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中国斑岩铜(钼)矿床中辉钼矿 Re 含量变化及控制因素*

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摘 要 铼作为战略性关键金属之一,越来越受到人们的关注。Re 主要以类质同象的形式赋存在辉钼矿中,然而,不同成因、不同类型矿床的辉钼矿中 Re 含量差异较大。在钨、锡矿床中 Re 含量较低,在斑岩型铜(钼)矿床中 Re 含量较高,后者是全球 Re 资源的主要载体。前人对于辉钼矿中 Re 元素的研究主要基于 Re-Os 同位素年代学,而对于不同区域、不同时代、不同类型斑岩型铜矿床中辉钼矿 Re 含量的变化规律及其控制因素的研究较少。文章通过汇总前人发表的斑岩型铜(钼)矿床的 Re-Os 同位素数据,从含矿斑岩的 Sr、Nd、Hf 等数据与辉钼矿中平均 Re 含量的关系等角度,探讨了其变化规律及控制因素。结果表明:中国斑岩型铜(钼)中 Re 含量随着成矿物质从地幔到地壳,依次减少;成矿流体的氧逸度、辉钼矿的产状、与其伴生的硫化物种类及不同的成矿阶段等因素共同控制了辉钼矿中 Re 的含量。

关键词 地球化学;斑岩型矿床;辉钼矿;Re 含量;成矿带;物质来源

中图分类号:P618.41;P618.65;P597 **文献标志码**:A

Variations and controlling factors of Re content of molybdenite in porphyry Cu (Mo) deposits of China

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Abstract

Re (rhenium), as one of the key strategic metals, has attracted more and more attention among researchers. Re occurs mainly in molybdenite in the form of isomorph. However, Re content in molybdenite varies with different geneses and types of deposits. Re content in tungsten and tin deposits is relatively low, while that in porphyry copper (molybdenum) deposits is relatively high, which serve as the main carrier of Re resources in the world. Previous studies of Re in molybdenite have been mainly based on Re-Os isotope chronology, but the studies of the variation rules and controlling factors of Re content in molybdenite of porphyry copper deposits in different regions, ages and types have been very insufficient. In this study, by collecting the available Re-Os isotope data of porphyry copper (copper-molybdenum) deposits, the relationship between Sr-Nd-Hf of ore-bearing rocks and

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the average Re content in molybdenite was investigated. The results show that the Re content in porphyry copper (copper-molybdenum) deposits in China decreases with the change of metallogenic material from the mantle to the crust. Re content in molybdenite is controlled by oxygen fugacity of ore-forming fluid, the modes of occurrence of molybdenite, the types of sulfides associated with molybdenite, different metallogenic stages and other factors.

Key words: geochemistry, porphyry deposit, molybdenite, Re content, metallogenic belt, material source

斑岩型铜矿主要分布在环太平洋、特提斯-喜马拉雅、古亚洲(中亚成矿带)3 个全球性成矿域(Yang et al., 2019;王瑞等,2020)。斑岩型铜矿床约占所有类型铜矿的 42%(Chen et al., 2013),提供了世界上近 75% 的 Cu、50% 的 Mo 和 20% 的 Au(Sillitoe, 2010; Sun et al., 2015)。另外,还包括一些关键金属,如铼(Re)、硒(Se)和碲(Te)等在一些斑岩型铜矿床中富集。虽然在一些斑岩型矿床中 Re 平均品位较低(通常 w(Re) < 10 μg/g),但储量较大,约 80% 的 Re 都来自于斑岩型矿床。Re 主要以类质同象形式取代 Mo 进入辉钼矿晶格中(Stein et al., 2001; 2003; 李超等,2011)。然而,不同矿床辉钼矿中的 Re 含量差异较大,在钨锡矿床中的辉钼矿 Re 含量较低,而在斑岩型铜(钼)矿床中的辉钼矿 Re 含量相对较高,是 Re 资源的主要载体。前人对于辉钼矿 Re-Os 同位素分析主要集中于成矿年代学研究(唐菊兴等,2009;Leng et al., 2013; Zhu et al., 2015),而关于辉钼矿微量元素含量的研究相对较少,特别是对于不同区域、不同时代、不同类型斑岩型铜矿床中辉钼矿 Re 含量的变化规律以及控制因素研究更少。

本文以中国斑岩型铜(钼)矿床为研究对象(图 1),收集了前人发表的中国冈底斯成矿带、玉龙成矿带、多龙成矿带、中甸成矿带、哀牢山成矿带、中亚成矿带、中条山成矿带、长江中下游成矿带、东南沿海带及其他一些成矿带的斑岩型铜(钼)矿中辉钼矿 Re-Os 同位素数据及含矿斑岩的 Sr、Nd 和 Hf 同位素数据(陈超等,2013;戴盼等,2018;高一鸣等,2012;高永宝等,2015;Hou et al., 2013; 贾丽琼等,2013;2015;郎兴海等,2010;冷成彪等,2007;冷秋锋等,2015;2016;李光明等,2005;2006;吕博等,2014;孟祥金等,2003a;2003b;芮宗瑶等,2002;孙燕等,2013;唐菊兴等,2009a;2010;王召林等,2008;吴云辉等,2013;辛洪波等,2009;杨志明等,2011;赵一鸣等,1997;赵元艺等,2009;曾普胜等,2004;2012;朱明田等,2010;祝向平等,2015a;2015b),探讨了辉钼矿中 Re 的分布行为及控制因素。

1 Re 含量变化规律及控制因素

关于中国斑岩型铜矿床的岩浆源区存在多种观点。有些研究者认为,含矿斑岩主要来自于加厚下地壳的部分熔融(Zhang et al., 2001; Hou et al., 2003; 2019; Wang et al., 2018)。而对于大陆环境,侯增谦等(2007)认为直接起源于古老下地壳的长英质岩浆一般不能形成斑岩型铜矿床,而含矿斑岩的岩浆源区主要为加厚的新生镁铁质下地壳或拆沉的古老下地壳与地幔物质的混合。铼在大陆地壳中的丰度为 w(Re) 0.18~2 ng/g, 平均为 0.4 ng/g(Taylor et al., 1995)。据估算,斑岩型铜(钼)矿床中 Re 的品位一般在 0.03~ 0.n g/t 之间(Millensifer et al., 2013)。斑岩型铜(钼)矿床中的 Re 大多数以类质同象的形式取代 Mo 进入辉钼矿(Stein et al., 2003; 李超等,2011)晶格中,w(Re)从<10 μg/g 到几万 μg/g 不等。相比之下,斑岩型钼矿尽管 Mo 的品位很高,但辉钼矿的 Re 含量通常较低(多数 w(Re)≤100 μg/g)。

Sr、Nd 以及 Hf 同位素具有重要的示踪意义,在矿床地质研究中常用于示踪成矿物质来源、含矿流体、深源熔体的壳幔混染作用(Tatsumoto et al., 1992; Zhang et al., 2002; Yang et al., 2006; Wang et al., 2018)。

统计结果显示(图 2a),中国斑岩型铜矿含矿斑岩的初始 Sr 同位素比值在 0.703~0.718 之间,说明成矿物质有地幔来源,也有壳幔混合源。$^{87}Sr/^{86}Sr$ 初始值与辉钼矿中 Re 的平均含量呈负相关,表明地壳物质大量参与斑岩型矿床的形成,不利于 Re 在辉钼矿中富集。由图 2b 可知,Re 含量随着 $\varepsilon_{Nd}(t)$ 变大,有增高的趋势,说明中国斑岩型铜矿的成矿物质来自于地幔,形成的辉钼矿中 Re 含量较高。在岩浆演化过程中,$\varepsilon_{Hf}(t)$ 示踪成矿物质来源类似于 $\varepsilon_{Nd}(t)$。由图 2c 可知,中国斑岩型矿床的成矿物质来源于地幔,则形成的辉钼矿 w(Re)较高,常大于 100 μg/g。随着 $\varepsilon_{Hf}(t)$ 增加,辉钼矿中 Re 含量有增加的趋势,说

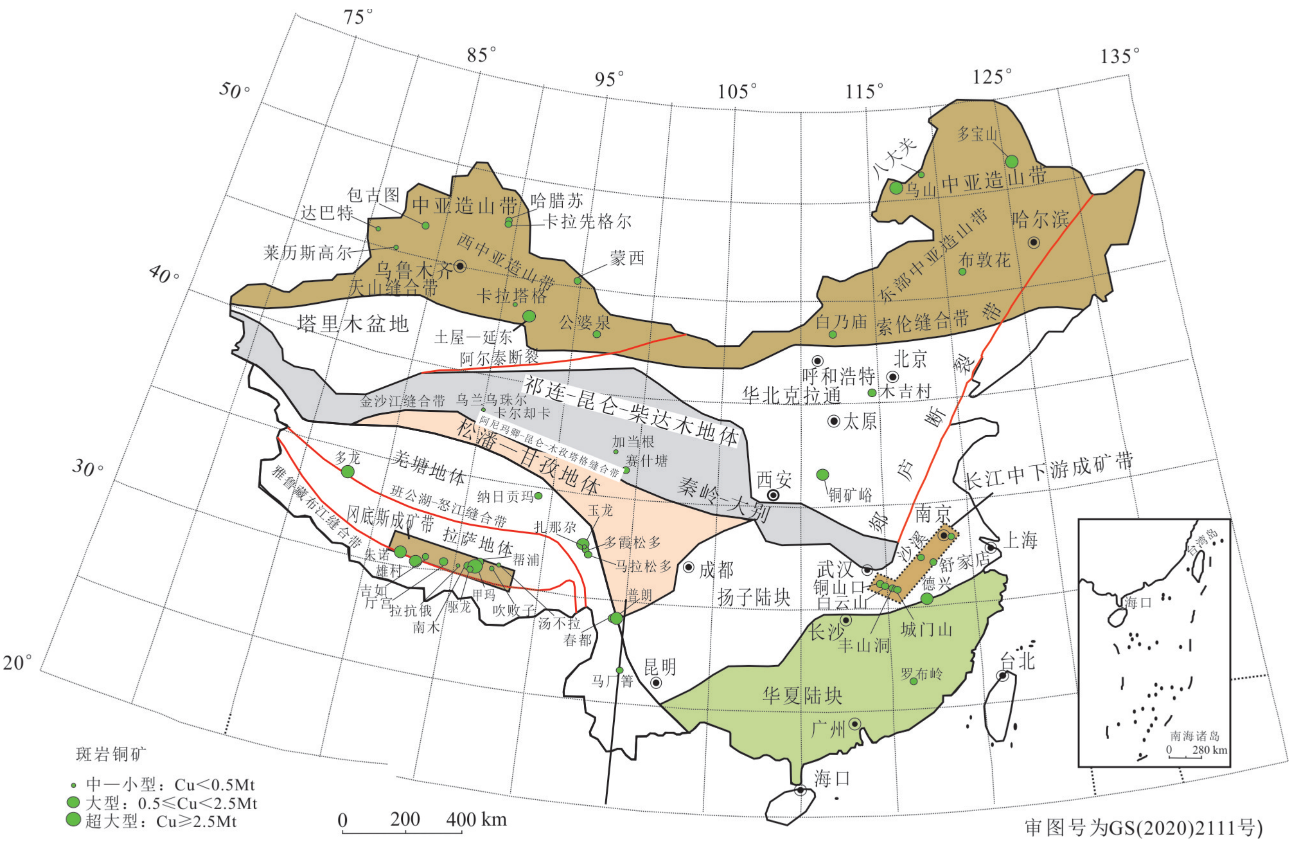

图1　中国斑岩型铜矿的分布(据 Yang et al., 2019；杨志明等，2020修改)

Fig. 1　Distribution of porphyry copper deposits in China (modified after Yang et al., 2019; Yang et al., 2020)

明随着地幔超镁铁-镁铁质熔体的不断分异演化，有利于Re的迁移和富集。Sr、Nd、Hf同位素统计结果表明，中国斑岩铜(钼)矿床的成矿物质有壳源、幔源和壳幔混合源3种，当成矿主体来源于地幔时，辉钼矿中Re含量最高，壳幔混合源次之，壳源含量最低。

如图3a所示，中国斑岩型铜(钼)矿床中辉钼矿平均Re含量与斑岩型铜(钼)矿中Cu的储量呈一定的正相关性。由图3b可知，含矿斑岩的Cu/Mo与斑岩体中辉钼矿的Re含量整体上呈正相关，说明Re和Mo的来源可能一致。矿床Re储量与Cu、Mo储量呈正相关(图3c、3d)，表明地幔物质大量参与斑岩型矿床的形成，有利于Re在辉钼矿中富集。据图3e，Cu与Mo储量没有相关性，可能反映了Cu与Mo的来源有差异。

图4表明，中国斑岩型铜(钼)矿床主要形成于新近纪、古近纪、白垩纪、侏罗纪、三叠纪、泥盆纪、志留纪、奥陶纪和寒武纪。其中，白垩纪、侏罗纪和三叠纪形成的斑岩矿床中辉钼矿Re平均含量最高，泥盆纪和志留纪次之，新近纪、古近纪、奥陶纪和寒武纪最低。据统计，二叠纪和志留纪目前没有发现斑岩型矿床，这可能与局部区域在这一时期没有发生大的地质构造作用有关，说明不同的地质构造背景可能会影响辉钼矿中的Re含量。

2　讨　论

2.1　成矿物质来源

Mao等(1999)研究表明：成矿岩浆来源于地幔形成的辉钼矿Re含量高于壳源和混合来源的辉钼矿。Stein等(2001)同样认为地幔的底侵或交代作用、基性和超基性岩的熔融，形成的辉钼矿Re含量要高于壳源。在板块俯冲过程，随着洋壳向深处运移，由于大洋沉积物、海水等组分的加入，使得地幔楔发生部分熔融。Sun等(2003；2004)研究表明，在岛弧环境中，地幔楔Re的富集实际上是在板块俯冲过程中加入的。Sun等(2004)证实了Re在俯冲带流体中是活动的，并且在俯冲板块脱水释放流体的同

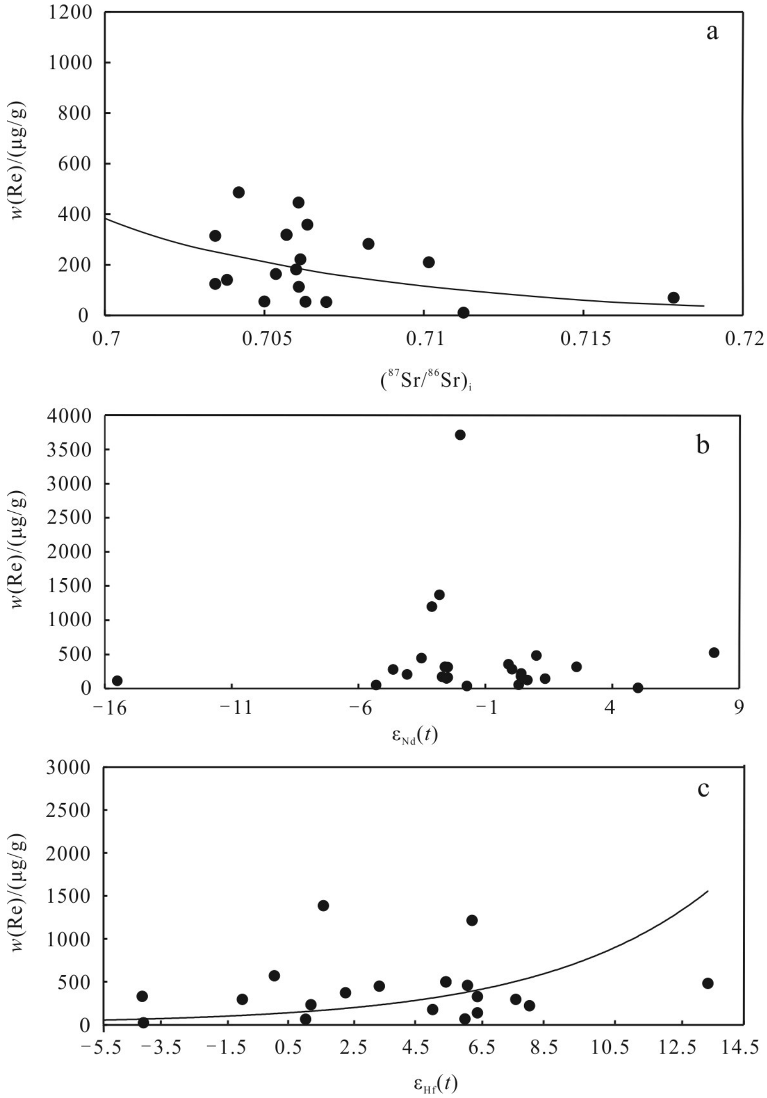

图2　含矿岩体的初始 $^{87}Sr/^{86}Sr$ (a)、$\varepsilon_{Nd}(t)$ (b)、$\varepsilon_{Hf}(t)$ (c)与辉钼矿中平均Re含量关系图解

图中数据来源：Guo et al., 2012; Huang et al., 1996; Huang et al., 2017; Leng et al., 2012; Li et al., 2005; Meng et al., 2003b; Wang et al., 2016; 陈超等，2013；陈华安等，2013；戴盼等，2018；高旭等，2018；高一鸣等，2012；高永宝等，2015；郭保健等，2006；郭周平等，2015；郝金华等，2012；何书跃等，2009；和文言等，2013；侯增谦等，2003；黄勇等，2015；贾丽琼等，2013，2015；康永建等，2014；冷成彪等，2007；冷秋锋等，2015; 2016；李利等，2018；梁清玲等，2012；林涛等，2017；吕博等，2014；屈迅等，2009；曲凯等，2014；任江波等，2011；任涛等，2014；佘宏全等，2009；孙燕等，2013；唐菊兴等，2009；王保弟等，2010；王世伟等，2012; 2014；吴良士等，1997；吴伟中等，2013；吴云辉等，2013；肖兵等，2017；谢桂青等，2006；薛春纪等，2011；杨富全等，2012；杨贵才等，2014；杨震等，2017；杨志明等，2011；袁顺达等，2013；张达玉等，2010；张刚阳等，2008；张连昌等，2013；张涛等，2015；张玉泉等，1998；张志欣等，2009；张作衡等，2006；赵晓燕等，2017；赵一鸣等，1997；赵元艺等，2009；赵云等，2013；郑有业等，2004；2007；朱明田等，2010；祝向平等，2011; 2015a

Fig. 2　Correlation diagram of $^{87}Sr/^{86}Sr$(a), $\varepsilon_{Nd}(t)$ (b), $\varepsilon_{Hf}(t)$ (c) in ore-bearing porphyry and average Re content in molybdenite

The data source: Guo et al., 2012; Huang et al., 1996; Huang et al., 2017; Leng et al., 2012; Li et al., 2005; Meng et al., 2003b; Wang et al., 2016; Chen C et al., 2013; Chen H A et al., 2013; Dai et al., 2018; Gao X et al., 2018; Gao Y M et al., 2012; Gao et al., 2015; Guo B et al., 2006; Guo et al., 2015; Hao et al., 2012; He S et al., 2009; He W et al., 2013; Hou et al., 2003; Huang et al., 2015; Jia et al., 2013, 2015; Kang et al., 2014; Leng C et al., 2007; Leng Q et al., 2015; 2016; Li et al., 2018; Liang et al., 2012; Lin et al., 2017; Lv et al., 2014; Qu X et al., 2009; Qu K et al., 2014; Ren J et al., 2011; Ren T et al., 2014; She et al., 2009; Sun et al., 2013; Tang et al., 2009; Wang B et al., 2010; Wang S et al., 2012; 2014; Wu L et al., 1997; Wu W Z et al., 2013; Wu Y H et al., 2013; Xiao et al., 2017; Xie et al., 2006; Xue et al., 2011; Yang F et al., 2012; Yang G et al., 2014; Yang Z et al., 2017; Yang Z M et al., 2011; Yuan et al., 2013; Zhang D et al., 2010; Zhang G et al., 2008; Zhang L et al., 2013; Zhang T et al., 2015; Zhang Y et al., 1998; Zhang Z et al., 2009; Zhang Z H et al., 2006; Zhao X et al., 2017; Zhao Y M et al., 1997; Zhao Y Y et al., 2009; Zhao Y et al., 2013; Zheng et al., 2004; 2007; Zhu et al., 2010; Zhu X P et al., 2011; 2015a

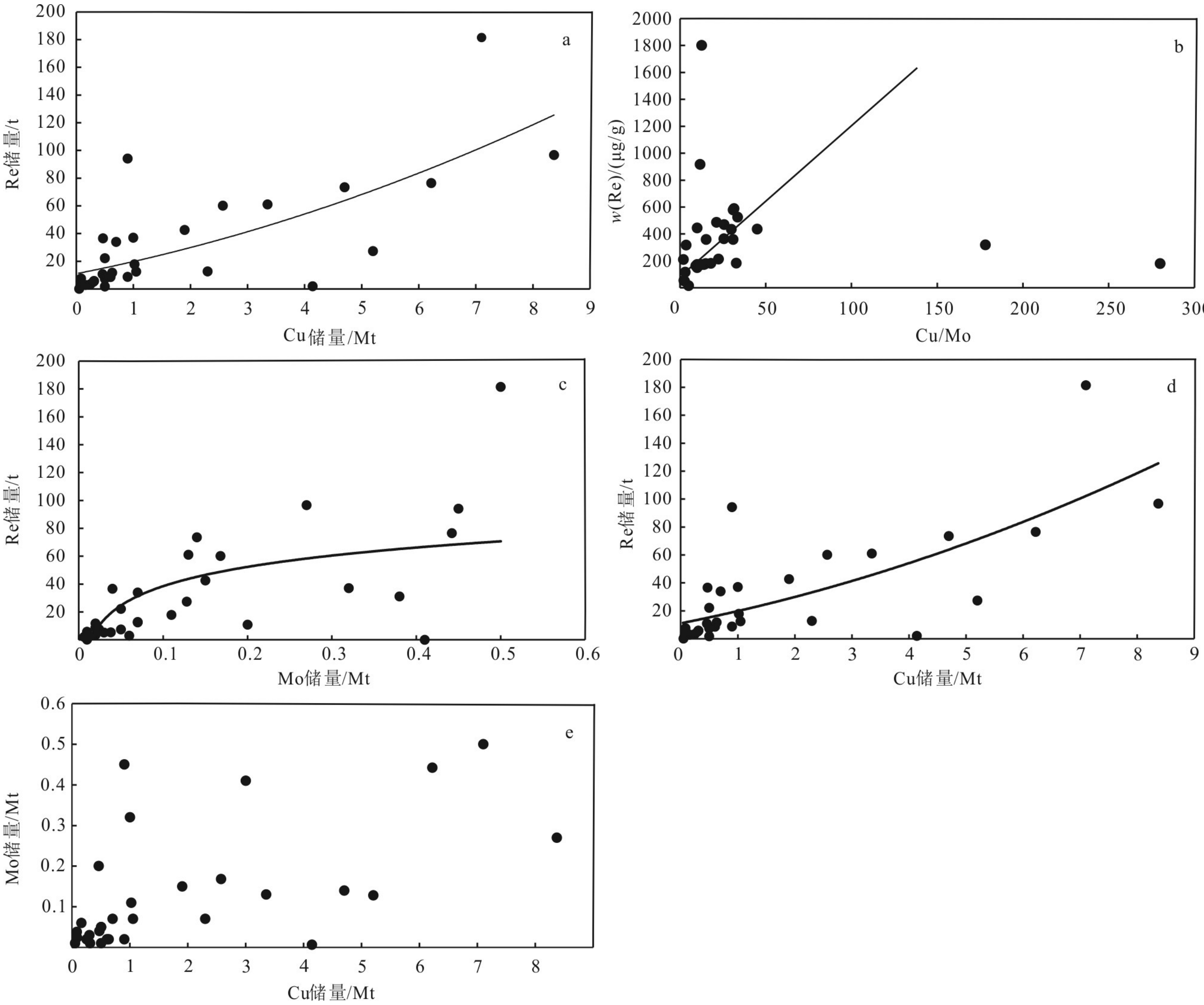

图3 Cu储量与Re储量(a)、Cu/Mo与辉钼矿Re含量(b)、Mo储量与Re储量(c)、Cu储量与Re储量(d)及Cu储量与Mo储量(e)图解

数据来源:高一鸣等,2012;侯增谦等,2003;黄勇等,2015;贾丽琼等,2015;康永建等,2014;Leng et al., 2013; 冷秋锋等,2015;李光明等,2005, 2006;Li et al., 2015; 孟祥金等,2003a; 2003b;Ouyang et al., 2014; 屈迅等,2009;芮宗瑶等,2002;王保弟等,2010;王立本等,1997;王世伟等, 2012; 2014;吴良士等,1997;谢桂青等,2006;Xie et al., 2007; 杨富全等,2012;杨贵才等,2014;Zhang et al., 2015; 张刚阳等,2008;张志欣等, 2009;赵冰爽,2018;赵一鸣等,1997;赵云等,2013;Zhao et al., 2014; 郑有业等,2004;周雄等,2013;朱明田等,2010

Fig. 3 The diagrams of Re reserves versus Cu reserves(a), Cu/Mo versus Re content in molybdenite(b), Mo reserves versus Re reserves(c), Cu reserves versus Re reserves(d) and Cu reserves versus Mo reserves(e)

The data source: Gao et al., 2012; Hou et al., 2003; Huang et al., 2015; Jia et al., 2015; Kang et al., 2014; Leng et al., 2013; Leng Q et al., 2015; Li G et al., 2005; 2006; Li et al., 2015; Meng et al., 2003a, 2003b; Ouyang et al., 2014; Qu et al., 2009; Rui et al., 2002; Wang B et al., 2010; Wang L et al., 1997; Wang S et al., 2012; 2014; Wu et al., 1997; Xie G et al., 2006, 2007; Yang F et al., 2012; Yang G et al., 2014; Zhang et al., 2015; Zhang G et al., 2008; Zhang Z et al.,2009; Zhao B et al.,2018; Zhao Y M et al., 1997; Zhao Y et al., 2013; Zhao et al., 2014; Zheng et al., 2004; Zhou et al., 2013; Zhu et al., 2010

时得到了富集。

富有机质黑色岩系为斑岩型铜矿(钼)的形成提供了一部分还原性物质(Rowins, 2000; Wilkinson, 2013; Richards et al., 2017; Shen et al., 2017)和少量的金属元素Cu、Mo等。黑色页岩等富有机质沉积岩中富含Re,如黑海和日本海黑色页岩的w(Re)分别为43 ng/g和12 ng/g(Crusius et al., 1996);挪威的黑色页岩w(Re) > 20 ng/g(Lipinski et al., 2003),而大

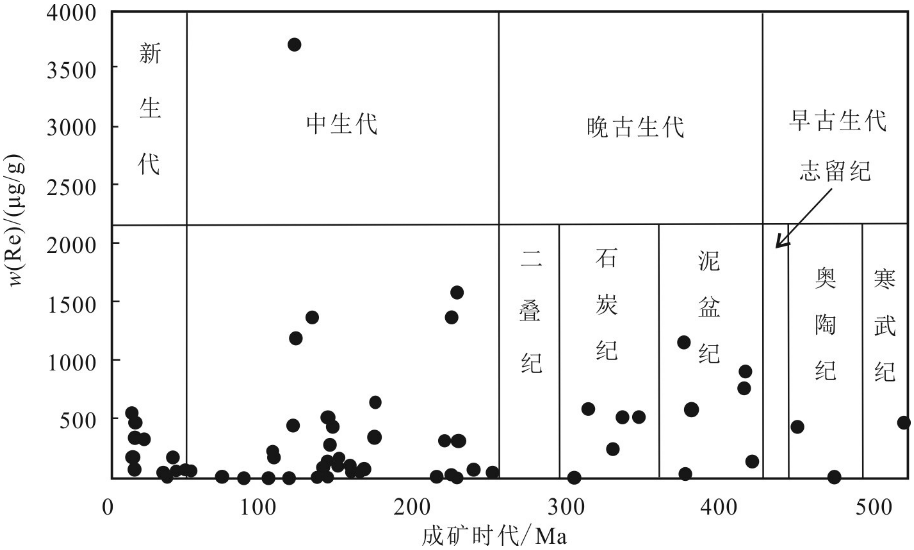

图4 不同时代矿床中Re含量变化图解

Fig. 4 Diagram of Re content changes in ore deposits of different ages

陆上地壳的w(Re)仅为2 ng/g (Sun et al., 2003)。黑色岩系作为Re的赋存迁移载体之一，很可能是斑岩型铜矿中Re的物质来源之一。

因此，成矿物质来源于地幔，如果在后期成矿过程有少量富有机质黑色岩系参与，会使得矿床中辉钼矿的Re含量增高。

2.2 Cu和Mo储量

由图3c可知，Mo在矿床中储量越高，其主要载体辉钼矿在矿体中所占比例就越多，则Re在矿体中就越分散。因此，所测单颗辉钼矿样品中Re含量就相对越低。Cu通常与Cl^-或SO_4^{2-}等结合成络合物在流体中迁移(Pokrovski et al., 2005; Berry et al., 2009; Webster et al., 2011)，Mo在流体中会与O、Cl^-等结合形成络合物(Ulrich et al., 2008)而稳定存在，Mo在流体中的稳定性主要受流体温度压力变化的影响(Klemm et al., 2008)，表明成矿温度可能是影响辉钼矿中Re含量的另一个关键因素(Berzina et al., 2005)。

Re主要赋存于辉钼矿中，Mo常与硫结合生成辉钼矿(MoS_2)，在辉钼矿大量结晶阶段，成矿岩浆或热液中赋存迁移的Re尽可能多的进入到辉钼矿晶格。在一定范围内(Mo储量约0.03 Mt)，随着矿床Mo储量的持续增加，Re储量急剧增加，这可能说明在这一阶段流体中的Re大规模进入辉钼矿晶格，使得矿体中Re储量明显增高。当超出此范围时，随着Mo储量的持续升高，矿体Re储量增加缓慢。说明在辉钼矿大量的结晶阶段，流体的氧逸度、温度和组分等发生变化，一些硫化物(黄铁矿、黄铜矿等)开始结晶，消耗残余流体中少量的Re，使得进入辉钼矿晶体中的Re减少。矿床中Mo储量与Cu储量没有明显的相关性(图3e)，可能反映了中国斑岩型铜(钼)矿床的Mo与Cu的来源存在差异，或者说明成矿物质在上升过程通过与围岩相互作用等，改变了含矿熔体的性质，促使Cu与Mo体系解耦。结合图3，可能说明金属Re不是单一的来源，有多个端员的贡献。

2.3 氧逸度

含辉钼矿较少的斑岩型Cu-Mo(Cu-Au或Cu-Mo-Au)体系中，辉钼矿Re含量通常较高，而辉钼矿含量较高的斑岩型Mo矿床中(如：Climax型钼矿)，Re在辉钼矿中的含量则相对较低。相比之下，斑岩型W-Mo(Mo-W)矿床中辉钼矿Re含量最低。Zhong等(2017)认为这主要与偏还原性的成矿流体有关，偏还原性的岩浆不利于Re在辉钼矿中富集，可能由以下几种因素控制：① Re具有亲硫(铜)的地球化学性质，在偏还原环境中，Re常与S^{2-}结合形成ReS_2而沉淀。因此，含还原性硫较多的岩浆或熔体不利于Re的迁移；② 相比于硅酸盐岩浆，Re更倾向于进入硫化物(Righter et al., 1998)；③ 在源区偏还原或还原环境下，还原性的硫很容易在硅酸盐体系达到饱和，而残留在岩浆源区，随岩浆迁移的S和Re含量较少，导致后期成矿过程进入辉钼矿中的Re含

量偏少。Sun 等(2013)研究表明:氧化性Fe^{3+}在后期斑岩型矿床形成时具有重要意义,而还原性的岩浆或熔体,Fe^{3+}通常含量较少,同样不利于Re在后期进入辉钼矿晶格。而斑岩型Cu-Mo-Au矿床,氧逸度相对高,S主要以SO_4^{2-}等形式出现,有利于Re进入硅酸盐岩浆。驱龙斑岩型Cu-Mo矿床是中国目前发现的最大的斑岩型矿床,含矿斑岩体中含有大量的岩浆成因石膏,说明此矿床的初始成矿岩浆或热液成矿系统具有较高的氧逸度(Yang et al., 2009; Wang et al., 2014)。

尽管地球的氧逸度在不同时期有一定的波动,但整体上呈上升趋势。可能反映了随着大气氧逸度的增加,对一些较为富集Re的矿物(辉钼矿、黄铁矿、黑色页岩及沥青等)剥蚀加剧,增大了大陆对成矿体系的补给量。Golden 等(2013)表明,在3.0 Ga以来,近地表的氧逸度逐渐增加,有利于Re在其中迁移富集,这可能说明岩浆的氧逸度在一定程度上影响了斑岩型铜(钼)矿床中辉钼矿的Re含量。

2.4　成矿时代

统计结果显示,在515 Ma以前,很少发现中国典型斑岩型铜矿(图4),这可能与新元古代(750~542 Ma)时期的全球性氧化事件(Reinhard et al., 2017)有关,或在这一时期内地层受到强烈的构造挤压,使得地层抬升剥蚀加剧。而斑岩矿床是一个浅成系统,使得早期形成的斑岩型矿体部分被剥蚀。Reinhard等(2017)也提出,新元古代出现过全球性大氧化事件。这一时期,相对富集Mo和Re的黑色页岩大量出现,黑色页岩等富集Re的矿物在板块俯冲环境下熔融,使得Re在局部发生富集作用。这些富含Re的岩浆或熔体在后期地质作用下参与了斑岩型铜(钼)矿床的形成,则辉钼矿中Re含量较高。李聪颖等(2020)认为,在500 Ma以前没有形成斑岩型Mo矿,也与这一时期的氧化事件有关联。揭示了岩浆缺氧在一定程度上影响了斑岩型铜矿中Re的含量。

总体来说,矿床形成时代越老,其辉钼矿中Re含量越低,Re属于变价元素,对氧化还原环境较为敏感。不同时代辉钼矿Re含量的变化可能由成矿系统的氧逸度控制。

2.5　不同区域成矿带

中国的斑岩型铜(钼)矿主要分布在冈底斯成矿带、中亚成矿带和长江中下游成矿带。本文主要探讨冈底斯、中亚和长江中下游3个成矿带的斑岩型矿床中辉钼矿平均Re含量的变化规律及其控制因素。

选取冈底斯成矿带中驱龙、朱诺、吉如、冲江、岗江、厅宫、南木、达布、帮浦、拉抗俄、尕尔穷、冲木达、汤不拉和沙让斑岩型矿床,来揭示这一成矿区辉钼矿中Re含量的变化及其控制因素。统计结果如图5所示,在冈底斯成矿带,多数矿床形成于新生代,少量形成于中生代。其中,新近纪形成的斑岩矿床,辉钼矿平均Re含量变化较大(最高的拉抗俄矿床中w(Re)为558 μg/g,最低的沙让矿床中辉钼矿w(Re)为54 μg/g),且多数含量较为集中。

张泽明等(2019)和Zhu等(2017a)研究表明,冈底斯成矿带的岩浆作用是幕式的,具有3个明显的峰期:晚白垩世(95~90 Ma)、早始新世(52~ 48 Ma)和早-中中新世(18~14 Ma),第二个峰期为大陆碰撞阶段(即65~48 Ma)。冈底斯成矿带斑岩型矿床主要形成于21~12 Ma,属于后碰撞阶段,此阶段大量的中酸性岩(如二长花岗斑岩、二长斑岩、英安岩和流纹岩等)形成,伴随少量的基性岩。这些具有埃达克质岩地球化学特征的中酸性岩石被认为是冈底斯弧新生的加厚下地壳部分熔融产物(Zhang et al., 2015; Yang et al., 2016a; Zeng et al., 2017)。但也有部分研究者认为这些具有埃达克质岩地球化学特征

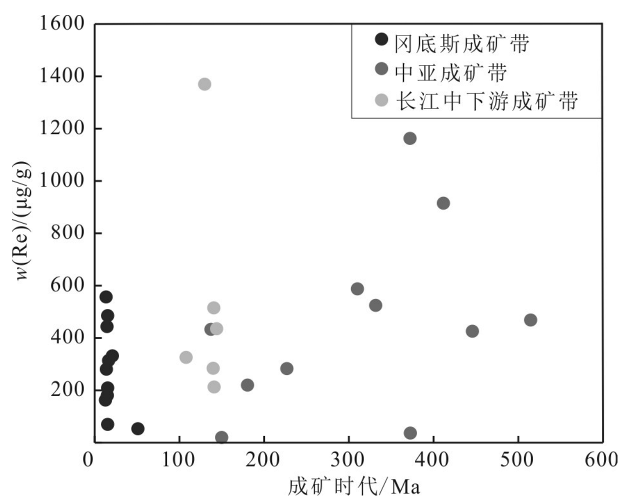

图5　冈底斯成矿带、中亚成矿带、长江中下游成矿带不同时代辉钼矿Re含量变化图解

Fig. 5　Correlation diagram of the Gangdise metallogenic belt, the Central Asian metallogenic belt and the Middle and Lower Yangtze River metallogenic belt with the changes of Re content in molybdenite of different ages

的岩石来源于俯冲板块熔体交代地幔楔(Qu et al., 2004),或幔源超钾质岩浆与壳源岩浆的混合产物(Yang et al., 2015; Wang et al., 2015;2016),表明冈底斯成矿带中大量斑岩型铜(钼)矿床形成于大陆后碰撞阶段,形成的辉钼矿以Re平均含量高、变化大且成矿期较为集中为特点。

中亚成矿带在中国主要包括新疆、甘肃北部和内蒙等地区,此矿带内发育有多处大型和超大型的斑岩型铜(钼)矿床。本次研究选取土屋-延东、包古图、蒙西云影山、白乃庙、莱历斯高尔、卡拉塔格、玉勒肯哈腊苏、多宝山、乌奴格吐山、布敦花和八大关等斑岩矿床,来探讨中亚成矿带斑岩型矿床中辉钼矿Re含量的变化规律及其控制因素。如图4所示,中亚成矿域斑岩型矿床的成矿期主要有早古生代、晚古生代、中生代和新生代。其中,二叠纪和志留纪没有形成储量较大的斑岩型矿床。而泥盆纪斑岩型矿床的辉钼矿中Re含量最高且差异较大,石炭纪、奥陶纪和寒武纪次之,中生代含量最少。另外,此成矿带斑岩型矿床的成矿高峰期为泥盆纪和石炭纪。中亚成矿域斑岩铜(钼)矿床的成矿构造地质背景主要为岛弧环境(朱永峰等,2007;申萍等,2015)。随着冈瓦那大陆的裂解,板块碎片逐渐形成了多数前寒武纪地质单元,然后漂过古亚洲洋,与东欧和西伯利亚板块拼合形成了中亚造山带。朱永峰等(2007)认为,中亚成矿域是由古特提斯洋俯冲消减造成的。从奥陶纪晚期到早二叠世,西伯利亚板块发生顺时针旋转,期间引起多期岩浆活动。加里东构造作用使得区域内大部分地区在晚古生代经受了不同的隆起和剥蚀,二叠纪时期大量地层处于抬升,造成中亚成矿带在这一时期没有斑岩型矿床的形成。结合图5,说明中亚成矿带内斑岩型铜(钼)矿床的成矿期较为分散,辉钼矿中Re含量差异大。

长江中下游成矿带作为为中国东部重要的斑岩型成矿带,其内有多个重要的斑岩型矿床,如:城门山铜-钼矿床、丰山洞铜-金矿床、沙溪铜-金矿床、铜山口铜-钼矿床、舒家店铜矿床、安基山铜矿床、马头钼-铜矿床和宝山铜多金属矿床。本次选取以上矿床来探讨本区域辉钼矿中Re的特征。统计结果如图5所示,长江中下游成矿带斑岩型铜矿主要形成于白垩纪,由燕山期陆内造山作用主导。各矿体间Re含量差异较大。周涛发等(2016)认为,该区域内与斑岩型矿床有关的岩浆活动主要发生于149~108 Ma,可以进一步分为早期(149~134 Ma)、中期(133~130 Ma)和晚期(120~108 Ma)三个阶段。其中,早期和晚期以斑岩-矽卡岩型矿化为主,中期以斑岩型矿化为主。常印佛等(2019)对长江中下游成矿带研究发现,本区自中侏罗世开始,由古太平洋板块向华南板块之下俯冲,使得该区域发生强烈的陆内造山运动,同时受华北板块和大别地块的影响,造成长江中下游成矿带内地层严重变形,岩石圈加厚。早白垩世开始,受太平洋板块俯冲的影响,导致岩石圈发生熔融,引发了岩浆活动且伴随一系列的成矿作用。因此,周涛发等(2016)认为,太平洋板块的俯冲作用是导致长江中下游成矿带在燕山期形成一系列斑岩型矿床的根本原因。长江中下游成矿带内斑岩型铜(钼)矿床主要形成于以下的地质过程,自燕山期开始,受太平洋板块俯冲的影响,使得该区域内地壳加厚(厚度 > 100 km),之后发生岩石圈的熔融、熔体上升和结晶分异等过程,成矿物质最后储存在地壳深部,并参与了斑岩型矿床的形成。该区域形成的斑岩型铜矿以成矿期较为集中,辉钼矿Re含量差异大为特征。

综上所述(图5),不同的地质构造背景可能会影响辉钼矿中Re的含量。

2.6 成矿母岩浆的演化程度(SiO_2含量)

由图6可以看出,随着含矿斑岩体中$w(SiO_2)$的增加,辉钼矿中Re含量下降,$w(SiO_2)$与Re含量呈负相关。说明成岩母岩浆演化程度越高,形成的斑岩型铜(钼)中辉钼矿Re含量越低。其中,$w(SiO_2)$在52%~65%之间,有几个矿区Re含量是最高的,这可能说明含矿斑岩的岩性在一定程度上也会影响Re在辉钼矿中的含量。Sillitoe(2010)研究表明与铜矿化有关的斑岩主要为中-酸性钙碱性岩浆,岩性变化于石英闪长岩与花岗岩之间。当$w(SiO_2) > 65\%$时,斑岩型铜矿床的数量最多,而辉钼矿中Re含量则减少,说明:① 参与形成斑岩型铜矿床的地壳物质越多,越不利于Re在斑岩型矿床中富集;② 硅酸盐体系贫Re且不利于Re迁移。Re为不相融元素,一般在岩浆演化的晚期富集,即热液流体中大量参与形成辉钼矿,基本上由硫化物控制,说明成矿母岩浆的演化程度可能会影响辉钼矿中的Re含量。

2.7 辉钼矿产状及成矿阶段

本次研究选取内蒙古东部白土营子钼-铜矿,探讨其不同成矿阶段形成的辉钼矿Re含量的规律及

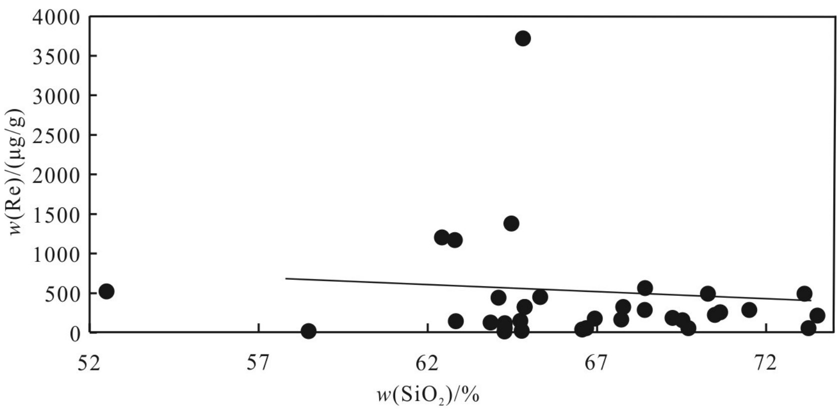

图6　斑岩体 $w(SiO_2)$ 与辉钼矿平均 $w(Re)$ 图解

数据来源：Leng et al., 2013; Li et al., 2005; Ouyang et al., 2014; Wang et al., 2016; Zeng et al., 2004; 陈超等，2013；陈文明等，1998；高永宝等，2018；郭保健等，2006；郝金华等，2012；康永建等，2014；冷成彪等，2007；冷秋锋等，2015；李志军等，2011；林涛等，2017；孟祥金等，2003b；任涛等，2014；芮宗瑶等，2002；佘宏全等，2009；谭钢等，2010；王保弟等，2010；王登红等，2004；王世伟等，2012；王召林等，2008；杨富全等，2012；杨震等，2017；袁顺达等，2013；张达玉等，2010；赵晓燕等，2017；赵云等，2013；郑有业等，2004; 2007；朱明田等，2010；祝向平等，2011; 2015b

Fig. 6　Correlation diagrams of SiO_2 content in magmatic rocks with the average Re content of molybdenite

The data source: Leng et al., 2013; Li et al., 2005; Ouyang et al., 2014; Wang et al., 2016; Zeng et al., 2004; Chen C et al., 2013; Chen W et al., 1998; Gao et al., 2018; Guo et al., 2006; Hao et al., 2012; Kang et al., 2014; Leng C et al., 2007; Leng Q et al., 2015; Li et al., 2011; Lin et al.,2017; Meng et al., 2003b; Ren et al., 2014; Rui et al., 2002; She et al., 2009; Tan et al., 2010; Wang B et al., 2010; Wang D et al., 2004; Wang S et al., 2012; Wang Z et al., 2008; Yang F Q et al.,2012; Yang Z et al., 2017; Yuan et al., 2013; Zhang et al., 2010; Zhao X et al., 2017; Zhao Y et al., 2013; Zheng et al., 2004; 2007; Zhu et al.,2010; Zhu et al., 2011; 2015b

其影响因素。在B脉石英期（主成矿期），以辉钼矿-黄铜矿发育，见有少量黄铁矿及斑铜矿为特征。D脉硫化物期（成矿晚期）黄铁矿绝对占优，常见黄铜矿、石英，有时可见少量的辉钼矿及其他硫化物为主。B脉石英期形成的辉钼矿相对于D脉硫化物期的辉钼矿Re含量较低。在主矿化期（即B脉期），大量的辉钼矿形成，熔体中大量的Re进入辉钼矿晶体，占据Mo的晶格位置。D脉硫化物期，仅有少量的辉钼矿生成，残余熔体中剩余的少量Re进入有限的辉钼矿晶体，使得Re含量高于B脉石英期（Austen et al., 2010; Shafiei et al., 2015; Ren et al., 2018）。

驱龙铜-钼矿位于西藏冈底斯成矿带，属于超大型斑岩铜-钼矿床。本次利用前人（孟祥金等，2003b）对西藏冈底斯成矿带驱龙铜-钼矿床（表1）研究结果，来探讨辉钼矿产状（细脉状、浸染状）是否会影响Re在其中的含量。以浸染状产出的辉钼矿，$w(Re)$为334~466 μg/g，平均为450 μg/g。以细脉状产出的辉钼矿，$w(Re)$为307~1218 μg/g，平均值为724 μg/g。结果表明，以浸染状产出的辉钼矿Re的含量高于细脉状的辉钼矿，说明辉钼矿的产状可能会影响Re的含量。

表1　驱龙斑岩型铜-钼矿床中不同产状辉钼矿的Re含量（据孟祥金等，2003a）

Table 1　Re content of molybdenite of different modes of occurrence in the Qulong copper-molybdenum porphyry deposit (after Meng et al., 2003a)

样品编号	$w(Re)$ /(μg/g)	模式年龄/Ma	样品描述
QK03	615.4	16.21	含浸染状辉钼矿、黄铜矿的二长花岗斑岩
QK06	333.9	15.99	浸染状辉钼矿化、黄铜矿化黑云母花岗岩
QK07	1218.2	16.17	含辉钼矿、黄铜矿的花岗闪长岩
QK09	465.7	16.11	浸染状辉钼矿化、黄铜矿化黑云母花岗岩
QK46	757.0	16.74	含浸染状辉钼矿、黄铜矿的二长花岗斑岩
QK52	306.7	16.42	含辉钼矿的石英细脉

3 结 论

（1）Re主要以类质同象的形式赋存在辉钼矿中。当成矿物质来源于地幔时，形成的辉钼矿中Re含量最高，来源于壳幔混合源的辉钼矿次之，来源于壳源的辉钼矿Re含量最低。

（2）中国斑岩型铜（钼）矿床主要形成于新近纪、古近纪、白垩纪、侏罗纪、三叠纪、泥盆纪、志留纪、奥陶纪和寒武纪，且年代越新，辉钼矿中Re含量越高。

（3）斑岩型矿床中辉钼矿常以浸染状、细脉状和网脉状为主，一般 w(Re)由 n μg/g~n×100 μg/g，且以浸染状产出的辉钼矿Re含量往往高于细脉状的辉钼矿Re含量。

（4）冈底斯、中亚及长江中下游3个成矿带中，辉钼矿Re含量差异较大，说明不同区域及不同地质构造背景可能会影响辉钼矿中Re含量。

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