

锡铜共生矿床的研究现状、问题与展望*

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摘要 文章在总结全球锡铜共生矿床时空分布规律的基础上,重点从成矿地质特征、热液蚀变组合、金属来源和成矿动力学背景等方面综述了锡铜共生这类矿床的研究进展,并总结了锡铜共生矿床中岩浆过程和热液过程。研究表明,锡铜矿床主要发育在与俯冲相关的板块边缘,弧后、后碰撞等岩石圈伸展环境,并伴随着强烈的壳幔相互作用。全球锡铜共生矿床的形成时代以晚古生代和中生代为主,其空间分布广泛但局部集中产出,主要分布在中国华南、南美玻利维亚、欧洲康沃尔和厄尔士以及俄罗斯远东地区。根据成矿特征,这类矿床可分为2类:第一类矿区除发育与锡成矿有关的高分异、还原性钛铁矿系列岩浆岩以外,还发育有大规模基性或碱性岩浆活动;第二类矿区则仅发育与锡成矿有关的岩浆岩,并未发育基性或碱性岩浆作用。目前对于锡和铜的物质起源仍有争议,其中锡主要来源为高分异花岗岩,而铜的物质来源比较复杂。在前人的研究基础上,文章提出对锡铜共生矿床的研究展望:①采用多种非传统稳定同位素(Sn、Cu、Ba同位素)进行联合示踪;②在开展精细矿物学特征研究的基础上,利用不同阶段的矿石矿物和脉石矿物,进行原位地球化学分析,查明锡铜共生的精细化过程和成矿物源归属。上述问题的深入研究或将提高对锡铜共生矿床成矿过程的认识,为该类型矿床的找矿勘查工作提供理论支撑。

关键词 锡铜共生;氧化还原条件;岩浆过程;热液过程;物质来源

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Research status, questions and prospects of Sn-Cu coexisting deposits

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Abstract

In this paper, based on the characteristics of the temporal and spatial distribution of Sn-Cu coexisting deposits in the world, we summarize the research progress of Sn-Cu deposits including metallogenic geological characteristics, hydrothermal alteration assemblages, metal sources and metallogenic dynamics, as well as the magmatic and hydrothermal processes. Previous studies have shown that Sn-Cu deposits are generally formed in the plate margin related to subduction, the lithospheric extensional environment such as post-arc and post-collision, with strongly crust-mantle interactions. Sn-Cu deposits were mainly formed in the Late Paleozoic and Mesozoic and distributed in several metallogenic belts including South China, western South America and Cornwall and Erzgebirge in Europe, and the Russian Far East. According to the mineralization characteristics, Sn-Cu deposits can be divided into two types; the first type develops coeval large-scale mafic or alkaline magmatic activities plus the Sn-

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related highly-fractionated reduced (ilmenite series) granitic rocks; the second type only develops Sn-related granitic rocks without mafic or alkaline magmatism. Currently, the metal source of Sn-Cu deposits still remains largely controversial; tin comes from highly fractionated granites but the Cu source is more complex. This paper suggests research prospect of Sn-Cu mineralization: ① combine multiple unconventional stable isotopes(e.g., Sn, Cu, Ba isotopes) as a tracer for metal source; ② based on detailed mineralogy characteristic, utilize in situ geochemical analysis of ore minerals and gangue minerals at different stages, to decipher the precise mineralization processes and metal source of Sn and Cu. Solving these problems may help us improve the understanding of the coexisting tin and copper mineralization processes and provide new basis for the exploration of Sn-Cu deposits.

Key words: coexisting Sn-Cu mineralization, redox condition, magmatic process, hydrothermal process, metal source

锡与铜具有迥然不同的地球化学性质。一般认为,锡矿化的发生都是与富F、B的过铝质或弱过铝质S型花岗岩类有关(Lehmann, 1990; Heinrich, 1990),岩浆作用主要由上地壳物质重熔形成的花岗岩浆,属钛铁矿(还原)系列,并具有高分异特征(Chappell et al., 1974; Ishihara, 1977; Taylor, 1979; Taylor, 1988; Lehmann, 1982; 徐克勤等, 1982)。而与铜矿化有关的准铝质I型花岗岩类与俯冲大洋板片或交代岩石圈地幔部分熔融形成的岩浆有关,属磁铁矿系列,并具有富水、低-中等分异氧化性特征(Gustafson et al., 1975; Ishihara, 1977; Mungall, 2002; Sillitoe, 2010; Richards, 2011; Sun et al., 2015)。传统观点认为铜矿热液体系为氧化性(Sillitoe, 2010; Richards, 2011; Blundy et al., 2015),氧逸度介于NNO(镍-氧化镍)和HM(赤铁矿-磁铁矿)缓冲线之间(Burnham et al., 1980)。而与花岗岩有关的锡矿热液体系一般为还原性,氧逸度位于FMQ(铁橄榄石-磁铁矿-石英)缓冲线之下(Taylor, 1988; Heinrich, 1990)。显然,就岩浆过程和热液过程而言,锡与铜很难出现于同一成矿系统之中。但现实并非如此,中国及全球不乏大型锡矿床中富含铜的实例,例如葡萄牙Neves Corvo锡成矿省、秘鲁San Rafael锡矿床、中国云南个旧和广西钦甲锡矿区均含有大量的铜矿资源(铜资源量均达中型以上)。那么,锡铜共生的成矿机理是什么?是多阶段多期次岩浆热液成矿作用的综合产物,还是同一成矿过程中不同阶段的演化结果?文章在综述前人研究工作和成果的基础上,主要介绍了锡铜共生矿床的时空分布特点、成矿地质特征以及热液蚀变组合,着重讨论了锡铜共生矿床中的岩浆过程、热液过程及成矿机制、成矿物质来源和成矿动力学背景等问题,旨在为锡铜共生矿床研究提供新的思路。

1 锡铜共生矿床的主要特点

1.1 成矿动力学背景

针对锡铜共生矿床的成矿动力学机制,学者目前已基本达成共识,即世界上绝大多数与花岗岩有关的锡铜矿床发育在与俯冲相关的板块边缘,其中包括大陆边缘陆内弧、弧后、后碰撞等岩石圈伸展环境(裴荣富等, 1989; Lehmann, 1990; Relvas et al., 2006a, b; Mao et al., 2018; Sillitoe et al., 2022)。这些伸展环境经历了板块俯冲折返、断裂和岩石圈拆沉,从而导致高温软流圈和地幔上升、减压熔融和镁铁质岩浆的产生,镁铁质岩浆的上涌侵位导致了中上地壳变质沉积岩发生部分熔融,强烈的壳幔相互作用为锡铜矿床的产生提供物质条件(Romer et al., 2016; Wolf et al., 2018; Mao et al., 2019)。

Zhang等(2017)认为在晚白垩世新特提斯板块的俯冲后撤造成了华南的成岩成矿事件,区域内可发现岩浆-热液活动与岩石圈伸展的构造背景存在密切联系。程彦博等(2008a; 2008b; 2009)对个旧地区开展系统年代学和地球化学工作,获得杂岩体的形成时代介于73~85 Ma,认为该地区双峰式火成岩的形成是华南西部晚白垩世岩浆-成矿热事件的结果;大厂矿区的相关岩体属于后造山花岗岩,成岩成矿时代属于95~90.4 Ma后造山向板内伸展转化阶段(蔡明海等, 2004a; 2006; 梁婷, 2008a; 张灵火等, 2017)。同时就区域构造而言,区内广泛存在的拉张盆地、变质核杂岩和镁铁质包体等现象,共同表明晚白垩世华南地区处于岩石圈构造伸展背景之下(蔡明海等, 2004b; 颜丹平等, 2005; 毛景文等, 2008)。相关地球物理学资料 and 同位素地球化学数据显示出锡铜矿床发育伴随着明显的壳幔

相互作用(赵永贵等,1992;彭聪等,2000;王永磊等,2012;廖时理等,2014)。

1.2 时空分布特点

从时间来看,全球锡铜共生矿床的成矿时代整体上跨度较大,从泥盆纪到新近纪普遍存在,成矿时代主要集中于晚古生代和中生代(Sillitoe et al.,2022)。

从空间来看,锡铜共生矿床的全球空间分布极不均一,常以成矿带或成矿省的形式集中产于环太平洋成矿带和特提斯成矿带(Sinclair et al.,2011;Lehmann,2021)(图1),主要分布在如下区域:①东亚锡矿带,主要包括中国华南、俄罗斯远东地区和日本中南部,例如:云南个旧超大型Sn-Cu矿床(Cheng et al.,2013a;b)、俄罗斯Sobolnoe(Gonevchuk et al.,2010)和日本Akenobe(Ishihara et al.,2012)的Sn-Cu矿床;②南美玻利维亚锡矿带和北美加拿大东南部,例如秘鲁San Rafael(Kontak et al.,2002)和加拿大Mount Pleasant(Yang et al.,2003)等Sn-Cu矿床;③英国Cornwall锡矿省以及中欧的厄尔士锡矿带,例如德国Sadisdorf矿床(Breiter et al.,1999)和葡萄牙Neves Corvo矿床(Relvas et al.,2006a;2006b)。

1.3 成矿地质特征

锡铜共生矿区内岩浆活动强烈,依据有无基性岩

出露可将矿区分为2类:一类为存在基性岩的矿区,以个旧矿区为例,其岩浆活动时间从印支期延续至燕山期,在空间上以个旧断裂为界,西区广泛出露燕山期斑状花岗岩、粒状花岗岩、基性火山岩和碱性岩,而东区大部分为隐伏岩体,少部分燕山期黑云母花岗岩以侵入体形式出露于白沙冲、北炮台和新山等地,老厂和卡房矿段附近分布有印支期幔源岩浆分异的碱性玄武岩并有少量燕山期煌斑岩脉出露于地表(程彦博等,2008b;杨宗喜等,2010;李肖龙等,2011;沈思联等,2016)。前人从岩石学、年代学和岩石地球化学等角度认为个旧花岗岩类是岩浆结晶分异的结果,其来自中元古代地壳重熔,并存在少量地幔组分的加入(程彦博等,2008a;2008b;Cheng et al.,2012b;2013b),进而形成个旧矿区具有多期次多阶段连续演化特征且规模巨大的杂岩体。成岩成矿时代相近表明锡铜矿化主要与晚白垩世岩浆活动有关(毛景文等,2008)。大厂矿区中部岩浆岩以黑云母花岗岩和细粒花岗岩为主,地表出露极少,多以隐伏岩株形式向铜坑-长坡矿床深部延伸,其两侧分别为花岗斑岩脉(东岩墙)和石英闪长玢岩脉(西岩墙),同时存在少量中性-基性岩(梁婷,2008;王新宇等,2015;Cai et al.,2023)。而另一类为无大规模基性岩出露的矿区,以秘鲁San Rafael矿床

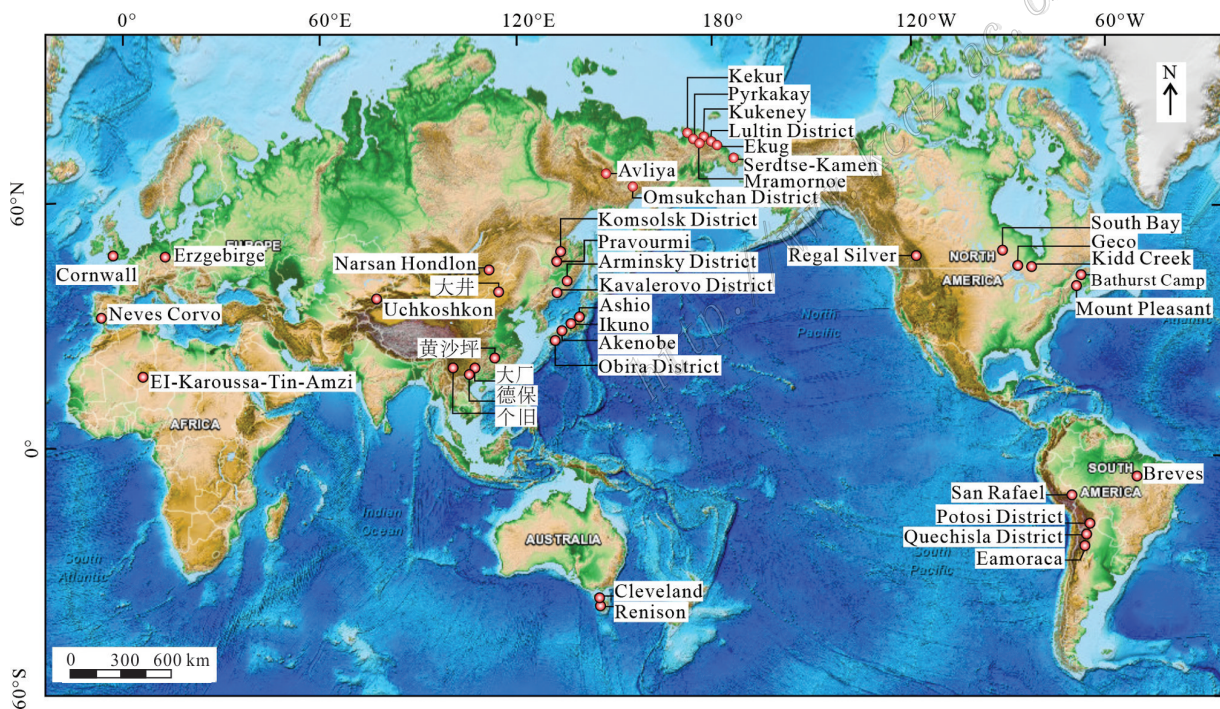


图1 世界锡铜共生矿床分布示意图
Fig. 1 Spatial distribution of Sn-Cu deposits in the world

为例,侵入体主要由粗粒钾长石巨晶黑云母-堇青石二长花岗岩和少量的细粒二长花岗岩-花岗闪长岩组成,同时含有少量的英云闪长岩、石英闪长岩以及煌斑岩包体,花岗岩体的形成是多次岩浆侵位的产物,岩浆源于变质沉积岩部分熔融形成的强过铝质的S型岩浆(Kontak et al., 2002; Mlynarczyk et al., 2003; Harlaux et al., 2021a)。矿化系统由北西向石英-锡石-硫化物组成,Sn矿化阶段的矿物组合为石英、锡石、绿泥石以及少量的电气石、磁黄铁矿和毒砂形成矿脉和角砾岩;而Cu矿化为主阶段的矿物组合为磁黄铁矿、黄铜矿、毒砂、方铅矿和闪锌矿(Harlaux et al., 2020)。

另一方面,按照锡铜矿床在成矿元素是否存在分带性,可将其分为2类:第一类为成矿元素具有明显分带性的矿区,以中国个旧和大厂矿区为例。前人总结了个旧矿区的地质特征,发现以花岗岩体为中心,在内接触带发育蚀变Be-Nb-Ta矿床,云英岩型Sn-W-Bi-Mo矿床和石英脉状矿床,在中接触带主要发育矽卡岩型Sn-Cu矿床,具有W、Bi、Pb、Zn和S等多元素共同富集的特征,矿石矿物主要为锡石和硫化物,伴生电气石、萤石,矿石呈块状构造和浸染状构造,矿化过程主要出现在退变质阶段。在外接触带形成脉状Sn-W-Mo矿化和层状矽卡岩Sn-Cu矿床,在花岗岩远端的围岩中发育含锡花岗岩型Sn矿化和热液脉型Cu-Pb-Zn-Ag矿床,其多以细脉浸染状或矿脉状充填交代于岩石裂隙中,矿石矿物主要为锡石(毛景文等, 2008; 解世雄, 2021)。而Cu矿化主要以接触带矿体和似层状矿体的形式发育于变玄武岩与碳酸盐岩夹层间,在花岗岩与变玄武岩的接触部位,矿体出现明显的铜富集特征,矿石矿物主要为磁黄铁矿和黄铜矿,伴生Sn、W、Pb、Bi、Ag、As等金属元素(杨宗喜等, 2010; 郭翔宇, 2017; 郭佳, 2019)。与个旧矿区相似,同样位于右江盆地的大厂矿区也呈现出成矿元素分带性的特征,其以龙箱盖花岗岩体为中心,向外依次为含Sn的近端矽卡岩型Zn-Cu-W-Sb中心矿化,中高温Sn-Pb-Zn-Sb-As多金属中间带矿化和外围Hg-Sb矿化的早期成矿作用的正向分带模式,该矿化分带模式与英国Cornwall锡多金属矿化分带基本吻合,是与花岗岩有关成矿的普遍特点。而在成矿作用晚阶段,形成了位于顶部围岩的中低温热液型W-Sb矿化,其叠加在矽卡岩型Zn-Cu矿化之上,并穿插锡多金属矿体,形成了晚期的逆向分带(陈毓川等, 1985; 成永生等, 2012; 梁婷等, 2014)。另一类Sn-Cu矿表现为Sn和Cu密切共

生且无明显的分带性,以葡萄牙Neves Corvo矿床与广西德保矿床为例,Neves Corvo矿床属于火山块状硫化物矿床,区域内存在一套双峰式火山岩,具体表现为上下两层的火山沉积层序,下部火山层序从底到顶依次为镁铁质辉绿岩和细碧岩、流纹岩、英安岩和枕状玄武岩和黑色页岩,上部火山层序为含磷酸盐结核、燧石和细粒火山沉积物的黑色页岩,硅质页岩和长英质火山岩(Oliveira et al., 2013)。矿石类型以网脉状、块状和条带状为主,网脉状矿体赋存于下部长英质火山沉积岩之中,块状矿体产于长英质火山岩或黑色页岩的顶部,条带状矿石是由强烈的逆冲推覆作用盖于网脉状矿石之上形成(Gaspar, 2002; Relvas et al., 2006b),矿石矿物包括黄铁矿、黄铜矿、闪锌矿和方铅矿,副矿物为黄锡矿、毒砂、磁黄铁矿和自然铋等,所有矿石矿物中均缺乏硫酸盐矿物(Relvas et al., 2006a; 2006b; Li et al., 2019)。而德保矿床以似层状或透镜状产出于钦甲花岗岩体的矽卡岩带,矿石呈浸染状、团块状和条带状,锡以锡石存在于脉石矿物之间或以类质同象的形式进入硫化物之中,铜主要以黄铜矿形式存在(王永磊等, 2010; 王晨光等, 2023)

1.4 热液蚀变特点(蚀变组合)

对于存在矿化分带的锡铜矿床,其往往具有典型蚀变分带特征。前人总结蚀变特征表现为由岩体向围岩依次划分为硅化带-钾化带(钾化-电气石化-萤石化)-绢英岩化带-大理岩化。矿体周围蚀变强烈,在此模式中,Sn-Cu矿化主要发生于钾化、萤石化、电气石化带中,其次产于钾化、绿帘石带中,呈现渐变过渡和蚀变组合混合的特征。当电气石化、钾化、黄铁矿化和萤石化共同出现时,则Sn-Cu矿化程度越高(陈守余等, 2011; 沈思联等, 2016; 赵月华, 2022)。

成矿过程中,当围岩为碳酸盐岩时,成矿流体与围岩发生水岩反应,在接触带形成矽卡岩型Sn-Cu矿化,围岩蚀变主要为矽卡岩化、云英岩化、绢云母化、绿泥石化等。在浅部形成脉状Sn矿化和云英岩型以及含锡白云岩型Sn矿化,该类矿化受岩层裂隙和构造带控制,矿体形态各异,从细脉状到网脉状均有分布,在花岗岩及碳酸盐岩裂隙带中围岩蚀变有钾长石化、云英岩化、碳酸盐化、绢云母化、萤石化以及电气石化(郭翔宇, 2017)。Cu矿化主要产于花岗岩凹陷构造带内及其附近的玄武岩和大理岩层间,围岩蚀变主要有硅化、阳起石化、金云母化、绿泥石化及透辉石化(杨宗喜等, 2010; 郭翔宇, 2017; 赵月华, 2022)。大厂矿区以龙箱盖岩体为中

心,向外依次为云英岩化、钾长石化-矽卡岩化、角岩化-硅化、电气石化、绢云母化、碳酸盐化(梁婷等,2014)。具体而言,Sn矿化主要以脉状矿体、层状-似层状和网脉状矿体形式产出,脉状矿化在两侧的围岩之中发生强烈的硅化、绢云母化和碳酸盐化,层状矿体围岩蚀变为硅化、碳酸盐化、电气石化、钾长石化,网脉状矿体产于泥灰岩和页岩的互层之中,该类型岩石普遍发育角岩化、矽卡岩化,且具有向深部蚀变增强的趋势(梁婷,2008)。以Cu矿化为主Zn-Cu矿主要以深部矽卡岩型层状矿体产出,该类矿化围岩蚀变主要发生矽卡岩化和角岩化,形成矽卡岩矿物组合(梁婷,2008)。对于无基性岩出露的San Rafael矿床和Sn-Cu密切共生的Neves Corvo矿床,其蚀变组合均表现为绿泥石化、钾长石化、钠长石化和绢云母化(Relvas et al., 2006a; Harlaux et al., 2021a)。

2 锡铜共生成矿机制

2.1 岩浆过程

Sn属于亲石元素和不相容元素,在岩浆演化过程中,不同氧逸度的岩浆中Sn的迁移与富集显著受制于Sn的不同价态的影响(Lehmann, 1990; Blevin et al., 1992; Linnen et al., 1996; Farges et al., 2006; Blevin, 2004)。具体表现为:在氧化岩浆中,Sn呈现相容元素的特征,以 Sn^{4+} 形式因类质同象赋存于早期结晶的铁-钛氧化物、黑云母和角闪石等矿物之中,而在还原岩浆中,Sn以 Sn^{2+} 形式存在保持不相容性,从而有利于元素运移并在晚期熔体中富集。由于岩浆中富含F、B等挥发组分,显著地降低了岩浆的黏度和固相线温度,延长了岩浆冷却和结晶分异的时间,促进了挥发分与Sn向残余熔体和流体中汇聚富集,进而有利于后期热液发生锡矿化(Burnham et al., 1980; Ishihara, 1981; Pollard et al., 1987; Lehmann, 1990; Dingwell et al., 1992)。

一般而言,与花岗岩相关的Sn矿床通常由高分异的长英质岩浆出溶含锡热液而成(Lehmann, 2021),然而,Harlaux等(2021a)在对San Rafael矿床研究时发现其花岗岩为中等分异程度,且地球化学指标不符合一般的锡矿床的形成模式,其更符合Wolf等(2018)提出可以通过对变质沉积岩中富Sn黑云母的多次熔融提取,出溶含Sn热液进而发生Sn矿化,而无需极端的岩浆分异过程。

Cu属于亲硫元素,在还原岩浆中硫元素主要以 S^{2-} 形式存在,Cu倾向与 S^{2-} 结合形成硫化物留存于源区的岩浆房之中,不利于Cu随着残余熔体以及流体向地壳浅部迁移富集,进而阻止Cu矿化的发生(Ballard et al., 2002; Lee et al., 2012)。然而,在含水的氧化性岩浆中,岩浆中的S绝大多数以 SO_4^{2-} 和 SO_2 的形式溶解在硅酸盐熔体中,Cu表现出不相容性,并且S在氧化环境比还原环境在硅酸盐熔体中的溶解度高一个数量级(Jugo, 2009)。Sun等(2004)研究发现当岩浆源区氧逸度保持较高的程度时,能够将早期还原环境形成的赋存在源区硫化物中的Cu重新活化,捕虏进岩浆体系之中,进一步导致Cu倾向于在残余熔体中逐渐富集演化并经由分离结晶作用,最终分配进入流体相上侵继而发生大规模的铜矿化作用(Richards, 2003; Simon et al., 2006; Sillitoe, 2010; 2022)。这表明与锡矿和铜矿相关的岩浆似乎一般具有差异较大的氧逸度。因此,岩浆氧逸度的计算对揭示锡铜共生矿床金属富集成矿的关键过程和成矿潜力研究均具有重要意义。锡铜共生矿床的氧逸度略高于花岗锡矿的氧逸度(图2)。

郭佳(2019)对大厂地区龙箱盖花岗岩研究发现其 $\text{Fe}_2\text{O}_3/\text{FeO}$ 值集中于0.27~0.53,与钛铁矿系列花岗岩的 $\text{Fe}_2\text{O}_3/\text{FeO}$ 比值接近(Ishihara, 1981),指示了较低的氧逸度环境,因此岩浆中的Sn主要以 Sn^{2+} 形式存在。近年来,一系列精确的同位素测定表明了锡铜矿床中锡矿化和铜矿化常形成于同期,是同一成矿事件的产物,尤其是辉钼矿Re-Os定年和锡石U-Pb定年在其中发挥了至关重要的作用。例如,杨宗喜等(2008)报道了个旧矿区辉钼矿Re-Os等时线年龄为(83.4±2.1)Ma;Guo等(2018a)获得了锡石原位U-Pb年龄为(84.3±1.4)Ma;Zhao等(2018)对大厂矿床中辉钼矿的形成时代进行了系统测定,获得Re-Os等时线年龄为(90.1±1.1)Ma;Guo等(2018b)获得锡石U-Pb年龄为(95.4±4.9)Ma~(90.3±1.8)Ma,年龄在误差范围内一致。然而,世界范围内锡铜共生矿床多与还原性的钛铁矿系列花岗岩有关(Sillitoe et al., 2022),这使得相关岩浆演化过程中铜的地球化学行为依然令人困惑。

2.2 热液过程

挥发分是岩浆热液成矿系统重要的矿化剂,在促进成矿物质源区的部分熔融、促进岩浆演化过程和成矿元素的迁移富集等方面发挥着关键作用。锡和铜迁移富集机制受温度、压力和氧逸度多种因素的综合影响(Dingwell et al., 1985; Eugster, 1986;

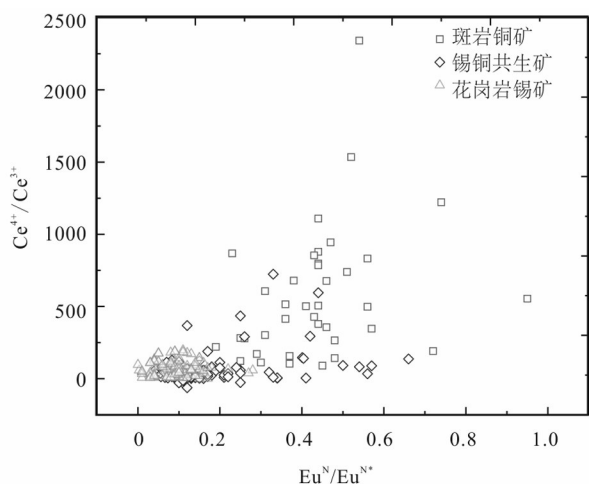


图2 不同矿区氧逸度 Ce^{4+}/Ce^{3+} vs. Eu^N/Eu^{N*} 示意图(数据来源:Ballard et al., 2002; Chen et al., 2016; 解世雄, 2021)

Fig. 2 Ce^{4+}/Ce^{3+} vs. Eu^N/Eu^{N*} (Date source: Ballard et al., 2002; Chen et al., 2016; Xie S X, 2021)

Webster, 1990), 其中氧逸度的变化是促使锡铜矿化的重要因素。

实验研究发现, Sn 在热液流体中的迁移富集行为主要依赖于流体中 Cl⁻ 的浓度, 在高氧逸度(HM)热液体系中, Sn 以 Sn⁴⁺ 形式与 Cl⁻ 和水结合形成 [SnCl₃(H₂O)₃]⁺、SnCl₅(H₂O)]⁻ 或 [SnCl₄(H₂O)₂]⁰ 进行迁移富集(Schmidt, 2018)。而 Sn 在还原性高温高盐度流体中主要以 Sn²⁺ 形式迁移, 且 Sn 在 H₂O+HCl 中的溶解度比 H₂O+NaCl 中的溶解度高出 2 个数量级(Duc-Tin et al., 2007), 当长石发生水解(云英岩化)或岩浆热液与大气降水发生混合导致流体中氧逸度升高, Sn²⁺ 转移电子形成 Sn⁴⁺, 从而以锡石(SnO₂) 的形式沉淀(Taylor, 1988; Heinrich, 1990; Audétat et al., 1998; Schmidt, 2018)。

Cu 可以在高盐度和氧化性的流体中与 Cl⁻ 结合进行迁移富集(Burnham et al., 1980; Pokrovski et al., 2005), 以发育磁铁矿、赤铁矿和硬石膏矿物组合为特征(Sillitoe, 2010; Richards, 2011; Sun et al., 2015)。但有学者研究表明, Cu 也可以与还原硫结合(HS⁻、H₂S 和 S²⁻) 进入气相进行迁移富集(Heinrich et al., 2004; Williams-Jones et al., 2005; Simon et al., 2006; Nagas-eki et al., 2008), 这一机制也可以解释发育极少量的还原性斑岩铜矿的形成过程(Rowins, 2000; Cao et al., 2014)。San Rafael 矿床中锡石和黄铜矿的沉淀主要发生在构造剪切带中, Harlaux 等(2020; 2021b)通过对其中发育的三期电气石进行原位 O

同位素研究指出, 还原性富 Sn 成矿流体与氧化性大气降水发生的流体混合导致氧逸度升高是导致 San Rafael 矿床形成的关键因素。王晨光等(2023)对德保矿床开展了地球化学和流体包裹体研究发现, 高氧逸度的成矿流体利于黄铜矿的沉淀, 但不利于 Sn 的运移与富集。最近的研究发现, 单相岩浆流体冷却引发的流体氧化还原缓冲可以在千年尺度内形成大型 Sn 矿床(Han et al., 2022)。前人对个旧矿区开展流体包裹体和 H-O 同位素研究发现, 成矿流体具有从还原的高温、中低盐度向氧化的低温、低盐度演化的特征, 天水与热液的混合是导致锡铜成矿的重要原因(莫国培, 2006; 杨宗喜等, 2010; 张娟等, 2012; Liao et al., 2014)。

3 问题与展望

3.1 成矿物质来源

目前, 针对锡铜共生矿床中铜的来源, 仍存在广泛争议, 一些学者推测是还原性、钛铁矿系列岩浆经高度分异出溶富锡的成矿流体, 并对矿区附近富铜的变质沉积原岩或镁铁质围岩进行淋滤萃取, 从而导致铜元素进入成矿流体, 进而形成锡铜共生矿床(毛景文等, 2008; 张娟等, 2012; Cheng et al., 2012a; Romer et al., 2016; Guo et al., 2018a; 李翔, 2019; 江丞曜等, 2021)。例如卡房矿床内老卡岩体平均 $w(Cu)$ 为 15.6×10^{-6} , 该矿段碳酸盐岩和马拉格矿段的碳酸盐岩 $w(Cu)$ 分别为 20×10^{-6} 和 19×10^{-6} , 而碱性玄武岩 $w(Cu)$ 高达 500×10^{-6} (彭张翔, 1992), 如此高的含铜量可以为成矿提供主要的物质来源(杨宗喜等, 2010)。但并非所有锡铜共生矿区及其周围都存在大规模基性-超基性岩浆岩, 例如, 秘鲁的 San Rafael 矿床发育西北走向的锡石-石英硫化物脉状矿体, 其产于过铝质花岗杂岩体和奥陶纪变质沉积岩中(Harlaux et al., 2021b)。如果这种观点成立, 那么需要何等条件的成矿流体可以将个旧锡矿区和 Cornwall 成矿省淋滤出超过百万吨的铜? 在成矿流体有限的条件下, 个旧锡矿区的玄武岩体淋滤形成此种超大规模的铜矿化还值得商榷。此外, 大规模的流体淋滤必会导致剧烈的热液蚀变现象发生, 但这与目前观察到的野外地质现象有所差异(Xu et al., 2001; Zhang et al., 2013)。其次, 对成矿年代学和流体包裹体研究表明锡和铜矿化常形成于同一成矿过程的不同阶段, 铜矿化的发生一般晚于锡矿化(Kontak et al., 2002; Liao et

al., 2014)。那么从锡矿化岩浆中出溶的成矿流体在经历温度、压力、氧逸度等物理化学条件的改变后是否还具有淋滤萃取围岩的能力,如果有那么水岩反应的过程如何?对于富锡成矿流体中铜的来源仍然需要进一步理论探索和实验探究,高温高压实验也许对探讨热液对富铜镁铁质围岩淋滤萃取的精细化过程可提供重要借鉴。

有学者指出锡与铜可能是从变质沉积原岩中继承下来,这些变质沉积岩发生部分熔融形成还原的钛铁矿系列岩浆(Sillitoe et al., 2022)。然而,铜在还原性岩浆中主要以硫化物的形式存在,很难被含锡的岩浆流体

所利用,当然,如果岩浆中的S含量极低,Cu含量极高,以至于铜仍有机会向残余熔体中迁移富集,那么该观点或许能够作为铜的可能来源,但是对于还原性岩浆而言,这种情况发生的可能性有多大我们不得而知。因此,对于此种观点的合理性还有待进一步证明。Clark等(1993)针对Cornwall成矿省提出,在弧后或碰撞后环境下通过地幔衍生的镁铁质岩浆供应到的中下地壳发生深熔作用造成地壳部分熔融,形成了过铝质钛铁矿系列岩浆,同时,镁铁质岩浆出溶的氧化性流体提供的铜进入到长英质岩浆房中,导致富铜流体与富锡流体发生混合,从而发生Sn-Cu矿化。但这一观点

表1 世界主要锡铜共生矿床特征表

Table 1 Characteristics of major Sn-Cu coexistence deposits in the world

矿床名称	矿床类型	成矿时代 /Ma	成矿动力 学背景	花岗岩体	中基性岩石	资源储量 /万t	品位	数据来源
英国 Cornwall 矿田	岩浆热液 脉型	270~295 (晚古生代)	碰撞伸展 环境	S型花岗岩	煌斑岩和玄 武岩熔岩,镁 铁质包体	锡矿:250 铜矿:200		Willis-Richards et al., 1989; Romer et al., 2016
葡萄牙 Neves Corvo 矿床	火山块状硫 化物型+岩 浆热液型	363~366 (晚古生代)	碰撞伸展 环境	隐伏S型 花岗岩	镁铁质火山 岩	锡矿:9.9 铜矿:324	锡:2.2% 铜:45Mt@6%+ 4.5Mt@12%	Relvas et al., 2006a; Martin-Izard et al., 2016; Li et al., 2019
德国 Sadisdorf 矿床	云英岩网 脉型	326 (晚古生代)	碰撞后伸 展环境	A型花岗 岩	煌斑岩脉	锡矿:1.5		Seltmann, 1994; Breiter et al., 1999
秘鲁 San Ra- fael 矿床	岩浆热液 脉型	24 (新生代)	俯冲相关 弧后环境	S型花岗岩	煌斑岩脉和 包体	锡矿:100 铜矿:37	锡:2% 铜:0.16%	Kontak et al., 2002; Mlynarczyk et al., 2003; Harlaux et al., 2020; 2021a
俄罗斯 Sobo- linoe 矿床	岩浆热液 脉型	85 (中生代)	俯冲相关 弧环境	I型花岗岩	闪长岩	锡矿:20 铜矿:0.6	锡:0.23%	Gonevchuk et al., 2010
加拿大 Mount Pleas- ant 矿床	云英岩网 脉型	370 (晚古生代)	碰撞后转 换伸展环 境	A型花岗 岩	拉斑玄武岩 和钙碱性安 山岩熔岩	锡矿:5.55 铜矿:1	锡:0.38% 铜:0.29%	Yang et al., 2003; Sinclair et al., 2006
日本 Akenobe 矿床	岩浆热液 脉型	73 (中生代)	俯冲相关 弧环境	隐伏I型花 岗岩	玄武岩、安山 质岩墙	锡矿:6.9 铜矿:17.8	锡:0.40% 铜:1.03%	Ishihara et al., 2012
云南个旧 矿床	矽卡岩型+ 岩浆热液型	85 (中生代)	俯冲弧后 伸展环境	S型花岗岩	玄武岩、镁铁 质包体	锡矿:327 铜矿:325	锡:1% 铜:2%	Cheng et al., 2013a; 2013b; Guo et al., 2018a; Mao et al., 2019; Wang et al., 2020
广西大厂 矿床	矽卡岩型+ 岩浆热液型	95.4~90.3 (中生代)	俯冲伸展 环境	S型花岗岩	石英闪长玢 岩、花岗斑岩	锡矿:110 铜矿:20	锡:1.1% 铜:0.28%	梁婷, 2008; 郭佳, 2019
湖南黄沙坪 矿床	矽卡岩型+ 岩浆热液型	159~154 (中生代)	后碰撞伸 展环境	A型花岗 岩	石英斑岩、花 岗斑岩和英 安斑岩	锡矿:3.82 铜矿:22.79	铜:1.12%	何厚强等, 2010; 赵盼捞等, 2018; 赵冻等, 2023
广西德保 矿床	矽卡岩型	435~438 (早古生代)	碰撞后伸 展环境	S型花岗岩	-	锡矿:3.21 铜矿:13.23	锡:0.24% 铜:1.05%	王永磊等, 2011; Chen et al., 2021; 王晨光等, 2023
澳大利亚 Cleveland 矿床	矽卡岩型	374 (晚古生代)	碰撞后伸 展环境	I型花岗岩	-	锡矿:7.56	锡:0.61%	Cox et al., 1988; Hong et al., 2017
澳大利亚 Re- nison 矿床	矽卡岩型	366 (晚古生代)	弧后伸展 环境	I型花岗岩	-	锡矿:34.6	锡:1.41%	Patterson et al., 1981; Hong et al., 2017

需要更多的岩相学证据支持,即矿床周围存在与含锡花岗岩时空相关的镁铁质岩体,包括暗色微粒包体、熔岩、岩墙和岩脉等产出形式(Cheng et al., 2013b; Wang et al., 2019),基本类似于斑岩型铜矿床的成矿过程(Sillitoe, 2010; Sun et al., 2015)。San Rafael 矿床的形成是由于软流圈异常热流和地幔衍生镁铁质岩浆的底侵作用,引起大陆地壳变质沉积岩的部分熔融,形成过铝质 S 型花岗岩岩浆(Sandeman et al., 1995; Kontak et al., 2002)。花岗岩岩浆在深部充分结晶形成了巨晶钾长石黑云母堇青石花岗岩体,高温镁铁质熔体补给注入更为还原、分异的晶粥体中引发了二次沸腾,导致富含金属的岩浆发生流体出溶,随后上升到地表形成花岗岩穹窿,在地表冷却并与对流的大气水混合,从而产生锡铜矿脉(Harlaux et al., 2021a)。对于世界著名的 Neves Corvo Sn-Cu 矿床,

前人运用锆石和锡石 U-Pb 定年得到长英质火山岩的年龄为 384~354 Ma(Oliveira et al., 2013),锡矿化年龄为 366~363 Ma(Li et al., 2019),成岩成矿时代相近。因此,前人认为高品位锡矿化的发生得益于岩浆热液的加入(Relvas et al., 2001; 2006a; 2006b; Huston et al., 2011),而非变质热液特殊贡献(Moura, 2008),其形成模式可能为深部隐伏的含锡花岗岩出溶富锡的岩浆热液,热液流体中 Sn 以氯化物形式络合喷入海底卤水池中遇冷而发生矿化,经循环海水萃取地层中的铜,铜以挥发性硫络合物的形式进入气相迁移,热液中的 H₂S 由于迅速冷却导致结晶程度不高,造成了少量硫化物沉淀。但是,成矿系统中 Sn 和 Cu 的矿化可在同一空间内叠加形成(Relvas et al., 2006b; Li et al., 2019),该来源能否支持 Sillitoe 等(2022)提出的来自基性岩浆的高氧化流体注入同时

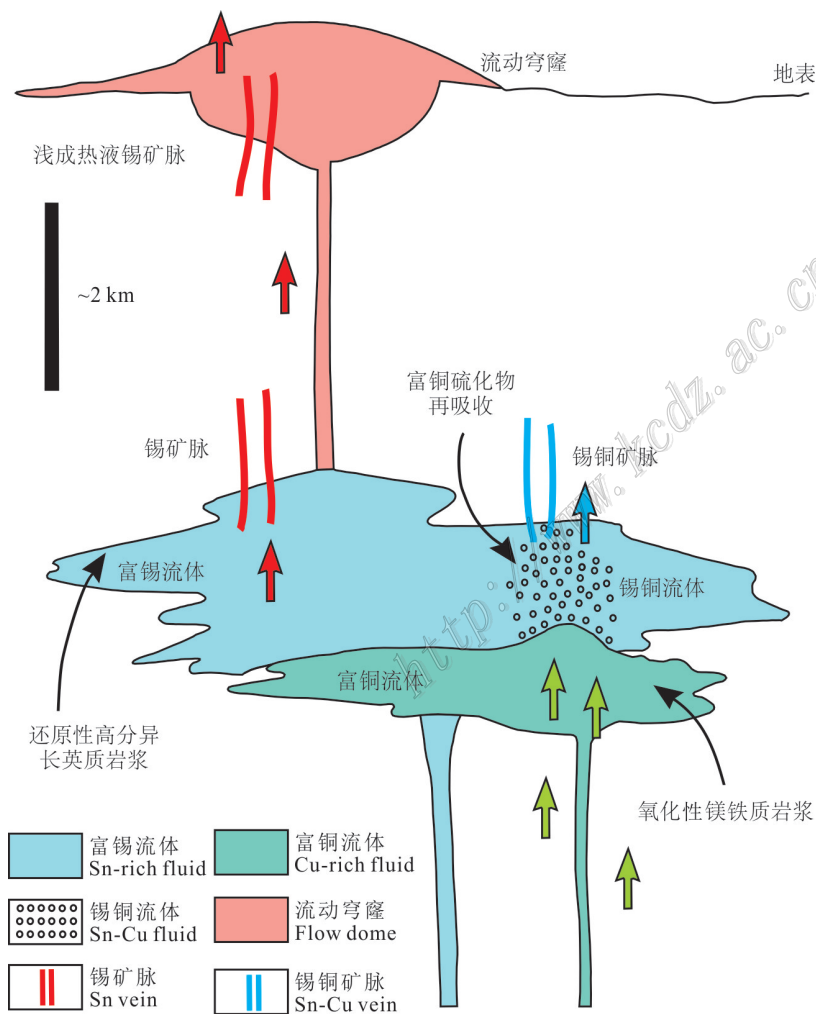


图 3 锡铜共生矿床形成模式图(据 Sillitoe et al., 2022)

Fig.3 Sn-Cu coexistence deposit formation model(after Sillitoe et al., 2022)

共存的长英质岩浆,进而导致出现锡铜共生的现象(图3),目前仍然存在于假设阶段,缺乏关键证据进行论证。

3.2 未来研究展望

目前,前人已经对锡铜共生矿床开展了诸多工作,但对于共生矿床的物质来源、成矿元素物质迁移与富集、矿床模型的构建等方面尚不完善,仍然存在一些科学问题有待揭示。展望未来,以下2个手段可能对揭示锡铜共生成矿机制可发挥作用。

其一,依靠多种非传统稳定同位素开展联合示踪,明确成矿物质来源。Sn、Cu同位素是解决岩浆阶段锡铜共生矿床中物质来源争议的重要手段。锡石Sn同位素的比值变化可以用来反演热液氧化还原演化过程(Yao et al., 2018)。Cu同位素的比值变化可以约束壳幔分异过程、追踪岩浆混合和同化混染物质来源,以及揭示热液矿化过程(Li et al., 2010; Liu et al., 2015)。Zheng等(2018)对藏南地区斑岩型铜矿床开展Cu同位素研究,为金属铜的来源和富集机制提供了直接约束,通过对比富矿岩体和贫矿岩体不同的Cu同位素组成,发现富矿岩体具有高Cu含量和较高的 $\delta^{65}\text{Cu}$ 值,其中的Cu可能来源于富含硫化物的再富集岩石圈,这表明岩浆源中的初始铜富集可能是大陆碰撞带形成巨型斑岩铜矿的关键步骤。此外,Ba同位素在示踪流体来源和再循环物质等方面具有广阔的应用前景(刘盛遨, 2022),对骑田岭3期花岗岩的Ba同位素研究表明,其存在显著的Ba同位素分馏,富集轻的Ba同位素的深部岩浆流体上涌注入浅部的晶粥体中,为锡矿床的形成提供丰富的物质来源(Deng et al., 2022)。因此,多种非传统稳定同位素的联合示踪有望解决锡铜共生矿床中成矿物质来源的问题。

其二,在开展精细矿物学特征研究的基础上,进行单矿物原位地球化学分析,利用不同阶段的矿石矿物和脉石矿物(锡石、闪锌矿、石榴子石、电气石),对不同阶段锡铜矿化的流体与物质来源进行界定。锡石作为成矿过程示踪矿物,其晶格内可容纳多种元素,锡石环带中微量元素的变化可以界定其生长环境并为锡矿化发生时的热液体系状态提供佐证(即温度、压力、氧逸度等)(Kempe et al., 2006; Gemmrich et al., 2021)。例如高松矿床中在相对还原条件下形成的原生锡石具有富W、U(Sb),贫Fe的特征,而在后期相对氧化环境中热液交代形成锡石具有富Fe,贫W、U的特征(Cheng et al., 2019);而根据大厂矿区中锡石富Fe、W,贫Nb、Ta的特征推断出

其形成于相对低温的热液环境(郭佳, 2019)。另外,电气石B同位素、闪锌矿、石榴子石和白钨矿微量元素在揭示物理化学条件,推断热液流体演化等方面发挥着重要作用(Ye et al., 2011; 叶霖等, 2018; Harlaux et al., 2021b; Xie et al., 2022)。因此,在精细矿物学特征研究的基础上,对不同矿物进行高空间分辨率的原位分析,有望对锡铜共生机制进行精细化探究和有效限定。

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