu、Sn、Rb、Zn、Ti、Li、Sr、V、Co、Ni、Sn 含量。

5.1 绿泥石温度计算结果

前人研究发现绿泥石成分中 Al^{IV} 含量与温度之间存在正相关关系,因此提出绿泥石固溶体温度计以研究成矿过程中热液的温度变化(Cathelineau and Nieva, 1985),本次研究使用 Winccac 绿泥石计算软件计算经验性绿泥石温度计,以此评估洪山沟铜金矿床中绿泥石的结晶温度。在经验性温度计中,以 Kranidiotis 等(1987)(TKML87- Al^{IV})及 Cathelineau(1988)(TC88- Al^{IV})方法计算出的绿泥石温度范围较为集中,Kavalieris 等(1990)(TK90-Si)、Jowett(1991)(TJ91- Al^{IV})、Hiller 和 Velde(1991)(THV91- Al^{IV})方法计算出的绿泥石温度差别较大,详细计算结果见表 3。

5.2 绿泥石 $\text{Al}/(\text{Al}+\text{Mg}+\text{Fe}^{2+})$ 与 $\text{Fe}/(\text{Fe}+\text{Mg})$ 值

$\text{Al}/(\text{Al}+\text{Mg}+\text{Fe}^{2+})$ 值可以判别绿泥石与母岩

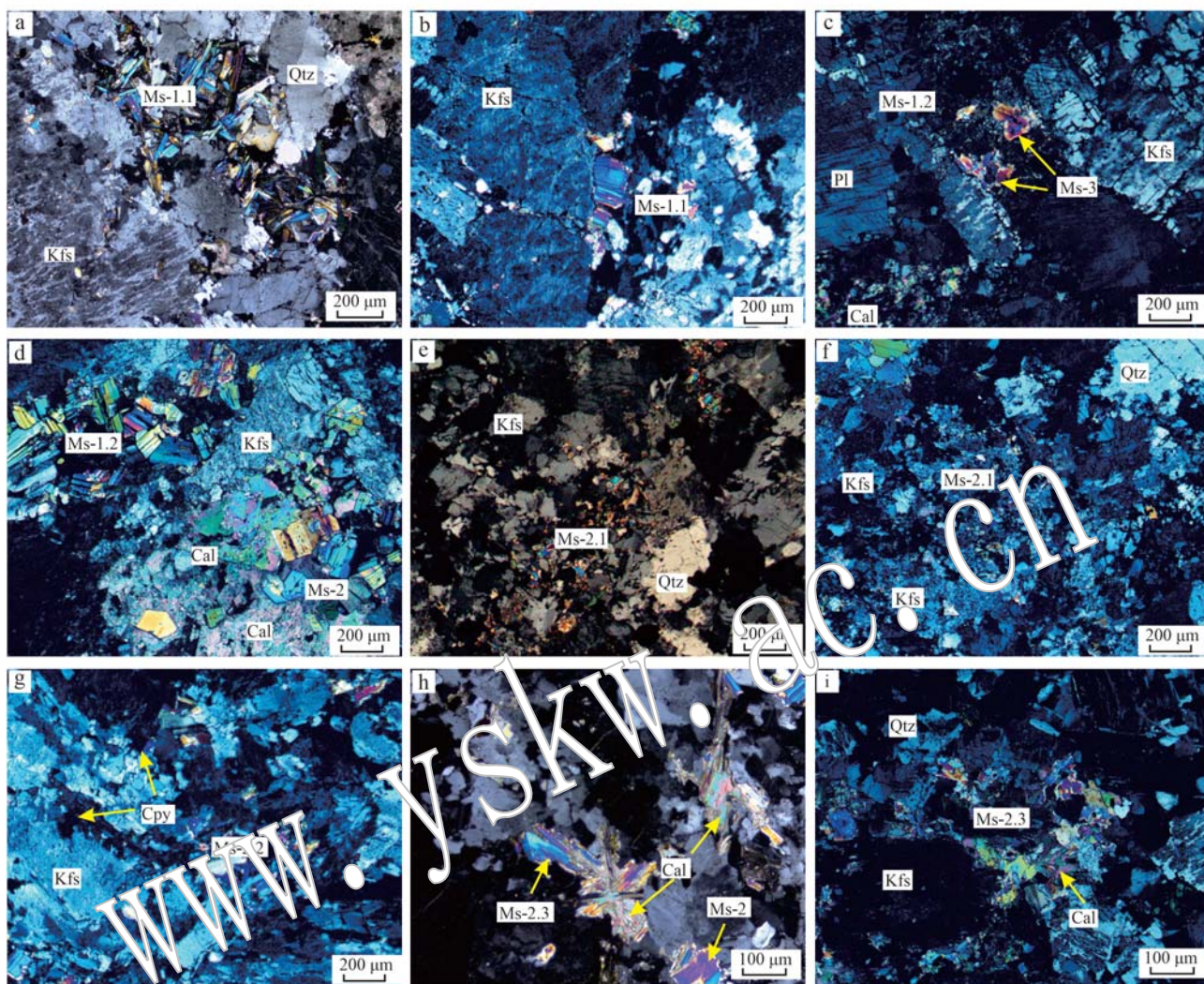


图4 白云母电子显微镜正交偏光照片

Fig. 4 Typical microphotographs (cross-polarized light) of muscovite

a—Ms-1.1, 白云母集合体与钾长石共生; b—Ms-1.1, 片状白云母与钾长石共生; c—Ms-1.2, 片状白云母与碳酸盐矿物、斜长石共生; d—Ms-1.2, 片状白云母集合体与碳酸盐、钾长石共生; e—Ms-2.1, 鳞片状白云母叠加钾长石之上, 与石英共生; f—Ms-2.1, 鳞片状白云母叠加钾长石之上, 与石英共生; g—Ms-2.2, 鳞片状白云母叠加于长石之上, 与碳酸盐矿物、黄铜矿共生; h—Ms-2.3, 片状白云母与碳酸盐矿物、黄铜矿共生; i—Ms-2.3, 片状白云母集合体与碳酸盐矿物、黄铜矿共生; Cal—方解石; Cpy—黄铜矿; Kfs—钾长石; Ms—白云母; Pl—斜长石; Qtz—石英

a—Ms-1.1, muscovite aggregates coexist with potassium feldspar; b—Ms-1.1, flaky muscovite coexists with potassium feldspar; c—Ms-1.2, flaky muscovite coexists with carbonate minerals and plagioclase; d—Ms-1.2, flaky muscovite aggregates coexist with carbonate and potassium feldspar; e—Ms-2.1, scaly muscovite superimposed on potassium feldspar, coexists with quartz; f—Ms-2.1, scaly muscovite superimposed on potassium feldspar, coexists with quartz; g—Ms-2.2, scaly muscovite superimposed on feldspar, coexists with carbonate minerals and chalcopyrite; h—Ms-2.3, flaky muscovite coexists with carbonate minerals and chalcopyrite; i—Ms-2.3, flaky muscovite aggregates coexist with carbonate minerals and chalcopyrite;

Cal—calcite; Cpy—chalcopyrite; Kfs—potassium feldspar; Ms—muscovite; Pl—plagioclase; Qtz—quartz

之间的关系, 一般认为 $Al/(Al+Mg+Fe) > 0.35$ 为泥质岩蚀变而成, $Al/(Al+Mg+Fe) < 0.35$ 则为铁镁质矿物蚀变 (Laird, 1988), 表3显示各类型绿泥石的 $Al/(Al+Mg+Fe)$ 值均小于 0.35, 表明洪山沟铜金矿床中的绿泥石均为铁镁质矿物蚀变。 $Fe/(Fe+Mg)$

值可判断绿泥石形成环境, 一般认为 $Fe/(Fe+Mg)$ 值越大, 环境的还原性越高 [$Fe/(Fe+Mg) > 0.5$], 易形成 Fe 绿泥石 (Inoue, 1952; Bryndzia and Scott, 1987; 郭国林等, 2012), Chl-1 的 $Fe/Fe+Mg$ 值在 0.57~0.65 之间, Chl-2 的 $Fe/(Fe+Mg)$ 值在 0.44~0.49 之

表 1 洪山沟铜金矿床绿泥石电子探针分析结果
Table 1 Electron microprobe analyses of chlorite from the Hongshangou copper-gold deposit

$w_B/\%$

类型 样品号	Chl-1						Chl-2						Chl-3	
	259-1	259-2	416. 1-1	416. 1-2	416. 1-3	416. 1-4	264. 3-1	346. 13-1	416. 1-1	419. 5-1	419. 5-2	419. 5-3	387. 2-1	387. 2-2
SiO ₂	26. 41	27. 06	28. 81	28. 66	27. 88	28. 12	30. 20	30. 31	29. 22	29. 17	29. 58	28. 58	34. 24	34. 41
TiO ₂	0. 12	0. 10	0. 22	0. 21	0. 20	0. 20	0. 45	0. 35	0. 06	0. 31	0. 30	0. 30	0. 39	0. 39
Al ₂ O ₃	12. 03	9. 75	11. 38	10. 91	11. 32	10. 80	8. 73	8. 99	11. 47	12. 66	12. 66	13. 16	8. 24	8. 40
Cr ₂ O ₃	0. 09	0. 18	0. 17	0. 28	0. 19	0. 11	0. 28	0. 18	0. 48	0. 36	0. 30	0. 26	1. 10	0. 51
FeO	35. 10	35. 67	31. 42	31. 08	31. 98	32. 30	25. 53	25. 73	26. 38	26. 26	26. 01	26. 06	25. 69	25. 78
MnO	1. 45	1. 15	1. 13	1. 04	1. 24	1. 17	0. 98	0. 66	1. 41	1. 03	1. 01	1. 10	1. 41	1. 39
MgO	10. 58	12. 20	12. 67	12. 95	12. 43	12. 57	18. 08	18. 63	16. 06	15. 55	15. 75	15. 52	13. 52	13. 66
CaO	0. 06	0. 05	0. 30	0. 36	0. 36	0. 30	0. 17	0. 17	0. 32	0. 51	0. 54	0. 33	0. 27	0. 28
Na ₂ O	0. 02	0. 04	0. 03	0. 04	0. 06	0. 03	0. 00	0. 03	0. 06	0. 06	0. 09	0. 08	0. 05	0. 03
K ₂ O	1. 16	0. 28	0. 01	0. 02	0. 70	0. 34	2. 32	2. 13	0. 59	2. 52	2. 24	2. 74	1. 04	1. 10
总和	87. 19	86. 72	86. 26	85. 74	86. 61	86. 08	87. 10	87. 59	86. 37	88. 67	88. 66	88. 36	86. 29	86. 30
Si	3. 03	3. 08	3. 23	3. 24	3. 16	3. 20	3. 15	3. 30	3. 21	3. 15	3. 17	3. 09	3. 72	3. 73
Ti	0. 01	0. 01	0. 02	0. 02	0. 02	0. 02	0. 03	0. 03	0. 00	0. 03	0. 02	0. 02	0. 03	0. 03
Al	1. 63	1. 31	1. 51	1. 45	1. 51	1. 45	1. 60	1. 15	1. 49	1. 61	1. 60	1. 61	1. 06	1. 07
Cr	0. 01	0. 02	0. 01	0. 03	0. 02	0. 01	0. 03	0. 02	0. 04	0. 03	0. 03	0. 02	0. 09	0. 04
Fe ²⁺	3. 28	2. 97	2. 95	2. 94	3. 03	3. 07	2. 42	2. 34	2. 43	2. 37	2. 33	2. 36	2. 34	2. 34
Mn	0. 14	0. 11	0. 11	0. 10	0. 12	0. 11	0. 09	0. 06	0. 13	0. 09	0. 09	0. 10	0. 13	0. 13
Mg	1. 81	2. 07	2. 12	2. 18	2. 10	2. 13	2. 55	3. 02	2. 33	2. 50	2. 52	2. 50	2. 19	2. 21
Ca	0. 01	0. 01	0. 04	0. 04	0. 04	0. 04	0. 05	0. 02	0. 04	0. 06	0. 06	0. 04	0. 03	0. 03
Na	0. 00	0. 01	0. 01	0. 01	0. 01	0. 01	0. 00	0. 01	0. 01	0. 01	0. 02	0. 02	0. 01	0. 01
K	0. 17	0. 04	0. 00	0. 00	0. 10	0. 05	0. 00	0. 00	0. 08	0. 35	0. 31	0. 38	0. 14	0. 15
F	0. 11	0. 14	0. 07	0. 10	0. 11	0. 06	0. 11	0. 24	0. 18	0. 11	0. 07	0. 08	0. 20	0. 22
Cl	0. 00	0. 00	0. 00	0. 01	0. 00	0. 00	0. 01	0. 00	0. 01	0. 01	0. 02	0. 00	0. 00	0. 00
X _{Fe}	0. 64	0. 59	0. 58	0. 57	0. 59	0. 59	0. 49	0. 44	0. 48	0. 49	0. 48	0. 49	0. 41	0. 40
X _{Mg}	0. 36	0. 41	0. 42	0. 43	0. 41	0. 41	0. 51	0. 56	0. 52	0. 51	0. 52	0. 51	0. 38	0. 38
Fe/(Fe+Mg)	0. 65	0. 52	0. 53	0. 57	0. 59	0. 59	0. 49	0. 44	0. 48	0. 49	0. 48	0. 49	0. 52	0. 51
Al/(Al+Mg+Fe ²⁺)	0. 24	0. 21	0. 23	0. 22	0. 23	0. 22	0. 24	0. 18	0. 23	0. 25	0. 25	0. 26	0. 19	0. 19
NaO+K ₂ O+CaO	0. 19	0. 06	0. 08	0. 10	0. 20	0. 13	0. 30	0. 34	0. 17	0. 48	0. 45	0. 47	0. 22	0. 22
Al+Mg+Fe	6. 81	6. 78	6. 57	6. 57	6. 64	6. 65	6. 56	6. 52	6. 54	6. 48	6. 45	6. 54	5. 58	5. 63

表 2 洪山沟铜金矿床绿泥石 LA-ICP-MS 分析结果
Table 2 LA-ICP-MS analysis results of chlorite in Hongshangou copper-gold deposit

$w_B/10^{-6}$

类型	编号	Li	Sn	Ga	Sc	Ti	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr
Chl-1	416. 1- 1	123. 00	1. 38	20. 46	16. 32	493. 08	121. 53	29. 02	22. 83	40. 48	2. 26	624. 13	0. 48	309. 03	327. 45
	419. 5-1	426. 74	6. 79	24. 91	19. 00	1 815. 11	321. 74	21. 7	61. 91	67. 26	0. 66	916. 93	0. 05	1 393. 04	6. 91
	264. 3-1	161. 16	0. 08	18. 08	1. 76	29. 62	12. 35	50. 01	0. 19	0. 06	0. 90	9. 43	0. 50	133. 89	14. 48
	264. 3-2	101. 20	0. 11	10. 68	1. 40	21. 66	12. 18	6. 08	0. 27	0. 36	1. 53	7. 75	0. 10	116. 36	6. 45
Chl-2	264. 3-3	106. 90	0. 46	13. 82	2. 72	327. 4	74. 74	12. 99	3. 00	1. 57	1. 85	76. 65	0. 14	175. 15	17. 97
	346. 13-1	17. 25	0. 43	9. 53	3. 72	6. 98	23. 65	160. 53	4. 07	6. 46	1. 33	64. 87	0. 04	10. 13	139. 29
	387. 2-1	243. 00	9. 55	29. 00	47. 07	1 630. 04	357. 13	166. 79	47. 12	62. 73	2. 71	1411. 14	0. 79	663. 65	34. 39

间, Chl-3 的 Fe/(Fe+Mg) 值为 0. 52、0. 51, 表明洪山沟铜金矿床主要成矿环境为还原性, 成矿流体经历了由氧化性→中性→还原性的演化过程。

5.3 绿泥石离子间置换关系

绿泥石中的离子常出现置换现象, 一般为 Al 与

四面体上的 Si、八面体上的 Fe 和 Mg 相互置换, 形成四次配位 Al^{IV}、六次配位 Al^{VI}, Fe、Mg 之间也可按任意比例互相置换(Inoue *et al.*, 2009)。根据绿泥石电子探针结果投图, 结果表明在 Al^{IV}-Si 图解中两者出现明显的线性负相关关系(图5a), 说明在绿泥石

表3 洪山沟铜金矿床绿泥石不同地温计计算结果 $^{\circ}\text{C}$
Table 3 Calculation results of different geothermometers
in the Hongshangou copper-gold deposit

类型	样品号	TKML87- Al^{IV}	TC88- Al^{IV}	TK90- Si	TJ91- Al^{IV}	THV91- Al^{IV}
Chl-1	259-1	272.00	250.00	150.00	261.00	158.00
	259-2	258.00	233.00	137.00	243.00	132.00
	416.1-1	243.00	185.00	113.00	194.00	58.00
	416.1-2	242.00	183.00	112.00	192.00	54.00
	416.1-3	240.00	209.00	122.00	218.00	94.00
	416.1-4	242.00	196.00	117.00	206.00	75.00
Chl-2	264.3-1	197.00	160.00	107.00	164.00	—
	346.13-1	199.00	164.00	108.00	169.00	—
	416.1-1	221.00	192.00	115.00	198.00	68.00
	419.5-1	235.00	213.00	125.00	219.00	101.00
	419.5-2	229.00	204.00	120.00	210.00	88.00
	419.5-3	246.00	230.00	135.00	236.00	127.00
Chl-3	387.2-1	115.00	—	163.00	164.00	176.00
	387.2-2	112.00	—	167.00	166.00	176.00

注: —表示未计算出结果。

中存在大量 Al^{IV} 对 Si 的置换(王玮等, 2021); 在 Fe-Mg 图解中两者出现明显负相关关系(图 1c), 说明在绿泥石中除存在 Al^{IV} 对 Si 的置换外还存在 Fe 与 Mg 的置换; Al^{VI} - Al^{IV} 图解中两者出现明显的非线性负相关关系(图 5e), 说明 Al^{IV} 对 Si 置换的同时出现 Fe-Mg 对 Al^{VI} 置换(Xie *et al.*, 1997; 王小雨等, 2014)。Kranidiotis 等(1987)研究发现, Al^{IV} 随着 $\text{Fe}/(\text{Fe}+\text{Mg})$ 的升高而升高, $\text{Fe}/(\text{Fe}+\text{Mg})$ - Al^{IV} 图解中出现相同趋势(图 5b), 说明绿泥石中 Al^{IV} -Si 置换的同时出现 Fe-Mg 置换并使更多的 Fe 置换 Mg 进入绿泥石(Kranidiotis *et al.*, 1987; Xie *et al.*, 1997)。绿泥石中的离子出现相互置换的现象主要因其所处环境的温度及酸碱度发生变化(艾永富等, 1998)。

5.4 绿泥石中主要阳离子与 Mg 的关系

前人研究证明若 Fe^{2+} 、 Fe^{3+} 、Si、Mn 等阳离子均与 Mg 呈负相关关系, 表明绿泥石形成于同一期热液活动(Battaglia, 1999)。洪山沟铜金矿床中绿泥石主要阳离子与 Mg 的关系图中, 仅 Al、 Fe^{2+} 与 Mg 呈弱负相关(图 6a、6b), 其他阳离子与 Mg 相关性不明显(图 6c、6d), 说明本区绿泥石经历了多期次的热液演化活动。

6 白云母化学成分特征

白云母电子探针分析结果详见表 4, 根据电子探针结果, Ms-1.1 的 SiO_2 含量(44.00%~45.21%)

较 Ms-1.2 (43.21%~43.66%)、Ms-2.1 (42.36%~44.23%)、Ms-2.2 (42.46%~44.15%)、Ms-2.3 (43.71%~44.40%) 的 SiO_2 含量偏高; Ms-1.1 的 Al_2O_3 含量(34.33%~37.12%)与 Ms-1.2 的 Al_2O_3 含量(35.17%~37.03%)相当, Ms-2.1 (30.20%~34.75%)、Ms-2.2 (32.47%~33.76%)、Ms-2.3 (30.47%~32.55%) 的 Al_2O_3 含量明显低于 Ms-1.1 与 Ms-1.2; Ms-1.1 的 FeO (0.42%~4.16%)、 MnO (0.01%~0.15%)、 MgO (0.02%~0.18%) 与 Ms-1.2 的 FeO (1.41%~4.37%)、 MnO (0.01%~0.07%)、 MgO (0.03%~0.36%) 较之 Ms-2.1 的 FeO (1.54%~5.73%)、 MnO (0.11%~0.34%)、 MgO (0.60%~2.68%), Ms-2.2 的 FeO (1.71%~5.76%)、 MnO (0.10%~0.35%)、 MgO (0.46%~2.05%), Ms-2.3 的 FeO (4.18%~6.33%)、 MnO (0.10%~0.18%)、 MgO (1.11%~3.34%) 含量较低。根据 Tislerchadoff 等(1999)提出的 $(\text{Fe}^{\text{tot}}+\text{Mn}+\text{Ti}-\text{Al}^{\text{VI}})-(\text{Mg}-\text{Li})$ 分类图对洪山沟铜金矿床中的白云母进行分类, 结果显示洪山沟铜金矿床中的白云母为普通白云母与多硅白云母(图 7)。

根据 Miller 等(1981)提出的 Ti-Na-Mg 三角分类图解进行投图, 结果表明: Ms-1.1、Ms-1.2 全部落在原生白云母范围内, 而 Ms-2.1、Ms-2.2、Ms-2.3 落在次生白云母范围内(图 8)(Miller *et al.*, 1981; Monier *et al.*, 1984; 王葆华等, 2021)。

白云母 LA-ICP-MS 分析结果详见表 5, 根据 LA-ICP-MS 结果, Ms-1.1 与 Ms-1.2 相比, Ms-1.1 具有较高的 Ga(最高 20.21×10^{-6})、Zn(最高 190.96×10^{-6})、Rb(最高 227.88×10^{-6}) 含量, Ms-1.2 具有较高的 Ba(最高 429.2×10^{-6})、Sn(最高 5.03×10^{-6})、Nb(最高 13.47×10^{-6})、Ti(最高 1313.43×10^{-6}) 含量, 二者的 Li、Zr、Cs、Cu、Sr 含量相近。

Ms-2.1 与 Ms-2.2、Ms-2.3 相比, Ms-2.1 具有较高的 W(最高 1.95×10^{-6})、Rb(最高 280.5×10^{-6})、Li(最高 309.85×10^{-6}) 含量, Ms-2.2 具有较高的 V(最高 311.64×10^{-6})、Ga(最高 25.47×10^{-6})、Sc(最高 39.89×10^{-6})、Zr(最高 77.01×10^{-6})、Cs(最高 13.87×10^{-6})、Zn(最高 987.57×10^{-6})、Sr(最高 327.45×10^{-6}) 含量, Ms-2.3 具有较高的 Ti(最高 1528.64×10^{-6}) 含量, 三者的 Sn、Cu 含量相近(图 9)。

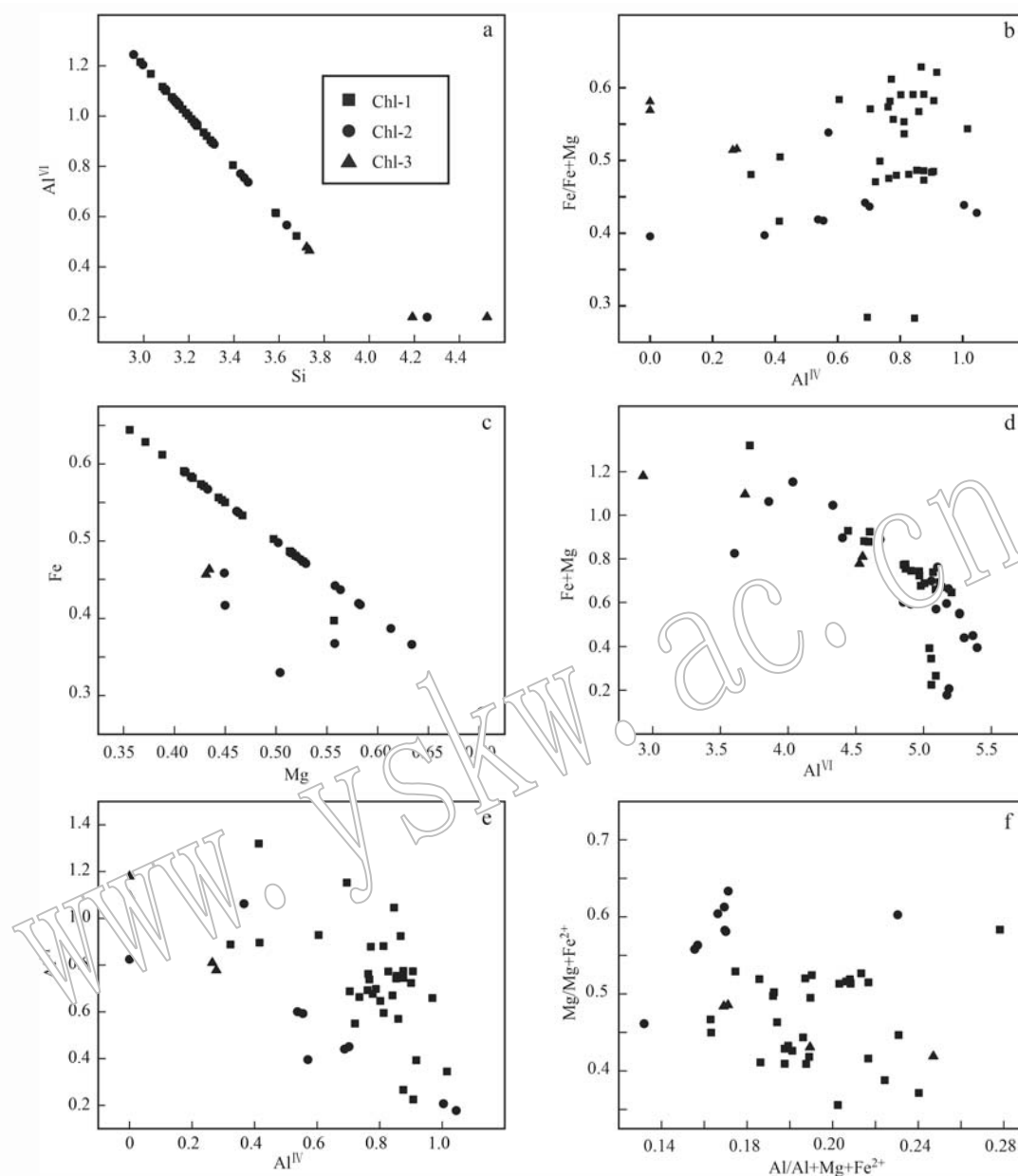


图5 洪山沟铜金矿床中绿泥石的主要阳离子(apfu)关系图解

Fig. 5 Correlation of main cations (apfu) in chlorite from the Hongshangou copper-gold deposit

7 讨论

7.1 绿泥石形成温度

绿泥石作为中低温变质作用的产物,成分对环境极其敏感,因此可利用其成分及结构反演环境温度(Kranidiotis and Maclean, 1987; Zang and Fyfe, 1995; Zhang *et al.*, 2022)。为验证各种绿泥石地质温度计准确性,将本次地质温度计计算结果与洪山

沟铜金矿床的石英流体包裹体测温结果(125~346℃)进行对比(刘昕曜, 2016), Kranidiotis 等(1987)所计算的温度与包裹体测温结果相符合,与洪山沟铜金矿床同属洪山地区的娄里金矿床(100~268℃)相近(李紫烨等, 2017)。综上,本文选择Kranidiotis 等(1987)提出的地质温度计作为本文的最终结果,确定绿泥石形成温度为112~272℃之间(图10i),属于中-低温热液成矿环境,变化范围较大,推测与矿区经历多期热液活动相关(张娟等,

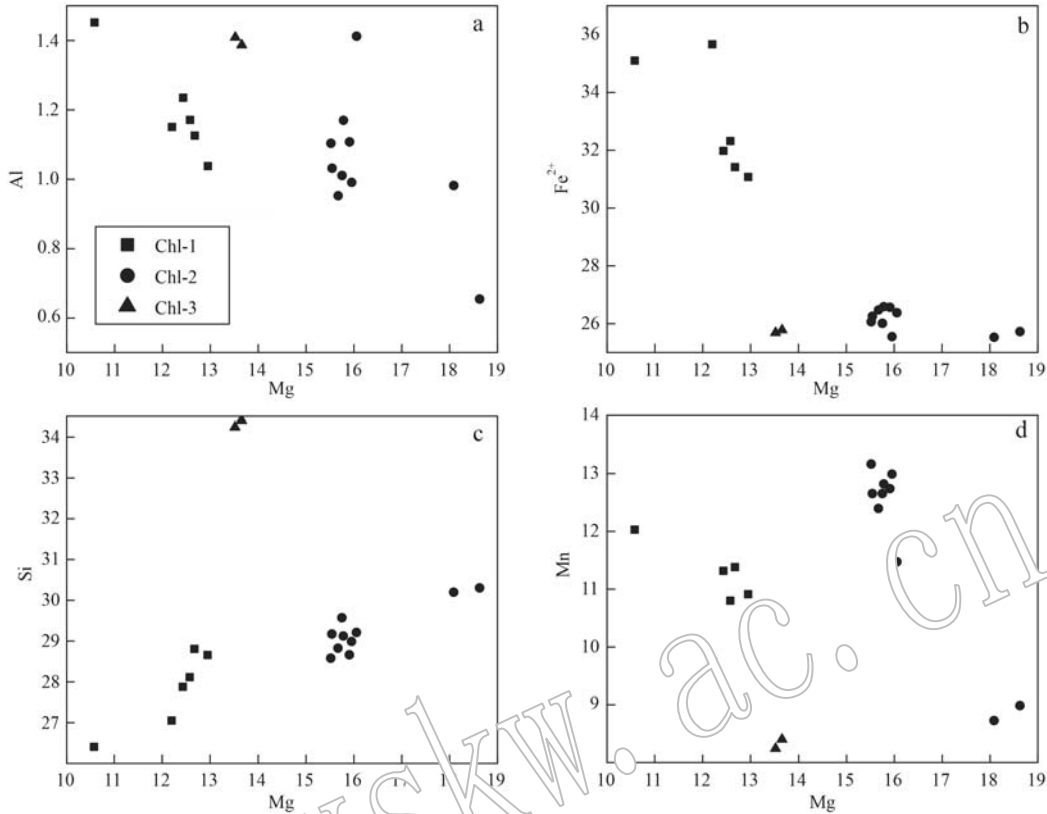


图 6 洪山沟矿床中绿泥石中主要阳离子与 Mg(apfu) 关系图解
Fig. 6 Correlation of the main cations and Mg(apfu) in chlorite in the Hongshangou deposit

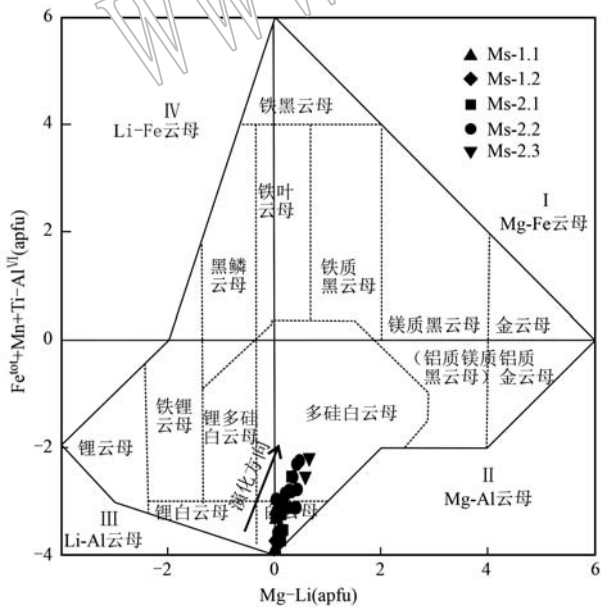


图 7 洪山沟矿床中白云母 $(\text{Fe}^{\text{tot}} + \text{Mn} + \text{Ti} - \text{Al}^{\text{VI}}) - (\text{Mg} - \text{Li})$ 分类简图 (据 Tischendorf *et al.*, 1999)

Fig. 7 The nomenclature of the micas from the Hongshangou deposit (modified from Tischendorf *et al.*, 1999)

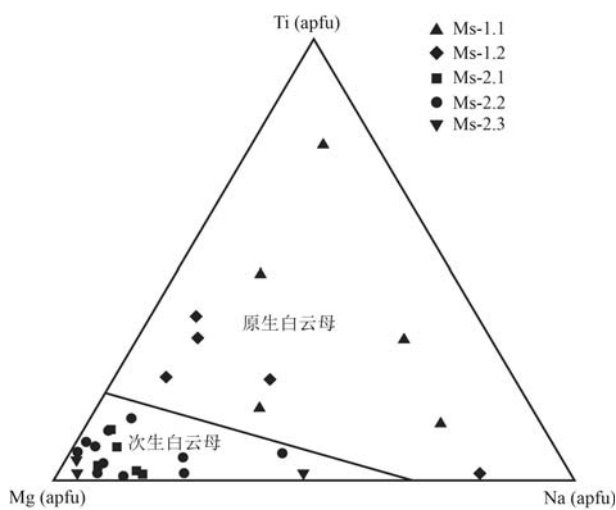


图 8 洪山沟矿床中白云母 Ti-Mg-Na 分类图
(据 Miller *et al.*, 1981)

Fig. 8 Ti-Mg-Na ternary classification diagram of muscovite from the Hongshangou deposit (modified from Miller *et al.*, 1981)

表 5 洪山沟铜金矿床白云母 LA-ICP-MS 分析结果
Table 5 The results of muscovite LA-ICP-MS analysis in Hongshangou copper-gold deposit

 $w_B/10^{-6}$

类型	样品号	Li	Sc	Ti	V	Cu	Zn	Ga	Rb	Sr	Zr	Nb	Sn	Cs	Ba	W
Ms-1.1	203.73-1	256.85	2.21	794.36	112.70	0.28	190.96	20.21	227.88	15.03	0.65	1.84	3.00	1.49	32.20	0.80
	203.73-2	109.41	1.85	599.37	40.45	0.24	45.86	13.23	158.61	7.45	0.11	3.25	2.82	0.47	27.59	0.40
	264.3-1	101.20	1.40	21.66	12.18	1.53	7.75	10.68	116.36	6.45	1.37	0.04	0.11	0.14	53.17	0.14
Ms-1.2	314.33-1	134.66	1.92	1 008.89	67.46	0.72	14.01	10.99	197.90	11.26	0.51	12.05	5.03	0.54	334.71	0.22
	314.33-2	145.05	1.83	1 313.43	59.21	1.85	15.52	11.75	214.72	8.27	0.55	13.47	4.04	0.31	429.20	0.18
	320.3-1	234.90	2.93	967.40	56.10	0.20	90.34	13.19	188.90	6.02	0.28	6.76	2.90	0.35	105.54	0.17
	320.3-2	258.11	3.12	1 170.53	57.91	0.32	82.59	13.50	200.44	5.92	0.28	8.16	3.25	0.40	112.58	0.17
Ms-2.1	222.5-1	131.23	3.67	510.70	21.54	0.32	29.60	9.56	181.51	10.07	0.30	0.43	1.19	1.03	132.13	0.95
	222.5-2	243.30	3.69	1 012.99	78.18	0.36	60.70	14.02	280.50	7.39	0.22	2.13	0.94	1.75	263.01	1.45
	280.3-1	112.95	2.95	562.67	12.60	1.11	8.69	3.49	169.10	35.07	0.47	0.74	1.11	0.31	482.85	0.76
	280.3-2	228.40	3.32	853.86	23.78	9.31	61.72	7.35	270.59	35.18	2.43	2.43	1.12	1.27	258.16	1.95
	364-2	309.85	2.98	31.15	5.08	0.16	18.81	10.82	196.86	68.34	0.65	0.40	1.13	0.53	5.44	0.21
Ms-2.2	203.73-1	294.36	2.08	1 314.74	64.22	0.19	43.70	14.14	190.19	27.33	8.72	19.57	5.03	0.43	48.19	0.38
	264.3-2	130.75	32.53	976.78	252.96	1.79	779.22	24.87	176.88	30.13	77.01	0.32	5.90	1.49	14.43	0.20
	416.1-1	122.20	39.89	515.72	311.64	0.83	987.57	25.47	183.18	109.72	45.57	0.75	0.76	9.36	7.14	0.03
	416.1-2	123.00	16.32	493.08	121.53	2.26	624.13	20.46	309.03	327.45	1.83	0.48	38	13.7	29.09	0.08
	416.1-3	20.23	3.40	169.79	129.07	18.84	3.91	10.76	33.88	151.03	96	3.23	3.23	0.26	99.60	1.20
Ms-2.3	264.3-3	106.90	2.72	327.40	74.74	1.85	76.65	13.82	175.15	17.9	1.18	3.23	0.46	0.41	83.32	0.22
	320.3-1	122.18	3.59	1 144.43	74.96	0.63	133.69	13.24	216.65	1.69	0.1	2.46	3.37	0.30	91.57	0.07
	320.3-2	116.16	4.09	1 528.64	84.20	0.67	139.16	15.42	241.47	1.16	0.27	2.63	4.95	0.36	92.69	0.12

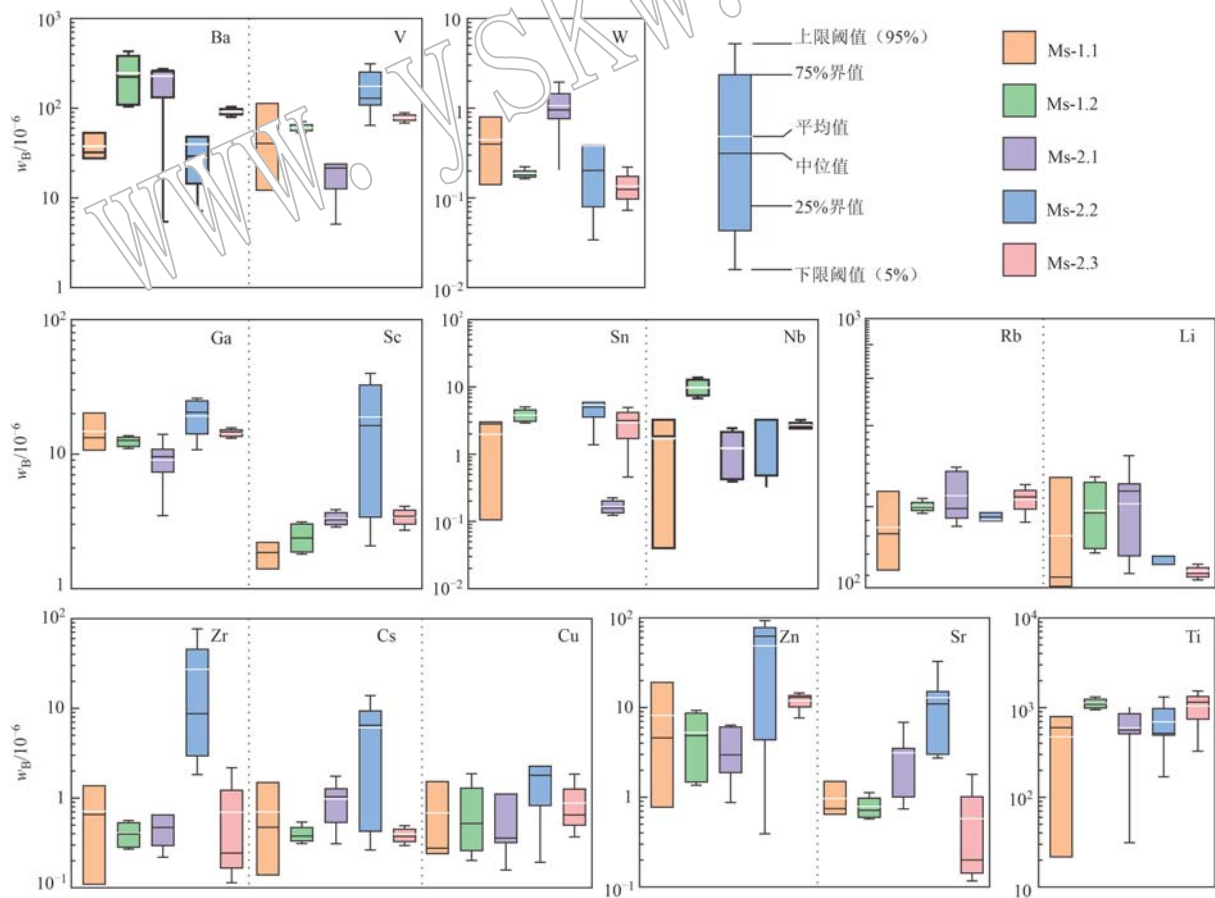


图 9 洪山沟铜金矿床各类型白云母微量元素成分箱状图

Fig. 9 Box diagrams of trace element composition of various types of muscovite in Hongshangou copper-gold deposit

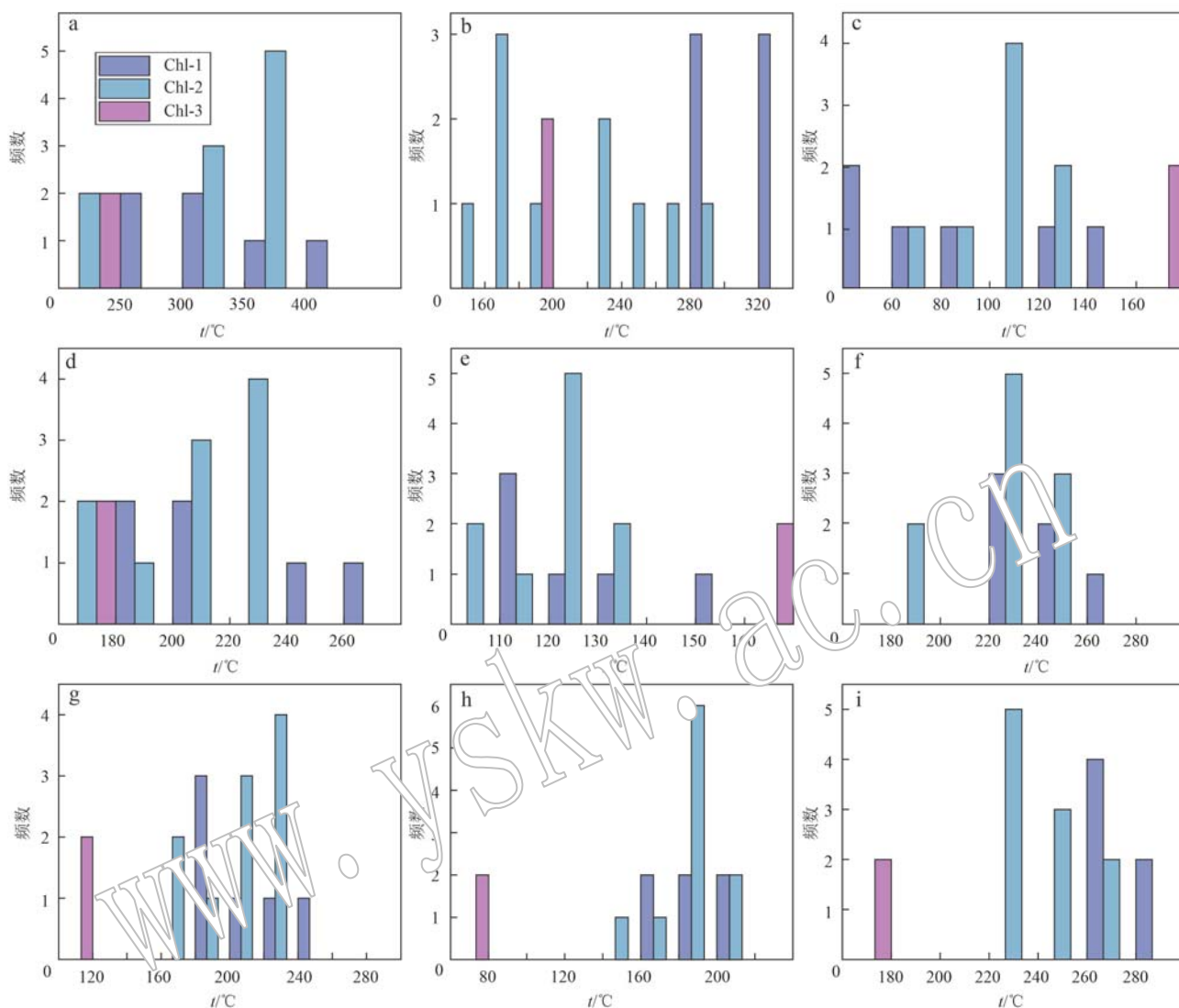


图 10 洪山沟矿床中绿泥石温度直方图

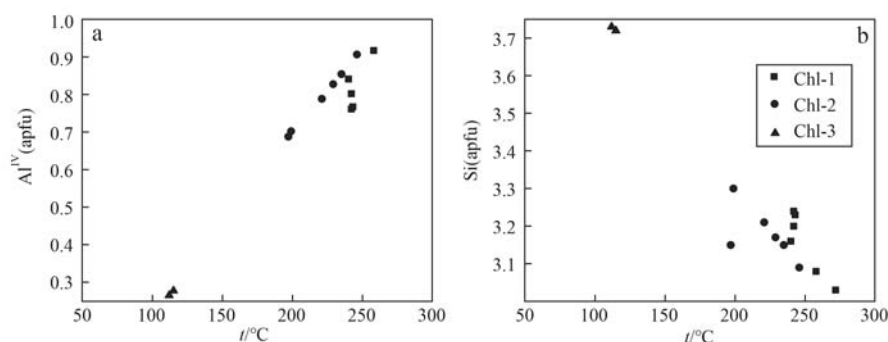
Fig. 10 Histograms showing the temperature of chlorite in the Hongshangou deposit

2021)。前人所做流体包裹体结果证明洪山沟铜矿成矿流体绝大部分测温结果集中于 210~310℃ 之间且晚期有大气水加入(刘昕曜, 2016), 铜沉淀的温度一般在 250~350℃ 之间, 其中 Chl-1 峰值比较集中, 在 242~280℃ 之间, Chl-2 较为分散, 在 197~246℃ 之间, 说明各绿泥石形成于各成矿阶段的晚期。推测成矿早期流体温度较高, 随着流体运移, 浅部大气降水与深部岩浆热液的流体混合导致成矿温度、压力逐渐下降, 进而导致隐爆作用的产生; 而大气降水的参与也使得流体 pH 值升高并偏于中性热液的溶解度降低, 导致金属硫化物析出沉淀。前人研究认为, 100~350℃ 内温度与绿泥石 Al^{IV} 值呈正相关关系, 而与八面体空位和 Al^{VI} 呈负相关关系

(Cathelineau and Nieva, 1985; Cathelineau, 1988)。洪山沟铜金矿床中的绿泥石形成温度与 Al^{IV} 、Si 均呈较好的线性相关关系(图 11), 该结果与前人研究成果相似, 证实了该温度体系的适用性(周栋等, 2018; 葛祥坤等, 2020; 张娟等, 2021; 刘松岩等, 2024)。

7.2 绿泥石形成环境

洪山沟铜金矿床中铜金矿均赋存于霓辉正长斑岩中, 且富矿的正长斑岩中绿泥石化较为发育, 可见明显的绿泥石交代作用, 热液侵入, 导致原岩中角闪石、黑云母发生蚀变交代, 从而形成大量的蚀变绿泥石。前人研究证明绿泥石成分中 Fe^{2+} 与 Mg^{2+} 会发生广泛的类质同象取代(艾永富等, 1998; Chu *et al.*, 2021)。

图 11 洪山沟矿床中绿泥石形成温度与 Si、Al^{IV} 相关性图解Fig. 11 Correlation of Si, Al^{IV} with temperature of chlorites in the Hongshangou deposit

2020), 在斑岩型矿床中, Fe 绿泥石倾向于在高温环境中形成, 随着温度降低与 pH 值升高, 导致绿泥石中出现 Fe、Mg 置换, 大量 Mg²⁺ 进入绿泥石晶格, 形成 Mg 绿泥石, 本次研究采用 Zane 等 (1998) 限定绿泥石结构类型和八面体占位主导阳离子的三角分类图解, 对洪山沟铜金矿床中绿泥石进行分类。据图 12 可知, 洪山沟铜金矿床中绿泥石均属三八面体 type-I 型绿泥石, 八面体中 Fe²⁺ 占主导地位, 为富 Fe 绿泥石, 指示洪山沟铜金矿床中的绿泥石形成于还原环境。在温度条件相近的中温热液矿床形成过程中, 溶液的酸碱度对绿泥石成分有明显影响, 前人证明 Fe/(Fe+Mg) 值可以反映绿泥石结晶时所处环境。一般认为 Fe/(Fe+Mg) 值越大, 环境的还原性越高 [Fe/(Fe+Mg) > 0.5], 更易形成 Fe 绿泥石。洪山沟

铜金矿床中 Chl-1 的 Fe/(Fe+Mg) 值为 0.57~0.65 (均值为 0.60), Chl-2 的 Fe/(Fe+Mg) 值为 0.44~0.49 (均值为 0.47), Chl-3 的 Fe/(Fe+Mg) 值为 0.51~0.52 (均值为 0.51), 指示绿泥石形成经历了流体还原性-近中性的演化过程, 黄铜矿沉淀于近还原性的环境。斑岩型矿床的含矿热液具氧化性, 赋存大量矿质 (Sun *et al.*, 2013, 2015; 贺文等, 2023), 在洪山沟成矿过程中, 热液向上运移蚀变侵入岩, 铁镁质矿物中的 Fe²⁺ 进入热液, 中和热液的氧化性, 导致金属硫化物沉淀, 此时成矿流体为近中性环境, 证明洪山沟铜金矿床成矿环境由氧化性到近还原性的转变。流体性质差异及成矿环境对金成矿起到抑制作用, 导致洪山沟铜金矿床中金见矿效果较差。

7.3 绿泥石微量元素对矿床的指示

已有众多学者证明绿泥石微量元素能够作为斑岩型矿床的勘查矢量工具 (Jago *et al.*, 2014; Pacey *et al.*, 2020; Xue *et al.*, 2021)。Wilkinson 等 (2015) 研究 Batu Hijau 矿床时发现绿泥石化学与斑岩热液中心呈系统性变化, 特别是在距斑岩 2.5 km 半径范围内, 随着距离的增加青磐岩化绿泥石中 Ti、V 等离子浓度呈指数级下降, 而 Li、Sr、Ba、Mn、Co、Ni、Zn 和 Pb 浓度呈指数级上升, 并提出 Ti 在斑岩系统中绿泥石元素空间变化规律可能与两种机制有关: ① 与热液流体的迁移扩散有关, 如斑岩矿床矿体外围经常出现的贵、贱金属异常; ② 由温度控制的元素替换。国内外众多学者对绿泥石微量元素的研究表明, 由于矿床不同形成环境, Zn、Mn、Sc、Sr、Li 与温度呈正相关性或负相关性, 但都证明了 Ti、V 会随着远离热液矿化中心逐渐降低 (Xiao *et al.*, 2018; Xiao and Chen, 2020)。据绿泥石微量元素箱状图 (图 13) 可看出, 洪山沟矿床中完全蚀变的绿泥石

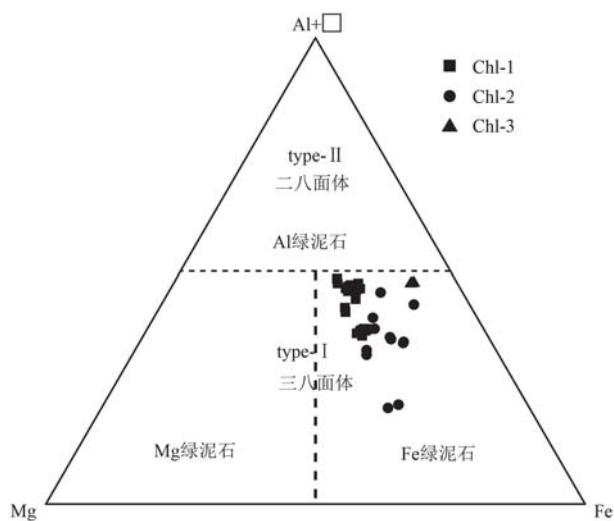


图 12 洪山沟矿床中绿泥石分类图解 (底图据 Zane and Weiss, 1998)

Fig. 12 Classification diagram for chlorite from the Hongshangou deposit (base map after Zane and Weiss, 1998)

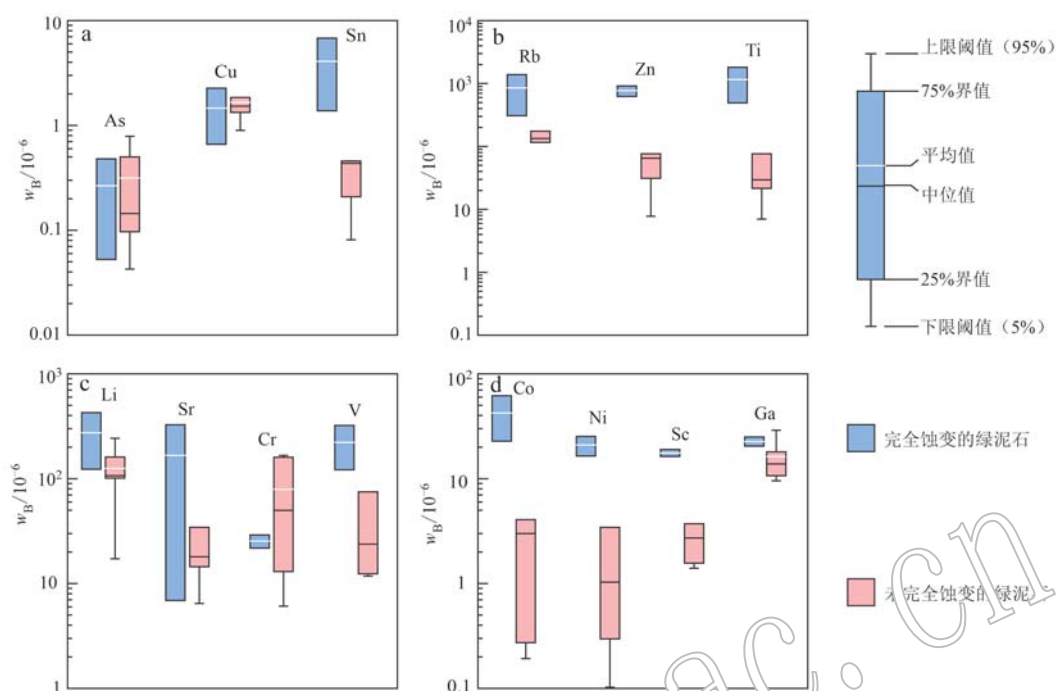


图 13 洪山沟铜金矿床各类型绿泥石微量元素成分箱状图

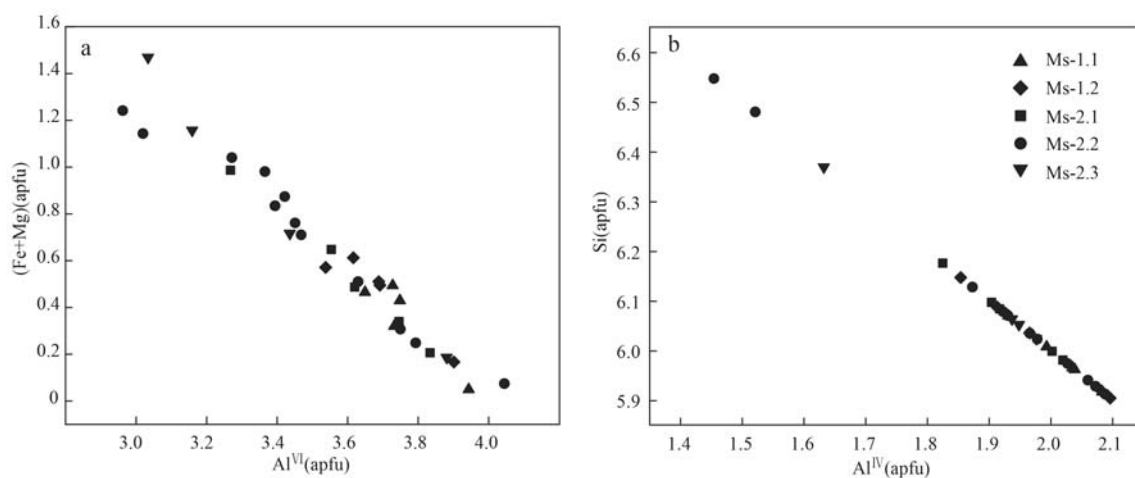
Fig. 13 Box diagrams of trace element composition of various types of chlorite in Hongshangou copper-gold deposit

中, Sn、Rb、Zn、Ti、V、Co、Ni、Sc 的含量均明显高于未完全蚀变的绿泥石, 完全蚀变的绿泥石比未完全蚀变的绿泥石的深度要深。尽管本次研究中绿泥石微量元素样品较少, 但微量元素变化趋势明显, 推测洪山沟铜金矿床的矿化热液中心还在深部。

7.4 白云母形成环境

白云母是含水层状硅酸盐矿物, 常见于热液蚀变环境, 其形成受热液性质 (成分、温度、压力、pH 值等)、围岩性质及水/岩比例等因素影响 (Guidotti *et al.*, 1994; Duke, 1994; Halley *et al.*, 2015; 郭娜

等, 2017; 贺文等, 2023)。洪山沟铜金矿床中, 白云母与多硅白云母共存。电子探针结果显示, 白云母八面体位置发生 Fe、Mg 对 Al^{VI} 的置换, 四面体位置存在 Si 对 Al^{IV} 的置换 (图 14)。多硅白云母与矿化关系密切, 而无矿岩体中主要为普通白云母。深部流体富含 CO_2 , 水解后呈酸性, 促进水岩反应, 形成高 Al 低 Si 的白云母; 随着流体上移, Fe^{2+} 进入降低氧化性, pH 值升高, 导致 Fe、Mg 置换 Al^{VI} 及 Si 置换 Al^{IV} , 形成高 Si 低 Al 的多硅白云母, Cu 随之沉淀成矿。

图 14 白云母 (Fe+Mg) 与 Al^{VI} (a) 和 Si 与 Al^{IV} (b) 的关系图Fig. 14 Correlation of the (Fe+Mg) and Al^{VI} (a), Si and Al^{IV} (b) of muscovite

多硅白云母是变质和热液交代作用的产物,可在低压低温及中压低温环境下稳定存在(叶美芳等, 2016)。洪山沟矿床中 Cu 在中低温-近中性环境下沉淀,金属硫化物更倾向于在此条件下沉淀(Hemley and Jones, 1964; Portela *et al.*, 2021)。随着流体上移, Fe^{2+} 降低氧化性, 流体近中性, 金属硫化物开始沉淀(Li *et al.*, 2013), pH 值升高促使 Fe、Mg 置换 Al^{VI} 及 Si 置换 Al^{IV} , 形成富 Si 贫 Al 的白云母。

洪山沟矿床白云母微量元素差异显著。原生白云母 Ms-1.1、Ms-1.2 中 Li、Zr、Cs、Cu、Sr 含量接近, 次生白云母 Ms-2.1、Ms-2.2、Ms-2.3 中 Sn、Cu 含量接近, V、W、Sc、Zn、Ti 在次生白云母中富集。V、Sc 差异反映白云母形成时期(Urabe-Mogollon and Maher, 2018, 2020), Ti、V、W、Sn 等高价元素在高氧化条件下不易进入云母晶格, Sc 在高氧逸度下更易进入磁铁矿或赤铁矿, 早期云母亏损 V、Sc, 晚期云母富集 V、Sc。Ms-2.1 的 V、Sc 含量高于 Ms-2.2、Ms-2.3。Zn 在高温蚀变中不易进入云母晶格, 高温中心云母具低 Cu、Zn 特征(Chaffee, 1982; Mailey

et al., 2015)。Ms-2.3 的 Zn 含量低于 Ms-2.1、Ms-2.2, 表明其形成于早期高温蚀变, Ms-2.1、Ms-2.2 形成于成矿中晚期。

白云母微量元素相关性图解(图 15)显示, 微量元素变化反映白云母共生阶段、围岩和流体组成、pH 值、压力、温度条件及共沉淀相元素分配(Ayuso, 1987; Loucks, 2014; Benavides, 2017; Alva-Jimenez *et al.*, 2020)。Ms-2.3 较 Ms-2.1、Ms-2.2 富集 Sn, 亏损 V、W、Zn, 表明其形成于早期低 pH 值、氧化性条件(Mallmann and O'Neill, 2013)。综上, 洪山沟矿床成矿流体早期具高氧逸度、低 pH 值特征, Ms-2.3 伴随少量矿化形成; 后期富 Sc、V 的 Ms-2.1 形成, 表明成矿流体后期有大气降水加入, 热液温度与氧逸度降低。

7.5 流体演化及成矿指示意义

斑岩型矿床中, 矿化中心的成矿流体具高温高氧化特征, 向外围水-岩反应导致岩浆中的硫酸盐矿物发生还原反应生成氧化性的含铁矿物(Ohmoto, 1997)。在洪山沟铜金矿床成矿过程中, 与白云母共生

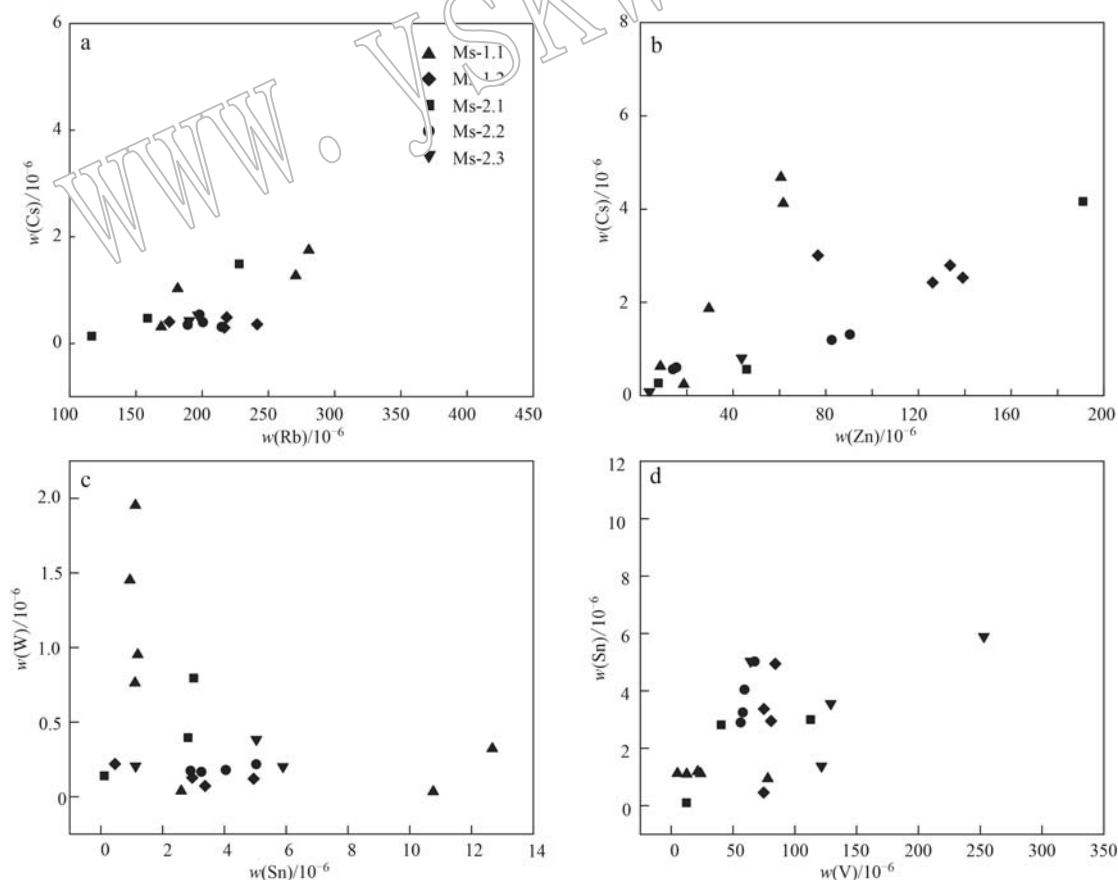


图 15 洪山沟铜金矿床白云母微量元素二元图解

Fig. 15 Binary diagrams of muscovite trace elements in Hongshangou copper-gold deposit

的方解石指示在成矿初期流体富含 CO_2 , 流体呈酸性, 温度较高抑制白云母离子间发生契尔马克置换 (唐楠等, 2021; 田成华等, 2022), 此时白云母为富Al贫Si的白云母, Cu与Cl形成氯络合物进行运移, 随着大气水的加入, 流体温度下降, 高温钾化蚀变逐渐向低温绢云母化、青磐岩化蚀变发展, Fe^{2+} 进入流体使流体从氧化性向中性转变, Cu开始沉淀并富集成矿 (杨航等, 2023; 李发桥等, 2024), 与矿物共生的绿泥石 Chl-1 的形成温度为 $270 \sim 280^\circ\text{C}$, 此时流体温度降低, pH值升高, 白云母为高Si低Al的多硅白云母, 表明洪山沟铜金矿床主要成矿环境为中-低温近中性环境。

8 结论

(1) 洪山沟铜金矿床中3类绿泥石形成温度在 $112 \sim 272^\circ\text{C}$ 之间, 其中与金属矿物共(伴)生的绿泥石温度在 $242 \sim 272^\circ\text{C}$ 之间, 微量元素指示洪山沟铜金矿床形成于中-低温热液成矿环境;

(2) 绿泥石微量结果表明完全蚀变的绿泥石更富 Sn、Rb、Zn、Ti、V、Co、Ni、Sc, 暗示深部还有热源的可能;

(3) 洪山沟铜金矿床中与长石共生的片状白云母、与方解石共生片状白云母为岩浆演化形成的普通白云母。与长石共生细小鳞片状白云母, 与长石、黄铜矿共生的片状白云母以及与方解石、黄铜矿共生鳞片状-片状白云母为热液蚀变形成的多硅白云母。与矿化密切相关的白云母具高 Si、Fe、V、W 低 Al、Sn 的特征, 指示洪山沟铜金矿床成矿流体早期呈酸性, 氧逸度较高, 后期随着大气降水的加入导致流体逐渐向中性转变, 氧逸度降低。表明洪山沟铜金矿床成矿环境为近中性环境。

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