CO_2 fluctuations in two Wombeyan caves and implications for Speleothem growth

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Abstract

CO_2 is being seen as an increasingly important factor in calcite development and hence speleothem growth. However, a better understanding is needed in order to fully understand the use of speleothems as recorders of palaeoclimate information.

Despite several cave CO_2 studies undertaken in the Northern Hemisphere, each emphasising the specificity of each site, there is a paucity of data on CO_{2cave} distribution in the southern hemisphere, especially in Australia. To date only one NSW CO_{2cave} study has been conducted and published and this study is the first to be undertaken at Wombeyan Caves.

Introduction

The objectives of my honours thesis were to measure CO_2 fluctuations throughout two touristic caves within the Wombeyan Caves Conservation Reserve, to determine preferential pCO_2 conditions for calcite growth, consider impacts of site hydrology on calcite (speleothem) growth and to investigate anthropogenic contribution to cave pCO_2.

Impacts on Calcite Development

The impacts on calcite development begin with the rainfall reacting with atmospheric and soil CO_2 produced by bioproductivity (Moore, 1962). The percolating waters dissolve CO_2 forming carbonic acid, which is the key driver of carbonate dissolution, until the fluid becomes saturated with respect to calcite. The now saturated dripwaters enter a cave with lower CO_2 partial pressure (pCO_2), preferentially, causing the CO_2 to degas and precipitate calcite as a speleothem (Moore, 1962). The rate of each of the aforementioned process will impact the hydrochemistry and equilibrium state of the dripwater which will determine the growth rate, geochemistry and petrography of the calcite (Fairchild *et al*., 2000; Frisia *et al*., 2000; Spötl *et al*., 2005). The pCO_{2cave} is known to impact the dripwaters ability to degas and deposit calcite, therefore preferable conditions for growth occur when pCO_{2cave} is lower than $pCO_{2dripwater}$. At CO_2 levels above the limestone threshold (2400ppm) the reaction reverses and dissolution occurs causing irreparable damage to the modern speleothems (Dragovich and Grose, 1990). As pCO_{2cave} has been known to show seasonal variability it can be assumed that during periods of lower CO_{2cave} (cooler months) would be preferential for the enhanced degassing of dripwaters and more conducive to calcite growth (Baldini *et al*., 2008). This implies that speleothems may preferentially record a winter climate signal, which will have implications for interpretation of palaeoclimate records.

Site Location and Climate

The Wombeyan Karst Conservation Reserve is located on a dissected plateau east of the Great Dividing Range, 125km SW of Sydney. The marble is approximately 200m thick and covers an area of 4km2. It is highly jointed providing important starting points for enlargement by solutional processes (McDonald, 2005).The two caves studied were Wollondilly and Kooringa. Wollondilly is a complex three levelled cave, with over a km of ladders and stairs, whilst Kooringa Cave is a small collapsed chamber. Local climate is warm to cool temperate but hydrology is highly variable and aseasonal rainfall patterns provides a constraint on calcite growth. Long term hydrology indicates that there is greater recharge in the cooler months where there is less evaporation. However, this is not always the case there can be lower precipitation in winter and high precipitation in summer depending on the El Niño Southern Oscillation conditions (ENSO). As an example, this year (2012) there was heavy rainfall in February and March, when the highest temperatures were recorded, and a water deficit occurred in the cooler months. At this site rainfall is strongly correlated to La Nina/El Niño phases. Since calcite deposition is also dependent on discharge and discharge is known to be ‘aseasonal’ at Wombeyan, speleothem growth rate at this site is also deemed to be highly variable. This has potential implications for derivation of climate histories from calcite precipitated from this drip and other similar drips at Wombeyan (McDonald *et al*., 2004).

Carbon Dioxide Measurements

Measurement of cave CO_2 levels was undertaken using a hand held Vaisala GM70 CO_2 monitor. Potential error by operator respiration was minimised by placing the probe in a designated area and the removal of the operator from the cave. Temperature, Humidity and Dew Point were measured synchronously with CO_2 using an EasyLog USB Probe. For the most part there appeared to be no strong relationship between CO_2 and other atmospheric conditions within the cave.

Two types of surveys were undertaken: Firstly, 8 hour surveys with readings taken at 20m intervals to quantify CO_2 distribution throughout the Wollondilly and Kooringa cave systems. This was performed on three occasions with the aim of quantifying seasonal cave CO_2 variability. And secondly surveys were undertaken initially overnight and then for more extensive periods to determine the impacts that the external diurnal temperature and pressure fluctuations had on the cave atmosphere.

Wollondilly Survey Results

The results of the Wollondilly surveys (Figure 1a-c) indicate that the CO_2 levels follow similar trends throughout the year. During each survey CO_2 levels are consistently higher in the Mulwaree Extension and lower in the Paddy Fields. The similarity between internal and external temperatures (±2°C) in April will decrease cave breathing by limiting the density driven exchange of air masses, from surface to cave and vice-versa. The possible high CO_2 build up in the upper passages are unequivocally characterized by the presence of roots penetrating through fractures in the cave, as the roots breathe and produce CO_2. This CO_2 is then trapped in the upper passages of the Mulwaree Extension due to the bottleneck that occurs upon entry to this area. Lower Wollondilly experiences the lowest levels of CO_2 because it is well ventilated. However, there is a slight yet consistently higher level of CO_2 in the Coronation Extension due to constricted flow. Due to an increase in contrast between external and internal temperatures (±6°C) increased cave breathing occurred in both July and in August and as a result there are consistently lower levels of CO_2 seen throughout the system due to continual effects of cave breathing. The findings of Baldini and others (2006) show a consistent increase in CO_2 with increasing distance from the entry. Comparatively, the CO_2 variations in Wollondilly Cave do not conform due to the complexity of the cave system. Overall it can be seen that CO_2 fluxes in Wollondilly

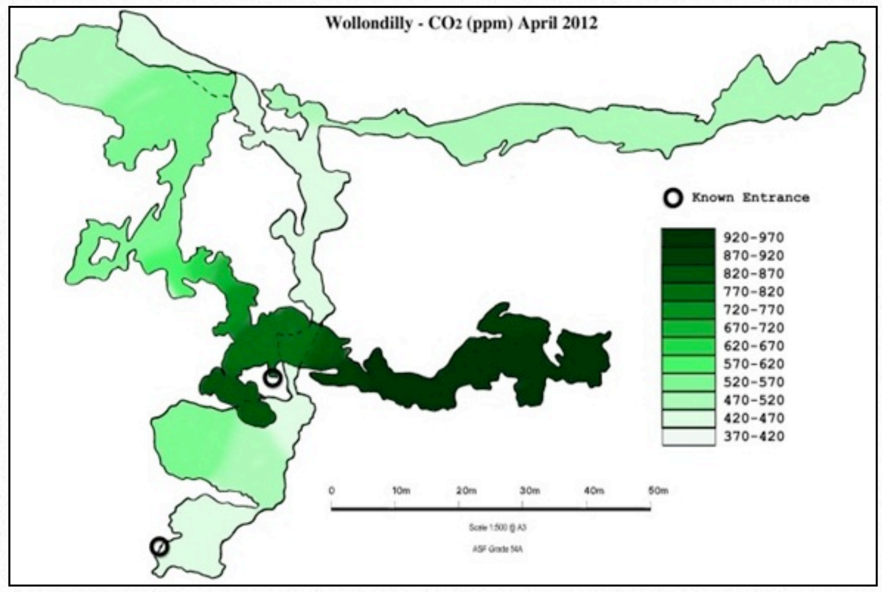


FIGURE 1 *a. Cave carbon dioxide (CO_2 ppm) distribution map for Wollondilly cave, April 2012.*

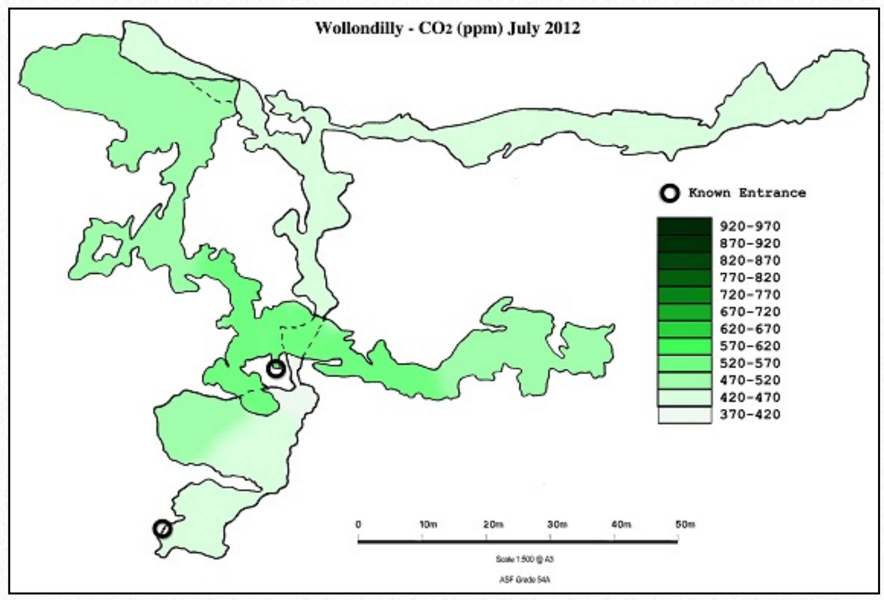


FIGURE 1 *b. Cave carbon dioxide (CO_2 ppm) distribution map for Wollondilly cave, July 2012*

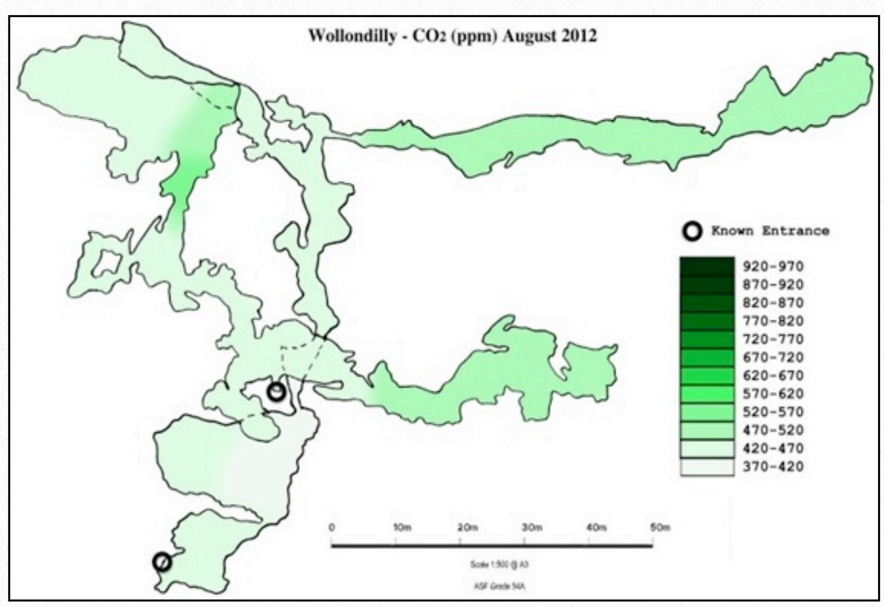


FIGURE 1 *c. Cave carbon dioxide (CO_2 ppm) distribution map for Wollondilly cave, August 2012.*

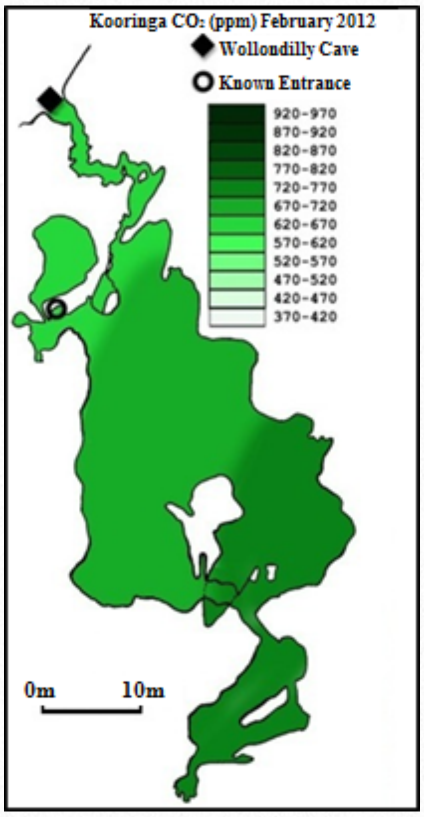


FIGURE 2 a. *Cave carbon dioxide (CO_2 ppm) distribution map for Kooringa cave, February 2012.*

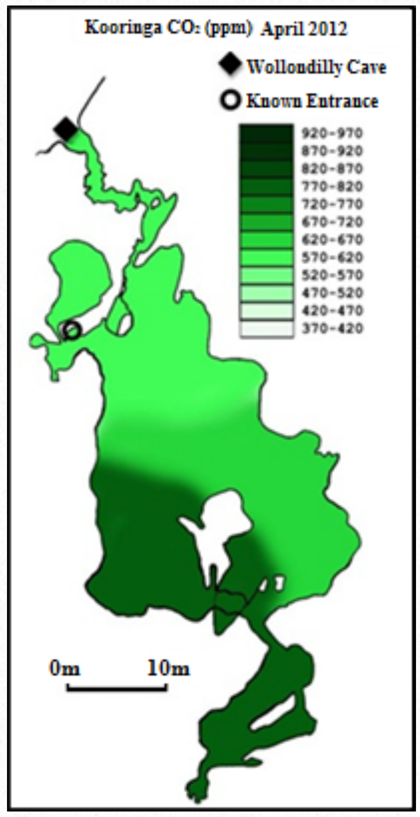


FIGURE 2 b. *Cave carbon dioxide (CO_2 ppm) distribution map for Kooringa cave, April 2012.*

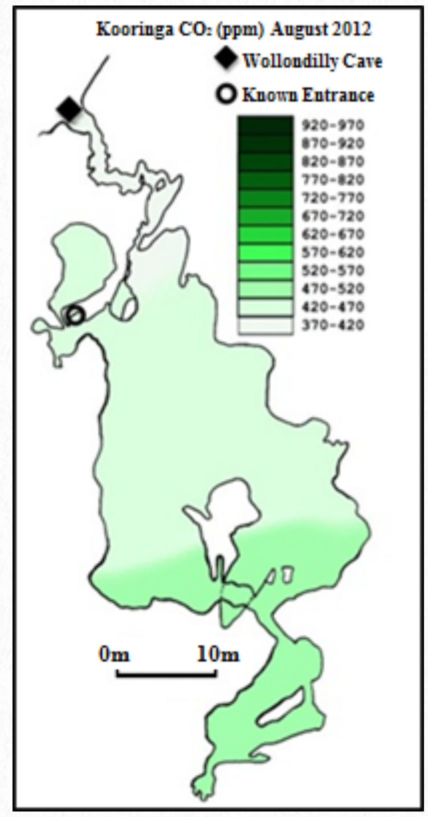


FIGURE 2 c. *Cave carbon dioxide (CO_2 ppm) distribution map for Kooringa cave, August 2012.*

Cave are constrained by the cave architecture and it is not sufficient to say that CO_2 concentrations increase with distance from entrance in this cave. The system is very complex and increased frequency of CO_2 surveys is recommended so as to quantify the CO_2 fluctuations.

Kooringa Survey Results

Unlike Wollondilly Cave, Kooringa Cave is a collapsed chamber and is open to the external atmosphere via an open gate and a tight connection to Wollondilly cave. Due to these features and the lack of tight passages CO_2 levels recorded are consistently lower than those recorded in Wollondilly and increase with distance from the main entrance, in line with the findings of Baldini *et al.* (2006). Three CO_2 surveys were carried out in Kooringa Cave (Figures 2a-c) and while trends remain the same a distinct change the levels of CO_2 during the colder months can also be observed in this cave. With a more consistent and complete data set than is acquirable in an honours year the potential seasonality of the pCO_2 of the caves would be more discernible. The limited findings infer that Wombeyan stalagmites may preferentially preserve a cold season signal due to the seasonal fluctuations in cave CO_2 and hydrology.

Anthropogenic CO_2 Input

An extended CO_2 survey undertaken in Upper Wollondilly (Figure 3) showed peaks occurring between the 8-11th of June, coinciding with the Queen's Birthday long weekend when there is an increase in visitor numbers to the cave. The constant presence of tourists in the caves limits the ability of the CO_{2cave} to return to its base levels. This, in turn, means that the input of anthropogenic CO_2 on the days following will steadily increase the 'base' level each day. Figure 3 indicates that the Mulwaree Extension took two days to fully recover from 3 days of intensive visitations. The location in which this survey was taken is bypassed by tourist groups. Inferring that the levels of CO_2 through the entire system must be impacted greatly in order for this section, which has

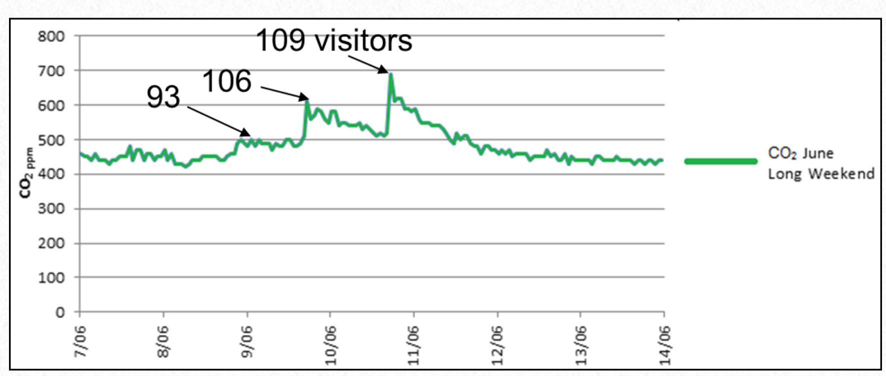
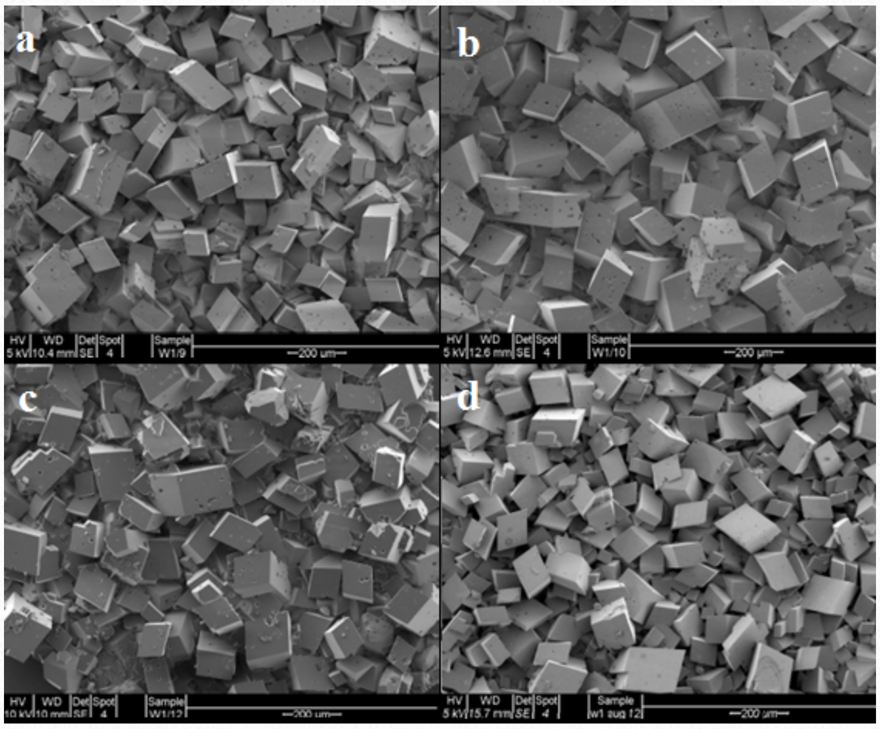


FIGURE 3. *Anthropogenic impacts on pCO_{2cave} due to increased tourist activity over the June long weekend, 2012. CO_2 values returned to baseline values within 36 hours.*



FIGURES 4 *a-d. SEM Images of Calcite samples collected from site W1 between 2009 and 2012.*

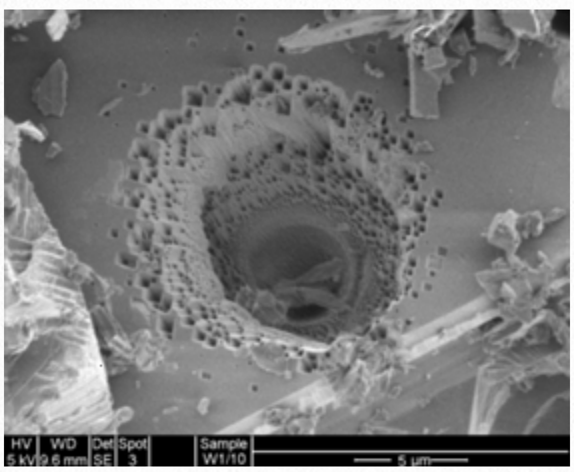
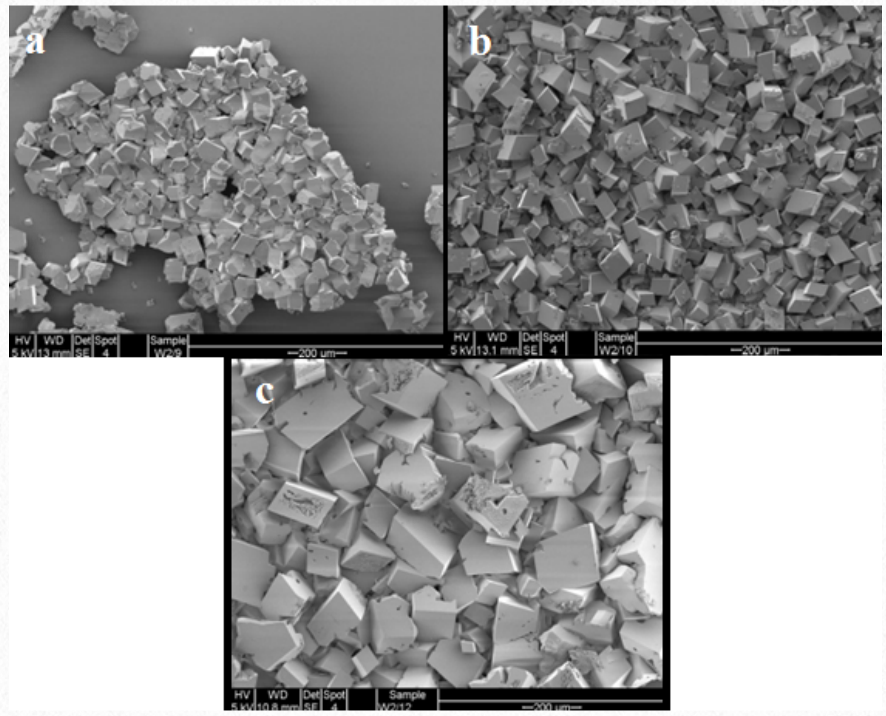


FIGURE 4 *e. SEM Image of the unusual surface features of Wombeyan calcite.*

previously been proven to respond differently to circulation compared to the rest of the cave, to have such elevated pCO_2 (Figures 1a-c). Preferably, measurements should be taken at several locations through the system, especially those areas in which there is high tourist activity, during intensive periods of visitation.

Results of Calcite Analysis

Multiple experiments were undertaken to discern the major impacts on calcite developing in the Wombeyan Karst. However, I will only discuss the results of the Scanning Electron Microscope (SEM). Past research has shown that by observing the shape of the calcite crystals clues of the depositional environment can be explained (Frisia *et al.*, 2000). Crystals with a well formed structure can be indicative of a more stable environment with a slower drip rate and lower oxygen lev-



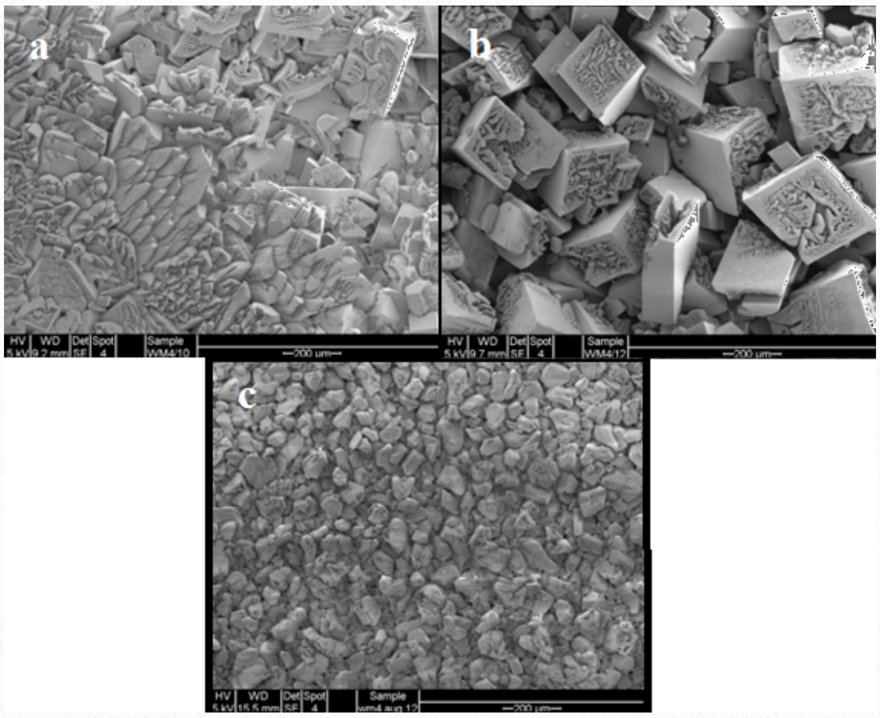
FIGURES 5 *a-c. SEM Images of Calcite samples collected from site W2 between 2009 and 2012.*

els. However, crystals with an erratic shape are indicative of a highly active environment with a regular influx of fresh oxygenated air (Frisia *et al.*, 2000).

Wollondilly Cave

Three sites were studied in Wollondilly cave (W1, W2, WM4) are all located within 2-5m of each other in the Mulwaree Extension and this provides an ideal circumstance in which to study calcite crystal morphology and clarify reasons for differences between the drips. According to theory of crystal growth, the rhombohedra form observed in this precipitate crystal experiment are consistent with a relatively low supersaturation and/or low presence of inhibitors (Frisia *et al.*, 2000).

Figures 4a-e indicate a relatively constant balance between degassing and drip rate in modulating calcite growth in all W1 samples from 2009-2012 (Figures 4a-d). Noticeable in all samples from W1 are circular holes (Figure 4e), which are a constant feature of the Wombeyan Karst. A possible explanation for these abnormalities is that organic colloidal matter has disturbed the crystal growth. The outside of the crystal has continued growing by screw dislocation which is highlighted by this feature while this impurity has inhibited growth on the inside of the crystal (Frisia pers. comm., 2012). This may have implications for the distribution of trace elements within the calcite if selected species are incorporated within the colloidal material. Another possible explanation by Aquilano *et al.* (2003) describes the development of screw

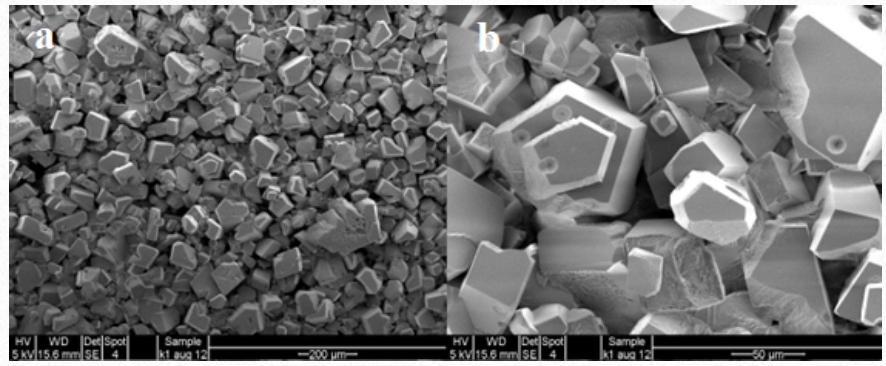


FIGURES 6 *a-c. SEM Images of Calcite samples collected from site WM4 between 2009 and 2012.*

dislocation growth around the surface of a gas bubble forming spherical cavities in the surface of the calcite crystal, and eventual encompassing of cavities within the crystal. More research is needed to clarify the cause of anomalies such as these and the samples at Wombeyan are ideal to try and solve the problem.

Samples from W2 show a variation in the concentration and average size of the crystals. When there are more crystals of a smaller size it can be inferred that an increase in supersaturation will lead to an increase in nucleation of crystal structures (Frisia *pers. comm.*, 2012). Thus, when comparing the W2 samples from 2009 (Figure 5a) to the samples collected in 2012 (Figure 5c) there has been a decrease in supersaturation based on crystal size and number. The drip water samples for 2012 collected at this site showed depletion in calcium concentration, thus supporting the theory of decreasing supersaturation.

The crystals of drip WM4 (figures 6a-c) are very distinct due to unusual features on the faces of the calcite. WM4 has a rapid drip rate and the defected surfaces may potentially be the result of not being fully immersed in the supersaturated film fluid preventing the crystals from growing with flat surfaces. The presence of incipient dendritic structure points to instability at the crystal/liquid interface (Frisia *et al.*, 2000). Having no data on the flushing of organics at the drip site, I can only speculate that both the supersaturation and the pres-



FIGURES 7 *a-b. SEM Images of Calcite samples collected from site K1.*

ence of impurities are higher here than in the other two drip sites.

Kooringa Cave

Two sites were studied in Kooringa, however, only K1 precipitated sufficient calcite for analysis (Figures 7a-b). Rounded crystal faces indicate that the film fluid is out of equilibrium due to an increase in supersaturation or, potentially high levels of organic molecules or high Mg concentrations restricting growth (Frisia, 2012).The most significant finding of the SEM work was that calcite developed in Kooringa Cave also displays the same holes that are common throughout Wollondilly and should be a focus of future research.

Conclusions

To conclude the complex nature of Wollondilly Cave greatly restricts the natural breathing of the system in contrast to Kooringa Cave which was found to concur with past research and increase in levels with increasing distance from the entrances.

Despite CO_2 spatial variability due to the cave architecture, there is a distinct seasonality in CO_2 levels in both caves at Wombeyan which indicates that the speleothems may record a seasonal signal instead of annual climate characteristics.

The natural levels of CO_2 in both caves were not found to impact or inhibit developing calcite, however, anthropogenic inputs greatly increased the CO_{2cave} implying that levels may approach the limestone threshold in areas of higher tourist traffic.

Calcite collected from sites in the same cave atmospheric conditions were shown to reflect variances in drip rate, flow patterns, supersaturation and film fluid thickness.

Overall, this project is good starting point for more intensive future studies. The field component of the project (7 months) was insufficient to gain a robust understanding of seasonal cave CO_2 variability. By contrast, the benchmark study at Grotta di Ernesto (Frisia *et al.*, 2011) required a decadal monitoring program.

Funding proved a constraint on the number and type of surveys that could be undertaken. Still, this pilot project shows the potential of monitoring as a tool to understand speleothem proxies. This study has highlighted the need for more monitoring and shown that speleothem proxies from the Wombeyan karst can be better understood in terms of seasonality if future research is carried out.

Future research would have to be carried out regularly over at least 2 years and would require access to more CO_2 monitoring equipment, funding and interdisciplinary collaboration, in order to gain a greater perspective on the seasonal nature of CO_2 concentration variability.

Acknowledgements

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