利用Picarro测试石笋包裹体水氢、氧同位素的方法

田野¹, 张海伟^{1*}, 宗保云¹, 段鹏珍¹, Hubert B. Vonhof², Yuri V. Dublyansky³, 宁有丰¹, Christoph Spötl³, 蔡演军¹, 程海^{1*}

1. 西安交通大学全球环境变化研究院, 西安 710054;

2. Department of Climate Geochemistry, Max Planck Institute for Chemistry, Mainz 55128, Germany;

3. Institute of Geology, University of Innsbruck, Innsbruck 6020, Austria

* 联系人, E-mail: zhanghaiwei@xjtu.edu.cn; cheng021@xjtu.edu.cn

2020-02-29 收稿, 2020-07-28 修回, 2020-07-29 接受, 2020-08-03 网络版发表

国家自然科学基金(41972186)和国家自然科学基金基础科学中心项目(41888101)资助

摘要 基于当前石笋包裹体水提取测试过程中面临的制约条件, 本研究设计了用于提取石笋包裹体水的真空装置, 将其与水同位素分析仪Picarro L2140-i相连接组成石笋包裹体水氢、氧同位素(δD 、 $\delta^{18}O$)测试系统. 该系统能够快速提取石笋包裹体中的水, 并对其 δD 和 $\delta^{18}O$ 的值进行测量. 包裹体水真空提取装置使用了以高压气缸为驱动的破碎研磨器, 具有良好的破碎效果; 在120°C真空条件下破碎获得的包裹体水随后被高纯氮气带入到Picarro L2140-i中进行测量分析. 为了验证包裹体水测试系统的可靠性和准确性, 本研究分别将石笋包裹体水真空提取装置以及Picarro液态水自动进样器与Picarro L2140-i主机连接, 对相同的水样品进行了对比测试. 两种方法测得的 $\delta^{18}O$ 和 δD 值在误差范围内接近. 使用该系统对东亚季风区石笋样品进行的测试结果显示: 石笋包裹体水的 $\delta^{18}O$ 和 δD 值分布在全球大气降水线附近, 表明测试过程中分馏作用较小; 包裹体含水量对测试精度有一定影响, 对于水汽浓度为2500~50000 ppm(1 ppm=1 $\mu L/L$)的样品, $\delta^{18}O$ 、 δD 的标准差分别为0.5‰、2‰, 与同类型系统相当. 研究结果表明该系统能如实测量石笋包裹体水的 $\delta^{18}O$ 和 δD 值, 将为利用水-碳酸盐平衡分馏方程重建古温度提供重要的技术支撑.

关键词 石笋包裹体, 稳定同位素, 水同位素分析仪(Picarro), 波长扫描光腔衰荡光谱, 古温度

石笋作为分布广泛、生长稳定、信息丰富的古气候研究重要载体, 可以利用U/Th定年方法进行高精度、高分辨率的绝对年代测定^[1~3]. 过去30年, 众多学者在利用石笋碳、氧稳定同位素($\delta^{13}C$ 、 $\delta^{18}O$)^[4~7]、微量元素^[8~11]、纹层厚度^[12]等指标重建区域环境和气候变化及相关指标与全球气候变化的联系方面取得了一系列重要研究进展. 但上述气候指标多用于指示水文气候变化, 且指标的气候意义仍存在争议. 例如, 有研究指出石笋 $\delta^{13}C$ 并不总是单一地指代洞穴上覆植被的变化^[13~16], 还可能受到碳酸盐先期沉淀等其他因素影响^[9,17]. 在亚洲季风区, 轨道-千年尺度的石笋 $\delta^{18}O$ 变化

通常被用于指示亚洲季风强度或从水汽源区至研究洞穴之间大范围降水变化^[7,18], 年代际-百年尺度上的季风边缘区石笋 $\delta^{18}O$ 记录被用于重建研究地区降水量的变化^[19~21]. 然而, 近来多项研究认为东亚季风区石笋 $\delta^{18}O$ 还可能受到冬季温度、水汽源或路径、水汽源区对流强度等因素的影响^[22~26]. 因此, 亟须开发其他影响因素较为单一的石笋代用指标. 另外, 目前较少有用于古温度重建的石笋代用指标, 尽管有研究利用石笋纹层厚度进行古温度重建^[12], 但是仅适用于生长纹层清晰的少数石笋样品. 利用石笋包裹体水重建古温度记录为解决该问题提供了可能. 例如, Zhang等人^[27]利用

引用格式: 田野, 张海伟, 宗保云, 等. 利用Picarro测试石笋包裹体水氢、氧同位素的方法. 科学通报, 2020, 65: 3626–3634

Tian Y, Zhang H W, Zong B Y, et al. Measurement of oxygen and hydrogen isotopic ratios of speleothem fluid inclusion water using Picarro (in Chinese). Chin Sci Bull, 2020, 65: 3626–3634, doi: 10.1360/TB-2020-0201

加拿大Jacklah Jill洞穴石笋包裹体水 δD 和 $\delta^{18}O$ 测试结果重建当地10~6 ka BP温度记录,并验证了结果的可靠性,证实了获得的古温度数据能够真实反映当地古气候变化记录。Griffiths等人^[28]利用石笋包裹体水 $\delta^{18}O$ 值重建了印度尼西亚南部Liang Luar洞穴全新世的平均温度,与利用印度洋-太平洋浮游有孔虫Mg/Ca记录重建的海表温度相一致。

石笋包裹体是洞穴石笋在生长过程中由于碳酸钙晶体结构的缺陷,将气体和液体封闭在晶格结构之中而形成的,他们保存了沉积物在形成时的原始信息,且在包裹体形成后较少受到外界环境影响。包裹体水的同位素组成继承于洞外大气降水,在石笋碳酸盐形成过程中与周边晶体发生水-碳酸钙平衡分馏^[29]。因此,通过分别测量包裹体水和石笋的 $\delta^{18}O$ 值,利用水-碳酸钙平衡分馏方程便可以计算包裹体形成时的洞穴温度^[30,31],即可推算出洞外的平均温度,进而重建研究地区的温度变化历史^[32~37]。利用 $\delta^{18}O$ 和 δD 还可以进一步计算氘盈余(d-excess),这一指标可以用来反映海水蒸发的情况(如海表温度、湿度等)^[38,39]。但因包裹体水提取难度大,同时也存在较大的分析误差,使得利用石笋包裹体水重建古温度的技术方法一直受到制约。

制约石笋包裹体水 $\delta^{18}O$ 和 δD 测试分析的关键在于:(1)包裹体水的提取;(2) $\delta^{18}O$ 和 δD 测试分析方法。包裹体水的提取主要有热爆裂法、直接提取法以及真空机械压碎研磨法。热爆裂法主要是将2 mm左右大小的石笋样品放置在真空高温加热条件下使其发生分解,从而释放包裹体内的水分^[40~42]。热爆裂过程的温度很高,可能会引起同位素的分馏。研究发现热爆裂法测得的现代石笋包裹体水 δD 的值比直接测定石笋所在洞穴滴水 δD 的值偏轻20%~30%^[40,43]。因此,目前热爆裂方法较少被采用。直接提取法则需要将石笋制成薄片,在显微镜下选取合适的包裹体并用微钻进行钻孔,使用注射器抽取包裹体水进行测试^[44]。该方法可以提取单一包裹体水的信息,避免了多个包裹体水混合对 $\delta^{18}O$ 和 δD 值造成干扰,但这一方法对样品的要求较为苛刻,需要有较大的包裹体才能进行测试,适用性差^[45]。真空机械压碎研磨法是在120~150°C真空条件下,通过施加压力将样品进行破碎^[4,46]。该方法在一定程度上能够避免高温热爆裂法产生的同位素分馏(δD 值偏轻)问题,操作简单、测试速度快、且适用于大多数石笋样品。

在石笋包裹体水测试分析方法方面,Bigeleisen等人^[47]和Friedman^[48]较早建立了将水转化为氢气并利用

质谱仪进行测试的方法。Schwarcz等人^[4]、Harmon等人^[49]以及Norman和Sawkins^[50]在此基础上开展了石笋包裹体水的测试。Dennis等人^[46]首先引入了包裹体水氢、氧同位素混合测试方法。目前对石笋包裹体水的测试方法主要使用双入口同位素比质谱(dual-inlet isotope ratio mass spectrometry)和连续流同位素比质谱(continuous-flow isotope ratio mass spectrometry, CF-IRMS)两种方法。这两种方法都需要将水分子通过化学方法转化成适合氢氧同位素质谱仪测试的气体。Vonhof等人^[51]使用CF-IRMS方法成功得到了包裹体水的氢氧同位素比值,其系统使用的包裹体水提取装置包含破碎器、冷阱和快速加热模块,通过载气直接将水在~200°C温度下输送至高温元素转换分析仪(high-temperature conversion-elemental analyzer, TC-EA)中。水分子在TC-EA中与玻璃碳反应转化为 H_2 和 CO ,随后被填充气相色谱柱分离,依次进入质谱仪进行测试。Dublyansky和Spötl^[52]在此基础上改进了破碎器,使系统能够测试更加少量(0.1~0.2 μL)的包裹体水,其测得的 $\delta^{18}O$ 和 δD 标准差分别为0.5‰、1.5‰。Wainer等人^[53]分别利用上述两套系统进行测试后发现二者之间的 $\delta^{18}O$ 、 δD 值分别存在1‰和3‰的偏差。

近年来,波长扫描光腔衰荡光谱技术(wavelength scanned cavity ring-down spectroscopy, WS-CRDS)凭借其在水体 δD 、 $\delta^{18}O$ 测试中分析速度快、样品处理简单、便于维护等优点受到广泛应用。WS-CRDS技术的原理是由单频激光二极管激发的光束在由3面高反射率反射镜构成的衰荡腔中进行多次循环反射,为光线与待测气体之间的相互作用创造了长达数千米的有效吸收光程,大大提升了痕量气体测量的灵敏度并缩短了测量时间。WS-CRDS方法和IRMS方法之间的区别在于前者可以直接吸收与 $H_2^{16}O$ 、 $H_2^{18}O$ 和 $H_2^{16}O$ 分子振动频率相对应的特定波长的激光,不需要将水分子转化为其他分子。实验表明,利用WS-CRDS进行水同位素分析的精度优于传统的IRMS系统^[54]。Arienzo等人^[55]使用WS-CRDS技术进行石笋包裹体水测试,并设计了石笋包裹体水提取装置,将其与使用WS-CRDS技术进行工作的水同位素分析仪Picarro L2130-i(Picarro, Inc., Santa Clara, CA, 美国)连接组成包裹体水测试系统,利用该系统测得的 $\delta^{18}O$ 、 δD 标准差分别为0.5‰、2‰。随后,Affolter等人^[56]设计了连续稳定水汽流的包裹体水提取装置,并和Picarro L1102-i相连接组成包裹体水测试系统,其测得的 $\delta^{18}O$ 、 δD 标准差分别为

0.4‰、1.5‰。

本研究所建立的石笋包裹体水 δD 和 $\delta^{18}\text{O}$ 测试系统在Arienzo等人^[55]的基础上进行了改进,使用了更加先进的水同位素分析仪Picarro L2140-i,并使用以气缸作为驱动的破碎研磨器;同时还改进了测试流程。

1 系统设计

石笋包裹体水 δD 和 $\delta^{18}\text{O}$ 测试系统可分为两部分,系统前半部分为石笋包裹体水真空提取装置,后半部分为进行 $\delta^{18}\text{O}$ 和 δD 测试的水同位素分析仪Picarro L2140-i(图1(a)).包裹体水真空提取装置由不锈钢制作,包括注射口、破碎研磨器、过滤器、缓冲瓶、真空泵等(图1(b)).此外,还通过设置进气阀(图1(b), V1)、真空阀(图1(b), V2)、三通阀门(图1(b), V5)、排气阀(图1(b), V6)等阀门控制系统内气体的流动过程.系统使用干燥的高纯氮气(N_2)作为载气.装置外侧由温度为 120°C 的伴热带包裹,目的是使从包裹体中释放的水迅速汽化并在输送过程中始终保持气体状态,确保没有因水蒸气凝结而发生分馏。

(i) 注射口.注射口设置在破碎研磨器前(图1(a)中黄色框内),由隔膜垫密封,一般使用 $1\ \mu\text{L}$ 注射器进行注射。

(ii) 破碎研磨器.破碎研磨器由气缸、活塞、加热底座以及密封部分组成(图1(c)).加热底座温度保持在 120°C ,通过控制操纵杆使活塞垂直上下运动,活塞杆在 $400\ \text{kPa}$ 压力驱动下能够产生 $4.1\ \text{kg}/\text{cm}^2$ 的压力,可以快速地粉碎放置于基座内部的块状石笋样品.在活塞和底座连接处,通过聚四氟乙烯密封圈进行密封。

(iii) 缓冲瓶.为使水汽与载气充分混合,在气体进入仪器前放置了体积为 $40\ \text{mL}$ 的缓冲瓶(图1(a)中蓝色框内),在缓冲瓶前后分别设置1个阀门,将缓冲瓶与破碎研磨器和仪器隔离(图1(b), V3, V4)。

(iv) 真空泵和排气口.真空泵接口位于破碎研磨器和缓冲瓶之间,通过真空阀(图1(b), V2)与系统相连接.真空泵的主要作用是在每个样品测试结束后快速除去管路中残留气体,使整个装置中的水汽浓度降至本底值以下.排气口位于载气入口处,压力表之前,由排气阀(图1(b), V6)控制,是为了防止装置内部压力过大,对仪器造成损坏,一般情况下阀门始终保持关闭状态。

(v) 三通阀门.石笋包裹体水真空提取装置与水同位素分析仪Picarro L2140-i通过三通阀门(图1(b), V5)相连接.阀门一端连接Picarro L2140-i主机(图1(a)中绿色框内),一端与阀门(图1(b), V4)连接,另一端连接至载气瓶与进气阀(图1(b), V1)之间.这一设计是为

图1 石笋包裹体水测试系统. (a) 石笋包裹体水 δD 和 $\delta^{18}\text{O}$ 测试系统实物图,绿色框内为Picarro L2140-i水同位素分析仪,黄色框内为注射口,红色框内为破碎研磨器,蓝色框内为 $40\ \text{mL}$ 缓冲瓶. (b) 石笋包裹体水 δD 和 $\delta^{18}\text{O}$ 测试系统示意图.包裹体水真空提取装置在 120°C 下进行加热,以确保系统内无水分残留. (c) 以气缸为驱动的破碎研磨器示意图,气缸通过操纵杆与活塞连接,使其上下运动,将样品破碎,释放包裹体水。

Figure 1 Fluid inclusion isotope analysis system. (a) Photograph of the fluid inclusion isotope (δD , $\delta^{18}\text{O}$) analysis system consisting of a Picarro L2140-i analyzer (green box), syringe injection unit (yellow box), crusher (red box) and a $40\ \text{mL}$ homogenization volume (blue box). (b) Schematic of fluid inclusion isotope (δD , $\delta^{18}\text{O}$) analysis system. The entire vacuum extraction device is heated to 120°C to minimize the absorption of water. (c) Schematic of the assembled crusher. A pneumatically operated piston finely crushes chips of speleothem calcite that are placed in the sample chamber, thus releasing the fluid inclusion water.

确保当包裹体水提取装置处于真空状态而使载气无法通过装置进入仪器时, 载气可以直接通过三通阀门进入Picarro L2140-i主机, 从而防止空气中的水进入仪器。

2 测试方法

由于不同石笋样品含水量不同, 首先应对样品包裹体含水量进行预判, 根据含水量确定测试石笋样品的大小。将块状石笋样品放置于破碎研磨器中并检查气密性后, 打开进气阀V1通入载气(17 kPa)进行吹扫。

待Picarro中的水汽浓度背景值低于100 ppm(1 ppm=1 $\mu\text{L/L}$)时, 关闭V1并转换三通阀V5使载气直接进入Picarro主机中而不通过真空提取装置, 打开真空阀V2将装置抽至真空后, 关闭V2及V4, 开始对样品进行破碎研磨。

当样品被压碎后, 立即打开V1通入载气, 当压力表显示气压达到17 kPa时, 关闭V1。等待90 s后, 打开V4并转换V5与缓冲瓶连通, 使与载气充分混合的包裹体水进入水同位素分析仪, 当Picarro显示水汽浓度>5000 ppm时, 关闭V3。

当Picarro显示的水汽浓度达到平稳状态后, 等待250 s, 打开V3并转换V5使载气直接进入水同位素分析

仪中, 降低系统中的水汽浓度, 同时打开压碎研磨器, 清理已破碎的样品粉末, 测试结束。

每次进行石笋样品测试前, 需要先通过注射口注射不同浓度的标准水建立校正方程, 测试所选取的标准水的 δD 与 $\delta^{18}\text{O}$ 值需与待测石笋包裹体水的 δD 、 $\delta^{18}\text{O}$ 值接近。Johnson等人^[57]指出, 当进入仪器中的水汽含量低于2500 ppm时, 仪器测量结果误差显著增大, 在本研究中也发现有类似现象。故本实验室使用SEG 1 μL (SGE analytical science syringe)注射器, 对每种标准水随机注射0.2、0.4、0.6、0.8、1.0 μL 各至少2次, 直到校正方程符合测试标准值为止。每次更换新的样品后, 还需连续注射至少2次0.6 μL (~20000 ppm)标准水检测系统稳定性。样品测试完毕后, 需再注射2次与样品水汽浓度相当的标准水进行对照, 方可进行下一样品的测试。

3 结果与讨论

3.1 水样品测试

为了验证系统测试结果的可靠性和准确性, 本研究分别利用石笋包裹体水真空提取装置以及Picarro液态水自动进样器与Picarro L2140-i主机连接, 选取西安

图 2 石笋SN40包裹体水测试结果. (a) 石笋SN40样品及采样位置(红色矩形); (b) 石笋SN40不同层位包裹体水 $\delta^{18}\text{O}$ 和 δD 平均值分布(黑色圆形). 黑色线为GMWL, 灰色线为 $\delta^{18}\text{O} \pm 0.5\text{‰}$ 区间

Figure 2 Fluid inclusion testing results of stalagmite SN40. (a) Picture of stalagmite SN40, red squares show the sampling positions of the fluid inclusion samples; (b) $\delta^{18}\text{O}$ and δD values (VSMOW) plotted for fluid inclusions from SN40 (black dots). Black line represents the GMWL and the two grey lines are $\pm 0.5\text{‰}$ $\delta^{18}\text{O}$

交通大学同位素实验室标准水LAB1、LAB2以及LAB3分别进行对比测试. 3种标准水样品 δD 与 $\delta^{18}O$ 的值均通过国际原子能机构(IAEA)标准进行标定获得. 首先将实验室标准水样品手动注射进入包裹体水真空提取装置, 并按照上述测试流程使其进入仪器进行测试. 作为对照, 将同样的标准水样品通过Picarro液态水自动进样器抽取并注射至汽化室内, 再进入仪器进行测试. 两种方法都须保证注射的水汽浓度在20000 ppm左右. 结果显示两种方法测得的 $\delta^{18}O$ 和 δD 的值相近(表S1).

3.2 石笋样品测试

本研究对位于东亚季风区的江西神农宫洞穴1根石笋样品(SN40)进行测试. 该石笋底部和顶部的 ^{230}Th 年龄分别为 7648 ± 80 和 4202 ± 47 a BP. 该样品生长速率较快, 孔隙含水量较大, 适用于包裹体水的提取、测试. 在石笋不同深度的生长层分别切割包裹体样品(图2(a)), 每个生长层采集3块样品进行测试. 从测试结果(表1)可以看出, $\delta^{18}O$ 最大标准差为0.7‰, δD 最大标准差为2.0‰, 且每一生长层的3块样品水汽含量越接近, 测试结果的标准差值越小. 对于一些包裹体水含量较少的石笋样品, 测试结果的精度较低, 可通过增加样品量以确保水汽量达到仪器测试的最佳区间, 从而提升测试精度. 但不论样品含水量高或低, 测试结果都具有一定的重现性. 同时, 石笋SN40每一层位的包裹体水 $\delta^{18}O$ 和 δD 平均值分布在全球大气降水线(global meteoric water line, GMWL) $\delta^{18}O \pm 0.5\%$ 范围内(图2(b)). 这表明 $\delta^{18}O$ 和 δD 在测试过程中受到同位素分馏的影响很小, 这与前人的研究成果一致^[36,37,55,56,58]. 因此, 该测试结果能够如实反映石笋包裹体形成时原始水的同位素组成.

综合以上测试结果可以看出, 本研究使用的包裹体水测试系统(简称为“XJTU System”)对石笋包裹体水测试的 $\delta^{18}O$ 值的标准差为0.5‰, δD 值的标准差为2‰. 该精度与其他同类型系统测试结果的精度相当(表2).

4 结论

本研究利用水同位素分析仪Picarro L2140-i建立了石笋包裹体水 δD 和 $\delta^{18}O$ 测试系统, 在包裹体水真空提取装置中使用以气缸为驱动的破碎研磨器, 具有较好的破碎效果. 本系统能够快速、准确地测定石笋包裹体水的 $\delta^{18}O$ 和 δD 值, 测试分析流程相对简单且结果稳定.

表 1 神农宫石笋SN40包裹体水 $\delta^{18}O$ 和 δD 测试结果

Table 1 $\delta^{18}O$ and δD values of the fluid inclusions from SN40, Shennong Cave

样品编号	水汽含量(ppm)	$\delta^{18}O$ (‰, VSMOW)	δD (‰, VSMOW)
SN40-28	26790	-5.55	-37.78
SN40-28	4409	-6.46	-40.30
SN40-28	20750	-6.10	-40.62
标准差		0.46	1.56
SN40-B	21550	-5.76	-39.72
SN40-B	13300	-6.62	-41.74
SN40-B	5740	-7.14	-42.11
标准差		0.70	1.29
SN40-C	20020	-5.73	-44.14
SN40-C	28330	-6.16	-43.93
SN40-C	31410	-6.19	-44.89
标准差		0.26	0.50
SN40-D	20460	-6.59	-41.88
SN40-D	13940	-6.91	-42.71
SN40-D	21570	-6.83	-43.51
标准差		0.17	0.82
SN40-F	23590	-6.11	-41.36
SN40-F	8034	-7.20	-42.97
SN40-F	29620	-6.61	-43.24
标准差		0.54	1.01
SN40-G	28200	-5.97	-38.73
SN40-G	6731	-6.21	-40.82
SN40-G	32670	-5.24	-36.80
标准差		0.51	2.01

表 2 本研究使用的石笋包裹体水 δD 和 $\delta^{18}O$ 测试系统(XJTU System)与其他测试系统测试精度对比

Table 2 Comparison of the standard deviation of $\delta^{18}O$ and δD between XJTU System used in this study and other published systems

系统名称	$\delta^{18}O$ (‰)	δD (‰)
Amsterdam Device ^[50]	0.7	2.0
Innsbruck System ^[51]	0.5	1.5
Miami Device ^[54]	0.5	2.0
Bern Line ^[55]	0.4	1.5
XJTU System	0.5	2.0

使用包裹体水真空提取装置和Picarro自动进样器分别与Picarro L2140-i主机相连接, 对相同的水样品进行测试, 两种方法获得的 $\delta^{18}O$ 和 δD 值有良好的一致性,

表明本系统的测试分析方法是可靠、准确的。对同一层位的石笋样品进行多次测试,结果表明本系统对包裹体含水量在合理区间(2500~50000 ppm)的样品测试 $\delta^{18}\text{O}$ 、 δD 的标准差分别为0.5‰、2‰,与同类型测试系

统的精确度相当。本系统测得的 $\delta^{18}\text{O}$ 和 δD 值位于GMWL附近,说明测试过程受到同位素分馏的影响较小。以上结果表明本研究所使用的系统可以很好地应用于石笋包裹体水 $\delta^{18}\text{O}$ 和 δD 值的测定。

参考文献

- 1 Edwards R L, Chen J H, Wasserburg G J. ^{238}U - ^{234}U - ^{230}Th - ^{232}Th systematics and the precise measurement of time over the past 500000 years. *Earth Planet Sci Lett*, 1987, 81: 175-192
- 2 Cheng H, Edwards R L, Hoff J, et al. The half-lives of uranium-234 and thorium-230. *Chem Geol*, 2000, 169: 17-33
- 3 Cheng H, Edwards R L, Shen C C, et al. Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth Planet Sci Lett*, 2013, 371-372: 82-91
- 4 Schwarcz H P, Harmon R S, Thompson P, et al. Stable isotope studies of fluid inclusions in speleothems and their paleoclimatic significance. *Geochim Cosmochim Acta*, 1976, 40: 657-665
- 5 Wang Y J, Cheng H, Edwards R L, et al. A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. *Science*, 2001, 294: 2345-2348
- 6 Fleitmann D, Burns S J, Mudelsee M, et al. Holocene forcing of the Indian monsoon recorded in a stalagmite from Southern Oman. *Science*, 2003, 300: 1737-1739
- 7 Cheng H, Edwards R L, Sinha A, et al. 640000 years and ice age terminations. *Nature*, 2016, 534: 640-646
- 8 McIntire W L. Trace element partition coefficients—A review of theory and applications to geology. *Geochim Cosmochim Acta*, 1963, 27: 1209-1264
- 9 Fairchild I J, Borsato A, Tooth A F, et al. Controls on trace element (Sr-Mg) compositions of carbonate cave waters: Implications for speleothem climatic records. *Chem Geol*, 2000, 166: 255-269
- 10 Fairchild I J, Smith C L, Baker A, et al. Modification and preservation of environmental signals in speleothems. *Earth-Sci Rev*, 2006, 75: 105-153
- 11 Fairchild I J, Treble P C. Trace elements in speleothems as recorders of environmental change. *Quat Sci Rev*, 2009, 28: 1-20
- 12 Tan M, Baker A, Genty D, et al. Applications of stalagmite laminae to paleoclimate reconstructions: Comparison with dendrochronology/climatology. *Quat Sci Rev*, 2006, 25: 2103-2117
- 13 Salomons W, Mook W G. Isotope geochemistry of carbonates in the weathering zone. In: Fritz P, Fontes J C, eds. *Handbook of Environmental Isotope Geochemistry*. Amsterdam: Elsevier, 1986, 2: 239-269
- 14 Schwarcz H P. Geochronology and isotopic geochemistry of speleothems. In: Fritz P, Fontes J C, eds. *Handbook of Environmental Isotope Geochemistry*. Amsterdam: Elsevier, 1986, 2: 271-303
- 15 Dorale J A, González L A, Reagan M K, et al. A high-resolution record of Holocene climate change in speleothem calcite from Cold Water Cave, northeast Iowa. *Science*, 1992, 258: 1626-1630
- 16 Dorale J A, Edwards R L, Ito E, et al. Climate and vegetation history of the midcontinent from 75 to 25 ka: A speleothem record from Crevice Cave, Missouri, USA. *Science*, 1998, 282: 1871-1874
- 17 Cruz Jr F W, Burns S J, Karmann I, et al. A stalagmite record of changes in atmospheric circulation and soil processes in the Brazilian subtropics during the Late Pleistocene. *Quat Sci Rev*, 2006, 25: 2749-2761
- 18 Wang Y, Cheng H, Edwards R L, et al. Millennial- and orbital-scale changes in the East Asian monsoon over the past 224000 years. *Nature*, 2008, 451: 1090-1093
- 19 Zhang P, Cheng H, Edwards R L, et al. A test of climate, sun, and culture relationships from an 1810-year Chinese cave record. *Science*, 2008, 322: 940-942
- 20 Tan L, Cai Y, Cheng H, et al. Summer monsoon precipitation variations in central China over the past 750 years derived from a high-resolution absolute-dated stalagmite. *Palaeogeogr Palaeoclimatol Palaeoecol*, 2009, 280: 432-439
- 21 Tan L, An Z, Huh C A, et al. Cyclic precipitation variation on the western Loess Plateau of China during the past four centuries. *Sci Rep*, 2014, 4: 6381
- 22 Clemens S C, Prell W L, Sun Y. Orbital-scale timing and mechanisms driving Late Pleistocene Indo-Asian summer monsoons: Reinterpreting cave speleothem $\delta^{18}\text{O}$. *Paleoceanography*, 2010, 25: PA4207
- 23 Dayem K E, Molnar P, Battisti D S, et al. Lessons learned from oxygen isotopes in modern precipitation applied to interpretation of speleothem records of paleoclimate from eastern Asia. *Earth Planet Sci Lett*, 2010, 295: 219-230
- 24 Tan M. Circulation effect: Response of precipitation $\delta^{18}\text{O}$ to the ENSO cycle in monsoon regions of China. *Clim Dyn*, 2014, 42: 1067-1077

- 25 Tan M. Circulation background of climate patterns in the past millennium: Uncertainty analysis and re-reconstruction of ENSO-like state. *Sci China Earth Sci*, 2016, 59: 1225–1241
- 26 Maher B A. Holocene variability of the East Asian summer monsoon from Chinese cave records: A re-assessment. *Holocene*, 2008, 18: 861–866
- 27 Zhang R, Schwarcz H P, Ford D C, et al. An absolute paleotemperature record from 10 to 6 ka inferred from fluid inclusion D/H ratios of a stalagmite from Vancouver Island, British Columbia, Canada. *Geochim Cosmochim Acta*, 2008, 72: 1014–1026
- 28 Griffiths M L, Drysdale R N, Vonhof H B, et al. Younger Dryas-Holocene temperature and rainfall history of southern Indonesia from $\delta^{18}\text{O}$ in speleothem calcite and fluid inclusions. *Earth Planet Sci Lett*, 2010, 295: 30–36
- 29 Hendy C H. The isotopic geochemistry of speleothems—I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochim Cosmochim Acta*, 1971, 35: 801–824
- 30 O'Neil J R, Clayton R N, Mayeda T K. Oxygen isotope fractionation in divalent metal carbonates. *J Chem Phys*, 1969, 51: 5547–5558
- 31 Kim S T, O'Neil J R. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim Cosmochim Acta*, 1997, 61: 3461–3475
- 32 Fleitmann D, Burns S J, Mangini A, et al. Holocene ITCZ and Indian monsoon dynamics recorded in stalagmites from Oman and Yemen (Socotra). *Quat Sci Rev*, 2007, 26: 170–188
- 33 Johnston V E, Borsato A, Spötl C, et al. Stable isotopes in caves over altitudinal gradients: Fractionation behaviour and inferences for speleothem sensitivity to climate change. *Clim Past*, 2013, 9: 99–118
- 34 Labuhn I, Genty D, Vonhof H, et al. A high-resolution fluid inclusion $\delta^{18}\text{O}$ record from a stalagmite in SW France: Modern calibration and comparison with multiple proxies. *Quat Sci Rev*, 2015, 110: 152–165
- 35 Baker J L, Lachniet M S, Chervyatsova O, et al. Holocene warming in western continental Eurasia driven by glacial retreat and greenhouse forcing. *Nat Geosci*, 2017, 10: 430–435
- 36 Millo C, Strikis N M, Vonhof H B, et al. Last glacial and Holocene stable isotope record of fossil dripwater from subtropical Brazil based on analysis of fluid inclusions in stalagmites. *Chem Geol*, 2017, 468: 84–96
- 37 Johnston V E, Borsato A, Frisia S, et al. Evidence of thermophilisation and elevation-dependent warming during the Last Interglacial in the Italian Alps. *Sci Rep*, 2018, 8: 2680
- 38 Merlivat L, Jouzel J. Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. *J Geophys Res*, 1979, 84: 5029–5033
- 39 Vimeux F, Masson V, Jouzel J, et al. Glacial-interglacial changes in ocean surface conditions in the Southern Hemisphere. *Nature*, 1999, 398: 410–413
- 40 Yonge C J. Stable isotope studies of water extracted from speleothems. Doctor Dissertation. Hamilton: McMaster University, 1982
- 41 Schwarcz H, Yonge C. Isotopic composition of palaeowaters as inferred from speleothem and its fluid inclusions. In: International Atomic Energy Agency, ed. *Palaeoclimates and Palaeowaters: A Collection of Environmental Isotope Studies*. Vienna: IAEA, 1983. 115–133
- 42 Verheyden S, Genty D, Cattani O, et al. Water release patterns of heated speleothem calcite and hydrogen isotope composition of fluid inclusions. *Chem Geol*, 2008, 247: 266–281
- 43 Matthews A, Ayalon A, Bar-Matthews M. D/H ratios of fluid inclusions of Soreq cave (Israel) speleothems as a guide to the Eastern Mediterranean Meteoric Line relationships in the last 120 ky. *Chem Geol*, 2000, 166: 183–191
- 44 Genty D, Plagnes V, Causse C, et al. Fossil water in large stalagmite voids as a tool for paleoprecipitation stable isotope composition reconstitution and paleotemperature calculation. *Chem Geol*, 2002, 184: 83–95
- 45 Li Q, Hu C Y. Advances on paleo-temperature reconstruction from stalagmite inclusions (in Chinese). *Geol Sci Technol Inf*, 2010, 29: 8–14 [李琴, 胡超涌. 石笋包裹体重建古温度的研究进展. *地质科技情报*, 2010, 29: 8–14]
- 46 Dennis P F, Rowe P J, Atkinson T C. The recovery and isotopic measurement of water from fluid inclusions in speleothems. *Geochim Cosmochim Acta*, 2001, 65: 871–884
- 47 Bigeleisen J, Perlman M L, Prosser H C. Conversion of hydrogenic materials to hydrogen for isotopic analysis. *Anal Chem*, 1952, 24: 1356–1357
- 48 Friedman I. Deuterium content of natural waters and other substances. *Geochim Cosmochim Acta*, 1953, 4: 89–103
- 49 Harmon R S, Schwarcz H P, Ford D C. Stable isotope geochemistry of speleothems and cave waters from flint ridgemammoth cave system, Kentucky—Implications for terrestrial climate change during period 230000 to 100000 years BP. *J Geol*, 1978, 86: 373–384
- 50 Norman D I, Sawkins F J. Analysis of volatiles in fluid inclusions by mass spectrometry. *Chem Geol*, 1987, 61: 1–10
- 51 Vonhof H B, van Breukelen M R, Postma O, et al. A continuous-flow crushing device for on-line $\delta^2\text{H}$ analysis of fluid inclusion water in speleothems. *Rapid Commun Mass Spectrom*, 2006, 20: 2553–2558
- 52 Dublyansky Y V, Spötl C. Hydrogen and oxygen isotopes of water from inclusions in minerals: Design of a new crushing system and on-line continuous-flow isotope ratio mass spectrometric analysis. *Rapid Commun Mass Spectrom*, 2009, 23: 2605–2613
- 53 Wainer K, Genty D, Blamart D, et al. Speleothem record of the last 180 ka in Villars cave (SW France): Investigation of a large $\delta^{18}\text{O}$ shift between MIS6 and MIS5. *Quat Sci Rev*, 2011, 30: 130–146

-
- 54 Brand W A, Geilmann H, Crosson E R, et al. Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of pure water samples and alcohol/water mixtures. *Rapid Commun Mass Spectrom*, 2009, 23: 1879–1884
- 55 Arienzo M M, Swart P K, Vonhof H B. Measurement of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of fluid inclusion water in speleothems using cavity ring-down spectroscopy compared with isotope ratio mass spectrometry. *Rapid Commun Mass Spectrom*, 2013, 27: 2616–2624
- 56 Affolter S, Fleitmann D, Leuenberger M. New online method for water isotope analysis of speleothem fluid inclusions using laser absorption spectroscopy (WS-CRDS). *Clim Past*, 2014, 10: 1291–1304
- 57 Johnson L R, Sharp Z D, Galewsky J, et al. Hydrogen isotope correction for laser instrument measurement bias at low water vapor concentration using conventional isotope analyses: Application to measurements from Mauna Loa Observatory, Hawaii. *Rapid Commun Mass Spectrom*, 2011, 25: 608–616
- 58 van Breukelen M R, Vonhof H B, Hellstrom J C, et al. Fossil dripwater in stalagmites reveals Holocene temperature and rainfall variation in Amazonia. *Earth Planet Sci Lett*, 2008, 275: 54–60
-

补充材料

表S1 实验室标准水样品LAB1、LAB2、LAB3通过包裹体水真空提取装置手动注射与通过Picarro液态水自动进样器自动注射测试结果对比

本文以上补充材料见网络版csb.scichina.com. 补充材料为作者提供的原始数据, 作者对其学术质量和内容负责.

Summary for “利用Picarro测试石笋包裹体水氢、氧同位素的方法”

Measurement of oxygen and hydrogen isotopic ratios of speleothem fluid inclusion water using Picarro

Ye Tian¹, Haiwei Zhang^{1*}, Baoyun Zong¹, Pengzhen Duan¹, Hubert B. Vonhof², Yuri V. Dublyansky³, Youfeng Ning¹, Christoph Spötl³, Yanjun Cai¹ & Hai Cheng^{1*}

¹ Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710054, China;

² Department of Climate Geochemistry, Max Planck Institute for Chemistry, Mainz 55128, Germany;

³ Institute of Geology, University of Innsbruck, Innsbruck 6020, Austria

* Corresponding authors, E-mail: zhanghaiwei@xjtu.edu.cn; cheng021@xjtu.edu.cn

A speleothem fluid inclusion extraction and isotope analysis system was established based on a vacuum extraction device and a Picarro L2140-i wavelength scanned cavity ring-down spectroscopy (WS-CRDS) water isotope analyzer. WS-CRDS allows to measure the stable oxygen and hydrogen isotope composition ($\delta^{18}\text{O}$ and δD) of small water samples simultaneously, which is faster, simpler, and requires less maintenance compared to currently used continuous-flow isotope ratio mass spectrometry (CF-IRMS). The precision of water isotopic analysis utilizing the WS-CRDS is often superior to that of CF-IRMS. Therefore, the use of Picarro for isotope analysis has rapidly gained popularity.

The oxygen isotopic composition of speleothem calcite ($\delta^{18}\text{O}_\text{c}$) is one of the main proxies of speleothem-based paleoclimate reconstructions, but the interpretation of $\delta^{18}\text{O}_\text{c}$ remains complex as it can be influenced by many factors. Speleothem fluid inclusions contain the characteristics of cave drip water. The $\delta^{18}\text{O}$ and δD values of fluid inclusion water provide direct information about paleoprecipitation, and can be further used to reconstruct paleotemperature when combined with $\delta^{18}\text{O}_\text{c}$. The present paper contains a detailed description of the system as we have designed it, and provides an introduction to the system's performance. The vacuum extraction device, connected to the Picarro analyzer, is designed to release the water trapped in speleothem fluid inclusions by pneumatically-operated crushing of discrete speleothem calcite chips. The whole device is kept at a temperature of 120°C to ensure the total and instantaneous vaporization of the water without isotopic fractionation. The vaporized water is carried by a flow of high-purity nitrogen to a 40 mL volume for homogenization, and is then introduced into the Picarro analyzer for $\delta^{18}\text{O}$ and δD analysis. A syringe injection unit was added to the vacuum extraction device to be able to measure standard water, with $\delta^{18}\text{O}$ and δD values similar to the speleothem samples, before and during measurements. To verify the precision and accuracy of the system, the same standard water samples were measured with an automated Picarro L2140-i set-up that includes an autosampler and a Picarro evaporation unit. The $\delta^{18}\text{O}$ and δD values of standard waters as measured by both systems are comparable. Using the crushing device, speleothem samples from the East Asian Monsoon region yield paired $\delta^{18}\text{O}/\delta\text{D}$ values within $\pm 0.5\text{‰}$ of the Global Meteoric Water Line (GMWL), indicating no isotopic fractionation during the measurements. The precision is a function of the water amount released and of the isotopic composition of the sample. The reproducibility of crushed speleothem samples, whose water vapor concentration is between 2500 and 50000 ppm, is 0.5‰ for $\delta^{18}\text{O}$ and 2‰ for δD (1 SD), similar to results obtained from other published measuring systems.

speleothem fluid inclusions, stable isotopes, water isotope analyzer (Picarro), wavelength scanned cavity ring-down spectroscopy, paleotemperature

doi: [10.1360/TB-2020-0201](https://doi.org/10.1360/TB-2020-0201)