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近十年来中国矿床地球化学研究进展简述

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摘　要: 我国的矿床地球化学研究在近十年取得了众多重要进展。本文对中国岩浆型 Cu-Ni-(PGE) 硫化物和 Fe-Ti-V 矿床、斑岩型铜矿床、花岗岩型钨锡矿床、碳酸岩型稀土矿床、卡林型金矿床和密西西比河谷型(MVT)铅锌矿床等的一些相关研究进展,以及原位分析技术和实验地球化学在矿床研究方面的应用进展进行了扼要论述。近十年来,造山带铜镍硫化物矿床的寻找取得突破进展,岩浆通道系统被证实对巨量钒钛磁铁矿的堆积起关键作用;碰撞型斑岩铜矿的成矿模型更趋完善,花岗岩相关钨锡矿床的成矿过程与机制获得更精细刻画,碳酸岩型稀土矿床的形成时限被精确限定;华南大规模低温成矿的时限和动力学背景研究取得重大突破,成矿物质来源和流体演化的认识更为深入;原位微区元素-同位素组成对精细刻画成矿过程发挥重要作用,实验地球化学的应用初现端倪。此外,本文还对未来需要重视的几个方面的工作提出了初步建议。

关　键　词: 岩浆矿床;岩浆热液矿床;低温热液矿床;原位分析技术;矿床地球化学

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Summary of Progresses in the Study of Ore Deposit Geochemistry in China in the Past Decade

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Abstract: In recent decade, numerous important achievements for ore deposit geochemistry have been made in China. This paper briefly summarizes some progresses in the studies of magmatic Cu-Ni-(PGE) and Fe-Ti-V deposits, porphyry Cu deposits, granite-related W-Sn deposits, carbonatite-related REE deposits, Carlin-type Au deposits, and Mississippi Valley-type Pb-Zn deposits, and the implications of in-situ analytical methods and experimental geochemistry in researches of ore deposits. Notably, a breakthrough has been made in the exploration of magmatic Cu-Ni sulfide deposits in the orogenic belt, and a magma-conduit system has been confirmed to be critical for the huge accumulation of V-Ti-bearing magnetite. The metallogenic model for collision-type porphyry Cu deposits has been increasingly improved, and the ore-forming process and mechanism for granite-related W-Sn deposits has been more elaborately illustrated. The metallogenic timing for carbonatite-related REE deposits has been more precisely confined. Significant progresses in researches on timing and geodynamic background, as well as deep understandings on the sources of ore-forming materials and the evolution of ore-forming fluids for large-scale mineralizations of low-temperature hydrothermal deposits in South China have also been made. Moreover, in-situ micro-analyses of elemental and isotopic compositions have played important roles for elaborately illustrating the ore-forming processes, and applications of experimental geochemistry shed preliminary light on studies of ore-forming mechanisms of mineral deposits. In addition, several perspectives on future studies that need to be paid attention to have been proposed.

Key words: magmatic deposit; magmatic-hydrothermal deposit; low-temperature hydrothermal deposit; in-situ analytical method; ore deposit geochemistry

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0 引言

矿床地球化学是矿床学与地球化学交叉融合形成的分支学科。近十多年来,成矿作用与地球动力学过程的更密切结合、成矿过程的精细化研究和先进分析测试仪器和技术(尤其是原位微区技术)的研发和应用,拓展了矿床地球化学的研究领域,创新和发展了成矿理论。我国的矿床地球化学研究在此期间取得了众多重要进展。由于矿床类型繁多、研究成果海量,本文仅总结了中国岩浆型 Cu-Ni-(PGE) 和 Fe-Ti-V 矿床、斑岩型 Cu 矿床、花岗岩相关 W-Sn 矿床、碳酸岩型 REE 矿床、卡林型 Au 矿床、密西西比河谷型(MVT) Pb-Zn 矿床的进展,同时对原位分析技术和实验地球化学在矿床研究中的一些应用进行了初步的总结。限于时间、视角和认识,相关内容难免挂一漏万,有关论述或难免偏颇,尚需有关研究者谅解和读者批评指正。

1 岩浆矿床地球化学研究进展

岩浆矿床提供了全球最重要的 Ti、V、Ni、PGE 和 Cr 资源,也是 Fe、Co 等矿产的重要来源。我国岩浆矿床的成矿作用在全球独具特色,例如,晚二叠世峨眉山地幔柱活动形成了世界上最大的 Fe-Ti-V 氧化物矿集区和若干 Cu-Ni-PGE 硫化物矿床,以及 Nb-Ta-Zr-REE 富集和矿化,同一地幔柱发生三类成矿作用的现象全球罕见;甘肃金川是全球第三大 Cu-Ni 硫化物矿床,与新元古代地幔柱/裂谷活动有关;东天山、东昆仑造山带一系列大型-超大型Cu-Ni 硫化物矿床的发现而成为新的研究热点。

1.1 岩浆硫化物矿床

最近十年我国岩浆硫化物矿床的研究和找矿工作都取得了重要进展,主要体现在以下几个方面。

1.1.1 造山带找矿工作取得突破 最近十年世界新发现的最大的铜镍矿并非在大火成岩省,而是在我国青海省东昆仑造山带的夏日哈木超大型镍钴矿床。2015 年该矿床的探明矿石储量为 1.57 亿 t,镍金属储量超过 108 万 t,Ni、Cu、Co 的平均品位分别达 0.65%、0.14%和 0.013%,进入世界级规模镍矿床的行列(Song et al., 2016b)。2012 年西澳大利亚地调局根据土壤地球化学异常在 Fraser Range 地区发现了 Nova 铜镍矿床,其矿石量达 1460 万 t,镍金属储量达 32.5 万 t,Cu、Ni、Co 的平均品位分别达 0.9%,0.08%和 2.2%(Maier et al., 2016)。与大火成岩省铜镍硫化物矿床相比,造山带铜镍硫化物矿床大多铜镍品位较低、贫铂族元素,但这些发现还是点燃了各国在造山带寻找铜镍硫化物矿床的热情。鉴于造山带面积远大于大火成岩省,上述发现意义重大。

然而,关于造山带铜镍硫化物成矿规律和条件的认识却存在很大分歧。例如,我国新疆北部铜镍硫化物矿床究竟形成于俯冲阶段、碰撞或碰撞后阶段还是与地幔柱活动有关,一直存在较大争议(Qin et al., 2011; Su et al., 2011; Zhang et al., 2011; Li et al., 2012; Song et al., 2013a; Xie et al., 2014; Deng et al., 2017)。东昆仑夏日哈木矿床也存在形成于俯冲阶段还是碰撞或碰撞后阶段之争(Song et al., 2016b, 2020; Zhang et al., 2017b; Wang et al., 2019a)。扬子地块周缘元古代的铜镍硫化物矿床(矿化),例如,四川冷水箐矿床及桂北一系列矿化岩体的矿物化学组成均显示其与俯冲过程有关,但迄今为止发现的矿床规模仍很小(Zhu et al., 2006, 2007; Zhou et al., 2017; Yao et al., 2018b; Ding et al., 2019)。因此,造山带铜镍硫化物矿床成因研究还任重道远。

1.1.2 成矿构造背景的新认识 许多岩浆硫化物矿床(特别是超大型矿床)往往产于大陆岩石圈边缘。基于含矿岩体时代与地幔柱活动的耦合关系,Begg 等(2010)认为,大陆岩石圈厚度大而使地幔柱到达大陆岩石圈底部时难以发生减压熔融,从而迫使地幔柱向岩石圈较薄和强度较低的大陆岩石圈边缘运移,并在较小的深度发生强烈的减压熔融、形成巨量镁铁-超镁铁岩浆,为大规模岩浆硫化物提供物质和能量条件。

造山带演化过程中,特别是碰撞阶段常伴生有大规模区域性走滑断层的形成。Lightfoot 和 Evans-Lamswood(2015)认为,走滑构造对铜镍硫化物成矿具有控制作用。对中国新疆黄山和黄山东岩体边缘及围岩的韧性剪切构造及岩体内部的断裂构造的分析表明,区域性剪切作用形成的次一级张性构造为幔源岩浆上升提供了通道,并为岩浆房的形成提供了空间(Wang et al., 2014a)。宋谢炎等(2018)认为,同碰撞阶段发生大规模的区域性剪切走滑使上述俯冲洋壳的断离更加容易,剪切走滑产生的超壳断裂为幔源岩浆的上升提供了顺畅的通道,也在地壳为含矿岩体的形成创造了良好的空间。

1.1.3 揭示岩浆通道系统中硫化物熔体的运移和聚集机制 目前对岩浆通道揭露最充分的是加拿大 Voisey's Bay 和美国的 Eagle 矿床(Lightfoot and Evans-Lamswood, 2015),而更多矿床的岩浆通道,如我国甘肃金川,由于中新生代剧烈的构造作用,

含矿岩体及矿体的产状被强烈改造，对矿床成因分析影响很大。Song 等(2012)在对金川岩体不同矿段岩相的主、微量元素(含 Cu、Ni、S、PGE 等)组成对比及断裂构造分析基础上，对其原始产状进行了恢复，认为金川存在两个独立的含矿岩体，它们分别经历了不同的成岩成矿过程，并在此基础上建立了新的成岩成矿模式：东、西岩体位于岩浆通道系统的两个分枝；硫化物熔离均发生在不同的深部岩浆房；熔离的硫化物乳珠被岩浆携带到西岩体，堆积在岩体底部成矿，而东岩体的矿体更可能是有硫化物-橄榄石晶粥挤入形成(Song and Li，2009；Chen et al.，2013a)。

Mao 等(2019b)和 Deng 等(2017b)通过全岩及矿物主、微量元素、Sr-Nd-Os 同位素方法探讨了地幔源区特征、地壳同化混染、岩浆氧逸度等因素对新疆黄山矿床成矿作用的约束和贡献，认为俯冲过程对地幔源区的改造对原始岩浆地球化学特点，以及后来岩浆演化过程及硫化物熔离机制、成矿机制和矿床的各种特征都有很重要的影响。

1.1.4　贱金属硫化物中铂族元素的赋存状态新认识　岩浆硫化物矿床中铂族元素的赋存状态一直是这类矿床研究的热点问题，单矿物分析发现磁黄铁矿和镍黄铁矿中可能有很高的铂族元素含量，近年来的 LA-ICPMS 分析也发现铂族元素的分布是不均匀的，但铂族元素究竟是以纳米颗粒还是类质同象形式分布，与哪些元素耦合却并不清楚(Chen et al.，2015a)。Liang 等(2019)对峨眉山大火成岩省杨柳坪超大型铜镍铂族元素矿床中贱金属硫化物的铂族元素赋存状态进行了研究，认为铂族元素在结晶前就常常和半金属元素耦合、以配合物形式存在于硫化物熔体中。因此，尽管其含量很低，也会以液相线矿物形式最早结晶形成纳米颗粒。

1.2　岩浆氧化物矿床

钒钛磁铁矿矿床是 V 和 Ti 的主要来源，中国资源量分别占全球的 48% 和 25%，产量占全球 55% 和 16%(USGS，2019)。我国钒钛磁铁矿矿床主要赋存于与地幔柱相关的大型镁铁-超镁铁层状岩体中，如峨眉山大火成岩省内带的攀枝花岩体(Zhou et al.，2005；Zhang et al.，2014a)和塔里木大火成岩省的瓦吉里塔格岩体(Cao et al.，2014)及板内伸展环境的元古代斜长岩套中(如大庙斜长岩体；Chen et al.，2013b)。此外，汇聚板块边缘的镁铁质岩体，如扬子板块北缘的毕机沟岩体也表现出一定的钒钛磁铁矿成矿潜力(Zhao et al.，2018)。

1.2.1　成矿母岩浆恢复取得突破性进展　对峨眉山和塔里木大火成岩省相关钒钛磁铁矿矿床的矿物化学研究并结合 MELTs 模拟计算发现，成矿岩体的母岩浆是由原始的铁苦橄质岩浆在地壳深部经历了橄榄石和铬铁矿分离结晶而演化来的高钛铁玄武质岩浆(Bai et al.，2012；Song et al.，2013b；Cao et al.，2014；Wang et al.，2014b；Zhang et al.，2018a)。Bai 等(2014)通过单斜辉石成分结合分配系数的反演和边缘带成分估算了成矿岩体母岩浆成分，结果表明红格与攀枝花成矿岩体母岩浆分别类似于岩体附近的峨眉山玄武岩。对比发现成矿岩体母岩浆的成分差异导致了成矿岩体在含矿岩性和矿物组合的显著区别，该差异被解释为上升地幔柱岩浆对新俯冲洋壳的选择性同化。Hou 等(2011，2013)通过稀有气体同位素及 Re-Os 同位素揭示了地幔柱-俯冲/再循环洋壳(榴辉岩)相互作用对形成铁苦橄质岩浆的贡献，并强调了源区过程对钒钛磁铁矿矿床的大规模成矿的控制作用。与此类似，塔里木大火成岩省相关钒钛磁铁矿矿床的铁玄武质母岩浆也被认为存在俯冲改造的岩石圈地幔的贡献(Zhang et al.，2018a；Cao et al.，2019a)。

1.2.2　钒钛磁铁矿矿床的成因争议　钒钛磁铁矿的成矿过程存在明显的争议，目前主要的成因模式有 3 种。Howarth 等(2013)观察到钒钛磁铁矿矿层中硅酸盐矿物存在不平衡结构，提出攀枝花岩体内的主要钒钛磁铁矿矿层不是原地形成的，而是由深部岩浆房中产生的富含钛磁铁矿晶体的晶浆堆积而成；通过岩石显微结构以及运用原位微区分析技术对矿物微量元素及熔融包裹体的研究，一些学者提出镁铁-超镁铁层状岩体中赋存的钒钛磁铁矿矿床是由玄武质岩浆液态不混溶作用分离而成富铁熔体形成(Zhou et al.，2013；Liu et al.，2014；Xing et al.，2014；Wang et al.，2018a)。类似的机制也被用来解释赋存于斜长岩套中铁钛磷灰岩(nelsonite)及相关钒钛磁铁矿矿床的成因(Chen et al.，2013b；He et al.，2016)；第三种成因模式认为矿物化学垂向上的规律性变化反映磁铁矿和钛铁矿直接在玄武质岩浆演化的早期阶段结晶并发生重力分异而成矿。较高的氧逸度(Bai et al.，2012，2016，2019b；Ganino et al.，2013；Cao et al.，2014)、富水(Howarth and Prevec，2013；Zhang et al.，2018a)以及富 Fe、Ti 的母岩浆(Song et al.，2013b；She et al.，2015)成分以及周期性岩浆的补给(Bai et al.，2012；Song et al.，2013b)是导致磁铁矿较早结晶并成矿的关键控制因素。近年来，非传统同位素(如 Fe、Mg 同位素等)被应用于钒钛磁

铁矿矿床成因研究(Chen et al.,2014; Liu et al.,2014; Cao et al.,2019b)。详细的分析结果显示硅酸盐矿物与磁铁矿、钛铁矿之间存在明显的同位素不平衡,但其原因是液态不混溶还是亚固相再平衡还存在争议。

1.2.3 建立钒钛磁铁矿的岩浆通道成矿模型 研究发现,含矿层状岩体本身并不足以提供形成超大型钒钛磁铁矿矿床所需的成矿物质,说明有更多的岩浆参与了成矿过程。通过详细的矿物学和地球化学研究,Bai 等(2012)揭示了具有地球化学韵律性变化特征的赋矿层状岩体曾是多期玄武岩浆喷发的岩浆通道系统,并在此基础上建立了在岩浆通道系统中形成超大型钒钛磁铁矿矿床的成矿模式。巨量的玄武质岩浆在岩浆通道中多次卸载大量的成矿物质,是钒钛磁铁矿在一个较小岩体中超常富集的关键因素。

2 斑岩(矽卡岩)-浅成低温热液型铜矿床地球化学研究进展

作为全球主要的 Cu、Mo 及重要的 Au 等金属来源,斑岩铜矿系统(包括矽卡岩型矿床和浅成低温热液型 Au 矿床)长期是工业界和学术界重点关注的矿床类型之一(Sillitoe,2010)。就我国而言,斑岩铜矿系统供应了全国65%以上的 Cu、超过1/4的 Au 和约90%的 Mo(Chang et al.,2019; White et al.,2019; Yang and Cooke,2019)。

2.1 碰撞型斑岩铜矿成矿模型的创新

经典的斑岩铜矿模型认为其主要形成于与大洋俯冲有关的岛弧或陆缘弧环境(Richards,2003; Sun et al.,2013; 毛景文等,2014; 陈华勇和吴超,2020)。我国地处全球三大构造域即环太平洋、古亚洲洋和特提斯构造域的复合部位,增生、碰撞、陆内造山带均十分发育(Hou et al.,2007; 陈衍景,2013; 秦克章等,2017; 侯增谦等,2020),除俯冲型斑岩铜矿外,我国还发育众多非弧环境的斑岩铜矿(Yang and Cooke,2019)。

近十年来,随着对西藏冈底斯斑岩铜矿带、玉龙斑岩铜矿带一系列非弧环境斑岩铜矿的深入研究,我国学者逐步建立了碰撞斑岩铜矿的成矿模型(Hou et al.,2015a,2017; Yang et al.,2015,2016; Wang et al.,2018c; 侯增谦等,2020)。与俯冲型斑岩铜矿一样,碰撞斑岩铜矿的岩浆源区亦具有较高的氧逸度和水含量,这些条件能保证岩浆中硫化物不会过早饱和并最终在出溶流体中富集(Richards,2009; Hou et al.,2011; Wang et al.,2014c; Sun et al.,2017);两类斑岩铜矿的围岩蚀变和矿化特征也十分相似,但碰撞斑岩铜矿中的绢英岩化对早期钾化蚀变的叠加可能更显著,同时绢英岩化阶段可能也沉淀了大量的铜硫化物(Yang and Cooke,2019),这些新的认识丰富了斑岩铜矿的成矿理论。传统观点认为,弧环境斑岩铜矿岩浆的高氧逸度和富水特征主要来自于俯冲板片(Richards,2003; Sillitoe,2010);对碰撞斑岩铜矿而言,俯冲期形成的新生或加厚下地壳±岩石圈地幔的部分熔融可能对成矿十分关键(Li et al.,2011b; Deng et al.,2015; Zhou et al.,2015b; Hou et al.,2017),Hf-Nd 同位素填图也证实斑岩铜矿主要产出于较年轻的地壳分布区(Wang et al.,2016a; 侯增谦和王涛,2018),但目前就新生下地壳和岩石圈地幔对成矿所需挥发性组分(水、硫、氯等)和金属贡献比例尚不明确(Lu et al.,2015; Yang et al.,2015; Wang et al.,2018c; Li et al.,2020b; 侯增谦等,2020)。最近,一些学者尝试通过非传统稳定同位素解决上述争议。Zheng 等(2019)发现冈底斯带成矿斑岩及黄铜矿均具有较重的 Cu 同位素组成($\delta^{65}Cu$ 为0.18‰~1‰),据此提出具较重 Cu 同位素组成的下地壳硫化物重熔提供了冈底斯斑岩铜矿带所需的铜。值得一提的是,近年来俯冲型斑岩铜矿的成矿机理也受到了一些挑战,例如,Lee 等(2012)、Chiaradia(2014)和 Lee 和 Tang(2020)提出,下地壳富硫化物堆晶体的重熔是形成斑岩铜矿的关键,该可能与厚地壳产出更多大型斑岩铜矿这一地质事实相吻合。但就我国俯冲型斑岩铜矿而言,其初始岩浆可能更多来自于俯冲流体交代地幔楔的部分熔融(Wang et al.,2017; Yang and Cooke,2019)。此外,如前所述,传统认为硫化物过早饱和被抑制是斑岩铜矿成矿的先决条件之一,但 Du 和 Audétat(2020)通过对铜陵矿集区斑岩铜矿的研究,指出早期硫化物饱和熔离对成矿影响不大,而岩浆富水(高 Sr/Y 值)则可能对成矿更为关键;Bai 等(2020)通过铂族元素研究,发现紫金山矿集区火山岩的铂族元素较低,暗示硫化物饱和很早,但出溶流体将早期岩浆硫化物重新萃取也可能形成斑岩铜矿床。显然,有关硫化物饱和与斑岩铜矿的成因联系,仍需更多研究。

2.2 斑岩铜矿成矿过程的精细刻画

近十年来,原位元素-同位素及高精度定年分析技术的发展推动了对成矿流体来源和演化的精细刻画,同时丰富了找矿勘探手段。Mao 等(2017)通过不同阶段石英微量元素的研究,深刻阐述了南

岭大宝山斑岩 Mo-W 多金属矿床流体演化过程; Li 等(2017, 2018f) 通过对驱龙斑岩铜矿各蚀变带辉钼矿 Re-Os 定年并基于各期次石英氧同位素周期性变化规律,阐明了成矿事件的瞬时性而热液演化的周期性特点。此外,通过激光原位测定锆石(Ce^{4+}/Ce^{3+}值、δEu 等)、磷灰石(F-Cl-S 含量)、榍石(Ga 含量、Fe_2O_3/Al_2O_3 值)、角闪石等矿物的化学成分,限定岩浆氧逸度、挥发性元素组分进而研判斑岩铜矿成矿潜力(Cao et al., 2012, 2018; Xu et al., 2012; Lu et al., 2016; Pan et al., 2016, 2018; Zhu et al., 2018; 赵振华和严爽, 2019),利用绿泥石、绿帘石的成分以及通过短波红外光谱技术(SWIR)识别蚀变矿物,从而约束矿床热液/矿化中心等方面过去十年也取得了诸多进展(杨志明等, 2012; 陈华勇和吴超, 2020)。Zhu 等(2018) 通过研究加拿大 Red Chris 斑岩铜矿发现,相较于成矿前和成矿后,成矿期斑岩具有显著高的磷灰石 S-Cl 含量,暗示富 S-Cl 的基性岩浆注入可能是斑岩铜矿的成矿关键之一。杨志明等(2012) 利用 SWIR 测量,发现西藏念村矿区东北部伊利石结晶度较大(>1.6) 且 Al-OH 吸收峰位较小(<2 203 nm),暗示该区可能为矿化蚀变中心。另外值得指出的是,利用非传统稳定同位素如 K、Mg、Fe、Cu 等识别-示踪成矿流体,近十年来已有不少开创性研究,也为斑岩铜矿地球化学研究开辟了新的领域(Li et al., 2018f; He et al., 2020; 李伟强等, 2020)。李伟强等(2020) 通过对德兴斑岩铜矿成矿斑岩全岩 K-Mg 同位素分析,发现蚀变斑岩具有显著高的 K-Mg 同位素比值($\delta^{41}K$ 为 −1.02‰ ~ 0.38‰; $\delta^{26}Mg$ 为 −0.49‰ ~ 0.32‰),指示热液蚀变过程相对富集重的 K-Mg 同位素。

2.3 矽卡岩-浅成低温热液型矿床研究进展

矽卡岩型矿床是我国十分重要的 Sn、Cu、Pb-Zn 和 Au 等金属的来源(李建威等, 2019; Chang et al., 2019);浅成低温热液型金矿床提供了我国约 8% 的金资源(>1 460 t),其中绝大部分属于低硫型,但从金资源量上看,高硫型浅成低温热液矿床产出的金更多,如福建紫金山和台湾金瓜石矿床合计产出超过 800 t 的金(Chen et al., 2012; Pan et al., 2019a; White et al., 2019)。近十年来,除将上述两类矿床作为斑岩铜矿系统的重要组成部分开展研究之外,我国学者还在这两类矿床的成因机制、成矿元素共生分异及高温与低温矿床的成因联系研究方面取得了重要进展。Shu 等(2013) 和 Zhu 等(2015a) 分别对我国内蒙古白音诺尔铅锌矿和云南羊拉铜矿开展了系统的地质地球化学研究,S-Pb 同位素组成表明成矿物质具岩浆来源,成矿年代与矿区岩浆岩一致,从而明确了上述矿床为矽卡岩型矿床而不具同生沉积成因。Xie 等(2015a) 通过对长江中下游矽卡岩型 Cu-Fe 和 Fe 矿床的研究,发现 Fe 矿床具有显著高的 S 同位素组成,暗示膏盐层的加入可能是成铁矿的关键。Zhai 等(2018) 通过对黑龙江三道弯子浅成低温热液型金矿床的 H-O、S-Pb 研究和地球化学热力学模拟,证实富 Te 流体可能对迁移、富集 Au 具有重要意义。Xie 等(2019) 通过榍石的 U-Pb 定年,发现华南曹家坝矽卡岩型钨矿床与周边低温 Sb-Au 矿床时代高度一致,并具显著成因联系。

3 与花岗岩相关的钨锡矿床地球化学研究进展

钨锡金属近年已成为欧美等西方发达国家高度关注的新兴战略性矿产,相关成矿作用研究及找矿勘查工作受到国内外的高度关注(Zhou et al., 2018d; Mao et al., 2019a; Lehmann, 2020; 蒋少涌等, 2020)。我国是钨锡资源的重要产区,其储量和产量长期居世界首位。我国钨矿床主要以石英脉型、矽卡岩、斑岩和云英岩型产出,而锡矿床主要以矽卡岩和石英脉型及云英岩型产出(Mao et al., 2019a),分布在华南、冈底斯、三江、昆仑、秦岭、大别-苏鲁和中亚造山带等地区。

3.1 钨锡成矿时代的精确限定

近十年来,我国学者成功开发出了矿石矿物锡石和黑钨矿原位 U-Pb 同位素定年方法(Yuan et al., 2011b; Deng et al., 2019; Tang et al., 2020),结合一些脉石矿物的同位素定年,如辉钼矿 Re-Os、云母 Ar-Ar 等,更精确地限定了我国钨锡矿床的形成时代(Hu et al., 2012b; Mao et al., 2019a; Wang et al., 2019b)。新元古代 Sn(W) 矿床(850 ~ 790 Ma) 分布在华南扬子地块西缘和南缘,早古生代 W(Sn) 矿床(450 ~ 410 Ma) 主要分布在北秦岭和东昆仑,晚古生代 W-Sn 矿床(310 ~ 280 Ma) 主要分布在中亚造山带西部,三叠纪 W-Sn 矿床(250 ~ 210 Ma) 在全国各地都有出现,从早侏罗世到白垩纪的 W-Sn 矿床(198 ~ 80 Ma) 分布在中国东部,而晚白垩世到新生代 W-Sn 矿床(121 ~ 23 Ma) 主要出露在冈底斯-念青唐古拉山-三江造山带(Chen et al., 2015c; Yuan et al., 2018b; Mao et al., 2019a; Wang et al., 2019b, 阳杰华等, 2017)。

3.2 钨锡富集过程与机制的精细刻画

近年来新方法的开发和原位微区技术的快速

发展和不断完善，显著促进了岩浆演化 W-Sn 富集过程及 W-Sn 矿床形成与演化的精细刻画，丰富和完善了与花岗岩有关的钨锡成矿理论。传统观点认为，W-Sn 矿床与花岗岩具有密切的成因联系，但 W-Sn 在岩浆演化过程中如何迁移富集得不到有效约束。近年，随着微区技术的应用，许多学者通过研究花岗岩中稳定副矿物的矿物学和矿物化学特征(如，榍石、磷灰石和石榴子石)，明确揭示了岩浆演化过程存在岩浆-热液过程阶段，该阶段 W-Sn 从岩浆转移到热液流体体系并形成 W-Sn 矿床(Yang et al.，2013，2014a; Hulsbosch et al.，2016; Zeng et al.，2017; Zhao et al.，2019)。针对成矿流体性质研究，一些学者近年采用红外显微测温技术，建立起了不透明矿石矿物黑钨矿中流体包裹体的研究方法(Wei et al.，2012; Ni et al.，2015)，直接限定成矿流体性质，弥补了以往通过研究共生脉石矿物中流体包裹体间接推断成矿流体性质带来的不足。如 Wei 等(2012) 发现江西西华山钨矿床中黑钨矿流体包裹体均一温度和盐度均高于共生石英中包裹体的均一温度和盐度。针对成矿流体演化与钨锡沉淀过程研究，一些研究者对不同成矿阶段的脉石矿物(如云母、电气石等) 开展原位元素和 B 同位素分析(Zhao et al.，2019; Hong et al.，2020)，对矿石矿物(如锡石、黑钨矿和白钨矿) 开展原位微量元素和 Sr-Hf-O 同位素等分析(Kendall-Langley et al.，2020)，结合矿石矿物如黑钨矿和锡石中单个流体包裹体成分分析，确定流体演化过程有其它性质的流体加入，进一步明确了流体混合作用是钨锡沉淀的关键控制因素(Legros et al.，2016，2018，2019; Peng et al.，2018; Yang et al.，2019d; Zhao et al.，2019)。同时，非传统稳定同位素如 Fe、Li、Sn 等近年也逐渐应用于示踪 W-Sn 成矿流体演化与沉淀过程，取得了一些开创性研究成果，这为 W-Sn 成矿作用研究拓展了新的视角(Wawryk and Foden，2015; Chen et al.，2018a; Li et al.，2018c; Yao et al.，2018a)。

3.3 幔源物质参与钨锡成矿的新认识

稀有气体同位素被广泛应用于 W-Sn 矿床的成矿作用研究(Li et al.，2011a; Hu et al.，2012a; 翟伟等，2012; Wei et al.，2019b)。传统的认识是与 W 矿床有关的花岗岩是由地壳物质重熔形成(徐克勤等，1982)，但近年的稀有气体同位素研究发现，许多 W 矿床的成矿流体中存在大量幔源 He 和 Ar，如华南瑶岗仙、西华山和淘锡坑，而 W 矿床的成矿流体由花岗岩分异出来，进而推断花岗岩中必含有大量的幔源 He。因此，原被认为与 W 成矿有关的 S 型花岗岩，实际上是壳幔相互作用的产物，地幔至少提供了地壳物质重熔所需的热(Hu et al.，2012a; Wei et al.，2019b)。值得一提的是，Yuan 等(2019) 首次认为地幔来源的热有助于地壳物质中白云母发生熔融，同时发生 W 矿化作用; 而地幔物质的直接参与可导致地壳物质中黑云母和白云母同时熔融，可产生 Sn(W) 矿化作用，进一步明确了壳幔相互作用是驱使 W-Sn 共生分异的主要原因。

4 碳酸岩型稀土元素矿床地球化学研究进展

碳酸岩型稀土矿床是中国稀土的最主要来源(>90%)(Xie et al.，2016)，且具有易采、易选和易冶的特点，经济价值显著。目前为止，中国重要的碳酸岩型稀土矿床主要分布于白云鄂博、冕宁-德昌及山东微山等地区(Xie et al.，2016)，但近年来在秦岭造山带也陆续发现了一系列规模不等的碳酸岩型稀土矿床，稀土氧化物(REO) 总储量达 200 万吨，有望成为我国的又一重要稀土资源基地(Zhang et al.，2019c)。近十年来，随着分析技术的进步，该类矿床的成矿时代和背景、稀土富集机制和关键因素、流体演化过程等方面的研究也取得了一系列重要进展。

4.1 碳酸岩型稀土矿床成矿时限的精确厘定

作为世界上最大的稀土矿床，白云鄂博稀土-铌-铁矿床一直是国内外关注的焦点，但因其具有十分复杂的元素及矿物组成，同时又经历了多期地质事件的叠加改造，其成矿时代长期争论不断。随着近十年各种原位分析技术的进步，有关白云鄂博矿床的成矿时代有了一定清晰认识。例如，利用锆石 LA-ICPMS U-Pb 及独居石 LA-MC-ICPMS Sm-Nd 等时线定年，基本限定矿区内碳酸岩的侵位时间为 ~1.3 Ga(Yang et al.，2011，2019d; Fan et al.，2014)，代表了最早一期的稀土成矿/富集事件(Zhu et al.，2015b; Song et al.，2018)，可能与超大陆的裂解相关。然而，大多数稀土矿物的 LA-ICPMS 和 SIMS U-Th-Pb 定年获得了一系列小于 1.3 Ga 且连续的年龄(1000 ~ 350 Ma，峰期 ~440 Ma; Smith et al.，2015; Fan et al.，2016; Song et al.，2018)，被认为记录了与古亚洲洋俯冲流体有关的热液改造或成矿事件(Yang et al.，2017)。

四川冕宁-德昌稀土矿带是我国第二大稀土成矿带，发育有牦牛坪超大型、大陆槽大型、木落寨和里庄小型矿床等一系列碳酸岩型稀土矿床(Xie et al.,2016; Liu and Hou,2017)。稀土矿物(氟碳铈矿)的 U-Th-Pb 同位素直接定年已精确限定成矿带北部的牦牛坪、里庄和木落寨矿床主要形成于 22 ~ 27 Ma,而南部的大陆槽矿床形成于 12 Ma(Liu et al.,2015; Ling et al.,2016),均与青藏高原碰撞导致的走滑断裂相关。

秦岭造山带不同构造单元上都发现有碳酸岩型稀土矿床,包括南秦岭单元的庙垭和杀熊洞稀土-铌矿床、北秦岭单元的太平镇稀土矿床以及华北陆块南缘的黄龙铺、黄水庵和华阳川等 Mo-REE 矿床(吴昌雄等,2015; 高成等,2017; 李靖辉等,2017; Zhang et al.,2019c)。目前,利用锆石和稀土矿物(独居石和氟碳铈矿)的 LA-ICPMS U-Pb 已基本确定该带的稀土形成于 440 ~ 410 Ma(如,庙娅、杀熊洞和太平镇)和 220 ~ 200 Ma(华北南缘的 Mo-REE 矿床)两期(Zhang et al.,2019c),且后期事件在早期矿化上(尤其是南秦岭)可能局部有叠加。

4.2 揭示碳酸岩型稀土矿床的物质来源和成因机制

白云鄂博矿床的成因长期存在很大争议(Fan et al.,2014,2016; Smith et al.,2015; Zhu et al.,2015b; Yang et al.,2017)。尽管近十年来开展了大量的同位素地球化学和矿物学等工作(发表文章百余篇),有关稀土巨量富集原因、H8 白云岩围岩的成因、稀土与铌-铁的关系等关键问题仍未形成共识。根据现有矿物学(如岩浆矿物)研究和岩浆特点的 Sr-Nd-O 同位素组成等以及不同碳酸岩地球化学成分连续变化的特点,大多数学者倾向于认为 H8 白云岩为致矿的 ~1.3Ga 岩浆碳酸岩体、稀土成矿与岩浆碳酸岩的演化密切相关(Wang et al.,2010; Fan et al.,2016; Yang et al.,2019d; Liu et al.,2020),而与古亚洲洋俯冲流体有关的热液事件对稀土成矿有何种贡献仍存在很大争论(Smith et al.,2015; Fan et al.,2016; Yang et al.,2017),亟待进一步研究。例如,部分研究者通过不同矿石中混合的 C-O 同位素特点认为该期热液极富稀土、通过交代 H8 围岩导致稀土成矿,代表了主成矿期(Ling et al.,2013; Yang et al.,2017);而另一些研究者通过矿石和矿物 Nd 同位素与 1.3 Ga 火成碳酸岩相似的特点,认为该期热液贫稀土、仅对早期火成碳酸岩成因的稀土矿石进行了不同程度的改造,无明显的稀土贡献(Liu et al.,2018b; Song et al.,2018)。

有研究者利用 Li 同位素证据证实,冕宁-德昌稀土成矿带致矿岩体的原始岩浆是受俯冲沉积物交代过的岩石圈地幔部分熔融的产物(Hou et al.,2015b; Tian et al.,2015),且原始岩浆演化过程中发生的碳酸岩与碱性岩浆不混溶作用进一步导致了稀土富集(Liu and Hou,2017)。尤其是近年来众多学者针对不同类型熔-流体包裹体开展了大量系统显微测温、SEM、激光拉曼和 LA-ICP-MS 成分等研究工作,初步确立该矿带不同矿床中成矿过程涉及流体沸腾作用而形成富稀土的高盐度流体;确定成矿流体为富 CO_2 和 SO_4^{2-} 的体系,硫酸盐对稀土的搬运和富集起重要作用;也证实温度的降低或压力释放以及浅部流体混合导致稀土矿物在晚期沉淀成矿(Xie et al.,2015b; Liu et al.,2019a; Guo and Liu,2019; Shu and Liu,2019)。然而,迄今仍有不少关键问题如流体出溶机制、稀土运移方式、硫酸盐的作用等(Cui et al.,2020b)仍需进一步研究。

对华北南缘 Mo-(REE) 矿床的同位素地球化学研究表明,致矿碳酸岩的形成可能与富碳酸盐俯冲板片熔体并交代加厚榴辉岩下地壳有关(Song et al.,2016a)、并在上升过程中可能有少量基底岩石的混染(Bai et al.,2019a);稀土成矿则与熔-流体演化形成的富 LREE/HREE、Mo、Pb 和 S 流体以及伴随的矿物结晶分异过程和后期热液活化等相关(Song et al.,2016a; Bai et al.,2019a)。另外,新近的元素和同位素地球化学研究表明,南秦岭单元庙垭和杀熊洞杂岩体的母岩浆可能源于被地壳物质(如碳酸盐物质)改造过的地幔源区(Xu et al.,2014; Çimen et al.,2018; Chen et al.,2018b),并在上升过程中通过结晶分异或液态不混溶作用促使稀土元素富集成矿(Zhu et al.,2017; Su et al.,2019)。但必须提及的是,新近矿物学和 LA-ICPMS 原位定年工作揭示,庙娅岩体中的稀土矿化在时代及矿物共生特点上却与 220 ~ 200 Ma 期热液叠加事件更为密切,可能存在后期稀土的活化和再富集(Ying et al.,2017,2020; Zhang et al.,2019c),抑或代表了与庙娅成岩过程无关的晚期稀土成矿事件(Çimen et al.,2018; Ying et al.,2020)。

5 低温矿床地球化学研究进展

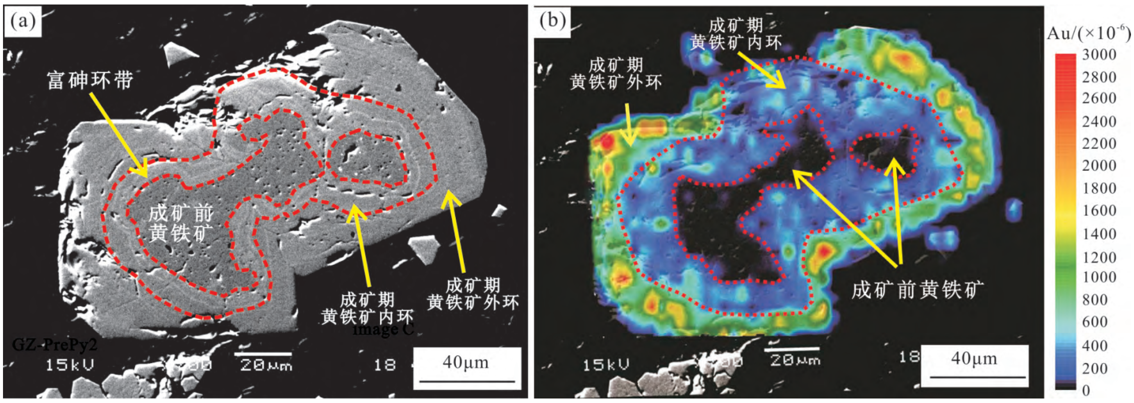
扬子地块及邻区尤其是扬子地块西南缘矿产资源非常丰富,在面积约 50 万 km^2 的范围内,卡林型金矿和锑、汞、铅、锌等低温热液矿床广泛发育,其中不乏大型-超大型矿床,构成了全球罕见的世界级多金属成矿域。区内锑矿储量占全球的 50% 以上,金矿储量约占全国的 1/5,同时还是我国铅锌矿的主要产区之一。

5.1 卡林型金矿床

全球卡林型金矿的主要产区是美国内华达和

我国滇黔桂地区(右江盆地)。滇黔桂地区的卡林型金矿是我国华南低温成矿域的重要组成部分(胡瑞忠等,2016)。近十来年,由于微区-原位分析等技术的快速发展和应用,滇黔桂地区的卡林型金矿取得了重要进展。

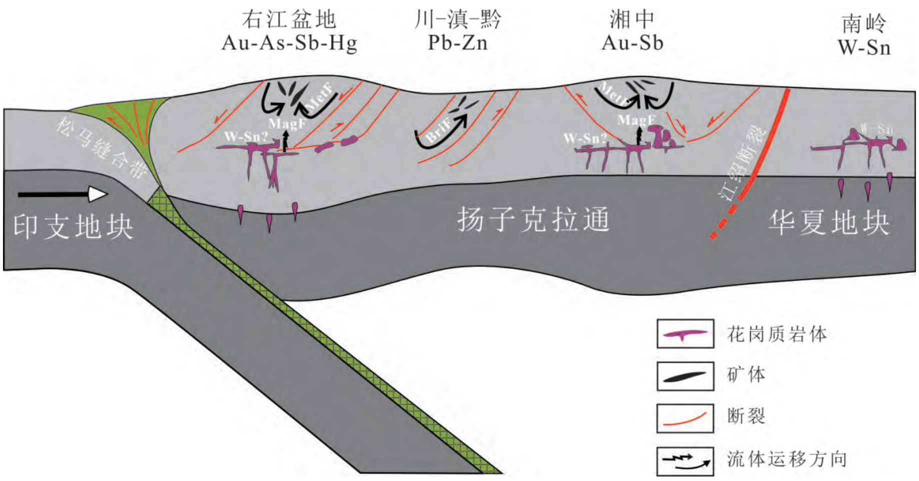
5.1.1 成矿年代和动力学背景 诸多学者早期尝试了多种方法对滇黔桂地区的卡林型金矿进行成矿年代学研究,但由于该类型金矿固有特点(矿物颗粒细、多期次、多环带、浸染状分布)(图1)和早期定年方法的局限,其成矿年龄一直没有得到很好的限定(胡瑞忠等,2007)。Hu等(2017)系统总结了滇黔桂地区卡林型金矿的成矿年龄,认为该区金矿主要有两期成矿作用,分别为200~230 Ma(相当于印支期)和130~150 Ma(相当于燕山期)。近年来,不同研究者基于金红石和锆石SIMS U-Pb、磷灰石SIMS Th-Pb、磷灰石和方解石LA-ICPMS U-Pb、锆石U-Th/He及绢云母Ar-Ar等方法,获得滇黔桂地区卡林型金矿床的成矿年龄集中在205~239 Ma和129~160 Ma(Pi et al.,2017; 高伟,2018; 黄勇,2019; Chen et al.,2019a; Zhu et al.,2020)。该区目前已发现少量200~230 Ma岩浆作用(Wu et al.,2019),并且继承锆石年龄分析显示深部有130~140 Ma和190~220 Ma的岩体(朱经经等,2016; 高伟,2018)。上述精确定年结果很好地证实了Hu和Zhou(2012)及Hu等(2017)提出的模式,即两期大规模低温成矿作用与其东侧华夏地块中与花岗岩浆活动有关的两期钨锡多金属成矿基本同时,扬子的低温成矿与华夏的钨锡高温成矿具有相似的成矿动力学背景(图2)(Hu and Zhou,2012; Hu et al.,2017; 胡瑞忠等,2020)。



(a)背散射图;(b)LA-ICP-MS金面扫描图。成矿期黄铁矿通常具有内环As高Au低、外环As低Au高的特征,说明Au在早期As含量较高的成矿流体中并未大量沉淀,而在晚期As含量较低的成矿流体中发生大规模沉淀。引自Xie等(2018a)

图1 锦丰金矿黄铁矿的多期次、多环带特征

Fig. 1 Micrographs exhibiting multi-stage and multi-band characteristics of a pyrite from the Jinfeng Au deposi



MetF-雨水成因流体; BriF-卤水成因流体; MagF-岩浆成因流体。引自Hu等(2017)和胡瑞忠等(2020)

图2 扬子克拉通印支期(200~230 Ma)大规模低温成矿动力学模型

Fig. 2 A proposed metallogenic dynamic model for the Indosinian (200-230 Ma) large-scale low-temperature mineralization in the Yangtze Craton

5.1.2 成矿物质来源、流体演化和成矿作用过程 原位微区分析技术可分析不同期次、不同环带矿物的元素和同位素组成,进而能有效限定成矿物质来源和反演成矿作用过程。诸多研究者利用 EPMA、SIMS 和 LA-ICPMS 对该区多个矿床中不同期次、不同环带黄铁矿/毒砂开展了精细的成分研究,发现成矿前与成矿期黄铁矿及矿物不同环带均具有显著的成分差异(图1)(Su et al., 2012; Hou et al., 2016; Hu et al., 2017; Xie et al., 2018b; Yan et al., 2018; Li et al., 2020c; Wei et al., 2020),说明成矿物质不是直接来源于赋矿地层。成矿期矿物不同环带的成分记录了成矿流体从早期到晚期的演化及 Au 的沉淀过程(图1)。此外,不少学者利用 SIMS、SHRIMP 和 LA-MC-ICPMS 对黄铁矿/毒砂开展微区-原位硫同位素组成分析,发现成矿期黄铁矿/毒砂的硫同位素组成主要集中在-5‰~5‰(Hou et al., 2016; Xie et al., 2018b; Yan et al., 2018; Li et al., 2020c; Wei et al., 2020),并与成矿晚期硫化物(如辉锑矿、雄黄、雌黄等)的硫同位组成数据相一致(Tan et al., 2015b);但不同学者对这些数据的解释不一致,主要有三种成矿物质来源的认识,包含:岩浆热液来源(Xie et al., 2018b; Yan et al., 2018)、变质热液来源(Su et al., 2018; Li et al., 2020c; Wei et al., 2020)和盆地水萃取地层物质(Hu et al., 2017)。此外,Hg 同位素(Yin et al., 2019)和惰性气体分析(Jin et al., 2020)均显示成矿流体有岩浆流体的贡献。

5.1.3 区域成矿作用对比 Su 等(2018)系统总结和对比了右江盆地北缘和南缘的卡林型金矿,发现盆地南缘的金矿形成于印支期(232~212 Ma),富含毒砂,其 Au/As 值低(1:1000~1:100000),硫同位素值较高($\delta^{34}S$ 为 12‰~18‰),成矿流体具有较高温度(~245 ℃)、低盐度(~2% $NaCl_{eqv}$)和富 CO_2 等特点;而盆地北缘金矿形成于燕山期(148~134 Ma),Au/As 值较高(1:10~1:1000),硫同位素组成接近零值,成矿流体为低温(~210 ℃)、中-低盐度(~5% $NaCl_{eqv}$)成矿流体。根据以上特征,Su 等(2018)提出印支期和燕山期造山作用释放的变质流体形成该区两期卡林型金矿。Xie 等(2018a)根据对滇黔桂地区和美国内华达卡林型金矿进行的对比研究,指出两地金矿在区域岩浆作用、蚀变特征、载金黄铁矿形貌和化学组成、成矿流体特征等方面都有差异,尤其是滇黔桂地区的金矿具有白云石化蚀变特征、流体温度-压力更高、更富集 CO_2,从而提出滇黔桂金矿的形成温度-压力-流体性质介于典型卡林型和造山型金矿之间(Xie et al., 2017, 2018a)。Wang 和 Grove(2018)从矿床、矿区和成矿省尺度对两地的卡林型金矿进行对比研究,发现二者具有高度相似性,从而认为滇黔桂地区的金矿应为卡林型金矿。

5.2 密西西比河谷型(MVT)铅锌矿床

扬子地台西南缘的川滇黔接壤区内成群成带分布有400多个大、中、小型铅锌矿床、矿点和矿化点,总面积约17万 km^2(柳贺昌和林文达,1999),是我国重要的 Pb、Zn、Ag 及多种分散元素生产基地之一。该矿集区是我国华南大面积低温成矿域的重要组成部分(黄智龙等,2011; Hu et al., 2017),也是我国密西西比河谷型(Mississippi Valley-type, MVT)铅锌矿床最为集中的分布区域(Zhang et al., 2015; Hu et al., 2017)。通过对矿集区近十年的研究,在成矿理论方面取得一批新认识,成矿预测方面也取得一批新突破。

5.2.1 成矿年代学与成矿动力学背景 由于川滇黔接壤铅锌矿集区缺乏精确可靠的成矿年代学数据,其成矿动力学背景长期存在争议(黄智龙等,2011; 张长青,2008; 毛景文等,2012; 吴越,2013; Hu et al., 2017)。不同研究者利用方解石和萤石 Sm-Nd、闪锌矿 Rb-Sr、沥青 Re-Os 和低 Re 含量硫化物 Re-Os 等时线及碳酸盐矿物原位 U-Th-Pb 等多种定年方法(文献略),获得矿集区赋存于不同时代地层的15个代表性矿床的成矿年龄大多集中在190~230 Ma 范围。该年龄与扬子地块西南缘古特提洋闭合时代205~240 Ma(钟大赉,1998)相近,为矿集区成矿动力学背景可能为印支期碰撞造山作用提供了年代学证据。Hu 等(2017)的研究表明,川滇黔接壤 Pb-Zn 矿集区成矿时代为190~230 Ma,华南低温成矿域内的右江盆地 Au-As-Sb-Hg 矿集区(Chen et al., 2015b, 2019a; Pi et al., 2017; 黄勇,2019)和湘中盆地 Sb-Au 矿集区(李华芹等,2008)也普遍存在该年龄段的成矿作用,并据此认为印支期奠定了华南大规模低温成矿的主体格架。

5.2.2 硫化物微量元素组成及矿床成因类型 LA-ICPMS 技术的发展使原位准确测定硫化物的微量元素组分成为可能,因而被广泛用于矿床成因类型划分、成矿流体来源与演化、成矿预测信息提取以及伴生关键金属分布与赋存状态等研究(Cook et al., 2009; Ye et al., 2011; George et al., 2015)。不同研究者对川滇黔接壤铅锌矿集区(叶霖等,2016; Wei et al., 2018, 2019a; 胡宇思等,2019; 李珍立等,2019)不同铅锌矿床的硫化物原位微量

元素组成研究表明,其明显不同于前人(Cook et al.,2009; Ye et al.,2011)总结的喷流沉积型、矽卡岩型和岩浆热液型铅锌矿床,而与 MVT 铅锌矿床总体相似;基于不同类型铅锌矿床闪锌矿的 Mn-Fe、Mn-Co、Cd/Fe-Mn 和 In/Ge-Mn 关系图,进一步确定这些矿床为 MVT 型铅锌矿床。

川滇黔接壤矿集区许多矿床都富含 Ge、Cd 等分散元素,是我国这些元素的重要生产基地之一,其分布规律、富集机理、赋存状态和综合利用长期是研究热点(温汉捷等,2019; 吴越等,2019; Wei et al.,2019a)。原位硫化物微量元素组成研究揭示,矿集区内许多铅锌矿床富含 Ge、Ge 富集于闪锌矿之中(吴越等,2019 及其中参考文献)。进一步的研究发现,区内富集 Ge 的闪锌矿也相对富集 Cu,且 Ge 与 Cu 之间存在明显的正相关关系(叶霖等,2016; 胡宇思等,2019; 李珍立等,2019; Wei et al.,2019a)等矿床。因 Cu^{2+} 较 Ge^{2+} 更易进入闪锌矿晶格(刘英俊等,1984),两者结合的平均离子半径更接近 Zn^{2+} 离子半径而有利于类质同象置换,这可能是矿集区内闪锌矿不同程度富集 Ge 的主要原因之一(Wei et al.,2019a)。

5.2.3 成矿物质基础和成矿流体来源与演化

(1)成矿物质来源。前人对川滇黔接壤铅锌矿集区成矿物质来源有多种认识,如赋矿地层(柳贺昌和林文达,1999)、峨眉山玄武岩(沈苏等,1988)、基底地层(Zhou et al.,2001)、多来源(黄智龙等,2004);近年来大量 Pb 同位素地球化学研究成果表明,该区成矿物质主要来源于基底地层,如赋存于震旦系的天宝山(何承真等,2016; 孙海瑞等,2016; Tan et al.,2019)、茂租(Wang et al.,2018b; Zhang et al.,2019a)和银厂沟(Li et al.,2016a; Tan et al.,2017),赋存于震旦-寒武系的乌斯河(Zhang et al.,2019b; Luo et al.,2020)和金沙厂(Zhou et al.,2015a),赋存于寒武系的麻栗坪(Luo et al.,2019a)和那雍枝(金中国等,2016; Zhou et al.,2018c),赋存于泥盆-石炭系的毛坪(谈树成等,2019; Xiang et al.,2020)和黔西北成矿区众多典型矿床(Li et al.,2015; Zhou et al.,2018b),赋存于石炭系的会泽矿床(Bao et al.,2017)和二叠系的富乐矿床(崔银亮等,2018; Zhou et al.,2018a; 任涛等,2019)。Bao 等(2017)对昆阳群不同岩石及水岩反应的淋滤液进行了成矿元素含量及 Pb 同位素组成研究,认为这套基底地层中富含成矿物质的岩石为铅锌矿床的主要矿源岩。

川滇黔接壤铅锌矿集区矿化与峨眉山玄武岩在空间上密切共生,很有特色。尽管玄武岩与铅锌矿床无直接成因联系,但已有研究表明峨眉山玄武岩在铅锌成矿过程中可能主要起“遮挡层”作用,为大规模流体运移、成矿元素活化-迁移-沉淀成矿营造了有利环境,还可能“保护”其下层位中的铅锌矿床免遭后期地壳全面隆升剥蚀的影响(崔银亮等,2018; 李珍立等,2019; Li et al.,2018g,2020c; Zhou et al.,2018a; 任涛等,2019)。

(2)碳酸盐岩在成矿过程中的作用。川滇黔接壤铅锌矿集区的一个明显特征是容矿岩石为不同时代(震旦纪-二叠纪)地层中的碳酸盐岩。前人对国内外许多地区的 MVT 铅锌矿床进行过深入研究(文献众多,略),在成矿背景、成矿条件、成矿机制、成矿规律和成矿预测等方面都取得丰富研究成果,但有关这类铅锌矿床容矿碳酸盐岩在成矿过程中的作用,以往的研究很少深入讨论。近年来,不同研究者对矿集区典型矿床容矿碳酸盐岩进行了系统研究(Zhou et al.,2018b; Luo et al.,2019a,2020; Xiang et al.,2020),结合水/岩相互作用 C-O 同位素组成模拟计算结果,揭示 MVT 铅锌矿床成矿过程中碳酸盐岩发挥了关键作用,主要表现为:①成矿前,碳酸盐岩与成矿流体间的水/岩相互作用,形成了强烈的白云岩化,为成矿准备了岩性、物质和空间等必要条件;②成矿期,碳酸盐矿物溶解-重结晶的循环过程,对金属大量沉淀导致成矿环境(如 pH)的改变起到了缓冲作用,因而形成大量雪花状(方解石/白云石斑点)典型 MVT 铅锌矿床的特征矿石;③成矿后,碳酸盐矿物充填、胶结矿化场所,利于矿石保存,同时成为重要的找矿标志矿物。

(3)成矿流体来源与演化。基于川滇黔铅锌矿集区典型矿床的流体包裹体及 C-H-O-S 同位素组成的研究(Zhou et al.,2014,2018a,2018c; Luo et al.,2019a,2020),对成矿流体性质、来源及演化形成了较为一致的认识:成矿流体具有中-低、中-低盐度特征,成矿物质主要由基底地层提供,成矿流体中的 S 主要来源于赋矿地层中硫酸盐热化学还原作用(TSR)、CO_2 主要来源于碳酸盐岩地层、H_2O 为盆地热卤水,流体混合作用是成矿元素沉淀成矿的重要机制。对流体混合作用成矿机制,主要证据是在矿床流体包裹体中发现流体混合现象(Zhou et al.,2014; Luo et al.,2019a),如多相流体包裹体并存、均一温度存在 2 个(或多个)峰值、盐度存在 2 个(或多个)区间。原位 S 同位素组成结果显示(金中国等,2016; Zhou et al.,2018c; Luo et al., 2019a),单颗粒硫化物中心和边缘 $\delta^{34}S_{CDT}$ 存在很大差异,被认为是高 $\delta^{34}S_{CDT}$ 流体与低 $\delta^{34}S_{CDT}$ 流体混合作用的产物;刘莹莹(2017)的成矿实验也初步证实:本区富铅锌矿床可能为含 Pb、Zn 卤水与富还原硫流体在有利的成矿空间(如断裂带、层间破碎带、溶洞等)相互的混合结果。

5.2.4 区域成矿模型 近年来,通过对川滇黔矿集区代表性矿床的深入剖析,大都建立了矿床成因模式,如金沙厂(Zhou et al.,2015a)、天宝山(何承真等,2016)、那雍枝(金中国等,2017;Zhou et al.,2018c)、银厂沟(Tan et al.,2017)、富乐(Zhou et al.,2018a)、黔西北成矿区(Zhou et al.,2018b)、乌斯河和麻栗坪(罗开,2019)、茂租(Zhang et al.,2019b)等,这些模式都具有以下特征:①矿床或矿体受构造和岩性控制,区域构造为导矿构造、层间破碎带为容矿构造,控矿岩性主要为粗晶白云岩;②成矿物质主要来源于基底地层;③成矿流体中 S 和 CO_2 具有不同来源;④矿体顶部存在"遮挡层"。

黄智龙(2020,未发表资料)对这些成矿模式进行高度概括,建立了区域成矿模型,简述为:印支期印支地块与华南陆块后碰撞伸展作用引发大规模流体运移,大规模运移的流体淋滤基底地层中的成矿元素形成成矿流体,成矿流体沿构造通道向上运移过程中遇"遮挡层"受阻折返沿碳酸盐岩地层层间破碎带等有利空间运移,与富还原硫流体发生混合作用成矿元素沉淀成矿。

6 原位分析技术在矿床研究中的应用

最近十年,随着仪器设备的发展,从更微观尺度更高精度地示踪成矿过程,从本质上揭示成矿机理成为矿床学研究的热点及重要趋势,各种微区原位分析技术迅速发展并被广泛应用,特别是激光剥蚀-电感耦合等离子质谱(LA-ICP-MS)和离子探针(SIMS)分析技术,我国在微区原位定年以及元素-同位素分析方面取得诸多重要进展,极大地促进了成矿理论的发展。

6.1 矿石矿物/副矿物微区原位 U-Pb 定年

成矿时代的原位研究主要集中在含 U 矿物上,一些适用于矿床学定年的含 U 或低 U 矿物定年方法被国内学者率先开发出来并广泛应用,代表性方法有:LA-ICP-MS 锡石(Yuan et al.,2011b;李惠民等,2013;Li et al.,2016b;Zhang et al.,2017a)、黑钨矿(Deng et al.,2019;Luo et al.,2019b;Tang et al.,2020;Yang et al.,2020)、石榴子石(Deng et al.,2017a;Yang et al.,2018)和氟碳铈矿(Yang et al.,2014b,2019c;Ling et al.,2016;涂家润等,2017)U-Pb 定年。国内近年来也建立了磷钇矿(Liu et al,2011;Li et al.,2013)、铌钽铁矿(Che et al.,2015)以及铀矿物(晶质铀矿、沥青铀矿和铀钍矿等)(邹东风等,2011;宗克清等,2015;肖志斌等,2020a,2020b;叶丽娟等,2019)的 LA-ICP-MS U-Pb 定年方法,尽管这些方法国外已较早开展工作。碳酸盐 LA-ICP-MS U-Pb 定年是国际上最近几年发展起来的新方法(Li et al.,2014),国内已有实验室初步建立了相关方法并开展了沉积碳酸盐定年的应用研究(Shen et al.,2019;沈安江等,2019;程婷等,2020)。鉴于碳酸盐在各种热液矿床中普遍存在,其在矿床学领域具有广泛的应用前景。

6.2 同位素组成微区原位分析

矿床学研究中常用的同位素示踪体系包括 H-O-C-S 稳定同位素、Sr-Nd-Pb-Hf-Os 放射性同位素及 He-Ar 稀有气体同位素体系等,这些体系和新的同位素体系微区原位分析方法被不断开发出来,并被应用于精细揭示成矿物质来源及成矿过程研究,代表性的分析方法有 SIMS 或 LA-ICP-MS 硫化物/硫酸盐 S 同位素分析(Zhu et al.,2016;Chen et al.,2017;Fu et al.,2017;Feng et al.,2018;Yuan et al.,2018a),富 Sr(如磷灰石、长石、白钨矿、钙钛矿等)和富 Nd(如独居石、榍石、氟碳铈矿等)矿物 Sr、Nd 同位素分析(Liu et al.,2012;Xu et al.,2015;Huang et al.,2015,2020;Xu and Jiang,2017;Li et al.,2018a;Yang et al.,2019c),硫化物 Pb 和 Os 同位素分析(Hu et al.,2015;Yuan et al.,2015,2018a;Feng et al.,2018;Zhu et al.,2019),石英或硅酸盐 Si 同位素分析(Liu et al.,2019b),碳酸盐 Ca 同位素分析(Zhang et al.,2019d)以及电气石 B 和 Li 同位素分析(Hou et al.,2010;Yang and Jiang,2012;Lin et al.,2019)等。值得一提的是,多种同位素(如 Sr-Nd、S-Pb、Sr-Pb)、同位素与 U-Pb 定年以及同位素与微量元素同时原位分析方法被越来越多地开发出来(Huang et al.,2015,2020;Yuan et al.,2018a),在综合示踪成矿过程、揭示矿床成因方面具有独特优势。此外,在仪器设备方面,一个显著的趋势是纳米离子探针以及飞秒激光被越来越多地应用于同位素微区原位分析(Zhang et al.,2014b;杨蔚等,2015;袁洪林等,2015;杨文武等,2017),纳米离子探针极大地提高了空间分辨率,飞秒激光能有效地减少或消除基体效应。

6.3 单矿物微量元素组成微区原位分析

矿物微量元素可以很好地记录成矿过程及反映物质来源，随着微区原位分析技术的发展，特别是 LA-ICP-MS 方法的应用，其受到越来越多的研究和应用(刘勇胜等，2013)。近十年来，代表性分析方法包括氧化物(如磁铁矿、锡石、白钨矿、黑钨矿和石英等)(张德贤等，2012; 付宇等，2013; 孟郁苗等，2016; 蓝廷广等，2017; Zhang et al.，2018b; Ke et al.，2019; Song et al.，2019)、硫化物(Ding et al.，2011; 袁继海等，2011; Zhu et al.，2016; 范宏瑞等，2018)、硅酸盐(Yuan et al.，2011a; 陈春飞等，2014; 柴发达等，2018; Cao et al.，2018)、碳酸盐矿物(Chen et al.，2011b; Duan et al.，2017; Yang et al.，2019b)和副矿物(如锆石、磷灰石、榍石、金红石、独居石)(He et al.，2016; She et al.，2016; Song et al.，2019)等的 LA-ICP-MS 或 SIMS 微量元素分析，特别是黄铁矿和磁铁矿微量元素，被广泛应用于矿床成因分类、成矿物质来源、精细成矿过程、物理化学条件以及勘探找矿研究(范宏瑞等，2018; Huang et al.，2019; Huang and Beaudoin，2019)。值得一提的是，微量元素 LA-ICP-MS mapping 分析方法(Zhu et al.，2016; 汪方跃等，2017)，结合阴极发光(CL)或背散射图像(BSE)等显微结构研究，可为成矿过程提供更精细的信息，被越来越多的研究者所应用。

6.4 单个流体包裹体组成研究

LA-ICP-MS 分析是目前单个流体包裹体组成(主、微量元素)最主要的分析手段，该方法最初是在20世纪70年代中后期尝试使用 LA-ICP-MS 分析单个流体包裹体组成建立起来的(Tsui and Holland，1979)，随着仪器设备和技术的发展，越来越多的实验室建立了该方法，特别是近年来国内一些实验室建立了相关方法并开展了应用研究(孙小虹等，2013; 蓝廷广等，2017; Li et al.，2018b; Pan et al.，2019b)。我国学者使用国内实验室建立的方法对斑岩或矽卡岩矿床(Lan et al.，2018; Liu et al.，2018a; Chen et al.，2019b)、W-Sn 矿床(Pan et al.，2019b; Yang et al.，2019a)和造山型金矿床(Zhou et al.，2019)等开展了单个流体包裹体组成研究，对这些矿床成因有了新的认识。

7 实验地球化学在矿床研究中的应用

近十年来，我国实验地球化学研究在矿床学中的应用，根据实验技术或方法，主要有包括四个方面的进展: ①利用活塞圆筒开展了高温高压下金属元素(Cu、Mo、Au、Re、W、Nb 和 Ta 等)及挥发分元素(S、F 和 Cl 等)在矿物、熔体和热液之间的分配行为与成矿实验，对这些元素在壳幔相互作用过程中的富集机制提供了有效限定(Xiong et al.，2011; Liu et al.，2014，2015; Ni et al.，2018; Zhang et al.，2018; Feng and Li，2019; Li et al.，2019; Sun et al.，2020); ②通过内加热式高压釜在精确限定氧逸度的基础上，对铁氧化物-磷灰石矿床形成过程中富铁熔体和硅酸盐熔体不混溶作用、基性岩岩浆源区以及铁钛氧化物温度-氧逸度计的使用条件等方面进行了研究(Hou et al.，2017，2018，2021); ③水热高压釜中金属元素在水溶液中溶解度实验法，如 Cu 在气相中的溶解迁移实验(Shang et al.，2007)，W、Mo 等在水盐溶液体系及含 F 盐水溶液中溶解形式及溶解度的实验(Wang et al.，2019b，2021; Shang et al.，2020); ④原位激光拉曼观测技术，一方面以毛细石英管技术为代表，研究温度范围为 -196 ~ 500 ℃，压力 100 ~ 100000 kPa。该方法主要应用于水盐体系中，成矿过程氧逸度条件模拟(Shang et al.，2009)、硫酸盐热化学反应(TSR)观测(Yuan et al.，2013)、硫酸盐液相不混溶(Wang et al.，2013，2016b; Wan et al.，2017)、有机烃类氧化还原反应观测(Qiu et al.，2020)和成矿元素 W 在水盐体系中溶解形式研究(Wang et al.，2020b)等; 另一方面以热液金刚石压腔技术为代表，该技术具有极宽的研究温度和压力范围(-196 ~1 000 ℃和 100 ~ 4×10^6 kPa)，主要应用于含碳酸盐碱性熔体中金属元素 W 熔解形式研究(Li et al.，2018d)、水溶液中硫酸盐溶解控制条件及其对稀土元素溶解度的影响等研究(Cui et al.，2020b)。

8 结语

综上所述，我国的矿床地球化学研究立足中国大陆成矿特色，近年来取得了较多重要进展和创新成果。但是，矿床地球化学是一门理论性和实践性很强的交叉学科，且研究对象涉及极其复杂的地球各圈层起源和相互作用，我国的相关研究要总体进入国际领跑水平依然任重道远。未来的研究需要重点关注(但不限于)以下几个方面的工作。

(1) 大型-超大型矿床和大型矿集区的形成往往与地球的核-幔-壳分异及壳幔相互作用有关。查明核-幔-壳分异和层圈相互作用对金属元素初始富集、有效迁移和巨量聚集形成不同类型矿床的机理仍是矿床地球化学需要解决的重大科学问题。我国矿产资源类型的极不均匀分布很可能与此密

切相关。

(2) 精细化、定量化描述是矿床地球化学学科发展的必然趋势。在详细的矿床地质特征和控矿因素研究基础上,依据原位微量元素-同位素组成,综合应用实验模拟和数学模拟的方法精细刻画成矿作用的地球化学和热力学过程,将为深入揭示岩浆起源-演化和流体-岩石相互作用机理、元素迁移及沉淀机制,全面理解成矿作用本质开辟新的重要途径。

(3) 战略性新兴产业的蓬勃发展对新兴关键矿产(稀有、稀散、稀土、稀贵金属)需求急剧增大。目前对新兴关键矿产资源的元素行为、赋存状态、形成与分布规律、超常富集机理等基本规律的认识还很不够,制约了成矿远景区的预测和勘查突破。开展关键金属成矿背景、富集机制、控矿因素组合及勘查评价方法体系的研究是突破找矿瓶颈、保障资源安全的重要途径。

(4) 深部找矿勘查是国际矿床学和勘查学界的重大前沿领域。揭示岩石圈结构和组成对矿集区分布的控制,建立隐伏矿床的地球化学异常模式和深穿透地球化学与矿物地球化学探测技术,对于突破探矿技术瓶颈、提升隐伏矿的探测能力将起到至关重要的推动作用。

(5) 矿床类型和特征的多样性、区域差异性和空间不均一性要求矿床地球化学研究必须具有全球视野。我国以往的研究较少针对国外矿床和重点成矿区带。要实现成矿理论和模式的系统创新,产生具有国际影响力的原创性研究成果,系统的国际对比及全方位的国际合作势在必行。

(6) 外太空蕴藏的特殊矿产资源是人类将来可能开发利用的重要资源储库。近地小行星是近期太空探索与资源开发利用最有价值的目标之一,相关资源的研究、探测和评价将是地球科学的新兴前沿研究方向。揭示行星形成演化与元素聚集机理,查明地外矿产资源的分布、储量并建立相应评价标准,是我国矿床地球化学研究亟待开拓的新领域。

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