北京石花洞疏松-致密型石笋微层形成机理

班凤梅^{1,2*}, 谭明³, 韩晋仙¹, 翟艳峰¹, 赵旭红¹, 孙会国^{3,4}

1. 山西财经大学资源环境学院, 太原 030006;

2. 西安交通大学全球环境变化研究所, 西安 710049;

3. 中国科学院地质与地球物理研究所新生代地质与环境重点实验室, 北京 100029;

4. 中国科学院地球科学研究院, 北京 100029

* 联系人, E-mail: banfm@sxufe.edu.cn

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摘要 北京石花洞石笋物质旋回微层及其气候重建研究在古气候领域已有广泛报道. 而本文所研究的石笋(XMG), 自20世纪90年代初后突变发育了疏松-致密型微层, 这种微层类型以前在石花洞从未发现. 扫描电子显微镜(scanning electron microscope, SEM)观测显示, 这种疏松-致密层偶是由方解石组构(calcite fabric)差异引起, 不透光疏松层是粒状镶嵌结构微晶方解石, 而透光致密层是晶簇状纤维晶方解石. 在对该石笋观测站点的现生碳酸盐SEM分析后, 发现其可分为3种类型, I型是旱季1~3月沉积的晶粒较大且晶面较为平整的菱面体及其组合体; II型是旱-雨季过渡时期(4~5和10~12月)生长的大、小晶体混生型; III型是雨季生成的晶粒细小(粒径<4 μm)的微晶. 菱面晶体所含杂质少, 形成条件为滴水慢且稳定、方解石饱和指数偏高、洞穴CO₂浓度低以及洞穴扰动最小, 这类晶体构成了透光纤维晶方解石层; 而微晶伴有较多杂质, 当季新水补给、洞穴CO₂浓度升高以及旅游活动增加等因素均利于其生成. 由于疏松的微晶方解石亚层形成于洞穴开放之后, 故推测洞穴开放后人为干扰所引起的洞穴环境改变, 很可能是其突变发育的关键因素.

关键词 石笋, 疏松-致密微层, 微晶方解石, 人类活动, 石花洞

北京石花洞位于雨热同季的东亚季风气候区, 石笋矿物为方解石. 利用该洞石笋微层厚度变化序列, Tan等人^[1]重建了北京近2650年的夏季温度. 过去在该洞已发现的所有石笋为放射状纤维晶方解石, 微层具有典型的“北方型”微层特点^[2], 即在透光显微镜下, 很薄的不透光层与较厚的透光层形成年旋回, 且不透光层与荧光显微镜下的亮层一一对应, 故推测这种薄的不透光层为有机质层^[3], 并证明了由雨季降水对土壤有机质的脉冲淋洗引起^[4]. 而本文介绍和分析的石笋(编号XMG)其疏松-致密结构旋回变化微层, 在石花洞是首次发现, 类似于中国南方和尚洞的方解石石笋微

层类型^[5,6]. 根据分析, XMG的疏松-致密层偶旋回是年旋回^[7], 共有23±1层, 记录时间可追溯到20世纪90年代初(1991~1993年), 其时正值洞穴开放初期.

疏松-致密旋回微层的方解石组构(calcite fabric)差异特征见于国外的研究报道^[8~10]. 其中一类, 由不同的方解石组构形成疏松-致密层, 如西班牙Gibraltar洞的白色柱状方解石和暗色微晶方解石^[8]. 而另一类, 方解石组构即晶体类型、排列方式相同, 疏松-致密层偶由石笋表面孔洞或包裹体的密度差异造成, 如比利时Père Noël洞^[9]和奥地利Katerloch洞^[10]. 除方解石石笋外, Duan等人^[11,12]曾发现文石也有疏松-致密微层, 并结合

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现代碳酸盐沉积的观测发现其受到洞穴CO₂浓度和滴水速率、饱和度指数以及Mg/Ca的影响。

本文通过洞穴监测方法,初步揭示了石花洞方解石石笋疏松-致密型微层的晶体组合方式与形成机理,并对其突变发育的原因进行了合理推断。

1 研究区概况及方法

石花洞(39°47'N, 115°56'E)距北京市区约50 km, 围岩地层为奥陶系马家沟组灰岩, 有白云岩夹层; 上覆地层中有石炭系-二叠系煤层的不均匀分布^[13]。洞穴区域土壤为褐土, 山坡土层厚度0~50 cm; 山谷土层较厚, 约为60~100 cm; 土壤表层(0~15 cm)颜色深, 总有机碳含量较高。植被以灌丛和草被为主, 山谷中分布有柿子树和核桃树。

据1990~2017年气象记录显示(图1), 北京地区年均温介于10.9~14.1°C, 6~8月月均温最高, 平均在25°C以上, 年平均降水量为550 mm, 降水的年际变化较大。2016年降水量高达966 mm, 而1999年降水量仅为280 mm。虽夏季降水的空间分布有一定差异, 如石花洞所处的房山区, 降水量通常多于城区, 但降水年际变化趋势基本与北京一致。

洞穴系统整体呈北西西-南东东向展布, 自上而下分为5层^[14]。XMG位于第2~3层的过渡层, 洞道较窄, 空气流动性较强。洞穴顶板厚度介于30~130 m, 该滴水点

上覆顶板厚约60 m。

XMG石笋整体呈圆柱状, 矿物成分主要为方解石, 高约4 cm, 结合²³⁰Th定年^[15]及微量元素年层校准^[7], 已知该石笋共沉积约150 a。

将石笋剖面顶部用稀酸轻轻擦拭, 而后用蒸馏水冲洗、吹干, 再在酸擦拭后的表面上喷金, 增强其导电性, 然后用导电胶将石笋固定在托盘上, 用扫描电子显微镜(scanning electron microscope, SEM)对喷金的表面进行扫描拍照, SEM为德国蔡司EVO18型。

将沉积有现生碳酸盐的玻璃片表面直接喷金, 用导电胶固定在托盘上, 用SEM对喷金的表面进行扫描拍照。同时利用安装在SEM上的布鲁克Quantax能谱仪对沉积表面的颗粒较大的菱面体和较小的微晶进行了成分分析, 测试高压为20.0 kV, 最大脉冲为1.21 keps。

SEM及能谱分析实验在中国科学院地球环境研究所进行。

2 结果与分析

2.1 石笋疏松-致密层结构特征

如图2所示, 当光从XMG石笋剖面两侧射入时, 可看出其顶部4 mm较下面显著偏暗(图2(A)), 显示这一部分透光性差, 同时可以明显看到因透光性差异引起的亮暗条带; 而用稀盐酸擦拭表面后, 在SEM下可见,

图1 1990~2017年北京年降水量和年均温变化。虚线为平均降水量, 气象数据引自国家气候中心网站(<https://www.ncc-cma.net/cn/>)

Figure 1 Changes of annual precipitation and annual mean temperature in Beijing, 1990–2017. The dashed line is the multi-year average precipitation. Data is from the National Climate Center website (<https://www.ncc-cma.net/cn/>)

图2 XMG石笋透光情况及微层SEM影像。红色虚线框为XMG石笋顶部4 mm部分; (A) 光源从两侧投射通过石笋时的影像; (B) 石笋剖面SEM影像, 可见到上部4 mm清晰的疏松-致密微层; (b) 为(B)图中小白框处疏松-致密层的SEM影像, 白色箭头指纤维状方解石晶簇

Figure 2 The transparent and SEM images of the stalagmite laminae at its top 4 mm part. (A) The image of stalagmite with light penetrating the stalagmite from both sides; (B) The SEM image of stalagmite hand specimen. There are clear porous/compact laminae at the top of 4 mm. (b) The magnified SEM image of white square in (B): The upper and lower are the compact sub-layer and porous sub-layer respectively; the white arrows point to fibrous calcite clusters in microcrystalline calcite

顶部4 mm呈现有规律的凹凸旋回(图2(B)), 亦即疏松-致密层偶旋回. 在高倍SEM视场中可见(图2(b)), 致密亚层是排列整齐的纤维状方解石, 其生长方向几乎与生长断面垂直, 而疏松亚层是表面呈蜂窝状的微晶方解石, 其中伴生有纤维状方解石晶簇. 但在石笋顶部4 mm以下部分, 通体透光, 没有疏松-致密层偶旋回.

可见, 疏松的微晶亚层的突变式发育是顶部疏松-致密旋回结构形成的关键, 由于其与纤维状方解石亚层组成层偶, 所以降低了整个剖面的透光性.

2.2 现生碳酸盐晶体的时间变化

在SEM下观测, 现生碳酸盐的晶体呈现出明显的季节性变化(图S1, S2). 根据晶体颗粒大小及晶形, 将现代碳酸盐晶体划分为3个类型(图3): I型以颗粒较大菱面体晶粒为主要特征, 多形成于1~3月份(图3(A)), 多数晶体 c -轴(沿生长方向的轴)大于10 μm , 属于Riechelmann等人^[16]划分的方解石C型晶体, 由菱面体{104}和菱面体{031}结合而成. 进一步放大后(图3(a)), 可以看到沿生长方向的晶面有螺旋错位生长产生的台阶^[17], 顶部出现光滑平整的F-面(图3(a)). II型为早-雨季过渡期生长的大、小晶体混生为特征, 沉积于旱季的4~5和10~12月份(图3(B), (b)), 生成月份随每年雨季出现的时间可能存在差异, 超过10 μm 的晶体逐渐减少, 粒径小于4 μm 的微晶增加. III型以粒径不足1 μm 的粒状或碎屑状微晶为主(图3(C), (c)), 主要形成于雨季, 与新水的补给有关. 因此, 这种细小微晶形成时间会随每年雨季到来时间有所提前或推后. 如2016年, 微晶形成时间为8月下旬~10月份, 而2017年微晶形成于6月下旬~8月, 较上一年提前1~2个月, 后面讨论部分将对此作进一步分析. 值得注意的是, 2017年4月, 观测到玻璃片表面的沉积物以颗粒细小的微晶为主, 这可能与3月下旬发生的一次较强降雨有关(24 mm/12 h).

3 讨论

3.1 石笋疏松-致密层偶的组构及形成

方解石组构(calcite fabric)通常由晶体的空间排列和它们的习性决定. Frisia等人^[18]曾详细阐述了方解石不同组构的形成机理, 即纤维晶方解石或称为细长柱状方解石, 由较大的菱面体(4 μm <宽<100 μm)及其聚合体形成, 而构成微晶方解石的晶体通常杂质较多, 杂质吸附在晶面上, 改变不同晶面的生长速度, 造成晶体

图3 XMG点现代碳酸盐晶体3种类型的SEM影像图. (A)~(C) 现代碳酸盐沉积物沉积时间分别是2016-02-17~2016-03-29, 2016-05-08~2016-06-13和2017-08-05~2017-08-23; 左侧图中白色框a, b, c放大如右图(a), (b), (c)

Figure 3 The SEM images of three styles of the modern carbonate sediments in XMG. The modern carbonates in (A), (B) and (C) were deposited from Feb 17 to Mar 29 in 2016, May 8 to Jun 13 in 2016 and Aug 5 to Aug 23 in 2017 respectively. The white boxes a, b, c in the left images are enlarged to the right images (a), (b), (c), respectively

缺陷明显, 晶粒变小(粒径<4 μm). 在使用能谱仪对粒径较大的菱面体和较小的微晶检测后(图4), 可以明显看到颗粒较大的菱面体构成的元素仅有C, O和Ca, 几乎没有杂质, 而晶粒较小的微晶则含有多种元素. 如Si, Al, Mg, Fe以及S等. 据此推测, XMG石笋致密亚层即纤维晶方解石亚层, 由体积较大的菱面体生长形成, 而疏松亚层则有不同程度的微晶混入, 由现生碳酸盐的II型和III型构成, II型中颗粒较大的菱面体形成其中伴生的纤维状方解石晶簇.

3.2 现生碳酸盐晶体形成的影响因素

影响洞穴方解石组构的因素包括两个方面: 一是滴水的理化性质^[16,18], 包括滴率快慢及变幅、物质或者元素的含量以及方解石饱和指数等指标; 二是洞穴环境, 如通风状况、温湿度变化以及 CO_2 浓度等因素^[8,10,19]. 石花洞是一个旅游洞穴, 滴水结晶过程, 除受滴水影响外, 还可能受到洞穴环境及其空气流通的干扰. 1~3月份, 石花洞地区降水和温度均最低, 洞内游客稀少, CO_2 浓度最低(图5), 滴水补给以储存水为主, 滴

图 4 现代碳酸盐晶体的元素分析图谱. 左图中绿色“+”为取样位置, A为颗粒较大的菱面体, B为微晶. (a) 左图A位置的元素分析图谱; (b) 左图B位置的元素分析图谱

Figure 4 Elemental analysis of modern sediment crystals. In the left image, green “+” means the sampling loaction, A is the rhombohedron with larger particles, and B is the microcrystalline; (a) and (b) show the elemental analysis spectrums for position A and B in the left image

图 5 石花洞地区降水及XMG点CO₂浓度的变化. 星形代表劳动节和国庆节长假期间的CO₂浓度峰; 黑色圆圈代表2017年3月22日的降水事件; 灰色方框表示2016和2017年集中降雨期; 虚线为1000 ppmv的CO₂浓度线; 2005~2007年CO₂和降水数据引自文献[21]

Figure 5 Variations in precipitation in Shihua Cave and CO₂ concentration around XMG site. The stars represent the peaks of CO₂ concentration during Labour Day holiday and National holiday; black circle is the rainfall event on March 22, 2017; the gray boxes represent the rain season in 2016 and 2017; dashed line means the CO₂ concentration at 1000 ppmv; precipitation data for 2005–2007 are cited from Ref. [21]

率慢而稳定, 碳酸钙优先沉积作用明显(图S3), 滴水饱和指数较高, 其中溶解的物质相对简单, 再加上洞穴环境稳定, 利于颗粒较大的菱面体(I型)的形成. 而在雨季,

随着降水的增加, 集中的降水对土壤有机质脉冲淋洗后进入滴水, 滴水杂质增加, 方解石饱和指数降低, 是形成了颗粒细小的微晶(III型)的主要原因. 因每年雨季

出现的时间不同,微晶的形成时间也随之存在明显的年际差异.如图5所示,2017年雨季发生在6月下旬~8月下旬,期间连续发生多次较高强度的降水(图5灰色框),滴水因此得到新水补给,在6~8月生成颗粒细小的微晶,而该年3~4月份也生成微晶,可能与3月22日一次较强降雨有关.然而,2016年的集中降雨发生在7月19日以后,之前虽有几场降雨,但单次雨量最大没有超过15 mm,直到7月19~20日出现了单次雨量超过300 mm强暴雨事件,随后雨季持续到10月,因此这一年微晶(III型)形成于8~10月.大、小晶体混生(II型)时期,降水频率低,且降雨强度也没有达到土壤有机酸脉冲进入滴水的阈值(>25 mm/d)^[4],因此这段时期滴水对晶体形成几乎没有影响,可见除滴水外,微晶的形成还可能与其他干扰因素相关.结合石笋XMG的突变微层仅出现于洞穴开放后的事实,因此推测洞穴开放对微晶方解石层形成可能有重要作用.石花洞洞穴开放后,人工出口通道的打通,在一定程度上增加了洞内外空气的交换强度和速度;游客的进入会导致气溶胶增加^[19]、温度升高^[20]以及二氧化碳浓度增加^[21];而景观灯光会造成洞穴干湿度的变化^[22].在这些改变的环境要素中,可能气溶胶的嫌疑最大,因为现生碳酸钙微晶伴含有多种杂质元素.洞穴气溶胶(aerosol)粒径为0.01~100 μm ,

洞穴开放后洞内外的气流交换加快、大量游客频繁进出扰动等均可导致气溶胶发生变化^[19].不仅如此,游客活动会引起洞穴 CO_2 浓度大幅升高,如图5所示,2005~2007年高频率的 CO_2 观测数据可以看到长假期间(劳动节和国庆节),游客剧增致使洞穴 CO_2 浓度出现明显峰值,而 CO_2 浓度的升高也可能通过抑制滴水脱气而对其生成的晶体形态产生影响,由图5可以看出滴水形成微晶时段 CO_2 浓度超过1000 ppmv,但其对晶体形态的影响程度,还有待于进一步的证明.

4 结论

通过对石花洞石笋疏松-致密型微层的现代碳酸盐沉积物SEM分析,发现由晶体组构的差异引起.疏松层由微晶方解石组成,形成于4~12月份,微晶的形成降低了解石的透明度.根据沉积事实和观测事实,以及二者的联系,可以看出石花洞发现的这种方解石组构差异而显现的微层,既反映了滴水及其地球化学元素的变化,又记录了旅游活动带来的洞穴环境的改变,虽然它们之间的作用机制还需进一步研究证明.本文第一次讨论了非自然因素对方解石组构的影响,这不但对石笋微层气候学的发展具有重要意义,如果能够证明,对一般沉积动力学也具有重要意义.

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补充材料

图S1 2016年XMG点现代碳酸盐沉积物SEM影像图

图S2 2017年XMG点现代碳酸盐沉积物SEM影像图

图S3 XMG点滴水Mg/Ca, Sr/Ca随 Ca^{2+} 变化趋势与 CaCO_3 的优先沉积模型

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Summary for “北京石花洞疏松-致密型石笋微层形成机理”

The fabric and its formation mechanism of porous-compact laminae in the stalagmite from Shihua Cave, Beijing

Fengmei Ban^{1,2*}, Ming Tan³, Jinxian Han¹, Yanfeng Zhai¹, Xuhong Zhao¹ & Huiguo Sun^{3,4}¹ School of Resources and Environment, Shanxi University of Finance & Economics, Taiyuan 030006, China;² Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710049, China;³ Key Laboratory of Cenozoic Geology Environment, Institute of Geology and Geophysics, Chinese Academy of Science, Beijing 100029, China;⁴ Institutions of Earth Science, Chinese Academy of Sciences, Beijing 100029, China* Corresponding author, E-mail: banfm@sxufe.edu.cn

The stalagmites in Shihua Cave, Beijing have been intensely studied as archives of regional palaeoclimate. They yield high resolution time series of multi-proxy records which have greatly improved the understanding of the relationship between speleothem formation and climate changes. The stalagmites studied in this cave were composed of fibrous calcite with clear visible and fluorescent laminae. Recently, porous-compact layers at the top 4 mm were found on an actively growing stalagmite (XMG). It consists of visible transparent-opaque layers. A noteworthy observation is that the laminae of calcite fabrics occurred on the top of XMG which formed after the cave open for tourism. The results from scanning electron microscopy analysis on this stalagmite indicates that the opaque microcrystalline calcite (MCC) porous sub-layers are composed of granular mosaic structures, comparing to the compact transparent fibrous columnar calcite (FCC) sub-layers with structures almost oriented perpendicular to the growth surface. Further analysis on the modern carbonate of this site was carried to investigate its formation mechanisms. Based on the size and habit of crystal, these modern carbonate crystallite formations can be categorized into three types. Type I contains larger rhombohedral grains, most of which are formed in the dry season of January–March. Most crystals with *c*-axis (along the growth direction) represent scales larger than 10 μm and structures of FCC. Type II includes the mixture of large rhombohedrons and small microcrystalline with a scale of less than 4 μm during the transition period of dry to rainy season, with deposition in April–May and October–December. During this period, the scale of large crystals with a diameter of more than 10 μm gradually decreases and the microcrystalline crystals begin growing. Type III consists of calcite precipitates with a spherical habit in the rainy season of June–September. Crystallites with diameters of less than 1 μm can be observed in this period, which is highly related to the new water recharge during this season. To investigate their elemental compositions, both the rhombohedral crystallites and microcrystalline were analyzed through an elemental spectrum analyzer. The results show that the elemental consistency is highly associated with the scales of crystallites. Trace elements, including silicon, aluminum, magnesium, etc. could be obtained on the microcrystalline specimen. On the contrary, only the basic formation elements of calcium carbonate as carbon, oxygen and calcium are detected on rhombohedral structures. Based on these observations, there are two hypotheses on this formation mechanism. Hypothesis I is that, FCC corresponded to the relatively decreased drip rates. During the dry season, the recharge contains high calcite saturation from a stable soil-water-rock interaction over the cave. On the other hand, new water inputs during the rain seasons of increased drip rates result in increased variables including lower index of calcite saturation, complex soil-water-rock interaction and variable amounts of prior calcite precipitation. Hereby, it presents a result of increased MCC with more impurities. Hypothesis II is that, the changed structure might be related to the cave tourism conditions. As the new structure is observed after the cave open to the public, it is expected to suggest a correlation to the tourist patterns. Moreover, both the increased CO_2 level and aerosol levels inside cave systems are highly associated with increased visitors, which result in more venting as well as external air inputs. It is likely that the impurities from the external aerosol are the key factors of MCC Formation during the transition period. These anthropogenic factors might play a vital role in the thicker microcrystalline calcite layers formation.

stalagmite, porous-compact laminae, microcrystalline calcite, anthropogenic activities, Shihua Cavedoi: [10.1360/N972019-00137](https://doi.org/10.1360/N972019-00137)