Chapter 1

Introduction

1.1   Introduction to Cave Aragonite

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.

Aragonite is classified in the orthorhombic crystal system while calcite has been variously classified as belonging to the rhombohedral (Hurlbut 1970), hexagonal, trigonal (Berry, Mason & Dietrich 1983) or triclinic (Glazer 1987) crystal systems. Another polymorph of $CaCO_3$ which occurs in caves is vaterite. Vaterite is classified in the hexagonal crystal system and is less dense than calcite. It has been recorded from cave moonmilk and carbide dumps. It is not stable in the vadose environment and commonly reverts to calcite via aragonite. Vaterite also occurs in the shells of living gastropods. Other polymorphs of calcium carbonate include the high temperature and pressure Calcite-IV and Calcite-V which are not stable in near-surface environments (Carlson 1983).

Aragonite is harder and denser than calcite. The specific gravity of aragonite is 2.930 and for calcite it is 2.711. It often forms with a characteristic acicular habit known as "church steeples". It has one cleavage plane {010} (across the "steeples") while calcite has a perfect cleavage plane $\{10\bar{1}1\}$ producing angles of $75°$ and $105°$. Calcite readily twins on the cleavage plane whereas aragonite twins on {110}, producing pseudo-hexagonal columnar crystals. The hardness of aragonite is 3.5 to 4 and for calcite it is 3. Aragonite is more brittle than calcite (Berry et al. 1983).

Aragonite is mostly encountered in the marine environment, often the product of biological activity such as the growth of an organism's shell. When the organism dies proteins in the shell decay exposing the aragonite in the shell aragonite to the environment. 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 can also be the product of high pressure on calcite, or chemical influence.

Aragonite was said to be the third most common cave mineral after calcite and gypsum (Ford & Cullingford 1976, Siegel 1965). Hill & Forti (1997) stated that aragonite is the second most common cave mineral after calcite. The change in status may be due to the discovery of extensive aragonite deposits in caves such as Lechuguilla Cave (Carlsbad Caves National Park, U.S.A.).

In the cave environment, calcite deposits are frequently coloured by organic (humic and fulvic) acids whereas aragonite tends to be either white or coloured by metal impurities such as copper. It used to be thought that the brown colouration of cave calcite was due to iron oxy-hydroxide staining, but this has been shown to be incorrect (Hill & Forti 1997). The colour is mainly due to inclusions of organic material, including humic and fulvic acids. Kaolinite is frequently coloured by iron oxy-hydroxides and in some cases it is clay which coats speleothems.

The Cave Aragonite Problem

Aragonite is being actively deposited as a secondary mineral in the vadose zones of many limestone caves around the world (Hill & Forti 1997). Similarly, aragonite is also deposited in the phreatic zones of thermal and hydrothermal caves (Dublyansky 2000). Curl (1962) recognised that both these types of occurrence are problematic as aragonite is thermodynamically unstable in fresh water and readily reverts to calcite. So the problem is, why does aragonite exist at all in caves? What are the factors that allow aragonite to deposit in caves without reverting to calcite?

Curl suggested that aragonite forms and persists in caves because there is something present which prevents calcite from forming. Curl found one the earliest references to this concept was Saylor (1928) who suggested that various substances inhibited the crystallisation of calcite and thereby allowed the precipitation of aragonite.

Hill & Forti (1997) noted that in the thirty-five years since Curl's theoretical work on the subject, more experimental work has been done by others regarding the deposition of aragonite in both cave and non-cave environments, so by 1997 there was apparently some consensus determining what does and what does not cause aragonite to occur in caves. Hill and Forti discussed the following factors: magnesium, strontium, pH, supersaturation and rate of precipitation, temperature, pressure, speleothem surfaces and carbon dioxide content.

These aspects will be discussed in Section 1.2.

Aragonite is also reported to be present in the caves of NSW which have a vastly different geological history to those of Europe and North America. This thesis will investigate the presence of aragonite in cave deposits from both the local and international aspect.

1.2   Present Knowledge of Cave Aragonite

Introduction to Aragonite Studies

Most work on carbonate diagenesis has focused on the marine environment, where aragonite is a common mineral of great relevance to marine sediment diagenesis. Work on carbonate chemistry

is also extremely important to industry, for example the curing of concrete for structural stability.

Descriptions of work by various researchers on the chemistry of aragonite in general was summarised in Bathurst (1974) and Morse (1983). They referred to the experiments performed on solutions of calcium carbonate with varying amounts of chemical inhibitors such as magnesium ions. Bathurst noted that the solution needed to be supersaturated with respect to both calcite and aragonite in order for aragonite to deposit. Like Bathurst, Morse referred to the work of several others and compared some of the results. Bathurst also discussed the chemistry of aragonite precipitation in the marine setting, such as the precipitation of aragonite in lime muds, beachrock and mollusc shells. Tucker & Wright (1990) also discussed aragonite chemistry with more accent on diagenesis of marine carbonates.

Tucker (1991) defined low magnesium calcite to be calcite which contained less than 4 mole% $MgCO_3$, and high magnesium calcite which contained more than 4 mole% $MgCO_3$. More commonly, high magnesium calcites range between 11 and 19 mole% $MgCO_3$.

Walter (1985) compared the relative solubilities of several carbonate minerals and found that the theoretical dissolution rates of the minerals varied with pH.

For a given pH, high Mg-calcite dissolved at the fastest rate, then low Mg-calcite, then aragonite and then calcite which was the slowest. As the pH is lowered, first to dissolve is high Mg-calcite followed by low Mg-calcite then aragonite then calcite at the lowest pH. For a given dissolution rate, high Mg-calcite dissolves at a higher pH than does low Mg-calcite, or aragonite or calcite.

For the cave environment, a review and discussion of cave aragonite is given by Hill & Forti (1997). This is considered the main current reference for work on cave minerals compiled up to 1997. Hill and Forti summarised aragonite chemistry in the cave setting, and gave numerous references to work done on cave aragonite up to that date.

For either aragonite or calcite to deposit, there needs to be a source of bicarbonate ion, HCO_3^- in solution, a means of allowing carbon dioxide to outgas or be otherwise removed from the reaction, and the solution needs to be supersaturated with respect to calcium carbonate. In the cave environment, these conditions usually lead to the deposition of calcite, as that is the most stable polymorph of calcium carbonate for those environmental conditions.

Morse reviewed the work on kinetics in terms of dissolution of calcite, and noted that both precipitation and dissolution of calcite are hindered by the presence of chemical inhibitors. If these chemical inhibitors are available in the drip water of a cave, and the water is also supersaturated with respect to calcium carbonate, then calcite is prevented from precipitating and aragonite deposits instead.

Calcite-inhibitors work by blocking crystal growth points on the calcite lattice, allowing aragonite to deposit at the expense of calcite. Growth points on a crystal are frequently at edges or around dislocations (Mercer 1990). This concept is shown in Figure 1.1.

Morse noted that in general, inhibitors for calcite were found to have no effect on the aragonite crystal structure and may form solid solutions in the aragonite crystal. Both precipitation and
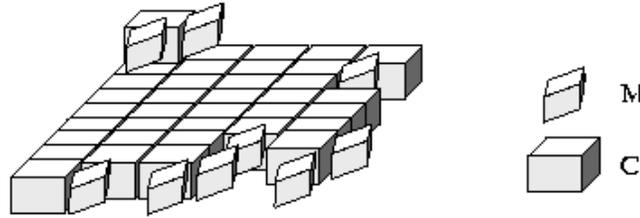
Figure 1.1: Schematic showing part of a developing crystal, with a sheet of unit cells such as calcite (C) whose growth points are being blocked by an inhibitor such as a magnesium compound (M). Based on ideas in Morse (1983) and Mercer (1990).

dissolution of calcite are affected by the presence of inhibitors. Some of the calcite-inhibitors listed by Morse include:

- magnesium

- heavy metals and rare earths (Cu, Sc, Pb, La, Y, Cd, Au, Zn, Ge, Mn, Ni, Ba, Co)

- sulfate, phosphate

Some organic compounds such as humic acids were mentioned by Morse as inhibiting the precipitation of aragonite. Other organic materials apparently inhibit both calcite and aragonite precipitation. However this appears to be due to the substances coating the mineral rather than any chemical kinetic effect.

Figure 1.2 illustrates the portion of the calcium carbonate phase diagram for the temperature and pressure ranges typical for caves in a meteoric environment. This is well within the stability region for calcite. For meteoric caves, the temperature of the cave is approximately that of the average annual temperature for the area. Included in this diagram are the typical ranges of temperatures for caves in a hydrothermal environment which are open to the atmosphere. In a closed environment, however, a water-filled cavity can experience much higher ranges of temperature and pressure.

Although Hill and Forti stated that temperature is not a factor in the precipitation of aragonite in caves, it is interesting to note the family of carbonate minerals which deposit at ambient pressures and low temperatures. The Pressure - Temperature (P-T) diagram of Carlson (1983) was extended by Tucker & Wright (1990) to include temperatures below $0°C$ and the hydrated calcium carbonates. They noted that at at sub-zero temperatures ikaite is stable (albeit at high pressure). Ikaite is $CaCO_3 \cdot 6H_2O$ which forms calcite pseudomorphs after ikaite as the temperature is increased above zero. Another hydrated mineral, monohydrocalcite $CaCO_3 \cdot H_2O$, is also unstable at the earth's surface and reverts to calcite. Monohydrocalcite has been recorded by Hill and Forti as occurring in some types of moonmilk and as hydrated spheroids in pools in cold caves. It is sometimes recorded along with aragonite. Aragonite is apparently not stable at sub-zero temperatures. Aragonite is stable, however, at much higher temperatures and pressures,
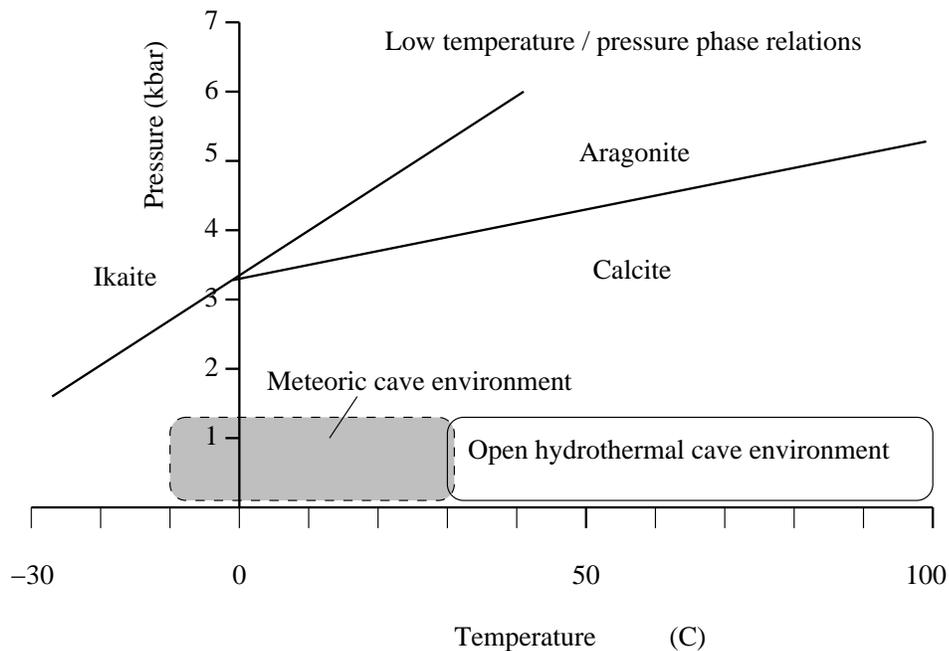
Figure 1.2: Stability Diagram for $CaCO_3$ at low temperatures and pressures shows that calcite is the expected polymorph in caves at atmospheric pressure. Based on Carlson (1983)

sufficiently to be useful as a guide to the P-T of formation of particular rocks such as blueschists around 4 to 6 kbar (Turner 1981, Essene 1983). The high magnesium content of serpentinites was noted by Essene to alter the P-T stability at which aragonite will form. The P-T stability for the formation of these rocks, however, is way above that found in meteoric caves.

For a given pressure, as temperature is increased, aragonite will generally convert to calcite. Similarly, for a given temperature, as pressure is increased, calcite will convert to aragonite.

In the marine environment, there are a number of factors that govern which polymorph of calcium carbonate is deposited. They include whether or not the deposition is related to the life processes of marine organisms and the chemistry of the water. Tucker (1991) discussed the Carbonate Compensation Depth (CCD) of the oceans. This depth is temperature dependent. It is the level at which calcium carbonate dissolution in sea water is matched by calcium carbonate deposition by organisms. For calcite, this depth in the tropics is about 4500 m to 5000 m. For aragonite in tropical oceans, the CCD is about 3500 m to 4000 m. This depth decreases as latitude increases, so that at seawater temperatures similar to those found near the polar regions, calcium carbonate dissolves in oceans at any level.

Palaeodeposits, Paramorphs and Marine Cave Cements

The aragonite crystal structure is sometimes preserved in sediments, even after the primary aragonite has been converted to calcite.

Kendall & Tucker (1973) described a crystal fabric found in limestones which resembled pseudomorphs of calcite after a "an acicular carbonate" which one assumes could be aragonite. The main arguments as to the precursor being an acicular carbonate included subcrystals diverging from the substrate, convergent optical axes, and curved twin lamellae.

Samples of marine aragonite were taken from a reef in Belize (British Honduras) (Ginsburg & James 1976). These were deposited in cavities and small caves within the barrier reef, at depths between 65 m and 120 m. The shape of the aragonite was as "mamelons": hemispherical aggregates of aragonite deposited on the ceilings of the voids in the reef bedrock. Occasionally they were deposited on the floors and sometimes filled the whole cavity. The limestone bedrock and the aragonite were both dated as Holocene (samples ranged from 7000 to 13000 years). The substrates to the aragonite included high Mg calcite, aragonitic coral or aragonitic algal plates. The development of needle crystals was influenced by the substrate, for example, oriented aragonite substrate grains produced larger mamelons than did unoriented grains. The strontium was present in the crystals in similar relative concentrations to that of Sr/Ca in sea water. Carbon and oxygen isotope ratios were consistent with that of marine limestones. The authors concluded that the mamelons were deposited shortly after the deposition of the limestone.

Robert Folk and Riccardo Assereto studied a piece of flowstone from Carlsbad Caverns, New Mexico (U.S.A.). In it were crystals of calcite which had once been aragonite. The original aragonite fabric such as feathery or squared terminations are preserved in the calcite. Small needle crystals were considered to be remaining aragonite. Unusually long length-slow calcite crystals were considered to have been previously aragonite or vaterite and have converted to calcite (Folk & Assereto 1976). Length-fast calcite crystals were described as being the most common type of calcite crystal development, with crystal elongation in the direction of the calcite optical axis (the c axis), and length-slow calcite crystals are elongated in the optically slower direction. They commonly exhibit undulatory optical extinction.

Assereto & Folk (1979) described the various aragonite, calcite and dolomite cements deposited in metre-sized cavities in marine shoreline tepee structures from the Triassic Calcare Rosso limestone of the Southern Alps of northern Italy. Although the original aragonite had been converted to calcite, all of the original fabric was preserved. The original depositional environment was described as near-marine semi-arid. The original aragonite was mainly deposited in the tops of the cavities as hemispherical crystal aggregates approximately 10 cm long, with aragonite flowstones deposited in the sides and bottoms. Aragonite hemispheres had been deposited on the bottoms of the cavities. Dolomite was deposited in small cavities within the original carbonate tepees. The aragonite became converted to calcite after the Mg/Ca ratios of water percolating through the deposit became less than about 2:1.

Braithwaite (1979) described crystal textures in a fluvial deposit in South Wales. This deposit was unusual in that the textures described were almost identical to those found in caves, yet these were in a surface stream associated with pisolites, stalactites and flowstone. The material was low-magnesium calcite. One of the crystal textures described was similar to an acicular calcium carbonate but Braithwaite did not consider that it had been aragonite as the growth faces were rhombohedral.

Mazzullo (1980) examined samples of limestone from the Capitan Limestone deposit, Guadalupe Mountains, New Mexico (U.S.A.) and found fan-shaped crystal aggregates in a replacement calcite fabric. The crystal terminations were squared, as is aragonite, but no curved twin lamellae could be found. Some fabrics had no uniform crystal optical extinction. Some inclusions followed the original aragonite crystal outlines.

Temperature

Cser & Fejérdy (1962) analysed samples from hydrothermal caves near Budapest and found that very few of their subaerial samples contained any aragonite at all. Dublyansky (2000) discussed the speleogenesis of hydrothermal caves of the Buda Hills in Hungary, and noted that thermal springs in the area had temperatures up to 65°C.

It was interesting to note that aragonite had been detected in the water coming out of nearby hot springs (subaqueous deposition). This aragonite converted to calcite when exposed to the surface environment.

In various aqueous solutions prepared from calcite or aragonite, calcite was found to be the only precipitate in a variety of temperature regimes (Siegel & Reams 1966). When carbon dioxide was bubbled through a solution prepared from artificially produced calcites and aragonites, there was a tendency to produce aragonite at higher temperatures e.g. above 65°C. This could be what is causing aragonite to precipitate (albeit temporarily) in the hydrothermal springs near Budapest. With solutions made from dolomite, Siegel and Reams found the precipitates were 90% magnesian calcite. More aragonite was precipitated as the temperature was increased above 50°C. Carbon dioxide exposure in this case did not affect the outcome.

Up until about 1962, an increase in temperature was thought to aid the formation of aragonite. This has been disputed by later researchers as summarised in Morse (1983). These researchers show that the long-term stability for aragonite at high temperatures is only achieved at high pressures. The stability diagram for aragonite (Figure 1.2) suggests that for the meteoric cave environment, temperature should not normally be a factor.

Temperature was not considered by Hill & Forti (1997) to be a factor in the occurrence of aragonite in meteoric caves. They noted that there appears to be more aragonite in cold caves than in tropical ones, which is the inverse of that suggested by previous researchers. Nearly all minerals listed in Hill and Forti were recorded from the vadose zone of caves.

Aragonite will convert back to calcite at high temperatures (e.g. over 100°C) and pressures around 3 kbar (conditions that do not apply to meteoric caves).

Leel-Ossy (1997) examined cave minerals occurring in the Jozsefhegy hydrothermal cave near Budapest, Hungary, and listed aragonite as one of the cave minerals associated with gypsum. However the aragonite and gypsum were considered to be much younger than the caves, and unrelated to the hydrothermal activity which formed the caves.

Association with Magnesium

The relationship between aragonite and magnesium has been described by Curl (1962) as being the strongest chemical influence in preventing calcite from depositing and allowing aragonite to deposit.

Eibengrotte is a cave in the Fränkische Schweiz (Germany) which is developed in massive dolostone. According to Fischbeck & Müller (1971), they found a number of minerals precipitating as surface coatings and as cave coral. These minerals were monohydrocalcite, hydromagnesite, nesquehonite, dolomite, aragonite and calcite. Both primary (from weathering of bedrock) and secondary dolomite was being deposited. The precipitation of aragonite was ascribed to the high magnesium content present in the cave seepage water. Monohydrocalcite was ascribed to an aerosol mode of formation after comparison with an industrial aerosol system.

Thrailkill (1971) sampled drip water and speleothems from various sites in Carlsbad Caverns and found that the "moonmilk" deposits were aragonite, hydromagnesite, huntite or dolomite and hydromagnesite. They did not contain calcite. Thrailkill found that the dripping water was considerably undersaturated with respect to hydromagnesite, but saturated with respect to calcite, aragonite, huntite and dolomite. Hydromagnesite only occurred where slow seepage allowed evaporation to take place. Dolomite and huntite are said to be formed by alteration from one of the other carbonates. Morse (1983) also listed magnesium as one of the calcite crystal poisoners.

Seemann included aragonite in a study of minerals of the Frauenmauer - Langstein cave system in Austria (Seemann 1985). He described its form in these caves as hard, small fine spikes, as coralloids and frostwork and as crusts. There was only a small amount noticed. These caves also had hydromagnesite and sulfate minerals.

Seemann wrote a summary of Austrian cave minerals (Seemann 1987). He included aragonite, and said that it occurred in many Austrian caves although not in large quantities. It occurred in conjuction with magnesium minerals as flowstone (often interlayered with calcite), in moonmilk growths, cave coral and anthodite type helictites. Seemann suggested that aragonite is deposited when the Mg/Ca ratio is 3:1 to 5:1.

The relationship between aragonite and magnesium compounds such as hydromagnesite has been described by others e.g. Hill (1987). Magnesium is one of the key components to aragonite deposition in many caves. Hill & Forti (1997) noted that with increasing percentage of magnesium in a mixed solution of magnesium and calcium carbonate, the following mineral se-

quence is deposited: calcite, high magnesium calcite, aragonite, huntite and hydromagnesite, magnesite. They noted that the presence of magnesium ions disrupts the calcite crystal lattice but not that of aragonite, and suggested that crystal poisoning by magnesium ions only affects the calcite crystal lattice, leaving aragonite to deposit freely given appropriate conditions of super-saturation. However Seemann (1985) showed that as the Mg content is increased, protodolomite and then dolomite can be produced (rather than aragonite, huntite and hydromagnesite).

In an overview of Venezuelan cave minerals, Urbani (1997) listed several caves as having aragonite present. One occurrence of aragonite was associated with sepiolite (a hydrated magnesium silicate) and another occurrence was developed in association with dolomite. Urbani also suggested that the aragonite crystallisation may have been promoted by a high concentration of strontium.

Frisia, Borsato, Fairchild & Longinelli (1997) examined a number of stalagmites and drip points in Clamouse cave (France). Aragonite speleothems were being precipitated only where there was dolomitic bedrock, and even then only when the drip rate was very low. The authors suggest that the role of magnesium is to inhibit the growth of calcite, either by crystal poisoning or by "difficulties in rapid dehydration of the Mg^{2+} ion". They found that the Clamouse cave water was not particularly high in dissolved Mg compared with other sites, and suggested that the structure of the nucleation sites may play a greater role. Frisia, Borsato, Fairchild & Selmo (2001) examined both aragonite and calcite speleothems in Clamouse cave. Calcite speleothems had transformed from aragonite precursors over about 100 years. They suggested speleothem aragonite is a palaeo-aridity indicator.

Niggeman, Habermann, Oelze & Richter (1997) examined coralloids deposited in windy areas of several caves in Germany and Austria. They found that more aragonite was deposited in the areas where the bedrock contained dolomite, either primary dolomite or from hydrothermal alteration of bedrock. They recorded the following data regarding the Mg/Ca ratio as mole % and the polymorph deposited:

At Site 1 with Mg/Ca <0.5: calcite
At Site 2 with Mg/Ca 2–3:   calcite + aragonite
At Site 3 with Mg/Ca 3–6:   calcite + aragonite
At Site 4 with Mg/Ca 3–23: calcite + aragonite

They also recorded the following minerals associated with Site 4 (Grauner Walls): Mg calcite, aragonite, monohydrocalcite, nesquehonite and hydromagnesite.

Bohemia Cave is in the Mount Owen Karst Area of the South Island of New Zealand. It was discovered in 1990 by members of the Czech speleological club Alberice. A large cavity was discovered in Bohemia Cave and its mineralogy was briefly summarised in Tásler (1998). The cavity itself was called "Dream of Alberice Cavers" and measures approximately 80 m wide by 650 m long which puts it in the list of large caverns by world standards. According to Tásler, most of the ceiling, walls and floor of this cavern are covered with aragonite speleothems of various sorts

together with hydromagnesite "snow". Tásler described the overlying bedrock as dolomitic Ordovician units of the Mount Arthur Group whereas the underlying rock was phyllite, with most of the cavern development apparently in the phyllite. Deposits of limonitised pyrrhotite were found near the junction area. According to Tásler, 90% of the speleothems are aragonite. Other minerals recorded include calcite, hydromagnesite, dolomite, opal, Fe- and Mn- hydroxides, gypsum and sepiolite. The contact area between the two different bedrock types was described as exceptionally rich in aragonite. Aragonite speleothem types recorded were stalactites, flowstone (including some yellow and yellow-red flowstone), stalagmites, soda straws, flos ferri (as thin intertwined branching forms), "winding needles", helictites, crystal coatings, linear needles, anthodites, "ball of threads", needle clusters. The needles and helictites were often hollow but there were also solid needles. The different speleothem types were often clustered together and sometimes with hydromagnesite coatings on the tips. Grass shaped aragonite crystals as ultra thin needles were found in the insides of some hollow speleothems such as straws.

In France, there are a number of caves with outstanding aragonite deposits. In most cases, the aragonite is associated with areas of metamorphosed dolostone. Some deposits are associated with gypsum and sulfur, and some with hydromagnesite (Cabrol, Gill & Gunn 2001).

In several caves near Waitomo, New Zealand, deposits of aragonite occur along with hydromagnesite or other magnesium-based compound: the mineralogy has apparently not been studied. Overlying pyroclastic deposits influence mineralogy and cave water chemistry at Waitimo Caves (P. Maynard, pers. comm.).

Strontium

Tucker & Wright (1990) found that strontium substitutes for calcium in both lattice and non-lattice sites for both calcite and aragonite. This complicates the chemistry. Strontium ions are a common trace constituent of seawater. However strontium often deposits as strontium sulfate and it may be the sulfate component which is the calcite-inhibitor rather than the strontium.

Strontium carbonate (strontianite) is rare in meteoric caves but celestite (strontium sulfate) is more common (Hill & Forti 1997). It sometimes occurs with aragonite and sometimes with high or low Mg calcite. Strontium has often been quoted as being a factor in the precipitation of aragonite, but Hill and Forti said that opinion was divided on the matter. They noted strontium readily substitutes for calcium without disrupting the aragonite crystal lattice so was unlikely to be a factor.

Association with Clay

Craig, Horton & Reams (1984) suggested that aragonite is nucleated by clastics in caves, based on their studies of speleothems from caves in Missouri (U.S.A.) but were unable to produce aragonite in an experiment mimicking current cave conditions. Instead, vaterite was produced.

In the aragonite caves of France, the aragonite is often associated with clays (Cabrol et al. 2001). Aragonite was found only in the clayey areas (David Gill, pers. comm.).

However, clays are one of the most common minerals found in caves, and they are frequently the substrate for a number of calcite speleothems such as flowstone and stalagmites.

Association with Vaterite

Hill & Forti (1997) noted that vaterite occurs in caves in association with moonmilk and sediments. Vaterite was said to be associated with the following minerals: hydromagnesite, baylissite, calcite, aragonite and monohydrocalcite. It was suggested that vaterite can form when calcium carbonate is precipitated under conditions of high CO_2 degassing. They suggest that vaterite reverts to aragonite and calcite over time.

Possible Association with Carbide Dumps

Carbide (calcium carbide) is used as a lighting source for caves in many parts of the world. The chemical reaction involves dripping water on calcium carbide to produce acetylene gas which is controlled and ignited to provide a bright flame. The solid waste product is mostly calcium hydroxide and this is occasionally dumped in caves. Cavers have noticed an unusual form of heligmite known as "carbidimites" associated with carbide dumps which have not been used for some time (Hill & Forti 1997). These are produced by the reaction between the spent calcium carbide dump (mostly calcium hydroxide and impurities such as arsenic) with cave seepage water. Carbidimites are characterised by an inverted horn shape, and a tendency to change shape over a short period of time (months) compared with other speleothems. Sarigu (1999) included photographs of carbidimites from a cave in Italy and discussed their mode of formation. Sarigu suggested that they form by the carbonation of calcium hydroxide with CO_2 to calcium carbonate and water, further carbonation to calcium bicarbonate and also the direct carbonation of calcium hydroxide to calcium bicarbonate. It was not stated as to which polymorph of calcium carbonate is taken. However the photographs and text note that the crystals deposited in the tubes as feathery shapes, rather unlike calcite and more like aragonite or possibly vaterite. Hill and Forti claim that most carbidimites are calcite but some are vaterite.

Influence by Sulfates

In caves containing gypsum (hydrated calcium sulfate), both calcite and aragonite can occur with the gypsum. Great Onyx Cave, Kentucky (U.S.A.) (Siegel 1965) contains this mineral association. Morse (1983) lists the sulfate ion as one of the calcite crystal inhibitors.

Carlsbad Caverns lie in the Guadalupe Mountains, Carlsbad National Park, U.S.A. Carlsbad Caverns contain extensive deposits of aragonite associated with gypsum and sulfur. This has been discussed in Thrailkill (1971) and Hill (1987). Thrailkill noticed that where there was gypsum,

there was very little calcite. According to Hill, the caves were formed in several stages. One of the later stages involved H_2S seeping though joints from nearby oil well brines. The reaction between H_2S and water formed sulfuric acid which corroded the porous limestone to form gypsum and large caves. The origin of this H_2S is apparently bacterial. Hill did not consider that the caves were formed at high temperatures (the present cave temperatures are about $20°C$).

According to Hill, aragonite in Carlsbad Caverns occurred as rims, stalactites, hollow stalagmites, moonmilk, frostwork, anthodites, flowstone, beaded helictites. Hill noted that there were not as much secondary sulfate in Carlsbad Caverns compared with carbonates, despite the large gypsum blocks present. The sulfate speleothems that were present apparently had a sulfur isotope signature closer to that of the overlying pyritic beds rather than that of the gypsum blocks.

Hill recorded the list of speleothems and minerals that were deposited near lakes in Carlsbad Caverns. In the pools were calcite "cave clouds" (a mammillary coating). Closest to the pools were rounded cave popcorn (mostly aragonite). Further up were shrub-shapes of aragonite frostwork and further up again were corroded speleothems.

Other outstanding caves which contain aragonite associated with gypsum include Cupp-Coutunn Cave (Turkmenistan) and Alum Cave (Vulcano Island, Sicily - Italy) Hill & Forti (1997).

Lechuguilla Cave in Carlsbad National Park was well illustrated in Speleo Projects (1998). This cave has a similar sulfuric acid speleogenesis as has Carlsbad Caverns. Both subaerial and subaqueous gypsum and aragonite speleothems occur in this cave, although they do not appear to occur together (or have not been photographed together). Possibly in the caves of the Guadalupe Mountains, aragonite speleothems and gypsum speleothems have a different origin. Lechuguilla cave has subaqueous speleothems such as selenite needles, calcite pool crystal and subaqueous calcite helictites. Aragonite has not been reported from the pool deposits. Calcite speleothems are apparently not as common in Lechuguilla Cave compared to other caves according to Speleo Projects (1998).

Cser & Fejérdy (1962) described aragonite precipitating in hot springs in hydrothermal caves in Hungary as well as subaerial deposits. Leel-Ossy (1997) mentioned that aragonite was a relatively young (subaerial) deposit in the in the Jozsefhegy Hydrothermal Cave (Hungary). Other reported minerals included calcite and gypsum.

Minerals of Humpleu cave in Romania were examined by Ghergari, Onac & Fratila (1997) as mainly wall crusts. Minerals included gypsum, calcite, aragonite and a variety of sulfate minerals, apparently the breakdown products of bat guano. They considered some of the calcite was a paramorph after aragonite.

However no aragonite was found by Turchinov (1997) in his description of cave minerals from the Western Ukraine gypsum caves. The minerals found included gypsum, celestite, calcite, rhodochrosite, quartz variety chalcedony, iron and manganese minerals and ice.

In Flower Cave, in the Puketiti district near Waitomo, New Zealand, cavers have reported aragonite deposits associated with large gypsum extrusions and crusts. The gypsum extrusions

are typically 200 mm long. Pool crystal deposits in that cave have been described as aragonite, but the actual mineralogy has not been confirmed. Photographs with cavers seem to indicate aragonite crystal sizes of around 20 to 30 mm long in aggregates and a hydrothermal influence on cave development has been suggested.

Influence by Humidity

Siegel & Reams (1966) cited the work of Pobéguin in 1955 and 1957 which suggested that aragonite precipitation is enhanced by high rates of evaporation. Aragonite is 16% more soluble than calcite, so to precipitate aragonite the solution must already be saturated with respect to calcite. One way of getting aragonite to precipitate first therefore would be to increase the rate of precipitation so that it is too fast for calcite precipitation. Siegel and Reams suggest that a rapid rate of evaporation can result in the solubility product of aragonite to be exceeded, allowing both calcite and aragonite to be deposited.

Hill & Forti (1997) described a "popcorn line" in Carlsbad Caverns as being due to a humidity effect. Cave Popcorn is a speleothem form which can be composed of calcite or aragonite, and according to Hill and Forti is formed by air moving over the speleothem surface, promoting mineral precipitation by evaporation of water at the outer surfaces. Some caves have a pronounced flow of cold dry air into the cave during winter, and this is apparently more significant to the development of this type of speleothem than is the loss of CO_2. Aragonite frostwork and coralloids are similar speleothem forms, with frostwork being formed at times of high humidity and coralloids formed when the humidity is lower and the rate of precipitation higher, producing a smaller crystal size.

On the other hand, Cilek, Bosak, Melka, Zak, Langrova & Osborne (1998) argued that the high humidity in the Ochtiná Aragonite Cave was one of the reasons why aragonite was depositing in the cave. The humidity in this case was kept constant by the buffering effect of saturated ochres. The ochres contained 47% to 56% water by weight, and this significantly influenced the cave's climate. This was said to aid the precipitation of large aragonite speleothems. However most caves have a high humidity buffered by clays and sediments. It is more likely that the constant high humidity controls the crystal size and growth rate of the deposited calcium carbonate rather than the polymorph.

Supersaturation and Rate of Deposition

Curl (1962) mentioned that only minute amounts of foreign material is required to alter the form deposited (both crystal shape and polymorph).

Siegel & Reams (1966) quoted Pobéguin's work of 1955 and 1957 which suggested that a high rate of deposition favours aragonite a little more than calcite (see related comments on humidity).

Theoretical growth rates of stalagmites with both stagnant and flowing water were calculated by Dreybrodt (1981). The limits to precipitation in the case of stagnant films was the ability for the film to outgas CO_2 whereas for running water, this was not a factor.

Supersaturation and rate of deposition were considered by Hill & Forti (1997) as being a factor in the precipitation of aragonite. They suggested that at very low rates of deposition, aragonite is favoured over calcite, in contrast to Siegel & Reams above.. At very high rates of deposition, vaterite is favoured and this may in time convert to aragonite. At other rates, calcite is the favoured polymorph. They noted that supersaturation can be achieved in dry caves with a high loss of CO_2 or a high evaporation rate, and suggest that these conditions also lead to increased percentage of magnesium in the remaining solution.

Supersaturation is a necessary requirement for the precipitation of either calcite or aragonite. Supersaturation can be achieved either by physical means (e.g. evaporation) or chemical means. By allowing CO_2 to escape, the solution may become supersaturated with respect to either calcite or aragonite (or vaterite). The solution can also become supersaturated by application of the common ion effect. For example, the addition of calcium sulfate to a supersaturated solution of calcium carbonate will cause the less soluble substance (calcium carbonate) to deposit.

Fast deposition commonly occurs near cave entrances where evaporation is highest, yet the material deposited is primarily calcite. Aragonite has been recorded from near cave entrances associated with monohydrocalcite according to Hill and Forti.

Aragonite can also occur in areas with slow deposition rates. An example of cave aragonite with an extremely slow rate of deposition was given by Bosák, Bella, Cílek, Ford, Hercman, Kadlec, Osborne & Pruner (2002) for the Ochtiná Aragonite Cave. Three generations of aragonite deposition were identified. The oldest generation detected (U/Th dating) was 138000 years old.

In Clamouse Cave (France), Frisia et al. (1997) found that the drip rate made the difference between aragonite and calcite precipitation. Aragonite was precipitated only under the slow drips in areas with dolomitic bedrock. Apparently the slower rate allows more takeup of magnesium from the bedrock, and reduces the rate of outgassing of CO_2.

Carbon Dioxide

Carbon dioxide content was also considered by Hill & Forti (1997) to be a factor in the precipitation of aragonite in caves. They quoted the work of Cabrol in 1978 and Courdry and Cabrol in 1982 in which a stratification line was noted in some caves in France. Above this line there was calcite but no aragonite whereas below the line, aragonite was deposited. This was ascribed to a lowering of the supersaturation of the seepage water to favour the deposition of aragonite over calcite.

Pressure

Pressure was considered to be a possible factor in the precipitation of aragonite in caves according to Hill & Forti (1997), referring to a personal comment by B. Rogers in which aragonite was described from an active fault in a cave. Calcite will readily convert to aragonite at high pressures. This situation is unlikely in most cave environments which are generally considered to be atmospheric temperature and pressure due to their near-surface location.

Speleothem Surfaces

Speleothem surfaces were also considered by Hill and Forti to be a factor in the deposition of aragonite. They referred to cases in which aragonite was formed over corrosion surfaces, or over older aragonite speleothems. They warned however that unless properly analysed, it can be impossible to distinguish between calcite and aragonite and mentioned that one researcher found one fifth of a supposedly aragonite collection was in fact calcite.

Speleothem surfaces and substrates are generally an important factor for the precipitation of most speleothems. The presence of seed crystals aids crystal growth, so calcite will tend to deposit on an existing calcite substrate following the pre-existing crystal boundaries, and aragonite may be similarly precipitated provided the solution is already supersaturated with respect to aragonite. Some substances, if present on the surface of a speleothem, inhibit the precipitation of either calcite or aragonite. Tucker & Wright (1990) noted that in the marine situation, oöids are frequently inhibited from developing larger than small grains because of a coating of organic material. Mineral fragments such as grains of quartz and clays were observed to be nucleation sites for aragonite in some Missouri (U.S.A.) speleothems (Craig et al. 1984). In an attempt to produce aragonite, they made a solutions of calcium carbonate and added various concentrations of clay in suspension. The clays comprised illite, kaolinite and chlorite (no carbonates or quartz). The resulting calcium carbonate precipitate was vaterite and calcite, not aragonite, with the ratio of vaterite to calcite increasing in proportion to the amount of clay present. Above 80 mg/l clay concentration, only vaterite was produced.

Associations with Biological Activity

"Moonmilk" is a white pasty material found in many meteoric caves around the world. In its typical form, it is a white pasty substance usually composed of fine rods of calcite deposited *en echelon*. A few minerals look superficially like moonmilk e.g. huntite, hydromagnesite and aragonite in suspension. It also occurs in caliche soils as described in Phillips & Self (1987). By definition, true moonmilk is at least 90% calcite (Fischer 1988). Moore & Sullivan (1997) described single needles of calcite from moonmilk as having a small microorganism body attached at one end of the fibre.

In the marine environment, aragonite is commonly produced as the result of biological activity, e.g. the influence of proteins in sea shells (Tucker & Wright 1990). The variety of carbonates precipitated in response to biological processes are calcite, Mg-calcite, aragonite, vaterite, monohydrocalcite, dolomite and amorphous carbonate.

Northup, Reyenback & Pace (1997) described evidence for microorganisms in meteoric cave moonmilk comprised of calcium carbonate as calcite or aragonite. Such microorganisms are not present in moonmilk composed of magnesium minerals.

Stable Isotope Studies

Cilek & Smejkal (1986) took samples from sectioned calcite-aragonite stalactites from the Stary hrad cave (Low Tatras) and from two Bohemian Karst caves. They analysed the stable C and O isotopes of the calcite and aragonite. The values for δ^{13}C were mostly negative for calcite and positive for aragonite. In general, the values for δ^{13}C and δ^{18}O for aragonite were greater than those for calcite. Generally, an enrichment in the heavier isotope can indicate a higher rate of evaporation. It is also temperature dependent. Cilek and Smejkal interpreted the difference as indicating a change in the way the two minerals had been precipitated. They suggested that the mode of formation for the calcite was based on the outgassing of CO_2 (the normal karst process) with minimal evaporation whereas the aragonite parts were mainly formed by very slow evaporation, so slow that biogenic effects are suppressed.

However, in Gillieson (1996), this same process was described and biological processes apparently enrich the calcite or aragonite with heavier oxygen isotopes. This process is also temperature dependent, with higher temperatures leading to heavier oxygen isotopes in precipitates.

Where the C and O isotopes are correlated (as is the case for these samples), both authors agreed that it is suggestive of an evaporative condition.

In Clamouse Cave (France), Frisia et al. (1997) similarly found that the isotope ratios suggested that the aragonite deposits were formed under more evaporative conditions than the calcite ones. They found it difficult to accept this standard interpretation because all their aragonite samples were collected in areas of no wind, constant temperature and very high ($\sim 99\%$) humidity. Instead, they suggested there is another mechanism responsible for the concentration of the heavier isotopes in the aragonite samples, and this is a chemical kinetic effect caused by the slow outgassing of CO_2. Apparently there is no data on the fractionation kinetics of oxygen isotopes as ions diffuse across the aragonite crystal surface.

Niggeman et al. (1997) compared the stable isotopes of calcite and aragonite coralloids. They also noted that the aragonite samples tended to have higher concentrations of these heavier isotopes. They attributed this to prior concentration of the isotopes in the solutions from which the carbonates were precipitated. This was because all samples were taken from draughty areas with apparently similar climatic conditions.

Cilek et al. (1998) also measured C and O isotopes in Ochtiná Aragonite Cave which has very little air movement and very high humidity. The isotope ratios for the aragonite were similar to those for calcite speleothems from the well-ventilated Starý hrad Cave. They concluded that the aragonite was deposited as a result of slow CO_2 outgassing.

Association with Phosphates

In a description of the mineralogy of Kartchner Caverns, Arizona (U.S.A.), Hill (1999) mentioned that the caves have some deposits of aragonite. There is little evidence of magnesium playing a part in its deposition as the limestones are particularly pure. Kartchner Caverns has large deposits of phosphatic minerals derived from bat guano, as well as a large quantity of iron oxides, silicates and unusual clays including rectorite. Sulphates were associated with the bat guano. It was suggested that the cave mineralisation may have had a partially hydrothermal origin. The aragonite deposits were located at the ends of passages where one would expect the humidity to be high. Little was said about the aragonite as it was not a major feature of the cave.

Humpleu cave in Romania also has an association of aragonite with bat guano phosphates. However Ghergari et al. (1997) considered the phosphate to be more recent than the aragonite based on the physical location of the minerals in the cave (the phosphate was on the lower parts of the passage whereas the aragonite was in the upper parts). Gypsum also occurred in association with the aragonite. Ochres were also detected.

Association with Ochres and Gossans

One of the photographs in Speleo Projects (1998) showed a cluster of aragonite popcorn and frostwork with a red, black and orange ochreous substrate, contrasting with the corroded and porous white bedrock.

In Slovakia there are extensive aragonite deposits in show caves. Some of these deposits are associated with "ochres" containing Fe, Mn and Mg as described in Cilek et al. (1998) and Bosák et al. (2002). Aragonite occurred as three forms: the oldest material was kidney-shaped and recrystallised; the intermediate aragonite speleothems occurred as long needles and helictites. The youngest generation occurred as small fan-shapes (frostwork) and helictites. Aragonite also occurred as flowstone. Ochtiná Aragonite Cave also has deposits of goethite and limonite, with the goethite of a particularly small crystal size. One aspect of the ochres in Ochtiná Aragonite Cave are their high water content, 47% to 56%, and it was thought that this material was buffering the humidity in the cave, keeping it at a constant high level. The two main factors leading to the deposition of aragonite in the cave were considered to be the presence of Fe and Mn in solutions, and the high humidity.

Interspersed with the ochres was black manganese oxides including asbolane and birnessite. Some of these manganese minerals were ascribed to microorganism activity. Hydromagnesite was found in small quantities associated with the ochres.

Although it is tempting to say that the presence of iron may influence the precipitation of aragonite, it is more likely that the aragonite is precipitated under the influence of other materials present in the iron oxides such as manganese, apatite or La-Nd-bearing phosphates which were also detected in the cave. Commonly, cave sediments are comprised of layers of clastics and calcite. The clastics usually include a component of iron oxy-hydroxides. The calcite layers usually contain no iron oxy-hydroxide (although they may be stained brown by humic acids). It is unusual to find aragonite present in such sediments. Where aragonite occurs with iron-rich sediments, the sediments are often hard yet porous, and it may be these physical qualities that make it possible for ions (e.g. magnesium or sulfate) to influence the form taken by precipitating calcium carbonate by keeping the humidity high, acting as a sturdy substrate and allowing slow movement of ions in solution.

Flos Ferri

Another aragonite occurrence outside of Australia is as flos ferri ("flowers of iron") in conjunction with cavities in iron mines. The Styrian (Steiermark, Austria) iron deposits had world-renown occurrences of aragonite in the form of tangled masses of helictites known as flos ferri.

There is a photograph of flos ferri aragonite from Styria on page 206 of Hurlbut (1970). Hurlbut stated

> "*When aragonite in coral-like aggregates is found on the walls of iron mines it is called "Flos Ferri," meaning* iron flower. *This specimen* (depicted) *is from Styria, Austria, which is famous for this variety of aragonite.*"
>
> (Hurlbut 1970)

Most of this material has now been mined away according to Stephan Kempe (pers. comm., August 1997). I have seen some large specimens of flos ferri aragonite in the private museum at the Glacier Gardens at Lucerne (Switzerland). Here, it is locally known as Eisernblut (iron blood) although it is white. It comprises tangled masses of helictites with a radius of curvature of around 5 to 10 mm. Other museums also have samples of this material, such as the Natural History museum at Lucerne. There is a sample of aragonite flos ferri from Steiermark (Austria) held in the Australian Museum collection, cat. no. D19158. It has a similar appearance to the Glacier Gardens sample.

Although Hurlbut (1970) did not say specifically which iron mineral was associated with flos ferri, he did say:

> *"the Austrian deposit at Erzberg in Styria is the only concentration of siderite of sufficient size and purity to be considered a major source of iron. Here a folded limestone has been replaced by massive siderite through the agency of iron-bearing waters to form a deposit of many tens of million tons."*
>
> (Hurlbut 1970)

Eisenerz is now a show-mine and is no longer worked (Austrian tourist bureau).

According to Shaw (1992), the word *flos ferri* was first used by John Hill in 1748 to describe a twisted form of helictite found in mines and in some Mendip (UK) caves. Shaw included two sketches by Patrin (1803) depicting "flos-ferri" and these resembled the flos ferri samples mentioned earlier. Shaw described flos ferri as a particularly slender variety of helictite which is made of aragonite and often found in iron mines. Hill and Forti described flos ferri, however, as a variety of anthodite which resembles a sea urchin (Hill & Forti 1997), and defined flos ferri in their Glossary as a quill-like variety of anthodite. These differences in terminology appear to be localised to particular countries and show caves.

This thesis will use the definition of flos ferri as used by Patrin, Shaw and Hurlbut.

Blue Speleothems

The copper ion can form a solid solution in the aragonite crystal structure (Morse 1983).

Aragonite in the form of blue speleothems occurs in conjunction with deposits of heavy metals (e.g. copper) e.g. the Blue Cave, France, (Hill & Forti 1997). Not all blue speleothems are aragonite, however, as a number of other cave minerals have been recorded in Hill & Forti (1997) such as allophane and some clays, and some calcite speleothems are described as "blue". The colour therefore cannot be used as a diagnostic tool to determine whether the speleothem is calcite or aragonite.

Blue "Larium stone" from a mine near Larium, Greece has been traded amongst mineral collectors. I have seen a sample of this material. It is aragonite with copper carbonate present as discrete centres rather than being dissolved in the aragonite. A photograph of this material held by collectors and advertised on the Internet shows a light blue stone with light and dark banding characteristic of a sedimentary deposit. Smithsonite was also mined near the town of Larium (Zn is one of the calcite-inhibitors listed by Morse (1983)).

Aragonite is typically white or colourless. It has also been recorded as blue, green, brown, yellow or orange depending on which trace metals are dissolved in the aragonite lattice.

1.3   Historical perspectives of aragonite in Australian caves

Shaw (1992) discussed cave aragonite in caves in a historical context. The earliest reference he found to cave aragonite was by Dr Charles S. Dolley (1887) describing aragonite spicules depositing in a hollow on a helictite in Luray Cavern (U.S.A.). Shaw also included earlier references to flos ferri speleothems by John Hill (1748) and sketches by Patrin (1803).

C.S. Wilkinson, NSW Government Geologist, visited the "Belubula Caves" (Walli Caves – see Figure 1.3) near Licking Hole Creek, which is a tributary of Liscombe Pools Creek, between Orange, Canowindra and Mandurama about 1870 shortly after their discovery by road contractors (Wilkinson 1892). This article was reproduced posthumously by the Department of Mines from an original publication in the Sydney *Town and Country Journal*, Sept. 9, 1876, p. 419. Concerning aragonite in "The Long Cave," Wilkinson said:

> *Another small cavern, rather difficult to get into, has a mound of white stalagmite with a tracery-marked surface, meeting which, and hanging in the centre are two stalactites covered with translucent spikes curving in all directions. These singular stalactites are seen in some of the other caverns; also groups of long radiating crystals of aragonite.*

> (Wilkinson 1892)

Whether Wilkinson actually sampled the aragonite is not known. From Wilkinson's report in 1876 there was very little reference to NSW cave aragonite until Frank (1974) described the Deep Hole (cave) at Walli almost a hundred years after Wilkinson's inspection of the same area. The lack of scientific interest in the subject in NSW is perplexing, given the amount of research being conducted in cave aragonite in other countries during that period. Historical aspects of cave science in NSW from 1830 to 1987 were discussed by Osborne (1991).

Dunlop (1977) described the show caves at Jenolan. In 1903 the Skeleton Cave (now Cerberus Cave, a branch of the southern show caves) was discovered, although other reports suggest an earlier date (Middleton 1991). It has a speleothem group known as the Arabesque: a combination of (apparently aragonite) stalactites, stalagmites and helictites. Also in 1903 the River Cave was discovered. This is also a branch of the southern show caves and has speleothems known as "Furze Bushes" which are very similar to the Arabesque. Dunlop described the spiky "Furze Bushes" in some detail, with pictures. They are now known to be aragonite (Ross Pogson pers. comm.).

The caves of Tasmania are well-known for their displays of aragonite, yet there was little scientific work done on their mineralogy in the 19th century. Most people visiting the caves did so out of curiosity and not research. Generally cavers and tourists are not mineralogists and do not have the resources to analyse minerals.
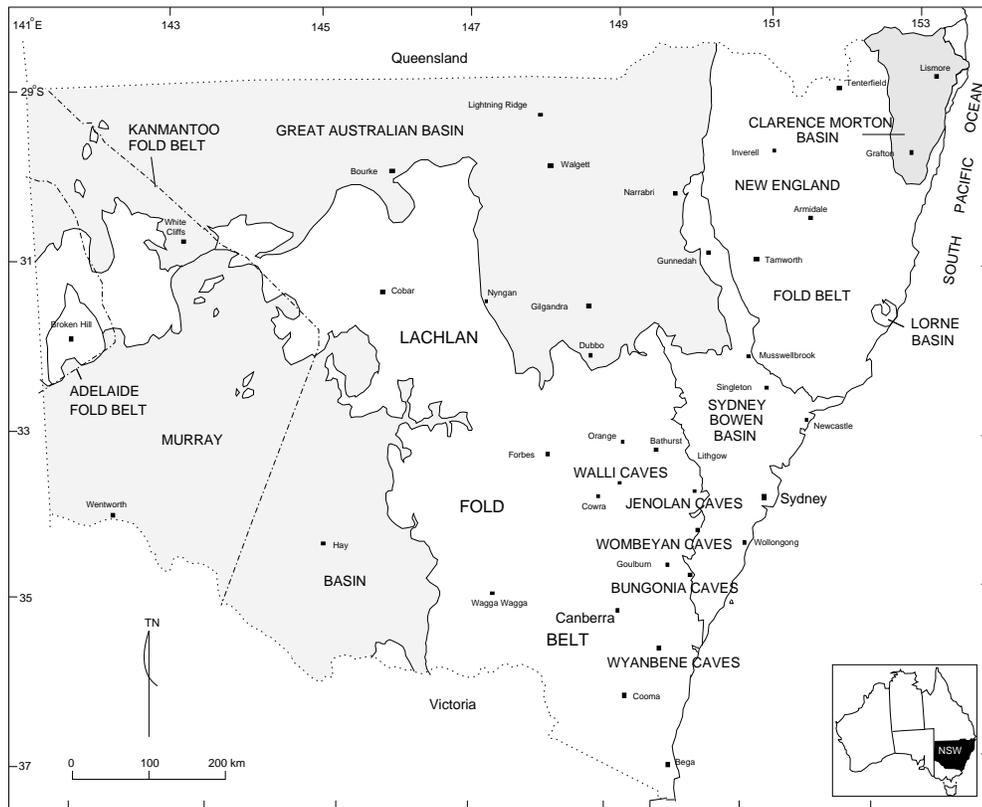
Figure 1.3: Map of NSW showing location of caves in this study, with major tectonic features. Tectonic overlay re-drawn from NSW Department of Mineral Resources; Australian map from Geosciences Australia.

One problem with reporting minerals from caves is an ethical one. Over-collecting is a world-wide problem coupled with the lack of protection for the caves' contents in many places. This has meant that discoverers of unusual cave minerals have often had to keep their discoveries secret.

Angel Cave, a small sea cave near Cape Schanck on the southern coast of Victoria was reported to contain pisolites of calcium carbonate (Baker & Frostick 1947). The acicular carbonates were analysed using wet chemical methods and found to be calcite, not aragonite. In the same article, pisoliths from a mine at Bendigo, Victoria were found to contain aragonite and possibly $MgCO_3$ associated with siderite.

Frank (1974) described the development of Walli caves based on work done in 1968 and 1969. This is the first published reference to the use of XRD to analyse aragonite from a NSW cave. Concerning aragonite in Deep Hole (Deep Cave), Frank said:

> *X-ray diffraction of some speleothems on the wall at 105036, Figure 5, showed them to be aragonite.*
>
> (Frank 1974)

Welch (1976) published a catalogue of caves at Jenolan, north of the show caves. Glass, Hennings and Wards Mistake caves were said to contain "aragonite". A photograph showed an acicular mineral in Hennings Cave.

Dunkley & Anderson (1978) included a photograph of "aragonite" near Upper Oolite Cavern, Mammoth Cave, Jenolan. Near the Pisa Chamber, there were "*a number of mud tunnels . . . one containing a unique cluster of aragonite crystals.*" (Dunkley & Anderson 1978)

Webb & Brush (1978) analysed aragonite from Wyanbene Cave near Braidwood, southern NSW. The samples were found loose on the ground underneath anthodites near Frustration Lake. XRD analysis showed the samples were both calcite and aragonite. SEM photographs showed the general habit of the anthodite fragments.

Osborne (1978) reported calcite which may have inverted from aragonite, in a geological description of Cliefden Caves, central NSW. He also described blue aragonite speleothems in the Australian Museum minerals collection, specimens D36380 and D23544 from Boonderoo Cave. There is no record of the substrate from which it was taken. A thin section (cat. No. USGD 54322) of the base of the small blue stalactite (specimen D36380) showed an inner sparry calcite layer coated with a blue aragonite layer, determined by XRD. The aragonite layer had radially oriented acicular crystals. The same radial structure was noted on the broken tip of the stalactite in Boonderoo Cave. The blue stalactites in both Boonderoo Cave and Murder Cave were developed at two different junctions of limestone members. Using revised stratigraphic nomenclature (Webby & Packham 1982), the one in Murder Cave is developed at the junction of two sub-units (upper and lower) of the Belubula Limestone, and the one in Boonderoo Cave is at the junction of the Belubula Limestone and Vandon Limestone.

Dyson, Ellis & James (1982) included a photograph of fine spiky "aragonite" helictite clusters on the walls of Shawl Cave, Wombeyan. There was no description of the substrate, or details of any tests applied.

Ralston (1989) recalled the discovery in 1964 of the Barralong Cave, Jenolan (southern show caves), saying on page 57: "*Hidden in its own little crevice is a Christmas Tree of aragonite.*"

Osborne (1990) examined palaeokarst deposits in the show caves at Jenolan. He mentioned that most of the Jenolan show cave's aragonite deposits were hosted on a substrate of laminated dolomitic internal sediments. Many of these sediments, found in River Cave, Mud Tunnels, Cerberus Cave, Imperial Cave, Jubilee Cave and Ribbon Cave, were unconformable with the Jenolan Caves Limestone and most had been dedolomitised.

In South Australia, aragonite occurs in caves associated with dolostone (Grant Gartrell, pers. comm.). Quarrying at Sellicks Hill Quarry uncovered a cave in September 1991. Photographs of the mined cave showed anthodites, popcorn, coralloids, and coatings of (apparently) dolomite and hydromagnesite. The cave has been closed by the quarry since 9th November 1991 and was the subject of a Parliamentary enquiry (Environment, Resources and Development Committee, Parliament of South Australia 1995).

Osborne (1993*a*) noted that dolomitic palaeokarst deposits are significant to the Jenolan show caves as they form the substrate for aragonite helictites.

Rowling (1993) sketched and described "aragonite" anthodites and helictites observed in Genghis Khan and Kubla Khan caves at Mole Creek, Tasmania.

Osborne (1994) noted that in eastern Australia, the longest cave systems, and the ones with most extensive deposits of aragonite and gypsum have been found to occur near areas of Permo-Triassic basinal sediments. Examples were given of caves with this association at Jenolan (NSW), Exit Cave at Ida Bay and caves at Mole Creek in Tasmania. Osborne suggested that dolomite in the palaeokarst was responsible for the deposition of aragonite speleothems instead of calcite ones at Jenolan. Aragonite speleothems at Jenolan with this association included the Furze Bush, possibly the Arabesque, and the helictites in Ribbon Cave. Osborne suggested that pyrite and dolomite were emplaced in buried palaeokarst deposits at low temperatures by basinal fluids from above. In both Tasmania and the Western edge of the Sydney Basin, this resulted in the association of Permian caprocks with large, well-decorated caves containing gypsum and aragonite speleothems.

Rowling (1995) described geological and mineralogical features of Wyanbene Cave, referring to rock chip analyses of Richardson, Byrnes & Degeling (1981). "Aragonite" anthodites and flos ferri were associated with "an oxide or weathered ore body".

Osborne (1996) described how the weathering of sulfides deposited in palaeokarst can lead to ochreous deposits associated with gypsum and red calcite speleothems. Examples were given from Wyanbene Cave, Jenolan Caves and caves in Tasmania. At Jenolan caves, aragonite helictites and other aragonite speleothems were developed on a dolomitic palaeokarst substrate. Aragonite occurred with gypsum in a number of places in eastern Australia. It was suggested that where caves are associated with ore bodies, the ore bodies act as aquicludes during initial speleogenesis. Later, as pyrite in the ore bodies is oxidised, it assists in breakdown of bedrock, exposing palaeokarst and aids speleothem development. It was suggested that large, well-decorated caves are often associated with ore bodies.

Bauer & Bauer (1998) reported "aragonite" at Bungonia in the Coffin Chamber of the B-4-5 Extension (cave).

Rowling (1998*a*) analysed "Ribbon helictites" from Jubilee Cave, Jenolan Caves, previously described by cave managers as "aragonite". Analyses by Maynard and Rowling showed them to be calcite. Their surface texture has bundles of needle-fibre calcite.

Vizjak (1998*b*) described the discovery of aragonite in a part of Mammoth Cave, Jenolan called "The World of Mud". The area lies near "a shale bed". Vizjak described their findings in 1997:

> *There lay the "Aragonite Snowfields" - a large, magnificent patch of white powdery formation covered in aragonite crystals as large as pencils.* (Further up, they found) *... several basketball sized clusters of aragonite crystals adorning the walls.*
>
> (Vizjak 1998*b*)

Breezes were noted in this area, although no cave entrances are known nearby. Vizjak described more "aragonite" speleothems in the area:

> *... at the "Mini Vortex" the aragonite clusters on the roof are spectacular, with crystals as big as chopsticks and there is an amazing white cross of calcite (or something) on the ceiling. ... Beyond the "Southern Cross", Turfa entered "Pure Dilemma". This small chamber is ... full of white crystal growths that are all over the walls.*
>
> (Vizjak 1998*a*)

Photographs of "The World of Mud" presented by Mark Bonwick (pers. comm.) showed that it contains extensive deposits of "aragonite" as anthodites and wall coatings. Some blue and green "aragonite" was present.

Rowling (1998*c*) described the discovery of Aragonite Canyon in Sigma Cave, Wombeyan with Sydney University Speleological Society. Although the surveyors were not the first people to find this part of the cave, they were the first to document it. This is discussed further in Section 3.1.

Members of Sydney University Speleological Society, I. Cooper, P. Maynard and others have reported (pers. comm.) on "aragonite" in Wiburds Lake Cave during a re-survey of the cave in 1999.

Rowling (1999*b*) described speleothems in the Chevalier Extension of Glass Cave, Jenolan. Some of the "aragonite" was associated with a white pasty material that looked like moonmilk. This is discussed further in Section 3.1.

Osborne (1999) mentioned Ribbon Cave (Jenolan) aragonite speleothems associated with magnesium rich minerals: huntite, dolomite and ferron dolomite. Dolomitic palaeokarst was considered the most likely source of magnesium. Sulfates were also deposited. Weathering of pyrite was the most likely source of the sulfate. The cave is wet and there is little evaporation. Aragonite was shown as spirals and spikes in the feature known as the "Lyrebirds Nest". Osborne suggested that pyrite was hydrothermally emplaced in palaeokarst sediments at Jenolan, and oxidation of this pyrite has formed sulfate and aragonite speleothems. It was suggested that pyrite was emplaced between mid Permian and Late Cretaceous to Early Tertiary, or could be related to hydrothermal activity associated with opening of the Tasman Sea (Late Cretaceous).

Osborne (2000) noted that aragonite in eastern Australian caves was mainly associated with dolomitic and pyritic palaeokarst and also with igneous dykes and other intrusions.

A photograph (Pryke 2000) of anthodites in Fife Cave, Church Creek, N.S.W. showed a helictite cluster resembling flos ferri. On the same page is a photograph by David Connard of anthodites in Genghis Khan Cave, Mole Creek, Tasmania.

England & Smith (2000) analysed moonmilk from several NSW caves and found the material was calcite in each case. Analyses used SEM and XRD. Samples were loose fragments taken from the floor of Barber Cave (CP-14) at Cooleman Plains, Horseshoe Cavern in Mammoth Cave (J-13) at Jenolan Caves and the Chevalier Extension of Glass Cave (J-17) at Jenolan Caves. Two main microscopic forms were found: a microcrystalline globular structure and several different sizes of fibrous structure.

Contos (2000) described microbial mantles with fine crystals embedded in the veils. These occurred in lakes in the following Nullarbor Plain Caves (South Australia and Western Australia): Cocklebiddy, Warbla, Weebubbie and Murra el Elevyn but not Tommy Graham, Koonalda or Nurina caves.

Contos, James, Heywood, Pitt & Rogers (2001) described biogenic calcite in Weebubbie cave. XRD indicated the mineral was calcite not aragonite. Organic acids were shown to alter the crystal shape of calcite.

Osborne, Pogson & Colchester (2002) examined the white pasty substance which occurs with aragonite at "The Lyrebirds Nest" (Ribbon Cave, Jenolan). It was huntite, not calcite "moonmilk". Aragonite was also found in Ribbon Cave as spherulites about 2 cm diameter, embedded in gossan. Locally, these are called "stars", and they also occur near the pool in the Orient Cave in a dark ochreous deposit (R.A. Osborne, pers. comm.). Pogson, Osborne and Colchester used XRD to analyse the aragonite from Ribbon Cave, the Furze Bush and small deposits in River Cave (R.A. Osborne, pers. comm.).

Turner (2002) analysed samples of blue and white speleothems from Cliefden Caves. One 40 mg sample from the blue aragonite stalactite in Boonderoo Cave, collected by the Orange Speleological Society in 1995 was found to contain copper. Other metals detected included barium, strontium, iron, zinc, magnesium, lead, nickel and uranium. Very small samples of blue speleothems and white speleothems from Taplow Maze cave were analysed. The blue speleothems contained copper, chromium and small quantities of nickel. These metals were also present in the white speleothem at much lower quantities. Turner suggested copper was the main element responsible for the blue colour. He did not determine whether the Taplow Maze blue material was aragonite or calcite. The substrate for the speleothems is not stated.

Rowling (2004) examined subaqueous helictites from Mullamullang cave, Nullarbor Plain, Western Australia. Minerals present, determined by XRD, were calcite, magnesian calcite, aragonite, hydromagnesite, gypsum, celestite and halite. A subaqueous helictite from another lake in the cave was found to comprise calcite, magnesian calcite, aragonite, hydromagnesite, gypsum,

huntite, cristobalite and halite.

Aragonite was reported (R.A. Osborne, pers. comm.) as the main constituent of boiler scale on heating elements in electric kettles at Jenolan Caves supplied by water from the Jenolan underground river. A small quantity of calcite was present. The polymorph was confirmed by XRD.

1.4   Why Study Aragonite in NSW Caves?

The bulk of calcium carbonate deposits in limestone caves in NSW are calcite. Aragonite is a minor deposit in most NSW caves, if it occurs at all. However, aragonite is being actively deposited in some NSW caves. This requires that some unknown factor in these caves is preventing the deposition of the stable form of $CaCO_3$ for these P-T conditions, that is calcite.

Chemical analyses of bulk NSW limestone from a variety of locations were listed by Carne & Jones (1919) and Lishmund, Dawood & Langley (1986). The purity of all the limestone deposits was high ($\leq 1\%$ $MgCO_3$) for all the areas in which aragonite has been reported from the caves. This infers that the conditions causing aragonite to be deposited is not common throughout the bulk of the limestone and instead may be localised to certain parts of the deposits. If the factors leading to aragonite deposition have something to do with the bedrock, as has been suggested by some researchers, then this is an important consideration for both the area's and caves' geomorphologies.

Another reason for studying aragonite in NSW caves is to fill in an apparent gap in the research on the occurrence of aragonite in a wider context, as most of the research on cave aragonite has been done in the northern hemisphere.

Despite the attractiveness of aragonite to cavers and tourists, and the lack of explanation as to its occurrence, there was little scientific work done on aragonite in NSW from the work of Wilkinson (1892) until the mid 20th century with the publications of Frank (1974), Osborne (1978) and Webb & Brush (1978).

In the show cave environment, aragonite has value as a tourist showpiece as the forms taken by aragonite speleothems are often attractive or unusual. Tourists like to visit show caves and this can be of economic importance to a local region.

1.5   Project Aims

The aims of this project are to:

- Investigate caves in NSW reported to contain aragonite

- Verify that the material is aragonite

- Analyse the substrate on which the aragonite is depositing

- Attempt to determine what factors lead to the deposition of aragonite in NSW caves.

Chapter 2

Materials and Methods

2.1 Introduction to Case Studies

The case studies concentrated on three main areas: Jenolan, Wombeyan and Walli. Additional areas were examined, either during the course of the research, or beforehand. These were useful as a comparison. It was important to concentrate on the main areas so that the work could be completed in a reasonable time.

2.2 Criteria for Chosen Areas

There are several factors that make one area more attractive as a study site compared to another area. The three main areas chosen had the following features which made them attractive as field sites:

- Reports that aragonite had been found at the site

- Preliminary site inspections showed aragonite may occur at the site

- Permission to sample the site was obtainable

- Permission to repeatedly visit the site was obtainable

- Ease of access

Reports that aragonite had been found at the site was a major reason for investigating the site in the first place. In some cases, this was the first study to report the occurrence of aragonite at the site but in most cases others have reported it. Typically, the occurrence of aragonite is reported in several ways:

- Reports in government publications

- Reports in scientific journals

- Reports in caving club journals

- Viewed on a previous visit

- Sampled and reported by other workers

Preliminary site inspections showed aragonite may occur at the site As far as possible, each of the reported sites was visited prior to deciding which ones should be chosen as study sites. This helped to cut down the number of study sites to a manageable size and choose the best sites representative of each area.

Permission to sample the site was obtainable Some land owners or managers do not allow sampling. In some cases this is because of previous bad experiences where far too much material was removed from a cave, and in other cases there is specific legislation governing sampling. In some cases it was possible to use already-collected material sampled by other workers as references. The sample size was kept within reasonable limits. In the case of the Jenolan and Wombeyan samples, the sampled material remains the property of the Jenolan Caves Reserve Trust.

Permission to repeatedly visit the site was obtainable. Some land owners or managers restrict visits to specific caves to once a year or less. Repeat visits are important to observe seasonal variations (if any) or changes after rainfall, etc. Repeat visits were also necessary in cases where there were no maps of the cave, and some time would be spent surveying it.

In the case of the chosen study sites, permission to repeatedly visit was granted provided the caves manager was aware of the visit and the appropriate forms were completed.

Ease of access is important to achieve a proper investigation. Not only is the ease of moving through the cave important, but also the ease of getting to the cave in the first place. The following are typical considerations regarding accessing the caves:

- Closeness to Sydney, to maximize time spent actually studying the site.

- Vehicular access to an area close to the caves, to minimise time taken to access the area.

- Difficulty of moving through the cave itself, how much equipment would be needed to access the aragonite site, how many people were needed to support the trip, how difficult was the route to the aragonite site.

- Accessibility to suspected aragonite occurrences within particular caves.

2.3 Methods Chosen

Field Methods

Caves are non-renewable, fragile environments and it was important that sampling was done carefully without destroying the visual appearance of the site. For each sampling site, small samples were obtained of aragonite material from the caves. Samples were also taken of the substrate and the bedrock.

Cave maps were required. In some cases, very good ones were already available and could be annotated. In other cases, a new map was made for this study following the Australian Speleological Federation standards for cave maps. A map of Contact Cave at Jenolan at a 1:100 scale has been prepared as part of this study. A map of Cow Pit was prepared prior to the start of this study. Maps of Wiburds Lake Cave, Sigma Cave, Piano Cave, Deep Hole (Deep Cave) and Flying Fortress Cave have been obtained. All field bearings were converted from magnetic north to True North for publication. Some included maps use Grid North and are indicated as such. Unless otherwise stated, bearings are relative to True North.

Photos and descriptions of the speleothems and their environment were made in the caves. The following notes were made of the aragonite in the field:

- What was the form taken by the speleothem, classified according to the criteria of Hill & Forti (1997).

- What was the CO_2 level at the site

- What was the temperature at the site

- What was the humidity at the site. Did there appear to be a boundary layer?

The following observations were made of the substrate:

- What was the physical relationship between the aragonite and the substrate?

- What type of geologic feature formed the substrate (e.g. sediment, dyke, speleothem, etc.)?

- The material was classified (e.g. gossan, bedrock, etc.) and described.

The following observations were made of the bedrock underlying or forming the substrate:

- What was its structure (e.g. dip, strike, relationship to aragonite deposits, etc.)

- The material was described (e.g. limestone, dolostone, etc.)

Temperature and Humidity Measurements

Temperature and humidity were mostly measured using the wet and dry bulb method. The instrument was a Zeal sling psychrometer with alcohol - in - glass capillary tubes. The tubes are graduated from -5°C to 50°C in increments of 0.5°C. With care, 0.25°C can be resolved. The conversion nomogram supplied with the instrument is graphed in 0.5°C increments over the same range with depression of wet bulb from -5 to 20°C. Humidity is show as an integer.

The wet bulb is moistened with distilled water. The unit was whirled for about 20 seconds, then the wet and dry thermometers were read. This was repeated for a total of three pairs of readings. Humidity was estimated later from a lookup table supplied with the instrument. The average of these three readings was used to determine the relative humidity. In general, sling psychrometers are inaccurate at high humidity levels such as are usually encountered in those parts of caves furthest from the entrance.

Some temperature measurements (e.g. some at Walli) were made using a Mercury-in-glass thermometer, graduated -10 to 110°C.

CO_2 measurements

CO_2 was measured with an Auer MSA metered pump 5146-950 to DIN33882, using Dräger tubes type "CO_2 0,1%/a CH23501" calibrated for CO_2 measurement For the 0 to 6% CO_2 scale, a single pump of the instrument bellows is sufficient. For the 0 to 1.2% scale, five pumps are required. The amount of CO_2 is indicated on the Dräger tubes by a purple colouring. The instrument is accurate to about 0.05% CO_2 on the n=5 scale, and 0.25% CO_2 on the n=1 scale.

Response to Hydrochloric Acid

This was sometimes used in the field or before other analyses to check for presence of carbonate. A small quantity of the specimen was crushed and placed in a test tube or high density polyethylene container. Two or three drops of 32% HCl were added and the resulting reaction observed. In most cases, the ambient temperature was recorded, as reaction rate slows with lowered temperatures. There was no attempt made to quantify the results. Solution colour was also used to note the presence of metals (e.g. iron or copper), which may be significant if carbonates contained other HCl-soluble impurities. Mostly, this technique was used to quickly identify non-carbonates (e.g. gypsum) which can sometimes look very similar to aragonite in the field. The technique was particularly useful for the Walli material which contained aragonite, gypsum, silicates and calcite.

Rock Slab

Bedrock hand specimens were slab-cut with a diamond rock saw. These cut pieces were used to identify those areas of interest for thin section. These were polished with wet and dry sandpapers

until smooth. Polished rock slabs are useful for examining opaque minerals such as pyrite and goethite, and also for examining larger scale structures that are generally too big to be recognised in standard thin section. Some speleothem structures were examined as slabs or small polished pieces.

Water-affected material was cut by Dr Osborne using an oil-cooled saw. Examples of material requiring this technique includes moist sediments with a high clay content, or speleothems with a high proportion of hydromagnesite. Both materials expand and destroy the sample if cut with a water-cooled saw. Some of the older high-clay samples were successfully cut using the water-cooled saw if they were thoroughly dry and potted with epoxy resin beforehand.

Thin Section

Thin sections were used to identify structural features of sediments and rocks (e.g. extent of dolomitisation) and to identify minerals present using optical techniques. Bedrock thin sections were made to examine the grain structure of the limestone, bioclasts and any alteration (e.g. dedolomitisation). Thin sections of nearby igneous rocks were made to examine the minerals present. Most thin sections for this study were prepared from rock slabs by the School of Geosciences Thin Section Technician, George Navratil. Thin sections of rocks from Bungonia were provided by Julie Bauer.

Thin sections can be made of speleothems to show the layering and crystal structure characteristic of the speleothem. This shows features which would otherwise be buried, such as acicular aragonite subsequently coated with finer aragonite or calcite. Two thin sections of aragonite speleothem were provided by Dr Osborne. Thin sections of substrates to the aragonite were made to examine the minerals present. Thin sections of other cave sediments were made to identify phosphate minerals, calcite cements, veins and to determine the order of deposition. Tables of all thin sections examined for this study are presented in the Appendix.

Optical Microscopy

Optical microscopy was used to examine the surfaces of speleothems such as aragonite anthodites, gypsum extrusions, crystal terminations and cleavage of small aragonite samples. Polarised light and crossed Nicols were used on thin sections to assist with mineral identification, aiding in the distinction between calcite, aragonite and gypsum. This was also one of the diagnostic tools used for identification of minerals present in igneous rocks close to the sample areas. Twinning often occurred in the calcite grains of the bedrock samples. The style of twinning appeared to be characteristic for each area. Optical microscopy was an essential tool to aid in the description of the sample's mineral structure.

Specimen photos were obtained using a variety of microscopes capable of camera attachment. A stereo zoom microscope was used for all initial hand specimen surface examinations and some thin section viewing. A polarizing petrology microscope with camera attachment was

used for most of the thin section examinations and photography, and some photographs of very small samples such as powders and grains. Other thin sections were examined and photographed using a polarizing stereo microscope. Some small specimens were examined and photographed using a stereo dissection microscope with timer and camera attachment but results were generally unsatisfactory. A stereo polarizing microscope and camera attachment at the Department of Chemistry, Materials and Forensic Science, University of Technology, Sydney was more suitable for this work and therefore used for most of the small sample photography. Larger specimens were either photographed directly in situ or on a bench setup with a scale. Some small specimens were digitally scanned on the flat bed of an Epson Perfection 2400 photo scanner.

X-Ray Diffration

X-Ray Diffraction (XRD) was the primary diagnostic tool used to identify particular mineral components of samples, including aragonite, substrates, dykes and bedrock minerals. It is one of the easiest methods of determining whether the specimen is calcite or aragonite. There are many different mineral catalogue entries for calcites and aragonites, and XRD can be used to identify which particular mineral is present. The differences in spectra amongst aragonites are due to aragonite crystal lattice dimensional variations caused by differences in trace element composition. Typically aragonite samples from one sample site will all have the same mineral catalogue entries, whereas aragonite samples from another limestone deposit or sometimes from another cave in the same deposit will have a different assemblage of aragonite catalogue entries due to trace elements or growth conditions. This technique could possibly be used to identify the location of an unknown aragonite sample.

Unfortunately the sample must be powdered for XRD analysis, thus destroying any gross structural information. However if a sample can be kept dry in its powdered state, it can be re-tested later if required. It was important to get sufficient material: a volume of at least two match-heads was adequate for preparing a powder slide. The more material present, the better the signal-to-noise ratio. If sufficient material is available, e.g. 1 cc, it can be loaded directly into the carrier well of the instrument. Powdering was done by grinding the specimen in an agate mortar and pestle. In some cases, the specimen was already a powder, so no grinding was necessary. Two types of powder samples were used. Where there was sufficient material, it was loaded directly into the carrier well. Where there was only a small amount of material available, it was placed on double-sided sticky tape mounted on a glass microscope slide and spread evenly. This was then attached to the carrier using double-sided tape. Potentially, specimen grinding may pose a problem for analysis of the powdered material by converting calcite to aragonite — this was discussed briefly in Webb & Brush (1978). However from the pressure/temperature stability diagram in Carlson (1983) at least 3 kbar pressure is required to do this at ambient temperature (see Figure 1.2). It seems unlikely that simple hand pressure could easily achieve such a transformation. However when specimens were ground for this study, care was taken to not grind too

hard or for too long. As none of the limestone or marble bedrock samples in this study showed aragonite in their X-ray spectra after grinding, it was assumed that all aragonite detected by XRD in other samples was from the sample itself and not an artefact of specimen grinding.

All XRD work was done at the Electron Microscope Unit at the University of Sydney. XRD (scanning) was performed using a 3kW Siemens Kristalloflex 710D X-Ray generator, model number 7kP5000-8AE, coupled with a Siemens D5000 Diffractometer and a small computer. The generator was operated at 40kV, 40mA, with a copper target. Slits used, in order: 1 mm at source, 1 mm, 0.2 mm, 0.6 mm (at receiver). The monochromator was a graphite crystal (2d = 0.2708 nm) for Cu Kα radiation. Kβ filters were nickel, 12 μm thickness. Scans were made from 2 to 70° 2θ in 28 minutes (2.4° per minute). The following software was used on a special version of Windows 95: For job control: Siemens Diffrac Plus Editjob version 2.00 1996. For status display: Siemens Status Display version 1.00 1994 written by Michael Jacob. For analysis: Bruker AXS EVA version 3.0 Diffrac*plus*. Care needed to be taken with analyses, as some components suggested by the software were unlikely in a cave situation. This could occur if 2θ spectral components were present at levels close to the baseline. The software tends to examine spectral components from lowest to highest 2θ value. A small sample can have a noisy spectrum, which can trick the software into suggesting unlikely components. For small samples with noisy spectra, a summary of "Cave Minerals of the World" was consulted, and the measured spectrum for each sample was compared with the most common and likely cave minerals before running a residual scan on the unidentified peaks. The largest peaks were considered first. Spectra were plotted in colour to aid identification in the lab. Raw scanned spectra were exported in UXD (Universal X-ray Diffraction) interchange format for publication.

Scanning Electron Microscopy

Some samples were prepared for Scanning Electron Microscopy (SEM). This was used to examine the surface of the samples and compare the aragonite and calcite specimens. The advantage of using the SEM instead of conventional optical microscopy is the enormous depth of field offered by the SEM. This was particularly useful when trying to obtain images of spiky aragonite. However, the SEM gives no information as to the specimen's colour, which must be determined using optical microscopy beforehand. The SEM was a particularly useful tool to aid in examining the crystal habits of normal calcite, needle-form calcite and aragonite, with XRD used to confirm the actual material. Some fine powdery specimens were examined with surprising results, especially with the needle-form calcites. The instrument used was the Philips SEM505 at the Electron Microscope Unit, the University of Sydney, coupled with a small computer running a version of Windows 95 software for image capture. In this case, the computer was only used for image capture and the operator had full control of the instrument.