Journal & Proceedings of the Royal Society of New South Wales, Vol. 137, p. 123–149, 2004
ISSN 0035-9173/04/0200123–27 $4.00/1

Studies on Aragonite and its Occurrence in Caves, including New South Wales Caves

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Abstract: Aragonite is a minor secondary mineral in many limestone caves throughout the world and is probably the second-most common cave mineral after calcite. It occurs 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 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 physically block the positions on the calcite crystal lattice which otherwise would develop into a larger crystal. Often an inhibitor for calcite has no effect on the aragonite crystal lattice, thus favouring aragonite depositition.

Several factors are 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.

Keywords: aragonite, cave minerals, calcite, New South Wales

INTRODUCTION

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

Aragonite often forms with a characteristic acicular habit known as "church steeples" (Figure 1). 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°. Aragonite twins on $\{110\}$, producing pseudo-hexagonal columnar crystals, whereas calcite readily twins on the cleavage plane. Compared with calcite, aragonite is harder (3.5 to 4 cf. 3), denser (specific gravity 2.930 cf. 2.711) and more brittle (Berry et al. 1983).

Aragonite is often produced in the growth of marine organisms, particularly in shells. When the organism dies, proteins in the shell decay exposing the aragonite. In time, aragonite reverts to calcite in the near surface environment in the presence of fresh water. The deposition of aragonite is also a the product of chemical influence, or high pressure on calcite. It also occurs in secondary deposits in caves (Siegel 1965, Ford & Cullingford 1976) and igneous rocks.

It is probably the second most common cave mineral after calcite Hill & Forti (1997). This reflects the discovery of extensive aragonite deposits in caves such as Lechuguilla Cave (Carlsbad Caves National Park, U.S.A.).

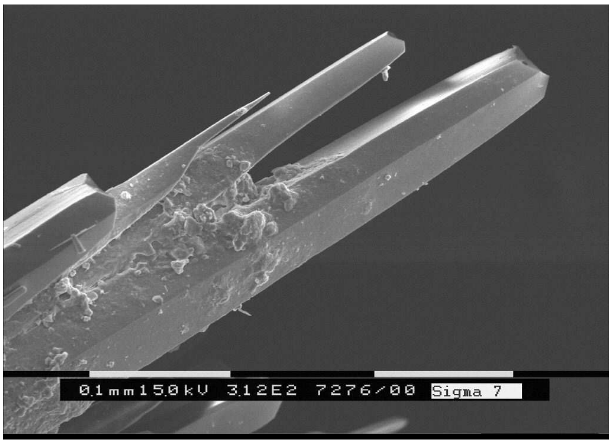

Figure 1. Aragonite from Sigma Cave, Wombeyan. SEM image by Jill Rowling and Dr Ian Kaplin.

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. In the cave environment, aragonite tends to be either white or coloured by metal impurities such as copper, whereas calcite deposits are frequently coloured by organic (humic and fulvic) acids. The brown colouration of cave calcite was often incorectly attributed to iron oxy-hydroxide staining (Hill & Forti 1997). 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 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 these occurrences are thermodynamically unstable in fresh water and readily revert to calcite. So, why does aragonite exist at all in caves? What allows aragonite to deposit in caves without reverting to calcite?

Curl suggested that aragonite forms and persists in caves because calcite is prevented from forming, a concept arising from Saylor in 1928 who suggested that various substances inhibited the crystallisation of calcite and thereby allowed the precipitation of aragonite.

Hill & Forti (1997) noted that since Curl's theoretical work, more experimental work was available on aragonite deposition in both cave and non-cave environments, so there was some consensus on determining the factors that 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 below.

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

PREVIOUS STUDIES ON ARAGONITE

Introduction to Studies

Shaw (1992) discussed cave aragonite in a historical context. The earliest reference he found was by Dr Charles S. Dolley in 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 in 1748 and sketches by Patrin in 1803.

Most work on carbonate diagenesis has focused on the marine environment, where aragonite is relevant to marine sediment diagenesis. Work on carbonate chemistry is also vital to industry, for example the curing of concrete for structural stability.

Descriptions of research on the chemistry of aragonite were summarised in Bathurst (1974) and Morse (1983). They referred to the experiments on solutions of calcium carbonate using 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, and discussed the chemistry of aragonite precipitation in the marine setting, in lime muds, beachrock and mollusc shells.

Tucker & Wright (1990) discussed aragonite chemistry with more accent on diagenesis of marine carbonates. Tucker (1991) defined low magnesium calcite as containing less than 4 mole% $MgCO_3$, while high magnesium calcites commonly ranged 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 fastest, then low Mg-calcite, then aragonite and then calcite which was the slowest. For a given dissolution rate, high Mg-calcite dissolves at a higher pH than does low Mg-calcite, aragonite or calcite.

Morse reviewed the kinetics in 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 aragonite deposits in preference to calcite.

Calcite-inhibitors work by blocking crystal growth points on the calcite lattice, which are frequently at edges or around dislocations (Mercer 1990). This concept is shown in Figure 2.

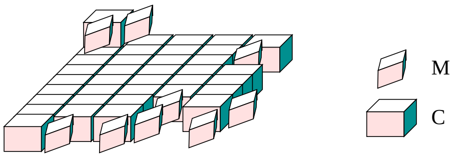

Figure 2. Schematic of a developing crystal, with a sheet of unit cells such as calcite (C) whose growth points are being blocked by an inhibitor such as a magnesium compound (M). Based on ideas in Morse (1983) and Mercer (1990).

Morse noted that inhibitors for calcite generally did not effect the aragonite crystal structure and may form solid solutions in the aragonite crystal. Both precipitation and dissolution of calcite are affected by inhibitors, including:

- 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 may inhibit precipitation of aragonite, while other organic materials apparently inhibit both calcite and aragonite precipitation. This may result from substances coating the mineral rather than any chemical kinetic effect.

For the cave environment, the review and discussion of cave aragonite by Hill & Forti (1997) is considered the main current reference.

For either aragonite or calcite to deposit, there needs to be bicarbonate ion, HCO_3^- in solution, a means of allowing carbon dioxide to outgas or be otherwise leave the reaction, and the solution needs to be supersaturated with respect to calcium carbonate. In caves, these conditions usually deposit calcite as the most stable polymorph of calcium carbonate.

Figure 3 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.

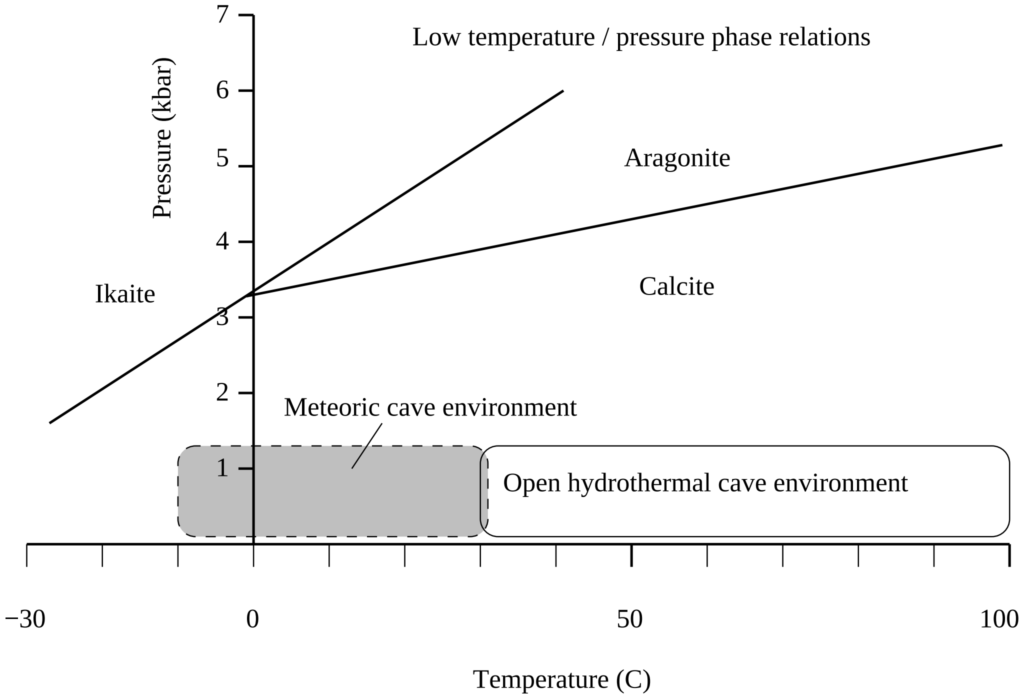

Figure 3. Stability Diagram for $CaCO_3$ at low temperatures and pressures shows that calcite is the expected polymorph in caves at atmospheric pressure. Based on Carlson (1983)

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. 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 occurs in some types of moonmilk and as hydrated spheroids in pools in cold caves and sometimes accompanies aragonite. Aragonite is apparently unstable at sub-zero temperatures, but at much higher temperatures and pressures is sufficiently stable to designate the P-T of formation of particular rocks such as blueschists at 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, but these P-T conditions are 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.

Palaeodeposits, Paramorphs and Marine Cave Cements

The aragonite crystal structure is sometimes preserved in sediments, even after conversion to calcite.

Kendall & Tucker (1973) described a crystal fabric in limestones which resembled pseudomorphs of calcite after a "an acicular carbonate", potentially 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 in a reef in Belize (British Honduras) (Ginsburg & James 1976) came from cavities and small caves within the barrier reef, at depths between 65 m and 120 m. The aragonite formed "mamelons": hemispherical aggregates of aragonite deposited on the ceilings of the voids in the reef bedrock. Some were deposited on the floors or 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 in the crystals was similar in 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 formed shortly after the deposition of the limestone.

A piece of flowstone from Carlsbad Caverns, New Mexico (U.S.A.) contained crystals of calcite which had once been aragonite (Folk & Assereto 1976). The original aragonite fabric such as feathery or squared terminations were preserved. Small needle crystals were considered to be remaining aragonite. Unusually long length-slow calcite crystals were attributed to previous aragonite or vaterite. Length-fast calcite crystals were 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 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 was now calcite, all of the original fabric was preserved. The original depositional environment was described as near-marine semi-arid. The original aragonite formed 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.

Mazzullo (1980) examined samples 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 but very few of their subaerial samples contained any aragonite. 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. Aragonite was detected in the water coming out of nearby hot springs (subaqueous deposition), but converted to calcite on exposure.

In various aqueous solutions prepared from calcite or aragonite, calcite was 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 explain the temporary aragonite precipitation 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 at temperatures above 50°C. Carbon dioxide exposure in this case did not affect the outcome.

Previously, an increase in temperature was thought to aid the formation of aragonite, but this became disputed (Morse 1983). Later research shows that the long-term stability for aragonite at high temperatures is only achieved at high pressures. The stability diagram for aragonite (Figure 3) suggests that for the meteoric cave environment, temperature should not normally be a factor. Temperature was not considered a factor by Hill & Forti (1997), but they noted that more aragonite appears 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 unlike meteoric caves).

Leel-Ossy (1997) examined cave minerals in the Jozsefhegy hydrothermal cave near Budapest, Hungary, that included aragonite with gypsum. However the aragonite and gypsum considerably post-dated both the caves and the hydrothermal activity which formed them.

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. Morse (1983) also listed magnesium as one of the calcite crystal poisoners.

Eibengrotte is a cave in the Fränkische Schweiz (Germany) which is developed in massive dolostone. Fischbeck & Müller (1971) found a number of minerals precipitating as surface coatings and as cave coral, including 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. 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.

Aragonite appears in minerals of the Frauenmauer - Langstein cave system in Austria (Seemann 1985). It forms in small amounts as hard, small fine spikes, coralloids, frostwork and crusts. These caves also had hydromagnesite and sulfate minerals. As the Mg content is increased, protodolomite and then dolomite can be produced (rather than aragonite, huntite and hydromagnesite).

A summary of Austrian cave minerals (Seemann 1987) shows aragonite occurs in many Austrian caves although not abundantly. It associates with magnesium minerals as flowstone (often interlayered with calcite), in moonmilk growths, cave coral and anthodite type helictites. 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 a key component to aragonite deposition in many caves. Hill & Forti (1997) noted that on increasing magnesium in a mixed solution of magnesium and calcium carbonate, the following mineral sequence is deposited: calcite, high magnesium calcite, aragonite, huntite and hydromagnesite, magnesite. The presence of magnesium ions disrupts the calcite crystal lattice but not that of aragonite, suggesting that crystal poisoning by magnesium ions only affects the calcite crystal lattice, leaving aragonite to deposit freely given appropriate conditions of supersaturation.

Urbani (1997) listed several Venezuelan caves as having aragonite. One occurrence was associated with sepiolite (a hydrated magnesium silicate) and another was associated with dolomite. Urbani suggested that the aragonite crystallisation was promoted by a high concentration of strontium.

Frisia, Borsato, Fairchild & Longinelli (1997) examined stalagmites and drip points in Clamouse cave (France). Aragonite speleothems were being precipitated only where there was dolomitic bedrock, and only when the drip rate was very low. The authors suggested that magnesium inhibited the growth of calcite, either by crystal poisoning or by “difficulties in rapid dehydration of the Mg^{2+} ion”. Clamouse cave water was not particularly high in dissolved Mg compared with other sites, so 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. 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 Sites 2, 3 and 4 with Mg/Ca increasingly > 2: calcite + aragonite, with Mg/Ca 3–23 at site 4. Site 4 (Grauner Walls) included Mg calcite, aragonite, monohydrocalcite, nesquehonite and hydromagnesite.

Bohemia Cave in the Mount Owen Karst Area of the South Island of New Zealand was discovered in 1990 by members of the Czech speleological club Alberice. A large cavity and its mineralogy was briefly summarised in Tásler (1998). The cavity, called “Dream of Alberice Cavers”, measures approximately 80 m wide by 650 m long which is a large cavern by world standards. Most of the ceiling, walls and floor of this cavern were covered with various aragonite speleothems together with hydromagnesite “snow”. The overlying bedrock was dolomitic Ordovician units of the Mount Arthur Group whereas the underlying rock to most of the cavern was phyllite. Deposits of limonitised pyrrhotite were found near the junction area. About 90% of the speleothems are aragonite, and other minerals include calcite, hydromagnesite, dolomite, opal, Fe- and Mn- hydroxides, gypsum and sepiolite. The contact area between the two bedrocks was exceptionally rich in aragonite. Aragonite speleothems include 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, with some 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 several caves near Waitomo, New Zealand, aragonite occurs with hydromagnesite or other magnesium-based mineral. Overlying pyroclastic deposits influence mineralogy and cave water chemistry at Waitimo Caves (P. Maynard, pers. comm.).

In France, several caves have outstanding aragonite deposits, usually associated with metamorphosed dolostone. Some deposits are associated with gypsum and sulfur, and some with hydromagnesite (Cabrol, Gill & Gunn 2001).

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.

Strontium carbonate (strontianite) is rarer in meteoric caves than strontium sulfate (celestite) (Hill & Forti 1997), but can occur with aragonite and sometimes with high or low Mg calcite. Strontium is often considered a factor in the precipitation of aragonite, but Hill and Forti noted strontium readily substitutes for calcium without disrupting the aragonite crystal lattice.

Association with Clastics and Clay

Craig, Horton & Reams (1984) suggested that aragonite is nucleated by clastics in caves, after studying speleothems from caves in Missouri (U.S.A.) but were only able to produce vaterite in an experiment mimicking current cave conditions.

In the aragonite caves of France, the aragonite is often associated with clays (Cabrol et al. 2001), exclusively in the clayey areas (David Gill, pers. comm. in 2001). However, clays are common minerals in caves, often as 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 associated with moonmilk and sediments, and is found with hydromagnesite, baylissite, calcite, aragonite and monohydrocalcite. Vaterite can form when calcium carbonate is precipitated under conditions of high CO_2 degassing, but 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. Dripping water on calcium carbide produces acetylene gas which is controlled and ignited to provide a bright flame. The solid waste is mostly calcium hydroxide with minor arsenic, and is occasionally dumped in caves. Cavers have noticed an unusual heligmite known as "carbidimites" associated with disused carbide dumps (Hill & Forti 1997). These form by the reaction between the spent calcium carbide dump with cave seepage water. Carbidimites have an inverted horn shape, and a tendency to change shape over months compared with other speleothems (decades). Sarigu (1999) included photographs of carbidimites from a cave in Italy and discussed their 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. The photographs and text note that the crystals deposited in the tubes as feathery shapes, more like aragonite or possibly vaterite rather than calcite. 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, e.g. Great Onyx Cave, Kentucky, U.S.A. (Siegel 1965). Morse (1983) lists the sulfate ion as a calcite crystal inhibitor.

Carlsbad Caverns in the Guadalupe Mountains, Carlsbad National Park, U.S.A., contain extensive deposits of aragonite associated with gypsum and sulfur (Thrailkill 1971, Hill 1987). Thrailkill noticed that where there was gypsum, there was very little calcite. According to Hill, the caves were formed in several stages. A late stage 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. The caves were probably not 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. Secondary sulfate in Carlsbad Caverns was less than carbonates, despite the large gypsum blocks present. The sulfate speleothems apparently had a sulfur isotope signature closer to that of the overlying pyritic beds rather than that of the gypsum blocks.

Hill listed 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.

Lechuguilla Cave in Carlsbad National Park was well illustrated in Speleo Projects (1998) and has a similar sulfuric acid speleogenesis to Carlsbad Caverns. Both subaerial and subaqueous gypsum and aragonite speleothems occur, but not together (or not photographed together). Possibly in these caves, aragonite and gypsum speleothems have a different origin. Lechuguilla cave has subaqueous speleothems such as selenite needles, calcite pool crystal and subaqueous calcite helictites, but lacks aragonite in pool deposits. Calcite speleothems are less common in Lechuguilla Cave compared to other caves (Speleo Projects 1998).

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

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.

Wall crusts in Humpleu cave in Romania (Ghergari, Onac & Fratila 1997) included gypsum, calcite, aragonite and a variety of sulfate minerals, apparently the breakdown products of bat guano. Some of the calcite was a paramorph after aragonite.

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 there have been described as aragonite, but require confirmation. Photographs with cavers suggest 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. To get aragonite to precipitate first needs an increased rate of precipitation, 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 form.

Hill & Forti (1997) described a "popcorn line" in Carlsbad Caverns as being due to a humidity effect. Cave Popcorn is a speleothem form of either calcite or aragonite, and probably forms 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, which may be more significant to the development of this 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 helped aragonite to deposit in the cave. The humidity 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, which could 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

Only minute amounts of foreign material is required to alter the form deposited (both crystal shape and polymorph) (Curl 1962), while a high rate of deposition favours aragonite a little more than calcite (Siegel & Reams 1966). 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, which did not occur for running water.

Supersaturation and rate of deposition are factors in the precipitation of aragonite Hill & Forti (1997). Unlike Siegel & Reams, Hill & Forti considered very low rates of deposition favour aragonite over calcite, while very high rates of deposition favour vaterite which may 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, which could lead to increased percentage of magnesium in the remaining solution.

Supersaturation is necessary for the precipitation of either calcite or aragonite, and can be achieved either by physical means (e.g. evaporation) or chemical means. By allowing CO_2 to escape, or by application of the common ion effect, the solution may become supersaturated with respect to either calcite or aragonite (or vaterite). 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 found near cave entrances associated with monohydrocalcite (Hill & Forti 1997). Aragonite also occurs in areas with slow deposition rates, e.g. Ochtiná Aragonite Cave (Bosák, Bella, Cílek, Ford, Hercman, Kadlec, Osborne & Pruner 2002) in which 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 controlled aragonite or calcite precipitation. Aragonite formed only under the slow drips in areas with dolomitic bedrock, which allowed more takeup of magnesium from the bedrock, and reduced the rate of outgassing of CO_2.

Carbon Dioxide

Carbon dioxide content is also a factor in the precipitation of aragonite in caves, based on the work of Cabrol in 1978 and Courdry and Cabrol in 1982 in which a stratification line was noted in some caves in France (Hill & Forti 1997). Above this line was only calcite 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.

Pressure

Pressure was also a possible factor in the precipitation of aragonite in caves (B. Rogers, pers. comm. in Hill & Forti (1997)). Aragonite was described from an active fault in a cave. Calcite will readily convert to aragonite at high pressures. This situation is unlikely for most cave environments.

Speleothem Surfaces

Speleothem surfaces may also assist the deposition of aragonite, where aragonite was formed over corrosion surfaces, or over older aragonite speleothems. However, it can be difficult to distinguish between calcite and aragonite and one researcher found one fifth of a supposedly aragonite collection was in fact calcite (Hill & Forti 1997).

Speleothem surfaces and substrates aid the precipitation of most speleothems. Seed crystals start crystal growth, so calcite accumulates on an existing calcite substrate following the pre-existing crystal boundaries, while aragonite may be similarly precipitated from solutions already supersaturated with respect to aragonite. Some substances, if present on the surface of a speleothem, inhibit the precipitation of either polymorph. Tucker & Wright (1990) noted that in the marine situation, oöids are frequently inhibited in development because of a coating of organic material. 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 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 precipitate was vaterite and calcite, not aragonite, with the ratio of vaterite to calcite increasing in proportion to the clay present. Above 80 mg/l clay concentration, only vaterite was produced.

Associations with Biological Activity

In the marine environment, aragonite often forms due to 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.

"Moonmilk" is a white pasty material found in many meteoric caves. 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) sectioned calcite-aragonite stalactites from the Starý 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 a change in the way the two minerals had been precipitated. Formation of the calcite was based on the outgassing of CO_2 (the normal karst process) with minimal evaporation whereas the aragonite mainly formed by very slow evaporation, so slow that biogenic effects are suppressed.

However, in Gillieson (1996), such 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 in these samples), both authors favoured an evaporative condition. In Clamouse Cave (France), Frisia et al. (1997) similarly found isotope ratios that suggested that the aragonite deposits were formed under more evaporative conditions. They found this interpretation difficult because all their aragonite samples were collected in areas of no wind, constant temperature and very high (∼99%) humidity. Instead, they suggested another mechanism concentrated the heavier isotopes in the aragonite samples, a chemical kinetic effect caused by the slow outgassing of CO_2.

Niggeman et al. (1997) compared the stable isotopes of calcite and aragonite coralloids. 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, because all samples came from draughty areas with 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 describing the mineralogy of Kartchner Caverns, Arizona (U.S.A.), Hill (1999) mentioned some deposits of aragonite. Magnesium plays little 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. 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.

Humpleu cave in Romania also has aragonite with bat guano phosphates. However Ghergari et al. (1997) considered the phosphate to be more recent than the aragonite, with phosphate on the lower parts of the passage and aragonite in the upper parts. Gypsum, aragonite and ochres were also present.

Association with Ochres and Gossans

A photograph 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, extensive aragonite deposits in show caves are associated with "ochres" containing Fe, Mn and Mg (Cilek et al. 1998, Bosák et al. 2002). Aragonite occurred as three forms: the oldest material was kidney-shaped and recrystallised; the intermediate aragonite speleothems form long needles and helictites; the youngest 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. The ochres have high water content, 47% to 56%, which may buffer the humidity in the cave, keeping it at a constant high level. The two main factors in the deposition of aragonite in the cave were the presence of Fe and Mn in solutions, and the high humidity. Interspersed with the ochres were 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.

Iron was not one of the elements listed by Morse (1983) which could cause aragonite to precipitate. It is more likely that it precipitates under the influence of other materials present such as manganese, apatite or La-Nd-bearing phosphates. Commonly, cave sediments contain 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) and aragonite is rarely present in such sediments. Where aragonite occurs with iron-rich sediments, the sediments are often hard yet porous, and these physical qualities may assist ions (e.g. magnesium or sulfate) to influence the form of precipitating calcium carbonate by keeping the humidity high, acting as a sturdy substrate and allowing slow movement of ions in solution.

Flos Ferri

On page 206 of Hurlbut (1970) is a photograph of tangled aragonite helictites (*"flos ferri"* from Styria (Steiermark, Austria):

> "*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.*"

Most of this material has now been mined away (Stephan Kempe, pers. comm., August 1997). Rowling saw large specimens of flos ferri aragonite in the private museum at the Glacier Gardens at Lucerne (Switzerland) in 1997. Here, it is known as *Eisernblut* (iron blood) although it is white. The tangled masses of helictites have a radius of curvature of around 5 to 10 mm. Other museums also hold this material, such as the Natural History museum at Lucerne and the Australian Museum collection, cat. no. D19158.

Although Hurlbut (1970) did not specify 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."*

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

According to Shaw (1992), the term *flos ferri* was first used by John Hill in 1748 for a twisted form of helictite found in mines and in some Mendip (UK) caves. Shaw included two sketches by Patrin (1803) depicting "flos-ferri" which 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. In contrast, Hill & Forti (1997) described flos ferri as a variety of anthodite which resembles a sea urchin (Hill & Forti 1997), and defined it as a quill-like variety of anthodite. These differences in terminology appear to be localised to particular countries and show caves.

This article follows the definition of flos ferri as used by Patrin, Shaw and Hurlbut. Flos ferri occurs at Jenolan Caves (Figure 4).

Figure 4. Part of The Arabesque, behind wire netting at Cerberus Cave, Jenolan Caves, featuring flos ferri. Speleothem is about 20 cm high.

Blue Speleothems

The copper ion can form a solid solution in the aragonite crystal structure (Morse 1983). Blue aragonite speleothems occur 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, but can include minerals such as allophane and some clays, and some calcite speleothems are described as "blue". The colour is not diagnostic tool as to whether the speleothem is calcite or aragonite.

Blue "Larium stone" from a mine near Larium, Greece has been traded amongst mineral collectors. Material I have seen 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 Larium. Zn is one of the calcite-inhibitors listed by Morse (1983).

HISTORICAL PERSPECTIVES OF ARAGONITE IN NSW CAVES

C.S. Wilkinson, NSW Government Geologist, visited the "Belubula Caves" (Walli Caves – see Figure 5) 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.*

There was very little further reference to NSW cave aragonite until Frank (1974) described the Deep Hole (cave) at Walli. The lack of scientific interest in the subject in NSW in the interim is perplexing, given the amount of research on 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 (Figures 4 and 6). 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. They are now known to be aragonite (Ross Pogson pers. comm.).

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.*

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*". 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 identified both aragonite and calcite. SEM photographs showed the general habit of the anthodite fragments.

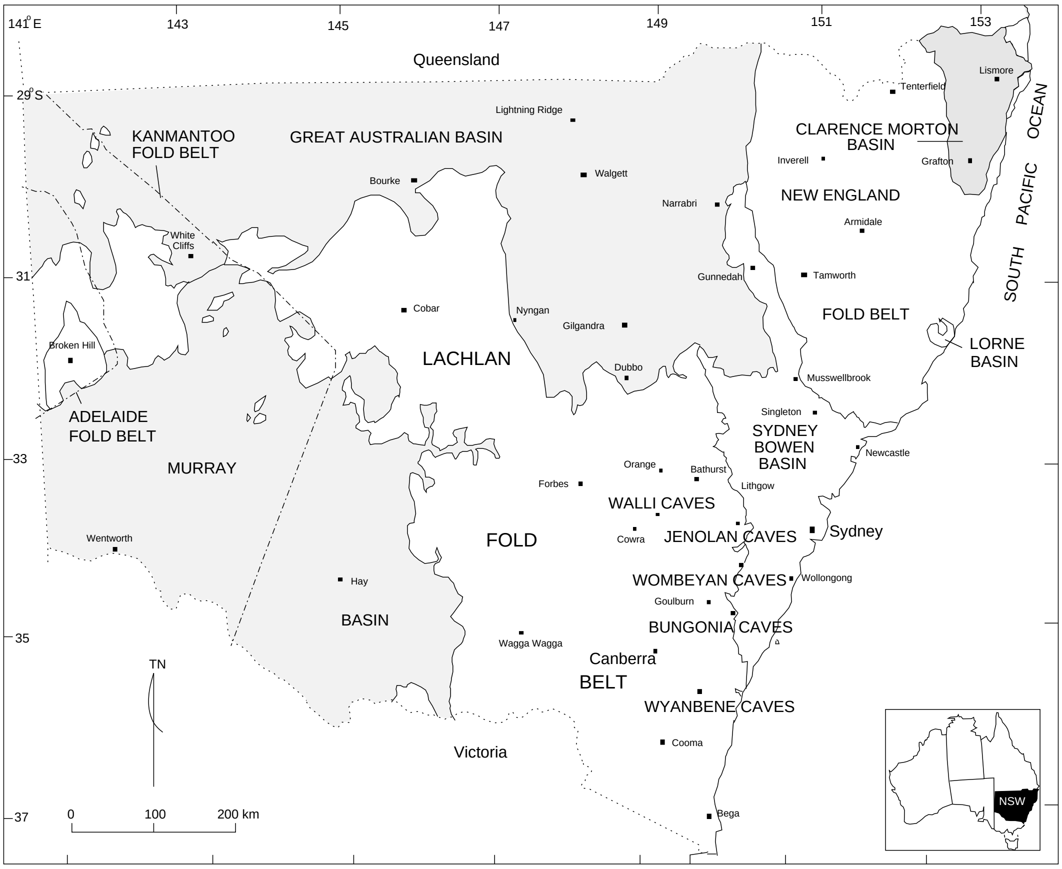

Figure 5. Map of NSW showing location of caves mentioned, with major tectonic features. Tectonic overlay re-drawn from NSW Department of Mineral Resources; Australian map from Geosciences Australia.

Osborne (1978) reported calcite which may have inverted from aragonite, from Cliefden Caves, central NSW. He also described blue aragonite speleothems in the Australian Museum minerals collection, specimens D36380 and D23544 from Boonderoo Cave. 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. 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), Osborne (1993) examined palaeokarst deposits in the show caves at Jenolan and mentioned aragonite deposits (helictites) were hosted on a substrate of laminated dolomitic internal sediments and palaeokarst deposits. 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.

Figure 6. The Arabesque, Cerberus Cave, Jenolan Caves. Speleothem is about 30 cm high and features flos ferri, ribbed stalactites and beaded helictites.

Osborne (1994) noted that in eastern Australia, the longest cave systems, and the ones with most extensive deposits of aragonite and gypsum occur near areas of Permo-Triassic basinal sediments, e.g. at Jenolan Caves (NSW), Exit Cave at Ida Bay and caves at Mole Creek in Tasmania. Osborne suggested that dolomite in the palaeokarst produced aragonite speleothems instead of calcite ones at Jenolan, such as the Furze Bush, possibly the Arabesque, and the helictites in Ribbon Cave. He suggested that pyrite and dolomite were emplaced in buried palaeokarst deposits at low temperatures by basinal fluids from above. In both the Western edge of the Sydney Basin, and in Tasmania, 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 weathering of sulfides deposited in palaeokarst can lead to ochreous deposits associated with gypsum and red calcite speleothems, as in Wyanbene Cave, Jenolan Caves and caves in Tasmania. Aragonite occurred with gypsum in a number of places in eastern Australia and where caves are associated with ore bodies. These bodies act as aquicludes: they prevent water from penetrating the rock during initial speleogenesis. Later, as pyrite in the ore bodies is oxidised, it assists in breakdown of bedrock, exposing palaeokarst and aids speleothem development. Thus, 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). "Ribbon helictites" from Jubilee Cave, Jenolan Caves, were described as "aragonite", but Rowling (1998*a*) showed them to be calcite.

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

> *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.*

Breezes were noted in this area, although no cave entrances are known nearby. Vizjak (1998*a*) 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.*

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*b*) described the discovery of Aragonite Canyon in Sigma Cave, Wombeyan with Sydney University Speleological Society. Although the surveyors did not discover this part of the cave, they were the first to document it. 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) described speleothems in the Chevalier Extension of Glass Cave, Jenolan. Some of the "aragonite" was associated with a white moonmilk-like material.

Osborne (1999) mentioned Ribbon Cave (Jenolan) aragonite speleothems associated with magnesium rich minerals: huntite, dolomite and ferroan dolomite. Dolomitic palaeokarst was 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" (Figure 7). Osborne suggested that pyrite was hydrothermally emplaced in palaeokarst sediments and its oxidation has formed sulfate and aragonite speleothems. The pyrite was emplaced between mid Permian and Late Cretaceous to Early Tertiary, or related to hydrothermal activity during 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 of anthodites in Fife Cave, Church Creek, N.S.W. (Pryke 2000) showed a helictite cluster resembling flos ferri. On the same page is a photograph by David Connard of aragonite anthodites in Genghis Khan Cave, Mole Creek, Tasmania.

Figure 7. Aragonite helictites (small, twisting bunches) and other speleothems at the Lyre Birds Nest, Ribbon Cave, Jenolan Caves. Area depicted is about 1 m high.

Osborne, Pogson & Colchester (2002) examined the white pasty substance found with aragonite at "The Lyrebirds Nest" (Ribbon Cave, Jenolan). It was huntite. Aragonite occurs 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 contained copper, 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 minor nickel at higher levels than in the white speleothem. Turner suggested copper caused the blue colour, but did not determine whether the Taplow Maze blue material was aragonite or calcite.

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

ARAGONITE IN OTHER AUSTRALIAN CAVES

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.

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.

Pisoliths from a mine at Bendigo, Victoria were found to contain aragonite and possibly $MgCO_3$ associated with siderite (Baker & Frostick 1947).

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).

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

Rowling (2003) examined subaqueous helictites found by cave divers from lakes in Mullamullang cave, Nullarbor Plain, Western Australia. Minerals in one helictite, determined by XRD, were calcite, magnesian calcite, aragonite, hydromagnesite, gypsum, celestite and halite. A subaqueous helictite from another lake in the cave contained calcite, magnesian calcite, aragonite, hydromagnesite, gypsum, huntite, cristobalite and halite.

RECENT STUDIES ON CAVE ARAGONITE IN NSW

Rowling (2004) examined aragonite in NSW caves, including Jenolan, Wombeyan and Walli. Aragonite in some NSW caves appeared to be associated with high evaporation rates allowing calcite, aragonite and vaterite to deposit, e.g. in cave sediments in areas with low humidity in Wollondilly Cave, Wombeyan. Several factors influence the deposition of aragonite instead of calcite speleothems in NSW caves, such as presence of ferroan dolomite, calcite-inhibitors (in particular ions of magnesium, manganese, phosphate, sulfate and heavy metals), and both air movement and humidity.

Several reported aragonite deposits were examined to confirm whether the material is aragonite. Substrates to the deposits 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. The study sites were all within Palaeozoic rocks in the Lachlan Fold Belt. Two 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.

Contact Cave lies near the eastern boundary of the Late Silurian Jenolan Caves Limestone, in steeply bedded and partially dolomitised limestone 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 was associated with a concentration of calcite-inhibiting ions, mainly magnesium, manganese and to a lesser extent, phosphates. Aragonite, dolomite and rhodochrosite are being actively deposited where these minerals are present. Calcite forms where minerals lack magnesium ions. The inhibitors appeared 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 lies near the western boundary of the Jenolan Caves Limestone, close to its faulted western boundary with Ordovician cherts. Aragonite here 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 included Glass Cave, Mammoth Cave, Spider Cave and the show caves. Aragonite in Glass Cave may be associated with 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, in metamorphosed Silurian Wombeyan Caves Limestone. Three sites were examined 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 end of the cave and in some other sites. In Sigma Cave, aragonite deposition involves 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, in the eastern part of the Wombeyan marble, has anthodites and helictites in an inaccessible area of the cave. Paramorphs of calcite after aragonite occurred 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 areas. The presence of vaterite and aragonite in fluffy coatings suggests vaterite inverting to aragonite. Calcite-inhibitors in the sediments included 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 in red phosphatic sediments with minor hydromagnesite and huntite. At cave W43, aragonite and paramorphs were detected in a coralloid speleothem. Dolomite in the bedrock may be a source of magnesium-rich minerals here.

Walli Caves are developed in the massive Belubula Limestone of the Ordovician Cliefden Caves Limestone Subgroup (Barrajin Group). Here, the limestone is steeply bedded, contains chert nodules with dolomite inclusions, and has gypsum and barite in veins. In Piano Cave and Deep Hole (Deep Cave), gypsum occurs both as a surface coating and as fine selenite needles on chert nodules in areas with low humidity. 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 were not major study sites, but sufficient information was available for a preliminary assessment as to why they may contain aragonite. These 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 low grade ore bodies which include several known calcite-inhibitors and aragonite occurs with both features. Brief notes were made of aragonite-like speleothems at Colong Caves (between Jenolan and Wombeyan), a cave at Jaunter (west of Jenolan) and at Wellington (240 km NW of Sydney).

ACKNOWLEDGMENTS

This research began in July 1999 as a part-time project and was completed in July 2004. Particular thanks are given to my supervisors Dr Tom Hubble (School of Geosciences, University of Sydney) and Dr Armstrong Osborne (School of Development and Learning, University of Sydney). Dr Ian Kaplin (Electron Microscope Unit, Sydney University) patiently showed how to use the electron microscope. The text has been greatly improved, thanks to helpful suggestions by the editor and reviewers.

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APPENDIX: GLOSSARY OF TERMS

Some terms used in speleology may be unfamiliar to the general scientist. Most speleothem terms used here are those defined by Hill & Forti (1997) and are recognised internationally. Other terms are used in Australian caving.

anthodite: Speleothem, usually made of aragonite, with an acicular and often branching appearance. Usually, anthodites develop from the cave's ceiling. Anthodites often have a solid core of aragonite, and may have huntite or hydromagnesite deposited near the ends of their branches. Anthodites vary in size from a few millimetres to about a metre.

cave: A natural cavity in rock that a person can enter. Some show caves are subdivided into convenient sections, each called a "cave", although this terminology is not encouraged. Thus, all the Jenolan show caves could be called one "cave" as they are all interconnected via underground passages, including the Grand Arch.

chamber: A cavity that a person can stand in, varies from about 4 m diameter to about 20 m diameter.

coral, cave: Speleothem characterised by hemispherical to globular appearance. Cave coral is often calcite, deposited on surfaces where there is some air movement. Deposition is mostly by capillary movement across the surface, with the main deposit occurring at the outside edge of the speleothem. Sizes usually vary from a few millimetres to a couple of centimetres diameter.

coralloid: Speleothem resembling coral but not sufficiently analysed to determine its make-up. Examples occur near the entrance areas of caves where there is a mixture of deposits and deposition mechanisms at work, resulting in speleothems with a mixture of characteristics and mineral content. The term is also used for the transition forms taken by some aragonite speleothems which alternate between anthodite-like and coral-like depending on the growth conditions.

flowstone: A deposit of (usually) calcite as a surface coating on any substrate in a cave so that the mass resembles melted wax. The overall shape is controlled by gravity and the surface tension of water. Surface textures range from completely smooth to deeply pocketed depending on carbonate concentration, flow rate and other factors. Flowstone is usually built up from thin layers of calcite, caused by seepage or dripping water containing HCO_3 outgassing CO_2 into the cave to precipitate $CaCO_3$. Depending on the source of water, flowstone can grade into stalagmites and where flowstone builds up over steep drops, furled shapes can resemble draperies.

flos ferri: Helictite characterised by slender tightly twisted forms, usually aragonite. Three different usages of this term include its first usage in 1748 by John Hill for a twisting variety of speleothem from mines and some Mendip (UK) caves (Shaw 1992). Hurlbut (1970) used a similar definition for aragonite in iron ore mines in Austria. Hill & Forti (1997) define flos ferri as a quill-like variety of anthodite, and define the earlier usage as "an ancient word for aragonite and for frostwork and helictites growing in the cavities of iron deposits". Herein, flos ferri means the tightly twisted form of aragonite helictite associated with iron ores.

furze bush Combination helictite, stalagmite and anthodite characterised by a vertical carbonate deposit (stalagmite/tite or column), usually of aragonite, together with finely twisting (usually aragonite) helictites. The helictites' diameter is typically about 1 to 5 mm and their radius of curvature ranges from about 10 mm to 100 mm. The name was given by Jenolan Caves guides for the fancied resemblance to a fir tree, and a name was needed in the show caves.

helictite: Speleothem with a fine capillary tube surrounded by usually either calcite or aragonite. Helictites are often wormlike, with typical diameter of a few millimetres and typical length of a few centimetres. Development is usually outwards from a wall. Beaded helictites have alternating deposits of calcite and aragonite giving the speleothem a pipe-cleaner appearance. Ribbon helictites are flattened calcite helictites.

heligmite: Helictite that develops from the floor of a cave, like small stalagmites, but they retain a fine capillary tube and develop by mineral-rich water flowing gradually through the capillary and onto the surface of the heligmite where it can outgas CO_2.

moonmilk: Speleothem with a pasty appearance, with a texture like cottage cheese when rubbed in the fingers. This material has a high water content. Most moonmilk is made of needle-fibre calcite, some contain hydromagnesite and other minerals. Moonmilk may be biogenic. True moonmilk has to be at least 90% calcite (Fischer 1988).

oolite: A loose spherical concretion, often pea-sized but can be larger. Usually found in pools or underground creeks where calcite or aragonite is precipitating. Oolites are rarely cube shaped. Outside of speleology, the conventional term for similar concretions is "pisolites". Oöids are smaller concretions (of any material) with a diameter of 0.2 to 0.5 mm.

passage: Part of a cave which is much longer than it is wide, like a corridor and generally of walk-through dimensions. In Australian speleology, a passage with reduced width is a "rift", and one with reduced height is a "crawlway" or a "flattener" depending on the way a person moved through it.

popcorn: A speleothem which vaguely resembles the snack, popcorn. Similar to "coralloid". A "popcorn line" is a horizontal deposit of popcorn in a cave passage which marks a humidity change or layer. Hydromagnesite and huntite may occur with aragonite.

spathite: A stalactite of aragonite with a wider central tube than the conventional calcite stalactite. This is caused by the flaring of the aragonite crystal compared to calcite. Sometimes a spathite comprises a series of aragonite "petals" overlapping each other to form a wide (2 or 3 cm) tube.

speleothem: Secondary mineral deposit in a cave. May be subaerial or subaqueous. They are classified according to mineral and shape, for example, a calcite stalactite. Commonly calcite, but can be other carbonates, sulfates, phosphates, oxy-hydroxides, etc. Most carbonate speleothems are formed by bicarbonate-rich water outgassing CO_2.

stalactite: Speleothem, usually of calcite, deposited on the ceiling of a cave. Characterised by general conical shape and usually a central hollow tube of calcite with the C-axis pointing downwards. This is surrounded by layers of calcite with the C-axis pointing at 90° to the surface.

stalactite, straw: Also known as "soda straws", these are central hollow tubes of stalactites without surrounding deposits. They usually occur where bicarbonate-rich water comes from a single point or crack, rather than running across the ceiling. Diameters are typically 4 or 5 mm and lengths vary from a few cm to metres.

stalagmite: Deposit on the floor of a cave under a drip point, resulting in a pile of carbonate (usually calcite) that is often higher than it is wide. Often roughly cylindrical symmetry, they vary from a flat disc about 4 cm diameter to massive deposits that are tens of metres high. The calcite C-axis is always directed at 90° to the stalagmite surface.

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(Manuscript received 28.09.2004)
(Manuscript received in final form 25.11.2004)