骆正骅, 李超, 赖正,等. 树脂柱串联法分离地质样品中 Sr-Nd-U[J]. 岩矿测试,2023,42(1):102-113.
LUO Zhenghua, LI Chao, LAI Zheng, et al. Separation of Sr, Nd, and U from Geological Samples Using Tandem Resin Column[J]. Rock and Mineral Analysis,2023,42(1):102-113. 【DOI: 10.15898/j.cnki.11-2131/td.202204060072】

树脂柱串联法分离地质样品中 Sr-Nd-U

骆正骅[1], 李超[1,2*], 赖正[1], 王晨羽[3], 郭玉龙[1], 段知非[1], 徐娟[1,2], 杨守业[1,2]
(1. 海洋地质国家重点实验室(同济大学), 上海 200092;
2. 同济大学海洋与地球科学学院, 上海 200092;
3. GFZ German Research Centre for Geosciences, Earth Surface Geochemistry, Telegrafenberg, Postdam 14473, Germany)

摘要: Sr、Nd、U 等同位素体系被广泛应用于地球表生过程中年代测定及物源示踪等研究,高效地分离这些同位素体系,对于推广这些同位素方法的应用具有重要现实意义。若要同时分析地质样品中 Sr、Nd、U 三种元素的同位素,现有方法往往需要消解两份样品,一份用于 Sr-Nd 而另一份用于 U 的分离提纯。这种方法不但增加了样品用量,而且需要多次蒸干溶液转换介质,既延长了分离流程也增加了样品被污染的风险。为了提高样品利用率和分析效率,本文通过将树脂柱串联改进了分离流程,提出一种仅需消解一份样品,便可同时提取 Sr、Nd、U 三种元素的新方法。本方法中 Sr 的分离采用 Sr 特效树脂,包含 Nd 在内的稀土元素(REE)的分离采用 AG50W-X8 树脂,U 的分离采用 UTEVA 特效树脂。实验中将三种树脂柱串联,采用 3mol/L 硝酸淋洗液淋洗,同步进行平衡树脂、上样、洗杂志,避免了蒸干操作。分离后的淋出液使用电感耦合等离子体质谱仪(ICP-MS)测试元素含量。结果表明:U 的回收率接近 99.9%,Sr 的回收率超过 90%,Nd 的回收率超过 80%;同时三种树脂柱串联的分离流程,主要基体元素(K、Ca、Na、Ba、Fe、Rb 等)的去除率均超过 99%,降低了对 Sr、Nd、U 高精度同位素分析的干扰;REE 中的 Sm 则可以通过后续使用 Ln 树脂等进一步去除。此外,本文还交换了 Sr 特效树脂和 UTEVA 树脂的位置,比对两种不同串联顺序对分离结果的影响,结果表明两种树脂柱串联顺序对目标元素的分离并无显著影响。使用该方法可以有效地实现 Sr、Nd、U 的分离,在减少操作步骤的同时节省约一半的样品用量,提高了同位素分析效率。

关键词: Sr; Nd; U; 串联树脂; 柱回收率; 同位素分离; 电感耦合等离子体质谱法

要点:

(1) 将树脂柱串联,采用相同淋洗液同步进行平衡树脂、上样、洗杂质,避免了蒸干操作。

(2) UTEVA 特效树脂和 Sr 特效树脂的上下串联顺序,对 Sr、Nd、U 元素的回收率并无显著影响。

(3) 多次重复回收利用树脂可能导致树脂柱失效,影响对目标元素的吸附能力,需要及时更换新树脂。

中图分类号: O657.63 **文献标识码:** A

铀系核素是自然界三大放射性衰变体系之一,其衰变长链中不同半衰期的核素,适用于不同时间尺度地质过程的研究[1]。近年来随着测试技术的发展,铀系同位素已被广泛应用于海洋[2]、河流[3]、黄土[4]、冰川[5]等沉积物的表生地球化学研究,为沉积物搬运、流域风化和土壤侵蚀等过程提供了有效的定量约束。除了铀同位素体系,$^{87}Sr/^{86}Sr$ 和 $^{143}Nd/^{144}Nd$ 同位素(简称 Sr-Nd 同位素)也是常见的两种同位素组合,由于它们在地表的独特行为[6-7],而成为岩石定年[8-9]、化学风化评估[10]和沉

收稿日期: 2022-04-06; **修回日期:** 2022-05-17; **接受日期:** 2022-05-23
基金项目: 国家自然科学基金项目(42076063, 41991324); 上海市自然科学基金项目(20ZR1460400, 21590712700)

第一作者: 骆正骅,硕士研究生,海洋地球化学专业。E-mail: luozh@tongji.edu.cn。
通信作者: 李超,博士,副教授,从事边缘海沉积地球化学研究。E-mail: cli@tongji.edu.cn。

积物来源示踪[11-13]等研究的有效手段。鉴于单一同位素指标的多解性和不确定性,近些年多同位素体系联合示踪的方法逐渐兴起,这对同位素测试分析提出了更高的要求。以$^{234}U/^{238}U$和 Sr-Nd 同位素为例,这些同位素指标的结合可以从多角度更全面地指示沉积物在地表的循环过程,有助于深化对沉积物“从源到汇”过程的理解[14-15]。

使用离子交换树脂对目标元素分离提纯是最常见的同位素富集分离方法,其原理是使用不同浓度种类的淋洗介质,改变树脂柱对元素的吸附能力来分离提纯目标元素。前人已经利用不同离子交换树脂以及不同淋洗流程建立了许多 Sr-Nd 同位素[16-18]以及 U 同位素[19-21]的独立分离方法,而对于同步分离多种元素的联合分离方法,目前主要集中于分离 Sr、Nd、Pb、Hf 等元素[22-24]。但对 Sr、Nd、U 元素的分离,大多数学者仍然是消解两份样品,一份用于分离 Sr-Nd 而另一份用于分离 U[25];或者是消解一份样品,中间通过蒸干样品转换介质,从而进行两次过柱分离[26]。前者增加了样品用量,不利于对珍贵样品(如大洋沉积物、极地钻孔等)的研究;后者增加了额外的蒸干操作,不仅耗费时间也增加了样品损失和受污染的风险。

本文在前人研究提出的分离方案基础上[27-29],尝试建立一种 Sr-Nd-U 联合分离提取的新方案。通过将三种树脂柱串联组合,用相同酸介质来平衡树脂联合过柱,随后将树脂柱分开,对三种树脂柱分别淋洗得到 Sr、Nd、U 三种元素。该方法仅需溶解一份样品,避免了多次蒸干溶液转换介质的步骤,在减少样品用量的同时提高了三种元素分离提纯的效率。

1　实验部分

1.1　仪器及工作条件

为了防止污染,本实验中所有样品的化学处理过程均在千级洁净度的超净分析室内进行,元素分离纯化所用的通风橱为百级工作台。分离流程所得各馏分,取 1mL 稀释约 10 倍后使用 Agilent 7900 电感耦合等离子体质谱仪(ICP-MS,美国 Agilent 公司)测试主量和微量元素含量,用于监控流程中元素回收率情况。仪器基本工作条件为:射频功率 1600W,等离子气流速 15L/min,载气流速 0.86L/min,辅助气流速 0.21L/min,采样深度 8mm,雾化器为微流石英雾化器,采样时间 200ms/mass。所有实验均在海洋地质国家重点实验室(同济大学)完成。

1.2　实验材料与主要试剂

Sr-Nd 同位素的分离使用 Sr 特效树脂(50~100μm,法国 Triskem 公司)以及 AG50W-X8 阳离子交换树脂(100~200 目,美国 Bio-Rad 公司);U 同位素的分离使用 UTEVA 特效树脂(100~150μm,法国 Triskem 公司)。本实验均采用 7mm 内径聚丙烯材质的树脂柱进行装填,Sr 特效树脂的装填高度为 1.6cm,UTEVA 特效树脂的装填高度为 4.2cm,AG50W-X8 树脂的装填高度为 5.6cm。

为有效监控样品的回收率,本实验使用玄武岩标准物质 BCR-2(美国地质调查局,USGS)为实验样品,该标准物质是较常用的岩石 Sr、Nd、U 同位素测定标准。

所用浓硝酸、浓氢氟酸和浓盐酸(优纯级,国药集团)在使用前均通过 Savillex 的酸蒸馏装置进行两次亚沸蒸馏纯化。实验用水经 Millipore 净化系统纯化,出水的电阻率不高于 18.2MΩ · cm。

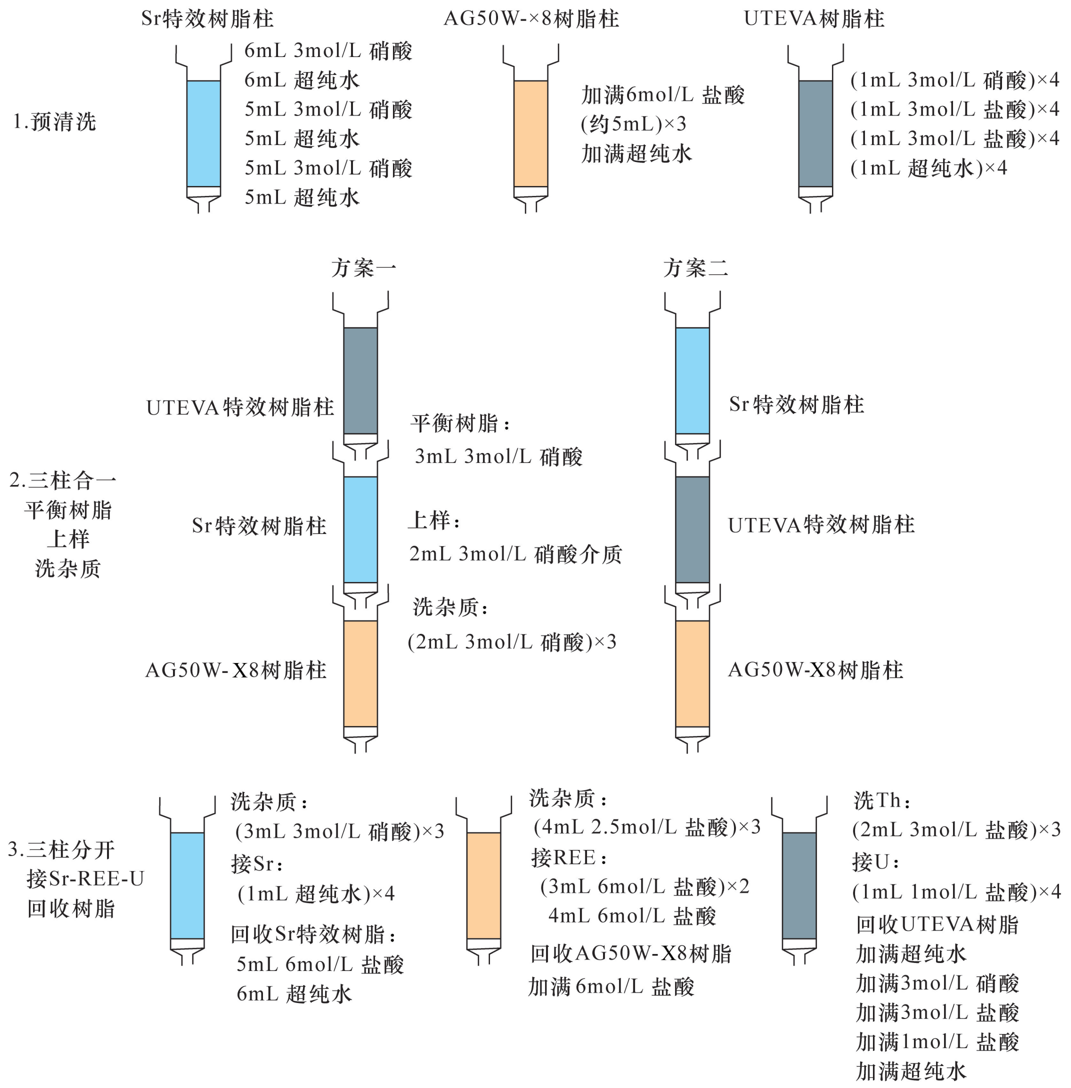
1.3　实验方法

1.3.1　样品消解

准确称取 50mg 粉末状标准物质 BCR-2,转移到聚四氟乙烯(Teflon™)材质的消解罐中。加入浓硝酸和浓氢氟酸各 1mL,盖紧消解罐盖子后放入配套的钢套内,拧紧后一同置于 190℃烘箱中加热 48h。消解后的样品置于电热板上蒸干,加入 1mL 浓硝酸重溶后再次蒸干。加入 2mL 30%的硝酸,再次将消解罐放入钢套内,拧紧后放入 190℃的烘箱中加热 12h。最后将消解完全的溶液转移至 15mL 可溶性聚四氟乙烯(PFA)接样罐中,置于电热板上蒸干。过柱分离前,向装有样品的接样罐中加入 2mL 的 3mol/L 硝酸,密封后置于 115℃电热板上加热 2h,保证样品完全溶解[30-31]。

1.3.2　化学分离

本文所采用的 Sr-Nd-U 联合过柱分离方案,参考了前人的 Sr-Nd 分离和 U 分离纯化流程[21,27-30,32],并加以综合和改进。前人研究表明,在 3mol/L 硝酸环境中,Sr 特效树脂能够高效吸附 Sr[33-34],同样环境下 AG50W-X8 阳离子树脂也能高效吸附 Nd[27,35],UTEVA 特效树脂则能高效吸附 U[21,28],同时都可以使用 3mol/L 硝酸进行洗杂质(但用量不同)。基于以上树脂特性,考虑将 UTEVA 特效树脂柱、Sr 特效树脂柱以及 AG50W-X8 树脂柱串联,采用 3mol/L 硝酸同步进行三根树脂柱的“平衡树脂”、“上样”和“洗杂质”的操作。通过以上操作实现了仅消解一份样品,通过一次过柱,便可以使



步骤 1:对三根树脂柱分别进行预清洗,降低本底。步骤 2:三柱串联,同步进行平衡树脂、上样、洗杂质。
步骤 3:三柱分离单独淋洗接取目标元素。

图 1 Sr、Nd、U **同位素联合分离流程示意图**

Fig. 1 Schematic diagrams of the combined Sr, Nd, U isotopes separation procedure.

目标元素吸附于不同树脂柱上。相比需要消解两份样品的传统做法,采用本文改进的方法仅需消解一份样品,减少了约一半的样品用量。

为了消除本底,各树脂柱在上样前,分别进行预清洗。洗柱后,将三种树脂柱串联(图 1),同步进行平衡树脂、上样和洗杂质操作。随后将三柱分开,Sr 特效树脂用于分离 Sr,AG50W-X8 阳离子交换树脂用于分离 REE,UTEVA 特效树脂用于分离 U。以上每一步分别接取淋出液,留待测试分析,具体流程见图 1 和表 1。其中馏分 1 表示三柱串联阶段上样、洗杂质所得淋出液;馏分 2、5、8 分别表示三柱分离后 Sr 特效树脂、AG50W-X8 树脂、UTEVA 特效树脂单独洗杂质所得淋出液;馏分 3、6、9 则表示接收 Sr、REE、U 的淋出液;馏分 4、7、10 表示各树脂回收阶段所得淋出液。

不同树脂柱自上而下的连接顺序,可能会对目标元素的回收产生相互干扰。由于富集 REE 的阳离子树脂吸附的元素种类最为复杂,因此本文将其置于最底部。为了比较 UTEVA 特效树脂柱和 Sr 特效树脂柱上下组合顺序对元素分离效果的影响,本文设计了两种树脂柱串联方案。方案一将 UTEVA 特效树脂置于 Sr 特效树脂上方,自上而下组合顺序为:UTEVA 特效树脂柱、Sr 特效树脂柱、AG50W-X8 树脂柱(图 1)。方案二将 UTEVA 特效树脂柱和 Sr 特效树脂柱位置交换,自上而下组合顺序为:Sr 特效树脂柱、UTEVA 特效树脂柱和 AG50W-X8 树脂柱(图 1)。

表 1　Sr、Nd、U 同位素联合过柱分离流程

Table 1　Procedure of combined Sr, Nd, U isotopes separation

流程	分离步骤	树脂柱	淋洗试剂	试剂总体积（mL）	馏分编号
①预清洗	本底清洗	Sr 特效树脂	3mol/L 硝酸	6	–
			超纯水	6	–
			3mol/L 硝酸	5	–
			超纯水	5	–
			3mol/L 硝酸	5	–
			超纯水	5	–
		AG50W-X8 树脂	6mol/L 盐酸	15	–
			超纯水	5	–
		UTEVA 特效树脂	3mol/L 硝酸	4	–
			3mol/L 盐酸	4	–
			3mol/L 盐酸	4	–
			超纯水	4	–
②三柱串联	平衡树脂	–	3mol/L 硝酸	3	–
	上样		3mol/L 硝酸	2	1
	洗杂质		3mol/L 硝酸	6	
③三柱分离	洗杂质	Sr 特效树脂	3mol/L 硝酸	9	2
	收集 Sr		超纯水	4	3
	回收树脂		6mol/L 盐酸+超纯水	11	4
	洗杂质	AG50W-X8 树脂	2. 5mol/L 盐酸	4	5
	收集 REE		6mol/L 盐酸	10	6
	回收树脂		6mol/L 盐酸	5	7
	洗杂质	UTEVA 特效树脂	3mol/L 盐酸	6	8
	收集 U		1mol/L 盐酸	4	9
	回收树脂		超纯水+3mol/L 硝酸 +3mol/L 盐酸 +1mol/L 盐酸	20	10

1. 3. 3　淋出液中主量和微量元素含量分析

取适量淋出液分别转移到对应的离心管中,用 3%硝酸稀释到合适浓度后用 ICP-MS 进行主量和微量元素测试。主量和微量元素测试采用多元素混标进行标线校准,分析过程中采用标样 BCR-2 进行校正。同时前后各测量一个 3%硝酸空白样品,监测环境本底,仪器测试误差小于 5%。全流程空白测试结果显示 U 本底值小于 0. 042ng,Nd 本底值小于 0. 081ng,Sr 本底值小于 0. 409ng。依据所有馏分中测得各元素的含量,计算出各元素占全流程总接收量的百分比即为该元素的回收率。

2　结果与讨论

2. 1　树脂柱串联法对 Sr-Nd-U 的纯化效果

高精度同位素测试对样品中元素的纯度有较高要求,基体元素以及待测同位素的同质异位素会对测试产生很大干扰[36-37]。本实验采用玄武岩标准样品 BCR-2 作为测试样品进行分析,每步操作的淋出溶液通过 ICP-MS 进行测试,根据各步骤所得馏分测试结果计算过柱流程中的元素回收率,见图 2 和图 3。馏分 1 为三柱串联上样、洗杂质所得淋出液;馏分 2、3、4 为分离 Sr 环节所得淋出液;馏分 5、6、7 为分离 REE 环节所得淋出液;馏分 8、9、10 为分离 U 环节所得淋出液。

由图 2 和图 3 可知,无论是在方案一还是方案二中,大部分基体元素(含量较高的 K、Ca、Na、Mg、Al、Fe、Ti、P 以及含量较低的 Rb、Hf、Th 等)主要集中在馏分 1 中,即在上样后的洗杂质阶段就被淋洗出去。其中 Na、Ti、Rb、Hf 洗脱率高达 99%;K、Ca 洗脱率稍低,约 85%;Fe 洗脱率约为 56%。此外本研究在三柱分离后,对各个树脂柱单独进行洗杂质操作,所得馏分编号为 2、5、8,进一步洗脱了残余的少部分杂质如 K、Ca、Ba、Fe。通过以上操作,成功去除了容易对后续目标元素测试产生影响的基体元素(Ca、Ba、Fe 等)[24]。因此,两种树脂柱串联方案都可以有效地淋洗掉绝大部分的基体元素,并且目标元素 Sr、Nd、U 能够被高效地吸附在树脂柱上。

Sr 元素主要集中于馏分 3 中,该馏分仅含有极少量的 P、Ba 元素。杂质中含量最高的 Ba 也不足 2000ng,对 Sr 同位素主要产生干扰的 Rb[17] 则被完全去除,这验证了前人利用 Sr 特效树脂高效分离 Sr、Rb 的结果[27]。

U 元素主要集中于馏分 9,该馏分仅含有极少量的 P 和 Pb 元素,这也证实了 Wang 等(2013)[28] 成功利用 UTEVA 特效树脂高纯度分离 U 的结果。

Nd 元素主要集中于馏分 6 中,该馏分中还含有 Sm 和 Ce。其中^{144}Sm 对^{144}Nd 产生干扰,^{142}Ce 则主要对^{142}Nd 产生干扰,因此 Ce 不会对^{143}Nd/^{144}Nd 的测试产生明显影响[38-39]。同时杨岳衡等(2007)[40] 通过测试一系列不同 Ce/Nd 比例的混合溶液,证实了虽然 Ce 的化学性质与 Nd 十分相似,难以在交换柱分离过程中分开,但高含量的 Ce($Ce/Nd>3$,一般地质样品 Ce/Nd 约为 3)不会影响后续对 Nd 同位素(^{143}Nd/^{144}Nd)的测试[40]。当 Sm 的含量远小于 Nd($Sm/Nd<0.04$)[40],也可以通过传统方法校正(利用^{147}Sm/^{144}Nd)得到 Nd 的含量,从而去除 Sm 的影响[24,41-42];而若 Sm 含量过高,前人也提出了多种解决方法[27,35,43],通过 Ln、P507 等树脂都可以进一步纯化分离 Nd、Sm 和 Ce。

2. 2　树脂柱串联法对 Sr-Nd-U 的分离效果

方案一中 Sr 元素的回收率为 92. 5%,而 U 回收率接近 99. 9%。方案二中 Sr 元素的回收率为 94. 3%,U 回收率高达 99. 8%。本文 U 的回收率很

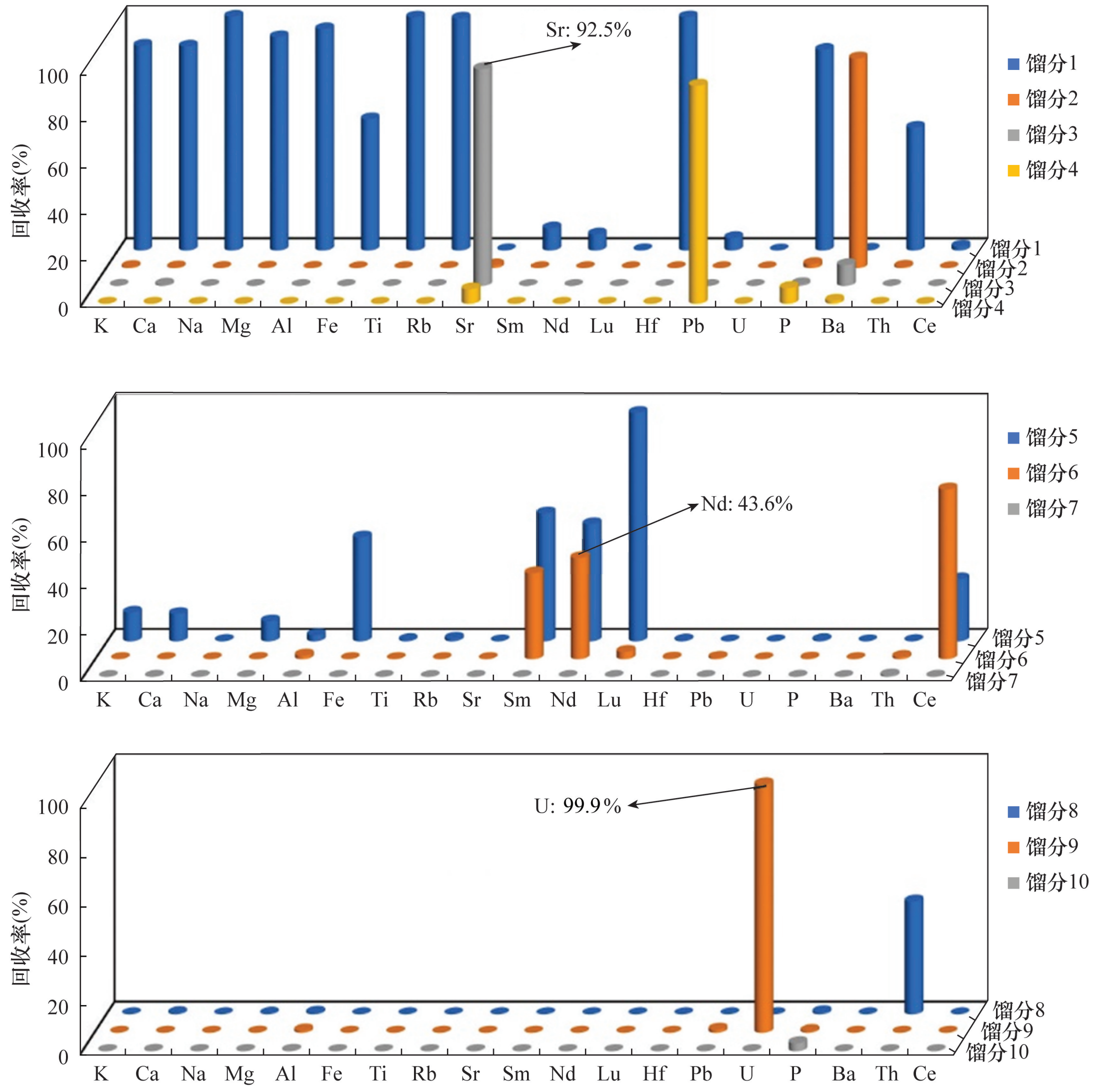


图 2　方案一中 Sr-Nd-U 在不同馏分中的回收率

Fig. 2　Recoveries of Sr-Nd-U in different fractions in procedure Ⅰ. The Sr and U recoveries are over 90%, while the Nd recovery is only 43.6% and need further separation with Sm.

高,适用于 U 含量较低的大部分沉积物样品。Nd 元素回收率较低,方案一中 Nd 回收率为 43.6%,方案二为 53.7%。

由图 2 可知,串联上样洗杂质所获得的馏分 1 中,大约有 6.8% 的 Nd 淋失;收集 REE 阶段洗杂质获得的馏分 5 也有接近 49.6% 的 Nd 淋失。结合袁永海等(2018)[44]研究发现,AG50W-X8 阳离子树脂经过 10 次回收再利用后,Nd 元素的回收率会从 90% 下降到 50%。通过对实验环境、材料、操作流程和仪器状态的检查核实,我们初步推测本文方法获得的 Nd 元素回收率较低,可能是因为 AG50W-X8 阳离子树脂经多次回收重复利用,使得树脂对 Nd 的吸附能力减弱所致。

2.3　Nd 元素回收率的重新检验

为进一步查明 Nd 元素回收率偏低的原因,本文选用了新的 AG50W-X8 树脂重新充填制作色谱柱。按照方案一的流程,更新树脂后 Sr 的回收率为 91.9%,U 的回收率为 99.3%,而 Nd 的分离回收率已经达到 82.1%(图 4)。参考前人的回收率结果[18],一般回收率超过 70% 便可以满足后续 Nd 同位素测试需要。该实验结果证实了在先前实验中 Nd 元素回收率偏低确实是由于 AG50W-X8 树脂失效导致,这也与前人结果相吻合。Zhu 等[45]指出阳离子树脂柱使用超过 6~7 次后,目标元素回收率会低于 60%;Li 等[46]指出树脂柱过多地重复使用(超过 5 次)将会导致严重的交叉污染以及低回收率等现象。树脂柱残留的基体元素,可能会与树脂本身

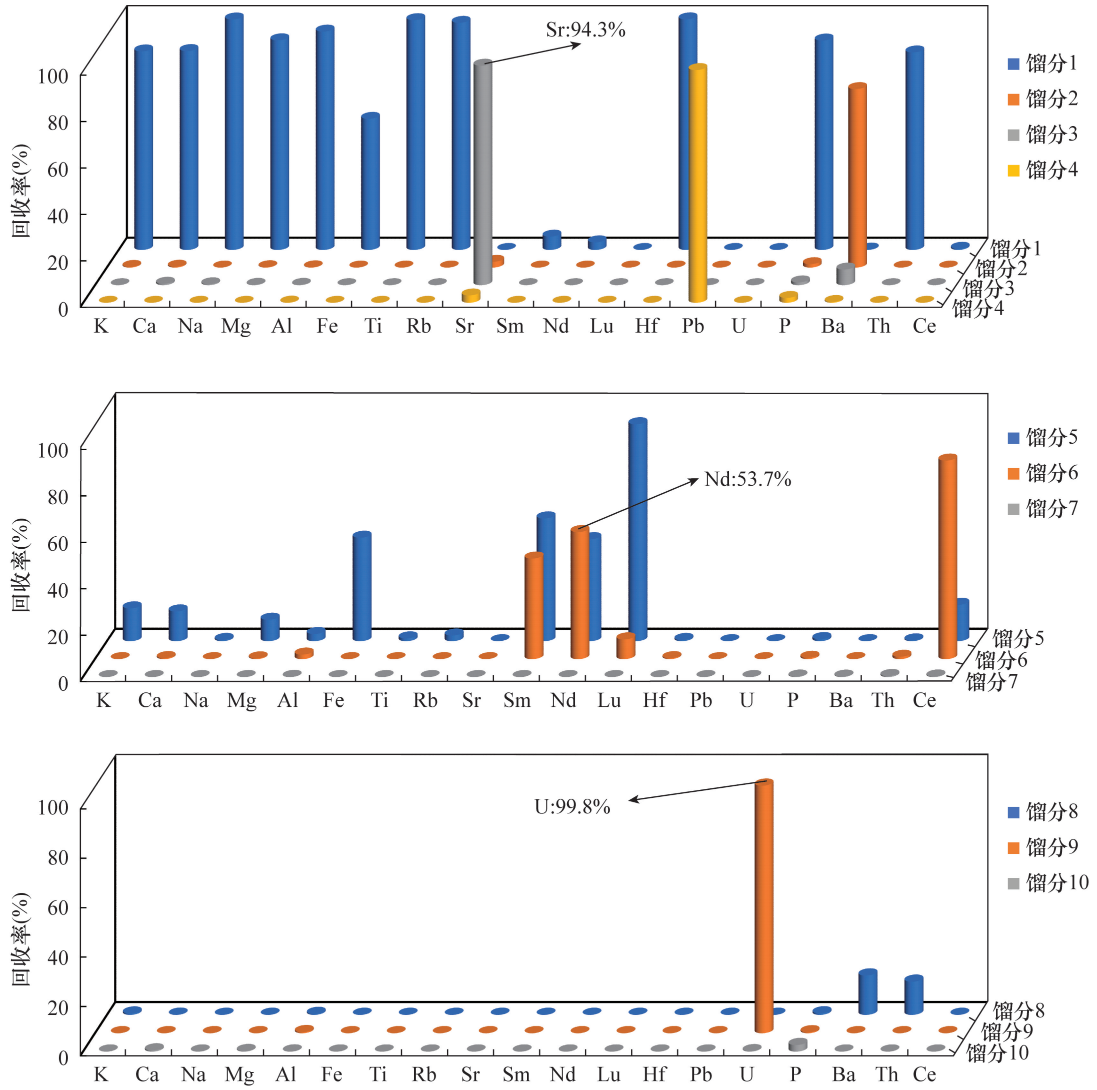


图 3　方案二中 Sr-Nd-U 在不同馏分中的回收率

Fig. 3　Recoveries of Sr-Nd-U in different fractions in procedure Ⅱ. The Sr and U recoveries are over 90%, while the Nd recovery is only 53.7% and need further separation with Sm.

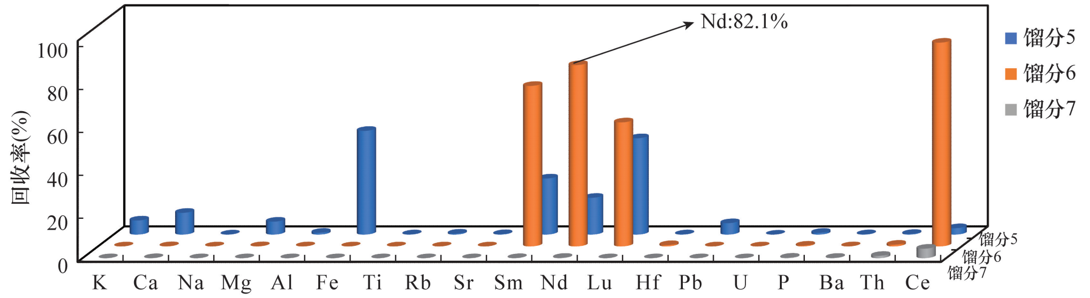


图 4　更新 AG50W-X8 树脂后 Nd 的回收率

Fig. 4　Nd recovery using renewed AG50W-X8 resin. The updated recovery for Nd is increased to 82.1%.

络合进而破坏树脂结构，降低树脂柱对关键元素的吸附能力[35]。若树脂使用后采用适当的酸进行清洗（如参照表 1 树脂回收流程），可以有效地去除本底，延长树脂柱使用寿命。同时对于放射性 Sr、Nd 同位素，不要求全部回收[47]，因此本文的分离效果并不影响后续同位素的测试。

2.4　树脂柱的串联顺序对分离效果的影响

树脂柱的设置顺序是串联法的一个关键，各树

脂柱在上下不同的位置，可能会改变不同元素的吸附行为，增加淋洗液的用量[24,41]。本文通过改变Sr特效树脂柱和UTEVA特效树脂柱的摆放顺序设计了两种过柱方案，以此比较二者的分离效果。在方案一中Sr元素的回收率为92.5%，Nd的回收率为43.6%，U回收率接近99.9%。方案二中Sr元素的回收率为94.3%，Nd的回收率为53.7%，U回收率接近99.8%。本文首轮实验中方案一和方案二都以较高的回收率分离出高纯度的Sr和U元素。而对于Nd元素，虽然其回收率偏低，但回收的含量(495.8ng)也已经可以满足多次Nd同位素测试的需求。不过偏低的回收率仍然会对低含量Nd样品的分析测试造成困难，为此本文通过重新充填树脂柱证实了偏低的Nd回收率是AG50W-X8树脂失效引起的。综合以上分析，结合Sr和U的联合过柱回收率，本文认为此次实验中设计的两种不同树脂柱串联方式对Sr-Nd-U元素的回收率并无显著影响。

3　结论

本文提出了一种只需一次溶样的三柱串联Sr-Nd-U联合分离方法，该方法可以快速高效地将Sr、Nd、U元素从硅酸盐岩样品中分离出来，其中U回收率最高接近99.9%，Sr回收率为92.5%，Nd回收率为82.1%，该回收率水平完全可以满足后续的同位素分析要求。

三柱串联Sr-Nd-U联合分离方法相比于传统的分离方法，减少了约一半的样品用量，有利于珍贵稀有样品(如大洋沉积物和极地样品)的分析；同时避免了蒸干转换介质操作，缩短了过柱时间，显著提高了化学分离效率。本文方法为Sr-Nd-U多同位素分离提供了新思路，未来可以尝试增加对流程中馏分4内Pb元素的回收，进一步拓展本文技术的应用范围。

致谢：感谢同济大学海洋与地球科学学院马松阳硕士对本文撰写提供的指导和建议，同时感谢两位匿名审稿人提出的宝贵意见。

4　参考文献

[1] Bourdon B, Henderson G M, Lundstrom C C, et al. Uranium-series geochemistry [M]. Washington D C: Publisher Mineralogical Society of America, 2003.

[2] Li C, Francois R, Yang S, et al. Constraining the transport time of lithogenic sediments to the Okinawa Trough (East China Sea) [J]. Chemical Geology, 2016, 445: 199-207.

[3] Martin A N, Dosseto A, May J H, et al. Sediment residence times in catchments draining to the Gulf of Carpentaria, northern Australia, inferred by uranium comminution dating [J]. Geochimica et Cosmochimica Acta, 2019, 244: 264-291.

[4] Li L, Liu X J, Li T, et al. Uranium comminution age tested by the eolian deposits on the Chinese Loess Plateau [J]. Earth and Planetary Science Letters, 2017, 467: 64-71.

[5] Cogez A, Herman F, Pelt É, et al. U-Th and ^{10}Be constraints on sediment recycling in proglacial settings, Lago Buenos Aires, Patagonia [J]. Earth Surface Dynamics, 2018, 6(1): 121-140.

[6] Banner J L. Radiogenic isotopes: Systematics and applications to earth surface processes and chemical stratigraphy [J]. Earth-Science Reviews, 2004, 65(3-4): 141-194.

[7] Tripathy G R, Singh S K, Krishnaswami S. Sr and Nd isotopes as tracers of chemical and physical erosion [M]//Handbook of environmental isotope geochemistry. Springer, 2012: 521-552.

[8] Anderson F S, Levine J, Whitaker T J. Rb-Sr resonance ionization geochronology of the Duluth Gabbro: A proof of concept for *in situ* dating on the Moon [J]. Rapid Communications in Mass Spectrometry, 2015, 29(16): 1457-1464.

[9] Cao J Y, Yang X Y, Lu Y Y, et al. Zircon U-Pb and Sm-Nd geochronology and geochemistry of the Sn-W deposits in the northern Guposhan ore field, Nanling Range, southern China [J]. Ore Geology Reviews, 2020, 118: 103323.

[10] Xu Z K, Li T G, Clift P D, et al. Bathyal records of enhanced silicate erosion and weathering on the exposed Luzon shelf during glacial lowstands and their significance for atmospheric CO_2 sink [J]. Chemical Geology, 2018, 476: 302-315.

[11] Dou Y G, Yang S Y, Shi X F, et al. Provenance weathering and erosion records in southern Okinawa Trough sediments since 28ka: Geochemical and Sr-Nd-Pb isotopic evidences [J]. Chemical Geology, 2016, 425: 93-109.

[12] Li J R, Liu S F, Shi X F, et al. Clay minerals and Sr-Nd isotopic composition of the Bay of Bengal sediments: Implications for sediment provenance and climate control since 40ka [J]. Quaternary International, 2018, 493: 50-58.

[13] Hu S Y,Zeng Z G,Fang X,et al. Increasing terrigenous sediment supply from Taiwan to the southern Okinawa Trough over the last 3000 years evidenced by Sr-Nd isotopes and geochemistry[J]. Sedimentary Geology, 2020,406:105725.

[14] Li C, Yang S Y, Lian E G, et al. A review of comminution age method and its potential application in the East China Sea to constrain the time scale of sediment source-to-sink process[J]. Journal of Ocean University of China,2015,14(3):399-406.

[15] Li L,Chen J,Chen Y,et al. Uranium isotopic constraints on the provenance of dust on the Chinese Loess Plateau [J]. Geology,2018,46(9):747-750.

[16] Guéguen F, Stille P, Dietze V, et al. Chemical and isotopic properties and origin of coarse airborne particles collected by passive samplers in industrial, urban, and rural environments [J]. Atmospheric Environment, 2012,62:631-645.

[17] 刘文刚,刘卉,李国占,等. 离子交换树脂在地质样品 Sr-Nd 同位素测定中的应用[J]. 地质学报,2017,91(11):2584-2592.

Liu W G, Liu H, Li G Z, et al. The application of ion exchange resins in Sr-Nd isotopic assay of geological samples[J]. Acta Geologica Sinica, 2017, 91(11): 2584-2592.

[18] 何连花,张俊,高晶晶,等. 地质样品 Sr 和 Nd 同位素的化学分离方法改进[J]. 海洋科学进展,2014,32(1):78-83.

He L H, Zhang J, Gao J J, et al. Improvement of the method for chemical separations of Sr and Nd in geological samples[J]. Advances in Marine Science, 2014,32(1):78-83.

[19] Rovan L,Štrok M. Optimization of the sample preparation and measurement protocol for the analysis of uranium isotopes by MC-ICP-MS without spike addition[J]. Journal of Analytical Atomic Spectrometry, 2019, 34(9):1882-1891.

[20] Granet M,Chabaux F,Stille P,et al. U-series disequilibria in suspended river sediments and implication for sediment transfer time in alluvial plains: The case of the Himalayan Rivers [J]. Geochimica et Cosmochimica Acta,2010,74(10):2851-2865.

[21] 廖泽波,邵庆丰,李春华,等. MC-ICP-MS 标样-样品交叉测试法测定石笋样品的^{230}Th/U 年龄[J]. 质谱学报,2018,39(3):295-309.

Liao Z B,Shao Q F,Li C H,et al. Measurement of U/Th isotopic compositions in stalagmites for ^{230}Th/U geochronology using MC-ICP-MS by standard-sample bracketing method [J]. Journal of Chinese Mass Spectrometry Society,2018,39(3):295-309.

[22] Pin C,Gannoun A,Dupont A. Rapid,simultaneous separation of Sr,Pb,and Nd by extraction chromatography prior to isotope ratios determination by TIMS and MC-ICP-MS [J]. Journal of Analytical and Atomic Spectrometry, 2014,29(10):1858-1870.

[23] Bast R,Scherer E,Sprung P,et al. A rapid and efficient ion-exchange chromatography for Lu-Hf,Sm-Nd,and Rb-Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS[J]. Journal of Analytical and Atomic Spectrometry, 2015, 30(11): 2323-2333.

[24] Li C F, Wang X C, Guo J H, et al. Rapid separation scheme of Sr,Nd,Pb,and Hf from a single rock digest using a tandem chromatography column prior to isotope ratio measurements by mass spectrometry[J]. Journal of Analytical Atomic Spectrometry, 2016, 31(5): 1150-1159.

[25] Moragues-Quiroga C,Juilleret J,Gourdol L,et al. Genesis and evolution of regoliths:Evidence from trace and major elements and Sr-Nd-Pb-U isotopes[J]. Catena, 2017,149:185-198.

[26] Aciego S M,Bourdon B,Lupker M,et al. A new procedure for separating and measuring radiogenic isotopes (U,Th,Pa,Ra,Sr,Nd,Hf) in ice cores[J]. Chemical Geology,2009,266(3-4):194-204.

[27] 韦刚健,刘颖,涂湘林,等. 利用选择性特效树脂富集分离岩石样品中的锶钐和钕[J]. 岩矿测试,2004,23(1):11-14.

Wei G J,Liu Y,Tu X L,et al. Separation of Sr,Sm and Nd in mineral and rock samples using selective specific resins[J]. Rock and Mineral Analysis,2004,23(1): 11-14.

[28] Wang R M,You C F. Precise determination of U isotopic compositions in low concentration carbonate samples by MC-ICP-MS[J]. Talanta,2013,107:67-73.

[29] Shao Q F, Pons Branchu E, Zhu Q P, et al. High precision U/Th dating of the rock paintings at Mt. Huashan, Guangxi, southern China [J]. Quaternary Research,2017,88(1):1-13.

[30] 马松阳,李超,王晨羽,等. 两种硅酸盐碎屑组分^{234}U/^{238}U 测试前处理方法的比较及启示[J]. 矿物岩石地球化学通报,2022,41(1):127-134.

Ma S Y,Li C,Wang C Y,et al. The comparison of two pre-treatment methods for the ^{234}U/^{238}U measurement of silicate detrital fractions and its enlightment significance

[J]. Bulletin of Mineralogy, Petrology and Geochemistry, 2022, 41(1): 127-134.

[31] Deng K, Yang S Y, Bi L, et al. Small dynamic mountainous rivers in Taiwan exhibit large sedimentary geochemical and provenance heterogeneity over multi-spatial scales[J]. Earth and Planetary Science Letters, 2019, 505: 96-109.

[32] Xu J, Yang S Y, Yang Y H, et al. Determination of stable strontium isotopic compositions by MC-ICP-MS[J]. Atomic Spectroscopy, 2020, 41(2): 64-73.

[33] Misawa K, Yamazaki F, Ihira N, et al. Separation of rare earth elements and strontium from chondritic meteorites by miniaturized extraction chromatography for elemental and isotopic analyses[J]. Geochemical Journal, 2000, 34(1): 11-21.

[34] Deniel C, Pin C. Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements[J]. Analytica Chimica Acta, 2001, 426(1): 95-103.

[35] 尹鹏, 何倩, 何会军, 等. 离子交换树脂法分离沉积物中锶和钕的影响因素研究[J]. 岩矿测试, 2018, 37(4): 379-387.

Yin P, He Q, He H J, et al. Study on the factors influencing the separation of Sr and Nd in sediments by ion exchange resin[J]. Rock and Mineral Analysis, 2018, 37(4): 379-387.

[36] 宗春蕾, 袁洪林, 戴梦宁. 一次溶样分离地质样品中 Pb-Sr-Nd 方法的可行性研究[J]. 岩矿测试, 2012, 31(6): 945-949.

Zong C L, Yuan H L, Dai M N. A feasibility study on chemical separation of Pb, Sr and Nd from the same single dissolution of geological sample[J]. Rock and Mineral Analysis, 2012, 31(6): 945-949.

[37] 刘婉, 李丹丹, 刘盛遨. 多接收器电感耦合等离子体质谱法测定土壤标准物质铜同位素组成[J]. 岩矿测试, 2021, 40(4): 561-569.

Liu W, Li D D, Liu S A. Determination of copper isotope composition of soil reference materials by MC-ICP-MS[J]. Rock and Mineral Analysis, 2021, 40(4): 561-569.

[38] Pin C, Gannoun A. A triple tandem columns extraction chromatography method for isolation of highly purified neodymium prior to ^{143}Nd/^{144}Nd and ^{142}Nd/^{144}Nd isotope ratios determinations[J]. Journal of Analytical Atomic Spectrometry, 2019, 34(2): 310-318.

[39] 朱志勇, 潘辰旭, 朱祥坤. 利用套柱法快速分离提纯 Sr 和 Nd 元素[J]. 岩矿测试, 2020, 39(4): 515-524.

Zhu Z Y, Pan C X, Zhu X K. Rapid purification of Sr and Nd for isotope analysis with multiple-column method[J]. Rock and Mineral Analysis, 2020, 39(4): 515-524.

[40] 杨岳衡, 张宏福, 谢烈文, 等. 多接收器电感耦合等离子质谱精确测定钕同位素组成[J]. 分析化学, 2007, 35(1): 71-74.

Yang Y H, Zhang H F, Xie L W, et al. Accurate measurement of neodymium isotopic composition using neptune multiple collector inductively coupled plasma mass spectrometry[J]. Chinese Journal of Analytical Chemistry, 2007, 35(1): 71-74.

[41] Li C F, Chu Z Y, Guo J H, et al. A rapid single column separation scheme for high-precision Sr-Nd-Pb isotopic analysis in geological samples using thermal ionization mass spectrometry[J]. Analytical Methods, 2015, 7(11): 4793-4802.

[42] Lin J, Liu Y S, Yang Y H, et al. Calibration and correction of LA-ICP-MS and LA-MC-ICP-MS analyses for element contents and isotopic ratios[J]. Solid Earth Sciences, 2016, 1(1): 5-27.

[43] Pin C, Briot D, Bassin C, et al. Concomitant separation of strontium and samarium-neodymium for isotopic analysis in silicate samples, based on specific extraction chromatography[J]. Analytica Chimica Acta, 1994, 298(2): 209-217.

[44] 袁永海, 杨锋, 余红霞, 等. 微波消解-多接收电感耦合等离子体质谱高精度测定锶钕同位素组成[J]. 岩矿测试, 2018, 37(4): 356-363.

Yuan Y H, Yang F, Yu H X, et al. High-precision measurement of strontium and neodymium isotopic composition by multi-collector inductively coupled plasma-mass spectrometry with microwave digestion[J]. Rock and Mineral Analysis, 2018, 37(4): 356-363.

[45] Zhu J M, Wu G L, Wang X L, et al. An improved method of Cr purification for high precision measurement of Cr isotopes by double spike MC-ICP-MS[J]. Journal of Analytical Atomic Spectrometry, 2018, 33(5): 809-821.

[46] Li X Q, Han G L, Zhang Q, et al. An optimal separation method for high-precision K isotope analysis by using MC-ICP-MS with a dummy bucket[J]. Journal of Analytical Atomic Spectrometry, 2020, 35(7): 1330-1339.

[47] Zhang Z Y, Ma J L, Zhang L, et al. Rubidium purification *via* a single chemical column and its isotope measurement on geological standard materials by MC-ICP-MS[J]. Journal of Analytical Atomic Spectrometry, 2018, 33(2): 322-328.

Separation of Sr, Nd, and U from Geological Samples Using Tandem Resin Column

LUO Zhenghua[1], *LI Chao*[1,2*], *LAI Zheng*[1], *WANG Chenyu*[3], *GUO Yulong*[1], *DUAN Zhifei*[1], *XU Juan*[1,2], *YANG Shouye*[1,2]

(1. State Key Laboratory of Marine Geology (Tongji University), Shanghai 200092, China;
2. School of Ocean and Earth Sciences, Tongji University, Shanghai 200092, China;
3. GFZ German Research Centre for Geosciences, Earth Surface Geochemistry, Telegrafenberg, Potsdam 14473, Germany)

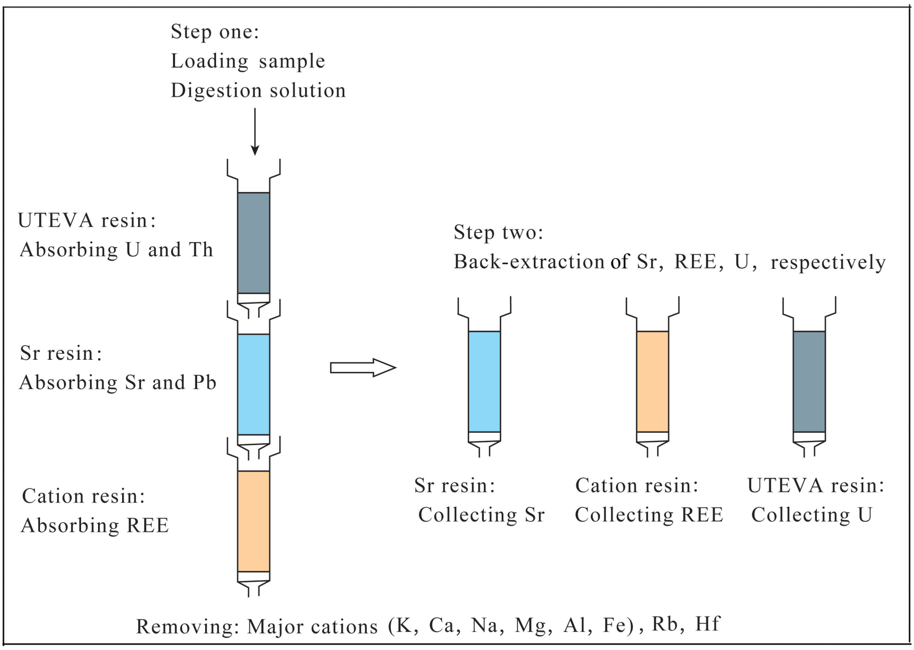
HIGHLIGHTS

(1) The resin columns are connected in series, and the same eluent is used to balance the resin, load the sample, and wash the impurities simultaneously, avoiding the operation of evaporation to dryness.

(2) Reversing the column positions, UTEVA column and Sr column, has no effect on Sr, Nd and U separation and the column recovery.

(3) Multiple reuse of resin can lead to resin column lapse, affecting the adsorption capacity of the target element, thus new resins should be used in a timely manner.

Tandem column scheme



ABSTRACT

BACKGROUND: Uranium-series nuclides are one of the three major radioactive decay systems, which are suitable for studying various geological processes at different time scales. In addition, $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotopes (Sr-Nd isotopes for short) are two commonly used isotopes, for rock dating, chemical weathering assessment and tracing sediment sources. In this case, the combination of Sr-Nd-U isotopes can provide more comprehensively knowledge of the element cycle on the earth's surface and deepen our understanding of the sediment "Source to Sink" processes.

Most previous studies involving the Sr-Nd-U isotopes have been established by separating Sr-Nd and U isotopes respectively. In this way, the digestion operation must be performed twice, one for separating Sr-Nd and the other for separating U. Alternatively, if only one sample is digested for measuring all three isotopes, between each element separation, the residue must be dried and dissolved in another solution so as to start a new column work. The former increases the amount of samples, which is not conducive to analysis of precious and trace samples; the latter adds additional drying operation, which is time consuming and increases the risk of sample loss and contamination.

OBJECTIVES: To establish a new Sr-Nd-U combined separation scheme. In this method, only one sample is dissolved, avoiding solution transfer between each separation, so as to reduce sample amount and improve the efficiency of separation and purification of Sr-Nd-U isotopes.

METHODS: A new chromatographic scheme of separating Sr-Nd-U with one sample digestion using a tandem column scheme is presented. Three columns were overlain sequentially to separate Sr in Sr Spec column, Nd in AG50W-X8 column and U in UTEVA column. 3mol/L HNO_3 was used to pre-condition, load the sample, and rinse the matrix. After rinsing the matrix, the tandem column was separated to 3 independent columns to elute the target elements (Sr, Nd, U) respectively.

As the connection sequence of different resin columns may interfere with the recovery of target elements, two different chromatographic schemes were compared. In Scheme 1, U column was placed on top of Sr column, while in Scheme 2 the positions of U column and Sr resin column were exchanged. In both schemes, the AG50W-X8 resin column was set at the bottom as the cationic resin can adsorb the most complex elements.

All separated elution was tested for element concentration using inductively coupled plasma-mass spectrometry (ICP-MS). The basalt standard sample (BCR-2) was used to examine the behavior and recovery of each element in the separation procedure.

RESULTS: A total of 10 fractions were recovered from the tandem column scheme, among which fraction 1 represented the leachate recovered by loading samples and rinsing matrix from the tandem three columns. Fraction 2, 5 and 8 represented the leachate recovered by Sr Spec resin, AG50W-X8 resin and UTEVA resin respectively rinsing matrix after separation of the three columns. Fraction 3, 6 and 9 represented the leachate recovered by Sr, REE and U columns, which was Sr, Nd and U collection. Fraction 4, 7 and 10 represented the leachate from each resin recycle stage.

In either Scheme 1 or Scheme 2, most matrix elements (high content of K, Ca, Na, Mg, Al, Fe, Ti and P and low content of Rb, Hf and Th) were mainly concentrated in fraction 1. The elution rate of Na, Ti, Rb and Hf was up to 99%. The elution rate of K and Ca was slightly lower at about 85% and the elution rate of Fe was about 56%. Sr was mainly concentrated in fraction 3, which contained only a small amount of P and Ba. Nd was mainly concentrated in fraction 6, which also contained both Sm and Ce. U was mainly concentrated in fraction 9, which only contained a very small amount of P and Pb. The column recovery was almost 99.9% for U, 90% for Sr and over 80% for Nd.

The removal rate of major matrix elements (K,Ca, Na, Ba, Fe, Rb, etc.) exceeded 99%, which reduced interference with high-precision isotope analysis of Sr, Nd, and U. The recovery and purity of Sr, Nd, U were all quite high. A very small amount of P and Ba in fraction 3 had no interference with Sr isotopes ($^{87}Sr/^{86}Sr$). The Rb which was isomorphism of Sr was removed completely. With regard to Sm and Ce in fraction 6, previous studies had shown that ^{142}Ce could not interfere with Nd isotope ($^{143}Nd/^{144}Nd$), and Sm could be further separated by Ln resin, so as not to affect Nd isotopic test. Fraction 9 contained nearly 100% U with no other elements.

The sequence of resin column splicing is a crucial consideration which may impact the element separation. Hence, the position of Sr Spec column and UTEVA column was exchanged to compare the influence of different column sequences on eluting target elements. Both Scheme 1 and Scheme 2 can effectively wash off most of the matrix elements, and the target elements Sr, Nd and U can be efficiently adsorbed on the resin. There is no significant difference on target element separation between the two different column sequences. This indicates that Sr Spec and UTEVA resins do not interfere with each other on the target elements.

CONCLUSIONS: The new chromatographic scheme of separating Sr-Nd-U with one sample digestion using a tandem column scheme can be used to quickly and efficiently separate Sr, Nd and U elements from silicate rock samples. The recovery rate for U, Sr and Nd is 99.9%, 92.5% and 82.1%, respectively, which meet the requirements of subsequent isotope analysis. This Sr-Nd-U combined separation method can be used to reduce the sample consumption by about 50%, which is beneficial to the analysis of precious and trace samples. Meanwhile, as no solution transfer is needed between each column separation, this method can also save time for column work and increase the efficiency of chemical separation. A new idea for Sr-Nd-U multi-isotope separation is provided. If the recovery of Pb in the fraction 4 of this chromatographic scheme can be improved in further studies, the application of this new method may be expanded to more fields in the future.

KEY WORDS: Sr; Nd, U; tandem resin column; column recovery; isotopic separation; inductively coupled plasma-mass spectrometry