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Calcium Carbonate Rafts, Cones and Conulites: Speleothems and Calthemites

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Abstract

Cave rafts are found on the surface of still pools, usually in parts of caves or mines with little air movement. They are most commonly composed of calcium carbonate ($CaCO_3$) in the form of calcite or aragonite, however there have been documented occurrences of gypsum, native sulphur and oxide rafts. Cave rafts are precipitated from supersaturated water in many settings including caves, mines, spring-fed rivers and under man-made concrete structures. Despite being very thin and fragile, rafts can create incredible structures that look like stalagmites when sunk in a constant location under a drip.

Degassing of carbon dioxide (CO_2) from solution is the prominent driving force causing the deposition of rafts in caves and mines, whereas deposition from solution derived from concrete is driven by absorption of CO_2 from the atmosphere into solution.

Free floating rafts can be classified as fine floating rafts, whereas rafts that are attached to a pool bank can grow thicker and develop into what are considered to be massive calcite crusts. Rafts in caves are classified as 'speleothems', however rafts created outside the cave environment are excluded due to the definition of the term. It is proposed that rafts created in or around man-made environments (outside caves) be classified as 'calthemites'.

It is proposed that a drip hole resembling a splash cup, created in a pile of rafts, where the flakes have become fused together or lined with calcite should be called a "raft splash cup" a subtype of conulite.

Key Words: cave raft, calcite raft, calcium carbonate, raft cone, tower cone, calcium hydroxide, micro raft, volcano cones, conulite, speleothem, calthemite

Introduction

Delicate calcium carbonate rafts are often encountered floating on the surface of still pools, usually in parts of caves or mines with little air movement (Figure 1). They are described by Hill and Forti (1997) as, "thin planar speleothems of crystalline material that float on the surfaces of pools." De Saussure (1779) was the first to mention them as looking "like a scattered dust" on the surface of a pool. Commonly known as "cave rafts" they have also been called other names in publications, including: calcite rafts, snowflakes, floe calcite/aragonite, lime/calcite ice, mineral film, crusts, water table speleothems and calcite platelets (Hill and Forti 1997; Faimon and others 2022).

Rafts in caves are classified as speleothems along with other secondary deposits such as stalactites, stalagmites and flowstone. They are most commonly composed of calcium carbonate ($CaCO_3$) in the form of calcite crystals and the less common polymorph, aragonite; however worldwide there are documented occurrences of gypsum, native sulphur and oxide rafts (Hill and Forti 1997). Even in Australia there are examples of unusual siderite cave rafts in Odyssey Cave B24, Bungonia, NSW (James 1975).

The study of rafts has been used to record local water and/or seawater levels, decipher palaeohydrological conditions, paleoenvironmental reconstructions, archaeological research of human activities in periodically flooded caves and to determine the geochemistry of contemporaneous water.

Figure 1. Large rafts on a pool in Glass Cave W9, Wombeyan, NSW. Photo Garry K. Smith

Formation of calcium carbonate rafts

While the chemistry involved in the creation of calcium carbonate speleothems is well documented, a brief overview of the processes may be in order.

After entering a cave through cracks and voids, water saturated with calcium irons can be trapped in pools over many weeks, months or longer. As the water degasses carbon dioxide (CO_2) and evaporates, it causes an increase in the saturation level of the solution to the point where $CaCO_3$ is deposited out of solution (usually as calcite). In calcium carbonate caves, CO_2 degassing is the leading mechanism causing $CaCO_3$ deposition, compared to evaporation which is limited by relatively high humidity atmospheres approaching 100% (Faimon and others 2022).

However, degassing is not necessarily the main driving force creating rafts of other minerals. For example, Calaforra and others (2008), found that evaporation remains a major factor in the creation of gypsum rafts. Their study of gypsum karst in Czechia, identified that "calcite speleothem evolution is mainly controlled by CO_2 diffusion, while gypsum deposits develop mostly due to evaporation" (Calaforra and others 2008).

Slow deposition may aid the growth of pool crystals (e.g. dog tooth spar) under the water and smaller crystals may be deposited at the pool edge along the thin top of rimstone dams. Faster deposition will result in the creation of cave rafts at the pool surface. Rafts typically appear in pools that don't have water flow (i.e. not overflowing a rimstone dam) and in environments with little air movement.

At the water surface of supersaturated pools, degassing of CO_2 causes deposition of small calcite crystals to start forming around a nucleus, which may be a minute speck of dust or other particles on the surface. As more calcite is deposited out of solution at the surface, the pool-water surface tension keeps the forming raft of minute crystals afloat despite the calcite density exceeding that of water.

The upper side of a raft exposed to the air is generally flat, smooth and shiny, whereas the underside has pointy crystals forming a dentate structure. Raft growth can be rapid, occurring over weeks to months.

There may be literally hundreds or more of these rafts forming at the same time (Figure 2). Their creation is driven by the ever-increasing saturation of the pool water surface as degassing and evaporation continue.

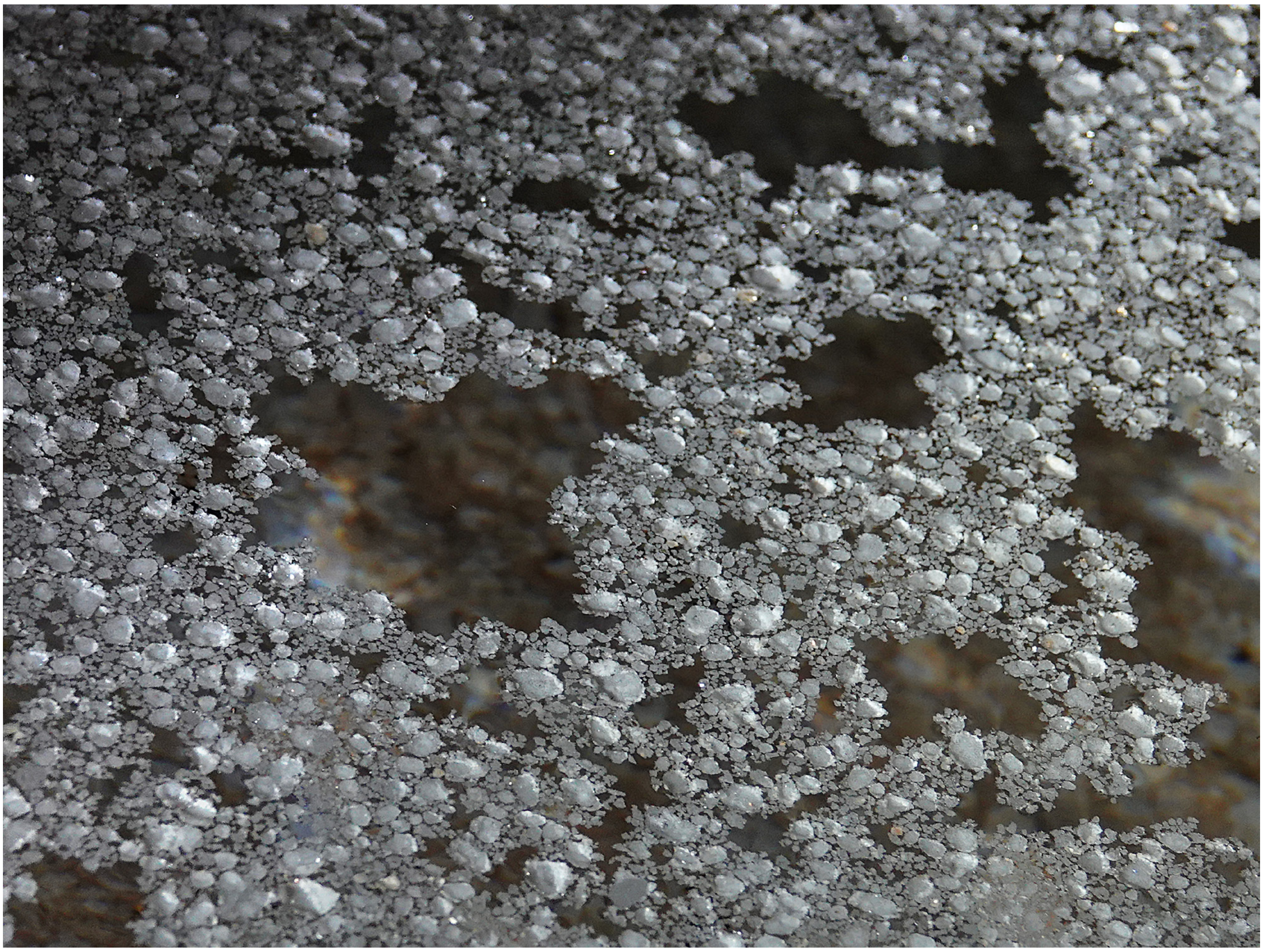


Figure 2. Many calcite rafts (<8 mm diameter) forming at the same time in Apple Tree Cave A79, Abercrombie, NSW. Photo Garry K. Smith

Small rafts can join to create larger ones, however there becomes a point where the mass of the growing raft cannot be supported by the water surface tension, and the rafts will sink either intact or break up on their way to the bottom. Very thin pure white rafts that have sunk, then left stranded when the pool water level drops, are called 'snowflakes' as they resemble new-fallen snow. An accumulation of sunken rafts can result in a litter of thin calcite platelets across the bottom of a pool.

Free floating rafts usually don't exceed 15 cm diameter and 1 mm thick (Hill and Forti 1997) before they sink under their own weight (Figure 3). However, rafts that have become attached to the pool edge (Figure 1) can grow much larger and thicker than those that remain free floating (Faimon and others 2022).

A thick layer of sunken rafts may become cemented together over time and form a hard mass.

Some of the small rafts that have settled on the bottom of a cave pool, which are not cemented together when the water level drops (to allow them to become dry), may float again when the water level rises again (Viehmann 1992).

As pools gradually drain away or evaporate, once-floating rafts will be left stranded on the bank of the receding pool (Figure 4). If left undisturbed these fragile rafts can remain intact after drying (Figure 5).

To float or sink

Fragile rafts rely on the surface tension of the pool water to remain afloat, so if disturbed with just the slightest movement they generally sink to the bottom. Even a single water drop falling from a stalactite is enough to break up and sink rafts at the drop impact location (Figure 6). The disruption of the pool-water surface tension by the impact of a drop is enough to also cause some rafts to sink in close proximity to the impact point.

Divers have observed rafts sinking in deep water due to their exhaled bubbles causing turbulence at the surface. The broken up rafts slowly sink through the water like delicate snowflakes and form a white carpet on the bottom.

Figure 3. Large rafts up to 15 cm in diameter, forming on a deep pool in Bullio Cave W2, Wombeyan, NSW. Photo Garry K. Smith

Figure 4. Calcite rafts left behind on bank as pool level drops in Apple Tree Cave A79, Abercrombie NSW. Photo Garry K. Smith

Raft cones and towers (also known as cave cones/towers)

An occasional drop from a stalactite is enough to break up and sink rafts directly beneath the drip point. After a raft sinks, a small section of clear water surface is created, however it is soon filled by newly forming rafts or others that slowly drift in to fill up the space. The rafts that have sunk to the bottom beneath a drip point, will gradually accumulate to form a mound (Figures 7, 8) called a "raft cone" or "cave cone". Raft cones can be very small (of less than a centimetre), but may reach over a metre in height. Some examples in Carlsbad Cavern, New Mexico are over 3 m in height and typically shingled at about 45° to the vertical (Hill 1981).

Figure 5. Calcite rafts left behind after pool dries up in Apple Tree Cave A79, Abercrombie, NSW. Note AA battery for scale. Photo Garry K. Smith

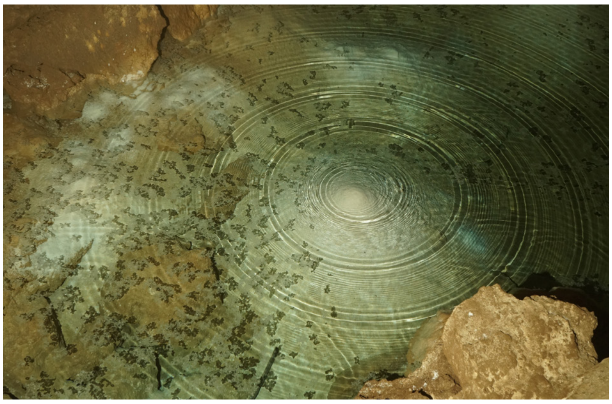


Figure 6. Radiating ripples caused by drips from an active stalactite show where rafts have been made to sink at the apex of a raft cone in Caverne Gastonia, Rodrigues, Mauritius. Photo Greg Middleton

Figure 7. Raft cone formed under a drip point, now dry after pool level dropped in Apple Tree Cave A79, Abercrombie, NSW. Note AA battery for scale. Photo Garry K. Smith

Figure 8. Raft cone with hole in top created under drip point in Moores Lake Cave TR27, 30, Timor, NSW. This cone is gradually being transformed into a volcano cone. Photo Garry K. Smith

Tyc Andrzej (2004), reported many exceptionally large cones over a metre in height, in the Gran Caverna de Santo Tomás, Cuba, which are made of calcite rafts that had sunk to the cave lake floor under drip points. These raft cones look even more dramatic when the lake water level drops, leaving the cones high and dry. Such large cones have not been recorded in Australian caves.

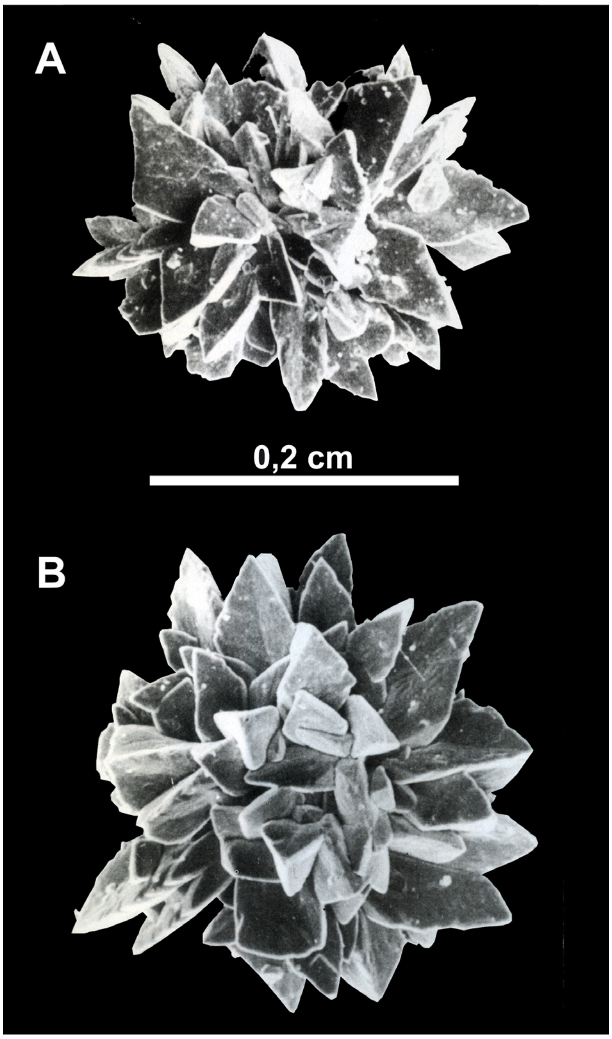
Raft cones that are exposed to the air by a lowering water level, can have holes drilled into their apex by a constant drop at the same location (Figure 8), particularly if the drip water becomes under-saturated with calcite. Called "volcano cones" as the name suggests, they take on the appearance of a miniature volcano with the central hole as the crater. These have been reported from quite a few caves around the world. Variations on this type of speleothem are volcano cones that have had rafts comprising their central drip hole cemented together, then the outer flakes of the volcano are washed away, leaving a central core with a little cup at the top (Hill and Forti 1997). This speleothem can be mistaken for a stalagmite.

Tower cones are a tall and slender variation of the raft cone speleothem. They have been reported in a number of caves around the world, with the most notable being in Grotta Giusti di Monsummano Terme (Tuscany, Italy) with towers measuring up to 3.5 m in height (Figure 9). The slender conical tapering shape of the towers have a shingle angle of only 20-25° to the vertical. They were created in the same manner as raft cones, except that the rafts being sunk under a drip point have been rapidly compacted, cemented and consolidated together in thermal (35°C) water. The cave rafts giving rise to

Figure 9. Grotta Giusti di Monsummano. The tower cones which are now inactive in the no longer submerged area of the cave. Some towers have developed until they came into contact with the folia now on the ceiling, which were developing following the progressive lowering of the air-water interface. The largest tower cones can reach two metres in height, but those in the photo are about 1 metre. Photo Paolo Forti

these cones are extremely small - about 2 mm or even less in diameter.

Paolo Forti has kindly provided SEM images (Figures 10A, B) showing the underside of two rafts from tower cones in Grotta Giusti. As is typical of this type of speleothem, both cave rafts have an almost flat upper face (not visible in the images) which is in direct contact with the cave atmosphere when forming (their C axis laying on the contact plane and being radially oriented). Figures 10A and 10B show the calcite crystals which have grown in all directions at the same speed to form a hemispherical shape structure, while immersed in the supersaturated water. Figure 10A is a raft which was recovered from inside a broken tower cone now dry, after the water level receded, and Figure 10B is a raft that has recently formed in the thermal water. The two rafts are practically identical, except that the crystalline surfaces of the ancient raft (Figure



Figures 10A, B. Photos by Paolo Forti.

A: SEM image of the lower part of a cave raft that was recovered from inside a broken tower cone in the Grotta Giusti area currently dry after the thermal water receded.

B: SEM image of a cave raft that recently formed on the surface of the thermal lake currently at the bottom of Grotta Giusti.

10A) are much rougher than those of the recently formed raft (Figure 10B). The ancient cave raft has undergone a partial diagenesis during the tower cone formation process by the accreting thermal waters (Paolo Forti, personal communication 5 Jan., 2023).

Tower cones up to 60 cm high have also been reported in Wanhuayan Cave, Hunan Province, China, however the rafts were created in a normal cave environment rather than a thermal one (Forti and Utili 1984).

Splash or drip cones

There may be a layer of broken rafts remaining on the ground after a pool has evaporated or slowly drained away. These layers may be centimetres thick as the pool that had supported the development of calcite rafts, filled and emptied with seasonal conditions. When the bed of rafts is dry, an occasional drip from a stalactite may rearrange the broken raft fragments into a splash cup shape and even cement the calcite fragments together. Such structures may only be a couple of centimetres in diameter and height (Figure 11). Are they just another variation of a conulite? These speleothems are described by Thayer (1967) as “simple drip-drilled mud pits …lined with calcite.” Peck (1976) suggested that the term ‘conulite’ could be broadened to “include any drop-drilled pit in sediments with walls which have been secondarily impregnated and, perhaps, lined by a mineral”. In later literature the term has been expanded to include “simple drip-tube pits in mud or other soft material which later becomes lined with calcite or other minerals” (Hill and Forti 1997). Therefore this definition can broadly encompass the speleothem depicted in Figure 11 which consists of broken calcite rafts sculptured by drip water and cemented together. However, as this type of conulite is specifically made of rafts it could be better described as a “raft splash cup”. This suggested name reflects the speleothem origin as the shape is influenced by the rebounding splash of drip water.

Figure 11. Raft splash cup created by drips from a stalactite, rearranging calcite rafts now in a dried pool, Lake Cave WA42, Walli, NSW. The rearranged rafts then become cemented together over time. Note AA battery for scale. Photo by Garry K. Smith

Rafts on spring water

Taylor and others (2004) reported calcite rafts on spring-fed rivers in the Barkly Karst of Northern Australia. The Middle Cambrian age karst consists of dolomites and dolomitic limestones. Patches of extremely fragile rafts just a few tens of microns thick were forming on the surface of large quiescent pools along the river, particularly behind tufa dams (also called travertine). One such waterhole (Homestead Waterhole) where calcite rafts were observed, measured 3 km long x 20-50 m wide and up to 6 m deep. Precipitation of rafts at the water-air interface were being primarily precipitated from supersaturated water, as occurs in caves, due to CO_2 degassing and evaporation. Taylor and others determined that the rafts were forming due to a combination of physical, chemical and biological processes. “The rafts are readily inhabited by microorganisms, particularly diatoms, which frequently become entombed by calcite as the rafts develop” (Taylor and others 2004). As with calcite rafts in caves, the upper surface was flat at the water-air interface, while the crystals growing downwards into the water have a dentate structure. Their morphology is similar to rafts formed in cave pools.

However, rafts found in caves and mines don’t appear to have biological (microorganism) involvement in the creation process as do the rafts formed in above-ground environments.

Rafts in mines and under man-made structures.

In mines and man-made structures, calcite rafts can also form. In mines, the chemistry involved may be the same as in limestone caves, however if below or inside concrete structures, the chemistry involved in the deposition of calcite rafts is completely different. In caves, secondary deposits (typically calcite) are called speleothems, and encompass stalactites, stalagmites, flowstone, calcite rafts, etc. However the widely accepted definition of the word “speleothem”, as introduced by Moore (1952), derived from Greek (*speleon*, a cave and *them*, deposit), excluded secondary deposits outside the natural cave environment.

This quandary became a dilemma for the author when writing a paper about straw stalactites composed of calcium carbonate attached to the underside of concrete buildings (Smith 2015, 2016). As a result, the term ‘calthemite’ (plural ‘calthemites’), was introduced to encompass the varied secondary deposits found in and under structures of human origin (including mines and tunnels), consisting primarily of calcite but which may contain other trace elements such as iron, copper and zinc or minerals, e.g. gypsum. Typically calthemites are secondary deposits associated with dissolution of concrete, lime, mortar or another calcareous material outside the cave environment. Calthemites mimic the shapes and forms of speleothems, such as stalactites, stalagmites and flowstone.

The word ‘calthemite’ is derived from the Latin *calx* (genitive *calcis*) “lime” + Latin, from Greek *théma*, “deposit” meaning ‘something laid down’, (also Medieval Latin *thema,* “deposit”) and the Latin *–ita* from Greek *-itēs* – used as a suffix indicating a mineral or rock.

Calthemites may form in tunnels and mines excavated into limestone or other calcareous rock. In these circumstances the secondary deposit of $CaCO_3$ may be derived from the calcareous rocks (not concrete), so the chemistry creating these calthemites is the same as speleothem deposition in limestone caves.

Figure 12 shows calcite rafts which have formed on a pool surface in an abandoned antimony mine near Nundle, NSW. There, water has seeped through the surrounding rock, dissolving small traces of calcium carbonate on its way to the pool. As calcium-rich pool water became more saturated through evaporation and degassing, rafts began to form. However, despite the calcite raft deposition process being the same as the formation of cave rafts, they are technically not classed as speleothems and must be considered calthemites (Smith 2016, 2021).

Figure 12. Calcite rafts in an abandoned antimony mine, Nundle, NSW. Photo Garry K. Smith

Faimon and others (2022) studied calcite rafts in an abandoned wartime adit, located in the Moravian karst (Czechia). The near-horizontal tunnel intersected limestone strata at the location where the rafts were forming, thus the chemistry depositing calcite is the same as in limestone caves, however, as with the previous example, the secondary deposits (rafts) are still considered to be calthemites. This study identified two different types of calcite rafts: fine floating rafts (FF rafts) and massive calcite crusts (MC rafts). The FF rafts consisted of a web of individual 100-200 μm large calcite crystals interconnected by crystalline edges and the MC rafts consisted of relatively firm and massive calcite crusts. The FF rafts transitioned to MC rafts after they became anchored to the bank of the pool. The study found that once anchored, the FF rafts could continue growing at the surface with the added support of the pool edge to remain afloat. They could grow on both top and bottom of the original air-water interface to form MC rafts up to several millimetres thick and mechanically strong. The top faces of MC rafts are considerably rougher than the FF rafts.

Faimon and others (2022) proposed several hypotheses, the most likely of which was that growth of calcite at the top face was due to rising capillary waters passing between the raft crystals. CO_2 degassing remained the main contributor to the deposition of calcite. Crystals on the underside of the raft grew more slowly because CO_2 can't diffuse into the atmosphere as rapidly as it can from crystals forming on the smooth top of the raft.

Rafts derived from hydrated lime (calcium hydroxide) solution

People who are involved in the bricklaying or concreting trades may notice a thin crusty layer covering the water surface the day after washing cement-covered shovels and trowels in a water bucket. Calcite rafts derived from lime, mortar or cement products appear very similar to rafts in limestone caves, however the chemistry involved in their creation is very different.

The deposition of calcium carbonate is a result of CO_2 absorption from the atmosphere reacting with calcium hydroxide, as opposed to rafts in limestone caves that are created by degassing CO_2 from calcium ion-rich solution. Like the rafts found in a bricklayer's wash bucket, the calcite rafts in pool water within a concrete tunnel or beneath a concrete building, are created where CO_2 is absorbed into solution. Under these circumstances, deposition of calcium carbonate is usually associated with hyperalkaline solution (pH > 9) as opposed to the near neutral pH to mildly alkaline solutions (pH 7.5 – 8.5) that commonly deposit speleothems. Refer to Smith (2015, 2016) for more information about the chemistry.

Micro calcite rafts – calthemites

The chemistry creating calthemites (precipitation of calcium carbonate $CaCO_3$ from solution) is a relatively rapid reaction allowing micro rafts to form on the surface of solution drops hanging from calthemite straws below concrete structures. After a solution drop has fallen, the next suspended drop begins to slowly grow in size. If the drop has not fallen, after about 5 minutes the first micro rafts can be seen with the naked eye on the drop surface.

The relatively rapid absorption of CO_2 from the atmosphere into the solution drop results in the creation of the calcium carbonate ($CaCO_3$) micro rafts. If there has been almost no air movement when the drip rate is very slow (>12 minutes between drips), the rafts join up and form a latticework pattern over the drop surface (Figure 13).

Figure 13. Drip with calcite rafts latticework formed on a very slow-dripping calthemite straw (≈ >12 minutes between drops) on a day with no wind or vehicle movement. Photo Garry K. Smith

Figure 14. Calcite rafts are broken up and spinning around the drip surface, influenced by air movement. Photo Garry K. Smith

Air movement, or internal solution pulses from the straw, will break up the raft latticework causing sporadic movement of the micro rafts around the drop surface (Figure 14). These rafts can influence the thickness and irregularities of a calthemite straw's outside diameter (Smith 2021). A 34-second video showing $CaCO_3$ micro rafts whirling around the surface of a straw drop can be viewed at www.youtube.com/watch?v=G-gm_kN5Xes.

Conclusion

Cave rafts are most commonly composed of calcium carbonate in the form of calcite, however worldwide there are documented occurrences of rafts composed of gypsum, of native sulphur and of oxide.

Rafts consisting of calcium carbonate and other minerals occur in both natural and artificial environments. In caves they are classified as 'speleothems', being a secondary deposit in a cave, however the definition of this term excludes secondary deposits (i.e. rafts) created outside the natural cave environment. The differences between these environments are sufficient to justify the use of the term 'calthemites' (first introduced by Smith (2015)) for rafts and other secondary deposit forms created in artificial environments, such as concrete buildings and man-made mines or tunnels.

As the term 'speleothem', specifically refers to secondary deposits in caves, the term should not be used to describe straws, stalactites, flowstone and other secondary deposits associated with dissolution of concrete, mortar, lime or calcareous material outside the cave environment.

In supersaturated pool water, calcite or aragonite can precipitate at the water-air interface to form 'rafts' with nucleation occurring on dust and other particles resting on the pool surface.

Fine floating rafts (FF rafts) can grow to approximately 15 cm in diameter and 1 mm thick before sinking, however if they attach to a pool edge they can continue to grow substantially larger to become massive calcite crusts (MC rafts) with a thickness of several millimetres.

Rafts that sink under a drip point can build up on a pool bottom to form raft cones or towers. When the pools dry out these cones can be mistaken for stalagmites. Drips from a stalactite can rearrange the broken raft fragments into a splash cup shape and even cement the calcite fragments together. It is proposed that this type of conulite made of rafts should be called a "raft splash cup", as the shape is influenced by the rebounding splash of drip water.

Apart from caves, calcite rafts can form in mines and above ground in quiescent spring water. The prominent driving force causing deposition of $CaCO_3$ in such cases is degassing of CO_2 as opposed to evaporation of solution.

However, calcite rafts forming on supersaturated hyperalkaline solution derived from lime, mortar or cement products are created by different chemistry that involves the absorption of CO_2 into solution to cause the formation of rafts. The creation of calthemite rafts can take just minutes when hyperalkaline solution ($pH > 9$) is involved in the deposition of calcium carbonate, whereas it can take days or longer for near neutral pH to mildly alkaline solutions (pH 7.5 – 8.5) that commonly deposit speleothem rafts.

Definition

Calcite Raft. *n.* A thin layer speleothem of crystalline calcite material which forms and floats on the surface of still cave-pools. Disturbance of the pool surface often sinks the rafts. This speleothem forms on the pool surface due to degassing of CO_2 from solution which causes saturation of solution and deposition of calcite at the surface. Rafts may also form on the surface of supersaturated hyperalkaline solution outside the cave environment due to CO_2 absorption.

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