

Chromophores Producing Blue Speleothems at Cliefden, NSW.

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Abstract

Osborne (1978) has described in some detail the blue stalactites that occur in Murder and Boonderoo Caves at Cliefden, NSW and reports “that the colour is due to some impurity in the aragonite and not to refractive effects”. In this study, small samples from the Boonderoo and Taplow Maze blue speleothems have been chemically analysed. Based on these chemical analyses it is suggested that the major chromophore is copper, with secondary contributions from chromium (Taplow Maze only) and perhaps nickel.

INTRODUCTION

Blue speleothems occur in Murder (CL2), Boonderoo (CL3) and Taplow Maze (CL5) Caves in the Cliefden Karst area in Central Western NSW (Figure 1). The caves are located in the Belubula River valley about 30 km north east of Cowra. The sky-blue stalactites (Figure 2) in Murder and Boonderoo Caves are reported to occur at the boundaries of the Upper and Lower Units of the Boonderoo Limestone Member and the Boonderoo and Large Flat Limestone Members respectively (Osborne, 1978). Osborne examined an Australian Museum sample (specimen number D36380) of the Boonderoo blue stalactite using optical microscopy and X-ray powder diffraction and found that the stalactite consisted of an inner zone of sparry calcite and an outer zone of aragonite. The author further concluded that “the blue colour is due to some impurity in the aragonite”. In addition to the blue stalactites discussed by Osborne, a number of blue speleothems occur in Taplow Maze Cave, including two aqua-blue columns (approx. 250 mm high) and two pale-sky-blue columns (approx. 300 mm high) surrounded by some flowstone. These are the only reported occurrences of blue speleothems in the Cliefden Caves system. The straight line distance from Murder to Taplow Maze cave is about 1.1 km (Central Mapping Authority, 1978). Note that the scale bar on Osborne’s topographic map is in error.

It was considered that the only way to establish the origin of the blue colour in the Cliefden Caves speleothems was to chemically analyse samples of the material. Fortunately, modern chemical analysis techniques, which have very high sensitivity, have made the study of *in situ* speleothems feasible. Meaningful chemical analysis data can be obtained from samples of only a few milligrams. Such samples can be carefully collected (essentially without causing damage) from the surface of an *in situ* speleothem. In conjunction with the Orange Speleological Society, arrangements were made to collect and analyse representative samples of the blue speleothems. To avoid ambiguity and to provide

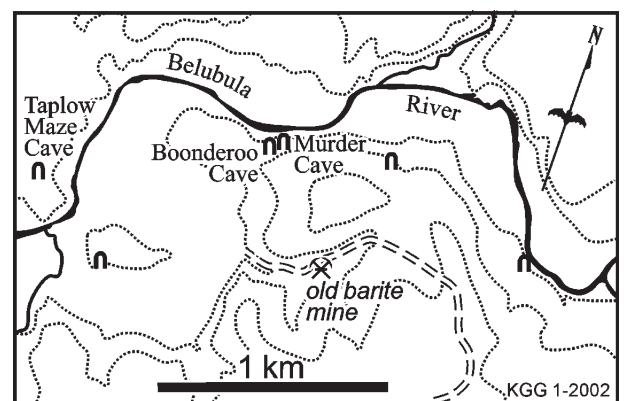


Figure 1: Location of Boonderoo, Murder and Taplow Maze Caves and nearby abandoned Barite Mine.

baseline compositional data, samples of adjacent white speleothems were also included in the study.

SAMPLE COLLECTION AND CHEMICAL ANALYSIS

Boonderoo Cave

In late 1995 members of the Orange Speleological Society collected a sample weighing approximately 40 milligrams from the blue stalactite located in Boonderoo Cave. The sample was carefully scraped from a small area of the stalactite using a steel blade. The sample was subsequently analysed using laser ablation inductively coupled plasma mass spectrometry (laser ablation ICP-MS), which is a technique well suited to the analysis of small solid samples. However, it is difficult to fully quantify the results and the data should be treated as semi-quantitative. Concentrations are expressed in parts per million (ppm). An extremely small (less than 10 mg) reserve sample was subsequently analysed using graphite furnace atomic absorption spectrometry (GFAAS). GFAAS is a very sensitive technique for the determination of trace elements. The limited sample mass restricted the analysis to copper and reduced the accuracy of the analysis. Results are summarised in Table 1.

Blue Speleothems



Figure 2: Blue stalactite in Murder Cave (CL3), Cliefden Caves. Photo by Garry K. Smith.

In addition, a sample from Boonderoo Cave was also available from the Australian Museum collection (specimen D23544). In this instance it was decided to try to obtain a more accurate analysis by using conventional solution-based ICP-MS rather than laser ablation ICP-MS. The samples were dissolved using a mixed acid digestion prior to analysis. Unfortunately, severe interference from the high levels of calcium present, coupled with the very small sample masses available resulted in unreliable analytical results from this approach.

Taplow Maze Cave

More extensive sampling was carried out in Taplow Maze Cave by members of the Newcastle and Hunter Valley Speleological Society in November 1996. Six samples were collected from a blue column and adjacent fallen broken white stalactite, two areas of blue flowstone and two areas of adjoining white flowstone. All samples were collected using a titanium scraper to carefully scrape material from the surface of the speleothem onto clean glazed sampling paper. The sample was then transferred to a zip seal plastic bag. Sample mass ranged from about 30 to 80 mg for all samples except the fallen broken white stalactite, from which a sample mass of about 5 g was collected.

As with the Boonderoo material, these samples were analysed using conventional solution based ICP-MS but again with disappointing results. Fortunately, reserve samples were available for the blue column and adjacent fallen broken white stalactite. These reserve samples were subsequently analysed using GFAAS. Due to the very limited sample mass, analysis was restricted to the elements considered most likely to contribute to the blue colour of the speleothems. The GFAAS results were validated using Certified Reference Materials. Results of this analysis are summarised in Table 2. Concentrations are expressed in ppm.

RESULTS AND DISCUSSION

The chemical analyses show high levels of copper in the Taplow Maze Cave sample and detectable levels of copper in the Boonderoo Cave sample. Most copper compounds are blue, blue green or green in colour and hence it can be concluded with some confidence that copper is the predominant chromophore. The Cu^{2+} ion can substitute for Ca^{2+} in the calcite or aragonite lattice (White, 1997). Cu^{2+} substitution in aragonite has been reported to produce blue (Cabrol, 1997 and White, 1997) and blue-green (Eraso, 1977) colourations. The presence of copper is not surprising given the extensive copper mineralisation in the general geographical area (Markham, 1975).

The Taplow Maze Cave sample also has significant levels of chromium and detectable levels of nickel. Most chromium and nickel compounds containing the Cr^{2+} and Ni^{2+} ions, respectively, are green or blue green and it is thus likely that these elements are secondary chromophores. Cr^{2+} is easily oxidised and as a result extremely unstable in water. It is rare in the cave environment (White, 1997). It is thus unlikely that Cr^{2+} will replace Ca^{2+} in calcite or aragonite in speleothems. However, Cr^{2+} is reported to impart deep blue colours to silicate minerals (White, 1997). While most compounds containing the Ni^{2+} ion are green, substitution of Ca^{2+} by Ni^{2+} in calcite results in a yellow colour (White, 1997). This is due to the ionic radius of Ni^{2+} being smaller than that of Ca^{2+} (Weast and Selby, 1967). The resultant distortion of the Ni^{2+} -substituted Ca^{2+} site causes the changes in the observed colour. White (1997) reports that a green aragonite in Timpanogos Cave, Utah, is due to minor amounts of a silicate mineral mixed with the aragonite. It is thus reasonable to assume that if the chromium and nickel are acting as chromophores, then they are probably present as the Cr^{2+} and Ni^{2+} ions in minor amounts of admixed silicate minerals.

The Boonderoo Cave sample also contains significant levels of strontium and barium. While these elements are unlikely to contribute to the blue colour, their presence is not unexpected. Both strontium and barium can isomorphously replace calcium in the aragonite lattice and strontium is a common minor constituent of

Table 1
Boonderoo Cave Blue Stalactite Analysis
Concentration in Stalactite (ppm)

Element	Semi-quantitative Laser Ablation ICP-MS Analysis	GFAAS Analysis (validated using Certified Reference Materials)
Iron #	46	
Magnesium	2	
Nickel	1	
Copper	2	65
Zinc	26	
Strontium	130	
Barium	150	
Lead	2	
Uranium	1	
Manganese, zirconium & antimony	Probably present (not conclusive)	
Rare earths	Not detected	

The iron detected in this sample may be present in the sample or could, at least in part, be due to contamination from the steel blade used to collect the specimen and/or the abundant red (iron-rich) cave sediments.

Table 2
Graphite Furnace Atomic Absorption Spectrometric Analysis
Taplow Maze Cave Blue Column and Adjacent (Fallen) White Stalactite.

Element	Concentration in Blue Column (ppm)	Concentration in White Stalactite (ppm)
Chromium	27	<1
Copper	2520	<1
Nickel	4	2

aragonite. Significant barium mineralisation occurs in the area with a barite mine once being operated close to the karst area (Figure 1).

The colour of the blue speleothems varies from very pale blue flowstone in Taplow Maze Cave to the azure blue stalactites in Boonderoo and Murder Cave and columns in Taplow Maze Cave. This variation in depth of colour may be due to variation in the concentration of the chromophores and/or thickness of the blue layer.

ACKNOWLEDGMENTS

I would like to thank all those who contributed to this project, including members of the Orange Speleological and the Newcastle and Hunter Valley Speleological Societies who assisted with specimen collection. Dr John Watling (Chemistry Centre of WA) ran the ICP-MS analyses, and Wayne Aurisch and Christine Foster (BHP Integrated Steel Laboratory Services, Hunter Laboratory) provided the GFAAS data. Australian Museum specimen D23544 was kindly made available

by Mr Ross Pogson (Collection Manager). Brian England provided a critical review of the manuscript during various stages of its preparation. The ongoing assistance and access privileges to these caves extended by Rosalin and Anthony Dunhill, owners of "Boonderoo" is gratefully acknowledged. Russell Drysdale is thanked for his review of a draft of this paper.

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