富含钴矿床研究进展与问题分析

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摘要 钴是各主要工业国家政府定义的重要战略金属. 全球钴矿可分为大陆钴矿和现代海底钴矿两大类. 大陆钴矿主要为沉积岩赋矿层控型、风化型和岩浆铜镍硫化物伴生矿, 其余类型也有独立/共/伴生钴矿产出. 在海底富钴的铁锰结壳和结核中虽有大量资源却无法开采. 不同构造背景和岩浆含水量下钴的配分系数较稳定, 其在岩浆铜镍硫化物矿床形成过程中更容易进入橄榄石中. 在热液环境下, 钴的溶解度与流体温度和盐度密切相关, 流体冷却和流体稀释过程均能造成钴金属沉淀. 研究发现富钴矿床成因争论表现同生成因与后期叠加之争. 除了少数脉状、黑色页岩型、密西西比河谷型和铁氧化物铜金矿床, 钴富集过程均与基性-超基性岩有关. 岩浆演化、后期热液过程和风化作用均有利于富集钴元素. 而钴的超常富集则往往与多期次成矿作用相关. 在今后研究工作中, 应尽快研究我国各类钴矿其形成在造山带和克拉通演化中所代表的地球动力学意义, 确定我国各类型矿床中钴富集的关键控制因素, 厘定钴在高-中-低温热液环境的迁移机制, 关注地球系统各圈层间的相互作用与钴矿的形成关系, 重视现代海底铁-锰-钴结核分布控制因素研究.

关键词 钴矿床, 矿床类型, 富集机制, 矿床成因

钴是各主要工业国家政府定义的重要战略金属. 它是制造高温合金、硬质合金、磁性合金和含钴化合物的重要原料, 被广泛应用于国防、原子能、航天、电子等工业以及高温磁性合金等高科技领域, 在国民经济和社会发展中具有特殊的意义. 同时, 钴在中国和美国同为紧缺资源^[1], 我国《全国矿产资源规划(2016~2020年)》首次将金属钴列入战略性矿产目录. 中国钴消费居世界第一^[2], 95%依靠进口. 钴在“中国制造2025”提出的“五大工程”(高端装备创新工程)和“十大领域”(航空航天装备、节能与新能源汽车和新材料)均有涉及. 现今我国的钴资源紧缺, 保障程度低. 据自然资源部《中国矿产资源报告(2018)》, 2017年我国钴

矿查明资源储量为68.78万t, 约占世界总储量的9.7%^[3]. 2012年起中国年产钴约7000 t, 年消耗2.5万t^[3], 但仅2017年上半年中国消费钴2.5万t(安泰科数据), 可见我国对钴的消费呈现加速式增长.

钴位于元素周期表第四周期第八副族, 具有一个稳定同位素Co58, 钴的电子构型为 $3d^7 4s^2$, 因此易失去最外层2个s电子氧化为 Co^{2+} ; 具有亲硫亲铁双重属性, 在自然界具有3种赋存形式^[4]: (1) 钴独立矿物-砷化物、硫化物、硫砷化物及其相似化合物-锑化物、硫锑化物、硒化物和碲化物等; (2) 类质同象, Co^{2+} 易以类质同象替代 Mn^{4+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} 等; (3) 矿物包体. 钴在地球及各层圈中的丰度与镍和铁有相

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似的分布规律,由地核向地壳迅速递减。钴在地壳中的丰度为17.3 ppm^[5](1 ppm=1 μg/g,下同),相当于上地幔的1/6(102 ppm^[6])。十分明显,钴是一个典型的地幔型元素。同时,具迁移能力强的特点,在地壳中主要呈分散状态。因此钴除少量以独立矿床产出外,主要作为其他矿床的伴生金属产出。钴在各类岩石中呈现出从超镁铁岩(~110 ppm),到玄武质岩石(48 ppm),到页岩(~10 ppm),到花岗岩(1 ppm)依次降低的趋势^[4,7,8]。主要的原生含钴矿物包括硫铜钴矿、硫钴矿、镍黄铁矿、辉砷钴矿、镍辉砷钴矿、钴辉砷镍矿、块硫镍钴矿、辉钴矿、钴硫砷铁矿、斜方砷钴矿、方钴矿、黄铁矿和磁黄铁矿等。次生含钴矿物主要有含钴白云石、钴土、钴华、水钴矿和含钴的针铁矿、褐铁矿等。

钴少见独立矿床,目前主要为镍矿及铜矿的副产品,生产量受市场对铜和镍需求影响,因而会导致周期性供给不平衡。我国钴矿资源分布地区较多^[9],其中伴生于岩浆铜镍硫化物矿中的钴主要分布在甘肃、新疆、吉林、陕西、云南、四川等地;与铁、铜矿伴生的钴资源分布在四川、青海、山西、河南、广东、安徽等地^[10];钴铜矿主要是吉林大横路钴矿^[11]和湖南东部独立钴矿^[12];富钴矽卡岩矿床主要发育在东昆仑地区^[13]、长江中下游^[14]和冈底斯地区^[15]。本文对钴的地球化学特征、各类钴矿的地质特征、钴元素的迁移-富集机制和各类富钴矿床的成因进行综合分析,并提出下一步对富钴矿床研究的展望。

1 富钴矿床的地质特征

全球主要钴矿床类型按照产出的背景,可分为大陆钴矿和现代海底钴矿两种(表1)。全球范围内钴矿资源比较丰富,目前陆地保有探明储量约为710万t^[2],而海底铁-锰-钴结核和结壳之中还有3.97~7.93亿t的钴矿资源^[16]。虽然各国都在研制开采深海富钴结壳的新技

术,但是目前可利用的仍是陆地的钴矿资源(主要分类见表1,大陆各类型钴矿的代表性矿床品位和金属量等见图1^[17~19])。下面对富钴矿床的主要类型和特点进行论述:

(i) 沉积岩赋矿层控型Cu-Co矿床。这类矿床包含了全球超过50%的钴资源储量,产量约占全球的65%以上^[2,20]。主要集中在中非的赞比亚-刚果(金)铜-钴矿带中,具有规模大、品位高的特点,品位一般为0.1%左右。矿层由浸染状硫化物和块状矿石组成,具有沉积结构特征。主要金属矿物是黄铜矿、黄铁矿、辉铜矿、硫钴矿、硫铜钴矿等^[21]。我国东川式铜矿^[22]和江西五宝山钴矿床^[23]是这种类型典型代表。

(ii) 风化型红土Ni-Co矿床。全球最具有经济价值的风化型红土镍-钴矿床主要集中分布在23.6°N~23°S之间的热带地区^[24],包括喀麦隆、古巴、新喀里多尼亚、印度尼西亚、菲律宾、澳大利亚、美国、马达加斯加等国家。这类矿床钴平均品位为0.06%~0.09%。其成因主要是由超基性侵入岩和玄武岩经长期强烈的风化和侵蚀作用形成富含铁、镍、钴的红土。富钴主要矿物是钴土矿、含镍钴土矿和含钴的铁氢氧化物。钴常常聚集在镍矿石或铁矿石中,偶尔形成一些独立矿物。我国代表矿床是云南元江-墨江镍钴矿、海南文昌蓬莱和安定居丁钴土矿。

(iii) 岩浆Cu-Ni硫化物矿床。大多位于克拉通边部或造山带内,与基性-超基性岩有直接联系^[25]。块状和浸染状镍-铜硫化物矿石是该类矿床的重要矿石类型。绝大部分钴都集中在镍黄铁矿中,有时富集在岩体边缘早期形成的黄铁矿带内的辉砷钴矿。该类矿床镍钴比值变化大。钴的含量高低与镍品位密切相关,镍品位越高,钴的含量也就越高。中国岩浆铜镍硫化物矿床伴生钴,品位变化大且较低(0.01%~0.04%),钴主要富集在镍黄铁矿中,也发育独立Co矿物^[26],如东天山图拉

表1 全球钴矿床主要类型^{a)}

Table 1 The classification of the globe cobalt deposits

大陆钴矿主要类型	大陆钴矿其他类型	现代海底钴矿床类型
沉积岩赋矿层控型Cu-Co	黑色页岩赋矿型(Ni-Cu-Zn-Co)	Fe-Mn(Ni-Cu-Co-Mo)结核
红土型Ni-Co	铁氧化物铜金型(Cu-Au-Ag-U-REE-Co-Ni)	Fe-Mn(Co-Mo-REE)
岩浆Cu-Ni硫化物型(Co-PGE)	变质沉积岩型(Co-Cu-Au)	结壳
	火山岩块状硫化物(Cu (Zn-Co-Ag-Au))	Cu(Zn-Co-Ag-Au)
	密西西比型(Zn-Pb(Co-Ni))	火山岩块状硫化物
	Fe-Cu-Co矽卡岩和交代型	
	多金属(Ag-Ni-Co-As-Bi)及其他富钴脉型	

a) 来自The Cobalt Conference 2015会议中Shedd的分类

图1 世界各主要钴矿矿石量和品位图解, 图中斜线表示金属量。图中矿床品位和矿石量数据来自文献[17~19]

Figure 1 The tonnage and grade of the main cobalt deposits, based on the data from refs. [17~19]

尔根铜镍矿含Co达0.03%, 伴生钴达到中型规模。

(iv) 黑色页岩赋矿型Ni-Cu-Zn-Co矿床。钴元素在黑色页岩中一般以类质同象或微粒杂质的形式赋存于黄铁矿、黄铜矿、砷镍矿等矿物中, 少部分以方钴矿和辉砷钴矿形式存在。如芬兰的Talvivaara矿床^[27]和我国广西金秀罗丹铜钴矿^[28]。

(v) 矽卡岩和交代型矿床。虽然矽卡岩中钴的平均品位小于50 ppm^[29], 但富钴的矽卡岩型矿床在世界许多地区均有分布, 特别是在矽卡岩铁矿中, 如西阿尔卑斯的Sesia-Lanzo成矿带^[30]、俄罗斯图瓦-蒙古地区^[31]、俄罗斯萨彦岭地区^[32]、日本的Yamato矿区^[33]、东欧(罗马尼亚)Banatitic成矿带^[34]、我国湖北大冶铜绿山^[14,35]等。在矽卡岩矿床中钴的赋存主要有两种形式: (1) 钴独立矿物, 如辉钴矿、方钴矿、辉砷钴矿、钴毒砂、水钴矿、钴镍矿和菱钴矿等; (2) 类质同象形式: 赋存于砷化物、硫化物矿物中替代其他元素, 主要有铁硫砷钴矿、钴镍黄铁矿、钴黄铁矿、钴毒砂、铁硫砷镍钴矿、斜方砷钴矿、斜硫砷钴矿等^[10]。近年来在我国青海东昆仑地区(肯德可克含钴矿化集中区^[36])和西藏冈底斯地区(浦桑果矽卡岩Cu-Pb-Zn-Co矿床^[15])均报道有富钴的矽卡岩矿床。

(vi) 变质沉积岩型Co-Cu-Au矿床。大多赋存在元古代裂谷环境的硅质碎屑变沉积岩中, 主要的赋钴矿物为Co-As-Ni的硫化物, 包括辉钴矿、钴硫砷铁矿、方钴矿、斜方砷钴矿、砷钴矿、硫铜钴矿等。这类矿床钴平均品位大于0.1%, 我国吉林大横路钴矿可能为该种类型^[17]。

(vii) 铁氧化物铜金矿床(简称IOCG矿床)。钴元素主要富集在IOCG矿床中的黄铁矿、磁黄铁矿或者砷化物中^[37~39]。在加拿大Great Bear岩浆带的少数Co-Ag-As(-Ni-U)矿床中富集钴元素^[40]。在美国Idaho钴矿带的磁铁矿-黑云母-硫化物矿石^[41]和Pennsylvania部分矿床中的富钴黄铁矿^[42]为美国供应主要的钴元素。我国海南石碌铁矿中钴矿体可能是此类型^[43]。

(viii) 火山岩块状硫化物Cu(Zn-Co-Ag-Au)矿床。这类与基性-中性火山喷发有关的钴多金属矿床多位于古陆边缘裂谷带内, 矿层产于火山-沉积建造中, 火山作用过程中的喷流岩及喷流沉积岩是主要的含矿岩石, 矿物组合类型有Cu-Co, Cu-Co-Au, Co-Bi-Au, Fe-Co, Zn-Au型, 矿石矿物为黄铜矿、黄铁矿、磁铁矿等^[44], 主要是弧前盆地或海沟背景的别子型火山块状硫化物矿床中^[45], 或大洋中脊蛇绿岩套超基性岩中的黄铁矿型Cu-Co(-Zn)矿床^[46~48](德尔尼型), 少数为塞浦路斯型。钴主要赋存在黄铁矿中。

(ix) 脉状或热液交代矿床。如加拿大安大略省的Ni-Co-As-Ag-Bi五元素脉状矿床^[49,50], 和摩洛哥Bou Azzer超大型特富Co(Ni-Au)矿床^[51]等。其中Bou Azzer是目前世界唯一以Co为主要开采产物的矿床, 矿体主要为镍钴砷矿物-石英-碳酸盐脉产于构造破碎带中, Co品位在1.0%~1.6%之间, 最高可达18%。而五元素脉状矿床中镍钴砷化物和自然银共生, 且矿床与岩浆岩没有成因联系^[52]。

(x) 密西西比河谷型铅锌矿(简称MVT型铅锌矿)。中钴主要赋存在硫镍钴矿中, 目前含有钴矿的MVT型铅锌矿主要分布在美国密苏里东南部的铅成矿区(Old Lead Belt和Viburnum Trend成矿区)。该地区矿床中铅含量远大于锌, 并且有一定规模的铜、钴、镍。其成矿物质可能来源于邻区前寒武纪基底^[53]。而其他碳酸盐容矿的MVT型矿床中基本不含有钴。而其他碳酸盐容矿的铅锌矿中, 少数如阿拉斯加Ruby Creek^[54]、澳大利亚的Mt. Isa^[55,56]矿床中均含有一定的钴。

(xi) 海底富Co的Fe-Mn结壳和结核。生长在大洋硬质基岩上的壳状沉积物, 主要分布在碳酸盐补偿深度以上、最低含氧层以下水深500~3500 m的平顶海山、海台顶部和斜坡上^[57]。富钴结壳主要分为铁锰矿物相、碎屑组分相、生物成因相和无定形铁的氢氧化物^[58]。主要矿物包括含铁的水羟锰矿和非晶质的FeOOH·xH₂O^[59], 而钴元素是以离子吸附态赋存在水羟锰矿中, 部分Co³⁺置换Mn⁴⁺进入水羟锰矿的晶格

中^[60]. 世界大洋富钴结壳的平均Co含量高达0.63%^[61].

本文将收集到的我国各类钴矿的矿床类型、规模、品位和主要含钴矿物等信息, 依据上述类型分类收集和整理列于图2、3和表2中. 这里不拟一一描述其地质特征, 仅对若干代表性钴矿床进行简要介绍.

(i) 金川岩浆铜镍硫化物型Ni-Cu-Co矿. 甘肃省金昌市金川镍铜钴矿是世界第三大镍硫化物矿床, 其赋存于侵入于白家嘴子组的金川超镁铁岩岩体中, 该岩体为多期岩浆侵位的复式岩体, 钴以镍辉砷钴矿、铁镍辉钴矿、斜方辉砷钴矿、辉钴矿、含钴辉砷镍矿等矿物, 赋存于产出岩体底部或根部的深部熔离-贯入型矿体中, 该类型矿体呈似板状、透镜状产出于纯橄岩中^[63].

(ii) 元江-墨江红土型Ni-Co矿. 云南省元江-墨江县交界处的红土型Ni-Co矿, 钴主要赋存在绿高岭石化蛇纹岩层和蛇纹岩残余层, 占风化壳面积25%, 矿体厚度数米至十余米, 最大埋深30~60 m, 品位中部富, 向下变贫^[68].

(iii) 大横路变质沉积岩型Cu-Co矿. 吉林省白山市大横路铜钴矿为近年来探明的以钴为主的大型铜钴矿. 矿体主要赋存在元古界大栗组下端含碳绢云千枚岩中(第二岩性段), 受复式褶皱控制, 矿体呈层状、似层状、分枝状和分枝复合状, 具层控特征^[78,79]. 矿化蚀变主要为硅化、绢云母化、绿泥石化、钠长石化和碳酸盐化等.

(iv) 周家沉积岩赋矿层控型Cu-Co矿. 辽宁省营口市周家铜钴矿赋存在古元古界里尔峪组浅粒岩中, 矿体形态呈层状、似层状、扁豆状和透镜体状, 其中钴矿体位于铜矿体的下部, 受层控特征明显, 产状与围岩产状一致^[79]. 矿化主要与硅化、绢云母化、绿泥石化和碳酸盐化有关.

(v) 德尔尼火山岩块状硫化物型Cu-Co-Zn矿. 青海省玛沁县德尔尼矿床为以大型铜、钴矿, 中型锌矿、伴生金银分别达到大、中型规模. 4个主矿体呈透镜状或似层状, 产出在阿玛尼卿超镁铁质岩带东段的德尔尼超基性岩的角砾状蛇纹岩带中, 并受后期构造影响^[71]. 围岩蚀变以蛇纹石化、碳酸盐化、滑石化、绿泥石化、硅化、金云母化、黑云母化、钠-透闪石化等.

(vi) 石碌铁氧化物-Cu(Au)-Co矿床. 海南省昌江县石碌铁矿是以铁矿石为主(主要为赤铁矿, 少量磁铁矿等), 共生或伴生有钴、铜、镍、铅锌、银(金)等金属矿产的大型矿床. 其赋矿围岩青白口纪石碌群为一套

低绿片岩相变质为主的火山-碎屑沉积岩和碳酸盐岩, 钴铜矿提主要赋存在第5层底部与第6层底部的过渡带或构造破碎带中^[43]. 矿区共计有钴矿体17个及铜矿体41个, 各矿体呈层状、似层状透镜体产出, 空间上其中钴铜矿体在铁矿体下方, 蚀变以镁质矽卡岩化为主^[43].

(vii) 驼路沟热液脉状Co-Au矿. 青海省格尔木市驼路沟钴(金)矿中15个钴(金)矿体呈陡倾角(70°~86°)、斜列式透镜体展布于下-中志留统绢云母石英片岩、绿泥绢云石英片岩和硅质钠长岩中, 矿体受晚期的构造变形改造^[44,84]. 矿化蚀变主要为硅化、钠长石化、黄铁矿化、碳酸盐化和绢云母化, 成因存在热液脉状^[44]和喷流沉积^[84]争论.

(viii) 大冶铁山矽卡岩型Fe-Cu(-Co)矿. 湖北省黄石市大冶铁山铁铜矿主要产出于铁山岩体和大冶群的接触带中, 矿区6个矿体呈似层状、透镜状产出于接触带内, 蚀变主要为矽卡岩化, 钴赋存在黄铁矿中^[92].

2 钴元素的富集机理及钴矿床的成因争论

2.1 钴元素的迁移-富集-沉淀机理

钴在地幔楔部分熔融过程中, 其在液态硫化物与硅酸盐熔体之间(30~50), 和在单硫化物固溶体与硅酸盐熔体之间(30~60)的配分系数相近^[95], 且受氧逸度影响较小. 这说明钴在含硫化物硅酸盐熔体中的行为并不受硫化物种类的控制. 该配分系数(30~60)与液态硫化物和洋中脊玄武岩之间的配分系数相近^[96,97], 说明不同构造背景和岩浆含水量下, 钴的配分系数较稳定, 且该值远低于铜和镍在硫化物与硅酸盐熔体相的配分系数^[98]. 在岩浆铜镍硫化物矿床形成过程中^[99], 钴更容易进入橄榄石中^[100], 但在结晶过程的最后阶段岩浆中的钴含量仅表现为少量下降^[101~103], 如Noril'sk和Voisey's Bay^[104]矿床. 因此, 岩浆中是否富集钴可能与岩浆量^[105], 或岩浆后期热液过程有关^[106].

在热液环境下钴主要以正二价氯络合物迁移^[107~109](35~440°C), 并随着体系Cl含量增多和温度升高, 钴的氯络合物配位数从八次配位变为四次配位^[110,111]. 在体系有H₂S的条件下, 钴在200~300°C条件下以氯络合物CoCl₄²⁻为主迁移, 在<200°C条件下以硫氢络合物Co(HS)⁺为主迁移^[112]. 另外, 钴的氢氧化物(如Co(OH)⁺, Co(OH)₂(aq), Co(OH)(NH₃)⁺)在高温流体(<288°C)中的稳定性、溶解度和热力学参数已有很好的限定^[113,114]. 由于钴的溶解度与流体的温度和盐度密

图2 我国主要钴矿床分布图. 图中矿床对应编号请参见表2

Figure 2 The distribution of the main cobalt deposits in China, with the numbers of the deposits shown in the Table 2

切相关, 因此流体冷却和流体稀释过程均能够造成热液中钴的溶解度和 CoCl_4^{2-} 稳定性下降, 进而造成钴金属沉淀^[109]. 但是目前缺乏各种含钴矿物(如硫铜钴矿 CuCo_2S_4 等)的热力学参数限定^[115,116], 仅能靠与钴矿物共生的黄铜矿和斑铜矿的热力学计算, 推断钴矿物的沉淀机制^[117].

2.2 富含钴矿床的成因争论

作为钴矿床的主要类型——沉积变质铜-钴矿, 其

区域地层、构造背景和成矿流体循环等方面研究都比较清晰; 但是, 对于成矿金属来源、流体循环、后期变质作用对具体矿床的成矿贡献等方面研究还存在争议^[20,118]. 沉积变质铜-钴矿主要形成于新元古代, 其成因认识以沉积成因观点为主, 但富矿成因争论较大, 包括同生成矿(成岩和成矿作用同时发生)^[79,119–122]; 后生成因或同造山成因成矿(成矿作用在沉积作用之后, 成矿物质来源于深部岩浆)^[123–125]; 叠加(多期)成矿, 即同生与晚期变质变形及热液作用(成矿至少两

图3 中国主要钴矿金属量和品位图解。图中矿床编号、矿床品位和金属量数据来自表2的相关文献

Figure 3 The tonnage and grade of the main cobalt deposits, based on the data from references listed in Table 2

期)^[78,126-133]。虽然中非铜(-钴)矿的巨量物质来自加丹加超群之前的陆壳岩石^[134-136],但后期变质作用形成的硫化物在某些矿床中占主导地位(如赞比亚Kansanshi和Kipushi矿床^[130])。原位测试技术揭示赞比亚Nchanga矿床中含铜-钴硫化物与共生的黄铁矿的硫同位素并不平衡,指示硫化物形成的多期性,并存在不同性质含矿流体的混合作用^[123]。因此,如何考量后期热液-变形-变质作用对沉积变质型铜-钴矿床中钴元素富集的影响,需要首先对矿床中钴矿石的成因类型(同生或后生)及所占比例进行判断。

在黑色页岩中富钴的矿体多为热液型的矿脉,其形成可能与基性-超基性岩体、中酸性岩浆期后热液或区域构造热液活动有关。热液流体提供了成矿物质来源^[137,138],但有些矿床成矿物质来源于原始沉积的黑色页岩^[139]。目前,矿床成因模式争论主要集中在海底热液喷流沉积成矿^[140-142]、海水沉积成矿^[138,143,144]、叠加成矿(包括热液、海水、生物作用以及复合叠加作用等)^[145-150]。目前是黑色页岩本身富含钴元素,还是

由于富钴的基性-超基性岩侵位,亦或热液过程富集钴元素,仍没有定论。

岩浆铜镍硫化物矿床中钴的富集争论主要在于,部分矿床中后期热液过程与钴矿体产出部位和品位、矿石主要金属矿物和矿体的镍钴比值的相关性^[106]等。

火山岩块状硫化物矿床中钴作为伴生组分,富集过程可能与热液叠加过程有关,这符合德尔尼型铜钴矿床中矿体边部钴增加、围岩蚀变强烈和热液活动明显等地质特征^[48,151]。但未发生变质作用的别子型矿床中钴是在块状Cu-Zn矿体形成阶段富集的,如最大的别子型矿床加拿大Windy Craggy矿床中钴是在磁黄铁矿和黄铁矿中富集,草莓状黄铁矿中钴含量更高^[152]。加拿大Soucy#1矿床中钴和金均在大量铜-锌矿体形成时富集^[153]。同时,退变质流体的确能影响先存块状硫化物矿床中金属元素的分布^[154](如西班牙Tharsis),进而影响钴元素的富集。

红土型镍钴矿中钴和镍均依靠超基性岩的化学和机械风化作用次生富集,钴主要富集在铁、锰的氧化物或氢氧化物中^[18,155]。

矽卡岩型富钴多金属矿床中钴趋向于在退变矽卡岩阶段形成,特别是在硫化物开始形成时^[30,33,156]。若为早期喷流沉积之后矽卡岩叠加形成的矿床(东昆仑骆驼路沟、肯德可克等矿床^[44,157]),往往更具工业价值。

虽然海底富钴结壳或结核的成因和物质来源有争论(水生成因^[158,159]、生物成因^[160]、基岩成因^[161]),但是结壳(结核)中钴的富集在表层,主要是由含铁的水羟锰矿的强烈吸附海水中的Co离子,或置换Mn离子进而富集钴元素^[61]。而富集过程主要与其形成的地质要素(如海山形成-迁移-沉降和水道开合等)^[162,163]和海洋要素(如最小含氧带、碳酸盐补偿深度等)^[164,165]有关。

部分脉状富Co矿床呈现多期次富集成矿的特点,如摩洛哥Bou Azzer 超大型特富Co(Ni-Au)矿床^[31,166],中国的东昆仑的骆驼路沟镜铁矿钴矿和督冷沟铜钴矿^[44]。如Bou Azzer矿床可能在从晚元古代-早寒武世(富钴蛇绿岩)到泛非期(蛇纹石化富集钴)到风化作用进一步富集,最后海西期中酸性岩浆热液迁移钴元素成矿^[167,168]。而安大略省的五元素矿床中,Ni-Co-Ag阶段矿化可能发生在300~500°C条件下,成矿与多期流体作用相关,矿质沉淀发生在浅部(沸腾包裹体群显示深度为0.7 km^[169]。另外部分热液交代元古代的火山岩形成绿泥石化热液蚀变型Co多金属矿床^[170]。

综合上述富含钴矿床的研究不难看出:(1)除了少

表2 中国主要钴矿床列表

Table 2 The list of the cobalt-bearing deposits in China

图中 序号	矿床名称	类型	矿床 规模 ^{a)}	含钴矿物	备注 ^{b)}	文献
岩浆铜镍硫化物型						
1	新疆图拉尔根Ni-Cu-Co矿	岩浆铜镍硫化物型	中型	含钴磁黄铁矿、镍辉砷钴矿、钴辉砷镍矿	伴生	[26]
2	新疆黄山Ni-Cu-Co矿	岩浆铜镍硫化物型	中型	含钴磁黄铁矿、含钴镍黄铁矿、钴辉砷镍矿	伴生	[62]
3	新疆黄山东Ni-Cu-Co矿	岩浆铜镍硫化物型	中型	含钴磁黄铁矿、含钴镍黄铁矿、钴辉砷镍矿	伴生	[62]
5	甘肃金川Ni-Cu-Co矿	岩浆铜镍硫化物型	大型	镍辉砷钴矿、铁镍辉钴矿、斜方辉砷钴矿、辉钴矿、含钴辉砷镍矿	伴生	[63]
19	吉林红旗岭Ni-Cu-Co矿	岩浆铜镍硫化物型	中型	含钴磁黄铁矿、硫镍钴矿、镍黄铁矿(7号岩体)	伴生	[64]
24	青海夏日哈木Ni-Cu(-Co)矿	岩浆铜镍硫化物型	中型	含钴辉砷镍矿、含钴镍黄铁矿	伴生	[65]
25	陕西煎茶岭Ni(-Co)矿	岩浆铜镍硫化物型	中型	含钴镍黄铁矿、含钴黄铁矿、含钴磁黄铁矿	伴生	[66]
37	云南白马寨Ni-Cu(-PGE-Co)矿	岩浆铜镍硫化物型	中型	含钴磁黄铁矿	伴生	[67,68]
4	新疆磁海Fe(Co)矿	岩浆铜镍硫化物型或砂卡岩型?	中型	含钴黄铁矿、含钴磁黄铁矿、斜方砷钴矿、辉砷钴矿	伴生	[69]
32	四川攀枝花地区V-Ti-Fe(-Co)矿	岩浆型	大型	含钴黄铁矿、含钴磁黄铁矿	伴生	[70]
风化型						
6	青海元石山NiFe(-Co)矿	风化型	中型	赋存在针铁矿、水针铁矿、褐铁矿等铁矿物	伴生	[71]
36	云南元江-墨江Ni-Co矿	风化型	中型	以氧化物和氢氧化物赋存在黏土矿物中、钴土矿	伴生	[68]
43	海南文昌蓬莱钴土矿	风化型	中型	钴土矿	共生	[72]
44	玉龙斑岩Cu-Mo(-Co)矿	风化型?(V号矿体氧化矿中)	中型	锰的水合氧化物中、钴华、碱式碳酸铜、褐铁矿和黄铁矿中	伴生	[73,74]
变质沉积岩型						
8	山西中条山篦子沟Cu-Co矿	变质沉积岩型	中型	辉钴矿	伴生	[75,76]
9	山西中条山桐木沟Cu-Co矿	变质沉积岩型	小型	辉钴矿	伴生	[76]
10	山西中条山胡家峪Cu-Co矿	变质沉积岩型	小型	辉钴矿、硫镍钴矿、含钴黄铁矿	伴生	[76,77]
18	吉林大横路Cu-Co矿	变质沉积岩型	大型	硫镍钴矿、辉钴矿、方钴矿、含钴黄铁矿	共生	[78,79]
7	山西中条山铜矿峪Cu-Co矿	变质沉积岩型(后期改造)?	大型	辉钴矿	伴生	[80]
沉积岩赋矿层控型						
17	辽宁营口周家Cu-Co矿	沉积岩赋矿层控型	中型	含钴黄铁矿、硫钴矿、铜硫钴矿	共生	[79]
34	云南永平厂街Cu-Co矿	沉积岩赋矿层控型	中型	含钴黄铁矿、镍辉砷钴矿、含钴毒砂、钴黄铁矿、钴毒砂、辉钴矿	共生	[67,81]
39	江西五宝山-七宝山Co-Pb-Zn矿 ^{c)}	沉积岩赋矿层控型	中型	辉钴矿、辉砷钴矿、钴毒砂、含钴黄铁矿	共生	[23,82]
火山岩块状硫化物型						
23	青海德尔尼Cu-Co-Zn矿	火山岩块状硫化物型	大型	钴镍黄铁矿	共生	[71]
脉状或热液交代型						
21	青海驼路沟Co(Au)矿	脉状或热液交代型或者火山岩块状硫化物型?	中型	含钴黄铁矿、硫钴矿、硫铜钴矿	独立	[83,84]
22	青海督冷沟Cu-Co矿	脉状或热液交代型或者火山岩块状硫化物型?	小型	铁硫砷钴矿、铁硫砷镍钴矿、钴黄铁矿、钴镍黄铁矿辉钴矿、硫钴镍矿	共生	[85]
35	云南大红山Fe-Cu-Co矿	脉状或热液交代型	小型	辉钴矿、硫钴矿、硫砷钴矿	伴生	[67]
38	湖南普乐-横洞Co矿	脉状或热液交代型	中型	含钴黄铁矿、辉钴矿	独立	[9,86]
41	广东河源铁岗钴矿	脉状或热液交代型	小型	辉钴矿	独立	[87]
铁氧化物铜金型						
33	四川拉拉Cu-Co-Au矿	铁氧化物铜金型	大型	含钴黄铁矿、辉钴矿、硫钴镍矿、方硫镍钴矿	伴生	[88]
42	海南石碌Fe-Co-Cu矿	铁氧化物铜金型?	中型	含钴黄铁矿、含钴磁黄铁矿、辉钴矿	共生	[43]

(续表2)

图中 序号	矿床名称	类型	矿床 规模 ^{a)}	含钴矿物	备注 ^{b)}	文献
矽卡岩型						
11	河北武安玉石洼Fe(Co)矿	矽卡岩型	中型	含钴黄铁矿、含钴磁黄铁矿	伴生	[89]
12	河北武安中关Fe(Co)矿	矽卡岩型	中型	含钴黄铁矿	伴生	[35]
13	山东莱芜张家洼Fe(Co)矿	矽卡岩型	大型	含钴黄铁矿	伴生	[90]
14	山东莱芜顾家台Fe(Co)矿	矽卡岩型	中型	含钴黄铁矿	伴生	[90]
15	山东莱芜西尚庄Fe(Co)矿	矽卡岩型	中型	含钴黄铁矿	伴生	[90]
16	山东淄博金岭Fe(Co)矿	矽卡岩型	大型	含钴黄铁矿、含钴磁铁矿、硫钴镍矿	伴生	[91]
20	青海肯德克Co-Bi-Au矿	矽卡岩型	中型	方钴矿、辉砷钴矿	共生	[44]
26	湖北大冶铁山Fe-Cu(-Co)矿	矽卡岩型	大型	含钴黄铁矿	伴生	[92]
27	湖北大冶铜绿山Fe-Cu(-Co)矿	矽卡岩型	中型	硫铜钴矿、含钴黄铁矿、辉钴矿、铁硫砷钴矿、斜方砷钴矿	伴生	[35,93]
28	湖北程潮Fe(-Co)矿	矽卡岩型	中型	含钴黄铁矿	伴生	[92]
29	湖北大冶大广山Fe(-Co)矿	矽卡岩型	中型	含钴黄铁矿	伴生	[92]
30	安徽安庆西马鞍山Cu-Fe-Co矿	矽卡岩型	中型	含钴黄铁矿	伴生	[94]
31	安徽铜陵药园山Cu-Fe-Co矿	矽卡岩型	中型	含钴黄铁矿	伴生	[94]
45	西藏普桑果Cu-Pb-Zn-Co-Ni矿	矽卡岩型	小型	镍辉砷钴矿	共生	[15]
黑色页岩赋矿型						
40	广西金秀罗丹Cu-Co矿	黑色页岩赋矿型		辉砷钴矿	独立	[28]

a) 20000 t以上为大型, 2000~20000 t为中型, 小于2000 t为小型; b) 硫化钴和砷化钴边界品位0.02%, 工业品位为0.03%~0.06%; 钴土矿边界品位0.3%, 工业品位0.5%。伴生钴矿的评价指标尚无统一规定, 一般选冶性能好的矿石, 含钴品位大于0.01%; c) 五宝山为层控热液型, 而七宝山为热液叠加层控型

数脉状矿床、黑色页岩型、MVT型和IIOCG型矿床, 钴元素富集过程或多或少与基性-超基性岩有关, 无论是岩浆过程、后期热液过程和风化作用均有利于富集钴元素; (2) 钴的超常富集往往与多期次成矿作用相关。另外限于对钴矿床的成因模型和勘查模型研究太少, 目前缺乏有效的地球物理方法对富钴矿产开展勘查工作。

3 研究展望

我国目前对富含钴矿床的研究程度和水平处于起步阶段, 全国各类富含钴矿床的时空分布特征、成因类型和钴的赋存状态等虽有一定的收集整理^[9], 但缺乏系统性的研究工作, 这与当今国家对钴日益增长的需求不相适应。在综合分析前人对钴的元素行为和富钴矿床成因研究的基础上, 我们认为目前亟需从如下几点开展研究: (1) 虽然对我国各类钴矿的空间分布特征和钴元素的赋存状态已有研究, 但应尽快查证相同区带中同类型矿床是否存在共伴生钴矿及其形成时代,

并探讨钴矿的形成在造山带和克拉通演化中的地球动力学意义; (2) 确定我国各类型钴元素富集过程的关键控制因素, 如地幔源区和岩浆过程对钴富集的控制(岩浆铜镍硫化物型)、赋矿火山岩层序(火山岩容矿块状硫化物型)、风化剖面分带(红土型矿床)、沉积与后期变质-变形作用(沉积变质型、黑色页岩型)、热液富集过程等, 特别是变形过程中对于矿体富集起到重要作用(如海南石碌铁矿^[43]), 重视基性-超基性岩在富钴矿床形成中的贡献; (3) 从实验和计算模拟的角度厘定钴元素在高-中-低温热液环境的迁移机制, 确定主要含钴矿物和热液中各类含钴络合物的热力学参数; (4) 关注地球系统各圈层间的相互作用与富钴矿床的形成关系, 从深部幔源岩浆作用, 到地壳浅部岩浆-热液成矿, 再到表生风化作用和海洋过程, 均涉及钴元素的富集, 如何从地球系统科学的角度解读富钴矿床形成的动力学机制; (5) 重视现代海底Fe-Mn-Co结核分布控制因素研究, 开发海底钴资源合适的开采技术。

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Summary for “富含钴矿床研究进展与问题分析”

A review of the types and ore mechanism of the cobalt deposits

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Cobalt is an important strategic metal of major industrial countries. In order to invoke the importance of the cobalt deposits to the strategic industries in China, this paper aims to introduce the different types of the cobalt deposits in the worldwide, to review the ore mechanism of the cobalt deposits and to propose the research directions of the future studies for the cobalt deposits. Global cobalt resources can be grouped into two deposit types: terrestrial and seafloor deposits. The major terrestrial cobalt deposits include sediment-hosted stratiform copper-cobalt, nickel-cobalt laterite, and magmatic sulfide copper-nickel deposits. Other sources include black shales hosted, skarn and replacement, metasedimentary rocks hosted, iron oxide copper-gold deposits, volcanic massive sulfides, polymetallic veins (five-element veins and other vein types), and Mississippi Valley-Type lead-zinc deposits. Seafloor cobalt-related deposits are mainly iron-manganese-cobalt nodules and crusts, which are hardly explored and productive. The detailed information of the major cobalt deposits is also listed, presenting the tonnage and grade of various types of the cobalt deposits in China. The polymetallic veins and black shales hosted types have the highest grade, and both types should be paid more attentions during the mineral exploration. For the geochemical behavior of the cobalt during the magmatic and hydrothermal environment, the partition coefficient of cobalt in the process of mantle melting under different tectonic background and water contents are relatively stable. Also, during the fractional crystallization of ultramafic-mafic magmas in the magmatic sulfide deposits, cobalt has a slight preference for olivine relative to basalt. In hydrothermal ore system, aqueous Cobalt(II) chloride complexes play a crucial role in cobalt transport and deposition, and their solubility has a close relationship with the temperature and salinity of the fluids. The debate on the genesis of various cobalt-rich deposits can be considered as the debate on the evaluation between diagenetic and superimposed processes in the ore formation. Besides some polymetallic veins, black-shale hosted, Mississippi Valley-Type lead-zinc, and iron oxide copper-gold deposits, the process of cobalt enrichment has close relationships with the ultramafic-mafic intrusions or volcanic during the magmatic processes, hydrothermal processes, or weathering. Moreover, the multiple-stage hydrothermal processes are also critical to cobalt enrichment. We suggest that the spatial-temporal distribution of different cobalt deposits in China and how their formations are related to the tectonic evolution of the craton and orogenic belt should be investigated immediately to determine the controlling geological factors in different cobalt deposits. Also, the thermodynamic properties of different cobalt-bearing speciation under different physico-chemical environments should be identified. The relationship between geodynamic processes and formation of cobalt-rich deposits needs to be considered. Finally, great attention should be paid to the study of marine iron-manganese-cobalt nodules and crusts and their proper mining technology.

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