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硫同位素非质量分馏记录地幔不均一性及其地球动力学意义

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摘要: 硫是一种挥发性元素, 在浅部岩浆过程(如分离结晶、岩浆脱气)中易产生硫同位素质量分馏效应(Mass-dependent fractionation of sulfur isotopes, MDF-S), 对使用硫同位素组成来约束地幔主要化学储库的属性产生干扰。硫同位素非质量分馏效应(Mass-independent fractionation of sulfur isotopes, MIF-S)是硫同位素分馏行为偏离质量依赖关系的现象, 主要通过含硫分子在高能紫外线照射下发生光化学反应产生, 其分馏机制与地球早期大气演化关系密切。值得注意的是, MIF-S 信号在太古代沉积岩中普遍存在, 而在大氧化事件之后该信号却消失不见。硫同位素非质量分馏(MIF-S)不依赖地幔氧化还原状态和高温过程(如部分熔融、分离结晶、岩浆脱气), 能够很好地规避浅部岩浆过程导致的硫同位素质量分馏, 对理解板块构造启动、地幔氧化还原状态和深部物质循环至关重要。在简要介绍硫同位素质量和非质量分馏理论的基础上, 本文梳理了地幔主要地球化学储库的硫同位素组成, 重点评述了近 20 年来硫同位素非质量分馏效应在地幔不均一性和板块构造启动时限等研究上的重要进展。

关键词: 硫同位素; 地幔不均一; 同位素非质量分馏; 同位素质量分馏; 地球化学。

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Mantle Heterogeneity Recorded by Mass-Independent Fractionation of Sulfur Isotopes and Dynamic Implications

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Abstract: Sulfur is a volatile element that is prone to mass-dependent fractionation of sulfur isotopes (MDF-S) during shallow magmatic processes (e.g., fractional crystallization and magma degassing), which limits us to constrain the properties of major mantle chemical reservoirs. The mass-independent fractionation of sulfur isotopes (MIF-S) is a phenomenon in which the fractionation behavior of sulfur isotopes deviates from the mass dependent relationship. MIF-S is mainly produced through photochemical reactions of sulfur-containing molecules under high-energy ultraviolet radiation, and its fractionation mechanism is closely related to the atmospheric evolution on early Earth. It is worth noting that MIF-S signals are commonly preserved

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in Archean sedimentary rocks, but they disappeared after the Great Oxidation Event (GOE). MIF-S does not rely on mantle redox states and high-temperature processes (such as partial melting, fractional crystallization, magma degassing), and can effectively avoid MDF-S driven by shallow magma processes. And so, MIF-S is crucial for understanding the onset of plate tectonics, mantle redox states, and deep material cycling. On the basis of a brief introduction to the theories of MDF-S and MIF-S, this review summarizes the sulfur isotope composition of major mantle chemical reservoirs, and focuses on the important progress in mantle heterogeneity and onset of plate tectonics recorded by MIF-S in the past two decades.

Key words: sulfur isotope; mantle heterogeneity; plate tectonics; mass-dependent fractionation; mass-independent fractionation; geochemistry.

0 引言

硫(S)是位于元素周期表第六主族的非金属元素,广泛分布于地球和太阳系中,它既是挥发性元素,容易受到岩浆脱气过程的影响(Beaudry *et al.*, 2018; Taracsák *et al.*, 2025);也是亲铜元素,在地球早期地核和硅酸盐地幔发生分异的过程中进入金属地核(Lodders, 2003; Wood and Halliday, 2010).自然界中硫以 ^{32}S 、 ^{33}S 、 ^{34}S 、 ^{36}S 四种稳定同位素存在,其丰度分别为95.02%、0.75%、4.21%、0.02%。天然样品硫同位素通常由 $^{34}\text{S}/^{32}\text{S}$ 比值确定的 $\delta^{34}\text{S}$ 表示: $\delta^{34}\text{S}_{\text{V-CDT}}(\text{‰}) = [(^{34}\text{S}/^{32}\text{S})_{\text{样品}} / (^{34}\text{S}/^{32}\text{S})_{\text{标样}} - 1] \times 1000$,其中 $(^{34}\text{S}/^{32}\text{S})_{\text{样品}}$ 代表测试样品的 $^{34}\text{S}/^{32}\text{S}$, $(^{34}\text{S}/^{32}\text{S})_{\text{标样}}$ 代表美国代阿布洛大峡谷(Canyon Diablo)铁陨石中陨硫铁(Troilite)的硫同位素组成($^{34}\text{S}/^{32}\text{S}=0.044163$)。

地球上绝大多数物质的硫同位素分馏过程是质量依赖的,即硫同位素变化通常遵循质量依赖分馏(MDF: Mass-dependent fractionation)的规律(图1),这意味着硫同位素比率的相对变化与所涉及同位素的质量差异成比例。在四硫同位素($\delta^{34}\text{S}$ 、 $\delta^{33}\text{S}$ 、 $\delta^{36}\text{S}$)关系图中,大部分地球样品落在硫同位素质量分馏(Mass-dependent fractionation of sulfur isotopes, MDF-S)线上(图1),关系式可以表示为: $\delta^{33}\text{S}=0.515 \times \delta^{34}\text{S}$ 和 $\delta^{36}\text{S}=1.90 \times \delta^{34}\text{S}$ (Farquhar *et al.*, 2000; Johnston, 2011)。

硫是地球系统中常见的挥发分之一,在自然界中通常以硫化物、硫酸盐、单质硫或分子硫的形式存在,也是构成生命有机体的主要元素。硫的丰度、价态、赋存状态(硫酸盐 vs. 硫化物)和同位素比值得到地球和行星科学研究领域的广泛关注,是研究地球深部和浅表系统物质循环的有效载体,在行星演化与分异(Wang and Becker, 2013; Wang *et al.*, 2021; Heiny *et al.*, 2025)、金属-稀土元素富集成矿(Cui *et al.*, 2020; Wan *et al.*, 2021; Wan *et al.*,

2023; Chen *et al.*, 2025; Farsang and Zajacz, 2025)、地幔氧化还原状态(Jugo *et al.*, 2010; Bénard *et al.*, 2018; Li *et al.*, 2020; Meng *et al.*, 2022)和地球宜居性演化(Farquhar *et al.*, 2000; Hattori *et al.*, 2013; Luo *et al.*, 2016)等方面起到了关键作用。本文旨在梳理地幔主要储库的硫同位素组成,详细总结了近年来硫同

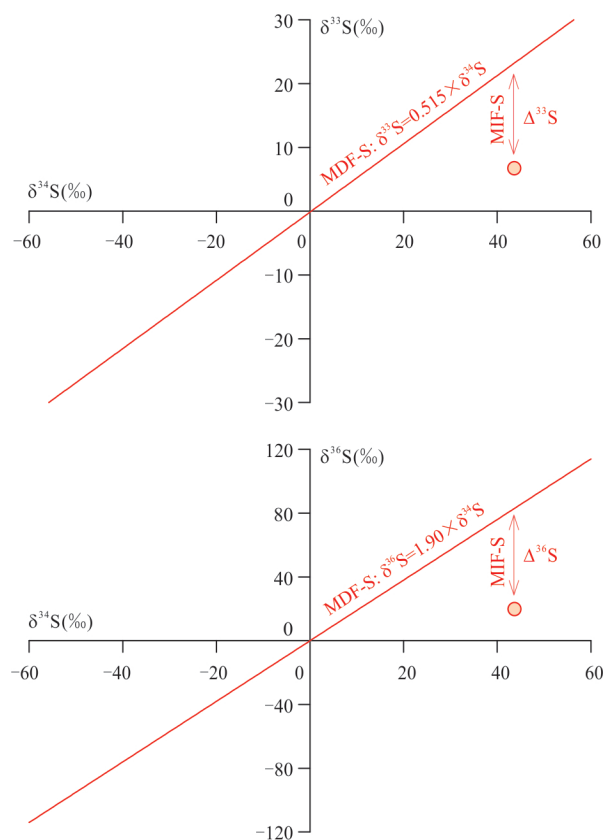


图1 年轻地质样品(<2 Ga)多硫同位素($\delta^{33}\text{S}$ 、 $\delta^{34}\text{S}$ 、 $\delta^{36}\text{S}$)之间的相关性

Fig.1 Relationships among multiple sulfur isotopes ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$) in young terrestrial samples (<2 Ga)

硫同位素质量分馏(MDF-S, $\Delta^{33}\text{S}=0$, $\Delta^{36}\text{S}=0$)和硫同位素非质量分馏(MIF-S, $\Delta^{33}\text{S} \neq 0$, $\Delta^{36}\text{S} \neq 0$)的定义来自文献(Farquhar *et al.*, 2000; Johnston, 2011)

位素非质量分馏效应在地幔不均一性和板块构造启动时限等方面的最新研究进展。

1 地幔化学不均一性

了解地幔化学不均一性及其成因机制是地幔地球化学的主要研究内容,也是固体地球科学的前沿研究领域,对理解地球内部运行机制、结构和物理-化学性质具有重要意义(Weiss *et al.*, 2016; Mazza *et al.*, 2019; 陈立辉等, 2022; Zhang *et al.*, 2024)。地幔地球化学研究在 20 世纪 80 年代取得突破性进展,基于洋脊玄武岩(mid-ocean ridge basalt, MORB)和洋岛玄武岩(ocean island basalt, OIB)的 Sr-Nd-Pb 放射性同位素体系研究,已揭示出全球地幔广泛存在纵向与横向化学不均一性,可以划分为多个地幔端元组分:亏损的 MORB 型地幔端元(depleted MORB mantle,

DMM)、I 型富集地幔(enriched mantle I, EM I)、II 型富集地幔(enriched mantle II, EM II)、高 ²³⁸U/²⁰⁴Pb 地幔端元(HIMU; ²⁰⁶Pb/²⁰⁴Pb≥20)和 FOZO(Focal Zone; 未显著脱气的、高 ³He/⁴He 比值)(Hart, 1984; Zindler and Hart, 1986; Hofmann, 1997; Stracke, 2012)(图 2)。地幔主要组成端元(EM I、EM II、HIMU)的不均一性一般被认为是因俯冲作用而发生的洋壳再循环导致的(Hofmann, 1997; Sobolev *et al.*, 2000)。然而,在大洋和大陆玄武岩地幔源区中也识别出了再循环陆壳组分的信息(Jackson *et al.*, 2007; Chen *et al.*, 2009; Zhang *et al.*, 2017)。近年来,随着高精度金属稳定同位素(如 Ca-Zn-Mg)在地幔地球化学研究中的广泛应用,越来越多的研究支持再循环地表碳酸盐对地幔不均一性的贡献(Liu *et al.*, 2016; Xu *et al.*, 2022; Zhang *et al.*, 2022; Zhou *et al.*, 2025),突破了对地幔端元模型的传统认知。

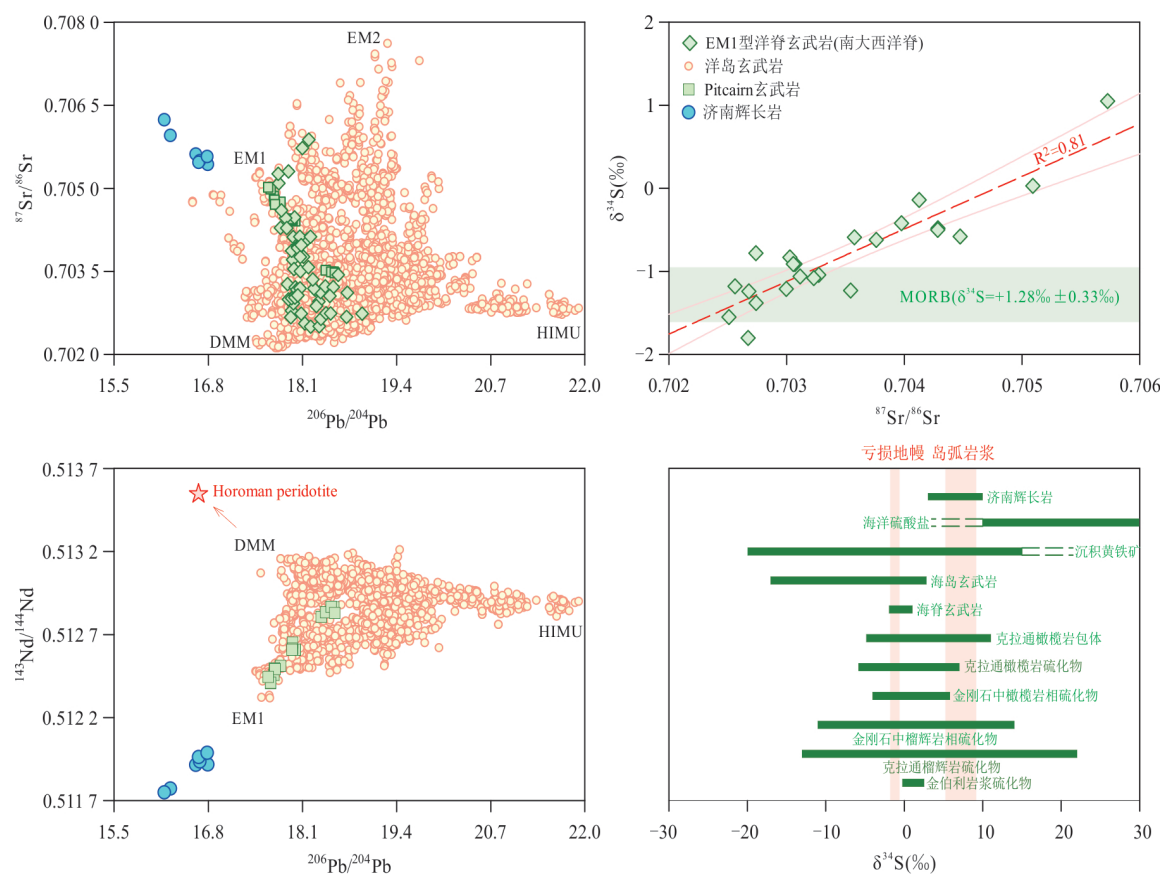


图 2 洋岛玄武岩 Pb-Sr-Nd-S 同位素组成和地幔端元组分

Fig.2 Pb-Sr-Nd-S isotopes of oceanic-island basalts (OIBs) and mantle end members

MORB. 洋脊玄武岩; OIB. 洋岛玄武岩; EM1.I 型富集地幔端元; EM2. II 型富集地幔端元; HIMU. 高铀/铅比值地幔端元. 数据源: 洋脊玄武岩和洋岛玄武岩数据分别引自 PetDB 数据库(<http://www.earthchem.org/petdb>)和 GEOROC 数据库(<http://georoc.mpch-mainz.gwdg.de/georoc>); Pitcairn 洋岛玄武岩数据引自 Delavault *et al.* (2016); 南大西洋 EM1 型洋脊玄武岩数据引自 Labidi *et al.* (2013); 亏损地幔(DMM)和岛弧玄武岩 $\delta^{34}\text{S}$ 数据分别引自 Labidi *et al.* (2013)和 Muth and Wallace (2021); 济南辉长岩和其余 $\delta^{34}\text{S}$ 数据引自 Zhang *et al.* (2020)

金伯利岩普遍具有类似于洋岛玄武岩的微量元素分布特征,一般被认为是150 km以下碳酸盐化软流圈地幔低程度部分熔融($<1\%$)的产物(Tappe *et al.*, 2012),是研究地球碳-硫循环的有效载体和探索深部地幔物质组成的重要探针.近年来对全球范围内不同年龄的金伯利岩Nd-Hf同位素的研究表明,大部分原始金伯利岩(>2 亿年)Nd-Hf同位素都落在同一条演化线上(接近于球粒陨石),揭示金伯利岩来源于一个共同的、长期的(>25 亿年)、未去气的原始地幔储库(未遭受再循环地表物质大规模混染作用的影响),而显生宙(<2 亿年)异常金伯利岩源区开始混入了地表碳酸盐组分(Woodhead *et al.*, 2019).然而,通过分析全球161件不同时代的金伯利岩碳同位素组成,Giuliani *et al.* (2022)发现金伯利在7.5亿年前显示地幔碳同位素的印记,而在7.5亿年之后开始富集轻的碳同位素,暗示显生宙以来的金伯利岩源区普遍受到了再循环有机碳而不是沉积碳酸盐的影响.考虑到寒武纪生命大爆发对有机质埋藏的正反馈,Giuliani *et al.* (2022)进一步提出寒武纪后增加的有机碳俯冲通量改造了地球深部碳储库,从而重构了深部碳循环与生命演化的因果链条.另外,金伯利岩携带的超深金刚石(形成于410~660 km,其包裹体具有地幔转换带的矿物组合,如林伍德石、钙钛矿和超硅石榴石等)普遍显示地表有机碳同位素特征($\delta^{13}\text{C}$ 低至 -27%),远低于典型地幔值($\delta^{13}\text{C}=-5\%\pm 1\%$) (Walter *et al.*, 2011; Timmerman *et al.*, 2019),指示地表有机碳可被俯冲输送至地幔过渡带经历氧化还原反应转化为金刚石(Walter *et al.*, 2011; Timmerman *et al.*, 2019).由此可见,大洋板块携带蚀变洋壳、碳酸盐岩或有机沉积物通过俯冲作用进入深部地幔,这些物质因密度差异可长期滞留于地幔转换带或核幔边界,形成化学异常体.值得注意的是,深部地幔化学异常体与地震波速异常耦合,容易被地球物理探测技术所捕捉(Torsvik *et al.*, 2010; Yang and Faccenda, 2020; Xu *et al.*, 2025).

2 地幔主要化学储库的硫同位素组成(MDF-S)

已有研究发现,碳质球粒陨石中含有丰富的硫(包括硫化物、硫酸盐、单质硫或分子硫),蕴含着太阳系早期高温环境下的丰富信息(Labidi *et al.*, 2017; Wang *et al.*, 2021; Heiny *et al.*, 2025).

Labidi *et al.* (2017)报道了13个碳质球粒陨石全岩的硫含量和同位素数据,结果显示这些碳质球粒陨石具有极高的硫含量(平均值 $S=2.11\%\pm 0.39\%$, 1σ , $n=13$)和相对均一的硫同位素组成(平均值 $\delta^{34}\text{S}=-0.08\%\pm 0.44\%$, 1σ , $n=13$). Labidi *et al.* (2013)研究了南大西洋洋脊玄武岩的全岩硫同位素组成(平均值 $\delta^{34}\text{S}=-1.28\%\pm 0.33\%$;图2),反映全硅酸盐地球(Bulk Silicate Earth,简称为BSE)具有明显低于球粒陨石的硫同位素特征(Labidi *et al.*, 2017).考虑到高温高压实验结果已经证实了液态金属核会优先富集重硫同位素 ^{34}S (Labidi *et al.*, 2013, 2016),Labidi *et al.* (2013)进一步将BSE与球粒陨石之间的 $\delta^{34}\text{S}$ 差异归因于核-幔分异,即重硫同位素在核-幔分异过程中倾向于进入地核,使得BSE具有低于球粒陨石的 $\delta^{34}\text{S}$ 值.然而,Wang *et al.* (2021)最近依据密度泛函理论的第一性原理计算获得了核-幔间硫同位素分馏系数,发现核-幔分异引起的硫同位素分馏几乎可以忽略不计.结合热力学计算结果,Wang *et al.* (2021)最终提出BSE与地核之间的 $\delta^{34}\text{S}$ 值差异不是由核-幔分异造成的,而是在早期太阳系 H_2 未完全散去的情况下,星胚发生部分熔融,硫主要以 H_2S 的形式挥发,并带走重硫同位素,使得残留硅酸盐富集轻硫同位素.

相比球粒陨石和洋脊玄武岩,地表物质、地幔主要化学储库和金刚石中硫化物包裹体的硫同位素组成展现高度的可变性(图2).在地质历史时期,海水硫酸盐的浓度和硫同位素组成变化与海洋的氧化还原状态密切相关:地球从缺氧向氧化环境的转型常伴随着海水硫酸盐浓度上升和 $\delta^{34}\text{S}$ 正向偏移(Claire *et al.*, 2014; Algeo *et al.*, 2015).例如,现代海水硫酸盐浓度明显高于早期缺氧海洋且显著富集重硫同位素(平均值 $\delta^{34}\text{S}=+20.9\%\pm 0.6\%$) (Claire *et al.*, 2014; Algeo *et al.*, 2015).因此,硫作为流体活动性元素可以通过板片俯冲和变质脱水迁移到深部地幔,驱动地幔氧逸度升高和硫同位素转变,也可以通过岛弧岩浆返回到地表(李继磊等, 2022).大量的理论计算和高温高压实验研究表明,氧逸度控制熔体中硫的赋存状态和迁移富集:氧逸度增加导致熔体中硫的溶解度增加,溶解硫从硫化物(S^{2-})为主导转变为硫酸盐(S^{6+})为主导(Jugo *et al.*, 2010; Li *et al.*, 2021; Xu and Li, 2021; Kleinsasser *et al.*, 2022).相较于洋脊玄武岩(ΔFMQ 为 -0.26 ± 0.44),现代岛弧火山岩具有更高的氧逸度

(Aulbach and Stagno, 2016)、更高的硫含量(可达 3 000 ppm)和富集重硫同位素($\delta^{34}\text{S} = 5.2\text{‰} \sim 9.5\text{‰}$; 图 2), 这反映了现代俯冲板片输入到地幔楔中的硫主要以硫酸盐(S^{6+})形式存在(Pons *et al.*, 2016; Walters *et al.*, 2019; Muth and Wallace, 2021). Lee *et al.* (2018) 发现大陆弧深部堆晶的石榴辉石岩具有高于亏损地幔的硫同位素组成($\delta^{34}\text{S} = -0.07\text{‰} \sim 4.54\text{‰}$), 表明俯冲板片释放的重硫同位素通过流体交代进入大陆弧地幔. 此外, 地幔捕虏体中硫酸盐的出现, 也被认为是俯冲板片派生的氧化性流体携带了硫酸盐进入了地幔楔(Pons *et al.*, 2016; Bénard *et al.*, 2018). 在地幔交代过程中, 俯冲富硫流体驱动地幔氧逸度升高并伴随着硫同位素的转变(Pons *et al.*, 2016; Bénard *et al.*, 2018).

虽然普遍认为地球表面和地幔硫储库是通过俯冲作用、地壳再循环和火山作用连接起来的(Kagoshima *et al.*, 2015; Hutchison *et al.*, 2019), 但是不同地幔端元的明确成因一直以来有所争议. 如图 2 所示, 南大西洋 EM1 型洋脊玄武岩的 $\delta^{34}\text{S}$ 与 $^{87}\text{Sr}/^{86}\text{Sr}$ 之间呈明显正相关性, 表明硫同位素分馏与源区性质存在内在联系, 支持 EM1 型地幔源区存在再循环地壳物质(Labidi *et al.*, 2013). Zhang *et al.* (2020) 通过研究济南 EMI 型辉长岩的重硫同位素($\delta^{34}\text{S} = +3\text{‰} \sim 10\text{‰}$) 和高非放射性成因铅(图 2), 提出地表的硫和铅可随俯冲过程进入浅部克拉通地幔, 经过长期储存之后可形成 EM1 型富集地幔. Beaudry *et al.* (2018) 以加那利群岛 HIMU 型洋岛玄武岩为研究对象, 发现受脱气作用影响有限的原始岩浆具有高于 MORB 的硫同位素特征($\delta^{34}\text{S} \approx +3\text{‰}$), 支持加那利地幔柱存在年轻的富含 ^{34}S 的再循环洋壳. Ranta *et al.* (2022) 发现冰岛地幔柱岩浆具有和球粒陨石相似的硫同位素($\delta^{34}\text{S} \approx 0\text{‰}$), 结合其高 $^3\text{He}/^4\text{He}$ (高达 25.9 R/R_a) 和负 $\mu^{182}\text{W}$ 异常, 反映原始地幔硫同位素($\delta^{34}\text{S}$ 趋近 0‰) 继承自未分异的硅酸盐地球储库, 这也暗示核-幔分异过程未引发显著的 MDF-S. 然而, 硫同位素在岩浆演化过程中存在质量分馏现象(Beaudry *et al.*, 2018), 严重制约了对地幔硫储库属性的准确限定.

3 MDF-S 确定地幔硫储库属性的局限性

岩浆氧逸度是驱动硫化物(S^{2-})与硫酸盐(SO_4^{2-})相互转化的重要参数, 易受浅部岩浆过程(如结晶

分异、脱气作用)的影响. 值得注意的是, 硫的赋存状态转变也会影响硫在岩浆中溶解度(Jugo *et al.*, 2010; Lee *et al.*, 2016; Hutchison *et al.*, 2019; Reekie *et al.*, 2019; Chen *et al.*, 2020; Lee and Tang, 2020) 和硫同位素质量分馏(Beaudry *et al.*, 2018; Tang *et al.*, 2020; Saal and Hauri, 2021; Liu *et al.*, 2022; Taracsák *et al.*, 2025), 干扰了对深部地幔源区硫同位素组成的理解. Tang *et al.* (2020) 从美国亚利桑那州大陆弧石榴辉石岩堆晶出发, 提出增厚的地壳高压环境下, 深部岩浆房石榴子石等高压矿物的结晶, 消耗了早期岩浆中大量二价铁, 使得分异岩浆中三价铁含量升高, 从而实现大陆的内生氧化, 氧化指标可通过磷灰石的硫含量进行表征(磷灰石倾向于富集氧化的硫(以硫酸根的形式存在)). 硫同位素可能与此过程同步发生质量分馏: 石榴石等高压矿物结晶会升高岩浆氧逸度, 促使硫价态转变, 进而影响岩浆硫同位素质量分馏($\delta^{34}\text{S}$ 值升高)(Lee *et al.*, 2018).

岩浆脱气作用也会诱导硫同位素质量分馏. Beaudry *et al.* (2018) 通过系统性分析加那利群岛玄武岩的熔体包裹体(未脱气岩浆)、基质玻璃(脱气后残留熔体)和硫化物微晶硫同位素组成($\delta^{34}\text{S}$), 发现岩浆脱气过程导致 $\delta^{34}\text{S}$ 值显著负向分馏(图 3). 另外, Saal and Hauri (2021) 首次通过对阿波罗 15 号和 17 号任务采集的月球原始火山玻璃及橄榄石熔体包裹体进行原位硫同位素分析, 观察到了显著的 MDF-S 现象($\delta^{34}\text{S}$ 变化范围大; 图 3), 发现 $\delta^{34}\text{S}$ 与硫含量、钛含量呈正相关关系: 高钛玄武岩硫含量(平均 $\text{S} > 1\,000\text{ ppm}$) 对应高 $\delta^{34}\text{S}$ 值($+1.3\text{‰} \sim -1.8\text{‰}$), 低钛玄武岩硫含量($\text{S} = 800 \sim 300\text{ ppm}$) 对应低 $\delta^{34}\text{S}$ 值($-0.27\text{‰} \sim -4.70\text{‰}$), 极低钛玄武岩硫含量(平均 $\text{S} < 400\text{ ppm}$) 对应极低 $\delta^{34}\text{S}$ 值($-4.80\text{‰} \sim -14\text{‰}$). 近期的高温高压实验结果表明, 在月球极低氧逸度条件下, 较低的硫含量仍有可能形成富铁贫硫的硫化物(Brenan *et al.*, 2019). 基于此硫化物饱和模型, Saal and Hauri (2021) 提出月幔硫同位素是不均匀的, 预测高钛玄武岩源区具有高硫含量(900 ppm) 和高 $\delta^{34}\text{S}$ 值($+1.7\text{‰}$), 而低钛玄武岩源区具有低硫含量(700 ppm) 和低 $\delta^{34}\text{S}$ 值(-1.5‰). 这个结果表明, 月幔中的硫含量显著低于地幔但其 $\delta^{34}\text{S}$ 值高于地幔(平均值 $\delta^{34}\text{S} = -1.28\text{‰} \pm 0.33\text{‰}$; 图 2) 约 3‰, 暗示月球核-幔分异改变了原始月幔的硫同位素组成(Saal

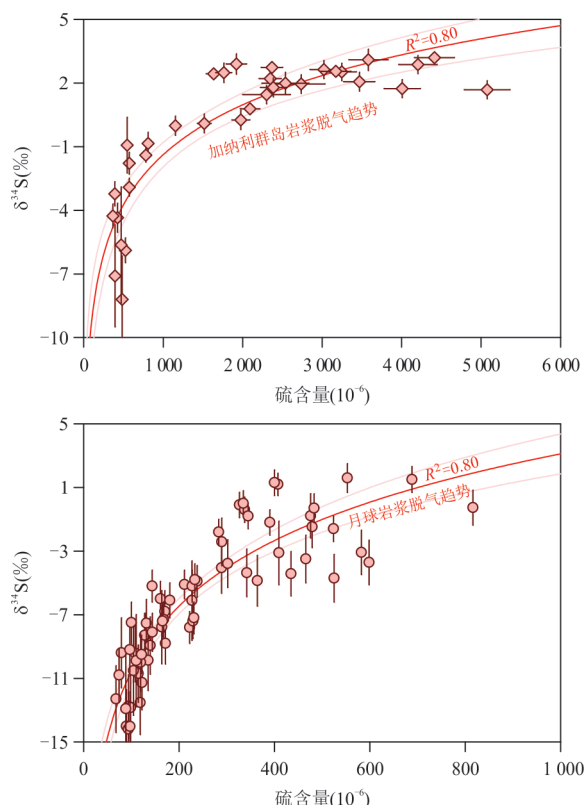


图3 岩浆脱气诱导硫同位素质量分馏

Fig.3 Degassing-induced mass-dependent fractionation of sulfur isotopes

加那利群岛和月球硫同位素数据分别引自 Beaudry *et al.* (2018) 和 Saal and Hauri (2021)

and Hauri, 2021). 月球高钛-低钛玄武岩硫同位素质量分馏幅度大, 反映月球经历了极端挥发分丢失, 支持 MDF-S 与月球岩浆海结晶和岩浆脱气过程有关 (Saal and Hauri, 2021).

综上所述, 浅部岩浆过程如分离结晶、岩浆脱气等可改变原始岩浆氧逸度及硫的赋存形态, 掩盖了原始岩浆的 MDF-S 信号. 因此, 在使用 $\delta^{34}\text{S}$ 准确解析深部地幔源区属性时, 需排除浅部岩浆过程 (如结晶分异、脱气作用) 的潜在干扰, 有必要更多地采用微区分析技术 (NanoSIMS) 直接测定未脱气硫化物包裹体的硫同位素组成, 或综合多同位素体系 (放射性同位素和金属稳定同位素) 进行联合示踪.

4 硫同位素非质量分馏效应(MIF-S)与早期地球演化

已有研究表明, 早期地球大气圈是极端缺氧的, 可供呼吸的自由氧气分子的含量不及现今大

气含氧量的 0.001% (Lyons *et al.*, 2014; Zhang *et al.*, 2020). 在一次全球规模的大氧化事件 (Great Oxidation Event, 简称为 GOE; 距今 23~24 亿年前) 之后, 大气中的游离氧含量急剧增加 (Lyons *et al.*, 2014; Luo *et al.*, 2016; Zhang *et al.*, 2020) (图 4). 这次早古元古代大氧化事件为地表环境的宜居性和生命的快速演化奠定了重要基础 (Holland, 2006; Och and Shields-Zhou, 2012; Lyons *et al.*, 2014; Poulton *et al.*, 2021), 也显著改变了陆地-海洋的矿物成分、元素和同位素组成 (Frei *et al.*, 2009; Bindeman *et al.*, 2018; Stolper and Keller, 2018; Wang *et al.*, 2019). 例如, 海水中金属铀 (U) 对氧浓度非常敏感: 当 GOE 之前海水中的氧气浓度较低时, 海水贫铀 (主要以不溶于水的 U^{4+} 形式存在) 和相应的大洋沉积物富集非放射性成因铅; 当 GOE 之后海水中的氧气浓度较高时, 海水明显更富铀 (主要以溶于水的 U^{6+} 形式存在; 图 4) 和相应的大洋沉积物富集放射成因铅 ($^{206}\text{Pb}/^{204}\text{Pb}$ 比值高达 43) (Zhang *et al.*, 2020).

大氧化事件作为地质历史时期的关键转折点, 对理解地表物质循环与深部地幔氧逸度演变规律之间的耦合关系具有重要意义. Aulbach and Stagno (2016) 通过太古代 (40~25 亿年前) 与元古代/现代洋脊玄武岩的 V/Sc 比值系统对比, 发现太古代样品 V/Sc 平均值 (5.2 ± 0.4 , 2σ , $n=5$) 显著低于元古代 (7.0 ± 1.4 , 2σ , $n=6$) 和现代 MORB (6.8 ± 1.6). 这一差异表明太古代上地幔整体呈现低氧逸度特征 (ΔFMQ 为 -1.19 ± 0.33), 其相对氧逸度普遍低于元古代/现代地幔值 (如现代 MORB ΔFMQ 为 -0.26 ± 0.44 ; 图 4). 另外, Moreira *et al.* (2023) 利用硫 K-edge 微 X 射线吸收近边结构光谱 (sulfur K-edge micro XANES spectroscopy), 测定了巴西 Mineiro Belt 地区 24~21 亿年前岛弧岩浆锆石中磷灰石包裹体的硫价态 (包括 S^{6+} 、 S^{4+} 和 S^{2-} 的相对丰度), 发现岩浆由 GOE 前的还原状态 (对应低 $\text{S}^{6+}/\Sigma\text{S}$) 转变为 GOE 后的氧化状态 (对应高 $\text{S}^{6+}/\Sigma\text{S}$), 提出古元古代氧化的沉积物通过俯冲作用显著提升了弧下地幔氧逸度. 因此, 早古元古代大氧化事件与地幔氧化还原状态转变在时间上紧密衔接, 印证了地表大氧化事件在深部地幔氧化过程中扮演着极为重要的角色 (Aulbach and Stagno, 2016; Stolper and Keller, 2018; Spencer *et al.*, 2019).

除此之外, Zhang *et al.* (2020) 选取华北克拉通

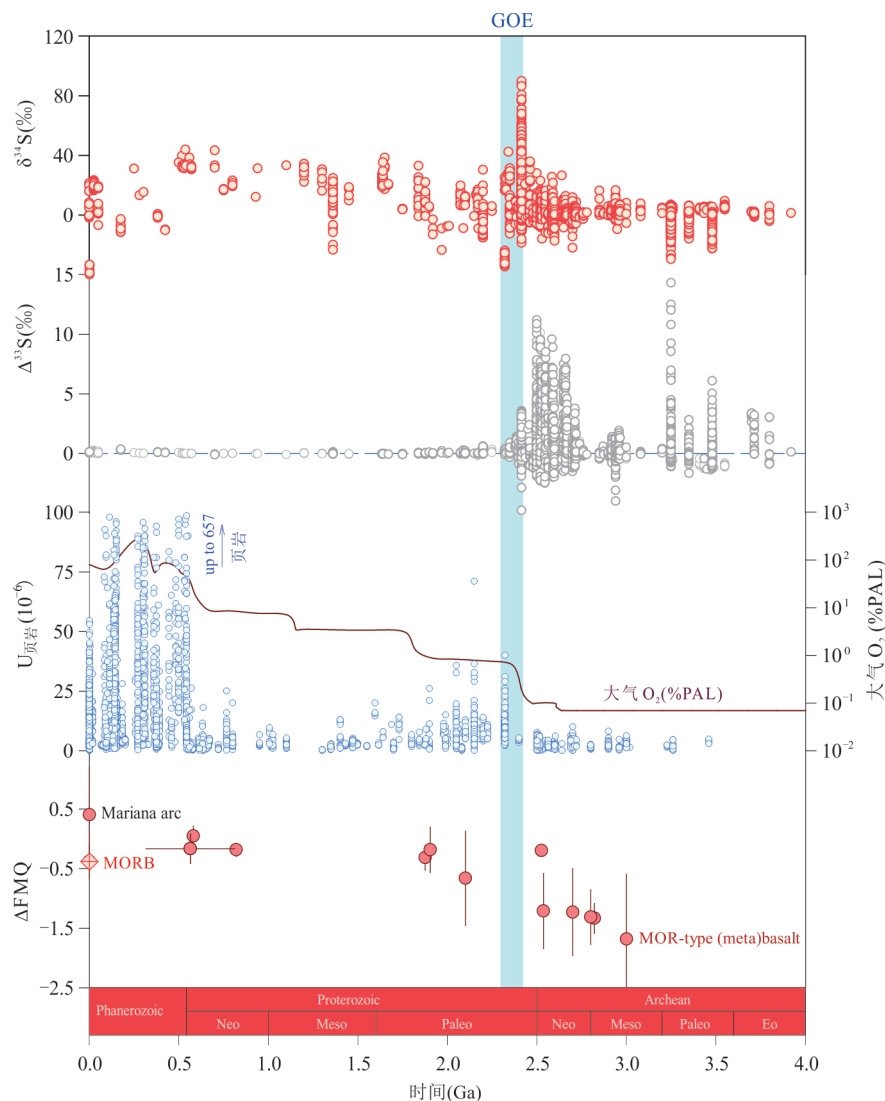


图 4 沉积物中 $\delta^{34}\text{S}$ 和 $\Delta^{33}\text{S}$ 随时间的演化序列
Fig.4 $\delta^{34}\text{S}$ 和 $\Delta^{33}\text{S}$ versus sedimentary age

沉积物多硫同位素数据引自 Claire *et al.* (2014); 地质历史时期大气氧浓度和页岩 U 含量数据引自 Zhang *et al.* (2020); 地幔氧逸度数据引自 Aulbach and Stagno (2016)

东部济南早白垩世富镁辉长岩为研究对象,通过全岩主-微量元素、锶-钕-铅同位素和硫化物硫同位素的原位微区分析研究表明,浅部克拉通地幔(EMI型地幔)的非放射性成因铅来自俯冲交代的太古代、还原的含水流体.该研究将浅部地幔铅储库的形成与表生氧化事件直接关联,阐明地球内部化学分异与地表环境演化存在协同作用,为理解早期地球壳幔物质循环提供了新视角.

硫同位素非质量分馏效应(Mass-independent fractionation of sulfur isotopes, MIF-S)是硫同位素(^{32}S 、 ^{33}S 、 ^{34}S 、 ^{36}S)分馏行为偏离质量依赖关系的现象,主要通过含硫分子(如二氧化硫或硫化氢)在短波紫外线(Ultraviolet, UV)照射下发生光化学反应

产生 ^{33}S 、 ^{36}S 异常.MIF-S表现为非零的 $\Delta^{33}\text{S}$ 和 $\Delta^{34}\text{S}$ 值($\Delta^{33}\text{S}\neq 0$, $\Delta^{36}\text{S}\neq 0$),学界通常使用 $\Delta^{33}\text{S}=\delta^{33}\text{S}-[(1+\delta^{34}\text{S})^{0.515}-1]$ 和 $\Delta^{36}\text{S}=\delta^{36}\text{S}-[(1+\delta^{34}\text{S})^{1.9}-1]$ 来定量描述多硫同位素的MIF幅度(图1).

在早期地球或火星等缺氧环境中,由于缺乏 O_2/O_3 的光子屏蔽作用,短波紫外光可穿透大气层引发硫同位素光化学分馏(Farquhar *et al.*, 2000; Ono, 2017; Bindeman *et al.*, 2018).该光化学反应会分别产生携带正 $\Delta^{33}\text{S}$ 值的还原态硫(S^0/S_8)和携带负 $\Delta^{33}\text{S}$ 值的氧化态硫(H_2SO_4)(Farquhar *et al.*, 2000; Ono, 2017).科学家已经发现太古代沉积岩中普遍存在MIF-S信号,表现为 $\Delta^{33}\text{S}\neq 0$ 且 $\Delta^{36}\text{S}\neq 0$,但是这些MIF-S信号在GOE之后年轻的沉积岩

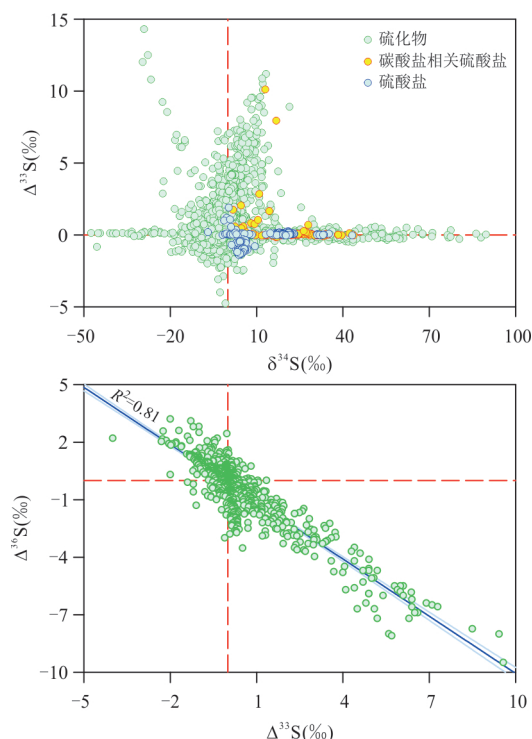


图5 沉积物中硫化物和硫酸盐的多硫同位素组成

Fig.5 $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ for sedimentary sulfides and sulfates

沉积硫同位素数据引自 Claire *et al.* (2014)

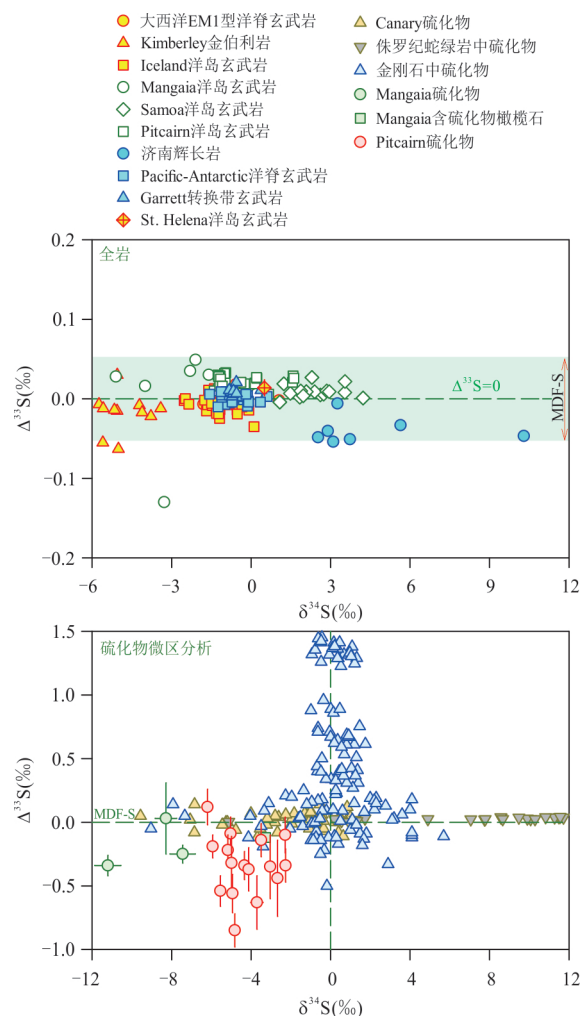
(Farquhar *et al.*, 2000; Pavlov and Kasting, 2002; Luo *et al.*, 2016; Ono, 2017; Poulton *et al.*, 2021) 或海水蚀变洋壳 (Genot *et al.*, 2024) 里面却消失不见 ($\Delta^{33}\text{S} \approx 0$, $\Delta^{36}\text{S} \approx 0$), 标志着大氧化事件的开启 (图4). 另外, 太古代沉积物亦可见 $\delta^{34}\text{S}$ 与 $\Delta^{33}\text{S}$ 的协同变化和 $\Delta^{33}\text{S}$ 与 $\Delta^{36}\text{S}$ 的同步偏负异常 (图5). 由于不同波长紫外光化学反应导致的 $\Delta^{33}\text{S}$ 与 $\Delta^{36}\text{S}$ 分馏幅度呈非线性关系, 使得 $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ 比值成为追溯早期地球硫循环模式 (还原性硫循环 vs. 氧化性硫循环) 的关键指标 (Ono, 2017). 同时, 缺氧环境可显著提升还原态硫气溶胶产率, 抑制氧化态硫气溶胶生成, 较大程度避免了含硫光化学衍生物的均质化作用 (MIF-S 信号将因还原态与氧化态气溶胶同比率沉积而抵消) (De Witt *et al.*, 2010), 从而提升 MIF-S 信号的保存潜力及进入沉积记录的几率 (Ono, 2017), 这也与太古代沉积岩保存较多正 $\Delta^{33}\text{S}$ 异常相一致 (图4和图5). 因此, 学界普遍认为 MIF-S 信号的生成与地质保存过程与低浓度大气氧存在多重关联, 是揭示地球大氧化事件前缺氧大气状态 ($\text{O}_2 < \text{现代 } 0.001\%$) 的关键证据 (图4和图5).

5 MIF-S 记录地幔不均一性

硫同位素非质量分馏效应 (MIF-S) 普遍认为 是由大气光化学反应主导, 能够很好地规避岩浆过程 (如部分熔融、分离结晶、岩浆脱气等) 导致的硫同位素质量分馏效应 (MDF-S), 为板块构造启动、地幔不均一性、太阳系原行星盘演化等研究提供了新的有效工具 (Farquhar *et al.*, 2000; Antonelli *et al.*, 2014; Ono, 2017; Heiny *et al.*, 2025). 近 20 年来, 随着大型二次离子质谱分析技术的发展, 同位素地球化学家陆续在地幔金刚石和洋岛玄武岩中观测到 MIF-S 信号, 为识别再循环古老的地表物质 (如沉积物) 和约束俯冲过程对地幔演化的影响提供了新范式, 深化了对地幔不均一性的认知.

如前文所述, 相较于 MDF-S, MIF-S 在探究地幔化学储库的属性方面明显更具优势. Cabral *et al.* (2013) 以 Austral-Cook 群岛中 Mangaia 岛年轻的 (~ 20 Ma) HIMU 型洋岛玄武岩 ($^{206}\text{Pb}/^{204}\text{Pb} > 20.5$) 为研究对象, 利用硫同位素微区分析技术, 发现橄榄石包裹的硫化物存在明显偏负的 MIF-S 信号 ($\Delta^{33}\text{S} = -0.34\text{‰} \pm 0.08\text{‰}$; 图6), 提出太古代热液蚀变洋壳在深部地幔可长期储存 (超过 20 亿年). 考虑到曼加亚岛玄武岩表现出明显偏离地幔阵列的 $\epsilon_{\text{Hf}} - \epsilon_{\text{Nd}}$ 同位素和铅同位素模型计算, 已有研究指出其地幔源区存在太古代 (> 3.2 Ga) 循环洋壳物质 (Nebel *et al.*, 2013). 需要指出的是, MIF-S 信号的发现无疑提供了更为直接的证据, 确认了 HIMU 型地幔源区存在太古代洋壳物质 (Cabral *et al.*, 2013). 另外, Zhang *et al.* (2022) 发现 Austral-Cook 群岛、St. Helena 岛和 Louisville 海山岛链 HIMU 型洋岛玄武岩普遍携带重的 Zn 同位素 ($\delta^{66}\text{Zn} = 0.38\text{‰} \pm 0.03\text{‰}$), 意味着其源区存在再循环的沉积碳酸盐. 因此, HIMU 地幔源区可能普遍存在太古代再循环洋壳 (蚀变玄武岩 ± 碳酸盐).

同样地, 利用硫同位素微区分析技术, Delavault *et al.* (2016) 发现 Pitcairn EM1 型玄武岩 (图2) 中橄榄石和斜长石的硫化物包裹体和基质硫化物表现出偏负的 $\Delta^{33}\text{S}$ 值 (低至 -0.8‰ ; 图6). 结合全岩铅同位素模拟计算, Delavault *et al.* (2016) 直接证明了 Pitcairn 地幔柱中存在太古代 (2.5~2.6 Ga) 沉积物的再循环组分, 进一步深化了对地球深部物质循环时限与机制的理解. 鉴于 Pitcairn 玄武岩显示出比正常地幔偏轻的镁同位素组成 ($\delta^{26}\text{Mg}$ 低至

图6 洋岛玄武岩的 $\Delta^{33}\text{S}$ 和 $\delta^{34}\text{S}$ 组成Fig.6 $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ for oceanic-island basalts (OIBs)

原位硫同位素数据来源: Mangaia 洋岛玄武岩数据引自 Cabral *et al.* (2013); Pitcairn 洋岛玄武岩数据引自 Delavault *et al.* (2016); 金刚石中硫化物包裹体 (Farquhar *et al.*, 2002; Cartigny *et al.*, 2009; Thomassot *et al.*, 2009; Smit *et al.*, 2019); 侏罗纪蛇纹岩中硫化物 (Genot *et al.*, 2024). 全岩硫同位素数据来源: 南大西洋 EM1 型洋脊玄武岩数据 (Labidi *et al.*, 2013); Mangaia 洋岛玄武岩 (Dottin III *et al.*, 2020a); Pitcairn 洋岛玄武岩 (Labidi *et al.*, 2022); 冰岛玄武岩 (Ranta *et al.*, 2022); Samoa 洋岛玄武岩 (Labidi *et al.*, 2015; Dottin III *et al.*, 2020b); St. Helena 洋岛玄武岩 ($\Delta^{33}\text{S} = 0.014\text{‰} \pm 0.010\text{‰}$; $\delta^{34}\text{S} > 0.5\text{‰}$) (Cartigny, 2015); Canary 洋岛玄武岩 (Beaudry *et al.*, 2018); Garrett 玄武岩 (Labidi and Cartigny, 2016); Pacific-Antarctic 洋脊玄武岩 (Labidi *et al.*, 2014); Kimberley 金伯利岩 (Fitzpayne *et al.*, 2021); 济南辉长岩 (Zhang *et al.*, 2020)

-0.40‰) 和偏低的 $\text{CaO}/\text{Al}_2\text{O}_3$ 比值 (与预期的含碳酸盐地幔熔融产生的熔体成分不符), Wang *et al.* (2018) 发现碳酸盐沉积物在 EM1 地幔端元的形成过程中也扮演了重要角色, 提出早期板块俯冲过程中的脱碳反应导致碳酸盐矿物分解, 但其轻镁同位素特征通过元素迁移被再循环的硅酸盐物质所

继承, 即沉积碳酸盐是以“幽灵”的形式循环进入 Pitcairn EM1 型地幔源区, 并未直接参与熔融. 这一“幽灵”碳酸盐循环机制与效应迥异于 HIMU 型地幔 (碳酸盐直接参与熔融或交代).

HIMU 和 EM1 型地幔源区属性的差异也体现在汞同位素非质量分馏 (MIF-Hg) 信号上. 与硫同位素相似, MIF-Hg 主要受光化学反应控制, 不受浅部岩浆作用影响, 是示踪深部地幔物质来源的重要指标. 最近, Moynier *et al.* (2021) 发现 Cook-Austral 群岛中 Tubuai 岛 HIMU 型洋岛玄武岩携带正的 MIF-Hg 信号 ($\Delta^{199}\text{Hg} = +0.23\text{‰} \pm 0.07\text{‰}$; $\Delta^{201}\text{Hg} = +0.18\text{‰} \pm 0.1\text{‰}$), 而 Pitcairn EM1 型玄武岩表现为负的 MIF-Hg 信号 ($\Delta^{199}\text{Hg} = -0.45\text{‰} \pm 0.01\text{‰}$; $\Delta^{201}\text{Hg} = -0.38\text{‰} \pm 0.06\text{‰}$), 暗示 HIMU 和 EM1 型地幔源区再循环的沉积物分别具有海洋和陆源的印记. 总之, HIMU 型地幔由太古代再循环洋壳 (蚀变玄武岩 ± 碳酸盐) 直接熔融主导, 而 EM1 型地幔源区存在的是太古代再循环陆源含碳酸盐沉积物 (碳酸盐已分解, 未参与熔融), 二者在碳循环机制、路径和效应上存在本质差别.

不同于洋岛玄武岩 MIF-S 信号, Smit *et al.* (2019) 聚焦多个克拉通地区 (包括 Kaapvaal、Zimbabwe 和 West Africa 克拉通) 的幔源金刚石, 发现硫化物包裹体普遍含有正的 MIF-S 信号 ($\Delta^{33}\text{S}$ 变化范围为 $-0.5\text{‰} \sim +1.5\text{‰}$; 图 6), 指示其硫源可能源自太古代大气循环, 暗示金刚石形成与早期地表物质再循环相关联. 尽管洋岛玄武岩 (Mangaia 和 Pitcairn) 和地幔金刚石中硫化物的原位硫同位素分析为太古代地表物质循环进入深部地幔提供了可靠的时空框架, 但是笔者统计了多个典型地区的洋岛玄武岩 (如 Iceland、Canary、Samoa、Mangai、Pitcairn、St. Helena)、洋脊玄武岩和金伯利岩的全岩硫同位素数据, 未发现明显的硫同位素非质量分馏信号 (全岩 $\Delta^{33}\text{S}$ 趋近于 0‰ ; 图 6). 全岩样品普遍无显著 $\Delta^{33}\text{S}$ 异常, 表明 MIF-S 信号可能被全岩信息掩盖 (例如, Mangaia 玄武岩中硫化物的 MIF-S 信号不均匀, 大部分并未展示 MIF-S 信号或信号很弱), 又或者地幔主要化学储库 (包括 DMM、EM1、EM2、HIMU、FOZO) 可能未显著混入太古代循环地表物质, 被认为代表的是原始地幔 (Labidi *et al.*, 2013, 2015; Dottin III *et al.*, 2020b; Ranta *et al.*, 2022) 或后太古代循环地表物质 (Dottin III *et al.*, 2020a; Labidi *et al.*, 2022; Genot *et al.*, 2024) 的硫同位素

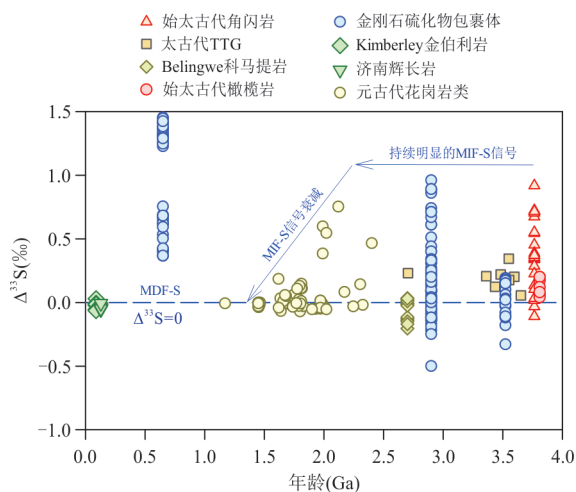


图7 金刚石中硫化物包裹体、橄榄岩和岩浆岩记录的 MIF-S($\Delta^{33}\text{S}$)信号随时间的演化

Fig. 7 MIF-S ($\Delta^{33}\text{S}$) signature of sulfide inclusions in diamonds, peridotites and magmatic rocks changed with time

数据来源:始太古代角闪岩(Caro *et al.*, 2025);始太古代橄榄岩(Lewis *et al.*, 2023);金刚石中硫化物包裹体(Farquhar *et al.*, 2002; Cartigny *et al.*, 2009; Thomassot *et al.*, 2009; Smit *et al.*, 2019);太古代 TTG(Caro *et al.*, 2025);元古代花岗岩类(LaFlamme *et al.*, 2018);Belingwe 科马提岩(Kubota *et al.*, 2022);Kimberley 金伯利岩(Fitzpayne *et al.*, 2021)

信号.以上研究显示,全岩硫同位素分析会不同程度地掩盖样品的 MIF-S 信号,可能会干扰对地球深部物质循环时限的界定.需要说明的是,地幔主要储库的化学不均一性并未能在大洋玄武岩全岩的 MIF-S 信号(全岩 $\Delta^{33}\text{S} \approx 0\text{‰}$;图 6)完全反映出来,可能是由长期的地幔对流或岩浆演化过程对 MIF-S 信号的均一化或缩小效应造成的,今后需加强地幔硫化物的原位多硫同位素分析.

6 MIF-S 对板块构造启动时限的约束

板块构造是地球区别于太阳系其他类地行星的独特标志,不仅塑造了地球的地表形态,还促进了地球宜居性的演变.然而,关于板块构造启动的时间,目前地质学界仍存在显著争议(Shirey and Richardson, 2011; Tang *et al.*, 2016; Smit *et al.*, 2019; Sobolev *et al.*, 2019; Lewis *et al.*, 2023; Caro *et al.*, 2025).前人研究认为,金刚石中硫化物包裹体的 $\Delta^{33}\text{S}$ 异常是揭示早期地球壳幔物质循环和板块构造启动时限的重要指标(Smit *et al.*, 2019).通过分析金刚石中硫化物包裹体的多硫同位素(图 7),Smit *et al.* (2019)发现形成于古太古代(~ 35 亿年前)的 Slave 克拉通金刚石不含 MIF-S 信号,反映以地幔原生岩浆持续增生为主导,缺乏显著地表物质再循环;相比之下,形成于中太古代至新元古代(29 $\sim$ 6.5 亿年前)的 Kaapvaal、津巴布韦和西非克拉通的金刚石含有 $\Delta^{33}\text{S}$ 异常,指示中太古代地表硫通过俯冲作用循环至深部地幔,从而将地球上板块构造启动的时间限制在约 30 亿年前(图 8).最近,Caro *et al.* (2025)和 Lewis *et al.* (2023)在北美始太古代(~ 38 亿年前)角闪岩和橄榄岩中也发现了 MIF-S 信号,进一步将金刚石包裹体约束的板块构造启动时间提前了约 10 亿年(图 7).同时,笔者也收集了 38 亿年之后出现的古太古代 TTG 岩系、新太古代科马提岩、古元古代花岗岩类和中生代金伯利岩/辉长岩的 $\Delta^{33}\text{S}$ 数据,观察到明显的 MIF-S 信号(图 7).这些 MIF-S 异常从始太古代开始稳定存在到古元古代,而在大氧化事件后开始持

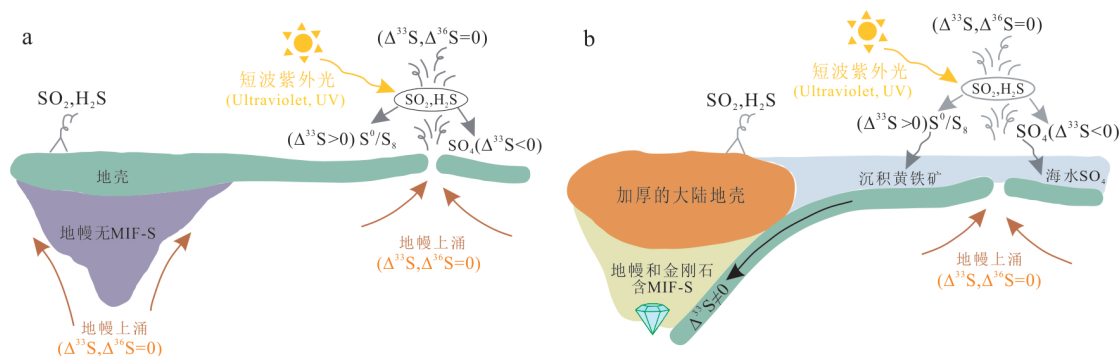


图8 太古代硫循环与板块构造启动的概念模型

Fig.8 Model of the Archean sulfur cycle and the onset of plate tectonics

a. 始太古代无板块构造,地表物质无法进入地球内部,对应的古老克拉通地幔没有 MIF-S 信号;b. 始太古代以来板块构造启动,地表物质随俯冲作用进入地球内部,在始太古代-古元古代地幔岩石和金刚石中显示 MIF-S 信号.修改自 Smit *et al.* (2019)

续衰减($\Delta^{33}\text{S}$ 趋近于 0; 图 7)。值得注意的是, 太古代-元古代岩石中 MIF-S 信号随时间演化的规律与大气氧气浓度、沉积物 MIF-S 信号和地幔氧逸度变化同步(图 4 和图 7), 这也为早期地球大气演化和板块构造启动提供了关键耦合证据(图 8)。考虑到地幔对流驱动的均一化效应, 软流圈可能因此未能有效保存 MIF-S 信号(仅限于局部硫化物); 相反, 克拉通岩石圈因其独特性质(如密度小、刚性强)未参与地幔对流均一化, 为 MIF-S 信号提供了地球最持久的天然储库。

7 总结与展望

硫同位素非质量分馏效应(MIF-S)普遍认为是由大气光化学反应主导, 能够很好地规避岩浆过程(如部分熔融、分离结晶、岩浆脱气等)导致的硫同位素质量分馏效应(MDF-S), 是揭示地幔不均一性和板块构造启动的重要指标。如何界定地球深部物质循环时限取决于硫同位素非质量分馏效应(MIF-S)的有效识别。考虑到岩浆硫化物脱气和混合对原始硫同位素信号的干扰, 有必要更多地利用硫同位素微区分析技术(NanoSIMS)加强对地幔主要化学储库属性的认识。

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