

应用Cu-Fe-Mg-Mo-Zn同位素示踪岩浆硫化物矿床的形成过程：原理、应用与展望

Matthew Jacek BRZOZOWSKI (马修)^{1*}, 刘晓凤¹, 肖菲¹, 王国一¹, 穆合塔尔·麦麦提尼亚孜², 吴昌志^{1,3*}

1. 西部矿产资源与地质工程教育部重点实验室, 长安大学地球科学与资源学院, 西安 710054

2. 中国科学院新疆生态与地理研究所, 新疆矿产资源研究中心, 乌鲁木齐 830011

3. 新疆自然资源与生态环境研究中心, 乌鲁木齐 830000

* 通讯作者, E-mail: mjbrzozo@chd.edu.cn (Matthew Jacek BRZOZOWSKI), wucz@chd.edu.cn (吴昌志)

2025-08-29收稿, 2025-12-05修回, 2025-12-22接受, 2026-05-21网络版发表

国家自然科学基金项目(U2444203)和长安大学中央高校基本科研业务费专项项目(300102274301)资助

摘要 半个世纪以来, 前人通过传统地球化学和同位素技术(如Sr-Nd-Hf-Os-S)对岩浆硫化物矿床的形成过程进行了较好的约束。然而, 目前关于世界级矿床的幔源组成特征及其形成机制, 尤其是地幔交代作用在富金属熔体形成过程中的关键控制因素方面仍存在一些重要科学问题亟待解决。值得关注的是, Cu-Fe-Mg-Mo-Zn等非传统金属稳定同位素体系的应用, 为解决上述关键科学问题提供了新的研究途径。这类同位素体系具有以下显著优势: (1)不受地质时代制约; (2)对部分熔融和分离结晶作用表现出较强的抗干扰性; (3)兼具亲石元素、亲铁元素和亲铜元素的同位素地球化学行为特征; (4)在不同端元储库(包括大陆地壳、蚀变洋壳及俯冲带流体等)中呈现显著的分馏特征差异。迄今为止, Cu、Fe及Mg同位素体系已被成功应用于岩浆硫化物矿床成因研究, 其中Mg同位素的应用相对有限。这些同位素体系为解决以下关键科学问题提供了重要约束: (1)成矿母岩浆地幔源区的交代改造过程(Cu-Fe-Mg); (2)成矿金属的物质来源(Cu); (3)金属元素的富集机制(Cu-Fe); (4)成矿系统的氧化还原状态(Cu-Fe); (5)硫化物熔体的演化过程(Fe)。尽管Mo和Zn同位素尚未直接应用于该类矿床研究, 但其在示踪地幔交代作用及鉴别交代介质类型(如俯冲带流体、碳酸盐熔体、榴辉岩组分)方面已展现出独特优势。因此, Mo-Zn同位素的引入有望深化对多类型地幔交代作用在全球典型岩浆硫化物矿床形成过程中贡献程度的认识。

关键词 岩浆硫化物矿床, 金属稳定同位素, 同位素分馏, 成矿过程

1 引言

岩浆硫化物矿床是全球铂族元素(PGE)和镍(Ni)的主要来源(Mudd和Jowitt, 2014; Mudd等, 2018)。虽然钴(Co)资源主要来源于沉积岩赋矿层控型Cu-Co矿床(~63%)和红土型Ni-Co矿床(~20%), 但岩浆硫化物矿床也是其重要来源(~14%)(Mudd等, 2013; Petavratzi等, 2019)。鉴于全球PGE、Ni和Co资源的供应主要集中于三个国家——南非(Bushveld杂岩体中的岩浆硫化物矿床)、

俄罗斯(Norilsk的Talnakh铜镍硫化物矿床)和刚果民主共和国(例如Tenke Fungurume的沉积岩型赋钴矿床), 这些资源在其他地区被认为存在供应中断和/或短缺的风险(Mudd等, 2013, 2018; Mudd和Jowitt, 2014; Petavratzi等, 2019)。此外, 由于这些元素在低碳技术、国防、能源、航空航天和电子工业中具有重要价值, 使得包括中国、加拿大以及欧洲等国家和地区将其列为“关键矿产”(Humphreys, 2014; Reich和Simon, 2024)。由此可见, 发现更多的Ni-Cu-Co-PGE资源对于支持低碳经济的

中文引用格式: Brzowski M J, 刘晓凤, 肖菲, 王国一, 穆合塔尔·麦麦提尼亚孜, 吴昌志. 2026. 应用Cu-Fe-Mg-Mo-Zn同位素示踪岩浆硫化物矿床的形成过程：原理、应用与展望. 中国科学：地球科学, 56(6): 2003–2024, doi: [10.1360/SSTe-2025-0267](https://doi.org/10.1360/SSTe-2025-0267)

英文引用格式: Brzowski M J, Liu X, Xiao F, Wang G, Muhtar M N, Wu C. 2026. Using Cu-Fe-Mg-Mo-Zn isotopes to trace the formation of magmatic sulfide deposits: Principles, applications, and future directions. Science China Earth Sciences, 69(6): 1961–1979, <https://doi.org/10.1007/s11430-025-1811-2>

持续转型至关重要,且有助于减少人类发展对全球气候造成的负面影响。

目前已发现的岩浆硫化物矿床主要形成于与地幔柱相关的岩浆系统,且在时空上多与大火成岩省(LIPs)(如西伯利亚、大峨眉山和Keweenaw等)密切相关(Campbell和Griffiths, 1990; Campbell, 2005; Campbell和Kerr, 2007; Ernst和Jowitt, 2013),例如: Norilsk的Talnakh铜镍硫化物矿床(Lightfoot等, 1993; Naldrett和Lightfoot, 1999), 金川铜镍硫化物矿床(Chai和Naldrett, 1992a, 1992b; Mao等, 2019), Bushveld杂岩体中的Ni-Cu-PGE硫化物矿床(Von Gruenewaldt等, 1985; Cawthorn, 1999)和Stillwater硫化物矿床(Lambert等, 1994; Horan等, 2001; Jenkins等, 2021), 以及Midcontinent Rift中的硫化物矿床(Bleeker等, 2020; Woodruff等, 2020)(图1)。然而,越来越多的证据表明,岩浆硫化物矿床并不局限于克拉通内部环境,许多具有重要经济价值的岩浆硫化物矿床发现于造山带环境中。典型实例包括: 中亚造山带(包括黄山东矿床、喀拉通克矿床、图拉尔根矿床; Zhou等, 2004; Han等, 2007; Li等, 2012; Gao和Zhou, 2013; Wang等, 2022)、中国的夏日哈木矿床(Li等, 2015; He等, 2022)、西班牙的Aguablanca矿床(Casquet等, 2001; Piña等, 2010)、不列颠哥伦比亚省的Giant Mascot矿床(Manor等, 2016)和Turnagain矿床(Jackson-Brown, 2017)、加拿大的E&L矿床(Brzoowski和Zaborniak, 2024)以及芬兰的Vammala矿床(Peltonen, 1995)(图1)。尽管形成这些矿床的构造背景不同,但其成矿均涉及以下4个关键过程: (1)地幔部分熔融形成富金属岩浆; (2)岩浆达到硫化物熔体饱和; (3)硫化物熔体通过与富金属岩浆相互作用富集金属元素(即R因子; Campbell和Naldrett, 1979); (4)硫化物熔体富集成矿发生在有限的空间内(Naldrett, 2010)。

过去半个世纪以来,岩浆硫化物矿床的特征和形成过程主要通过全岩和矿物化学分析、Sr-Nd-Pb-Os放射性同位素以及S稳定同位素来表征。全岩地球化学和放射性同位素为理解地幔来源岩浆的源区特征、地壳混染以及结晶分异-堆晶作用过程提供了重要研究手段(Shirey等, 1994; Lambert等, 1994; Shirey, 1997; Hollings等, 2007b, 2007a; Ding等, 2012; Lu等, 2019及其参考文献; Barnes等, 2021; Rooney等, 2022; Brzoowski等, 2023b, 2024)。岩浆补给对岩浆硫化物成矿系统的重要性已通过矿物结构及其化学成分的详细研究得到证实(包括斜长石(Shahabi Far等, 2019)、辉石(Shahabi Far等, 2019; Schoneveld等, 2025)和氧化物(Brzoowski等, 2021c))。硫化物和全岩中金属含量的变化可以用于表征

硫化物熔体和硅酸盐熔体相互作用的程度,以及这一相互作用对高品位矿化发展的重要性(例如, Naldrett等, 2000, 2009; Piña等, 2008, 2012, 2016; Dare等, 2014; Duran等, 2015, 2016; Barnes和Ripley, 2016及其参考文献; Good等, 2017; Lu等, 2019及其参考文献; Brzoowski等, 2020, 2023a; Cao等, 2021)。硫化物化学成分和S同位素对于深入理解岩浆如何达到硫化物饱和起到了关键作用(Penniston-Dorland等, 2008, 2012; Bekker等, 2009, 2016; Hanski等, 2011; Ding等, 2012; Konnunaho等, 2013; Hofmann等, 2014; Donoghue等, 2014; Sharman等, 2015; Duan等, 2016; Hiebert等, 2016; Shahabi Far等, 2018; Lu等, 2019及其参考文献; Benson等, 2020; Brzoowski等, 2023a, 2025)。我们之所以依赖于上述同位素地球化学体系,部分是源于对它们的地球化学行为有比较深刻的理解,也与早期分析技术限制了我们对其他同位素的准确测定有关。然而,随着多接收器电感耦合等离子体质谱(MC-ICP-MS)技术的持续进步,人们已能够以优于 $\pm 0.1\%$ ($\delta^{26}\text{Mg}$ 、 $\delta^{56}\text{Fe}$ 、 $\delta^{65}\text{Cu}$ 、 $\delta^{66}\text{Zn}$ 和 $\delta^{98}\text{Mo}$)的精度测定 $^{26/24}\text{Mg}$ 、 $^{56/54}\text{Fe}$ 、 $^{65/63}\text{Cu}$ 、 $^{66/64}\text{Zn}$ 和 $^{98/95}\text{Mo}$ 等同位素比值(Albarède, 2004; Albarède和Beard, 2004; Willbold等, 2016; Dauphas等, 2017; Moynier等, 2017; Teng, 2017; Johnson等, 2020)。因此,这些稳定金属同位素体系可作为不受时间约束的岩石成因示踪剂,用于揭示不同矿化程度的镁铁质-超镁铁质岩石的地幔源区特征和岩浆硫化物矿床的形成过程。

2 铜铁镁锌钼(Cu-Fe-Mg-Zn-Mo)同位素的高温行为

在应用金属同位素示踪岩浆硫化物矿床形成过程之前,必须明确这些同位素在岩浆作用过程中的分馏行为,以便有效识别与成矿作用相关的同位素变化。为此,下文将简要综述铜铁镁锌钼(Cu-Fe-Mg-Zn-Mo)同位素在地幔部分熔融、岩浆结晶分异以及地幔交代作用过程中的地球化学行为。

2.1 铜(Cu)同位素

基于未受交代作用的橄榄岩、洋中脊玄武岩(MORB)及洋岛玄武岩(OIB)的铜同位素组成, Liu等(2015)估算出全硅酸盐地球(BSE)的铜同位素($\delta^{65}\text{Cu}$)组成为 $0.06\text{‰} \pm 0.20\text{‰}$ 。在陆壳岩浆体系中,铜以+1和+2价态存在,在 $\Delta\text{FMQ} < 1.2$ 时以 Cu^{+1} 形式为主,在 $\Delta\text{FMQ} > 1.2$ 时以 Cu^{+2} 形式为主(Liu等, 2014)。因此,与氧化还原相关的过程中可能导致铜同位素的显著分馏。俯冲带环境

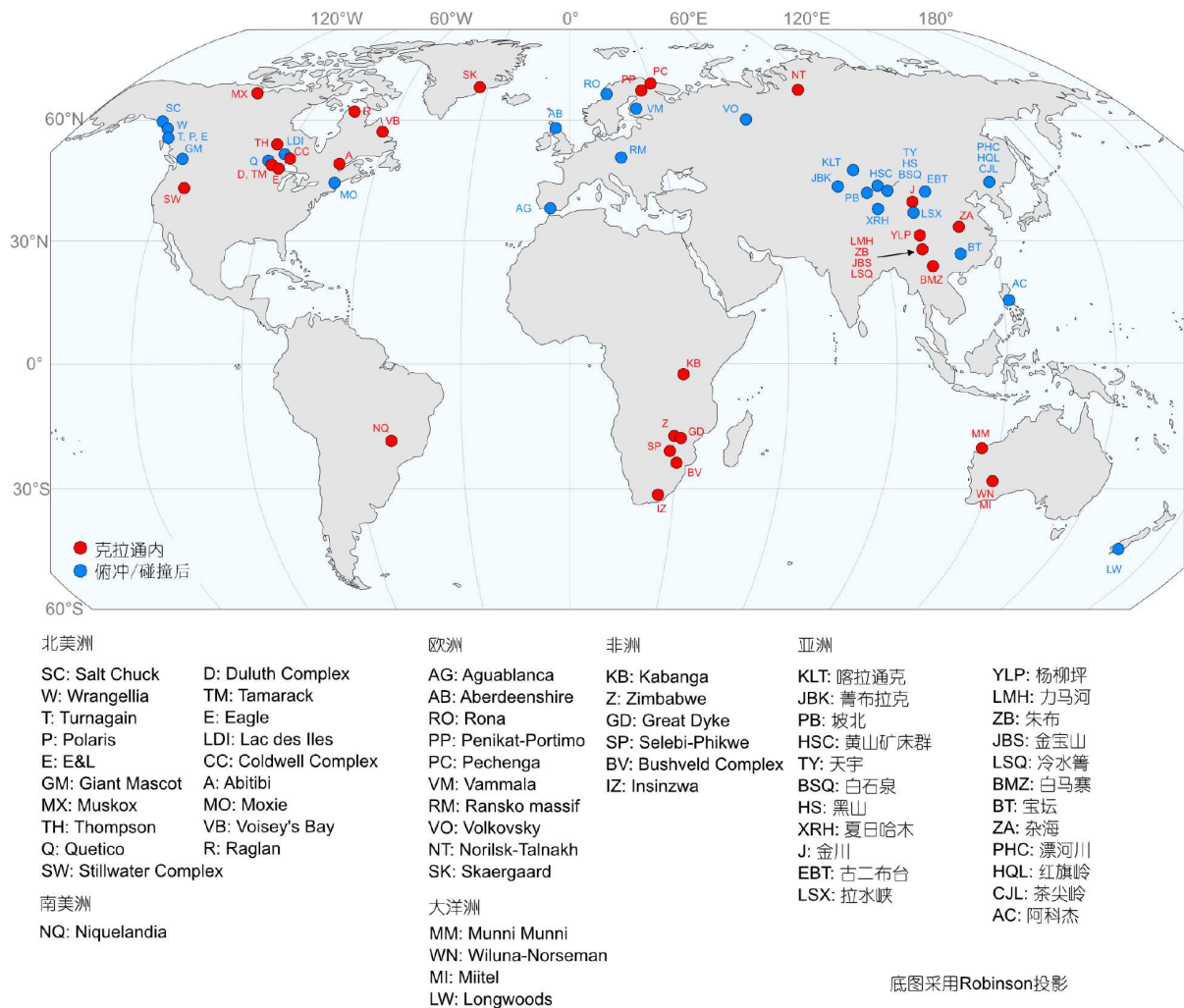


图1 全球典型克拉通内与俯冲带/碰撞后Ni-Cu-PGE矿床分布图, 据Naldrett(2011)修改

以较高的氧逸度为特征(平均 ΔFMQ 为1), 而板内环境则具有显著较低的氧逸度(平均 ΔFMQ 为0.1)(Cottrell等, 2021)。因此, 地幔部分熔融过程中氧化还原条件的变化只可能影响俯冲带岩浆的Cu同位素组成, 而板内岩浆的铜同位素基本不受此类过程影响(Huang等, 2017; Sun等, 2023)。鉴于地幔中大部分铜主要赋存于硫化物相(Hughes等, 2017; Kiseeva等, 2017), 且硫化物优先富集 ^{63}Cu ($\Delta^{65}\text{Cu}_{\text{sul-sil}}$ 为-0.2‰左右; Savage等, 2015; Xia等, 2019), 因而在地幔熔融过程, 主导铜同位素行为的关键物相是硫化物相, 而非硅酸盐或氧化物相。因此可见, 当熔融体系不存在硫化物相时, 部分熔融作用不会导致显著的铜同位素分馏, 这与对地幔橄榄岩、MORB和OIB铜同位素组成的观测结果相吻合(Liu等, 2015)。这一机制也被Huang等(2017)用以解释Balmuccia和Baldissero地块中 $\delta^{65}\text{Cu}$ 值的部分变化: 较重的 $\delta^{65}\text{Cu}$ 值(高达0.379‰)反映了含硫化物地幔源区的部分熔融, 而较轻的

$\delta^{65}\text{Cu}$ 值(低至-0.133‰)反映了熔体-橄榄岩相互作用过程中硫化物的沉淀。鉴于硅酸盐、氧化物和磷酸盐的Cu含量较低, 硫化物相同样是控制岩浆结晶过程中铜含量及铜同位素变化的主导相。Huang等(2016)对Laacher See火山灰的研究首次证实了这一现象: 该区不同演化程度的响岩具有相对均一的 $\delta^{65}\text{Cu}$ 值, 而代表它们母岩浆组成的碧玄岩中较轻的铜同位素组成被认为是硫化物熔体的分异作用所导致的。Sun等(2023)和Zou等(2024)对MORB及其伴生辉长质堆晶岩的研究也得出了相似结论。这些研究均证实, 在橄榄石、单斜辉石和斜长石作为液相线矿物的硫化物不饱和岩浆演化过程中, 不存在可检测的铜同位素分馏。然而, 一旦硫化物熔体形成(例如由钛铁氧化物结晶相关的氧化还原变化引发), ^{63}Cu 优先进入硫化物相的特性便会使体系因硫化物分离和聚集而产生显著的铜同位素变化。尽管铜同位素分馏与分离结晶作用无直接关联, 但Zhang W Q等(2024)的研究表明, 堆晶间

隙熔体与硫化物熔体之间的相互作用(如硫化物的溶解、迁移和再沉淀)可在堆晶岩中产生显著的铜同位素变化。上述研究的核心结论在于:只有当硫化物熔体参与时,结晶分异作用才会显著影响熔体的铜同位素组成。与部分熔融和结晶分异作用不同,地幔源区经历的交代作用可导致显著的铜同位素分馏。[Liu等\(2015\)](#)的研究证实,受交代橄榄岩的 $\delta^{65}\text{Cu}$ 值变化范围可达 -0.64‰ – 1.82‰ 。交代地幔的铜同位素变化可能源自多种地质过程,包括地幔硫化物氧化还原条件相关的溶解-再沉淀作用和地幔中次生硅酸盐矿物的形成过程([Liu等, 2015](#));板片流体中以氯络合物形式迁移的富集重铜同位素过程([Kendrick等, 2020](#); [Kempton等, 2022](#); [Chen Z等, 2022](#));熔体-橄榄岩反应过程中轻铜同位素硫化物的沉淀或掺入过程([Huang等, 2017](#); [Zou等, 2019](#))。

2.2 铁(Fe)同位素

当前学术界普遍认为,地幔由具有球粒陨石特征的铁同位素($\delta^{56}\text{Fe}$)组成,平均值为 $-0.005\text{‰}\pm 0.006\text{‰}$ ([Dauphas等, 2017](#))。铁是一种氧化还原敏感元素,在自然界中以自然铁(Fe^0)、 Fe^{2+} 和 Fe^{3+} 的形式存在,因此对影响体系氧化还原状态的地质过程(例如分离结晶和地幔交代)较为敏感([Johnson等, 2020](#))。与镁同位素不同的是,岩浆体系的铁同位素组成同时受部分熔融程度和分离结晶程度的双重控制。大量研究已充分证实:由于玄武岩的铁同位素组成系统地重于橄榄岩,因此部分熔融所产生的熔体具有相对于残留相更重的铁同位素组成([Williams等, 2005](#); [Weyer等, 2005](#); [Weyer和Ionov, 2007](#); [Teng等, 2013b](#); [Sossi等, 2016](#); [Johnson等, 2020](#)及其参考文献)。[Dauphas等\(2009\)](#)通过建立首个数值模型定量验证了这一结论,该模型成功模拟了不同部分熔融程度、 $\text{Fe}^{3+}/\text{Fe}^{2+}$ 比值和地幔缓冲能力条件下的铁同位素分馏行为。在结晶分异作用方面,通过Kilauea Iki熔岩流、Hekla火山喷发产物和Red Hill侵入体的研究证明,熔体的铁同位素组成与分异程度呈显著正相关([Teng等, 2008](#); [Schuessler等, 2009](#); [Sossi等, 2012](#))。这种系统性变化应是含 Fe^{2+} 的硅酸盐(即橄榄石和辉石)的分离结晶导致演化熔体中 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 比值持续升高的结果([Weyer, 2008](#); [Sossi等, 2012](#))。由于部分熔融和分离结晶作用对幔源岩浆铁同位素组成的显著影响,地幔交代作用对铁同位素组成的改造往往更难识别。研究表明,无论是硅酸盐熔体还是碳酸盐熔体交代作用,均可产生既低于又高于典型幔源岩石的 $\delta^{56}\text{Fe}$ 值([Beard和Johnson, 2004](#); [Poitrasson等, 2004](#); [Weyer和Ionov, 2007](#); [Weyer, 2008](#); [Zhao等, 2010, 2012](#); [Debret等, 2016, 2018, 2021](#))。就硅

酸盐熔体交代而言,较重的 $\delta^{56}\text{Fe}$ 值被认为是二辉橄榄岩地幔与硅不饱和但富钙铁熔体反应的结果,从而导致斜方辉石被单斜辉石替代,而较轻的 $\delta^{56}\text{Fe}$ 值则源于渗流熔体与地幔围岩之间 ^{54}Fe 的同位素交换([Weyer和Ionov, 2007](#); [Huang等, 2011](#); [Zhao等, 2012](#))。除上述岩浆过程外,幔源岩石的铁同位素组成还可能受到地壳岩石同化混染的影响——地壳岩石通常具有显著偏重且高度不均一的 $\delta^{56}\text{Fe}$ 值,最高可达约 0.6‰ ([Poitrasson和Freydier, 2005](#); [Schoenberg和Blanckenburg, 2006](#); [Heimann等, 2008](#); [Schuessler等, 2009](#); [Sossi等, 2012](#); [Telus等, 2012](#); [Zambardi等, 2014](#); [Foden等, 2015](#); [Du等, 2017](#); [He等, 2017](#); [Xu等, 2017](#); [Xia等, 2017](#))。

2.3 镁(Mg)同位素

根据MORB、OIB、橄榄岩捕虏体以及碳质、普通辉石和顽火辉石球粒陨石的镁同位素组成,[Teng等\(2010\)](#)推测地幔的镁同位素组成相对稳定,并估算其 $\delta^{26}\text{Mg}$ 值为 $-0.25\text{‰}\pm 0.07\text{‰}$ 。鉴于OIB和橄榄岩的镁同位素组成缺乏显著变化,该研究同时证实镁同位素对地幔部分熔融程度的变化基本不敏感。唯一例外是,当石榴子石作为残留相存在时,由于石榴子石优先富集 ^{24}Mg ,此环境下部分熔融所产生的熔体可能比典型地幔具有更重的镁同位素组成([Teng等, 2010](#); [Liu等, 2011](#); [Wang S J等, 2012, 2015b, 2016](#))。尽管钛铁氧化物具有镁同位素显著偏重的特性($\delta^{26}\text{Mg}$ 最高达 2.94‰),辉石呈镁同位素偏轻的特征(最低至 -0.49‰),橄榄石保持类似地幔的镁同位素组成([Chen等, 2018, 2021](#); [Tian等, 2020](#); [Ding等, 2021](#)),但[Teng等\(2007\)](#)基于Kilauea Iki火山不同演化程度的玄武岩(MgO 含量为 $2.37\text{--}26.87\text{ wt.}\%$)样品的 $\delta^{26}\text{Mg}$ 值无明显差异,证实了岩浆演化过程中镁同位素并不发生显著分馏。这种对部分熔融和结晶分异的不敏感性,在一定程度上与镁在岩浆体系中仅以单一价态存在而导致其同位素组成不受氧化还原过程的影响有关。除地壳物质混染(通常重于地幔镁同位素组成;[Shen等, 2009](#); [Liu等, 2010](#); [Li等, 2010, 2014](#); [Huang等, 2013](#); [Teng等, 2013a](#); [Wimpenny等, 2014](#); [Wang等, 2015a, 2015b](#); [Yang等, 2016](#))外,扰动幔源岩浆镁同位素组成的主要过程为地幔交代。该过程引发的同位素变化方向取决交代介质类型。硅酸盐熔体交代可产生轻于或重于典型地幔的 $\delta^{26}\text{Mg}$ 值变化([Yang等, 2009](#); [Huang等, 2011](#); [Pogge von Strandmann等, 2011](#); [Xiao等, 2013](#); [Hu等, 2015](#); [Lai等, 2015](#); [Su等, 2015](#); [Yu等, 2021](#)),碳酸盐熔体交代通常形成轻于典型地幔的 $\delta^{26}\text{Mg}$ 值([Yang等, 2012](#); [Hu等, 2015](#); [Huang等, 2015](#); [Wang](#)

Z Z等, 2016; Sun等, 2021; Yu等, 2021), 而板片流体交代可产生重于典型地幔的 $\delta^{26}\text{Mg}$ 值(Pogge von Strandmann等, 2011; Li等, 2018; Brzozowski等, 2022)。

2.4 锌(Zn)同位素

地幔捕虏体与造山带地块($\delta^{66}\text{Zn}=-0.06\text{‰}-0.42\text{‰}$)、地幔柱($0\text{‰}-0.63\text{‰}$)、洋中脊($0.21\text{‰}-0.44\text{‰}$)及岛弧($0.03\text{‰}-0.38\text{‰}$)等不同构造背景环境下的超镁铁质-长英质幔源岩类以及花岗质岩类($0.15\text{‰}-0.88\text{‰}$)的锌同位素组成已得到很好地限定, 且BSE与大陆地壳具有相近的平均 $\delta^{66}\text{Zn}$ 值(分别为 $0.2\text{‰}\pm 0.05\text{‰}$ 和 $0.23\text{‰}\pm 0.07\text{‰}$; Sossi等, 2018; Pickard等, 2022)。锌在陆壳环境中仅以+2价存在, 因此不涉及氧化还原相关的同位素分馏。同样, 基于Hekla和Kilauea Iki火山熔岩的研究, Chen等(2013)证实岩浆结晶分异过程中的锌同位素分馏效应微弱(变化 $<0.1\text{‰}$)。然而, 幔源岩浆的锌同位素组成受地幔部分熔融程度(取决于熔融深度, 即压力条件)和源区矿物组成(如尖晶石或石榴子石稳定域)(Chen等, 2013)的影响。总体而言, 部分熔融产生的熔体相较于残留相具有更轻的锌同位素组成(最大可达 0.4‰)。其中以尖晶石稳定域所发生熔融过程的同位素分馏程度最为显著(Doucet等, 2016; Wang等, 2017; Day等, 2022)。据此, 可得出以下两个重要认识: (1)上地幔存在锌同位素组成的非均质性; (2)幔源岩石中观测到的锌同位素变化主要与不同富集或难熔程度的地幔源区不同程度的部分熔融作用有关(Wang等, 2017; Day等, 2022)。关于地幔源区交代作用(即源区成分变化)导致岩浆锌同位素组成变化的研究, 目前主要集中于俯冲带环境或经俯冲改造的地幔源区。尽管具体的效应和程度存在差异, 但前人已识别出三种能显著影响俯冲改造地幔及其部分熔融产物锌同位素组成的关键过程: (1)含碳物质的加入导致 $\delta^{66}\text{Zn}$ 值升高(Liu等, 2016, 2020; Beunon等, 2020; Qu等, 2022; Shu等, 2022); (2)硅质碎屑物质的混入引起 $\delta^{66}\text{Zn}$ 值降低(Liu等, 2020); (3)来自俯冲板片流体的交代通常使 $\delta^{66}\text{Zn}$ 值系统性偏重(Pons等, 2016; Debret等, 2018, 2021)。此外, 岩浆中含锌的挥发分逸失也会改变岩浆锌同位素组成, 导致残余岩浆呈现出显著偏重的 $\delta^{66}\text{Zn}$ 值, 但该过程可能仅局限于陆上喷发环境(John等, 2008; Toutain等, 2008; Chen等, 2013)。

2.5 钼(Mo)同位素

BSE和MORB的钼同位素组成($\delta^{98/95}\text{Mo}$)已被精确限定为 $-0.15\text{‰}\pm 0.01\text{‰}$ 和 $-0.22\text{‰}\pm 0.03\text{‰}$ (95%置信度)(Hin等, 2022)。尽管对上陆壳的钼同位素组成的研究程度低

于幔源岩石, 但其 $\delta^{98/95}\text{Mo}$ 值显著偏重(约为 0.15‰), 且大陆地壳平均值介于 $0.1\text{‰}-0.35\text{‰}$ 之间(Willbold和Elliott, 2017及其参考文献)。地幔与地壳的钼同位素组成的显著差异表明, 地壳物质同化混染可导致幔源熔体 $\delta^{98/95}\text{Mo}$ 值显著升高。作为典型的氧化-还原敏感和流体活动性的过渡族元素, 钼在自然界可表现为亲铜性、亲铁性或亲石性特征(Richter等, 2010; Barnes, 2018)。然而, 在岩浆体系中, 钼主要呈亲石性, 其地球化学行为与稀土元素相似(即不相容性)(Greaney等, 2017)。虽然钼具有氧化还原敏感元素特征(在陆壳环境中主要以 Mo^{2+} 和 Mo^{6+} 价态存在), 但在硅酸盐熔体中钼主要以四面体配位的 Mo^{6+} 形式存在(Candela和Holland, 1984; Holzheid等, 1994; O' Neill和Eggins, 2002; Farges等, 2006)。上述结果表明, 与近地表条件下观察到的显著钼同位素分馏现象(Kendall等, 2017及其参考文献)不同, 钼的氧化还原状态变化在高温岩浆体系中不太可能导致显著的钼同位素分馏。类似地, 虽然已有研究证实, 从高度演化的硅酸盐岩浆中含水矿物相(如角闪石、黑云母)的分离结晶会导致钼同位素向更重的组成方向分馏(Voegelin等, 2014; Yang等, 2017; Wille等, 2018; Fan等, 2022), 但镁铁质-超镁铁质岩浆的钼同位素组成对分离结晶作用基本不敏感(Yang等, 2015; Chen S等, 2022; Rojas-Kolomiets等, 2023)。部分熔融对熔体中钼同位素组成的影响取决于源区的氧逸度。在还原环境中, 大于90%的钼以 Mo^{6+} 形式存在, 仅在低程度部分熔融时($<10\%$)才可能使熔体的 $\delta^{98/95}\text{Mo}$ 值与源区发生分馏(最大可偏重 1‰)(McCoy-West等, 2019)。然而随着熔融程度升高, 这种分馏效应显著减弱, 熔体的 $\delta^{98/95}\text{Mo}$ 值通常与源区组成相差不超过 0.07‰ (McCoy-West等, 2019)。与上述过程不同, 地幔中与俯冲作用/交代作用相关的过程对幔源岩石钼同位素组成的变化具有重要控制作用, 并可根据交代介质的不同, 产生从重于到轻于BSE值的一系列同位素组成变化(Freymuth等, 2015; König等, 2016; Gaschnig等, 2017; Villalobos-Orchard等, 2020; Ahmad等, 2021; Li等, 2021; Chen S等, 2022; Chen C等, 2025; Yu等, 2022; Fang等, 2022, Fang等, 2023; Hin等, 2022; Rojas-Kolomiets等, 2023; Willbold和Messling, 2023; Marfin等, 2024)。上述过程引起的钼同位素组成变化可依据交代介质类型分为四类: 低程度部分熔融所形成的熔体、俯冲板片流体、俯冲板片镁铁质地壳以及板片沉积物。鉴于低程度部分熔融($<10\%$)所产生熔体的钼同位素组成较源区偏重(McCoy-West等, 2019), 此类熔体在地幔中的渗透作用会提升源区的 $\delta^{98/95}\text{Mo}$ 值。大量研究证实, 大洋板片脱水作用产生的流体优先迁移重钼同位素

(^{98}Mo)，因此向地幔源区加入此类流体会导致其 $\delta^{98/95}\text{Mo}$ 值高于典型地幔值。由于脱水作用优先活化 ^{98}Mo ，残留板片将继承较轻的 $\delta^{98/95}\text{Mo}$ 值，因而脱水板片熔体可使地幔源区获得较典型地幔更轻的钼同位素组成。类似地，榴辉岩组分的加入同样会导致地幔源区钼同位素组成偏轻。最后，洋壳沉积物及蚀变洋壳(AOC)通常以轻钼同位素组成(低 $\delta^{98/95}\text{Mo}$ 值)为特征(也有少数例外; Gaschnig等, 2017; Yu等, 2022)，因此这些沉积物或AOC熔融产物的加入会导致地幔源区的钼同位素组成相对于典型地幔偏轻。尽管与俯冲作用相关的钼同位素变化在俯冲带最为显著，但在受古俯冲事件影响的其他构造背景中亦被识别，如西伯利亚大火成岩省(Marfin等, 2024)和大洋中脊(Hin等, 2022; Chen Z等, 2025)，这凸显了钼同位素作为俯冲/交代作用示踪剂的高灵敏度特性。

3 铜铁镁(Cu-Fe-Mg)同位素与岩浆硫化物矿床成因

基于上述讨论可知，Cu、Fe、Mg、Zn和Mo等同位素体系在地幔与地壳尺度地球化学过程中的行为已得到相对较为系统的约束，它们为理解这些过程提供了互补的视角。然而，这些同位素体系在岩浆硫化物矿床成因研究中的应用仍较为有限，其中Cu、Fe和Mg同位素的应用相对较多，而Mo和Zn同位素则尚未得到充分重视。鉴于Cu、Fe、Mg、Zn和Mo兼具变化的亲石性(Mg、Mo、Zn)、亲铜性(Cu、Fe)及亲铁性(Cu、Fe、Zn)特征，它们在地幔交代、岩浆结晶分异等过程中表现出不同的地球化学行为，以及在幔源与壳源岩石中呈现出显著的组成差异，因此这些同位素体系在揭示岩浆硫化物矿床成因方面具有重要的潜力。具体而言，它们可用于评估以下关键问题：板内与俯冲带环境中矿床形成过程中地幔尺度作用的差异、地幔交代对富金属岩浆形成的影响、不同类型交代过程对金属富集的贡献，以及地壳混染和氧化还原条件在硫化物熔体形成中的作用。阐明上述问题对于理解和深化岩浆硫化物矿床的成矿机制至关重要，既涉及初始富金属岩浆的生成——此为成矿过程中最关键且最具挑战性的环节，也包括后续的成矿作用过程。因此，下文将分为两部分展开论述：第一部分系统评述Cu、Fe和Mg同位素在全球典型岩浆硫化物矿床成因中的应用进展；第二部分探讨Mo和Zn同位素在该类成矿系统中作为成因示踪工具的潜在价值和应用前景。

3.1 岩浆型硫化物矿床的Cu-Fe-Mg同位素组成特征

岩浆型硫化物矿床的铜同位素变化范围($\delta^{65}\text{Cu}=-2.3\text{‰}-1.84\text{‰}$)远超过未受交代地幔($\delta^{65}\text{Cu}=0.06\pm 0.20\text{‰}$;

Liu等, 2015)和交代地幔($\delta^{65}\text{Cu}=-0.64\text{‰}-1.82\text{‰}$; Liu等, 2015)的组成范围(图2A)。同时，岩浆型硫化物矿床 $\delta^{65}\text{Cu}$ 值的变化范围远大于硫化物熔体与硅酸盐熔体之间通过平衡同位素分馏所能产生的范围(详见第3.2节“同位素分馏因子”部分)。正因如此，必定存在某些机制显著影响岩浆型硫化物矿床形成过程中铜同位素的分馏，如地壳混染作用(详见第3.3节“同化混染与金属富集”部分)以及与氧化还原相关的过程(详见第3.5节“氧化还原过程”部分)。同样地，岩浆型硫化物矿床中 $\delta^{56}\text{Fe}$ 值的变化范围($-2.06\text{‰}-2.53\text{‰}$)也远大于地幔平均铁同位素值($-0.005\pm 0.006\text{‰}$; Dauphas等, 2017)(图2B)。然而，与铜主要赋存于黄铜矿中不同，铁在多种硫化物中均具有较高的含量。这意味着由于不同硫化物中Fe化学键的差异(详见第3.4节“硫化物熔体的演化”部分)(Schauble, 2004)，这些含铁硫化物的结晶过程可能会导致铁同位素的分馏。这至少可以在一定程度上解释为什么磁黄铁矿($\delta^{56}\text{Fe}=-2.06\text{‰}-1.68\text{‰}$)、镍黄铁矿($\delta^{56}\text{Fe}=-1.73\text{‰}-2.53\text{‰}$)和黄铜矿($\delta^{56}\text{Fe}=-0.65\text{‰}-2.35\text{‰}$)同位素组成的显著变化，且磁黄铁矿的铁同位素组成总是系统性地轻于共生的黄铜矿和镍黄铁矿(图2B)。需要指出的是，对于铜同位素或者铁同位素，这种显著变化并不局限于某个特定的构造背景，无论是在克拉通内(例如Coldwell杂岩体、Duluth杂岩体、Norilsk-Talnakh、金川)还是造山带(例如黄山、喀拉通克、图拉尔根)的矿床，均表现出显著的矿床内部同位素分馏(图2A和2B)。相较于铜和铁同位素，岩浆型硫化物矿床的镁同位素组成的研究相对较少，目前仅在金川、夏日哈木矿床及Coldwell杂岩体中获得了相关数据。尽管许多全岩样品和单矿物的 $\delta^{26}\text{Mg}$ 值与地幔值难以区分，但未受混染样品($\delta^{26}\text{Mg}=-0.49\text{‰}-0.05\text{‰}$)和受混染样品($\delta^{26}\text{Mg}=-1.69\text{‰}-0.92\text{‰}$)的 $\delta^{26}\text{Mg}$ 值变化范围均超出了地幔平均值($-0.25\text{‰}\pm 0.07\text{‰}$; Teng等, 2010)(图2C)。考虑到镁同位素在地幔部分熔融或分离结晶作用过程中不会发生显著分馏，且硫化物的熔离作用对镁同位素的影响也较小(详见第2.3节“镁同位素”部分)，由此推测，混染作用(详见第3.3节“同化混染与金属富集”部分)或地幔交代作用(详见第3.6节“源区组成与地幔交代作用”部分)，以及母岩浆演化过程会改变镁同位素组成。在下文中，我们将解释岩浆型硫化物矿床体系中同位素值变化的相关机制。

3.2 同位素分馏因子

与在演化过程中硅酸盐熔体和硅酸盐矿物共存的硫不饱和岩浆不同，形成岩浆型硫化物矿床的母岩浆在演化过程中还与硫化物熔体共存。正是这种硫化物熔体不

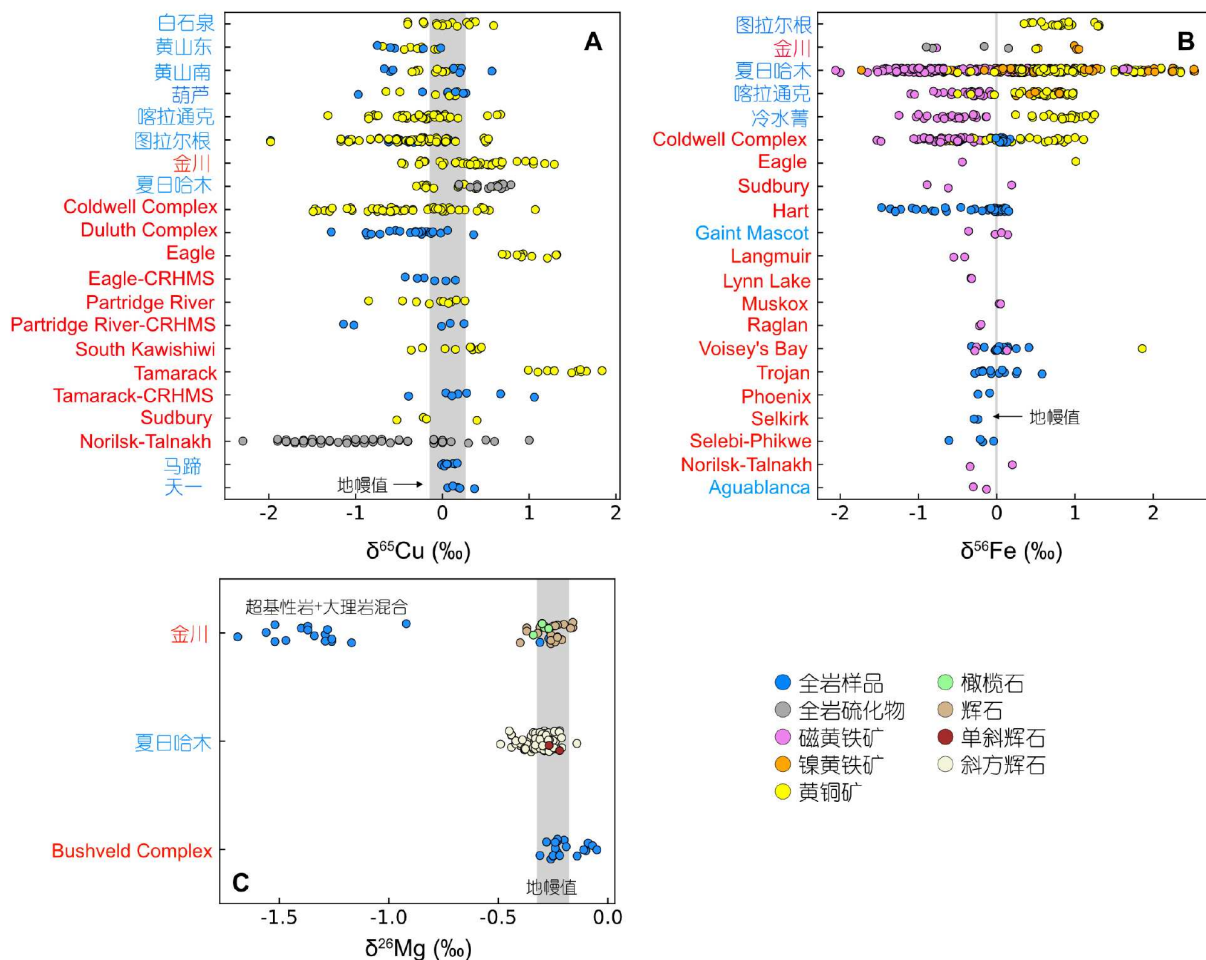


图2 全球Ni-Cu-PGE矿床中硫化物、全岩及硅酸盐矿物的Cu-Fe-Mg同位素组成。灰色区域分别代表地幔的Cu($0.06‰ \pm 0.20‰$; Liu等, 2015)、Fe($-0.005‰ \pm 0.006‰$; Dauphas等, 2017)和Mg($-0.25‰ \pm 0.07‰$; Teng等, 2010)同位素组成范围。铜同位素数据引自Zhu等(2000)、Malitch等(2014)、Ripley等(2015)、Asp(2016)、Zhao等(2017)、Zhao等(2019)、Tang等(2020)、Brzozowski等(2021a)、Smith等(2022)、Zhao等(2022a)、Zhao等(2022b)、Tang D等(2024)、Zhao等(2024)和Tang D等(2025), 铁同位素数据引自Fiorentini等(2012)、Hiebert等(2013)、Hofmann等(2014)、Hiebert等(2016)、Bilenker等(2018)、Ding等(2019)、Zhao等(2019)、Brzozowski等(2021b)、Wang等(2021)、Brzozowski等(2022)、Bao等(2024)、Tang D等(2024)和Tang Q等(2025), 镁同位素数据引自Tang等(2018)、Chen等(2021)、Ding等(2021)、Brzozowski等(2022)和Tang Q等(2025)。红色标签表示克拉通内环境矿床, 蓝色标签表示俯冲带相关环境(含碰撞后)矿床。缩写: CRHMS, 赋存于围岩中的块状硫化物

断从硅酸盐熔体中萃取金属元素, 并将其富集于小体积岩石内, 才能成矿(Naldrett, 1989, 1999, 2010; Barnes和Ripley, 2016; Barnes等, 2017)。因此, 理解Cu、Fe、Zn(即具亲铁与亲铜元素性质)同位素在硫化物熔体与硅酸盐熔体间的分馏行为, 对其作为成因示踪工具的有效性至关重要。已有研究表明, 硫化物熔体-硅酸盐熔体间的铜同位素分馏因子($\Delta^{65}\text{Cu}_{\text{sul-sil}}$)为负值, 表明硫化物优先富集轻铜同位素(^{63}Cu)(Savage等, 2015; Huang等, 2016; Xia等, 2019)。Savage等(2015)在地核形成的相关温度条件下, 将硫化物-硅酸盐体系间的铜同位素分馏因子($\Delta^{65}\text{Cu}_{\text{sul-sil}}$)限定为超过 $-1‰$ 。Xia等(2019)通过不同温度的高温实验进一步明确该分馏因子的绝对值与温度呈

负相关, 在 $1700\text{--}1500\text{ }^{\circ}\text{C}$ 范围内, $\Delta^{65}\text{Cu}_{\text{sul-sil}}$ 介于 $-0.27‰\text{--}-0.54‰$ 之间。锌同位素在硫化物熔体-硅酸盐熔体间表现出与铜同位素相似的分馏特征, 其分馏因子($\Delta^{66}\text{Zn}_{\text{sul-sil}}$)亦为负值。硫化物熔体优先富集轻同位素 ^{64}Zn , 且分馏程度随温度的降低而增大。当温度为 $1700\text{--}1500\text{ }^{\circ}\text{C}$ 时, $\Delta^{66}\text{Zn}_{\text{sul-sil}}$ 介于 $-0.21‰\text{--}-0.47‰$ 之间(Xia等, 2019)。研究还发现, 除温度外, 硫化物熔体的镍含量对铜和锌同位素的分馏程度具有控制作用: 高镍硫化物熔体($\sim 25\text{ wt.}\%$ Ni)的铜和锌同位素分馏程度显著低于低镍硫化物熔体($0.1\text{--}1.2\text{ wt.}\%$ Ni)(Xia等, 2019)。Schuessler等(2007)基于在 $1000\text{--}840\text{ }^{\circ}\text{C}$ 时的天然磁黄铁矿颗粒与流纹质玻璃的平衡实验研究, 证实了磁黄铁矿优先富集轻铁同位素

(^{54}Fe)，其与硅酸盐熔体的铁同位素分馏因子($\Delta^{56}\text{Fe}_{\text{po-sil}}$)平均值为 $-0.35\text{‰}\pm 0.04\text{‰}$ 。但是，该实验所用的熔体的 $\text{Fe}^{2+}/\Sigma\text{Fe}$ 比值较低(0.38 ± 0.02)，因此在镁铁-超镁铁质岩体系中常见的高 $\text{Fe}^{2+}/\Sigma\text{Fe}$ 比值条件下，预期的分馏因子绝对值会有所降低(Schuessler等, 2007)。Ding等(2019)对中国冷水箐铜镍硫化物矿床中硫化物矿化岩石($\sim 2\text{ wt.}\%$ S)的研究也得出类似的同位素分馏值($\Delta^{56}\text{Fe}_{\text{po-sil}}=-0.4\text{‰}\pm 0.2\text{‰}$)。鉴于硫化物熔体主要由FeS组成，磁黄铁矿-硅酸盐熔体之间的分馏因子通常被等效为硫化物熔体-硅酸盐熔体之间分馏因子($\Delta^{56}\text{Fe}_{\text{sul-sil}}$)。

岩浆硫化物熔体在冷却过程中会经历明确的结晶分异序列：首先结晶出单硫化物固溶体(MSS)并生成富铜残余熔体；随后从富铜熔体中结晶出中间固溶体(ISS)；最终，MSS和ISS再分别重结晶为磁黄铁矿+镍黄铁矿和黄铜矿(Kellerud等, 1969; Cabri, 1973; Dutrizac, 1976; Ebel和Naldrett, 1996; Lusk和Bray, 2002; Tsujimura和Kitakaze, 2004)。同位素分馏可发生于上述硫化物演化过程的多个阶段。因此，要准确解译硫化物的同位素变化，需理解硫化物在不同阶段的分异机制。其中，铁同位素的分馏效应尤为关键，因为铁作为主要成分存在于岩浆硫化物矿床中所有的常见硫化物相(磁黄铁矿、镍黄铁矿和黄铜矿)中。迄今为止，仅Zhao等(2019)基于中国图拉尔根矿床中浸染状及富铁、富铜的块状硫化物的成分，估算了残余硫化物熔体与MSS之间铜和铁同位素的分馏因子。他们通过瑞利分馏模拟表明，残余硫化物熔体与MSS的铜同位素分馏因子($\Delta^{65}\text{Cu}_{\text{residual sulfide-MSS}}$)和铁同位素分馏因子($\Delta^{56}\text{Fe}_{\text{residual sulfide-MSS}}$)分别约为 1.1‰ 和 0.5‰ ，证实MSS分异过程会产生同位素偏重的残余熔体。

3.3 同化混染与金属富集

由于硫化物饱和和所需的硫含量(SCSS)与压力呈负相关关系(Mavrogenes和O'Neill, 1999)，绝大多数岩浆在上升至浅部地壳时均处于硫不饱和状态，因而需有某种特定机制促使岩浆向硫化物饱和状态演化。虽然岩浆硫化物饱和可通过多种途径实现，如封闭体系的分离结晶作用、岩浆氧逸度变化、岩浆混合作用或外部硅源的加入，但通过地壳物质混染(在深部或就位位置)导致岩浆中外源硫的加入被视为其中最重要的机制之一。这是因为，其他过程通常仅能产生少量硫化物熔体而难以形成大规模矿化(Ripley和Li, 2013)。这一结论得到众多岩浆硫化物矿床硫同位素($\Delta^{33}\text{S}$ 、 $\delta^{34}\text{S}$)组成明显超出地幔范围这一现象的支持(见Brzozowski等, 2025中的图1)。外源硫的加入可以通过全岩同化混染作用、围岩硫化物的优

先溶解或硫化物异源熔体(即代表围岩硫化物的熔融所产生的硫化物熔体)的形成来实现(Robertson等, 2015; Lesher, 2017)。然而无论机制如何，外源硫化物加入岩浆系统不仅会提供硫，还可能同时携带铜和铁等其他金属元素。鉴于沉积岩和硅质岩宽泛的铜同位素($\delta^{65}\text{Cu}=-3\text{‰}\sim 3\text{‰}$)(Albarède, 2004; Asael等, 2007, 2009; Li等, 2009; Ripley等, 2015; Chi Fru等, 2016; Smith等, 2021)和铁同位素($\delta^{56}\text{Fe}=-2.5\text{‰}\sim 0.5\text{‰}$)(Beard等, 2003; Poitrasson和Freydier, 2005; Yamaguchi等, 2005; Schoenberg和Blanckenburg, 2006; Heimann等, 2008; Sossi等, 2012; Telus等, 2012; Zambardi等, 2014; Foden等, 2015; Du等, 2017; Xu等, 2017; Xia等, 2017)组成，此类地壳混染作用对最终的硫化物铜和铁同位素组成的变化发挥了重要作用。

多数(但非全部)岩浆硫化物矿床确实存在地壳混染。Brzozowski等(2021a)曾提出，Midcontinent Rift区Marathon Cu-PGE矿床Footwall带中黄铜矿的负 $\delta^{65}\text{Cu}$ 值($-1.49\text{‰}\sim -0.75\text{‰}$)指示了太古宙沉积物来源铜对成矿系统的加入。然而，上述地壳混染作用并未在黄铜矿($\delta^{56}\text{Fe}=-0.65\text{‰}\sim -1.11\text{‰}$)和磁黄铁矿($\delta^{56}\text{Fe}=-1.48\text{‰}\sim -0.16\text{‰}$)的铁同位素组成中留下记录，这与这两种硫化物的铁同位素组成主要受控于硫化物熔体的演化有关(讨论见后文)(Brzozowski等, 2021b)。相比之下，俄罗斯Kharaelakh($\delta^{65}\text{Cu}=-2.3\text{‰}\sim -0.9\text{‰}$)与Talnakh岩体($\delta^{65}\text{Cu}=-1.1\text{‰}\sim -0.1\text{‰}$)轻的铜同位素组成特征被认为是母岩浆原始特征(Malitch等, 2014)，但他们并未排除同化混染的可能性，因为 $\delta^{65}\text{Cu}$ 与 $\delta^{34}\text{S}$ 之间存在显著的负相关性。对于Midcontinent Rift区Duluth杂岩体($\delta^{65}\text{Cu}=-0.85\text{‰}\sim -0.45\text{‰}$)以及Eagle($\delta^{65}\text{Cu}=0.69\text{‰}\sim 1.32\text{‰}$)和Tamarack侵入体($\delta^{65}\text{Cu}=0.99\text{‰}\sim 1.84\text{‰}$)铜同位素组成的显著变化，Ripley等(2015)认为是源于地幔源区不均一性而非同化混染，因为同化混染需要假设一个具有极低 $\delta^{65}\text{Cu}$ 值(远低于 -0.25‰)的地幔源区。在此基础上，Smith等(2021)进一步指出，Eagle($\delta^{65}\text{Cu}=-0.43\text{‰}\sim -0.15\text{‰}$)和Tamarack($\delta^{65}\text{Cu}=-0.39\text{‰}\sim -1.06\text{‰}$)岩体附近围岩中的块状硫化物的地幔型 $\delta^{65}\text{Cu}$ 值暗示其缺乏地壳混染作用，而Duluth杂岩体附近硫化物较轻的铜同位素组成($\delta^{65}\text{Cu}=-1.14\text{‰}\sim -0.25\text{‰}$)源自地幔低程度部分熔融而非沉积岩中铜的同化，因为该地区Virginia组和Thomson组沉积物的铜同位素偏重($\delta^{65}\text{Cu}=-0.33\text{‰}\sim -3.12\text{‰}$)。Zhao等(2022b)也提出金川矿床的浸染状-海绵陨铁状硫化物($\delta^{65}\text{Cu}=-0.47\text{‰}\sim -1.29\text{‰}$)与块状硫化物($\delta^{65}\text{Cu}=-0.91\text{‰}\sim -0.09\text{‰}$)的铜同位素变化源于地幔交代过程而非同化混染作用，因为当地围岩(混合岩和大理岩)铜含量低且 $\delta^{65}\text{Cu}$ 值为分布局限的正值

(0.21‰–0.23‰)，无法产生观测到的变化范围。基于亏损地幔与大陆地壳混合作用的 $\delta^{65}\text{Cu}$ - $\delta^{34}\text{S}$ -S/Se-Cu/Pd变化模拟及随钻孔深度变化的 $\delta^{65}\text{Cu}$ - $\delta^{34}\text{S}$ 分析，Tang Q等(2024)认为中国夏日哈木矿床中硫化物系统偏重的铜同位素组成($\delta^{65}\text{Cu}$ =0.19‰–0.79‰)是5%–15%地壳混染的结果。然而，Tang D等(2025)的新模型提出，夏日哈木矿床硫化物的铜同位素组成偏重($\delta^{65}\text{Cu}$ =–0.30‰–0.67‰)是源自俯冲交代地幔源区的母岩浆与富铜的下地壳物质(同位素组成偏轻)发生60%–80%的同化混染的结果。两项研究估算的混染程度存在差异的根源可能在于所采用的熔体与混染端元 $\delta^{65}\text{Cu}$ 值不同。Tang Q等(2024)采用与典型地幔值相近的初始熔体 $\delta^{65}\text{Cu}$ 值(0.06‰±0.20‰；Liu等，2015)，并将地壳端元设定为重于典型地幔的 $\delta^{65}\text{Cu}$ 值(未提供具体数值)。与之相反，Tang D等(2025)采用了显著偏重的熔体端元 $\delta^{65}\text{Cu}$ 值(1.82‰)以体现源区的交代特征，并将富铜的下地壳端元设定为偏轻的 $\delta^{65}\text{Cu}$ 值(–3.17‰)。若假设两项研究的铜含量相近，后者的模型中幔源与壳源端元之间更大的同位素差异会导致更高的混染程度估算值。考虑到该地区围岩($\delta^{56}\text{Fe}$ =0.131‰–0.177‰)和下地壳($\delta^{56}\text{Fe}$ =0.1‰–0.3‰；Telus等，2012)相对较轻的铁同位素组成，他们认为下地壳同化混染作用对母岩浆铁同位素组成($\delta^{56}\text{Fe}$ =0.04‰–0.49‰；按 $\Delta^{56}\text{Fe}_{\text{sul-sil}}$ =0.4‰计算)的影响可以忽略不计，并指出铁同位素的变化主要反映了硫化物熔体分异和 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 比值的变化(下文讨论)。Tang D等(2024)认为，喀拉通克矿床的铁和铜同位素组成的变化是成矿岩浆对下地壳物质的选择性同化混染。基于对幔源岩浆与不同 $\delta^{65}\text{Cu}$ 值地壳岩石的混合模拟计算，Zhao等(2024)认为同化混染作用无法解释东天山铜镍矿化侵入体 $\delta^{65}\text{Cu}$ 值的显著变化(–0.97‰–0.57‰)，因为需要近100%的混染比例才能达成这种变化，显然不符合地质事实，并认为其铜同位素组成是继承了交代地幔源区的特征(详见下文讨论)。在加拿大与科马提岩相关的Hart矿床中，Hiebert等(2016)根据矿化科马提岩 $\delta^{56}\text{Fe}$ 值(–1.5‰–0.2‰)与全岩La/Nb、Zr/Ti比值(地壳混染指标)的弱负相关性，认为其铁同位素组成的负偏特征源于地壳混染。基于科马提岩浆流中 $\delta^{56}\text{Fe}$ - $\Delta^{33}\text{S}$ - $\delta^{34}\text{S}$ 的空间变化特征以及喷流岩($\delta^{56}\text{Fe}$: –2.1‰–0.9‰； $\Delta^{33}\text{S}$: –1.4‰–0.3‰； $\delta^{34}\text{S}$: –11.4‰–7.6‰)与碳质泥岩($\delta^{56}\text{Fe}$: –2.0‰–1.7‰； $\Delta^{33}\text{S}$: –0.9‰–0.2‰； $\delta^{34}\text{S}$: 1.6‰–5.0‰)的铁和硫同位素的组成差异性，Hiebert等(2016)认为这两类岩性是主要的同化混染端元，而科马提岩浆流在不同区段同化了二者的不同比例物质。

尽管部分岩浆硫化物矿床的铁和铜同位素组成记录了同化混染的同位素特征，但此类特征的缺失并不能意

味着同化混染作用未曾发生。其原因在于，硫化物熔体的铜和铁同位素组成(与其硫同位素组成和S/Se比值类似)受控于其在与侵入体系中未受混染的岩浆脉冲相互作用时所发生的同位素交换过程(即R因子；Campbell和Nal-drett, 1979；Lesher和Burnham, 2001；Ripley和Li, 2003)。前人对包括Eastern Gabbro岩体(Shahabi Far等, 2018；Brzozowski等, 2020, 2025)、博茨瓦纳东部Tati绿岩带与Phikwe杂岩体(Fiorentini等, 2012)、Voisey's Bay矿床(Hiebert等, 2013)、Bushveld杂岩体的Platreef岩系(Sharman等, 2013)、Hart科马提岩矿床(Hiebert等, 2016)及Eagle矿床(Ding等, 2012)在内的多个岩浆硫化物矿床的研究已证实，该过程可部分至完全破坏硫同位素与S/Se所携带的同化混染信号。为定量揭示R因子对硫化物熔体Cu-Fe-S同位素及S/Se比值的影响机制，本研究采用Ripley和Li(2003)提出的开放体系同位素交换方程：

$$\delta M_{\text{sulR}} = \frac{\delta M_{\text{sil}_1} + R^0 \times (\delta M_{\text{sil}_1} + \Delta M_{\text{sul-sil}})}{(1 + R^0)} \quad (1)$$

$$R^0 = \frac{C_{\text{sil}_1}^M}{C_{\text{sil}_1}^M} \times R$$

为模拟S/Se比值的变化过程，本研究采用Ripley和Li(2003)提出的封闭体系R因子方程进行建模，并应用分步批量平衡法进行计算。这意味着每一步平衡计算的结果将作为下一步的新初始值代入，具体的数学公式表达为

$$C_{\text{sulR}}^{\text{metal}} = \frac{C_{\text{sil}_1}^M + (R \times C_{\text{sil}_1}^M)}{1 + \frac{R}{D_{\text{sul-sil}}^M}} \quad (2)$$

在式(1)和(2)中， δM_{sulR} 代表硫化物熔体与硅酸盐熔体相互作用后的Cu-Fe-S同位素组成， δM_{sil_1} 和 δM_{sil_1} 分别为硅酸盐熔体与硫化物熔体的初始同位素组成； $\Delta M_{\text{sul-sil}}$ 和 $D_{\text{sul-sil}}^M$ 分别代表硫化物熔体-硅酸盐熔体分馏因子和分配系数； $C_{\text{sil}_1}^M$ 和 $C_{\text{sil}_1}^M$ 对应硅酸盐熔体与硫化物熔体中的Cu-Fe-S-Se的浓度， R 为瞬时R因子(单次岩浆脉冲的熔体/硫化物质量比)， R^0 为累积R因子(所有岩浆脉冲R因子之和)。尽管我们本次研究的重点是铁和铜同位素组成变化与R因子的关系，但我们也提供了硫同位素与S/Se比值的变化特征，因为这两种指标的地球化学行为已得到充分限定，并被广泛应用于岩浆硫化物矿床的特征分析中。为简化表述，模型使用的全部假设参数已列于表1。

图3清晰展示了元素-同位素交换反应的两个关键方面。首先，随着R因子增大，硫化物熔体的 $\delta^{65}\text{Cu}$ - $\delta^{56}\text{Fe}$ - $\Delta^{33}\text{S}$ -S/Se值逐渐趋近于流经该系统的脉冲式岩浆组成(此处假设该组成与地幔值相似)。其次，完全消除混染作用

表1 模型中的硅酸盐-硫化物熔体组分与分配系数

分类	参量	数值	依据	参考文献
硅酸盐熔体组分	$\Delta^{33}\text{S}_{\text{sil}}$	0‰	地幔平均组成	Ripley和Li(2003), Dauphas等(2017), Liu等(2015)
	$\delta^{56}\text{Fe}_{\text{sil}}$	-0.005‰		
	$\delta^{65}\text{Cu}_{\text{sil}}$	0.06‰		
	S_{sil}	260 ppm	与Coldwell杂岩体Eastern Gabbro中的变玄武岩的S、Fe、Cu含量相似	Good和Lightfoot(2019)
	Fe_{sil}	150000 ppm		
	Cu_{sil}	160 ppm		
	Se_{sil}	0.099 ppm	采用Coldwell变玄武岩的S含量与地幔平均S/Se值计算得出	-
	$\Delta^{33}\text{S}_{\text{sul}}$	2‰	为简化对比, 设定为混染值	-
	$\delta^{56}\text{Fe}_{\text{sul}}$	2‰		-
	$\delta^{65}\text{Cu}_{\text{sul}}$	2‰		-
硫化物熔体组分	S_{sul}	360000 ppm	与磁黄铁矿、镍黄铁矿及黄铜矿的S含量相似	-
	Fe_{sul}	440000 ppm	假设硫化物熔体为磁黄铁矿、镍黄铁矿与黄铜矿的混合物	-
	Cu_{sul}	200000 ppm	与Marathon矿床金属品位相似	Ruthart(2013)
	Se_{sul}	3 ppm	设定为混染值; S/Se比值为120000	-
	$\Delta^{33}\text{S}_{\text{sul-sil}}$	0‰	-	Ripley和Li(2003)
硫化物熔体-硅酸盐熔体之间的分馏因子及分配系数	$\Delta^{56}\text{Fe}_{\text{sul-sil}}$	-0.4‰	-	Schuessler等(2007), Ding等(2019), Brzozowski等(2021b)
	$\Delta^{65}\text{Cu}_{\text{sul-sil}}$	-0.2‰	-	Savage等(2015), Xia等(2019)
	$D_{\text{sul-sil}}^{\text{Se}}$	2339	-	Barnes和Ripley(2016)
	$D_{\text{sul-sil}}^{\text{Cu}}$	2130	-	
	$D_{\text{sul-sil}}^{\text{Fe}}$	2339	-	Ripley等(2002)

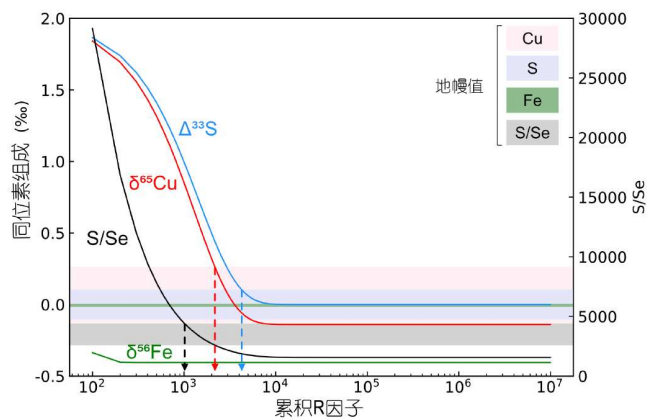


图3 不同R因子条件下硫化物熔体 $\delta^{65}\text{Cu}$ 、 $\delta^{56}\text{Fe}$ 、 $\Delta^{33}\text{S}$ 及S/Se比值的数值模拟结果。彩色区域分别代表 $\delta^{65}\text{Cu}$ (0.06‰±0.20‰; Liu等, 2015)、 $\delta^{56}\text{Fe}$ (-0.005‰±0.006‰; Dauphas等, 2017)、 $\Delta^{33}\text{S}$ (0‰±0.1‰; Lesher和Burnham, 2001; Farquhar等, 2002; Ripley和Li, 2003)以及S/Se比值(2850-4350; Eckstrand和Hulbert, 2007; Palme和O'Neil, 2014)的地幔标准值范围

的地球化学和同位素证据所需的R因子值因不同示踪指标而异。具体而言, 铜同位素、硫同位素和S/Se比值分别在R因子达到约2000、4000和1000时趋近地幔特征值(实际R因子值会因混染程度的不同而略有变化)。然而, 铁

同位素的表现与其他指标截然不同: 无论R因子如何变化(即使考虑了同化混染程度的影响), 其同位素组成均低于地幔特征值, 这与硫化物熔体-硅酸盐熔体之间分馏因子有关。这种差异行为的根本原因在于, Cu-Fe-S-Se元素在硫化物熔体/硅酸盐熔体中的浓度比存在显著差异(铜(2000)、硫(1385)和硒(30)远高于铁(3), 基于模型参数), 从而使得铁同位素能更快地与流动岩浆之间达到同位素平衡(Hiebert等, 2013; Brzozowski等, 2021b)。

目前, 关于R因子对岩浆硫化物矿床铁和铜同位素组成影响的研究仍较为有限。Brzozowski等(2021a)的研究表明, Marathon矿床中黄铜矿的 $\delta^{65}\text{Cu}$ 值从Footwall带(-1.49‰-0.75‰)到Main带(-1.04‰-0.08‰)再到W矿带(-0.34‰-1.07‰)呈系统性升高的趋势, 并将这一现象归因于在R因子约为100-1000000的范围内, 硫化物熔体与未混染岩浆持续相互作用, 从而导致同化混染信号被逐步消除。尽管铜同位素呈现上述系统性变化特征, 但Brzozowski等(2021b)发现Marathon矿床中硫化物的铁同位素组成几乎不受R因子影响。Tang D等(2024)将新疆喀拉通克矿床中浸染状黄铜矿铜同位素组成的变化($\delta^{65}\text{Cu}$ =-0.85‰-0.67‰)解释为R因子的变化, 尽管其变化范围仅为~100-1000。在Voisey's Bay矿床中, Hiebert等(2013)

认为,若硫化物在R因子约400时已达到平衡,则任何由同化混染引起的 $\delta^{56}\text{Fe}$ 值变化必然已被消除,因为铁同位素平衡所需的R因子远低于400。对Hart科马提岩型矿床的研究则显示,随着R因子从~5增至250,浸染状至块状硫化物样品的全岩 $\delta^{56}\text{Fe}$ 值由-1.5‰系统性升高至0‰(Hiebert等, 2016)。鉴于夏日哈木矿床硫化物中Pd含量显著差异及 $\delta^{56}\text{Fe}$ 值的有限变化, Tang Q等(2025)推断该矿床中硫化物矿石的铁同位素组成主要受控于最高达500的R因子。与图3的模拟结果及前人关于R因子影响硫化物铁同位素的研究结果不同, Ding等(2019)提出,中国冷水管矿床浸染状磁黄铁矿的 $\delta^{56}\text{Fe}$ 值(-1.25‰—-0.13‰)随R因子增大而降低。这是由于该模型假设 $\Delta^{56}\text{Fe}_{\text{sul-sil}}$ 随R因子增加而负向偏移,以解释硫化物熔体与硅酸盐熔体达到铁同位素平衡所需的临界质量。尽管此类模型可能适用于部分矿床,但普适性显然受限,因为在高R因子(>1000)条件下,模型会计算出不切实际的极端负 $\delta^{56}\text{Fe}$ 值(Brzoowski等, 2021b)。

镁作为亲石元素,其同位素组成不受硫化物熔体相关过程的影响。因此,镁同位素不会经历硫化物熔体与硅酸盐熔体之间的同位素交换反应,而此类反应通常能破坏Cu-Fe同位素记录的同化混染信号。鉴于这一特性,加之镁同位素组成在壳源组分中具有显著差异,使其可作为示踪岩浆混染作用的可靠指标。Tang等(2018)研究发现,中国金川矿床全岩、辉石和橄榄石的镁同位素系统地偏负($\delta^{26}\text{Mg}$ 值为-0.4‰—-0.26‰),且围岩大理岩为显著的负值(-2.0‰—-1.17‰)。据此, Tang等(2018)提出金川岩浆在浅部地壳过程中同化了<10%的大理岩,并结合10%—20%的下地壳物质同化混染作用,认为同化混染过程通过降低SCSS值对金川岩浆中硫化物的饱和起到了关键作用。然而, Ding等(2021)基于距侵入岩-大理岩接触带不同距离的辉石具地幔特征的 $\delta^{26}\text{Mg}$ 值(-0.32‰—-0.16‰),认为金川岩体的大理岩同化混染范围可能仅限于岩体与大理岩的接触带。在中国夏日哈木矿床, Chen等(2021)通过Mg-Sr-Nd同位素体系识别出两类不同的同化混染端元。边缘相斜方辉石呈现轻镁同位素组成($\delta^{26}\text{Mg}$ =-0.44‰—-0.3‰),结合其全岩较高的($^{87}\text{Sr}/^{86}\text{Sr}$)_i(0.7127—0.7172)与负 ϵ_{Nd} 值(-5.4—-4.8),指示岩体在侵位过程中受到片麻岩和大理岩的局部混染。而斜方辉石岩中斜方辉石具有接近地幔的 $\delta^{26}\text{Mg}$ 值(-0.34‰—-0.21‰),结合其全岩相对较低的($^{87}\text{Sr}/^{86}\text{Sr}$)_i(0.7087—0.7118)和偏负程度较小的 ϵ_{Nd} 值(-4—-1.4),反映其深部岩浆房经历的地壳物质混染。值得注意的是, Tang Q等(2025)虽然同样将夏日哈木矿床中辉石轻于地幔的 $\delta^{26}\text{Mg}$ 值(-0.376‰—-0.141‰)归因于地壳混染(因为样品同时具有较高的 $\delta^{34}\text{S}$

值),但也提出至少部分镁同位素的变化反映了母岩浆源自碳酸盐化地幔源区。

3.4 硫化物熔体的演化

尽管岩浆分离结晶过程中铜和铁同位素的行为已被充分表征(Teng等, 2008; Schuessler等, 2009; Sossi等, 2012; Huang等, 2016; Sun等, 2023; Zou等, 2024),但硫化物熔体演化如何控制最终结晶硫化物的铜和铁同位素组成仍缺乏系统研究。硫化物熔体结晶包括一系列步骤(Kellerud等, 1969; Cabri, 1973; Dutrizac, 1976; Ebel和Naldrett, 1996; Lusk和Bray, 2002; Tsujimura和Kitakaze, 2004)。在1180—900 °C温度区间, MSS从硫化物熔体中晶出,残余富铜熔体随后在900—800 °C析出ISS。在650—200 °C温度范围内,磁黄铁矿与镍黄铁矿从MSS中重结晶而成,黄铜矿(±斑铜矿)则从ISS中重结晶而成。当温度低于210 °C时,黄铜矿中出溶方黄铜矿,磁黄铁矿在<145 °C时出溶陨硫铁。这一结晶序列清晰表明,所有硫化物相均含铁,而铜主要赋存于黄铜矿(斑铜矿与方黄铜矿在全球矿床中相对少见)。因此,硫化物熔体演化对硫化物铁同位素组成的影响远大于对铜同位素的影响。尽管不同硫化物矿物中铁的成键环境(如磁黄铁矿中的 Fe^{2+} 与黄铜矿中的 Fe^{3+} ; Goh等, 2006)及非零的 $\Delta^{56}\text{Fe}_{\text{Ccp-po}}$ (Zhao等, 2019; Ding等, 2019)预示着不同硫化物之间会发生铁同位素分馏,但Brzoowski等(2021b)首次通过加拿大Marathon矿床的具有矿物学分带特征的Footwall带(磁黄铁矿>黄铜矿)、Main带(黄铜矿>磁黄铁矿)和W Horizon带(黄铜矿+斑铜矿)作为典型案例,揭示了硫化物熔体演化对硫化物铁同位素组成的影响。Brzoowski等(2021b)通过分离结晶模型证明,随着硫化物熔体中晶出的MSS比例的减少,黄铜矿的 $\delta^{56}\text{Fe}$ 值也同步下降。这是因为MSS较ISS早结晶且优先富集 ^{54}Fe ,从而导致残余富铜熔体中可供黄铜矿晶体结合的 ^{54}Fe 减少。因此, MSS结晶比例越高, ISS的铁同位素组成越重。据此, Marathon矿床中黄铜矿的 $\delta^{56}\text{Fe}$ 值从Footwall带(+0.75‰—1.11‰)到Main带(+0.01‰—0.81‰)再到W Horizon带(-0.65‰—-0.01‰)呈现的系统性降低趋势被解释为硫化物熔体中MSS结晶比例逐渐降低的结果。特别值得注意的是, W Horizon带黄铜矿普遍呈现负 $\delta^{56}\text{Fe}$ 值,表明该带硫化物熔体几乎未经历MSS结晶阶段(这一解释与该带矿物组合特征高度吻合)。尽管未明确涉及硫化物熔体的具体结晶序列, Tang D等(2025)通过数值模拟证明,假设硫化物矿物与熔体间的分馏系数 $\alpha(\text{Fe})=0.99997$, $\alpha(\text{Cu})=0.99999$,夏日哈木矿床中浸染状硫化物 $\delta^{56}\text{Fe}$ 与 $\delta^{65}\text{Cu}$ 的变化可通过高达20%(Fe)与40%(Cu)的硫化物熔体分离结晶来解释。

3.5 氧化还原过程

铜和铁在地球中均呈多价态特征,暗示他们的同位素可能受氧化还原过程而发生分馏。这一现象在低温环境中已得到充分验证(Marechal和Sheppard, 2002; Zhu等, 2002; Ehrlich等, 2004; Mathur等, 2005; Markl等, 2006),但直至近年才在高温岩浆硫化物矿床中得到证实。Zhao等(2017, 2019)提出,新疆图拉尔根矿床中浸染状黄铜矿 $\delta^{65}\text{Cu}$ (-1.98‰ — -0.04‰)和 $\delta^{56}\text{Fe}$ (0.35‰ — 0.92‰)值的变化与全岩Cu-S含量呈相关性,且晚期形成的硫化物具有更高的 $\delta^{65}\text{Cu}$ 值和更低的 $\delta^{56}\text{Fe}$ 值,这些特征被解释为硫化物-岩浆分异过程中伴随的氧化还原变化所致。在这一模型中,图拉尔根矿床的母岩浆通过橄榄石和辉石的结晶以及硫化物熔体的分离,导致岩浆中 Fe^{2+} 持续消耗,残余熔体中 Fe^{3+} 相对富集。这种岩浆体系的氧化过程促使反应 $\text{Cu}^{1+} + \text{Fe}^{3+} \rightleftharpoons \text{Cu}^{2+} + \text{Fe}^{2+}$ 向右进行,进而使熔体中 Cu^{2+} 浓度显著增加。两种可能的机制可以解释这种同位素变化。Zhao等(2017)认为,基于黄铜矿以 Cu^{1+} 为主导(Goh等, 2006),熔体中 Cu^{2+} 进入黄铜矿时被还原为 Cu^{1+} (Cu^{1+} 优先结合 ^{63}Cu ; Schauble, 2004),导致残余熔体逐渐贫 ^{63}Cu ,因而晚期形成的黄铜矿 $\delta^{65}\text{Cu}$ 更重。Zhao等(2019)则强调黄铜矿中Cu-Fe价态差异(Klekovkina等, 2014),早期形成的黄铜矿($\text{Cu}^{1+}\text{Fe}^{3+}\text{S}_2^{-}$)相较于晚期形成的黄铜矿($\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{-}$)具有更低的 $\delta^{65}\text{Cu}$ 值和更高的 $\delta^{56}\text{Fe}$ 值。类似的模型被用于解释东天山黄山(-0.69‰ — -0.05‰)、黄山东(-0.35‰ — -0.18‰)和葫芦(-0.65‰ — -0.17‰)矿床中黄铜矿的 $\delta^{65}\text{Cu}$ 值与所估算氧逸度(QFM分别为 -0.7 至 0 、 -1.4 — -0.2 和 -1.2 — -0.6)的正相关关系(Zhao等, 2022a)。然而,这些模型难以解释Marathon、夏日哈木及东天山多个岩浆硫化物矿床的同位素特征。例如,Marathon矿床的辉长岩(-1.49‰ — -1.07‰)与辉石岩(-0.59‰ — -0.47‰)中黄铜矿的 $\delta^{65}\text{Cu}$ 值几乎完全重叠,但按氧化还原分馏理论,镁铁质岩(低 $\text{Fe}^{2+}/\text{Fe}^{3+}$)应比超镁铁质岩具有更轻的铜同位素组成(Brzoowski等, 2021a)。在铁同位素方面, $\delta^{56}\text{Fe}$ 值变化于 -0.65‰ — $+1.11\text{‰}$ 之间的黄铜矿大多产自单一岩相(Two Duck Lake辉长岩),该岩体由多期次晶粥脉冲而非单一分异岩浆脉冲结晶形成,排除了氧化还原控制的可能(Brzoowski等, 2021b)。在喀拉通克矿床,块状与浸染状矿石的黄铜矿 $\delta^{65}\text{Cu}$ 值相似且与 $\delta^{65}\text{Cu}$ - $\delta^{56}\text{Fe}$ 无相关性,表明氧化还原过程并未主导黄铜矿的Cu-Fe同位素组成(Tang D等, 2024)。夏日哈木矿床最原始的浸染状矿石(斜方辉石 $\text{Mg}^{\#} \approx 89$)出现高 $\delta^{65}\text{Cu}$ 值(0.64‰),且 $\delta^{65}\text{Cu}$ 与 $f\text{O}_2$ (基于橄榄石-硫化物氧压计计算; Barnes等, 2013)无相关性,同样排除了氧化还原的重要

影响(Tang Q等, 2024)。在更大尺度上,东天山地区铜镍矿化镁铁-超镁铁质岩体 $\delta^{65}\text{Cu}$ 与 SiO_2 (岩浆演化指标)缺乏相关性,表明了由岩浆分异作用引起的氧化还原条件变化对铜同位素组成的控制作用并不显著(Zhao等, 2024)。然而就矿化岩体而言,地幔源区的氧化作用对其母岩浆初始铜同位素组成可能具有关键控制意义。由于 ^{65}Cu 优先赋存于 Cu^{2+} ,地幔硫化物的非均一交代与氧化分解会产生具有变化的铜同位素组成的部分熔体,该特征可作为判别矿化岩体的标志性指标(矿化岩体的 $\delta^{65}\text{Cu}$ 为 -0.97‰ — -0.57‰ ,贫矿岩体的 $\delta^{65}\text{Cu}$ 为 -0.01‰ — -0.37‰),且与其变化的Ba/Nb(矿化岩体为 40 — 756 ,贫矿岩体为 2 — 59)和Ba/La比值(矿化岩体为 16 — 219 ,贫矿岩体为 1 — 26)相吻合(Zhao等, 2024)。Tang D等(2025)提出夏日哈木矿床中磁黄铁矿和黄铜矿的 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 比值(反映硫化物熔体氧化状态)可能控制了其铜和铁同位素组成。海绵陨铁状和块状矿石中磁黄铁矿的 $\delta^{56}\text{Fe}$ 与 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 呈正相关,且较浸染状矿石中的磁黄铁矿的 $\delta^{56}\text{Fe}$ 值更高,表明从氧化程度渐增的熔体中结晶的磁黄铁矿通过吸纳更多 Fe^{3+} (富集 ^{56}Fe)导致同位素变重。虽未直接测定黄铜矿中铜和铁的价态,但黄铜矿的 $\delta^{65}\text{Cu}$ 值从浸染状到块状矿石逐渐升高,推测与其 Fe^{3+} 比例相关。

总体而言,尽管一些证据支持氧化还原过程对硫化物及其赋存岩体的铜和铁同位素组成的调控作用,但其影响程度具有可变性,且对于上述讨论的以通道型侵入体为特征的岩浆系统而言可能相对次要。究其原因,通道型侵入体本质上代表了一种以多期次岩浆补给为特征的贯穿式“flow-through”流动系统。而这一特性正是许多小体积矿床能形成高金属品位的必要条件(Barnes和Lightfoot, 2005; Naldrett, 2010; Barnes等, 2015; Barnes和Ripley, 2016)。在此类开放体系的演化过程中,由于更原始岩浆的持续注入能够有效补充分离结晶消耗的元素(包括 Fe^{2+} 等氧化还原敏感元素),从而抑制了分离结晶作用可能导致的氧逸度显著变化。尽管此类模型可能适用于部分镁铁质-超镁铁质Ni-Cu-PGE成矿系统(例如Coldwell杂岩体东部辉长岩中的矿床; Brzoowski等, 2021a),但其普适性仍显不足。中亚造山带内多个岩浆型铜镍硫化物矿化岩体所呈现的分离结晶引起氧化还原变化的证据,即表明该类氧化还原过程可能对铜和铁同位素分馏产生重要影响。例如, Cao等(2019)通过揭示计算的氧逸度(FMQ+0.2至FMQ+1.5)与橄榄石Fo值(84 — 91)之间的负相关关系,论证了坡一岩体(可能包括红旗岭与黄山西岩体)的母岩浆在经历低程度分离结晶作用($<6\%$)后氧化程度增强。在此基础上, Cao等(2020)对中亚造山带内更多与俯冲环境(菁布拉克、黑山、额布图)及碰撞

后环境(喀拉通克、白鑫滩、黄山东、黄山、坡一、坡十、图拉尔根、红旗岭)相关的铜镍硫化物矿床开展了系统的氧逸度研究,研究表明:(1)这些矿化岩体的地幔源区氧逸度($\sim$ FMQ至FMQ+1)与MORB的氧逸度相当或略高($<$ FMQ+0.5; Cottrell和Kelley, 2011; Zhang等, 2018; Cottrell等, 2021); (2)岩体氧逸度与橄榄石Fo值呈负相关关系。这些证据共同指示,岩体的氧化特征主要源自相对还原性岩浆的分离结晶作用。基于上述研究,王焰等(2025)进一步提出,中亚造山带内洋内型与安第斯型汇聚板块边缘镁铁质-超镁铁质岩体的高氧逸度并非源于氧化的地幔源区,而是由其富水母岩浆演化所致。具体而言,洋内型汇聚板块边缘镁铁-超镁铁质岩体的岩浆高氧逸度被解释为水的解离或挥发分逸散过程中带出部分 Fe^{2+} 所致;而安第斯型汇聚板块边缘镁铁-超镁铁质岩体的岩浆氧逸度变化,则被归因于该构造背景下更厚的岩石圈所导致的石榴子石分离结晶作用。鉴于通道型岩浆硫化物成矿系统中地质过程的复杂性,单一模型显然难以合理解释该类系统中铜和铁同位素组成的变化机制,需结合具体矿床的地质背景与控制因素进行个案评估。

3.6 源区组成与地幔交代作用

Cu-Fe-Mg同位素体系在岩浆硫化物矿床研究的应用主要集中于解析成矿过程(如地壳混染、金属富集及硫化物熔体演化等)。尽管这些同位素体系在示踪成矿母岩浆源区特征方面的应用仍相对有限,但为揭示岩浆硫化物矿床的地幔源区特征提供了新的视角。基于Marathon矿床富铂族元素的W矿带中黄铜矿铜同位素组成显著偏重的($\delta^{65}\text{Cu}=-0.34\text{‰}-1.07\text{‰}$)特征,Brzowski等(2021a)提出,至少部分参与成矿系统的母岩浆脉冲应源自于重铜同位素组成($\delta^{65}\text{Cu}>1\text{‰}$)的交代地幔源区(Liu等, 2015)。这一推论的理论基础在于,在W矿带特有的高R因子条件下(>100000),硫化物熔体与硅酸盐熔体的铜同位素会达到完全平衡。换言之, W矿带硫化物熔体的铜同位素组成直接反映了母岩浆的铜同位素特征。因此,硫化物熔体所表现出的偏重的铜同位素组成表明其母岩浆同样具有偏重的铜同位素特征,而这正是交代地幔的典型属性之一(Liu等, 2015)。Brzowski等(2022)通过对加拿大Coldwell杂岩体中贫矿变玄武岩和层状岩系,以及矿化Marathon岩系的全岩Mg-Fe同位素组成开展了系统分析,深入评估了研究区地幔交代介质的性质。结果表明,尽管这些岩石显示出与典型玄武岩一致的铁同位素组成($\delta^{56}\text{Fe}=0.07\text{‰}\pm 0.08\text{‰}$),但其镁同位素组成($\delta^{26}\text{Mg}=-0.31\text{‰}-0.05\text{‰}$)却呈现偏重特征。基于此,我们排除了碳酸盐熔体(产生低 $\delta^{26}\text{Mg}$ 值)和俯冲蚀变洋壳/沉积物(导

致 $\delta^{56}\text{Fe}$ 分馏)作为主要交代介质的可能性,并提出俯冲板片来源的流体才是最可能的地幔交代介质,而不同岩石组合 $\delta^{26}\text{Mg}$ 值的变化,则是岩浆对同位素组成不均一的地幔源区进行熔融抽取的结果。

Tang等(2020)根据对新疆喀拉通克和白石泉矿床中黄铜矿的低 $\delta^{65}\text{Cu}$ 值特征,同样提出成矿母岩浆源自受俯冲板片流体交代的地幔源区的认识。这一结论主要基于以下两点关键证据:其一,矿床的 $\delta^{65}\text{Cu}$ 值显著轻于区域沉积岩,排除了地壳混染作为轻铜同位素组成主要来源的可能性;其二,采用具有轻 $\delta^{65}\text{Cu}$ 特征(最低达 -1.82‰)的母岩浆进行R因子模拟,可以重现矿床中观测到的铜同位素组成变化范围。和Brzowski等(2021a)的思路类似,Zhao等(2022b)提出金川矿床偏重的铜同位素组成($\delta^{65}\text{Cu}=-0.44\text{‰}\pm 0.28\text{‰}$)同样指示其成矿母岩浆源自受俯冲板片流体交代的地幔源区。他们认为,这些流体既能从俯冲板片中萃取重铜同位素(^{65}Cu),也可通过溶解原生硫化物从上覆地幔橄榄岩中活化 ^{65}Cu ,进而在金川矿床的岩浆源区(即大陆岩石圈地幔, SCLM)形成具有重铜同位素组成特征的次生硫化物。为进一步评估地幔交代作用对东天山岩浆硫化物矿床成矿的控制作用,Zhao等(2024)系统研究了康古尔-黄山剪切带沿线时空相关的含矿(图拉尔根、葫芦、黄山东、黄山)与贫矿(马蹄、天一)岩体的铜同位素组成。研究发现,含矿岩体的铜同位素组成($\delta^{65}\text{Cu}=-0.97\text{‰}-0.57\text{‰}$)的变化范围明显大于贫矿岩体($\delta^{65}\text{Cu}=-0.06\text{‰}-0.49\text{‰}$),被解释为前者的母岩浆源自俯冲板片流体交代的地幔源区——该流体通过氧化分解地幔硫化物,促使铜及其他金属在原始岩浆中富集。尽管上述研究未明确强调,但流体加入地幔源区的一个关键效应在于其能显著提高源区部分熔融程度(Mungall和Brenan, 2014),从而形成富含成矿金属的熔体。因此,流体对地幔的交代作用很可能是形成Ni-Cu-PGE矿床所需富金属岩浆的关键初始步骤。

4 岩浆硫化物矿床成因研究展望与钼(Mo)和锌(Zn)同位素应用前景

岩浆硫化物矿床主要发育于克拉通(Campbell和Griffiths, 1990; Campbell, 2005; Campbell和Kerr, 2007; Ernst和Jowitt, 2013),也可形成于造山带背景(Lu等, 2019; 薛胜超等, 2022),并被认为是分别主要源自地幔柱和俯冲改造过的幔源岩浆(图4)。在俯冲带环境,交代(含水)地幔的部分熔融通常可产生具有地球化学性质多样化且富含成矿金属的母岩浆(Fiorentini和Beresford, 2008; Zhao等, 2018; Yao等, 2018)。然而,越来越多的证据表明,许多板内岩浆并非完全源自地幔柱,而是

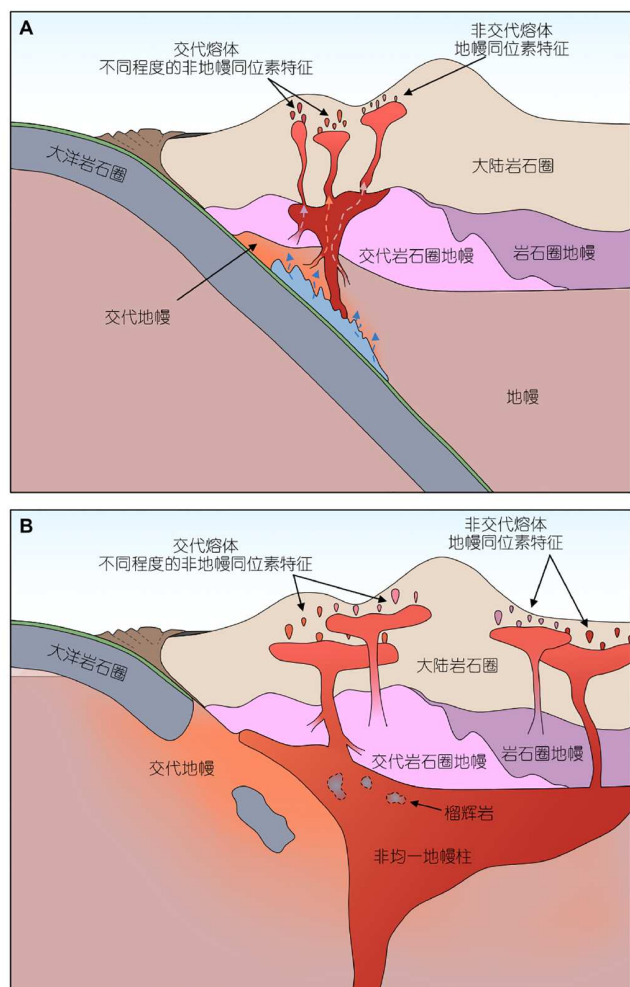


图4 岩浆硫化物矿床成矿动力学模型。(A) 板片来源物质对弧下地幔的改造及弧岩浆生成过程；(B) 地幔柱与不同程度交代岩石圈地幔(SCLM)相互作用，形成地球化学性质各异的熔体，其源区分别包括：未受改造的地幔柱熔体、与交代地幔相互作用的地幔柱熔体，以及交代/未交代的SCLM

由地幔柱与不同程度的交代型SCLM混合形成(图4)(Elam等, 1992; Shirey, 1997; Zhang等, 2008; Liu等, 2017; Good和Lightfoot, 2019; Rooney等, 2022; Brzozowski等, 2022, 2023b, 2024; Marfin等, 2024)。尽管关于SCLM在岩浆硫化物矿床形成过程中所起的作用仍存在争议(Zhang等, 2008; Maier和Groves, 2011; Arndt, 2013; Maier等, 2017)，但大量研究已在这些成矿系统中识别出源区含有不同交代程度的SCLM组分。这些实例包括Midcontinent Rift中Keweenaw大火成岩省相关的矿床(如Current、Escape、Marathon)(Good和Lightfoot, 2019; Rooney等, 2022; Brzozowski等, 2022, 2023b, 2024)、金川矿床(Zhao等, 2022b)以及西伯利亚大火成岩省的Norilsk-Talnakh矿床(Lightfoot等, 1993; Naldrett和Light-

foot, 1999; Marfin等, 2024)。准确评估地幔交代作用和SCLM对岩浆硫化物矿床成因的贡献，对于深入理解这类重要矿床的形成机制，进而提高相关矿床的勘查效率具有重要意义。鉴于新型稳定同位素体系(如Mo和Zn)对交代过程的高度敏感性(图4)，其应用将为解决这一科学问题提供新的研究途径。

尽管Cu-Fe-Mg同位素已被广泛应用于岩浆硫化物矿床的成因研究，但目前尚未有研究直接利用钼和锌同位素开展此类工作。值得注意的是，已有少数研究尝试将钼同位素应用于与Ni-Cu-PGE硫化物矿化无关的层状侵入体的成因分析(Nebel-Jacobsen等, 2021; Zhang L等, 2024)。鉴于这些同位素体系在记录与俯冲相关过程和地幔交代作用方面的独特作用(详见第2.5和2.4节)，以及岩浆硫化物矿床的形成过程与地幔交代、俯冲过程和SCLM的贡献之间的成因联系(详见第3.6节)，钼和锌同位素组成有望为揭示上述地质过程的成因联系提供新的关键性约束。

截至目前，Marfin等(2024)是唯一应用钼同位素开展Ni-Cu-PGE成矿作用相关的岩石成因的研究。该研究聚焦西伯利亚大火成岩省玄武岩，而这些玄武岩在时空分布上与俄罗斯Norilsk的Talnakh铜镍硫化物矿床密切相关。将全岩钼同位素数据与地球化学及Sr-Nd-Hf同位素体系结合，Marfin等(2024)成功识别出西伯利亚大火成岩省玄武岩的源区存在与俯冲相关的特殊组分。值得注意的是，Ivakinsky组和Gudchikhinsky组大部分玄武岩样品的轻钼同位素组成($\delta^{98}\text{Mo}=-0.4\text{‰}-0.08\text{‰}$)和低Mo/Ce比值(0.016–0.023)被解释为源区存在榴辉岩脱水熔融组分的贡献，而Gudchikhinsky组少数玄武岩样品表现出的重钼同位素组成($\delta^{98}\text{Mo}=0.07\text{‰}$)和高Mo/Ce比值(0.049)则反映了经历流体交代改造的地幔源区的贡献。尽管西伯利亚大火成岩省玄武岩与Norilsk-Talnakh矿床可能不存在直接成因联系(Malitch等, 2020; Krivolutsckaya等, 2021)，但二者在西伯利亚大火成岩省中的时空共生关系暗示，成矿系统的源区可能同样经历了交代改造作用。该研究凸显了钼同位素的双重指示作用——既可作为地幔源区物质贡献的有效指标，又能作为识别源区改造过程的工具，为未来利用钼和锌等其他新型同位素体系开展相关研究奠定了重要基础。

致谢 感谢责任编辑和两位审稿人的建设性意见。

参考文献

王焰, 魏博, 曹勇华, 等. 2025. 汇聚板块边缘镁铁-超镁铁质岩浆作用与铜镍硫化物矿床成因. 大地构造与成矿学, 49: 753–776

- 薛胜超, 王庆飞, 唐冬梅, 等. 2022. 造山带岩浆铜镍硫化物矿床的混染模式——以天山-北山二叠纪铜镍矿为例. *矿床地质*, 41: 1–20
- Ahmad Q, Wille M, König S, et al. 2021. The molybdenum isotope subduction recycling conundrum: A case study from the Tongan subduction zone, Western Alps and Alpine Corsica. *Chem Geol*, 576: 120231
- Albarède F. 2004. The Stable Isotope Geochemistry of Copper and Zinc. In: *Geochemistry of Non-Traditional Stable Isotopes*. Mineralogical Society of America, 409–427
- Albarède F, Beard B. 2004. Analytical methods for non-traditional isotopes. *Rev Mineral Geochem*, 55: 113–152
- Arndt N. 2013. The lithospheric mantle plays no active role in the formation of orthomagmatic ore deposits. *Econ Geol*, 108: 1953–1970
- Asael D, Matthews A, Bar-Matthews M, et al. 2007. Copper isotope fractionation in sedimentary copper mineralization (Timna Valley, Israel). *Chem Geol*, 243: 238–254
- Asael D, Matthews A, Oszczepalski S, et al. 2009. Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits. *Chem Geol*, 262: 147–158
- Asp K. 2016. An investigation of Ni and Cu isotopic fractionation in Basal Duluth Complex Cu-Ni-PGE mineralization, northeastern Minnesota. Dissertation for Master's Degree. Duluth: University of Minnesota Duluth
- Bao Y W, Feng Y T, Zhang M J, et al. 2024. Enrichment of cobalt in the Xiarihamu Ni-Co sulfide deposit in the East Kunlun orogenic belt, Western China: Constraints from distribution of cobalt in sulfides and Fe and S isotopes of sulfides. *J Asian Earth Sci*, 259: 105886
- Barnes S J, Lightfoot P C. 2005. Formation of magmatic nickel sulfide ore deposits and processes affecting their copper and platinum group element contents. In: Hedenquist J W, Thompson J F H, Goldfarb R J, et al., eds. *Economic Geology 100th Anniversary Volume*. 179–213
- Barnes S J, Godel B, Gurer D, et al. 2013. Sulfide-olivine Fe-Ni exchange and the origin of anomalously Ni rich magmatic sulfides. *Econ Geol*, 108: 1971–1982
- Barnes S J, Cruden A R, Arndt N, et al. 2015. The mineral system approach applied to magmatic Ni-Cu-PGE sulphide deposits. *Ore Geol Rev*, 76: 296–316
- Barnes S J, Ripley E M. 2016. Highly siderophile and strongly chalcophile elements in magmatic ore deposits. *Rev Mineral Geochem*, 81: 725–774
- Barnes S J, Holwell D A, Le Vaillant M. 2017. Magmatic sulfide ore deposits. *Elements*, 13: 89–95
- Barnes S J. 2018. Chalcophile elements. In: White W M, ed. *Encyclopedia of Geochemistry: A Comprehensive Reference Source on the Chemistry of the Earth*. Cham: Springer International Publishing
- Barnes S J, Williams M, Smithies R H, et al. 2021. Trace element contents of mantle-derived magmas through time. *J Petrol*, 62: egab024
- Beard B L, Johnson C M, Skulan J L, et al. 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chem Geol*, 195: 87–117
- Beard B L, Johnson C M. 2004. Fe isotope variations in the modern and ancient Earth and other planetary bodies. In: *Geochemistry of Non-Traditional Stable Isotopes*. Mineralogical Society of America, 319–357
- Bekker A, Barley M E, Fiorentini M L, et al. 2009. Atmospheric sulfur in Archean Komatiite-hosted nickel deposits. *Science*, 326: 1086–1089
- Bekker A, Grokhovskaya T L, Hiebert R, et al. 2016. Multiple sulfur isotope and mineralogical constraints on the genesis of Ni-Cu-PGE magmatic sulfide mineralization of the Monchegorsk Igneous Complex, Kola Peninsula, Russia. *Miner Depos*, 51: 1035–1053
- Benson E K, Ripley E M, Li C, et al. 2020. Multiple S isotopes and S isotope heterogeneity at the east eagle Ni-Cu-platinum group element deposit, northern Michigan. *Econ Geol*, 115: 527–541
- Beunon H, Mattioli N, Doucet L S, et al. 2020. Mantle heterogeneity through Zn systematics in oceanic basalts: Evidence for a deep carbon cycling. *Earth-Sci Rev*, 205: 103174
- Bilenker L D, Weis D, Scoates J S, et al. 2018. The application of stable Fe isotopes to magmatic sulfide systems: Constraints on the Fe isotope composition of magmatic pyrrhotite. *Econ Geol*, 113: 1181–1192
- Bleeker W, Smith J, Hamilton M, et al. 2020. The Midcontinent Rift and its mineral systems: Overview and temporal constraints of Ni-Cu-PGE mineralized intrusions. Geological Survey of Canada
- Brzozowski M J, Samson I M, Gagnon J E, et al. 2020. On the mechanisms for low-sulfide, high-platinum group element and high-sulfide, low-platinum group element mineralization in the Eastern Gabbro, Coldwell Complex, Canada: Evidence from textural associations, S/Se values, and platinum group element concentrations of base metal sulfides. *Econ Geol*, 115: 355–384
- Brzozowski M J, Good D J, Wu C, et al. 2021a. Cu isotope systematics of conduit-type Cu-PGE mineralization in the Eastern Gabbro, Coldwell Complex, Canada. *Miner Depos*, 56: 707–724
- Brzozowski M J, Good D J, Wu C, et al. 2021b. Iron isotope fractionation during sulfide liquid evolution in Cu-PGE mineralization of the Eastern Gabbro, Coldwell Complex, Canada. *Chem Geol*, 576: 120282
- Brzozowski M J, Samson I M, Gagnon J E, et al. 2021c. Oxide mineralogy and trace element chemistry as an index to magma evolution and Marathon-type mineralization in the Eastern Gabbro of the alkaline Coldwell Complex, Canada. *Miner Depos*, 56: 621–642
- Brzozowski M J, Good D J, Yan W, et al. 2022. Mg-Fe isotopes link the geochemical complexity of the Coldwell Complex, Midcontinent Rift to metasomatic processes in the mantle. *J Petrol*, 63: 1–23
- Brzozowski M J, Hollings P, Heggie G, et al. 2023a. Characterizing the supra- and subsolidus processes that generated the Current PGE-Cu-Ni deposit, Thunder Bay north intrusive complex, Canada: Insights from trace elements and multiple S isotopes of sulfides. *Miner Depos*, 58: 1559–1581
- Brzozowski M J, Hollings P, Zhu J J, et al. 2023b. Osmium isotopes record a complex magmatic history during the early stages of formation of the North American Midcontinent Rift—Implications for rift initiation. *Lithos*, 436–437: 106966
- Brzozowski M J, Hollings P, Hamilton M, et al. 2024. Petrogenetic relationship of the variably Ni-Cu-platinum-group element (PGE)-mineralized intrusions of the Thunder Bay North Intrusive Complex, Midcontinent Rift, Canada: Implications for mineral exploration in mafic-ultramafic complexes. *Geol Soc Am Bull*, 137: 1747–1762
- Brzozowski M J, Zaborniak K. 2024. Sulphide mineralization at the E&L magmatic Ni-Cu-PGE deposit: Textural evidence for contamination, vapour saturation, fluid immiscibility, and metal remobilization. In: *Geological Fieldwork 2023*. British Columbia Ministry of Energy, Mines and Low Carbon Innovation, British Columbia Geological Survey Paper 2024-01. 65–78
- Brzozowski M J, Hollings P, Good D J, et al. 2025. Sulfur isotopes as a record of complex sulfide saturation histories in conduit-type Ni-Cu-PGE deposits: An example from the Eastern Gabbro, Coldwell Complex, Canada. *Econ Geol*, 120: 385–401
- Cabri L J. 1973. New data on phase relations in the Cu-Fe-S system. *Econ Geol*, 68: 443–454
- Campbell I H, Naldrett A J. 1979. The influence of silicate:sulfide ratios on the geochemistry of magmatic sulfides. *Econ Geol*, 74: 1503–1506
- Campbell I H, Griffiths R W. 1990. Implications of mantle plume structure for the evolution of flood basalts. *Earth Planet Sci Lett*, 99: 79–93
- Campbell I H. 2005. Large igneous provinces and the mantle plume hypothesis. *Elements*, 1: 265–269
- Campbell I H, Kerr A C. 2007. The Great Plume Debate: Testing the plume theory. *Chem Geol*, 241: 149–152
- Candela P A, Holland H D. 1984. The partitioning of copper and

- molybdenum between silicate melts and aqueous fluids. *Geochim Cosmochim Acta*, 48: 373–380
- Cao Y, Wang C Y, Wei B. 2019. Magma oxygen fugacity of Permian to Triassic Ni-Cu sulfide-bearing mafic-ultramafic intrusions in the central Asian orogenic belt, North China. *J Asian Earth Sci*, 173: 250–262
- Cao Y, Wang C Y, Wei B. 2020. Magma oxygen fugacity of mafic-ultramafic intrusions in convergent margin settings: Insights for the role of magma oxidation states on magmatic Ni-Cu sulfide mineralization. *Am Mineral*, 105: 1841–1856
- Cao Y, Good D, Linnen R, et al. 2021. Genesis of the low sulfide-high-grade PGE mineralization in the W Horizon, Coldwell Complex, Canada: Quantitative modeling for PGE reef-style mineralization in syn-magmatic sills. *Miner Depos*, 56: 1151–1176
- Casquet C, Galindo C, Tornos F, et al. 2001. The Aguablanca Cu-Ni ore deposit (Extremadura, Spain), a case of synorogenic orthomagmatic mineralization: Age and isotope composition of magmas (Sr, Nd) and ore (S). *Ore Geol Rev*, 18: 237–250
- Cawthorn R G. 1999. Platinum-group element mineralization in the Bushveld Complex—A critical reassessment of geochemical models. *S Afr J Geol*, 102: 268–281
- Chai G, Naldrett A J. 1992a. The Jinchuan ultramafic intrusion: Cumulate of a high-Mg basaltic magma. *J Petrol*, 33: 277–303
- Chai G, Naldrett A J. 1992b. Characteristics of Ni-Cu-PGE mineralization and genesis of the Jinchuan Deposit, Northwest China. *Econ Geol*, 87: 1475–1495
- Chen C, Förster M W, Shcheka S S, et al. 2025. Sulfide-rich continental roots at cratonic margins formed by carbonated melts. *Nature*, 637: 615–621
- Chen H, Savage P S, Teng F Z, et al. 2013. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth Planet Sci Lett*, 369–370: 34–42
- Chen L M, Teng F Z, Song X Y, et al. 2018. Magnesium isotopic evidence for chemical disequilibrium among cumulus minerals in layered mafic intrusion. *Earth Planet Sci Lett*, 487: 74–83
- Chen L M, Song X Y, Hu R Z, et al. 2021. Mg-Sr-Nd isotopic insights into petrogenesis of the Xiarihamu mafic-ultramafic intrusion, Northern Tibetan Plateau, China. *J Petrol*, 62: ega113
- Chen S, Sun P, Niu Y, et al. 2022. Molybdenum isotope systematics of lavas from the East Pacific Rise: Constraints on the source of enriched mid-ocean ridge basalt. *Earth Planet Sci Lett*, 578: 117283
- Chen Z, Chen J, Tameh L S, et al. 2022. Heavy copper isotopes in arc-related lavas from cold subduction zones uncover a sub-arc mantle metasomatized by serpentinite-derived sulfate-rich fluids. *J Geophys Res-Solid Earth*, 127: e2022JB024910
- Chen Z, Teng F Z, Stern R J, et al. 2025. Molybdenum isotope evidence for subduction-modified mantle beneath mid-ocean ridges. *Earth Planet Sci Lett*, 658: 119294
- Chi Fru E, Rodríguez N P, Partin C A, et al. 2016. Cu isotopes in marine black shales record the Great Oxidation Event. *Proc Natl Acad Sci USA*, 113: 4941–4946
- Cottrell E, Birner S K, Brounce M, et al. 2021. Oxygen fugacity across tectonic settings. In: Moretti R, Neuville D R, eds. *Geophysical Monograph Series*. Wiley, 33–61
- Cottrell E, Kelley K A. 2011. The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth Planet Sci Lett*, 305: 270–282
- Dare S A S, Barnes S J, Prichard H M, et al. 2014. Mineralogy and geochemistry of Cu-rich ores from the McCreedy East Ni-Cu-PGE deposit (Sudbury, Canada): Implications for the behavior of platinum group and chalcophile elements at the end of crystallization of a sulfide liquid. *Econ Geol*, 109: 343–366
- Dauphas N, Craddock P R, Asimow P D, et al. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth Planet Sci Lett*, 288: 255–267
- Dauphas N, John S G, Rouxel O. 2017. Iron isotope systematics. *Rev Mineral Geochem*, 82: 415–510
- Day J M D, Moynier F, Ishizuka O. 2022. A partial melting control on the Zn isotope composition of basalts. *Geochem Persp Lett*, 23: 11–16
- Debret B, Millet M A, Pons M L, et al. 2016. Isotopic evidence for iron mobility during subduction. *Geology*, 44: 215–218
- Debret B, Bouilhol P, Pons M L, et al. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *J Petrol*, 59: 1145–1166
- Debret B, Garrido C J, Pons M L, et al. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochim Cosmochim Acta*, 296: 210–225
- Ding X, Ripley E M, Shirey S B, et al. 2012. Os, Nd, O and S isotope constraints on country rock contamination in the conduit-related Eagle Cu-Ni-(PGE) deposit, Midcontinent Rift System, Upper Michigan. *Geochim Cosmochim Acta*, 89: 10–30
- Ding X, Ripley E M, Wang W, et al. 2019. Iron isotope fractionation during sulfide liquid segregation and crystallization at the Lengshuiqing Ni-Cu magmatic sulfide deposit, SW China. *Geochim Cosmochim Acta*, 261: 327–341
- Ding X, Ripley E M, Underwood B S, et al. 2021. Behavior of Mg and C-O isotopes during mafic magma-carbonate interaction at the Jinchuan Ni-Cu deposit, North China Craton. *Chem Geol*, 562: 120044
- Donoghue K A, Ripley E M, Li C. 2014. Sulfur isotope and mineralogical studies of Ni-Cu sulfide mineralization in the Bovine Igneous Complex Intrusion, Baraga Basin, Northern Michigan. *Econ Geol*, 109: 325–341
- Doucet L S, Mattielli N, Ionov D A, et al. 2016. Zn isotopic heterogeneity in the mantle: A melting control? *Earth Planet Sci Lett*, 451: 232–240
- Du D H, Wang X L, Yang T, et al. 2017. Origin of heavy Fe isotope compositions in high-silica igneous rocks: A rhyolite perspective. *Geochim Cosmochim Acta*, 218: 58–72
- Duan J, Li C, Qian Z, et al. 2016. Multiple S isotopes, zircon Hf isotopes, whole-rock Sr-Nd isotopes, and spatial variations of PGE tenors in the Jinchuan Ni-Cu-PGE deposit, NW China. *Miner Depos*, 51: 557–574
- Duran C J, Barnes S J, Corkery J T. 2015. Chalcophile and platinum-group element distribution in pyrites from the sulfide-rich pods of the Lac des Iles Pd deposits, Western Ontario, Canada: Implications for post-cumulus re-equilibration of the ore and the use of pyrite compositions in exploration. *J Geochem Explor*, 158: 223–242
- Duran C J, Barnes S J, Corkery J T. 2016. Trace element distribution in primary sulfides and Fe-Ti oxides from the sulfide-rich pods of the Lac des Iles Pd deposits, Western Ontario, Canada: Constraints on processes controlling the composition of the ore and the use of pentlandite compositions in exploration. *J Geochem Explor*, 166: 45–63
- Dutrizac J E. 1976. Reactions in cubanite and chalcopyrite. *Can Mineral*, 14: 172–181
- Ebel D S, Naldrett A J. 1996. Fractional crystallization of sulfide ore liquids at high temperature. *Econ Geol*, 91: 607–621
- Eckstrand O R, Hulbert L J. 2007. Magmatic nickel-copper-platinum group element deposits. In: Goodfellow W D, ed. *Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods*. Geological Association of Canada. 205–222
- Ehrlich S, Butler I, Halicz L, et al. 2004. Experimental study of the copper isotope fractionation between aqueous Cu(II) and covellite, CuS. *Chem Geol*, 209: 259–269
- Ellam R M, Carlson R W, Shirey S B. 1992. Evidence from Re-Os isotopes for plume-lithosphere mixing in Karoo flood basalt genesis. *Nature*, 359: 718–721

- Ernst R E, Jowitt S M. 2013. Large Igneous Provinces (LIPs) and Metallogeny. In: *Tectonics, Metallogeny, and Discovery: The North American Cordillera and Similar Accretionary Settings*. Society of Economic Geologists, volume 17. 17–51
- Fan J J, Wang Q, Ma L, et al. 2022. Extreme Mo isotope variations recorded in high-SiO₂ granites: Insights into magmatic differentiation and melt–fluid interaction. *Geochim Cosmochim Acta*, 334: 241–258
- Fang W, Dai L Q, Zheng Y F, et al. 2022. Basalt Mo isotope evidence for crustal recycling in continental subduction zone. *Geochim Cosmochim Acta*, 334: 273–292
- Fang W, Dai L Q, Zhao Z F. 2023. Molybdenum isotopic heterogeneity for intraplate basalts and its origin. *Chem Geol*, 641: 121784
- Farges F, Linnen R L, Brown G E. 2006. Redox and speciation of tin in hydrous silicate glasses: A comparison with Nb, Ta, Mo and W. *Canadian Miner*, 44: 795–810
- Farquhar J, Wing B A, McKeegan K D, et al. 2002. Mass-independent sulfur of inclusions in diamond and sulfur recycling on early earth. *Science*, 298: 2369–2372
- Fiorentini M L, Beresford S W. 2008. Role of volatiles and metasomatized subcontinental lithospheric mantle in the genesis of magmatic Ni-Cu-PGE mineralization: Insights from *in situ* H, Li, B analyses of hydromagmatic phases from the Valmaggia ultramafic pipe, Ivrea-Verbano Zone (NW Italy). *Terra Nova*, 20: 333–340
- Fiorentini M L, Bekker A, Rouxel O, et al. 2012. Multiple sulfur and iron isotope composition of magmatic Ni-Cu-(PGE) sulfide mineralization from Eastern Botswana. *Econ Geol*, 107: 105–116
- Foden J, Sossi P A, Wawryk C M. 2015. Fe isotopes and the contrasting petrogenesis of A-, I- and S-type granite. *Lithos*, 212–215: 32–44
- Freyer H, Vils F, Willbold M, et al. 2015. Molybdenum mobility and isotopic fractionation during subduction at the Mariana arc. *Earth Planet Sci Lett*, 432: 176–186
- Gao J F, Zhou M F. 2013. Generation and evolution of siliceous high magnesium basaltic magmas in the formation of the Permian Huangshandong intrusion (Xinjiang, NW China). *Lithos*, 162–163: 128–139
- Gaschnig R M, Reinhard C T, Planavsky N J, et al. 2017. The molybdenum isotope system as a tracer of slab input in subduction zones: An example from Martinique, Lesser Antilles Arc. *Geochim Geophys Geosyst*, 18: 4674–4689
- Goh S W, Buckley A N, Lamb R N, et al. 2006. The oxidation states of copper and iron in mineral sulfides, and the oxides formed on initial exposure of chalcopyrite and bornite to air. *Geochim Cosmochim Acta*, 70: 2210–2228
- Good D J, Cabri L J, Ames D E. 2017. PGM Facies variations for Cu-PGE deposits in the Coldwell Alkaline Complex, Ontario, Canada. *Ore Geol Rev*, 90: 748–771
- Good D J, Lightfoot P C. 2019. Significance of the metasomatized lithospheric mantle in the formation of early basalts and Cu-platinum group element sulfide mineralization in the Coldwell Complex, Midcontinent Rift, Canada. *Can J Earth Sci*, 56: 693–714
- Greaney A T, Rudnick R L, Helz R T, et al. 2017. The behavior of chalcophile elements during magmatic differentiation as observed in Kilauea Iki lava lake, Hawaii. *Geochim Cosmochim Acta*, 210: 71–96
- Han C, Xiao W, Zhao G, et al. 2007. Re-Os dating of the Kalatongke Cu-Ni deposit, Altay Shan, NW China, and resulting geodynamic implications. *Ore Geol Rev*, 32: 452–468
- Hanski E J, Luo Z Y, Oduro H, et al. 2011. The Pechenga Ni-Cu sulfide deposits, Northwestern Russia: A review with new constraints from the feeder dikes. In: *Magmatic Ni-Cu and PGE Deposits: Geology, Geochemistry, and Genesis*. Society of Economic Geologists
- He H L, Chen L M, Song X Y, et al. 2022. Genesis of the Xiarihamu magmatic Ni-Co sulfide deposit in the East Kunlun Orogen, Northern Tibetan Plateau: *In situ* oxygen isotope and geochemical perspectives. *Econ Geol*, 117: 1827–1844
- He Y, Wu H, Ke S, et al. 2017. Iron isotopic compositions of adakitic and non-adakitic granitic magmas: Magma compositional control and subtle residual garnet effect. *Geochim Cosmochim Acta*, 203: 89–102
- Heimann A, Beard B L, Johnson C M. 2008. The role of volatile exsolution and sub-solidus fluid/rock interactions in producing high ⁵⁶Fe/⁵⁴Fe ratios in siliceous igneous rocks. *Geochim Cosmochim Acta*, 72: 4379–4396
- Hiebert R S, Bekker A, Wing B A, et al. 2013. The role of paragneiss assimilation in the origin of the Voisey's Bay Ni-Cu sulfide deposit, Labrador: Multiple S and Fe isotope evidence. *Econ Geol*, 108: 1459–1469
- Hiebert R S, Bekker A, Houllé M G, et al. 2016. Tracing sources of crustal contamination using multiple S and Fe isotopes in the Hart komatiite-associated Ni-Cu-PGE sulfide deposit, Abitibi greenstone belt, Ontario, Canada. *Miner Depos*, 51: 919–935
- Hin R C, Hibbert K E J, Chen S, et al. 2022. The influence of crustal recycling on the molybdenum isotope composition of the Earth's mantle. *Earth Planet Sci Lett*, 595: 117760
- Hofmann A, Bekker A, Dirks P, et al. 2014. Comparing orthomagmatic and hydrothermal mineralization models for komatiite-hosted nickel deposits in Zimbabwe using multiple-sulfur, iron, and nickel isotope data. *Miner Depos*, 49: 75–100
- Hollings P, Hart T, Richardson A, et al. 2007a. Geochemistry of the Mesoproterozoic intrusive rocks of the Nipigon Embayment, northwestern Ontario: Evaluating the earliest phases of rift development. *Can J Earth Sci*, 44: 1087–1110
- Hollings P, Richardson A, Creaser R A, et al. 2007b. Radiogenic isotope characteristics of the Mesoproterozoic intrusive rocks of the Nipigon Embayment, northwestern Ontario. *Can J Earth Sci*, 44: 1111–1129
- Holzheid A, Borisov A, Palme H. 1994. The effect of oxygen fugacity and temperature on solubilities of nickel, cobalt, and molybdenum in silicate melts. *Geochim Cosmochim Acta*, 58: 1975–1981
- Horan M F, Morgan J W, Walker R J, et al. 2001. Re-Os isotopic constraints on magma mixing in the Peridotite Zone of the Stillwater Complex, Montana, USA. *Contrib Miner Petrol*, 141: 446–457
- Hu Y, Teng F Z, Zhang H F, et al. 2015. Metasomatism-induced mantle magnesium isotopic heterogeneity: Evidence from pyroxenites. *Geochim Cosmochim Acta*, 185: 88–111
- Huang F, Zhang Z, Lundstrom C C, et al. 2011. Iron and magnesium isotopic compositions of peridotite xenoliths from Eastern China. *Geochim Cosmochim Acta*, 75: 3318–3334
- Huang J, Ke S, Gao Y, et al. 2015. Magnesium isotopic compositions of altered oceanic basalts and gabbros from IODP site 1256 at the East Pacific Rise. *Lithos*, 231: 53–61
- Huang J, Liu S A, Wörner G, et al. 2016. Copper isotope behavior during extreme magma differentiation and degassing: A case study on Laacher See phonolite tephra (East Eifel, Germany). *Contrib Miner Petrol*, 171: 1–6
- Huang J, Huang F, Wang Z, et al. 2017. Copper isotope fractionation during partial melting and melt percolation in the upper mantle: Evidence from massif peridotites in Ivrea-Verbano Zone, Italian Alps. *Geochim Cosmochim Acta*, 211: 48–63
- Huang K J, Teng F Z, Elsenouy A, et al. 2013. Magnesium isotopic variations in loess: Origins and implications. *Earth Planet Sci Lett*, 374: 60–70
- Hughes H S R, McDonald I, Looke M, et al. 2017. Paradoxical co-existing base metal sulphides in the mantle: The multi-event record preserved in Loch Roag peridotite xenoliths, North Atlantic Craton. *Lithos*, 276: 103–121
- Humphreys D. 2014. The mining industry and the supply of critical

- minerals. In: Gunn G, ed. *Critical Metals Handbook*. Hoboken: John Wiley & Sons
- Jackson-Brown S. 2017. Origin of Cu-PGE-rich sulphide mineralization in the DJ/DB zone of the Turnagain Alaskan-type intrusion, British Columbia. Dissertation for Master's Degree. Vancouver: The University of British Columbia
- Jenkins M C, Mungall J E, Zientek M L, et al. 2021. Origin of the J-M Reef and Lower Banded series, Stillwater Complex, Montana, USA. *Precambrian Res*, 367: 106457
- John S G, Rouxel O J, Craddock P R, et al. 2008. Zinc stable isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth Planet Sci Lett*, 269: 17–28
- Johnson C, Beard B, Weyer S. 2020. *Iron Geochemistry: An Isotopic Perspective*. Cham: Springer International Publishing
- Kellerud G, Yund R A, Moh G H. 1969. Phase relations in the Cu-Fe-S, Cu-Ni-S, and Fe-Ni-S systems. *Econ Geol Monogr*, 4: 323
- Kempton P D, Mathur R, Harmon R S, et al. 2022. Cu-isotope evidence for subduction modification of lithospheric mantle. *Geochem Geophys Geosyst*, 23: e2022GC010436
- Kendall B, Dahl T W, Anbar A D. 2017. The stable isotope geochemistry of molybdenum. *Rev Mineral Geochem*, 82: 683–732
- Kendrick M A, Danyushevsky L V, Falloon T J, et al. 2020. SW Pacific arc and backarc lavas and the role of slab-bend serpentinites in the global halogen cycle. *Earth Planet Sci Lett*, 530: 115921
- Kiseeva E S, Fonseca R O C, Smythe D J. 2017. Chalcophile elements and sulfides in the upper mantle. *Elements*, 13: 111–116
- Klekovkina V V, Gainov R R, Vagizov F G, et al. 2014. Oxidation and magnetic states of chalcopyrite CuFeS_2 : A first principles calculation. *Opt Spectrosc*, 116: 885–888
- König S, Wille M, Voegelin A, et al. 2016. Molybdenum isotope systematics in subduction zones. *Earth Planet Sci Lett*, 447: 95–102
- Konnunaho J P, Hanski E J, Bekker A, et al. 2013. The Archean komatiite-hosted, PGE-bearing Ni-Cu sulfide deposit at Vaara, eastern Finland: Evidence for assimilation of external sulfur and post-depositional desulfurization. *Miner Depos*, 48: 967–989
- Krivolutskaya N, Makvandi S, Gongalsky B, et al. 2021. Chemical characteristics of ore-bearing intrusions and the origin of PGE-Cu-Ni mineralization in the Norilsk Area. *Minerals*, 11: 819
- Lai Y J, Pogge von Strandmann P A E, Dohmen R, et al. 2015. The influence of melt infiltration on the Li and Mg isotopic composition of the Horoman Peridotite Massif. *Geochim Cosmochim Acta*, 164: 318–332
- Lambert D D, Walker R J, Morgan J W, et al. 1994. Re-Os and Sm-Nd isotope geochemistry of the Stillwater Complex, Montana: Implications for the petrogenesis of the J-M Reef. *J Petrol*, 35: 1717–1753
- Leshner C M, Burnham O M. 2001. Multicomponent elemental and isotopic mixing in Ni Cu (PGE) ores at Kambalda, Western Australia. *Canadian Miner*, 39: 421–446
- Leshner C M. 2017. Roles of xenomelts, xenoliths, xenocrysts, xenovolatiles, residues, and skarns in the genesis, transport, and localization of magmatic Fe-Ni-Cu-PGE sulfides and chromite. *Ore Geol Rev*, 90: 465–484
- Li C, Zhang M, Fu P, et al. 2012. The Kalatongke magmatic Ni-Cu deposits in the Central Asian Orogenic Belt, NW China: Product of slab window magmatism? *Miner Depos*, 47: 51–67
- Li C, Zhang Z, Li W, et al. 2015. Geochronology, petrology and Hf-S isotope geochemistry of the newly-discovered Xiarihamu magmatic Ni-Cu sulfide deposit in the Qinghai-Tibet Plateau, western China. *Lithos*, 216–217: 224–240
- Li H Y, Zhao R P, Li J, et al. 2021. Molybdenum isotopes unmask slab dehydration and melting beneath the Mariana arc. *Nat Commun*, 12: 6015
- Li W, Jackson S E, Pearson N J, et al. 2009. The Cu isotopic signature of granites from the Lachlan Fold Belt, SE Australia. *Chem Geol*, 258: 38–49
- Li W, Teng F, Wing B A, et al. 2014. Limited magnesium isotope fractionation during metamorphic dehydration in metapelites from the Onawa contact aureole, Maine. *Geochem Geophys Geosyst*, 15: 408–415
- Li W Y, Teng F Z, Ke S, et al. 2010. Heterogeneous magnesium isotopic composition of the upper continental crust. *Geochim Cosmochim Acta*, 74: 6867–6884
- Li W Y, Teng F Z, Xiao Y. 2018. Magnesium isotope record of fluid metasomatism along the slab-mantle interface in subduction zones. *Geochim Cosmochim Acta*, 237: 312–319
- Lightfoot P C, Hawkesworth C J, Hergt J, et al. 1993. Remobilisation of the continental lithosphere by a mantle plume: Major-, trace-element, and Sr-, Nd-, and Pb-isotope evidence from picritic and tholeiitic lavas of the Noril'sk District, Siberian Trap, Russia. *Contrib Mineral Petrol*, 114: 171–188
- Liu J, Xia Q K, Kuritani T, et al. 2017. Mantle hydration and the role of water in the generation of large igneous provinces. *Nat Commun*, 8: 1824
- Liu S, Wang Z, Yang C, et al. 2020. Mg and Zn isotope evidence for two types of mantle metasomatism and deep recycling of magnesium carbonates. *J Geophys Res-Solid Earth*, 125: e2020JB020684
- Liu S A, Teng F Z, He Y, et al. 2010. Investigation of magnesium isotope fractionation during granite differentiation: Implication for Mg isotopic composition of the continental crust. *Earth Planet Sci Lett*, 297: 646–654
- Liu S A, Teng F Z, Yang W, et al. 2011. High-temperature inter-mineral magnesium isotope fractionation in mantle xenoliths from the North China Craton. *Earth Planet Sci Lett*, 308: 131–140
- Liu S A, Huang J, Liu J, et al. 2015. Copper isotopic composition of the silicate Earth. *Earth Planet Sci Lett*, 427: 95–103
- Liu S A, Wang Z Z, Li S G, et al. 2016. Zinc isotope evidence for a large-scale carbonated mantle beneath eastern China. *Earth Planet Sci Lett*, 444: 169–178
- Liu X, Xiong X, Audétat A, et al. 2014. Partitioning of copper between olivine, orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. *Geochim Cosmochim Acta*, 125: 1–22
- Lu Y, Leshner C M, Deng J. 2019. Geochemistry and genesis of magmatic Ni-Cu-(PGE) and PGE-(Cu)-(Ni) deposits in China. *Ore Geol Rev*, 107: 863–887
- Lusk J, Bray D M. 2002. Phase relations and the electrochemical determination of sulfur fugacity for selected reactions in the Cu-Fe-S and Fe-S systems at 1 bar and temperatures between 185 and 460 °C. *Chem Geol*, 192: 227–248
- Maier W D, Groves D I. 2011. Temporal and spatial controls on the formation of magmatic PGE and Ni-Cu deposits. *Miner Depos*, 46: 841–857
- Maier W D, O'Brien H, Peltonen P, et al. 2017. Platinum-group element contents of Karelian kimberlites: Implications for the PGE budget of the sub-continental lithospheric mantle. *Geochim Cosmochim Acta*, 216: 358–371
- Malitch K N, Latypov R M, Badanina I Y, et al. 2014. Insights into ore genesis of Ni-Cu-PGE sulfide deposits of the Noril'sk Province (Russia): Evidence from copper and sulfur isotopes. *Lithos*, 204: 172–187
- Malitch K N, Belousova E A, Griffin W L, et al. 2020. Oxygen-hafnium-neodymium isotope constraints on the origin of the Talnakh Ultramafic-Mafic Intrusion (Norilsk Province, Russia). *Econ Geol*, 115: 1195–1212
- Manor M J, Scoates J S, Nixon G T, et al. 2016. The Giant Mascot Ni-Cu-PGE deposit, British Columbia: mineralized conduits in a convergent margin tectonic setting. *Econ Geol*, 111: 57–87
- Mao X, Li L, Liu Z, et al. 2019. Multiple magma conduits model of the Jinchuan Ni-Cu-(PGE) deposit, Northwestern China: Constraints from

- the geochemistry of platinum-group elements. *Minerals*, 9: 187
- Marechal C N, Sheppard S M F. 2002. Isotopic fractionation of Cu and Zn between chloride and nitrate solutions and malachite or smithsonite at 30°C and 50°C. *Geochim Cosmochim Acta*, 66: A484
- Marfin A E, Bizimis M, Lightfoot P C, et al. 2024. Constraints on the source of Siberian Trap magmas from Mo isotope evidence. *Geochim Cosmochim Acta*, 375: 106–122
- Markl G, Lahaye Y, Schwinn G. 2006. Copper isotopes as monitors of redox processes in hydrothermal mineralization. *Geochim Cosmochim Acta*, 70: 4215–4228
- Mathur R, Ruiz J, Tittley S, et al. 2005. Cu isotopic fractionation in the supergene environment with and without bacteria. *Geochim Cosmochim Acta*, 69: 5233–5246
- Mavrogenes J A, O'Neill H S C. 1999. The relative effects of pressure, temperature and oxygen fugacity on the solubility of sulfide in mafic magmas. *Geochim Cosmochim Acta*, 63: 1173–1180
- McCoy-West A J, Chowdhury P, Burton K W, et al. 2019. Extensive crustal extraction in Earth's early history inferred from molybdenum isotopes. *Nat Geosci*, 12: 946–951
- Moynier F, Vance D, Fujii T, et al. 2017. The isotope geochemistry of zinc and copper. *Rev Mineral Geochem*, 82: 543–600
- Mudd G M, Weng Z, Jowitt S M, et al. 2013. Quantifying the recoverable resources of by-product metals: The case of cobalt. *Ore Geol Rev*, 55: 87–98
- Mudd G M, Jowitt S M. 2014. A detailed assessment of global nickel resource trends and endowments. *Econ Geol*, 109: 1813–1841
- Mudd G M, Jowitt S M, Werner T T. 2018. Global platinum group element resources, reserves and mining—A critical assessment. *Sci Total Environ*, 622–623: 614–625
- Mungall J E, Brenan J M. 2014. Partitioning of platinum-group elements and Au between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile elements. *Geochim Cosmochim Acta*, 125: 265–289
- Naldrett A J. 1989. *Magmatic Sulfide Deposits*. Oxford: Clarendon Press
- Naldrett A J. 1999. World-class Ni-Cu-PGE deposits: Key factors in their genesis. *Miner Depos*, 34: 227–240
- Naldrett A J, Lightfoot P C. 1999. Ni-Cu-PGE deposits of the Norilsk Region, Siberia: Their formation in conduits for flood basalt volcanism. In: Keays R R, Lesher C M, Lightfoot P C, et al., eds. *Dynamic Processes in Magmatic Ore Deposits and their Application in Mineral Exploration*. Geological Association of Canada, Short Course Notes. 195–249
- Naldrett A J, Asif M, Krstic S, et al. 2000. The composition of mineralization at the Voisey's Bay Ni-Cu sulfide deposit, with special reference to platinum-group elements. *Econ Geol*, 95: 845–865
- Naldrett A J, Wilson A, Kinnaird J, et al. 2009. PGE Tenor and Metal Ratios within and below the Merensky Reef, Bushveld Complex: Implications for its genesis. *J Petrol*, 50: 625–659
- Naldrett A J. 2010. From the mantle to the bank: The life of a Ni-Cu-(PGE) sulfide deposit. *South African J Geol*, 113: 1–32
- Naldrett A J. 2011. Fundamentals of Magmatic Sulfide Deposits. In: *Magmatic Ni-Cu and PGE Deposits: Geology, Geochemistry, and Genesis*. Reviews in Economic Geology, Volume 17. 1–50
- Nebel-Jacobsen Y, Wille M, Ivanic T, et al. 2021. Molybdenum isotope systematics in cumulate rock of the 2.8 Windimurra layered intrusion: A test for igneous differentiation and the composition of the Archean mantle. *Precambrian Res*, 355: 106087
- O'Neill H S C, Eggins S M. 2002. The effect of melt composition on trace element partitioning: An experimental investigation of the activity coefficients of FeO, NiO, CoO, MoO₂ and MoO₃ in silicate melts. *Chem Geol*, 186: 151–181
- Palme H, O'Neil H S C. 2014. Cosmochemical estimates of mantle composition. In: Holland H D, Turekian K K, eds. *Treatise on Geochemistry*. 2nd ed. Elsevier. 1–39
- Peltonen P. 1995. Magma-country rock interaction and the genesis of Ni-Cu deposits in the Vammala Nickel Belt, SW Finland. *Mineral Petrol*, 52: 1–24
- Penniston-Dorland S C, Wing B A, Nex P A M, et al. 2008. Multiple sulfur isotopes reveal a magmatic origin for the Platreef platinum group element deposit, Bushveld Complex, South Africa. *Geology*, 36: 979–982
- Penniston-Dorland S C, Mathez E A, Wing B A, et al. 2012. Multiple sulfur isotope evidence for surface-derived sulfur in the Bushveld Complex. *Earth Planet Sci Lett*, 337–338: 236–242
- Petavratzi E, Gunn G, Kresse C. 2019. Commodity Review: Cobalt. British Geological Survey
- Pickard H, Palk E, Schönbächler M, et al. 2022. The cadmium and zinc isotope compositions of the silicate Earth—Implications for terrestrial volatile accretion. *Geochim Cosmochim Acta*, 338: 165–180
- Piña R, Gervilla F, Ortega L, et al. 2008. Mineralogy and geochemistry of platinum-group elements in the Aguablanca Ni-Cu deposit (SW Spain). *Mineral Petrol*, 92: 259–282
- Piña R, Romeo I, Ortega L, et al. 2010. Origin and emplacement of the Aguablanca magmatic Ni-Cu-(PGE) sulfide deposit, SW Iberia: A multidisciplinary approach. *Geol Soc Am Bull*, 122: 915–925
- Piña R, Gervilla F, Barnes S J, et al. 2012. Distribution of platinum-group and chalcophile elements in the Aguablanca Ni-Cu sulfide deposit (SW Spain): Evidence from a LA-ICP-MS study. *Chem Geol*, 302–303: 61–75
- Piña R, Gervilla F, Barnes S J, et al. 2016. Platinum-group element concentrations in pyrite from the Main Sulfide Zone of the Great Dyke of Zimbabwe. *Miner Depos*, 51: 853–872
- Pogge von Strandmann P A E, Elliott T, Marschall H R, et al. 2011. Variations of Li and Mg isotope ratios in bulk chondrites and mantle xenoliths. *Geochim Cosmochim Acta*, 75: 5247–5268
- Poitrasson F, Halliday A N, Lee D C, et al. 2004. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth Planet Sci Lett*, 223: 253–266
- Poitrasson F, Freydisier R. 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. *Chem Geol*, 222: 132–147
- Pons M L, Debret B, Bouilhol P, et al. 2016. Zinc isotope evidence for sulfate-rich fluid transfer across subduction zones. *Nat Commun*, 7: 13794
- Qu Y R, Liu S A, Wu H, et al. 2022. Tracing carbonate dissolution in subducting sediments by zinc and magnesium isotopes. *Geochim Cosmochim Acta*, 319: 56–72
- Reich M, Simon A C. 2024. Critical minerals. *Annu Rev Earth Planet Sci*, 53: 141
- Righter K, Pando K M, Danielson L, et al. 2010. Partitioning of Mo, P and other siderophile elements (Cu, Ga, Sn, Ni, Co, Cr, Mn, V, and W) between metal and silicate melt as a function of temperature and silicate melt composition. *Earth Planet Sci Lett*, 291: 1–9
- Ripley E M, Brophy J G, Li C. 2002. Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. *Geochim Cosmochim Acta*, 66: 2791–2800
- Ripley E M, Li C. 2003. Sulfur isotope exchange and metal enrichment in the formation of magmatic Cu-Ni-(PGE) deposits. *Econ Geol*, 98: 635–641
- Ripley E M, Li C. 2013. Sulfide saturation in mafic magmas: Is external sulfur required for magmatic Ni-Cu-(PGE) ore genesis? *Econ Geol*, 108: 45–58
- Ripley E M, Dong S, Li C, et al. 2015. Cu isotope variations between conduit and sheet-style Ni-Cu-PGE sulfide mineralization in the Midcontinent Rift System, North America. *Chem Geol*, 414: 59–68
- Robertson J, Ripley E M, Barnes S J, et al. 2015. Sulfur liberation from

- country rocks and incorporation in mafic magmas. *Econ Geol*, 110: 1111–1123
- Rojas-Kolomiets E, Jensen O, Bizimis M, et al. 2023. Serpentine fluids and slab-melting in the Aleutian arc: Evidence from molybdenum isotopes and boron systematics. *Earth Planet Sci Lett*, 603: 117970
- Rooney T O, Konter J G, Finlayson V A, et al. 2022. Constraining the isotopic endmembers contributing to 1.1 Ga Keweenaw large igneous province magmatism. *Contrib Miner Petrol*, 177: 49
- Ruthart R. 2013. Characterization of high-PGE low-sulfur mineralization at the Marathon PGE-Cu deposit, Ontario. Dissertation for Master's Degree. Waterloo: University of Waterloo
- Savage P S, Moynier F, Chen H, et al. 2015. Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation. *Geochem Persp Lett*, 53: 53–64
- Schauble E A. 2004. Applying stable isotope fractionation theory to new systems. *Rev Mineral Geochem*, 55: 65–111
- Schoenberg R, Blanckenburg F V. 2006. Modes of planetary-scale Fe isotope fractionation. *Earth Planet Sci Lett*, 252: 342–359
- Schoneveld L, Barnes S J, Luolavirta K, et al. 2025. Extent and survival of zoned pyroxene within intrusions hosting magmatic sulfides: Implications for zoned pyroxene as a prospectivity indicator. *Miner Depos*, 60: 533–549
- Schuessler J A, Schoenberg R, Behrens H, et al. 2007. The experimental calibration of the iron isotope fractionation factor between pyrrhotite and peralkaline rhyolitic melt. *Geochim Cosmochim Acta*, 71: 417–433
- Schuessler J A, Schoenberg R, Sigmarsson O. 2009. Iron and lithium isotope systematics of the Hekla volcano, Iceland—Evidence for Fe isotope fractionation during magma differentiation. *Chem Geol*, 258: 78–91
- Shahabi Far M, Samson I M, Gagnon J E, et al. 2018. Identifying externally derived sulfur in conduit-type Cu-platinum-group element deposits: The importance of multiple sulfur isotope studies. *Geology*, 46: 235–238
- Shahabi Far M, Samson I M, Gagnon J E, et al. 2019. Evolution of a conduit system at the Marathon PGE-Cu Deposit: Insights from silicate mineral textures and chemistry. *J Petrol*, 60: 1427–1460
- Sharman E R, Penniston-Dorland S C, Kinnaid J A, et al. 2013. Primary origin of marginal Ni-Cu-(PGE) mineralization in layered intrusions: $\Delta^{33}\text{S}$ evidence from the Platreef, Bushveld, South Africa. *Econ Geol*, 108: 365–377
- Sharman E R, Taylor B E, Minarik W G, et al. 2015. Sulfur isotope and trace element data from ore sulfides in the Noranda district (Abitibi, Canada): Implications for volcanogenic massive sulfide deposit genesis. *Miner Depos*, 50: 591–606
- Shen B, Jacobsen B, Lee C T A, et al. 2009. The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation. *Proc Natl Acad Sci USA*, 106: 20652–20657
- Shirey S B, Klewin K W, Berg J H, et al. 1994. Temporal changes in the sources of flood basalts: Isotopic and trace element evidence from the 1100 Ma old Keweenaw Mainainse Point Formation, Ontario, Canada. *Geochim Cosmochim Acta*, 58: 4475–4490
- Shirey S B. 1997. Re-Os isotopic compositions of Midcontinent rift system picrites: Implications for plume—Lithosphere interaction and enriched mantle sources. *Can J Earth Sci*, 34: 489–503
- Shu Z T, Liu S A, Prelević D, et al. 2022. Recycling of carbonates into the deep mantle beneath central Balkan Peninsula: Mg-Zn isotope evidence. *Lithos*, 432–433: 106899
- Smith J M, Ripley E M, Li C, et al. 2021. Cu and Ni isotope variations of country rock-hosted massive sulfides located near midcontinent rift intrusions. *Econ Geol*, 117: 195–211
- Smith J M, Ripley E M, Li C, et al. 2022. Magmatic origin for the massive sulfide ores in the sedimentary country rocks of mafic-ultramafic intrusions in the Midcontinent Rift System. *Miner Depos*, 57: 1189–1210
- Sossi P A, Foden J D, Halverson G P. 2012. Redox-controlled iron isotope fractionation during magmatic differentiation: An example from the Red Hill intrusion, S. Tasmania. *Contrib Miner Petrol*, 164: 757–772
- Sossi P A, Nebel O, Foden J. 2016. Iron isotope systematics in planetary reservoirs. *Earth Planet Sci Lett*, 452: 295–308
- Sossi P A, Nebel O, O'Neill H S C, et al. 2018. Zinc isotope composition of the Earth and its behaviour during planetary accretion. *Chem Geol*, 477: 73–84
- Su B X, Teng F Z, Hu Y, et al. 2015. Iron and magnesium isotope fractionation in oceanic lithosphere and sub-arc mantle: Perspectives from ophiolites. *Earth Planet Sci Lett*, 430: 523–532
- Sun P, Niu Y, Chen S, et al. 2023. Copper isotope fractionation during magma differentiation: Evidence from lavas on the East Pacific Rise at 10°30'N. *Geochim Cosmochim Acta*, 356: 93–104
- Sun Y, Teng F Z, Pang K N, et al. 2021. Multistage mantle metasomatism deciphered by Mg-Sr-Nd-Pb isotopes in the Leucite Hills lamproites. *Contrib Miner Petrol*, 176: 45
- Tang D, Qin K, Su B, et al. 2020. Sulfur and copper isotopic signatures of chalcopyrite at Kalatongke and Baishiquan: Insights into the origin of magmatic Ni-Cu sulfide deposits. *Geochim Cosmochim Acta*, 275: 209–228
- Tang D, Qin K, Evans N J, et al. 2024. Sulfide copper-iron isotopic fractionation during formation of the Kalatongke magmatic Cu-Ni sulfide deposit in the Central Asian Orogenic Belt. *Geochem Geophys Geosyst*, 25: e2023GC011406
- Tang D, Lazarov M, Wang D, et al. 2025. Response of Fe-Ni-Cu isotope systematics to sulfide liquid oxygen content: Implications for magmatic sulfide Co enrichment in orogenic settings. *Geochim Cosmochim Acta*, 390: 1–23
- Tang Q, Bao J, Dang Y, et al. 2018. Mg-Sr-Nd isotopic constraints on the genesis of the giant Jinchuan Ni-Cu-(PGE) sulfide deposit, NW China. *Earth Planet Sci Lett*, 502: 221–230
- Tang Q, Bao J, Zhang Y, et al. 2024. Copper isotope fractionation during magmatic evolution in a convergent tectonic setting: Constraints from sulfide Cu-S isotopes and whole-rock PGE of the Xiarihamu Ni-Cu sulfide deposit. *Chem Geol*, 668: 122348
- Tang Q, Zhang Y, Li L, et al. 2025. Fe and Mg isotopes as tracers of the mantle sources and ore-forming processes of the Xiarihamu magmatic Ni-Cu sulfide deposit. *Lithos*, 508–509: 108095
- Telus M, Dauphas N, Moynier F, et al. 2012. Iron, zinc, magnesium and uranium isotopic fractionation during continental crust differentiation: The tale from migmatites, granitoids, and pegmatites. *Geochim Cosmochim Acta*, 97: 247–265
- Teng F, Yang W, Rudnick R L, et al. 2013a. Heterogeneous magnesium isotopic composition of the lower continental crust: A xenolith perspective. *Geochem Geophys Geosyst*, 14: 3844–3856
- Teng F Z, Wadhwa M, Helz R T. 2007. Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth Planet Sci Lett*, 261: 84–92
- Teng F Z, Dauphas N, Helz R T. 2008. Iron isotope fractionation during magmatic differentiation in Kilauea Iki Lava Lake. *Science*, 320: 1620–1622
- Teng F Z, Li W Y, Ke S, et al. 2010. Magnesium isotopic composition of the Earth and chondrites. *Geochim Cosmochim Acta*, 74: 4150–4166
- Teng F Z, Dauphas N, Huang S, et al. 2013b. Iron isotopic systematics of oceanic basalts. *Geochim Cosmochim Acta*, 107: 12–26
- Teng F Z. 2017. Magnesium isotope geochemistry. *Rev Mineral Geochem*, 82: 219–287
- Tian H C, Zhang C, Teng F Z, et al. 2020. Diffusion-driven extreme Mg and Fe isotope fractionation in Panzhihua ilmenite: Implications for the origin of mafic intrusion. *Geochim Cosmochim Acta*, 278: 361–375
- Toutain J P, Sonke J, Munoz M, et al. 2008. Evidence for Zn isotopic

- fractionation at Merapi volcano. *Chem Geol*, 253: 74–82
- Tsujimura T, Kitakaze A. 2004. New phase relations in the Cu-Fe-S system at 800°C; constraint of fractional crystallization of a sulfide liquid. *N Jb Mineral Monatsh*, 2004(10): 433–444
- Villalobos-Orchard J, Freymuth H, O'Driscoll B, et al. 2020. Molybdenum isotope ratios in Izu arc basalts: The control of subduction zone fluids on compositional variations in arc volcanic systems. *Geochim Cosmochim Acta*, 288: 68–82
- Voegelin A R, Pettke T, Greber N D, et al. 2014. Magma differentiation fractionates Mo isotope ratios: Evidence from the Kos Plateau Tuff (Aegean Arc). *Lithos*, 190–191: 440–448
- Von Gruenewaldt G, Sharpe M R, Hatton C J. 1985. The Bushveld Complex; introduction and review. *Econ Geol*, 80: 803–812
- Wang P, Niu Y, Sun P, et al. 2021. Iron isotope compositions of coexisting sulfide and silicate minerals in sudbury-type ores from the Jinchuan Ni-Cu sulfide deposit: A perspective on possible core-mantle iron isotope fractionation. *Minerals*, 11: 464
- Wang S J, Teng F Z, Williams H M, et al. 2012. Magnesium isotopic variations in cratonic eclogites: Origins and implications. *Earth Planet Sci Lett*, 359–360: 219–226
- Wang S J, Teng F Z, Bea F. 2015a. Magnesium isotopic systematics of metapelite in the deep crust and implications for granite petrogenesis. *Geochim Persp Lett*, 1: 75–83
- Wang S J, Teng F Z, Rudnick R L, et al. 2015b. The behavior of magnesium isotopes in low-grade metamorphosed mudrocks. *Geochim Cosmochim Acta*, 165: 435–448
- Wang S J, Teng F Z, Scott J M. 2016. Tracing the origin of continental HIMU-like intraplate volcanism using magnesium isotope systematics. *Geochim Cosmochim Acta*, 185: 78–87
- Wang Y, Li C, Li W, et al. 2022. Geology and geochemistry of the Tulaergen conduit-style magmatic Ni-Cu sulfide deposit in the Central Asian Orogenic Belt, northwestern China. *Miner Depos*, 57: 319–342
- Wang Z Z, Liu S A, Ke S, et al. 2016. Magnesium isotopic heterogeneity across the cratonic lithosphere in eastern China and its origins. *Earth Planet Sci Lett*, 451: 77–88
- Wang Z Z, Liu S A, Liu J, et al. 2017. Zinc isotope fractionation during mantle melting and constraints on the Zn isotope composition of Earth's upper mantle. *Geochim Cosmochim Acta*, 198: 151–167
- Weyer S, Anbar A, Brey G, et al. 2005. Iron isotope fractionation during planetary differentiation. *Earth Planet Sci Lett*, 240: 251–264
- Weyer S, Ionov D A. 2007. Partial melting and melt percolation in the mantle: The message from Fe isotopes. *Earth Planet Sci Lett*, 259: 119–133
- Weyer S. 2008. What Drives Iron Isotope Fractionation in Magma? *Science*, 320: 1600–1601
- Willbold M, Hibbert K, Lai Y J, et al. 2016. High-precision mass-dependent molybdenum isotope variations in magmatic rocks determined by double-spike MC-ICP-MS. *Geostand Geoanal Res*, 40: 389–403
- Willbold M, Elliott T. 2017. Molybdenum isotope variations in magmatic rocks. *Chem Geol*, 449: 253–268
- Willbold M, Messling N. 2023. Systematic across-arc variations of molybdenum isotopes in a fluid-dominated subduction zone system. *Geochim Geophys Geosyst*, 24: e2023GC011007
- Wille M, Nebel O, Pettke T, et al. 2018. Molybdenum isotope variations in calc-alkaline lavas from the Banda arc, Indonesia: Assessing the effect of crystal fractionation in creating isotopically heavy continental crust. *Chem Geol*, 485: 1–13
- Williams H, Peslier A, Mccammon C, et al. 2005. Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity. *Earth Planet Sci Lett*, 235: 435–452
- Wimpenny J, Yin Q Z, Tollstrup D, et al. 2014. Using Mg isotope ratios to trace Cenozoic weathering changes: A case study from the Chinese Loess Plateau. *Chem Geol*, 376: 31–43
- Woodruff L G, Schulz K J, Nicholson S W, et al. 2020. Mineral deposits of the Mesoproterozoic Midcontinent Rift system in the Lake Superior region—A space and time classification. *Ore Geol Rev*, 126: 103716
- Xia Y, Li S, Huang F. 2017. Iron and Zinc isotope fractionation during magmatism in the continental crust: Evidence from bimodal volcanic rocks from Hailar basin, NE China. *Geochim Cosmochim Acta*, 213: 35–46
- Xia Y, Kiseeva E S, Wade J, et al. 2019. The effect of core segregation on the Cu and Zn isotope composition of the silicate Moon. *Geochim Persp Lett*, 12: 12–17
- Xiao Y, Teng F Z, Zhang H F, et al. 2013. Large magnesium isotope fractionation in peridotite xenoliths from eastern North China craton: Product of melt-rock interaction. *Geochim Cosmochim Acta*, 115: 241–261
- Xu L J, He Y, Wang S J, et al. 2017. Iron isotope fractionation during crustal anatexis: Constraints from migmatites from the Dabie orogen, Central China. *Lithos*, 284–285: 171–179
- Yamaguchi K E, Johnson C M, Beard B L, et al. 2005. Biogeochemical cycling of iron in the Archean-Paleoproterozoic Earth: Constraints from iron isotope variations in sedimentary rocks from the Kaapvaal and Pilbara Cratons. *Chem Geol*, 218: 135–169
- Yang J, Siebert C, Barling J, et al. 2015. Absence of molybdenum isotope fractionation during magmatic differentiation at Hekla volcano, Iceland. *Geochim Cosmochim Acta*, 162: 126–136
- Yang J, Barling J, Siebert C, et al. 2017. The molybdenum isotopic compositions of I-, S- and A-type granitic suites. *Geochim Cosmochim Acta*, 205: 168–186
- Yang W, Teng F Z, Zhang H F. 2009. Chondritic magnesium isotopic composition of the terrestrial mantle: A case study of peridotite xenoliths from the North China craton. *Earth Planet Sci Lett*, 288: 475–482
- Yang W, Teng F Z, Zhang H F, et al. 2012. Magnesium isotopic systematics of continental basalts from the North China Craton: Implications for tracing subducted carbonate in the mantle. *Chem Geol*, 328: 185–194
- Yang W, Teng F Z, Li W Y, et al. 2016. Magnesium isotopic composition of the deep continental crust. *Am Mineral*, 101: 243–252
- Yao Z, Qin K, Mungall J E. 2018. Tectonic controls on Ni and Cu contents of primary mantle-derived magmas for the formation of magmatic sulfide deposits. *Am Mineral*, 103: 1545–1567
- Yu S Y, Xu Y G, Huang K J, et al. 2021. Magnesium isotope constraints on contributions of recycled oceanic crust and lithospheric mantle to generation of intraplate basalts in a big mantle wedge. *Lithos*, 398–399: 106327
- Yu Y, Huang X L, Chung S L, et al. 2022. Molybdenum isotopic constraint from Java on slab inputs to subduction zone magmatism. *Geochim Cosmochim Acta*, 332: 1–18
- Zambardi T, Lundstrom C C, Li X X, et al. 2014. Fe and Si isotope variations at Cedar Butte volcano; insight into magmatic differentiation. *Earth Planet Sci Lett*, 405: 169–179
- Zhang H L, Cottrell E, Solheid P A, et al. 2018. Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state of iron in MORB. *Chem Geol*, 479: 166–175
- Zhang L, Li J, Zhang Y, et al. 2024. Molybdenum isotopic fractionation in the Panzhihua mafic layered intrusion in the Emeishan large igneous province, southwest China. *Am Mineral*, 109: 628–632
- Zhang M, O'Reilly S Y, Wang K L, et al. 2008. Flood basalts and metallogeny: The lithospheric mantle connection. *Earth-Sci Rev*, 86: 145–174
- Zhang W Q, Liu C Z, Johan Lissenberg C, et al. 2024. Post-cumulus control on copper isotopic fractionation during oceanic intra-crustal magmatic differentiation. *Geochim Cosmochim Acta*, 369: 35–50

- Zhao X, Zhang H, Zhu X, et al. 2010. Iron isotope variations in spinel peridotite xenoliths from North China Craton: Implications for mantle metasomatism. *Contrib Miner Petrol*, 160: 1–14
- Zhao X, Zhang H, Zhu X, et al. 2012. Iron isotope evidence for multistage melt–peridotite interactions in the lithospheric mantle of eastern China. *Chem Geol*, 292–293: 127–139
- Zhao Y, Xue C, Liu S A, et al. 2017. Copper isotope fractionation during sulfide-magma differentiation in the Tulaergen magmatic Ni-Cu deposit, NW China. *Lithos*, 286–287: 206–215
- Zhao Y, Xue C, Symons D T A, et al. 2018. Temporal variations in the mantle source beneath the Eastern Tianshan nickel belt and implications for Ni-Cu mineralization potential. *Lithos*, 314–315: 597–616
- Zhao Y, Xue C, Liu S A, et al. 2019. Redox reactions control Cu and Fe isotope fractionation in a magmatic Ni-Cu mineralization system. *Geochim Cosmochim Acta*, 249: 42–58
- Zhao Y, Liu S A, Xue C, et al. 2022a. Copper isotope fractionation in magmatic Ni-Cu mineralization systems associated with the variation of oxygen fugacity in silicate magmas. *Geochim Cosmochim Acta*, 338: 250–263
- Zhao Y, Liu S A, Xue C, et al. 2022b. Copper isotope evidence for a Cu-rich mantle source of the world-class Jinchuan magmatic Ni-Cu deposit. *Am Mineral*, 107: 673–683
- Zhao Y, Liu S A, Xue C, et al. 2024. Metasomatized mantle facilitates the genesis of magmatic nickel-copper sulfide deposits in orogenic belts: A copper isotope perspective. *Geochim Cosmochim Acta*, 366: 128–140
- Zhou M F, Michael Lesher C, Yang Z, et al. 2004. Geochemistry and petrogenesis of 270 Ma Ni-Cu-(PGE) sulfide-bearing mafic intrusions in the Huangshan district, Eastern Xinjiang, Northwest China: Implications for the tectonic evolution of the Central Asian orogenic belt. *Chem Geol*, 209: 233–257
- Zhu X K, O’Nions R K, Guo Y, et al. 2000. Determination of natural Cu-isotope variation by plasma-source mass spectrometry: Implications for use as geochemical tracers. *Chem Geol*, 163: 139–149
- Zhu X K, Guo Y, Williams R J P, et al. 2002. Mass fractionation processes of transition metal isotopes. *Earth Planet Sci Lett*, 200: 47–62
- Zou Z, Wang Z, Li M, et al. 2019. Copper isotope variations during magmatic migration in the mantle: Insights from mantle pyroxenites in Balmuccia Peridotite Massif. *J Geophys Res-Solid Earth*, 124: 11130–11149
- Zou Z, Wang Z, Xu Y G, et al. 2024. Contrasting Cu isotopes in mid-ocean ridge basalts and lower oceanic crust: Insights into the oceanic crustal magma plumbing systems. *Earth Planet Sci Lett*, 627: 118563

(责任编辑: 王瑞)