

深入下地幔：高温高压下的新反应与成分、结构分层

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摘要: 本文总结了过去二十多年矿物学研究在下地幔结构相变和矿物反应的研究进展, 集中讨论了富Ca布里奇曼石形成以及(Al, H)-SiO₂结构相变对下地幔物理性质、物质组成的影响。首先, 讨论了富Ca布里奇曼石的形成条件, 明确了过往研究中, 温压条件及元素组成对其形成深度的影响存在的矛盾和问题。其次, 指出该反应可能导致下地幔物相组成的分层, 但其对下地幔速度密度与元素分配的影响尚需进一步研究。第三, 通过总结俯冲洋壳中Al和水对SiO₂结构相变的影响, 以及洋壳碳酸盐与SiO₂的反应, 探讨了这些变化与下地幔中部不同深度和尺度的低速体之间的关系。最后, 提出在地幔相关温压条件下进一步研究铝和水对SiO₂结构相变前后速度的影响, 这对理解下地幔中部小尺度散射体的形成至关重要。

关键词: 下地幔; 物质和结构分层; 布里奇曼石-毛钙硅石互溶; 斯石英; Al和水

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Deep into the lower mantle: its new reactions, compositional changes, and structural layering under high temperature and high pressure

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Abstract: In this paper, we have summarized the progresses in mineralogical researches over the past two decades regarding to the structural phase transitions and mineral reactions in the lower mantle, and emphatically discussed the formation of Ca-rich bridgmanite and the influence of its structural phase transitions of (Al, H)-SiO₂, on the physical properties and chemical compositions of the lower mantle. Firstly, we have discussed the formation conditions of Ca-rich bridgmanite, clarified contradictions and problems in previous studies regarding to the influences of temperature, pressure, and elemental composition on the depth of the formation reaction of Ca-rich bridgmanite, suggested that this reaction could lead to stratification of phase compositions in the lower mantle, pointed out that its effects on the velocity, density, and element partitioning of the lower mantle should be further researched. By summarizing the influence of Al and water on structural phase transitions of SiO₂ in subducted oceanic crust and the reactions between carbonates and SiO₂, we have further discussed relationships between these variations and the low velocity bodies in the middle part of the lower mantle at different depths and scales, and have proposed that further investigation of the influence of Al and water on the structural phase transitions of SiO₂ under relevant mantle temperature and

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pressure conditions is crucial for understanding the formation of small-scaled scatterers in the middle part of the lower mantle.

Key words: lower mantle; material and structural layering; Ca-rich bridgmanite; stishovite; Al and water

0 引言

下地幔是地球内部最大的连续圈层,深度从660 km延伸至2890 km,温度变化覆盖1800~4400 K (Brown and Shankland, 1981; Hernlund et al., 2005)。由于除了极少量的金刚石包裹体能够携带来自下地幔物质组成的信息,我们几乎无法直接获得下地幔岩石组成的信息。因此对下地幔的研究主要依赖于地震学观测、地球动力学模拟、高温高压矿物学实验等手段 (Bercovici, 2007; Lay, 2007; Price, 2007)。认识下地幔的结构和物质组成,对推动理解基本的地球物理过程,尤其是内外物质交换、热量传递和地球内部动力学过程,揭示深层地球系统的复杂性和演化机制具有重要意义。

研究表明下地幔主要由布里奇曼石[(Mg, Fe)(Si, Al, Fe)O₃],铁方镁石[(Mg, Fe)O]和毛钙硅石(CaSiO₃)组成 (McDonough and Sun, 1995; Irifune et al., 2010; McDonough, 2016)。在地幔岩模型中,布里奇曼石在下地幔的含量高达75%(体积分数),铁方镁石和毛钙硅石的占比分别为~17%和~8%(体积分数) (McDonough and Sun, 1995; Ricolleau et al., 2009; Irifune et al., 2010; McDonough, 2016)。由于这些矿物在下地幔温压范围内不发生结构相变,因此在一维地震学速度图像中,下地幔不存在全球性的速度间断面 (Dziewonski and Anderson, 1981)。过去对下地幔速度异常研究的关注点主要在核幔边界。例如,地震学在核幔边界上方100~300 km处观察到的横波和纵波波速0.5%~3%的跳变,定义为D"不连续面 (Lay and Helmberger, 1983; Wyssession et al., 1998)。D"不连续面只在核幔边界某些地方被观测到,并在不同区域呈现出复杂的波速特征 (Li et al., 1998; Lay and Garnero, 2004; Hutko et al., 2008; Sun D Y et al., 2016)。除了典型的速度跳变,有的区域仅观测到波速斜率的变化 (Sun D Y et al., 2016)。虽然D"不连续面的形成被认为与布里奇曼石向后钙钛矿结构相变密切相关,但D"不连续面复杂的波速结构更表明核幔边界存在强烈的横向速度和温度分布不均一 (Murakami et al., 2004, 2007; Oganov and Ono, 2004; Hirose, 2006; Ono and Oganov, 2005; Catalli et al., 2009; Sun et al., 2018)。

除了D"不连续面,大型低剪切波速省(LLSVPs,

Large Low Shear Velocity Provinces)和超低速带(ULVZs, Ultra-low Velocity Zones)是下地幔研究的另外两个热点和难点问题。LLSVPs位于太平洋和非洲板块下方的核幔边界处,横波波速(V_S)比周围地幔低大约1%~3% (Ni et al., 2002; Ni and Helmberger, 2003; He and Wen, 2009, 2012)。LLSVPs的形成机制目前存在很大的争议。在地幔主要矿物中,四方晶型毛钙硅石、富Fe布里奇曼石,以及含Fe布里奇曼石的歧化反应都被认为可能与LLSVPs的形成有关 (Zhang et al., 2014; Wu, 2016; Thomson et al., 2019; Wang et al., 2021)。此外地球动力学研究提出,LLSVPs可能是岩浆冷却过程或核幔分异过程中残留的物质堆积形成 (Labrosse et al., 2007; Lee et al., 2010; Nomura et al., 2011)。这些物质比周围地幔更加致密,因此可以避免被地幔对流冲散 (Labrosse et al., 2007; Lee et al., 2010; Nomura et al., 2011)。也有研究认为,来自外核的致密Fe-Ni-S流体进入下地幔底部也可能造成LLSVPs,但是Fe合金流体在地幔中的含量还存在较大争议 (Shi et al., 2013; Zhang et al., 2016)。对于核幔边界速度比周围地幔低10%~30%的ULVZs,其可能的形成机制包括含水矿物脱水导致的部分熔融、富Fe流体,以及富Fe后钙钛矿、富Fe铁方镁石、低波速Fe-H化合物的富集等,目前也没有统一的认识 (Williams and Garnero, 1996; Zhang and Fei, 2008; Hu et al., 2016; Liu et al., 2016, 2017; Mao et al., 2017; Fu et al., 2023; Esdaille and Chen, 2024)。

除了核幔边界,地震学还在下地幔中部观测到诸多小尺度散射体 (Kaneshima and Helffrich, 1999; Niu et al., 2003; Niu, 2014; Haugland et al., 2017; Zhang et al., 2020)。这些散射体的横波波速(V_S)通常比周围地幔低2%~6%,纵波波速(V_P)低~1%,密度差异在0.6%~9%之间 (Kaneshima and Helffrich, 1999; Niu et al., 2003; Niu, 2014)。在南美洲等区域,小尺度散射体和周边下地幔 V_S 差高达10%~12% (Haugland et al., 2017)。这些小尺度散射体是否与下沉俯冲板片带来的物质分布不均一相关,也存在争议 (Sun et al., 2019; Wang et al., 2020; Zhang et al., 2021; Yu et al., 2024)。

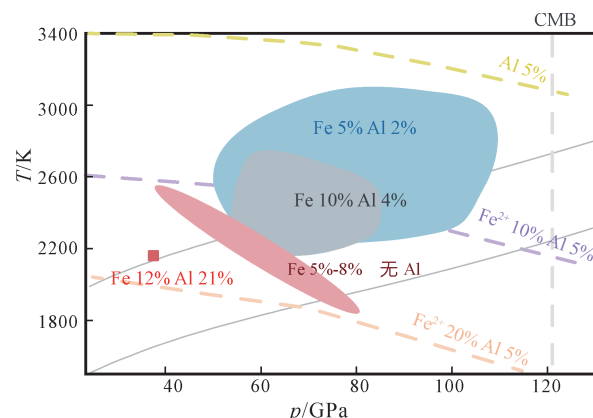
近年来,新的高温高压实验结果为下地幔带来了全新认识。水、碳等挥发分可能跟随俯冲洋壳进入地球深部,并且影响地幔局部区域的物质组成与地震学

信号(Zheng et al., 2016; Maeda et al., 2017; Li et al., 2018; Lv et al., 2021)。尤其是近年来实验和理论计算发现, 毛钙硅石会在下地幔中部深度溶入布里奇曼石, 这为我们理解下地幔的结构与物质组成都提供了全新的认识(Creasy et al., 2020; Muir et al., 2021; Ko et al., 2022; Zhang et al., 2023)。本文中总结了近期高温高压矿物学在下地幔深度的实验和理论计算新结果, 以期下地幔结构和物质分层带来新的理解和认识。

1 毛钙硅石和布里奇曼石的互溶与下地幔分层

早在20世纪就有相关研究提出, 下地幔1600 km深度处可能存在成分分层(Kellogg et al., 1999)。如果下地幔中部存在一个化学成分的分层, 可以更好地解释下地幔洋中脊与洋岛玄武岩的同位素差异以及现有地幔岩模型产热与地表观测不符的问题(Kellogg et al., 1999)。但在核幔边界以上, 下地幔中没有被观测到的全球性速度不连续面。

下地幔的几种主要矿物可能会在下地幔条件下发生结构变化或自旋转变, 但这些变化会带来多大尺度的地震学异常, 还仍存在争议。Badro等(2003)发现铁方镁石中Fe的3d层电子在60~70 GPa会发生高自旋到低自旋的转变, 该项研究也掀起了对Fe自旋转变所引发的地球物理效应的研究热潮(Lin et al., 2005; Marquardt et al., 2009; Mao et al., 2011; Yang et al., 2015; Wu, 2016)。虽然在300 K下铁方镁石中铁的自旋转变宽度较窄, 可以引起体积模量和纵波速度~10%的陡然下降和密度陡增; 但温度升高至下地幔中部温度后, 铁方镁石自旋转变宽度将增加到~1200 km(Lin et al., 2005; Mao et al., 2011)。因此, 其Fe自旋转变是否能产生可被探测的地震学信号还存在较大争议(Lin et al., 2005; Marquardt et al., 2009; Antonangeli et al., 2011; Mao et al., 2011; Yang et al., 2015; Wu, 2016)。作为下地幔中含量最多的矿物, 布里奇曼石中Fe同样存在自旋转变, 但自旋转变发生的条件颇为苛刻(Dobson and Brodholt, 2005; Catalli et al., 2011; Mao et al., 2015)。只有当布里奇曼石中的 Fe^{3+} 出现在B位才能在40~50 GPa发生自旋转变(Dobson and Brodholt, 2005; Catalli et al., 2011; Mao et al., 2015)。虽然布里奇曼石中 Fe^{3+} 的自旋转变同样可以引发密度的增加和纵波波速的降低, 但由于布里奇曼石中的Al限制了B位 Fe^{3+} 的含量, 布里奇曼石中 Fe^{3+} 自旋转变对速度的影响有限, 在下地幔很难引起可被观测到的速度结构分层(Dobson and Brodholt, 2005; Catalli et al., 2011; Mao et al., 2015; Fu et al., 2018)。毛钙硅石作



阴影区域为高温高压实验中, 不同成分样品富-Ca布里奇曼石形成的条件。其中, 蓝色阴影为Fe含量5% Al含量2%; 灰色阴影为Fe含量10% Al含量4%; 红色阴影为Fe含量5%~8%不含Al; 红色点为Fe含量12% Al含量21% (Creasy et al., 2020; Fujino et al., 2004; Ko et al., 2022)。

虚线为理论计算中富-Ca布里奇曼石形成的温度随Fe含量的变化 (Muir et al., 2021)。其中, 黄色虚线为Al含量5%; 紫色虚线为 Fe^{2+} 含量10% Al含量5%; 桔黄色虚线为 Fe^{2+} 含量20% Al含量5%。灰色实线为正常和冷的俯冲板片低温曲线(Brown and Shankland, 1981)。CMB—核幔边界

图1 Fe、Al等元素对富-Ca布里奇曼石形成条件的影响

Fig.1 The Influence of elements such as Fe and Al on the formation conditions of Ca-rich Bridgmanite

为下地幔中含量第三的矿物, 在常温高压下处于四方晶型结构, 在高温的下地幔会相变为立方晶型结构(Sun N Y et al., 2016)。近年来有研究陆续指出, Al和Ti元素的加入可以使四方晶型毛钙硅石的稳定性提高, 使其可以在冷俯冲环境下存在于下地幔(Kurashina et al., 2004; Thomson et al., 2019)。但Al、Ti等元素在下地幔储量有限, 其在下地幔温度和压强条件下对毛钙硅石结构相变的影响还亟待进一步深入研究, 这样的结构相变是否能够引起下地幔全球性的速度分层也不清楚。

Ko等(2022)在自然杂志发表的高温高压结果指出, 下地幔压强超过39 GPa、温度超过2200 K后毛钙硅石将溶入布里奇曼石形成一个单相。这与下地幔由毛钙硅石、布里奇曼石和铁方镁石三种矿物独立存在的传统认识截然不同。该研究结果发表后, 引起了对下地幔是否存在物质形态分层的新关注。实际上早在20世纪末, Miyajima等(1999)就以富Al石榴石作为起始样品, 在35 GPa高温加热后, 发现毛钙硅石和部分NAL相溶入了布里奇曼石。但后续利用透辉石作为起始物质的研究发现, 毛钙硅石在布里奇曼石中的溶解度只有0.02(Irifuue et al., 2000)。

目前看来, 毛钙硅石是否能够溶入布里奇曼石受多种条件影响。首先, 毛钙硅石和布里奇曼石发生互溶的压强在~35 GPa(900 km深度)以上, 温度均超过1900 K(Creasy et al., 2020; Fujino et al., 2004; Ko et

al., 2022; Muir et al., 2021; Zhang et al., 2023)。例如, Fujino等(2004)在以铁铝榴石与钙铁榴石的混合物作为起始样品的高温高压实验中观察到, 毛钙硅石和布里奇曼石在~30 GPa、1900~2200 K下还几乎完全不互溶; 而当温压达到~78 GPa、1900~2200 K后, 毛钙硅石中被检测到有~9% Mg(摩尔质量, 下同)以及~8% Fe。随后的实验与计算研究都指出, 温度对Ca溶入布里奇曼石有极大的促进作用(Miyajima et al., 1999; Fujino et al., 2004; Creasy et al., 2020; Muir et al., 2021; Ko et al., 2022; Zhang et al., 2023)。在Ko等(2022)的研究中, 他们观察到所有富Ca布里奇曼石都出现在2200 K以上; 理论计算结果发现, 在125 GPa、2042 K, 仅1%的毛钙硅石可以溶入布里奇曼石, 在2675 K时有10%的毛钙硅石溶入, 但当温度升高至2743 K, 则有50%的毛钙硅石可以溶入(Muir et al., 2021)。

下地幔布里奇曼石是Fe和Al的重要储库, Fe和Al含量的多少也对毛钙硅石和布里奇曼石的互溶有显著影响(Miyajima et al., 1999; Creasy et al., 2020; Muir et al., 2021)。首先, 布里奇曼石中的Fe对毛钙硅石的溶入有促进作用(图1)(Ko et al., 2022)。含铁量10%的布里奇曼石与毛钙硅石完全互溶发生在39 GPa、1900 K, 形成 $\text{Ca}_{0.1}\text{Mg}_{0.8}\text{Fe}_{0.1}\text{SiO}_3$, 互溶温度比理论计算中预测的纯 MgSiO_3 - CaSiO_3 体系低~400 K(Muir et al., 2021)。但是, 对于互溶过程中究竟是 Fe^{2+} 还是 Fe^{3+} 扮演了更重要的角色, 目前存在较大不确定性(Miyajima et al., 1999; Creasy et al., 2020; Muir et al., 2021)。理论计算研究指出, 布里奇曼石中 Fe^{2+} 可以促进富Ca布里奇曼石的形成(Muir et al., 2021)。增加5%的 Fe^{2+} 可以使二辉橄榄岩体系中毛钙硅石溶入布里奇曼石的温度降低~700 K(Muir et al., 2021)。但实验结果倾向认为 Fe^{3+} 对富Ca布里奇曼石的形成更有利(Miyajima et al., 1999; Creasy et al., 2020)。Miyajima等(1999)的起始样品中只含有 Fe^{2+} , 但是他们在回收的样品中发现了歧化反应产生的 Fe^{3+} 。因此他们推测, 在毛钙硅石溶入布里奇曼石中起决定性作用的是歧化反应产生的 Fe^{3+} (Miyajima et al., 1999)。不仅如此, Creasy等(2020)发现在 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 仅为11%的起始样品中, 即使温度和压强达到2000~2300 K和35~40 GPa也没出现毛钙硅石溶入布里奇曼石的现象; 但当起始辉石样品中 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 增加到55%后, 在相同温压条件下出现了富Ca布里奇曼石。

另一方面, 作为布里奇曼石中的重要组成元素之一, Al被认为会抑制富Ca布里奇曼石的形成(Fujino et al., 2004; Muir et al., 2021; Ko et al., 2022)。理论计算

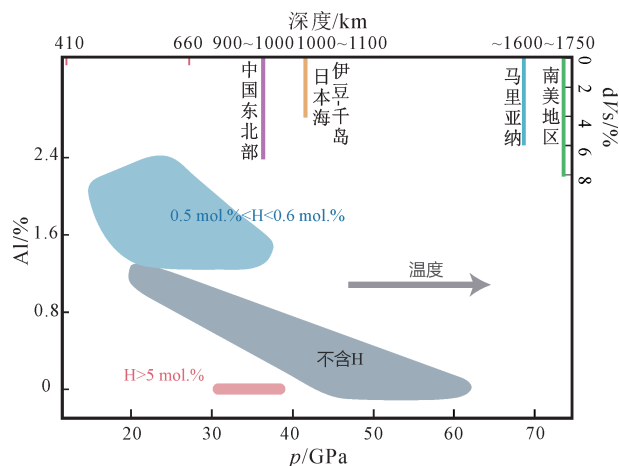
则发现, 含有10% Fe^{2+} 和5% Al^{3+} 的样品比仅含有8% Fe^{2+} , 以及 $\text{Fe}^{3+} + \text{Al}^{3+}$ 含量仅为2%的样品的互溶温度高~200 K(Muir et al., 2021)。Ko等(2022)发现, 在同时含有Fe和Al的科马提岩样品中, 布里奇曼石-毛钙硅石发生互溶的温度比纯Fe体系高~400 K。因此, 这两项研究均认为Al对毛钙硅石溶入布里奇曼石有抑制作用(Muir et al., 2021; Ko et al., 2022)。

一旦毛钙硅石与布里奇曼石的互溶在下地幔发生, 下地幔将被分割为由布里奇曼石、铁方镁石、毛钙硅石三相共存的上层, 以及由布里奇曼石-毛钙硅石和铁方镁石两相构成的下层。如前所述, 虽然这种分层发生的深度受成分、温度和布里奇曼石中Fe价态的影响, 但据估计会发生在下地幔中部1500~2200 km深度。目前, 该分层反应可能带来的下地幔物理性质变化尚不清楚。根据过往的实验研究, Ko等(2022)指出, 该反应可能带来0.6%的密度变化, 反应前后的体积模量几乎没有变化, 因此该反应不会产生可以观测的地震学信号。而根据理论计算的结果, 该反应可能使纵波和横波波速分别产生-0.5%~1.2%和-1.5%~3.5%的变化(Muir et al., 2021)。但这是否会产生全球性的地震学异常, 则尚不确定。如前所述, 温度是引起这种物相分层的核心因素之一。在早期地球拥有更热的地幔的条件下, 富Ca布里奇曼石可能在很浅的下地幔深度形成(Ko et al., 2022)。在地球逐渐冷却的过程中, 下地幔富Ca布里奇曼石层会逐渐变薄, 集中在下地幔深部(Ko et al., 2022)。这种在演化过程中深度不断变化的物相分层如何影响下地幔的热量传输、元素分配、粘滞系数等物理性质, 则亟待地球物理和矿物学研究的进一步探索。

2 俯冲洋壳与下地幔中部小尺度散射体

除了核幔边界处广泛存在的速度异常, 地震学数据显示下地幔中部900~1900 km深度存在一些横波低于周围地幔2%~12%的速度异常体(Kaneshima and Helffrich, 1999; Niu et al., 2003; Niu, 2014; Haugland et al., 2017; Zhang et al., 2020)。这些发生在下地幔不同深度, 具有多变横波波速特征的异常结构或者速度界面是否代表着下地幔不同深度和区域存在物质分布的异常? 这些物质异常是否与洋壳的俯冲有关? 这些都成为理解下地幔物质循环和组成的热点和难点问题。

在化学成分上, 俯冲洋壳较正常地幔贫Mg, 但富Si、Fe、Al、Ca等元素, 并且还携带了大量的挥发分(Ricolleau et al., 2010; Ishii et al., 2022b)。这种成分的差异使得俯冲洋壳具有明显区别于正常地幔的密度和速



蓝色阴影为斯石英H含量0.5%~0.6%;红色阴影为斯石英中H含量大于5%;灰色阴影为不含H的斯石英。彩色短线为地震学观测到的下地幔中部速度异常的深度以及 V_S 变化。其中,紫色为中国东北部(Zhang et al., 2020);橙色为日本海(Niu, 2014)和伊豆—千岛地区(Niu et al., 2003);蓝色为马里亚纳地区(Kaneshima and Helffrich, 1999);绿色为南美地区(Haugland et al., 2017)

图2 常温高压下Al元素和H元素对斯石英相变条件的影响及地震学观测在不同区域发现的低横波散射体

Fig. 2 The influence of Al and H elements on the phase transition conditions of stishovite under ambient temperature and high pressure, and seismologically observed low S-wave scatterers in different regions

度结构(Wang et al., 2020; Yu et al., 2024)。特别是和正常地幔相比,俯冲洋壳中含有大量的 SiO_2 ,它的结构相变对俯冲洋壳及周围地幔有巨大影响(Harte, 2010; Sun et al., 2019; Zhang et al., 2021)。 SiO_2 以斯石英存在于俯冲至下地幔的洋壳中,其含量可以达到16%~25%(体积分数)(Harte, 2010)。在下地幔中部温压条件下(~1800 km, 2200 K),斯石英会进一步相变为具有 CaCl_2 型结构的后斯石英相(Kingma et al., 1995; Prakapenka et al., 2004; Shieh et al., 2005; Nomura et al., 2010; Wang et al., 2012; Fischer et al., 2018; Sun et al., 2019)。虽然这一相变是铁弹性的二级相变,不会引起明显的密度跳变,但在相变过程中会导致剪切模量的大幅度降低,带来1.2%的纵波和6.3%的横波低速异常(Zhang et al., 2021; Yu et al., 2024)。因此,这一相变被认为是中下地幔小尺度散射体的主要成因(Sun et al., 2019; Zhang et al., 2021)。但地震学观测到的小尺度散射体分布在900~1900 km不同深度(Kaneshima and Helffrich, 1999; Niu et al., 2003; Niu, 2014; Haugland et al., 2017; Zhang et al., 2020)。考虑到斯石英至 CaCl_2 型后斯石英相变具有正的克拉波龙斜率,该相变在低温下可能发生在更浅的区域。虽然在较冷俯冲条件下洋壳温度低于正常地幔800 K时,

这一相变发生的深度可以浅至~1500 km,但仍很难解释一些深度在900~1500 km,横波异常高达10%~12%的小尺度散射体(Haugland et al., 2017)。

值得一提的是, SiO_2 是Al和水在下地幔的重要载体(Lakshtanov et al., 2007; Litasov et al., 2007; Bolfan-Casanova et al., 2009; Nisr et al., 2020; Ishii et al., 2022a; Lin et al., 2022)。实验研究观察到,下地幔斯石英可以容纳接近10%(质量分数,下同)的水,而后斯石英的Al含量可以达到9% (Ishii et al., 2022a; Lin et al., 2022)。Al的出现能大幅度降低斯石英至后斯石英相变的压强(Nisr et al., 2020; Zhang et al., 2021; Ishii et al., 2022a)。在300 K下,含有3%Al(摩尔质量,下同)的斯石英在~35 GPa(900 km)就相变为后斯石英,相变压强远低于纯 SiO_2 斯石英的55 GPa(Zhang et al., 2021)。对于不含Al的体系,H主要以 $4\text{H}^+ \leftrightarrow \text{Si}^{4+}$ 的取代机制进入斯石英,但已有实验对H如何影响斯石英的相变压强存在争议(Nisr et al., 2020; Lin et al., 2022)。例如,Nisr等(2020)认为H和Al类似,可大幅降低斯石英的相变压力。在只含14% H的 SiO_2 中,斯石英在~24 GPa, 1500 K(660 km)就会转变为后斯石英相。但Lin等(2022)却认为H对后斯石英相变的影响较小。目前看,至少在Al和H同时存在的 SiO_2 中(2.37(2)% Al, 0.53% H),相变压强可低至24.3 GPa(~660 km)(Lakshtanov et al., 2007; Bolfan-Casanova et al., 2009; Nisr et al., 2020; Lin et al., 2022; Zhang et al., 2022)。但上述关于含Al和H斯石英相变条件的研究结果基本来自于常温高压实验。温度的升高如何影响这一相变的发生深度? Al和H是否引发相变过程中速度陡降幅度的变化? 这都极大影响了我们对下地幔小尺度散射体形成机制的理解。

有趣的是,洋壳俯冲至下地幔后还可能携带类似菱镁矿(MgCO_3)的挥发分(Maeda et al., 2017; Drewitt et al., 2019; Lv et al., 2021)。这些挥发分在下地幔不同深度会与洋壳以及地幔物质发生反应,影响下地幔在局部区域的物质组成(Seto et al., 2008; Maeda et al., 2017; Drewitt et al., 2019)。例如,菱镁矿就会与 SiO_2 在下地幔中部50~80 GPa(1200~1800 km)发生反应,生成 CO_2 和 MgSiO_3 ,反应的克拉波龙斜率为147 MPa/K(Seto et al., 2008; Maeda et al., 2017; Drewitt et al., 2019)。Fe的加入会降低菱镁矿与 SiO_2 反应的发生温度(Drewitt et al., 2019)。含 FeCO_3 为15.38%(质量分数)的菱镁铁矿将在46 GPa, 1900 K与 SiO_2 发生反应,克拉波龙斜率为74 MPa/K;反应发生的温度低于 MgCO_3 体系在该深度的~2100 K(Drewitt et al., 2019)。如果白云石能被输运至下地幔,铁含量为

16.89% (质量分数) FeCO_3 的白云石会在 50 GPa、1880 K 与 SiO_2 发生反应 (Drewitt et al., 2019)。

碳酸盐与 SiO_2 反应能极大的改变俯冲洋壳中 SiO_2 的含量,进而影响斯石英至后斯石英相变时速度异常的幅度。当 SiO_2 中不含有任何 Al 和 H 时,在正常下地幔温度下,菱镁矿- SiO_2 的反应相较于斯石英相变发生在更浅的 ~1000 km 深度 (Maeda et al., 2017)。如果俯冲洋壳中 CO_2 的含量为 2.5%~5.0% (质量分数),菱镁矿与 SiO_2 的反应将消耗掉俯冲洋壳中 4.5%~9.0% 的 SiO_2 (Yu et al., 2024)。相较于不含碳的俯冲洋壳, SiO_2 被消耗后,其相变过程中产生的横波低速也将由 ~6% 降低到 2.5%~4.5% (Yu et al., 2024)。对于较冷的俯冲板片,当其温度比正常地幔低 500 K 时,菱镁矿与 SiO_2 的反应发生在斯石英相变之后 (Nomura et al., 2010; Sun et al., 2019)。结合碳酸盐本身对俯冲洋壳的速度密度影响,在含碳俯冲洋壳中发生斯石英相变能造成 4.4%~6.4(4)% 的横波波速陡降 (Yu et al., 2024)。如果再考虑 Al 和 H 对斯石英相变深度的影响,俯冲洋壳含碳量的不同以及温度的变化可以解释在日本海、伊豆—千岛和马里亚纳等区域观测到的 900~1800 km 深度范围内,具有 2%~7% 横波低速异常的小尺度散射体的形成 (Kaneshima and Helffrich, 1999; Niu, 2014; Niu et al., 2003; Yu et al., 2024)。

因此,下地幔低横波波速小尺度散射体的形成可能与俯冲洋壳的成分差异以及在下地幔温度压强下经历的复杂化学反应密切相关。当然,Al 和 H 含量以及温度变化是如何影响斯石英至 CaCl_2 型结构相变深度、波速等物理性质目前还缺乏足够的实验研究。对于一些横波低速异常达到 10%~12% 的小尺度散射体也无法用上述 SiO_2 相变来解释。这些都需要未来的实验和理论计算研究来帮助我们进一步深入认识存在于下地幔不同深度的速度异常体的形成机制。

3 总结

本文回顾了过去二十多年在高温高压矿物学实验和理论计算方面在下地幔条件下的研究进展,重点探讨了这些研究在结构相变和矿物反应方面的新发现,以及它们对我们深入理解下地幔物质组成和速度结构的重要意义。文章主要总结了布里奇曼石-毛钙硅石互溶和 (Al, H)- SiO_2 结构相变在揭示下地幔潜在物质分层、不同深度速度异常体以及界面重要性的研究成果。分析了温度、Fe 和 Al 含量以及 Fe 价态对布里奇曼石-毛钙硅石在下地幔互溶发生深度的影响,指出目前已有实验和理论计算还存在的矛盾和不足。特别指出目前大部分研究仍集中在明确布里奇曼石-毛钙

硅石互溶的发生条件,但对互溶发生后是否影响下地幔的演化历程、元素分配和输运以及速度密度结构仍不清楚,亟须进一步研究。虽然斯石英结构相变与下地幔中部深度小尺度低横波波速散射体的形成密切相关,但在地幔相应温度下,Al 和水如何影响斯石英结构相变深度,以及它们对相变前后波速的影响等问题,仍需要未来的实验和理论计算进行深入研究。这些新反应和新的结构相变不断更新我们对下地幔物质组成和结构的认识,对明确地球深内部演化过程至关重要。

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