

# 硼的地球化学性质及其在俯冲带的循环与成矿初探\*

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**Abstract** Boron is an important element widely used in chemical engineering, agriculture, material sciences, and nuclear industries. The nuclear fusion reactions of hydrogen (H) with the boron isotope <sup>11</sup>B can be potential as an ideal clean energy in the future. There are amounts of boron strongly enriched in subducted sediments, altered oceanic crust and serpentinized lithospheric mantle. Boron is an incompatible lithophile and soluble element. Boron can be readily transported during subduction dehydration, resulting in the serpentinization of forearc mantle wedge with such boron-rich fluids. The mantle wedge is extensively serpentinized by fluids derived from forearc dehydration of the subducting slab, with boron captured in the serpentinized mantle wedge. Most of borate deposit seemingly primarily occur along the collision suture zone, especially along that continent-continent collision develops after ocean-continent subduction. Therefore, the primary known economic borate deposits mainly occur in the high altitude intermontane basins developed at the convergent plate margins. Anatolia Plateau in Turkey hosts the largest borate reserves around the world which may be associated with the massive forearc serpentinite or serpentinized mélange recycled to magma source during subduction erosion. The erupted volcanic magmas transport boron-rich volcanic rocks, ashes and hydrothermal fluids to the surface, from which boron is leached into closed basins, the typical byproducts of orogeny. Combined with extensive evaporation and, dry and cold climate, borate deposits eventually develop in orogen. The boron reserves of China are only 3% of the global ones, mainly from the Liaodong Peninsula, Qaidam Basin of Qinghai, Tibet, Sichuan, and Hunan Province. There may be more potential boron resources for China. We thus call on more efforts on the research and exploration of borate deposits and purchase of abroad boron resources as strategic reserves.

**Key words** Boron; Borate deposits, Serpentinite; Mantle wedge; Volcanic arc

**摘要** 硼是广泛应用于化工、农业、材料科学及核工业领域的重要元素。硼与氢的核聚变反应是未来具备运用潜力的清洁能源。硼作为典型的亲石元素,是高度不相容元素。硼元素容易富集于蚀变洋壳及蛇纹石化地幔橄榄岩中。而在板块俯冲过程中,由于硼具有强的流体活动性,会优先赋存于流体中。因此,当蛇纹石化的大洋岩石圈及覆于其上的沉积物在俯冲过程中发生脱水,这使得弧前地幔楔发生大规模的蛇纹石化。此时大量硼元素很可能随俯冲流体释放并封存于弧前地幔楔中。目前已发现的超大型硼矿床主要位于聚合型板块边缘,尤其土耳其拥有世界上最大的硼酸盐储量。我们推测这些矿床

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的形成基础条件之一可能与弧前高度蛇纹石化的地幔楔有关。尤其是在洋-陆俯冲环境,弧前蛇纹岩或蛇绿混杂岩首先通过俯冲侵蚀再循环到火山弧岩浆中,使得岩浆更富集硼。随后弧火山喷发大量富硼的火山岩、岩浆热液及水气。在岩浆冷却过程中,硼元素析出、沉淀于火山表面,并伴随风化、侵蚀过程汇聚至碰撞造山带的封闭湖盆之中。此外,干冷的气候条件下也进一步促进了硼的成矿。我国具有形成大型、超大型硼矿的地质条件,应加大研究及探勘力度,并适当购买硼作为战略储备。

**关键词** 硼;硼矿床;蛇纹岩;地幔楔;火山弧

**中图法分类号** P541; P78.93

硼为典型的亲石元素。硼能与 VIIA 族(卤组元素)直接化合,形成卤化硼。与 IVA 族(碳、硅、锡)、VA 族(氮、磷、砷)、VIA 族(硫)元素形成的化合物具有熔点高的特性。此外,高温下硼能与过渡金属或金属氧化物反应,形成金属硼化物。这些化合物通常具有高硬度、耐熔、高电导率的性质,被广泛应用在化工、农业、材料科学及核工业领域,价值远高于天然硼。例如:二硼化铼( $\text{ReB}_2$ )、碳化硼( $\text{B}_4\text{C}$ )、钕铁硼( $\text{Nd}_2\text{Fe}_{14}\text{B}$ )。前两者的硬度皆可超过摩氏硬度 9,可应用于坦克车装甲、防弹衣等军事工业产品中,后者则是当今磁性最强的永久性磁铁,在电子技术产业中亦被广泛的应用。值得注意的是,在核工领域,碳化硼是理想的中子吸收剂,因而可用来控制核裂变的速率。此外,硼与氢的核聚变反应会产生氦四,不会释放具危害性的高能中子,是和平利用核聚变的优质材料,也是未来值得期待的清洁能源(Hora *et al.*, 2017)。

硼矿床类型主要有火山沉积型、火山热泉型、沉积变质型、现代盐湖型、砂卡岩型(唐尧等, 2013)。目前世界上发现的超大型硼矿床也主要集中于聚合型板块边界(Helvacı *et al.*, 2017)。火山活动对于硼矿床的形成有重要的影响(Smith and Medrano, 1996; Helvacı, 2005),即使是现代盐湖沉积的硼矿床,也被认为与火山活动或热液活动有直接或间接的关系(Helvacı and Alonso, 2000; Pueyo *et al.*, 2001; Risacher and Alonso, 2001; Warren, 2010)。我国虽然具有形成大型、超大型硼矿的地质条件,但从目前探明储量看硼矿资源却只占了全球硼矿储量的 3%(USGS, MRDS 数据库<sup>①</sup>)。为增进对硼成矿机制的了解以提供将来探采硼矿的研究参考,本文将讨论硼在俯冲带中的循环机理,并提出硼元素在聚合型板块边界周边成矿的可能模式。

## 1 硼的元素地球化学性质

硼的原子序数为 5,原子质量为 10.81 mol/g (Baxter and Scott, 1921)。在元素周期表中,硼位于第 2 周期、IIIA 族。硼的密度约为 2.34 g/cm<sup>3</sup>,熔点 2076℃,沸点 3927℃。晶体结构为三方晶系,摩氏硬度 > 9,在非结晶状况之下,硼的粉末呈棕黄色,而晶体为黑色并带金属光泽。硼的价态主要为 +3 价,为易溶元素,流体活动性较强,会优先进入到流体中,是岩浆和热液过程中重要的挥发性组分。硼在自然界中鲜少以单质存在,通常以硼砂( $\text{Borax}$ :  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )、四水硼砂(Kernite:  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ )或硼酸(Sassolite:  $\text{H}_3\text{BO}_3$ )的

形式赋存,或进入多种含硼矿物之中,例如电气石、白云母、蛇纹石等。过去针对硼在气-液体中的分配、迁移能力和存在形式的实验表明,硼的气-液分配能力受液体或熔体中硼含量的影响较小,且随着温度上升,硼的分配系数增加(张生等, 2014)。硼砂是硼酸盐工业中最重要的含硼矿物(Kistler and Helvacı, 1994),主要发现于非海相蒸发岩中(Smith and Medrano, 1996; Garrett, 1998)。此外,硼酸易溶于水,其溶解度随着温度升高而增加。在火山活动地区,天然硼酸主要在温度下降的过程中自高温水蒸气中逐步凝析并沉淀于火山岩表面(张生等, 2014)。

硼有 14 个同位素,其中两个为稳定同位素<sup>11</sup>B 及<sup>10</sup>B (Aston, 1920),在自然界的丰度分别为 80.1% 及 19.9% (Baxter and Scott, 1921; Briscoe and Robinson, 1925),两者相对质量差异较大(Aston, 1927)。实验及理论计算证明硼同位素可以在地质过程中发生显著的分馏(Kakihana *et al.*, 1977; Marschall *et al.*, 2007),其分馏主要受控于 B(OH)<sub>3</sub> 和 B(OH)<sub>4</sub> 的相对含量。重同位素<sup>11</sup>B 主要富集在 B(OH)<sub>3</sub> 中,轻同位素<sup>10</sup>B 主要富集在 B(OH)<sub>4</sub> 中(Kakihana *et al.*, 1977; Jiang and Palmer, 1998; 蒋少涌, 2000; Jiang, 2001; Jiang *et al.*, 2008; Marschall and Jiang, 2011)。硼同位素组成主要以  $\delta^{11}\text{B}$  表示:  $\delta^{11}\text{B} (\text{‰}) = [(\frac{^{11}\text{B}}{^{10}\text{B}})_{\text{样品}} / (\frac{^{11}\text{B}}{^{10}\text{B}})_{\text{NIST-SRM951}} - 1] \times 1000$ 。低温条件之下硼显著的分馏,其广泛应用于示踪地球表生过程(Hemming and Hanson, 1992; Barth, 1998)、海底热液系统及俯冲带中的水岩反应过程等研究(Spivack and Edmond, 1987; Ishikawa and Nakamura, 1994; Xiao *et al.*, 2011; Scambelluri and Tonarini, 2012)。

## 2 全球硼矿分布

根据美国 USGS 统计,2018 年全球硼矿资源储量约为 11 亿吨,主要分布于土耳其、美国、智利、秘鲁、俄罗斯、哈萨克斯坦。图 1 为全球硼矿床分布与全球大地构造的关系图,其中清楚展现了硼矿床的主要产区主要分布于洋-陆俯冲的聚合型板块边界处。环太平洋构造火山活动带的硼矿床主要集中于南、北美西部,阿尔卑斯-喜马拉雅造山带著名的硼成矿区则分布于土耳其安那托利亚高原及我国青藏高原。这意味着研究俯冲带硼循环与碰撞造山过程对于寻找硼矿是

① USGS. Mineral Resources Data System (MRDS). <https://mrdata.usgs.gov/mrds/find-mrds.php>

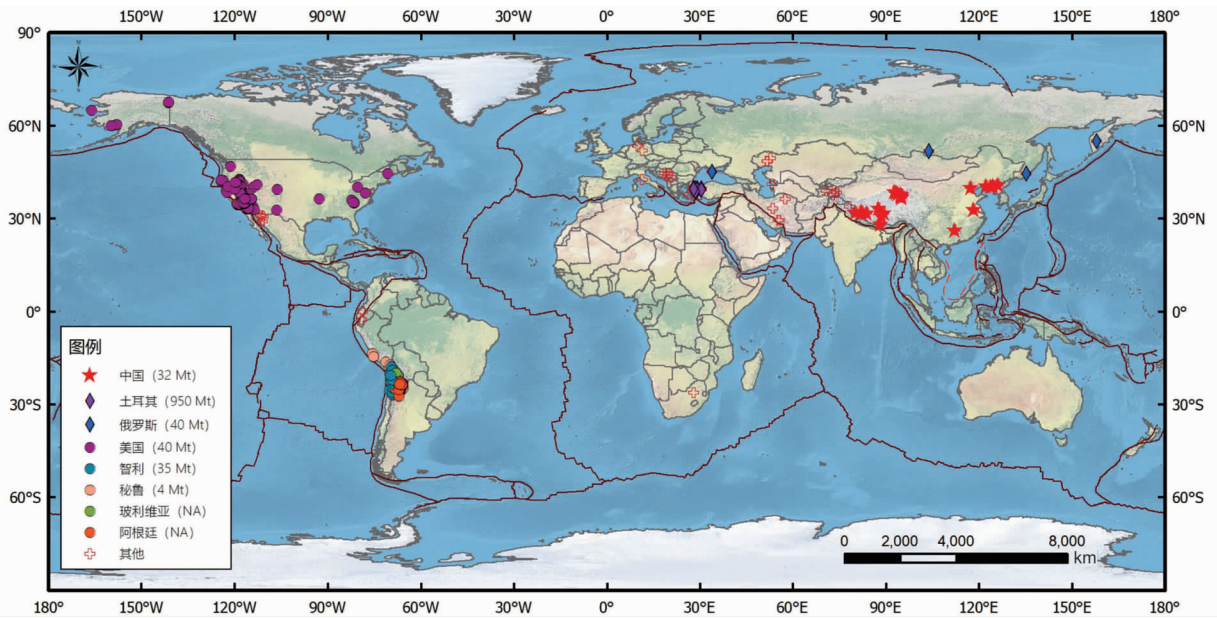


图1 全球硼矿床分布与板块边界图(数据来源于MRDS, USGS)

Fig.1 Worldwide distribution of major borate deposits (data source: MRDS, USGS)

必要的。

至目前为止已知约有86%的硼分布在土耳其安纳托利亚高原(Anatolia Plateau),该地区拥有全球最大的超大型的硼矿床(Helvacı, 1995, 2015; Orti *et al.*, 2016; Helvacı *et al.*, 2017)。土耳其硼矿床主要形成于中新世时期,为火山沉积型硼矿床,主要发育高盐度及高碱度的湖盆中(Helvacı and Firman, 1976; Helvacı, 1986, 1989; Helvacı and Alonso, 2000)。这是由于与阿拉伯板块和欧亚板块于此碰撞所孕育出的一系列地堑断陷盆地形成新生湖盆,为硼酸岩的沉积提供了条件。这些盆地中填充着来自弧岩浆的凝灰岩、熔岩等,同时,富硼的流体亦沿着断层循环流入盆地之中(Helvacı, 1986, 1989; Helvacı and Alonso, 2000),即强烈的火山活动将热泉注入湖盆并与火山碎屑沉积物混合最终形成了该地区的硼矿床(Helvacı, 1984, 1986; Helvacı and Alonso, 2000)。此外,位于加利福尼亚南部及安地斯山西部的硼矿床,与土耳其硼矿的成矿背景相似,亦属于火山沉积及盐湖沉积复合的硼矿床(Helvacı and Alonso, 2000; 申军, 2013)。根据前人研究(Warren, 2010),目前大多数已开采的大型层状硼酸盐矿床几乎均位于干燥气候地区,并且产出于火山及断层活动所形成的山间洼地的盐湖或盐沼中,例如:分布于南美洲安地斯山的沙漠地区(如:阿根廷、秘鲁、智利)的硼矿带。然而,这些地区的硼储量却远不及于土耳其,说明土耳其的成矿条件应有其特殊性,而不仅是受到邻近俯冲带火山弧及封闭湖盆等成矿因素的影响。

我国硼的储量仅为全球储量的3%,约为3200万吨,主要集中在辽东、青海柴达木盆地,西藏、四川、湖南等地区。

其中辽宁省、吉林省的硼矿床属沉积变质型,其储量约占全国的40%以上。此处硼矿床为含硼的变质火成岩系,原岩系由酸性熔岩与海相蒸发岩交互的沉积旋回,形成于断陷盆地之中(Peng and Palmer, 2002)。同时,受到海底热泉的影响,造成含硼矿物以热水沉积和粘土吸附的方式开始富集,为此区硼矿的形成提供了重要基础(邵世宁和熊先孝, 2010)。青海柴达木盆地为现代盐湖硼矿成矿区,盆地基底为变质岩组成并中酸性侵入岩及陆缘碎屑。青藏高原所产的硼矿主要来自第四纪盐湖型硼矿,储量约占全国的50%,位于冈底斯弧盆系的狮泉河-申扎-嘉黎混杂岩带、革吉-则弄火山弧、班戈-伯舒拉岭-高黎贡山岩浆弧等构造带中的山间构造盆地中(邵世宁和熊先孝, 2010)。其成矿条件与前述土耳其及南、北美硼矿床极为类似,主要与俯冲带火山物质及热液带来的硼元素有关,断层活动导致的断陷湖盆提供了成矿空间,尤其辅以干冷气候与高海拔等要素综合决定了硼的富集与成矿(Warren, 2010)。

### 3 硼元素的储库

硼元素富集于现代海水( $4.5 \times 10^{-6}$ ; Spivack and Edmond, 1987)、俯冲沉积物( $1 \times 10^{-6} \sim 150 \times 10^{-6}$ )、大陆地壳( $10 \times 10^{-6} \sim 11 \times 10^{-6}$ ; Rudnick and Gao, 2003; Marschall *et al.*, 2017)、蚀变洋壳( $9 \times 10^{-6} \sim 70 \times 10^{-6}$ ; Marschall *et al.*, 2017)及亏损地幔( $0.060 \times 10^{-6} \sim 0.173 \times 10^{-6}$ ; Marschall *et al.*, 2017)等各种不同的储库中,且不同储库的硼同位素组成亦有很大的不同。因此,硼同位素体系成为研



$10^{-6}$ ; Benton *et al.*, 2001; Deschamps *et al.*, 2010; Harvey *et al.*, 2014; De Hoog and Savov, 2018), 且随着俯冲深度增加残余板片硼元素则逐渐减少(图 2)。

蚀变的大洋岩石圈在俯冲过程中, 从板片释放的流体一部分沿着楔形裂缝和断层排出(Martin *et al.*, 2016), 一部分则交代弧前地幔楔使之发生蛇纹石化(Wu *et al.*, 2018)。板片脱水过程伴随着硼同位素分馏, 重的硼同位素进入流体, 残余蚀变洋壳和沉积物便具更轻的硼同位素特征。这使得弧前蛇纹岩中硼浓度高( $6.6 \times 10^{-6} \sim 126 \times 10^{-6}$ ), 且普遍有较富重硼同位素( $\delta^{11}\text{B} > +20\text{‰}$ )。由于局部蛇纹岩具有正向浮力, 可以上升并加积到增生楔及弧前混杂岩中, 形成富硼的蛇纹岩海山或蛇纹石泥(Benton *et al.*, 2001; Savov *et al.*, 2007), 造成弧前地幔楔及蛇绿混杂岩中富集了大量的硼(Benton *et al.*, 2001; Savov *et al.*, 2005, 2007; Kodolányi and Pettke, 2011; Pabst *et al.* 2012; De Hoog and Savov, 2018)。因此, 一些研究认为火山弧中重硼同位素主要来源于俯冲侵蚀(subduction erosion)与弧前蛇绿混杂岩(forearc serpentinitized mélangé)的复合贡献(Harvey *et al.*, 2014; Martin *et al.*, 2016; De Hoog and Savov, 2018)。然而, 在最近的研究中指出并不是所有的地幔楔都具有高的 $\delta^{11}\text{B}$ 值, 反而其值具有很广的分布区间( $-15.3\text{‰} \sim 9.7\text{‰}$ ), 而这主要与沉积物中的流体交代作用会降低 $\delta^{11}\text{B}$ 值(Cannaò *et al.*, 2015, 2016)有关。

#### 4.2 硼在俯冲及碰撞造山带的成矿机制

硼矿床的成因与俯冲带之间的关联性很早就被提出(Ozol, 1978), 尤其以与火山岛弧之间的关联更被关注。目前已知火山弧岩石中硼的浓度范围介于 $1.3\text{‰} \sim 36.6\text{‰}$ , 平均值为 $12 \times 10^{-6} \sim 15 \times 10^{-6}$ ,  $\delta^{11}\text{B}$ 值大于 $+18\text{‰}$ 。硼同位素组成在高温岩浆过程中几乎没有分馏, 因而火山弧玄武岩的同位素特征应与地幔楔熔融形成的熔体相似。弧岩浆产物被认为是硼矿的主要成矿物质来源(Ersoy *et al.*, 2010)。火山弧中丰富的硼显示了岩浆源中广泛存在的流体-岩石相互作用(Ryan and Langmuir, 1993), 而这些硼元素主要来自大洋岩石圈物质及覆于其上的沉积物受到俯冲带区域变质及热液蚀变的过程(Warren, 2010)。前述已知在俯冲过程中受到板片脱水的影响, 造成硼元素伴随着流体而富集在弧前蛇纹石化地幔楔中, 本文认为这可能是造成聚合型板块边界易发生硼成矿的条件之一。根据世界硼矿的分布趋势, 我们发现在洋-陆俯冲转变为陆-陆碰撞的区域地质条件之下似乎更容易形成硼矿带。部分文献指出, 硼倾向于优先富集在后期花岗岩浆、伟晶岩浆以及出溶的富挥发分流体中(Černý, 1992; Grew and Anovitz, 1996; Thomas, 2002; 张生等, 2014)。而大陆地壳的主要组成为花岗岩, 因此我们认为洋-陆俯冲带相较于洋-洋俯冲更容易在碰撞的过程中通过岩石圈加厚增温, 使得弧前蛇纹石化地幔岩石逐步发生脱水熔融, 将富硼特征转移至浅表, 使得早期的弧岩浆岩更加富硼。

一方面随着俯冲结束转为碰撞造山之后易于造山带边缘发育断陷盆地; 另一方面, 当火山喷发物及热液汇入邻近构造活动形成的湖盆中, 尤其在干燥气候与高海拔的气候条件之下, 再通过表生蒸发作用进而促使硼元素进一步富集成矿。

根据上述有关俯冲带中硼循环的研究结果, 本文提出几种土耳其硼矿床相较于其他国家更富集硼的可能假设: (1)  $\delta^{11}\text{B}$ 的富集主要取决于俯冲角度: 从 $\delta^{11}\text{B}$ 与倾角的变化关系已知, 平板俯冲所发育的火山弧比在陡峭俯冲板片上的火山弧其 $\delta^{11}\text{B}$ 值更低(De Hoog and Savov, 2018)。(2) 俯冲板片释出的流体中的 $\delta^{11}\text{B}$ 值大小与沟弧前缘距离呈负相关: 研究(Leeman *et al.*, 2004; Marschall *et al.*, 2007; Pabst *et al.*, 2012)表明, 远离海沟的火山弧受到俯冲板片释出的流体影响较小, 流体主要是在接近海沟处释放(Savov *et al.*, 2007; Hyndman *et al.*, 2015)。以上两者皆可能导致弧前地幔楔蛇纹石化的位置与程度有所差异。目前的研究表明, 出露于弧前地区的蛇纹岩及蛇绿混杂岩富含重硼同位素(Benton *et al.*, 2001; Savov *et al.*, 2004, 2005, 2007; Tonarini *et al.*, 2007, 2011)。这些相对富硼的弧前地幔楔物质, 在透过俯冲剥蚀或地幔楔角搬运到深地幔楔的过程中, 会再伴随着脱水及熔融过程而进入水气、热液等流体之中(Tatsumi, 1989; Straub and Layne, 2002, 2003; Hattori and Guillot, 2003; Deschamps *et al.*, 2010; De Hoog and Savov, 2018)。研究还表明, 在火山喷气温度约为 $105 \sim 886^\circ\text{C}$ 的气体中硼含量范围介于 $13 \times 10^{-6} \sim 700 \times 10^{-6}$ 之间(Kracek *et al.*, 1938; Kanzaki *et al.*, 1979; Quisefit *et al.*, 1989; Taran *et al.*, 1995; Leeman *et al.*, 2005), 远低于硼酸在 $100^\circ\text{C}$ 水中的饱和溶解度(张生等, 2014)。火山气体的冷却和凝结过程中, 水气和硼酸发生分离, 随着温度的降低, 硼酸从高温蒸气中凝析、沉淀于火山岩石表面(张生等, 2014)。本文认为世界著名的大型硼矿床的形成可能与火山弧物质及热液流体本身就具有相对高浓度的硼有关, 而地幔楔与岛弧火山岩的硼的浓度可能取决于特定的俯冲参数。有关硼的成矿, 则取决于后续是否能够在造山带中发育出利于硼成矿的构造环境及气候等条件(包括封闭湖盆、干燥及高海拔等)。

## 5 结语

从全球大地构造的角度可以观察到, 目前已知的大型硼矿床主要位于聚合型板块边缘, 尤其在洋-陆俯冲转变为陆-陆碰撞的造山带。俯冲板片脱水及弧前地幔楔蛇纹石化对硼在弧前地幔楔的富集起着关键作用。

土耳其安纳托利亚高原的硼储量占了全球的86%以上, 其形成可能与板片的俯冲角度较陡, 并与板片释出的流体及弧前物质的俯冲侵蚀有关。高的俯冲角度使得该处地幔楔蛇纹石化程度更高、更富集硼。这些富集硼的弧前蛇纹岩伴随着俯冲侵蚀携带硼元素进入火山弧, 其火山产物中的成矿物质经风化、淋滤汇入干旱气候带内的封闭蒸发盆地, 最终

成矿。

我国青藏高原除了具备高海拔及干燥等气候条件,还具有典型自洋-陆俯冲转化为陆-陆碰撞的区域地质背景,发育由断层活动而形成的断陷湖盆,为形成大型、超大型硼矿提供了良好的成矿的空间和条件,建议应加强其硼矿基础地质方面的研究及探勘力度,并适当购买国外硼矿以作为战略储备。

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