扬子地块西南部关键金属元素成矿作用

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摘要 在自元古代以来的长期地质演化过程中, 扬子地块西南部形成了多样化的富含In、Ge、Ga、Cd、Re、Sn、Li、Nb、REE(rare earth element)和PGE(platinum group elements)等不同种类关键金属元素的矿床类型. 通过总结以往的研究, 本文认为该区除晚二叠世与峨眉山地区幔柱活动有关的Cu-Ni-PGE岩浆硫化物矿床和新生代与印-亚大陆后碰撞造山作用有关的碳酸岩型REE矿床外, 富含关键金属元素矿床的成矿作用主要显示四大特点: (1) 古-中元古代发育我国首个被确认的富稀土IOCG成矿省; (2) 燕山晚期与花岗岩有关的富In锡石硫化物矿床在面积很小的区域大爆发成矿; (3) 印支期和燕山早期花岗岩岩浆活动微弱, 富Ge低温Pb-Zn矿床和低温Au-As-Sb-Hg-Tl矿床广泛发育; (4) 埃迪卡拉纪以来的海相沉积岩尤其是黑色页岩和碳酸盐岩广布, 多时代富Li、Nb、Zr、Ga、Re、REE、PGE等的沉积和/或风化-沉积矿床大面积分布. 在此基础上, 进一步总结了区域地质事件与成矿事件的相互关系, 提出了一些重要成矿系统值得进一步探索的领域.

关键词 扬子地块, 关键金属, 矿床类型, 成矿作用

关键金属(critical metals)是国际上近年提出的新概念, 指当今社会必需、安全供应存在高风险的一类金属. 虽然各国定义的关键矿产种类不一, 但主要包括稀有金属、稀散金属、稀土金属和PGE、Co、Cr等^[1]. 因其独特的材料性能, 它们在新能源、新材料、信息技术和国防军工等行业具有不可替代的重大用途. 近年来, 欧盟、美国、俄罗斯、英国、澳大利亚、日本等重要国际组织和国家, 均提出相关发展战略或设立重大计划加强对关键金属的研究, 以扩大关键金属矿产的新来源, 创新高效利用的新途径和强化对关键金属的控制力. 扬子地块在国内外矿产资源格局中占据重要地位, 自古元古代以来的长期地质演化过程中, 岩浆成矿作用、岩浆热液成矿作用、低温热液成矿作用、风化沉积成矿作用等均很发育, 形成了多样化的富含不同种类

关键金属元素的矿床或某些关键金属元素的独立矿床, 涉及的关键金属元素主要包括In、Ge、Ga、Cd、Re、W、Sn、Li、Nb、REE(rare earth element)和PGE等. 不少学者已对这些关键金属元素的成矿作用开展了较深入的研究, 取得重要成果. 本文概述了其中主要矿床类型的成矿特征以及前人对其成矿背景、过程和规律的一些认识. 在此基础上, 初步总结了区域构造-环境事件与成矿事件的相互关系和一些重要成矿系统值得深入探索的领域, 以期今后对关键金属元素超常富集成矿机制及其资源评价和找矿预测的深入研究, 为建立关键金属元素成矿、预测和利用的理论方法体系提供参考.

1 地质背景

华南陆块由扬子地块和华夏地块在新元古代

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(~830 Ma)沿江南造山带碰撞拼贴而形成^[2],北面以秦岭-大别造山带为界与华北克拉通相连,西南面沿松马-哀牢山缝合带与印支地块连接,西面由龙门山断裂与西部的松潘-甘孜地块分开,东面紧邻太平洋。虽然学界对扬子与华夏的分界仍有不同认识,最近有研究认为江绍-郴州-临武断裂可能是其边界^[3](图1)。

扬子地块由前寒武纪基底和显生宙盖层组成。前寒武纪基底岩石主要包括三部分:太古代-古元古代结晶基底(如崆岭杂岩)、围绕结晶基底的中-新元古代褶皱变质岩、局部不整合于其上的新元古代弱变质岩(如板溪群、冷家溪群等)和埃迪卡拉纪未变质地层。新元古代的这套弱变质和未变质地层被认为是陆内裂谷即南华裂谷内的沉积产物^[3]。显生宙盖层主要是寒武纪到三叠纪的海相碳酸盐岩夹碎屑岩和泥质岩,以及侏

罗纪到第四纪的陆相沉积岩^[5]。其中,寒武系黑色页岩和显生宙碳酸盐岩极其发育^[6,7],二叠纪末期的峨眉山玄武岩在扬子地块西半部广泛分布^[8,9]。

扬子地块历经多次重要构造事件影响^[4],自老到新主要包括:(1)发生于古元古代约2.05~1.90 Ga和1.7~1.5 Ga的哥伦比亚超大陆聚合和裂解作用^[10,11];(2)中-新元古代约1.0~0.75 Ga期间发生于不同区域的造山或裂解作用^[12~15];(3)早古生代约480~390 Ma的加里东运动^[16];(4)晚二叠世约260 Ma的峨眉山地幔柱活动^[8,9];(5)早中生代约255~200 Ma的印支运动^[16,17];(6)晚中生代的燕山运动,在华夏地块和扬子地块西南部分别形成了峰期年龄分别为160~150和100~80 Ma的花岗岩^[16,18,19];(7)新生代约40~25 Ma的印-亚大陆后碰撞造山作用^[20,21]。上述构造事件从宏观上控制了扬子地

图1 华南构造格架和扬子地块西南部富关键金属元素矿床分布略图^[3,4]

Figure 1 A simplified geological map of South China showing the structural framework and the distribution of critical metal-rich deposits in the southwestern Yangtze Block^[3,4]

块多期次大规模成矿作用的发生^[4].

2 关键金属主要成矿类型

扬子地块富含关键金属元素的矿床广布、类型多样(图1), 主要有岩浆成因Cu-Ni-PGE硫化物矿床、碳酸岩型REE矿床、IOCG矿床、岩浆热液成因锡石硫化物矿床、低温热液矿床、沉积矿床和风化-沉积矿床. 因川西冕宁-德昌喜山期稀土成矿带和晚二叠世峨眉地幔柱相关岩浆矿床有另文讨论, 本文主要介绍其他几类矿床.

2.1 富REE磷块岩矿床

国内外的磷块岩矿床常伴生REE, 且部分矿床中稀土相当富集^[22]. 我国磷块岩的稀土也较富集, 在贵州织金磷块岩矿床中目前查明的稀土(REE₂O₃, 平均含量为0.11%)资源量已达300余万t, 其中重稀土(Y₂O₃, 平均含量为0.04%)资源量100余万t, 占稀土总量30%以上^[23], 达到超大型稀土矿床资源规模, 具有巨大潜在价值.

织金富稀土磷块岩矿床产于下寒武统梅树村期戈仲伍组(C₁gz)含磷地层中, 主要由灰色、暗灰色含磷白云岩、白云质磷块岩和磷块岩组成. REE和Y含量受岩

石类型控制, 从白云岩→含磷白云岩→磷质白云岩→白云质磷块岩→磷块岩, REE和Y含量依次增加. 研究表明, 海相缓坡盆地最利于稀土富集, 缓坡盆后缘则一般不富稀土^[24]. 白云质磷块岩、条带状磷块岩和块状磷块岩中的稀土表现为中、重(Y)稀土富集的模式(图2)^[25], 与现代深海富稀土沉积物的稀土模式^[26]基本相似. 研究表明, 稀土元素主要类质同象磷灰石中的钙而赋存于氟磷灰石中^[27,28]. 在高稀土含量(>527 ppm, 1 ppm=1 μg/g)的磷块岩中, 与REE和P₂O₅具有较好相关性不同, Y与P₂O₅不相关, 可能反映Y存在与REE不一致的富集过程.

Re-Os法确定矿床形成的时间上限为522.9±8.6 Ma^[29]. 通常认为, 矿床的形成与上升洋流携带的 Fe-P-(REE+Y)水团由深水盆地往浅水台地运移密切相关. 深部铁磷复合物(FeOOH·PO₄)被还原并释放所吸附的磷和REE, 随上升洋流迁移到台地边缘大陆斜坡带较浅部位的氧化区域发生沉淀^[30]. 磷块岩中稀土的富集主要受控于海水介质条件^[31]和后期成岩作用的改造^[32].

2.2 富PGE、Re黑色岩系

黑色岩系指有机碳含量较高的未变质或浅变质碎

图2 织金富稀土磷块岩矿床磷块岩样品稀土模式^[25]

Figure 2 PAAS (post-Archean Australian shale)-normalized rare earth element (REE) patterns for REE-rich phosphorite deposits in the Zhijin County^[25]

屑岩系。全球范围内黑色岩系均呈现PGE和Re的一定富集,甚至具工业价值^[33]。扬子地块西南缘广泛发育黑色岩系,包括成冰系大塘坡组、埃迪卡拉系陡山沱组、寒武系牛蹄塘组和志留系五峰-龙马溪组黑色页岩。已有研究显示,湘黔地区陡山沱组和牛蹄塘组黑色岩系具有PGE和Re的超常富集^[34-36]。

牛蹄塘组黑色页岩沉积于南华裂谷盆地,与下覆灯影组不整合接触。这套黑色页岩沿扬子地块东侧从云南至浙江不连续延伸近2000 km。牛蹄塘组黑色页岩中Pd含量为1~100 ppb(1 ppb=1 ng/g),Pt为6~60 ppb,Re为100~680 ppb^[35,37]。厚约几至数十厘米的Ni-Mo-PGE多金属层(Ni~3%; Mo~5%; PGE~1 g/t)顺层产出在牛蹄塘组底部的黑色页岩中。形成年龄为521±5 Ma,属于寒武纪早期^[38]。主要矿点包括遵义地区黄家湾、天鹅山、新土沟等,张家界地区大坪、三岔、后坪、柑子坪等。此外,云南德泽、江西上饶和浙江诸暨等地区也有分布。目前在Ni-Mo-PGE多金属层中尚未发现PGE的独立矿物,PGE通常呈分散形式赋存在含镍钼的硫化物和黄铁矿中^[39,40]。关于其中PGE和Re的来源,主要有海水和热液之争。类似于现代海水的PGE配分模式暗示,这些元素可通过化学沉淀从海水中自生富集^[35,38,41]。但是,Jiang等人^[35]认为黑色页岩中的Ni-Mo-PGE多金属层与洋底现代铁锰结壳沉积于不同的环境,PGE和Re不可能主要源自海水。Han等人^[41]发现,Ni-Mo-PGE多金属层的PGE配分模式和Pd/Pt(0.94)更类似于洋中脊玄武岩和洋岛玄武岩,而Pd/Ir(124)和Pt/Ir(133)比值更类似于海底热液系统中富铜的硫化物,因此指出PGE可能来源于淋滤基性岩的热液流体。显然,这些差异性的结论还有待对PGE地球化学行为的进一步研究加以证实。

目前,仅鄂西地区黑色页岩中Re的远景资源量可达万吨以上^[42]。根据古地理分析,寒武纪早期湖南和贵州处于斜坡相和盆地相,黑色页岩的平均厚度大于鄂西地区。最近在贵州剑河和湖南袁家地区陡山沱组黑色页岩中发现Re含量可达2000 ppb^[36]。另外,根据Ni-Mo-PGE多金属层中PGE和Re的品位估算,仅遵义黄家湾(图1)的PGE和Re资源量已近6和60 t,华南黑色岩系中PGE和Re可能具有较大潜在资源前景。

2.3 碳酸盐黏土型Li-Ga-REE矿床

扬子地块西南部广泛发育古生代碳酸盐岩地层,受后期构造活动(如加里东运动)影响抬升地表^[43]。随后

的风化剥蚀作用(喀斯特化)形成大量古岩溶洼地/岩溶盆地等负地形并接受碎屑沉积,常形成黏土型锂矿和铝土矿^[44-46]。其中又以沉积型铝土矿最成规模,累计探明储量超过10亿t(图1)。沉积型铝土矿指由基底碳酸盐岩(白云岩、灰岩)经强烈化学风化形成的富铝风化壳物质,随后被搬运沉积到碳酸盐岩不整合面上,再经成岩成矿作用形成的地质体^[47-49]。通常情况是,活动性强的碱性和碱土元素(K、Ca、Na等)被迁出,化学性质相对稳定的元素(Al、Ga、REEs等)则发生相对富集,形成铝土矿并伴生一些关键金属元素^[47,50]。特殊的是,活泼元素Li在铝土矿中也存在富集现象,被认为主要是其中黏土矿物吸附Li的结果^[51]。

温汉捷等人^[46]在前人研究基础上,对黔中下石炭统九架炉组及滇中下二叠统倒石头组富Li-Ga-REE铝土岩/黏土岩(图3)进行了系统研究,通过千余件样品的分析发现,Li₂O最高含量分别可达0.74%和1.10%。这一类黏土型锂资源的主要地质地球化学特征是:(1)成矿物质来自黏土岩基底的泥质灰岩和白云岩;(2)主要以吸附方式赋存在黏土矿物蒙脱石中;(3)沉积环境对锂的富集具有重要控制作用,封闭的陆相(滨海)盆地有利于锂的聚集;(4)除Li外还有Ga和REE的富集。基于其成因和赋存状态与国外火山岩黏土型锂矿存在本质区别,可将这一类锂矿定义为碳酸盐黏土型锂资源,是国际锂矿资源新类型。

事实上,碳酸盐黏土型锂矿与铝土矿常相伴产出,它们产于同一层位,均与碳酸盐岩基底具有密切成因联系,富锂黏土岩与铝土矿的形成密切相关,但两者在风化程度上存在显著区别,相对于铝土矿而言富锂黏土岩的铝/硅(A/S)更小(图4)。一般而言,黏土岩中Li₂O含量最高(可高达约1.1%;图4),铝土矿中Ga最富集(可高达200 ppm),而REE则在黏土岩和铝土矿中同步富集(可高达3700 ppm)^[46,48]。

扬子地块西南部大面积分布古生代碳酸盐岩地层,其不整合面上大规模产出沉积型铝土矿并伴生Li-Ga-REE等关键矿产。这类矿床通常具有分布面积广、产出层位稳定、厚度较大、开采成本低(多露天开采)等特点,经过深入研究和勘查,可望成为这些关键金属矿产资源的最重要来源之一。

2.4 玄武岩风化型Nb-Ga-Zr-REE矿床

扬子地块西南部滇黔地区上二叠统宣威组底部与峨眉山玄武岩不整合接触面上,常形成一套Nb、

图 3 早二叠世滇中倒石头组(a)和早石炭世黔中九架炉组(b)铝土矿/富锂黏土岩分布图^[46]
Figure 3 Distribution of lithium-rich clay rocks of the lower Permian Daoshitou formation in Yunnan Province (a) and the lower Carboniferous Jiujialu formation in Guizhou Province (b)^[46]

图 4 黏土岩铝/硅(A/S)与锂含量相关图^[46]
Figure 4 Correlation of the aluminum/silicon (A/S) content ratio and Li_2O content^[46]

REE、Zr、Ga等多种关键金属元素富集的古风化壳(图5)^[52], 其中铌平均含量约220 ppm(Nb_2O_5)(自测), 已超过风化壳型铌(钽)矿床的工业品位(160~200 ppm, 《稀有金属矿产地质勘查规范DZ/T 0202-2002》), 有的甚至超常富集至1000 ppm; 稀土含量也高, 其中LREE约850~5500 ppm, 达到风化壳型稀土矿床工业品

位(800~1500 ppm); 镓平均含量约50 ppm, 也超过铝土矿中镓的工业品位(20 ppm). 同时, 该类风化壳分布广、厚度大、延伸稳定^[52,53], 形成了Nb-REE-Zr-Ga共生富集的矿点或矿床, 如四川昭觉、美姑地区的铌钽矿点、滇东-黔西地区的铌-稀土多金属富集层、贵州西部风化壳型稀土矿床等^[52,53], 具有很大资源远景.

代世峰等人^[54]认为, 多金属富集层中的稀土主要赋存于以下载体中: (1) 源区的碎屑矿物(如独居石、磷钇矿、锆石、磷灰石); (2) 成岩或后生阶段形成的含稀土磷酸盐和碳酸盐等自生矿物(如水磷铀石和氟碳铈矿); (3) 煤系地层中的有机质; (4) 部分可能以离子吸附态存在, 这与Zhang等人^[53]报道的贵州宣威组底部稀土元素赋存状态一致. 关于其中铌、钽的赋存状态, Dai等人^[52]的研究表明, 可能以离子吸附态被黏土矿物吸附. 对Nb-REE-Zr-Ga的来源, 目前主要有3种观点: (1) 多金属富集层底部峨眉山玄武岩直接风化的结果^[55,56]; (2) 来自峨眉山大火成岩省顶部的酸性岩^[57,58]; (3) 来自火山灰-热液流体的混合作用^[52]. 这些观点还需研究进一步证实.

图5 扬子地块滇黔地区二叠系宣威组与底部峨眉山玄武岩空间展布(a, b)及Nb-REE-Zr-Ga多金属矿床矿化特征(c)^[8,57,61]

Figure 5 Distributions of the upper Permian Xuanwei formation and its underlying Emeishan basalt in the Dian-Qian region of Yangtze Block (a, b) and the cartoon showing the characteristics of Nb-REE-Zr-Ga polymetallic mineralization (c)^[8,57,61]

近期的研究发现, 宣威组底部的峨眉山高钛玄武岩主要含钛矿物除钛铁矿和磁铁矿外, 还有一类重要的高钛矿物——榍石^[59]. 杜胜江等人^[60]通过对峨眉山玄武岩中榍石的研究发现, 其中极富铌、稀土、锆等, 很可能是成矿物质的主要贡献者. 但是, 研究区玄武岩中广泛发育的榍石如何形成并在风化蚀变过程中如何控制铌、稀土等多元素的富集, 目前尚不清楚. 该问题的解决不仅有助于深刻认识成矿物质来源及表生成矿过程, 而且可为古风化壳型铌-稀土矿床找矿勘查目标的选定提供较合理的地质依据.

2.5 富In锡石硫化物矿床

热液成因锡石硫化物矿床是全球最重要的富钨矿床类型^[62,63]. 我国这类矿床主要分布在桂北-滇东南锡多金属成矿带的锡石硫化物矿床中, 包括广西大厂和云南个旧、都龙、白牛厂等世界级超大型矿床, 是我国和全球In资源的主要来源. 大厂矿床In探明储量已超8000 t, 是我国In储量最高的矿床^[64], 都龙保有钨金属量>6000 t, 是我国钨资源探明量第二、保有量第一的矿床^[64].

这些锡(钨)多金属矿床常产于花岗岩体内外接触带(图6), 与燕山晚期花岗岩有关, 属于岩浆热液矿床,

成岩成矿时代约为100~80 Ma, 相当于晚白垩世^[18,19]. 该类矿床中的闪锌矿是In的主要载体矿物, 类质同象是其赋存形式, 各矿床中目前尚未发现In的独立矿物, 也未发现锡石富集In的现象. 但是, 闪锌矿中In分布很不均匀, 大厂、都龙、白牛厂、个旧矿床闪锌矿的In含量分别为 1020 ± 240 ^[66]、 $3.3 \sim 3535$ ^[67]、 $3.0 \sim 234$ ^[68]和 $434 \sim 4781$ ppm^[69]. 不同温度和成矿阶段闪锌矿中的In含量存在明显差异, 黑色铁闪锌矿通常最富In^[64,67].

值得注意的是, 华南南岭地区也存在许多重要的锡多金属矿床. 它们与燕山早期花岗岩(约160~150 Ma)有关^[18,19]. 以往认为这类矿床In含量较低, 但最近在柿竹园^[70]、昆仑关、香花岭和七宝山等矿床中均发现较好的In矿化, 暗示华南地区In的矿化可能从燕山早期就已开始. 然而, 受花岗岩浆活动期次以及花岗岩岩性、源区和演化程度等的影响, 各矿床In矿化存在显著差异, 燕山早期的锡多金属矿床是否伴随大规模In矿化, 还有待更深入的研究. 事实上, 关于“In与Sn的耦合关系”目前仍不清楚^[62,63,71,72], 两者的成因联系可能是由于In与Sn具有相似的地球化学性质, 富Sn花岗质岩浆在结晶分异演化过程中导致了两者在成矿流体中的共同迁移和富集.

图6 云南都龙锡锌铜多金属矿床剖面图^[65]。1, 南温河花岗岩; 2, 新寨岩组第一段下亚段; 3, 新寨岩组第一段上亚段; 4, 新寨岩组第二段; 5, 燕山晚期花岗岩(y_b^{3a-b}); 6, 燕山晚期花岗岩斑岩(y_b^{3c}); 7, 硅化壳; 8, 石榴石透辉砂卡岩; 9, 绿泥石阳起砂卡岩; 10, W矿体; 11, 铜矿体; 12, 锡锌(铜)矿体; 13, 地质界线; 14, 断层

Figure 6 Cross section of the Dulong Sn-polymetallic deposit, Yunnan Province^[65]. 1, Nanwenhe granite; 2, lower segment of member 1 of the Xinzhai formation-complex; 3, upper segment of member 1 of the Xinzhai formation-complex; 4, member 2 of the Xinzhai formation-complex; 5, late Yanshanian granite (y_b^{3a-b}); 6, late Yanshanian granite porphyry (y_b^{3c}); 7, weathered siliceous crust; 8, garnet-diopside skarn; 9, chlorite-actinolite skarn; 10, tungsten ore body; 11, copper ore body; 12, Sn-Zn (In) ore body; 13, geological boundary; 14, fault

2.6 富稀土IOCG矿床

铁氧化物-铜-金(即IOCG)矿床是过去20年新提出的重要矿床类型^[73]。不少IOCG矿床除特征的Fe、Cu和Au矿化, 通常还富集REE。据最新统计, IOCG矿床中稀土储量占世界总储量的8.7%^[74]。尽管经济价值显著, 有关REE异常富集的原因长期缺乏关注, 一些关键问题如矿床中REE的赋存状态及其与Fe、Cu矿化的关系和REE来源等目前仍缺乏制约。我国西南康滇地区的古元古代地层(如东川群、河口群和大红山群)中, 产有一系列矿化特征相似且出现明显REE富集的Fe-Cu矿床^[15](图1和7)。近年来, 通过对该区典型矿床的研究, 基本明确了它们类似于典型IOCG矿床且共同构成中国第一个IOCG成矿省——康滇IOCG成矿省^[15,69,75,76]。针对其中稀土矿化的研究虽起步较晚, 但仍取得不少进展^[77,78]。

研究显示, 这些IOCG矿床均有不同程度的稀土矿化, 但以拉拉和迤纳厂矿床最为显著(平均REE含量分

别为0.25wt%和0.11wt%)^[77]。典型稀土矿物以独居石为主, 其次为氟碳铈矿、氟碳钙铈矿、褐帘石和榍石等, 而重稀土矿物如磷钇矿极少。这些矿物分布于Fe-Cu矿石中, 但更倾向于与Cu矿化期矿物如黄铜矿、辉钼矿等紧密共生, 说明稀土与Cu矿化同期、稍晚于Fe矿化^[69,75,77]。矿物学研究进一步揭示, 矿床早期Fe阶段及围岩中的富稀土磷灰石常不同程度地被热液交代, 是Cu矿化流体交代早期磷灰石时导致REE活化并重新沉淀的结果^[77,78]。Cu矿化流体具有活化或获取稀土的能力。Sr-Nd同位素数据和质量平衡模拟也证实, 矿床中的稀土除来源于岩浆-热液流体外, 富稀土的围岩也通过水-岩作用提供了部分稀土^[77,78]。

2.7 富Ti低温热液矿床

目前工业利用的铌主要从含铌矿床中作为伴生组分回收。全球各类铌及含铌矿床常具低温成矿特征, 主要分布在扬子地块西南部和美国内华达州等低温成矿省内。在我国西南部, 铌不仅作为共生组分富集于低温

图7 康滇IOCG成矿省地质及矿床分布略图(a)、拉拉Fe-Cu-(REE)矿床地质略图(b)、迤纳厂Fe-Cu-(REE)矿床地质略图(c)^[75,79]
 Figure 7 Simplified geological map and distribution of IOCG deposits in the Kangdian IOCG province (a) and geological sketch maps of the Lala (b) and Yinachang (c) Fe-Cu-(REE) deposits^[75,79]

热液金、汞、锑、砷矿床中，而且形成了两个世界罕见的铊矿床——贵州滥木厂铊汞矿床和云南南华铊砷矿床^[71]。

扬子地块西南部的滇黔桂接壤区，分布大量以卡林型金矿为主的金、汞、锑、砷等低温(多为120~250℃)热液矿床，是我国扬子地块中生代大面积低温成矿省的重要组成部分(图1)。该区目前探明金储量近1000 t，是我国的主要金矿基地之一，也是除美国内华达低温成矿省外的全球第二大卡林型金矿集中区^[7]。这些金矿床主要产于沉积岩地层中，少数矿床中偶见硫铊铊汞矿，热液期载金黄铁矿含铊可达100余ppm，形成卡林型金矿典型的Au、As、Sb、Hg、Tl等低温成矿元素组合。滥木厂铊汞矿床产于卡林型金矿集中分布的贵州贞丰县灰家堡背斜的二叠统龙潭组-大隆组地层中，赋矿围岩岩性为钙质粉砂岩和泥质灰岩，矿体呈似

层状或透镜状，矿石矿物有红铊矿、辰砂、雌黄、雄黄、黄铁矿和毒砂，以及少量斜硫铊汞矿、硫铊铊矿和铊明矾。铊主要赋存于红铊矿等铊矿物中，少量以类质同象或吸附形式赋存于辰砂、黄铁矿等矿物中^[80]。富铊矿石铊品位可达0.1%~5%，而汞铊共生矿床铊品位可达0.01%。已初步探明该矿床的铊储量为>500 t，共生金、汞储量超过1和4800 t^[81]。

目前尚无滥木厂铊汞矿床的成矿年龄数据，因其成矿特征与区内卡林型金矿相似，推测铊成矿应发生于160~130 Ma^[82]。该矿床的成矿流体具有低温(107~194℃)、低盐度和偏酸性特征^[83]，以往认为铊的源岩是赋矿地层本身，地层中的化石或含钾矿物富含铊并被后期流体改造而富集成矿^[81,84]。然而，Tan等人^[85]的研究表明，滥木厂未蚀变的龙潭组-大隆组地层铊含量接近克拉克值，地层剖面元素填图显示铊在背

斜核部发生了自下而上的运移,因此赋矿地层可能不是铈的矿源层。

2.8 富锗(Ge)等的Pb-Zn矿床

全球锗资源多来源于富锗煤和富锗贱金属硫化物矿床^[86],MVT(Mississippi valley-type)型铅锌矿床是全球锗资源最重要的来源之一^[87]。作为我国扬子地块中生代大面积低温成矿省的重要组成部分,川滇黔接壤区面积约17万km²,分布400余个MVT铅锌矿床(点)^[7,71,88](图1)。这些低温热液铅锌矿床均不同程度富集Ge。其中,会泽铅锌矿床中Ge储量超过386 t,与毛坪(17 t)、富乐(129 t)、茂租(136 t)等矿床一起构成滇东北锗资源基地^[89]。除Ge外,该区的铅锌矿床中Cd、Ga等关键金属亦存在相对富集现象,多数已达伴生组分综合利用要求。

研究表明,矿床中的闪锌矿是Ge等关键金属元素的主要载体。闪锌矿中Ge含量变化较大,多在1~500 ppm之间,最高可达近1000 ppm,高度富Ge的闪锌矿通常只集中在矿物组合中的某些特定世代^[68,88,90](图8)。此外,闪锌矿中也不同程度地富集Cu。元素Mapping面分析显示,Ge和Cu在闪锌矿中的富集区域一致,Ge与Cu具有很好的正相关(图8)。在乐红、富乐、麻栗坪和天宝山矿床闪锌矿中Ge-Cu的相关系数分别可达0.95、0.93、0.81和0.73。这可能表明Ge与Cu呈耦合方式类质同象替代了闪锌矿中的Zn。Cu作为与Ge共同替代Zn的伙伴,对铅锌矿床中Ge的富集至关重要^[88]。

研究表明,这些富锗Pb-Zn矿床主要形成于约230~200 Ma的印支期^[7]。基底地层是该区矿床的主要物源区^[91]。但是,该区的这些矿床均产于富铜的峨眉山玄武岩的下伏地层中,至少玄武岩中的Cu对矿床的形成可能发挥了重要作用,值得进一步研究。

3 扬子地块西南部关键金属成矿与主要地质事件的关系

如前所述,扬子地块西南部富含不同种类关键金属元素的各类矿床广泛分布。近年来,这些矿床的年代学研究取得重要进展。研究表明,它们是不同的时期构造-岩浆-环境事件的产物。

(i) 古-中元古代IOCG矿床。这些富REE的Fe-Cu矿床分布于扬子地块西缘古元古代变质岩地层中,构成南北向展布的康滇IOCG成矿省(图1和7)。纳纳厂和拉拉矿床中褐帘石U-Pb和辉钼矿Re-Os年龄显示,稀土

图8 川滇黔接壤区铅锌矿床闪锌矿Cu-Ge关系图^[88]

Figure 8 Correlation of Cu and Ge contents of sphalerite in the Pb-Zn deposits from the border area of Sichuan, Yunnan and Guizhou provinces^[88]

矿化分别发生于1.7和约1.1 Ga,它们代表了该成矿省两期重要的稀土矿化事件,是古元古代哥伦比亚超大陆裂解和中元古代裂谷活动驱动的两期陆内岩浆活动的产物^[75,91~93]。

(ii) 新元古代至早古生代富REE磷块岩矿床和富PGE、Re黑色页岩。这些矿床或矿化主要沿扬子地块西南缘分布(图1),寒武纪织金富稀土磷块岩矿床和黑色页岩中Ni-Mo-PGE多金属层的Re-Os年龄分别为522.9±8.6^[29]和521±5 Ma^[29],可能与新元古代大陆裂解——雪球事件等相关联的大氧化事件的后续效应有关。例如,地质历史时期海相深部缺氧沉积物和辉钼矿中Re含量的增加与两次大氧化事件相耦合,地球表层的氧化过程由于超基性岩和斑岩型矿床的风化,可能为海洋PGE和Re储库的增加提供了重要物源^[94~96]。

(iii) 晚古生代风化-沉积矿床。这类矿床包括3个时期:黔中下石炭统九架炉组的碳酸盐黏土型Li-Ga-REE矿床、滇中下二叠统倒石头组的碳酸盐黏土型Li-Ga-REE矿床、滇黔地区上二叠统宣威组玄武岩风化型Nb-Ga-Zr-REE矿床。它们的形成可能与晚古生代冰期密切相关。晚古生代冰期是显生宙持续时间最长、影响范围最广、强度最大的一次全球性冰川事件^[97,98]。在全球晚古生代冰期背景下,冰期海平面下降导致位于低纬度的黔中、滇中的早古生代碳酸盐岩基底和二叠纪玄武岩发生暴露风化,并在适宜的古气候与较稳定的构造背景中,形成喀斯特风化壳和玄武岩风化壳,继而形成相应的风化-沉积矿床。

(iv) 中生代热液矿床。中生代是扬子地块最重要的成矿时期,形成了大量低温矿床和锡石硫化物矿床。

这一时期的成矿作用主要有两种动力驱动机制^[7,16,18,19]。(1) 印支期(约230~200 Ma)受制于多陆块相互作用的陆内造山,驱动盆地流体和大气成因流体循环,分别形成了川滇黔矿集区富Ge的Pb-Zn矿床和滇黔桂接壤区右江盆地的部分卡林型Au矿床;(2) 燕山早期(约160~130 Ma)和燕山晚期(约100~80 Ma)的陆内岩石圈伸展,先后驱动低温流体循环和花岗岩浆活动,而在右江盆地内部及其南、东周边分别形成了第二期的低温Au-As-Sg-Hg-Tl矿床和与花岗岩有关的富In锡石硫化物矿床。

4 结论和展望

自元古代以来,扬子地块西南部的多次重大地质-环境事件导致地壳再造和环境突变,造就了富含关键金属元素的多种矿床类型。相对于我国其他地质单元,扬子地块西南部富含关键金属元素矿床的成矿作用主要显示四大特点:(1) 古-中元古代发育我国首个被确认的富稀土IOCG成矿省;(2) 燕山晚期与花岗岩有关的富In锡石硫化物矿床在面积很小的区域大爆发成矿;(3) 印支期和燕山早期花岗岩浆活动微弱,富Ge低温Pb-Zn矿床和低温Au-As-Sb-Hg-Tl矿床广泛发育;(4) 埃迪卡拉纪以来的海相沉积岩尤其是黑色页岩和碳酸盐岩广布,多时代富Li、Nb、Zr、Ga、Re、REE、

PGE等的沉积和风化-沉积矿床大面积分布。

这些成矿作用在我国有的甚至在全球都具典型性,需要针对上述四大成矿系统各自的研究现状,有重点地加强布局。(1) 对IOCG成矿省重点探讨REE的富集机制和资源潜力;(2) 该区在云南与广西交界的很小区域,形成了与晚白垩世花岗岩有关的4个超大型锡石硫化物矿床且高度富In,是世界In的主要产地,同时也是发展In成矿理论的理想场所,需要从壳幔循环、岩浆结晶分异、元素地球化学性质和结晶矿物学等多维度开展深入研究,以解决为什么In与锡石硫化物矿床有关、闪锌矿选择性富In的“铜窗效应”本质是什么、哪些锡石硫化物矿床才富In等科学难题;(3) 扬子地块的中生代低温成矿省,是全球两个主要低温成矿省之一,该区富Ge、Ga、Cd、Tl等关键金属元素的大量低温矿床的形成,在其他有利因素配合下,可能与元素地球化学背景密切相关,但这些研究是以往的薄弱环节;(4) 该区的沉积和风化-沉积矿床,例如碳酸盐黏土型Li-Ga-REE矿床和玄武岩风化型Nb-Ga-Zr-REE矿床等,很可能是具有巨大资源潜力的新类型矿床,除成矿机制的深入研究外,元素赋存状态和可利用性研究尤其重要;(5) 已有的勘查技术和评价方法多为针对主矿种而研发,亟须进一步开发面向关键金属找矿信息集成-预测-定位和评价的技术方法。

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Summary for “扬子地块西南部关键金属元素成矿作用”

Metallogeny of critical metals in the Southwestern Yangtze Block

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The Yangtze Block is one of the major geological units in China. Numerous and diverse mineralization are extensively distributed in this block, making the Yangtze Block be one of the well-known providers of mineral-resources worldwide. In the southwestern Yangtze Block, since Proterozoic, the diverse mineralization involves magmatic, magmatic-hydrothermal, low-temperature hydrothermal and weathering-sedimentary processes were extensively developed, of which critical metal mineralization (e.g., In, Ge, Ga, Cd, Re, W, Sn, Li, Nb, REE, and PGE) is generally present as by-products in some basic or precious deposits or as independent deposits. Previous studies have revealed ten types of critical metal mineralization in the region, specifically including the REE-rich phosphorite, PGE-Re-rich black shales, carbonate clay-type Li-Ga-REE, basalt weathering-type Nb-Ga-Zr-REE, In-rich cassiterite sulfide, REE-rich IOCG, Tl-rich low-temperature hydrothermal, Ge-rich Pb-Zn, Cu-Ni-PGE sulfides and carbonatite-related REE deposits. In the past decade, numerous studies have advanced our understanding of the mineralization styles, timing and ore genesis of these types of critical-metal mineralization, and are summarized in this paper. It was indicated that the Cu-Ni-PGE sulfide deposits are genetically related to the late Permian E'meishan mantle plume, whereas the carbonatite-related REE deposits are Cenozoic in age and have formed during post-collision between the Indian and Asian continents. Moreover, the REE-rich IOCG deposits were newly identified, constituting a Proterozoic IOCG metallogenic province that was first documented in China, and enrichments of REEs were suggested to be related to the chemical attributes of the late Cu mineralizing fluids; the In-rich sulfide deposits, distributed in a small area of the SW Yangtze Block, were suggested to be genetically related to late Yanshanian granites; the low-temperature hydrothermal mineralization, characterized mainly by the Pb-Zn and Au-As-Sb-Hg-Tl deposits that define one of the two world-largest low-temperature metallogenic provinces, was mainly formed at the Indosinian and Yanshanian periods during which granitic activities are relatively weak; numerous marine-facies sedimentary rocks particularly including the black shales and carbonate rocks are associated with the development of multi-episodes of sedimentary and/or weathering-sedimentary deposits that are uniquely enriched in Li, Nb, Zr, Ga, Re, REE and PGE.

We also proposed some issues that are important but currently poorly addressed, including aspects of the evaluation of REE resource potential and mechanisms of REE concentrations in IOCG deposits, and key factors controlling the extreme enrichment of Ge, Ga, Cd and Tl in the Mesozoic low-temperature metallogenic province, with focuses on the background values of these elements in the region. Moreover, available studies show that In is extremely enriched in four giant cassiterite-rich, granite-related sulfide deposits distributed in the border area of Yunnan and Guangxi, making this area a unique In metallogenic province in the world. However, it is currently not clear why In is enriched in cassiterite-rich sulfide deposits and why In is enriched in the sphalerite as a function of “indium window” effect, which should be constrained through a combined study involving crust-mantle circulation, crystallization fractionation of magma, geochemical behaviors of metals and mineralogy. We also proposed that the weathering-sedimentary deposits, such as the clay-type Li-Ga-REE and basalt weathering-type Nb-Ga-Zr-REE ones, are likely brand-new types with huge potential of critical metal resources, and emphasized that in addition to ore genesis studies, researches on the distributions of metals and potential utilization of resources should also be paid more attention. We also highlight that current prospecting techniques and methods that are mostly used for exploration of some common basic or precious deposits are likely not applicable for the exploration of critical metal deposits. As such, new techniques and methods involving the integration of prospecting information, predication and locating of ore bodies and evaluation of resources should also be developed for critical metal deposits.

Yangtze Block, critical metal, deposit types, metallogeny

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