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同位素技术应用于示踪矿山环境污染研究进展

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摘要: 随着采矿等矿业活动在全球范围内的大面积进行,人们对矿山及其周边环境问题的关注度持续增加。电感耦合多接收等离子体质谱仪(MC-ICP-MS)的出现推动了同位素的地球化学研究,也使得同位素示踪技术被广泛应用于探究矿山环境中的各类问题。为强调同位素示踪技术在复杂矿山环境中应用的重要性及其能解决科学问题的多样性,本文调研和分析了截至 2022 年 7 月国内外学者公开发表的借助同位素示踪技术测试、分析矿山水文环境中的地球化学过程及污染物来源/影响等方面的论文及其数据,研究区涵盖二十多个国家、四十多个地区。通过总结发现:水体氢、氧同位素示踪技术是矿山水源解析、水力联系研究及酸性矿山废水(AMD)源识别的有效工具;硫酸盐硫、氧同位素示踪技术为研究矿山环境中的硫酸盐来源、AMD 酸化过程及污染、细菌硫酸盐的还原作用与元素迁移转化等提供重要支持;重金属(铅、镉、锌、汞等)同位素示踪技术是探究矿山及附近环境中的金属污染来源及不同来源贡献率的有效手段。大量研究表明,虽然同位素技术在解析矿山环境污染物来源和特征污染物迁移转化机制以及揭示矿山水文地球化学过程等方面起到重要作用,但目前的大部分研究局限于应用单一/少数同位素对矿山环境介质进行短时间示踪研究。因此,未来需进一步发展多同位素示踪技术,并对矿山环境中存在的各类问题进行长期、持续地监测调查,提出有效的污染防治新方法。

关键词: 矿山环境; 同位素; MC-ICP-MS; 酸化过程; 重金属

要点:

(1) MC-ICP-MS 的出现推动了同位素在环境、化学行为等方面的研究。

(2) 同位素示踪技术是矿山污染物源解析和环境地球化学过程研究的重要手段。

(3) 多同位素联合示踪为识别复杂矿山环境问题和研究其过程机制提供多维度支撑。

中图分类号: X820.4 **文献标识码:** A

矿产资源既是自然资源的重要组成部分,也是社会经济发展的重要物质基础与保证[1],开发利用矿产资源作为建设、发展的必然要求,是许多发展中国家的重要经济支柱[2]。有学者估计,大约有 0.2%的地球陆地面积(3.7 万 km^2)被用于矿业活动[3],而由采矿、冶炼等人为活动所引发的矿山及其周边区域环境变化与污染问题,也引起越来越多学者的关注。有关矿山环境的研究自 20 世纪 70 年代起已步入初期阶段[4],目前,国内外已有众多学者采用多种方法(地球化学分析法、多元统计分析、同位素示踪技术等),对矿区环境污染[5-7]、元素的迁移转化[8-9]等地球化学过程及其影响因素展开研究。如 Cao 等[5]采用因子分析与层次分析法等方法,对湖南省衡阳市甘溪镇铅锌矿区及周边土壤污

收稿日期: 2022-03-10; **修回日期:** 2022-07-19; **接受日期:** 2022-08-20
基金项目: 国家重点研发计划项目(2018YFC1801705); 国家自然科学基金委员会—贵州省人民政府喀斯特科学研究中心项目(U1612442); 贵州省人才基地建设项目(RCJD2018-21)
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染进行溯源与评估;Zhang 等[10]通过地球化学分析/建模与统计分析,发现水岩反应及人为的煤矿开采活动是影响山西省娘子关泉集水区岩溶水化学的主要因素。

然而,由于矿山环境具有复杂性,物质与元素的迁移转化等地球化学过程受到诸多因素的影响,同位素示踪技术相较于其他传统方法而言,是评估与量化矿山环境问题更为有效的手段。Urey[11]于 1947 年首次进行稳定同位素的地球化学研究。其后的几十年间,研究者们陆续对碳(C)、氢(H)、氧(O)、氮(N)等质量较小元素的传统稳定同位素进行分析测试[12]。二十世纪末,随着电感耦合多接收等离子体质谱仪(MC-ICP-MS)的出现,人们对非传统稳定同位素的研究进入了一个新的阶段[13],该技术为人们准确地了解与认识这些元素的环境、化学行为等提供了重要手段。近十年来,已有上百篇文献就同位素示踪技术在探究矿山水来源/联系[14-16]、酸性矿山废水的排放[17-18]、金属富集[19-21]等方面问题进行报道。

本文调研了截至 2022 年 7 月公开发表的应用同位素示踪法研究矿山环境污染来源、过程等方面的文献,研究区涉及二十多个国家、四十多个地区,系统地总结了基于同位素特征数值,在矿山环境中通过同位素示踪技术对矿山水环境、硫酸盐及酸性矿山废水来源与成因、金属污染等方面开展的各类研究。旨在突出同位素示踪技术在复杂的矿山环境中应用的重要性及其能解决科学问题的多样性,并对该领域今后的发展提供建议。

1　水体氢氧同位素示踪技术在矿山环境中的应用

采矿活动产生的废弃物往往被堆放于地表或倾倒在地下[22],通过地表径流、淋滤等过程对矿山水环境造成污染[23],另外,地下水位以下的采矿活动为地下含水层及酸性矿山废水(AMD)提供通道[24],加快了污染物的迁移与扩散。因此,查明矿山水的补给来源与不同区域间的水力联系,对于了解矿山的水文循环过程及污染源识别等具有重要意义。

天然水环境中含有氢氧稳定同位素[14],来源相同的水体中氢氧稳定同位素特征具有相似的线性关系,而不同位置水体(如大气降水、河流/湖泊水体与地下水等)中的氢氧稳定同位素组成的变化规律往往不同,水的蒸发则会引起同位素分馏[25]。因此,可以通过分析水中氢氧稳定同位素特征对区域内水体来源/混合、水力联系及是否存在蒸发作用等进行探究[15,26]。此前已有较多学者[8,14-18,27-42]在该方面开展研究工作。查君珍等[27]采集安徽省淮南市 4 个采煤沉陷区积水、地下水、河水及大气降水等共计 59 个水样,使用液态水和水汽同位素分析仪测试氢氧稳定同位素($\delta^{18}O$ 和 δD),发现沉陷区积水氢氧稳定同位素值与大气降水及浅层地下水相近,因此这二者为沉陷区积水水源,其中大气降水是其主要来源,与此前张磊等[32]的研究结果相同。另外,沉陷区积水可能同时受降水、蒸发作用、补给水源等的影响。与河水相比,沉陷区积水沉陷时间越长,积水同位素值的变化越大[27]。李小倩等[6]借助液态水同位素分析仪测定广西合山煤矿矿井水体中的氢氧同位素,指出合山矿区水体补给来源以夏季降雨为主,且均受到明显蒸发作用的影响,地下水和地表水间存在密切的水力联系。此外,有研究发现,将水体氢氧稳定同位素与锶同位素相结合,通过构建数学模型,可识别与量化矿山水体的混合情况[33-34]。由此可见,利用水体氢氧同位素示踪发现矿山水主要来源于大气降水,且补给受发生在过去不同气候条件下当时的大气降水同位素组成、沉陷时间及蒸发作用所引起的同位素分馏等因素共同影响;分析矿山不同水体间氢氧同位素的线性特征,能够探究其间的相互关系。

同时,水体氢氧同位素示踪也是识别酸性矿山废水(AMD)来源与污染的有效手段[7,17-18,40]。Marco 等[7]指出矿区位于阿普安阿尔卑斯山脉南部(意大利托斯卡纳地区)的 Baccatoio 溪流集水区,由于岩溶系统的淡水受到黄铁矿等硫化矿物的影响,从而形成 AMD,暴雨期的渗透雨水促进了 AMD 流出;隧道中的酸性滴落物表现出氢氧稳定同位素值的位移,考虑是由于黄铁矿氧化与铁水解造成的。

2　硫酸盐硫氧同位素示踪技术在矿山环境中的应用

2.1　示踪硫酸盐来源及迁移转化等过程

来源不同的硫酸盐硫同位素特征存在差异[43],可被用于识别硫酸盐的来源及其与地下水间的地球化学行为,氧同位素同样是示踪硫酸盐来源及其与地下水含水层的混合过程的有效工具[6,8,35,41,44-65]。Haubrich 等[47]和 Junghans 等[48]分别在不同时期研究测试了德国多金属硫化物矿床 Freiberg 矿山酸性废水中的硫酸盐硫、氧同位素,Haubrich 等[47]发现

大气降水和硫化物的氧化是其硫酸盐的主要来源,其中低品位矿石更容易受到大气降水的淋滤影响从而释放 SO_4^{2-};Junghans 等[48]同样指出硫化物氧化是矿井水中 SO_4^{2-} 的主要来源,且矿山酸性废水在矿脉水位最深可达处约有 50%(±10%)的硫来自硫化物氧化,但同时地下水及土壤渗水中的 SO_4^{2-} 也是其硫酸盐的主要来源。后来 Tichomirowa 等[49]利用硫酸盐硫氧同位素及锶同位素($^{87}Sr/^{86}Sr$)探究这座矿山在十年间(1997—2008 年)硫酸盐的来源,除了获得与 Haubrich 等[47]和 Junghans 等[48]相同的结果外(地下水中的硫酸盐及当地矿石硫化物氧化产生的硫酸盐),还存在从该地区采矿和工业留下的矿渣等废物中释放出的硫酸盐。上述研究表明,在以硫化物矿床为主的矿山中,硫化物矿物氧化是其环境中硫酸盐的主要来源。

除硫化物矿物氧化外,石膏溶解也是矿山环境中硫酸盐的主要来源之一,另外可能还伴有大气降雨/酸沉降、地下水渗透、淋滤等过程。此前报道表明,土壤和废弃物淋滤作用及大气硫酸沉降是波兰 Holy Cross 山区 Wisniówka Mala(主要由石英岩与石英砂岩组成)矿坑湖水中的 SO_4^{2-} 的重要来源[50]。任坤等[51]通过对广西八步地下河流域中硫氧同位素进行分析,发现石膏溶解、硫化物氧化与大气降雨是地表水与地下水中硫酸盐的主要来源;这三种来源在枯水期对流域硫酸盐的贡献率分别为 43%、39%和 18%,与丰水期没有显著差异。同样地,Roesler 等[41]指出,蒙大拿州巴特的世界级多金属矿床(以菱锰矿为主,另外还包括石英、闪锌矿及少量黄铁矿等)西营地矿山硫酸盐部分也来源于硬石膏溶解,同时还有黄铁矿的氧化物与之混合。Zhang 等[52]发现贵州碳酸盐岩地区杉树林铅锌矿山下游河流水体中的硫同样来自石膏溶解,另外还来自尾矿溶解、大气降雨等。

同时,人为采矿活动的扰动与排放也是矿山环境中硫酸盐的重要来源。2013 年 Miao 等[53]发现美国亚利桑那州 Monument Valley 铀矿区地下水中存在两种不同的硫酸盐来源:采矿过程释放其中 74%的硫酸盐(平均值 427mg/L);另外 26%的硫酸盐则来自硫化矿物氧化(平均值 147mg/L),其成分主要源自研究区域含水层水源主要补给区裸露基岩中的硫化物矿物氧化,而在与尾矿相关的部分,氧化作用则相对较小。后来,2015 年 Killingsworth 等[54]对北美密西西比河中的硫酸盐来源进行探究,认为其中自然来源的硫酸盐占硫酸盐总量的 25%,其余 75%均为人为来源,而认为来源中因煤矿开采产生的硫酸盐占比为 47%。

综上所述,矿山环境中的硫酸盐大都来源于以下五方面:①硫化物矿物氧化;②石膏溶解;③大气降雨、酸沉降;④地下水渗透、淋滤;⑤采矿等人为活动。现将其总结于图 1。

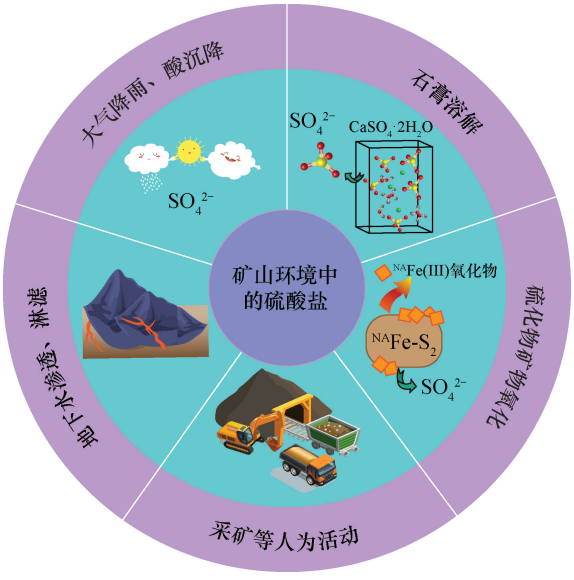

图 1　矿山环境中硫酸盐的主要来源

Fig. 1　Main sources of sulfate in the mine environment

2.2　示踪矿山废水酸化及元素迁移等地球化学过程

2.2.1　研究酸性矿山废水来源及对周边环境的影响

矿山开采活动产生的酸性矿山废水(AMD)是现在所面临的严峻的环境污染问题[66],具有较难预防且治理成本高昂的特点,会对矿区及周边环境产生严重破坏[67-69]。硫酸盐硫、氧同位素是示踪采矿活动对水环境污染的有效方法[64],可用于研究 AMD 的成因及其对区域地下水和含水层的影响[6,70-71],且可以反映水体受污染程度、范围以及硫化物氧化的地球化学过程等[72]。有学者证实,相较于普通水质测定或水体稳定同位素,采用硫酸盐稳定同位素示踪 AMD 污染更具灵敏性[31]。

诸多研究表明,矿物氧化与地下水混合是造成水体酸化进而形成 AMD、污染地下水的主要原因[58]。早期报道认为,AMD 在渗入地下含水层时会得到一定的缓冲,但也可能对含水层产生污染[59]。如曾祥颖等[73]利用 MAT 252 质谱仪测定贵州省独山县独山半坡锑矿的$^{34}S/^{32}S$,证实辉锑矿和硫铁矿的氧化是导致研究区域内水体酸化的原因。

此外,产生的 AMD 会对矿区含水层造成污染。Gammons 等[30-31]在两个不同时期对美国蒙大拿 Great Falls-Lewistown 废弃煤矿区 Madison 酸性矿山废水(AMD)中的硫酸盐硫、氧同位素($\delta^{18}O$、$\delta^{34}S$)进行测试,发现研究区域 AMD 来自黄铁矿氧化,同时其含水层可能存在 AMD 串层污染现象。近期的一项研究基于地下水化学与同位素数据分析,建立了中国四川省与云贵高原之间的黄铁矿水文地球化学概念模型[74],指出黄铁矿氧化产生的 AMD 促进了金属溶解,且碳酸盐岩对 AMD 具有缓冲处理能力;利用硫酸盐硫同位素与水体氢氧稳定同位素构建的质量平衡模型,发现通过岩溶裂隙/管道渗透的 AMD 是地下水污染的主要原因。

同时,AMD 也是导致矿山及周边地区中河流、湖泊污染的重要端元。Butler[75]研究表明美国加利福尼亚州奥克兰 Leona Heights 硫磺矿区 Leona 河中的硫酸根与金属是由硫化物氧化产生的 AMD 进入河流,从而导致的结果。同样地,Vengosh 等[76]通过测试硫、碳及锶同位素组成特征发现,美国西弗吉尼亚州 Mud 河流域中有一些河流受到山顶开矿采煤活动的影响,并提出这些同位素可示踪矿区对河流产生的污染等影响。

2.2.2　揭示矿区水环境细菌硫酸盐的还原作用

硫化物矿物的氧化与石膏溶解等过程几乎不会使硫同位素分馏[31,77],而细菌硫酸盐的还原作用会使硫酸盐硫、氧同位素变重[50],进而发生分馏。故一些研究者[21,35,41,56,59,78-79]采用硫酸盐硫、氧同位素示踪研究区域内是否存在硫酸盐细菌的还原作用。

此前有研究指出,美国蒙大拿州 Butte 斑岩铜矿存在硫酸盐细菌的还原作用,这影响了淹没矿井中 AMD 的同位素分布以及地球化学过程[79]。Migaszewski 等[35]研究发现波兰中南部 Holy Cross 山区 Podwisniówka 矿山中的矿山废水同样受到硫酸盐细菌还原作用的影响,另外还存在黄铁矿氧化(受细菌驱动作用)及硫酸盐风化等。由此可见,AMD 特征受硫酸盐细菌的还原作用影响,因此,有学者就是否可以利用细菌硫酸盐的还原作用修复酸性矿山水体展开了研究。Knoller 等[56]指出德国 Lusatia 亚褐煤区采矿湖 ML111 的硫酸盐硫、氧同位素及硫同位素数据反映出硫酸盐细菌的还原作用对湖泊以西含水层的流动方向具有重要影响,同时还可以改善水质;而在湖泊以东的 Dump 含水层中,硫酸盐还原菌则没有那么广泛的影响;此外,在湖泊 ML111 的水柱中,细菌硫酸盐的还原作用仅存在于占湖泊体积不足 1%的永滞带里,因此借助硫酸盐还原菌来修复高酸度采矿湖这一办法的可行性目前还很低。

另外,矿山环境中金属元素的富集与细菌硫酸盐的还原作用也密切相关。有研究报道,当耐酸型硫酸盐还原细菌存在于厌氧且有足量有机碳的 AMD(pH ≈4)环境中时,由于细菌硫酸盐的还原作用,一些微量金属会衰减或被去除,由此提出可以通过向自然酸性系统中添加有机碳基质来提高微生物呼吸作用,进而导致金属衰减[78]。并且,硫酸盐还原菌也可作用于溶解金属进而产生金属硫化物矿物沉淀,这些沉淀聚集在矿山地下通道中,导致进入地下水体中的有毒金属浓度降低[41]。但在降低水体中金属浓度的同时,细菌硫酸盐与金属作用产生的沉淀可能会导致沉积物中的金属浓度升高。如汪福顺等[21]研究表明,贵阳阿哈湖的微生物硫酸盐还原大多发生在表层沉积物中,这种不同于以往研究的分布特征可能是造成重金属元素在表层沉积物中富集的原因。

2.2.3　分析矿区元素迁移转化过程

在矿区进行采矿等活动导致环境的生物地球化学过程与某些元素的迁移转化密切相关,硫酸盐硫、氧同位素能够示踪环境中的地球化学过程[8],分析矿区元素的迁移转化过程及影响因素。有研究指出,矿山环境中受 AMD 影响的河流中的单位离子通量远高于未受影响的河流[80],且因 AMD 具有较高的硫酸盐含量,当其进入湖泊时,可通过提高湖泊中硫酸盐还原型细菌的活性,进而使 Hg^{2+} 甲基化,从而具有更高的毒性和生物可利用度。因此,提出可以通过控制 AMD 流入湖泊来降低汞对矿山及周边生态环境的影响[81]。Zhang 等[52]对贵州省杉树林碳酸盐岩地区铅锌矿区展开研究,发现下游地表河流悬浮物的吸附与解吸作用会对水体与沉积物间的重金属(铅、锌、铜)行为产生影响,且与环境 pH 有关,而碳酸盐岩对重金属的迁移则具有抑制作用。同时,金属循环与 pH 值的调节可能依赖于生物地球化学循环[82],离子交换、矿物相反应(金属氢氧化物的还原溶解)与氧化还原等过程均会影响微量元素的迁移率[83]。

此外,有学者将硫同位素特征与地下水流动模型、反应性输运模型相结合,分析西澳大利亚 Perth 盆地附近的 6 处水井(一处用于含水层的储存与回采(ASR),另外 5 处为监测井;所有水井含水层矿物岩性中均存在黄铁矿)含水层中的地下水流动与多

组分迁移转化等水文地球化学过程[46]。指出在含水层储存过程中存在黄铁矿氧化行为,除一处监测井外,其余水井含水层中的溶质浓度大都保持不变;而在回采期间,因地下水回流,溶质浓度回归初值。该研究强调了同位素特征数值与建模方法联用在复杂环境中探究地下水流动与溶质元素迁移转化等过程的可行性。

3　重金属同位素示踪技术在矿山环境中的应用

随着金属矿山的开采与冶炼,由此导致的重金属污染问题也日益严重,环境中重金属成分含量在过去的几十年间大量增加[84],这些重金属元素广泛地存在于土壤、河流、大气等环境介质中[85-86],继而进入动植物、人类等生命体内,威胁生命健康并对生态系统造成严重破坏[87-88]。因此,重金属污染防控与治理刻不容缓。

对环境中已存在的重金属污染溯源是防控的关键[19,89]。此前已有较多学者利用重金属同位素示踪技术探究采矿活动导致的铅[90-99]、镉[96,100-105]等重金属污染来源并量化其对周边环境、生物的影响,取得了较好的成果。同时,金属汞污染及其危害也逐渐引起人们的重视。近十年来,不少研究者采用汞同位素对矿山生态系统中的汞进行源解析,进而对其环境影响作出评价[106-118]。另外,锌同位素示踪技术同样可用于识别环境介质中的锌来源[105,119-121],但与铅、镉、汞三者相比,其应用研究较少。

3.1　铅同位素

铅(Pb)同位素示踪是判断当地甚至全球铅污染来源和途径的有效手段。自然环境中,铅有 4 种稳定的同位素:^{206}Pb、^{207}Pb、^{208}Pb 和^{204}Pb,其中,因^{206}Pb、^{207}Pb、^{208}Pb 与^{204}Pb 相比具有丰度随时间增加的特性[122],故通常使用其比值作为示踪剂[98],该项分析技术已被广泛应用于追踪和量化各种环境中的铅污染[123]。

目前已有较多研究表明,矿山及其周边环境中的铅主要来源于采矿、冶炼活动排放的酸性矿山废水等废弃物,并且会对河流造成较大区域/较远距离的污染。早期报道指出,美国加利福尼亚州 West Shasta 铜矿区排放的矿山废水是 Sacramento 河流上游 60km 内铅的主要来源,其他河段内的铅则主要来自汽油燃烧(60%)与 Sierra Nevadan 铜矿山的废水排放(40%)[90]。Bird 等[91]发现 Maritsa 河流泥沙量的 42%~63%来自受采矿活动直接影响的支流;且支流的泥沙在下游 200km 甚至更远的河段内均有分布。Lin 等[92]采集了中国福建省九龙江表层沉积物样品,基于其铅同位素组成特征与潜在来源分析表明,九龙江表层沉积物中的铅主要来自母岩(34%)、煤的燃烧(34%)以及福建铅锌矿床(32%)。同时,有学者认为人为矿业活动产生的铅污染也是扰动湖泊生态系统的重要端元。Monna 等[93]对法国 Cévennes 山脉国家公园河中捕捞的野生褐鳟鱼组织中的铅同位素组成特征进行测试,结果表明它们生活在受研究区域内多金属硫化物矿山采矿与工业排放废物污染的环境中,这影响到鱼类的生长发育。

另外,通过铅同位素示踪还可解释矿区及附近土壤、植物等环境介质中的铅污染来源。Tang 等[94]根据铅同位素示踪与二元混合模型,发现中国北京市密云水库上游历史金矿区的土壤和沉积物中的铅污染主要来自采矿活动。揭示了历史采矿活动对周边环境的持续污染,实现了铅同位素示踪和多元统计分析联用对采矿活动产生污染的定量研究。张怡悦[95]也利用铅同位素指纹和贝叶斯模型,识别与定量分析了该水库上游金/铁矿产密集区域受污染土壤及植物中的污染来源,发现土壤与植物根部的铅污染主要来源于尾砂,贡献率分别为 43%~75%和 32%~50%。此外,采矿活动产生的粉尘可能会通过污染大气进而危害土壤与植物生长发育。如 Wen 等[96]证实人为采矿和冶炼过程中排放的灰尘沉积是造成中国云南省兰坪县金顶铅锌矿区周围土壤中的铅和镉污染的主要缘由,铅锌矿开采活动产生的粉尘污染了距矿山约 5 公里范围内土壤的大部分区域。同样地,Wang 等[97]认为中国东部铜陵铜铁金矿区植物生长环境中的大气与土壤均遭受柴油燃烧与采矿冶炼活动排放的铅污染,而后通过叶面吸收等途径进入植物体内,致使铅富集。

3.2　镉同位素

从人为来源释放到环境中的镉会影响污染区的镉同位素组成[104],例如人为的采矿、冶炼等活动会导致镉同位素的分馏,因此矿区及周围土壤、沉积物等环境中的重金属污染可借助镉同位素示踪技术进行溯源研究[122]。

有研究指出,镉稳定同位素示踪可用于识别地质和水文条件较复杂的矿山环境河流中的镉污染源识别及迁移转化等过程[100]。Gao 等[102]为测定中国北江镉污染情况,在沿江不同样点采集河流沉积

物样品,发现 2 个位于铅锌矿附近的沉积物样品镉同位素值($^{114/110}$Cd)明显高于其他沉积物样品(与标准溶液相比);后来同样利用镉同位素示踪技术,指出北河(珠江水系)沉积物中镉污染来源于上游采矿活动及该地区其他工业生产的输入[103]。值得注意的是,在使用镉同位素示踪分析矿山流域镉污染时,需结合环境中可能导致镉同位素分馏的因素,进行综合考量评估。Zhang 等[104]对中国云南省流经兰坪县金顶铅锌矿附近被污染河流(碧江)沉积物样品与河岸土壤样品测试发现,不论是在自然还是模拟实验条件下,表生风化均会导致明显的镉同位素分馏。因此,在利用镉同位素比值对河流(水体或沉积物等)镉污染进行源识别与源解析时,应考虑由于环境影响可能出现的镉同位素分馏的情况。结合 Wen 等[96]之前的研究结果,综合考虑,铅锌矿污染区河流沉积物中镉的一个重要来源是洪水期进入碧江的大气粉尘和微细土壤颗粒。

3.3　汞同位素

与铅、镉同位素一样,汞同位素也被广泛应用于示踪汞污染源及其对环境影响等方面[124]。有学者利用汞同位素示踪技术对矿山环境中的汞污染进行源识别与源解析,发现周边流域及地下水中的汞污染大部分来源于矿业活动,并对流域生态系统造成影响,另外,可采用二元混合模型计算不同汞污染来源对矿区流域汞浓度的贡献率[106]。Foucher 等[107]采集斯洛文尼亚 Idrija 汞矿区附近的 Idrijca 河、Soca/Isonzo 河与 Trieste 湾的沉积物样品,测定样品与周围不同汞矿的汞同位素比值,并利用二元混合模型进行计算,发现两条河流以及 Trieste 湾北部的汞大都来源于 Idrijca 地区的汞矿,该地区的汞矿对 Trieste 湾的汞的贡献率从北部(>90%)到南部(40%~50%)逐渐下降。Gehrke 等[108-109]发现 San Francisco 海湾的汞污染来自 New Almaden 和 New Idria 汞矿区的冶炼废料以及矿业活动产生的汞;其中有部分汞随径流从 New Idria 汞矿区流出后进入下游 San Carlos 河流,并影响河流生态系统[110]。同时,矿山环境中的 Hg 同位素组成与 Hg 物种的迁移、分布密切相关,Hg 物种或物种转化可能使汞同位素特征发生变化[111]。

人为采矿、冶炼等活动造成的汞污染同样会影响土壤、大气等环境介质,进而危害农作物的生长发育。Yin 等[112-114]研究表明中国西南部贵州省万山汞矿区土壤汞污染主要来源于采矿冶炼废渣;基于二元混合模型,提出汞煅烧(导致汞同位素分馏)、未经氧化的汞矿石与自然地质是矿区河流大水溪沉积物中汞污染的来源,且主要汞污染来源随距离变化;水稻植株中的汞污染来自大气汞(23%±4%)和土壤汞的混合。Li 等[115]同样根据二元混合模型更具体地指出该矿区大气汞对水稻的无机汞和总汞的贡献率分别为 31%±16%和 17%±11%。宋正城[116]对该矿区土壤汞污染来源进行量化溯源后发现,其中有 92%的汞污染来自矿区的采矿活动(汞矿石 78%,冶炼废料 15%),这一结果与 Yin 等[112-114]此前的研究结论一致。

3.4　锌同位素

早期研究发现,Zn 和 Cd 同位素示踪技术均可用于环境 Zn、Cd 污染溯源[105]。目前已有一些研究者利用锌同位素示踪,识别矿山河流、大气等环境中的锌污染来源。如 Borrok 等[119]在美国科罗拉多州 Animas 河上游采用锌和铁同位素对河水中的重金属进行源识别,指出河流中的锌来源于多金属硫化物矿山废弃物淋滤,铁由富铁地下水补给。Weiss 等[120]研究芬兰三个变质泥炭:Hietajärvi(背景值)、Outokumpu(靠近采矿场地)、Harjavalta(靠近冶炼厂),发现其中靠近采矿场地的 Outokumpu 与冶炼厂附近的 Harjavalta 二者岩心顶部的锌同位素比值(^{66}Zn/^{64}Zn)与其锌浓度相关,指出锌同位素可用来示踪人类活动等不同的大气锌来源。

同时,环境中锌的迁移转化等过程可能会影响其同位素特征。Aranda 等[121]采集该州 Rocky 山脉 Waldor 银铅矿区地表水与土壤孔隙水样品,分析发现地表水样品均具有近似的锌同位素特征,而土壤孔隙水样品的锌同位素值(δ^{66}Zn)则变化较大。该学者认为矿区锌具有相同的最终来源,但土壤层的吸附作用、有机质络合、沉淀及植物吸收等可能会对孔隙水中的锌同位素产生影响。

3.5　其他金属同位素

除前文中提到 Vengosh 等[76]认为锶同位素等可用于示踪美国西弗吉尼亚州 Mud 河流域(Appalachian 盆地)因煤矿区废石导致的河流污染外,还有一些学者也利用锶同位素对矿山污染来源及影响因素展开研究。在 Vengosh 等[76]研究的同一时期,Chapman 等[125-126]也将锶同位素用于示踪 Appalachian 盆地煤、油、气开采区废弃矿井排水调查,指出 AMD 是该开采区矿井排水的主要来源,并提出锶同位素可作为污染源识别的有效示踪剂,用于识别复杂环境中水岩交互作用的过程。Jeon[99]通过锶同位素与铅同位素示踪韩国 Dongjin 废弃

Au-Ag-Cu矿山 AMD 污染河流的地球化学过程,发现影响河流中重金属与主要离子迁移的有两个主要因素,即铁铝氢化物的吸附沉淀作用及未被污染水体的稀释。

同样,锑、铁同位素组成特征也是矿山环境中污染源解析、表征元素地球化学过程的有效工具。因自然来源的锑同位素组成不同于人为来源,因此锑同位素可被用于区分环境中 Sb 的自然来源与人类来源[127]。Resongles 等[128]指出法国南部锑矿区地表 Orb 河流上游和 Gardon 河流 Sb 同位素均发生显著变化,考虑可能与 Sb 从矿山、沉积物向水体迁移途中的地球化学过程有关。此前,Herbert 等[129]在瑞典 Kristineberg 矿山通过铁同位素特征示踪研究矿山中的铁循环过程,结果表明尾矿水和盐酸羟胺萃取固相间存在较大的铁同位素分馏,考虑是水相铁平衡、微生物氧化以及 $Fe(OH)_3$ 沉淀等因素的影响。并提出铁同位素可用于识别矿山中的铁循环过程及防控酸性矿山废水。另外,多同位素示踪技术在矿山中的应用也引起了人们的关注。Talavera 等[130]在墨西哥 Taxco 银矿区示踪矿区利用多同位素(H、O、S、Sr、Pb)示踪水-岩-尾矿相互作用以及硫和有毒金属来源,指出多同位素技术是矿区复杂水-岩-尾矿相互作用以及污染来源的重要工具。

4　存在问题和发展方向

近年来,国内外众多学者采用同位素示踪技术对矿山环境中的各类问题开展了一系列研究,并在矿山水体源解析、硫酸盐溯源与 AMD 成因分析、重金属源识别及污染评价等方面取得一些进展和成果:①利用水体氢氧稳定同位素示踪发现矿山水主要来源于大气降水,同时受时间、蒸发作用等多种因素的影响;另外,氢氧稳定同位素示踪技术也是查明矿山水间的水力联系以及对 AMD 溯源的有效工具。②通过硫酸盐硫、氧同位素示踪研究表明矿山环境中硫酸盐来源于矿物硫化物的氧化、石膏溶解、人为采矿活动、大气降水和地下水渗透等,其中前三个因素是其主要来源;且 AMD 主要由矿物氧化与地下水混合产生,也与硫酸盐细菌还原作用有关。同时,矿区金属富集与 AMD 及硫酸盐细菌的还原作用密切相关,因此硫酸盐硫氧同位素也能够揭示矿区元素的迁移转化过程。③采用重金属同位素示踪技术不仅可以对环境中的重金属污染进行溯源,还能够查明不同污染源的贡献率,为重金属污染防治指明方向;与传统方法相比,在矿区环境中应用同位素示踪技术能够得到不同端元的贡献率,并对其作出定量分析,在矿山环境污染源识别、变迁机制及探究矿山水文地球化学过程等方面具有重要作用。

然而,当前国内外关于同位素示踪技术在矿山环境中的应用研究还存在许多局限性与不足,建议今后加强以下三方面的研究。

(1)以往的研究时间尺度较短、时间不连续,缺少对矿山同位素研究领域的全面认识。在未来的工作中,可采用该技术对矿山环境问题进行长期监测。

(2)大多学者在研究中往往使用单一同位素或少数几个同位素进行示踪,今后可发展多同位素联用示踪技术,同时对矿山环境进行多方面研究。

(3)在同位素示踪矿山环境中污染物来源的基础上,提出切实可行的污染防治新思路。

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A Review of Research Progress of Isotope Technology in Tracing Pollution Process in the Mine Environment

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HIGHLIGHTS

(1) The advent of MC-ICP-MS has promoted the study of isotopes in the environment, their chemical behavior, and so on.

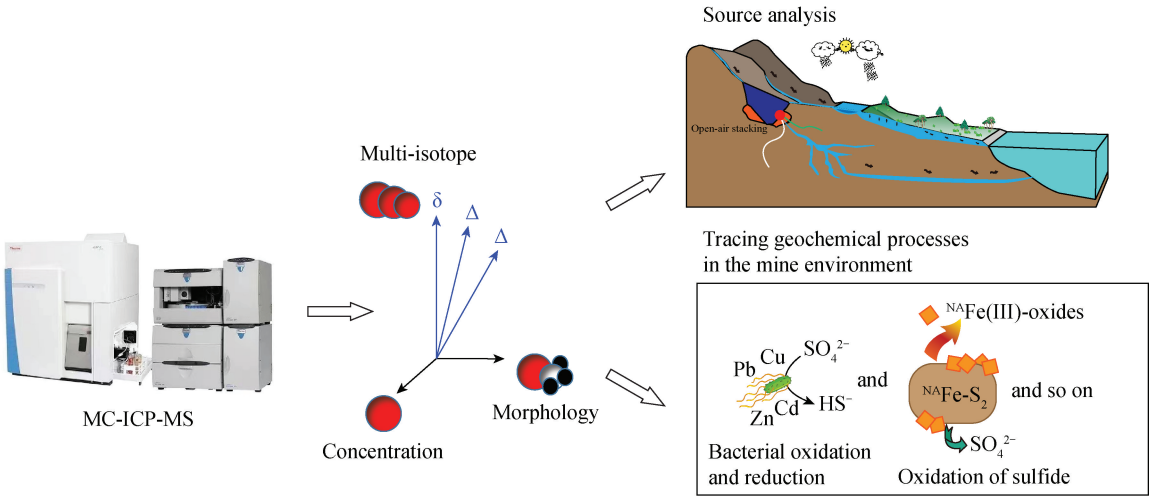
(2) Isotope tracing technology is an important tool for source analysis of mine contaminants and studying environmental geochemical processes.

(3) Combined multi-isotope tracing provides multidimensional support for identifying complex mine environmental problems and studying their process mechanisms.

ABSTRACT

BACKGROUND: With mining activities taking place on a global scale, the concern for environmental issues within and around mines continues to increase. The advent of multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) has promoted the geochemical study of isotopes and has led to the widespread use of isotope tracing techniques to investigate various issues in the mining environment.

OBJECTIVES: To systematically summarize the various types of studies currently conducted on the application of isotope tracing technology in mining environments, with the aim of highlighting the importance of the application of isotope tracing technology in complex mining environments and the diversity of scientific problems it can solve.



METHODS: Data published by scholars at home and abroad by July 2022 has been collected and compiled on testing and analyzing the supply source/connection of mine water body, sulfate/carbonate source and the cause of acid mine wastewater (AMD), migration and transformation of mining elements, different sources and contribution rates of heavy metal pollution with the help of isotope tracer technology. The study area covers more than 40 regions in 20 countries.

RESULTS: It is found that hydrogen and oxygen isotope tracing techniques in water bodies are effective tools for mine water source analysis, hydraulic linkage studies and AMD source identification. Sulfate sulfur and oxygen isotope tracing techniques provide important support for the study of sulfate sources in mine environments, AMD acidification processes and pollution, bacterial sulfate reduction and elemental migration transformation. Heavy metal isotope (Pb, Cd, Zn, Hg isotopes) tracing technology is an effective way to investigate the sources of metal pollution in mines and nearby environments and the contribution of different sources.

CONCLUSIONS: Although isotope techniques play an important role in resolving the sources of environmental pollutants in mines and the mechanisms of migration and transformation of characteristic pollutants and revealing the hydrogeochemical processes in mines, most of the current studies are limited to the application of single/few isotopes for short time tracing studies of environmental media in mines. Therefore, further development of multi-isotope tracing technology is needed in the future, as well as long-term and continuous monitoring and investigation of various problems in the mine environment. New and effective methods for pollution prevention and control are also proposed.

KEY WORDS: mine environment; isotopes; MC-ICP-MS; acidification process; heavy metals