**The University of Sydney**
Faculty of Science
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# Cave Aragonites of New South Wales

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for the degree of Master of Science

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# Preface

### Sources of material

Sources of material are from my fieldwork unless specifically stated otherwise. Unless otherwise stated explicitly in the text, I was wholly responsible for the following: Cave maps and diagrams, collection of samples, photography, specimen preparation for powder XRD and thesis typing. All XRD scanning and analysis was done by myself on the University's equipment unless otherwise stated. I cut some of the smaller samples and polished the slabs. I mounted the samples for electron microscopy. I operated the electron microscope and obtained pictures of specimens. Where there was assistance for any picture, it has been acknowledged. I later edited my pictures on my computer to crop the image and generally prepare it for publication. All opinions and statements are my own, unless specifically acknowledged.

### Permissions and Ethics

Samples of cave minerals collected from Jenolan and Wombeyan Caves are the property of the Jenolan Caves Reserve Trust. All samples collected by me were done so with the permission of the relevant cave management authorities. All caving trips were undertaken using minimal impact and safety guidelines as per the Australian Speleological Federation.

### Work done by others

George Navratil prepared most of the thin sections; others were on loan from Julie Bauer and prepared by her. All have been individually acknowledged. George also cut most of the rock specimens and slabs using the rock saw at the Department of Geosciences. Dr Armstrong Osborne also cut some of the rock specimens and slabs. The samples which were to be examined using electron microscopy were coated by the staff of the Electron Microscope Unit at the University of Sydney. All film photos were processed and printed by a commercial film laboratory.

Thesis typesetting was done by myself, with assistance from Dr Mike Lake for occasional help with layout and LaTeX $2\varepsilon$ typographical coding. Proofreading was done by Dr Phil Maynard and Dr Lake, with helpful suggestions from Dr Osborne and Dr Tom Hubble regarding grammar and organisation.

## Abstract

Aragonite is a minor secondary mineral in many limestone caves throughout the world. It has been claimed that it is the second-most common cave mineral after calcite (Hill & Forti 1997). Aragonite occurs as a secondary mineral in the vadose zone of some caves in New South Wales. Aragonite is unstable in fresh water and usually reverts to calcite, but it is actively depositing in some NSW caves.

A review of current literature on the cave aragonite problem showed that chemical inhibitors to calcite deposition assist in the precipitation of calcium carbonate as aragonite instead of calcite. Chemical inhibitors work by physically blocking the positions on the calcite crystal lattice which would have otherwise allowed calcite to develop into a larger crystal. Often an inhibitor for calcite has no effect on the aragonite crystal lattice, thus aragonite may deposit where calcite deposition is inhibited.

Another association with aragonite in some NSW caves appears to be high evaporation rates allowing calcite, aragonite and vaterite to deposit. Vaterite is another unstable polymorph of calcium carbonate, which reverts to aragonite and calcite over time. Vaterite, aragonite and calcite were found together in cave sediments in areas with low humidity in Wollondilly Cave, Wombeyan.

Several factors were found to be associated with the deposition of aragonite instead of calcite speleothems in NSW caves. They included the presence of ferroan dolomite, calcite-inhibitors (in particular ions of magnesium, manganese, phosphate, sulfate and heavy metals), and both air movement and humidity.

Aragonite deposits in several NSW caves were examined to determine whether the material is or is not aragonite. Substrates to the aragonite were examined, as was the nature of the bedrock. The work concentrated on Contact Cave and Wiburds Lake Cave at Jenolan, Sigma Cave, Wollondilly Cave and Cow Pit at Wombeyan and Piano Cave and Deep Hole (Cave) at Walli. Comparisons are made with other caves. The study sites are all located in Palaeozoic rocks within the Lachlan Fold Belt tectonic region. Two of the sites, Jenolan and Wombeyan, are close to the western edge of the Sydney Basin. The third site, Walli, is close to a warm spring. The physical, climatic, chemical and mineralogical influences on calcium carbonate deposition in the caves were investigated. Where cave maps were unavailable, they were prepared on site as part of the study.

Contact Cave is located near the eastern boundary of the Late Silurian Jenolan Caves Limestone, in an area of steeply bedded and partially dolomitised limestone very close to its eastern boundary with the Jenolan volcanics. Aragonite in Contact Cave is precipitated on the ceiling as anthodites, helictites and coatings. The substrate for the aragonite is porous, altered, dolomitised limestone which is wedged apart by aragonite crystals. Aragonite deposition in Contact Cave is associated with a concentration of calcite-inhibiting ions, mainly minerals containing ions of magnesium, manganese and to a lesser extent, phosphates. Aragonite, dolomite and rhodochros-

ite are being actively deposited where these minerals are present. Calcite is being deposited where minerals containing magnesium ions are not present. The inhibitors appear to be mobilised by fresh water entering the cave as seepage along the steep bedding and jointing. During winter, cold dry air pooling in the lower part of the cave may concentrate minerals by evaporation and is most likely associated with the "popcorn line" seen in the cave.

Wiburds Lake Cave is located near the western boundary of the Jenolan Caves Limestone, very close to its faulted western boundary with Ordovician cherts. Aragonite at Wiburds Lake Cave is associated with weathered pyritic dolomitised limestone, an altered, dolomitised mafic dyke in a fault shear zone, and also with bat guano minerals. Aragonite speleothems include a spathite, cavity fills, vughs, surface coatings and anthodites. Calcite occurs in small quantities at the aragonite sites. Calcite-inhibitors associated with aragonite include ions of magnesium, manganese and sulfate. Phosphate is significant in some areas. Low humidity is significant in two areas.

Other sites briefly examined at Jenolan include Glass Cave, Mammoth Cave, Spider Cave and the show caves. Aragonite in Glass Cave may be associated with both weathering of dolomitised limestone (resulting in anthodites) and with bat guano (resulting in small cryptic forms). Aragonite in the show caves, and possibly in Mammoth and Spider Cave is associated with weathering of pyritic dolomitised limestone.

Wombeyan Caves are developed in saccharoidal marble, metamorphosed Silurian Wombeyan Caves Limestone. Three sites were examined in detail at Wombeyan Caves: Sigma Cave, Wollondilly Cave and Cow Pit (a steep sided doline with a dark zone). Sigma Cave is close to the south east boundary of the Wombeyan marble, close to its unconformable boundary with effusive hypersthene porphyry and intrusive gabbro, and contains some unmarmorised limestone. Aragonite occurs mainly in a canyon at the southern extremity of the cave and in some other sites. In Sigma Cave, aragonite deposition is mainly associated with minerals containing calcite-inhibitors, as well as some air movement in the cave. Calcite-inhibitors at Sigma Cave include ions of magnesium, manganese, sulfate and phosphate (possibly bat origin), partly from bedrock veins and partly from breakdown of minerals in sediments sourced from mafic igneous rocks. Substrates to aragonite speleothems include corroded speleothem, bedrock, ochres, mud and clastics. There is air movement at times in the canyon, it has higher levels of $CO_2$ than other parts of the cave and humidity is high. Air movement may assist in the rapid exchange of $CO_2$ at speleothem surfaces.

Wollondilly Cave is located in the eastern part of the Wombeyan marble. At Wollondilly Cave, anthodites and helictites were seen in an inaccessible area of the cave. Paramorphs of calcite after aragonite were found at Jacobs Ladder and the Pantheon. Aragonite at Star Chamber is associated with huntite and hydromagnesite. In The Loft, speleothem corrosion is characteristic of bat guano deposits. Aragonite, vaterite and calcite were detected in surface coatings in this area. Air movement between the two entrances of this cave has a drying effect which may serve to concentrate minerals by evaporation in some parts of the cave. The presence of vaterite and aragonite in fluffy coatings infers that vaterite may be inverting to aragonite. Calcite-inhibitors in the sediments include ions of phosphate, sulphate, magnesium and manganese. Cave sediment includes material sourced from detrital mafic rocks.

Cow Pit is located near Wollondilly Cave, and cave W43 is located near the northern boundary of the Wombeyan marble. At Cow Pit, paramorphs of calcite after aragonite occur in the walls as spheroids with minor huntite. Aragonite is a minor mineral in white wall coatings and red phosphatic sediments with minor hydromagnesite and huntite. At cave W43, aragonite was detected in the base of a coralloid speleothem. Paramorphs of calcite after aragonite were observed in the same speleothem. Dolomite in the bedrock may be a source of magnesium-rich minerals at cave W43.

Walli Caves are developed in the massive Belubula Limestone of the Ordovician Cliefden Caves Limestone Subgroup (Barrajin Group). At the caves, the limestone is steeply bedded and contains chert nodules with dolomite inclusions. Gypsum and barite occur in veins in the limestone. At Walli Caves, Piano Cave and Deep Hole (Deep Cave) were examined for aragonite. Gypsum occurs both as a surface coating and as fine selenite needles on chert nodules in areas with low humidity in the caves. Aragonite at Walli caves was associated with vein minerals and coatings containing calcite-inhibitors and, in some areas, low humidity. Calcite-inhibitors include sulfate (mostly as gypsum), magnesium, manganese and barium.

Other caves which contain aragonite are mentioned. Although these were not major study sites, sufficient information is available on them to make a preliminary assessment as to why they may contain aragonite. These other caves include Flying Fortress Cave and the B4-5 Extension at Bungonia near Goulburn, and Wyanbene Cave south of Braidwood. Aragonite deposition at Bungonia has some similarities with that at Jenolan in that dolomitisation of the bedrock has occurred, and the bedding or jointing is steep allowing seepage of water into the cave, with possible oxidation of pyrite. Aragonite is also associated with a mafic dyke. Wyanbene cave features some bedrock dolomitisation, and also features low grade ore bodies which include several known calcite-inhibitors. Aragonite appears to be associated with both features. Finally, brief notes are made of aragonite-like speleothems at Colong Caves (between Jenolan and Wombeyan), a cave at Jaunter (west of Jenolan) and Wellington (240 km NW of Sydney).

## Acknowledgments

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Analysis of samples was done with the assistance of several people and laboratories. These people are thanked for their contributions to this project: Mr George Navratil (School of Geosciences, University of Sydney) prepared the excellent thin sections from various rock samples. Mr Adam Sikorsky (Electron Microscope Unit, Sydney University) assisted with introduction to specimen preparation and how to get the most out of the X Ray Diffractometer. Dr Ian Kaplin (Electron Microscope Unit, Sydney University) patiently showed how to use the electron microscope. Mr Tom Savage (School of Geosciences, University of Sydney) assisted with lab equipment for grinding rock samples. Dr Phil Maynard (Dept. of Chemistry, Materials and Forensic Science, University of Technology, Sydney) assisted with photo scanning and after-hours use of microscope and camera, Raman spectrometer and printer. Dr Mike Lake (Chemistry Dept., University of Technology, Sydney) assisted with after hours use of the mortar and pestle for sample grinding. Dr Armstrong Osborne provided microscopes with camera attachment and also cut some of the softer specimens using an oil cooled saw. Dr Osborne is also thanked for supplying some of the underground equipment. Dr Derek Wyman (School of Geosciences, University of Sydney) assisted with interpretation of the granitic thin sections from Wombeyan.

Julie Bauer is thanked for the loan of the valuable thin sections of rocks from Bungonia which she prepared for her Honours work at the University of Wollongong. Additional thanks are given to Dr Mike Lake for patiently showing how to typeset using LaTeX 2$\varepsilon$.

Doing a proper academic study of this subject has required several repeat visits to the more important sites. For permission to visit and sample, many thanks are made to the following cave management people and organisations: at Jenolan Caves: Jenolan Caves Reserve Trust, Steve Riley and Dan Cove; at Wombeyan Caves: Jenolan Caves Reserve Trust, Mike and Annette Chalker; at Walli Caves: The Sydney Speleological Society and Peter Wellings; at Bungonia Caves: The NSW National Parks and Wildlife Service and members of the Bungonia Recreation Activities Group, Senior Rangers Jackie Taylor and Brian Richardson.

Visits to some of the study sites involved considerable logistical effort to move both the scientists and the equipment safely into and out of the cave. This also involved setting up ropes and ladders. Many thanks are given to the numerous cave surveyors, riggers, pack haulers, photographers and cheerful people from caving clubs who assisted on these trips. Particular thanks for logistical support is given to the following people and organisations: Sydney University Speleological Society members Dr Phil Maynard, Dr Mike Lake and Mr Geoff McDonnell are thanked for their help with rigging, surveying and equipment. Sydney Speleological Society members Peter Wellings, Ernie Byrnes, John Bonwick and Ian Wilde are thanked for their expertise as underground guides. Dr Armstrong Osborne is thanked for taking the time to discuss the underground features in situ, even though there were so many unexplained features in the caves that require further work.

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