

**BLACK COLOUR OF AUSTRALIAN SPELEOTHEM:  
ORIGIN AND PALAEO-ENVIRONMENTAL IMPLICATIONS**

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Speleothem (precipitated calcite) deposits from caves and the proxies preserved within them are widely used in palaeo-environmental and palaeo-climatic reconstruction. Isotope-geochemical analyses of dated growth rings have proven particularly valuable, whereas methods for exploiting information gained from organic (and inorganic) trace constituents are in their early stage of development (Blyth *et al.*, 2006). A particular challenge is presented by so called ‘black’ speleothem of the Nullarbor Plain in Australia (Webb and James, 2006). Speleothem such as stalactites tend to vary in colour from white to yellow or brown, but are rarely very dark or black except when covered by organic overgrowth. The Nullarbor is the only region known globally where thoroughly black speleothem (sometimes interspersed by white layers) occur widely and in abundance. Due to climatic change, speleothem formation has long ceased in this region and recent advances in U-Pb dating techniques have established an age of ~ 4 Ma for a Nullarbor specimen (Woodhead *et al.*, 2006). This sample is one or more orders of magnitudes older than most speleothem analysed from other locations to date and demonstrates the unprecedented opportunity Nullarbor speleothem analysis may provide for palaeo-environmental reconstruction.

There have been various attempts to establish the origin of the unusual black colour in Nullarbor speleothem (summarised in Webb and James, 2006), but none to date have provided unequivocal evidence for the origin of this colour. A key problem in establishing its origin is the fact that a very small amount of substance within or between the lattice of otherwise colourless calcite crystals may be sufficient to intensely colour a speleothem. Suggestions for colouring agents include inorganic residue from the weathering of the host limestone such as Mn, Fe or S compounds; or organic traces such as organic acids released from decaying vegetation, or airborne black carbon soot from wildfires drawn into caves by the strong barometric cave draughts that typify the Nullarbor.

In this study, we aim to test the above hypotheses on the origin of the black colour based on a series of analyses of samples from the same region of the Nullarbor by teams in

Australia and the UK. In these samples, two superimposed mechanisms of ‘darkening’ are evident (Figure 1): a brown colour within the matrix (zone A) and distinct to cloudy black inclusions (B). Methods used include optical examination by Raman Microscopy, SEM and environmental SEM of thin sections and of residue following removal of the calcium carbonate ‘matrix’, X-ray Photoelectron Spectroscopy, GC-MS, Isotope MS and ICP-MS of residue; and also solid state NMR of powdered speleothem material. The nature, potential origin and their contribution to the overall sample colour of both ‘darkening’ agents are evaluated and their implications for palaeo-environmental reconstruction are discussed.

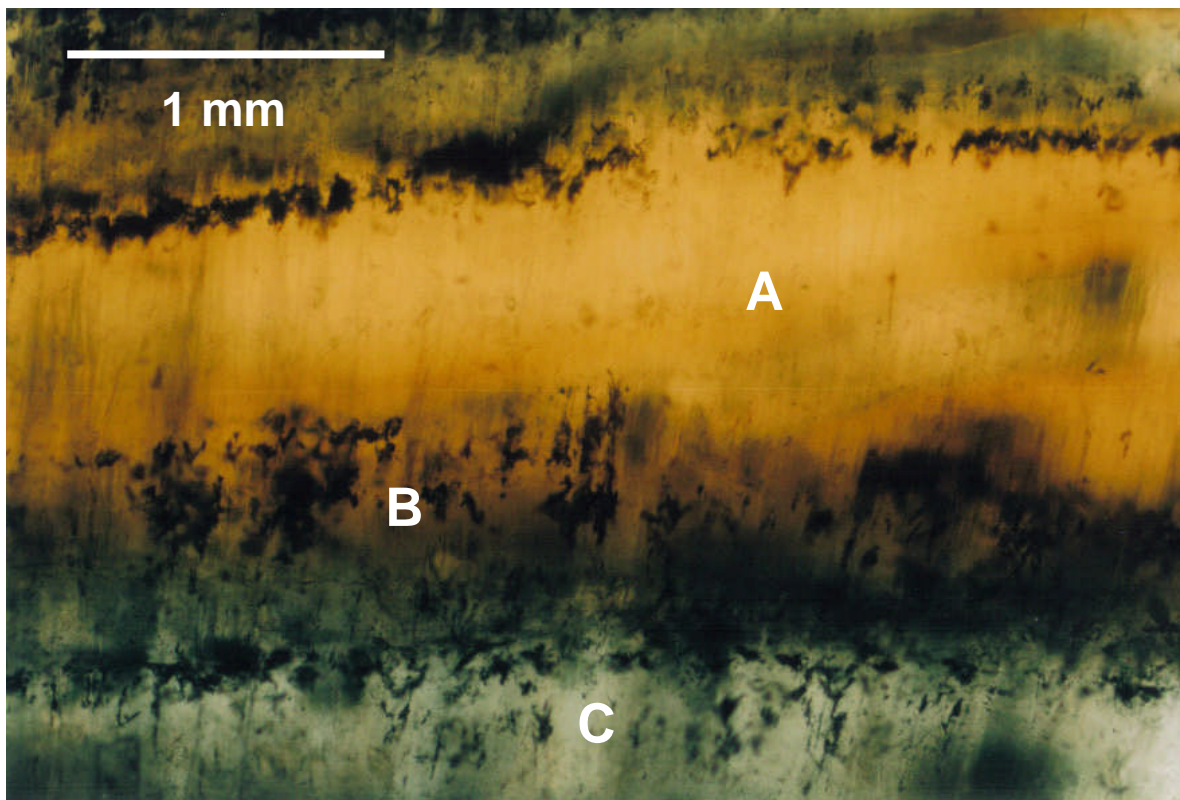


Figure 1. Thin section of a banded ‘black’ speleothem sample from the Nullarbor Plain, Australia. Three distinct zones are evident: brown (A), uncoloured (C) and layers with black inclusions (B).

## REFERENCES

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