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Moonmilk: Sample analysis and review of the literature

***Garry K. Smith*[1]**

[1]Newcastle and Hunter Valley Speleological Society Inc.
P.O. Box 15, Broadmeadow, N.S.W. 2292, Australia. gksmith29@icloud.com

Abstract

Moonmilk is a relatively common speleothem that usually has the appearance of a white clumpy substance or a thin coating on cave surfaces. It is defined by its appearance and physical properties, not its composition. This paper reviews the properties of moonmilk, as well as the definition, including its physical characteristics, composition, phosphorescence and origin. A review of historical references to moonmilk reveals that many conflicting research conclusions have appeared in publications over the years, and that it is difficult to identify how moonmilk is created.

Analyses of several moonmilk samples from NSW caves are presented that confirm just how variable moonmilk can be. A sample from Victoria, confirms that even rare minerals can be deposited as Moonmilk. Future research will no doubt shed further light on aspects of moonmilk's formation.

What is moonmilk?

Moonmilk is a secondary mineral deposit formed within caves (a speleothem), although it is not found in all caves. Most cavers have probably seen clumps of soft white material on cave walls or floors, but never thought much about it. Experienced cavers may generalize and refer to all white fluffy-looking material in caves as 'moonmilk', but the novice who has never seen it before, will be none the wiser. This is where a definition may help:

"Moonmilk is a term used to describe aggregates of microcrystalline substances of varying composition" (Hill and Forti 1997a). A particular morphology and texture, not composition, is implied by the term 'moonmilk'.

Physical properties

Moonmilk consists of fine-grained particles, and is typically soft and mouldable when damp. When wet, it looks like white cream cheese and is pasty when rubbed between the fingers, but if just moist it may feel like fairy floss (cotton candy). When dry it can be crumbly and resemble chalk or talcum powder. Moonmilk in caves typically retains a high water content, thus giving it plasticity, but when moonmilk is mixed into water, the fine particles become suspended and the mixture looks like milk.

Figure 1. Kevin Mott surrounded by moonmilk in cave 5L-339, South Australia. Photo by Garry K. Smith

Figure 2. Henry Shannon has a close look at moonmilk in cave 5L-339. Photo by Garry K. Smith

Moonmilk can be found as just a thin coating on cave surfaces or in layers many centimetres thick, as in 5L-339 cave (in South Australia's Lower South-East) where moonmilk has formed on the walls and ceiling (Figures 1 & 2). Some chunks of moonmilk up to 5 cm thick have naturally fallen or been dislodged by humans or animals and now lie on the floor (Smith 1995, 2007). Moonmilk is a very fragile speleothem that can be easily damaged, so cavers must be careful as carelessness or intentionally touching it can cause irreparable damage, as has occurred in parts of 5L-339 cave (Smith 2007).

Most moonmilks are white or cream in colour, however it can occur in other colour variations including black. It can be formed in the shape of shawls, stalactites, stalagmites, columns, flowstone, coralloids and even as cave pearls. Most occurrences are found in subaerial locations (Figure 3), however there are a number of occurrences where it has formed in permanent pools of still water e.g. Cataract Cave, Prince of Wales Island, southeastern Alaska, where balls of moonmilk, locally called "cottonballs", up to 10 cm in diameter have formed (Hill and Forti 1997a).

Figure 3. David Stuckey and Marcia Kaye in the Moonmilk Chamber of Stable Cave (A26-27), Abercrombie, NSW. Photo by Garry K. Smith

Composition

In limestone caves moonmilk usually consists of calcium carbonate ($CaCO_3$) in the form of calcite or aragonite, while in dolomite caves it is typically hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \bullet 4(H_2O)$. Moonmilk can consist of many other carbonate minerals, either singularly or in combination. Less frequently it may consist of sulphates, phosphates, silicates and other minerals, particularly in non-carbonate caves (Hill and Forti 1997a).

Phosphorescence

Moonmilk typically possesses the property of luminescence, but more specifically, phosphoresence. Luminescence is the glowing (emission of light) of an object due to an increased energy level of its atoms, occurring without perceptible heat. The electrons orbiting the atom's nucleus can be excited by radiation (such as light from a camera flash or by electricity) and this radiation can be re-emitted at any wavelength, though is most familiar as visible light. Two forms of luminescence are "fluorescence" and "phosphorescence". Fluorescence is when light is emitted during absorption of radiation of some other (invisible) wavelength, but stops when the energy source is removed. Phosphorescent material can store the absorbed light energy (usually visible light) for some time and release light later (usually at a different wavelength - that is to say, colour), resulting in an afterglow that persists when the initial energy source has been removed.

Moonmilk's phosphorescent properties can be observed with the naked eye in a cave. The trick is to turn off all lights, cover your eyes with your hand while an electronic flash is set off close to and pointing toward the moonmilk. Make sure not to physically touch the moonmilk while in the dark. Immediately after the electronic flash is fired, take your hand away and look at the moonmilk. In most circumstances it will glow a bright green or blue for several seconds and in some cases up to 7 seconds (Smith 1995) as was the case in cave 5L-339, and also in Belfry Cave (TR-2), NSW (Smith 1996). The moonmilk remains glowing as its atom's electrons, with increased energy from the bright flash of light having moved them to higher orbits, then emit light as they return to their normal orbits around the nuclei.

If the moonmilk is of a very porous nature, the phosphorescent glow appears to last longer as the light from the camera flash and re-emitted light bounces around inside the moonmilk structure.

Historical references and medicinal uses of moonmilk

The likely first written reference to moonmilk in a cave was by Ko Hung about 300 AD (Shaw 1992). Agricola (1546, p. 465) described material that was probably moonmilk (which he called *galactites* = milk stone). Conrad Gesner (1555) provided a very clear description of moonmilk from a cave in Switzerland named Mondmilchloch (Moonmilk Cave) but he called the substance *fungus petraeus* (stone fungus) while recording that the locals called it *mondmilch* (Shaw 1992). Since then many articles have been written, discussing this material's properties and speculating about its origin.

Heller (1966) determined through literature searches that at least 79 names have been used to describe the speleothem moonmilk. Among them are *montmilch* gnomes's milk, *lac lunae*, *bergmilch* and rock milk.

Over the centuries humans have used moonmilk for medicinal purposes with various degrees of success as a remedy for many aliments and conditions including: haemorrhages, diarrhoea, dysentery, malignant fevers, to dry up ulcers and to stop wounds bleeding.

Origin of Moonmilk

Both biotic and abiotic mechanisms have been proposed to explain the formation of moonmilk. They include the effects of freezing, disintegration of bedrock or speleothems and microorganisms causing the material to precipitate.

Many studies have been undertaken which conclude that microbes, bacteria and/or other microorganisms are involved in the creation of moonmilk. A study by Danielli and Edington (1983) investigated the role of microbes in the formation of moonmilk. They isolated a wide range of colony types (the majority of them Gram-negative cells) from three caves in Wales, where calcite moonmilk was a common occurrence. These authors suggested that the cells were using the organic salt (negatively charged ions) for energy and dumping the calcium as a waste product. Calcite precipitation occurred when the solution saturation point was exceeded.

A study by Gradziñski and others (1997) that found *in vitro* culture of collected samples involved numerous genera of bacteria and fungi forming the microbial mat of moonmilk deposits. They concluded that, "The so called 'knallgas-bacteria', belonging to the chemoautolithotrophes, seem to play decisive role in calcification processes" and that other genera support the mineralisation processes.

A wide range of microbes, particularly bacteria and streptomycetes, but also fungi, algae and protozoa, can be cultured from moonmilk, often in very high densities (Northup and others 2000). However a later paper by Northup and Lavoie (2001) reviewing available literature concluded that "The evidence that microbes may play a role in formation of moonmilk is largely circumstantial and based on presence".

Northup and Lavoie (2001) also noted that, "Putative cells and an organic matrix can frequently be seen with SEM or in thin sections, but not in all cases. There is no known benefit of calcium carbonate precipitation in bacterial metabolism, although detoxification of calcium has been suggested (Simkiss 1986)."

However, culture studies have demonstrated the ability of bacteria from caves to precipitate calcium carbonate. The wide variety of physicochemical conditions and mineral types that have been identified indicates that microbes are clearly involved in the formation of moonmilk by dissolution or acting as nucleation sites, and they may play a minor or negligible role in other cases (Northup and Lavoie 2001).

A study by Borsato and others (2000), determined that moonmilk samples collected from 14 caves in the Italian Alps (1500 - 1900 m asl.) were created through crystal growth triggered by slow degassing of solution and capillary flow under very low discharge. The optimal microclimatic conditions for the formation of calcite moonmilk in the caves they studied were temperatures of 3.5-5.5°C and relative humidity that is at or close to 100%. "Available evidence from these deposits indicates that microbes did not play a direct role in the calcite precipitation" of the moonmilk. The calcite crystals making up the moonmilk, ranged between 50 and 500 nm wide and 1 to >10 µm long.

Hill and Forti (1997a) list four methods by which moonmilk may originate:

1. *Freezing of limestone by water ice causes carbon dioxide to be expelled from the limestone, and a milky fluid is produced on the limestone wall.* (However, they accept that this method of moonmilk creation would only apply to caves which experience temperatures that drop to below freezing point.)

2. *Moonmilk is formed as part of the life cycle of microorganisms. Species of bacteria, algae and fungi have all been isolated from moonmilk deposits.* (As previously mentioned, the existence of microorganisms in moonmilk samples does not automatically imply the organisms played a part in its creation. There is still much research that needs to be undertaken to conclusively determine the role of various life forms.)

3. *Moonmilk is a disintegration product of bedrock or speleothems (i.e., it is a rotten concretion).* (This method of moonmilk creation has only been attributed to a very few documented instances and typically does not stand up to the analysis of most moonmilk deposits.)

4. *.... Moonmilk precipitates directly from groundwater as do other speleothems such as stalactites and stalagmites, but that, for some reason, the crystals in the deposit never grow large.* (This theory explains the majority of moonmilk deposits, particularly the magnesium carbonate minerals, that

naturally form as finely microcrystalline to cryptocrystalline deposits. However this theory does not readily explain calcite and aragonite moonmilks that form as microcrystalline or cryptocrystalline deposits. This is contrary to the typical deposition of these two minerals that usually form large crystals when deposited as stalagmites and stalactites etc.)

Forti (2009) suggests that microbiological reactions frequently seem to be responsible for moonmilk deposition by: “1. biochemical corrosion of bedrock by organic acid produced by microorganisms (*Arthrobacter, Flavobacterium, Pseudomonas)*; 2. active precipitation of moonmilk by bacteria (*Macromonas bipunctata*).” Bacteria that utilize CO_2 (like *othrix* in the sulphur cycle) have been found to cause accelerated carbonate speleothem growth.

Given the many conflicting research conclusions that have appeared in publications over the years, it is impossible to identify a single cause for the formation of moonmilk. No doubt there is still much research to be undertaken before science can fully explain how different moonmilks are created.

SEM and XRD analysis of moonmilk from NSW caves

Twenty pea-size samples of moonmilk were collected by the author from caves across NSW. Samples collected in National Parks were covered under an agency permit, while those from private property required permission from individual owners. Scanning Electron Microscope (SEM) images were prepared and chemical analyses were undertaken by Brian M. England (Principal Geological Consultant) at BHP Billiton Research Laboratories in Newcastle, NSW (England 2000).

Part of each original sample was prepared as a fresh fracture surface, coated with a layer of gold (around 40 nanometres thick) and examined by SEM to determine its morphology (England 2000). This data was recorded as micrographs, both as hard copy (Polaroid prints) and digital images. Some of these very high resolution SEM images are reproduced here. Analysis of each sample was achieved by X-ray powder diffraction (XRD), using a Siemens D500 diffractometer and then Fein-Marquart Associates µPDSM search/match software was used to interpret the pattern and determine its mineralogy. Part of each sample was then analysed by energy dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM), to determine its chemical composition, especially the presence of major impurity elements such as strontium, manganese and iron, which may influence growth and morphology.

Many of the moonmilk samples were of similar needle-like shape and size as shown in Figure 4. Some other variations of moonmilk fibres are shown in Figures 5 to 11.

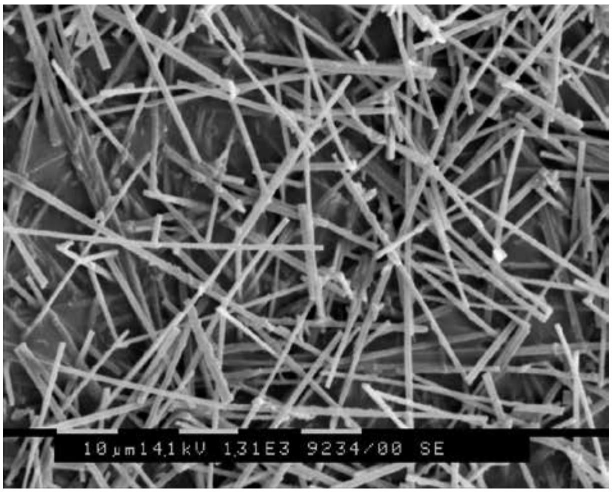


Figure 4. Moonmilk from Barber Cave (GP14), Cooleman Plains NSW. Average fibre size is ≈1.4µm (0.0014 mm) wide. The sample only contains calcium carbonate. Image by Brian England

Figure 5. Moonmilk from B4, Kunderang Brook, NSW. Calcium carbonate strands are approx. 7.08µm (0.00708 mm) thick. Image by Brian England

All images are greatly magnified under an SEM. Note the many variations in shape of the microcrystalline to cryptocrystalline crystals. Out of many samples collected across NSW, there was only one sample which clearly showed evidence of being produced by a life-form, most likely bacterial. The calcite micro-structures are tubular with a spiralling shape (Figure 10).

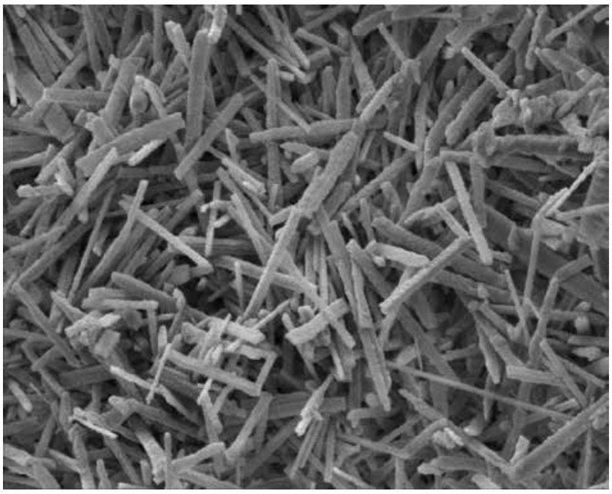


Figure 6. Moonmilk from Rock-me Cave (TR52), Timor, NSW. The thickest fibre in this photo is ≈ 2μm (0.002 mm) wide. The sample only contains calcite fibres.   Image by Brian England

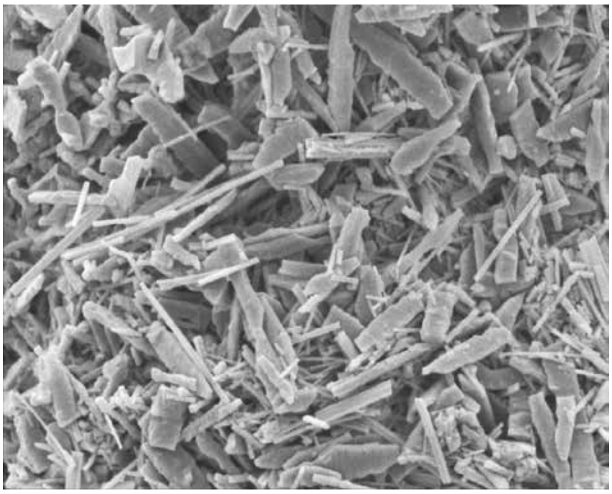


Figure 7. Moonmilk from Rock-me Cave (TR52), Timor Caves. The thickest calcite fibres of moonmilk are ≈ 4μm (0.004 mm) wide. Image by Brian England

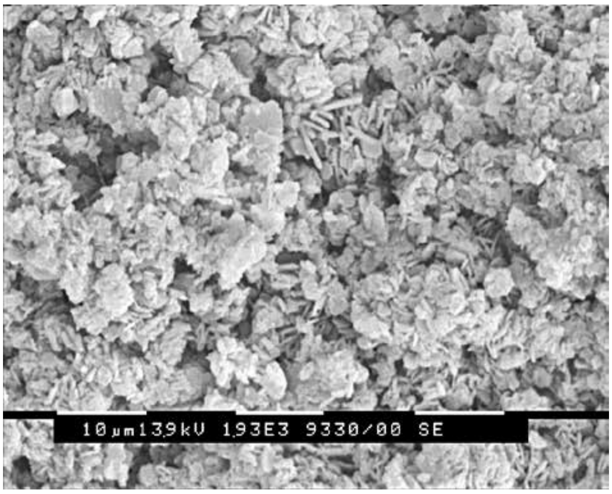


Figure 8. Moonmilk from Wiburds Lake Cave (J58), Jenolan NSW. White section on scale bar is 2μm (0.002 mm) long.   Image by Brian England

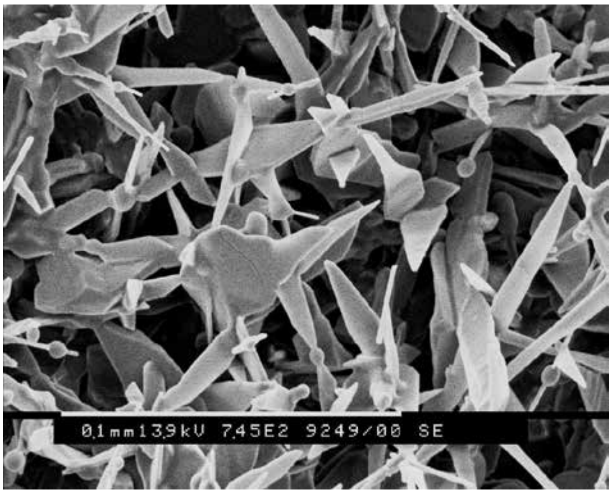


Figure 9. Moonmilk from Punchbowl Cave (WJ8), Wee Jasper. Analysis indicates that the majority of this sample is calcite, however some calcium sulphate hydrate (Gypsum) CaSO4.2H20 is also present. The largest calcium carbonate fibre of moonmilk in photo is approximately 24.3μm (0.0243 mm) wide. No Gypsum is present.   Image by Brian England

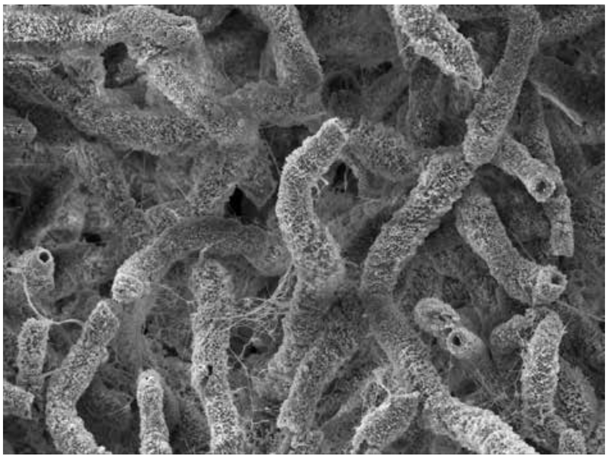


Figure 10. Moonmilk from Moses Cave (MP7), Moparrabah NSW. Image width is 250μm (0.25mm). Sample that indicates a biological influence in the creation of moonmilk. Each of these worm-like hollow structures are approximately 20μm in diameter with a 3.8μm hole in the middle.   Image by Brian England

Figure 11. Moonmilk from Mammoth Cave (J13) Jenolan NSW. Sample contained both calcite and aragonite. Fibrous calcite strands are approximately 1.5μm thick.   Image by Brian England

Most samples consisted of calcite with no trace of aragonite. From the 20 samples, only one from Deep Hole at Walli (WA-17), showed aragonite to be present as a major phase.

The results of a sample collected from Mammoth Cave (J-13), NSW clearly showed that the sample contained both calcite and aragonite (Figures 11 & 12). One could assume that the rice-grain size speleothem was first deposited as aragonite and over thousands or millions of years, the outside crystal structure changed to calcite while the internal crystal structure remained as aragonite. The external appearance of the sample kept the needle-like shape of the original aragonite (England 1997, Smith 1997).

In addition to the abovementioned samples from NSW limestone caves, a pee-size sample of moonmilk was collected from amongst the floor scoria of Tunnel Cave (3H-9) a lava cave at Mt Eccles, Victoria. Although the look and feel of the moonmilk was the same as the samples collected from limestone caves, the analysis revealed that it was a rare mineral called Taranakite, $K_3(Al,Fe)_5(HPO_4)_6(PO_4)_2{\bullet}18(H_2O)$ (Figures 13 & 14) (England 1999). This is a good example of how the term moonmilk applies only to morphology and texture, not composition.

Figure 13. Taranakite, $K_3(Al,Fe)_5(HPO_4)_6(PO_4)_2{\bullet}18(H_2O)$, moonmilk from Tunnel Cave (3H-9) a lava cave at Mt Eccles, Victoria. White section on scale bar is 2µm (0.002 mm) long. Image by Brian England.

Discussion: $CaCO_3$ polymorphs

Calcium carbonate has three polymorphs: calcite, aragonite and vaterite. This means that all three of these minerals have the same composition ($CaCO_3$), however they crystallise with different atomic structures. Vaterite is rarely found in caves because it requires temperatures above 35°C to form. On the other hand calcite is the most abundant, since cave temperatures and pressures fall completely within its stability field.

Aragonite is the second most common mineral in caves after calcite. Because cave temperatures and pressures fall below the range at which aragonite crystallises, it theoretically should not exist in caves. However it does form even in caves at high altitude where the temperature approaches 0°C. Given enough time (thousands to millions of years) aragonite will change its internal crystal structure to calcite, while externally keeping the needle-like shape of the original aragonite (Hill and Forti 1997a).

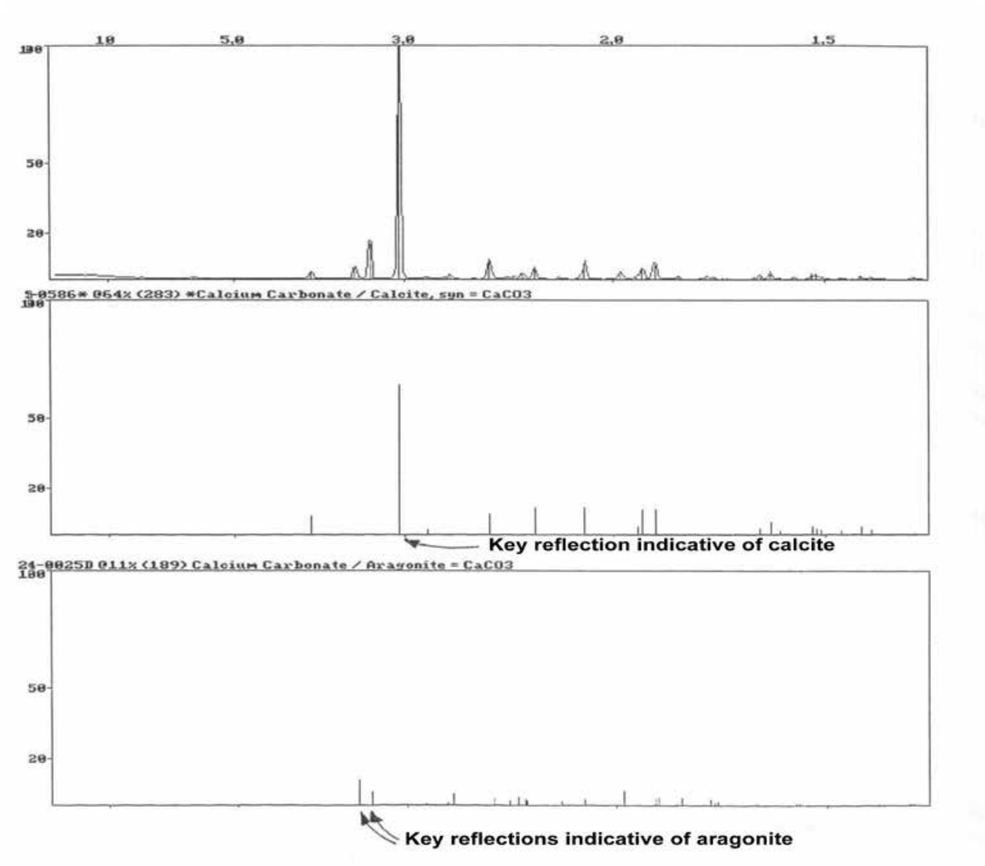
It is now generally accepted that the presence of magnesium (Mg) and\or strontium (Sr), in the precipitating solution is the prime factor which influences aragonite deposition in preference to calcite (England 1984). However another factor that may cause aragonite to precipitate is the degree of supersaturation with respect to the rate of CO_2 loss from the solution.

In 1971, Fishbeck and Müller found that when the Mg/Ca ratio reached about 2.9:1, aragonite is the main calcium carbonate mineral to form, and at a ratio of 4.4:1, it is the only calcium carbonate mineral to form. Evaporation of the precipitating solution (rather than carbon dioxide loss) has a large effect in determining which $CaCO_3$ polymorph or magnesium carbonate mineral is deposited. Ironically, the magnesium ion is excluded from the aragonite crystal structure. One theory is that the magnesium ion poisons the crystal growth of calcite, allowing the supersaturation level to build up to the point where aragonite can precipitate (Hill and Forti 1997b).

Conclusion

Moonmilk consists of microcrystalline particles that can vary considerably in shape and composition. As moonmilk has four known modes of creation it is almost impossible without thorough research, to identify how an *in-situ* moonmilk has formed in a cave. The texture and feel of moonmilk can vary considerably depending on its moisture content. Also the mineral composition can't be determined merely by observation or from its location in a cave.

The presence of microbes in analysed moonmilk samples, is not a basis to automatically assume that they have played a role in its creation. There is still much research to be undertaken before science can fully explain how different moonmilks are created.

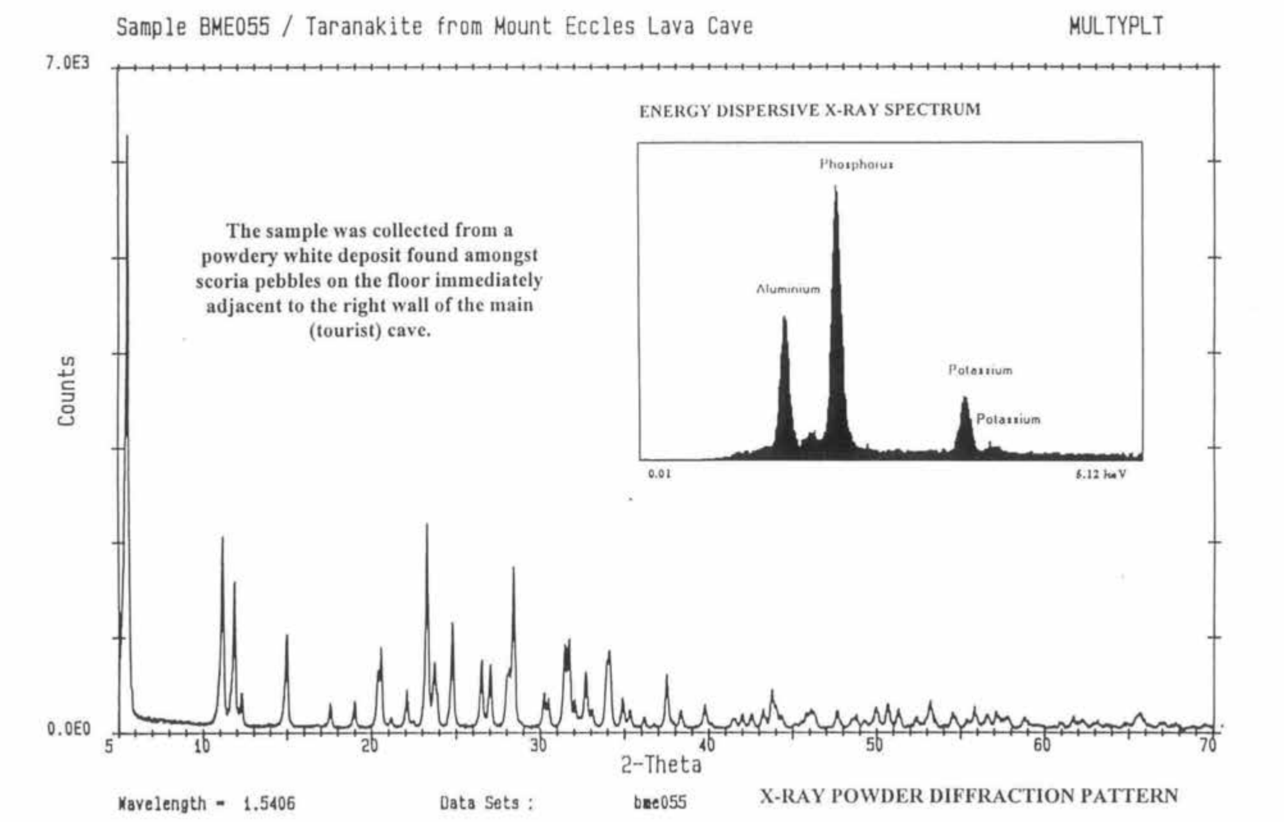


Key reflection indicative of calcite

Key reflections indicative of aragonite

Figure 12. Moonmilk analysis by X-ray diffraction (XRD), using a Siemens D500 diffractometer and then Fein-Marquart Associates µPDSM search/match software to interpret the pattern.

The first chart shows the actual X-ray reflections from the atomic lattice structure. The second chart is the normal X-ray pattern for Calcite. The third chart is the normal X-ray pattern for Aragonite. Graphs by Brian England.



The sample was collected from a powdery white deposit found amongst scoria pebbles on the floor immediately adjacent to the right wall of the main (tourist) cave.

Figure 14. X-ray diffraction (XRD) analysis, that determined the moonmilk sample from Tunnel Cave (3H-9) is rare mineral called Taranakite. Diffractogram by Brian England

Acknowledgements

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