关键矿产资源铟研究进展

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2020-01-20 收稿, 2020-03-28 修回, 2020-03-30 接受, 2020-04-02 网络版发表

国家重点研发计划(2017YFC0602501)和中国科学院地质与地球物理研究所重点自主部署项目(IGGCAS-201902)资助

摘要 铟是一种稀有金属, 被广泛应用于电子工业、航空航天、合金制造、太阳能电池新材料等高科技领域, 是现代工业、国防和尖端科技领域不可缺少的支撑材料, 被许多国家称之为21世纪的“关键矿产资源”。在过去的10多年间, 铟资源的相关基础研究主要体现在: (1) 岩浆分异演化与铟的富集关系; (2) 岩浆热液过程与铟的富集和分散; (3) 铟的赋存状态及其选择性超常富集的关键机制。全面评价不同地质体铟的富集分布规律、铟选择性超常富集机制研究, 以及铟的二次回收技术研发是未来铟资源研究的主要方向。

关键词 铟, 矿床类型, 富集机制, 时空分布, 回收利用

元素铟(indium)属于第五周期第ⅢA族, 是由德国学者Reich和Richter于1863年在测定锌矿石中的铟时发现的。铟在地壳中的丰度仅为0.01 ppm(1 ppm=1 μg/g), 在不同的地质环境下, 既可表现出亲硫元素的特征, 又表现为亲石元素的特征。铟在岩浆分馏过程中, 属于不相容元素, 在岩浆结晶分馏晚期, 大部分铟倾向保留在熔体中, 其分馏演化机制可能与锡类似。

21世纪以来, 金属铟在高新技术(例如, 红外探测、微波通讯、太阳能电池、靶材ITO等)、电子工业以及医疗、国防、新能源等领域的应用日益广泛, 尤其是在新兴产业技术和国防安全领域的作用极为重要, 因而被西方经济发达体称之为“关键金属”或者“关键矿产资源”。金属铟业已成为支撑我国战略性新兴产业蓬勃发展的金属材料之一。

我国是目前全球最大铟生产国, 产量约占全球的44%以上。日本和韩国是铟最大的消费国。预计未来全球透明电极涂层和铜铟镓硒薄膜太阳能电池专用原材

的ITO靶材对金属铟的需求将会超过700 t/a^[1], 供需矛盾将日益突出。未来铟资源将成为世界发达国家为发展战略性新兴产业而争夺的对象^[2]。因此, 寻找新的铟资源量或者发现潜在的战略储备资源基地已经迫在眉睫。

1 全球铟资源配置格局以及我国铟产业局面

世界上铟的资源量极其有限且产地高度集中, 分布十分不均。至今为止, 世界上还没有专门开采铟的矿山。世界上大约90%的金属铟主要来自铅锌冶炼厂的副产物。在冶炼过程中, 铟主要从闪锌矿、黝锡矿、黄铜矿等硫化物中回收, 部分来自含铟的矿物(如硫铟铜矿、铟石、铟黄锡矿(sakuraiite)等)。富铟的矿床主要分布在与岩浆活动有关的具有明显地温梯度的活动洋壳、大陆边缘或者造山带中。这些矿床的形成时间与造山带的峰期或与俯冲作用和碰撞有关的区域成矿作用的时限一致^[3]。中国已经探明的铟资源主要集中于华南褶皱带和古亚洲褶皱带, 主要分布于广西、云南、

引用格式: 李晓峰, 朱艺婷, 徐净. 关键矿产资源铟研究进展. 科学通报, 2020, 65: 3678–3687

Li X F, Zhu Y T, Xu J. Indium as a critical mineral: A research progress report (in Chinese). Chin Sci Bull, 2020, 65: 3678–3687, doi: 10.1360/TB-2020-0058

内蒙古、广东、青海、湖南、江西、贵州和四川等省区,其中广西、云南、内蒙古和广东等4个省区的铜资源量占全国总储量的80%。

全球探明的铜储量约79000 t。铜资源比较丰富的国家有中国、玻利维亚、美国、加拿大和俄罗斯等,上述国家铜资源量占全球铜资源量的80.6%。中国铜资源量约占全球铜资源量的18.2%^[4]。目前世界上含铜的矿石主要来自加拿大新不伦瑞克Mount Pleasant硫化物脉型、角砾岩型和交代型Sn-W-In矿床、加拿大Kidd Creek火山成因块状硫化物Zn-Cu-Pb矿床、我国大厂矽卡岩型Sn-Zn-Cu矿床和都龙矽卡岩型Sn-Zn矿床、日本Toyaha浅成低温Zn-Pb-Cu-Ag-In矿床^[5]、俄罗斯Gaiskoye VMS Cu-Zn矿床^[6]、阿根廷San Roque浅成低温热液Au-Cu-Zn-Pb-Ag矿床等^[7,8]。

虽然中国是世界上铜资源储量和铜金属产量的第一大国,长期保持着铜资源大国的地位,但是我国在国际铜市场上缺乏相应的主导权、市场“话语权”不足。由于铜生产企业盲目扩张、无序竞争、冶炼铜的意愿不高,铜的高端产品开发不足等因素,导致我国铜资源安全面临严重威胁。目前,国内只能生产中低端ITO靶材,铜的高端产品大量进口,铜资源二次回收率较低导致资源浪费严重。相反,日本、韩国等铜消费强国具备完善的产业链,依靠自身技术优势,尤其是铜二次循环利用技术和资源储备政策等措施,使这些国家并没有由于铜高消费量而造成对铜资源进口的过度依赖。随着国际上铜需求量的日益增大,若不尽早采取对策,我国将会失去固有的铜资源优势,从而威胁到我国铜资源的安全供给。

2 我国铜资源主要类型、特点及其时空分布

世界上铜资源的矿床分类还没有统一的认识和标准,已有的矿床分类,大多是不同学者根据研究需要而划分的。如,德国学者Schwarz-Schampera等人^[3]根据富铜矿床地质特征,把铜矿床分为8种类型:(1)与脉状-网脉状锡矿、钨矿以及斑岩锡矿有关;(2)与火山成因块状硫化物(VMS)矿床有关;(3)与喷流沉积(SEDEX)矿床有关;(4)与多金属脉状矿床有关;(5)与浅成低温矿床有关;(6)与活动的岩浆系统有关;(7)与斑岩铜矿有关;(8)与矽卡岩矿床有关。日本学者Ishihara等人^[9]把铜矿床划分为与块状硫化物矿床有关(如Kidd Creek、Broken Hill、Sullivan、Brunswick等)和与浸染状、脉状和矽卡岩矿床有关(如Mt. Pleasant、Toyoha、Iku-

no、Akenobe、Kawayama、Nakatatsu和Taishu)的两种类型。我国富铜矿床主要分为:(1)以海底喷流沉积成矿作用为主的矿床;(2)与岩浆作用有关的矿床^[10,11]。Werner等人^[4]提出了与花岗岩相关的铜矿床(如澳大利亚Baal Gammon),以及与沉积(变质)砂页岩型铜矿床有关的铜矿床(如澳大利亚昆士兰Waterloo)的分类方案。然而,在不同类型的划分方案中,矽卡岩型和块状硫化物型矿床均是铜资源的主要来源,分别占全球铜资源量的29.2%和28%,其次为浅成低温热液型和喷流沉积型铅锌矿床,分别占全球铜资源量19.9%和18.0%^[4]。

我国铜资源主要分布在广西、云南、广东、湖南、内蒙古以及青藏高原等地。云南和广西是我国最主要的铜资源基地,广西大厂、云南都龙和个旧占我国已探明铜资源量的70%。我国铜资源有关的矿床类型主要为矽卡岩型,其次为热液脉型(包括浅成低温热液脉型),且以锡多金属矿化为主;在成矿时代上主要集中于燕山期;在空间分布上主要富集于古陆边缘位置,其中扬子板块西南缘是我国乃至世界上最主要富铜矿床聚集区^[12]。

近年来,我国一些地区相继发现了铜的矿化,如华北板块北缘内蒙古孟恩陶勒盖与大井热液脉型锡多金属矿床^[13,14]、华南南岭野鸡尾斑岩-矽卡岩型锡多金属矿床^[15-17]、西藏班公湖-怒江成矿带拉屋矽卡岩型Cu-Zn矿床^[18,19]。另外,在福建紫金山斑岩铜矿的深部也发现了硫铜矿等含铜矿物^[20]。这些含铜地质体和含铜矿物的发现对我国未来寻找和发现新的铜资源提供了重要的线索。

3 铜资源相关基础研究的主要进展

3.1 岩浆结晶分异与铜的富集关系

铜主要来源于岩浆热液成矿系统^[7,14,21-25],尤其是富锡的岩浆热液矿床^[1,26-28]。该类型矿床主要是与花岗岩有关的矽卡岩型与浅成低温热液型(热液脉型)。Gion等人^[29]的研究显示,铜矿床主要与A型或S型花岗岩相关,这些花岗岩均表现出高度结晶分异的特点^[29,30];除了一些不含角闪石等暗色矿物的高演化I型花岗岩(如白岗岩等)外,I型花岗岩形成铜矿床的潜力较小。Simons等人^[31]研究了英国西南部与岩浆热液相关的稀有金属矿化(In、Sn、Li、Be等),指出铜主要富集在结晶分异程度较高的黑云母花岗岩中,黑云母是其主要的载体矿物,但铜的富集程度并不完全随着结晶分异程

度的增加而增加,这说明铟在岩浆演化过程中其地球化学行为是比较复杂的. 铟在熔体与镁铁质矿物之间的配分模拟实验表明,在岩浆演化过程中,铟在黑云母和熔体之间的分配系数与黑云母八面体位置 Fe^{2+} 含量、Al四面体含量以及Ti的含量成反比^[32]. 黑云母和角闪石能够富集一定程度的铟. 铟进入黑云母和角闪石晶格中的置换机制主要为: $\text{Mg}^{2+} + \text{In}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Fe}^{2+} + \text{Ti}^{4+} + \text{Al}^{3+}$ (黑云母) 和 $2\text{In}^{3+} + 2\text{Al}^{3+} + (\text{空位}) \leftrightarrow 4\text{R}^{2+} + \text{Si}^{4+}$ 与 $\text{In}^{3+} + \text{Al}^{3+} \leftrightarrow \text{R}^{2+} + \text{Si}^{4+}$ (角闪石). 花岗岩中镁铁质矿物含量越高,花岗岩形成铟矿化的潜力就越低. 黑云母中镁含量增加也会降低铟成矿的潜力^[29]. 因此,岩浆热液流体中是否具有足够的铟形成铟矿床可能与早期长英质岩浆房中结晶分异的镁铁质矿物含量有关^[32]. 对不同类型矿床(石英-锡石脉型和锡石硫化物型)锡石中铟的富集分布研究发现,碱性-亚碱性镁铁质源区和花岗岩的共同作用是形成高品位铟矿床的重要前提条件^[33],火山环境更有利于铟的富集^[7]. 最近研究发现一些与铟成矿有关的花岗岩中镁铁质包体中铟的富集程度明显高于寄主花岗岩. 如云南薄竹山花岗岩铟的含量为0.019~0.084 ppm,而其中镁铁质包体中铟的含量为0.048~0.178 ppm^[34]. 因此,需进一步开展镁铁质岩石与铟的富集成矿的关系研究,厘清铁镁质岩浆的侵入对长英质岩浆分异过程中铟的富集与分散的控制因素.

3.2 岩浆热液过程中铟的富集与分散

在岩浆热液系统中,铟主要以 InCl^{4-} 和 InClOH^+ 络合离子的形式在流体中迁移,温度的增加有利于提高铟与络合物离子的结合能力,且在300~350°C达到最大^[35].

以前人们较多关注硫化物中铟的富集和分布特征,而对铟在高温硅酸盐矿物中富集分布的研究较少,仅在矽卡岩矿床研究中有少量报道,如新疆白干湖W-Sn矽卡岩矿床石榴子石铟含量在2~30 ppm之间,且多数小于2 ppm^[36];西藏冈底斯知不拉Cu矽卡岩矿床石榴子石中铟含量显示不均一特征,可高达20 ppm^[37];加多捕勒Fe-Cu矽卡岩矿床石榴子石的铟含量较低,平均值在0.29~4.6 ppm之间. 云南都龙锡锌多金属矿床中矽卡岩矿物(包括钙铁榴石、钙铝榴石、钙铁辉石、透辉石、钙铁辉石、符山石、斜黝帘石、阳起石、透闪石)LA-ICP-MS分析表明:发现石榴子石是最主要的含铟和锡矿物,且不同类型、不同世代的石榴子石具有

差异性. 早期的钙铁榴石中铟含量在166~629 ppm之间,而晚期的钙铝榴石中的铟含量在1.6~10 ppm之间. 而辉石和其他含水矽卡岩矿物均显示不含铟或者低铟含量特征. LA-ICP-MS面扫描结果显示早期钙铁榴石富铟、富锡而晚期钙铝榴石贫铟、贫锡;铟与锡显示一定的协变关系,而与铝呈明显的反相关关系(图1). 这说明铟在岩浆-热液演化过程中主要表现为亲硫的地球化学性质. 在演化早期高温条件下铟在富锡的热液体系中迁移,而较低温度下,铟与锡分道扬镳^[12]. 日本Ikuno矿床中铟主要集中于早期结晶的闪锌矿结晶带内带,而锡倾向富集于晚期结晶的闪锌矿结晶带外带^[9],也说明了在较低温度条件下铟与锡的分离沉淀的存在.

越来越多的研究表明,岩浆热液演化过程中的多阶段流体叠加作用是铟超常富集的关键,矿化过程的多期次叠加是形成高品位铟矿床的重要前提条件^[33]. 阿根廷Pinguino矿床主要经历了两个矿化阶段,早期的Cu-Au-As-Sn-W-Bi矿化,主要形成锡硫化物、铜金硫化物以及银铅铋硫盐类(308~327°C, 2 wt%~5 wt% NaCl);晚期的Zn-Pb-Ag-In-Sb-Cd矿化,主要形成闪锌矿、方铅矿以及银铅硫盐类(255~312°C, 4 wt%~9 wt% NaCl)^[38,39]. 日本Toyoha矿床铟早期在高温富铟、铜、银和锡的流体中运移($\geq 300^\circ\text{C}$),主要分散于富铜的矿石中;而晚期由于流体的交代作用,形成富铟闪锌矿^[5]. 德国Hämmerlein矽卡岩多金属矿床中富In闪锌矿主要围绕早阶段不含In的闪锌矿边缘及其中裂隙生长,是富In流体交代早阶段不富In的闪锌矿的结果^[40]. 日本的Toyoha、Ashio及Akenobe等含In矿床和玻利维亚Potosi、Huari Huari、Porco等含In矿床闪锌矿颗粒中复杂的铟成分分带均表明流体演化的周期性和后期叠加改造特征. 早阶段的闪锌矿主要呈立方晶系,稍晚阶段的闪锌矿富铟,晶体结构向六方晶系(纤锌矿)转变^[41,42].

虽然铟的富集大多与锡石硫化物矿床有关,但是越来越多的证据表明,一些富铟的矿床几乎不含锡或者与锡呈反相关关系,如与铟矿化有关的块状硫化物矿床(VMS)和喷流沉积矿床(SEDEX)^[43]. 玻利维亚Huari Huarik矿床黄锡矿表现出铟与锡呈反相关关系的特点,In可能存在类质同象替代Sn和Cu的现象^[44]. 湖南七宝山Pb-Zn-Cu贫锡矽卡岩矿床中铟主要富集在闪锌矿中及铅锌矿石中(铟含量为28.0~203.0 ppm,平均122.8 ppm),西藏拉屋矿床大型矽卡岩型Cu-Zn矿床中其铟含量平均为45 ppm^[18].

图1 云南都龙锡锌多金属矿床石榴子石. 元素铝、锡、镱LA-ICP-MS面扫描图像. 早期钙铁榴石明显富In和Sn, 而晚期钙铝榴石贫In和Sn. And: 钙铁榴石; Gr: 钙铝榴石; Chl: 绿泥石; Cp: 黄铜矿; Mt: 磁铁矿. 元素浓度: ppm

Figure 1 LA-ICP-MS maps of element Al, In, and Sn in garnet grain at Dulong Sn-Zn polymetallic deposit, Yunnan Province, China. In and Sn are rich in earlier generation of andradite, but they are poor in the later generation of grossular. And, andradite; Chl, chlorite; Cp, chalcopyrite; Gr, grossular; Mt, magnetite. Concentration scales in parts-per-million

3.3 铟的赋存状态和选择性富集机制研究

作为铟的主要载体矿物, 闪锌矿中铟含量可高达24.73 wt%^[40], 因此, 铟的赋存状态和选择性富集机制的研究主要围绕闪锌矿来开展^[7,22,42,45,46]. 铟在闪锌矿中最普遍的替代机制为 $\text{Cu}^+ + \text{In}^{3+} \leftrightarrow 2\text{Zn}^{2+}$ ^[46,47]. 由于不同类型矿床中成矿元素组合的差异(Cu、Ag、Sn、Ga、Ge等), 铟在闪锌矿中的富集机理也略有差异.

在闪锌矿中铟替代锌的方式主要有3种: (1) $\text{Cu}^+ + \text{In}^{3+} \leftrightarrow 2\text{Zn}^{2+}$, 如日本Toyaha矿床^[46]、中国的大厂矿床^[7,22]、玻利维亚Ashio矿床^[42]、Potosi矿床^[45]等. (2) $\text{Cu}^+/\text{Ag}^+ + \text{In}^{3+} \leftrightarrow 2\text{Zn}^{2+}$, 如玻利维亚Akenobek矿床^[42]和中国都龙矿床^[7,42]等. (3) $\text{In}^{3+} + \text{Sn}^{3+} + (\text{空位}) \leftrightarrow 3\text{Zn}^{2+}$, 如法国Saint-Salvy矿床等^[48]. 由于闪锌矿沉淀环境的差异导致锡可以不同的价态与其他元素替代锌^[49], 如 $\text{In}^{3+} + (\text{Cu}, \text{Ag})^+ + \text{Sn}^{2+} \leftrightarrow 3\text{Zn}^{2+}$ 、 $\text{In}^{3+} + \text{Sn}^{4+} + (\text{Cu}, \text{Ag})^+ + (\text{空位}) \leftrightarrow 4\text{Zn}^{2+}$. 而锡石中铟的替代机制主要有两种^[50]: 2

$(\text{Sn}^{4+}, \text{Ti}^{4+}) \leftrightarrow (\text{Fe}^{3+}, \text{In}^{3+}) + (\text{Nb}^{5+}, \text{Ta}^{5+})$ 替代和 $\text{Fe}^{2+} + (\text{Nb}, \text{Ta})^{5+} \leftrightarrow \text{In}^{3+} + (\text{Ti}, \text{Sn})^{4+}$. 锡石中铟的替代机制同样反映了热液体系的氧化还原程度. 现代测试分析技术的发展有力地揭示了闪锌矿In的替代机制和复杂的成分分带的原因, 如Cook等人^[47]利用同步辐射X射线吸收近边结构(XANES)实验证实了闪锌矿中 $\text{Cu}^+ + \text{In}^{3+} \leftrightarrow 2\text{Zn}^{2+}$ 替代机制的存在. Sahlström等人^[51]利用高光谱阴极发光技术揭示含铟闪锌矿1 μm宽的胶状环带化学成分的变化. 胶状环带中存在 $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + (\text{In}, \text{Ga})^{3+}$ 的耦合替代关系; 高强度阴极发光与富In-Cu-(Ga)的闪锌矿有关, 其波长介于500~600 nm; 当闪锌矿中铟的含量相对铜增加时, 阴极发光的波峰向高波长位置迁移; 愈向胶状环带的边部铟相对于铜逐渐增加.

铟除了以类质同象的形式选择性富集于硫化物中外, 还可以铟独立矿物的形式存在. 已发现含铟矿物主要有硫铟铜矿、铟石、羟铟石等18种^[52]. 含铟矿物多以显微出溶物的形式产出于闪锌矿^[24,53,54]或者斑铜矿

中^[55]. Shimizu和Kato^[56]通过温度-硫活度相图模拟显示硫铜矿的形成温度主要在285~310℃之间, 硫活度($-\log a_{S_2}$)在 10^{-8} ~ 10^{-6} atm之间. 在In/Zn比值较高时(In/Zn>50), 铜相对于锌过饱和, 使硫铜矿在高温时从闪锌矿中出溶; 当In/Zn比值较低(In/Zn<50)时, 铜多以类质同象赋存于闪锌矿和黄铜矿的晶格中^[24,53,54]. 由于黄铜矿和硫铜矿具有相似的晶体结构, 它们在与立方晶系的闪锌矿共存时, 铜优先进入闪锌矿中; 但当闪锌矿缺乏时, 黄铜矿可成为铜的主要载体矿物^[57].

岩浆热液演化过程中物理化学条件的变化可使铜的赋存状态由矿物中的晶格铜向独立铜矿物转换. 铜的富集总是位于闪锌矿-硫铜矿以及闪锌矿-黝锡矿固溶体分离演化线之间^[25,40]. 最近的原子探针实验表明: 虽然德国Hämmerlein矿床闪锌矿中铜含量高达24.7 wt%, 但其形成机制并不是晚阶段富铜流体交代早阶段贫铜闪锌矿的结果^[40]; 而是以硫铜矿纳米颗粒的形式赋存于闪锌矿中^[58].

另外, 铜在硫化物中赋存状态的实验模拟研究取得了较大进展, 有力地揭示了铜在闪锌矿中的赋存状态. Filimonova等人^[59]用实验合成方法研究了金、铜和铜在闪锌矿中的赋存状态, 并与自然界中的高铜闪锌矿进行对比. 结果显示: 虽然金、铜、铜在合成的闪锌矿中均一分布, 但是其结构和化学态却不相同. 因此, 对于闪锌矿中微量元素均一分布特征, 不能简单地认为是微量元素以固溶体的形式存在于矿物晶格中的结果, 它们有可能以元素聚合物或纳米颗粒的形式存在于闪锌矿中.

3.4 铜由类质同象形式向独立矿物转变: “铜窗”效应和“铜爆”现象可能的关键机制

Dill等人^[8]在研究阿根廷浅成低温热液型Au-Cu-Zn-Pb-Ag-In矿化时, 发现当闪锌矿中的铜含量在0.2 wt%~0.6 wt%之间时, 其中相应的铜含量大幅增高, 从而提出了闪锌矿沉淀过程中存在“铜窗”效应. Liu等人^[16]认为在湖南香花岭锡矿同样存在“铜窗效应”(当闪锌矿中Cd含量在0.35 wt%~0.45 wt%时, 其中铜的含量明显增加). 铜窗效应的产生是在温度和硫逸度降低过程中, 闪锌矿由立方晶系向六方晶系转换过程中晶格参数的变化引起的^[8].

都龙锡矿EMPA面扫描显示闪锌矿中铜的分布是均匀的, 而不具有成分分带^[41]. 研究结果表明^[60], 云南都龙锡矿床中闪锌矿可以分为5种类型, 但并不是每

种类型的闪锌矿都富铜. 赋存于磁黄铁矿中的闪锌矿中铜含量可达0.20 wt%~14.75 wt%, 且显示出明显不均匀分布的特点, 元素In的分布与元素Cu的分布较为相似, 而与元素Sn的分布明显不同(图2), 这意味在闪锌矿成矿作用的某个阶段中存在着铜大量富集沉淀的“铜爆”现象. 高角度环形暗场扫描透射电子显微镜高分辨原子图像显示磁黄铁矿中高铜(14.74 wt%)的闪锌矿主要呈显微-纳米颗粒形式存在, 而不是硫铜矿的出溶物. 铜主要以离子交换的形式赋存闪锌矿晶格中; 主要沿着{111}方向在闪锌矿中富集, 并导致闪锌矿中出现晶格缺陷(位移)和少量空位的存在(图3). 研究结果进一步证实了前人提出铜在闪锌矿晶格中的空位替代机制^[48,49]. 这种铜爆现象是在合适的物理化学条件下, 闪锌矿中 In^{3+} 与 Cu^{+} 离子或者 Ag^{+} 替代 Zn^{2+} 离子的数量达到较大的值, 从而引起铜在闪锌矿中超常富集, 产生“铜爆”现象. 若成矿流体中有足够的铜和铜, 而闪锌矿晶格中所能替代的数量已不能增加时(即在一定的物理化学条件下闪锌矿中 In^{3+} 和 Cu^{+} 所能替代 Zn^{2+} 的最大值), 则可能导致铜以硫铜矿的形式沉淀.

4 展望

高新技术产业和清洁能源技术的快速发展, 对铜的需求量必将会越来越大, 铜资源安全稳定供给是满足我国战略性新兴产业蓬勃、健康发展的重要保障. 因此, 未来铜资源的相关研究应注重以下几个方面:

(1) 加强铜资源相关的基础理论研究, 提高对In超常富集过程的认识, 为铜资源的找矿勘查提供理论依据. 从全球尺度、矿集区尺度、矿床尺度等全方位研究富铜矿床类型、富铜矿物及其元素组合、铜的赋存状态、富铜矿床成矿时代、与铜成矿有关的花岗岩成岩时代和岩石成因, 揭示不同尺度利于富铜成矿的地质条件; 开展不同成矿区带、不同类型矿床之间的对比研究, 揭示富铜矿床的富集分布规律及其形成的特殊地质背景. 全面评价不同地质体铜的富集与分布规律, 提出未来铜资源的找矿勘查方向, 发现潜在的铜资源战略储备基地.

(2) 铜的赋存状态和选择性超常富集机制是将来一段时间内铜成矿作用研究中的热点. 铜的赋存状态研究是合理利用铜资源, 提高铜资源利用率的重要途径. 在不同类型的矿床中, 铜对矿物具有选择性富集的特点, 因此, 在不同类型地质体中如何准确识别出铜的载体矿物及其分布规律是研究中的难点和重点. LA-

图2 云南都龙锡锌矿床磁黄铁矿颗粒中富铜的闪锌矿(a)中元素Zn(b)、Fe(c)、Cu(d)、In(e)和Sn(f)EMPA面扫描图像。Po: 磁黄铁矿; Sp: 闪锌矿; Cp: 黄铜矿

Figure 2 The EMPA maps (Zn-Fe-Cu-In-Sn) of the indium-bearing sphalerite (a) in pyrrhotite at Dulong Sn-Zn polymetallic deposit, Yunnan Province, China. (b) Element Zn, (c) element Fe, (d) element Cu, (e) element In and (f) element Sn. Po, pyrrhotite; Sp, sphalerite; Cp, chalcopyrite

图3 云南都龙锡锌矿床磁黄铁矿颗粒中富铜闪锌矿高角度环形暗场扫描透射电子显微镜高分辨原子图像显示晶格错位(a)与空位(b)特征

Figure 3 High-resolution HAADF STEM image of indium-rich sphalerite in pyrrhotite at Dulong Sn-Zn polymetallic deposit, Yunnan Province, showing the presence of lattice dislocation (a) and vacancies (b) in sphalerite lattice

ICP-MS原位定量分析技术、高光谱阴极发光技术(hyperspectral cathodoluminescence)、X射线吸收近边结构光谱技术(XANES)等现代分析技术是解决铜在载体

矿物中的分布及其超常富集机制的重要手段。这些问题的解决能够揭示铜选择不同载体矿物富集沉淀的原因, 阐明控制“铜窗”效应和“铜爆”现象产生的关键

因素.

(3) 加强钢资源回收利用与替代品的研发. 随着全球对钢需求的剧增, 一些发达国家投入了大量的资金进行钢资源的二次回收利用和钢金属替代材料的研发, 如日本对钢资源的二次利用占到其钢资源利用的70%

以上. 国际上钢的最有潜力替代材料“石墨烯”和“银纳米线”的研发成功, 标志着我国钢资源开发利用与发达国家还存在明显的差距, 因此, 加强钢资源的二次回收利用技术及其替代产品的研发, 是实现钢资源安全的重要途径之一.

致谢 对两位匿名审稿人提出的建设性修改意见深表感谢.

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Summary for “关键矿产资源研究进展”

Indium as a critical mineral: A research progress report

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Indium (In) is a post-transition metal of Group 13 in the Periodic Table. It is a highly volatile chalcophile element which behaves in a moderately to highly incompatible manner. Abundance of indium in the continental crust is estimated at 0.01 ppm.

Indium has been widely used in high-tech products, especially in emerging industry technology and national defense and security sectors. Therefore, it is called “critical mineral” in developed countries. Indium becomes one of the critical metals to support vigorous development of China’s emerging strategic industries.

More than 90% of indium is recovered as a by-product of zinc mining. The most recent assessment of global indium reserves in 2018 was 79000 tonnes. China accounts for more than 18.2% of global indium reserves, while Peru, Canada, USA and Russia together own more than 62.4%. Indium occurs in different types of ore deposits. Indium-rich deposits include volcanic- and sediment-hosted exhalative massive sulfide deposits, epithermal deposits, polymetallic base metal vein-type deposits, granite-related tin-base-metal deposits, skarn deposits and porphyry copper deposits. These deposits are commonly associated with active oceanic or continental plate margins and orogenic belts with steep geothermal gradients due to enhanced magmatic activities.

Most of indium deposits are associated with highly differentiated granites. Biotite is the main carrier mineral of indium. Recent research indicates that the enrichment of indium does not increase with the increase of crystallization differentiation in felsic magmatic systems. The increase of magnesium concentration in biotite reduces the potential of indium mineralization. The joint action of alkaline and sub-alkaline mafic and granitic magmas is an important prerequisite for the formation of high-grade indium deposits. Volcanic systems provide favorable conducive environment for the enrichment of indium.

There are few studies on the enrichment of indium in silicate minerals. Garnet is a major tin-bearing skarn mineral at the Dulong Sn-Zn deposit of Yunan Province. Based on LA-ICP-MS analysis, indium concentration is 166.0–629.0 ppm in the garnet that was formed in the early skarn stage and 1.6–10.0 ppm in the garnet that was formed in the late skarn stage. The data indicate that the earlier garnet is enriched in indium than the later one. The data also show that indium has an apparent covariant relationship with tin, but an inverse correlation with aluminum.

Multi-stage fluid activities in the evolution of magmatic hydrothermal processes are the key to enrichment of indium. Overprinting of multi-stage hydrothermal processes plays an important role in the formation of high-grade indium deposits. For example, indium-rich sphalerite in the Hämmerlein skarn polymetallic deposit in Germany occurs around the early indium-free sphalerite grain, demonstrating overprinting of later indium-rich ore fluids.

There are three ways for indium to substitute for zinc in sphalerite: (1) $\text{Cu}^+ + \text{In}^{3+} \leftrightarrow 2\text{Zn}^{2+}$, (2) $\text{Cu}^+ / \text{Ag}^+ + \text{In}^{2+} \leftrightarrow 2\text{Zn}^{2+}$, and (3) $\text{In}^{3+} + \text{Sn}^{3+} + (\text{vacancy}) \leftrightarrow 3\text{Zn}^{2+}$. The substitute of indium for zinc in sphalerite is slightly different due to the ore-forming element (Cu, Ag, Sn, Ga, Ge, etc.). Tin can replace zinc with different valence state and other elements depending on the precipitation environment of sphalerite. Recent studies have shown that there are “indium window” and “indium explosion” that exist during the process of indium mineralization. Modern analytical technology and experimental simulation reveal the mechanism for “indium explosion” effect in the Dulong Sn-Zn deposit of Yunan Province. In this mechanism, lattice displacement and vacancies in small number within sphalerite facilitate indium enrichment in {111} direction in sphalerite.

In summary, several items should be followed for the future research and exploration of resources of critical mineral indium: (1) Fully understand the occurrence state of indium in major carrier minerals and reveal mechanism for selective super-enrichment of indium; (2) improve our understanding of indium enrichment mechanism in different geological settings, which would effectively guide future exploration of indium deposits; (3) renovate indium recycling technologies and seek its substitutes.

indium, deposit type, enrichment mechanism, spatial and temporal distribution, recycling

doi: [10.1360/TB-2020-0058](https://doi.org/10.1360/TB-2020-0058)