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超高压榴辉岩-脉体体系成因和俯冲带变质流体演化

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摘 要: 超高压岩石-脉体体系是认识俯冲带流体性质和行为的天然实验室. 通过总结大别超高压变质带 3 个榴辉岩(角闪岩)-脉体体系的研究成果, 探讨了大陆俯冲带变质流体的溶解-结晶过程和氧逸度变化规律以及流体对轻元素硼的迁移过程. 对榴辉岩-复合高压脉体的研究发现超高压流体通过溶解矿物富集溶质组分, 流体随后经历 3 期结晶过程, 分别形成绿帘石-绿帘石脉、绿帘石-石英脉和蓝晶石-绿帘石-石英脉. 绿帘石 La、Cr 和 δE_u 值是判断结晶次序的关键指标. 对榴辉岩-角闪岩-低压脉体研究表明大陆俯冲带低压变质流体的氧逸度明显高于高压-超高压变质流体. 高氧逸度条件也导致一些反常矿物(如退变金红石)的生长. 对含电气石榴辉岩-脉体研究揭示变质碳酸盐岩是大陆俯冲板片中重硼同位素的重要储库, 其在汇聚板块边界的脱硼作用显著影响深部硼循环. 上述研究成果为理解俯冲带变质流体演化和物质循环提供重要科学依据.

关键词: 超高压榴辉岩; 脉体; 俯冲带流体; 结晶; 氧逸度; 岩石学; 元素迁移.

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Genesis of UHP Eclogite-Vein System and Metamorphic Fluid Evolution in Subduction Zones

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Abstract: The system of ultrahigh-pressure (UHP) metamorphic rocks and veins is a natural laboratory to understand the nature and behavior of metamorphic fluids in subduction zones. This paper presents a review of the studies on three suits of eclogite (amphibolite)-vein system from the Dabie UHP terrane in order to discuss the dissolution and crystallization processes of subduction-zone metamorphic fluids, variation in fluid oxygen fugacity (f_{O_2}), and fluid-assisted boron (B) transfer. The study of UHP eclogites and enclosed multiple veins indicates that UHP fluid transferred materials by the dissolution of various components. This solute-rich fluid then experienced a three-stage crystallization process, which produced omphacite-epidote vein, epidote-quartz vein, and kyanite-epidote-quartz vein. La and Cr contents and δE_u values of vein epidote are critical geochemical indicators for assessing the precipitating sequence of veins. The investigation on an eclogite-amphibolite-vein system indicates that low-

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pressure fluids have much higher f_{O_2} conditions than high-pressure (HP) and UHP fluids in continental subduction zones. Such high f_{O_2} conditions also lead to the growth of some unusual minerals (e. g., low pressure retrograde rutile). The investigation on tourmaline-bearing eclogite-vein system indicates that metacarbonate is an important reservoir of isotopically heavy boron (B) in subducted continental crust, and the release of B of metacarbonate at convergent boundary exerts a significant influence on deep B cycling. The studies above provide important insights into the fluid evolution and material cycling in subduction zones.

Key words: UHP eclogite; vein; subduction-zone fluid; crystallization; oxygen fugacity; petrology; boron transfer.

0 引言

俯冲带是连接地球内部圈层和表生圈层的枢纽,深刻影响地球内部的演化、物质—能量的平衡和人类宜居环境.板片向下俯冲过程中发生高压—超高压变质作用,同时释放俯冲带变质流体(Poli and Schmidt, 2004).这些流体是引发俯冲带重要地质过程的关键因素.在宏观尺度上,俯冲带变质流体活动导致了地幔楔部分熔融、壳/幔相互作用、中—深源地震和汇聚板块边界的元素迁移(McCulloch and Gamble, 1991; Davies, 1999; Beinlich *et al.*, 2010; Zheng *et al.*, 2012; Chen *et al.*, 2015);在微观尺度上,这些流体直接参与了变质反应并改变反应速率、同位素平衡状态和矿物—岩石物理化学性质(Glodny *et al.*, 2003; Putnis and John, 2010; John *et al.*, 2012; Ni *et al.*, 2017).准确限定俯冲带流体的形成和演化以及流体运移过程中引发的物质循环是正确认识上述重要地质过程的前提和关键.

高压—超高压变质岩是深俯冲板片折返至地表的直接产物.这些岩石中发育的变质脉体代表了俯冲板片中流体曾经的运移通道和部分结晶产物.同时,脉体与其寄主岩石之间的反应带记录了成脉流体与岩石相互作用的直接信息(Spandler and Hermann, 2006; Beinlich *et al.*, 2010).因此,变质脉体和高压—超高压围岩(包括二者之间的反应带)为我们探究深俯冲—折返过程中流体活动和俯冲隧道内物质迁移提供了理想样品.

大别—苏鲁造山带是全球超高压岩石出露面积最大、岩石种类最齐全的变质带(Zhang *et al.*, 2009; Zheng *et al.*, 2012).该变质带超高压榴辉岩(及其退变产物)中发育了大量不同结构和矿物组合的变质脉体(Franz *et al.*, 2001; Li *et al.*, 2004; Zheng *et al.*, 2007; Zhang *et al.*, 2008; Wu *et al.*, 2009; 盛英明等, 2011; Xiao *et al.*, 2011; Chen *et al.*, 2012; Guo *et al.*, 2014; Zhao *et al.*, 2016; Wang *et al.*, 2017),使该地区成为国际俯冲带变质流体研究

的一个重要基地(Zheng and Hermann, 2014).然而,已有的研究主要针对俯冲带变质流体源区、条件和时代,缺乏对于变质流体结晶过程中矿物和元素行为的研究;再者,对于变质流体的一些重要物理化学性质,如氧逸度条件(f_{O_2}),仍以定性估计为主,缺乏定量约束;此外,现有的研究工作主要关注简单组分(如Si-Al-Na-K)和常见微量元素(大离子亲石元素、稀土元素和高场强元素等)的迁移过程,对于一些轻元素(如硼)在俯冲变质流体演化过程中的行为仍缺乏足够的认识.围绕这些重要科学问题,本文总结了大别造山带3处典型超高压榴辉岩(角闪岩)和脉体的研究成果,结合国际最新研究进展,对大陆俯冲带超高压流体的溶解和多阶段结晶过程、流体的氧逸度变化以及流体对轻元素硼的迁移过程进行阐述和讨论(本文矿物缩写根据Whitney and Evans, 2010).

1 俯冲带超高压流体溶解—结晶过程

大别造山带花凉亭地区的超高压榴辉岩发育了一套独特的复合多期高压变质脉体.Guo *et al.* (2015)对多个露头的野外观察表明,榴辉岩和复合脉体显示了规律性的岩石学特征(图1a):(1)复合多期高压脉体由3类高压脉体组成,从脉体—榴辉岩的边界向脉体内部依次为绿辉石—绿帘石脉(Omp-Ep vein)、绿帘石—石英脉(Ep-Qz vein)和蓝晶石—绿帘石—石英脉(Ky-Ep-Qz vein);(2)沿上述脉体出现次序,脉体绿帘石(3类脉体共有的矿物)含量逐渐降低、颗粒逐渐变大、颗粒的形态从他形变为自形—半自形;(3)靠近脉体的榴辉岩发育典型的水/岩反应结构特征,表现为逐渐靠近脉体,榴辉岩中绿帘石和蓝晶石含量明显降低.进一步的岩相学观察、相平衡模拟计算以及矿物原位同位素分析表明形成复合多期脉体的流体均来源于寄主榴辉岩,由榴辉岩中硬柱石在2.7~3.0 GPa和660~720 °C条件下脱水分解形成.形成的流体在运移过

程中与榴辉岩发生水/岩反应,导致各类元素发生了不同程度迁移.其中Si(-33%)、Ca(-45%)、Al(-32%)、Ti(-20%)和挥发分(-60%)从榴辉岩中迁出;而Mn和Na迁移程度较低(~5%).这些结果表明,榴辉岩中绿帘石、蓝晶石、石英和金红石被溶解进入超高压流体,而石榴石和绿辉石在流体中的溶解程度较低.此外,超高压流体溶解作用导致大离子亲石元素(LILE, -85%)、轻稀土元素(LREE, -60%)、高场强元素(HFSE, -20%)和过渡族金属元素(TME, -20%)也发生不同程度的迁移.

3类高压脉体的全岩和矿物成分都显示了系统的变化,表明均一的超高压流体在结晶过程中发生了显著的化学分异.从脉体-榴辉岩边界到脉体的内部,脉体的难溶元素(如Mg、Mn、HFSE、TME和重稀土元素HREE)含量逐渐降低;而流体活动元素(如U、LILE和LREE)含量逐渐升高.脉体绿帘石的轻稀土(如La)含量逐渐升高,而过渡族相容元素Cr含量和 δEu 值 $[\delta\text{Eu} = 2\text{Eu}_N / (\text{Sm}_N + \text{Gd}_N)]$ 逐渐降低(图1b和1c).实验岩石学结果表明,如果绿帘石与俯冲带流体达到平衡,轻稀土元素更倾向于进入流

体相,Cr更倾向于进入绿帘石,而流体的 δEu 值低于绿帘石的 δEu 值(Martin *et al.*, 2011).因此,花凉亭复合脉体的成分变化反映了多期脉体的结晶次序.其中具有最高Cr含量和 δEu 值,最低La含量的绿辉石-绿帘石脉最先从超高压流体中结晶出来;绿帘石-石英脉是由绿辉石-绿帘石脉结晶之后的残余流体形成的;而具有最低Cr含量和 δEu 值以及最高La含量的蓝晶石-绿帘石-石英脉形成最晚,由绿帘石-石英脉结晶之后再残余的流体形成.上述推断与模拟计算的结晶过程中流体成分演化结果一致.

上述研究表明,俯冲带均一成分的流体经历了多阶段结晶过程和显著的元素分异.因此,任何变质脉体的化学成分不能简单等同于原始流体的成分.重建原始流体的成分需要准确限定流体多期结晶历史.俯冲带流体的多期结晶行为可能是导致自然界高压脉体多样性的一个重要原因.考虑到绿帘石是俯冲带变质脉体中一个常见矿物,该矿物的Cr、La含量和 δEu 值可以作为判断脉体沉淀次序的关键地球化学指标(Guo *et al.*, 2015).

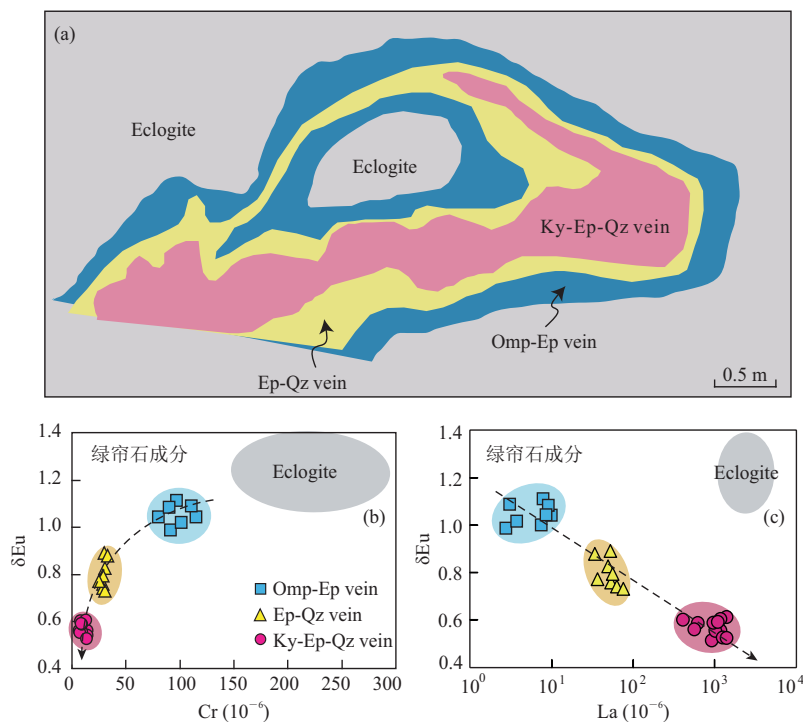


图1 花凉亭超高压榴辉岩和复合多期高压脉体的野外分布(a)和绿帘石矿物成分(b和c)

Fig.1 The field distribution (a) and epidote compositions (b and c) of Hualiangting UHP eclogites and multiple HP veins

引自 Guo *et al.*(2015)

2 大陆俯冲带变质流体的氧逸度变化

流体的氧逸度(f_{O_2})条件是影响流体地球化学行为的重要参数.氧逸度不仅控制流体中变价元素的赋存状态和溶解能力(Pawley *et al.*, 1992; Sun *et al.*, 2004; Bali *et al.*, 2010),也极大制约着流体、岩石反应过程中的相平衡关系和同位素分馏行为(Arculus, 1985; Mattinson *et al.*, 2004; Williams *et al.*, 2005).因此,俯冲带流体的 f_{O_2} 条件是控制俯冲带物理化学性质和地质过程的关键因素.然而,俯冲板片中的流体活动往往是幕式的,可能具有不同的源区、形成机制和时代.特别是大陆俯冲板片岩石普遍经历了折返和后期退变质流体的改造,对这些流体的 f_{O_2} 条件及其引发的岩石学效应仍缺乏系统的研究.

绿帘石 [这里指 $Ca_2Al_3Si_5O_{12}(OH) - Ca_2Al_2Fe^{3+}Si_5O_{12}(OH)$ 固溶体] 中的铁主要以三价

形式存在(Enami *et al.*, 2004).因此,绿帘石 Fe 含量与流体的 f_{O_2} 密切相关(Mattinson *et al.*, 2004; Poli and Schmidt, 2004; Cao *et al.*, 2011).花凉亭地区榴辉岩-角闪岩-退变脉体体系发育大量绿帘石,为研究大陆板片深俯冲-折返过程中流体 f_{O_2} 变化提供了良好的研究载体.退变质脉体主要由铁钛氧化物(铁钛矿-赤铁矿固溶体)和斜长石组成.铁钛氧化物边缘发育更晚期的绿片岩相矿物组合.Guo *et al.* (2017) 的分析测试表明,榴辉岩相和高角闪岩相绿帘石的 X_{Fe} 值 [=Fe/(Fe+Al)=0.20~0.26] 普遍较低;而低角闪岩相和绿片岩相绿帘石具有明显更高的 X_{Fe} 值(0.30~0.36).在此基础上的热力学模拟计算表明,低角闪岩相至绿片岩相流体的 f_{O_2} 为 $\Delta FMQ + (2.5\sim 4.5)$ (FMQ 代表 fayalite-magnetite-quartz 参考标准)(图 2a),显著高于峰期高压和超高压流体的 f_{O_2} (接近 FMQ).此外,高 Fe 的绿帘石普遍具有明显的 Ce 负异常,进一步支持参与绿帘石形成

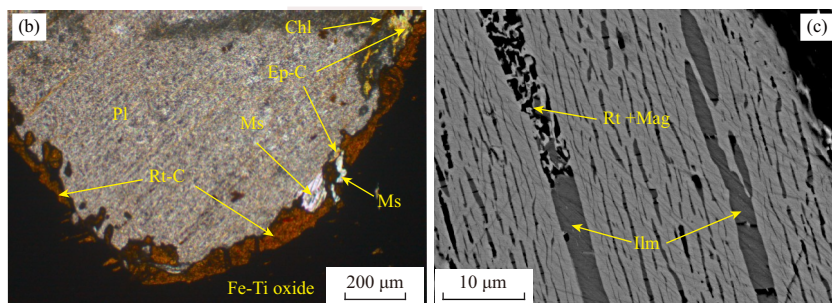
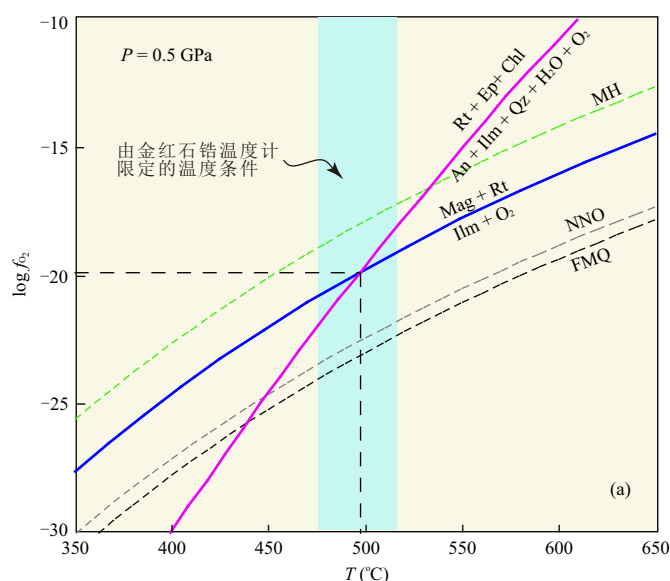


图 2 计算的绿片岩相变质流体的氧逸度条件(a)和绿片岩相条件下退变质金红石的形成(b和c)

Fig.2 Calculated oxygen fugacity conditions of the greenschist-facies retrograde fluid (a) and the growth of retrograde rutile at the greenschist-facies condition (b and c)

引自 Guo *et al.*(2017)

的流体具有高的 f_{O_2} (Guo *et al.*, 2016).

退变过程中流体 f_{O_2} 的升高也导致岩石中出现一些特殊的反应结构和矿物组合.例如在基性岩体系中,金红石主要稳定在高温高压条件下,由进变质过程中钛铁矿、榭石和黑云母等矿物分解形成(Luvizotto and Zack, 2009; John *et al.*, 2010; 陈意等, 2018);而在退变质过程中,金红石将被上述矿物取代.然而,花凉亭变质基性岩和脉体中高 f_{O_2} 流体活动则引发了退变质金红石的形成(475~515 °C; Guo *et al.*, 2017).这些金红石由钛铁氧化物氧化形成(图 2b, 2c),机制为变质流体参与下的界面耦合溶解-再沉淀(interface-coupled dissolution-precipitation)(Putnis and John, 2010).

上述研究表明大陆俯冲板片在折返晚期经历了高 f_{O_2} 流体的渗透.考虑到绿帘石在变质基性岩石中广泛存在,绿帘石 Fe 含量变化以及相关特殊结构和矿物(如低压退变质金红石)的出现可以指示俯冲带变质流体的氧逸度变化.

3 大陆俯冲带富硼流体形成和重硼同位素循环

挥发性元素硼(B)是一个质量较轻的非金属亲石元素,在熔/流体活动中容易发生迁移(Marschall, 2018).硼有两个稳定同位素(^{10}B 和 ^{11}B),二者之间较大的质量差(~10%)导致俯冲带各个端元之间硼同位素组成差异明显($\delta^{11}\text{B}$ 从-30‰到+40‰)(蒋少涌等, 2000; De Hoog and

Savov, 2018; Trumbull and Slack, 2018).因此,硼及其同位素在示踪俯冲带熔/流体活动和深部物质循环等过程中发挥重要作用.海水是地球上最重要的重硼同位素储库($B=4.5\mu\text{g/g}$, $\delta^{11}\text{B}=\sim+40\%$; Foster *et al.*, 2010),因此与海水相关的岩石端元,如俯冲的蛇纹化岩石圈地幔和蚀变洋壳,具有相对高的硼含量(分别为10~90 $\mu\text{g/g}$ 和9~70 $\mu\text{g/g}$)和重硼同位素组成(分别为+7‰~+20‰和-4‰~+25‰)(Marschall, 2018).岛弧岩浆岩和交代地幔楔相对于亏损地幔($B<0.1\mu\text{g/g}$, $\delta^{11}\text{B}=-7.1\%$)具有更高的B含量(1.3~37 $\mu\text{g/g}$)和 $\delta^{11}\text{B}$ 值(从-5‰~+15‰),也进一步指示俯冲大洋板片释放的变质流体具有重硼同位素特征(Palmer, 2017; De Hoog and Savov, 2018).相反,大陆俯冲板片主要由大陆表壳岩石和沉积物组成,这些岩石具有轻的硼同位素组成(平均 $\delta^{11}\text{B}=-9.1\%$; Trumbull and Slack, 2018).因此,传统观点普遍认为大陆俯冲带发育的熔/流体具有低的 $\delta^{11}\text{B}$ 值.然而,越来越多的证据指示一些与俯冲大陆地壳相关的流体也可以显著富集重B同位素(Ota *et al.*, 2008a; Marschall *et al.*, 2009).因此,俯冲带高 $\delta^{11}\text{B}$ 流体来源和B同位素分馏效应仍是目前俯冲带研究领域的未解之谜.

电气石是地壳岩石中硼的主要载体(~3% B),是记录流体中硼迁移的最理想矿物(Dutrow and Henry, 2011).电气石在硅饱和体系中可以稳定在较高的温度和压力条件下(达4.0~4.5 GPa/700~800 °C; Ota *et al.*, 2008b).因此含电气石的超高压岩石-脉体系统为理解俯冲带含硼流体活动提供了

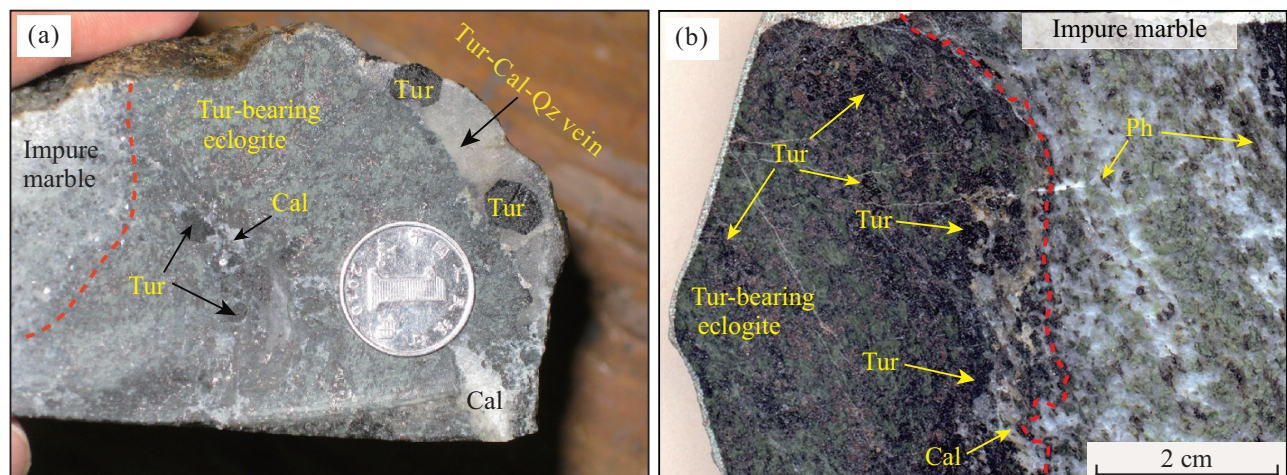


图 3 白羊岭含电气石超高压榴辉岩和脉体的手标本(a)和榴辉岩-围岩大理岩的手标本(b)

Fig.3 Hand specimens of the Baiyangling UHP eclogite-vein system (a) and eclogite-marble system (b)

引自 Guo *et al.*(2019)

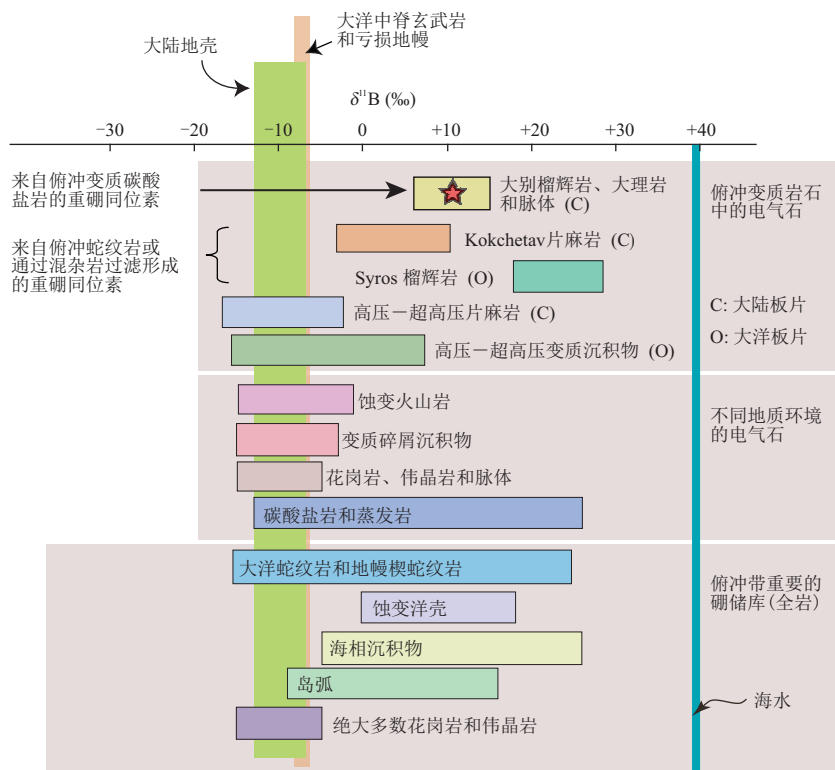


图 4 大别超高压岩石中电气石的硼同位素与主要硼储库的硼同位素对比

Fig.4 Boron isotopic compositions of tourmaline from the Dabie UHP rocks in comparison with major boron reservoirs
引自 Guo *et al.*(2019)

一个重要窗口。

Guo *et al.* (2019)首次报道了大别山白羊岭地区的含电气石超高压榴辉岩和脉体样品(图 3a)。这也是目前全球首例出露于大理岩中的含电气石榴辉岩样品(图 3b)。岩石学、全岩微量元素和 Sr-Nd 同位素结果表明,榴辉岩中电气石由不纯大理岩中白云母在 2.2~2.6 GPa 和 610~660 °C 条件下释放的富硼流体交代形成。榴辉岩中发育的电气石—方解石—石英脉是这些富硼流体的直接结晶产物。交代过程导致大量的 B、C、LILE 等从大理岩进入榴辉岩体系。矿物成分分析指示,电气石属于镁电气石 ($X_{Mg}=0.7\sim 0.8$),与已报道的高压岩石中电气石成分相似(Marschall *et al.*, 2009)。激光原位分析显示,榴辉岩和脉体中单颗粒电气石具有均一的硼同位素比值,表明流体交代过程和结晶过程不引起硼同位素分馏。这些电气石均具有非常高的 $\delta^{11}B$ 值 ($+6\text{‰}\sim +15\text{‰}$;图 4),表明俯冲变质碳酸盐岩释放的流体具有重 B 同位素特征。定量的模拟计算表明这些流体中硼含量可达 700 $\mu\text{g/g}$ (亏损地幔楔硼含量的至少 7 000 倍)。因此,变质碳酸盐岩不仅是深俯冲板片中碳的主要载体,也是硼的重要储库。大

陆俯冲带同样可以引发显著的重硼同位素迁移。

这一研究表明不纯变质碳酸盐岩是俯冲板片一个重要的重硼同位素储库,其在汇聚板块边界的脱硼或再循环过程将显著改变地幔楔和衍生岩浆的硼含量以及硼同位素组成。

4 总结

我们综述了大别超高压变质带 3 个代表性榴辉岩(角闪岩)—脉体体系的研究成果,探讨了俯冲带变质流体的溶解—结晶历史、氧逸度变化和硼迁移等重要科学问题,取得了如下认识。

(1)花凉亭超高压榴辉岩和复合多期高压脉体记录了榴辉岩释放的超高压流体溶解和多期次结晶过程。流体的溶解作用使其富集多种溶质组分。随后的降温降压过程导致流体发生 3 个阶段的结晶过程,形成复合高压脉体;该过程也引发流体成分不断变化和元素分异。绿帘石的 La 和 Cr 含量及 δEu 值能够有效判断流体的结晶次序。

(2)花凉亭榴辉岩—角闪岩—低压脉体体系研究表明俯冲大陆板片在折返过程中发育的低压退

变质流体具有比峰期高压—超高压流体明显高的氧逸度条件. 绿帘石 Fe 含量变化和低压退变质金红石的出现可以指示俯冲板片中流体的氧逸度变化.

(3) 白羊岭含电气石的超高压榴辉岩—脉体体系记录了俯冲带富硼流体与榴辉岩反应的岩石学过程和地球化学效应. 这些富硼流体来源于围岩不纯大理岩. 变质碳酸盐岩是大陆俯冲板片中重硼同位素的重要储库, 其在深俯冲—折返过程中可以释放富硼、高 $\delta^{11}\text{B}$ 的高压—超高压流体. 因此变质碳酸盐岩对俯冲带硼及其同位素的收支平衡具有重要意义.

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