Cave Aragonites of New South Wales

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INTRODUCTION

Although cavers and cave managers have reported aragonite from a number of NSW caves, there is surprisingly little literature in the scientific community regarding its occurrence in NSW caves. The aims of this project are to:

- Investigate caves reported to contain aragonite
- Verify that the material either is or is not aragonite
- Analyse the substrate on which the aragonite is depositing
- Determine what factors lead to the deposition of aragonite in NSW caves.

INVESTIGATING REPORTS OF ARAGONITE IN NSW CAVES

Walli

C.S. Wilkinson, NSW Government Geologist, visited caves near the Belubula River near Orange and Canowindra in about 1870 (Wilkinson 1892). He visited three caves: the small Bone Cave, the "Long Cave" and a "Deep Cave" (believed to be Deep Hole, WA17, also known as Deep Cave). His investigations of the "Deep Cave" were limited to the bottom of the first pitch as the party had insufficient rope to see the rest of the cave. He reported aragonite deposits in "Long Cave" although he did not report about the substrate on which it was depositing, nor is there any record of either the analysis or the sampled material. The cave which most resembles Wilkinson's description and map is Piano Cave (WA12) at Walli on the "Bingera" farm property.

These caves are not open to the public, however permission to visit may be obtained through the Sydney Speleological Society (SSS) who manage the caves. The specific sites at Piano Cave that may have been sampled by Wilkinson are damaged to some extent however this is not unusual to expect in a cave which has been well visited for over a hundred years.

In both Piano Cave and Deep Hole, aragonite occurs as a surface coating mixed with gypsum and barite. In Deep Hole, aragonite also occurs as small anthodites associated with seams and joints.The Walli Limestone is a tough dark (foetid) limestone of Ordovician age containing numerous chert nodules. In the chert nodules there are dolomite (or de-dolomite) rhombs and pyrite cubes / goethite pseudomorphs. Barite occurs throughout the limestone and also in the nearby Walli Andesite. An abandoned barite mine at Walli is developed in the Andesite (Anon. various years' reports).

Piano Cave and Deep Hole have been selected as study sites for this project because they contain aragonite and are the earliest reference to aragonite in NSW caves.

Wyanbene

In 1978, Webb and Brush analysed aragonite collected from the ground near an anthodite at Frustration Lake in Wyanbene Cave and found that the material was a mixture of calcite and aragonite (Webb & Brush 1978). The substrate on which it was depositing was not analysed.

The author has reported what appear to be aragonite deposits in the form of *flos ferri* “flowers of iron” helictites at Wyanbene (Rowling 1995, Osborne 1996). Aragonite appears to be present in several forms: as surface coatings, stalactites, helictites, anthodites, columns and possibly a coralloid. Some of these speleothems are coloured blue or green. The substrate appears to be a type of gossan.

A report on the rock chip geochemistry of the Wyanbene deposit was done by Richardson (May 1981). Analysis by the Dept. Mineral Resources shows that the deposit contains quantities of ironstones as either gossans or hydrothermally deposited minerals which include heavy metals and sulphides.

The limestone has steeply-dipping joints filled with this material. It also has some dolomitised areas. In Wyanbene Cave, aragonite is mostly associated with areas of the cave which expose these joints, as reported by Rowling (Rowling 1995). Gypsum occurs in parts of the cave, often as fine needles on sediment banks.

The chemical influences on aragonite development at Wyanbene cave appear to be heavy metals: gold, lead, zinc, nickel, cobalt, cadmium, with sulphate and magnesium.

Jenolan
Welch (1976) and Dunkley & Anderson (1978) have produced guidebooks to the caves at Jenolan. There are reports and photographs of aragonite in some of the caves at Jenolan but the authors did not confirm that the material was actually aragonite. There is aragonite in the tourist caves and at least five other caves. Two caves (Contact Cave and Wiburds Lake Cave) have been selected as study sites for the cave aragonite project.

The Jenolan limestone deposit is mostly a fairly pure Silurian limestone. It also has some impure and dolomitised areas, especially towards the eastern and western edges of the deposit. Other parts of the deposit have been intruded by igneous dykes. This is most pronounced in Wiburds Lake Cave.

Despite the long period of time that some of the aragonite speleothems at Jenolan have been known, there has been little in print about it. One of the earliest references to aragonite deposits in the tourist caves at Jenolan is Osborne (1993). The earliest printed reference to aragonite anywhere at Jenolan is Welch (1976) and concerns the undeveloped caves. There are, however, over a hundred years' worth of tourist guidebooks and photographs of speleothems now known to be aragonite (such as the Lyrebirds Nest, the Arabesque and the Furze Bushes).

- ***Wiburds Lake Cave***
  Members of Sydney University Speleological Society, I. Cooper, Dr P. Maynard and others have reported (pers. comm.) over the last ten years on aragonite deposits in Wiburds Lake Cave. Some of these deposits are difficult to get to, but at the sites I have visited, aragonite takes the form of beaded helictites, anthodites and a spathite. Areas visited include "Neddys Knock" area and "The Maze". Thin sections and XRD (Xray diffraction) of material from "Neddys Knock" shows that the aragonite is deposited in a matrix of what appears to be de-dolomite, weathered pyrite and fine sediment, giving the appearance of a gossan. Chemical influences on the deposition of aragonite in Wiburds Lake Cave appear to be magnesium (as hydromagnesite) from de-dolomitisation of brecciated dolomitic bedrock with manganese(as braunite, todorokite and others) associated with a devonian mafic dyke; sulphate (as gypsum) from oxidation of pyrite in both the bedrock and the dyke, and phosphate (from bat guano).

- ***Contact Cave***
  Aragonite in the small Contact Cave takes the form of anthodites, helictites and surface coatings, mainly on the low, flat ceiling. The speleothems are liberally coated in white pasty hydromagnesite and huntite, with rhodochrosite and dolomite as sands and other coatings on the speleothems. There are also dark manganese minerals present such as todorokite and pyrolusite. There are also phosphates (from bat guano). Contact Cave is very close to the limestone / shale contact. Here, the bedrock is dolomitised and corroded in places; there are also goethite cubes (pseudomorphed after pyrite) in the dolomitised areas.

  Contact Cave also has a "popcorn line" below which aragonite is deposited. This may infer that air humidity may be an influence on the type of speleothems deposited, and whether supersaturation may be achieved with respect to calcium carbonate.

  The main chemical influences on aragonite at Contact Cave appear to be magnesium and manganese, and possibly phosphate.

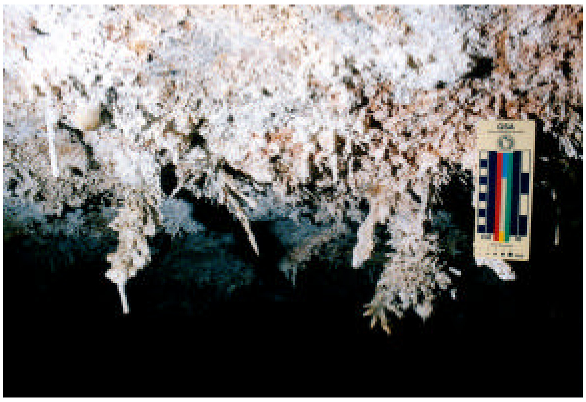

Figure 1 - Scene from Contact Cave showing various coated aragonite speleothems

- ***Mammoth Cave***

  Cavers' reports from Jenolan include M. Vizjak on Mammoth Cave's World of Mud Extension. This recently-discovered area of Mammoth Cave was still being explored and mapped by members of the Sydney Speleological Society up till the end of 2001 (Vizjak 1998b, Vizjak 1998a). Photographs of the site indicate that it contains fairly extensive deposits of what appears to be aragonite in the form ofanthodites and wall coatings. Some blue and green aragonite is present. During a visit to "The World of Mud" I saw what appeared to be aragonite anthodites, helictites and coatings. The areas visited were "Toms Kitchen" and part of the rockpile heading upwards from that area. Other cavers have reported gypsum ramshorns from higher in the deposit.

  Interestingly, aragonite also occurs in the lower rockpile of this large chamber, as a coating on large boulders. There is also a slightly blue flowstone ("the Blue Lady") and some unusual orange cave pearls in a side chamber. These are also possibly aragonite.

  The mud is unusually dark in some areas and appears to contain manganese oxides. In other areas it is almost red. Like Contact Cave, this part of Mammoth Cave is very close to the steeply-dipping limestone / shale contact and appears to be developed along the boundary.

  The bedrock appears to be highly corroded in places. As the shale contains a lot of manganese oxides, this is assumed to be the source of it in the mud; the corrosion may be from weathering pyrite. Some of the large helictites are almost black, presumably because of manganese oxides. Many have white efflorescences (assumed to be huntite and / or hydromagnesite). One such large helictite mass has about half a dozen branches, each about 400 mm long but only about 5 mm diameter. They are very dark brown. In this same area, aragonite "stars" protrude from red ochrous sediment at the ends of bedrock blocks.

  Another smaller dark helictite mass resembles a sea urchin. The spines are about 100 mm long and about 3 mm diameter. The tips are white with blobs of hydromagnesite, and each has a small growth ofaragonite at the tip, angled back towards the wall. This shows that the mass of helictites form part of a single speleothem with a common hydrological influence.

  One characteristic of aragonite is it is slightly harder than calcite. This may enable speleothems such as helictites to reach a greater length than is normally achieved with calcite.

  As the entrance to this part of the cave was dug out, it is unlikely that phosphates from bat guano would be present, however none of the "World of Mud" has been sampled so this cannot be confirmed.

  It would appear that chemical influences on the deposition of aragonite in this area are magnesium, sulphate and manganese.

- ***Other Caves at Jenolan***
  Although not analysed, there are speleothems in Spider Cave which appear to be aragonite. These occur in Helictite Chamber, as beaded helictites, anthodites and thickened straw stalactites. The substrates in this case appear to be rusty-coloured ochreous deposits. They occur in a relatively dry section of the cave.

  I have also visited Glass Cave (Jenolan) and described the aragonite anthodites therein (Rowling 1999). These are deposited on a rusty red and black coloured, porous substrate which looks superficially the same as that which can be seen in the tourist caves, in particular "The Jungle" area of Orient Cave. A grain from the floor, and moonmilk recovered from clothing, have been tested. XRD has confirmed the presence of aragonite, gypsum, phosphates and hydromagnesite.

  Osborne, Pogson and Colchester have been investigating minerals in the Jenolan Tourist caves. They reported aragonite from Ribbon Cave, the Mud Tunnels and other sites (Osborne, Pogson & Colchester 2002). The substrate is also being investigated. Their work is ongoing.

Cliefden
In a geological description of the caves at Cliefden, Osborne reported calcite which may have inverted from aragonite (Osborne 1978). The article also includes a description of the sample of a blue aragonite speleothem from Boonderoo Cave which is held by the Australian Museum. This was analysed and found to be blue aragonite coating a white calcite core. There is no description of the substrate from which it was taken. I have not visited this cave; access is not presently permitted.

In Turner (2002), Australian Museum samples of this material were analysed to find out what caused the blue colour. Metals detected in the blue material (apart from calcium) were copper, chromium, nickel, iron, zinc, strontium, barium, with small amounts of magnesium, lead and uranium.

Barite occurs both in the limestone and in the local andesite. There is an abandoned barite mine at Cliefden, about 500 m to the south of Boonderoo Cave, in the andesite.

Also at Cliefden, aragonite has been reported from Taplow Maze (cave) and from Murder Cave in the form of blue stalactites.

Colong
A deposit of what appears to be aragonite has been reported near the dyke in Colong Cave (R.A. Osborne, A. Pryke pers. comm.). Xray diffraction work by the author shows that this material is mainly calcite and clays, with minor aragonite, calcium silicates, phosphates and manganese. The spiky nature of the material was mainly due to needle-form calcite.

Bungonia
J. Bauer & P. Bauer reported aragonite in a cave at Bungonia, "The B4-5 Extension", but the specific site was not sampled so there is no confirmation that the material is actually aragonite (Bauer & Bauer 1998). R. A. Osborne has also reported (pers. comm.) *flos ferri* from Flying Fortress Cave (B17) at Bungonia. J. Bauer reports that the material in Flying Fortress Cave is aragonite, determined by XRD (J. Bauer, pers. comm.). I have visited the sites in Flying Fortress Cave, and it appears that the aragonite is associated with steeply-dipping, weathered dolomitic beds. This is in the fossiliferous Lookdown limestone, identified by J. Bauer. The forms taken by the aragonite include helictites (*flos ferri*), stalactites and spathites. The colour ranges from white to orange-brown and may be a mixture of calcite and aragonite.

A sample from near the dyke has been analysed using Raman spectroscopy and appears to be aragonite with a calcite coating, and hydromagnesite.

Jaunter
M. Scott (pers. comm. approx. 1989) has shown the author "Crystal Cave" with what appeared to be extensive deposits of aragonite in the form of large anthodites. This is in the Silurian Jaunter limestone at "Tarakuanna" (previously known as "Iona") in the Jaunter region to the west of Jenolan Caves. In this case, the aragonite was deposited below a porous, rusty coloured substrate, resembling a gossan. The property owner no longer allows access to this cave,

however there are plenty of photographs showing the range of anthodites present. The chemical influence on aragonite deposition in this cave appears to be magnesium, judging by the white material deposited on the ends of many of the anthodites.

Another cave in the same area, Tugellella Cave, is also said to contain aragonite but the aragonite is apparently nowhere near as extensive as in the "Crystal Cave".

Wombeyan
Cavers around the world have often mentioned hollow spheroids - "cave turnips", which often occur near cave entrances. They are briefly described in Hill & Forti (1997). At Wombeyan Caves, they are often found naturally broken. A Swiss caver has reported via the internet that the material inside these balls is aragonite but has not confirmed this.

I have visited sites with these spheroids at Wombeyan Caves (Sigma Cave and Cow Pit) (Rowling 1998b). These sites also appear to have aragonite deposits in the form of surface coatings. The surface coatings in Sigma Cave have been confirmed as being aragonite (by XRD) but the spheroids in Cow Pit are calcite. Under the microscope the material resembles aragonite. Some of the material from the "turnips" appears to have been influenced by biological activity. Either the deposit was originally aragonite and has reverted to calcite, or it was originally deposited as needle-form calcite. As the insides of these "turnips" appears to be mud with occasional white hydromagnesite and / or huntite one can guess that in some cases, aragonite may be deposited. Clearly more work needs to be done on these speleothems before an accurate assessment can be made.

- **Wollondilly Cave**
  Aragonite has been reported at Wollondilly Cave. There are four places of interest: an anthodite in "the Cathedral", spiky stalactite tips near "Star Chamber", fluffy and crusty coatings in "the Loft" and a spiky pool crystal deposit at the base of "Jacobs Ladder".

  The lower "Cathedral" anthodite is high on a ceiling and thus out of reach, however access is possible to the area about 15 m directly above the apparent aragonite deposit. This is called "The Loft". In "The Loft", there is a perched deposit of allogenic gravel and cobbles. Older speleothems have been corroded by bat guano. The grey crusty coatings here have been analysed with XRD; they contain calcite, aragonite, vaterite and various phosphates. Also in this area is a white fluffy material which is mostly needle-form calcite but also contains aragonite, phosphates, calcium silicates and hydromagnesite.

  The nearby "Star Chamber" spiky coatings are mainly calcite with huntite and hydromagnesite. The calcite grains appear to be recrystallised from aragonite. They are more brittle than normal calcite crystals.

  Although the spiky pool crystal at the base of "Jacobs Ladder" XRDs as calcite, it appears to be recrystallised from aragonite. There is hydromagnesite in the nearby clays, determined by XRD. Possibly in this pool, calcium carbonate can deposit either as calcite or aragonite depending on the amount of magnesium ions present in the pool solution.

  Another white deposit that looked like aragonite was sampled; this turned out to be calcite also. The chemical influences allowing aragonite to precipitate at Wollondilly Cave appear to be phosphate and magnesium.

- **Sigma Cave**
  Also at Wombeyan Caves, Sigma Cave is located towards the southern end of the marble deposit. A trip to Sigma was organised in 2002 to examine the aragonite in one part of the cave. Some material was sampled, including bedrock veins, pieces of anthodite, wall coatings and stalactite pieces. Much of the material sampled was from the floor, that is, it was taken from material already broken. Some small pieces of material were taken from the walls. The samples were analysed wth XRD, with interesting results. The aragonite samples taken from the wall were almost pure aragonite with traces of huntite and hydromagnesite. Their surfaces were spiky with good aragonite crystal form.

Figure 2 - SEM image of a number of aragonite crystals from the wall of Aragonite Canyon, Sigma Cave

The samples that had lain on the floor in the mud were a mixture of calcite, aragonite and calcium silicates (scawtite). The surface of these samples appeared to have been recrystallised. A fallen stalactite was sampled; it consists of layers of chalky phosphates, hydromagnesite, with crystalline aragonite and calcite. Most likely the phosphates are derived from bat guano. An interesting spathite (also broken) was examined. This comprised a hollow tube of aragonite, surrounded by twisted needles of aragonite. Longer needles (also aragonite) projected from the main shaft of the stalactite giving it a bottle-brush appearance.

It is suggested that the samples obtained by Webb and Brush at Wyanbene may have been altered to aragonite after they fell from the original anthodite, and this suggests that there is something special about the anthodite that keeps calcium carbonate precipitating as aragonite rather than calcite. In the case of Wyanbene, this is most likely to be magnesium-based chemicals such as hydromagnesite and copper-based chemicals such as copper carbonate which will poison a calcite crystal's development. In the case of Sigma Cave the chemical poisoning appears to be from phosphates and manganese, as well as from magnesium.

PRESENT KNOWLEDGE ON ARAGONITE OCCURRENCE IN CAVES

Association with Ochres and Gossans

In Slovakia there are extensive aragonite deposits in show caves. Some of these deposits are associated with "ochres" containing Fe, Mn and Mg eg. Cilek, Bosak, Melka, Zak, Langrova & Osborne (1998). Some of these deposits were ascribed to microorganism activity, especially the manganese-based compounds.

Another type of aragonite occurrence overseas is in conjunction with iron mines. In particular, the Styrian (Austria) iron deposits had world-renowned occurrences of aragonite in the form of tangled masses of helictites known as *flos ferri* (flowers of iron). There is a sample of this material in the Australian Museum, and it is aragonite as tested using XRD, according to the Minerals Curator, Ross Pogson (pers. comm.).

As there are examples of *flos ferri* in NSW caves the association of this form of aragonite with iron oxides and aragonite occurrence was investigated at Wyanbene (Rowling 1995) and the "Lyrebirds Nest" at Jenolan (Osborne et al 2002). Although it is tempting to say that iron may influence the precipitation of aragonite, it is more likely that the aragonite is precipitated under the influence of other materials such as magnesium, cobalt or manganese. Iron is not a recognised calcite inhibitor (Morse 1983). Iron is an extremely common element in cave sediments yet aragonite is not. The iron-rich sediments associated with aragonite are hard, yet porous, and it may be these physical qualities that make it possible for other chemical influences (eg. magnesium or sulphate) to dictate the form taken by precipitating calcium carbonate. In Rowling (1998a), SEM/EDX work performed by Maynard showed that ribbon helictites from Jubilee Cave, Jenolan, contained iron, however they were calcite, not aragonite.

There are several goethite deposits at Jenolan Caves. They occur either as massive deposits or as concretions. In-cave massive deposits include the western areas of Glass Cave where the aragonite deposits occur, Orient Cave and Ribbon Cave (also associated with aragonite). Concretionary deposits in caves include the roof near the Diamond Mines area of Imperial Cave. Outside the caves, goethite occurs as nodules and concretions at Lucas Rocks, on the tourist track along the western margin of the limestone and as both concretions and massive deposits behind two of the houses on Burma Road. The latter deposit is associated with apparently weathered de-dolomite.

A similar but much smaller deposit occurs near Contact Cave on the eastern margin of the limestone. Thin sections show that the iron is associated with de-dolomitisation; basically as ferroan dolomite weathers, the magnesium seems to be released first, and this may be the local source of hydromagnesite at Contact Cave. What is left in the bedrock is porous iron oxides, forming diamond-shaped patterns after the original dolomitic texture. Different iron oxidation states colour the material variously from yellows and browns through to reds and black. The black areas also contain significant quantities of manganese oxides. Weathering is presumably enhanced by sulphuric acid from oxidising pyrite: also a good source of sulphate, eg. gypsum. At Contact Cave the de-dolomite contains small cubes of goethite pseudomorphed after pyrite.

Association with Magnesium

According to Morse (1983), magnesium is a significant poisoner of calcite crystal growth so it is not surprising to find aragonite being deposited at the expense of calcite in caves with significant amounts of magnesium.

In France, there are a number of outstanding caves with aragonite. In most cases, the aragonite is associated with areas of metamorphosed dolostone. Some of these French deposits are associated with gypsum and sulphur, and some with hydromagnesite. The aragonite was often associated with clays. Where there was no clay, there was no aragonite (D.W. Gill, pers. comm.). An unpublished report concerning these caves (Cabrol, Gill & Gunn 2001) has been circulated to interested members of the International Union of Speleology.

In South Australia, aragonite occurs in caves associated with dolostone (G. Gartrell, pers. comm.).

The relationship between aragonite and hydromagnesite has been described by others eg. Hill (1987) and it has been confirmed by XRD that in several caves at Jenolan, this relationship exists (Contact Cave, Glass Cave, Wiburds Lake Cave). Huntite in the tourist caves is also associated with aragonite (Osborne et al 2002). Other caves at Jenolan appear to contain magnesium minerals but they have not been analysed. Normally, dolomite and dolostone is more resistant to weathering than limestone however magnesium compunds can be released if the dolomite is subjected to strong acids such as sulphuric acid (from the weathering of pyrite), nitric and phosphoric acid (present in fresh bat guano). Both pyrite and bat guano occur at Jenolan, Walli, Bungonia and Wombeyan Caves.

Blue Speleothems

Aragonite in the form of blue speleothems occurs eg. the Blue Cave, France, (Hill & Forti 1997) in conjunction with deposits of heavy metals (eg. copper). This appears also to be the case with blue aragonite speleothems in some NSW caves such as at Cliefden and Wyanbene. The copper ion can form a solid solution in the aragonite crystal structure but not in calcite, where it precipitates instead as malachite or azurite separately from the calcite structure. Turner (2002) describes how copper is most likely the main heavy metal colouring in blue aragonite speleothems at Cliefden.

Influence by Sulphates

The author has visited several well-decorated caves at Mole Creek, Tasmania which contain aragonite deposits in the form of rock coatings, "donkey tail" stalactites, anthodites and helictites. These are in Gordon Limestone which contains magnesium carbonates and pyrite (I. Cooper, pers. comm.). These caves also contain deposits of gypsum.

Carlsbad Caverns and Lechuguilla Cave (Carlsbad National Park) contain extensive deposits of aragonite. This has been discussed in Hill (1987), Thrailkill (1971), Hill & Forti (1997) and well illustrated in Speleo Projects (1998). In these cases, evaporation is said to be the primary cause of aragonite deposition.

The caves at Carlsbad also contain significant deposits of gypsum and sulphur. There are two effects of gypsum in solution. One is the common ion effect, which causes calcium carbonate to deposit first in a mixture of calcium carbonate and calcium sulphate. The second effect is the crystal poisoning effect, where the sulphate molecule adheres to the growth points of the calcite crystal. This prevents calcite from depositing. Instead, calcium carbonate deposits as aragonite which is not affected by crystal growth poisoning by sulphate.

Independence to Biological Activity?
In the marine environment, aragonite is commonly produced as the result of biological activity (eg. sea shells) whereas in the spelean environment, biological activity has been implicated in calcium carbonate deposition as moonmilk (needle form calcite) and other calcite deposits rather than aragonite. It could be worthwhile comparing the microbial activity on aragonite speleothems compared with calcite ones in the vicinity. Biogenic calcite in the caves of the Nullarbor as described by Contos (2000) implies organic acids in the alteration of the crystal shape of calcite, but XRD indicates the mineral is calcite not aragonite.

The only examples of possible biogenic deposits seen by the author at Jenolan are some pasty "moonmilk" or hydromagnesite deposits. Where aragonite is associated with these deposits (eg. in Glass Cave, Jenolan), it appears to be secondary to the pasty deposit. That is, the aragonite appears to be deposited instead of conventional calcite as a result of the chemical influence of the pasty material.

Temperature Independence?
There are caves in Hungary which are hydrothermal and are reported to contain aragonite deposits eg. Leel-Ossy (1997). Temperature is said to aid the formation of aragonite however this is disputed by other researchers eg. Morse (1983).

In Australia, aragonite occurs in caves in South Australia, Western Australia, Tasmania and NSW, with average cave temperatures ranging from 8°C (Mole Creek, Tasmania) to 19°C (Cliefden and Walli, NSW). In NSW at least, temperature does not seem to be a factor in aragonite deposition.

Humidity and Air Movement
Cave climate (temperature and relative humidity) was measured at the study sites, however there was no strong correlation between these measurements and the presence or absence of aragonite.

At Jenolan, Wombeyan and Wyanbene, aragonite appeared to be concentrated in areas where a breeze can occur due to air movement in the cave, or where humidity could potentially be lowered due to the position of the site with respect to the entrance of the cave. It also occurred in areas where there is no air movement.

When the humidity was measured, it was usually over 98% however one site (The Loft) had relatively low humidity. Possibly if a high reading instrument were available, more meaningful results could be gained.

It should be noted that in each case where there was aragonite, there were chemicals present (eg. hydromagnesite) which would contribute to the development of aragonite.

The area of the cave with the lowest humidity and highest air movement is the entrance area, however aragonite was not detected there except in one case (Cow Pit), where it was a minor constituent of cave fill. Generally, calcium carbonate deposits near the entrance were as calcite, sometimes as needle-form calcite.

Effect Of CO_2
CO_2 concentration was measured at each study site using Draeger tubes. Some sites would be classified as "fresh air" whereas other sites visited measured 0.5%. There was no correlation between the CO_2 concentration and the presence or abscence of aragonite.

METHODOLOGY

The methodology being used to investigate aragonite is as follows:

- Literature search
- Visit field sites
- Obtain permission from site owners to sample
- Select field study sites
- Analyse samples
- Determine what factors lead to the deposition of aragonite in NSW caves.

Literature Search

A literature search was started in 1999 for all references to cave aragonite in NSW. There was not a great deal written on the subject.

Other sources of NSW material included cavers' trip reports. Personal observations from cave guides, other researchers and sport cavers were investigated. This led to the realisation that aragonite may be more common than originally thought in caves, especially at Jenolan.

The literature was examined on cave aragonites, and aragonite formation in general. There has been a lot of work done on the chemistry of aragonite in the marine setting eg. Bathurst (1974), also Tucker & Wright (1990) however for the spelean environment, a very good summary of references is Hill & Forti (1997). The best reference so far on aragonite chemistry kinetics is Morse (1983).

A list has been compiled of caves (based on trip reports etc.) which are reported as having aragonite.

Field Study Sites

From the list of caves said to contain aragonite, a short list was compiled of caves which would be relevant to this study.

Many of these cave sites have been visited to determine the extent of the deposit. Some of these sites have already been visited over the past 10 years.

Reported sightings of aragonite in caves have been checked, as some cavers report anything spiky as aragonite (could be gypsum, calcite, etc.). The only sites which were not checked were those which were considered to be either insignificant or extremely difficult to visit, either because of physical difficulty or landowner policy.

Three cave areas were identified as being worthy of further investigation to become case studies (i.e. they form the majority of the study work). These sites were identified as being relatively accessible both physically and with permission of the owner.

Study sites were chosen on the following basis:

- Ease of access to site
- Significance of aragonite at the site
- Preferably each of the sites is in different limestone deposits so that comparisons can be made of them.

Caves chosen are Wiburds Lake Cave and Contact Cave at Jenolan, Sigma Cave and Wollondilly Cave at Wombeyan, and Piano Cave and Deep Hole at Walli.

In some cases, there are samples of cave aragonite already held in museum collections so further sampling of aragonite at the original site was not necessary however sampling of the substrate and the speleothem water (if possible) was required. One of the problems the author has encountered is that the aragonite speleothems are often fairly dry. Museum samples have been located in the Australian Museum and inspected. There was little data associated with the samples apart from the general collection information (date, collector, region).

For each sampling site, small samples were obtained of aragonite material from the caves. Also samples have been taken of the substrate and the bedrock. The following investigations are being made of the aragonite in the field:

- What is the form taken by the speleothem, classified as per Hill & Forti (1997)?
- What is the CO_2 level at the site?
- What is the temperature at the site?
- What is the humidity at the site. Is there a boundary layer?

The following investigations are being made of the substrate:

- What is the physical relationship between the aragonite and the substrate?
- What is its structure (eg. sediment, dyke, speleothem, etc.)?
- Description of the material (eg. gossan, bedrock, etc.)

The following investigations are being made of the bedrock:

- What is its structure (eg. dip, strike, relationship to aragonite deposits, etc.)?
- Description of the material (eg. limestone, dolostone, etc.)

Field Work

Where museum or other samples were not available, field samples were obtained of:

- The substrate material (mud, rock etc.) on which the aragonite is depositing
- The host rock
- The aragonite (only a very small quantity is required).

Caves are non-renewable, fragile environments and it is important that sampling be done carefully without destroying the visual appearance of the site.

Photos and descriptions of the speleothems and their environment were made in the caves. In-situ measurements have been made of temperature, and CO_2 levels. Relative humidity was checked in the caves using a whirling hygrometer. If possible, samples were to be made of water from actively wet aragonite speleothems however during the course of this project none have been found in a wet state as NSW was in drought.

Cave maps were required. In some cases, very good ones were already available and just needed to be annotated however in other cases, the author made her own.

The geological setting of each study site is being described (where it hasn't already been done).

I also looked at paleokarst fills and prepared geological descriptions of the sites. In many cases it appeared that the best aragonite was to be found associated with these fills.

Sample Analysis

Thin sections and polished slabs of selected host rock material were examined using optical microscopy.

Most samples were analysed using XRD, using a Siemens D5000 diffractometer. Some soft specimens and wall deposits were examined using a Philips SEM505 scanning electron microscope. The substrate was checked for carbonate content by simple test with HCl. Substrate composition was determined by XRD.

For the aragonite specimens, the overall appearance was described and the material was determined to be aragonite (or not) using XRD.

WHAT THIS PROJECT WILL CONTRIBUTE TO KNOWLEDGE IN THIS FIELD

- A list will be compiled of caves in NSW which contain aragonite.
- Reported sightings of aragonite in caves will be checked and verified as to whether or not the material is aragonite.
- More information will be known about the type and composition of the substrates at these sites.
- The cave environment at each site will be described. (eg. temperature, humidity, chemical, physical and geological factors).
- Common factors leading to the deposition of aragonite will be discussed.
- Ideally, the extent and mode of formation of NSW cave aragonites will be determined.

APPENDIX - LIST OF CAVES REPORTED AS CONTAINING ARAGONITE IN NSW

(*cfm*): confirmed by XRD.

- Bungonia: B4-5 Extension; Flying Fortress Cave (*cfm*).
- Cliefden: Murder Cave; Boonderoo Cave (*cfm*); Taplow Maze.
- Colong: Colong Caves (*cfm*).
- Jaunter Limestone: "Tarakuanna", Crystal Cave.
- Jenolan: Ribbon Cave (*cfm*), mud tunnels (*cfm*), Orient Cave; Mammoth Cave; Glass Cave (*cfm*); Hennings Cave; Wiburds Lake Cave (*cfm*); Contact Cave (*cfm*); Spider Cave; Dwyers Cave.
- Timor: Hill Cave.
- Walli: Piano Cave (*cfm*); Deep Hole (*cfm*).
- Wee Jasper: Careys Cave; Nice Cave; Dip Cave.
- Wombeyan: Sigma Cave (*cfm*); Cow Pit (*cfm*); Guineacor Cave; Wollondilly Cave (*cfm*); Kooringa Cave; Blackberry Hole/Dutchmans Cave; Lantern Cave, Bullio Cave.
- Wyanbene: Wyanbene Main Cave (*cfm*).
- Yarrangobilly: North Glory Hole; Eagles Nest.

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