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岩浆-热液系统中铟的成矿作用*

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摘　要　铟作为支撑新兴高科技产业发展的关键金属,主要应用于电子工业、半导体、焊料合金及航空航天等领域,对国家安全和经济发展至关重要。当前铟的重要来源是与花岗质岩浆有关的锡多金属矿床,其中铟的富集程度远超其他类型矿床。文章在简要概括铟矿床类型的基础上,探讨了铟在岩浆-热液系统各演化阶段的富集过程以及锡、铟同步富集的原因。在岩浆演化过程中,如果有黑云母、角闪石等铟的主要载体矿物发生分离结晶,铟的成矿潜力便会被大大削弱。当铟进入成矿流体后,铟的氯化物、氟化物和氢氧化物对铟的搬运有重要作用,流体的温度、pH 值以及金属配体的种类和浓度是控制铟迁移和沉淀的重要因素。而当铟从流体中沉淀时,因四次配位的 In^{3+} 与贱金属硫化物(闪锌矿、黄铜矿、黝铜矿等矿物)中四次配位的金属离子更相似,造成大量的铟以类质同象替换的方式进入硫化物而与锡发生分离;沉淀后的含铟矿物在后期地质过程中可能经历铟的重新活化、迁移和扩散等过程,导致铟再次富集。铟的富集过程与锡有关,这可能是由于铟和锡具有相似的地球化学性质,二者在表生环境中活动性弱,会滞留在经历化学风化的富黏土的沉积岩中,这样的沉积岩经变质作用会形成大量的云母类矿物,而黑云母作为铟和锡的共同载体,其在高温条件下发生分解可能是导致铟和锡在矿床中同步富集的根本原因。此外,新近在一些贫锡岩浆热液矿床中发现铟也能够超常富集,其机理尚不清楚。加强表生环境中锡与铟预富集过程的研究以及贫锡矿床中铟富集机制的研究,对查明铟-锡共生、分离机制和完善铟成矿理论至关重要。

关键词　地质学;关键金属;岩浆热液;铟矿床;闪锌矿;富集机制

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Metallogenesis of indium in magmatic hydrothermal system

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Abstract

Indium, as one of critical elements, is widely used in such high-tech industries as electronic industry, semiconductors, solder alloys and aerospace industries, thus playing a significant role in national security and economy. Since the indium concentration in granite-related tin polymetallic deposits are much higher than that in other types of deposits, the In-Sn polymetallic deposits are ideal for studying indium mineralization. Indium-rich deposits are known to be genetically associated with granitic magmatism. During magmatic evolution, the potentiality of indium ore formation decreases greatly if the main host minerals of indium, such as biotite and hornblende, crystallize and separate from the melt. In hydrothermal fluid, indium, which is closely associated with tin, can be transported in the form of chlorides, fluorides and hydroxides of indium. Such a process is controlled by tempera-

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ture, pH as well as types and concentrations of ligands in ore-forming fluids. When indium precipitates, it mainly enters sulfides (e.g. sphalerite, chalcopyrite and tetrahedrite) due to similar ionic radius of In^{3+} to metal elements in Zn-Cu-bearing sulfides and decouples with tin. After precipitation, these indium-bearing minerals might undergo subsequent geological processes, resulting in reactivation, migration and diffusion of indium and contributing to further indium enrichment. The close association of tin and indium might result from similar geochemical behaviors. They are immobile in surficial environments and tend to remain in clay-rich sediments during chemical weathering, which would form biotite and muscovite during metamorphism. Then the breakdown of biotite at high temperature would result in synchronous enrichment of indium and tin in magma source. Recently, significant indium enrichments have been found in tin-poor polymetallic deposits associated with granitic magmatic hydrothermal systems, but the enrichment mechanism of indium in such a system remains unclear. Consequently, future studies should focus on the pre-enrichment processes of indium and tin as well as the enrichment mechanisms of indium in tin-poor polymetallic deposits so as to obtain a better understanding of the coupling and decoupling of tin-indium enrichment and the metallogenesis of indium.

Key words: geology, critical metal, magmatic hydrothermal fluids, indium deposits, sphalerite, enrichment mechanisms

铟(Indium,In)是一种柔软、有光泽的银白色金属,具有良好的导电性和光渗透性,被广泛应用于电子工业、半导体、焊料合金及航空航天等高科技领域,尤其是在锡铟氧化物(Indium Tin Oxides, ITO)靶材的生产制造业中发挥着重要作用(Schwarz-Schampera, 2014; 张伟波等, 2019)。21世纪以来,铟作为重要战略资源已经被日本、美国、欧盟、澳大利亚等国列为关键金属之一(毛景文等, 2019; 李晓峰等, 2019)。据Werner等(2017)的统计结果,全球至少有356 kt的铟(包括探明的76 kt和潜在的280 kt)。按照当前的消费水平,这些铟可以满足本世纪的需求。但是,全球铟资源分布不均以及受主要铟资源大国资源政策的影响,未来的铟资源市场仍然存在供应风险(Werner et al., 2017)。因此,加强铟成矿理论的研究、拓展新的资源基地以确保铟资源安全供应,显得十分必要。

铟作为稀散元素,在地壳中的丰度极低,常作为伴生矿种产出(Schwarz-Schampera et al., 2002; 涂光炽等, 2004)。由于In^{3+}与Sn^{2+}具有相近的地球化学性质(刘英俊, 1984),许多重要的铟矿均与锡矿伴生(朱笑青, 2006; Zhang et al., 2007; Ishihara et al., 2011a; 2011b)。目前,关于铟成矿作用的认识也主要基于对锡铟多金属矿床的研究。近年还报道了贫锡富铟的矿床,说明在贫锡的环境中铟仍可发生超常富集(Liu, 2017)。但目前仍不清楚锡铟矿床中锡在铟的迁移和富集过程中所发挥的作用,贫锡矿床中铟的富集机制作为铟成矿理论的一部分也未被充分重视,这严重制约了铟成矿理论的建立和铟资源的高效开发利用(李晓峰等, 2007; 2019;徐净等, 2018)。

1　铟的矿床类型

铟元素在元素周期表中位于第五周期,第三主族,有2种同位素^{113}In和^{115}In,分别占4.3%和95.7%,其氧化态有+1价和+3价2种,以+3价作为常见价态,属亲铜元素(Schwarz-Schampera, 2014)。铟在地壳、洋壳、球粒陨石以及海水中的丰度极低,$w(In)$分别为0.056×10^{-6}、0.072×10^{-6}、0.08×10^{-6}和0.2×10^{-9}~0.7×10^{-9} (Rudnick et al., 2014; Schwarz-Schampera, 2014)。但是在一些富铟矿床中,铟可以出现数千至数万倍的超常富集。

在地球化学性质上,In^{3+}与Sn^{2+}十分相近(刘英俊, 1984)。全球许多重要的锡矿带也是重要的铟产地(Ishihara et al., 2011a;Torró et al., 2019a; 李真真等, 2019),但锡在矿床中多以锡石(SnO_2)的形式出现,铟却倾向于进入具有四面体结构的矿物,如闪锌矿、黄铜矿、黝铜矿、黄锡矿等硫化物,其中,闪锌矿是铟最重要的载体矿物(Zhang et al., 1998;Werner et al., 2017)。由于这些含铟的贱金属硫化物在很多矿床中广泛存在,以及目前对铟矿工业品位的要求比较低($w(In)$ 5~10 g/t),意味着不同类型的矿床均可能作为铟的来源,不同学者对铟矿类型也有不同的划分方案。Schwarz-Schampera等(2002)和Werner

等(2017)对铟矿的类型做了较为详细的划分，可总结为以下8类：脉状-网脉状W-Sn矿、与火山岩有关块状硫化矿床、与喷流沉积作用有关的块状硫化物矿床、多金属脉型矿床、矽卡岩矿床、斑岩矿床、砂页岩型铜矿以及与现代活动的岩浆系统有关的矿床。

上述铟矿类型主要是基于对铟来源的划分，并非铟在这些矿床类型中都能够达到超常富集的程度。例如，锌矿石是铟的重要来源，但并非所有的铅锌矿中的铟都具有工业价值。Zhang (1987)在对国内外60多个铅锌矿床微量元素研究后发现，不含锡的矿床中铟含量都很低，只有富锡矿床中的铟含量才可达到富铟矿床的标准（w(In)>50~100 g/t)(张乾等, 2003; 涂光炽等, 2004)，并提出构成富铟矿床至少要具备以下2个条件：① 锡石硫化物矿床或含锡铅锌矿床的存在；② 闪锌矿大量堆积(张乾等, 2003)。近年来，对各类矿床中闪锌矿开展的研究工作表明，富铟的闪锌矿往往形成温度较高，多与相对高温的岩浆热液过程有关，而在与岩浆活动无明显成因联系的矿床中，闪锌矿的铟含量往往偏低(图1; 伍永田, 2009; Cook et al., 2009; Ye et al., 2011; Frenzel et al., 2016; Bauer et al., 2019a)。因此，与岩浆活动有关的锡(锌)多金属矿床是铟矿化最有利的场所，这类矿床是中国和世界铟资源最主要的来源，也是当前铟矿研究的主要对象。

2 岩浆-热液过程中铟的富集

2.1 岩浆活动与铟矿化

研究表明，铟在地幔部分熔融过程中表现出不相容性和挥发性(Sun, 1982)。在前人建立的铟矿成因模式中(图2)，铟在地壳中的富集多与花岗质岩浆活动关系密切，暗示了铟主要来源于岩浆 (Schwarz-Schampera et al., 2002; 李晓峰等, 2010)。

由于铟在含氧化合物中与Fe^{2+}关系紧密(刘英俊, 1984)，在岩浆的结晶分异过程中，角闪石、黑云母等镁铁质矿物的大量结晶会导致铟的分散而不利于铟矿化的发生，尤其是角闪石的结晶，会大大降低

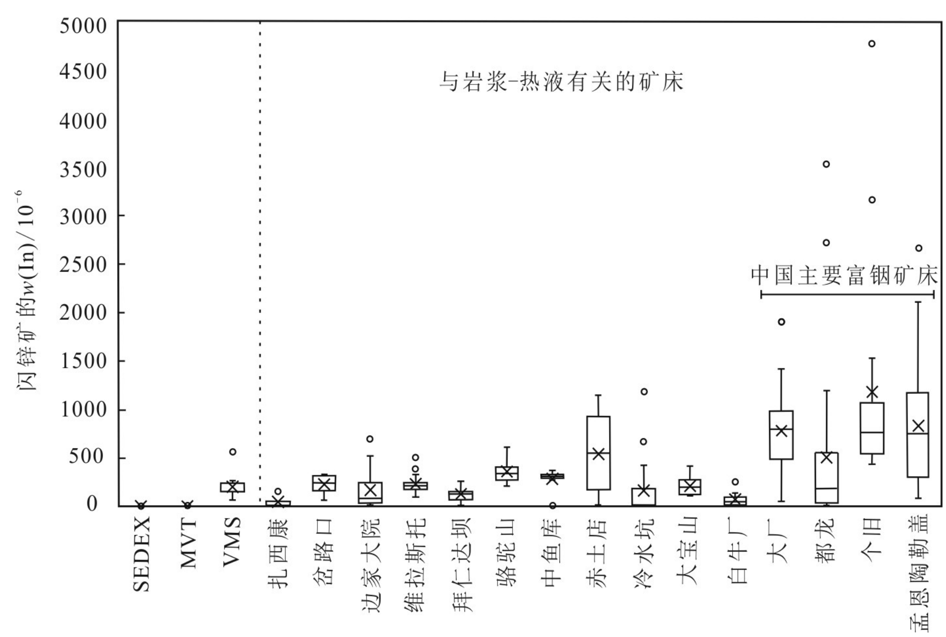

图1 不同类型含铟矿床的闪锌矿铟含量

数据引自：张乾等, 2004; 李厚民等, 2009; 承斯, 2011; Ye et al., 2011; 曹华文等, 2014; 程泽锋, 2015; Li et al., 2015; 裴秋明等, 2015; 皮桥辉等, 2015; 田浩浩等, 2015; 张政等, 2016; 金露英, 2016; 钱孟轩, 2017; 陶兰初, 2017; 邢波等, 2017; 叶霖等, 2017; 陈翠华等, 2019; 张含等, 2019

Fig. 1 Indium content of sphalerite from different types of deposits

Date Source: Zhang et al., 2004; Li et al., 2009; Cheng, 2011; Ye et al., 2011; Cao et al., 2014; Cheng, 2015; Li et al., 2015; Pei et al., 2015; Pi et al., 2015; Tian et al., 2015; Zhang et al., 2016; Jin, 2016; Qian, 2017; Tao, 2017; Xin et al., 2017; Ye et al., 2017; Chen et al., 2019; Zhang H et al., 2019

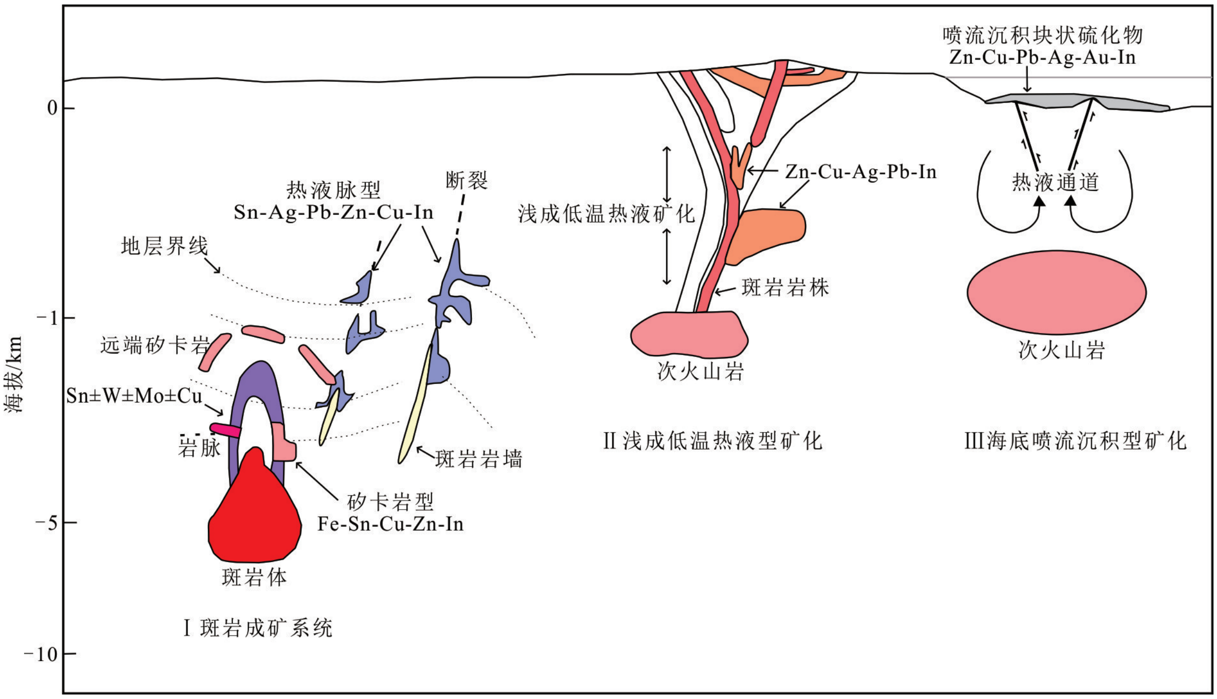

图2　铟矿的成因模式图(修改自 Schwarz-Schampera et al., 2002)

Fig. 2　Genetic models of indium deposits (modified after Schwarz-Schampera et al., 2002)

铟矿化的可能性(Gion et al., 2019)。Gion 等(2018)测定了铟在角闪石与熔体之间的分配系数约为36,且角闪石的成分对分配系数影响不大,而铟在黑云母与熔体之间的分配系数受黑云母成分(八面体位置 Fe^{2+} 的含量和四面体 Al 含量)的影响(图 3a、b),分配系数在 0.6~16 之间变化(Gion et al., 2018)。对于I型花岗岩,其形成过程中除伴有黑云母的结晶分异之外,还常常伴随着角闪石的结晶;而S型和A型花岗岩中的镁铁矿物以黑云母为主,缺少角闪石,所以I型花岗岩的铟矿化潜力较低(Cook et al., 2011a; Simons et al., 2017; Gion et al., 2019)。值得注意的是,在花岗质岩浆中,尽管铟会进入结晶的黑云母,但随着岩浆的演化,黑云母对铟的相容性会逐渐变低,这就造成那些缺少角闪石的熔体随着黑云母的结晶反而会具有更高的铟含量(王大鹏等,2019),这也符合铟矿化常与高分异花岗岩有关的事实。

此外,熔体中的挥发分(F、Cl、B、P 等)也是制约铟矿化的重要因素。在源区部分熔融过程中,F、Cl、B 等矿化剂的存在,可降低矿物的固相线温度,使成矿元素在熔体中的溶解度增大,有利于成矿元素进入熔体相中(Hu et al., 2009; Moura et al., 2014; Valkama et al., 2016; Gion et al., 2019)。当这些挥发分进入熔体后,进一步降低熔体的固相线、延长岩浆的结晶分异过程,使熔体聚合度减小、粘度降低,增加了成矿元素在熔体中的扩散性能(Keppler et al., 1991; London, 1997; Simons et al., 2017),有利于铟在残余熔体中富集。对于I型花岗岩,由于挥发分增加会造成岩浆结晶分异过程的延长,这会使得更多的铟进入结晶的角闪石和黑云母中,不利于铟矿化的发生,但部分缺少角闪石结晶的I型花岗岩仍具备铟矿化的潜力;对于A型和S型花岗岩,由于它们缺少可容纳铟的暗色矿物,随着挥发分的增加,流体出溶时,这些挥发分作为铟的重要配体会把更多的铟带入成矿流体,从而抵消了因延缓结晶造成的不利影响(Simons et al., 2017; Gion et al., 2019)。

2.2　铟在成矿流体中的迁移和富集

根据 Pearson(1963)的"软硬酸碱理论",In^{3+}属于硬酸,在不同的流体条件下,可与之结合的配体离子有 OH^-、F^-、Cl^- 以及 SO_4^{2-} 等强碱(Pearson, 1963; Wood et al., 2006)。Seward 等(2000)认为,In^{3+}在热液流体中主要以氯的络合物($InCl_4^-$)和水合物($InClOH^-$)的形式存在,在 300~350℃的热液流体中,$InCl_4^-$的含量达到最高。最新研究也指出,在酸性、高氯的流体中,以 $InCl_3$ 形式存在的铟要比近中性、

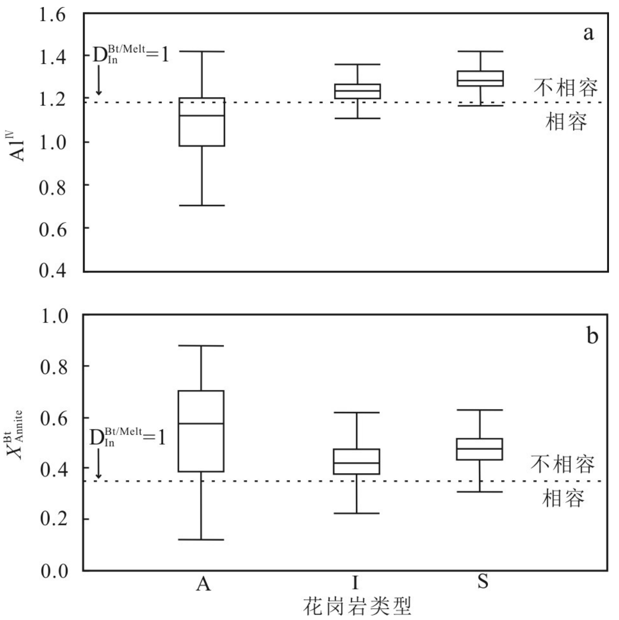

图3 A、I、S型花岗岩中黑云母四面体Al含量(Al^{IV})(a)和黑云母八面体位置Fe^{2+}含量(X_{Annite}^{Bt})(b)对铟在花岗质岩浆中相容性的影响(修改自Gion et al., 2019)

Fig. 3 The influence of tetrahedral aluminum (Al^{IV}) (a) and the proportion of Fe^{2+} in the octahedral site (X_{Annite}^{Bt}) (b) of biotite from A, I, S-type granites on the compatibility of indium in granitic magma(modified after Gion et al., 2019)

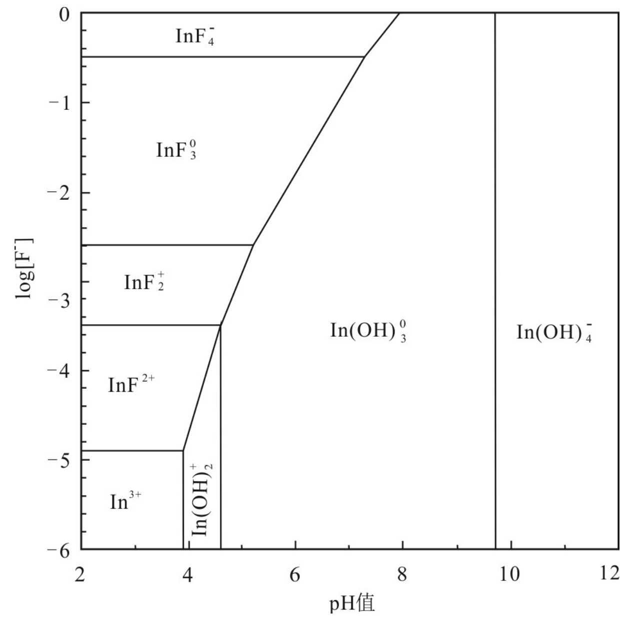

图4 在25℃、10^5 Pa条件下In^{3+}的氟化物和氢氧化物的稳定域(修改自Wood et al., 2006)

Fig. 4 The fields of predominance of fluoride and hydroxide complexes of In^{3+} at 25°C and 10^5 Pa (modified after Wood et al., 2006)

低氯的流体中以InO_2H和InO_2^-形式存在的铟含量更高,而形成锡石硫化物矿床的流体就具有酸性、高氯的特征,并且降温和pH升高是铟从这种酸性、高氯流体中沉淀分离的有效机制(Gaskov et al., 2020)。

就铟的各种配体离子而言,氯是自然界各类热液矿床中普遍存在的一种矿化剂。如果铟在成矿热液中仅以简单的氯的络合物的形式迁移,那铟就有可能在任何矿床中富集,然而事实并非如此(朱笑青等, 2006)。在实际情况中,铟矿化多与高分异的花岗岩有关,这种高分异的特征很大程度上与岩浆中的氟含量有关(Simons et al., 2017)。Wood等(2006)也指出,在标准条件下(温度25℃,压力100 Pa),当pH=5、氟的活度大于10^{-3}时,铟的氟化物对铟的迁移起关键作用(图4),并推测在酸性、富氟的条件下(如云英岩化),氟化物也是In^{3+}在热液流体中迁移的一种重要形式(Wood et al., 2006; Broman et al., 2018)。Moura等(2014)认为巴西Mangabeira地区的In-Sn矿化与富氟的流体和云英岩化有关(Moura et al., 2014)。因此,氟对铟的迁移,特别是对铟在岩浆阶段的富集也有重要影响,但中高温岩浆-热液中氟如何控制铟的迁移和富集,还缺乏实验验证。

如前所述,流体的物理化学条件和金属配体的种类、浓度,对铟在流体中的迁移形式有重要影响(Gaskov et al., 2020)。但在许多铟矿床中,成矿流体中其他金属离子的活度也会制约铟的富集。例如,富铜的铅锌矿比贫铜的铅锌矿更富铟,成矿流体Cu^+的活度升高会促进铟进入闪锌矿(Cherniak, 2010; Cook et al., 2012; Shimizu et al., 2012; Andersen et al., 2016; Frenzel et al., 2016; Torró et al., 2019b);锌的含量会控制铟的存在形式,当锌含量高时,铟主要进入闪锌矿,反之,铟以独立矿物的形式出现(Cook et al., 2011a; 2011b);铁对铟的富集也有影响,高铁闪锌矿往往具有较高的铟含量(Seifert et al., 2006; Pavlova et al., 2015; Li et al., 2015; Valkama et al., 2016);当w(Cd)在0.2%~0.6%时,闪锌矿的晶体结构会发生变形,此时的闪锌矿具有最高的铟含量,此现象被称为"铟窗效应"(Dill et al., 2013)。由此可见,成矿流体中其他金属离子的活度不但控制了铟的赋存形式,还会造成铟在不同阶段闪锌矿中的选择性富集(Cook et al., 2011b; 戴塔根等, 2012; 熊伊曲等, 2015; Liu, 2017)。

不可忽略的一个事实是,在绝大多数矿床中,锡对铟的富集似乎具有更重要的影响。研究表明,花岗岩浆从结晶成岩→分异出成矿流体→遭受变质与蚀变→与围岩发生接触交代的全过程,In与Sn始终保持正相关性(王大鹏等, 2019),说明当流体体系中有锡存在时,铟更容易进入流体并发生富集(Zhang et al., 2007; 王大鹏等, 2019)。Zhang等(2007)推测铟和锡在成矿流体中可能以某种化合物的形式共同迁移,但在成矿物质沉淀时,锡在矿床中主要以氧化物的形式锡石出现,铟则主要以硫化物的形式存在。关于铟和锡在流体中共存和在矿物中分离的机制目前尚无定论。从与铟矿化有关的这些元素的地球化学性质来看,锡在大多数地质过程中有+2价和+4价,其中Sn^{2+}和Sn^{4+}六次配位的离子半径分别为0.93 Å和0.69 Å(Shannon, 1976)。由于锡矿多与还原性的钛铁矿系列花岗岩关系密切,锡在演化晚期的熔体和流体中多以Sn^{2+}的形式存在,而In^{3+}六次配位的离子半径为0.94 Å,与Sn^{2+}相近,此时成矿流体中搬运Sn^{2+}的配体也有利于In^{3+}的迁移。当成矿元素沉淀时,主要含铟硫化物(闪锌矿、黄铜矿、黝铜矿等)中的金属离子是四次配位,如四次配位的Zn^{2+}、Cu^{+}、Fe^{2+}的离子半径分别为0.74 Å、0.74 Å、0.78 Å,这与In^{3+}四次配位的离子半径(0.76 Å)相似,因此大量的In^{3+}会进入硫化物(王大鹏等, 2019),这就造成了铟矿化与锌矿化和铜矿化紧密相关。

除了这些含锡富铟的多金属矿床外,近年来还报道了贫锡富铟的实例。其中湖南七宝山斑岩-矽卡岩型铜多金属矿伴生的铟也达到了大型规模(>500 t),矿床中黄铁矿-闪锌矿矿石的w(In)平均达122.9×10^{-6}(Liu , 2017; Yuan et al., 2018b)。尽管该矿床贫锡,但却富集Cu、Pb、Zn、Ag、Cd、Fe、Mn、Te、Ga、Ge、In等。在这样复杂的多金属流体系统中,铟和其他金属离子如何迁移和富集,以及流体演化的各个阶段中铟与其他元素的相关性如何仍缺乏研究。

3　铟的赋存状态

与其他稀散元素相似,铟在自然界的富集也有明显的专属性(张乾等, 2003),主要存在于闪锌矿、黄铜矿、黄锡矿和锌黄锡矿等具有四面体结构的硫化物中,其中又以闪锌矿中的铟最为重要,占目前全球铟资源的95%(Zhang et al., 1998; Werner et al., 2017)。目前报道的铟矿物共有18种,但只有极少数铟矿的载铟矿物为铟的独立矿物,如日本的Kawazu矿床,铟主要以硫铟铜矿和羟铟石的形式存在(Andersen et al., 2016; Lerouge et al., 2017)。

在有大量闪锌矿形成的富铟矿床中,铟更倾向于以类质同象的方式进入闪锌矿。近年来针对In进入闪锌矿的方式开展了大量的研究工作,不同学者提出了不同的机制,包括:①$In^{3+}+Cu^{+}\leftrightarrow 2Zn^{2+}$;②$In^{3+}+Sn^{3+}+\square\leftrightarrow 3Zn^{2+}$;③$In^{3+}+Cu^{+}+Sn^{2+}\leftrightarrow 3Zn^{2+}$和$In^{3+}+Cu^{+}+Sn^{4+}+\square\leftrightarrow 4Zn^{2+}$。几种替换方式中与$In^{3+}$一同进入闪锌矿的一价金属离子除$Cu^{+}$外,还可能有少量的$Ag^{+}$ (Cook et al., 2009; Ye et al., 2011; Cook et al., 2011b; Cook et al., 2012; Murakami et al., 2013; Belissont et al., 2014; Belissont et al., 2016; Frenzel et al., 2017; Xu et al., 2020a)。其中,方式①已得到多方面证据的支持,对于方式②和③,闪锌矿中的锡到底以何种形式出现,有待进一步研究(Belissont et al., 2014; Wei et al., 2018)。

对于这种以类质同象替换方式存在于闪锌矿中的铟而言,当In^{3+}和Cu^{+}/Ag^{+}对闪锌矿中Zn^{2+}离子的替代达到较高程度时,便会出现铟爆发式富集的现象(如"铟爆效应"或"铟窗效应")(李晓峰等,2020)。若成矿流体中的Cu、In足够高,这种替换超过上限便可能导致铟的独立矿物(如硫铟铜矿)出现。由于闪锌矿是等轴晶系的矿物,而硫铟铜矿是具有黄铜矿结构型的四方晶系矿物,铟由类质同像形式向独立矿物转变过程中,闪锌矿晶体形态和晶胞参数也会由等轴晶系/六方晶系的闪锌矿/纤锌矿向四方晶系的硫铟铜矿/黄铜矿转变(Dill et al., 2013)。与富铟闪锌矿的晶格结构存在各向异性的认识一致(Ohta et al., 1989),最近对富铟闪锌矿开展的扫描透射电镜(STEM)的研究也表明,由于Cu、In进入闪锌矿,导致闪锌矿中出现晶格缺陷(变形),而铟的富集和闪锌矿的结构改变(由等轴晶系转为四方晶系)往往就发生在这些晶格变形的部位(Xu et al., 2020b)。

对于贫锌矿床,由于缺少主要载铟矿物,出现独立铟矿物的可能性便会大大增加(Cook et al., 2011a; 2011b)。当矿石In/Zn比值>50(单位分别是10^{-6}和%),w(In)>40×10^{-6}时,有利于铟矿物的形成(Valkama et al., 2016a; 2016b)。硫铟铜矿($CuInS_2$)作为内生矿床中最常见的独立铟矿物,其形成需要大量铜离子的参与,矿床的铜含量也是制约独立铟矿物形成的重要因素。如在芬兰Sarvlaxviken地区富铜贫

锌的矿脉中，铟主要以独立矿物（硫铟铜矿）形式出现，而在Jungfrubergen和Getmossmalmen地区的矿脉中有大量闪锌矿，铜相对缺少，铟则主要赋存在闪锌矿中（Cook et al., 2011a）。Toyoha多金属矿是日本最大的铟矿床，该矿床中的硫铟铜矿只在富铜的矿石中出现(Ishihara et al., 2006; Shimizu et al., 2012)。近年来，中国的福建紫金山铜金矿、西藏班公-怒江铜多金属成矿带和青海赛什塘-日龙沟铜多金属矿田等地，也报道了硫铟铜矿、羟铟石、自然铟等独立铟矿物的存在(赵元艺等, 2010; 王少怀等, 2014; Liu et al., 2016)，而扬子板块南-西南缘的锡多金属矿集区作为中国最主要的铟产地却未报道有铟的独立矿物存在。这也说明，富铜铟、贫锌的环境有利于硫铟铜矿的形成。此外，在被斑铜矿、石英等不含铟的矿物交代过的闪锌矿、黄铜矿附近也会出现铟的独立矿物(Andersen et al., 2016)。这主要是由于In不能进入斑铜矿、石英等矿物的晶格而被排斥，使铟在被交代的矿物周围富集，最终导致独立铟矿物的形成。

除了稀有的独立铟矿物，铟还能以很高的含量赋存在其他矿物中。如欧洲华力西褶皱带的一些Sn±W矿床中，黄铜矿、黄锡矿、黄铁矿、砷黄铁矿及金红石相对于闪锌矿均具有较高的铟含量(Lerouge et al., 2017)；葡萄牙Neves Corvo锡铜矿床中，黝锡矿的w(In)高达0.7%(Benzaazoua et al., 2003)；玻利维亚的Poopó多金属矿中，锡石的w(In)最高也可达18%(Torres et al., 2019a)。有学者提出铟进入锡石的方式可能为：$2(Sn, Ti)^{4+} \leftrightarrow (In, Fe)^{3+} + (Nb, Ta)^{5+}$和$Fe^{2+} + (Nb, Ta)^{5+} \leftrightarrow In^{3+} + (Sn, Ti)^{4+}$ (Lerouge et al., 2017)，认为铟能否进入锡石取决于体系中Nb、Ta的活度，当体系中缺少Nb、Ta时，铟仍主要进入闪锌矿。值得关注的是，常与闪锌矿共生的方铅矿为NaCl型结构，且铅离子半径与铟相差太大，被认为不利于类质同象替换（刘英俊, 1984）。最近的研究发现，在芬兰西南地区含铟和稀土元素的矿脉中，硫铟铜矿多以微小颗粒的形式包裹在方铅矿中，Al-Ani等（2018）据此认为铟初始富集在方铅矿中，方铅矿和硫铟铜矿可形成固溶体。除这些金属矿物外，一些矽卡岩矿床中的石榴子石也具有较高的铟含量，如都龙Zn-Sn-In多金属矿床的石榴子石中，w(In)为166×10^{-6}~629×10^{-6}（Xu et al., 2020a）。综上所述，尽管铟在绝大多数矿床中的主要载体是闪锌矿，但不局限于此，铟的赋存状态以及影响铟赋存状态的物理化学条件仍然是一个值得探讨的问题。

4 铟的多阶段富集

近年来，许多学者利用EMPA、LA-ICP-MS以及同步辐射X射线吸收近边结构（XANES）等方法对相关矿物微区开展了一系列的研究工作，发现即使在同一富铟闪锌矿内部也具有明显的不均一性，表现为铟在闪锌矿的某个部位或者具有某种结构（如环带结构、交代残余结构）中富集(Murakami et al., 2013; Belissont et al., 2014; Bauer et al., 2019b)。研究表明，当温度为300~500℃时，在Cu-Fe-Zn-S体系中，闪锌矿的CuS溶解度非常有限，摩尔分数最高不超过2.4%（对应w(Cu)约为1.58%），当闪锌矿的原始铜含量超过该溶解度极限，闪锌矿中便会出现黄铜矿的显微包体 (Kojima et al., 1984; 1985; Sugaki et al., 1987; Keith et al., 2014)。若富铟闪锌矿沉淀时，Cu^{+}和In^{3+}按照1∶1的比例进入闪锌矿晶体，闪锌矿中铟的含量也极为有限（w(In)不超过2.81%），但是在富铟矿床中，闪锌矿局部的w(In)可超过20%，w(Cu)可超过10%(Liu et al., 2017)。如湖南柿竹园和香花岭矿田内的闪锌矿、黄铜矿等矿物均存在边部比核部更加富集铟的现象，且香花岭矿田内的闪锌矿w(In)最高达21.96%(Liu et al., 2017; 2018)，这说明一定存在其他地质过程使得铟发生如此高强度的富集。

Bauer等(2019b)在德国Freiberg地区的矽卡岩型矿床中发现，与闪锌矿共生的富铟黄铜矿发生分解后，释放出来的铟会扩散进入附近闪锌矿的边部，造成闪锌矿边部的w(In)超过17%。Torró等(2019c)发现玻利维亚Huari Huari矿床中的众多含铟矿脉中，只有铜含量较高的Antón Bravo矿脉才具有高的铟含量，认为富铜流体的加入是使Antón Bravo矿脉富铟的重要原因。此外，有证据表明，成矿后的构造变质事件也会造成铜、铟等元素在矿床中重新分配，导致铟在矿床的局部再次高度富集，甚至形成硫铟铜矿等独立铟矿物 (Jonsson et al., 2013; Lockington et al., 2014; Carvalho et al., 2018)。这种因流体叠加、交代、矿物分解以及变质事件造成铟发生再富集的现象，在阿根廷San Roque地区、芬兰西南部、加拿大Mount Pleasant地区以及日本Toyoha矿床均有报道(Sinclair et al., 2006; Cook et al., 2011; Shimizu et al., 2012; Dill et al., 2013)。

后期的地质事件之所以能使铟发生超常富集,其本质在于后期地质过程改变了先存含铟硫化物所处的物理化学条件,促进了铟在共存矿物之间发生迁移、扩散等过程,进而使铟发生再富集(Shimizu et al., 2012; Carvalho et al., 2018; Bauer et al., 2019a)。由于单独的In^{3+}进入闪锌矿较为困难,往往需要一价金属离子(以Cu^{+}为主等)的参与。在许多富铟矿床中,闪锌矿中常出现规则或不规则的富铟环带(Murakami et al., 2013; Liu et al., 2017; 2018; Bauer et al., 2019b)。这种富铟环带与矿物中由微量元素组成和含量差异造成的韵律环带不同,后者可能由流体性质发生周期性变化导致 (Peterson et al., 2014),前者还可能受控于元素在矿物之间的扩散速率。相对于Cu^{+}而言,In^{3+}的扩散能力弱(Cherniak, 2010),通过扩散过程进入闪锌矿的In主要集中在闪锌矿的边部,形成富Cu+In的不规则环带 (Bente et al., 1995)。在这样的扩散过程中,元素的扩散会随着硫逸度、闪锌矿的铁含量的升高以及水的存在而增强(Bente et al., 1995; Yuan et al., 2018a; Torró et al., 2019c)。在多阶段矿化过程中,由于后期流体的叠加还会带来一定的水,这在一定程度上也促进了铟在矿物之间的扩散。

5　锡、铟的同步富集

5.1　锡铟的预富集过程

铟在锡多金属矿中的富集程度远远超过其他类型的矿床。很自然的一个问题是,导致铟和锡在这类矿床中同步富集的根本原因是什么?从二者的地球化学性质来看,锡在母岩化学风化过程中的溶解度低且容易被黏土矿物吸附(Romer et al., 2014; 2016)。与锡类似,铟在表生过程中的活动性也很弱,在母岩风化后迁移不远,多在原地残积(刘英俊, 1984; Lopez et al., 2015)。

最新研究指出,个旧锡多金属矿区的层间氧化矿石更富集铟元素(郭志娟等, 2020),说明矿石在表生氧化过程中随着其他易迁移元素的流失,铟由于活动性差而在原地富集。因此,经强化学风化形成的富黏土沉积岩有利于铟、锡的初始富集,这些富黏土沉积岩再经过变质作用,便会形成富云母类矿物的副变质岩(Wolf et al., 2018)。在造岩矿物中,锡的主要载体是黑云母、榍石、钛铁矿等含钛矿物,铟的主要载体是黑云母和角闪石,其中黑云母是二者共同的载体矿物(刘英俊, 1984; Gion et al., 2018; 2019)。在构造热事件中如果有这些矿物的分解,尤其是黑云母的分解,初始熔体就可能同时出现Sn、In的富集。在随后的地质过程中,由于In^{3+}与Sn^{2+}地球化学性质相似,二者便共同迁移,直至成矿元素沉淀时发生分离。但是,这些镁铁质矿物的分解需要在高温熔融过程(>800℃)中实现(Wolf et al., 2018; Yuan et al., 2019),而要达到这样的高温就需要来自地幔的热量输入(Romer et al., 2016),仅靠增厚地壳内部的热量难以使这些矿物发生分解(Clark et al., 2011)。因此,地幔提供高温使富Sn、In的镁铁质矿物分解释放Sn、In等元素,可能是导致锡、铟同步富集的重要前提。

5.2　华南板块南缘锡、铟的超常富集

中国是铟资源大国,铟矿主要分布在华南板块南缘和大兴安岭南段,其中以华南板块南缘的铟矿最为重要,主要的富铟矿床有大厂、都龙、个旧等锡多金属矿床(伍永田, 2009; 李晓峰等, 2010; 皮桥辉等, 2015; 叶霖等, 2017)。这些矿床的成岩成矿时代集中在晚白垩世(98~82 Ma)(徐容等, 2018; 许赛华等, 2019),与成矿有关的岩体主要为A型或S型花岗岩,形成这些花岗岩的原岩为富黏土的碎屑岩(徐斌, 2015; 赵振宇, 2017; 陈薇, 2019)。

最新的研究表明,新特提斯板块的俯冲后撤是华南板块南缘晚白垩世大规模成岩成矿的动力学机制(Zhang et al., 2017; 2018; 徐荣等, 2018; Huang et al., 2019)。在新特提斯板块后撤过程中,软流圈地幔上涌使上覆地壳中的变沉积岩发生高温部分熔融的同时,还伴有大量黑云母的分解(郭佳, 2019),形成的富锡(铟)的长英质岩浆(可能有少量地幔物质贡献)经历不同程度的结晶分异作用,最终就位于地壳浅部,形成相关的锡铟多金属矿化。由于铟在地壳中的丰度极低(0.056×10^{-6}),富铟的岩浆源区的存在为最终的铟矿化提供了重要的物质基础。成矿岩体高的锆石饱和温度(800±20)℃和其中幔源暗色包体的存在,暗示了地幔为与锡成矿有关的花岗岩的形成提供了充足的热量(Yuan et al., 2019; Liu et al., 2020)。

除华南板块南缘外,由中国西南三江向缅甸、泰国、马来西亚、印尼延伸的东南亚巨型锡矿带也是世界上锡的重要来源。锆石Ti温度计显示该成矿带上与锡矿化有关的花岗岩的温度(700~800℃)比贫矿花岗岩的温度(590~689℃)更高,且该带上的花岗岩主要也源自变泥质沉积岩的部分熔融,同期地幔来

源的镁铁质岩墙的存在暗示了地幔为部分熔融提供了充足的热量(Liu et al., 2020; Yang et al., 2020)。该巨型锡矿带也具备锡、铟同步富集的有利条件,其铟成矿潜力也值得关注。因此,富铟源区的存在以及地幔提供高温诱发部分熔融是Sn-In矿化有利条件,但目前的研究工作更多关注了成矿过程中铟和锡的相关关系,对于铟和锡在成岩过程中的富集行为讨论较少。查明不同类型母岩经化学风化向富黏土沉积岩转化过程中锡铟的预富集过程是揭示锡、铟同步富集、铟超常富集的关键,这对理解铟的成矿物质来源也有重要的启示意义。

6 结 论

(1)铟在岩浆岩中的主要载体是角闪石、黑云母等镁铁质矿物。由于铟在角闪石和熔体之间的分配系数高且稳定,I型花岗岩在形成过程中因常伴有角闪石的结晶,其铟矿化潜力低于S型和A型花岗岩。

(2)酸性、高氯的流体最有利于铟的搬运;流体中铜、镉、铁的活度控制了铟在闪锌矿中的富集程度;流体中铜和锌的相对含量制约了独立铟矿物(如硫铟铜矿)的形成。研究多金属流体系统中铟的富集过程和控制铟富集的物理化学条件等,是揭示铟超常富集的关键环节。

(3)闪锌矿是最主要的载铟矿物,$In^{3+} + (Cu^{+}, Ag^{+}) \leftrightarrow 2Zn^{2+}$是铟进入闪锌矿的主要方式。除闪锌矿外,铟也可以在黄铜矿、黝铜矿、黝锡矿、锡石、石榴子石等其他矿物中富集。

(4)后期的变质事件、流体的叠加交代、矿物的分解、Cu+In的扩散以及表生环境的风化/氧化作用,是一些矿床中的闪锌矿或矿石超常富铟的重要原因。

(5)锡铟同步富集是富铟矿床的显著特点,导致这一现象的根本原因可能是由于二者在表生环境中的活动性弱,易残留在富黏土的沉积岩中,这样的源岩再发生熔融便为Sn-In矿化提供了物质基础。

References

Andersen J C Ø, Stickland R J, Rollinson G K and Shail R K. 2016. Indium mineralisation in SW England: Host parageneses and mineralogical relations[J]. Ore Geology Reviews, 78: 213-238.

Al-Ani T, Ahtola T, Kuusela J and Al-Ansari N. 2018. Mineralogical and petrographic characteristics of Indium and REE-bearing accessory phases in the Kymi granite stock, southern Finland[J]. Natural Resources, 9(2): 23-41.

Bauer M E, Burisch M, Ostendorf J, Krause J, Frenzel M, Seifert T and Gutzmer J. 2019a. Trace element geochemistry of sphalerite in contrasting hydrothermal fluid systems of the Freiberg district, Germany: Insights from LA-ICP-MS analysis, near-infrared light microthermometry of sphalerite-hosted fluid inclusions, and sulfur isotope geochemistry[J]. Mineralium Deposita, 54(2): 237-262.

Bauer M E, Seifert T, Burisch M, Krause J, Richter N and Gutzmer J. 2019b. Indium-bearing sulfides from the Hämmerlein skarn deposit, Erzgebirge, Germany: Evidence for late-stage diffusion of indium into sphalerite[J]. Mineralium Deposita, 54(2): 175-192.

Belissont R, Boiron M, Luais B and Cathelineau M. 2014. LA-ICP-MS analyses of minor and trace elements and bulk Ge isotopes in zoned Ge-rich sphalerites from the Noailhac-Saint-Salvy deposit (France): Insights into incorporation mechanisms and ore deposition processes[J]. Geochimica et Cosmochimica Acta, 126: 518-540.

Belissont R, Muñoz M, Boiron M, Luais B and Mathon O. 2016. Distribution and oxidation state of Ge, Cu and Fe in sphalerite by μ-XRF and K-edge μ-XANES: insights into Ge incorporation, partitioning and isotopic fractionation[J]. Geochimica et Cosmochimica Acta, 177: 298-314.

Bente K and Doering T. 1995. Experimental studies on the solid state diffusion of Cu+In in ZnS and on "Disease", DIS (Diffusion Induced Segregations), in sphalerite and their geological applications[J]. Mineralogy and Petrology, 53(4): 285-305.

Benzaazoua M, Marion L P, Pinto A, Migeon H and Wangnor F E. 2003. Tin and indium mineralogy within selected sampes from the Neves Corvo ore deosit (Portugal) : A multidisciplinary study[J]. Mineral Engineering, 16(11): 1291-1302.

Broman C, Sundblad K, Valkama M and Villar A. 2018. Deposition conditions for the indium-bearing polymetallic quartz veins at Sarvlaxviken, south-eastern Finland[J]. Mineralogical Magazine, 82(S1): S43-S59.

Cacho A, Melgarejo J, Camprubí A, Torró L, Castillo-Oliver M, Torres B, Artiaga D, Tauler E, Martínez Á, Campeny M, Alfonso P and Arce-Burgoa O R. 2019. Mineralogy and distribution of critical elements in the Sn-W-Pb-Ag-Zn Huanuni deposit, Bolivia[J]. Minerals, 9(12): 753.

Cao H W, Zhang S T, Zheng G, Liu R P, Tian H H, Zhang X H and Li J J. Geochemical characteristics of trace element of sphalerite in the Zhongyuku (Pb)-Zn deposit of the Luanchuan, southwest of China[J]. Journal of Mineralogy and Petrology, 34(3): 50-59(in Chinese with English abstract).

Chen C H, Song Z J, Yang Y L, Yang D P, Gu Y and Chen X J. 2019. The trace elements characteristics of sphalerite and genetic analysis of Dongzigou lead-zinc deposit in Xishui County, Guizhou Province[J]. Acta Mineralogica Sinica, 39(5): 1-9(in Chinese with

English abstract).

Chen W. 2019. The granitic magmatism and its significance of mineralization in Gejiu, Yunnan (Dissertation for Master degree)[D]. Supervisor: Dong G C and Ding X Z. Beijing: China University of Geosciences. 38-52(in Chinese with English abstract).

Chen Z F. Zinc isotopes and minor element s in sphalerite from magmatic hydrothermal deposit in the Middle-southern Part of Da Hinggan Mountains, China (Dissertation for Master degree) [D]. Supervisor: Yang Y Q and Zhang A L. Beijing: China University of Geosciences. 14-20(in Chinese with English abstract).

Cheng S. 2011. The Mineralogical study of sphalerite of Xiabao deposit in Lengshuikeng silver-lead zinc ore ficld, Jiangxi province (Dissertation for master degree)[D]. Supervisor: He M Y. Beijing: China University of Geosciences. 18-31(in Chinese with English abstract).

Cherniak D J. 2010. Diffusion in carbonates, fluorite, sulfide minerals, and diamond[J]. Reviews in Mineralogy and Geochemistry, 72(1): 871-897.

Clark C, Fitzsimons I C, Healy D and Harley S L. 2011. How does the continental crust get really hot[J]? Elements, 7: 235-240.

Cook N J, Ciobanu C L, Pring A, Skinner W, Shimizu M, Danyushevsky L, Saini-Eidukat B and Melcher F. 2009. Trace and minor elements in sphalerite: A LA-ICPMS study[J]. Geochimica et Cosmochimica Acta, 73(16): 4761-4791.

Cook N J, Ciobanu C L and Williams T. 2011a. The mineralogy and mineral chemistry of indium in sulphide deposits and implications for mineral processing[J]. Hydrometallurgy, 108(3-4): 226-228.

Cook N J, Sundblad K, Valkama M, Nygård R, Ciobanu C L and Danyushevsky L. 2011b. Indium mineralisation in A-type granites in southeastern Finland: Insights into mineralogy and partitioning between coexisting minerals[J]. Chemical Geology, 284(1-2): 62-73.

Cook N J, Ciobanu C L, Brugger J, Etschmann B, Howard D L, de Jonge M D, Ryan C and Paterson D. 2012. Determination of the oxidation state of Cu in substituted Cu-In-Fe-bearing sphalerite via-XANES spectroscopy[J]. American Mineralogist, 97(2-3): 476-479.

Dai T G, Du G F, Zhang D X and Wang M Y. 2012. Indium distribution in Dachang tin-polymetallic deposit of Guangxi Province[J]. The Chinese Journal of Nonferrous Metals, 22(3): 703-714(in Chinese with English abstract).

Dill H G, Garrido M M, Melcher F, Gomez M C, Weber B, Luna L I and Bahr A. 2013. Sulfidic and non-sulfidic indium mineralization of the epithermal Au-Cu-Zn-Pb-Ag deposit San Roque (Provincia Rio Negro, SE Argentina)—with special reference to the "indium window" in zinc sulfide[J]. Ore Geology Reviews, 51: 103-128.

Guo Z J, Song Y T, Xu R T, Wang C W, Yang F, Wang Q L, Han W, Liu H H and Kong M. 2020. Characteristics of distribution and Enrichment of indium in Gejiu tin polymetallic ore-concentrated area in Yunnan Province[J]. Geoscience, DOI:10.19657/j.geoscience.1000-8527.2020.048.

Guo J. 2019. Tin mineralization events and fertility of granitoids in theYoujiang Basin, South China: The Gejiu and Dachang Sn-polymetalic districts as examples(Dissertation for Ph.D)[D]. Supervisor: Sun W D. Guangzhou: University of Chinese Academy of Sciences(Guangzhou Institute of Geochemistry,Chinese Academy of Sciences). 113-140(in Chinese with English abstract).

Frenzel M, Hirsch T and Gutzmer J. 2016. Gallium, germanium, indium, and other trace and minor elements in sphalerite as a function of deposit type—A meta-analysis[J]. Ore Geology Reviews, 76: 52-78.

Gaskov I V and Gushchina L V. 2020. Physicochemical Conditions of the formation of elevated indium contents in the ores of tin-sulfide and base-metal deposits in Siberia and Far East: Evidence from thermodynamic modeling[J]. Geochemistry International, 58(3): 291-307.

George L L, Cook N J and Ciobanu C L. 2016. Partitioning of trace elements in co-crystallized sphalerite-galena-chalcopyrite hydrothermal ores[J]. Ore Geology Reviews, 77: 97-116.

Gion A M, Piccoli P M and Candela P A. 2018. Partitioning of indium between ferromagnesian minerals and a silicate melt[J]. Chemical Geology, 500: 30-45.

Gion A M, Piccoli P M and Candela P A. 2019. Constraints on the formation of granite-related indium deposits[J]. Econ. Geol., 114(5): 993-1003.

Hu X Y, Bi X W, Shang L B, Hu R Z, Cai G S and Chen Y W. 2009. An experimental study of tin partition between melt and aqueous fluid in F/Cl-coexisting magma[J]. Science Bulletin, 54(6): 1087-1097.

Huang W T, Lianga H Y, Zhang J, Wu J, Chen X L and Ren L. 2019. Genesis of the Dachang Sn-polymetallic and Baoshan Cu ore deposits, and formation of a Cretaceous Sn-Cu ore belt from southwest China to western Myanmar[J]. Ore Geology Reviews, 112: 1-17.

Ishihara S, Hoshino K, Murakami H and Endo Y. 2006. Resource evaluation and some genetic aspects of indium in the Japanese ore deposits[J]. Resource Geology, 56(3): 347-364.

Ishihara S, Murakami H and Li X. 2011a. Indium concentration in zinc ores in plutonic and volcanic environments: examples at the Dulong and Dachang mines, South China[J]. Bulletin of the Geological Survey of Japan, 7/8(62): 259-272.

Ishihara S, Murakami H and Marquez-Zavalia M F. 2011b. Inferred indium resources of the Bolivian tin-polymetallic deposits[J]. Resource Geology, 61(2): 174-191.

Jin L Y. 2016. Metallogenesis of Chalukou porphyry Mo-vein type Zn-Pb mineralization system in northern Great Xing'an Range (Dissertation for Ph.D)[D]. Supervisor: Qin K Z and Li G M. Beijing: Chinese Academy of Sciences (Institute of Geology and Geophysics, Chinese Academy of Sciences). 201p(in Chinese with English abstract).

Jonsson E, Högdahl K, Majka J and Lindeberg T. 2013. Roquesite and associated indium-bearing sulfides from a Paleoproterozoic carbonate-hosted mineralization: Lindbom's prospect, Ergslagen, Sweden[J]. The Canadian Mineralogist, 51(4):629-641.

Keith M, Haase K M, Schwarz-Schampera U, Klemd R, Petersen S and Bach W. 2014. Effects of temperature, sulfur, and oxygen fugacity on the composition of sphalerite from submarine hydrothermal vents[J]. Geology, 42(8): 699-702.

Keppler H and Wyllie P J. 1991. Partitioning of Cu, Sn, Mo, W, U, and Th between melt and aqueous fluid in the systems haplogranite-H_2O-HCl and haplogranite-H_2O-HF[J]. Contributions to Mineralogy and Petrology, 109(2): 139-150.

Kojima S and Asahiko S. 1984. Phase relations in the central portion of the Cu-Fe-Zn-S system between 800 and 500℃[J]. Mineralogical Joumal, 12(1): 15-28.

Kojima S and Asahiko S. 1985. Phase relations in the Cu-Fe-Zn-S System between 500℃ and 300℃ under hydrothermal conditions[J]. Econ. Geol., 80: 158-171.

Lerouge C, Gloaguen E, Wille G and Bailly L. 2017. Distribution of In and other rare metals in cassiterite and associated minerals in Sn ± W ore deposits of the western Variscan Belt[J]. European Journal of Mineralogy, 29(4): 739-753.

Li H M, Wang D H, Zhang C Q, Chen Y C and Li L X. 2009. Characteristics of trace and rare earth elements in minerals from some typical lead-zinc deposits of Shaanxi Province[J]. Mineral Deposits, 28(4): 434-448(in Chinese with English abstract).

Li X F, Yasushi W and Mao J W. 2007. Research situation and economic value of indium deposits[J]. Mineral Deposits, 26(4): 475-480(in Chinese with English abstract).

Li X F, Yang F, Chen Z Y, Bu G J and Wang Y T. 2010. A tentative discussion on geochemistry and genesis of indium in Dachang tin ore district, Guangxi[J]. Mineral Deposits, 29(5): 903-914(in Chinese with English abs tract).

Li X F, Xu J, Zhu Y T and Lü Y H. 2019. Critical minerals of indium: Major ore types and scientific issues[J]. Acta Petrologica Sinica, 35: 3292-3302(in Chinese with English abstract).

Li X F, Zhu Y T and Xu J. 2020. Indium as a critical mineral: A research progress report[J]. Chinese Science Bulletin, Doi: https://doi.org/10.1360/TB-2020-0058.

Li Y B, Tao Y, Zhu F L, Liao M Y, Xiong F and Deng X Z. 2015. Distribution and existing state of indium in the Gejiu Tin polymetallic deposit, Yunnan Province, SW China[J]. Chinese Journal of Geochemistry, 34(4): 469-483.

Li Z Z, Qin K Z, Zhao J X, Li G M and Su S Q. 2019. Basic characteristics, research progresses and prospects of Sn-Ag-basemetal metallogenic system[J]. Acta Petrologica Sinica, 35(7):1979-1998.

Liu J P, Gu X P, Shao Y J, Feng Y Z and Lai J Q. 2016. Indium mineralization in copper-tin stratiform skarn ores at the Saishitang-Rilonggou ore field, Qinghai, northwest China[J]. Resource Geology, 66(4): 351-367.

Liu J P. 2017. Indium mineralization in a Sn-Poor skarn deposit: A case study of the Qibaoshan deposit, South China[J]. Minerals, 7(5): 76.

Liu J P, Rong Y N, Zhang S G, Liu Z F and Chen W K. 2017. Indium mineralization in the Xianghualing Sn-polymetallic orefield in southern Hunan, southern China[J]. Minerals, 7(9): 173.

Liu J P, Rong Y N, Gu X P, Shao Y J, Lai J Q and Chen W K. 2018. Indium mineralization in the Yejiwei Sn-polymetallic deposit of the Shizhuyuan orefield, southern Hunan, China[J]. Resource Geology, 68(1): 22-36.

Liu L, Hu R Z, Zhong H, Yang J H, Kang L F, Zhang X C, Fu Y Z, Mao W and Tang Y W. 2020. Petrogenesis of multistage S-type granites from the Malay Peninsula in the southeast Asian tin belt and their relationship to Tethyan evolution[J]. Gondwana Research. https://doi.org/10.1016/j.gr.2020.02.013.

Liu Y J, Cao L M, Li Z J, Wang H N, Chu T Q and Li J R. 1984. Element geochemistry[M]. Beijing: Science Press. 387-393(in Chinese).

Lockington J A, Cook N J and Ciobanu C L. 2014. Trace and minor elements in sphalerite from metamorphosed sulphide deposits[J]. Mineralogy and Petrology, 108(6): 873-890.

London D. 1997. Estimating abundances of volatile and other mobile components in evolved silicic melts through mineral-melt equilibria[J]. Journal of Petrology, 38: 1691-1706.

Lopez L, Jovic S M, Guido D M, Permuy Vidal C, Páez G N and Ruiz R. 2015. Geochemical distribution and supergene behavior of indium at the Pingüino epithermal polymetallic vein system, Patagonia, Argentina[J]. Ore Geology Reviews, 64: 747-755.

Mao J W, Yang Z X, Xie G Q, Yuan S D and Zhou Z H. 2019. Critical minerals: International trends and thinking[J]. Mineral Deposits, 38(4): 689-698(in Chinese with English abstract).

Moura M A, Botelho N F, Olivo G R, Kyser K and Pontes R M. 2014. Genesis of the Proterozoic Mangabeira tin-indium mineralization, Central Brazil: Evidence from geology, petrology, fluid inclusion and stable isotope data[J]. Ore Geology Reviews, 60: 36-49.

Murakami H and Ishihara S. 2013. Trace elements of Indium-bearing sphalerite from tin-polymetallic deposits in Bolivia, China and Japan: A femto-second LA-ICPMS study[J]. Ore Geology Reviews, 53: 223-243.

Ohta E. 1989. Occurrence and chemistry of indium-containing minerals from the Toyoha mine, Hokkaido, Japan[J]. Mining Geology, 39:355-371.

Pavlova G G, Palessky S V, Borisenko A S, Vladimirov A G, Seifert T and Phan L A. 2015. Indium in cassiterite and ores of tin deposits[J]. Ore Geology Reviews, 66: 99-113.

Pei Q M, Cao H W, Zhang S T, Tang L, Xu T, Li J J, Zhang X H and Guo N N. 2015. Trace element geochemistry of the Luotuoshan sulfur-zinc polymetallic deposit in Luanchuan, western Henan, and its geological implications[J]. Acta Petrologica et Mineralogica, 34(5): 741-754(in Chinese with English abstract).

Peterson E C and Mavrogenes J A. 2014. Linking high-grade gold mineralization to earthquake-induced fault-valve processes in the Porgera gold deposit, Papua New Guinea[J]. Geology, 42(5): 383-386.

Pearson R G. 1963. Hard and soft acids and bases [J]. Journal of The American Chemical Society, 85: 3533-3539.

Pi Q H, Hu R Z, Wang D H, Miao B K, Qin X F and Chen H Y.2015. Enrichment of indium in west ore belt of Dachang orefield: Evidence from ore textures and sphalerite geochemistry[J]. Mineral Deposits, 34(2): 379-396(in Chinese with English abstract).

Qian M X. 2017. The study of geological characteristics, geochemical characteristics and Metallogenic system of The Bianjiadayuan Pb-Zn polymetallic deposit in Inner Mongolia, China(Dissertation for Master degree) [D]. Supervisor: Yang Y Q and Zhang A L. Beijing: China University of Geosciences(Beijing). 43-49(in Chinese with English abstract).

Romer R L and Kroner U. 2016. Phanerozoic tin and tungsten mineralization—Tectonic controls on the distribution of enriched protoliths and heat sources for crustal melting[J]. Gondwana Research, 31: 60-95.

Romer R L and Kroner U. 2014. Sediment and weathering control on the distribution of Paleozoic magmatic tin-tungsten mineralization[J]. Mineralium Deposita, 50(3): 327-338.

Rudnick R L and Gao S. 2014. 4.1 - Composition of the continental crust[A]. In: Holland H D and Turekian K K, eds.Treatise on geochemistry (Second Edition)[M]. Oxford:Elsevier. 1-51.

Schwarz-Schampera U. 2014. Indium[A]. In: In: G. Gun, ed. "Critical metals handbook" [M]. John Wiley & Sons. 204-209.

Schwarz-Schampera U and Herzig P M. 2002. Indium:Geology, mineralogy, and economics[M]. Springer, Berlin, Heidelberg.

Seifert T and Sandmann D. 2006. Mineralogy and geochemistry of indium-bearing polymetallic vein-type deposits: Implications for host minerals from the Freiberg district, eastern Erzgebirge, Germany[J]. Ore Geology Reviews, 28(1): 1-31.

Seward T M, Henderson C and Charnock J M. 2000. Indium(Ⅲ) chloride complexing and solvation in hydrothermal solutions to 350 degrees C: An EXAFS study[J]. Chemical Geology, 167(1-2): 117-127.

Shannon R D. 1976. Revised effective ionic radii and systematic study of inter atomic distances in Halides and Chalcogenides[J]. Acta Crystallographica, 32: 751-767.

Shimizu T and Morishita Y. 2012. Petrography, chemistry, and near-infrared microthermometry of indium-bearing sphalerite from the Toyoha polymetallic deposit, Japan[J]. Econ. Geol., 107(4): 723-735.

Simons B, Andersen J C Ø, Shail R K and Jenner F E. 2017. Fractionation of Li, Be, Ga, Nb, Ta, In, Sn, Sb, W and Bi in the peraluminous Early Permian Variscan granites of the Cornubian Batholith: Precursor processes to magmatic-hydrothermal mineralisation[J]. Lithos, 278-281: 491-512.

Sinclair W D, Kooiman G J A, Martin D A and Kjarsgaard I M. 2006. Geology, geochemistry and mineralogy of indium resources at Mount Pleasant, New Brunswick, Canada[J]. Ore Geology Reviews, 28(1): 123-145.

Sugaki A, Kitakaze A and Kojima S. 1987. Bulk compositions of intimate intergrowths of chalcopyrite and sphalerite and their genetic implications[J]. Mineralium Deposita, 22(1): 26-32.

Sui Q L, Zhu L H, Sun S J, Chen D H, Zhao X J and Wang Z F. 2020. The geochemical behavior of tin and Late Cretaceous tin mineralization in South China[J]. Acta Petrologica Sinica, 36(01): 23-34 (in Chinese with English abstract).

Sun S S. 1982. Chemical-composition and origin of the Earths primitive mantle[J]. Geochimica et Cosmochimica Acta, 46(2): 179-192.

Tao L C. 2017. Research on the supply and demand pattern of global indium resources in the future (Dissertation for Master degree)[D]. Supervisor: Li J W and Li Y. Beijing: China University of Geosciences(Beijing). 45-49(in Chinese with English abstract)45-49.

Tian H H, Zhang S T, Cao H W, Han J W, Lü P D and Zhang Y H. 2015. Geochemical characteristics of trace elements of sphalerite in the Chitudian Pb-Zn deposit , West Henan Province[J]. Bulletin of Mineralogy, Petrology and Ceochermistry. 34(2): 334-342(in Chinese with English abstract).

Torres B, Melgarejo J, Torró L, Camprubí A, Castillo-Oliver M, Artiaga D, Campeny M, Tauler E, Jiménez-Franco A, Alfonso P, Osvaldo and Arce-Burgoa. 2019a. The Poopó polymetallic epithermal deposit, Bolivia: Mineralogy, genetic constraints, and distribution of critical elements[J]. Minerals, 9(8): 472.

Torró L, Cazorla M, Melgarejo J C, Camprubí A, Tarrés M, Gemmrich L, Campeny M, Artiaga D, Torres B, Martínez Á, Mollinedo D, Alfonso P and Arce-Burgoa O R. 2019b. Indium mineralization in the volcanic dome-hosted Ánimas-Chocaya-Siete Suyos polymetallic deposit, Potosí, Bolivia[J]. Minerals, 9(10): 604.

Torró L, Melgarejo J, Gemmrich L, Mollinedo D, Cazorla M, Martínez Á, Pujol-Solà N, Farré-De-Pablo J, Camprubí A, Artiaga D, Torres B, Alfonso P and Arce O. 2019c. Spatial and temporal controls on the distribution of indium in xenothermal vein-deposits: The Huari Huari district, Potosí, Bolivia[J]. Minerals, 9(5): 304.

Tu G C. 2004. The geochemistry and ore-forming mechanism of the dispersed elements[M].Beijing:Geological Publishing House.317-367(in Chinese).

Valkama M, Sundblad K, Nygård R and Cook N. 2016a. Mineralogy and geochemistry of indium-bearing polymetallic veins in the Sarvlaxviken area, Lovisa, Finland[J]. Ore Geology Reviews, 75: 206-219.

Valkama M, Sundblad K, Cook N J and Ivashchenko V I. 2016b. Geochemistry and petrology of the indium-bearing polymetallic skarn ores at Pitkäranta, Ladoga Karelia, Russia[J]. Mineralium Deposita, 51: 823-839.

Wang D P, Zhang Q, Wu L Y, Ye L, Liu Y P and Lan J B.2019. The relationship between indium and tin, copper, lead and zinc in granite and its significance to indium mineralization[J]. Acta Petrologica Sinica, 35(11): 3317-3332(in Chinese with English abstract).

Wang S H, H S and Huang H X. 2014. Discovery of roquesite in the Zijinshan Cu-Au deposit, Fujian Province, and its implications for deep exploration[J]. Geological Bulletin of China, 33(9): 1425-1429(in Chinese with English abstract).

Wei C, Huang Z L, Yan Z F, Hu Y S and Ye L. 2018. Trace element contents in sphalerite from the Nayongzhi Zn-Pb deposit, Northwestern Guizhou, China: Insights into incorporation mechanisms, metallogenic temperature and ore genesis[J]. Minerals, 8(11): 490.

Werner T T, Mudd G M and Jowitt S M. 2017. The world's by-product and critical metal resources part Ⅲ: A global assessment of indium[J]. Ore Geology Reviews, 86: 939-956.

Wolf M, Romer R L, Franz L and López-Moro F J. 2018. Tin in granitic melts: The role of melting temperature and protolith cormposition[J]. Lithos, 310-311: 20-30.

Wood S A and Samson I M. 2006. The aqueous geochemistry of gallium, germanium, indium and scandium[J]. Ore Geology Reviews, 28 (1): 57-102.

Wu Y T. 2009. Study on the enrichment regularity of indium in Dachang ore-field, Guangxi (Dissertation for Ph. D) [D]. Supervisor: Chen S L. Changsha: Central South University. 1-124(in Chinese with English abstract).

Xing B, Xiang J F, Ye H S, Chen X D, Zhang G S, Yang C Y, Jin X and Hu Z Z. 2017. Genesis of Luotuoshan sulfur polymetallic deposit in western Henan Province: Evidence from trace elements of sulfide revealed by using LA-ICP-MS in lamellar ores[J]. Mineral Deposits, 36(1): 83-106(in Chinese with English abstract).

Xiong Y Q, Liu J P, Shao Y J, Feng Y Z, Xing X H and Hu S X. 2015. Distribution of Qibaoshan copper polymetallic deposit in northeast Hunan Province[J]. Acta Mineralogica Sinica, 35(Supp.): 355 (in Chinese).

Xu B. 2015. Multi-stage magmatism in Laoiunshan of SE Yunnan, China: Geochemistry, geodynamic implication and related mineralization(Dissertation for Ph. D) [D]. Supervisor: Jiang S Y. Nanjing: Nanjing University. 21-68(in Chinese with English abstract).

Xu J and Li X F. 2018. Spatial and temporal distributions, metallogenic backgrounds and processes of indium deposits[J]. Acta Petrologica Sinica, 34(12): 3611-3626(in Chinese with English abstract).

Xu J, Cook N J, Ciobanu C L, Li X F, Kontonikas-Charos A, Gilbert S and Lü Y H. 2020a. Indium distribution in sphalerite from sulfide-oxide-silicate skarn assemblages: A case study of the Dulong Zn-Sn-In deposit, southwest China[J]. Mineralium Deposita, Doi: https://doi.org/10.107/s00 126-020-00972-y.

Xu J, Ciobanu C L, Cook N J, Slattery A and Li X F. 2020b. Phase relationships in the system ZnS-CuInS: Insights from a nanoscale study of indium-bearing sphalerite[J]. American Mineralogist, Doi: https:/ldoi.org/10.2138lam-2020-7488.

Xu R, Deng J, Cheng H Y, Cui X L and Wang C B. 2018. Geochronology, geochemistry and geodynamic setting of Late Cretaceous magmatism and Sn mineralization in the western South China and Tengchong Baoshan[J]. Acta Petrologica Sinica, 34(5): 1271-1284 (in Chinese with English abstract).

Xu S H, Ren T, Lv C L, Shi W M and Wang C Y. 2019. Research progress on the cretaceous highly fractionated S-type granite in the southeastern Yunnan, China[J]. Acta Mineralogica Sinica, 39(2): 149-165(in Chinese with English abstract).

Yang, J H, Zhou M F, Hu R Z, Williams-Jones A E, Liu L, Zhang X C, Fu Y Z and Mao W. 2020. Granite-related Tin metallogenic events and key controlling factors in Peninsular Malaysia, southeast Asia: New insights from cassiterite U-Pb dating and zircon geochemistry[J]. Econ. Geol., 115 (3): 581-601.

Ye L, Cook N J, Ciobanu C L, Liu Y P, Zhang Q, Liu T G, Gao W, Yang Y L and Danyushevskiy L. 2011. Trace and minor elements in sphalerite from base metal deposits in South China: A LA-ICPMS study[J]. Ore Geology Reviews, 39(4): 188-217.

Ye L, Liu Y P, Zhang Q, Bao T, He F, Wang X J, Wang D P and Lan J B. 2017. Trace and rare earth elements characteristics of sphalerite in Dulong super large Sn-Zn polymetallic ore deposit, Yunnan Province[J]. Journal of Jilin University(Earth Science Edition), 47 (3): 734-750(in Chinese with English abstract).

Yuan B, Zhang C Q, Yu H J, Yang Y M, Zhao Y X, Zhu C C, Ding Q F, Zhou Y B, Yang J C and Xu Y. 2018a. Element enrichment characteristics: Insights from element geochemistry of sphalerite in Daliangzi Pb-Zn deposit, Sichuan, southwest China[J]. Journal of Geochemical Exploration, 186: 187-201.

Yuan S D, Mao J W, Zhao P L and Yuan Y B. 2018b. Geochronology and petrogenesis of the Qibaoshan Cu-polymetallic deposit, northeastern Hunan Province: Implications for the metal source and metallogenic evolution of the intracontinental Qinhang Cu-polymetallic belt, South China[J]. Lithos, 302-303: 519-534.

Yuan S D, Williams-Jones A E, Romer R L, Zhao P L and Mao J W. 2019. Protolith-related thermal controls on the decoupling of Sn and W in Sn-W metallogenic Provinces: Insights from the Nanling Region, China[J]. Econ. Geol., 114(5): 1005-1012.

Zhang L P, Zhang R, Hu Y B, Liang J L, Ouyang Z X, He J J, Chen Y X, Guo J and Sun W D. 2017. The formation of the Late Cretaceous Xishan Sn-W deposit, South China: Geochronological and geochemical perspectives[J]. Lithos, 290-291: 253-286.

Zhang L P, Zhang R Q, Wu K, Chen Y X, Li C Y, Hu Y B, He J J, Liang J L and Sun W D. 2018. Late Cretaceous granitic magmatism and mineralization in the Yingwuling W-Sn deposit, South China: Constraints from zircon and cassiterite U-Pb geochronology and whole-rock geochemistry[J]. Ore Geology Reviews, 96: 115-129.

Zhang Q. 1987. Trace elements in galena and sphalerite and their geochemical significance in distinguishing the genetic types of Pb-Zn ore deposits[J]. Chinese Journal of Geochemistry, 6(2): 177-190.

Zhang Q, Zhan X Z, Pan J Y and Shao S X. 1998. Geochemical enrichment and mineralization of indium[J]. Chinese Journal of Geochemistry, 17(3): 221-225.

Zhang Q, Liu Z H, Zhan X Z and Shao S X. 2003. Specialization of ore deposit types and minerals for enrichment of indium[J]. Mineral Deposits, 22(3): 309-316(in Chinese with English abstract).

Zhang Q, Liu Z H, Zhan X Z and Shao S X. 2004. Trace element geochemistry of Meng'entaolegai Ag-Pb-Zn-in deposit, Inner Mongolia, China[J]. Acta Mineralogica Sinica. 24(1): 39-47(in Chinese with English abstract).

Zhang Q, Zhu X Q, He Y H, Jiang J J and Wang D P. 2006. Indium enrichment in the Meng'entaolegai Ag-Pb-Zn deposit, Inner Mongolia, China[J]. Resource Geology, 56(3): 337-346.

Zhang Q, Zhu X Q, He Y L and Zhu Z H. 2007. In, Sn, Pb and Zn contents and their relationships in ore-forming fluids from some in-rich and in-poor deposits in China[J]. Acta Geologica Sinica (English Edition), 81(3): 450-462.

Zhang Z, Tang J X, Lin B, Zheng W B, Lin X, Tang X Q, Gao Y M, Wang Y Y, Yang H H and Huang J. 2016. Geochemical characteristics of trace elements of sphalerite in the Zhaxikang deposit, southern Tibet, and their geological significances[J]. Bulletin of Mineralogy, Petrology and Geochemistry, 35(6): 1203-1216(in Chinese with English abstract).

Zhao Y Y, Liu Y, Cui Y B, Lü L N, Song L and Qu X M. 2010. Discovery and significance of indium mineralization belt in Bangong Lake—Nujiang River metallogenic belt and adjacent regions in Xizang(Tibet)[J]. Geological Review, 56(4): 568-578(in Chinese with English abstract).

Zhao Z Y. 2017. The magmatism and genesis of Dulong Zn-Sn polymetallic deposit in Maguan, Yunnan Province(Dissertation for Ph. D)[D]. Supervisor: Ding J. Beijing: China University of Geosciences (Beijing). 30-52(in Chinese with English abstract).

Zhu X Q, Zhang Q, He Y L and Zhu C H. 2006. Relationships between indium and tin, zinc and lead in ore-forming fluid from the indium-rich and -poor deposits in China[J]. Geochimica, 35(1): 6-12 (in Chinese with English abstract).

附中文参考文献

曹华文,张寿庭,郑硌,刘瑞萍,田浩浩,张旭晃,李军军. 2014. 河南栾川矿集区中鱼库(铅)锌矿床闪锌矿微量元素地球化学特征[J]. 矿物岩石, 34(3): 50-59.

陈翠华,宋志娇,杨玉龙,杨德平,辜鹰,陈宵杰. 2019. 贵州习水洞子沟铅锌矿床闪锌矿微量元素特征与成因[J]. 矿物学报, 39(5): 1-9.

陈薇. 2019. 云南个旧花岗岩浆作用及其成矿意义(硕士论文)[D]. 导师: 董国臣,丁孝忠. 北京:中国地质大学(北京). 38-52.

承斯. 2011. 江西冷水坑银铅锌矿下鲍矿区闪锌矿的矿物学特征研究(硕士论文)[D]. 导师: 何明跃. 北京: 中国地质大学(北京). 18-31.

程泽锋. 2015. 闪锌矿锌同位素和微量元素在岩浆热液矿床中的初步研究(硕士论文)[D]. 导师:杨永强,张安立. 北京: 中国地质大学(北京). 14-20.

戴塔根,杜高峰,张德贤,王明艳. 2012. 广西大厂锡多金属矿床中铟的富集规律[J]. 中国有色金属学报, 22(3): 703-714.

郭佳. 2019. 华南右江盆地锡成矿事件与花岗岩锡成矿能力——以个旧和大厂锡多金属矿区为例(博士论文)[D]. 导师: 孙卫东. 广州: 中国科学院大学(中国科学院广州地球化学研究所). 113-140.

郭志娟,宋云涛,徐仁廷,王成文,杨帆,王乔林,韩伟,刘华忠,孔牧. 2020. 云南个旧锡多金属矿集区稀散元素铟的分布富集特征[J]. 现代地质. DOI:10.19657/j.geoscience.1000-8527.2020.048.

金露英. 2016. 大兴安岭北段岔路口斑岩钼矿-脉状锌铅矿成矿系统结构与成矿作用研究(博士论文)[D]. 导师: 秦克章,李光明. 北京: 中国科学院大学(中国科学院地质与地球物理研究所). 201页.

李厚民,王登红,张长青,陈毓川,李立兴. 2009. 陕西几类重要铅锌矿床的矿物微量元素和稀土元素特征[J]. 矿床地质, 28(4): 434-448.

李晓峰,Yasushi Watanabe,毛景文. 2007. 铟矿床研究现状及其展望[J]. 矿床地质, 26(4): 475-480.

李晓峰,杨锋,陈振宇,卜国基,王义天. 2010. 广西大厂锡矿铟的地球化学特征及成因机制初探[J]. 矿床地质, 29(5): 903-914.

李晓峰,徐净,朱艺婷,吕友虎. 2019. 关键矿产资源铟:主要成矿类型及关键科学问题[J]. 岩石学报, 35(11): 3292-3302.

李晓峰,朱艺婷,徐净. 2020. 关键矿产资源铟研究进展[J]. 科学通报, doi:10.1360/TB-2020-0058

李真真,秦克章,赵俊兴,李光明,苏仕强. 2019. 锡-银多金属成矿系统的基本特征、研究进展与展望[J]. 岩石学报. 35(7): 1979-1998.

刘英俊,曹励明,李兆麟,王鹤年,储同庆,李景荣. 1984. 元素地球化学[M]. 北京:科学出版社.387-393.

毛景文,杨宗喜,谢桂青,袁顺达,周振华. 2019. 关键矿产——国际动向与思考[J]. 矿床地质, 38(4): 689-698.

裴秋明,张寿庭,曹华文,唐利,许腾,李军军,张旭晃,郭娜娜. 2015. 豫西栾川县骆驼山硫锌多金属矿床闪锌矿微量元素地球化学特征及其地质意义[J]. 岩石矿物学杂志, 34(5): 741-754.

皮桥辉,胡瑞忠,王登红,缪秉魁,覃小峰,陈宏毅. 2015. 广西大厂锡多金属矿田西矿带稀散元素铟的富集规律研究——来自矿石组构和闪锌矿地球化学的证据[J]. 矿床地质, 34(2): 379-396.

钱孟轩. 2017. 内蒙古边家大院铅锌多金属矿矿床地质特征、地球化学特征及成矿模式(硕士论文)[D]. 导师: 杨永强,张安立. 北京: 中国地质大学(北京). 43-49.

隋清霖,祝红丽,孙赛军,陈登辉,赵晓健,王钊飞. 2020. 锡的地球化学性质与华南晚白垩世锡矿成因[J]. 岩石学报, 36(1): 23-34.

陶兰初. 2017. 维拉斯托多金属矿床硫化物LA-ICP-MS微量元素特征及其意义(硕士论文)[D]. 导师: 侯青叶. 北京: 中国地质大学(北京). 45-49.

田浩浩,张寿庭,曹华文,韩江伟,吕鹏瑞,张云辉. 2015. 豫西赤土店铅锌矿床闪锌矿微量元素地球化学特征[J]. 矿物岩石地球化学通报, 34(2): 334-342.

涂光炽,等. 2004. 分散元素地球化学及成矿机制[M]. 北京: 地质出版社. 317-367.

王大鹏,张乾,武丽艳,叶霖,刘玉平,蓝江波. 2019. 花岗岩中铟与锡铜铅锌的关系及其富集成矿意义[J]. 岩石学报, 35(11): 3317-3332.

王少怀,何升,黄宏祥. 2014. 硫铜铜矿在福建紫金山铜金矿床的发现及深部找矿意义[J]. 地质通报, 33(9): 1425-1429.

伍永田. 2009. 广西大厂矿田铟的富集规律研究(博士论文)[D]. 导师: 陈松龄. 长沙: 中南大学. 1-124.

邢波,向君峰,叶会寿,陈小丹,张国苏,杨晨英,金雪,胡志中. 2017. 豫西骆驼山硫多金属矿床的成因——来自纹层状矿石中硫化物LA-ICP-MS微量元素证据[J]. 矿床地质, 36(1): 83-106.

熊伊曲,刘建平,邵拥军,冯雨周,星显宏,胡祥昭. 2015. 湘东北七宝山铜多金属矿床铟的分布规律[J]. 矿物学报, 35(S1): 355.

徐斌. 2015. 滇东南老君山地区多期岩浆作用地球化学(博士论文)[D]. 导师: 蒋少涌. 南京: 南京大. 学21-68.

徐净,李晓峰. 2018. 铟矿床时空分布、成矿背景及其成矿过程[J]. 岩石学报, 34(12): 3611-3626.

徐容,邓军,程韩宇,崔晓琳,王传斌. 2018. 华南板块西缘和腾冲-保山地块晚白垩世岩浆活动及Sn成矿作用对比:年代学、地球化学和动力学背景[J]. 岩石学报, 34(5): 1271-1284.

许赛华,任涛,吕昶良,石伟民,王彩艳. 2019. 滇东南白垩纪高分异S型花岗岩研究进展[J]. 矿物学报, 39(2): 149-165.

叶霖,刘玉平,张乾,鲍谈,何芳,王小娟,王大鹏,蓝江波. 2017. 云南都龙超大型锡锌多金属矿床中闪锌矿微量及稀土元素地球化学特征[J]. 吉林大学学报(地球科学版), 47(3): 734-750.

张含,胡家刚,蔡明海,邵主助,刘嘉兴,胡志戍. 2019. 广西铜坑富锡铟矿床中闪锌矿的微量元素赋存特征[J]. 科学技术与工程, 19(19): 34-45.

张乾,刘志浩,战新志,邵树勋. 2003. 分散元素铟富集的矿床类型和矿物专属性[J]. 矿床地质, 22(3): 309-316.

张乾,刘志浩,战新志,邵树勋. 2004. 内蒙古孟恩陶勒盖银铅锌铟矿床的微量元素地球化学[J]. 矿物学报, 24(1): 39-47.

张伟波,陈秀法,陈玉明,曹艳华,何学洲,黄霞,邓攀. 2019. 全球铟矿资源供需现状与我国开发利用建议[J]. 矿产保护与利用, 39(5): 1-8.

张政,唐菊兴,林彬,郑文宝,林鑫,唐晓倩,高一鸣,王艺云,杨欢欢,黄建. 2016. 藏南扎西康矿床闪锌矿微量元素地球化学特征及地质意义[J]. 矿物岩石地球化学通报, 35(6): 1203-1216.

赵元艺,刘妍,崔玉斌,吕立娜,宋亮,曲晓明. 2010. 西藏班公湖-怒江成矿带与邻区铟矿化带的发现及意义[J]. 地质论评, 56(4): 568-578.

赵震宇. 2017. 云南省马关县都龙锌锡多金属矿床——岩浆作用及矿床成因研究(博士论文)[D]. 导师: 丁俊. 北京: 中国地质大学(北京). 30-52.

朱笑青,张乾,何玉良,祝朝辉. 2006. 富铟及贫铟矿床成矿流体中铟与锡铅锌的关系研究[J]. 地球化学, 35(1): 6-12.