长江中下游成矿带关键金属矿产研究现状与进展

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摘要 关键金属已成为全球争夺的战略性关键矿产资源, 其矿化特点和成矿规律等研究受到高度关注. 长江中下游是我国重要的铁铜金多金属成矿带, 产出多个大中型斑岩-矽卡岩铜金铁矿床和矽卡岩型铁矿床. 矿床中除了主要成矿元素铜、金、铁和硫富集成矿, 关键金属资源种类很多, 目前可利用的主要有镉、钴、硒、碲和铼等, 它们是我国战略亟需, 且有待重点研究和突破的关键金属资源. 近年来长江经济带内大型矿业公司对伴生关键金属的综合利用日益重视, 矿床中关键金属的开发利用亟待理论和技术支撑, 因此开展成矿带内关键金属矿产综合研究具有重要的理论价值和现实意义. 在系统收集成矿带矿床中关键金属已有研究成果和资料的基础上, 对成矿带内矿床中关键金属富集特征进行了调查评价, 绘制了长江中下游成矿带含伴生关键金属元素矿床分布图, 初步总结了矿床主矿种和伴生关键金属元素的对应关系. 通过对成矿带内斑岩-矽卡岩型铜铁金矿床中镉、钴、硒、碲和铼等关键金属元素矿产的赋存状态及富集特征进行总结, 明确了上述关键金属元素的主要寄主矿物和其中含量特征. 在综合分析成矿带关键金属已有研究成果的基础上, 提出了成矿带斑岩-矽卡岩型矿床中关键金属下一步重点关注和研究的主要科学问题.

关键词 关键金属, 关键金属矿产分布特征, 赋存状态, 长江中下游成矿带

关键金属(critical metals)和关键矿产资源(critical minerals)是国际上近年来提出的新概念, 是指对战略性新兴产业的发展至关重要的一类金属元素及其矿床的总称, 其成矿特点和成矿机制研究已成为国际矿床学研究的热点^[1~4]. 长江中下游成矿带作为环太平洋成矿域的重要组成部分, 在中生代转换复合的构造体制、强烈壳幔相互作用等复杂的大陆动力学过程和岩浆活动背景下, 形成了多个大中型斑岩-矽卡岩型铜铁金矿床. 在此大规模成矿作用过程中, 矿床中除了主要成矿元素铜、金、铁和硫富集成矿, 还以伴生形式富

集了较大规模的镉、硒、钴、铼、铋、锗、镓、铟和铊等关键金属资源, 其中可伴生利用的关键金属资源主要有镉、钴、硒、碲和铼等, 它们是我国战略亟需, 且有待重点研究和突破的关键金属资源^[5~20]. 长江中下游成矿带作为我国矿床学研究程度和矿产利用技术水平最高的成矿带之一, 近年来在关键金属综合利用方面也走在前沿, 因此在成矿带开展关键金属研究具有重要的理论价值和现实意义.

长江中下游成矿带是典型的陆内成矿带, 明显有别于陆缘弧及岛弧带内大型-超大型斑岩-矽卡岩型矿

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床成矿带,以往研究集中在铜、铁、金、硫等元素成矿作用的深部过程和末端效应,矿床中伴生的关键金属的成矿背景与元素行为,成矿过程和富集机制研究则相对零散。毛景文等人^[4]系统地总结了我国进入21世纪以来不同类型关键金属矿床的主要勘查成果及全球关键金属矿产研究新进展,列举了长江中下游斑岩-矽卡岩Cu-Au-Mo-Fe成矿带中发现在铜多金属矿床外围镓、锑、铋、锗、硒、铟、碲和铼多种稀散元素富集。谢桂青等人^[21]提出长江中下游成矿带有两种不同类型含稀散金属矿床:一类呈伴生于斑岩-矽卡岩铜铁金和铅锌矿床,以多种稀散金属为特征;另一类呈独立稀散金属矿床,以前者为主。但总体上,成矿带关键金属元素赋存状态和共生分异机制等研究则相对薄弱,相关研究亟待开展。本文简要回顾了区内关键金属研究历史,并对成矿带内典型矿床中关键金属富集特征进行了调查评价,绘制了长江中下游成矿带含伴生关键金属元素矿床分布图。重点对关键金属元素镓、锑、硒、碲和铼在斑岩-矽卡岩型矿床中分布特征和赋存状态进行了分析总结,阐明上述关键金属元素的主要寄主矿物和其中含量特征。在总结目前成矿带关键金属研究现状的基础上,提出了成矿带关键金属矿产资源领域值得重点关注和研究的3个主要科学问题。

1 长江中下游成矿带关键金属勘查与研究现状

长江中下游成矿带关键金属(稀有、稀散元素)矿产勘查工作始于20世纪50年代末,如安徽省专门成立了稀有分散元素工作队,与安徽省地质局、华东地质局和合肥工业大学地质队,分别对安徽省沿江地区主要的铁铜铅锌矿床共伴生的稀散元素开展了调查评价工作,发现了矽卡岩型铜矿床及玢岩型铁矿床中伴生有镓、硒等元素,及若干镓、锗等元素的富集线索。

20世纪60~90年代,随着国民经济的高速发展,工业对稀有稀散元素的需求大量增加,成矿带稀有稀散元素勘查工作进入高峰期。江西、湖北、安徽、江苏四省地勘、科研单位对成矿带开展了稀有、稀散元素的调查评价工作,先后发现了宣城荞麦山含锗铁矿床、铜陵金口岭铜矿(伴生镓)、铜陵狮子山铜矿(伴生硒)、青阳寺门口硫铁矿(伴生硒)、铜陵市鸡冠石银金矿(伴生镓)、铜陵市冬瓜山铜矿(伴生硒)、江西城门山铜矿(伴生碲)等。

21世纪以来,各省地勘部门下属地质队开始注重

在矿床勘探过程中寻找关键金属矿产。在勘查过程中对2000年以后发现的大中型矿床开展了共伴生稀有、稀散元素的综合评价工作,先后发现了铜陵市姚家岭铜金多金属矿(伴生硒碲镓)、荷花山铅锌矿(伴生镓镓)和繁昌县浮城墩铜矿(伴生镓)。

建国以后至2010年,成矿带的稀散元素的地质工作以矿点为主,区域上的面积性调查评价工作并未开展。随着2011年全国三稀资源战略调查项目的启动,沿江各省也开始注重三稀资源的调查评价工作。如安徽省分别在2014与2015年于铜陵地区、青阳-贵池地区、宣城地区开展了三稀及稀有金属矿产资源的调查评价工作,取得了诸多区域性调查成果。程志中等人^[22]绘制了中国南方地区碲地球化学图,发现了安庆-铜陵和黄石-九江两个碲地球化学异常,与斑岩-矽卡岩型铜多金属矿有关;成矿带内镓元素异常分布范围广,浓集中心主要与多金属矿床和矿田相对应,且表现出与特定层位的相关性。

长江中下游成矿带作为我国矿床学研究程度和矿产利用技术水平最高的成矿带之一,近年来在关键金属综合利用方面也走在前沿。如2010年初,湖北大冶有色公司下属贵稀厂正式启动铼回收项目,2019年4月,稀贵厂新建精制硒项目正式投料,进入试生产,可以生产精制铼、精制碲、精制硒等一系列关键金属产品;2019年8月,铜陵有色集团与中国航空发动机集团有限公司合作,成立铜陵铜冠优创特种材料有限公司,投资5000万元建设每年2 t高纯度精制铼项目,专供中国航空发动机集团有限公司(国内最大铼金属需求方)。这将对我国未来对战略性关键金属资源的重大需求起到支撑和保障作用。

相比成矿带铜金矿床成矿作用研究,前人对长江中下游成矿带中关键金属成矿作用的研究则相对较少,且已有研究主要集中在关键金属的矿物学研究方面。Xie等人^[23]在丰山矿田发现鸡笼山矽卡岩铜金矿床中产出丰富的碲铋矿物、碲银矿和碲汞矿。韩颖霄和谢桂青^[24]发现产于灰岩的低温金矿——曹家山和竹林塘金矿床中产出丰富的碲金矿、碲金银矿、碲银矿、碲铅矿、碲汞矿和自然碲等碲化物,灰岩中含金方解石脉产出碲铅矿、碲金银矿、碲金矿和银金矿的矿物组合;张伟等人^[25]通过电子探针和扫描电子显微镜等手段,厘定出鸡冠嘴矽卡岩铜金矿床中产出硒银矿、硒铅矿、碲铋矿和碲银矿等碲化物和硒化物;钟国雄^[26]在姚家岭矿床方铅矿中发现碲银矿、碲金银矿、碲金

矿、辉碲铋矿和碲铋矿。谢桂青等人^[21]绘制了长江中下游成矿带含稀散金属矿床的分布图,提出长江中下游成矿带有两种不同类型含稀散金属矿床。

2 成矿带关键金属矿产分布特征

长江中下游成矿带可划分为大体上平行延伸的南、北、中3个亚带(图1),分别受成矿带的南北边界断裂及“中轴线”的主干断裂所控制。主带即中亚带(沿江成矿亚带)为长江中下游成矿带的主体,延长纵贯全区,宽度达数十千米,集中了区内主要的铜、铁、硫铁矿、金、银、铅锌等矿床。根据湖北、江西、安徽和江苏四省矿床发现史的资料^[27~30],结合已发表的文献和矿产勘探报告,可知成矿带内大中型斑岩-矽卡岩型矿床(图1)的铜金矿石中普遍伴生有镉、钴、硒、碲和铋等关键金属元素,部分矿床中伴生的关键金属资源量已达到大型规模。如城门山矿床伴生有超大型-大型的碲和镉等关键金属矿产资源,碲资源储量5571 t^[30];铜绿山多金属矿石中碲的含量达136 ppm(1 ppm=1 μg/g),达到工业品位;江西省碲资源储量占全国71%^[31];铜陵冬瓜山矿床中普遍含硒、镉和钴,其中,硒含量一般在10~300 ppm之间,最高可达500 ppm;镉含量一般在30 ppm以上,最高可达300 ppm,钴含量平均为30 ppm,最高可达100 ppm。且选矿试验表明,矿床中各主要矿体镉、硒和钴平均含量均能达到综合利用的要求^[32],勘探报告估算伴生硒资源量1652 t、镉资源量618 t、和钴资源量8077 t;铜陵新桥矿床中已探明伴生的硒资源量1340 t、镉资源量725 t、钴资源量6077 t;姚家岭矿床中伴生的镉资源量为1415 t。成矿带中这些矿床中伴生的关键金属均已达大型规模。

在前人资料基础上,本次工作通过对长江中下游成矿带内典型矿床中主要类型矿石中关键金属含量分析,开展了矿产中伴生关键金属概略调查(表1)。发现矽卡岩型矿床中关键金属元素伴生种类较多,主矿种不同,伴生关键金属元素也具有一定的差异。矽卡岩型铜多金属矿伴生关键金属元素以硒为主,碲次之,还少量伴生铋和铟;以城门山矿床、铜绿山矿床、金口岭矿床、狮子山矿床、琅琊山矿床等为代表。矽卡岩型硫铁矿伴生关键金属元素主要为硒和钴,以新桥矿床为代表。矽卡岩型钨钼矿床伴生关键金属元素以镓、锗为主,少量伴生铟、镉、碲,以阮家湾矿床、东顾山矿床、桂林郑矿床为代表。矽卡岩型铅锌矿床伴生关键金属元素以镉为主,镓、锗次之,少量伴生铟、碲,以

姚家岭矿床、栖霞山矿床、黄山岭矿床和荷花山矿床为代表。矽卡岩型矿床主要分布于鄂东南矿集区、九瑞矿集区、铜陵矿集区。斑岩型铜金矿床伴生关键金属元素以硒为主,镉和铋次之,以庐江县沙溪铜矿和宣城市茶亭铜矿为代表,主要分布在庐枞矿集区和宣城矿集区。矽卡岩型和斑岩型矿床中伴生的关键金属元素均主要赋存于主矿种的硫化物中。

成矿带中部分玢岩型和矽卡岩型铁矿床中伴生关键金属镓,但通常难以利用。如鄂东南矿集区程潮矽卡岩铁矿的镓资源量为1482 t^[33],相当于3个大型镓矿床。本次调查评价也发现宁芜矿集区凹山铁矿、姑山铁矿、庐枞矿集区罗河铁矿床、泥河铁矿床和小包庄铁矿床中均伴生关键金属镓,同时还伴生少量硒和镉。

此外,本研究还发现,长江中下游成矿带庐枞矿集区内部分布的脉状铜矿普遍伴生硒元素,以井边铜矿、石门庵铜矿为代表;与浅成低温热液成矿作用有关的明矾石矿床中普遍伴生关键金属元素镓,以庐江县矾山明矾石矿为代表。成矿带内还产出若干关键金属独立矿床,以安徽和县香泉铌矿床和江苏南京浦口区万寿山锗矿床为代表,但暂时无开发利用价值。

3 成矿带关键金属赋存状态及富集特征

如前文所述,尽管长江中下游成矿带中关键金属矿产分布广、种类多,寄主矿床类型多样,但成矿带内矿床具有伴生利用价值的关键金属主要有镉、钴、硒、碲和铋等,均主要赋存在斑岩-矽卡岩型矿床中,下文重点对成矿带内上述5种关键金属的赋存特征进行初步分析和总结。

3.1 钴的赋存状态及赋存特征

钴主要作为伴生元素产出于铜矿床内,钴在铜铁矿床中最富集。据刘宝娣^[34]统计,铜矿床中钴在矿石中平均含量为19~190 ppm,相当于其克拉克值的1~10倍,其中,矽卡岩型铜矿含钴较高,为克拉克值的5~10倍。主要富集钴的矿石类型为磁黄铁矿型铜矿石、磁铁矿型铜矿石、黄铁矿型铜矿石和矽卡岩型铜矿石。

研究表明,长江中下游成矿带与成矿有关的岩浆岩中钴丰度较低,而成矿过程中钴主要富集在金属硫化物和金属氧化物中,通常主要赋存于毒砂、黄铁矿、磁黄铁矿、黄铜矿、磁铁矿等金属矿物中,矿物中钴的含量高低次序为毒砂>黄铁矿>黄铜矿>磁黄铁矿>磁铁矿。刘宝娣^[34]通过测定多个铜矿床中金属矿物

图 1 长江中下游成矿带含共伴生关键金属元素矿床分布图^[20]。含稀散金属的矿床据湖北、江西、安徽和江苏四省矿床发现史、作者未发表资料修编。1, 程潮铁矿床(伴生铈); 2, 张福山铁矿床(伴生铈); 3, 铜山口铜金矿床(伴生硒/碲); 4, 鸡冠咀金矿床(伴生硒/碲); 5, 铜绿山铁铜矿床(伴生硒/碲); 6, 阮家湾钨矿床(伴生铈/钨); 7, 鸡笼山金铜矿床(伴生硒/碲); 8, 封三洞金铜矿床(伴生硒/碲); 9, 洋鸡山金矿床(伴生硒/碲); 10, 城门山铜金矿床(伴生硒/碲); 11, 东顾山钨钼矿床(伴生铈); 12, 沙溪铜金矿床(伴生铈); 13, 罗河-小包庄铁矿床(伴生铈); 14, 泥河铁矿床(伴生铈); 15, 矾山明矾石矿床(伴生铈); 16, 石门庵铜矿床(伴生铈/钨); 17, 井边铜矿床(伴生铈/钨); 18, 黄山岭-桂林郑铅锌钼矿床(伴生钨); 19, 湛岭钼矿床(伴生铈); 20, 金口岭铜金矿床(伴生铈); 21, 狮子山铜金矿床(伴生铈/碲/钨); 22, 荷花山铅锌矿床(伴生铈/钨); 23, 新桥硫铁矿床(伴生铈/钨/钼); 24, 姚家岭铜锌矿床(伴生铈/钨/钼); 25, 茶亭铜金矿床(伴生钨); 26, 姑山铁矿床(伴生铈); 27, 凹山铁矿床(伴生铈); 28, 香泉铀矿床; 29, 琅琊山铜金矿床(伴生铈); 30, 万寿山锗矿床; 31, 栖霞山铅锌矿床(伴生钨)

Figure 1 Distribution of deposits containing critical metals resource in the Middle-Lower Yangtze River Valley metallogenic belt^[20]. Information refer to discovery history of mineral deposits in Hubei, Jiangsu, Anhui and Jiangxi and authors' unpublished data. 1, Chengchao iron deposit (associated gallium); 2, Zhangfushan iron deposit (associated gallium); 3, Tongshankou copper-gold deposit (associated selenium/tellurium); 4, Jiguanzui gold deposit (associated selenium/tellurium); 5, Tonglushan iron-copper deposit (associated selenium/tellurium); 6, Ruanjiawan tungsten deposit (associated gallium/cadmium); 7, Jilongshan gold-copper deposit (associated selenium/tellurium); 8, Fengsandong gold-copper deposit (associated selenium/tellurium); 9, Yangjishan gold deposit (associated selenium/tellurium); 10, Chengmenshan copper-gold deposit (associated selenium/tellurium); 11, Donggushan tungsten-molybdenum deposit (associated rhenium); 12, Shaxi copper-gold deposit (associated selenium); 13, Luohe-Xiaobaozhuang iron deposit (associated gallium); 14, Nihe iron deposit (associated gallium); 15, Fanshan alunite deposit (associated gallium); 16, Shimen'an copper deposit (associated selenium/gallium); 17, Jingbian copper deposit (associated selenium/gallium); 18, Huangshanling-Guilinzheng lead-zinc-molybdenum deposit (associated cadmium); 19, Zhanling rhenium-molybdenum deposit (associated rhenium); 20, Jinkouling copper-gold deposit (associated gallium); 21, Shizishan copper-gold deposit (associated selenium/tellurium/cobalt); 22, Hehuashan lead-zinc deposit (associated cadmium); 23, Xinqiao sulfur deposit (associated selenium/cadmium/cobalt); 24, Yaojialing copper-zinc-gold deposit (associated selenium/cadmium/cobalt); 25, Chating gold-copper deposit (associated cadmium/gallium); 26, Gushan iron deposit (associated gallium); 27, Washan iron deposit (associated gallium); 28, Xiangquan thallium deposit; 29, Langyashan copper-gold deposit (associated selenium); 30, Wanshoushan germanium deposit; 31, Qixiashan lead-zinc deposit (associated cadmium)

的钴含量平均值, 得出黄铜矿含钴114 ppm、黄铁矿含钴611 ppm、磁黄铁矿含钴548 ppm、毒砂中平均含钴5900 ppm、磁铁矿含钴95 ppm。近年来, 部分学者对区内不同矿床中的金属矿物开展了电子探针主量分析和LA-ICP-MS微量元素分析。李红阳等人^[35]通过对新桥

矿床中含硫磁铁矿体的主要磁铁矿和黄铁矿单矿物电子探针测定, 得出磁铁矿中含有少量的钴(含量为20 ppm), 黄铁矿中钴含量较高(210 ppm)。

Monteiro等人^[36]曾对硫化物中钴的富集机制进行了探讨, 认为其主要由钴的地球化学性质决定, 钴的地

表 1 长江中下游成矿带代表性含共伴生关键金属元素矿床特征一览表^{[27-33]a)}**Table 1** Summary of characteristics of representative deposits containing critical metal resources in the Middle-Lower Yangtze River Valley metallogenic belt^[27-33]

矿床类型	矿床名称	Se	Te	Re	Co	Cd	Ga	勘探报告 资源量	资料来源
矽卡岩-斑岩型 铁铜金矿床	新桥硫铁金矿床	10~300	—	—	10~100	10~100	—	Se: 1340 t Cd: 725 t Co: 6077 t	**
	琅琊山铜矿床	20~100	—	200~800	—	—	—	—	本研究
	安庆铜铁矿床	20~200	—	—	50~200	—	—	Se: 675 t Co: 3250 t	**
	铜陵凤凰山铜矿床	50~150	10~100	—	—	—	—	—	本研究
	庐江沙溪铜矿床	50~150	—	—	—	—	—	—	本研究
	庐江茶亭铜矿床	50~150	—	—	—	—	—	—	本研究
	铜陵冬瓜山铜矿床	10~300	—	—	30~100	30~300	—	Se: 1652 t Cd: 618 t Co: 8077 t	**
	城门山铜金矿床	—	50~200	—	—	—	—	Te: 5571 t	[33]
	程潮铁矿床	—	—	—	—	—	10~100	Ga: 1482 t	[33]
	罗河-小包庄铁矿床	—	10~50	—	—	—	—	—	本研究
玢岩型铁矿床	泥河矿床	—	10~50	—	—	—	—	—	本研究
	凹山矿床	—	10~50	—	—	—	—	—	本研究
	姑山矿床	—	10~50	—	—	—	—	—	本研究
	东顾山钨钼矿	—	—	100~500	—	—	—	—	本研究
其他类型矿床	湛岭钼矿床	—	—	100~500	—	—	—	Re: 30 t	**
	庐枞井边-石门庵脉状铜金矿	50~150	—	—	—	—	—	—	本研究
	庐江大矾山明矾石矿	—	—	—	—	—	50~200	Ga: 380.3 t	**
	香泉铌矿床	—	—	—	—	—	—	Tl: 250 t	**
	万寿山锗矿床	—	—	—	—	—	—	Ge: 69 t	**

a) 表中数据为矿床中主要类型矿石中关键金属含量, 单位为ppm; **表示矿床勘查地质报告(内部资料); “—”表示低于检出限

球化学性质既有亲铁性又有亲硫性, 因此常富集于与Fe-Cu-S有关的矿床中。铁、钴、镍的离子半径及负电性极为相似, 故可产生广泛的类质同象置换, 在内生成矿作用中, 钴置换铁的硫化物及氧化物中铁而呈类质同象混入。周涛发等人^[37]通过对新桥层状硫化物矿体中不同类型黄铁矿的微量元素分析发现, 黄铁矿是主要的赋钴矿物, 钴主要赋存于胶状黄铁矿和细粒黄铁矿内(钴含量介于150~700 ppm), 矿物元素面扫描表明, 钴以类质同象形式进入黄铁矿内(图2(a), (b))。黄铁矿中钴含量明显受成矿温度控制, 钴主要富集于成矿温度较高的早期黄铁矿和黄铜矿等矿物中, 随着成矿温度下降, 硫化物中钴含量降低。如在罗河铁矿床中, 不同类型黄铁矿中钴含量有明显变化, 早阶段高温黄铁矿中钴含量可达1000~5000 ppm, 而晚阶段低温黄铁矿

钴含量只有1~10 ppm(图2(c), (d))。

3.2 硒和碲的赋存状态及赋存特征

硒和碲的地球化学性质较为相似, 所以二者常常被视为同一个地球化学对^[38], 硒-碲、硒-硫能较广泛地产生类质同象置换。前人对铜陵矿集区不同矿床中的硫化物开展了电子探针和LA-ICP-MS的研究, 均表明硒主要赋存于硫化物中, 硫化物的微量元素特征指示, 硒主要以内置同象的形式存在于硫化物中^[37,39-41], 未发现作为独立的矿物。黄铁矿是主要的富硒矿物, 黄铁矿中硒含量变化范围在10~100 ppm。碲通常在成矿带斑岩-矽卡岩矿床硫化物中含量较高, 已达综合利用标准^[34,41-43]。分析表明, 碲主要以类质同象形式取代硫赋存于斑铜矿、磁黄铁矿、黄铁矿及黄铜矿中, 各矿

图2 新桥和罗河矿床中黄铁矿钴的赋存特征。(a), (b) 新桥矿床黄铁矿中钴以类质同象形式产出; (c), (d) 罗河铁矿床不同类型黄铁矿中钴含量具有明显差异

Figure 2 Occurrence of cobalt in pyrite of different stages in Xinqiao and Luohe deposit. (a), (b) Isomorphism is the main occurrence of cobalt in pyrite from Xinqiao deposit; (c), (d) contents of cobalt varies considerably in different types of pyrite from Luohe deposit

物中斑铜矿含碲最高, 其次是黄铁矿, 上述矿物中碲含量高低顺序为斑铜矿>黄铁矿>黄铜矿>磁黄铁矿。

成矿带内部分矿床中硒和碲与金密切共生。储国正和曹奋扬^[44]在铜陵鸡冠石矿床银(金)矿床自然金、自然银、银金矿研究中通过电子探针分析发现, 自然金、自然银和银金矿中均检测到较高的硒和碲含量, 含量介于0.01%~0.1%^[44]。

碲在矿床中还经常以独立矿物形式产出, 例如姚家岭矿床中产出大量的辉碲铋矿, 其形成于早硫化物阶段, 存在多种赋存形式(图3): (1) 主要呈长条状、不规则柱状包裹于闪锌矿中, 粒径一般为15~30 μm; (2) 以板状包裹于黄铁矿中, 粒径可达200 μm; (3) 少量以不规则状、小团状形式与闪锌矿相伴, 共同分布于方解石细脉中, 粒径一般介于5~30 μm之间; (4) 呈不规则团状包裹于黄铜矿中或沿着黄铜矿边界镶嵌分布, 粒径一般为~50 μm; (5) 呈板条状嵌布于黄铁矿与闪锌矿晶粒之间, 粒径10~30 μm之间; (6) 呈长条状分布于方解石与闪锌矿之间, 粒径大者达50 μm, 闪锌矿形成略早于其余两种矿物。其中, (1)和(4)是辉碲铋矿的主要赋存状态。电子探针分析显示此矿物主量元素铋含量为

60.53%~60.57%, 碲含量为28.70%~30.74%, 硫含量为4.55%~4.62%, 有少量的硒, 含量为1.53%~2.78%。

3.3 镉的赋存状态及赋存特征

镉具有典型的分散元素地球化学性质, 至今尚未发现镉的独立矿床。镉主要伴生在其他金属矿床中, 尤其是中低温铅锌矿床^[38]。目前针对长江中下游成矿带内镉的分布特征的研究较少。Liu等人^[45]对铜陵狮子山矿区荷花山铅锌矿床中闪锌矿开展LA-ICP-MS分析, 发现闪锌矿中伴生较高含量镉, 含量介于0.1%~1.5%之间, 提出镉主要类质同象赋存于闪锌矿中。此外, 在铜金矿床硫化物中也发现镉的赋存, 在新桥矿床黄铁矿中发现存在少量的镉, 含量范围为10~50 ppm^[37]。

3.4 铋的赋存状态及赋存特征

铋和钼的元素性质相近, 铋通常以类质同象形式在辉钼矿中富集。为了确定长江中下游成矿带矿床的成矿时代, 前人系统开展了辉钼矿Re-Os同位素定年, 基本查明了成矿带内主要矿床辉钼矿的铋含量。如铜陵矿集区大团山矽卡岩型铜矿床中辉钼矿铋含量为

图3 (网络版彩色)姚家岭矿床辉碲铋矿赋存特征。Sp, 闪锌矿; Tet, 辉碲铋矿; Py, 黄铁矿; Cal, 方解石

Figure 3 (Color online) The occurrence of the tetradymite in Yaojialing deposit. Sp, sphalerite; Tet, tetradymite; Py, pyrite; Cal, calcite

149~1000 ppm^[46]; 舒家店斑岩铜金矿床辉钼矿中铋平均含量为516 ppm^[47]; 凤凰山矽卡岩铜矿床辉钼矿中铋的含量在54~190 ppm之间^[48]; 姚家岭矽卡岩锌金矿床辉钼矿中铋含量在242~1142 ppm之间^[49,50]。鄂东南矿集区矽卡岩型铜矿床阮家湾、千家湾、铜绿山和斑岩型铜山口等矿床中辉钼矿铋的含量分别为24.8、334、305~665、203~224 ppm^[51]。九瑞矿集区丰山洞、东雷湾、宝山、城门山和武山等矿床中辉钼矿铋的含量分别为436^[51]、34.1~57.9、28.0~204^[52]、4.9~14.9^[53]和267~678 ppm^[54]。另外, 也有学者尝试开展黄铁矿Re-Os同位素定年, 但黄铁矿中铋含量很低, 均为ppb级别。从统计学上看, 成矿带内同一矿床中辉钼矿中铋含量变

化范围较大, 大部分矽卡岩斑岩矿床中铋含量通常为100~1000 ppm, 但无明显的分布规律。

近年来在长江中下游成矿带南亚热带新发现了湛岭斑岩型铋钼矿床, 勘探报告提交铋金属资源量为30 t, 是成矿带内目前发现的最大的关键金属铋矿床。本工作对矿床的辉钼矿中铋赋存状态开展了初步研究。矿物原位LA-ICP-MS点分析和面扫描结果显示, 湛岭辉钼矿中的铋存在明显的不均匀分布特点, 在同一叶片的核部铋含量高于边部, 不同叶片中铋含量也存在很大差异(图4(a))。利用FIB切割技术, 对经过LA-ICP-MS面扫描区域中铋最富集的区域进行切割, 借助SEM和TEM分析方法, 在辉钼矿中尚未发现存在细小矿物晶

图4 湛岭辉钼矿床Re元素的LA-ICP-MS含量面扫描图(a)和透射电子显微镜下的高分辨率图(b)

Figure 4 LA-ICP-MS mapping diagram (a) and high resolution diagram under transmission electron microscope (b) of Re element in Zhanling molybdenite deposit

体或者团块(图4(b)). 因此, 铼可能是以类质同象的形式存在于辉钼矿的晶格中.

4 研究展望

虽然关键金属成矿机制已成为国际矿床学研究的热点^[1~4], 但包括镉、钴、硒、碲和铼等在内的关键金属矿床的成矿机制研究总体程度较低. 与之类似, 长江中下游成矿带内关键金属的研究还属于起步阶段, 目前还仅局限于调查评价和关键金属在矿床中分布特征等初步研究. 翟明国等人^[1]提出关键矿产资源研究在地质方面主要科学问题包括: 元素地球化学性质和赋存状态、重大地质事件和层圈物质循环与成矿物质基础、超常富集的苛刻条件和成矿规律, 对长江中下游成矿带关键金属矿产而言, 主要有以下几个重点关注的科学问题.

(1) 2003~2008年, 国际地质科学联合会(IUGS)曾设立IGCP项目, 主要研究碲和硒在矿床中的成矿机制^[55], 项目系统地分析了世界典型的富含碲化物和硒化物的岩浆型铜镍硫化物矿床、铁氧化铜金型矿床、火山岩块状硫化型矿床、斑岩型矿床、矽卡岩型矿床、浅成低温型矿床、造山型金矿床和卡林型金矿床的成矿类型、成矿物质来源、成矿流体特征和矿石物质富集机理, 为成矿带碲和硒的研究提供了良好的研

究基础. 长江中下游成矿带是典型的陆内成矿带, 明显有别于陆缘弧及岛弧带内的大型-超大型斑岩矿床组成的成矿带, 以往研究主要集中在铜铁金硫等元素成矿作用的深部过程和末端(浅部)效应. 对成矿作用过程中关键金属元素的地球化学行为、富集机制等认识仍很肤浅. 亟待开展陆内构造环境下斑岩-矽卡岩型铜金矿床成矿系统形成与演化过程中关键金属的来源与富集机制研究.

(2) 长江中下游成矿带关键金属元素矿产资源以“稀、伴、细”为特征, 主要以3种赋存状态产出: 独立矿物、以微量元素呈类质同象和固溶体形态、以极细小矿物与其他矿物形成复杂共生组合形成的独立矿物. 成矿带内目前发现的关键金属元素独立矿物只具有矿物学和矿床学意义, 可经济回收利用的关键金属元素均富集在硫化物中, 且特定的关键金属与某个矿物有明确的对应性. 如铼从辉钼矿中回收、硒和碲从黄铜矿中回收、镉主要从闪锌矿中回收、钴从黄铁矿中回收. 目前, 以往矿床学研究主要通过LA-ICP-MS和电子探针来分析矿物微区中元素的含量, 但对于元素在矿物中具体是类质同象还是纳米级矿物包裹体形式往往无法给出准确的判断.

近年来, 材料学在微纳检测技术上取得了长足的进步. 采用扫描电子显微镜^[56,57]、扫描隧道电子显微镜^[58,59]、高分辨透射电子显微镜^[60,61]、球差矫正高分辨透射电子显微镜^[62,63]可对微纳尺度到原子级别的团聚体进行直接的观测, 并结合微区成分分析, 可直接分析不同尺度微区的成分、结构以及界面结合情况. 因此, 将材料科学领域最尖端微区微纳分析技术应用到矿床学领域, 建立系统的镉、钴、硒、碲和铼等关键金属的赋存状态表征的分析技术与方法流程. 确定特定硫化物中关键金属的赋存状态是成矿带关键金属元素富集机理研究和资源的有效利用的核心问题和难点.

(3) 矿床学研究对象为自然界地质过程形成的天然产物, 关键金属元素的成矿模拟实验开展较少. 材料学研究对象为人工合成物, 通过现代材料合成, 可以在不同基体上进行单原子催化剂的制备并进行原子尺度赋存状态分析^[64,65]. Liu等人^[66]利用扫描透射电子显微镜结合高角度环形暗场像, 分析了沸石结构中单原子催化剂Pt、Pd、Ru、Rh、Co、Ni和Cu等的赋存状态. 采用第一性原理计算方法来获得各种不同材料的晶格常数、形成能、弹性模量、电子密度等结构及性能方面已有很多报道^[67,68]. 材料学的相关研究为关键金

属成矿机制的研究提供了一种具有指导意义的研究思路。根据成矿带关键金属矿产的特征, 有针对性地开展成矿模式实验, 将理论计算与相关模拟实验相结合, 充分利用微纳表征技术的先进手段和相关理论对人工合

成的主矿物中关键金属元素赋存状态的精确分析与确定, 并根据其与主矿物相及其他元素的晶体学关系及界面相关性, 有望为阐明关键金属富集机理提供有说服力的依据。

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Summary for “长江中下游成矿带关键金属矿产研究现状与进展”

Critical metal resources in the Middle-Lower Yangtze River Valley metallogenic belt

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Critical metals are strategic key mineral resources for global competition, with research on mineralization characteristics and metallogenic regularity attracting attention. The Middle-Lower Yangtze River Valley metallogenic belt (MLYB) is a part of the circum-Pacific magmatic belt. Under complex continental dynamic setting, such as the Mesozoic transformation of structural systems and intensive crust-mantle interactions, a large amount of porphyry-skarn Cu-Fe-Au deposits have been formed. During large-scale mineralization processes, critical resources, including Cr, Co, Se, Re, and Te, are produced from these deposits, in addition to bulk metals such as Cu, Ag, Fe, and S-rich ores. These critical metals are urgently needed in China's strategy. Therefore, research should receive emphasis to achieve new breakthroughs. In recent years, large mining companies in the Yangtze River economic belt have paid special attention to the comprehensive use of critical metals. Therefore, studies on critical metals in the belt have important theoretical and economic significance. This paper has systematically reviewed and summarized the research outcomes and literature related to the exploration and research work of critical metals in MLYB and preliminarily investigated the enrichment characteristics of the critical metals in the deposits in the belt. The preliminary investigation indicates that if the dominant metals in skarn deposits differ, the subsequent byproduct critical metals also differ. Most critical metals are hosted in sulfides in these skarn deposits. This paper shows a spatial distribution map of the critical metal deposits. Based on this map, the relationships between the dominant metal and the associated critical metal elements are summarized. Moreover, this paper has reviewed and summarized the deportment and enrichment mechanism of Cr, Co, Se, Re, and Te in the porphyry-skarn Cu-Fe-Au deposits in the belt and clarified the key host minerals and their abundances by referring to the five critical elements. Based on comprehensive analyses of previous studies on critical metals in the belt, we have raised three key scientific points that should be the focus of future studies on related topics. First, the primary research clue about sources and enrichment mechanisms should consider the systematic evolution of the porphyry-skarn Cu-Au deposits in the intracontinental setting. The second is a key question and challenging issue regarding the recovery and comprehensive utilization of the critical metals in specific sulfides. Finally, the full use of microscale to nanoscale lab analyses and related theories about the synthesized host minerals bearing critical metals may provide important evidence that can help interpret the enrichment mechanism of the critical metals. This point should be based on research on the crystallinity relationships and interface correlations between the host and critical metal elements.

critical metals, distribution characteristics of critical metal resources, occurrence, the Middle-Lower Yangtze River Valley metallogenic belt

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