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A high-resolution spatial survey of cave air carbon dioxide concentrations in Scoska Cave (North Yorkshire, UK): implications for calcite deposition and re-dissolution.

Tom WHITAKER[1,2], Daniel JONES [1,3], James U L BALDINI[1] and Alex J BAKER[1]
[1] Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK.
[2] Current address: Department of Earth Sciences, Royal Holloway University of London, Egham, TW20 0EX, UK.
[3] Current address: Flat 41E, Wyre House, Chancellors Wharf, Aldcliffe Road, Lancaster, LA1 1WB, UK.

Abstract: Carbon dioxide concentration variability in caves has implications for palaeoclimatic research involving stalagmites, the conservation of cave art, condensation corrosion, and safety during cave exploration. Here we present a high-resolution spatial survey of cave air carbon dioxide partial pressure (P_{CO_2}) in the 1.5km Scoska Cave system in North Yorkshire, UK, constructed using measurements taken during the interval of July 1 – July 5, 2008. According to the spatial P_{CO_2} survey, 76% of the cave air P_{CO_2} increase occurred within the first ~50 metres; consequently the P_{CO_2} gradient throughout the rest of the cave was slight. As is the case in other caves, this suggests that a 'front' exists at this site between high P_{CO_2} cave air and low P_{CO_2} outside air, where the P_{CO_2} increases dramatically over a short distance. Temperature data support this interpretation. This CO_2 'front' is thought to represent the farthest point reached by large-scale advection of air out of the cave, and its position is hypothesized to fluctuate depending on atmospheric conditions. Thus, distinct P_{CO_2} trends characterize sections of the Scoska Cave system, which result in spatial variability in calcite deposition and redissolution. Modelled stalagmite growth rates vary between negligible and 0.21 mm yr^{-1}, depending on unconstrained drip water [Ca^{2+}] values and cave atmosphere P_{CO_2}. Assuming constant drip water [Ca^{2+}], optimum calcite deposition occurs near to the cave entrance, where ventilation and advection reduce P_{CO_2} levels most effectively. However, calcite precipitation on the roof of the cave may partially control the [Ca^{2+}] of drip water that reaches the floor, so although the link between overall calcite deposition (i.e., on the roof and the floor) and P_{CO_2} appears robust, the effect of variable cave air P_{CO_2} on stalagmite growth rates requires more research. These calculations suggest that calcite precipitation rates in different areas of Scoska Cave may differ due to local P_{CO_2} and temperature variability, highlighting the benefits of thoroughly understanding site-specific cave environmental factors prior to the interpretation of stalagmite-based palaeoclimate records.

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Currently 0.039% of the Earth's atmosphere is comprised of carbon dioxide, which is present either in gaseous or dissolved phases in most environments. Carbon dioxide concentration is a critical rate-determining variable in a variety of natural processes occurring in karstic environments, including speleogenesis, condensation corrosion and carbonate speleothem deposition. Speleothems, particularly stalagmites, are increasingly used as important archives of terrestrial climate (Cruz *et al.*, 2006; Henderson, 2006; McDermott *et al.*, 2005; Wang *et al.*, 2005) and, because their growth is partly controlled by cave air P_{CO_2}, it is necessary to understand fully how this gas behaves in the subsurface. Limestone primarily dissolves following the hydrolysis of CO_2 and subsequent formation of carbonic acid (H_2CO_3), which is responsible for the chemical weathering of most rocks (Dreybrodt, 1988; White, 1988). The CO_2 that ultimately forms carbonic acid is derived primarily from the interaction and percolation of water moving down through the soil. Soil air P_{CO_2} is much higher than either atmospheric air (outside air) or cave air. Soil air can be up to 100 times more enriched than outside air, depending on prevailing climate and vegetation conditions on the surface (Brook *et al.*, 1983; Rightmire, 1978). Soil CO_2 is derived largely from the decomposition of organic matter by micro-organisms and root respiration (Dreybrodt, 1988; Gillieson, 1996). Water percolating through the unsaturated zone can act as both a source and sink of P_{CO_2} depending on the P_{CO_2} of the surrounding air. Water equilibrates with the ambient atmosphere, so many karst waters have a high dissolved CO_2 concentrations, having travelled through the high P_{CO_2} soil zone. These waters then dissolve limestone until the waters become saturated with respect to calcite. When the vadose water enters a void space in the limestone, the water degasses to equilibrate to a typically lower ambient P_{CO_2}, and consequently deposits calcite (or, more rarely, aragonite). CO_2 degassing from drip water is potentially one of the principal sources of CO_2 into a cave system. Similarly, soil zone CO_2 may diffuse via fractures and conduits into the cave system, but the relative importance of this source may depend on the depth of the cave as well as the size and number of the secondary fractures. Microbial decomposition of organic material contained within sediments deposited within the cave passageways and aerobic respiration of certain organisms (e.g. bats, etc.) may also increase the amount of CO_2 within the cave system, but these are likely to be locally important rather than affecting an entire cave system. However, cave air P_{CO_2} would eventually reach a maximum and cease to increase if no CO_2 sinks existed. The most important CO_2 sink in typical cave systems is ventilation, which can operate on a variety of timescales (Mattey *et al.*, 2008; Spötl *et al.*, 2005) and is generally controlled by air mass density or pressure differences (Kowalczk, 2010). Other sinks include streams, which can absorb cave air CO_2 if the stream water has a low dissolved CO_2 content; however, streams can also act as sources if the dissolved P_{CO_2} is greater than in the ambient cave air.

Previous research demonstrates that cave air P_{CO_2} influences the growth rate of stalagmites (Baker *et al.*, 1998; Baldini *et al.*, 2008; Buhmann and Dreybrodt, 1985). Stalagmite and stalactite growth rates can vary within and between different cave systems, karst types, and in different climates. For stalagmites to achieve their full potential as palaeoclimate proxies, the response of cave air P_{CO_2} to climate fluctuations needs to be better understood, and an excellent first step is to characterize the distribution of CO_2 in various cave sites. Additionally, because high cave air P_{CO_2} exacerbates condensation corrosion, the research presented here also has ramifications for the preservation of cave artwork of cultural significance in heavily visited tourist caves

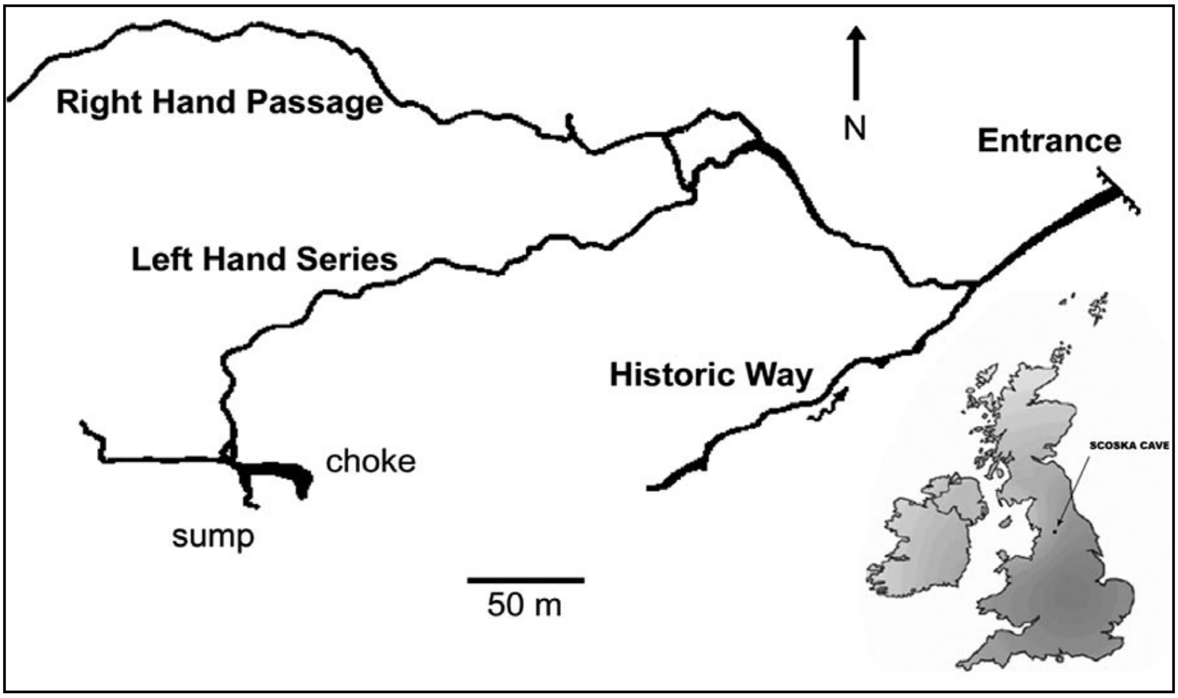


***Figure 1**: Location and survey of Scoska Cave, Littondale (North Yorkshire,) [based on survey by University of Leeds Speleological Association; adapted from Chandler (1989).]*

(Hoyos *et al.*, 1998). The results presented are also relevant for cave exploration; foul air (air with low levels of oxygen within it) can occur within some cave systems. Very few high resolution spatial datasets of the CO_2 concentrations within cave systems exist. Gewelt and Ek (1983) produced a spatial comparison of two caves in Belgium, and the results demonstrated that a linear relationship existed between distance from the cave entrances and cave air P_{CO2} at these sites. Another study by Ek and Gewelt (1985) suggested that P_{CO_2} concentrations are generally higher nearer the ceiling of passages. Fernandez-Cortes *et al.* (2006) compared cave atmospheric conditions before and after tourist activity and noted that convection replenishment of cave air can accompany changing cave air–outside air thermal gradient. Baldini *et al.* (2006) presented a high-resolution dataset for Ballynamintra Cave, a c.95m-long cave in Ireland, constructed using a precise infrared CO_2 probe in conjunction with breathing apparatus (to mitigate the effects of operator respiration). This study applies the same field methodology of Baldini *et al.* (2006) to develop another high-resolution CO_2 spatial variability survey of a longer cave system – Scoska Cave.

Site Description

Scoska cave (54° 8.859′ N, 2° 7.860′ W) is situated approximately 1.5km NW of Arncliffe village in Littondale, North Yorkshire, UK. The mean annual rainfall at Malham Tarn Meteorological Station (approximately 5.7km southsouthwest of Scoska Cave) is 1502mm, and the mean temperature is 6.9°C (Burt and Horton, 2003). Currently the precise stratigraphical level of the cave is unknown, but it appears to lie within the Malham Formation (Great Scar Limestone Group), possibly at or close to the boundary between the Gordale Limestone and Cove Limestone members (see Arthurton *et al.,* 1988). These limestones were deposited in clear, shallow tropical seas towards the close of Early Carboniferous (Asbian) times. Scoska Cave is predominantly made up of bedding plane-guided passages and contains 1.5km of surveyed passage (Fig.1; Chandler, 1989). After about 80m, the wide entrance passage leads to a chamber approximately 1.8m high and approximately 4m wide. The chamber splits into two passages to the right and left. The left passage, known as the ‘Historic Way’, maintains an average width of 1.5 – 2.5m for its entire 400m length. However, the height of the passage decreases from 1.2m at its start to 0.43m at its end. The Historic Way contains a small stream, which runs down the centre of the passage. A passage branches off to the right from the Historic Way and is approximately 2m high by 1m wide; again the width remains generally constant but the height decreases to about 0.8m. This passage continues for 110m until the passage splits into left and right passages. The left passage, known as the ‘Left Hand Series’, extends for 410m until a low, ~1m-high, 1.63m-wide and 47.6m-long chamber is reached. At the end of this chamber, a subterranean waterfall is present, with a stream running through the chamber down the bedrock to a sump, which has been dived to c.10m. In the far left of the chamber another small passage leads to another sump. Both sumps are likely connected hydrologically with the resurgence in the nearby Bown Scar Cave. The passage leading to the right is called the ‘Right Hand Passage’, is approximately 500m long, and is also thought to terminate in a sump. The Left Hand Series and Right Hand Passage are connected by a small passage named ‘Bears Passage’, which is approximately 1m high by 1m wide, and 30m long. Most of the known cave sections are included in the CO_2 survey; however, some areas were not surveyed because the excessive water present within some very low passages precluded effective use of the breathing apparatus (see below), without which the readings would potentially have been biased.

Distribution of cave vegetation in relation to light intensity was studied by Pentecost and Zhaohui (2001). The cave was found to contain 59 species of vegetation, with bryophytes comprising the majority of this cave biota. Scoska Cave is therefore the richest cave bryologically currently known in Britain, and one of the richest in Europe (Pentecost and Zhaohui, 2001). Scoska Cave is also currently the site of a study in which temperature sensors were placed every 10m between the entrance and about 200m into the cave to help elucidate the pattern of moth growth and habitats (Hodgson, 2007). This latter research was ongoing during the gathering of the data being considered here.

Methodology

This study uses temperature and P_{CO_2} data measurements that were made between 01 July 1 and 05 July 2008. The spatial P_{CO_2} and temperature data were collected using a calibrated Vaisala GM70 CO_2 probe connected to a Vaisala MI70 datalogger, and have a precision of ±30 ppm. The meter calculates P_{CO2} within the atmosphere by measuring the absorption of an infrared beam by CO_2 molecules; the amount absorbed is proportional to the P_{CO2} of the air in the probe at the time of measurement. The temperature was measured using a Vaisala HM70 probe connected to the Vaisala MI70 datalogger; the precision of the temperature measurement is excellent, ±0.05°C. All the P_{CO_2} data are presented in units of ppm and have been corrected for the barometric pressure within the cave. Potential error caused by the addition of operator-respired CO_2 into the cave atmosphere was minimized by using breathing apparatus, which allowed normal inhalation but expelled respired air along a 20m-long flexible tube that was pulled through the cave behind the operators. The tube ran into previously surveyed sections of the cave, allowing sufficient time for measuring the cave air P_{CO_2} at the different sites (approximately 30 – 45 seconds per data point). Electric lights were used exclusively.

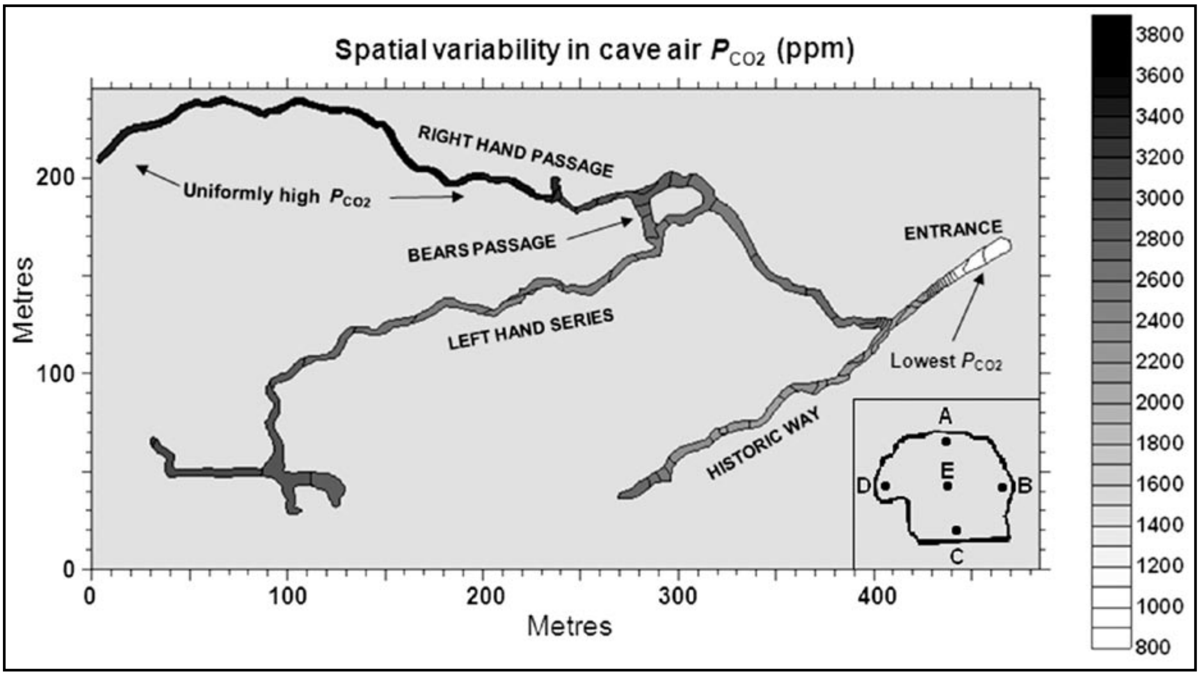


Figure 2: Contour map of the spatial distribution of cave atmosphere P_{CO_2}. Inset: Schematic illustration of the cave entrance in cross-section (entrance of Scoska Cave measures 6.16m high and 6.47m wide), where A, B, C, D and E are, respectively, the ceiling, right side, floor, left side, and middle. These points represent locations of P_{CO_2} measurements at each location comprising this spatial survey. Measurements at A, B, C, and D could be taken at nearly every location; E could be taken only where passages are high enough. An average of all measurements at each location was used in the creation of the P_{CO_2} contour map.

To produce the most accurate map of spatial cave air P_{CO_2} and temperature values possible, measurements were taken at several points along the passage cross-section at every location (Fig.2, inset). These values were then averaged to produce the x–y cave-scale survey.

The distance between the surveyed locations was 10m. All distances were measured using a Leica DISTO™ D3, which has a precision of ±1.0mm within 10m; this instrument was also used to measure the passage width and height at each location. The direction of the survey shot along that passage were taken using a compass. The Leica DISTO™ D3 was also used to measure the angle of the shot as well as the dip of bedding planes in the cave. These data points allowed the drafting of a new line-survey plan of Scoska Cave; this plan compared very well with a previous cave survey (Chandler, 1989). The cave air P_{CO_2} and temperature data were then incorporated into the drafted map to construct two- and three-dimensional contour maps. All contour maps were created using Surfer 8®.

Results and Interpretations

Impact of operator presence

The potential impact of operator-respired CO_2 on the accuracy of the results was assessed by removing the breathing apparatus when approximately 420m from the cave entrance within the Right Hand Passage, which is 2.3m wide and 0.68m high at this point. P_{CO_2} and temperature measurements were taken over a three minute period. A steady 12.5% increase in cave air P_{CO_2} from 3650 ppm to 4100 ppm was recorded (Fig.3), which is consistent with the results of previous research showing an increase of 16% over two minutes in a smaller cave (Baldini *et al.*, 2006). Similarly, temperature readings showed an increase over the same recording period. These indicate that the presence of two people within this same passage increased the temperature by at least 0.27°C. The value might be slightly lower due to the humidity within the cave, which may affect heat transfer through the air (Laguerre *et al.*, 2009). This figure is also consistent with previous studies that recorded an increase of at least 0.3°C over a period of two minutes (Baldini *et al.*, 2006). Due to the constant impact of body temperature, and because methods of limiting a human body's heat signature while caving are generally impractical, the reported temperature data are probably higher than the cave air temperature would have been without the presence of two cavers, though this error is not easily quantifiable. Owing to this potential error, no temperature contour map is presented; however, broad trends throughout the cave system and within passages are probably real and will be discussed generally. Changes in cave air P_{CO_2} while the breathing apparatus was in use were quantified; the operator remained still for fifteen minutes while wearing the breathing apparatus, measuring the P_{CO_2} levels every thirty seconds. There was no increase through that period, suggesting strongly that the P_{CO_2} results gathered while using the above-described apparatus are valid.

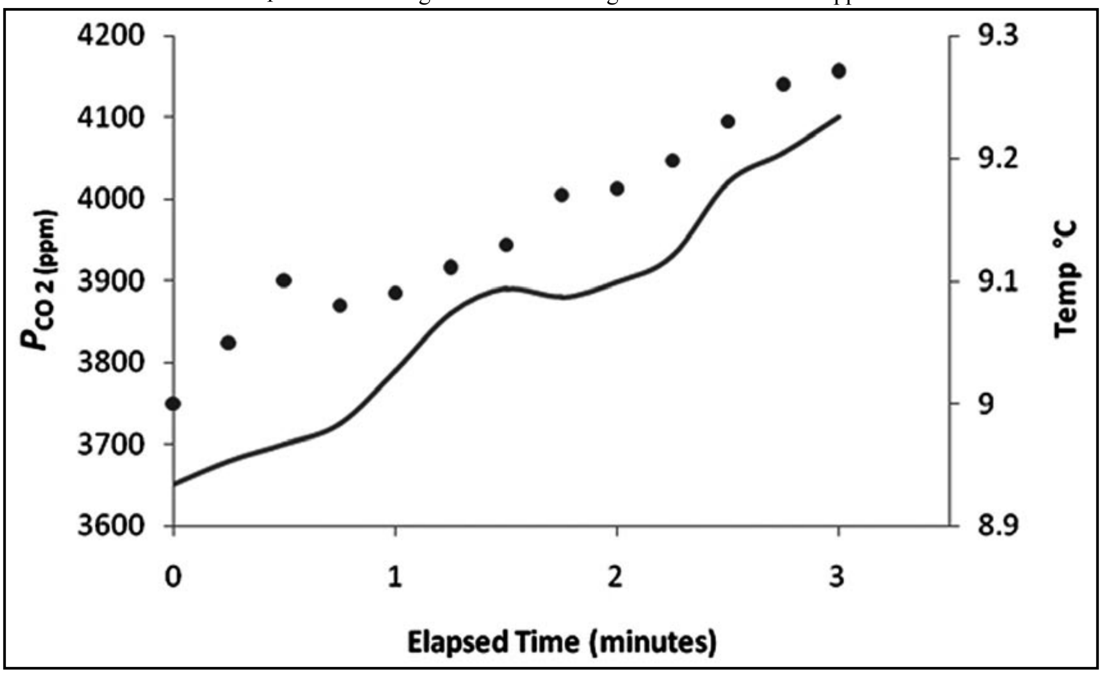


Figure 3: Time-series of cave atmosphere P_{CO_2} (solid line) and temperature (circular dots) quantifying the increases associated with removal of breathing apparatus and operator respiration. Apparatus was removed at time = 0. However, measurements had already been made in this section of Scoska Cave and it is likely that temperature values were slightly lower (~0.5 – 1°C) prior to operator presence.

Cave air P_{CO_2} variability within Scoska Cave

The Entrance and the Historic Way

Ventilation of the cave via the large cave opening leads to Scoska Cave's entrance having the lowest P_{CO_2} measurements of any section of the cave (Fig.3). However, the relatively low cave air P_{CO_2} (of about 600 ppm) characteristic of the cave entrance, persists for only a short distance. Just 200m into the cave, values reach 2900 ppm, representing 76% of the total P_{CO_2} increase observed throughout the entire cave. This demonstrates that the influence of the outside atmosphere does not extend very far into the cave, and that at this site ventilation was not actively affecting deeper sections of the cave system for the duration of this study.

A transect through the Historic Way (Fig.4) illustrates that cave air P_{CO_2} values increase with distance from the entrance. A small stream noted in the centre of this broad, low passage eventually flows out of the cave entrance. The maximum P_{CO_2} value recorded (3100 ppm) in the Historic Way is from the final location in the passage. This *maximum* reading was obtained to the right of the passage, in close proximity to the small stream. However, the *mean* value at the final measuring location in this passage is 2736 ppm, suggesting that the stream in the Historic Way is a possible CO_2 source. The measurement taken next to the stream was significantly higher than the other measurements taken at the same station. On the basis of the chemistry of the host rock and of the streamwater itself, the likely source of the stream is water percolating through the limestone, but with possible admixture of swallet water (Ternan, 1974). Due to the potential swallet water influence, the stream might introduce a flux of organic material (faecal or plant matter, etc) into the Scoska system. Microbial breakdown of this material would provide a potent source of cave atmosphere CO_2 compared to values related to vadose seepage. The first 15m stretch of this cave apparently contains abundant bryophytes (Pentecost and Zhaohui, 2001). Whereas these might also act as a CO_2 sink by absorbing CO_2 from the atmosphere, decomposition of bryophytes in the area could provide a source of CO_2. However, it is probable that most of the CO_2 at this site is derived from advection and diffusion of air from deeper in the cave.

The Left Hand Series

This is a much narrower passage than the Historic Way, measuring c.2m initially and tapering down to c.0.6m farther from the entrance. The transect through the Left Hand Series begins at its intersection with the Historic Way, and extends back to the sump at the far southwestern limit of the known cave system. Unlike the Historic Way, which demonstrated a rapid rise in P_{CO_2}, the Left Hand Series experiences only a gradual increase in values from 2600 ppm to just over 3000 ppm, despite it being, at 470m, more than twice as long as the Historic Way. The P_{CO_2} gradient is therefore c.1 ppm per metre, and the highest values are measured close to the sump. Second-order variability superimposed onto this first-order trend seem to coincide with locations containing standing pools of water, suggesting once again that the water might act as a source or a sink for CO_2. The water could essentially have a 'memory' of the cave air P_{CO_2} conditions prevailing a few hours or days previously, and until re-equilibration with a changed atmosphere is achieved, the water will either degas or absorb CO_2. Such pools became progressively deeper and more abundant with increasing distance from the entrance, starting at depths of 0.15m and increasing to 0.2m. During the study cave air P_{CO_2} actually decreased slightly to a point 380m from the cave entrance, from where values increased dramatically. The cave passage became much smaller and more tortuous here, potentially impeding advective transport of CO_2 out of the cave (ventilation). The Left Hand Series terminates at a sump at the end of a 47.6m-long, 1m-high passage that contains a fast-flowing stream running towards the east. The stream enters the cave via a waterfall down a 0.15m-diameter shaft. P_{CO_2} was measured as 2890 ppm at this shaft. The highest P_{CO_2} reading taken in the cave was measured at the sump, located beyond a narrow gap (c.0.5m) in the rock that the stream flows down. The chamber containing the sump is 1.09m high and 4.05m wide, with the sump is located in its left-hand corner. The maximum P_{CO_2} value of 3500 ppm was measured directly over the sump.

The stream leading to the sump most likely originates as a surface stream sinking into a doline. Overall, the chamber has relatively low P_{CO_2} considering its distance from the entrance. Readings directly above the stream were lower (2850 ppm) compared to readings taken away from the stream (3080 ppm), suggesting that the stream is absorbing a small amount of CO_2 from the atmosphere and supporting the interpretation that the stream originates as a surface stream flowing in the subsurface for too short a time to equilibrate with the ambient P_{CO_2}.

The Right Hand Passage

The Right Hand Passage transect begins at the passage's intersection with Bears Passage, and extends towards the farthest northern section of the cave. This transect is characterized by a gradual increase in cave air P_{CO_2} with increasing distance from the entrance (Fig.4). Unlike the Left Hand Series the height stays relatively constant (0.8 – 1m) throughout the Right Hand Passage. The Right Hand Passage is the muddiest section of Scoska Cave. A pool of standing water occurs approximately 290m from the entrance; however, the P_{CO_2} reading over the water is almost identical to that of the cave air to either side (~2860 ppm), suggesting that this water has little effect on P_{CO_2} concentrations and has equilibrated fully with the ambient cave atmosphere. Approximately 430m from the entrance, close to the end of the Right Hand Passage, the highest cave air P_{CO_2} value of the Scoska system was measured, giving an average at the specific station of 3550 ppm. Perhaps significantly, this location is also at the muddiest point in Scoska Cave; whether or not this is linked to the elevated values will be discussed below.

Controls on Cave Air P_{CO_2}

The overall trend through Scoska Cave is one of increasing P_{CO_2} with increasing distance from the entrance, consistent with studies based on other sites (Baldini *et al.*, 2006; Ek, 1979; Ek and Gewelt, 1985). This implies that at Scoska Cave the predominant controls on the spatial cave air P_{CO_2} levels at any one instant are the amount of ventilation and proximity to the entrance. In other words, the amount of mixing between the high P_{CO_2} air in the vadose zone of the aquifer and outside air determines the cave air P_{CO_2} at specific points in the cave, and the influence of outside air is greatest near the entrance.

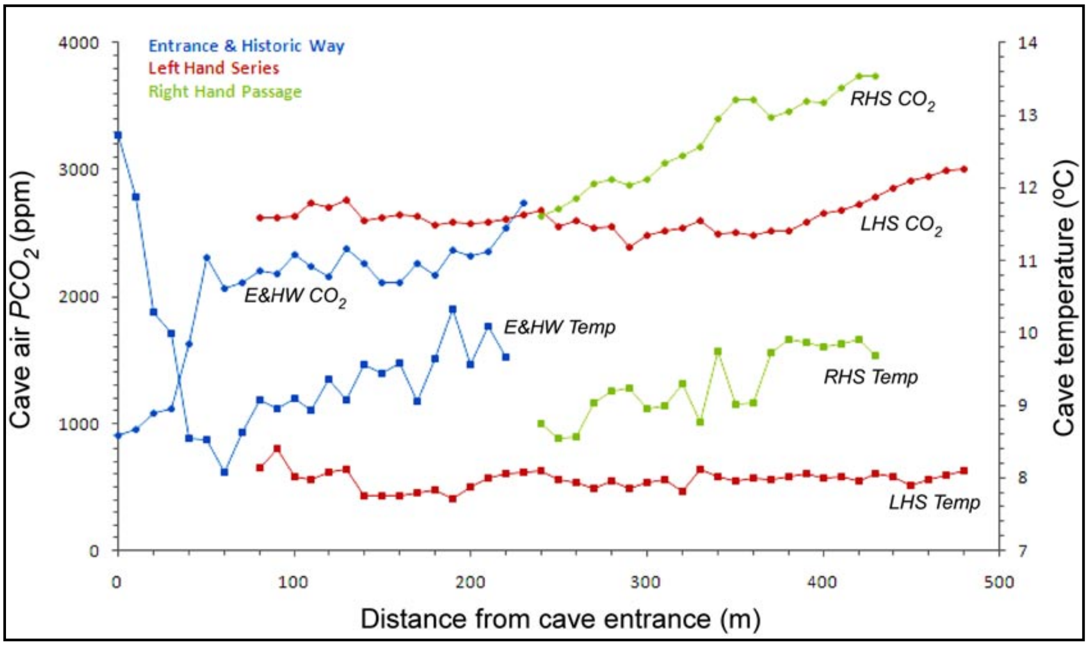
It is noted that Scoska Cave has only one entrance that is accessible for cavers. Most caves also exchange air with the surface through smaller voids and this can influence circulation and P_{CO_2} concentrations in the cave system significantly. As in previous high-resolution spatial 'snapshots' of cave air P_{CO_2} (e.g., Baldini *et al.*, 2006), there exists a short transition zone near the entrance between air composed predominantly of outside air and air composed predominantly of high P_{CO_2} cave air. Beyond and before this transition zone, the P_{CO_2} gradient is comparatively subdued.

The location of such a transition zone, or 'front', between cave and outside air in Scoska Cave is likely to result, at least in part, from passage morphology, and might form where the cave passages become significantly constricted. However, it is hypothesized here that this 'front' might migrate towards or away from the cave entrance depending on factors such as relative air temperature, air density, and barometric pressure. These temporal trends will be described in detail, with their implications for stalagmite growth rates and oxygen isotope proxy records, in a subsequent publication.

In addition to the first-order trend of increasing P_{CO_2} with distance from the cave entrance, some smaller-scale secondary variability also exists. For example, although the Right Hand Passage is characterized by a slow increase in concentration with distance, some locally high concentrations also suggest that a control other than simple, large-scale advection of air is responsible. Physical constraints such as dips in the cave passage might obstruct the flow of circulating air in these cave segments, and locally-important sources of CO_2 could include organic decomposition within mud deposits located in this passage.

The density of carbon dioxide is 1.98kg m^{-3}, about 1.5 times that of normal air. Regardless of this density contrast, CO_2 in caves rarely 'sinks'. Instead, the vibrational energy of the CO_2 molecules causes them to mix thoroughly with the other gas molecules in the cave atmosphere (Badino, 2009; Berger, 1988). Only in cases where a significant volume of CO_2 is flowing from a ceiling fissure would the gas mirror the behaviour of a liquid and flow as a column to the floor

Figure 4:
Cave atmosphere P_{CO_2} (circle data point markers) and temperature (square data point markers) for the entrance passage and Historic Way (blue; 'E&HW'), Left Hand Series (red; 'LHS'), and Right Hand Passage (green; 'RHS'), plotted against the distance (m) from the cave entrance. Data for Left Hand Series and Right Hand Passage begin at 80 and 230m from the cave entrance, respectively. Excepting Historic Way, the decrease in temperature with distance from the cave entrance is generally associated with reductions in cave passage height and width. Importantly, temperature data are increasingly vulnerable to influence of operator presence with decreasing cross-sectional area of the passage.



(Berger, 1988). In general, locally-elevated P_{CO_2} values measured at floor level are caused by rapid drips degassing preferentially nearer the floor. The gas then begins to diffuse upwards into the cave atmosphere. Similarly, locally-elevated cave air P_{CO_2} measurements in deeper sections of caves result from poorer ventilation in these areas rather than from gravity-induced 'sinking' of CO_2. This is illustrated by cave sites where a secluded passage leads *upwards* from the main passage and yet still has elevated cave air P_{CO_2} values, as is the case for Le Trou Joney, Belgium (Ek, 1979). In Scoska Cave, CO_2 appears evenly distributed around the cave passages (Figs 3 and 5), indicating that the air is well mixed, or that few 'point' sources of CO_2 (e.g., a fissure releasing a column of CO_2 gas) exist. The only readings that deviated significantly from the general background levels were high readings taken near the floor of the Entrance and Right Hand Passages where a stream or sediment deposit was present. A variety of general CO_2 sources exist in caves, including:

i) degassing of dissolved CO_2 from vadose water;
ii) production of CO_2 from respiration of micro-organisms within the soil;
iii) CO_2 flow through fractures present in the rock;
iv) production of CO_2 from decomposition of organic matter carried into the cave from a surface stream;
v) seepage of geothermal CO_2 through fractures, although geothermal CO_2 is unlikely to be present in Scoska Cave.

Currently the Right Hand Passage is the muddiest in Scoska Cave, with the mud deposits beginning at the end of Bears Passage. The presence of mud suggests that either: *i)* a stream once ran through the passage, though at present it is uncertain whether the stream continues to be active intermittently or is no longer active, or *ii)* the sediment was deposited from static water that flowed into the passage from a flood in an adjacent passage. The latter possibility is most likely because flowing water is unlikely to deposit the fine clay and silt found in the passage. If this is the case, the sediment likely represents a large number of successive flood events depositing small amounts of sediment. Beyond a very muddy section with static pools the Right Hand Passage ends in a sump, as does the Left Hand Series. The mud in the passage has a very fine-grained matrix and contains few large clasts, but it might also contain a large amount of organic matter derived from the surface and carried into the cave by sinking water. It is proposed that the high P_{CO_2} levels (the highest in Scoska Cave) recorded within this passage originate from microbial decomposition of the organic matter present within the sediment. However, microbes (particularly bacteria) will only continue decomposing the organic matter until either there is no more organic matter left to decompose (Potter *et al.*, 2005). Consequently, for this explanation to be correct, the organic matter in the sediment must be replenished periodically in order to enable bacterial decomposition to continue.

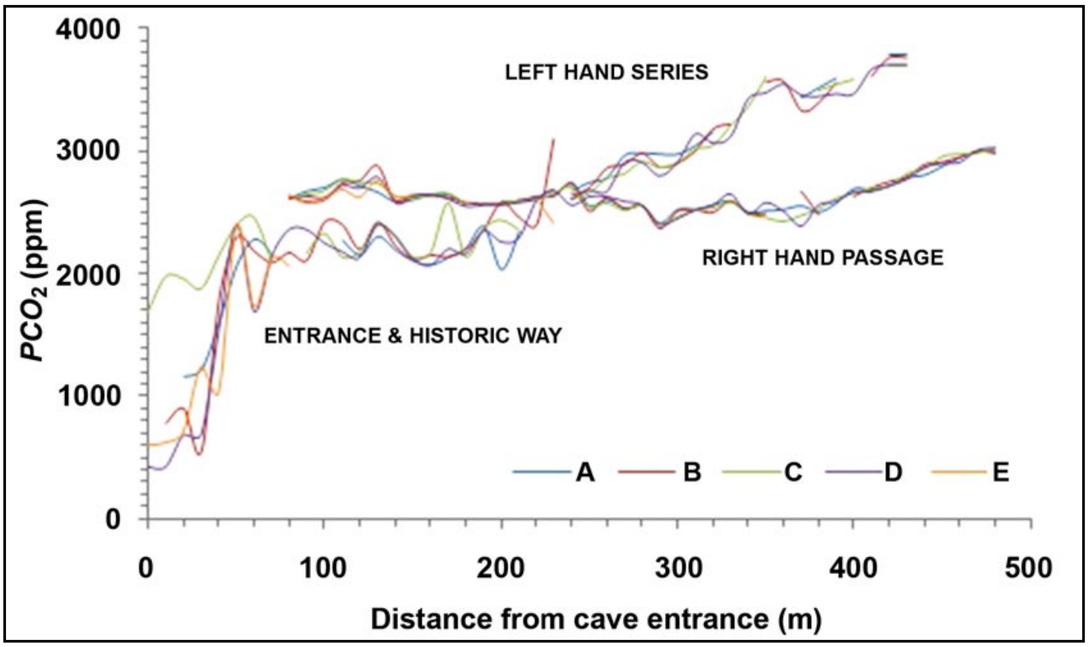


Figure 5:
Variability in the cave air P_{CO_2} measured at different cross-sectional locations (designated A, B, C, D and E) within cave passages, as illustrated in Figure 3. These data show that general trends in P_{CO_2} are cross-sectionally uniform for the entire cave system. A notable exception is found, however, up to ~40m from the entrance, where data for C (floor) are higher than the overall pattern.

Temperature distribution

All the temperature data shown in the figures are mean values for the temperature data gathered at each location. The temperature inside and outside the cave was averaged from hourly temperature readings taken from *in situ* temperature loggers. Outside a mean of 19.5°C was recorded, which is only 6°C higher than the temperature recorded directly within the entrance to the cave. A more thorough investigation of the temperature variation between outside and inside the cave will be presented in a subsequent publication. Temperature values decrease steadily from the entrance through to the end of the Historic Way, and this trend broadly follows the same trend as cave air P_{CO_2} through the same passage (Fig.4). The temperature gradient is particularly strong across the transition zone identified in cave air P_{CO_2}, further demonstrating that this zone probably reflects the mixing of cave air and outside air.

Temperature generally increases gradually after the first 50m of the Historic Way further back into the cave down both the Left Hand Series and the Right Hand Passage. Some second-order variability is superimposed onto this trend of gradually increasing temperatures. However, because the increase corresponds with a gradual reduction in passage cross-sectional area, it is likely that this is caused by the presence of two researchers in the small passages. Ultimately, these data show a clear association between cave atmosphere CO_2 concentration and temperature, strongly suggesting mixing between cave air and outside air.

Implications

Effects on calcite deposition

In the Historic Way, the most heavily decorated passage in Scoska Cave, stalactites are the predominant speleothems. It is possible that the stream hindered stalagmite deposition or is currently redissolving stalagmite calcite (Ternan, 1974). The stalactites are fed by vadose water that has equilibrated with a soil and/or epikarstic P_{CO_2}, which is almost certainly significantly higher than the cave air P_{CO_2}. When this percolation water reaches the cave atmosphere, it equilibrates with the lower P_{CO_2} by degassing. It is likely that, other than advection of cave air deeper in the system, this is the major CO_2 source within the Historic Way. However, some CO_2 might be added to the system from the breakdown of organic matter transported by the stream, though the concentrations put into the system through this mechanism are still likely to be less than those derived from stream degassing. The large difference between the dissolved CO_2 present in the drips and the cave air P_{CO_2} in the Historic Way promotes degassing and subsequent calcite deposition according to the equation:

$$\mathbf{Ca^{2+}_{(aq)} + 2HCO_3{}^{2-}_{(aq)} \leftrightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}} \qquad \textbf{\textit{(Eq. 1)}}$$

If spatial homogeneity of drip water hydrochemistry is assumed throughout the entire cave (no evidence for localized flow that would concentrate calcite deposition in one place exists), then the abundant speleothem deposition in the Historic Way is probably due to an increased differential between dripwater P_{CO_2} and cave air P_{CO_2}. In other words, the increased ventilation characteristic of this section of Scoska Cave would promote speleothem deposition by decreasing ambient P_{CO_2}.

The essential controls on speleothem deposition (e.g. temperature, drip rate, drip hydrochemistry, soil and cave air P_{CO_2}, and solution film thickness) are well-quantified (Dreybrodt, 1999); however, spatiotemporal variability in these controls, particularly in cave air P_{CO_2}, is not well constrained (Baldini, in press; Fairchild *et al.*, 2006). Researchers have now begun to consider the implications of cave air P_{CO_2} dynamics for palaeoclimate studies that utilize speleothem. Recently, several studies (Baldini *et al.*, 2002; Polyak and Asmerom, 2001; Proctor *et al.*, 2000; Spötl *et al.*, 2002) have employed stalagmite growth rate itself as a palaeoclimate proxy. Others have linked seasonality in stalagmite stable isotope signals to seasonally variable cave air P_{CO_2} (Johnson *et al.*, 2006; Mattey *et al.*, 2008). Changes in calcite deposition rates can affect net proxy signals (Baldini, *in press*). Therefore, rapid or seasonal shifts in cave air P_{CO_2}, which engender variability in the growth rates of stalagmites, might skew the geochemical proxy records 'encoded' within them towards the season of preferential deposition (Baldini *et al.*, 2006, 2008; Banner *et al.*, 2007; Frisia *et al.*, 2000; Mattey *et al.*, 2008; Spötl *et al.*, 2005).

From the high-resolution survey of cave air P_{CO_2} presented here, spatial variability in stalagmite growth rates has been modelled, using the approach of Baldini (in press). The following equation describes vertical calcite growth rate (R_o) theoretically (Baker *et al.*, 1998; Baldini *et al.*, 2008; Dreybrodt, 1999):

$$R_o = 1174 \times \left(Ca - Ca_{app}\right) \times \left(\delta \times \Delta T^{-1}\right) \times \left(1 - e^{-(\alpha)(\Delta T)(\delta^{-1})}\right) \qquad \textbf{\textit{(Eq. 2)}}$$

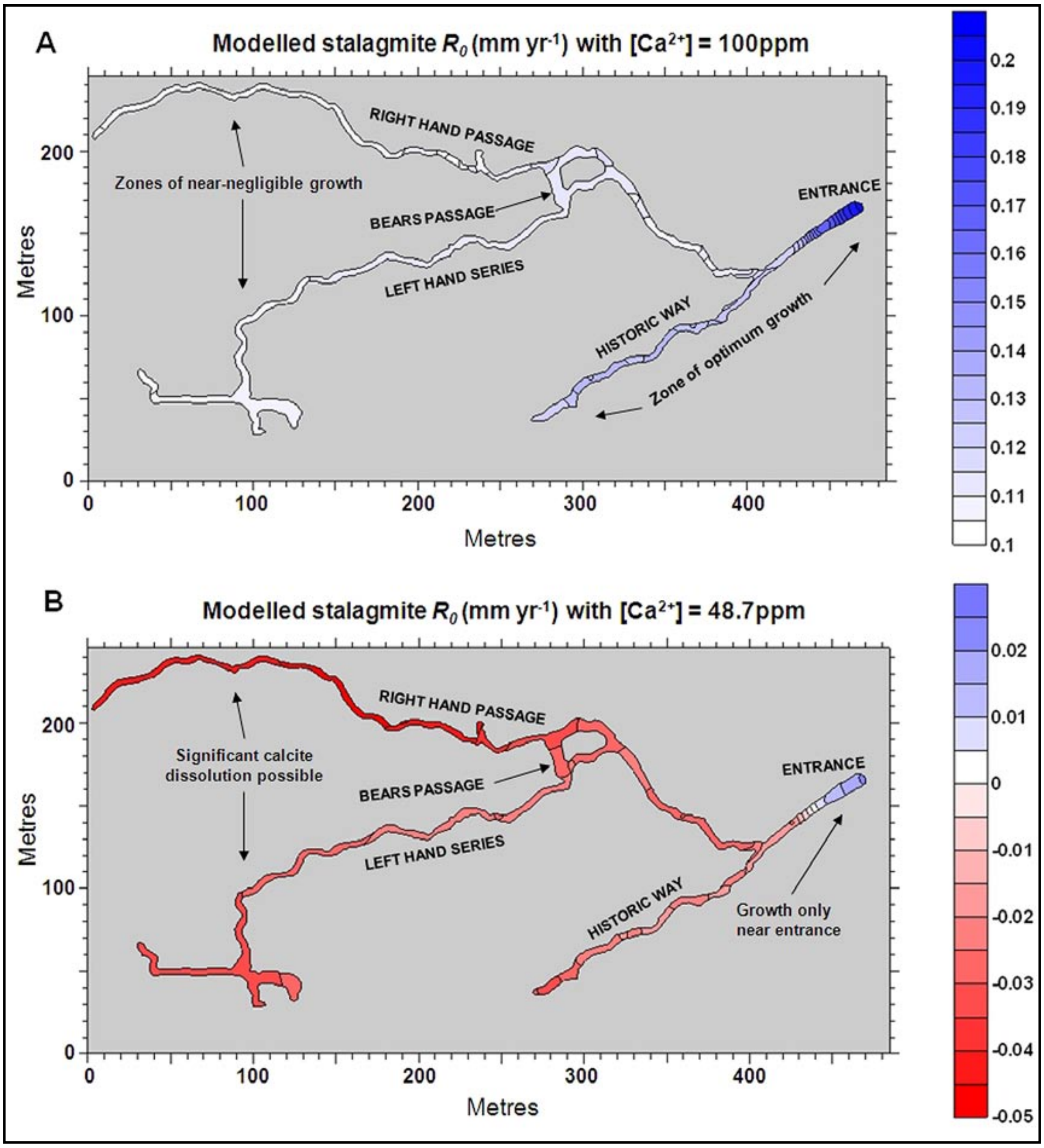
where: the constant 1174 converts molecular accumulation rate of calcite (mmol mm^{-1} s^{-1}) into growth rate (mm yr^{-1}); *Ca* is the initial calcium ion concentration [Ca^{2+}] of the dripwater (mmol L^{-1}); Ca_{app} is the dripwater [Ca^{2+}] at equilibrium with a given (cave) atmospheric P_{CO_2} (mmol L^{-1}); δ is the thickness (mm) of the film of calcite-saturated dripwater covering the apex of a growing stalagmite from which calcite precipitates by Equation 1; ΔT is the drip interval (s); and α is a 'kinetic constant' (mm s^{-1}) that is sensitive to change in δ and ambient cave temperature.

An important unconstrained variable in this modelling is the calcium ion concentration of dripwater, [Ca^{2+}]. This is likely to change through time, and is also likely to vary spatially throughout the cave, affecting growth rates potentially independently of cave air P_{CO_2} effects. To compensate for this lack of information, two different values of dripwater [Ca^{2+}] are used to map stalagmite growth rates through the cave: 2.5 and 1.25 mmol L^{-1} (100 and 50 ppm, respectively). Modelling suggests that the elevated P_{CO_2} concentrations prevalent in the deeper sections of the cave, or close to sumps, result in the lowest growth rates (Fig.6A). Conversely, sections characterized by lower cave air P_{CO_2}, such as the entrance passage, are predicted to promote faster growth, owing to the increased degassing drive of dissolved CO_2 from dripwaters (Fig.6A). This observation presents an apparent paradox: if a major source of cave atmosphere CO_2 in Scoska Cave is degassing from speleothem-forming dripwaters, why are growth rate and ambient cave air P_{CO_2} level inversely related? This would serve to create a negative feedback, where rising CO_2 retards calcite deposition and associated degassing, and, eventually, the source of that CO_2 itself. For this negative feedback to operate, it must be regularly 'reset' by ventilation events, which are hypothesized to influence the entrance passage and the Historic Way more strongly than deeper sections of the cave system. This offers one possible explanation for decreased speleothem abundance beyond sections proximal to the cave entrance. When the lower initial dripwater [Ca^{2+}] is used, calcite dissolution would apparently occur throughout the entire cave except from within ~40m from the entrance (Fig.6B). This [Ca^{2+}] value is significantly lower than typical cave dripwater values, and suggests that in this scenario dripwaters would largely be undersaturated with respect to calcite. Incremental increases in dripwater [Ca^{2+}] from this low value of 1.25 mmol L^{-1} (while still remaining below 2.5 mmol L^{-1}) increase the proportion of the cave where stalagmite growth may occur. In both 'end-member' cases shown (1.25 and 2.5 mmol L^{-1}), it is assumed that initial dripwater [Ca^{2+}] is spatially invariant, which is undoubtedly unrealistic for most cave systems. Particularly worth mentioning is the fact that some calcite deposition might occur on the cave roof before the drip reaches the floor. This prior calcite precipitation will undoubtedly exert an influence on dripwater [Ca^{2+}] and consequently may decrease growth rates on stalagmites. The relative importance of cave air P_{CO_2} modulated prior calcite precipitation on stalagmite growth rates needs to be researched further. It is acknowledged that these model scenarios are overly simplistic; nevertheless, the direct dependence of growth rates on the interrelated influences of dripwater saturation state and cave air P_{CO_2} is demonstrated.

Condensation corrosion

It is also interesting to consider condensation corrosion, which may occur most often near the entrance of caves due to moisture laden outside air mixing with colder cave air. This condensed water absorbs CO_2 from the air, forms carbonic acid, and dissolves calcite rather than depositing it. However, the abundant stalactite deposition present in the Historic Way in Scoska Cave appears to argue against significant condensation corrosion in this part of the cave. It is not clear why condensation corrosion does not play a larger role in Scoska Cave,

Figure 6:
Contour maps illustrating spatial variability in modelled vertical calcite growth rate, R_o (mm yr^{-1}) for:
*(**A**) initial dripwater [Ca^{2+}] = 2.5 mmol L^{-1} = 100 ppm, and*
*(**B**) initial dripwater [Ca^{2+}] = 1.25 mmol L^{-1} = 48.7 ppm. Blue map colouration indicates the rate of calcite precipitation; red colouration indicates 'negative growth rate' (i.e. where calcite dissolution is possible). For both maps, invariant growth-determining factors are taken to be ΔT = 60 s, δ = 0.1mm, and α = 1.275x10^{-4} mm s^{-1}.*



though the explanation might involve the stream in the Historic Way or that the condensation corrosion is limited to the area immediately around the entrance. It might also be that condensation corrosion only affects inactively growing stalagmites whose surfaces are not covered by saturated-to-oversaturated solutions.

Conclusions

This study of CO_2 variability in Scoska Cave has shown that concentrations increase with distance from the entrance. However, the CO_2 concentrations within individual passages are affected by local sources and sinks. The three passages within this cave system present different ways by which CO_2 can enter a cave.

In the Historic Way, the CO_2 sources were degassing from supersaturated drip waters and fracture flow of supersaturated water through the limestone. The main source in the Left Hand Series is the degassing of the water from pools. However, the stream running through the chamber at the inner limit of this passage appears to act as a CO_2 sink. In the Right Hand Passage, microbial decomposition of organic material within the mud might act as a CO_2 source. However, both the Left and Right Hand Passages gain CO_2 from water and air flow through fractures.

These results demonstrate that only a few P_{CO_2} readings will rarely give an accurate indication of the spatial distribution of CO_2 within a cave system, corroborating previous research (e.g., Baldini *et al.*, 2006). Caves that ventilate efficiently might be characterized by fewer data, though this efficiency may change over time. Although clarifying the factors affecting CO_2 distribution throughout a cave system, the spatial dataset presented here offers only a 'snapshot' in time of the CO_2 distribution throughout this cave system. Strategically-placed CO_2 loggers would be required to detect repositioning of a CO_2 'front' through time as it responds to atmospheric and climatic shifts.

A valid indication of the sources, sinks, and distribution of CO_2 for a moderate-length cave system in a temperate karst landscape is presented in this paper. However, more research into other caves of varying lengths and in other environments (e.g., a tropical environment) needs to be undertaken better to understand the systematics of CO_2 behaviour in other cave systems.

The distribution of cave air P_{CO_2} might play a role in controlling deposition rates of calcite throughout the Scoska system. It is surmised that, as a result of P_{CO_2} and temperature variability, calcite precipitation rates in separate areas of Scoska Cave might differ substantially, highlighting the importance of site-specific cave environmental factors, such as ventilation, in the interpretation of speleothem-based palaeoclimate records.

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