geoconvention Virtual Event September 13 - 15 2021

Interior architecture of anthropogenic stalactite-form deposits

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Introduction

Calthemites are carbonate accumulations resulting from weathering of cement, lime and other cement-based construction materials associated with concrete structures and mortar used to bind building blocks. They are widely distributed as stalactite-form deposits on undersides of concrete structures (Macleod et al., 1990; Dow, 2003; Smith, 2016), but their interior microstructure fabrics and mineralogy have received little attention (Broughton, 2020). These deposits consist of calcite, but also include minerals such as tona, portlandite and halite. Calthemite structures develop as calcareous crusts that follow cracks along the underside of concrete structures, resulting from precipitation from water seepage having chemistry altered by partially dissolved concrete. Soda straws are commonplace with external morphologies consistent with similar limestone cave speleothems (Kendall and Broughton, 1978). In contrast, these concrete-derived deposits have interior microstructure architecture that is markedly different from cave deposits because of the high porosities, 40-60%, and a differing mineralogy. The interior microstructures of these blister-like crusts consist of concentric and curvilinear calcite laminae capable of supporting external forms including the weight of soda straw attachment areas extending downward from the encrustation. Calcite fabrics not previously observed with calthemite deposits are reported, including dendritic shrubs that have variously coalesced into concentric growth rings along central canals of soda straws.

Study area

An underground car parking garage was selected because of the 100s of soda straw type calthemites present on the overlying concrete ceiling. The building is located near the town of Cranbrook in southeastern British Columbia. The location along the eastern slopes of the Rocky Mountains receives a variable but multi-meter thick annual snow pack. The deposit resulted from migration of salt-saturated water to the exterior concrete surface where precipitation occurs.

Mineralogy

These secondary carbonate deposits accumulate as calcite but also include minor percentages of other hydrous carbonate compounds resulting from dissolution of portlandite cement chemicals by meteoric and groundwater seeps into and along fractures of the concrete structures. XRD of a bulk sample, consisting of 20 specimens of calcareous crusts and soda straws, records a composition of 93.8% calcite [$CaCO_3$]; 4.2% halite [NaCl], 1.8% trona [$Na_3(CO_3)(HCO_3)\cdot 2H_2O$]; 0.2% portlandite [$Ca(OH)_2$].

External Form

The external morphologies of calthemite deposits from the study area have of up to four components: (1) efflorescence consisting of irregular multiple cm long encrustation with low relief, 1-3 mm thick, extending along and partially covering over a crack formed along the underside of a concrete ceiling; (2) ellipsoidal to oval or round basin-form on the ceiling crust, each with a blister-like shell commonly 1-4 cm long and up to 0.5 cm height; (3) tubular soda straw structure extending vertically downward from a low point of the basin-form ceiling crust; (4) bulbous to botryoidal deposits covering external areas of soda straw surfaces. The soda straw structures attached at the lowest point of a basin-forms have lengths ranging from <1 to 10 cm, but are typically 4-6 cm. Width of these tubular structures is consistent, typically in the range of 0.5 cm.

Soda straw lengths consist of thin overlapping calcite laminae of microcrystalline calcite, resulting in diminished translucency. Fe-oxide staining and non-carbonate minerals, mostly halite, accumulate on external surfaces, also reducing the translucency of otherwise pure calcite tubular structures. Almost all calthemite soda straws observed from the study area have external surfaces that are partially enveloped by botryoidal to coralloid deposits having a variable but dominantly calcite-halite mineralogy. The external surfaces of the soda straws may display ridges, 1-3 mm high and 3-6 mm wide that concentrically ring the tubular structure. Many of these concentric calcite ridges are enveloped by irregular to bulbous botryoidal buildups of halite, but with traces of trona and portlandite.

Sparse segments of calthemite soda straw-lengths have sufficient translucency such that interior growth layers can be observed. There are two types of intra-tubular calcite fabrics that can be observed at the surface of translucent soda straws, provided there are no opaque laminae encrustations. Concentric growth rings consisting of microcrystalline calcite accumulated as cement layers, resulting in growth fabrics superficially comparable to soda straws in limestone caves, except for their ultra-fine crystalline texture and micro-porosity.

The external surfaces of most soda straw develop of several mm-thick bulbous or botryoidal growth forms, in contrast to the lack of such buildups on the external surfaces of adjoined ceiling crust. These diminutive bulbous forms, 1-3 mm thick, have external morphologies. In contrast, well-developed coralloid-like botryoidal growths on the calthemite soda straw surfaces are mostly to entirely consist of crystalline halite aggregates. The bulk mineralogy of these botryoidal buildups consists of halite, not calcite.

Interior architecture

The architecture of a soda straw consists of a basal segment that protrudes downward from a more fully developed basin-form crust where successive builds of concentric shells consist of calcite laminae that are sufficiently thick or numerous as to provide foundation support for the straw base (Fig. 1). Concentric growth layers are characteristic of both the interior and external soda straw surfaces. The interior micro-structure of the ceiling crusts consist of bulbous cm-scale chambers with multiple curvilinear partitions of microcrystalline calcite laminae that are effective load-bearing walls that provide structural integrity for the basin-from chambers that are standalone or adjoined, and interconnected by micro-channel conduits. The interior walls of the oval to circular basin-forms, necessarily provide levels of sufficient structural stability for foundation support of soda straw attachment areas. These interior support structures constitute only 40-60% of the interior volume, resulting in a fragile structure. These interior partitions also have pervasive intra-crystalline micro-porosity. Many of the basin-form ceiling crusts have breached walls resulting from lateral interconnectivity by micro-canals between adjacent structures or because the low point of the structure was insufficient to support the weight of the attached soda straw, resulting in collapsed bubble structures. The basin-forms structures consist of concentric shells of continuous laminae with intervening open spaces lined with these bulbous micro-protuberances of calcite. These protuberances entirely cover over sections of the curvilinear laminae wall of the channel pathways. The inner surfaces of both the basin-forms and the interconnecting channels vary from smooth at the 10s micron scale to being covered with bulbous micro-protuberances consisting of stacked microcrystalline calcite platelets (Fig. 2). These are randomly distributed, but also accumulate as beaded structures entrained parallel with concentric growth layers in the tube substrate. Botryoidal coralloid forms on soda straw external surfaces have an interior architecture consisting of aggregates of microcrystalline halite that are characterized by extensive canal induced micro-porosity.

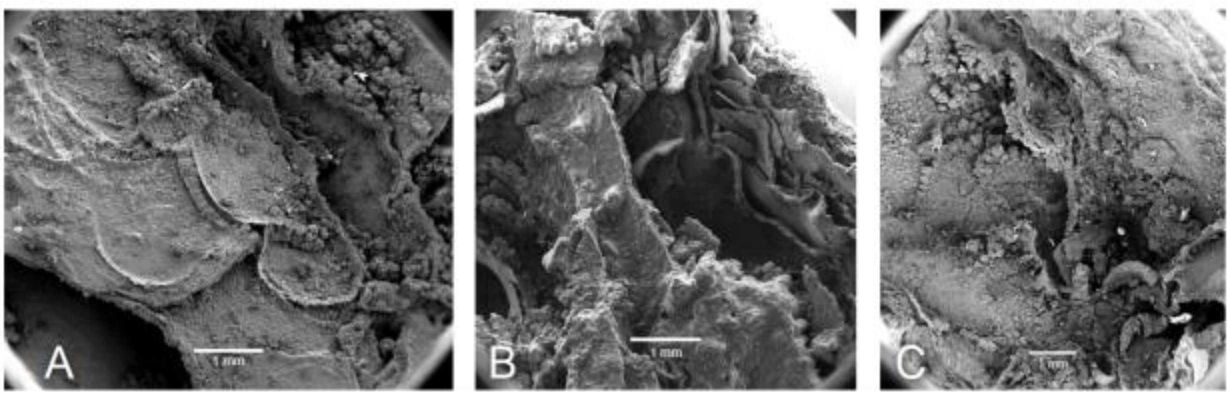

Figure 1. Microstructure of interior calcite walls that partition the ceiling crust and result in high interior porosities of 30-60%. Structural walls consist of overlapping concave partitions that result from calcite precipitation with degassing along migrations of water-gas interfaces. The structure of the walls consists of curvilinear arrays of partially coalesced micro-crystalline calcite protuberances (A-B) with extensive micro-porous areas (C).

Morphogenesis

The genesis of a calthemite deposit consists of four stages:

Stage 1. Encrustation. Degassing of water films and drops seeping downward from multi-cm to multi-meter-long ceiling cracks results in the deposition of a surface crust consisting entirely of calcite, but only limited levels of halite, trona and portlandite at this early stage because of their elevated solubility. A series of disconnected to partially adjoined basin-form encrustations develops along the overlying ceiling crack. Calcite precipitation along the water-gas interface results in thin, fractions of mm-thick, calcite rims, and bubble-like crusts with multiple thin interior calcite walls or partitions that provide varying degrees of structural support. This interior architecture consists of multiple paralleling walls or partitions that form canal-like channels or conduits connecting the basin-forms, permitting interior sub-horizontal pathways for the water film flow. Interior walls develop as overlapping composites of multiple thin curvilinear laminae characterized by offset partitioned and paralleling voids, resulting from the lateral and vertical migrations of the water-gas interfaces. Protuberances emanating from these partitions provide bridge-like structural support across such void areas. This process results in extensive distribution of bulbous protuberances lining the inner surfaces of the channel walls and the basin-forms. Clusters of these bulbous protrusions aggregate to provide strut-like bridges, resulting in a markedly increased structural rigidity for the channel-basin crust complex without significantly blocking interior water flow along these pathways. Most calcareous crusts at this early stage lack sufficient thickness and structural rigidity as to provide foundation support permitting straw development.

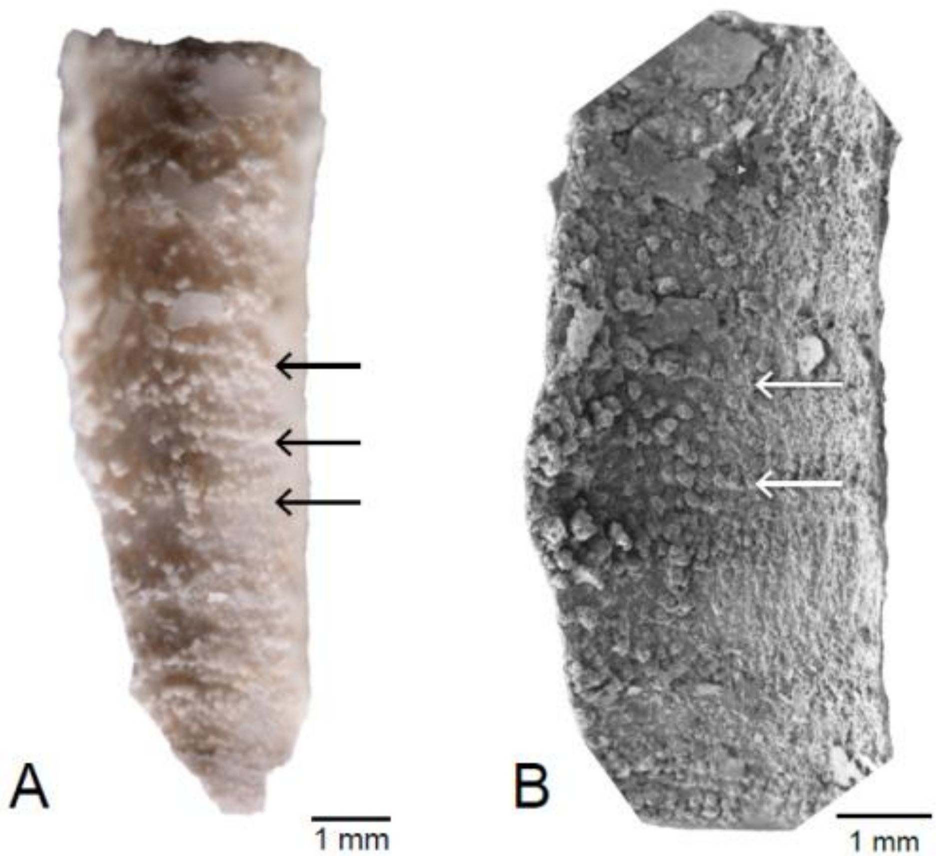

Figure 2. Interior surface of soda straw, characterized by bulbous protrusions consisting of stacked microcrystalline platelets of calcite. Photomicrograph (A) and SEM image (B) of a section of soda straw canal surface illustrating linear arrays of bulbous protrusions (arrows), aligned parallel to the interior concentric growth layers.

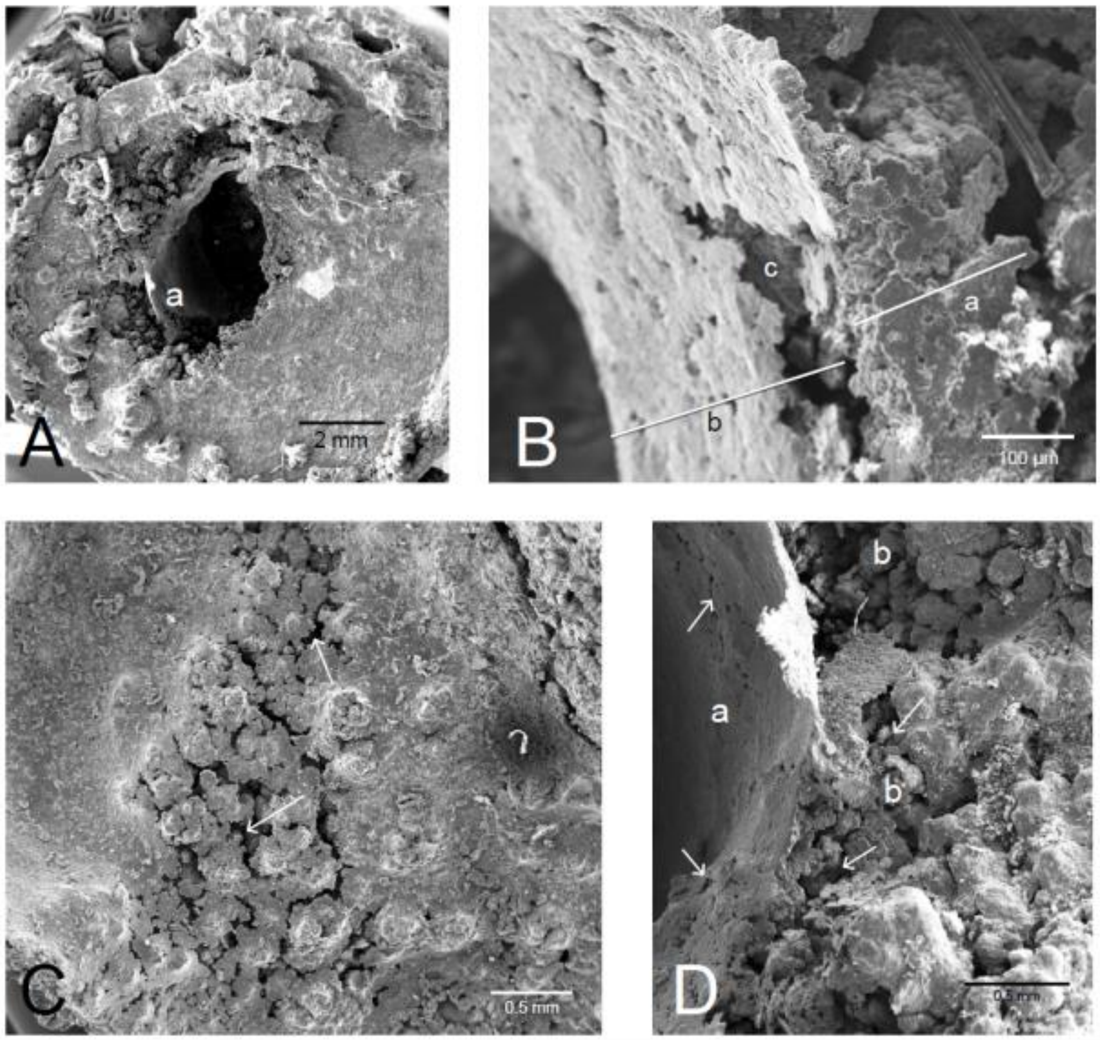

Figure 3. Interior microstructure of soda straw walls. (A) The uppermost attachment area of tubular structure develops at the low point of a shallow saucer-shaped crust. The upper rim of the tubular straw structure (a) lacks contact with overlying concrete ceiling. (B) Cross-section of a tubular wall. The tubular wall (a) and the interior surface of the soda straw canal (b) consist of stacked microcrystalline platelets of calcite with extensive micro-porosity (c) within the fabric. (C-D) Interior surface areas of a tubular structure (a) develop clusters of micro-porosity channels (arrows) that provide capillary driven thin film communication within the straw (b) outward to the external surface, and permitting buildups of halite protuberances on the external surface.

Stage 2. Soda straw development. Soda straws lengthen and thicken with degassing of the water droplet at the straw tip and degassing of the hydrostatic water film flow along capillary conduits of the micro-porosity of the straw tube. This contrasts with the dense crystalline structure of straws

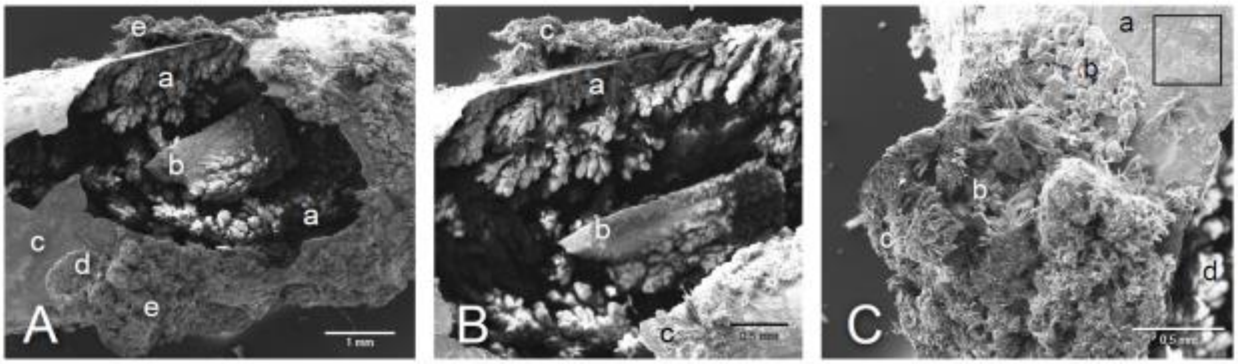

Figure 4. Soda straw mineralogy and crystalline structure. (A-B) Dendritic calcite shrub fabrics (a) developed along the inner surface of a straw central canal, subsequently coalesced into concentric growth layers (b). (C) External straw surface with fan-shaped shrub (frame) substrate (a) covered over by halite crystals (b) and acicular portlandite crystals (c-d).

in natural limestone caves. Buildups of cement along the walls of larger blister-basin forms permit early stage development of a soda straw foundation that is not initiated at the ceiling crack, but 1-2 mm to as much as 5 mm below and within the encrustation (Fig. 3). The base of the soda straw necessarily forms as a completely circular structure of calcite displaced downward from the level of the overlying concrete ceiling. Rapid degassing of the water drop meniscus results in additional calcite precipitation around the breach point-drain hole. This build of the straw stub effectively dikes the breach hole and directs gravity-driven water droplets downward. If incipient breach point at or near the bottom of the basin-form crust has insufficient thickness and interior wall supports, then breakage occurs and straw lengthening does not proceed. This process causes the fluid flow in adjacent areas of the crust to be partially drained, and results in water-gas interface fluctuations. Localized degassing controls on sites of rapid calcite precipitation, such as the continued development of interior wall protuberances within the crust complex as drainage is directed towards the incipient straw central canal. There are fan-shaped crystal growth surfaces resulting from arrays of coalesced dendritic shrubs (Fig. 4), a fabric not previously described from soda straws but common to travertine fabrics (Erthal et al., 2017).

Stage 3. External surface laminae. Water film flow across the exterior surface of a soda straw attachment area would have been sourced from micro-cracks or patchy areas of high inter-crystalline porosity at the base of the soda straw canal. This results in calcite deposition across and outward from an attachment area. These thin films rapidly degas and deposit thin calcite laminae, enhancing the slight concave curvature across the base of the soda straw, but not to the extent as to be identified as conical-form structures commonplace as limestone cave stalactites. Intermittent thin film flows directed downward along the external surface of the straw permits various sheaths of calcite laminae to accumulate. Variations in film thicknesses can result in subtle corrugated-like depositions, including concentric curvilinear ridges at the micron-scale.

Stage 4. Bulbous botryoidal surface deposits. Botryoidal and other irregular buildups are commonly observed on the external surfaces of most soda straws. These multi-mm scale growths result from the buildup of microcrystalline aggregates of halite on the external surface, particularly where micro-porosity conduits extend from the central canal to the outer surface (Fig. 5). Hydrostatic pressure-driven flows along these capillary conduits permit seepage of water films from the central canal onto the outer surface. The patchy distribution of these bulbous structures on external straw surfaces is constrained to a specific segment of the straw length, and may result in halite or calcite depositions that circumscribe the straw. Deposition and preservation of such halite deposits are late stage events because of the high solubility of the mineral, remaining in solution during the earlier stages of calcite deposition. Only when water film flow is nearly terminal can halite accumulate as the evaporation induces precipitation. The halite crystallization is largely preserved with cessation of water seepage.

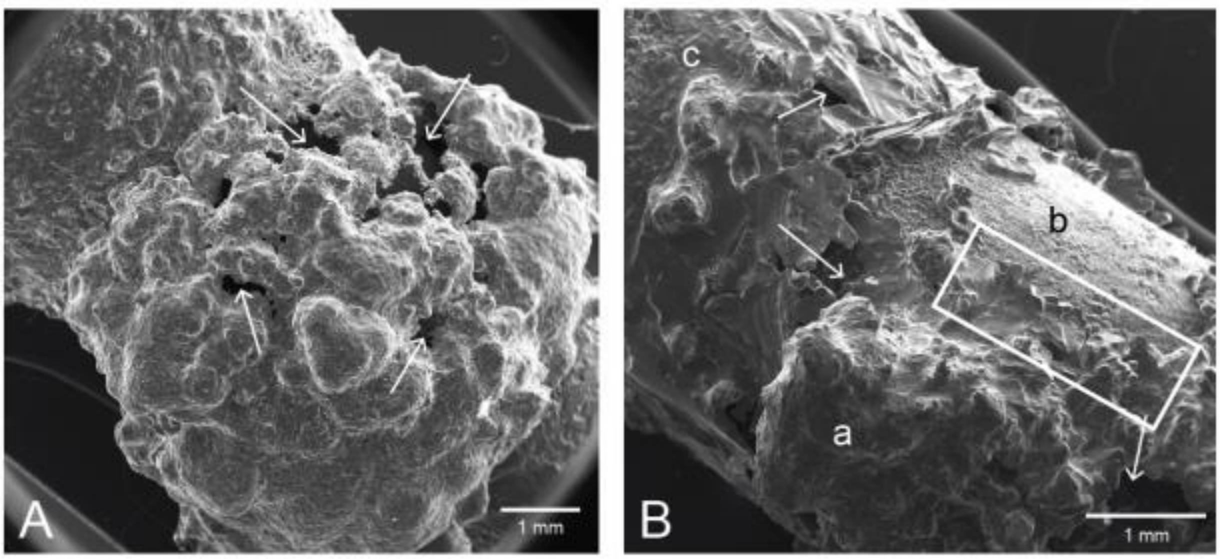

Figure 5. External morphologies of bulbous and botryoidal deposits accumulated on soda straw surfaces with SEM imaging. Buildups consist of coarsely crystalline halite at areas where the micro-porosity canals within the tubular structure of the calcite soda straw are concentrated. (A-B) Bulbous and botryoidal buildups of halite (a) on the calcite soda straw external surface (b), and areas with disseminated micro-crystals of halite (c). Clusters of cubic halite crystals are commonplace (frame). Micro-porosity channels (arrows) provide communication between the straw central canal and the external surface.

Conclusions

The mineralogical and microstructural studies indicate that calthemite deposits of the study area occur mostly as nearly hollow crusts of calcite, characterized by interior partition and walls for structural support. The external morphologies of these deposits have similarities to those formed in natural limestone caves, but their interior microstructural architecture and mineralogy are not comparable, a widely underappreciated distinction. Containerized water-gas interfaces control microcrystalline calcite depositional fronts. The curvilinear walls partition the interior architecture into sub-parallel network of micro-conduits or canals that interconnects multiple basin-forms. This crust microstructure results in a highly porous and fragile interior architecture consisting of curvilinear calcite growth fabrics that partially regulate water-gas interface levels. Nonetheless, these interior calcite walls retain significant micro-porosity as to permit hydrostatic pressure driven capillary flows and result in arrays of sub-parallel or concentric wall structures. These layered calcite laminae partitions are often separated by parallel fluid-filled panels linked together by bridges of bulbous micro-protuberances consisting of micron scale platelets. The depositional processes result in a crust with an elevated interior porosity. These concrete ceiling crusts are not comparable to calcite crusts accumulated on ceilings of limestone caves, which are characterized by growth layers having minimal porosity, such as flowstone.

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