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俯冲板片稳定同位素(Fe-K-Li-B-Ba)的分馏行为

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摘 要: 俯冲带是壳幔循环的重要场所,K、Ba、B和Li作为流体活动性元素,富集在俯冲带流体中;同时各个储库的同位素差异使得其成为研究各种俯冲带流体的良好示踪剂.总结了近年来有关俯冲带Fe同位素与俯冲带变质流体氧化还原状态的研究进展,以及K、Ba、Li和B同位素在俯冲各个阶段的地球化学行为,包括俯冲物质的同位素组成,俯冲板片变质流体的稳定同位素分馏,及俯冲板片物质再循环沉积物、蚀变洋壳及俯冲带蛇纹岩与上覆地幔楔的相互作用再循环过程中伴随的元素分配和稳定同位素分馏.随着稳定同位素测试精度的提升和以上同位素在不同地质储库和地质过程的数据完善,可以更有助于理解俯冲带中的相关物理化学变化过程.

关键词: 稳定同位素;俯冲带;同位素示踪;地壳物质再循环;地球化学.

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Fractionation Behavior of Stable Isotopes (Fe-K-Li-B-Ba) in Subducted Plates

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Abstract: Subduction zones are important sites for recycled material, K, Ba, B and Li, as fluid-mobile elements, are enriched in melts and fluids. At the same time, the isotopic difference of each geochemical reservoir makes it a good tracer for studying various fluid in subduction zone. In recent years, research progresses of Fe isotopetracing the redox state of fluid in subduction zone and K, Ba, Li, B isotope behaviors in the subduction zone are summarized and stable isotopic behavior in a series of geochemical process, including isotopic composition of subducted materials, isotopic fractionation with dehydrated fluid during subduction, interactions between recycled sediments, altered oceanic crust and serpentinite and overlying mantle wedge and elements and stable isotope fractionation in subduction zones. With the improvement in measurement and the improvement of sample data in geochemical reservoir and geochemical sample, stable isotope is helpful to understand the physico chemical processes in subduction zones.

Key words: stable isotope; subduction zone; isotopic tracing; crustal material recycled; geochemistry.

俯冲带是地表与地幔之间物质迁移的重要通道,洋壳和陆壳再循环进入地幔的重要场所,同时可以控制地幔楔与俯冲板片之间物质传递的物理化学过程.俯冲板片在俯冲过程中通过一系列变质脱水反应释放流体,并诱发地幔楔部分熔融进而产生岛弧火山作用.大洋板片在俯冲过程中,其主要组分蚀变洋壳和沉积物中的含水矿物分解所产生的流体具有富集大离子亲石元素和轻稀土元素、亏损高场强元素和重稀土元素的特征,并可以反映到弧岩浆的地球化学特征上(徐义刚等,2020).同时,

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俯冲板片的变质脱水过程会显著影响残余板片的化学组成(魏春景和郑永飞，2020)，是造成深部地幔不均一性的重要原因(Hofmann，1997)；而且能够影响俯冲带变质过程中元素和同位素的地球化学行为，可以造成显著的流体活动性元素迁移及其同位素分馏(Elliott，2003)，所以认识流体活动性元素的行为是俯冲带元素地球化学循环的关键.此外，由于地表低温过程中显著的同位素分馏，导致在地幔中加入少量的再循环地壳物质就可以显著改变其同位素组成.因此稳定同位素成为识别再循环组分的有力工具，在约束地幔中地壳物质的再循环中可以发挥重要作用.据此，本文对Fe，K，Ba，B和Li同位素体系进行综述，以探讨其在俯冲过程中的同位素行为.

1 Fe同位素与俯冲带氧化还原状态

俯冲带在对氧化还原敏感的变价元素(如Fe、S等)循环方面也起着重要作用.这些元素在俯冲板片和地幔楔之间的化学交换会改变地幔楔和弧岩浆的氧化还原状态，也会改变某些成矿元素的富集状态进而影响其成矿行为.目前对Fe在俯冲带的运移方式以及俯冲带流体的氧化还原状态的认识有限，但铁同位素分馏对流体中Fe的氧化还原状态十分敏感，为研究流体的氧逸度(fO_2)提供了可能(Williams *et al.*，2004；Teng *et al.*，2008；Debret *et al.*，2015，2016；Chen *et al.*，2019b；Deng *et al.*，2022).

蛇纹石是俯冲带中循环进入地幔的重要含水矿物之一，进变质过程中利蛇纹石、纤蛇纹石转化为叶蛇纹石再转化为次生橄榄石的过程中会释放大量流体进入地幔楔(Hattori and Guillot，2007)，流体的性质受氧化还原反应控制(Debret *et al.*，2015)，所以蛇纹石矿物中Fe提供了相对直接的氧化还原状态约束手段(Debret *et al.*，2016，2020).Debret *et al.*(2015，2016)发现利蛇纹石向叶蛇纹石转变过程中$Fe^{3+}/\sum Fe$值逐渐降低，表明俯冲带深部更加还原，与板片中硫化物将三价铁还原为二价铁导致Fe^{3+}减少有关.西阿尔卑斯变质蛇纹岩的$\delta^{56}Fe$与全岩$Fe^{3+}/\sum Fe$值呈显著负相关，这一变化是由于蛇纹石脱挥发物过程中释放了富硫酸盐、碳酸盐和/或高盐流体，硫、碳或氯结合的氧化性轻Fe进入流体相导致的，为蛇纹岩中铁在俯冲相关进变质过程中的开放体系流体行为首次提供了直接证据(Debret *et al.*，2015，2016).希腊锡夫诺斯的石榴石环带铁同位素也显示出了轻Fe伴随着硬柱石分解流体的流失.但是在实验和理论研究中，在平衡状态下含Fe^{2+}组分比含Fe^{3+}组分具有更低的$\delta^{56}Fe$值(Polyakov and Mineev，2000；Hill *et al.*，2010)，这说明释放轻铁流体是由更轻的二价Fe优先与流体中碳、硫、氯络合的动力学同位素分馏作用导致的(Hill *et al.*，2010；Debret *et al.*，2016)，对应的重铁同位素可以残留在蛇纹石中，轻铁同位素流体迁移到上覆地幔楔或地幔熔融区产生轻Fe同位素岛弧岩浆(Deng *et al.*，2022).同时脱水流体中S的运移需要相对高的氧逸度(FMQ +1～+4，FMQ为铁橄榄石－磁铁矿－石英氧逸度缓冲对)(Debret *et al.*，2015)，从而脱出的流体高度氧化，进而氧化弧下地幔(Debret *et al.*，2016).

近年来，俯冲带中也发现有还原性流体(Chen *et al.*，2019b).相平衡模拟显示，流体的氧化还原状态取决于蛇纹石的成分，在有硫化物和金属元素存在的条件下，氧逸度可以低至FMQ-4，甚至更低并在俯冲过程中持续存在(Klein and Bach，2009；Debret and Sverjensky，2017)，同时在俯冲过程中释放出含H_2的还原性流体(Evans *et al.*，2017).西阿尔卑斯造山带白片岩受到了俯冲带地幔楔富滑石蛇纹岩流体的交代，具有较寄主变质花岗岩更高的Fe同位素组成(Chen *et al.*，2019b).在流体交代过程中Fe^{3+}的溶解度非常有限，Fe的活动以Fe^{2+}为主(Evans，2012)，白片岩Fe同位素分馏系数与前人模拟的以Fe^{2+}-Cl和Fe^{2+}-(HS)为主的流体瑞利分馏模型相一致(Chen *et al.*，2019b)，轻铁以Fe^{2+}-Cl和Fe^{2+}-(HS)络合物形式运移，表明俯冲带深部流体局部应为高盐度的还原性流体(Chen *et al.*，2019b)，而与之前普遍认为的俯冲带流体为高氧化性不一致(Debret *et al.*，2016，2020).因此，Fe同位素结果表明，俯冲板片和地幔交界处的氧逸度在局部具有高度的非均一性.

2 K同位素与俯冲带物质循环

2.1 K同位素自然界储库

钾是在弧岩浆中明显富集的元素之一，其参与了板块脱水、熔融和流体的运移过程.不同地质单元的K同位素组成差异明显(图1)，MORB的K同位素值$\delta^{41}K=-0.44‰\pm0.09‰$(Parendo *et al.*，2017；Tuller-Ross *et al.*，2019a；Liu *et al.*，2020a)，上地壳K同位素组成较不均一，平均值为$\delta^{41}K=-0.44‰\pm0.05‰$

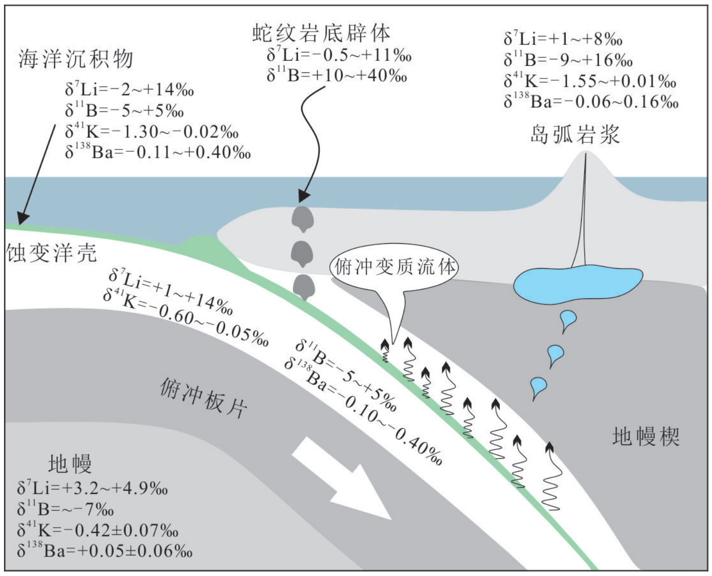

图 1　俯冲带中的 K，Ba，B 和 Li 同位素体系

Fig. 1　Schematic illustration of K，Ba，B，Li isotope systematics in a subduction-zone setting

K 同位素数据来自 Hu *et al*.(2020，2021); Wang *et al*.(2020);Ba 同位素数据来自 Bridgestock *et al*.(2018); Li *et al*.(2019a); Nielsen *et al*.(2018，2020); B 同位素数据来自 Ryan and Chauvel(2014);Palmer(2017);Marschall and Foster(2018);Li 同位素数据来自 Millot *et al*.，(2004); Ottolini *et al*.，(2004); Magna *et al*.(2006); Jeffcoate *et al*.(2007); Tang *et al*.(2007)

(Li *et al*.，2019b；Huang *et al*.，2020). 海水 K 同位素组成 δ^{41}K＝－0.42‰±0.07‰(Wang *et al*.，2020)，Hu*et al*.(2021)对发表的大洋玄武岩数据进行了统计分析，得到原始地幔的 K 同位素值为 δ^{41}K＝－0.42‰±0.07‰. 远洋沉积物的 K 同位素组成为 δ^{41}K＝－1.30‰～－0.02‰. 蚀变洋壳(AOC)的 K 同位素组成为 δ^{41}K＝－0.60‰～－0.05‰，平均值－0.32‰(Hu *et al*.，2020).

2.2　K 同位素与地幔熔融

K 是地幔熔融过程中高度不相容的大离子亲石元素，在部分熔融过程中会富集于熔体中，其分馏作用很小，因此能够继承地幔源区的 K 同位素特征. 理论计算证实，在 1 100 ℃时，硅酸盐熔体和矿物之间的平衡分馏小于 0.1‰(Zeng *et al*.，2019). 全球大洋玄武岩 K 同位素组成 δ^{41}K＝－0.43‰±0.09‰，表明地幔部分熔融过程中没有显著的 K 同位素分馏(Tuller-Ross *et al*.，2019a，2019b).

2.3　K 同位素板片流体脱水过程

俯冲板片在变质脱水过程中 K 随着含水矿物(如云母和角闪石等)的分解而释放到流体中(Becker *et al*.，2000；Zack *et al*.，2001). 西藏松多榴辉岩的 δ^{41}K 值与 K_2O 含量和 K/Nb 比值均呈正相关，表明其低 δ^{41}K 值很可能与俯冲过程中的脱水相关，所脱出的流体富集重 K(Liu *et al*.，2020a). 日本伊豆岛弧岩浆岩的 K 同位素比上地幔、沉积物和洋壳都偏重，且表现出从弧前到弧后 δ^{41}K 值较上地幔重但逐渐变轻的趋势，反映了随俯冲深度增加，含 K 矿物相逐渐脱水，重 K 优先进入流体使得残余板片逐渐亏损重 K(Parendo *et al*.，2022). 此外，宝鸡超钾质岩石起源于俯冲板片流体加入交代上覆地幔，具有较亏损地幔更高的 K 同位素组成，也表明了板片流体具有重 K 同位素组成的特征(Liu *et al*.，2021). 因此，K 同位素体系可能具有示踪源区流体交代过程的潜力.

2.4　K 同位素在弧岩浆的应用

在大陆风化过程中，重钾同位素优先进入水圈中，使残余相富集轻钾同位素(Chen *et al*.，2020；Teng *et al*.，2020)，经历中度至强烈风化作用的陆源沉积物 δ^{41}K 值在－0.70‰～－0.35‰ 之间(Hu *et al*.，2020). 在到达弧岩浆产生的深度前，沉积物中的 K 元素没有显著的脱水流失(Busigny *et al*.，2003). 因为部分熔体不会对 K 同位素进行分馏(Tuller-Ross *et al*.，2019b)，沉积物熔体会继承沉积物低 K 特征，Hu *et al*.(2020)通过二元混合计算来评估再循环物质对地幔 K 同位素的改造，沉积物熔体加入地幔产生的 δ^{41}K 始终低于地幔值，因此低 δ^{41}K 是沉积物输入的敏感指标(Hu *et al*.，2020). 同时，数据模拟计算显示添加 3% 的蚀变洋壳流体就

会导致明显的高于地幔的 $\delta^{41}K$ 特征(Hu *et al.*, 2020).这使得K同位素具有示踪俯冲带物质循环的潜力.

阿尔卑斯和喜马拉雅造山带的钾质和超钾质火成岩和马提尼克岛弧岩浆岩的K-Pb-Sr-Hf-Nd同位素间相关性可以识别出有沉积物流体的加入,且根据K同位素定量估算出地幔源区有高达5%的沉积物再循环加入(Hu *et al.*, 2021; Wang *et al.*, 2021).我国东北地区不同类型的新生代玄武岩也表现出不同的K同位素组成,可归因于地幔源区中不同俯冲物质的加入;其中钾质熔岩的轻钾同位素组成与再循环的沉积物有关,而钠质熔岩的重钾同位素组成归因于蚀变洋壳的加入(Sun *et al.*, 2020).

因此,K同位素地球化学可以作为研究幔源岩浆地壳再循环的有效工具,有助于进一步认识不同俯冲组分在富集地幔端元的作用.

3 Ba同位素与俯冲带物质循环

3.1 Ba同位素自然界储库

碱土金属元素钡(Ba)由于在地幔部分熔融过程中的高度不相容性而在地壳中强烈富集(Sun and McDonough, 1989).因此Ba同位素是潜在的示踪地壳物质再循环和壳幔相互作用的有效工具.俯冲带相关地质单元具有不同的Ba同位素组成(图1),地幔 $\delta^{138/134}Ba$ 同位素组成为 $\delta^{138/134}Ba=0.05‰\pm0.06‰$(Nielsen *et al.*, 2018; Li *et al.*, 2019a);远洋沉积物Ba同位素值范围为 $\delta^{138/134}Ba=-0.11‰\sim+0.10‰$,平均值为 $\delta^{138/134}Ba=0.02‰\pm0.10‰$(Bridgestock *et al.*, 2018; Nielsen *et al.*, 2018, 2020);而蚀变洋壳(AOC)的Ba同位素值变化范围较大,为 $\delta^{138/134}Ba=-0.10‰\sim+0.40‰$(Nielsen *et al.*, 2018, 2020);花岗岩、花岗闪长岩、黄土、冰碛岩和河流沉积物样品与上地壳组成类似且钡同位素较为均一,$\delta^{138/134}Ba=0.00\pm0.03‰$(Nan *et al.*, 2018).

3.2 俯冲板片Ba同位素特征及岛弧成因模型

Ba是不相容的流体活动性元素,高度富集在岛弧岩浆中,Ba/Th比值被用来识别岛弧岩浆中所加入流体的特征(Wu *et al.*, 2020).由于不同的循环物质(蚀变洋壳,沉积物等)以及地幔储库具有不同的Ba同位素组成,所以再循环的俯冲沉积物和AOC在地幔不均一性中起着重要作用.据此Ba同位素可被用作识别俯冲板片释放流体的灵敏指标,用来识别地幔中各种再循环组分.

重晶石矿物是大洋沉积物中主要的含Ba组分(Plank and Langmuir, 1998),其在板片俯冲早期发生分解,此过程中无明显分馏(Bridgestock *et al.*, 2018; Nielsen *et al.*, 2018).多硅白云母是沉积物和蚀变洋壳Ba的主要寄主矿物,显著影响着深俯冲的沉积物和蚀变洋壳释放的交代流体(Zack *et al.*, 2001; Hermann, 2002).实验研究表明,多硅白云母矿物可以稳定于较宽的温度和压力范围内,深度可达300 km(Hermann, 2002),在多硅白云母的稳定域中,俯冲的蚀变洋壳和沉积物的Ba同位素组成没有明显变化(Zhao *et al.*, 2021).由于Ba在地幔熔融过程中高度不相容,全岩分配系数 $D_{Ba}^{solid/melt}=0.000\,12$,当发生1%的部分熔融时99%以上的Ba将进入熔体,这意味着地幔源和玄武岩浆之间的Ba同位素分馏很小.

Rb和Ba元素在地幔熔融过程中元素行为类似,因此,洋中脊玄武岩(MORB)和上地幔具有一致的比值Rb/Ba=0.09(Sun and McDonough, 1989; Gale *et al.*, 2013),大多数俯冲沉积物的Rb/Ba<0.1(Plank and Langmuir, 1998),而AOC组分的Rb/Ba值一般>0.35(Plank and Langmuir, 1998),使得Ba同位素结合Rb/Ba比值能识别出沉积物和蚀变洋壳物质的加入.已经发表的文章中,Rb/Ba-Ba同位素及Ba-Sr-Nd同位素值二元模拟曲线都识别出了不同比例的大洋沉积物以及蚀变洋壳的加入,为大洋沉积物以及蚀变洋壳再循环提供了强有力的证据(Wu *et al.*, 2020; Zhao *et al.*, 2021).我们统计了已发表的岛弧岩浆岩的Ba同位素以及放射性Sr和Pb同位素值(Nielsen *et al.*, 2020; Wu *et al.*, 2020),发现岛弧岩浆岩的Ba-Sr-Pb同位素特征指示其源区有俯冲带蚀变洋壳流体和沉积物熔体组分的加入(图2).但是,蚀变洋壳和沉积物组分加入并不能完全解释所有的岛弧岩浆岩的Ba同位素组成,有可能存在一个未被识别的更富集轻Ba的端元,因此需要后续更多研究.

对于俯冲带岛弧岩浆岩的产生目前有两种不同的俯冲带板片端元混合模型,较为传统的是交代地幔楔熔融模型,即沉积物熔体、蚀变洋壳(AOC)和/或蛇纹石脱出的流体交代地幔楔(Ryan and Chauvel, 2014).蚀变洋壳和沉积物脱水或熔融产生俯冲带流体,发生微量元素(如Sr/Nd, Ba/Th, U/Nb)分异特征,在弧下方与地幔楔熔体混合,形

成岛弧岩浆(Nielsen and Marschall, 2017). 在混杂岩(mélange)模型中,俯冲大洋岩石圈板片物质(沉积物、蚀变洋壳等)由于受地幔楔隧道壁的机械刮削作用而拆离成不同大小的地壳碎块进入大洋俯冲隧道内发生混合,同时经历不同程度的变形和变质,从而形成不同型式的高压-超高压构造混杂岩(Marschall and Schumacher, 2012). 混杂岩随后以底辟的形式上升进入地幔楔,并熔融形成具有微量元素分异特征的弧岩浆(Nielsen and Marschall, 2017). 以上这两种模型的关键区别在于混合和熔融的相对时间,它们分别独立影响微量元素分配和同位素分馏. 交代地幔楔成因的蚀变洋壳沉积物形成的俯冲带流体首先发生微量元素分异,再加入弧岩浆的源区,发生同位素混合. 相反,在混杂岩熔融模型中,这些组分首先机械混合形成一个新的混杂岩石,从而确定其放射性同位素组成,然后在第二步中熔融,从而对微量元素进行分异(Nielsen and Marschall, 2017). 不过我们可以利用$^{87}Sr/^{86}Sr$和$^{143}Nd/^{144}Nd$来区分这两种模式,因为沉积物和蚀变洋壳全岩的Nd/Sr值相对于蚀变洋壳流体和沉积物熔体差别很大(Kessel *et al.*, 2005; Hermann and Rubatto, 2009),导致地幔和这些组分之间的Sr/Nd同位素混合曲线具有明显不同的曲率(Nielsen and Marschall, 2017).

最近,有研究展现出Ba同位素在区分交代地幔楔熔融模型和混杂岩底辟模型的巨大潜力(Nielsen *et al.*, 2018, 2020; Wu *et al.*, 2020). 汤加－克马德克岛弧熔岩(Tonga-Kermadec)岛弧岩浆Ba-Sr-Pb同位素二元混合模型显示沉积物熔体和蚀变洋壳流体加入地幔,且沉积物成分在蚀变洋壳流体加入之前被添加到地幔中,为汤加－克马德克岛弧为传统的板片熔流体交代地幔楔模型提供了Ba同位素证据(Wu *et al.*, 2020).

3.3　俯冲板片流体的Ba同位素特征

在俯冲带中,Ba同样存在于俯冲带流体中参与壳幔物质循环. 有研究人员对中大别岗河和碧溪岭两地榴辉岩的高压脉体进行了Ba同位素分析,表明在变质脱水过程中,随着轻Ba绿帘石矿物的结晶,残余流体逐渐富集重的Ba同位素,产生的Ba同位素分馏$\Delta^{138}Ba$可以高达0.70‰. 所以俯冲板片高压-超高压脱水会发生显著的Ba同位素分馏,流体会具有相对俯冲板片更重的Ba同位素组成. 所以在用Ba同位素示踪俯冲板片物质加入的过程中,尤其是缺少多硅白云母矿物时,要考虑到俯冲板片熔融和流体脱水过程的分馏影响.

目前Ba同位素的发展还处于初期阶段,其在俯冲带中的行为仍需更多后续研究.

4　B同位素与俯冲带物质循环

4.1　B同位素自然界储库

B元素在大陆地壳中富集,而在地幔中显著亏损(Marschall and Foster, 2018). 硼主要富集于大陆地壳、大洋沉积物和蛇纹石中(Scambelluri and Tonarini, 2012; Palmer, 2017),经过与海水相互作用,洋壳与沉积物都具有较高的B含量和较重的硼同位素特征$\delta^{11}B$

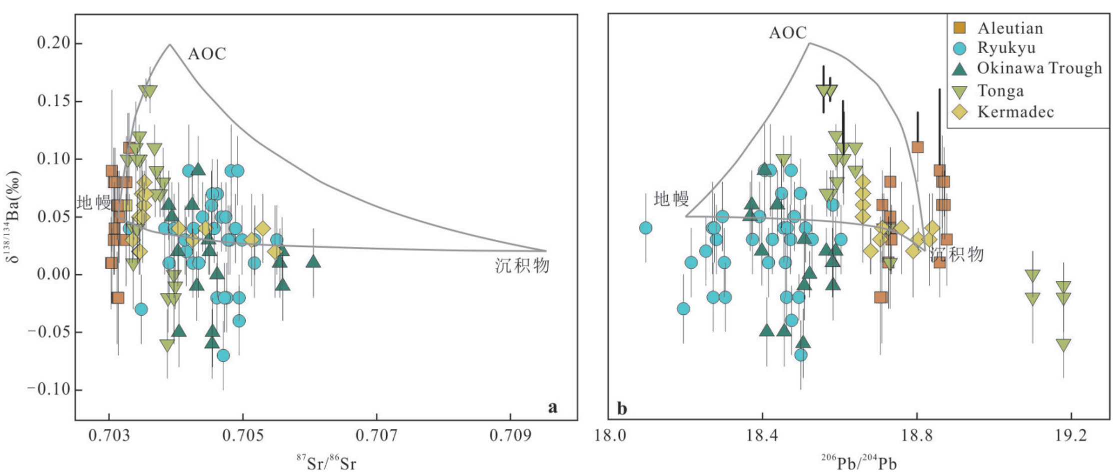

图2　岛弧岩浆岩$\delta^{138}Ba$值与$^{87}Sr/^{86}Sr$ (a)和$^{206}Pb/^{204}Pb$ (b)的关系图

Fig. 2　$\delta^{138/134}Ba$ data versus $^{87}Sr/^{86}Sr$(a) and $^{206}Pb/^{204}Pb$ (b) of arc volcanic lavas

Ba, Sr, Pb同位素数据来源Nielsen *et al.*(2018, 2020); Wu *et al.*(2020); 地幔值来自Nielsen *et al.*, (2018), Li *et al.*(2019a); 蚀变洋壳值来自Wu *et al.*(2020); 沉积物值来自Plank and Langmuir., (1998); Bridgestock *et al.*(2018); Nielsen *et al.*(2018, 2020)

$=-5‰\sim+5‰$(Palmer, 2017),蛇纹岩硼同位素组成$\delta^{11}B=+10‰\sim+40‰$(Scambelluri and Tonarini, 2012; Bebout *et al.*, 2014;Palmer, 2017).大陆地壳$\delta^{11}B$值较低,约为$-16‰\sim0$,平均值为$-10‰$(Marschall and Foster, 2018).同时岛弧岩浆岩的硼同位素组成为$\delta^{11}B=-9‰\sim+16‰$(Ryan and Chauvel, 2014; Marschall and Foster, 2018).未蚀变的洋中脊玄武岩硼同位素组成为$\delta^{11}B=-7.1‰\pm0.9‰$(Marschall *et al.*, 2017).洋底蛇纹岩具有重B同位素组成,$\delta^{11}B=+7.0‰\sim+19.9‰$(Marschall and Foster, 2018).在沉积物、蚀变洋壳和地幔楔蛇纹岩中的显著分馏(图1),使得B同位素有潜力示踪俯冲带流体.

4.2 俯冲物质的B同位素特征

在俯冲前期,沉积物在浅部的压实和成岩过程中,~70%的B会在弧前丢失(Savov *et al.*, 2007; Bebout, 2014).在成岩作用和化学风化过程中,流体活动性更高的^{11}B通过河流或地下水被溶解并输送到海洋中,而^{10}B较多残留在大陆风化层中(Muttik *et al.*, 2011).这些残余物质(云母和粘土)有着较原岩及大陆地壳更低的$\delta^{11}B$值(Romer *et al.*, 2014).尽管在浅层弧前区域大量流失,但剩余的沉积B可被白云母和电气石俯冲到更深处(Bebout *et al.*, 2007).实验和自然观测结果表明,在SiO_2饱和体系中,在700~800 ℃时,电气石可以在4.0~4.5 GPa稳定存在(Henry and Dutrow, 1996; Berryman *et al.*, 2015),在泥质岩体系中电气石在压力为4.5~5.0 GPa (700 ℃) 和4~4.5 GPa (800 ℃)时分解,同时释放出的富B流体分配进入白云母矿物俯冲进入深部地幔(Ota *et al.*, 2008; Xu *et al.*, 2022).

在俯冲沉积物和蚀变洋壳中,粘土、云母和电气石是主要的含B矿物,其中电气石中B含量可达~3%(Bebout and Nakamura, 2003).电气石一旦形成,就不容易通过体积扩散重新调整其化学组成(Henry and Dutrow, 1996).B在电气石和流体中的配位均为三次配位,所以电气石和流体间的B同位素分馏不大(Bebout and Nakamura, 2003),结合电气石常发育的生长环带和其中的矿物包裹体可以有效地记录变质作用期间不同来源富B流体的参与和交代过程(Bebout and Nakamura, 2003; Marschall *et al.*, 2009; Guo *et al.*, 2019; Liu *et al.*, 2022;Xiong *et al.*, 2022; Xu *et al.*, 2022).如在电气石单矿物环带原位B同位素的研究中,可以用不同B同位素特征来源的流体(如蛇纹岩流体、沉积物熔体及蚀变洋壳流体)来解释电气石边缘比核更轻或更重的现象(Trumbull *et al.*, 2008).同时电气石在脱挥发分过程中,会显示出从核到边$\delta^{11}B$递减的变化(Nakano and Nakamura, 2001; Bebout and Nakamura, 2003; Berryman *et al.*, 2017).

4.3 岛弧岩浆的B同位素特征

关于硼元素是否循环进入深部地幔的问题,可以通过在岛弧岩浆中寻找俯冲的$\delta^{11}B$特征来解决,结合其他放射性同位素数据(如Sr,Nd或Pb),能够识别出不同再循环物质的贡献.早期对岛弧岩浆硼同位素组成的研究认为源区存在高$\delta^{11}B$的俯冲沉积物流体与地幔二元混合过程(Ishikawa and Nakamura, 1994; Leeman, 1996).然而,来自深俯冲沉积物和蚀变洋壳的板片流体的B同位素组成随着深度的增加而逐渐变轻(Rosner *et al.* 2003),很难与在岛弧中观察到的重B同位素组成相一致.随着更多全球范围内的岛弧岩浆岩B同位素数据的发表,Marschall and Foster (2018)对全球的弧岩浆岩B同位素进行了统计,B-Sr-Nd同位素显示弧岩浆未落在MORB和全球沉积物(GLOSS)二元混合线上,相反岛弧岩浆岩落在了马里亚纳群岛(大洋钻探计划ODP Leg125)弧前变质蛇纹岩(Savov *et al.*, 2005, 2007)与MORB的二元混合线上(图3),从而证明了蛇纹石脱水对弧岩浆的重要贡献(Scambelluri and Tonarini, 2012).蛇纹岩也被证明俯冲到了弧下深度,脱水形成岛弧岩浆源区(Scambelluri and Tonarini, 2012; Bebout *et al.*, 2014).蛇纹石流体可能来源于俯冲带弧前变质的蛇纹岩(Savov *et al.*, 2005, 2007),也可能是俯冲带上覆的蛇纹岩混杂岩(Marschall and Schumacher, 2012; Martin *et al.*, 2016),也可能是俯冲板块下部的深海蛇纹岩(Konrad-Schmolke *et al.*, 2016).在大陆俯冲带中,也显示出了橄榄岩对B的贡献.变质橄榄石具有与蛇纹岩原岩相似的高$\delta^{11}B$,表明橄榄石可能是蛇纹石分解中同位素重B的重要富集矿物(Harvey *et al.*, 2014).西藏高原南部拉萨地块的后碰撞超钾质岩显示出B同位素具有区分大洋俯冲和大陆俯冲的潜力(Hao *et al.*, 2022).大别地区钾质岩Sr-Nd-Pb-B同位素数据显示由地幔楔橄榄岩和再循环脱水的大陆地壳混合形成的(Ma *et al.*, 2021).所以在俯冲带中,蛇纹岩是岛弧以及大陆俯冲带中B循环过程中非常重要的组分.

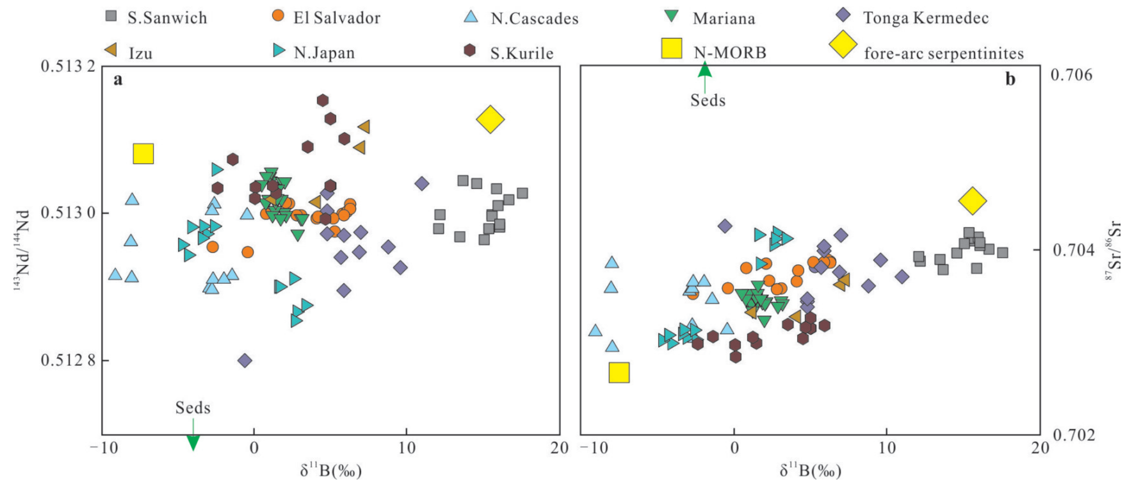

图 3　岛弧熔岩 $\delta^{11}B$ 值与放射性同位素 $^{143}Nd/^{144}Nd$ (a), $^{87}Sr/^{86}Sr$ (b)的关系图

Fig. 3　$\delta^{11}B$ data versus $^{143}Nd/^{144}Nd$ (a) and $^{87}Sr/^{86}Sr$ (b) of arc volcanic lavas

岛弧岩浆岩 $\delta^{11}B$, $^{143}Nd/^{144}Nd$, $^{87}Sr/^{86}Sr$ 数据来源 Ewart and Hawkesworth, (1987); Woodhead(1989); Ishikawa and Nakamura(1994); Shibata and Nakamura(1997); Ishikawa and Tera(1997, 1999); Taylor and Nesbitt(1998); Ishikawa *et al.*(2001); Straub and Layne(2002); Rosner *et al.*(2003); Leeman *et al.*(2004, 2017); Moriguti *et al.*(2004); Barry *et al.*(2006); Tonarini *et al.*(2007, 2011), 平均俯冲沉积物(GLOSS II)值来自 Plank(2014),弧前蛇纹石化地幔橄榄岩值来自 Benton *et al.*(2004); Savov *et al.*(2004, 2005, 2007)

5 Li同位素与俯冲带物质循环

5.1　Li同位素自然界储库

锂(Li)元素有两个稳定同位素,分别为 ^6Li 和 ^7Li,自然界中丰度分别为 7.5% 和 92.5%. ^6Li 和 ^7Li 两种稳定同位素表现出高达 16% 的相对质量差异,因此,质量依赖的同位素分馏很大,使其成为研究俯冲带各种地质过程的良好示踪剂(Penniston-Dorland *et al.*, 2010). Li元素在部分熔融过程中为中等不相容元素 $D^{melt\text{-}rock}$=0.25~0.35 (Ryan and Langmuir, 1987),具有较强的流体活动性,Li元素倾向于进入液相(Brenan *et al.*, 1998). 地幔 Li 同位素组成为 δ^7Li=+3.2‰~+4.9‰(Ottolini *et al.*, 2004; Magna *et al.*, 2006; Jeffcoate *et al.*, 2007; Marschall *et al.*, 2017),现代海水 Li 同位素组成 δ^7Li=+31~+32‰(Millot *et al.*, 2004;付露露等, 2021),蚀变洋壳 Li 同位素组成 δ^7Li=+1‰~+14‰(Tang *et al.*, 2007),海洋沉积物Li同位素组成 δ^7Li=-2‰~+14‰(Tang *et al.*, 2007)(图 1).

5.2　俯冲板片的 Li 同位素特征

在俯冲过程中,绿片岩相-角闪岩相-蓝片岩相没有显著的Li同位素分馏,说明俯冲板片在早期脱水过程中,流体能继承原岩的Li同位素组成(Qiu *et al.*, 2009; Penniston-Dorland *et al.*, 2010). Zack *et al.*(2003)首先报道了俯冲带极低Li榴辉岩(低至-11‰),其用开放体系瑞利分馏模型模拟板片脱水过程中Li元素分配和同位素分馏,表明 ^7Li 倾向于进入液相从而使残余板片富集轻Li. 板片脱水高Li流体交代地幔楔,使得弧前地幔楔强烈富集Li且具有重Li同位素(Tomascak *et al.*, 2002; Marschall *et al.*, 2007). 然而,模拟计算表明俯冲带进变质脱水过程中,Li同位素最大分馏仅为3‰(Marschall *et al.*, 2007; Wunder *et al.*, 2007). 同时对变质岩自然样品的研究也发现在不同程度的变质脱水过程中Li同位素的分馏同样有限(Teng *et al.*, 2007; Qiu *et al.*, 2009, 2011). 据此,Marschall *et al.* (2007)认为榴辉岩极低的Li同位素值不是由俯冲变质脱水过程主导的,而是变质流体-岩石相互作用过程中Li扩散的结果.

在自然样品中,Li被认为在粒间流体的孔隙空间中移动,^6Li 比 ^7Li 扩散快 3% (Richter *et al.*, 2003),实验和自然岩石中都发现了扩散导致的Li同位素分馏,受扩散影响的距离可能长达30 m,相应的观测到的由扩散导致的分馏达~30‰(Zack *et al.*, 2003; Teng *et al.*, 2006; Marschall *et al.*, 2007, 2017; Penniston-Dorland *et al.*, 2010; John *et al.*, 2012). 所以Li同位素的扩散可以被用作地质速度计来限定流体-岩石相互作用等过程的持续时间.

Li同位素的扩散,与沉积流体的交代作用(Marschall *et al.*, 2007; Penniston-Dorland *et al.*, 2010; Simons *et al.*, 2010),以及由俯冲带蛇纹石脱

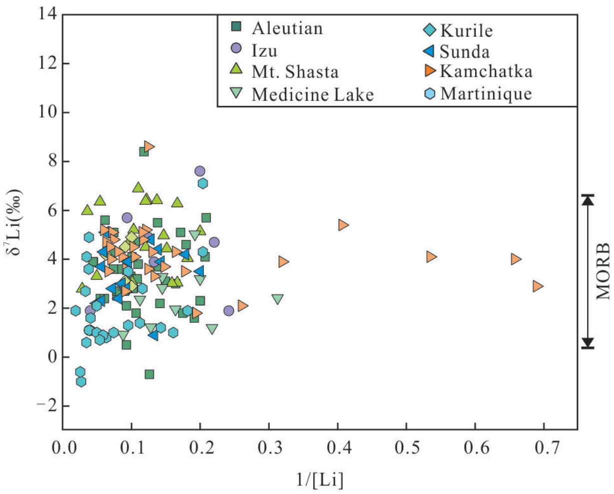

图4 岛弧熔岩δ^7Li值与1/[Li]关系图

Fig. 4 Correlations between δ^7Li and 1/[Li] of arc volcanic lavas

数据来源Moriguti and Nakamura(1998); Tomascak *et al.*(2002); Tomascak(2004); Magna *et al.*(2006); Tang *et al.*(2013); Hanna *et al.*(2020); Liu *et al.*(2020b)

水形成的低^{7}Li的变质流体的交代(Tian *et al.*, 2019)都会导致岩石具有低δ^7Li特征,脱水后的板片富含轻Li继续俯冲至深部地幔,从而导致Li同位素在地幔中的不均一性(Seitz *et al.*, 2004; Aulbach and Rudnick, 2009; Su *et al.*, 2012).同时地幔捕掳体中识别到的低δ^7Li信号,也证明了锂同位素在地幔中局部的不均一性(Zhang *et al.*, 2010; Su *et al.*, 2012; Tang *et al.*, 2013).

5.3 岛弧岩浆的Li同位素特征

全球岛弧岩石显示了均一的Li同位素组成δ^7Li=+2.1‰~+5.1‰(Tomascak *et al.*, 2002; Ryan and Kyle, 2004; Liu *et al.*, 2020b),与MORB组成相一致(图4).虽然板片流体具有高Li浓度和高δ^7Li值的特征,但由俯冲板片脱水所携带的高锂特征可能在地幔楔过程中发生了快速扩散并被均一化(Liu *et al.*, 2020b).但马提尼克(Martinique)岛弧岩浆岩和阿留申(Aleutian)岛弧岩浆岩通过Li-Sr-Nd同位素以及δ^7Li-Y/Li等元素比值进行模拟,发现源区存在少量的俯冲沉积物成分,有可能是俯冲带释放的未被再平衡的流体(Tang *et al.*, 2014; Hanna *et al.*, 2020).

6 结论

随着近10年分析技术的进步,稳定同位素得到了飞速发展.本文对氧化还原敏感元素Fe的同位素及流体活动性元素K, Ba, B和Li同位素在俯冲带流体活动中的行为进行了总结.

(1)Fe是俯冲带中对氧化还原敏感的变价元素,其对俯冲带的研究表明俯冲板片和地幔交界处的氧逸度是非均质的,局部可存在氧化性或还原性流体.因此,Fe同位素在示踪俯冲带复杂流体来源和活动性以及俯冲带深部各阶段流体岩石相互作用方面展示了巨大潜力和前景,但仍需更多后续研究.

(2)K在俯冲带变质脱水过程中,重K优先进入流体.全球大洋玄武岩K同位素均一,表明在地幔部分熔融的高温过程中没有显著的K同位素分馏.此外,在对岛弧岩浆岩的研究中,结合K同位素和放射性同位素识别出了沉积物熔体和蚀变洋壳流体的再循环对岛弧岩浆K同位素组成的再改造过程.K同位素在岛弧岩浆中的研究还处于初步阶段,还需发掘K同位素在岛弧岩浆中的独特优势.

(3)Ba同位素在识别俯冲带蚀变洋壳流体和沉积物熔体组分加入地幔形成岛弧岩浆岩以及区分交代地幔楔熔融模型和混杂岩底辟模型中展现出了巨大潜力.但是,最近的研究显示在大陆俯冲带脱水过程中,Ba同位素可以发生显著分馏,高达0.70‰.对于Ba元素在岛弧深度释放进入岛弧岩浆的比例以及会发生的同位素分馏的研究还较少,这使得Ba同位素识别俯冲再循环物质时可能存在不确定性,需要后续更多研究进行论证.

(4)沉积物在俯冲弧前阶段会丢失~70%的B,残余的B赋存于电气石和白云母中继续俯冲.对全球范围内岛弧岩浆的B同位素统计显示出变质蛇纹岩对岛弧B同位素的巨大贡献.B同位素研究还可以结合其他同位素手段对俯冲带蛇纹岩成因进行限定.此外,还需要做进一步有关典型变质矿物中的原位B同位素研究,以更好的了解深俯冲过程B同位素的行为.

(5)Li同位素在俯冲带早期变质过程中分馏较小.但在榴辉岩中发现的极负的Li同位素值,最开始被认为是脱水流体带走了重Li,但后续的研究表明可能是同位素扩散的结果.此外,Li同位素在全球岛弧岩浆岩中显示组成相对均一,表明其在地幔楔过程中可能发生了再平衡.Li同位素扩散对分馏的影响仍然是研究和讨论的热点,同时对于独特的未发生均一化的岛弧也是Li同位素研究的重点.

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