# Ribbon Helictites: A New Category Jill Rowling

# Abstract

This paper describes the size, shape, abundance and location of ribbon helictites and proposes possible growth mechanisms for them. SEM photographs of the surface of one ribbon helictite have shown an unusual crystal form for a calcite speleothem, together with apparent etching and pitting of surfaces. These surfaces exhibit some features found in organically deposited calcite. Further optical work has revealed that the stem of ribbon helictites is composed of a twinned pair of crystal aggregates, with the stem's central canal lying in this twin plane. The ribbon also appears to exhibit twinning. Oval features on the ribbon's surface appear to be twinned aggregates, originating from the ribbon's central canal.

It is proposed that ribbon helictites form by two growth stages: development of the stem and then a ribbon, with influences from acidic solutions. Overall shape is strongly controlled by crystal habit.

Keywords: helictite, calcite, twinning, Jenolan, lublinite.

# Introduction

Helictites are classified by Hill & Forti (1997) into four basic categories: filiform (thread-like), beaded (anemone-like), vermiform (worm-like) or antler (twig or rod-like). This paper describes a fifth form which is ribbon-like. It occurs at Jenolan Caves, Australia.

Jenolan Caves lie to the west of Sydney in the Blue Mountains (see Figure 1) in a band of massive dark Silurian limestone. Over 300 cave entrances have been recorded, the largest and most significant of which are in the tourist complex. The caves are horizontally developed with multiple levels. The lowest levels contain small streams and the upper levels are typically large, well-decorated chambers. Sediments in the caves are mostly partially cemented ancient stream gravels comprising quartz porphyry and shales.

In upper level areas of the tourist caves some of these sediments appear to have reacted with the limestone bedrock, resulting in unusual calcite crystal coatings. Whilst making a list of interesting speleothems at Jenolan Caves in 1994, I noticed unusual helictites in Jubilee Cave and Orient Cave and called them "ribbon helictites" on account of their flattened ribbon-like appearance as shown in Figure 2. Samples were taken from already broken pieces near an area of the Jubilee Cave called "The Pincushion". Tests showed that the material was calcite (not aragonite) with 0.5 % Fe in the tested sample (Rowling, 1997). Further work on these enigmatic speleothems has included SEM photographs of the surface of a ribbon helictite. This highlighted the similarity between the crystallites of ribbon helictites and some of those published for lublinite (a variety of calcite often associated with moonmilk, eg Moore and Sullivan (1997), also called needle-form calcite). Twinned crystal aggregates appear to be a common feature, with both the stem and the ribbon exhibiting crystal twinning.

This paper examines ribbon helictite structure, as a guided tour. It starts with the stem, pointing out features





Figure 2. A ribbon helictite from Jubilee Cave, Jenolan Caves. Size is about 7 mm x 7 mm. The broken stem is to the left of the picture and the tip is curled to the front right.

# **Ribbon Helictites**

along the way to the tip. Fine details are described, then the paper concludes with a discussion of their formation.

# Description & Characteristics of Ribbon Helictites

## **General Description**

Ribbon helictites are typically about 20 mm long, 5 mm wide and about 1 mm thick. They appear to grow



Figure 3. Part of a broken stem. Key shows location (circled) on a typical ribbon helictite. The beaded canal lies inside the stem and striations shown are crystal boundaries on the surface.



Figure 4. View down the end of a broken stem. In this sample, three crystal aggregates form columns with the central canal (arrowed) in the middle of them. There are apparently two halves to the stem with the change in cleavage defining the boundary.

from a fairly straight stem (like a miniature flagpole) and are made of calcite bundles which have a pronounced elongation of the calcite c [0001] axis. Like other helictite forms, ribbon helictites have a small central canal and appear to grow by capillary action. Unlike other helictite forms, ribbon helictites' calcite c axes are aligned parallel to each other, rather than evenly radial to the central canal. This results in the flattened appearance. They are usually white or clear, although grey, brown and yellow ones have been seen. Some blackened and inactive ones have been seen in Jubilee Cave, however it is unknown as to whether they are coated with soot or whether they grew that colour.

Although ribbon helictites are not particularly common, even in the Jubilee Cave, they are locally abundant. Jubilee Cave has about 50 well-formed examples, usually on the wall but also on roofs composed of infill. The substrate is usually partially cemented ancient stream gravels. Where ribbon helictites occur, vermiform, filiform and antler helictites were often found nearby.

## Stem Details

Some helicities have a smooth transition from surface coating to stem however often the stems are engulfed in surface coatings so as to be obscured. Figures 3 and 4 show two views of a broken section of stem. The habit of the crystals making up the stem's surface seem to be a combination of sheaf-like layers and a "fence paling" type (discussed later). The stem's central canal is irregular in cross section and lies in what appears to be a crystal twin plane. It is beaded (as shown in Figure 3). This beading occurs primarily in the supposed twin plane and is visible when looking perpendicular to the plane. There are also fine hairlike tubes (canalicules) running parallel to the central canal, but in the bulk of the stem (not just the twin plane). These are also a feature of the ribbon, described below.



Figure 5. The same helictite as Figure 2 using transmitted light. The central canal is visible as a darker line.



Figure 6. Broken surface of a ribbon. Characteristic of ribbon helictites are the elongated, roughly hexagonal cross section of the ribbon and the "tartan" parting surface texture.



Figure 7. SEM picture of the surface of a broken ribbon showing the "tartan" parting surface texture in more detail. Parting of crystallites alternates with perfect cleavage of thin layers of calcite. Scale bar is 100 µm. Electron illumination is from the right.

#### The Ribbon

The ribbon forms the main part of the helictite and can vary in length from about 5 mm up to about 120 mm, however its width (about 5 mm) and thickness (about 1 mm) are relatively constant over the entire length. Figure 2 shows the general shape of the ribbon with the central canal appearing as a lighter streak.

In general, the lower edge of the ribbon which curves from the stem exhibits flat crystal terminations giving a smooth surface. Some specimens have laminations along this edge. The upper edge and edges furthest from the stem usually have well-developed crystal terminations.

### The Ribbon's Central Canal

Figure 5 shows a transmitted-light view of the same sample as shown in Figure 2, with the central canal appearing as a dark line. The canal is approximately in the centre of the ribbon, with a tendency to be closer to the outside of bends. Unlike the stem's central canal, it has a roughly circular cross section, about 0.3 mm diameter, with a milky coloured calcite surround. This milky calcite has a drusy appearance in some broken samples. The ribbon's central canal also exhibits beading at right angles to its growth as shown in Figure 5 and 13. Beading appears to be associated with crystallite boundaries and often appears spiky as a consequence. Along the main part of the ribbon, the diameter of the central canal is much greater in the middle than at either the tip or the stem.

## **Cross Section of the Ribbon**

Figure 6 shows a sketch of a broken ribbon. Ribbon cross sections are approximately hexagonal but elongated in the calcite c axis direction, though occasionally they can be trapezoidal. Canalicules can be seen in this view, towards the bottom edge. Of the sample helictites, half had broken ribbons. This broken surface was similar in each case, having a parting surface at right angles to the ribbon and a calcite cleavage surface. Parts of the ribbon are more firmly cemented (cleavage surface) than other parts (parting surface). Figure 7 is a SEM photograph of detail from the parting surface of a broken ribbon, showing a "tartan pattern" which results from a combination of parting along loosely-cemented crystallite boundaries and conventional calcite cleavage of fine layers of calcite (perpendicular to the crystallites). Figure 7 also shows a long crystallite which may have a hole continuing under the material to the right.

#### **Growing Point (Tip)**

The general shape of the tip of a ribbon helictite is a tapering structure. Some specimens taper gradually (like conventional vermiform helictites) and others are more chisel-shaped as shown in Figure 8. At the tip, the calcite crystallites are narrower and appear needle-like in shape. Their relatively wide spacing suggests that this structure is porous. The needles are aligned in one direction which



Figure 8. Tip of a ribbon helictite. The central canal is the lighter area just before the tip, although the hole does not appear at the surface. The tip may have a slot as shown (arrow). Crystals near the tip are poorly cemented and very fine, needle form, whereas further away the crystals are larger.

is not the radial orientation one might expect from crystals growing at the tip of a capillary tube. The hole at the tip is not usually visible.

## Crystal Forms.

Figure 9 is a SEM picture showing typical pseudohexagonal crystals near the edge of a ribbon, looking down the c axis. Only the m {1010} faces (long sides) on these crystals are well developed and the other faces are relatively poorly defined with pits and holes visible. The crystals are irregular hexagonal prisms, flattened in one direction. They appear to be intergrown. This sample was found sitting loosely on a pile of old bat guano, so has probably been etched. Samples which were found fallen onto gravel showed shiny crystal terminations. Other crystal forms include wedge-shaped terminations and chisel-shaped terminations on fairly flat laths.



Figure 9. SEM picture of a group of pseudohexagonal columnar crystals near the edge of a ribbon. The ends are pitted and the faces poorly defined whereas the sides are well developed. The columns appear to be split. Scale bar is  $100 \ \mu m$ .

## "Fence Paling" Sides

One feature common to most ribbon helictites is the blocky crystallites making up the flat faces of the ribbon. Under the microscope, these appear like fence palings, where each crystallite is slightly offset from its neighbour. SEM picture, Figures 10 and 11 show how the long pseudohexagonal crystals can be arranged to form this pattern, and how it can vary. The "fence palings" are arranged in a regular pattern, although the step angle can vary across the face of a ribbon helictite.

The eroded appearance of the crystal terminations



Figure 10. SEM picture of part of a ribbon showing the "fence paling" crystallites and their diagonal surface texture. Scale bar is  $100 \ \mu m$ .



Figure 11. SEM picture of an area near the lower edge of a ribbon, showing the ends of flattened hexagonal crystallites arranged to form canalicules and "fence paling" sides. Scale bar is 100 µm.

could be an artefact of the guano deposit. It is difficult to determine whether the flat terminations are a growth feature or an etch feature; perhaps both mechanisms are at work here. The gaps between the crystallites are most likely the short, light flecks and tubes (canalicules) seen under the optical microscope on cleavage areas of broken ribbons. They would be able to conduct water, however it has not been proven that they connect with the central canal. The overall structure presumably leaks water out of both the tip and these canalicules. This would explain why in Jubilee Cave, the entire surface of ribbon helicities has been observed to be wet due to seepage of water through the helicitie.

Figure 12 shows more detail of one crystallite with diagonal lines which can be seen on the crystallite sides. They sometimes occur on only one side of a ribbon and are not visible on the other side. They are at about 90° to the cleavage plane of broken samples. These are similar to a feature of the lublinite variety of calcite (discussed later) and show up well with side lighting. Also shown are the two types of ribbon fracture: the parting surface and the cleavage surface.

#### Symmetry of a Double Ribbon Helictite

Figure 13 shows a double ribbon helictite. This beautiful helictite has two ribbons, both appearing to be mirror images, and indicating a common environmental influence, possibly the result of multiple twinning in the stem. Central canal beading is apparent, and the canals are not open at the tips.

#### **Apparent Twinning on Ribbon Faces**

In a few samples, on that part of the flat ribbon surface closest to the central canal, there is often a "zipper" pattern formed by interlocking crystal terminations either side of the central canal. Each side of the "zipper" exhibits different optical extinctions.



Figure 12. Broken ribbon showing "fence paling" sides and diagonal surface texture (stripes on upper half). Crystallites near the edges are much smaller than the ones near the centre.

#### Ovals

Several ribbon helictites have a structure which I have termed an "Oval" on their surface: see Figure 14. Ovals seem to be associated with a bend in the ribbon's growth direction and are often symmetrical. At the centre of an Oval is sometimes a field of spiky terminated calcite blades. This may be the start of a structure similar to some rod-shaped antler helictites.



Figure 13. Double ribbon helictite is about 9 mm x 6 mm, and about 2 mm thick.



Figure 14. An Oval feature on a ribbon helictite. The helictite is coated with platinum for the SEM. Note the apparent twinning of the Oval with the ribbon sides. In the centre of the Oval can be seen a bundle of thin pseudohexagonal calcite crystals. Broken stem is at top right. Photographed with normal light. Helictite is approximately 9 mm x 14 mm.

# Discussion

## **Unusual Crystal Structures**

The blocky and fine needle shaped features of ribbon helicities are formed from elongated pseudohexagonal calcite crystallites with interstitial canalicules (small gaps between the pseudohexagonal crystal bundles).

Many crystallites feature diagonal stripes, visible in normal light, polarised light and SEM (eg Figure 10). Previously, I interpreted the diagonal stripes to be cleavage lines, (Rowling, 1997) however they seem to be a growth feature. This diagonal striping is assumed to be polysynthetic twinning (ie twinning along the calcite cleavage plane) as described by Hurlbut & Klein (1977).

As each side of the ribbon's "zipper" exhibits different optical extinctions it is proposed that this feature may be basal plane {0001} twinning, which is common for calcite (Hurlbut & Klein, 1977). It is possible that water can leak from the central canal to the surface.

Ovals appear to have their origin near the central canal and seem to be twinned at approximately  $90^{\circ}$  with the long crystallites of the ribbon's face. Twinning in calcite is often caused by pressure and thus the Ovals are probably a growth or pressure feature rather than a dissolution feature.

Preferential growth of crystallites, their diagonal striping (like lublinite), twinning features and their overall shape may be influenced by chemical "poisoning" of the normal calcite structure, resulting in dislocations to the crystal lattice. The 0.5 % Fe in the tested sample may be sufficient to cause such dislocations, however it is not known whether this was a surface contaminant.

# Similarities found with Calcite Formed in the Presence of Microorganisms

The terminations of some of the long crystals on the thin edges of ribbon helictites are similar to spiky and "Gothic Arch" forms of calcite in biologically active travertines, described by Folk, Chafetz & Tiezzi (1985).

The diagonal lines noted before on the surface of the ribbon (Figures 10 and 12) have certain similarities with the needle form, lublinite variety of calcite often associated with microorganisms and moonmilk. The diagonal stripes on the pseudohexagonal crystallites resemble those of lublinite laths, although the crystallites on ribbon helicities are about two orders of magnitude larger than that published for the lublinite laths in moonmilk (Moore and Sullivan, 1997). Additionally, some ribbon helicities have a laminated edge almost as though it was made of stacked lublinite laths. Moonmilk is fairly common at Jenolan, although not particularly a feature where there are ribbon helicities, so the application to ribbon helicities is not conclusive.



Figure 15. Proposed growth mechanism for ribbon helictites. See text for details. Step 1: Initial deposition of pseudohexagonal calcite around a pore forms the wall attachment. Step 2: Development of basic helictite. Step 3: Development of ribbon. A = porous sediment; B = thin calcite coating; C = columnar calcite; D = surface water film; E = central canal.

### Growth Mechanisms.

A mechanism for the formation of helictites in general is summarised in Hill and Forti (1997). I have modified this theory to show how ribbon helictites might form:

**Porous substrate:** At Jenolan Caves, the ribbon helicities are associated with cave fill composed of porous, ancient river sediments.

Corrosion source within the substrate: The Jenolan substrate material possibly contains pyrite (as do other sediments at Jenolan: Armstrong Osborne, pers. comm.) and the limestone bedrock in contact with these sediments usually looks corroded. In the damp environment of the Jubilee Cave, a complex series of chemical reactions (eg Rowling, 1995) involves oxidising the pyrite, liberating sulphuric acid, eroding the bedrock, releasing CO<sub>2</sub> (both to air and in solution) and calcium sulphate (aqueous). Additional carbonate-rich water seeping over this sediment can deposit a thin film of calcite (common ion effect), however in places it can be eroded by sulphuric and/or carbonic acid again (at the sediment-calcite interface) which may create pin holes in the calcite film. Where the tourist cave track work has exposed layers of sediments, one can view this corrosion.

*Creation of a stem:* Instead of depositing calcite with its c axis evenly radial to the pin hole and the substrate as one might expect (and has been shown by Davis, Palmer & Palmer, 1991), ribbon helicities appear to initiate with the c axis perpendicular to the pin hole (Step 1 in Figure 15).

The stem's central canal forms the same as "normal" helictites, presumably from capillary action above the original pin hole in the substrate (Step 2 in Figure 15). This could occur randomly by competitive growth above the canalicules. The crystals of the stem are comprised of bundles which appear to be twinned. In the presumed twin composition surface lies the central canal. Growth proceeds in the direction perpendicular to the substrate, mainly from water seeping through the central canal under capillary action. To a lesser extent, water could pass through the canalicules and deposit calcite at their ends. Water could also travel by capillary action across the surface, depositing on the sides of the stem, with crystal alignment the same as the stem. The stem comprises at least two bundles of long pseudohexagonal calcite crystals with their c axes nearly aligned. These bundles appear to be twinned on an m face (unusual for calcite, but common for aragonite) and do not have the

overall cylindrical symmetry of common vermiform helictites. Deposition at the tip is such that the original twinning is reproduced. This could occur by repetition of the

is reproduced. This could occur by repetition of the crystal lattice dislocation during crystal growth. The beading of the stem's central canal is probably

due to periodic dissolution, eg if the tip becomes blocked, CO<sub>2</sub> would not escape to atmosphere and conditions may become such that chemical equilibrium tends towards dissolution (through carbonic acid) rather than precipitation of calcite. This would occur mainly in the direction of the c axis at the end blockage (which is the fastest growth/etch direction for calcite). This could etch back a "bead" (hole) at the tip. Unblocking the tip would result in a change of chemical equilibrium as CO<sub>2</sub> is allowed to escape: a calcite deposition phase results. Further growth may deposit calcite over the old tip, leaving a crystal grain boundary, possibly even leaving contaminants at the boundary. During a subsequent etch phase, the tip may re-open and etch back another "bead", also, if contaminants are present at previous grain boundaries, these previous "beads" may be enlarged also.

From stem to ribbon: The stem's central canal changes direction through approximately 90° (once or twice) to begin ribbon development. The initiation of this direction change appears to be at the edge of crystallites. The first 90° bend appears to be between pairs of crystallites and the second 90° bend (if present) is toward the side. In this part of the ribbon helictite, the surface crystallites' c axes remain aligned with those of the stem. During the process of central canal development, the axis of the central canal wanders within the stem's twin composition plane. During a canal enlargement phase, it is possible that the central canal may reach the side of the stem, and this is presumably what initiates ribbon growth. Canal wandering may also be aided by the density (or lack) of canalicules. Since the bulk of the water would be drawn by capillary action through the central canal, this side "leak" in the central canal may become the major growth point. Growth may still continue via canalicules and surface capillarity, however the latter may even block the original tip.

Deposition at the tip is with the calcite's c axis the same as the local substrate (ie the stem) producing the ribbon (Step 3 in Figure 15). It is highly likely that the apparent twinning of the ribbon is a continuation of the stem's twinning. Additionally, the upper and lower halves of the ribbon may be twinned, resulting in a four-way symmetry. Initially tiny needle-like crystals of calcite are deposited at the tip, but competitive crystal growth over time forms the larger crystallites of the ribbon. Similarly, the sides may grow due to spiky calcite being deposited at the edges, following the alignment of underlying crystallite terminations. The water for this edge development is assumed to come from canalicules as well as from the tip.

Central canal features: The central canal in the ribbon section is much larger than the central canal at either the tip or the stem. This could be due to preferential dissolution in the calcite c axis direction (at times), with the milky calcite being deposited (at other times). This would require changes to the chemistry of the solution in the central canal as ribbon growth progressed. Beading of "normal" helictites from Harz, Germany, has been examined by Kempe and Hartmann (1997) and was considered by them to be related to annual growth. In Germany, in winter, precipitation usually occurs as snow which means it is drier and less water is available for helictite growth. Unlike Germany, Jenolan does not have a definite predictable dry season, so the beading in ribbon helictites may simply be an indication of fluctuations in water availability rather than annual growth.

*Tips:* The tips of ribbon helicities are not usually visible; perhaps the hole gets periodically blocked by calcite and then unblocked as dissolved  $CO_2$  in the central canal water makes it more acidic from carbonic acid,  $H_2CO_3$ .

*Ovals:* At times, the ribbon's central canal may become blocked and subsequent dissolution of the central canal may be responsible for multiple tips, giving rise to multiple ribbon growth and development of Ovals. Ovals, in particular, are interesting as they share some characteristics with the stem (fence paling sides, long crystallites, symmetry about the oval axis, spiky calcite inside the oval). Ovals seem to be twinned with the ribbon sides, so could be influenced by pressure exerted by the growth of the ribbon surface.

Finally, *old age:* Ribbon helicities may "die" from their water supply drying up (ie changes to local hydrology), or become engulfed by flowstone, or they may continue to thicken, forming flattened loops, for a very long time.

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