Project Report for MSc.
Cave Aragonites of NSW

Jill Rowling

November 2000

Abstract:

A Part-Time MSc. Project at the University of Sydney, Geosciences Department. Supervisors: Tom Hubble and Dr Armstrong Osborne.

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; and to determine what factors lead to the deposition of aragonite in NSW caves.

There is surprisingly little scientific literature regarding its occurrence in NSW caves.

There are a number of chemical and physical factors which affect the stability of aragonite in the cave environment. Aragonite is unstable in the freshwater environment, so deposition of aragonite in the spelean environment is unexpected, however it has been reported from a number of NSW cave areas.

Aragonite can deposit at the expense of calcite when a calcite inhibitor is present.

The methodology being used to investigate aragonite involves a literature search; visits to cave areas and selection of suitable field sites; obtaining samples at field study sites; analysis of samples; and determining what factors lead to the deposition of aragonite in NSW caves.

The project was started in July 1999. This presentation was originally given as a progress report to the Geosciences Dept at the University of Sydney on Friday 1st December 2000.

1. Project Aims

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.

2. What is Aragonite?

Aragonite is a polymorph of calcium carbonate, $CaCO_3$. It was named after the province of Aragon, Spain, where it occurs as pseudo-hexagonal twins.

Calcite is the more common polymorph encountered in the environment. Aragonite is classified in the orthorhombic crystal system whereas calcite is variously classified as belonging to the in the triclinic (Glazer, 1987), hexagonal/trigonal (Berry, Mason, Dietrich, 1983) or rhombohedral (Hurlbut, 1970) crystal systems.

Other polymorphs of $CaCO_3$ include the unstable vaterite (hexagonal) which occurs in gastropods and carbide dumps, as well as the high temperature and pressure Calcite-IV and Calcite-V which are not stable in near-surface environments.

Aragonite is harder and more dense than calcite, and has a characteristic acicular habit. It has two cleavage angles whereas calcite has the familiar three perfect cleavage angles.

Aragonite is mostly encountered in the marine environment, often the product of biological chemical activity such as the development of an organism's shell. When the organism dies, shell aragonite will in time revert to calcite in the near surface environment in the presence of fresh water. Outside of biological influences, the deposition of aragonite is generally considered the product of high pressure and / or high temperature on calcite, or chemical influence.

Given its instability in the freshwater environment, deposition of aragonite in the spelean environment is unexpected. In the spelean environment, calcite deposits are frequently coloured

by humic acids whereas aragonite tends to be either white or coloured by metal impurities such as copper.

3. Stability

Carlson (1983), p192 shows a pressure-temperature stability diagram for various polymorphs of $CaCO_3$ however the scales are from 0 to 1200 °C temperature and 0 to 40 kbar pressure.

The spelean environment is about 15 °C and about 1 bar pressure only, which is in the stability range for calcite. At these temperatures and pressures, aragonite is unstable. Aragonite is stable above about 3 kbar pressure which does not occur in the surface environment.

Based on temperature and pressure alone, in the cave environment one would expect calcite to be the only form deposited yet aragonite does occur therefore there must be another factors other than temperature or pressure for aragonite to occur in caves.

4. Reasons for doing this project

Aragonite is chemically unstable in the normal cave environment, however it has been reported from a number of NSW cave areas as shown in Table 1.

Table 1: Caves reported to have Aragonite

Cave Area	Caves with aragonite
Jenolan	13
Wombeyan	7
Cliefden	3
Wee Jasper	3
Bungonia	2
Yarrangobilly	2
Colong	1
Jaunter	1
Walli	1
Wyanbene	1

There is surprisingly little scientific literature regarding its occurence in NSW caves.

There are a number of chemical and physical factors which affect the stability of aragonite in the cave environment. These include:

- humidity
- air movement and
- presence of calcite inhibitors (Morse, 1983) such as:
    - magnesium
    - manganese
    - sulphate
    - phosphate

Aragonite can deposit at the expense of calcite when a calcite inhibitor is present.

Other workers have mentioned strontium, temperature, rate of deposition or CO_2 concentration as being influential in the deposition of aragonite however the views are sometimes contradictory.

In limestone areas where aragonite has been reported, bulk sampling of the bedrock by the Mines Dept. has often shown high purity of limestone with insignificant concentrations of impurities.

The best aragonite seems to occur in those same limestone deposits in small areas featuring what is usually termed by cavers and cave guides as ``rotten rock''. Some of these sites at Jenolan have been described by Dr Osborne (Osborne, 1993 and 1999).

Identifying aragonite sites and their substrates may help to determine reasons for the aragonite occurence in these areas. It may also help to determine some of the geological events that have happened since the limestone was originally deposited.

5. Project Methodology

The methodology being used to investigate aragonite is as follows:

- Literature search
- Visit cave areas and select suitable field sites
- Obtain samples at field study sites
- Analyse samples
- Determine what factors lead to the deposition of aragonite in NSW caves.

6. Current Status of the Project

6.1 Literature Search

A literature search was started last year for all references to cave aragonite in NSW as well as aragonite in general, summarised in Table 2.

Table 2: References to aragonite in publications

Type of Publication	Refs
NSW Cavers' trip reports	4
Other publications on NSW Caves	15
Other spelean aragonite	9
Aragonite in general	27
Total references	55

Additionally, there are a number of unpublished accounts by cavers together with verbal reports and photographs showing what appears to be aragonite in NSW caves.

One of the most useful ``Other references'' was by Morse on the kinetics of aragonite precipitation. Morse lists a number of anions and cations which can assist in the deposition of aragonite by inhibiting the precipitation of calcite.

It has been encouraging to see evidence of some of these materials in caves where aragonite occurs, in particular magnesium, manganese, sulphate and phosphate.

6.2 Field Site Visits

I obtained permission from each of the site owners before visiting a site or sampling at a site.

The type of application varies from land owner to land owner, with some having no formal arrangements and others requiring specific forms to be filled in before permission is granted for a visit.

Usually a separate application is required for each visit.

Permission to sample is in some cases more difficult than others; it depends on the site owner. This is summarised in Table 3.

Table 3: Site Permits

Controlling Authority	Visiting Permit	Sampling Permit
JCRT	Yes	Yes
SSS	Yes	Yes
OSS	Yes*	Not yet
TK	Yes*	Not yet
NSW NPWS	Yes*	Not yet

* Had been visited prior to this study being undertaken

JCRT Jenolan Caves Reserve Trust, controls access to Jenolan, Wombeyan, Abercrombie and Borenore Caves.

SSS Sydney Speleological Society, controls access to Walli Caves through an arrangement with the property owner.

OSS Orange Speleological Society, controls access to Cliefden Caves through an arrangement with the property owner.

TK The Property owner, Tarakuanna. This property has changed ownership. Caves are part of the Jaunter limestone deposit.

6.3 Field Sites

The following field sites were visited over the period November 1999 to November 2000:

- Jenolan Caves:
  - Contact Cave
  - Wiburds Lake Cave
  - Ribbon Cave (joint trip with Australian Museum: David Colchester, Ross Pogson and Armstrong Osborne)
  - Mammoth Cave
- Wombeyan Caves:
  - Wollondilly Cave
  - Guineacor Cave
  - Cow Pit
- Walli Caves:
  - Piano Cave (after C. S. Wilkinson, NSW Government Geologist in 1876) (Wilkinson, 1892).
- Wellington Caves:
  - Phosphate Mine

6.4 Samples

Rather than duplicating work with relatively scarce material, I am trying to collaborate with other workers who have already studied cave minerals, as well as obtaining my own original samples where such work has not already been done.

For example, at Jenolan Caves, the Australian Museum has been sampling in the tourist caves and at Contact Cave. The analyses show that the material sampled is aragonite with magnesium carbonate (as huntite).

I have some very small samples of ``aragonite" from most of the caves visited, and also samples of some of the matrix in which the material was embedded.

Samples of speleothem need only be very small, eg pin head size. Samples of bedrock however need to be larger for thin section preparation, and care must be taken when taking the sample so as not to disturb or damage an important site.

6.5 Analysis

Preliminary optical work has shown that some of the matrix is very interesting and nothing like the ``normal" limestone bedrock. The material is considerably altered. Some samples appear to be dolomitic and other samples look more like a weathered low grade ore body.

Examining some of the ``aragonite" with optical microscopy shows that the material has the same form as that expected for aragonite, however full analysis will require X-ray techniques.

I am intending to undertake this work early next year (ie 2001).

6.6 Mapping

Cave maps are an essential tool for documenting sample locations and the cave's mineral deposits. In some cases, the caves have already been mapped but in other cases, original maps need to be prepared.

I have prepared maps of the following caves:

- Jenolan Caves: Contact Cave
- Wombeyan Caves: Cow Pit, parts of Wollondilly Cave.

Maps are drawn to 1:100 scale using standard Australian Speleological Federation symbols. Both plan and elevation are given, and sample points are being indicated on the maps. Geological features will be indicated as well (in prep.; some sketches were shown).

6.7 Problems Encountered

Some of the problems encountered during this study have included:

- Needle form calcite can sometimes look like aragonite so I need to await XRD analysis before deciding what it is!
- Not being able to fit into some parts of caves said to contain aragonite!
- Some speleothems are a mixture of calcite and aragonite.
- Some of the bedrock material is surprisingly hard. Special techniques may be required in some cases to get samples without making an obvious mark. This is important where the site is part of a tourist cave display or it is an important conservation site.
- Sometimes caving collegues fall asleep, get bored, cold or run away!

7. Future Plans

My plans for the future of this project include:

- Concentrate on the following caves as case studies:
    - Wombeyan: Sigma Cave
    - Bungonia: Flying Fortress Cave
    - Jenolan Caves: Wiburds Lake Cave and Contact Cave
    - Walli Caves: Piano Cave
- Obtain cave maps or survey and draw them as required

- Obtain samples of aragonite, matrix and bedrock
- Analyse precipitating fluids associated with aragonite deposits.
- Attend course in X-ray analysis, SEM and sample preparation
- Analyse samples for aragonite and trace elements
- Measure temperature, CO_2 and humidity in the caves to see if there is any correlation with the presence of aragonite.
- Study thin sections of bedrock and matrix (in prep.)
- Carbon - Oxygen isotope analysis will also need to be done.
- It has been suggested that I should also look for possible evidence of microbial activity associated with aragonite.

8. References

Berry, L.G., Mason, B. & Dietrich R.V. (1983). ``Mineralogy: Concepts, Descriptions, Determinations'' Freeman.

Carlson, W.D. ``The Polymorphs of $CaCO_3$ and the Aragonite - Calcite Transformation'' In: Richard J. Reeder (Ed.) ``Carbonates: Mineralogy and Chemistry'' Mineralogical Society of America 191-226.

Glazer, A.M. (1987). ``The Structures of Crystals''. Hilger.

Hurlbut, C.S. Jr. (1970). ``Minerals and Man'' Random House.

Morse, J.W. (1983). ``The Kinetics of Calcium Carbonate Dissolution and Precipitation'' In: Richard J. Reeder (Ed.) ``Carbonates: Mineralogy and Chemistry'' Mineralogical Society of America 227-264.

Osborne, R.A.L. (1993). ``Geological Note: Cave formation by exhumation of Palaeozoic palaeokarst deposits at Jenolan Caves, New South Wales'' Aust. J of Earth Sc. Vol 40. 591-593.

Osborne, R.A.L. (1999). ``The Origin of Jenolan Caves: Elements of a new synthesis and framework chronology'' Proc. Linn. Soc, NSW No 121 1-27.

Wilkinson, C.S. (1892). ``Description of the Belubula Caves, Parish of Malongulli, Co. Bathurst'' Records of the Geological Survey of NSW, Dept Mines, Sydney, Vol III Part 1. 1-5, plates I-III.

9. Contact details

Address for Correspondence: Jill Rowling, 2 Derribong Place, Thornleigh NSW 2120 Australia
work email: rowling@ali.com.au
home email: jillr@speleonics.com.au