火星陨石的岩石矿物学及源区特征

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内容提要:目前火星岩石样品的唯一来源是火星陨石,是研究火星物质组成和成分演化、物理化学性质、壳幔分异过程、岩浆过程等的重要窗口。火星角砾岩的成分与探测器和火星车获得的火星表面平均成分及部分表面岩石成分相似,代表了来源于火星壳的富集型样品。其他大部分火星陨石通常为基性岩浆岩,形成于幔源岩浆上涌后喷发至表面或侵入为岩墙或岩床,携带了火星幔的物质组成信息,不同的微量元素和同位素组成特征指示其来源于火星幔不同的源区。部分岩浆在上涌过程中经历了火星壳的混染作用,形成的陨石记录了火星壳的部分物质组成。火星陨石的研究已经获得了大量火星表面和深部的物质组成和演化信息,主要认识包括:①火星壳氧化程度较高,富集稀土元素, $^{238}\text{U}/^{204}\text{Pb}$ 比值较高, $\epsilon^{142}\text{Nd}$ 和 $\epsilon^{182}\text{W}$ 较低;②火星幔部的氧逸度和轻稀土元素富集程度高度不均一,同位素组成特征指示至少存在六个不同的源区(低 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 、高 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 、高 $^{147}\text{Sm}/^{144}\text{Nd}$ 低 $^{176}\text{Lu}/^{177}\text{Hf}$ 的三类辉玻无球粒陨石源区;较低 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 、较高 $\epsilon^{182}\text{W}$ 的辉橄与纯橄无球粒陨石源区;NWA 8159 的源区;NWA 7034 中部分组分的源区);③幔部不均一的特征可能形成于火星分异早期。目前发现的火星样品数量约 300 余块,大部分样品的结晶年龄小于 650 Ma,但是火星表面的地质单元主要为诺亚纪或西方纪产物。另外火星探测数据获得的表面岩石成分比火星陨石更富硅和碱性元素,且岩石种类更丰富,除玄武质岩石之外还有大量中性和酸性岩石。因此对火星物质组成和演化更全面、深入的研究还需要的探测任务(包括样品返回)的数据补充。

关键词:火星陨石;岩浆过程;火星幔源区;火星壳混染;玄武岩

火星陨石是研究火星物质组成的直接对象,据陨石协会公告,截至 2021 年 5 月,获得正式命名的火星陨石约有 300 余块,其中包含了很多配对的陨石。目击的降落型陨石仅 5 块,分别为 Chassigny、Nakhla、Shergotty、Tissint 和 Zagami。火星陨石一般根据矿物组成和岩相结构划分为辉玻无球粒陨石(Shergottite, S)、辉橄无球粒陨石(Nakhlite, N)、纯橄无球粒陨石(Chassignite, C)、斜方辉石岩质无球粒陨石(Orthopyroxenite, O)和角砾岩(Martian polymict breccia),因此火星陨石又被称为 SNC 或 SNCO 陨石(McSween et al., 1998; Agee et al., 2013)。种类的名称一般取自本类型的典型样品,例如辉玻无球粒陨石、辉橄无球粒陨石分别根据

Shergotty 和 Nakhla 命名。辉玻无球粒陨石是火星陨石中数量最多的种类,约有 255 块;其次为辉橄无球粒陨石,约 26 块;纯橄无球粒陨石有 3 块;斜方辉石岩质无球粒陨石目前仅 ALH 84001 一块样品;角砾岩的代表型样品主要为 NWA 7034,但该样品还有大约 17 块配对陨石,包括 NWA 7533、NWA 10922 等(Agee et al., 2013; Meteoritical Bulletin Database)。不同类别火星陨石的数量和代表性样品如表 1 所示。

McSween et al. (1980)首先提出 Shergotty 和 Zagami 是来源于火星的样品,它们的结晶年龄较为年轻,应当来源于行星大小的母体而非小行星(Ashwal et al., 1982)。直到在样品 EETA 79001

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和 Shergotty 中发现了与火星大气成分相符的 N_2 、稀有气体、 CO_2 及碳同位素组成等才确定其火星成因 (Bogard et al., 1983; Becker et al., 1984; Carr et al., 1985)。随着更多相似陨石的发现, 统计获得的氧同位素组成和矿物成分等 (例如辉石的 FeO/MnO 特征) 与其他母体来源的样品具有明显差异, 这为火星陨石的判定提供了更多有效途径 (Clayton et al., 1996; Treiman et al., 2000)。

遥感影像解译结果显示火星上广泛存在熔岩流、席状、叶状或坍塌等地貌特征, 表明火山活动是火星上重要的地质活动之一 (Tanaka et al., 2014)。火星陨石中除了火星角砾岩之外, 其他均为岩浆岩, 有助于了解火星的火山活动历史。另外, 虽

然卫星和火星车配备的光谱仪对火星表面进行了遥感和就位探测, 提供了大量火星表面成分和地球物理性质等信息, 但是无法追溯深部物质组成 (McLennan et al., 2014; Khayat et al., 2020; Lognonné et al., 2020)。而火星陨石在精细认识岩相结构和矿物成分上具有显著优势, 在此基础上分析结晶条件、岩浆成分及演化特征等, 可以了解岩浆运移过程和源区物质组成, 从而进一步制约深部物质组成、物理化学性质、早期壳幔分异过程等 (Udry et al., 2020a)。本文将介绍不同亚类火星陨石的岩相结构、成分特征、岩浆过程、结晶年龄和源区物质组成, 解析从火星陨石的角度获得的对火星壳和火星幔的物质组成和演化特征的认识。

表 1 不同种类火星陨石的数量和代表性样品

Table 1 Number and representative samples of different types of Martian meteorites

种类	亚类	数量 ^①	代表性样品	参考文献
辉玻无球粒陨石	玄武质	112	Los Angeles, NWA 480, QUE 94201	McSween et al., 1996 Barrat et al., 2002a; Warren et al., 2004 Combs et al., 2019; Rahib et al., 2019
	嵌晶质	47	NWA 10169, NWA 11065	Barrat et al., 2002b; Filiberto et al., 2012
	橄榄石斑晶质	66	NWA 1068, NWA 6234	Filiberto et al., 2014; Udry et al., 2017
	辉长质	21	NWA 6963, NWA 7320	Herd et al., 2017; Lapen et al., 2017
	其他 ^②	9	NWA 8159, NWA 7635	Udry et al., 2018
辉橄无球粒陨石	-	26	Nakhla, Lafayette, MIL 03346	Beck et al., 2006; Hewins et al., 2020
纯橄无球粒陨石	-	3	Chassigny, NWA 2737, NWA 8694	Mittlefehldt, 1994
斜方辉石岩质无球粒陨石	-	1	ALH 84001	Agee et al., 2013; Humayun et al., 2013
火星角砾岩	均为配对陨石	18	NWA 7034, NWA 7533, NWA 10922	

注: ①陨石数量根据陨石协会公告 (至 2021 年 5 月) 及部分文献统计获得; ②其他种类指与常见四个亚类辉玻无球粒陨石结构具有一定差异或者没有足够信息判断亚类的样品; “-”代表该种类未分亚类。

1 火星陨石的岩相结构与成分特征

火星陨石的矿物组成与地球上的玄武岩相似, 主要矿物为橄榄石、辉石、长石, 尖晶石族矿物 (铬铁矿和钛铁尖晶石等) 和钛铁矿的含量一般小于 5%, 磷酸盐一般小于 2%, 其他副矿物还有陨硫铁、镍黄铁矿、斜锆石、二氧化硅等。大部分长石由于冲击作用转变为熔长石, 仅有少量陨石中存在保留晶体结构的斜长石 (Udry et al., 2020b)。典型的火星陨石显微结构特征如图 1 所示。除了依据岩相和矿物组合分类之外, 还可以依据全岩 $Mg^{\#}$ 值和钙含量划分为三类: 镁铁质 (Mafic)、过镁铁质 (Permafic) 和超镁铁质 (Ultramafic) (图 2; Irving et al., 2011)。通常辉橄无球粒陨石为镁铁质, 纯橄无球粒陨石为超镁铁质, ALH 84001 为超镁铁质。辉玻无球粒陨石成分变化范围较大, 三种类型的样品均有。

1.1 辉玻无球粒陨石 (Shergottite)

不同辉玻无球粒陨石间的岩相结构、主要矿物

成分、主量及微量元素等都有显著的多样性 (Papike et al., 2009)。少量辉玻无球粒陨石中含有地外形成的次生盐类, 例如 EETA79001 中的地外次生碳酸盐、硫酸盐等, 是火星水化蚀变产物 (Gooding et al., 1988, 1990)。早期研究根据矿物组合以及有无斑状结构特征划分了三个亚类: 玄武质辉玻无球粒陨石 (Basaltic Shergottite)、二辉橄质辉玻无球粒陨石 (Lherzolic Shergottite) 和橄榄石斑晶质辉玻无球粒陨石 (Olivine-phyric Shergottite) (McSween et al., 1998; Goodrich, 2002; Papike et al., 2009)。随着更多火星陨石的发现, 一些二辉橄质辉玻无球粒陨石中斜长石的含量高于 10%, 例如 RBT 04261 中的斜长石高达 20% (Usui et al., 2010), 比地球上典型的二辉橄岩更多。为避免成因上的误解, 一般将此类样品称为“嵌晶质辉玻无球粒陨石 (Poikilitic shergottite)”。此外, 辉玻无球粒陨石 NWA 6963、NWA 7320 等具有典型的辉长结构, 新的研究认为应当增加一个“辉长质辉

图 1 火星陨石的背散射和元素假彩色图像

Fig. 1 Back scattered images and false color chemical maps of Martian meteorites

(a)—玄武质辉玻无球粒陨石 NWA 8653; (b)—嵌晶质辉玻无球粒陨石 GRV 020090; (c)—橄榄石斑晶质辉玻无球粒陨石 NWA 8716; (d)—辉长质辉玻无球粒陨石 NWA 7320 (据 Udry et al., 2017); (e)—富普通辉石辉玻无球粒陨石 NWA 8159 (据 Herd et al., 2017); (f)—橄榄石-长石斑晶质辉玻无球粒陨石 NWA 7635 (据 Lapen et al., 2017); (g, h)—橄榄石-斜方辉石斑晶质辉玻无球粒陨石 NWA 1195 (据 Irving et al., 2004); (i)—辉橄无球粒陨石 Nakhla; (j)—纯橄无球粒陨石 NWA 2737 (据 Beck et al., 2006); (k)—斜方辉石岩质无球粒陨石 ALH 84001 (据 Kring et al., 1998); (l)—角砾岩 NWA 7034 (据 Agee et al., 2013)

(a)—Basaltic shergottite NWA 8653; (b)—poikilitic shergottite GRV 020090; (c)—olivine-phyric shergottite NWA 8716; (d)—gabbroic shergottite NWA 7320 (after Udry et al., 2017); (e)—augite-rich shergottite NWA 8159 (after Herd et al., 2017); (f)—olivine-plagioclase-phyric shergottite NWA 7635 (after Lapen et al., 2017); (g, h)—olivine-orthopyroxene-phyric shergottite NWA 1195 (after Irving et al., 2004); (i)—Nakhlite Nakhla; (j)—Chassignite NWA 2737 (after Beck et al., 2006); (k)—orthopyroxenite ALH 84001 (after Kring et al., 1998); (l)—breccia NWA 7034 (after Agee et al., 2013)

玻无球粒陨石(Gabbroic shergottite)”亚类,用以强调其结构特征以及深成的来源(Udry et al., 2017; Filiberto et al., 2018)。另一方面,按照轻稀土元素(Light Rare Earth Element, LREE)的相对含量由大到小,辉玻无球粒陨石可分为富集型

(Enriched, $[La/Yb]_{CN} > 0.8$)、过渡型(Intermediate, $[La/Yb]_{CN} = 0.3 \sim 0.8$)和亏损型(Depleted, $[La/Yb]_{CN} < 0.3$),也可以分别称为轻微亏损型(Slightly depleted)、中度亏损型(Moderately depleted)与重度亏损型(Highly

图2 火星岩浆岩全岩 $Mg^{\#}$ 与钙含量关系示意图
(改自 Irving et al., 2011, 2020)

Fig. 2 Variation of $Mg^{\#}$ versus CaO for bulk Martian igneous rocks (modified from Irving et al., 2011, 2020) 数字对应于 NWA 样品, 其他代号对应样品如下 (Numbers refer to NWA samples and other abbreviations are): LA—Los Angeles; QUE—QUE 94201; S—Shergotty; Z—Zagami; DaG—DaG 476; Y98—Yamato 980459; RBT—RBT 04261; LEW88—LEW 88516; ALHA77—ALHA 77005

depleted) (Bridges et al., 2006; Papike et al., 2009)。典型的辉玻无球粒陨石稀土元素含量特征如图 3a 所示。

1.1.1 玄武质辉玻无球粒陨石 (Basaltic Shergottite, B-S)

玄武质辉玻无球粒陨石主要由较自形、具环带结构辉石与填隙状长石组成。橄榄石含量一般小于 5%，基本上为铁橄榄石。尖晶石族矿物主要为钛铁尖晶石，缺乏铬铁矿等早期结晶矿物。辉石含量约为 40%~73% 不等，以易变辉石和普通辉石为主，成分差异较大，但斜方辉石罕见 (图 4a)。长石约 22%~47% 不等，以中长石为主，少量样品 (例如 Zagami; McCoy et al., 1999) 含有非常富碱性元素的长石质填隙物 (图 4c)。有的样品中常见由钛铁矿、铁橄榄石、白磷钙矿等组成的晚期填隙物 (例如 NWA 8653; Wu Yunhua et al., 2021)。陨石的稀土元素含量差异较大 ($La_{CN} = 2 \sim 17$; $Lu_{CN} = 7 \sim 20$)，以富集型的配分模式为主，过渡型的代表样品为 NWA 480 (Barrat et al., 2002a)，亏损型的代表

样品为 QUE 94201 (Lodders, 1998)。

有 2 块特殊的样品 (NWA 8159 和 NWA 7635) 不同于常见的辉玻无球粒陨石。NWA 8159 同样主要由辉石和长石组成，但斑晶主要为普通辉石，可见斜方辉石，但易变辉石含量明显少于一般的玄武质辉玻无球粒陨石，称为普通辉石辉玻无球粒陨石 (Augite-rich shergottite; Herd et al., 2017)。NWA 7635 由铁橄榄石、普通辉石和自形的长石斑晶组成，粒径最大为 200 μm ，基质由较细粒的富铁普通辉石组成，虽然样品中不含易变辉石，但是其岩相特征和玄武质样品最为相似，通常称之为橄榄石-长石斑晶辉玻无球粒陨石 (Olivine-plagioclase-phyric shergottite; Lapen et al., 2017)。这两块样品的稀土元素含量均较低，且与亏损型的辉玻无球粒陨石一致 ($NWA 8159 La_{CN}/Lu_{CN} = 0.09$; $NWA 7635 La_{CN}/Lu_{CN} = 0.07$)。

1.1.2 嵌晶质辉玻无球粒陨石 (Poikilitic Shergottite, P-S)

嵌晶质辉玻无球粒陨石由嵌晶区和非嵌晶区组成，嵌晶区为粗粒辉石主晶 (粒径高达 10 mm) 包裹较细粒橄榄石或铬铁矿 (几百微米至几毫米)，并且多数辉石主晶的核部为低钙辉石，边缘可能有高钙辉石 (比例 1.4%~28% 不等)，橄榄石约含 11%~31% 不等，长石一般较少，有的嵌晶区内无长石；非嵌晶区则由较为自形的橄榄石 (粒径高达 4 mm)、辉石 (粒径高达 1 mm)、熔长石、磷酸盐、硫化物、铁氧化物等组成 (Lin Yangting et al., 2005; Usui et al., 2010; Jiang Yun et al., 2012)。一般认为非嵌晶区是结晶过程中相对晚期的产物，代表了演化程度更高的组分 (Rahib et al., 2019)。由于嵌晶区和非嵌晶区所占比例并不均一，因此不同样品整体的矿物含量差异较大，橄榄石约含 22%~63%，辉石约含 13%~61%，长石约含 4%~23%，部分样品中的冲击熔体可高达 14%。辉石的成分变化范围比玄武质辉玻无球粒陨石的更小 (图 4a)，长石的成分变化范围则更大 (图 4c)。同一样品中嵌晶区与非嵌晶区的辉石与橄榄石的成分有重叠，但一般最富镁的颗粒在嵌晶区，最富铁的颗粒在非嵌晶区。全岩 $Mg^{\#}$ 含量一般为 56~71 不等。目前发现的嵌晶质辉玻无球粒陨石多数为富集型 ($La_{CN} = 5 \sim 10$) 或过渡型 ($La_{CN} = 0.8 \sim 3$)，仅有 Asuka 12325 为亏损型 (Vinciane et al., 2019)。我国南极科考队在格罗夫山发现的两块火星陨石，GRV 020090 和 GRV 99027 均为嵌晶质辉玻无球粒陨石，分别为富集型

图 3 火星陨石稀土元素含量特征

Fig. 3 REE patterns for Martian meteorites

(a)—辉玻无球粒陨石(据 Lodders, 1998; Barrat et al., 2001, 2002a; Jambon et al., 2002; Anand et al., 2008; Lin et al., 2008; Rahib et al., 2019);(b)—辉橄和纯橄无球粒陨石(据 Nakamura et al., 1982a; Beck et al., 2006; Treiman et al., 2008; Jambon et al., 2016; Hewins et al., 2020);(c)——斜方辉石岩质无球粒陨石 ALH 84001 和角砾岩 NWA 7034/7533(据 Barrat et al., 2010; Agee et al., 2013; Humayun et al., 2013)

(a)——Shergottites (after Lodders, 1998; Barrat et al., 2001, 2002a; Jambon et al., 2002; Anand et al., 2008; Lin et al., 2008; Rahib et al., 2019); (b)——nakhilites and chassignites (after Nakamura et al., 1982a; Beck et al., 2006; Treiman et al., 2008; Jambon et al., 2016; Hewins et al., 2020); (c)——orthopyroxenite ALH 84001 and breccia NWA 7034/7533 (after Barrat et al., 2010; Agee et al., 2013; Humayun et al., 2013)

和过渡型,其中 GRV 99027 是目前发现的嵌晶质辉玻无球粒陨石中稀土元素含量最低的样品(Lin Yangting et al., 2008; Jiang Yun et al., 2012)。

1.1.3 橄榄石斑晶质辉玻无球粒陨石 (Olivine-phyric Shergottite, Ol-phyric S)

橄榄石斑晶质辉玻无球粒陨石主要由橄榄石(7%~29%)、辉石(52%~65%)、长石(12%~27%)组成。整体上,该类陨石中的橄榄石比其他火星陨石更富镁($Mg^{\#} = 85 \sim 50$)。易变辉石(~50%)的含量高于高钙辉石(<10%) (图 4a),少数样品的辉石成分范围较大,例如 LAR 06319,低钙辉石约含 32%(其中斜方辉石 4%),高钙辉石约含 22%(Basu Sarbadhikari et al., 2009)。长石的成分与玄武质辉玻无球粒陨石相近(图 4c)。其典

型的结构特征是具有两组粒径的斑晶:较大的橄榄石斑晶为毫米级,内部常有铬铁矿或熔体包裹体,具有明显的成分环带,核部富镁,边部相对富铁,可能与母岩共同结晶形成(例如 LAR 06319; Basu Sarbadhikari et al. 2009),或为捕虏晶(例如 SaU 005; Goodrich, 2003);较小的橄榄石斑晶普遍为几十至几百微米,成分环带不明显,但普遍比较大橄榄石斑晶更富铁。辉石粒径与较小的橄榄石斑晶相近,少数可达 1 mm,普遍有成分环带,例如 NWA 8716(Wu Yunhua et al., 2019)。多数陨石的稀土元素含量较低,且配分模式以亏损型为主($La_{CN} = 0.6 \sim 1$; $Lu_{CN} = 4 \sim 6$),过渡型的样品有 NWA 6234 (Filiberto et al., 2012)、NWA 7042 (Kizovski et al., 2020),富集型的样品有 NWA 1068(Barrat et

图4 火星陨石的辉石(a,b)和长石(c,d)的成分范围示意图

Fig. 4 Chemical composition of pyroxene (a, b) and plagioclase (c, d) in Martian meteorites

数据来源:玄武质(据 McSween Jr et al., 1996; McCoy et al., 1999; Barrat et al., 2002a, 2002b; Warren et al., 2004; Basu Sarbadhikari et al., 2009; Hui Hejiu et al., 2011),其中长石填隙物来自样品 Zagami;嵌晶质(据 Mikouchi et al., 1997; Mikouchi, 2005; Howarth et al., 2014; Rahib et al., 2019);橄榄石斑晶质(据 Peslier et al., 2010; Gross et al., 2011; Wu Yunhua et al., 2019),其中 NWA 5298 中的填隙物和富铁辉石边的成分未展示;辉橄和纯橄无球粒陨石(据 Floran et al., 1978; Beck et al., 2006; Hewins et al., 2020);ALH 84001(据 Mittlefehldt, 1994);NWA 7034/7533(据 Agee et al., 2013; Santos et al., 2015)

Data sources: basaltic shergottites(after McSween Jr et al., 1996; McCoy et al., 1999; Barrat et al., 2002a, 2002b; Warren et al., 2004; Basu Sarbadhikari et al., 2009; Hui Hejiu et al., 2011), feldspathic mesostases are from Zagami; poikilitic shergottites (after Mikouchi et al., 1997; Mikouchi, 2005; Howarth et al., 2014; Rahib et al., 2019); olivine-phyric shergottites (after Peslier et al., 2010; Gross et al., 2011; Wu Yunhua et al., 2019), the composition of mesostases and the outermost rims is not demonstrated; Nakhilites and Chassignites (after Floran et al., 1978; Beck et al., 2006; Hewins et al., 2020); ALH 84001 (after Mittlefehldt, 1994); NWA 7034/7533 (after Agee et al., 2013; Santos et al., 2015)

al., 2002b)、LAR 06319(Basu Sarbadhikari et al., 2009)。

1.1.4 辉长质辉玻无球粒陨石 (Gabbroic Shergottite, G-S)

辉长质辉玻无球粒陨石是基于结构的分类,有一部分陨石的矿物组成与玄武质辉玻无球粒陨石一致,但是结构特征却表明他们的形成过程有差别。与地球上典型的辉长岩相比,火星陨石的辉石含量

相对较高(地球:15%~50%,火星:46%~70%),例如 NWA 6963 (Filiberto et al., 2014, 2018) 和 NWA 7320(Udry et al., 2017),主要由半自形且粒径较大的辉石和熔长石组成,NWA 6963 中长石和辉石的粒径分别为 0.7 mm 和 1.1 mm,且长石最大长轴可达 5 mm。除此之外,Udry et al. (2017)认为部分长石含量大于 10%的含橄榄石嵌晶质辉玻无球粒陨石也可以称为橄辉长质辉玻无球粒陨石

(Olivine gabbroic shergottite), 例如 NWA 11509 (Irving et al., 2018)。NWA 6963 的稀土元素配分模式与富集型辉玻无球粒陨石一致 ($La_{CN} = 11$; $Lu_{CN} = 10$) (Filiberto et al., 2018)。NWA 7320 的含量在过渡型辉玻无球粒陨石的范围内 ($La_{CN} = 2$; $Lu_{CN} = 4$), 但是具有辉玻无球粒陨石中最高的正铕异常 ($Eu/Eu^* = 2.2$), 可能是由于较多斜长石堆晶导致 (约含 50%), 形成于侵入体而非喷出熔岩中 (Udry et al., 2017)。

1.2 辉橄无球粒陨石 (Nakhlite)

辉橄无球粒陨石为单斜辉石堆晶岩, 典型样品为 Nakhla, 辉石含量约 55%~81%, 主要为普通辉石、少量易变辉石、斜方辉石 (图 4b), 橄榄石 (1%~34%) 和长石 ($\leq 34\%$) 含量不等, 少量样品中的填隙物可高达 20% (Treiman, 2005; Day et al., 2006)。有的橄榄石含有包裹体, 常见板状或羽状铬铁矿、磁铁矿或辉石等。长石的成分较富钠, 可见少量富钾长石 (图 4d), 常呈放射板状, 并未完全转变为熔长石, 还有一部分保留其晶体结构, 反映陨石只经历了较弱的冲击作用。样品全岩的 $Mg^\#$ 约为 36~52, 是演化至一定程度的产物 (Udry et al., 2018)。陨石的稀土元素含量差异较大, 但配分模式一致, 轻稀土元素非常富集 ($La_{CN} = 4\sim 38$; $Lu_{CN} = 2\sim 6$; $[La/Lu]_{CN} = 3\sim 6$; 图 3b)。微量元素含量大致具有二分性, 可以分为含量较高 (NWA 6148、NWA 11013、NWA 10153、NWA 10645、NWA 817 和 Miller Range 辉橄无球粒陨石) 和含量较低 (Nakhla、Governador Valadares、Lafayette、NWA 998 和 Yamato 辉橄无球粒陨石) 的两组样品 (Udry et al., 2018)。

该类样品中常见有地外成因的次生矿物, 例如层状硅酸盐 (如蒙脱石等黏土矿物)、硬石膏、石膏、菱铁矿、黄钾铁矾、岩盐等, 这些矿物是了解火星表面环境、气候与宜居性的重要窗口, 对理解火星挥发分组成, 流体的活跃阶段、赋存状态等有重要的指示意义 (Treiman et al., 1993; Bridges et al., 2000)。

1.3 纯橄无球粒陨石 (Chassignite)

纯橄无球粒陨石主要由橄榄石堆晶组成, 此类陨石仅有 3 块: Chassigny、NWA 2737、NWA 8694。橄榄石约含 84%~91%, 一般呈自形或半自形, 可见含辉石、铬铁矿等包裹体, 此外还有少量普通辉石及易变辉石堆晶 (约 3%~11%), 长石一般少于 6%。单个样品的辉石成分较均一, 但不同样品间成分无重叠 (图 4b); 长石的变化范围则很大, 除斜长

石之外还有大量碱性长石 (图 4d; Floran et al., 1978; Beck et al., 2006; Udry et al., 2018; Hewins et al., 2020)。Chassigny ($Mg^\# = \sim 69$) 和 NWA 2737 ($Mg^\# = \sim 78$) 中的橄榄石非常富镁, 而 NWA 8694 则较富铁 ($Mg^\# = \sim 54$)。纯橄无球粒陨石的稀土元素配分模式与辉橄无球粒陨石十分相似, 但元素含量更低 ($La_{CN} = 2\sim 4$; $Lu_{CN} = 0.5\sim 0.8$; $[La/Lu]_{CN} = 3\sim 4$; 图 3b)。该类样品中较为特殊的矿物是钛角闪石以及含钛云母, 这类矿物在其他火星陨石中较为罕见, 是火星岩浆含水状况的重要指示物 (He Qi et al., 2013)。

1.4 斜方辉石岩质无球粒陨石 (Orthopyroxenite)

斜方辉石岩质无球粒陨石 ALH 84001 主要由粗粒斜方辉石构成, 粒径可达 5 mm, 约占 97%, 另外还含 2% 铬铁矿、1% 长石、0.15% 磷灰石和少量普通辉石等 (Mittelfehldt, 1994; Barrat et al., 2010)。辉石常具 120° 夹角的共结点结构, 成分均一程度很高, 斜方辉石为 $Fs_{27.3}En_{69.4}Wo_{3.3}$, 普通辉石为 $Fs_{12.7}En_{45.1}Wo_{42.2}$ (图 4b), 长石的成分与辉橄无球粒陨石相近 (图 4d)。全岩 $Mg^\#$ 约为 71, 稀土元素含量较低 ($La_{CN} = 0.8$, $Lu_{CN} = 2$), 受控于斜方辉石的稀土元素组成, 全岩具有重稀土元素富集的特征 ($[La/Lu]_{CN} = 0.4$; 图 3c)。该样品曾经因为内部含有状似细菌活动的产物受到大量关注 (McKay et al., 1996), 但是后期研究认为仅凭形貌特征是无法确凿判断是否具有生物成因的, 样品中的碳酸盐可能结晶于冲击熔体 (Scott et al., 1997) 或水环境中 (Halevy et al., 2011)。

1.5 火星角砾岩 (Polymict breccia)

火星角砾岩为复矿物碎屑角砾岩, 有矿物碎片、冲击熔体碎屑、角砾岩碎屑、岩浆岩碎屑 (玄武岩、粗安岩、玄武安山岩等) (Santos et al., 2015)。陨石中含量最高的矿物为辉石 (高钙与低钙辉石共约 44%), 其次是斜长石 (38%)、铁氧化物 (10%)、碱性长石 (5%) 和磷灰石 (4%), 基质中磁铁矿、磁赤铁矿等铁氧化物含量较高, 另外还有少量透长石、歪长石、氯磷灰石、钛铁矿、金红石、铬铁矿、黄铁矿、碳酸钙等 (Agee et al., 2013), 矿物组成十分复杂。辉石成分分布较广, 斜方辉石、易变辉石和普通辉石均有, 但是缺乏富铁的辉石 (图 4b), $Mg^\#$ 通常为 47~87, 此外仅有一个玄武安山岩质的角砾中的辉石铁含量较高 ($Mg^\# = 31$)。长石的成分变化范围非常大 ($An_{5\sim 55}Ab_{44\sim 88}Or_{1\sim 12}$, 图 4d), 其中嵌晶质、粗安岩质和富钛铁磷酸盐的角砾中有较富碱性元素的长

石($An_{1\sim7}Ab_{9\sim38}Or_{55\sim90}$)。全岩稀土元素含量较高,轻稀土元素相对较为富集,且有明显负铈异常($La_{CN}=58, Lu_{CN}=27, [La/Lu]_{CN}=2, Eu/Eu^*=0.3$, 图3c),表明曾经历长石质组分的分离。内部角砾以及基质的稀土元素含量和配分模式差异较大($La_{CN}=10\sim292, Lu_{CN}=9\sim67, [La/Lu]_{CN}=0.1\sim4, Eu/Eu^*=0.1\sim0.5$) (Agee et al., 2013; Humayun et al., 2013)。角砾岩中除了有与已知火星陨石种类一致的组分,也有未发现的组分,全岩成分与火星车和轨道探测获得的平均火星表面成分以及部分玄武岩成分一致,因此是代表火星壳组成的重要样本 (Agee et al., 2013)。

2 火星上的岩浆过程

2.1 氧逸度

氧逸度是衡量物质氧化程度的重要参数,可以影响变价元素的价态和赋存方式,是了解元素组成、分配行为、电导率等化学和物理性质,认识岩浆过程的重要窗口。对火星陨石氧逸度的认识主要通过矿物的成分特征定量或半定量的分析获得,例如:共生橄榄石—尖晶石—斜方辉石 (Ballhaus et al., 1991)和共生钛铁氧化物的主量元素含量 (Ghiorso et al., 1991)、辉石的铈、钆、铬含量 (Wadhwa, 2001; McCanta et al., 2004)、橄榄石或铬铁矿的钒含量 (Papike et al., 2004; Shearer et al., 2006)等。一般辉玻无球粒陨石的氧逸度差异较大,利用钛铁氧化物分析获得的氧逸度约 $QFM-4\sim+1$ 不等 (Herd et al., 2001; Herd, 2006); 辉橄无球粒陨石的氧逸度稍高,约 $QFM-2\sim+1.5$ (Dyar et al., 2005; Treiman et al., 2008; Szymanski et al., 2010); 纯橄无球粒陨石与辉橄无球粒陨石的氧逸度相似,约 $QFM-1\sim+1$ (Treiman et al., 2007; Lorand et al., 2018); ALH 84001 通过不同方式估算的氧逸度值由 $QFM-2.7\sim QFM$ 不等 (Herd et al., 1999; Righter et al., 2008)。

部分样品通过不同氧逸度计或不同区域分析获得不同的氧逸度值可能反映结晶过程中氧逸度的变化,例如 QUE 94201, 辉石 Eu 与 Gd 含量指示的氧逸度为 $IW-1$ (Wadhwa, 2001), 而共生的钛铁氧化物指示的氧逸度约为 $IW+1.19$ (Herd et al., 2001); 通过橄榄石—辉石—尖晶石氧逸度计获得 ALHA 77005 的嵌晶区氧逸度为 $IW-1$, 非嵌晶区的氧逸度为 $IW+1.38$ (Rahib et al., 2019)。这些情形均反映了样品结晶后期氧逸度的增加,并且氧

逸度可以变化几个数量级。角砾岩 NWA 7034/7533 的氧逸度则远高于其他火星陨石,约为 $QFM+2\sim3$ 或更高 (Leroux et al., 2016), 反映了火星壳明显较高的氧逸度环境,这与探测数据指示的表面氧化环境一致 (Schmidt et al., 2013)。

Herd et al. (2002) 发现辉玻无球粒陨石的氧逸度与样品的轻稀土元素亏损程度有关,亏损程度越高(也即 La/Yb 比值越低),氧逸度越低,呈现氧化且富集和还原且亏损两个端元混合的特征。地球地幔复杂的氧逸度组成通常归因于大陆或洋壳物质俯冲进入地幔 (Wood et al., 1990), 而火星上由于不受板块俯冲运动的影响,其幔部物质可能保留了核幔分异初期较还原的特征 ($IW-1.4\sim-0.9$, Brennan et al., 2020), 因此还原且亏损的端元应当来源于火星幔。氧化的端元可能来源于火星壳或火星幔内的分离结晶后的残余熔体,而且越氧化的组分轻稀土元素越富集 (Herd et al., 2002; Borg et al., 2003; Herd, 2003)。但是后期对更多样品的氧逸度分析削弱了辉玻无球粒陨石的稀土元素与氧逸度的相关性(图5),此外辉橄无球粒陨石的氧逸度和 La/Yb 比值特征也很难用两端元混合模式解释 (Szymanski et al., 2010; Herd et al., 2017; Howarth et al., 2017; Udry et al., 2017; Rahib et al., 2019)。有研究认为火星幔部氧逸度不均一的特征可能在火星分异阶段已经形成 (Nicklas et al., 2021)。总之,现阶段一般认为幔部氧逸度具有较复杂的组成特征,初期不均一的氧逸度,加上后期岩浆过程、去气作用、矿物在亚固相下重新平衡、大气作用等导致成岩过程中氧逸度发生变化 (Herd et al., 2001, 2017; Rahib et al., 2019)。目前对源区氧逸度的追溯难度依然很大,需要结合更多的限定条件综合判断。

2.2 岩浆的演化机制

火星岩浆在形成、上涌至成岩过程中经历了一系列的物理化学条件变化。例如 Zagami (McCoy et al., 1999)、GRV 020090 (Lin Yangting et al., 2013)、SaU 005 (Goodrich, 2003) 的岩相结构、晶体大小分布、矿物和全岩成分等信息都表明这些样品可能经历了多阶段的结晶过程,包括冷却速率改变、熔体结晶分离、外来物质加入等。了解岩浆的运移、化学演化过程等有助于解析火星深部的物理化学条件,认识火星幔和壳的组成特征。

火星岩浆岩的岩相结构和矿物组成可以反映岩浆侵位和喷发的特征。岩浆上涌后可能形成岩床、

图 5 辉玻无球粒陨石氧逸度值与 $[La/Yb]_{CN}$ 含量比值关系 (改自 Udry et al., 2017; Howarth et al., 2018)

Fig. 5 $\log fO_2$ relative to FMO buffer versus bulk-rock $[La/Yb]_{CN}$ normalized to CI-chondrite of shergottites (modified from Udry et al., 2017; Howarth et al., 2018)

岩株等不同深度的深成构造,也可能喷出表面(图 6)。一般情况下,玄武质和橄榄石斑晶质辉玻无球粒陨石为浅成或喷出岩,嵌晶质和辉长质辉玻无球粒陨石为侵入岩。例如玄武质 Los Angeles、QUE 94201 中的三斜铁辉石(Pyroxferroite)分解成为后成合晶集合体(铁橄榄石+二氧化硅+富铁辉石),可能是岩浆在地表或近地表冷却过程中形成(Aramovich et al., 2002)。辉长质 NWA 6963 中含有碱性长石与石英交生的结构,可能是长石和石英在共结点下同时结晶形成,这种产物常见于地球的侵入岩中,与文象花岗岩结构相似(Filiberto et al., 2014)。纯橄无球粒陨石的堆晶结构和均一的橄榄石成分表明其具有相对较缓慢的冷却速率,例如处于较厚的熔岩流或岩床底部等,与部分地球上的纯橄岩形成环境相似(Udry et al., 2018)。辉橄无球粒陨石中虽然也有堆晶,但是矿物比例和分布特征并不与重力分异的特征一致,而是富斑晶的熔岩在流动过程受动力作用的影响导致(Corrigan et al., 2015)。不同辉橄无球粒陨石间粒径分布特征进一步指示了样品形成于不同层序,例如部分同源辉橄无球粒陨石形成的顺序自上而下依次为: Nakhla、Governador Valadares、Lafayette、NWA

998(Corrigan et al., 2015)。

地球深成岩的矿物成分研究表明,结晶压力越大,辉石的 Ti/Al 比值越低,实验研究也给出了不同比值对应的压力参考值(Nekvasil et al., 2004)。辉玻无球粒陨石中辉石的 Ti/Al 比值变化范围较大,一般 0.21~0.7 不等,通常是普通辉石或辉石富铁边部 Ti/Al 比值更大,反映了随着结晶过程的进行,压力逐渐变小的环境,对应于岩浆上涌至浅部的过程。其中,嵌晶质辉玻无球粒陨石的嵌晶区一般结晶于深部(例如 NWA 7397, 1000 MPa),而非嵌晶区结晶于上涌过程中(Howarth et al., 2015)。部分橄榄石斑晶质陨石可能形成于浅表,并未喷发,例如 NWA 6234 的 Al/Ti 比值较为均一,形成于相对稳定的压力下,而 NWA 5789、Yamato 980459 则曾喷发至表面(Gross et al., 2013)。辉橄无球粒陨石中辉石核部的 Ti/Al 比值一般约为 0.16~0.22,部分橄榄石边部可高达 0.5,同样是变压结晶的产物,可能形成于熔岩流或较浅的侵入体中(Udry et al., 2018)。而纯橄无球粒陨石的辉石成分多数为 0.07~0.3,反映了整个结晶期间相对较高的形成压力(约为 930 MPa),可能位于火星下地壳或上地幔(Filiberto et al., 2010; Zuber et al., 2000; Udry et al., 2018)。ALH 84001 的辉石成分较为均一, Ti/Al 比值约为 0.1~0.2,同样对应深成的特征(Mittlefehldt, 1994)。

与地球上的岩浆岩相似,火星岩浆岩也经历了分离结晶、同化混染等过程。辉橄无球粒陨石和纯橄无球粒陨石均为典型的堆晶产物,虽然样品均经历了不同程度的元素扩散再平衡的过程,但是全岩的镁含量和稀土元素呈负相关,符合分离结晶趋势(Harvey et al., 1992; Udry et al., 2018)。辉玻无球粒陨石中,橄榄石斑晶质样品是镁含量最高的,而且常形成于氧逸度较低的环境中,可能是最为接近原始火星幔源岩浆成分的样品,但是很多样品内部的粗粒橄榄石斑晶可能来源不明,有外来物质加入。这个加入过程通常很复杂,例如在分离结晶的同时还可能注入更原始的岩浆,甚至加入来源于火星壳的物质,无法保留原始熔体成分信息(Castle et al., 2020)。根据粗粒橄榄石斑晶成分特征和同位素组成等可知,能代表原始熔体成分的样品可能仅有 Yamato 980459、NWA 5789、NWA 2990、NWA 1068、NWA 6234(Filiberto et al., 2011; Gross et al., 2013; Collinet et al., 2017)。玄武质样品如 Zagami、NWA 8653 中观察到富硅碱长石质玻璃、

图6 火星辉玻、辉橄和纯橄无球粒陨石的形成过程示意图(改编自 Mikouchi et al., 2008; Usui et al., 2008; Howarth et al., 2014; Udry et al., 2018; Combs et al., 2019; Rahib et al., 2019)

Fig. 6 Schematic illustration of the petrogenesis of shergottites, nakhlites and chassignites (modified from Mikouchi et al., 2008; Usui et al., 2008; Howarth et al., 2014; Udry et al., 2018; Combs et al., 2019; Rahib et al., 2019)

二氧化硅、铁橄榄石、磷酸盐、钛铁矿等的后期充填物,是当岩浆结晶分异完成了95%~98%时,剩余熔体不混熔导致的,代表了火星玄武岩岩浆演化到较高程度的物质组成特征(Neal et al., 1989; McCoy et al., 1999; Anand et al., 2003)。此外,辉玻无球粒陨石和纯橄无球粒陨石的氯同位素组成,辉橄无球粒陨石中火成硫化物的成分等证实了部分样品中存在同化混染火星壳物质的过程(Chevrier et al., 2011; Williams et al., 2016)。

总体上,火星和地球上的岩浆侵位机制、化学演化模式等均有相似之处,例如火星玄武岩岩浆随着演化过程的进行,逐渐富铁、碱性元素、稀土元素等。但由于火星深部温压条件、表面环境、挥发分含量、可能不存在板块活动等方面的差异,导致岩浆过程中部分元素分配行为等有差异,例如地球玄武岩中橄榄石的铁-镁分配系数一般为0.3,而火星玄武岩的值为0.35(Filiberto et al., 2011)。但是类地行星的整体岩浆演化规律一致,应当开展更为深入的比较行星学研究。

2.3 火星陨石的同位素年龄

现阶段通过Sm-Nd、Rb-Sr、K-Ar、U-Pb等体系对火星陨石进行了大量同位素年龄的分析,其地质

意义(结晶年龄/蚀变年龄)的解析需要结合陨石的岩相结构和矿物特征等综合考虑。大多数火星陨石的结晶年龄非常年轻,为亚马逊纪产物(图7),辉玻无球粒陨石一般形成于中一晚亚马逊纪(≤ 642 Ma),岩石类型与年龄大小间没有必然的相关性,但基于目前的样品特征,最年轻的样品一般为富集型或过渡型辉玻无球粒陨石,亏损型样品相对较老(Nyquist et al., 2001; Korochantseva et al., 2009)。含有地外蚀变产物的样品EETA 79001的结晶年龄约为 173 ± 3 Ma(Nyquist et al., 2001),表明火星自~180 Ma以来仍然有流体作用。但由于辉玻无球粒陨石中发现的蚀变现象有限,因此该作用可能并不普遍。2块特殊的辉玻无球粒陨石NWA 8159和NWA 7320的Sm-Nd年龄相近,分别约为 2370 ± 250 Ma(Herd et al., 2017)和 2403 ± 250 Ma(Lapen et al., 2017),为早亚马逊纪产物。

辉橄无球粒陨石和纯橄无球粒陨石的形成年龄较为一致,约为1.3 Ga(Nyquist et al., 2001)。辉橄无球粒陨石Lafayette和Yamato 000593内的次生矿物伊丁石的形成年龄大约为~650 Ma,代表了蚀变事件的发生时间(Shih et al., 1998, 2002;

Swindle et al., 2000; Borg et al., 2005), 但是 Lafayette 中还测出了多组 K-Ar 年龄, 从 670~0 Ma 不等, 其他年龄可能是受到热变质作用改造 (Borg et al., 2005), 或代表后期一次或多期次流体事件 (Swindle et al., 2000)。

角砾岩 NWA 7034 中的年龄组成较为复杂, 全岩和矿物的 Sm-Nd、锆石和磷灰石的 U-Pb 组成表明大部分组分都形成于~4.44 Ga (4428±25 Ma, Humayun et al., 2013; 4465±73 Ma, Hu Sen et al., 2019), 指示了火星早期的岩浆活动时间 (Nyquist et al., 2016)。后期部分组分受到多次事件的扰动, 例如部分锆石和磷灰石记录了 1.7~1.3 Ga 不等的变质年龄 (Humayun et al., 2013; Yin Qing-zhu et al., 2014; Bellucci et al., 2015a; Hu Sen et al., 2019)。

斜方辉石岩质 ALH 84001 的形成年龄也约为诺亚纪, 早期研究获得样品的 Sm-Nd 和 Rb-Sr 年龄为 4.5 Ga (Jagoutz et al., 1994; Nyquist et al., 1995), 但是其他研究获得 4.1~3.8 Ga 不等的结果, 例如 Lu-Hf (4091±30 Ma, Lapen et al., 2010)、Pb-Pb (4077±99 Ma, 4038±140 Ma, Bouvier et al., 2009)、U-Pb (4117.3±2.3 Ma, Jagoutz et al., 2009)、Rb-Sr (3840±50 Ma, Wadhwa et al., 1996)、Ar-Ar (4175±25 Ma, Knott et al., 1995)。Nyquist et al. (2001) 认为 4.5 Ga 代表 ALH 84001 的形成年龄, 而 4.1 Ga 反映了后期变质事件的时间, 但是现阶段的研究普遍认为后者代表了样品的结晶年龄, 前者可能是由于磷酸盐受到蚀变和风化作用的影响, 导致 Sm、Nd、Sr 等元素重新分配, 从而产生偏大的 Sm-Nd 年龄 (Lapen et al., 2010)。此外, 次生碳酸盐的形成时代也有大量研究, 例如 Mittlefehldt (1994) 根据对碳酸盐冲击特征和成分的观察认为存在两个期次的碳酸盐; 不同的定年分析获得的年龄约 4.04~1.39 Ga 不等 (Knott et al., 1995; Wadhwa et al., 1996; Borg et al., 1999)。结合辉玻无球粒陨石和辉橄无球粒陨石中次生矿物的形成时间来看, 火星上的流体过程每次持续的时间都很短, 可能是因为目前找到的火星陨石还不能完全代表火星岩石特征, 也可能是因为这些蚀变是由于局部的冲击、岩浆或全球气候变化事件的触发导致, 不是连续发生的 (Borg et al., 2015)。

通过分析撞击坑出现频率以及地层交叠特征等可以看出火星上的火山活动几乎贯穿了整个地质历

史时期 (Hartmann et al., 2001; Carr et al., 2010; Robbins et al., 2011; Tanaka et al., 2014)。但是目前发现的火星陨石的年龄基本上集中在 < 650 Ma、1.3 Ga、2.4 Ga 和 4.0 Ga 四组中, 并且超过半数的辉玻无球粒陨石年龄约为 180 Ma。同时, 大多数火星陨石的溅射年龄也较为集中 (McSween, 2015), 来源于有限的几次溅射事件, 因此目前的火星陨石代表的区域可能是有限的。另外, 部分火星陨石中不含有适用于精确定年的矿物 (例如斜锆石), 或者没有足够的样品量进行全岩同位素年代学分析, 因此未来对火星陨石结晶年龄的分析还依赖于高精度、低损耗量分析技术的发展。

3 源区特征

3.1 稀土元素和同位素组成特征

一般认为火星陨石中轻稀土元素亏损的组分来源于火星幔, 但是富集组分的来源存在不同的认识。虽然地壳是富集组分的重要来源 (Herd et al., 2002; Franz et al., 2014), 但是也有大量富集型样品的主微量元素含量、同位素组成和氧逸度特征等均未受到地壳混染过程的影响 (Ferdous et al., 2017), 因此火星幔中应当也存在富集型源区。由于火星上不存在板块活动, 难以像地球一样发生壳幔物质交换, 因此富集型的火星幔源区可能在火星分异早期就形成了。Borg et al. (2003) 认为在火星岩浆洋时期结晶形成亏损的堆晶和富集的晚期残余熔体 (Trapped, enriched residual liquids), 这些晚期产物类似月球岩浆洋中的 KREEP 组分, 可能是富集型源区的重要来源, 亏损型源区可能比富集型源区更深 (Borg et al., 2003; Brandon et al., 2012)。近年来也有少量研究认为火星壳在超过一定厚度且温度较低时, 可以通过拆沉的方式进入地幔, 从而实现壳幔物质的循环, 改变火星幔的成分 (Peters et al., 2015; Semprich et al., 2020)。

岩石的同位素组成对源区的特征有重要指示意义。例如: 从地球岩石的研究可知, Sm-Nd 和 Lu-Hf 体系相似, 在后期过程中 (包括变质作用等) 的同位素的分馏不强烈, 仍然保留源区信息; Rb-Sr 由于活动性有差异, 会在重熔等过程中进一步分馏。同时, Rb、Pb、Hf、Sm 等元素的不相容性存在差异, 可以指示不同的来源, 例如 Rb 最容易在地壳富集, 地壳中的 Rb 含量高于 Sr, 因此地壳物质中通常会有较高的 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值, 而 Sm 非常不相容, 亏损地幔中的 $^{143}\text{Nd}/^{144}\text{Nd}$ 一般较高。

图7 火星陨石的同位素年龄

Fig. 7 Isotopic ages of Martian meteorites

数据来源(data sources): Nyquist et al., 1979, 1995, 2000, 2009; Nakamura et al., 1982b; Jagoutz, 1989, 1996; Knott et al., 1995; Wadhwa et al., 1996; Borg et al., 1997, 1999, 2000, 2002, 2005, 2008; Shih et al., 1998, 2002, 2003, 2005, 2009; Bogard et al., 1999; Swindle et al., 2000; Terada et al., 2004; Misawa et al., 2005; Symes et al., 2008; Bouvier et al., 2009; Korochantseva et al., 2009; Lapen et al., 2010, 2017; Liu Tao et al., 2011; Jiang Yun et al., 2012; Agee et al., 2013; Humayun et al., 2013; Zhou Qin et al., 2013; Brennecka et al., 2014; Yin Qingzhu et al., 2014; Bellucci et al., 2015a; Herd et al., 2017; Hu Sen et al., 2019; Wu Yunhua et al., 2021

富集型、过渡型和亏损型辉玻无球粒陨石的 $\epsilon^{142}\text{Nd}$ 值分别约为 $-0.23 \sim -0.13$ 、 $0.03 \sim 0.23$ 和 $0.57 \sim 0.92$ ， $\epsilon^{182}\text{W}$ 值分别约为 $0.33 \sim 0.40$ 、 $0.29 \sim 0.51$ 和 $0.83 \sim 1.80$ ，亏损型样品与其他样品具有显著差异，如图8a所示(Kruijer et al., 2017)。源区的 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{87}\text{Rb}/^{86}\text{Sr}$ 比值以及 $\gamma^{187}\text{Os}$ 和 $\epsilon^{143}\text{Nd}$ 值均具有两端元混合的特征，但是 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 比值具有三个端元的混合特征，如图8b所示(Lapen et al., 2010; Brandon et al., 2012; Andreasen et al., 2015)。据此可将辉玻无球粒陨石源区分为三类：具有高 Sm/Nd 和高 Lu/Hf 比值的亏损型源区，具有高 Sm/Nd 和低 Lu/Hf 比值的亏损型源区，以及具有低 Sm/Nd 和低 Lu/Hf 比值的富集型源区(Debaille et al., 2008; Andreasen et al., 2015)。从更小的尺度来看，每个源区都是不均一的，例如富集型源区仍然存在微小的 Lu/Hf 和

Sm/Nd 差异，Los Angeles和NWA 856可能来源同一源区，而其他富集型样品来源于另一源区(Combs et al., 2019)。

ALH 84001的同位素组成特征与富集型辉玻无球粒陨石非常相似，二者的源区及成因可能密切相关(Lapen et al., 2010; Andreasen et al., 2015)。NWA 8159和NWA 7320的年龄相近(~ 2.4 Ga)且明显老于其他辉玻无球粒陨石，但是二者的成分、矿物组成、岩相结构等差异较大，应当形成于不同的源区和结晶过程。NWA 8159的 $\epsilon^{142}\text{Nd}$ (0.77 ± 0.02)和 $\epsilon^{182}\text{W}$ (1.13 ± 0.10)与亏损型的辉玻无球粒陨石相似，但样品的铬和铅同位素组成与辉玻无球粒陨石有差异，因此该样品可能来源于一个新的亏损型源区(Herd et al., 2017; Kruijer et al., 2017; Lapen et al., 2017; Bellucci et al., 2020)。而NWA 7230的源区 $^{147}\text{Sm}/^{144}\text{Nd}$ 和

图 8 火星陨石源区的同位素组成

Fig. 8 Isotopic composition of Martian meteorite source reservoirs

(a)— $\epsilon^{142}\text{Nd}$ 和 $\epsilon^{182}\text{W}$ (据 Kruijer et al., 2017); (b)— $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ (据 Andreassen et al., 2015); UM1—上地幔 1; UM2—上地幔 2; EN—富集地幔组分; SUM—较浅的上地幔; ◆—辉玻无球粒陨石的值

(a)— $\epsilon^{142}\text{Nd}$ versus $\epsilon^{182}\text{W}$ (after Kruijer et al., 2017); (b)— $^{147}\text{Sm}/^{144}\text{Nd}$ versus $^{176}\text{Lu}/^{177}\text{Hf}$ (after Andreassen et al., 2015); UM1—upper mantle 1; UM2—upper mantle 2; EN—enriched mantle materials; SUM—shallow upper mantle; ◆—data from shergottites

$^{176}\text{Lu}/^{177}\text{Hf}$ 组成与富集型辉玻无球粒陨石 Los Angeles 和 NWA 856 一致, 可能为同一源区产物 (Udry et al., 2017)。NWA 7034 的 $\epsilon^{142}\text{Nd}$ (-0.45 ± 0.06) 和 $\epsilon^{182}\text{W}$ (0.20 ± 0.05) 值低于火星幔, 是目前追溯到的富集程度最高的源区。另外, NWA 7034 中部分组分的源区 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 组成与其他火星陨石均不一致, 代表了另一种新源区 (Armytage et al., 2018)。

辉玻无球粒陨石和纯橄无球粒陨石的成分特征相似且同位素组成较为均一, 样品的 $\epsilon^{142}\text{Nd}$ 和 $\epsilon^{182}\text{W}$ 分别约为 $0.51 \sim 0.71$ 和 $2.14 \sim 3.35$, 后者明显高于辉玻无球粒陨石 (Foley et al., 2005; Caro et al., 2008)。最初这种差异被认为是早期由岩浆洋分异导致, 但是样品的 Nd 同位素组成并不满足两阶段演化模型, 也无法用岩浆过程或后期交代作用解释, 可能经历了诸如幔部倒转等更为复杂的演化过程 (Debaille et al., 2009)。源区的 $^{147}\text{Sm}/^{144}\text{Nd}$ 和 $^{176}\text{Lu}/^{177}\text{Hf}$ 分别约为 $0.2339 \sim 0.2358$ 和 $0.0392 \sim 0.0422$, $^{87}\text{Rb}/^{86}\text{Sr}$ 较低, 约为 $0.7023 \sim 0.7028$, 表明其来源于与辉玻无球粒陨石不同的亏损型源区 (Misawa et al., 2006; Debaille et al., 2009; Day et al., 2018)。

不同种类陨石的 μ ($^{238}\text{U}/^{204}\text{Pb}$) 值和源区的 $^{147}\text{Sm}/^{144}\text{Nd}$ 、 $^{176}\text{Lu}/^{177}\text{Hf}$ 、 $\epsilon^{142}\text{Nd}$ 、 $\epsilon^{182}\text{W}$ 等呈线性相关, 表明不同源区的铅同位素应当与其他同位素体一样, 不均一的组成可能形成于火星分异早期阶段 (Bellucci et al., 2018; Moriwaki et al., 2020)。

Bellucci et al. (2015b) 提出的两阶段铅演化模型可以解释大部分火星陨石的初始铅组成: 第一阶段从 4567 Ma 至 4504 Ma, μ 值为 1.8; 第二阶段从 4504 Ma 至矿物形成时期, 不同种类陨石的 μ 值为 1.4~4.7 不等 (Bellucci et al., 2015b, 2018)。一般亏损型辉玻无球粒陨石的 μ 值为 1.4~1.5, 过渡型和富集型辉玻无球粒陨石的 μ 值为 3.1~4.7 (Bellucci et al., 2018)。但是也有少量样品, 例如亏损型的 DaG 476 和 Yamato 980459 的 μ 值均约为 2.3, 反映了源区成分不均一 (Moriwaki et al., 2020)。另外, 辉橄和纯橄无球粒陨石、ALH 84001 的 μ 值一般分别为 2.5~2.8、4.0 (Bellucci et al., 2018)。角砾岩 NWA 7533 部分长石的 μ 值 ≥ 13.4 , 表明火星壳是一个高 μ 储库 (Bellucci et al., 2015a)。

但是辉玻无球粒陨石的 U-Pb 同位素体系组成一直存在争议, 因为早期研究发现辉玻无球粒陨石的全岩 Pb-Pb 年龄约为 4.1 Ga (Zagami, 4048 $\pm$ 17 Ma; Bouvier et al., 2005), 但是富 U 矿物的原位 U-Pb 分析获得的年龄约为 180 Ma (Zagami, 182.7 $\pm$ 6.9 Ma; Zhou Qin et al., 2013)。年轻的年龄可能代表岩石的结晶年龄 (Nyquist et al., 2001; Symes et al., 2008), 或者是受到后期撞击事件或蚀变事件的改造 (Shih et al., 1982; Bouvier et al., 2005)。Moser et al. (2013) 在冲击变质程度较高的玄武质陨石 NWA 5298 中找到了具有不同冲击特征的斜锆石, 其中具有明显变质结构 (例如粒状结

晶结构、斜锆石生长出锆石增生边等)颗粒的 U-Pb 年龄受到不同程度的扰动,其中改造最强烈的斜锆石年龄为 22 Ma;而保留了原生岩浆结构的斜锆石年龄为 187 Ma,应当代表结晶年龄。其 Pb-Pb 同位素组成可能反映了源区成分特征,或者是由于混入了一部分成因不明或不同来源的放射铅导致 (Bellucci et al., 2015a, 2016; Moriwaki et al., 2017; Tobita et al., 2017)。纯橄和辉橄无球粒陨石可能也混入了相似的组分,例如 Chassigny 中混入的放射铅的储库 μ 可能高于 9.25 (Bellucci et al., 2016; Jones et al., 2017),该组分的源区可能位于火星壳中。

目前较为公认的是火星幔的稀土元素、亲铁元素、同位素组成等都高度不均一,并且最早形成于火星分异早期,例如早期撞击物的加入、岩浆洋结晶过程等 (Armytage et al., 2018; Marchi et al., 2020; Yoshizaki et al., 2020; Zhang Zhongtian et al., 2021)。不同源区形成后保持了长时间的相互独立,并未发生明显的物质交换。火星陨石的同位素组成差异表明火星幔至少存在六个源区,其中辉玻无球粒陨石具有三个源区,ALH 84001 可能与富集型辉玻无球粒陨石来源于相似的源区,辉橄无球粒陨石和纯橄无球粒陨石来源于同一源区,NWA 8159 和 NWA 7034 中的部分组分分别来源于不同源区。未来对新火星陨石和火星返回样品的研究可能会识别出更多新的源区信息。

3.2 不同种类火星陨石的关联

辉玻无球粒陨石间的成因密切相关,一般认为具有相似结晶年龄、微量元素和同位素组成的不同亚类的辉玻无球粒陨石可能来源于同一源区,不同程度的分离结晶导致主量元素和矿物组成存在差异。例如玄武质样品 QUE 94201 可以由橄榄石斑晶质样品 Yamato 980459 经分离结晶形成 (Symes et al., 2008)。EET 79001 由橄榄石斑晶质岩相和玄武质岩相组成,为这两种亚类的成因关联提供了岩相学的依据 (Van Niekerk et al., 2007)。虽然 Papike et al. (2009) 提出单纯的分离结晶并不能解释部分微量元素的成分特征,因为 QUE 94201 和 Yamato 980459 辉石中的铬含量并不满足分离结晶的关系。但是大部分样品的主微量元素(例如 Lu、Th 等)特征都可以通过与 Yamato 980459 成分相似的亏损端元和与 NWA 1068 成分相似的富集端元混合后经分离结晶形成 (Treiman et al., 2015)。不同的混合方式和分离结晶程度导致了辉玻无球粒

陨石的成分多样性。通过同位素组成特征可知,亏损型的源区至少有两种,但是不排除两种源区的微量元素组成相似。

嵌晶质辉玻无球粒陨石由于含有大量堆晶,因此很难从主微量元素演化的角度上分析其与上述两种亚类的辉玻无球粒陨石的成因关联。最初认为富集型和过渡型的嵌晶质辉玻无球粒陨石均来自于同一岩浆岩套,富集型样品形成深度更浅、富含演化程度较高的熔体 (Mikouchi et al., 2008)。但是同位素组成揭示了二者具有不一样的源区,例如富集型的嵌晶质样品 NWA 10169 和 NWA 4468 与富集型玄武质样品 Shergotty 和橄榄石斑晶质样品 LAR 06319 等同源,过渡型嵌晶质样品 ALHA77005 和 LEW 88516 与过渡型玄武质样品 NWA 1460 可能同源 (Nyquist et al., 2009; Rahib et al., 2019)。此外,不同亚类的微量元素等也有相似性,例如嵌晶质 NWA 11065 的稀土元素成分与玄武质 NWA 480 和橄榄石斑晶质 NWA 6234 相近,并且其橄榄石的磷环带特征也与 NWA 6234 相似,表明了不同亚类的辉玻无球粒陨石源区高度相关 (Rahib et al., 2019)。

纯橄无球粒陨石和辉橄无球粒陨石都具有堆晶结构,且稀土元素配分模式、挥发组分含量、结晶年龄和溅射年龄等都非常相似,这些样品的主微量元素含量、岩相结构等具有连续变化的特征,因此一般认为这两种陨石具有成因关联 (Nyquist et al., 2001; Beck et al., 2006; McCubbin et al., 2013; Udry et al., 2018)。其同位素组成表明源区是亏损的,源区低程度地部分熔融导致样品富集轻稀土元素 (Day et al., 2018; Udry et al., 2018)。不同样品间矿物粒径、模式丰度的差异等表明样品形成于不同的层位中 (Corrigan et al., 2015)。此外,富铁的纯橄无球粒陨石 NWA 8694 的橄榄石堆晶中具有和辉橄无球粒陨石相似的填隙物,为二者的成因关联提供了岩相学证据 (Hewins et al., 2020)。目前认为辉玻无球粒陨石和辉橄及纯橄无球粒陨石来源于不同的地幔源区,火星幔部成分高度不均一,但是更进一步的关联性还没有完全的认识,有待进一步研究解决 (Udry et al., 2018)。

4 火星陨石研究中的问题与展望

目前已经有大量关于火星陨石岩相结构、矿物组成、结晶年龄等方面的研究成果,对火星上的岩浆过程、物质组成、源区成分、壳幔分异、火星表面的蚀

变作用等信息有了初步的了解,但是受限于火星陨石的数量和种类,仍有许多尚未解决的问题。几个典型的问题如下:

(1)火星陨石的代表性:火星陨石的多样性主要受控于源区特征、部分熔融条件、母岩浆的演化、冷凝过程等。目前探测获得的火星表面成分差异较大,从玄武质到安山质,或者更为酸性的英安岩或花岗质岩石均有分布,比火星陨石(火星角砾岩除外)更富硅和碱性元素,火星表面仅有 Bounce 岩石与火星陨石成分相近(McSween et al., 2009; Agee et al., 2013)。辉玻无球粒陨石(NWA 8159 和 NWA 7635 除外)结晶年龄基本都小于 ~ 650 Ma,其中大多数样品集中于 ~ 180 Ma(图 7)。但是火星表面大部分区域都为诺亚纪产物,而诺亚纪的火星陨石只有 ALH 84001 和火星角砾岩。另外,探测数据表明火星表面存在大量蚀变产物,包括赤铁矿、石膏、碳酸盐等,但是在火星角砾岩中的蚀变矿物常以铁的氧化物和氢氧化物为主,没有硫酸盐、氯化物等盐类(Carter et al., 2012; Loizeau et al., 2012)。火星角砾岩、辉玻无球粒陨石和火星表面的盖尔撞击坑出露的 Sheepbed 泥岩的蚀变特征和机制均有差异(Fu Xiaohui et al., 2020)。这一系列现象表明火星表面仍有大量组分未能直接在火星陨石中找到。

(2)火星表面环境:目前普遍接受的观点是火星早期(约 3.5 Ga 以前)湿润,发生过阶段性的液态水活动,当前表面干燥,存在浅表层水冰(Carr et al., 2010; Zhao Jiannan et al., 2016; Ramirez et al., 2018)。部分火星陨石中的氢同位素也表现出与火星壳部水相互作用的痕迹(Hu Sen et al., 2020)。但对火星环境的变化方式以及具体环境温湿度条件、流体性质等研究仍未达成共识。例如,火星上的大量辫状水系指示的是干燥还是湿润的环境一直存在争议(Edwards et al., 2016; Dundas, 2020),次生矿物中的同位素分馏机制不明,且流体活跃时间与期次缺乏更多数据的制约(Swindle et al., 2000; Bellucci et al., 2017)。

(3)火星幔部组成特征:通过对火星陨石的成分和同位素组成的分析认为火星幔部是不均一的,并且在火星分异早期就形成了不均一的幔部,但是其不均一程度、成分、形成机制、富集组分的来源和分布及其如何在整个地质历史时期保持幔部的不均一性等并未达成共识。

(4)火星岩浆过程:目前通过火星陨石的岩相结构、成分特征等的研究对岩浆的侵位、喷发等过程有

了一定的了解,但是仍缺乏精确的限定,讨论过程中存在很多假设前提,并且对同一样品的岩浆过程的认识可能不同。

此外,还有许多重要环节有待进一步研究验证,例如火星陨石中初始铅的辨识、火星幔中是否存在比现在认知的 μ 更高($\mu > 4.7$)的储库;火星幔中挥发分的组成和含量;火星撞击坑定年的准确度等。我国的火星探测任务“天问一号”探测器已于 2020 年 7 月成功发射,环绕器上搭载了探测雷达、火星离子与中性粒子分析仪、火星矿物光谱分析仪等,在火星车上还搭载了表面成分探测仪,其对火星表面元素分布、岩石类型的探测等将有助于对火星物质组成的进一步理解(Li Chunlai et al., 2018)。另外美国的火星陨石返回计划也将为火星表面岩石源区的对应、撞击坑年代学的校正等提供更丰富、更高精度的数据,进而推动人类对火星地质演化特征的认识(Clery et al., 2019)。

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Petrology, mineralogy of Martian meteorites and chemical signatures of source reservoirs

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Abstract

Martian meteorites are the only available rock samples from Mars. They provide direct evidence for the composition and chemical evolution of Martian materials, placing constraints on the physical and chemical properties, core-mantle differentiation, magmatic process, etc. Martian breccia is compositionally similar to basalts and average Martian crust measured by rover and orbiter missions, representing a geochemically enriched crust. Whereas other Martian meteorites are mainly mafic igneous rocks which formed from mantle-derived magma that may erupt to the surface or embed in the subsurface as dikes or sills. Variations of rare earth elements and isotopic compositions indicate heterogeneous mantle sources. Some meteorites have undergone crustal assimilation during ascent, recording chemical signatures of the Martian crust. Martian meteorites have expanded our knowledge on the composition of the exterior and interior, including ① the Martian crust is oxidized and enriched with relatively high $^{238}\text{U}/^{204}\text{Pb}$, low $\epsilon^{142}\text{Nd}$ and $\epsilon^{182}\text{W}$. ② The Martian mantle is diverse in oxygen fugacity and rare earth element abundance. At least six different source reservoirs have been identified: three reservoirs for shergottites (low $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$, high $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$, high $^{147}\text{Sm}/^{144}\text{Nd}$ and low $^{176}\text{Lu}/^{177}\text{Hf}$), one for nakhlites and chassignites (relatively low $^{147}\text{Sm}/^{144}\text{Nd}$, $^{176}\text{Lu}/^{177}\text{Hf}$ and high $\epsilon^{182}\text{W}$), one for NWA 8159, and one for some components of NWA 7034. ③ The heterogeneity of Martian mantle may have formed during early fractionation of Mars. Currently the number of Martian meteorites is around 300. The majority of Martian meteorites were crystallized within the last 650 Ma while the Martian surface is predominantly Hesperian and Noachian. In addition, the composition does not overlap with remote sensing results. The surface rocks have diverse rock types including intermediate to acidic rocks besides basalts, and generally more enriched in SiO_2 and alkali than meteorites. Therefore, new missions (including sample return) are recommended to undertake a complementary study of the composition and evolution of Mars.

Key words: Martian meteorite; magmatic process; Martian mantle source; Martian crustal assimilation; basalt