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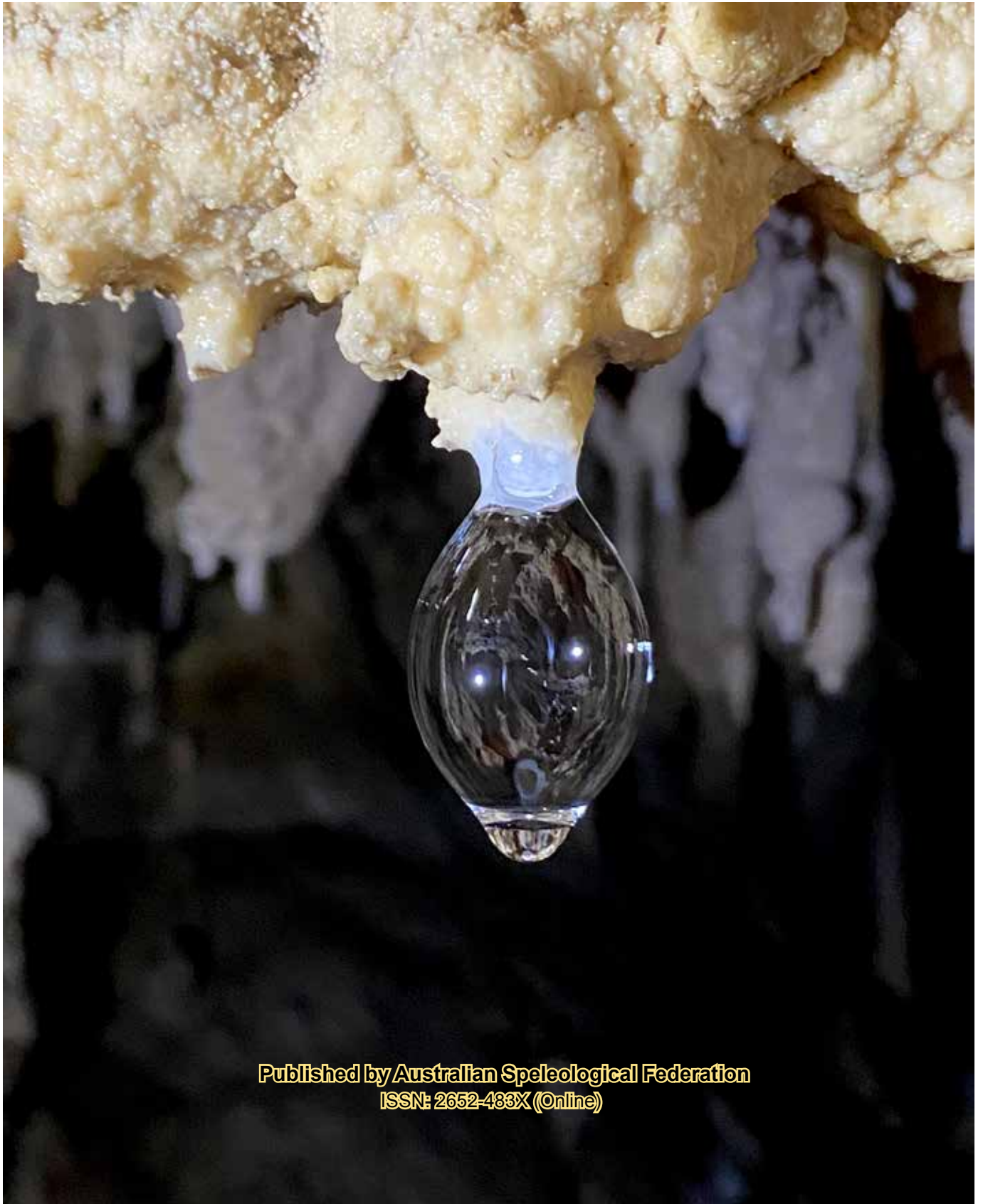
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Helictite was established in 1962 by its foundation editors, Edward A. Lane and Aola M. Richards. It is intended to be wide ranging in scope from the scientific study of caves and their contents, to the history of caves and cave areas and the technical aspects of cave study and exploration. The territory covered is Australasia – Australia, New Zealand, the near Pacific Islands, Papua New Guinea and surrounding areas, Indonesia and Borneo.

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All correspondence to: P.O. Box 269, Sandy Bay, Tasmania, Australia. E-mail: ozspeleo@iinet.net.au

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Calcium Carbonate Rafts, Cones and Conulites: Speleothems and Calthemites

*Garry K. Smith*¹

¹Newcastle and Hunter Valley Speleological Society.

P.O. Box 15, Broadmeadow, N.S.W. 2292, Australia gksmith29@icloud.com

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 (CaCO₃) 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 (CO₂) 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 CO₂ 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 (CaCO₃) 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 ions 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



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

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 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.

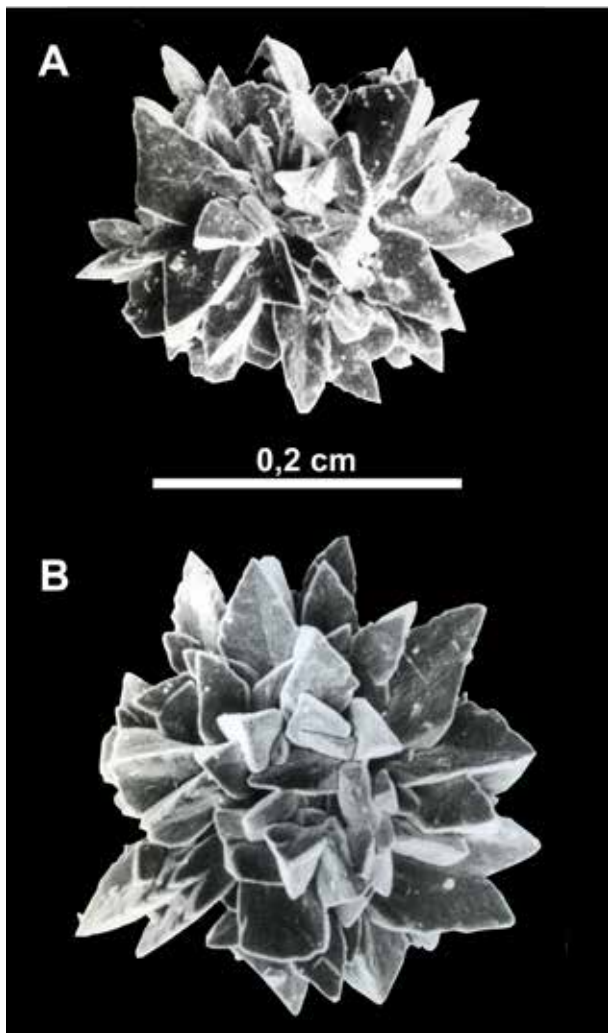
Tower cones are a tall and slender variation of the raft cone speleothem. They have been reported in a number of caves around the world, with the most notable being in Grotta Giusti di Monsummano Terme (Tuscany, Italy) with towers measuring up to 3.5 m in height (Figure 9). The slender conical tapering 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 CO₂ 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 CaCO₃ 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

Calcium carbonate rafts, cones & conulites

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 ($\text{pH} > 9$) as opposed to the near neutral pH to mildly alkaline solutions ($\text{pH} 7.5 - 8.5$) 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 ($\approx >12$ 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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Bubble-drip and Bubble-blowing Straw Stalactites - a small remarkable natural wonder

Garry K. Smith

Australasian Cave & Karst Management Assoc. and Newcastle & Hunter Valley Speleological Society
P.O. Box 15, Broadmeadow, N.S.W. 2292, Australia gksmith29@icloud.com

Abstract

Bubble-blowing straw stalactites are not common and are a result of solution pushing gas bubbles out the end of a straw. These bubbles consequently burst shortly after exiting the straw's central channel. However, a handful of these rare oddities have been recorded with a bubble that remains intact at the base of the straw, while solution flows over the bubble surface and drips from beneath. Some of these bubbles can be 20 mm or larger in diameter. It is proposed that these small remarkable natural wonders should be called 'bubble-drips' - if the bubble remains intact for several consecutive solution drips. This would distinguish the phenomenon from bubbles that burst upon exiting the straw and those which remain at the straw tip for some period of time. Research by Johnson (2022) suggests that the rare speleothems termed 'cave turnips' are created by bubble-blowing stalactites and, more specifically, the variant to be now called bubble-drips.

Very little research appears in available literature surrounding both bubble-drips and bubble-blowing straws. A number of hypotheses relating to the possible environmental conditions leading to the creation of bubble-drips are provided. This paper makes suggestions for research that could be undertaken to validate or disprove the hypotheses provided.

Introduction

On a recent trip to Takaka in the far north of New Zealand's South Island, while attending the ACKMA conference in 2023, the author was told about a nearby cave containing an unusual phenomenon of a *bubble-drip straw*. Several days later, Keiran Chandler and John (Oz) Patterson took a group of us to see the bubble drip in Elliots Cave, located on private property.

Our group was fortunate to see this unusual occurrence close up (Figure 1). Photographs and videos were taken of the relatively large air bubble hanging from a very short straw stalactite (with a flared tip) as solution flowed from the straw's central canal, over the surface of the bubble and dripped from the bottom of the bubble. This bubble remained intact as more solution ran over its surface and dripped from the bubble at a rate of approximately a drop every 4 seconds. As each drop of water fell from the vertically elongated bubble, the separation created a change in stress on the bubble causing it to rebound to a slightly horizontally-flattened ball, then back to round. As more solution was observed flowing over the bubble surface, it again became vertically elongated, until the next solution drop fell from the bottom and the process repeated (Figure 2).

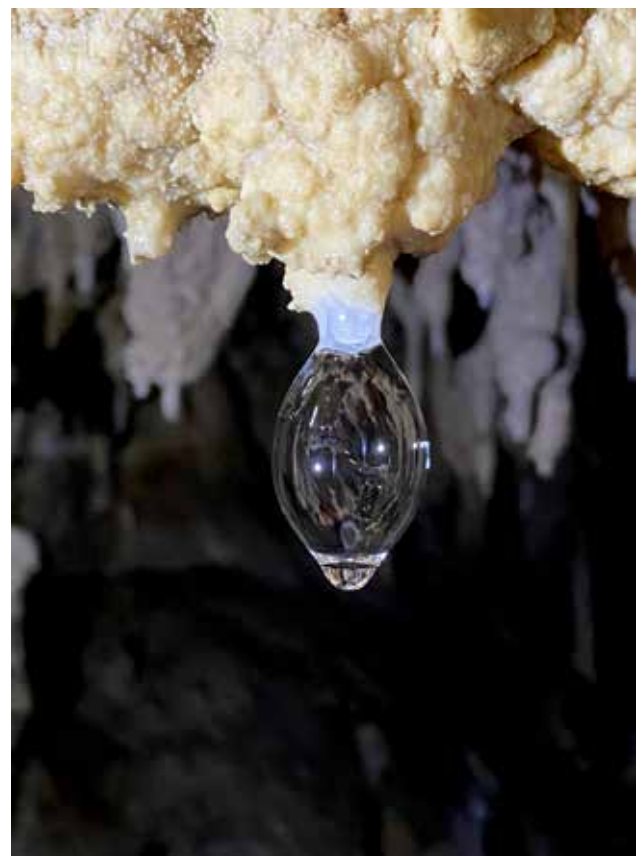


Figure 1. A solution bubble in Elliots Cave at Takaka in the far north of New Zealand's South Island.
Photo Garry K. Smith

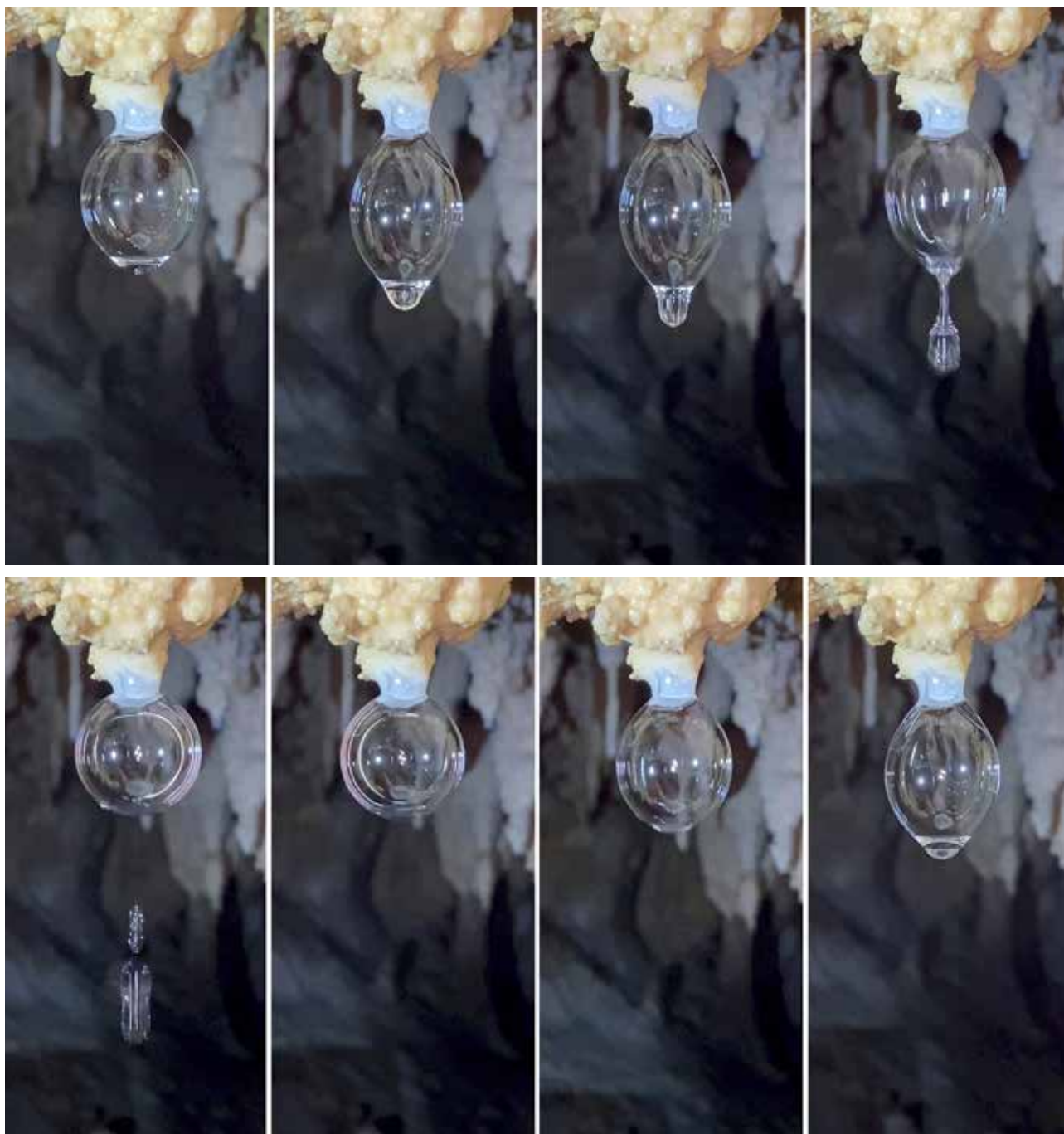


Figure 2. Sequence of a solution bubble beneath a short straw, showing a drop forming and falling from the base of the bubble that remains intact as the sequence is repeated many times before eventually bursting. Photo Garry K. Smith

This is certainly a small, but remarkable, natural wonder that is rarely seen.

So how does this happen without the bubble bursting every time a drop falls from the bottom of the air bubble? How does the gas get into the solution? Is there some chemistry involved that changes the solution's surface tension to maintain the bubble, despite the force exerted on it by the dripping solution? These questions and many others sent me on a quest for answers.

As an active caver for approximately 60 years, I have never before seen a bubble at the end of a straw with solution dripping from the bottom. Available literature broadly refers to this phenomenon as 'bubble-blowing soda straws' but does not make distinction between constantly bursting bubbles and those that remain intact. Hence this category is very broad and does not reflect the two distinct variants.

To clarify the phenomena, I propose that there should be two distinct categories: 'bubble-blowing straw', and the now-proposed variant to be called a 'bubble-drip':

1. Bubbles and solution come out the end of a straw, however the bubbles usually burst before, or as, a solution drop falls. To be referred to as ‘bubble-blowing straws’ in this paper.
2. The bubble at the bottom of the straw remains intact for a period of time while solution drops fall from the bottom of the bubble. These will be referred to here as ‘bubble-drips’.

This short paper has been written in the hope that other cavers who have observed this rare wonder will help shed more light on their occurrence and behaviour. If you have ever seen a bubble-drip or bubble-blowing straw, please contact the author.

The documented locations, some of which appear on the internet in social media, have been listed in this paper, along with the identified environmental conditions and morphology of the straw stalactites.

Known Occurrences

The earliest report found during literature searches for bubble-blowing stalactites dates from 1938. Custodian T.O. Thatcher at Lehman Caves, Great Basin National Park, Nevada, USA, observed bubbles issuing from a stalactite after hearing what he thought was water dripping into a pool in the Cypress Swamp section of Lehman Cave. Upon investigation he reported, “Both water and air were coming down the channel, about the size of a match, in the centre of the formation, thus forming bubbles which made the sound when bursting” (Anon. 1938, 1972). This example is not quite the same as the one in Elliotts Cave, NZ, in that the bubbles were not remaining intact while water continued dripping.

In their book *Cave Minerals of the World* (Second Edition), Hill and Forti (1997, p. 107), provide a photo by Michael Lichon of a “bubble-blowing soda straw” in Baldocks Cave, Mole Creek, Tasmania. This appears to be what is here termed a bubble-drip.

Internet searches have revealed just a few occurrences of bubble-drips in the USA, including several examples in Lehman Caves, Great Basin National Park, Nevada. Baker (2017) provides several images of bubble-drips in her blog ‘Desert Survivor’ (Figure 3a-d).

Also the website page at <<https://www.us-parks.com/great-basin-national-park/caves.html>> refers



Figure 3a, b. Bubble-blowing straws at Lehman Caves, Great Basin National Park, Nevada, USA. Photos Gretchen M. Baker.

to the Lodge Room area of Lehman Cave having some soda straws with a bubble on the end of each and water dripping from the bubbles. They occur at a depth of about 24 m below the surface (Baker, G.M., pers. comm). Pinyon pine and juniper grow on the surface above the chamber with the bubble drips.

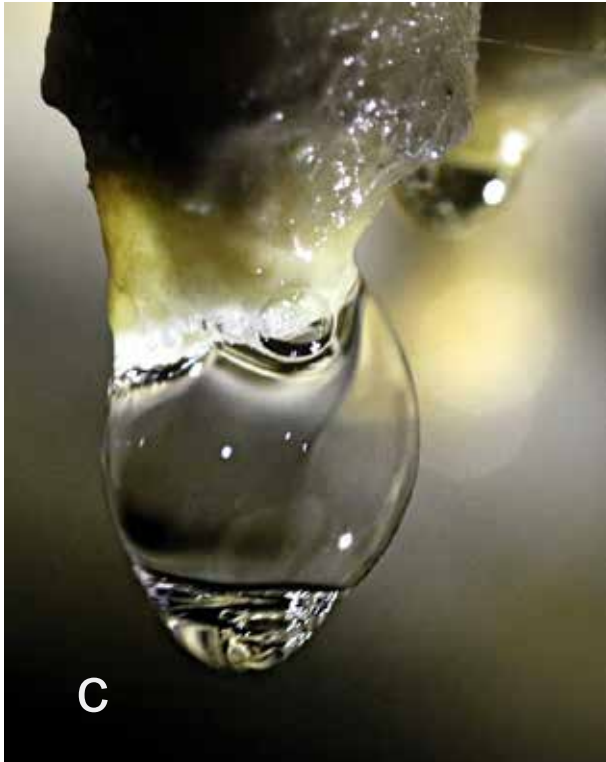


Figure 3c, d. Bubble-blowing straws at Lehman Caves, Great Basin National Park, Nevada, USA. Photos Gretchen M. Baker.

At Timpanogos Cave National Monument, Utah, USA, it is also reported that on rare occasions bubbles can form, at the end of soda-straws in Middle Cave, typically during wet springs such as in June 2019. A video of a bubble-blowing straw can be seen

at https://m.facebook.com/timpanogoscavenps/videos/cave-bubbles/347795159233822/?_se_imp=0x1NYp4Xwd5Vdo9Xe. And also at <https://www.facebook.com/reel/2901107923506582>

Another occurrence of a bubble-drip has been reported in Lewis and Clark Caverns State Park, Montana, US and a photo by Zack Story is posted at https://www.instagram.com/p/CQHMuXJLiMQ/?img_index=2.

There are two bubble-drips in close proximity to one another in a video posted on Facebook by “Indian Caverns” in October 2012. They both drip at rates faster than a drip every two seconds and there is a comment that the faster one of these bubble drips existed one year earlier. See https://www.facebook.com/100040793987008/videos/4365823336975/?__so__=permalink.

How do they occur?

The only explanation I have found as to how these bubble-drip and bubble-blowing straws occur is given by Hill and Forti (1997). They state that bubble-blowing stalactites are thought to be caused when the straw stalactite’s internal flow is temporarily interrupted while external flow continues. Capillary pressure may draw water and air into the end of the straw. When internal flow resumes, the result may be a bubble-blowing stalactite.

Observations

In the quest for more answers, the author searched the internet and located a couple of photos and videos of other bubble-drips to compare with the one in Elliots Cave, NZ. There appears to be a common theme across all the available images and videos, in that the straws from which the bubble-drips have formed are typically short in length and their diameter at the end is about 1-3 mm larger than standard speleothem straws which are typically between 4.5 and 6.45 mm (Smith 2019, 2021a, b). The solution drip rate is typically one drop every 2 to 4 seconds. The straws with bubble-blowing drips appear to be located in shallow depth caves (<15 m) with some vegetation at the surface in the solution catchment area. The videos on the internet and the bubble-drip video taken by the author in Elliots Cave, do not show any obvious solution flow on the outside of the straw which could be attributed to the high solution drip rate. This would suggest that something different is occurring, not capillary

pressure and solution flow on the outside of the straw as suggested in Hill and Forti (1997).

Hypotheses for Bubble-drip Formation

A possible explanation is that active bacteria breaking down rotting vegetation and growing tree roots (Smith 2022), are creating a significantly elevated carbon dioxide (CO₂) concentration in the soil above the cave. Another contributing factor may be that during winter the outside air temperature can be significantly colder than the cave air. This scenario is strengthened by the well documented fact that cold water can absorb and retain a higher concentration of CO₂ and other gasses than warmer water. If this is the case then rain water passing through the soil can absorb the high concentration of CO₂ and carry it down to the cave where degassing is occurring at a faster rate than usually occurs at a straw tip. Degassing in caves typically occurs because CO₂ in the drip solution at a higher concentration diffuses into the cave atmosphere with a lower concentration (generally without bubbles). However, physics shows that bubbles may form if the gas is forced out of solution too fast, such as when a solution is warmed up just a few degrees. Such conditions could well have created the bubble in Elliotts Cave as it had been very cold and raining for several days before our visit and the cave temperature was noticeably warmer than the above-ground temperature.

A simple demonstration of how gases and liquids interact is given when the cap is unscrewed from a cold bottle of carbonated water: the rapid reduction in pressure causes CO₂ bubbles to be released from solution. More bubbles continue to form as the soda water warms up to room temperature.

All the photo and video examples of bubble-drips I have located on the internet depict bubbles attached to short straws, which generally appear to be 1-3 mm larger than the average straw diameter. Certainly, the observed straw in Elliotts Cave was a larger diameter, very short and flared at the tip. This would suggest that the solution may be more acidic and as the drip rate was relatively fast, calcium carbonate is mostly being deposited on the cave floor and not at the straw stalactite tip.

In addition to the possible effect of an elevated concentration of CO₂ in the solution, there may be other chemistry involved that is altering the solution surface tension. Could there be an introduced compound from plant, algal or other microbial life,

that is decreasing the drip solution surface tension, thus increasing the bubble size and resistance to bursting when the drops fall from the bubble?

Contrary to what one would expect, decreasing the surface tension of water allows bubbles to form and resist bursting. For example, if air is blown into water with a drinking straw to create bubbles, they burst quickly because the surface tension of the water is relatively high and the water is not very stretchy. Adding soap decreases the surface tension so that the water can stay stretched around the bubble.

In nature there are substances such as saponins that act like soap and reduce water surface tension. Natural plant saponins are compounds that can dissolve in water, and will latch onto oils. Thus saponins have historically been extracted from some plants and used to make soaps. So, in summary saponins are a group of steroid or triterpenoid glycosides and related chemicals found in roots, shoots, seeds and flowers of many plant species. Saponins can be released into the soil by secretion from roots and/or leaching from living or decaying plant material (Mishustin and Naumova 1955; Oleszek and Jurzysta 1987).

The existence of saponins could be an explanation for the relatively large bubble-drip size in Elliotts Cave and why the bubble remains intact, while solution drips from the bottom of the bubble.

Given that bubble-drips appear to be rare worldwide, it may be that a number of conditions need to exist at the same time for this quirk of nature to occur.

These possible explanations are suggested on the basis of limited evidence and as a starting point for further investigation. It would be useful to analyse the bubble gas and the solution chemistry.

Gas bubbles influence speleothem morphology

A study documenting unusual bulbous speleothems called 'cave turnips', was undertaken in Lehman Caves, Nevada, USA, by Ryan J. Johnston (2022) and revealed a link with gas bubbles on straw stalactites. 'Cave turnips' are hollow inside and were named cave turnips by Dr. Louise Hose, a prominent Lehman Caves researcher. The research team identified and measured a total of 1017 cave turnips scattered over nine locations in the cave.

Bubble-drip and Bubble-blowing straw stalactites

Johnson hypothesized that the “turnip genesis begins as a soda straw, an abnormal bubble forms on the tip, and calcitic water flows over the bubble, creating the unique hollow turnip shape”. As calcite-rich water flows down the straw over the bubble, calcium carbonate is gradually deposited, causing the straw diameter to flare out, following the shape of the bubble. If the speleothem continues to grow, it may end up as a hollow turnip-shaped stalactite (Figures 4 and 5).



Figure 4. A cave turnip column in Lehman Caves, Nevada, USA. Photo Ryan J. Johnston.

While common in Lehman Cave, this type of turnip speleothem is relatively rare worldwide. The turnips at Lehman Caves have formed as a result of prolonged favourable conditions in past millennia. In today's present climate, “According to park geologists, these bubbles form during pluvial periods, the most recent occurring in 2018” (Johnson 2022).

Figure 6 shows examples of cave turnip speleothems in Hill Cave (TR7-8) at Timor Caves, NSW, Australia, that may have been created by this process.

Acknowledgements

The author thanks David Wools-Cobb for his suggestion of the possible influence of natural plant saponins; Cathi Humphrey-Hood, ASF



Figure 5. Photograph showing the hollow inside of a cave turnip caused by condensation corrosion removing the thin cave turnip wall. Lehman Caves, Nevada, USA. Photo Ryan J. Johnston.

Librarian, for sourcing the article in the publication *Cave Lights* and Gretchen M. Baker for granting permission to publish her bubble-drip images in this paper.

Special appreciation is expressed to Katerina Fulton for checking this article for grammar and readability.

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Figure 6. Cave turnips in Hill Cave (TR7-8) at Timor Caves NSW, that could have been created by bubble drips on straws. Note, on broken turnip, the internal crystals radiating inwards toward the centre of a ball-shaped speleothem. Photo Garry K. Smith.

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A late nineteenth century collection of fossils from the Naracoorte Caves highlights the role of the South Australian Museum in the history of the site.



Elizabeth H. Reed^{1,2}, Jessie-Briar Treloar¹, Mary-Anne N. Binnie² and Jennifer Thurmer³

¹Department of Ecology and Evolutionary Biology, School of Biological Sciences, The University of Adelaide, Adelaide, South Australia, 5005.

²Earth Sciences (Palaeontology), South Australian Museum, North Terrace, Adelaide, South Australia, 5000.

³South Australian Museum Archives, South Australian Museum, North Terrace, Adelaide, South Australia, 5000.

Corresponding author: liz.reed@adelaide.edu.au

Abstract

The Naracoorte Caves World Heritage site is renowned for its well-preserved deposits of fossil vertebrates spanning the last 500,000 years. Palaeontological research at the Caves began in earnest in 1969 following the discovery of the Fossil Chamber in Victoria Cave. Prior to that, records of fossil discoveries were largely restricted to incidental finds of material during caving activities or cave tourism developments in the Caves Reserve and the broader Naracoorte cave complex. The Reverend Julian Tenison-Woods first reported vertebrate fossils from Naracoorte Caves in 1858. However, there is no record of museum accession for this material and its current whereabouts is unknown. Discovery of megafauna fossil material was widely reported in 1908 and later, but there is very limited information regarding fossil collections made at Naracoorte during the middle to late nineteenth century. Here we report on fossil material collected from Naracoorte Caves and curated at the South Australian Museum by Amandus Zietz in 1888. The collection includes a range of small bones that are labelled and mounted, suggesting they were once used for public outreach or display. These fossils may represent the earliest museum collection currently known from Naracoorte Caves and highlight the South Australian Museum's long association with the caves and the early history of palaeontological investigation at this globally significant locality.

Keywords: Naracoorte Caves, fossils, Amandus Zietz, Quaternary, South Australian Museum, World Heritage.

1.0 Introduction

The Naracoorte Caves in South Australia is renowned for its Quaternary vertebrate fossil deposits (Wells and others 1984; Reed and Bourne 2000, 2009). The site was inscribed on the UNESCO World Heritage list in 1994 with Riversleigh in north-west Queensland as the Australian Fossil Mammal Sites (Riversleigh/Naracoorte). Throughout the Naracoorte cave complex, vast sediment deposits preserve deeply stratified assemblages of fossil vertebrates that span the last 500,000 to 600,000 years (Prideaux and others 2007; Arnold and others 2022; Weij and others 2022). In addition to the vertebrate fossils, multiple palaeoclimate and palaeoenvironmental proxies are preserved, including speleothems, pollen, diatoms, charcoal and macro plant fossils (e.g. Bampton 2021; Atkins and others 2022). Naracoorte's fossils are exceptionally well preserved, with over 135 species of amphibian, bird, reptile and mammal

identified to date (Reed 2019). The combination of multiple fossil sites at one locality, diversity of faunal and environmental records and tightly resolved site chronologies places Naracoorte Caves in an ideal position to address key questions relating to Quaternary biodiversity such as the causes and timing of megafauna extinction.

The first written records of caves at Naracoorte come from 1845, soon after European colonisation of the region (Reed and Bourne 2013). Originally known as the Mosquito Plains Caves, they have served as a major visitor attraction for the district and source of pride for the local community (Reed and Bourne 2013). The Naracoorte area holds Cultural significance for First Nations Peoples who have lived in the South East region of South Australia for thousands of years (Reed 2021). The Naracoorte area is the Traditional Country of the Potaruwutij, Jardwadjali, Boandik and Meintangk Peoples. Unfortunately, no archaeological record

1888 Naracoorte fossil bone collection

has been found in the caves so far, and information on specific interactions with the caves is limited. Our focus for this paper relates to the post-European colonisation history of the Naracoorte Caves, specifically the history of palaeontological study.

In 1857, Reverend Julian Tenison-Woods visited Blanche Cave at Naracoorte and later reported his discovery of fossil bones representing modern species of small mammals in *The South Australian Register* (Woods 1858). However, he did not recover any remains of extinct Pleistocene species, such as those previously found in the Wellington Caves in New South Wales (Reed and Gillieson 2003). Woods later expanded his description of the caves and fossils in his book *Geological Observations in South Australia: Principally in the district South-East of Adelaide* (Woods 1862). Despite providing a detailed account of what he found in the cave, Woods did not mention where the fossil material he collected was housed or if it was presented to a museum for registration. The South Australian Museum (located in Adelaide) became an entity in 1856, yet there is no record of this fossil material in the accession records. Woods may have sought to lodge it with another institution; however, we have not been able to find any record of this. Later records from the early twentieth century indicate that more fossil material had been discovered at Naracoorte Caves, and this was lodged with the South Australian Museum (Turner and Reed 2023). However, there remains a gap in knowledge regarding fossil collections made from Naracoorte during the middle to late nineteenth century.

Here we describe a collection of vertebrate fossils from Naracoorte Caves that is housed in the Palaeontology Collection of the South Australian Museum. The material is attributed to Mr Amandus Zietz, who was a Preparator and Assistant Director of the Museum and is well known for fossil discoveries made with the Museum Director, Edward Stirling. The fossil collection described here contains a selection of small bones accompanied by hand-written labels indicating the material was collected or curated in 1888. Palaeontology collection records indicate that it was retained for its potential historical value. Here we propose that this is the earliest museum curated fossil collection from Naracoorte Caves and present a description of the material and its significance, along with biographical information on Amandus Zietz. We also review early fossil discoveries at Naracoorte and the role of the South Australian Museum in palaeontological research in South Australia and its long association with the Naracoorte Caves.

2.0 The 1888 Zietz collection

2.1 Documentation and curation of the collection

We documented and photographed all individual elements of the collection, including the original packaging. Photographs were taken with a Nikon D7200 digital SLR camera and Nikon 50 mm lens. For each item we recorded the following details: description, size (dimensions in mm), condition and recommendations for conservation. Individual items were placed in an acid-free archival sleeve and then all collection items were placed in the original box with a Tyvek cover sheet and then placed in an acid-free archival storage box within a foam bed. We registered the collection with the Palaeontology Collection of the South Australian Museum and it was given the registration number SAMA P57488 (SAMA = South Australian Museum Adelaide; 'P' refers to the Palaeontology Collection). We documented 27 items which are all included under this registration number.

2.2 Description of the collection - SAMA P57488

The collection consists of a rectangular-shaped cardboard storage box containing 23 cards with small fossil bones glued to them, a glass vial containing cave sediment, and some loose fossil specimens in a small tray with hand-written and printed labels (Figure 1, Appendix). The storage box is a cardboard tray with lid (270 x 207 mm: Figure 2A, B). It is covered with reddish-brown coloured paper with a fine 'pebbled' texture. The tray is in reasonable condition, with bumping on the corners and peeling of the paper cover. It appears consistent in age with the collection, but we cannot confirm the precise association between the box and the contents. Fixed to the front of the tray is a modern white sticker labelled "Naracoorte Caves A. Zietz" in permanent marker (Figure 2C). The tray is lined with cotton wool and tissue which has yellowed with age (Figure 2D).

A small, glass-bottomed tray with white-paper-covered sides was found within the storage box (125 x 87 mm: Figure 3A, B). This style of tray was commonly used at the South Australian Museum for storing collection items in the nineteenth century. It contains loose bone material and some small limestone fragments (Figure 3B). The fossil material is from various small vertebrates, with one long bone fragment from a macropod, which appears to have a small word written in ink that possibly reads 'Zietz'. Two hand-written labels and one printed



Figure 1. Contents of the storage box in original position prior to documentation (SAMA P57488). Scale bar = 8 cm.

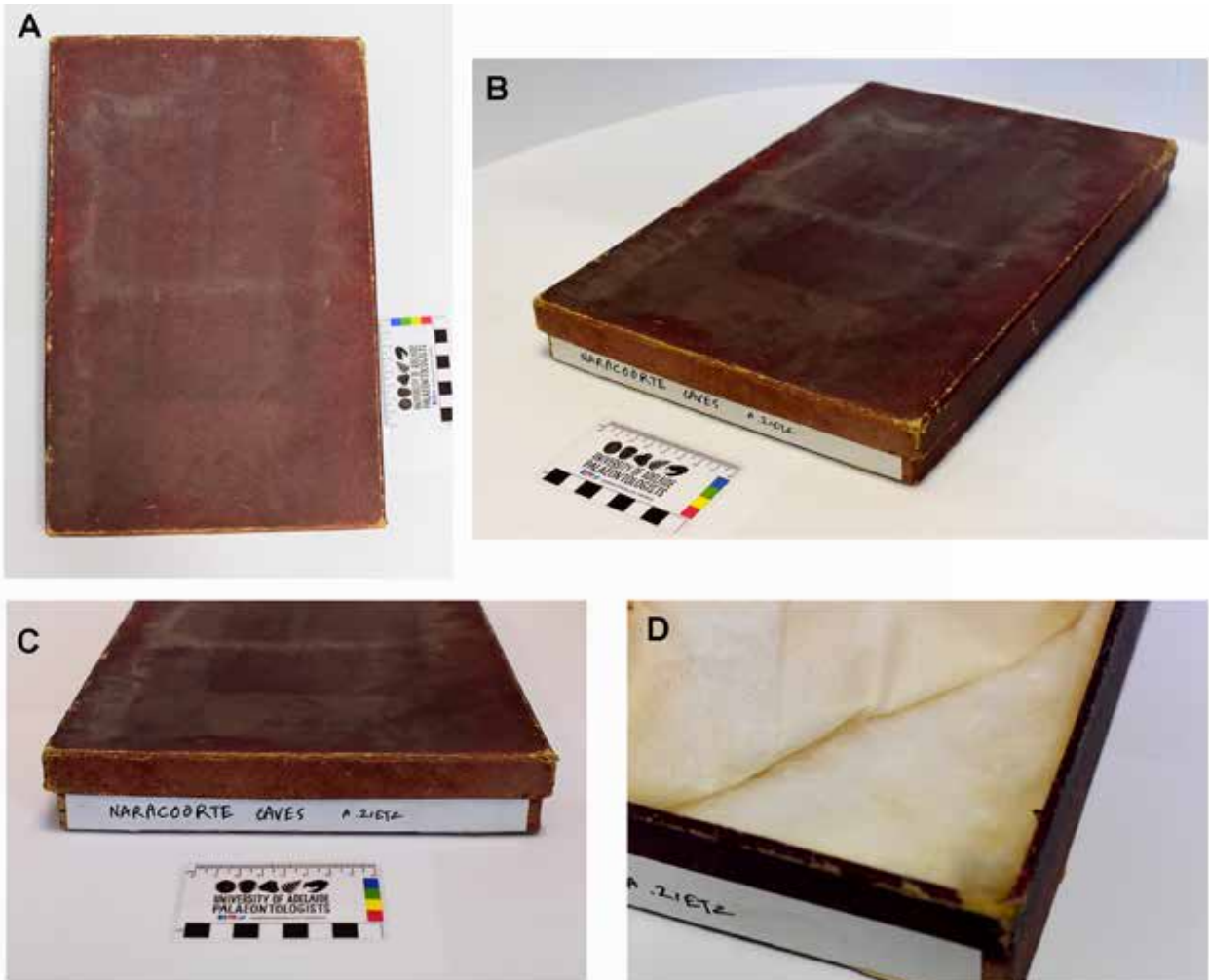


Figure 2. Storage box containing the Zietz material (SAMA P57488). A - view of box lid from above; B - view of entire box; C - front of box showing label; D - cotton and tissue padding lining the base of the box (specimens removed).



Figure 3. Descriptive labels associated with the collection (SAMA P57488). A. Printed label found within a small tray of assorted bones; B. Small tray of assorted bones with hand-written label; C. Hand-written label listing the contents of the collection and locality (signed A. Zietz 1888); D. Rear of label. Note that the preferred spelling of Naracoorte in the 19th Century was ‘Narracoorte’.

label are included with the fossil material (Figure 3). The printed label (113 x 87 mm; Figure 3A) reads: “Sample of GUANO from the Narracoorte Caves, containing Bones of small Mammals, Birds, Reptiles, &c.”. Note that the spelling of Naracoorte on the label – “Narracoorte” – was actively used in the 19th and early 20th centuries but is no longer in use. Labels such as this were printed in-house at the Museum or by local printers for items that would be exhibited, suggesting this collection may have been on display at some stage. The largest of two hand-written labels (60 x 45 mm; Figure 3C, D) reads: “Bones of various animals: Birds, Rodentia, Marsupialia, Saurians etc. sorted out from samples of dust, which was taken from the Narracoorte Caves. A. Zietz. 1888.”. Another smaller label, written on lined paper (35 x 26 mm; Figure 3B), reads: “Narracoorte Caves”. All labels, both card and paper, have yellowed with age.

Included in the collection is a glass vial with a cork stopper (Figure 4). It has a hand-written

label that reads “Narracoorte Caves” glued to the glass. The vial is 117 x 27 mm and contains a sample of very fine-grain cave sediment which is probably a sample of the sediment from which the fossils were picked. There are 23 individual cards with fossils glued on to them and these range in size from 45 x 28 mm to 114 x 74 mm (Figure 4, Table 1). The cards are in good condition; most are cream-coloured (yellowed with age), but one card is black. The cards have been labelled in pencil, describing the fossils attached (Figure 4, Table 1). Most of the fossils are in good condition, but a few are incomplete, and some are missing from their cards as indicated by glue spots without specimens. Some of the missing specimens were found in the glass-bottomed tray with the various small bones. A range of different small vertebrate bones are represented on the cards and are arranged either by skeletal element type (e.g. pelvis, vertebrae, ribs) or animal type (e.g. mammal, bird). Most of the bones are described using common vernacular such



Figure 4. All items from the collection (SAMA P57488) laid out. Scale bar = 5 cm.

as “shin bones”, “arm bones”, “leg bones” rather than formal anatomical terms. One card is labelled using the German spelling *Knie* bones rather than ‘knee’ and suggests Amandus Zietz may have labelled it as he was German (Figure 4). The use of simple terminology for the labels may support the suggestion that the specimens were on public display. The use of cards for display of specimens, known as visible curation, was commonly done in the early history of the South Australian Museum (Neville Pledge pers. comm. 2022). Another possibility, given that the cards are small, is that they were used for teaching, demonstrations or presentations to hand around to participants to inspect.

2.3 The fossil fauna represented in the collection

The fossil collection consists of a range of skeletal elements, mostly mammalian remains and some bird bones. Reptile and frog remains are absent from the collection. Bird bones include some cranial and post-cranial elements. Post-cranial mammalian bones represent much of the collection, with several cranial specimens. Only a handful of the specimens such as maxilla, dentaries and teeth are identifiable to genera or species. The rodents (Muridae) identified include *Pseudomys auritus*, *Pseudomys* (small, possibly *P. fumeus*) and *Rattus spp.* Marsupial specimens include species

1888 Naracoorte fossil bone collection

of the family Dasyuridae (e.g. *Sminthopsis spp.*), bandicoots (*Perameles spp.* including juveniles).

The bones and identified animals reflect the composition of many of the Quaternary age small vertebrate fossil deposits at Naracoorte (Reed and Bourne 2000; Macken and Reed 2013). The dominance of mammalian remains, particularly rodents, is characteristic of these deposits (Macken and Reed 2013). The prevalence of small bones and the faunal composition is also suggestive of the accumulating mode in the cave via owl pellets (regurgitates). Owls are well documented as accumulators of small vertebrate remains in caves at Naracoorte in modern times as well as in fossil taphonomic histories from the caves (Reed 2012; Macken and Reed 2013). Owl-pellet-derived fossil deposits form thick units on cave floors at Naracoorte and would have been easily accessible at the time of collection in 1888, particularly in the frequently visited Blanche Cave, which was the site of fossil collection by Woods in 1857.

2.4 Origin of the collection

We have compared the handwriting and signature on the labels with known examples from Amandus Zietz held in the South Australian Museum Archives and State Records of South Australia and it is consistent with his writing. It is unclear whether Zietz collected the fossil material himself or curated a collection submitted to the South Australian Museum by someone else. One of the labels suggests he sorted the bones from samples of cave “dust” (sediment) collected at Naracoorte. Zietz was known to be active in the field and travelled to museums in Melbourne and Sydney to purchase and exchange material including ethnographic and faunal material in late October and November in 1888 (Anon. 1888a; McCoy 1888; Zietz 1888; Turnbull 2017). Frederick McCoy (Director of the National Museum in Melbourne) wrote to Robert Kay (General Director and Secretary of the Public Library, Museum and Art Gallery of South Australia) on 22nd November 1888 to outline Mr Zietz’s recent trip, including some details of items for exchange between the two museums (McCoy 1888). There is mention of fossil shells from South Australia, but not of any vertebrate material from Naracoorte Caves. However, it is possible material was acquired by Zietz during this trip, although it is not mentioned in his correspondence (Zietz 1888). We have recently been made aware of a small collection of material from Naracoorte Caves that is housed in the Palaeontology Collections of

Museums Victoria and attributed to the collector George Sweet; however, there is no date with this material, making it difficult to align it with the collection discussed here.

In mid-1888, Zietz examined megafaunal fossil material collected from a cave in Mount Gambier in 1887 by Mr Ritter, which had been received as a donation to the Museum via Mr Basedow MP in March 1888 (Anon. 1888b, c). There is a record for the donation of a stalagmite from Naracoorte Caves to the Museum by Mr Lawrence in November or December 1887 (Anon. 1888d). These various donations may have motivated Zietz to visit the South-East region of South Australia and it is entirely possible that he visited the Naracoorte Caves. However, we cannot confirm from Museum travel records that he journeyed to Naracoorte or that he collected any material from Naracoorte Caves.

Zietz may have curated material submitted to the Museum by a member of the public, although we cannot find a donation record to support this. Another possibility is that the material was collected by a ‘Collector’ for the Museum, a practice that was common at the institution (Hale 1956). One such collector, Frederick William Andrews, had a keen interest in the Naracoorte Caves and he put forward an unsuccessful offer to the Forest Board to “take charge” of the caves in 1879 (Anon. 1879). Andrews was first commissioned as a Collector in 1864 by the Curator, Frederick George Waterhouse, and remained in this role until his tragic death in 1884 (Hale 1956). Anderson may have collected a sample of cave sediment which was later sorted, identified and curated by Zietz. However, we cannot find evidence to support this.

We propose that the fossil material was collected from what is now the Naracoorte Caves World Heritage Area, and possibly from Blanche Cave. In 1876 the caves were transferred to the management of the Forestry Board and declared the Caves Range Forest Reserve. The Forest Board later became the Woods and Forest Department, and in 1885 50 acres of land around the caves was declared as a reserve for the protection of the caves. In 1888, the Caretaker and Forester of the Caves Range Forest Reserve was William Reddan (Reed and Bourne 2013). If the material described in this paper was collected after 1885 then it would have been with permission of the caretaker. The labels use the formal name “Naracoorte Caves”, which was used at the time to describe the Reserve. Blanche Cave

(often called Old Cave or Big Cave) was the main cave that people visited at the park and had been since 1845. It is the cave in which Reverend Woods made his fossil discoveries in 1857. Blanche Cave is easily accessible when compared with others such as Bat Cave and Cathedral Cave which have deep vertical entrances. The sediment sample within the glass vial in the Zietz collection closely resembles the dry, fine-grained sandy sediments found on the floor of large chambers in Blanche Cave. It is possible that it came from one of the other caves; however, regardless it is most likely that it would have been collected from within the Caves Reserve at that time. William Reddan may have collected the material himself and forwarded it to the Museum; however, we so far have no evidence to confirm this.

3.0 Amandus Zietz (1839 – 1921) and Friedrich Zietz (1874 – 1922)

Amandus Heinrich Christian Zietz (Figure 5) was born in Schleswig-Holstein in 1839. A well-educated man, he reportedly studied under

the famed German zoologist and naturalist Ernst Haeckel (Anon. 1921). His early career was as a teacher, but this was not his main interest, and he later won a museum position at the Godeffroy Museum in Hamburg where he could pursue his passion for collecting. Zietz served as a preparator and curator at the Kiel Zoological Museum where he won awards for exhibitions he had prepared (Anon. 1921).

Doctor Wilhelm Haacke, Director of the South Australian Museum in Adelaide, recommended Zietz for appointment as Preparator. Zietz arrived in South Australia in 1883 (Anon. 1921). He later became Assistant Director, working under Professor Edward Stirling (Hale 1947; Hale 1956). Stirling and Zietz worked closely together and are well-known for expeditions to Lake Callabonna in the 1890s where they recovered fossils of megafauna, notably *Diprotodon optatum* and *Genyornis newtoni*. They published several monographs and papers on these finds (see Hale 1956 for an overview). Assisted by his son Friedrich, Zietz assembled a *Diprotodon* skeleton for display at the Museum (Anon. 1906).



Figure 5. Left. Amandus Zietz c. 1890 (State Library of South Australia B6817). Right. Friedrich Robert Zietz (State Library of South Australia B9387/35).

1888 Naracoorte fossil bone collection

Amandus Zietz made important contributions to the Museum's collections and exhibitions during his time, particularly with his studies of fish and birds (Hale 1956). He died in Adelaide in August 1921 (Anon. 1921).

Friedrich (Fritz) Robert Zietz (Figure 5), son of Amandus Zietz, was a well-known ornithologist in South Australia. He started working at the South Australian Museum in 1891 as an apprentice and was employed as an assistant in 1897 and later as ornithologist. He was a founding member of the Royal Australian Ornithologists' Union and a Fellow of the Royal Society of South Australia (Anon. 1922). In 1908, he visited Naracoorte Caves with Professor Stirling where he collected megafauna fossil material from Specimen Cave (Anon. 1908; Turner and Reed 2023).

4.0 The role of the South Australian Museum and its palaeontology collections.

4.1 Involvement of South Australian Museum scientists in fossil discoveries at Naracoorte.

In 1908, 50 years after Woods first reported bones from Blanche Cave, the park caretaker, William Reddan, discovered some remains of *Thylacoleo carnifex* and other species in Alexandra Cave and Specimen Cave (Reed and Bourne 2000; Turner and Reed 2023). The Director of the South Australian Museum, Edward Stirling, was notified by Reddan and visited the caves with Museum Preparator Friedrich Zietz (Figure 5). They collected material from Specimen Cave which was lodged in the Museum's collections (Anon. 1908; Turner and Reed 2023). Stirling later reported the finds to the South Australian Museum Board (Stirling 1908, 1912). These were the first records of extinct Pleistocene species found at Naracoorte Caves (Turner and Reed 2023) and the first fossil material publicly reported since Woods (1862).

Very little was subsequently reported about fossil collections from Naracoorte's caves until key discoveries were made in the 1950s and 1960s. A skeleton of the Pleistocene marsupial predator *Thylacoleo carnifex* was found in James Quarry (Naracoorte township) in 1956 and reported to the South Australian Museum by the quarry owner, Amos James (Daily 1960). The Curator of Anthropology, Norman Tindale, and Preparator Paul Lawson collected the specimen; a later collection was made in 1957 by Tindale and the

Curator of Fossils and Minerals, Brian Daily (Daily 1960). Additional specimens of *T. carnifex* were reported to the Museum in 1959 by Amos James, and Brian Daily and Peter Aitkin (Assistant Curator of Insects) collected further material from the quarry site (Daily 1960). At Naracoorte Caves Reserve, cave exploration led to the discovery of *T. carnifex* material in Cathedral Cave in 1959 and this was accessioned into the Museum collections. The formation of CEGSA (Cave Exploration Group of South Australia) in 1955 led to systematic exploration and mapping of the caves in the South East region and many more fossil discoveries, too numerous to summarise here. CEGSA was affiliated with the South Australian Museum and its members contributed to fossil collections over many years and greatly increased knowledge of the fossil values of South Australian caves.

Pleistocene fossil material was excavated from Haystall Cave in 1964 by CEGSA members, including Neville Pledge, who would become the Curator of Fossils at South Australian Museum in June 1969 (Mitchell 1969). The fossil material was registered with the Museum and some of the extinct sthenurine kangaroo specimens were described by Merrilees (1965). In 1969, a large cave deposit was uncovered during quarrying in Henschke Quarry in Naracoorte Township. Named the Henschke Fossil Cave, the site yielded a diverse array of Pleistocene fossils and was excavated by cavers and volunteers under the direction of Neville Pledge from 1969 to 1981, and later excavated by John Barrie (Pledge 1990; Barrie 1997). Volunteers from the Friends of the South Australian Museum group assisted with the excavations and some of these people joined CEGSA to further their interest in caves (Pledge 1980). In the same year, the most extensive Pleistocene deposit in the region was discovered by cave explorers Grant Gartrell, Roderick Wells and Robert Henzel in Victoria Cave (now known as Victoria Fossil Cave) within the Naracoorte Caves Reserve (Wells 1975; Wells and others 1984). Following the discovery, palaeontologist Rod Wells and colleagues from Flinders University spent several decades excavating and studying the Fossil Chamber deposits and documenting a diverse assemblage of Middle Pleistocene fauna (Wells and others 1984). Volunteers assisted with the excavations and included university students, members of the local community and CEGSA members.

In 1972 the Naracoorte Caves was designated as a Conservation Park and management was transferred

to the National Parks and Wildlife Service (NPWS) under the *National Parks and Wildlife Act 1972* (Wells and others 1980). Funding was acquired in 1974 to improve visitor infrastructure in the cave and build an interpretation centre at park headquarters. Planning and implementation of displays in the centre was a collaborative effort between NPWS, the South Australian Museum, CEGSA and Flinders University (Wells and others 1980). The construction of displays was directed by Museum Preparator, Paul Lawson, and included realistic cave displays moulded from latex peels of the walls in Alexandra Cave. The centre opened in 1979 and remained in operation until it was superseded by the Wonambi Fossil Centre which opened in 1998.

Fossil material from many sites at Naracoorte Caves, collected primarily by researchers from Flinders University and The University of Adelaide, forms a significant component of the South Australian Museum's Quaternary vertebrate fossil collection. The Naracoorte Caves is now internationally recognised as a UNESCO World Heritage site preserving a suite of Quaternary vertebrate fossil deposits spanning 500,000 years. South Australian Museum palaeontology researchers, including one of us (ER) and Diego Garcia-Bellido (Miocene marine fossils) are involved in research and public outreach at the site. The Museum is the responsible agency for the curation of fossil specimens from the Naracoorte Caves as is reflected in the park management plan which states: "These remain the property of South Australia and must be registered with the South Australian Museum" (Department for Environment and Heritage 2001). There is also a South Australian Museum representative serving on the Interagency Reference Group for Naracoorte Caves.

4.2 Palaeontology at the South Australian Museum.

The South Australian Museum is the custodian of South Australia's cultural and natural heritage. Legislated to collect and care for zoological and geological specimens, and objects of historical interest (*South Australian Museum Act 1976-1985*), the Museum has been acquiring specimens since 1856, with the purpose of increasing knowledge and understanding of the State's natural and cultural heritage. The Museum has a function to educate the public about the State's natural heritage, scientific research, biodiversity, environment and Aboriginal Culture. The specialised data

produced by its staff are available to national and international communities through online databases, public outreach and publications. Its Natural Science Collections play a vital role in documenting Earth's past and present. They are a valuable resource to examine and interpret, expanding current knowledge about the evolution of life. Research outcomes from the fossil collections will elucidate environmental changes linked to climate change thus enabling us to prepare for a sustainable future. Specimens collected over the last 167 years are being re-examined using the latest research technologies to produce new information, such as the use of stable isotope analysis of rodent teeth to reconstruct paleoenvironments (Bampton 2021). Research cannot be adequately undertaken without the collections and their significance as study material is evidenced by access requests for visiting researchers from all over the world. These collections are not only of scientific importance but are also a part of Australia's national heritage.

The Palaeontology Collection dates to the beginning of the Museum in 1856 (originally known as the South Australian Institute Museum). When plans for a museum were announced, colonists and amateur naturalists began donating specimens to populate an establishing institution (Hale 1956). The first recorded discovery of fossil vertebrates was in 1857 by a Thomas Wigley who found bones in the bank of the River Murray which were subsequently shipped to Professor Richard Owen in London for examination (Hale 1956). In 1869 fossils were purchased for £4 "from a quarry near Government House" (Hale 1956). Since then, opportunistic discoveries and donations from members of the public, pastoralists and mining activities provided a rich and diverse South Australian collection. The first Curator of the Museum, Frederick George Waterhouse (1860–1882), acquired material (real and casts) locally and worldwide to entertain and enlighten Adelaideans. This attitude has now shifted to conservation and a greater appreciation of scientific research. Few systematic searches for fossil vertebrates were done by South Australian Museum staff until the Hurst, Stirling and Zietz expeditions in 1893; then later in 1906 by A. Zietz and R. Zietz at Salt Creek/Normanville (Hale 1956). Other noted early expeditions include Stirling and Zietz to Naracoorte in 1908 (Turner and Reed 2023); Tindale's 1931 Tantoola Caves expedition; followed by the 1953 and 1954 expeditions by Professor Stirton to the Lake Eyre Basin (Hale 1956).

1888 Naracoorte fossil bone collection

Today, South Australian Museum staff, in collaboration with national and international researchers, continue the methodical search for fossils of national and global significance from South Australian localities such as the World Heritage Naracoorte Caves, the Nilpena Ediacara National Park in the Flinders Ranges, Lake Callabonna and Lake Palankarina Fossil Reserves, Emu Bay and Kelly Hill Conservation Park on Kangaroo Island and the Nullarbor Plain in South Australia. This ongoing and active research has expanded the collections over decades. The Palaeontology Collection currently has over 59,000 registered specimens and is one of Australia's key repositories of Ediacaran, Cambrian and Quaternary fossil collections. The primary focus is South Australian collections based on contemporary research and collection strengths. Items from outside South Australia are collected if considered necessary for better understanding of regional occurrences and for comparative studies. However, the collecting interests of other museums are respected and consultation with these institutions is undertaken when there are overlapping interests. To this day, the South Australian Museum receives generous donations of specimens from the general community and acknowledges this significant contribution to the State's natural heritage collections.

5.0 Conclusions

SAMA P57488 consists of a collection of vertebrate fossil material from Naracoorte Caves, curated by Mr Amandus Zietz in 1888. The fossil specimens are mostly mounted on cards and accompanied by hand-written and printed labels contained within a cardboard storage box. The collection is in good condition overall and the presence of labels and the mounting of specimens suggests the material may have been on display or used for public outreach at the South Australian Museum. The fossil material represents a variety of small vertebrates typical of Quaternary deposits at Naracoorte Caves. The collection is historically significant as it may represent the earliest accessioned museum collection from the Naracoorte Caves. Previous collections were made by the Reverend Julian Tenison-Woods in 1857, but the whereabouts of this material is unknown and there is no record of museum accession or further discoveries until 1908. The collection is associated with Mr Amandus Zietz who was a Preparator, and later Assistant Director, of the South Australian Museum. Zietz is a significant character in the

Museum's history, and the fields of palaeontology and zoology in South Australia.

The material described in this paper highlights the involvement of the South Australian Museum with the Naracoorte Caves over at least the last 135 years, and the important role of the Museum in palaeontological research at this globally important locality. We demonstrate the value of examining undescribed museum collections which may yield important historical information about fossil localities. The South Australian Museum is a key institution for palaeontological research in South Australia and its collections span the extensive history of life on earth recorded in the diverse fossil sites of the State.

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Author contributions

ER, JBT and MAB devised the study. ER and JBT documented the collection and identified the fossils. ER undertook archival research and wrote most of the manuscript with contributions from JBT and MAB. JT contributed historical research to the project. All authors contributed to editing the manuscript.

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APPENDIX - List of items registered in the 1888 Zietz collection SAMA P57488.

Item no.	Item	Size (mm)	Description	Label text (exact transcription)
1	Storage box with lid and cotton padding.	270 x 207 x 30 (tray); 280 x 219 (lid)	Small glass-bottomed tray of fossil bones; glass vial filled with cave sediment; 23 cards with bones glued to them	Naracoorte Caves. A. Zietz
2	Label	60 x 45	Label written in ink on card	Bones of various animals: Birds, Rodentia, Marsupials, Saurians etc. sorted from samples of dust, which was taken from the Naracoorte Caves. A. H. Zietz 1888
3	Tray of loose bones with two labels	125 x 87 (tray), 113 x 87 (printed label); 35 x 26 (label)	Glass bottomed tray containing loose fossil bones and two labels - one printed and the other hand-written on lined paper	1. Sample of GUANO from the Naracoorte Caves, containing Bones of small Mammals, Birds, Reptiles &c.; 2. Naracoorte Caves
4	Glass vial with cork stop	117 x 27	Glass vial containing sample of cave sediment. Cork stopper	Naracoorte Caves
5	Card with small bones glued on	60 x 45	Calcaneus; small mammals. 12 specimens	No label
6	Card with small bones glued on	90 x 60	Cranial bones and teeth, small mammals	Marsupial Naracoorte Caves
7	Card with small bones glued on	60 x 45	Manus and pes elements, small mammals; two caudal vertebrae. 42 specimens	Footbones etc Naracoorte Caves
8	Card with small bones glued on	90 x 60	Vertebrae - small mammal, bird, and frog. 30 specimens	Vertebra Naracoorte Caves
9	Card with small bones glued on	90 x 60	Bird bones - cranial and post-cranial. Three specimens	Bird Naracoorte
10	Card with small bones glued on	114 x 74	Rodent bones - dentaries and isolated teeth. 18 specimens	No label
11	Card with small bones glued on	60 x 45	Tibia - small mammals. Four specimens	Shinbones of small mammals Naracoorte Caves
12	Card with small bones glued on	45 x 28	Pelvis and scapula - small mammals Five specimens	No label
13	Card with small bones glued on	60 x 45	Epiphysis - small mammals. 24 specimens	No label
14	Card with small bones glued on	60 x 45	Ulna - small mammals. 11 specimens	Arm bones of small mammals Naracoorte Caves
15	Card with small bones glued on	75 x 55	Pelvis, sternum, fragments - small mammals. Eight specimens	Pelvis etc. Naracoorte Caves

16	Card with small bones glued on	60 x 45	Metatarsal - small mammals. Three specimens	No label
17	Card with small bones glued on	45 x 30	Patella - small mammals (bandicoot). 10 specimens	Knie bones Narracoorte
18	Card with small bones glued on	90 x 60	Sacrum, vertebrae - small mammals. 10 specimens	Sacrum vertebra of small mammals Narracoorte Caves
19	Card with small bones glued on	90 x 60	Vertebra (cervical, thoracic) - small mammals. 13 specimens	vertebra Narracoorte Caves
20	Card with small bones glued on	90 x 60	Vertebra (caudal + others) - small mammals. 50 specimens	tailbones of small mammals Narracoorte Caves
21	Card with small bones glued on	90 x 60	Tibia - small mammals. Four specimens	Shinbone of mammals. Narracoorte Caves
22	Card with small bones glued on	90 x 60	Petrous - small mammals 17 specimens	Earbones of small mammals Narracoorte Caves
23	Card with small bones glued on	60 x 45	Rib - small mammals. 12 specimens	ribs Narracoorte Caves
24	Card with small bones glued on	55 x 40	Molar teeth - small mammals. 19 specimens	molars of small Marsupials Narracoorte Caves
25	Card with small bones glued on	60 x 45	Humerus - small mammals. Two specimens	legbones of small mammals Narracoorte Caves
26	Card with small bones glued on	90 x 60	Cranial fragments - small mammals. 30 specimens	Skull bones Narracoorte Caves
27	Card with small bones glued on	90 x 60	Femur, humerus - small mammals. Five specimens	Leg bones of small mammals Narracoorte Caves

Australian Caves and Karst Systems

John Webb, Susan White and Garry K. Smith, Editors

Book Review by Andy Spate

This outstanding book will have set the scene describing our knowledge of Australia's karst resources for many decades to come. It is part of a series titled *Cave and Karst Systems of the World* which is edited by James W. LaMoreaux (P. E. LaMoreaux and Associates, Tuscaloosa, AL, USA). It is published by Springer in 2023 and runs to some 398 pages.

<https://link.springer.com/book/10.1007/978-3-031-24267-0>

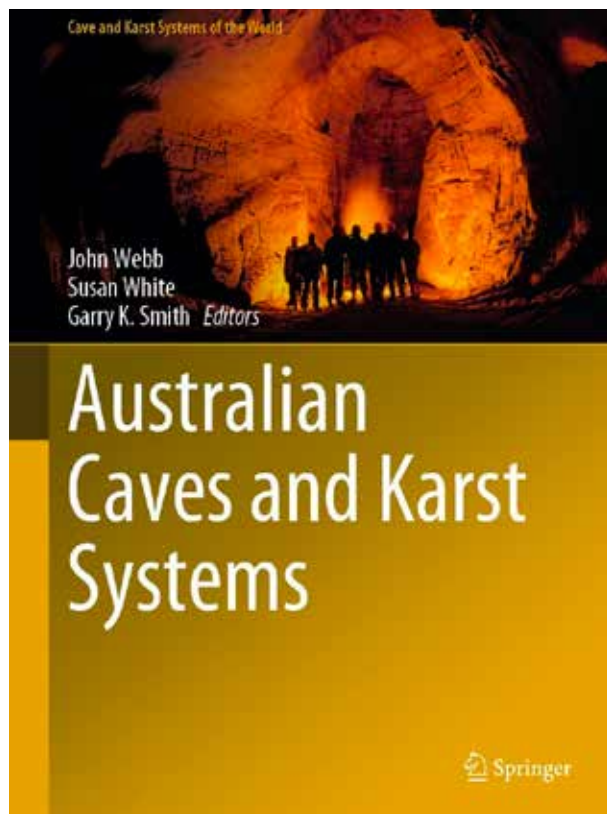


Figure 1. 'Australian Caves and Karst Systems' front cover

The series editors introduce this book with the following paragraph:

... Books in this series focus on a specific cave or karst system, on the cave or karst systems of a specific region, on a specific type of cave or karst system, or on any other perspective related to cave and karst systems of the world. The book series addresses a multidisciplinary audience involved in anthropology, archaeology, biology, chemistry, geography, geology, geomorphology, hydrogeology, paleontology, sedimentology, and

all other disciplines related to speleology and karst terrains.

Turning now to *Australian Caves and Karst Systems*. This is the 24th volume in the series and is the only one to deal with an entire continent – the other volumes relate to countries, to individual karst areas or to themes of karst interest such as speleogenesis or hypogene karst.

What better way to sum up this remarkable book than to quote at length the editor's preface below (I have taken the liberty of removing references):

Welcome to this book on Australian caves and karst. Although the Australian continent is not well-endowed with caves on a world scale, Australian karst is notable for its diversity. It encompasses the razor-sharp towers of north Queensland, the cold, deep shafts of southwest Tasmania, the carbonate dunes of southwest Western Australia, the clear cenote lakes of southeastern South Australia and the ancient reefs of northwest Western Australia. Australian karst has something for everyone.

This variety reflects diversity in carbonate rock types, climate and vegetation, and geological history. Firstly, carbonate rocks in Australia fall into two broad groups: strongly cemented Neoproterozoic and Palaeozoic limestones and dolomites ('hard' rock karst), and Tertiary and Quaternary limestones that are moderately well to poorly cemented ('soft' rock karst) (Figure 2). Mesozoic limestones are almost completely absent. The Neoproterozoic/ Palaeozoic carbonates can be divided into an eastern province of generally strongly deformed limestones and a northern province of flat-lying dolomites and limestones) (Figure 3).

Secondly, Australia has very diverse climate and vegetation, from monsoonal tropical rainforest to desert dunes and alpine grasslands, and this directly impacts karst development. Furthermore, because the Australian continent has been moving slowly northwards for tens of millions of years, the climate has changed greatly over this time, e.g. the inland Australian desert used to be covered with open forest.

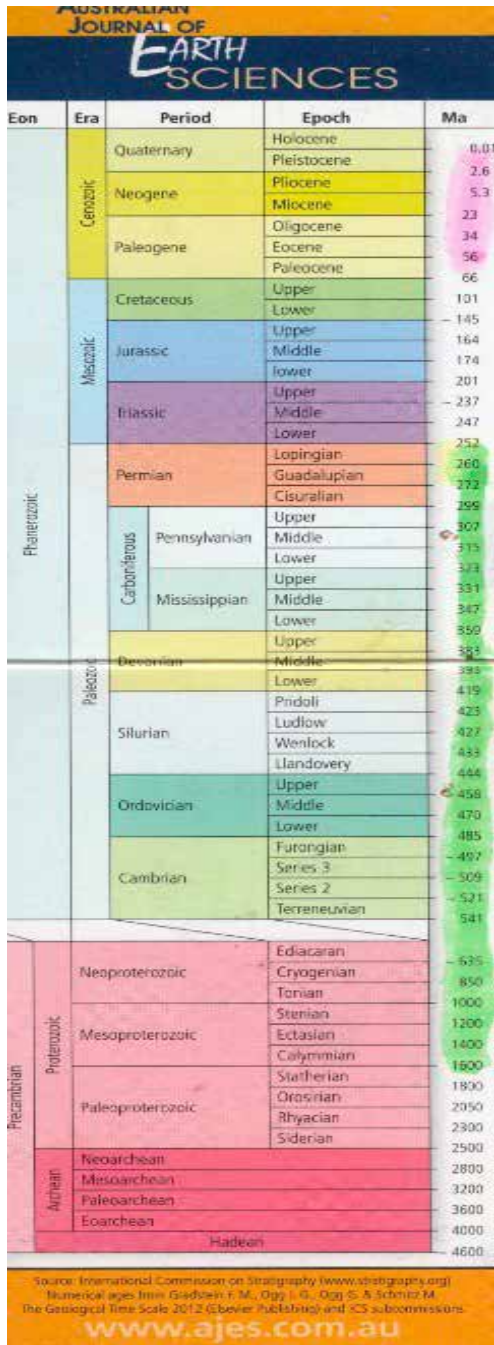


Figure 2. Ages of Australian karst-bearing carbonate rocks (left) – from the Australian Journal of Earth Sciences Geological Time Scale chart. Key to colours in far right column: Pink = ‘soft’ rock karst. Green = ‘hard’ rock karst.

Thirdly, Australian karst has been affected by the long geological history of the continent. Parts of Australia are an old, stable craton, with the oldest known mineral grains on Earth ... However, in the last 10 million years parts of southern and eastern Australia have seen extraordinary landscape change: hundreds of volcanic eruptions, numerous earthquakes that uplifted whole mountain ranges, advances and retreats of the coastline for hundreds of kilometres. These geological events have been imprinted on the karst.

As a result, there is more variety in Australian karst than any other area of equivalent size on Earth, and the [17] chapters in this book are organised to reflect that variety ... Following three chapters on the interaction between humans and caves in Australia, are seven chapters on ‘hard rock’ karst areas, starting in the south with Tasmania and proceeding anticlockwise around the continent to finish in South Australia

Next are five chapters on ‘soft rock’ karst, finishing with the youngest caves, followed by three chapters on non-carbonate caves, and concluding with three chapters on cave contents (speleothems, sediments and fossils) and two chapters on cave biology.”

Twenty-two authors have contributed to this remarkable book which supplants Finlayson and Hamilton-Smith’s *Beneath the Surface* (2003) – indeed some authors of that book provided contributions to *Australian Caves and Karst Systems*.

I have not read the ~400 pages cover to cover but have scrolled through and dipped into many chapters where I have expertise or interest. The book is a thoroughly professional and wide-ranging description of Australia’s karsts and their values. Great diagrams and images. Although the cover image (Figure 1), while evocative, may lack a little oomph?

I am most impressed!

But there is something lacking ... There is little discussion of the karsts developed in the sandstones, laterites and similar non-carbonate rocks of northern Australia other than in Chapter 18 ‘Non-Carbonate Caves’. I and another specialist were tasked with providing this chapter – but we were unable to contribute to this publication at the time. My apologies.

Interestingly the editor’s preface talks about the absence of Mesozoic karst-bearing limestones in Australia. John Webb tells me that ‘the best-known Mesozoic limestone in Australia is the Early Cretaceous Toolebuc Formation, which occurs across a large part of western Qld. It is a thin, dirty limestone with no known caves.’ Another reviewer, Dr Jo De Waele, also comments on this lack of Mesozoic limestones (<https://digitalcommons.usf.edu/kiparticles/>). Both the editors and De Waele imply that much of the world’s karst is to be found on Mesozoic carbonates. In spite of intensive

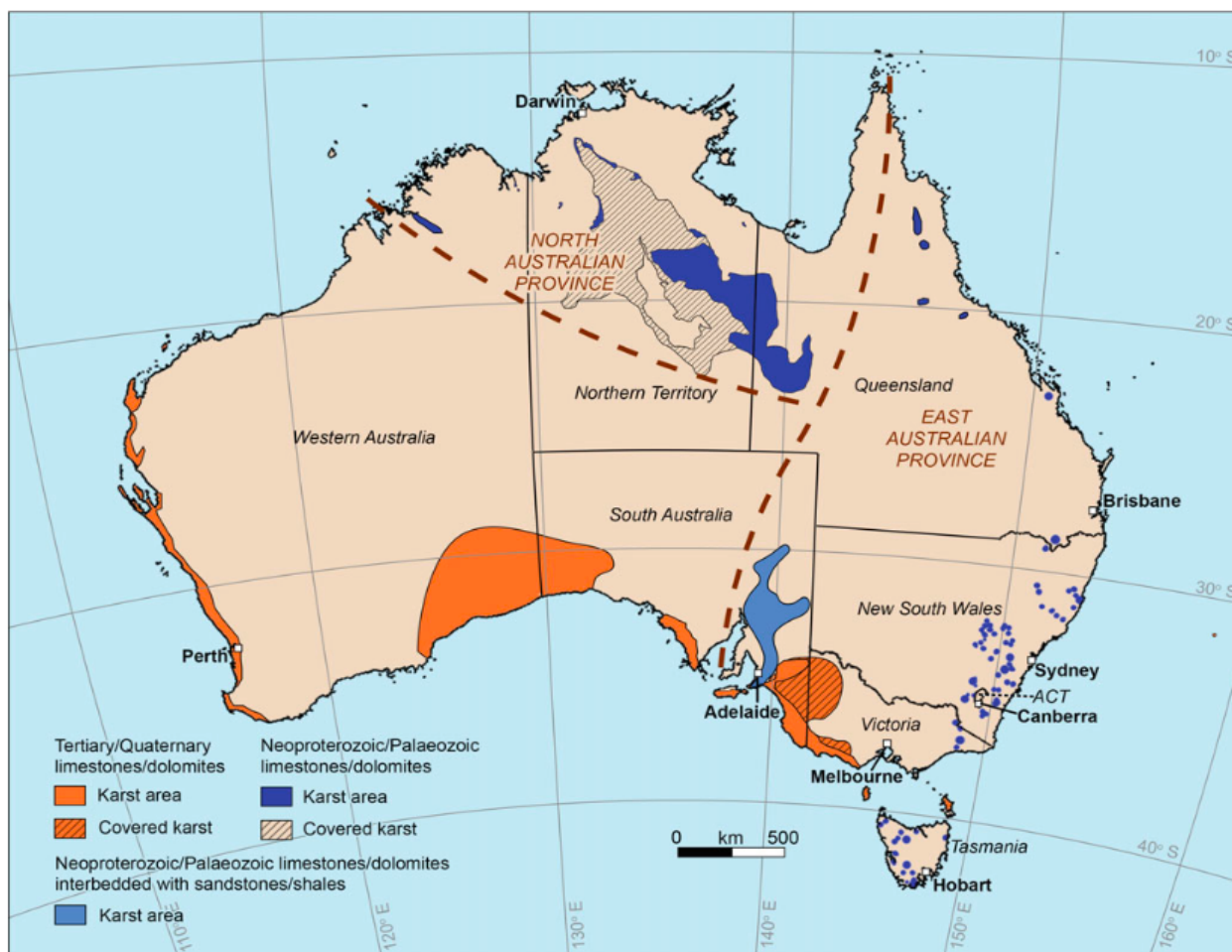


Fig. 1 Distribution of carbonate rocks in Australia (after Grimes 2009). Strongly cemented Neoproterozoic and Palaeozoic limestones and dolomites ('hard' rock karst) are divided into an eastern province of generally strongly deformed limestones and a northern province of flat-lying dolomites and limestones. Tertiary and Quaternary limestones are moderately well to poorly cemented ('soft' rock karst) and gently dipping to flat-lying

Figure 3. 'Distribution map of carbonate rocks in Australia' – taken from the Preface p. viii.

Googling, I have not found definitive statements or maps on the ages of carbonates worldwide ... but it would be good to see such information.

Each chapter is accompanied by its own set of references – presumably so that each chapter can be 'sold' separately. The chapters are followed by an Appendix 1 (a glossary), and three indexes – Cave Index, Main Index and a Stratigraphic Index listing each rock unit mentioned in the text.

This excellent book is very expensive – as of 1 Dec 2023 the eBook costs €139.09 (~\$230); the hardback €169.99 (~\$280). A softback version will

be available in 2024. Springer states that at least part of the high cost is due to the undoubtedly high quality of the maps, diagrams and photographs.

The Australian Speleological Federation Library is negotiating with Springer to see if the book can be made available digitally to ASF and ACKMA members.

Reference

FINLAYSON, Brian and HAMILTON-SMITH, Elery 2003 [eds] *Beneath the Surface: A natural history of Australian caves*. UNSW Press, 182 pp.

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