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湘南芙蓉锡矿床首次发现斧石:一个重要的含 B 矿物 及其指示意义^{*}

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Abstract Most of the Sn mineralization worldwide is commonly associated with highly-fractionated granites, especially with those granites rich in volatile components such as F, Cl, Li and B. However, previous researches paid little attention to the volatile B. The giant Furong tin deposit, located in the middle part of Nanling Region, is of great significance in China. Axinite was found in skarn in this deposit for the first time, which provides an ideal opportunity to explore the role of volatile B during the formation of tin deposit. By means of detailed mineralogical, petrological and geochemical studies, the petrographic characteristics, crystal structures and chemical compositions of axinites from Furong were depicted, followed by a discussion on the relationship between the volatile B and granite emplacement, as well as tin mineralization in this area. The axinite from Furong deposit is lilac brown in color, massive in texture, hard, colorless and light yellow under microscope, with self-shaped wedge shape, high protrusion and low interference color, and intergrown with vesuvianite, fluorite, garnet and sphene. It was revealed that the axinite belongs to axinite-(Fe), with a general $chemical \ formula \ of \ Ca_{2.\,22} \ (\ Fe_{0.\,52} \ , \ Mn_{0.\,41} \ , \ Mg_{0.\,13} \)_{1.\,06} \ Al_{2.\,11} \ B_{0.\,72} \ Si_{3.\,98} \ O_{15.\,5} \ . \ There \ are \ various \ B-rich \ minerals \ including \ axinite \ ,$ tourmaline and ludwigite in the Furong deposit, indicating that the Qitianling granitic pluton is rich in boron. The enrichment of the volatile B in granite can reduce the magma viscosity, and increase the degree of magma differentiation, which helps the enrichment of incompatible elements like Sn in the residual melt during the magma evolution. Boron is also closely related to tin mineralization, since the B enrichment can facilitate the extraction of Sn from source rocks, improving the Sn concentrations in the primary magma. Like F and Cl, boron can form a complex with Sn, which is beneficial to the long-distance migration for tin; and they can be enriched in residual melt during magma evolution because of similar geochemical behaviors of B and Sn during the fractional crystallization, and these magmas are considered to be the sources of the mineralizing fluid responsible for tin mineralization. In addition, with the continuous discovery of B-bearing minerals in the Furong tin deposit, it indicates that there is a good potential for the prospecting of associated boron ores in the studied area.

Key words Axinite; Mineralogical characteristics; Implication for tin mineralization; Furong tin deposit; Southern Hunan

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摘 要 世界上绝大部分锡矿床均与富 F、Cl、Li、B 等挥发份的高分异花岗岩有关,前人对 F、Cl、Li 等组份在花岗质岩浆演 化及锡成矿过程中的作用已有较为深入的认识,但对挥发份 B 关注较少。南岭中段的芙蓉超大型锡矿床是我国重要锡矿产 地,我们首次在该矿床发现了硼硅酸盐矿物中罕见的斧石,为研究挥发份 B 对锡成矿的作用提供了机会。通过详细的岩石 学、矿物学和地球化学研究,揭示了斧石的产出特征、晶体结构和化学成分特征,进而探讨了挥发份 B 与该区花岗岩成岩成矿 的关系。芙蓉锡矿床新发现的斧石为丁香褐色、块状构造、硬度较大,显微镜下呈无色、浅黄色等,主要为自形尖劈状的楔形、 长条状等自形结构、正高突起、干涉色较低,与符山石、萤石、石榴子石、榍石等矿物共生。电子探针分析表明,芙蓉矿床的斧 石属铁斧石,其平均化学式为 Ca₂₂(Fe_{0.52},Mn_{0.41},Mg_{0.13})_{1.06}Al₂₁₁B_{0.72}Si_{3.98}O_{15.5}。结合前人研究成果,芙蓉矿床斧石、电气石、 硼镁铁矿等富 B 矿物的广泛产出,指示了骑田岭花岗岩富含挥发份 B;硅酸盐熔体中挥发份 B 的存在,能降低岩浆粘度,增加 岩浆的结晶分异程度,延长岩浆寿命,进而有利于 Sn 等不相容元素在岩浆演化过程中向残余熔体富集。B 与锡成矿的关系密 切,岩浆中的 B 能提高源区 Sn 的萃取效率,增加原始岩浆中 Sn 的含量;B 能形成锡的络合物,有利于锡的长距离运移;B 与 Sn 具有相似的地球化学行为,在岩浆演化过程中,富集于残余熔体中,进一步演化后富集于成矿流体中。此外,在芙蓉锡矿床,随着含 B 矿物的不断被发现,表明该矿床可能具有寻找伴生硼矿的潜力。

关键词 斧石;矿物学特征;指示意义;芙蓉锡矿床;湘南

中图法分类号 P578.93;P618.44

锡,作为稀有金属,在地壳中的丰度很低,其上地壳的丰 度仅1.7×10⁻⁶(Rudnick and Gao,2003),但我国锡矿资源丰 富,其产量和储量均稳居世界首位(陈骏等,2000;陈郑辉等, 2015;Mao et al.,2019;蒋少涌等,2020;袁顺达等,2020)。我 国锡矿资源主要集中分布于华南地区,该地区虽面积不足世 界陆地总面积的1%,但却集中了全球22%的锡矿资源(陈 骏等,2000;袁顺达,2017;隋清霖等,2020;Mao et al.,2021)。

据统计,全球 95% 以上的锡矿床与花岗岩有着直接或间 接的关系(Lehmann, 1990; 陈骏等, 2000; Yuan et al., 2008; Kamilli et al., 2017; Zhao et al., 2018; 隋清霖等, 2020; 袁顺达 和赵盼捞, 2021); 特别是那些富 Li、F、B 的高分异花岗岩与 锡矿关系密切,通常被认为是锡成矿的物质提供者(朱金初 等, 2002; Yuan et al., 2008; 王汝成等, 2008; 隋清霖等, 2020; Zhao et al., 2022a)。目前人们对富 Li、F 花岗岩与锡矿的关 系已进行了较多研究(Thomas et al., 2000; 王联魁等, 2000; 朱金初等, 2002; 张德会等, 2004; 袁顺达, 2017), 但对富 B 花 岗岩研究较少, 挥发份 B 与花岗岩成岩、成矿的关系仍不 清楚。

斧石为三斜晶系的硼硅酸盐矿物,尽管在砂卡岩和其它 接触变质岩中均可产出(Grew,1996;Andreozzi et al.,2000; Frost et al.,2007;Sun et al.,2020),但由于其产出数量较少, 目前国内外有关斧石的研究并不多;且前人工作主要侧重于 斧石的成分、结构及分类等方面的研究(Sanero and Gottardi, 1968;Lumpkin and Ribbe,1979;Pringle and Kawachi,1980; Andreozzi et al.,2000,2004;Filip et al.,2006,2008;Matsubara et al.,2011),较少涉及其与成矿的关系。湖南芙蓉锡矿床位 于南岭中段骑田岭岩体的南缘(图1),前人已对其矿床地质 特征(许以明等,2000;黄革非等,2001;王登红等,2003;蔡锦 辉等,2004)、花岗岩成因(王联魁等,1982;朱金初等,2003; Zhao et al.,2005;邓希光等,2005;Chen et al.,2021)、成岩成 矿时代(毛景文等,2004;李华芹等,2006;彭建堂等,2007;朱 金初等,2009;袁顺达等,2010;Yuan et al.,2011;王志强等, 2014;Chen et al.,2021,2022a;Xing et al.,2022;Zhang et al., 2022)、成矿流体(李兆丽等,2006;毕献武等,2008;双燕等, 2009;单强等,2011,2014;王志强等,2014;Deng et al.,2022; Chen et al.,2023)和矿床成因(蒋少涌等,2006;Li et al., 2007;Chen et al.,2022b)等方面进行了详细的研究,但针对 该区花岗岩及岩浆期后热液体系中挥发份的研究较少,尤其 是挥发份 B 在锡成矿过程中所起的作用,目前仍不清楚。最 近我们首次在芙蓉矿区发现了斧石,该矿区斧石、电气石等 富 B 矿物的广泛存在,表明与该锡矿有关的骑田岭花岗岩富 含挥发份 B,这为研究挥发份 B 与花岗岩成岩、成矿关系提 供了理想的场所。因此,本文试图通过对该区新发现的斧石 进行系统的矿相学、矿物晶体结构和化学成分研究,进而探 讨挥发份 B 在成岩、成矿过程中的作用,以便揭示富 B 花岗 岩与锡矿的关系。

1 地质背景

1.1 骑田岭岩体

骑田岭岩体分布于华南腹地的南岭地区,在大地构造上 位于华夏板块的西侧(图1),是湘南地区出露面积最大的花 岗质岩体。该岩体大体呈等轴状,侵位于晚古生代-中生代 的碳酸盐岩和碎屑岩中,总出露面积约为520km²(图2a)。 骑田岭岩体为三阶段侵入的复式岩体(朱金初等,2009),按 侵入时间从早到晚,该岩体的岩性为中-粗粒角闪黑云母花 岗岩、中粒黑云母花岗岩和细粒花岗岩(图2a);大部分学者 认为前两种岩性的花岗岩与该区锡矿关系密切(朱金初等, 2003,2009;李华芹等,2006;赵葵东等,2006;李鸿莉等,2007; Yuan et al.,2011;Deng et al.,2022),但最新研究发现,晚期 侵入的细粒花岗岩可能与锡成矿关系更为直接(Chen et al., 2021,2022a)。该岩体的化学成分具有 SiO₂、Al₂O₃、Na₂O + K₂O、FeO 含量较高、分异指数较大、富含挥发份(F、Cl)等特 点(柏道远等,2005;邓希光等,2005;李鸿莉等,2007;单强



图 1 湘南地区地质简图和矿产分布图(据 Yuan et al., 2011 修改)

Fig. 1 Simplified geological map of southern Hunan, showing the distribution of ore deposits (modified after Yuan et al., 2011)

等,2011)。前人对骑田岭花岗岩进行了较多的年代学研究, 发现该岩体的成岩年龄为146~163Ma,主要集中在150~ 160Ma(刘义茂等,2002;朱金初等,2002,2009;毛景文等, 2004;赵葵东等,2006;单强等,2014;王志强等,2014;Chen *et al.*,2021)。

1.2 芙蓉锡矿床

芙蓉锡矿床,在构造上处于 NE 向炎陵-郴州-蓝山构造带与 NW 向郴州-邵阳构造带的交汇部位,为南岭中段 W-Sn 多金属成矿带的重要组成部分。除芙蓉锡矿床外,南岭中段成矿带还发育有一系列世界级的钨锡矿床,典型矿床有柿竹

园钨锡多金属矿床、瑶岗仙钨矿床、红旗岭钨锡多金属矿床 和香花岭钨锡多金属矿床(图1)。芙蓉矿区位于骑田岭岩 体南缘(图2a),距郴州市约40km;该矿床发现于20世纪90 年代,其锡资源量超过60万t(魏绍六等,2002),是南岭W-Sn成矿省中规模最大的锡矿床之一,为一世界级的超大型 锡矿床。

芙蓉矿区出露的地层主要为晚古生界-中生界的石炭系和二叠系,另有少量三叠系,岩性主要为碳酸盐岩、钙质页岩、白云岩、砂岩和灰岩等,其中碳酸盐岩为其主要的赋矿围岩。该矿区构造活动强烈,发育一系列 NE-NNE 向断裂,其次发育有 EW、NS 向断裂(图 2b),且 NE 向断裂为该区最主要的控矿构造。



图 2 骑田岭岩体地质图(a, 据 Xie *et al.*, 2010 修改)和芙蓉锡矿床地质简图(b, 据毛景文等, 2004;彭建堂等, 2007 修改) Fig. 2 Geological map of the Qitianling pluton (a, modified after Xie *et al.*, 2010) and simplified geological map of the Furong tin deposit (b, modified after Mao *et al.*, 2004; Peng *et al.*, 2007)

芙蓉矿区的锡矿化主要产于骑田岭岩体内部或岩体与 碳酸盐岩、砂岩的接触带,目前该区已发现有50多条矿脉 (图 2b),大体可分为白腊水-安源、黑山里-麻子坪和山门口-淘锡窝-狗头岭等三个 NE 向锡矿带(黄革非等,2001)。白腊 水-安源锡矿带为该区最主要的锡矿产地,该带锡矿主要赋 存于岩体中及内外接触带,现已发现锡矿脉20多条,锡资源 量预计在40万t以上(黄革非等,2001),为该矿提供了约 73%的锡矿资源量,特别是白腊水矿区的19号矿体,锡矿储 量巨大,其资源量约占整个矿床的32%(彭建堂等,2007)。 19 号矿脉产于二叠系碳酸盐岩和花岗岩的接触带,该矿脉长 可达1600m,宽约50~150m,为芙蓉矿区规模最大的矿脉;该 矿脉 Sn 资源量达到 27 万 t, 矿石中 SnO, 品位较高, 最高可 达21%(平均品位为0.79%)(蔡锦辉等,2004;毛景文等, 2004)。该矿的矿化类型主要为矽卡岩型、蚀变花岗岩型、构 造蚀变带型和云英岩型;矿体主要呈似层状、扁豆状、不规则 状等产出;矿石矿物主要有锡石、磁铁矿、黄铁矿及少量的黄 铜矿、方铅矿和闪锌矿等;脉石矿物主要为石榴子石、符山 石、云母、石英、透辉石、电气石、萤石和方解石等;矿石类型 主要有锡石矿石、磁铁矿-锡石矿石、透辉石-透闪石-锡石矿 石等。前人对芙蓉锡矿床进行了精细的成矿年代学研究,包 括云母和角闪石的 Ar-Ar 定年(毛景文等,2004;彭建堂等, 2007; Chen et al., 2022a)、锡石和符山石的 U-Pb 定年(Yuan et al., 2011; 王志强等, 2014; Chen et al., 2022a; Xing et al., 2022),所获得的年龄均表明该矿形成于150~160Ma。

2 样品的采集与分析

本次研究所使用的样品(PD-5、PD-6-1和PD-6-2),均采

自芙蓉锡矿床中的安源-白腊水锡矿带的 19 号矿体。具体 采样位置如图 2b 所示。

斧石的粉晶 X 射线衍射分析(XRD)实验在中国科学院 地球化学研究所矿床地球化学国家重点实验室完成;使用的 仪器为 D/Max-2200 型 X 射线衍射仪, Cu Kα 辐射电压 40kV,电流 20mA,最大功率为 2.2kw,扫描角度范围 2°~ 60°,步长 0.04°,分辨率为 0.028°(2θ)。电子探针分析 (EPMA)在中南大学地球科学与信息物理学院电子探针显 微分析实验室完成;使用的仪器为岛津 EPMA-1720H 型,加 速电压为 15.0kV,电流 20nA,束斑直径为 5μm,检出限为 0.01%,分析精度为 0.03%;值得说明地是,本次 B 含量测试 使用的是电气石标样。

3 斧石的矿物学特征

3.1 手标本及镜下特征

芙蓉矿区的斧石,在手标本中为丁香褐色,呈针簇状、放 射状或致密块状集合体产出,玻璃光泽,贝壳状断口,可见一 组解理,硬度较大,常与紫色萤石、红褐色石榴子石等矿物共 生(图3)。

偏光显微镜下,斧石为尖劈状的楔形(图4a)或长条状 (图4b-f),常呈无色、浅黄色或淡蓝色,具有微弱的多色性 (图4a),一组解理发育,可见双晶;正高突起,干涉色较低, 斜消光(图4)。镜下可见斧石与符山石(图4c-f)、石榴子石 (图4c,d)、萤石(图4e,f)、石英、电气石、榍石等矿物共生, 局部可见斧石蚀变为绿泥石的现象(图4b)。斧石与锡石均 形成于砂卡岩期,为共生关系,但遗憾的是,在手标本和镜下 均未找到两者的直接接触关系。



图 3 芙蓉锡矿床斧石的手标本照片

Fig. 3 Specimen photos of axinite collected from the Furong tin deposit



图 4 芙蓉锡矿床斧石的镜下照片

(a)尖劈状楔形斧石;(b)长条状斧石,少量蚀变为绿泥石;(c、d)斧石与石榴子石、符山石共生;(e、f)斧石与符山石、萤石、金云母和石英共 生.(a-c、e)为单偏光下;(d、f)为正交偏光下.Ax-斧石;Chl-绿泥石;Grt-石榴子石;Ves-符山石;Fl-萤石

Fig. 4 Micrographs of axinite collected from the Furong tin deposit

(a) axinite with wedge shape; (b) axinite with long strip, locally chloritization; (c, d) axinite coexisting with garnet and vesuvianite; (e, f) axinite intergrown with vesuvianite, fluorite, phlogopite and quartz. (a-c, e) under plane-polarized light; (d, f) under cross-polarized light. Ax-axinite; Chl-chlorite; Grt-garnet; Ves-vesuvianite; Fl-fluorite

3.2 粉晶 X 射线衍射分析(XRD)

本次研究对采自芙蓉矿区斧石样品(PD-5)进行了 X 射 线衍射分析,其 XRD 谱图如图 5a 所示。不难看出,该斧石 样品具有明显 d = 6.249nm、3.445nm、3.127nm、2.875nm、 2.791nm 等特征峰值,与铁斧石矿物的标准衍射谱图(图 5b; Dalnegorsk, Russia 1408, https://www.mindat.org/min-1459. html)较吻合,可初步确定其为铁斧石。



图 5 芙蓉锡矿床斧石的 X 射线衍射图谱

(a)样品 PD-5 的斧石;(b)铁斧石标准谱线,来自 https://www.mindat.org/min-1459.html

Fig. 5 X-ray diffraction spectrum of axinite from the Furong tin deposit

(a) axinite from Sample PD-5; (b) standard spectral line of axinite-Fe, come from https://www.mindat.org/min-1459.html

3.3 斧石的化学组成

利用电子探针对 3 件斧石样品 (PD-5、PD-6-1 和 PD-6-2)共53 个点进行了原位成分分析,测试结果如表 1 所示。 根据分析结果不难发现,该区斧石化学成分变化较大,其SiO₂变化范围为 35.96% ~40.18% (平均 38.57%),Al₂O₃为 16.20% ~18.85% (平均 17.29%),CaO 为 19.54% ~20.78% (平均 20.09%),MgO 为 0.05% ~1.37% (平均 0.87%),FeO^T 为 4.6% ~7.35% (平均 6.06%),B₂O₃ 为 2.61% ~5.36% (平均 4.06%),MnO 为 4.06% ~5.28% (平均 4.69%)。

本次电子探针分析未能获得 H₂O 的含量,因此,在计算 单位原子数时,有必要将 H₂O 含量从斧石分子式中剔除,故 需根据 O = 15.5(Matsubara *et al.*,2011)来计算其它阳离子 的含量。根据 EMPA 测试数据,可计算得到斧石样品 PD-5、 PD-6-1 和 PD-6-2 共 53 个点的分子式单位原子数(apfu)(表 1)。其中:3.81 < Si < 4.09 (3.98,平均值,下同),1.96 < Al $<2.36\ (2.11)\ ,2.15< Ca<2.31\ (2.22)\ ,0.41< Fe<0.65\\ (0.52)\ ,0.35< Mn<0.46\ (0.41)\ ,0.01< Mg<0.20\ (0.13)\ ,\\ 0.48< B<0.92\ (0.72)\ _{\circ}$

在剔除 H_2O 和 O = 15.5 的条件下, 计算得到 3 个斧石样 品(PD-5、PD-6-1 和 PD-6-2)的平均化学式分别为: $Ca_{2.22}$ ($Fe_{0.54}$, $Mn_{0.41}$, $Mg_{0.11}$)_{1.06} $Al_{2.09}$ $B_{0.76}$ $Si_{3.98}$ $O_{15.5}$, $Ca_{2.24}$ ($Fe_{0.50}$, $Mn_{0.43}$, $Mg_{0.15}$)_{1.08} $Al_{2.16}$ $B_{0.65}$ $Si_{3.98}$ $O_{15.5}$, $Ca_{2.20}$ ($Fe_{0.53}$, $Mn_{0.37}$, $Mg_{0.17}$)_{1.07} $Al_{2.05}$ $B_{0.77}$ $Si_{4.00}$ $O_{15.5}$; 芙蓉矿区斧石平均化学式可表 示为 $Ca_{2.22}$ ($Fe_{0.52}$, $Mn_{0.41}$, $Mg_{0.13}$)_{1.06} $Al_{2.11}$ $B_{0.72}$ $Si_{3.98}$ $O_{15.5}$.

值得一提地是,前人已有的研究表明,铁斧石中 Fe^{3+} << Fe^{2+} (甚至没有 Fe^{3+})(Andreozzi *et al.*,2004),因此我们对表 1 中数据进行处理时,将 FeO^{T} 中的 Fe全部视为 + 2 价的亚 Fe_{\circ} 与斧石标准化学式 Ca_{2} (Fe_{\circ} Mn,Mg)₂₁ Al₂BSi₄O_{15.5}(Andreozzi *et al.*,2004)比较,不难发现,芙蓉矿区斧石的 Fe_{\circ} Mn、Mg、Si 含量与其理论值相近,但同时表现出相对富 Ca_{\circ} 贫 B 的特征。

表1 芙蓉锡矿床斧石的化学成分(wt%)

Table 1 Chemical compositions of axinites from the Furong tin deposit (wt%)

样品号 PD-5													
测点号	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10	-11	-12	-13
SiO_2	37.12	39.24	39.81	39.40	39.43	39.98	39.81	39.03	38.99	39.30	38.79	38.50	37.57
B_2O_3	5.01	4.36	5.28	4.42	4.56	4.90	5.12	4.06	5.00	4.83	4.81	4.63	4.57
Al_2O_3	17.19	17.07	17.15	16.54	17.04	16.95	17.39	16.84	17.06	16.36	17.09	16.62	17.12
FeO ^T	6.10	6.06	6.22	7.23	5.96	6.28	6.37	6.64	6.25	6.53	6.51	5.61	5.32
MgO	0.91	0. 98	1.08	0.05	0.99	0.74	0.82	0.69	0.83	0.52	0.85	0.92	0.74
MnO	4.15	4.38	4.16	5.28	4.27	4.94	4.69	4.70	4.48	4.90	4.43	4.70	5.05
CaO	20.15	20.12	20.13	19.75	20.22	20.13	20.29	20.08	20.20	20.32	20.09	20.28	20.78
Total	90.63	92.22	93.83	92.67	92.47	93.92	94.48	92.05	92.80	92.76	92.57	91.26	91.14
O = 15.5条件下计算的原子数													
Si	3.86	4.01	3.97	4.04	4.01	4.01	3.96	4.02	3.95	4.00	3.95	3.97	3.90
В	0.90	0.77	0.91	0.78	0.80	0.85	0.88	0.72	0.87	0.85	0.85	0.83	0.82
Al	2.10	2.06	2.02	2.00	2.04	2.00	2.04	2.05	2.04	1.96	2.05	2.02	2.09
Fe	0.53	0.52	0.52	0.62	0.51	0.53	0.53	0.57	0.53	0.56	0.55	0.48	0.46
Mg	0.14	0.15	0.16	0.01	0.15	0.11	0.12	0.11	0.13	0.08	0.13	0.14	0.11
Mn	0.37	0.38	0.35	0.46	0.37	0.42	0.39	0.41	0.38	0.42	0.38	0.41	0.44
Са	2.24	2.20	2.15	2.17	2.20	2.16	2.16	2.22	2.19	2.22	2.19	2.24	2.31
样品号	PD-5									PD-	-6-1		
<u></u> 测占号	-14	-15	-16	-17	-18	-19	-20	-21	-2.2	-23	-24	-1	-2
SiO	39, 95	38, 76	37.06	38.09	38, 88	38.73	37.26	38, 90	38.04	38. 55	38.96	38.27	38.06
$B_2 O_2$	4 33	4 36	3 53	3.66	4.61	3 64	3 17	3 81	3.64	2.79	3 80	4 15	3.70
AlaOa	17 23	17 11	17 70	17 54	17 19	17 74	17 72	18 17	18 77	17 62	16 75	17 02	16 78
FeO ^T	5 84	5 64	6 15	6.26	6 61	6 63	6 12	6 71	6 32	7 35	6.82	6 32	6 19
MaO	1 00	0.80	0.43	0.52	0.58	0.62	0.75	0.29	0.52	0.08	0.61	0.83	0. 17
MpO	1.00	4 04	5.03	4.86	4 94	4 63	4.02	5.00	1 63	5 21	4.68	4 80	1 18
CaO	4.80 20.40	4. 94 20. 52	20 34	4.00 20.24	4. 94 20, 12	4.03	4. 92	20.31	4.05	10 01	4.00 20.04	10 08	20.00
Tatal	20.40	20. 32	20. 34	20. 24	20.12	01 01	19.92	02 20	01 00	01 50	20.04	01 44	20.00
0 = 15 5	95.00 : 冬仕玉井	92.22	90.24 kh	91.10	92.91	91.91	69. 65	93.29	91.99	91.50	91.00	<i>71.</i> 44	90.12
0 = 15.5	, 示 T 「 「 「 「 「 「 「 「 「 「 「	异时床 J 3	2 02	2 08	2.06	4.00	2.06	2 07	2 02	4 05	4.04	2 07	4 01
51 D	4.02	5.97	5.92	5.90	0.90	4.00	5.90	5.97	5.92	4.05	4.04	5.97	4.01
	0.75	0. 77	0.04	0.00	0.81	0.05	0.38	0.07	0.05	0.51	0.08	0.74	0.07
AI	2.04	2.07	2.21	2.10	2.06	2.10	2.22	2.18	2.28	2.18	2.05	2.08	2.08
ге	0.49	0.48	0.54	0.55	0.56	0.57	0.54	0.57	0.55	0. 65	0. 59	0.55	0.55
Mg	0.15	0. 14	0.07	0.08	0.09	0.09	0.12	0.04	0.11	0.01	0.09	0.13	0. 14
Mn	0.41	0.43	0.45	0.43	0.43	0.41	0.44	0.44	0.40	0.46	0.41	0.43	0.40
Са	2.20	2.25	2.31	2.26	2.19	2.21	2.27	2.22	2.20	2.24	2.23	2.22	2.26
件品亏							PD-6-1	10			10		
	-3	-4	-5	-6	-/	-8	-9	-10	-11	-12	-13	-14	-15
SIO ₂	37.79	38.06	38.06	36.57	39.06	39.07	37.32	38.06	39.25	37.84	38.25	38.45	39.26
B_2O_3	3.98	3.99	3.63	3.08	4.09	3.31	3.03	2.61	3.65	4.97	3.46	2.63	3.47
AI_2O_3	16.58	16. 37	16. 76	17.89	17.89	17.65	17.75	17.01	16.57	18.70	17.21	17.22	17.17
FeO ¹	5.94	5.83	5.99	5.74	5.78	5.90	5.23	5.81	5.80	5.58	6. 15	5.58	5.90
MgO	0.83	0.84	1.00	1.08	1.12	1.05	0.90	0.86	0.99	1.05	0.89	0.87	0.95
MnO	4.84	4. 59	4.50	4.62	4.43	4.46	4.70	4.65	4.82	5.11	5.09	5.15	5.23
CaO	19.99	19.97	19.54	20.02	20.16	19.99	20.02	19.81	19.53	20. 20	20.14	19.92	20.55
Total	89.95	89.63	89.48	88.98	92.52	91.42	88.94	88.81	90.60	93.44	91.18	89.81	92.53
0 = 15.5	5 条件下计	算的原子	釵										
Si	3.99	4.02	4.03	3.92	3.98	4.05	3.99	4.09	4.09	3.81	4.00	4.09	4.04
В	0.72	0.73	0.66	0.57	0.72	0.59	0.56	0.48	0.66	0.87	0.62	0.48	0.62
Al	2.06	2.04	2.09	2.26	2.15	2.16	2.24	2.15	2.04	2.22	2.12	2.16	2.08
Fe	0.52	0.52	0.53	0.51	0.49	0.51	0.47	0.52	0.51	0.47	0.54	0.50	0.51
Mg	0.13	0.13	0.16	0.17	0.17	0.16	0.14	0.14	0.15	0.16	0.14	0.14	0.15
Mn	0.43	0.41	0.40	0.42	0.38	0.39	0.43	0.42	0.43	0.44	0.45	0.46	0.46
Са	2.26	2.26	2.22	2.30	2.20	2.22	2.29	2.28	2.18	2.18	2.26	2.27	2.27

样品号		PD	-6-1		PD-6-2									
测点号	-16	-17	-18	-19	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10
SiO_2	37.61	35.96	37.68	37.88	38.86	37.46	38.78	39.49	38.53	39. 58	39.23	39.71	40.18	39.84
B_2O_3	4.71	3.31	3.28	3.29	4.30	3.51	3.11	5.25	4.54	4.61	4.31	4.40	4.58	5.36
$\mathrm{Al}_2\mathrm{O}_3$	17.15	18.74	18.85	18.65	16.61	16.20	17.91	16.90	17.51	17.01	17.17	17.60	16.68	16.81
$\rm FeO^{T}$	5.67	4.78	4.64	4.82	6.51	6.23	5.95	6.45	5.90	6.60	6.50	5.51	5.73	6.43
MgO	0.94	1.13	1.21	1.14	0.96	1.09	1.16	1.01	1.21	0.91	1.31	1.37	1.19	0.86
MnO	5.18	4.97	4.90	5.13	4.35	4.40	4.33	4.34	4.26	4.36	4.06	4.46	4.07	4.41
CaO	20.15	20.00	19. 94	19.89	20.03	19.96	19. 91	20.18	19.91	19. 94	20.23	20. 28	20.15	20.31
Total	91.41	88.89	90.49	90.80	91.62	88.85	91.14	93.62	91.86	93.01	92.81	93.32	92.58	94.02
O = 15.5条件下计算的原子数														
Si	3.89	3.85	3.94	3.95	4.01	4.02	4.04	3.96	3.94	4.01	3.99	4.00	4.06	3.97
В	0.84	0.61	0.59	0.59	0.77	0.65	0.56	0.91	0.80	0.81	0.76	0.76	0.80	0.92
Al	2.09	2.36	2.32	2.29	2.02	2.05	2.20	2.00	2.11	2.03	2.06	2.09	1.99	1.98
Fe	0.49	0.43	0.41	0.42	0.56	0.56	0.52	0.54	0.51	0.56	0.55	0.46	0.48	0.54
Mg	0.14	0.18	0.19	0.18	0.15	0.17	0.18	0.15	0.18	0.14	0.20	0.20	0.18	0.13
Mn	0.45	0.45	0.43	0.45	0.38	0.40	0.38	0.37	0.37	0.37	0.35	0.38	0.35	0.37
Са	2.23	2.29	2.23	2.22	2.21	2.29	2.22	2.17	2.18	2.16	2.20	2.19	2.18	2.17

4 讨论

4.1 斧石的分类

根据电子探针分析结果(表1),不难发现,芙蓉矿区斧石 Ca>1.5 且 Fe>Mn;在 Mg-Mn-Fe 三角图解中(图6),53 个样 品点中仅3 个点落入锰斧石范围,其余样品点均分布于铁斧 石区域,因此该区斧石应主要为铁斧石,这与前面的 X 射线衍 射分析结果相吻合。前人的研究表明,新疆、云南、广西等地 产出的斧石亦均为铁斧石(钱一雄,1990;黄仕华,2001;Sun et al.,2020);但与新疆亚曼苏铁矿床中的斧石相比(Sun et al., 2020),本次新发现斧石铁含量明显偏低(图6)。



图 6 芙蓉锡矿床斧石 Mg-Fe-Mn 三角图解

样品 Y7730-8 和 Y7801-5 亚曼苏铁矿床斧石数据来自 Sun et al., 2020

Fig. 6 Composition of axinite from Furong tin deposit in the Mg-Fe-Mn diagram

Data of Sample Y7730-8 and Sample Y7801-5 from the Yamansu deposit from Sun $et\ al.$, 2020

芙蓉矿区新发现的斧石明显富 Fe,可能与骑田岭岩体相 对富 Fe 有关。前人研究表明,骑田岭岩体 FeO^T 含量较高 (1.40% ~7.04%,平均为4.02%,邓希光等,2005),明显高 于邻近的千里山岩体(0.48% ~2.68%);骑田岭岩体中角闪 石黑云母花岗岩中的黑云母为铁黑云母,黑云母花岗岩中的 黑云母为铁叶云母(李鸿莉等,2007),该区花岗岩中这些富 铁的黑云母也证实该岩体的确富 Fe。值得一提地是,我们在 芙蓉矿区 19 号矿体中发现了较多的电气石,这些电气石颜 色深,大多为黑色和黑褐色,在镜下显示出蓝色、深蓝色,且 多色性很强(深蓝色-蓝色-蓝绿色-无色),这些特征均指示该 区的这些电气石铁含量很高,应为铁电气石。总之,芙蓉矿 区这些富 Fe 的斧石和电气石,均与骑田岭岩体相对富 Fe 特 征相吻合,表明骑田岭岩体应为芙蓉锡矿的成矿母岩。

4.2 挥发份 B 对花岗质岩浆演化的影响

芙蓉矿区广泛存在的电气石(Yang et al.,2015; Chen et al.,2023)、本次新发现的斧石以及最近该区发现的数种含 硼矿物(李小赛等,2021)均表明,芙蓉锡矿床中富 B 矿物分 布广泛。根据前人对成矿流体的研究(李鸿莉等,2007;毕献 武等,2008;双燕等,2009;袁顺达,2017),结合矿区电气石和 磷灰石的微量元素特征(Yang et al.,2015; Chen et al.,2023),不难发现该区成矿流体来自岩浆热液;该矿区电气石 和骑田岭花岗岩中电气石均富 B、且具有相近的 B 同位素比 值,同时花岗岩和矿区的电气石 B 含量远高于围岩地层中的 B 含量(Xu et al.,2021; Chen et al.,2023),均说明挥发份 B 亦来自花岗质岩浆。

已有的研究发现,挥发份 B 在熔体中的溶解度通常较低 (Pollard *et al.*,1987),但在部分含电气石的花岗岩中 B_2O_3 含量可高达 1% (Pichavant and Manning,1984);实验研究发

现,碱金属含量高的岩浆热液,其 B₂O₃含量更高(Smirnov et al.,2005)。大量理论和实验研究表明,挥发份物质 B 在花 岗岩的成岩过程中主要有以下两方面的作用:(1)能有效地 降低岩浆的粘度。前人实验表明,在花岗质岩浆中加入 1% B₂O₃,岩浆粘度至少可降低 1 个数量级(Dingwell et al., 1992);且岩浆的温度越高,粘度降低的幅度越大。(2)岩浆 中挥发份 B 的加入,能增大岩浆结晶分异的温度范围,从而 促使岩浆分异更加强烈彻底(Lehmann,1990; Gomes and Neiva,2002;陈骏等,2014;崔晓琳等,2022)。此外,B 的存在 亦可增加岩浆体系中水的溶解度,使得该岩浆体系中的含水 流体相富硅和碱金属(主要为钠)而贫铝(Pollard et al., 1987),从而会直接影响岩浆体系的演化过程。

尽管骑田岭岩体中 SiO₂ 含量(64.83% ~76.59%,平均 69.7%,邓希光等,2005;李鸿莉等,2007)明显低于华南改造 型花岗岩(平均72.82%,刘昌实和朱金初,1989),但由于岩 浆中 B 等挥发份含量较高,故该岩体的分异指数 D.I.较高, 其晚期花岗岩 D.I. 值可高达 93 ~94(李鸿莉等,2007)。前 人的研究表明,骑田岭花岗质岩浆来自黑云母脱水为主的地 壳物质重融,其温度可超过 800℃(Yuan *et al.*,2019;Zhao *et al.*,2022b;Chen *et al.*,2023),如此高温的岩浆体系,挥发份 B 能大幅降低其岩浆粘度,且延长岩浆结晶分异的时间;骑 田岭岩体是一复式岩体,其侵位时间前后相差 17Myr(朱金 初等,2009),也很可能与此有关。

4.3 挥发份 B 与锡成矿的关系

Sn 是亲石元素,具有中等不相容性,主要富集于地壳中 (Lehmann, 1990; 陈骏等, 2000; Yuan et al., 2019)。因此, 壳 源物质(尤其是变沉积岩)的部分熔融对形成有经济价值的 锡矿至关重要(Lehmann, 1990)。已有的研究显示, 我国南岭 地区是世界上最大的 W、Sn 成矿省,其成矿物质主要来自新 元古代-早古生代变质沉积岩(魏震洋等,2009;陈骏等, 2014),且南岭地区侏罗纪形成的金属物质 Sn 在以黑云母脱 水为主的地壳物质高温(800 ± 20℃)部分熔融过程中富集 (Wolf et al. ,2018; Huang et al. ,2019; Yuan et al. ,2019; Chen et al., 2023)。成矿元素 Sn 是亲石元素, 具有较强的亲熔体 性和亲流体性(Zajacz et al., 2008; 袁顺达和赵盼捞, 2021), 在地壳部分熔融过程中, Sn 会优先从变沉积岩进入岩浆中 形成原始的富 Sn 熔体,而在随后的熔体演化分异过程中,Sn 又会倾向于富集在共存的岩浆期后热液流体相中,最后富集 成矿 (Yuan et al., 2019; Deng et al., 2022; Zhao et al., 2022a)

大量研究显示,花岗岩能否形成具有经济价值的锡矿, 与部分熔融的温度条件、岩浆中初始 Sn 含量、以及岩浆演化 过程中 Sn 的迁移形式等因素密切相关(Yuan et al.,2019; Zhao et al.,2022c);而岩浆中 Li、F、B 等挥发份的含量能有 效地制约这些影响因素(隋清霖等,2020),因此挥发份在锡 成矿过程中的作用不容忽视。但由于岩浆-热液体系中 B 的 含量通常远低于 Li、F 等挥发份,因而其对成矿作用的影响 往往被忽视(Thomas *et al.*,2003;Smirnov *et al.*,2005)。

在骑田岭岩体和芙蓉锡矿床形成的整个过程中,挥发份 B可能起着至关重要的作用,具体表现在以下几方面:(1)在 源岩发生部分熔融形成含 Sn 岩浆的过程中,岩浆中高含量 B能有效降低黑云母等含锡矿物的固相线温度,从而提高源 岩中 Sn 的萃取率。(2) 正如前所言, B 的存在亦可提高岩浆 中水的溶解度(Pollard et al., 1987), 岩浆体系中 H₂O 含量的 增加无疑会提高整个硅酸盐熔体中 Sn 的含量,进而提高熔 体出溶时所释放的成矿流体规模和成矿金属量,这对芙蓉超 大型锡矿床的形成至关重要。(3)在B等挥发份含量较高的 岩浆演化过程中,岩浆分异程度越高,残留熔体相中 Sn 越富 集,其在岩浆中的含量可达到地壳丰度的10倍以上(陈骏 等,2000;崔晓琳等,2022)。(4)在酸性岩浆体系中,B与Sn 均是不相容元素,在岩浆发生出溶时均倾向富集于流体相中 (Hervig et al., 2002; 袁顺达和赵盼捞, 2021), 且流体中 B 的 存在有利于 Sn 的进一步富集(陈骏等, 2000; Hervig et al., 2002; Thomas et al., 2003; Zhao et al., 2022b)。最新实验结 果表明,在未加入Li、F、B等挥发份岩浆的人工合成包裹体 中, Sn 在流体-熔体中的分配系数(D^{fluid/melt})为5.4 左右(袁 顺达和赵盼捞,2021;Zhao et al.,2022a),而在富Li、F、B等挥 发份体系中流体-熔体的分配系数明显增高,最高可达42 (Zajacz et al., 2008)。(5) 在热液运移过程中, 挥发份 B 还 可能与 Sn 形成某些络合物(如 Sn(BF₄),)(Thomas et al., 2003),这为成矿流体中 Sn 长距离搬运和富集提供了重要保 障。总之,在芙蓉矿床锡成矿过程中,不论是对花岗质岩浆 中 Sn 的富集,还是岩浆-热液体系中 Sn 的富集及搬运,挥发 份B均扮演着至关重要的作用。

4.4 对矿床寻找 B 矿的指示意义

B 与 Sn 的地球化学行为相似,两者均具有亲石性,并具 有显著的亲流体性,在岩浆-热液作用过程中,两者均通过部 分熔融作用,从源岩进入岩浆,在随后的岩浆分异过程中又 从岩浆转移到热液流体中,最后发生沉淀富集,因此,锡矿床 形成过程中很可能有伴生硼矿的形成。

李小赛等(2021)在芙蓉矿区亦发现了数种含硼矿物,其 中工业价值较高的硼镁铁矿,其 B₂O₃ 品位达到了 9.5%,远 超我国硼矿的最低工业品位(5%)。本次研究在砂卡岩中首 次发现了 B 含量较高的斧石,且其与电气石等富 B 矿物共 生,因而在芙蓉矿区寻找硼矿的潜力较大。

值得注意的是,在南岭乃至华南地区,存在较多与高分 异花岗岩有关的 Sn 矿床,如柿竹园钨锡多金属矿床、红旗岭 钨锡多金属矿床、香花岭钨锡多金属矿床等,鉴于 B 与 Sn 往 往同时富集于晚期的岩浆热液体系中,因此,有必要加强该 区域锡矿带或锡矿床中的硼矿找矿工作。

5 结论

(1)首次在芙蓉锡矿区砂卡岩中发现了斧石。成分上, 其主要为铁斧石,具有富 Ca、贫 B 特征。

(2)挥发份 B 在骑田岭岩体成岩、成矿过程中起着至关 重要的作用。B 有利于提高源区 Sn 的萃取效率,提高原始 岩浆中 Sn 含量;能降低岩浆的粘度、促进岩浆的结晶分异演 化,促使 Sn 向晚期残余熔体中不断富集。

(3) 挥发份 B 有利于 Sn 在成矿流体中的富集及运移,B 能形成 Sn 的络合物,促进含锡流体的长距离迁移。

(4)在岩浆-热液体系中 B 与 Sn 地球化学行为类似,芙蓉锡矿区及华南类似的锡矿床中具有寻找伴生硼矿的潜力。

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