



现代河流碎屑磷灰石原位地球化学分析

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现代河流碎屑磷灰石原位地球化学分析 ——对长江物源示踪研究的启示

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摘要 长江是连接青藏高原和西太平洋的东亚最大河流,研究其源汇过程对于认识和理解沉积物剥蚀、搬运和沉积过程等方面具有重要科学意义。对河流沉积物中常见的磷灰石开展了原位微量元素和⁸⁷Sr/⁸⁶Sr比值分析,结果表明,金沙江的微量元素和⁸⁷Sr/⁸⁶Sr比值二维散点图的分布区域与大渡河、岷江和嘉陵江的明显不同;丰都段长江干流样品与大渡河、岷江和嘉陵江样品形成重叠区域,结合MDS(非矩阵多维标度)判断图结果,说明丰都段长江干流的物质主要来自龙门山。磷灰石原位地球化学分析方法可以有效区分发源于青藏高原东南的金沙江和发源于龙门山的大渡河、岷江和嘉陵江的物质。但由于金沙江梯级水电站的建设对其下游沉积物的组成起到重要影响,在今后使用该方法进行长江全流域物源示踪研究时需要谨慎。

关键词 磷灰石;微量元素;⁸⁷Sr/⁸⁶Sr比值;长江;物源示踪

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0 引言

河流是塑造地表形态,串联地球岩石圈、水圈、大气圈物质循环的重要介质^[1-4]。因而保存于河流中的碎屑沉积物(砾、砂、泥)对理解构造变形、气候变化和地表侵蚀作用之间的联系具有广泛意义^[5-12]。“亚洲水塔”青藏高原与多个亚洲边缘海盆地及亚洲内陆湖泊组成了规模巨大的源—汇系统^[13-14]。认识这一源—汇系统的发展过程,包括河流砾、砂、泥的产生、搬运与沉积过程,不仅为探索地球海陆交互作用等关键过程提供基础支撑,也能提供水系演化的信息^[15-23]。其中尤以亚洲最大河流,发源于青藏高原东部,流经云贵高原、四川盆地、江汉盆地和长江中下游平原,最终流入太平洋西部陆架边缘海(东海)的长江最受关注^[4,11,24](图1)。而长江的发育和形成综合反映东亚中—新生代以来构造体制转换、气候变化等重要信息,对中国三大地势阶梯的建立具有重要指示意义,也是探索青藏高原构造—气候—沉积系统科学研究的重要组成部分^[25-31]。因

而,国内外研究者从环境磁学^[11]、全岩地球化学^[18-20,24]、重矿物组成^[7,15,25,30]、黏土矿物组成^[31]、单颗粒矿物年龄谱对比^[8-10,32]等方面,对其源汇过程开展了广泛研究。然而,全岩地球化学组成更多代表沉积物均一化的物源信息;矿物组合研究,有时因流域内缺乏标型矿物,增加了物源解析的难度;锆石矿物硬度大,可以经历多期次物质沉积循环过程,仅仅依靠单一的U-Pb年龄谱对比,并不能很好的限定潜在物源区。

近年来,在河流沉积物物源示踪研究中,越来越多的学者开始对某一矿物(例如锆石和磷灰石)同时进行原位物源信息(U-Pb年龄,Sr-Nd同位素等)的获取^[33-39],已被证明在界定物源区,识别构造活动引起的水系变化等方面十分有效。进而避免分析单一矿物引起物源示踪结果的不确定性。尽管磷灰石在重矿物中的含量十分低,在搬运过程中也容易出现磨蚀,在大型河流物源示踪研究中会存在代表性不强的现象。但在大河流域的个别流域,比如流域内存在磷灰石成分特别高的母岩,或者不同支流流域中

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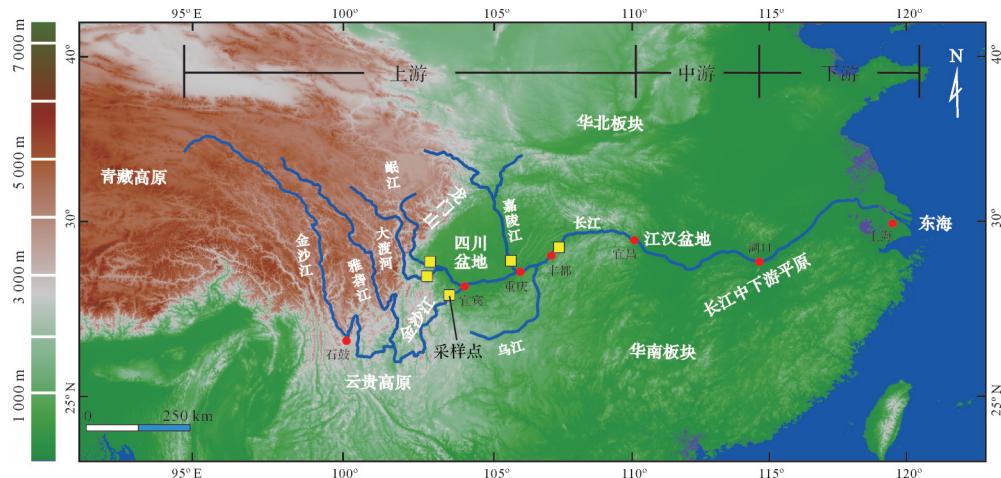


图1 长江流域位置分布图
Fig.1 Location of Yangtze River Basin

磷灰石含量差异巨大等情况,可以起到很好的物源示踪效果^[34-35]。分析河流下游或者沉积盆地中的碎屑磷灰石的原位地球化学元素组成,将其与上游河流或潜在源区进行对比,从而建立源汇关系。近年来,磷灰石这一物源示踪方法被广泛应用于河流物源示踪^[40-42]、盆地古流向重建^[36]等方面。但在长江流域这项工作还未开展。因而,我们对长江上游主要干支流开展碎屑磷灰石原位微量元素和Sr同位素分析,将金沙江、大渡河、岷江、嘉陵江支流与丰都段长江干流的结果进行对比,来探索这一方法在长江上游物源示踪研究的可行性。

1 研究背景

长江发源于青藏高原的唐古拉山脉,在上海市崇明岛以东注入东海,连接了地球上最高的高原和最大的大洋,全长约6 300 km,流域面积约 $1.8 \times 10^6 \text{ km}^2$,是亚洲最大河流。从源头到宜昌是其上游河段。伴随着晚新生代以来青藏高原的隆升,在亚洲东亚和南亚季风气候控制下,长江流域产生并携带巨量的水沙进入太平洋西岸陆架海,对流域生态环境和边缘海的海洋环境产生重大影响,在全球变化中扮演重要角色,是国内外众多重大研究计划的靶区^[4,43-44]。

宜昌以上长江流域面积为 $1.0 \times 10^6 \text{ km}^2$,1956—2007年的年均径流量达到 $4.3 \times 10^{11} \text{ m}^3$,年均输沙量为 $4.5 \times 10^8 \text{ t}$ ^[45]。长江上游的四大支流金沙江(图2)、岷江(包含大渡河)、嘉陵江和乌江流域面积分别为 $5 \times 10^5 \text{ km}^2$ 、 $2.2 \times 10^5 \text{ km}^2$ 、 $1.6 \times 10^5 \text{ km}^2$ 、 $0.87 \times 10^5 \text{ km}^2$,总

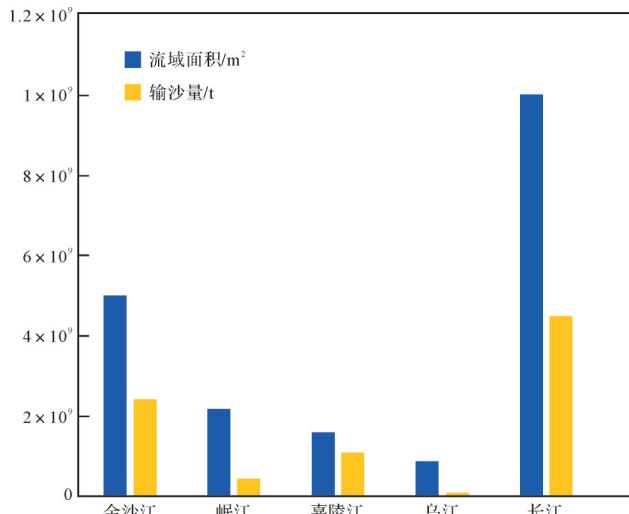


图2 长江上游干支流流域面积和1956—2007年的平均输沙量柱状图(数据来源于文献[45])
Fig.2 Column chart of basin area and mean sediment discharge 1956-2007 in the upper reaches of the Yangtze River (data from reference [45])

面积 $8.8 \times 10^5 \text{ km}^2$,占长江上游流域面积的87.9%。金沙江年均输沙量为 $2.4 \times 10^8 \text{ t}$,占长江宜昌水文站的54.2%。岷江年输沙量为 $0.47 \times 10^8 \text{ t}$,占宜昌水文站的10.4%。嘉陵江年输沙量($1.1 \times 10^8 \text{ t}$)占宜昌站的24.1%。乌江流域是长江南岸最大支流,但主要流经云贵高原的喀斯特高山地区,与上述河流相比,河流流域面积和年均输沙量小($0.05 \times 10^8 \text{ t}$),占宜昌站的5.6%。因而乌江并不是宜昌以上长江干流的主要物质输送河流,本次研究未对其开展样品分析。

2 样品来源和研究方法

2.1 样品采集

对宜昌以上长江干支流进行样品采集,每个点大约采集3~5 kg样品(图1)。为了采样更具有代表性,每一个样品由多个采样点组成,同时避免人为污染源。金沙江样品在宜宾市上游金沙江干流河漫滩采集($28^{\circ}44'36''$ N, $104^{\circ}35'50''$ E)。大渡河样品采自白岩坎镇河漫滩($29^{\circ}32'46''$ N, $103^{\circ}44'18''$ E),岷江样品采自乐山市岷江下游河漫滩($29^{\circ}37'44''$ N, $103^{\circ}45'11''$ E)。嘉陵江干流河漫滩样品采自施家梁镇($29^{\circ}47'36''$ N, $106^{\circ}28'25''$ E)。长江上游干流样品采自丰都河漫滩($29^{\circ}52'30''$ N, $107^{\circ}27'33''$ E)。上述样品主要采集砂级沉积物。

将野外采集回来的碎屑样品经重砂分析、磁性分选等一系列过程,将磷灰石分离出来,并在双目显微镜下进行人工挑选提纯。每个样品随机挑选>300颗制成环氧树脂靶,并对靶片进行表面抛光处理。然后对所有样品进行背散射图像拍摄,圈定磷灰石颗粒的分析位置,避开包裹体和裂隙部位,提高分析精度。

2.2 磷灰石微量元素分析

磷灰石原位微量元素和Sr同位素分析在南京宏创地质勘查技术服务有限公司微区分析实验室使用激光剥蚀—电感耦合等离子体质谱仪(LA-ICPMS)完成。激光剥蚀平台采用Resolution SE型193 nm深紫外激光剥蚀进样系统(Applied Spectra,美国),配备S155型双体积样品池。质谱仪采用Agilent 7900型电感耦合等离子体质谱仪(Agilent,美国),采用束斑直径50 μm 、剥蚀频率10 Hz、能量密度3.5 J/cm²、扫描速度3 $\mu\text{m}/\text{s}$ 的激光参数剥蚀NIST 612,调节气流以获得高信号强度(^{238}U 约为 6×10^5 cps)、低氧化物产率($\text{ThO}/\text{Th}<0.2\%$)。选用100 μm 束斑线扫NIST 610对待测元素进行P/A调谐。磷灰石样品固定在环氧树脂靶上,抛光后在超纯水中超声清洗,分析前用分析级甲醇擦拭样品表面。采用5个激光脉冲对每个剥蚀区域进行预剥蚀(剥蚀深度~0.3 μm),以去除样品表面可能的污染。在束斑直径50 μm 、剥蚀频率5 Hz、能量密度2 J/cm²的激光条件下分析样品。数据处理采用Iolite程序^[46],以NIST 610作为外标, ^{43}Ca 作为内标计算微量元素含量,内标值假定化学计量式。

采用L1、L2、L4、L4、H1、H2和H3法拉第杯组合接收Kr、Rb、Er、Yb和Sr相关质量数的信号。标准溶液NBS 987的 $^{87}\text{Sr}/^{86}\text{Sr}$ 测定值为 $0.710\ 245\pm 0.000\ 025$,与TIMS测定值0.710 236在不确定度范围内一致^[47]。测量前,测定并校正法拉第杯的电子噪音背景,以及放大器的接收增益。在束斑直径50 μm 、剥蚀频率8 Hz、能量密度6 J/cm²的激光条件下分析样品。通常采集20 s的气体空白,35~40 s的信号区间,信号积分时间0.262 s。剔除 ^{88}Sr 信号强度低于0.35 V低信号点以及超出两倍标准偏差的异常点。使用 $^{86}\text{Sr}/^{88}\text{Sr}=0.119\ 4$,按指数规律对其他同位素比值的仪器质量分馏进行在线校正。每隔10~15个样品测试两次Durango磷灰石标样,监控仪器状态。

磷灰石微量元素含量可直接使用非矩阵多维标度MDS(Multidimensional Scaling)统计分析^[48],它是基于K-S统计方法,利用数据之间的相似性对数据进行成分分析,这种相似性分析早已被广泛应用到了碎屑锆石U-Pb年龄、磷灰石微量元素组成、重矿物数据分析中,获得了较好的效果。因此,我们采用该方法对宜昌以上长江干支流碎屑磷灰石的微量元素组成进行MDS统计分析,进行磷灰石微量元素含量相似/向异性分析,从而判断各个支流的磷灰石组成与丰都段长江干流的磷灰石的相关关系。

3 实验结果

磷灰石颗粒的阴极发光图像如图3所示。金沙江、大渡河、岷江、嘉陵江和丰都段长江干流的碎屑磷灰石颗粒以次棱角和棱角长柱状为主,说明这些磷灰石没有经历多期次的沉积循环过程,反映了各自流域内最近磷灰石颗粒的外形特征。磷灰石微量元素和Sr同位素分析结果见表1。可以看出,金沙江的磷灰石P元素含量,尤其是平均值(178 486)与大渡河、岷江、嘉陵江和长江干流明显不同。金沙江的磷灰石Sr元素平均值含量为 $1\ 006\times 10^{-6}$,超过其他各个河流,而其稀土元素总量(ΣREE)又是本次所有河流中最低的(506.5×10^{-6})。在 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值结果中,来自龙门山的三条河流(大渡河、岷江和嘉陵江)要比金沙江和丰都段长江干流的高。因而,总体来说金沙江下游的磷灰石原位微量元素组成与龙门山的河流和长江干流明显不同。

在P元素和Sc元素含量(图4a)、P元素含量和 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值二维散点图中(图4b),金沙江的分布

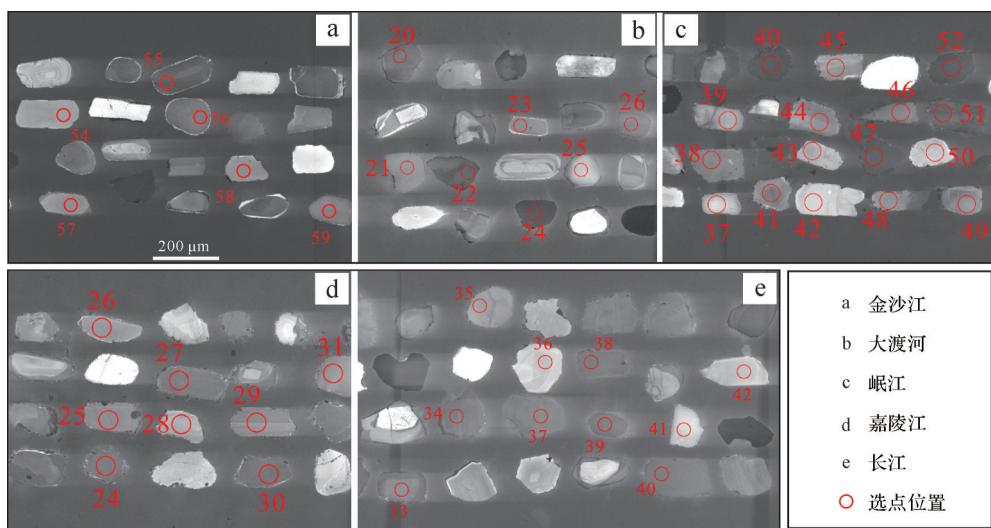


图3 磷灰石原位地球化学分析阴极发光图像

Fig.3 In situ geochemical analysis of apatite cathodoluminescence images

表1 磷灰石原位地球化学数据统计表

Table 1 Descriptive statistics of in situ geochemical data for apatite grains

样品元素	P/ $\times 10^{-6}$	Sc/ $\times 10^{-6}$	Sr/ $\times 10^{-6}$	Σ REE/ $\times 10^{-6}$	$^{87}\text{Sr}/^{86}\text{Sr}$ 比值
金沙江($n=60$)					
最小值	174 300	1.3	99.7	52.1	0.702 80
最大值	195 000	10.8	3 503	6 090.5	0.714 42
平均值	178 486	2.1	1 006	506.5	0.709 43
大渡河($n=60$)					
最小值	183 600	1.3	31.3	16.5	0.704 45
最大值	192 300	2.2	3 114	4 822	0.792 35
平均值	187 610	1.6	486	1 512.7	0.717 21
岷江($n=60$)					
最小值	178 600	1.5	82.6	19.2	0.704 19
最大值	193 100	4.1	5 592	20 879	0.761 44
平均值	188 244	1.9	748.9	2 461.4	0.710 36
嘉陵江($n=60$)					
最小值	168 300	1.3	58.4	61.9	0.703 23
最大值	191 200	16.9	5 816	7 744.2	0.779 79
平均值	186 237	2.1	657.5	2 470.7	0.714 97
长江($n=60$)					
最小值	169 100	1.3	81.1	20.6	0.703 62
最大值	191 800	6.2	13 220	7 742.7	0.738 37
平均值	187 138	1.7	751.5	2 367.9	0.709 84

区域与大渡河、岷江和嘉陵江的明显不同,而丰都段长江干流样品与大渡河、岷江和嘉陵江样品彼此间形成重叠区域。在 Σ REE 和 P 元素含量二维散点图中(图 4c),金沙江下游的磷灰石颗粒分布区域没有和其他流域重叠在一起。在 Sr 元素含量和 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值形成的二维散点图中(图 4d),尽管各个流域的分布区域相对

集中,但依然能看到金沙江形成特定的分布区域。

在 MDS 分析结果中(图 5),金沙江的磷灰石 P 元素含量与其他流域的磷灰石 P 元素含量判别距离较远,而嘉陵江、岷江和大渡河的磷灰石 P 元素含量与丰都段长江干流具有相近性。据此判断,长江上游干流的磷灰石主要来自发源于龙门山的河流。

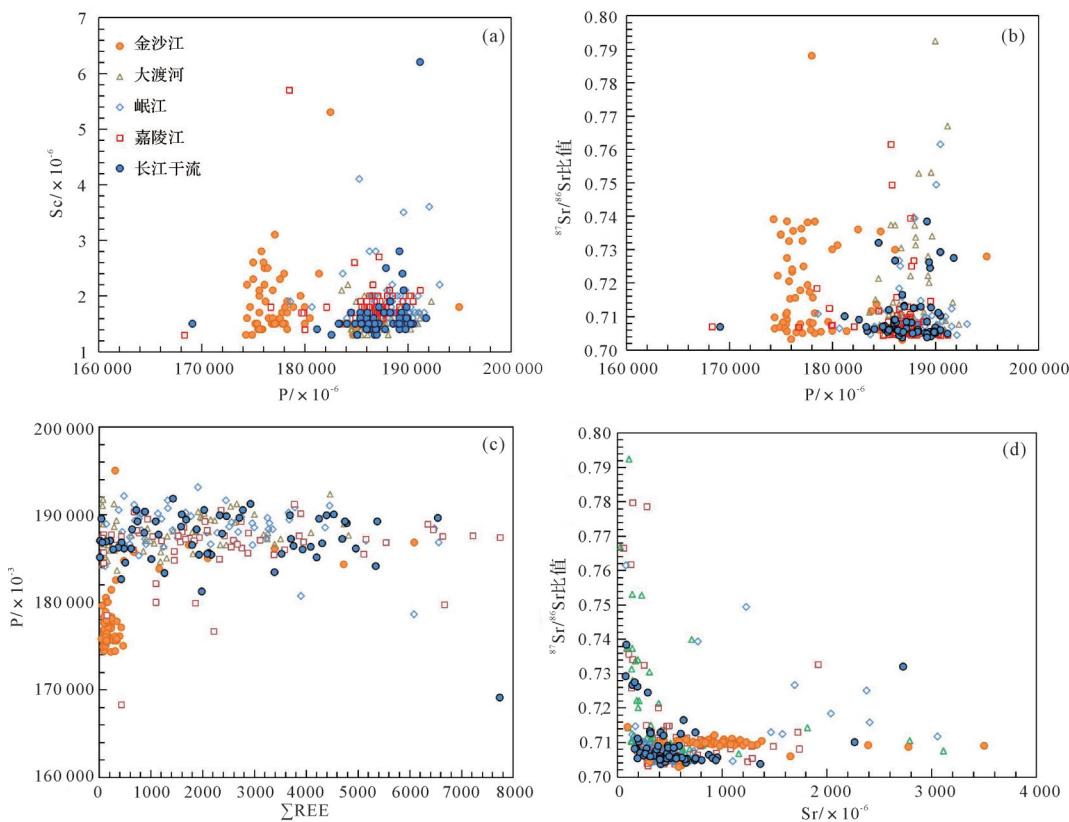


图4 磷灰石地球化学分析结果二维散点图

(a)P vs. Sc;(b)P vs. $^{87}\text{Sr}/^{86}\text{Sr}$;(c) ΣREE vs. P;(d)Sr vs. $^{87}\text{Sr}/^{86}\text{Sr}$

Fig.4 Two-dimensional scatter plots of (a) P and Sc; (b) P and $^{87}\text{Sr}/^{86}\text{Sr}$; (c) ΣREE and P;
(d) Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ contents of fluvial detrital apatite grains

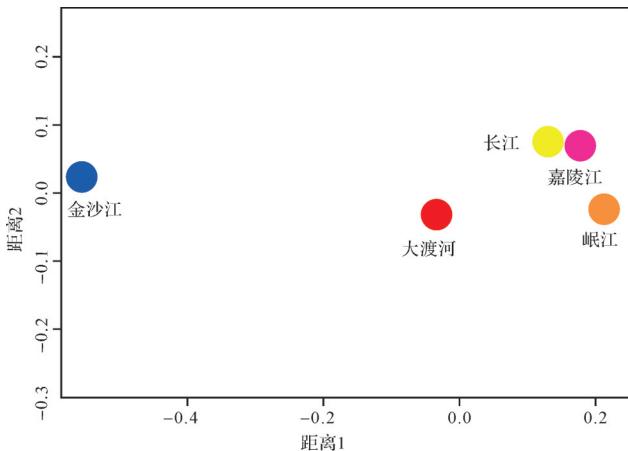


图5 磷灰石 MDS 判别图

Fig.5 MDS identification diagram of apatite grains

4 讨论

磷灰石富集P和Sr等不相容元素,其含量变化由全岩 SiO_2 含量和所在熔体的分配系数控制,因而母岩的分异程度是磷灰石化学组成的主要控制因

素^[49]。此外,磷灰石中的 ^{87}Rb 经过 β^- 衰变后变成 ^{87}Sr ,在剥蚀、搬运和沉积过程中最初的 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值不发生变化^[33]。而这一比值在不同地区、不同时代岩体有明显差异,这是将其运用于大河物源示踪研究的基础。稀土元素(REE)由15个镧系元素(La~Lu)组成,由于它们具有相似的物理和化学性质,在地质体中都倾向于成组出现,在自然界REE的分配形成存在差异^[50-51],这一差异也被广泛用来开展沉积物物源示踪研究。因而,将磷灰石的P、Sr、Sc和ΣREE元素含量或比值与其他元素做散点图的方法用于物源示踪研究最为普遍^[49-51]。对比碎屑磷灰石原位地球化学组成发现,丰都段长江干流的磷灰石颗粒的P、Sr、Sc和ΣREE元素含量与大渡河、岷江和嘉陵江的样品存在重叠,而与金沙江下游的磷灰石颗粒分布区域明显不同(图4)。另外,由于P元素是磷灰石的特征元素,对其进行MDS相似/向异性分析更具有代表性。金沙江下游磷灰石与丰都段长江干流磷灰石的P元素组成判别距离较远,而丰都段长江干流磷灰石

P元素组成和嘉陵江、岷江和大渡河的P元素组成判别距离相近(图5)。这说明丰都段长江物质主要来自发源于龙门山的河流,而金沙江对其碎屑物质的贡献不大。但长江流域的沉积物以轻矿物为主,作为重矿物的磷灰石所占比例低,将其用于长江水系的物源示踪研究时,需要考虑这一影响因素。

从石英成核素¹⁰Be物源示踪和地表侵蚀速率结果^[26,52]来看(图6a),金沙江流域的侵蚀速率较低,长江上游干流物质主要来自嘉陵江、大渡河和岷江;Vezzoli *et al.*^[27]的重矿物组合和主成分分析结果表明嘉陵江成为长江上游干流碎屑物质的主要输送河流。长江上游黏土矿物物源示踪结果显示,大渡河、嘉陵江、岷江对长江干流的物质贡献大^[31]。上述结果与水文站观察到的输沙量结果吻合^[45](图6b)。尽管碎屑锆石U-Pb年龄^[53]和磁铁矿化学组成^[54]物源示踪结果表明,长江上游干流的碎屑物质除了主要来自嘉陵江外,金沙江的作用也不可忽视。但考虑到随着金沙江中下游溪洛渡和向家坝水库的建设并投入

使用,其输沙量减少至 0.02×10^8 t^[55],泥沙主体部分被拦截在这些梯级水库内部,导致其输沙量甚至已经低于乌江(0.05×10^8 t)^[45],对长江干流的泥沙贡献率显著下降。He *et al.*^[53]分析的锆石U-Pb年龄封闭温度高,具有强抗风化性,先前保存于河床的碎屑锆石后期经历多期次沉积再循环过程;王中波等^[54]的采样时间早于金沙江下游溪洛渡和向家坝水库投入使用的时间(2012年)。因而,长江干流依然能出现金沙江以前输入的物质信号。此外,尽管嘉陵江^[56]、岷江^[57](包含大渡河)的输沙量由于人类活动、气候变化和修建水库显著下降,但下降的幅度低于金沙江,嘉陵江和岷江依然有相对充足的碎屑物质供给。嘉陵江及岷江进入丰都段长江的距离远小于金沙江,发源于龙门山的河流输入的碎屑物质“稀释”了金沙江的碎屑物质信号,导致丰都段长江干流现代河流物质主要受发源于龙门山河流的影响。因而,利用长江流域现代河流碎屑磷灰石原位地球化学组成,可以很好地区分龙门山和青藏高原东南缘的河流物质

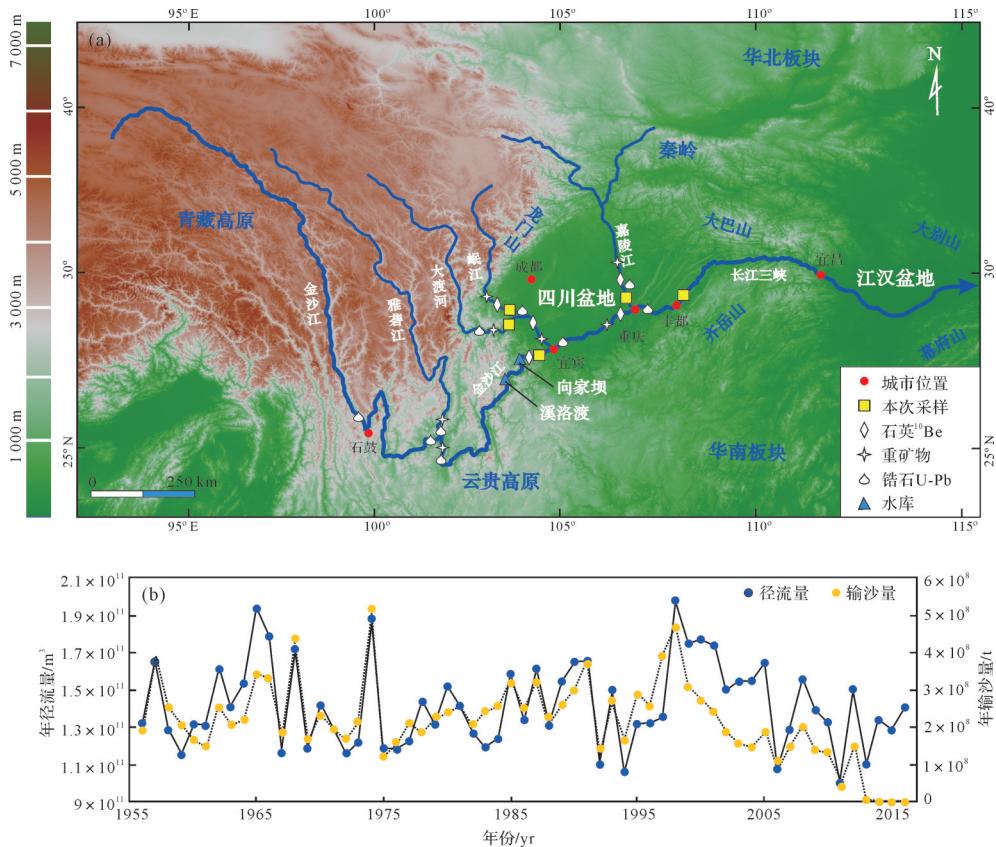


图6 (a)研究区已有研究采样点分布图,石英¹⁰Be^[26,52],重矿物^[27],锆石U-Pb年龄^[53];
(b)金沙江年径流量和年输沙量变化图(据文献[45]修改)

Fig.6 (a) Map of sampling points in the study area, quartz ¹⁰Be^[26,52], heavy minerals^[27], zircon U-Pb age^[53];
(b) Variation of annual runoff and sediment discharge in Jinsha River (modified from reference [45])

信号。利用这一方法在江汉盆地的新生代地层中识别金沙江的物质信号,可能具有很好的物源示踪效果,但该方法无法进一步有效区分发源于龙门山的各条河流的物质信号。因此,在今后利用该方法开展长江流域物源示踪研究时,结合其他方法可以达到精准建立长江源汇关系的研究目的。

5 结论

通过对长江上游干支流开展碎屑磷灰石原位微量元素和 $^{87}\text{Sr}/^{86}\text{Sr}$ 比值分析,在二维散点图中发现金沙江的分布区域与大渡河、岷江和嘉陵江的明显不同,而丰都段长江干流样品与大渡河、岷江和嘉陵江样品彼此间形成重叠区域;进一步结合MDS判断图结果揭示,丰都段长江干流的物质主要来自龙门山。磷灰石原位地球化学分析方法可以有效区分发源于青藏高原东南的金沙江和发源于龙门山的大渡河、岷江和嘉陵江的物质。但其无法进一步有效区分发源于龙门山的各条河流的物质信号。建议将这一方法与其他物源示踪方法联合使用,可以有效建立长江的源汇关系。

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In-situ Geochemical Analysis of Modern Fluvial Detrital Apatite: Implications for provenance tracing studies in the Yangtze River

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Abstract: The Yangtze River is the largest river in East Asia, connecting the Tibetan Plateau and the western Pacific Ocean. The study of its source and sink process is of great scientific significance for understanding the processes of sediment denudation, transport and deposition. In situ analysis of trace elements and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in apatite commonly found in river sediments found from a two-dimensional scatter plot that the distribution area of the Jinsha River was significantly different from that of the Dadu, Minjiang and Jialing Rivers. The Yangtze River mainstream samples in the Fengdu section overlap with those from the Dadu, Minjiang and Jialing Rivers. When combined with the results from a multidimensional scaling (MDS) judgement chart, it was indicated that the material in the main stream of the Yangtze River in the Fengdu Section mainly comes from the Longmen Mountain. The in situ geochemical analysis of apatite effectively distinguished the materials originating from the Jinsha River in the southeastern Tibetan Plateau and from the Dadu, Minjiang and Jialing Rivers in the Longmen Mountain. This provides a better reference for future provenance-tracing studies of the whole Yangtze River Basin. However, due to the important influence of current construction of the Jinsha River cascade hydropower station on the composition of its downstream sediment, caution should be exercised when applying this method in such future studies.

Key words: apatite; trace elements; $^{87}\text{Sr}/^{86}\text{Sr}$ ratio; Yangtze River; provenance tracing