名义上无水矿物中微量结构水的分析方法研究进展

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摘要 在地球内部, 氢主要以羟基和分子水的形式存在于矿物和熔体中, 构成各种活动和不活动的富水组分. 对于含水矿物来说, 氢主要占据正常的结构位置, 是矿物化学式中不可或缺的一部分. 对于名义上无水矿物来说, 尽管其化学式中不含氢, 但是在矿物结构位置和晶格缺陷中可以含有微量的结构水和分子水. 矿物晶格缺陷中的流体/熔体包裹体可含有可观量的水. 尽管名义上无水矿物的水含量很有限, 通常在 ppm 量级, 但是这些微量水对矿物乃至岩石体系的诸多物理化学性质均会产生极其显著的影响. 伴随现代分析技术手段的不断改进和提高, 针对名义上无水矿物中结构水含量及其氢同位素组成的探测表现为朝着更高的空间分辨率、更低的检出限以及多种分析方法综合应用的方向发展. 迄今为止, 显微红外光谱仍然是名义上无水矿物中结构水观察的最主要手段, 此外离子探针、连续流质谱法和弹性反冲探测分析技术等亦得到了更广泛的应用. 本文简要回顾近年来这些分析方法的研究进展及其应用情况.

关键词 名义上无水矿物, 水含量, 结构羟基, 分子水, 红外光谱

1 引言

研究发现上地幔和地壳的主要造岩矿物, 橄榄石、辉石、石榴石、长石和石英等名义上无水矿物, 均含有一定量的水在矿物结构位置和晶体缺陷中, 水的含量(通常表征为质量百万分之一, 即 parts per million)可以从数 ppm 至数千 ppm (Bell 和 Rossman,

1992a, 1992b; Beran, 2006; Johnson, 2006). 这些水通常以结构羟基和分子水的形式存在, 两者之间的比例随压力大小而变化. 考虑到这些造岩矿物在地球圈层中所占的质量权重, 它们构成了地球中最重要的水储库 (Kohlstedt 等, 1996; Withers 和 Hirschmann, 2008; Tenner 等, 2012a).

水的存在能够显著影响体系的熔融温度和流变

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学性质(Hirth和Kohlstedt, 1996; Kohlstedt, 2006)、降低地震波速和黏滞度、增强电导率、改变光和热辐射能效、影响其他离子的扩散速率、加深熔融的起始深度并影响熔融程度等。正是由于这些作用, 水的存在显著影响了地球内部的许多岩石学和动力学过程, 包括火山喷发在内的熔融事件、地幔对流、壳幔相互作用等(Asimow和Langmuir, 2003; Bercovici和Karato, 2003; Dixon等, 2004; Hauri等, 2006a; Karato, 2011; Grove等, 2012)。甚至有人提出, 没有水板块运动亦不会发生(Regenauer-Lieb等, 2001; Regenauer-Lieb和Kohl, 2003)。

2 名义上无水矿物的水含量分析

尽管前人针对名义上无水矿物中微量结构水含量的量化进行了多种途径的探测, 包括氢测压法(Bell等, 1995)、连续流质谱法(Gong等, 2007a; O'Leary等, 2007)、核反应分析法(Bell等, 2004)、弹性反冲探测分析法(Aubaud等, 2009; Bureau等, 2009; Withers等, 2012)、核磁共振法等(Keppler和Rauch, 2000; Johnson和Rossman, 2003), 显微傅里叶变换红外光谱仍然是迄今为止应用最广泛并且最便捷的观察手段(Rossman, 2006)。此外, 本底不断降低的离子探针/纳米离子探针技术受到日益广泛的重视(Stephant等, 2014; Hu等, 2015)。

2.1 红外光谱法

显微红外光谱技术因其制样相对简单, 一般需要晶格定向的矿物颗粒或者一定厚度的双面抛光岩石薄片, 并且具备较高的灵敏度和操作便捷而得到广泛的应用。红外光谱技术不仅能够获得矿物水含量的定量信息, 同时亦能给出氢在矿物中的赋存方式以及区分不同种型的水, 即结构羟基与分子水(Rossman, 2006)。前人应用红外光谱技术针对结构水及伴随的流体活动性开展了大量的研究, 并积累了大量的常见造岩矿物谱图数据, 便于研究者将获得的红外谱图与前人的工作进行对比研究。不同造山带超高压变质岩中常见名义上无水矿物石榴石、单斜辉石、金红石和石英的探测均发现了一定数量的水, 包括阿尔卑斯Dora Maira地块(Rossman等, 1989)、哈萨克斯坦 Kokchetav 地块(Katayama 和 Nakashima,

2003; Katayama等, 2006)以及中国大别-苏鲁造山带(Zhang等, 2001; Xia等, 2005; Chen等, 2007; Sheng等, 2007; Su等, 2008)。除了以结构羟基形式存在的结构水之外, 这些矿物中还发现微米/纳米级流体包裹体形式存在的分子水(Su等, 2002; Meng等, 2009), 这部分水可以采用高温裂解/元素和同位素在线连续流质谱法来进行探测(Gong等, 2007a)。矿物中的结构水和分子水共同构成了深俯冲大陆板块中变质流体的重要来源(Zheng, 2009; Zheng和Hermann, 2014)。

将显微红外光谱技术与冷热台相结合, 一般可实现的温度控制范围为液氮温度-196~600℃, 通过对比不同温度条件下矿物的红外吸收峰位置及其强度的变化, 可以深入探讨氢在名义上无水矿物缺陷结构中的配位、种型信息及其温度效应(Yang等, 2012, 2015)。例如: 单斜辉石从室温升值500℃时, 3620~3640 cm^{-1} 吸收峰表现为系统的降低, 而3520~3535和3450~3465 cm^{-1} 两组吸收峰位置则基本上保持不变, 这不仅指示了第一组与后两组吸收峰在氢结合强度上的显著差异, 同时说明高温下的红外吸收系数与室温下可能是不同的(Yang等, 2010)。金红石的两组吸收峰3279和3297 cm^{-1} 在升温过程中表现出后者吸收面积的降低的同时伴随着前者吸收面积的升高, 表明温度效应引起粒间形式氢的赋存方式的相互转化(Yang等, 2011)。

鉴于上地幔捕虏体矿物在伴随寄主金伯利岩浆或碱性岩浆上升途中可能发生氢的扩散丢失, 对存在水含量扩散剖面的捕虏体矿物进行精细的显微红外光谱观察, 进而通过扩散动力学模拟可获得寄主深源岩浆的抬升速率信息(Demouchy等, 2006; Peslier等, 2008, 2015)。智利Pali-Aike碱性玄武岩携带的地幔橄榄岩捕虏体中橄榄石存在明显的脱水扩散剖面, 这一方面暗示了利用橄榄石来反演上地幔的水含量可能明显被低估, 另一方面间接地制约了寄主岩浆从60~70km地幔深部喷出至地表的速率为(6±3)m/s(Demouchy等, 2006)。类似的, 南非金伯利岩和夏威夷岛霞石岩的抬升速率被分别限定在5~37m/s(Peslier等, 2008)和0.2~25.3m/s(Peslier等, 2015)。而与橄榄石共生的单斜辉石和斜方辉石水含量的大量红外观察数据则发现其保持了深部地幔的水含量配比, 似乎并没有受到抬升扩散影响, 可以用来反演上地幔的水含量(Peslier等, 2002; Grant等, 2007; Yang等,

2008; Gose等, 2009; Xia等, 2010, 2013; Sundvall和Stalder, 2011).

在应用红外光谱技术计算水含量时, Beer-Lambert定律要求已知吸收系数. 不同种类和化学组成的矿物红外吸收系数要么通过其他独立的方法来获得(Bell等, 1995, 2004), 要么通过羟基振动频率与吸收系数之间的相关性来计算得到(Paterson, 1982; Libowitzky和Rossman, 1997), 吸收系数的精准度决定了是否能够采用红外光谱技术来获得准确的水含量. 迄今为止, 常见造岩矿物橄榄石、单斜辉石、斜方辉石、石榴石、长石和石英等以及副矿物金红石和蓝晶石等都积累了相当数量的吸收系数数据(Rossman, 2006). 由于明显的空间分辨率优势, 离子探针在标定红外吸收系数上表现出日益强劲的发展潜力(Mosenfelder等, 2011).

利用Beer-Lambert定律 $c=A/(I \times t)$ 计算水含量时, 积分面积 $A(\text{cm})$ 为全部羟基振动吸收峰面积的总和, 对于是否有必要针对不同位置的吸收峰进行单独的吸收系数标定, 目前仍然存在争议(Kovacs等, 2010; Stalder等, 2012). 理论上, 应采用偏振红外光在三个晶轴方向上或者三个相互垂直方向上的吸收面积加和来获得准确的水含量(Libowitzky和Rossman, 1996), 但是针对粒径较小的天然或合成矿物颗粒来说, 在特定情况下, 采用非偏振光在非定向颗粒上进行多点(一般>10)采集并加权平均的做法在理论和实践上亦被证实是行之有效的办法(Kovacs等, 2008; Withers, 2013; Xia等, 2013; Liu等, 2015).

对于非均质矿物来说, 采用显微红外光谱有三种途径来获得吸收峰面积 A : (1) 偏振光作用于定向颗粒的三个晶轴方向, 将结果进行加和(Libowitzky和Rossman, 1996); (2) 两束相互垂直的偏振光作用于颗粒任意三个相互垂直的方向, 结果加和并除以2(Libowitzky和Rossman, 1996); (3) 颗粒任意方向的非偏振光多次测量(通常>10)的平均值, 结果乘以3(Kovacs等, 2008). 途径(1)适用于矿物颗粒含有足够大且不含杂质的可供分析的区域, 途径(2)适用于样品含有至少2颗以上水含量均一的颗粒, 针对粒径较小(一般<0.2mm)的天然和合成样品来说, 通常仅能够通过途径(3)来获得水含量. 当线性偏振吸收>0.3或者非偏振吸收>0.15, 矿物表现为强烈的各向异性时, 非偏振吸收与厚度不成线性关系, 即不再遵循

Beer-Lambert定律(Libowitzky和Rossman, 1996; Kovacs等, 2008; Sambridge等, 2008; Withers, 2013); 只有在偏振吸收<0.3, 矿物表现为弱的各向异性时(偏振吸收的最大值和最小值之间差别不显著), 非偏振光遵循Beer-Lambert定律并可获得较好的水含量精确度(Sambridge等, 2008).

费县玄武岩中单斜辉石斑晶的非偏振红外光谱多次测量结果发现(Xia等, 2013), 三组吸收峰的位置分别出现在大约3640、3530和3460 cm^{-1} . 利用与之相似化学组成和吸收峰位置及其相对强度的单斜辉石偏振红外分析结果的深度对比研究(Bell等, 1995; Sundvall和Stalder, 2011), Xia等(2013)提出费县单斜辉石的非定向颗粒进行单次非偏振光测量较之偏振光所引起的最大偏差将远小于20%, 即使综合考虑红外吸收系数和厚度测量的误差, 水含量的不确定性将小于30%. Liu等(2015)进一步通过理论计算和红外分析论证了该方法应用于太行单斜辉石和斜长石斑晶的可行性.

2.2 离子探针法

除了广泛应用的红外光谱技术之外, 近些年得益于仪器性能和制样技术的改进, 如采用 Cs^+ 离子源, 提高真空度(<10⁻⁹torr)以及无树脂制样技术(图1)等, 二次离子质谱(离子探针)技术日益成为名义上无水矿物中微量结构水探测的强有力手段, 其水含量常规检出限可降至<10ppm, 甚至低至2~4ppm(Hauri等, 2002, 2006b; Koga等, 2003). 红外光谱和离子探针可作为互补的技术手段, 二者既相互印证又各具所长(Aubaud等, 2007). 不同的红外吸收峰能够有效区分矿物中点缺陷形式的结构羟基和体缺陷形式的分子水(流体包裹体中水), 并指示羟基在缺陷中的确切赋存方式, 而离子探针则提供了更高的空间分辨率(特别是纳米离子探针), 无需做晶体定向, 并且可以同时获得矿物近表面层物质的水含量和其他元素/同位素, 如氢同位素组成(Hu等, 2015).

相对于显微红外光谱来说, 离子探针在直接探测共存的地幔矿物与含水硅酸盐熔体之间氢的配分系数方面发挥了巨大优势. 如运用离子探针技术获得了2GPa和1380℃熔融实验中橄榄石/熔体和斜方辉石/熔体之间氢的配分系数(Koga等, 2003); 同样采用离子探针得到1~4GPa和1000~1380℃条件下含水熔

图1 离子探针分析的矿物和玻璃标样以及样品金属钢靶 (Tenner 等, 2009)

融实验中橄榄石、单斜辉石、斜方辉石、石榴石与硅酸盐熔体之间氢的配分, 重新估算上地幔水的最大存储能力分别为橄榄岩0.6wt.%和榴辉岩0.4~0.5wt.% (Hauri等, 2006a). 类似的, 上地幔橄榄岩在不同温压、矿物化学组成以及体系初始水含量条件下的部分熔融实验进一步强化了对矿物/熔体之间氢的配分行

为的认识(Aubaud等, 2004, 2008; Tenner等, 2009, 2012b). 通过将离子探针与红外光谱、拉曼光谱、核反应分析法的水含量分析结果进行相互对比(图2), 使得离子探针水含量分析流程和校正方法日趋完善(Aubaud等, 2007; Mosenfelder等, 2011; Mosenfelder和Rossman, 2013a, 2013b).

最近几年颠覆传统地学观念的月球含水性发现亦离不开离子探针高精度分析的贡献. 月球火山玻璃中挥发份的分析发现其含有4~46ppm的水, 以各种扩散去气模型推测其喷发前的初始水含量为~750 ppm (Saal等, 2008). 月球玄武岩中晚期结晶磷灰石的探测(图3)分别发现了高达1600 (Boyce等, 2010)、6050 (Greenwood等, 2011)和7000ppm (McCubbin等, 2010)主要以羟基形式赋存的水, 指示其岩浆源区的水含量为64ppb~5ppm. 月球玄武岩橄榄石中熔体包裹体的探测也发现了615~1410ppm的水(Hauri等, 2011). 运用红外光谱和离子探针技术对月球表层土壤中玻璃的分析发现其水含量可达到~200ppm (Liu等, 2012). 而有限的质疑月球含有显著水的证据则来自月岩及磷灰石远远超过地球岩石和陨石变化范围的Cl同位素组成($\delta^{37}\text{Cl}=13.0\sim24.5\text{‰}$)的间接推断(Sharp等, 2010).

相比较红外光谱来说, 离子探针是准确获得微小的(一般<0.2mm)天然或合成矿物水含量的首选, 并且可以藉此重新用来标定红外吸收系数(Mosenfelder和Rossman, 2013a, 2013b). 理论和实验结果均表明, 由于化学组成和/或氢种型的差异所引起的平均波数的明显不同, 进而造成采用同种矿物红外吸

图2 斜方辉石中水含量(表征为 $^{16}\text{O}^1\text{H}/^{30}\text{Si} \times \text{SiO}_2$)的离子探针标定(Mosenfelder 和 Rossman, 2013)

(a) 按照 Bell 等(1995)的红外吸收系数来标定; (b) 按照 Libowitzky 和 Rossman(1997)计算的吸收系数来标定

图3 月球磷灰石样品水含量和氢同位素组成相关性的离子探针分析(Greenwood等, 2011)

收系数计算的水含量偏差可能达到30~50%甚至更高(Paterson, 1982; Bell等, 1995; Libowitzky和Rossman, 1997; Balan等, 2008). 以长石为例, 前人将 ^1H MAS核磁共振方法得到的斜长石、透长石和微斜长石水含量用来标定普适性的碱性长石红外吸收系数(Johnson和Rossman, 2003). 然而, 斜长石/歪长石和透长石中结构OH的平均波数分别为大约3200和3300 cm^{-1} , 微斜长石/正长石中结构 H_2O 的平均波数为大约3475 cm^{-1} , 结构OH和结构 H_2O 在波数上的差异必将引起红外吸收系数的明显不同(Koch-Muller和Rhede, 2010). 引入了新的长石红外光谱和离子探针分析结果, 进而重新标定的红外吸收系数分别为(Mosenfelder等, 2015), 微斜长石/正长石中结构 H_2O 为 $(120470 \pm 11360) \text{L mol}^{-1} \text{H}_2\text{O cm}^{-2}$, 斜长石/歪长石中结构OH为 $(150000 \pm 15000) \text{L mol}^{-1} \text{H}_2\text{O cm}^{-2}$, 透长石中结构OH为 $(202600 \pm 20260) \text{L mol}^{-1} \text{H}_2\text{O cm}^{-2}$.

经过不断的尝试和改进, 目前运用离子探针和/或纳米离子探针技术进行高精度的矿物水含量的分析流程已趋于成熟(Boyce等, 2012; Barnes等, 2013). 样品制备方面, 通过无树脂技术以实现有效降低氢的背景值, 即把岩石薄片或矿物单颗粒靶制作过程中所使用的树脂类物质都必须经过丙酮和酒精的反复清洗除去, 然后将样品压入铝金属环所固定的金属靶当中(Mosenfelder等, 2011). 标样方面, 采用前人通过不同方法已获得水含量的橄榄石、单斜辉

石、斜方辉石、石榴石、玄武岩玻璃和流纹岩玻璃等样品来监控背景和校正基质效应(Koga等, 2003; Aubaud等, 2007). 离子探针分析结果中部分表现异常高的水含量或较差内部精密度的分析点, 通常被解释为由亚显微的含水矿物包裹体所引起(Tenner等, 2009; O'Leary等, 2010; Mosenfelder等, 2011; De Hoog等, 2014). 鉴于无法区分不同种型的含氢相, 离子探针分析之前应用扫描电子显微镜的BSE图像有助于避开各种类型的包裹体被证明是行之有效的方法(Hu等, 2014). 尽管不同型号的离子探针(cameca-3f, -6f, -7f, nanoSIMS 50L)在具体仪器参数设置上略有差异, 但是总体上的仪器条件要求是一致的, 即: (1) 样品在交换气阀内应保持尽可能长的时间(24~72h以上); (2) 样品室需要达到超高的真空度(10^{-10} torr量级); (3) 采集 $^{16}\text{O}^1\text{H}$ 信号; (4) 采用 Cs^+ 初始离子源和分析之前的预吹扫和成像等(Tenner等, 2012b; Mosenfelder和Rossman, 2013a, 2013b; Gaetani等, 2014; Stephant等, 2014). Turner等(2015)尝试采用SHRIMP SI对6件天然玄武质玻璃和7件名义上无水矿物(橄榄石和辉石)进行水含量分析, 由于其较之cameca系列具有更大的样品仓和更长的离子束路径, 导致实现高真空度的难度增大以及样品表面水分子释放-吸附信号强度的降低, 目前可达到的检出限约为20~40ppm, 或许未来随着真空度的提高以及样品信号的增强, 采用SHRIMP来探测名义上无水矿物水含量的背景值可望进一步降低.

2.3 拉曼光谱和弹性反冲探测分析

拉曼光谱与红外光谱都是通过羟基的伸缩振动吸收来获得名义上无水矿物的水含量. 与红外光谱可低至1ppm的检出限不同(Libowitzky和Beran, 2006), 采用共聚焦显微激光拉曼光谱技术目前仅能够实现~50ppm的检出限(Di Muro等, 2006); 但相比于红外光谱 $>5\mu\text{m} \times 5\mu\text{m}$ 的空间分辨率来说(Xia等, 2013), 拉曼光谱可低至 $\sim 1\mu\text{m} \times 1\mu\text{m}$ (Thomas, 2000; Thomas等, 2008). 而纳米级的矿物和流体包裹体则只能有赖于场发射扫描电子显微镜的观察(Wirth, 2009). 与红外光谱类似, 显微拉曼光谱同样表现出无损分析、制样简单、操作便捷、高精度和高分辨率的特点, 并且可以获得40ppm~40wt.%的名义上无水矿物乃至含水玻璃的水含量(Thomas等, 2008). 利用

其他分析方法的相互校准, 拉曼光谱方法已应用于重新标定部分橄榄石和石榴石标样的红外吸收系数(Thomas等, 2008).

相对于其他方法来说, 弹性反冲探测分析(elastic recoil detection analysis)是近几年被应用于名义上无水矿物水含量探测上的新技术. 该方法将入射的 $^4\text{He}^+$ 聚焦到抛光的样品表面与氢相互作用引起弹性反冲, 氢原子核离开样品表面被检测到(Sweeney等, 1997; Bureau等, 2003). 在改进后的制样技术和仪器条件下, 目前的常规检出限可达到~100ppm(Aubaud等, 2009). 弹性反冲探测分析属于准无损分析, 且得到的是绝对的水含量, 因此可以用来标定检出限以上的名义上无水矿物和含水玻璃的红外吸收系数, 如天然橄榄石(82~260ppm)、实验合成橄榄石(240~790ppm)、斜方辉石(201~452ppm)、单斜辉石(159~716ppm)、石榴石(90ppm)以及流纹岩玻璃和熔体包裹体等(Bureau等, 2009). 这些名义上无水矿物的水含量与前人红外光谱和离子探针分析结果在实验误差范围内一致(图4). 更进一步, 18个高压实验水合橄榄石(270~2120ppm)亦被用来标定红外吸收系数(Withers等, 2012).

3 名义上无水矿物的氢同位素组成

3.1 连续流质谱法

就流体活动而言, 氢同位素组成能够提供最直接的制约条件. 得益于纳摩尔水量进样系统的连续流质谱(continuous flow isotope ratio mass spectrometry)的技术进步, 即将热分解元素分析仪与同位素气质谱仪联机进行矿物的水含量和氢同位素组成测定, 使得获取氢同位素组成的途径从含水矿物拓展到了名义上无水矿物. 相比于传统的真空压力计法(Bell和Ihinger, 2000), 连续流质谱技术所需要的样品量少, 更有利于挑选出纯净的矿物颗粒和降低杂质的干扰, 一般含水矿物的样品量仅需10~200 μg , 而名义上无水矿物为5~40mg(Gong等, 2007a; O'Leary等, 2007). 依据水含量的多少, 目前含水矿物氢同位素组成和水含量的常规分析精度可达到 $\pm 0.5\text{‰}$ 和 $\pm 0.3\text{wt.}\%$ (Eiler和Kitchen, 2001; Sharp等, 2001; Bauer和Vennemann, 2014), 而名义上无水矿物由于其低的水含量, 常规分析精度可达到 $\pm 5\text{‰}$ 和 $\pm 5\text{wt.}\%$ (Gong等,

图4 红外光谱法与弹性反冲探测分析水含量的相互标定 (Aubaud 等, 2009)

(a) 橄榄石; (b) 单斜辉石; (c) 斜方辉石

2007a, 2007b). 并且通过不同温度下的预加热处理并利用红外光谱技术进行水含量变化的监测, 可近似区分矿物中不同种型的水, 即流体包裹体形式存在的分子水和缺陷形式赋存的结构羟基(Bell和Ihinger, 2000; Gong等, 2007b). 这个方法已经用来分析大陆玄武岩中斑晶矿物的水含量和氢同位素组成(Xu等, 2014).

前人应用连续流质谱技术, 对大别-苏鲁造山带

及中国大陆科学钻探工程主孔岩芯各种类型岩石的含水矿物和名义上无水矿物进行了系统的全水含量(包含了矿物中所有的含氢相)及其氢同位素组成的分析发现(Chen等, 2007, 2011; Gong等, 2007c; 龚冰等, 2013): (1) 氢同位素表现出显著的变化范围, 从-155‰至-20‰, 记录了超高压变质岩原岩经历与古大气降水的高温热液蚀变; (2) 石榴石和绿辉石之间保存了平衡或非平衡的氢同位素分馏, 指示了板块折返过程中名义上无水矿物与退变质流体之间差异的氢同位素交换; (3) 石榴石、绿辉石和金红石等名义上无水矿物中的全水含量与氢同位素组成表现出负的相关性, 表明贫D的分子水通常较之结构羟基表现出更强烈的流体活动性, 由此造成后成合晶矿物较之寄主矿物更加贫D. 目前连续流质谱法在应用于变质岩名义上无水矿物的全水含量和氢同位素组成时有下列方面亟需提高和改进: (1) 分步加热时如何避免样品与大气接触造成可能的氧化还原反应; (2) 如何控制不同产状和化学成分的名义上无水矿物释放流体包裹体中分子水的差异温度, 从而近似获得结构羟基的水含量和氢同位素组成; (3) 如何最大限度降低含水矿物包体和后成合晶矿物对名义上无水矿物分析造成的影响.

3.2 离子探针法

尽管前人采用离子探针技术建立了完善的含水玻璃和熔体包裹体的氢同位素组成分析流程和基质效应校正(Hauri等, 2002; Hauri, 2002), 并将其广泛应用于各种地质产状岩石的母岩浆水含量示踪(Shaw等, 2008; Hauri等, 2011; Saal等, 2013). 然而, 相对于玻璃和熔体包裹体通常在数千ppm至wt.%量级的水含量, 名义上无水矿物仅含有ppm量级的结构水, 导致其氢同位素的分析精度急剧的降低, 从而限制了其在相对有限变化范围的地球样品中的广泛应用(Bell和Ihinger, 2000). 目前利用离子探针技术获得名义上无水矿物的氢同位素组成数据主要来自地外样品, 如: 火星陨石GRV 020090中磷灰石 δD 的最大值为(4239 $\pm$ 81)‰(Hu等, 2014), 月球含铁斜长岩和橄长岩中斜长石的氢同位素组成为(260 $\pm$ 110)‰(Hui等, 2015), 氢同位素组成分析的不确定性为50~100‰. 未来是否可利用离子探针技术进行更广泛的名义上无水矿物氢同位素分析, 一方面有赖于氢同位素

标样的不断积累, 另一方面有赖于真空度和多接受器的进步所带来的低丰度同位素D探测精度的显著提高.

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