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低铀碳酸盐矿物的 LA-MC-ICPMS 微区原位 U-Pb 定年方法

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摘要 碳酸盐矿物的同位素年代学研究具有广阔的应用前景, 但理想样品少、定年难度大(尤其是低铀样品)等因素限制了该方法的发展. 本研究利用激光剥蚀多接收电感耦合等离子体质谱技术(LA-MC-ICPMS), 建立了针对低铀碳酸盐矿物的微区原位 U-Pb 同位素定年方法. 通过 LA-ICPMS 预扫描, 可以快速筛选出适合定年的样品和最佳剥蚀点, 再借助为实现低铀含量的精确测量而对接收器配置优化设计的 Nu Plasma II MC-ICPMS 进行碳酸盐矿物的 U-Pb 年龄测定. 此外, 通过两种已报道的碳酸盐矿物标样 ASH15 和 WC-1, 标定出一种更加均一且适用对象更广的实验室内部标样 AHX-1a, 其与国际标样长期对比测量获得的年龄加权平均值为 209.8±1.3 Ma($2S_{总}$, n=21, $MSWD$=2.7). 此年龄结果是在半年内不同时期对样品靶不同部位 21 次独立标定的年龄结果的加权平均值, 每一次对测约有 50~150 组数据点, 总共 2000 多组数据点. 与此同时, 为了继续寻找其他理想碳酸盐矿物标样, 更进一步的同位素稀释法标定工作还有待开展.

关键词 碳酸盐矿物, U-Pb 年龄, LA-MC-ICPMS, 矿物标样

碳酸盐矿物(MCO_3, M代表金属阳离子)在地球上广泛分布, 从表生沉积环境到内生成矿环境均有生成. 自然界中, 碳酸盐矿物产状多样, 如碳酸盐脉、晶洞方解石、胶结物、微喀斯特等. 其定年技术具有广阔的应用范围, 不仅适用于记录古气候、古环境、古生态、古人类的洞穴石笋和海洋珊瑚的高精度定年[1~4], 而且能进行与断裂活动和古地震有关碳酸盐脉以及油气储层碳酸盐胶结物的定年[5~7]. 此外, 还有望应用于中低温内生矿床热液活动史和成矿年代学研究.

铀-铅(U-Pb)同位素测年是当下放射性地质年代学研究中应用最广的一种定年方法. 目前常用于U-Pb定年的矿物有锆石、斜锆石、独居石、榍石、磷灰石、磷钇矿和钙钛矿等富U副矿物. 理论上, 保存良好且未遭受后期蚀变的纯净碳酸盐矿物, 只要U/Pb足够高(比如对古生代到中生代样品来说, U/Pb>1)且有一定的变化范围(在Tera-Wassenburg $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$谐和图能够构筑良好的反向等时线), 或普通Pb足够低, 测试点能落在谐和线附近, 均能像上述矿物一样进行U-Pb同位素定年. 但是, 碳酸盐矿物的U含量非常低(一般比锆石低2~4个数量级), 加上普通Pb难以校正等问题, 导致碳酸盐矿物U-Pb定年难度大, 技术发展缓慢.

前人曾用同位素稀释法(isotope dilution, ID)成功对洞穴碳酸盐矿物进行U-Pb定年, 突破了U-Th法的测年范围(<0.5~0.6 Ma)[8,9]. 但ID溶液法要求定年样品拥有足够高的U含量、足够大

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的U/Pb比变化范围且实验室环境及化学处理流程具有足够低的Pb本底. 随着激光剥蚀(laser ablation, LA)技术的兴起, 有关碳酸盐矿物激光原位定年技术受到大量关注[7,10~13]. 与ID溶液法相比, LA原位法在碳酸盐矿物定年方面具有显著优势. 例如, 制样简单、可以预判最佳剥蚀点、微区微量取样、本底低且效率高. 然而, 碳酸盐矿物激光U-Pb定年法在实际开发中仍面临诸多挑战: 满足定年条件的样品少; 低U矿物的测量信号低; 理想矿物标样较缺乏. 目前该技术在国内尚属空白, 国际上也仅几家实验室有过相关报道, 且研究对象多针对高铀样品[10~13].

本研究在中国地质科学院北京离子探针中心和澳大利亚昆士兰大学放射成因同位素实验室共同支持下, 使用ASI RESOlution SE激光剥蚀系统和Nu Plasma II MC-ICPMS成功建立了低铀碳酸盐矿物的U-Pb定年方法(接收器配置和仪器参数见表S1). 对于大多数碳酸盐矿物, 采用的激光束斑直径为100 μm, 能量密度为2~3 J/cm^2, 剥蚀频率为10 Hz. 每测量10或5个未知样品点, 间插2或1次矿物标样点. 其中, NIST614国际玻璃标样用于^{207}Pb/^{206}Pb同位素分馏校正, 方解石矿物标样用于^{238}U/^{206}Pb元素分馏校正(同位素校正流程和方法见文献[11,14]). 再使用Tera-Wassenburg ^{238}U/^{206}Pb-^{207}Pb/^{206}Pb谐和图计算获得的下交点年龄即为碳酸盐矿物的U-Pb年龄[15]. 采用Tera-Wassenburg谐和图法的优点是不需要准确测量和扣除普通铅, 特别适合于古生代以来的碳酸盐矿物测年. 使用上述参数, 我们的Nu Plasma II MC-ICPMS目前可以实现如下灵敏度: U>500000 cps/ppm (1 ppm=1 μg/g), Pb>400000 cps/ppm, ^{207}Pb的本底一般在10~100 cps之间, 该方法具体有以下优点:

(1) LA-ICP-MS预扫描能有效解决选样、取样难的问题. 碳酸盐矿物通常具有复杂的生成历史且易遭受后期改造, 其U, Pb活动性比硅酸盐矿物更难预测. 故此, 选择同源、同时、封闭体系且U/Pb比有一定变化范围的理想定年样品非常困难. 而传统"微钻取样法"不适用于低铀碳酸盐矿物, 一是钻样量大且粉末样易污染; 二是大量样品粉末混合全溶后U/Pb比均一化, 导致不同小样的U/Pb比变化范围小, 在Tera-Wassenburg谐和图上难以构筑理想的等时线以获取精确的下交点年龄.

本研究采用ASI RESOlution SE激光剥蚀系统和Thermo iCap RQ四级杆ICP-MS对未知样品进行预扫描, 以便快速选出测量点^{238}U/^{206}Pb和^{207}Pb/^{206}Pb变化大(足以构筑良好的TW反向等时线)或普通Pb足够低, 测试点能落在谐和线附近的理想样品. 根据预扫描结果, 再使用LA-MC-ICPMS有的放矢地进行U-Pb测年, 可以避免浪费大量珍贵的MC-ICPMS机时. 一般而言, 至少有50%以上的样品因普通铅太高而不适用于U-Pb定年, 并且有一定地域性差别. 如某些地区适合定年的样品能超过90%, 而有些地区则不足10%(特别是具有铅锌矿分布的地区).

(2) 在离散打拿极倍增器或高灵敏度法拉第杯上测量^{238}U可实现不同铀含量的碳酸盐矿物的精确U-Pb同位素静态测量. 一般碳酸盐矿物具有明显低U特征(通常比锆石低2~4个数量级, 即其测量信号只有锆石的1/100~1/10000), 故检测难度非常大. 但碳酸盐矿物本身的铀含量会有几个数量级的变化, 分布范围从1~2 ppb(1 ppb=1×10^{-3} μg/g)到1~10 ppm(一般在0.05~0.5 ppm之间).

前人使用扇形场(sector-field)单接收ICP-MS(如Elements 2或Attom HR)[7,12,14], 或多接收MC-ICPMS(如Nu Plasma HR或modified Neptune)[10,11,13]进行碳酸盐矿物U-Pb同位素测定, 初见成效. 但是, 扇形场单接收ICP-MS的灵敏度没有MC-ICPMS高, 并且因采用跳峰法造成测量时接收效率低. 大多数MC-ICPMS虽能实现^{238}U-^{208}Pb-^{207}Pb-^{206}Pb离子流的高效同时静态测量, 但往往只有^{208}Pb-^{207}Pb-^{206}Pb是在离子计数器(如通道式电子倍增器、离散打拿极电子倍增器或Daly检测器)上检测, 而^{238}U则在10^{11} Ω通用法拉第杯上检测, 通常当U<0.2 ppm时, ^{238}U很难被精确测定. 为了解决这个问题, 我们在昆士兰大学的Nu Plasma II MC-ICPMS上最高质量端安装了10^{12} Ω的前置放大器(比通用的10^{11} Ω的前置放大器的灵敏度高10倍)和1个ETP离散打拿极倍增器(discrete dynode multiplier), 专用于静态测量^{238}U同位素. 当U含量足够高时(如>0.1 ppm), 采用高灵敏度法拉第杯测量; 而当U含量较低时(如<0.1 ppm), 则使用离散打拿极倍增器测量. 因离散打拿极倍增器的背景极低, 一般U含量高于1 ppb时就能精确测定. 除此以外, Nu Plasma II MC-ICPMS在低质量范围另配有5个离散打拿极倍增器, 分别用于静态同时接收^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb (和^{204}Hg干扰峰)以及^{202}Hg离子流. 目前, 如果待测样品的U/Pb比足够高, 即使其U含量低至1 ppb, 我们也能够对其有效定年.

(3) 开发合适的碳酸盐矿物标样. 在激光原位分析中, 寻找或制备基质匹配(matrix-matched)的合适标样是一项重大挑战. 目前国际报道的两种碳酸盐矿物标样分别是ASH15(洞穴钙板, 即flowstone)和WC-1(海相方解石胶结物). 国际上三家实验室采用同位素稀释法分别在TIMS和MC-ICPMS上对ASH15D进行了测量, 其所得年龄加权平均值为3.001±0.012 Ma[11,16]. 然而ASH15D标样, 因为样品极其年轻, 放射性成因Pb丰度低, 不是校正年老碳酸盐矿物的最佳选择. 前人对WC-1进行同位素稀释法标定的年龄结果254.4±6.4 Ma相对离散, U/Pb比变化小且缺少低U/Pb比的数据点, 故其下交点年龄误差大. 使用WC-1进行激光U-Pb定年时的数据点也比较离散, 所得年龄存在3%的不确定性[14]. 但由于碳酸盐矿物缺乏理想标样, WC-1仍被当作国际标样用于激光U-Pb测年. 鉴

于此, 我们尝试标定更加均一、适用范围更广的碳酸盐矿物标样AHX-1a(实验编号CT10), 以及产状和成分一致的其他潜在标样.

AHX-1a是采自塔里木盆地北缘的一种纯净充填孔洞方解石(主、微量数据见表S2), 它的平均U含量约为0.127 ppm, 比锆石标样91500的U含量约低超过700倍. 本研究通过LA-MC-ICPMS技术将潜在标样AHX-1a与已知标样ASH15E(ASH15标样的D和E是同一块标样上的连续生长的两个相邻部位, 间距约1 cm. 因洞穴钙板生长速率很快, D和E之间的年龄差一般不超过一千年, 在±0.012 Ma误差范围内一致)[11,16]长期交叉对测, 标定AHX-1a的年龄并评估该年龄的准确度和重现性.

使用LA-MC-ICPMS仪器, 在100 μm束斑直径、3 J/cm^{2}能量密度和10 Hz剥蚀频率条件下, 以NIST614和ASH15E (3.001 Ma)作外标, 采用样品-标样间插法对AHX-1a长期监测 21次. 结果表明, AHX-1a的U-Pb年龄在不同测试时期具有良好重现性, 其年龄加权平均值为209.8±1.3 Ma($2S_{总}$, N=21, $MSWD$=2.7).

$$S_{总}=\sqrt{\left(S_1^2+S_2^2\right)}, \quad (1)$$

其中S_1代表未知样品, S_2代表标准样品. 为了评估该年龄的准确性, 又以AHX-1a作已知标样, WC-1作未知样品进行多次对测, 使用AHX-1a的标定年龄209.8 Ma对WC-1进行^{238}U/^{206}Pb元素分馏校正, 最终获得WC-1的年龄值与前人的报道值在误差范围内高度一致[14](图1是其中某两次的对测结果, 相关数据参见表S3). 由此表明, 我们标定出的AHX-1a加权平均年龄209.8 Ma是准确可靠的.

与已报道标样ASH15和WC-1相比, AHX-1a标样的均一性更好、适用对象更广. 但鉴于AHX-1a原始样品量偏少, 在没有完全刻画出U-Th-Pb在样品中的空间分布特征之前, 不宜贸然进行同位素稀释法溶液法标定, 故目前暂时被用作实验室内部标样. 当下, 我们还在继续寻找并标定与AHX-1a性质类似、年龄接近但样品量足够大的

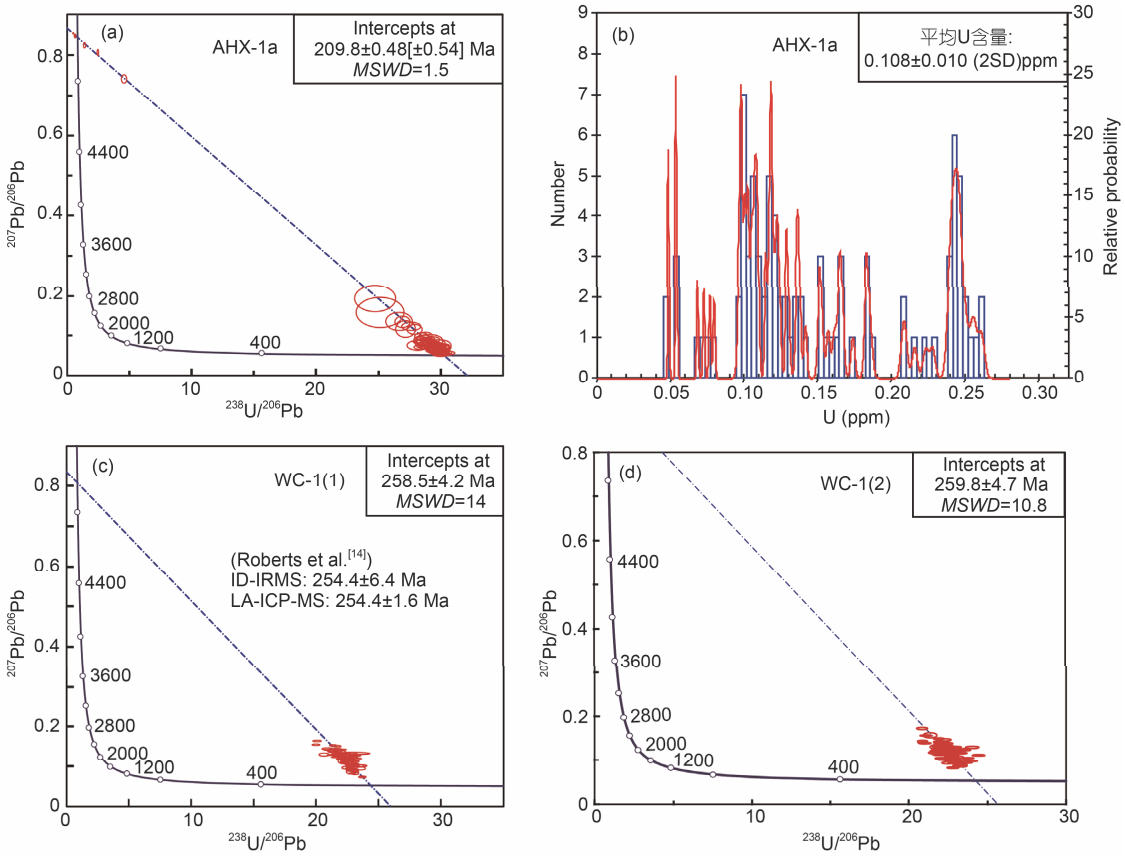


图 1 (网络版彩色)碳酸盐矿物 AHX-1a 和 WC-1 对测的 LA-MC-ICPMS U-Pb 定年结果. (a), (b) 分别是 AHX-1a 某一次的定年结果和所剥蚀点的平均 U 含量; (c), (d) 分别是 WC-1 某两次的定年结果. 以 AHX-1a 作已知标样, WC-1 作未知样品, 使用 NIST614 标准进行 ^{207}Pb/^{206}Pb 同位素分馏校正, 用 AHX-1a 标定年龄 209.8 Ma 对 WC-1 进行 ^{238}U/^{206}Pb 元素分馏校正. 元素分馏校正方法见文献[14]

Figure 1 (Color online) LA-MC-ICPMS U-Pb cross-calibration results for calcite minerals AHX-1a and WC-1, which used AHX-1a as the working standard and WC-1 as an unknown sample. (a), (b) The AHX-1a dating result and the mean U content in one session. (c), (d) The dating results in two sessions of WC-1. ^{207}Pb/^{206}Pb isotope fractionation was calibrated against the international glass standard NIST614, and ^{238}U/^{206}Pb elemental fractionation was corrected against the working standard AHX-1a using recommended age of 209.8 Ma, following the correction procedure described in Ref. [14]

其他潜在标样，并期望通过同位素稀释法使用已有的^{208}Pb-^{233}U混合稀释剂进行独立校正. 目前，我们已经在同一地区找到两块希望很大的潜在标样，更细致的同位素稀释法标定工作有待进一步开展. 一旦我们拥有了^{205}Pb-^{233}U混合稀释剂，不需要溶解掉太多样品时，我们就对AHX-1a进行同位素稀释法标定.

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补充材料

表S1 碳酸盐矿物LA-MC-ICPMS U-Pb同位素测年的接收器配置和仪器参数
表S2 碳酸盐矿物工作标样AHX-1a的LA-ICP-MS主、微量元素含量
表S3 碳酸盐矿物标样AHX-1a和WC-1的LA-MC-ICPMS U-Pb测年结果

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Summary for “低铀碳酸盐矿物的LA-MC-ICPMS微区原位U-Pb定年方法”

In-situ LA-MC-ICPMS U-Pb dating method for low-uranium carbonate minerals

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The *in-situ* U-Pb isotopic geochronology of carbonate minerals has some broad application prospects, not only for the recording of paleoclimate, paleoenvironment, paleoecology, ancient human caverns, calcium plate and marine coral, but also in carbonate vein dating associated with fault activity, neotectonics, paleoearthquake and hydrocarbon reservoirs. However, the development of this method is limited by many factors, such as, very few samples satisfying essential dating conditions, low-uranium carbonates having ultra-low concentrations; and lack of ideal mineral standards. Currently, this technology is still in development in both China and Australia, with only four laboratories in the world having reported results which are mostly for high-uranium (>0.1 ppm) carbonate samples.

In this study, Nu Plasma II multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) with ASI RESOlution SE laser ablation system (LA) is used to refine an *in-situ* U-Pb isotopic dating method for low-uranium carbonate minerals. Here, NIST614 international glass standard is used for $^{207}Pb/^{206}Pb$ isotopic fractionation calibration, and carbonate mineral standard is used for $^{238}U/^{206}Pb$ element fractionation calibration. The age of the lower intersection obtained by using the Tera-Wassenburg (TW) $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ diagram represents the U-Pb age of the carbonate mineral. The improvements made in this study are mainly completed on the following aspects. Firstly, pre-screening with LA-ICP-MS allows for rapid selection of suitable samples, which have large variations in $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ to construct a good TW reverse isochron or their common Pb is so low that measuring points can fall near the concordant line. Secondly, 10^{12} Ω preamplifier at the highest quality end of the Nu Plasma II MC-ICPMS (10 times more sensitive than a versatile 10^{11} Ω preamplifier) and an ETP (electron multiplier) discrete dynode multiplier dedicated to static measurement of ^{238}U isotope were installed. The high sensitivity Faraday cup measurement is used when the U content is sufficiently high (e.g. >0.1 ppm); while the discrete dynode multiplier is used if the U content is low (e.g. <0.1 ppm). Thirdly, a potential carbonate standard AHX-1a (calcite) has been characterized through cross-calibration with the international standard ASH15 (flowstone) and attained the recommended age of 209.8±1.3 Ma ($2S_{total}$, N=21, $MSWD$=2.7). This result is a weighted average age of 21 consecutive independent calibrations of different parts of the sample mount over a period of six months, with approximately 50–150 sets of data points at each time, for a total of approximately 2000 data points. In order to evaluate the accuracy of the recommended age (209.8 Ma) of AHX-1a, we have performed simultaneous measurement of AHX-1a and WC-1 (marine calcite cement) in different sessions, treating AHX-1a as the known standard and using the age of 209.8 Ma to correct element fractionation of WC-1. The dating results are highly consistent with previous results within the error range, which demonstrates that the recommended age (209.8 Ma) of the potential standard AHX-1a is accurate and reliable.

Compared with the reported standards ASH15 and WC-1, AHX-1a is more homogeneous and wider application potential. However, in view of the fact that the original sample size of AHX-1a is small, which makes it not suitable for isotope dilution calibration method before its spatial distribution characteristics of U-Th-Pb are completely delineated. Therefore, AHX-1a is temporarily used only as an in-house standard in our laboratory. Currently, we are continuing to search for and calibrate other potential standards with similar characteristics to AHX-1a, but of a larger sample size. To continuously characterize and identify suitable carbonate reference materials, further calibration using isotope dilution is planned.

carbonates, U-Pb age, LA-MC-ICPMS, carbonate reference material

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