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CARBON DIOXIDE SOURCES, SINKS, AND SPATIAL VARIABILITY IN SHALLOW TEMPERATE ZONE CAVES: EVIDENCE FROM BALLYNAMINTRA CAVE, IRELAND

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Carbon dioxide concentrations in Ballynamintra Cave, S. Ireland, generally increase with distance from the entrance, but this trend is non-linear because physical constrictions and slope changes compartmentalize the cave into zones with distinct P_{CO_2} signatures. In this cave, CO_2 originates from the soil and enters the cave by degassing from dripwater and by seeping through fractures, and is then transported throughout the cave by advection. Elevated concentrations in roof fissures, joints, and adjacent to walls suggest that these locations shelter CO_2 gas from advection and permit local accumulation. CO_2 enrichment was noted over a sediment accumulation, suggesting that microbial oxidation of organic compounds in the sediment provided an additional CO_2 source distinct from the soil zone above the cave. Advection driven by external barometric pressure variations caused ventilation, which is the principal CO_2 sink. The data presented here underscore the need for high resolution data to adequately characterize cave air P_{CO_2} variability.

Introduction

Carbon dioxide partial pressure (P_{CO_2}) in the unsaturated zone is an important rate-determining factor in a variety of geochemical processes occurring in the subsurface. Dissolution of atmospheric and soil CO_2 into percolation waters forms carbonic acid (H_2CO_3), the principal agent responsible for limestone dissolution and cave development. Generally, soil P_{CO_2} is substantially higher (typically 1,000–10,000 ppm) than atmospheric values (~380 ppm) (Troester and White, 1984; White, 1988), and is largely responsible for the total dissolved CO_2 in vadose water. In a closed system, limestone dissolution occurs until the dissolved carbon dioxide is completely consumed. Conversely, an open system maintains constant contact between the percolating water and soil CO_2, increasing the amount of total carbonate dissolution. In reality, most systems are open until a certain depth, past which contact with the soil zone stops and closed system behavior ensues. The geochemical system then remains at equilibrium until the water reaches void spaces with lower P_{CO_2} than the dissolved P_{CO_2} of the water, at which point degassing of the dissolved CO_2 occurs, followed by calcite precipitation. Thus, P_{CO_2} variability throughout a cave can influence the spatial distribution of calcite deposition. Previous research suggests that stalagmite growth rate is a proxy for paleotemperature (Genty *et al*., 2001), vegetation (Baldini *et al*., 2005), and rainfall (Genty and Quinif, 1996; Railsback *et al*., 1994). Thus, understanding CO_2 distribution and dynamics in caves is important for palaeoclimate research using stalagmites because their growth rates partially depend on cave atmosphere P_{CO_2} (Kaufmann, 2003; Kaufmann and Dreybrodt, 2004; Spötl *et al*., 2005).

While CO_2 degassing may cause calcite precipitation, water condensing from high-humidity cave air onto calcite surfaces in a cave may absorb CO_2 from the air, producing carbonic acid and subsequent calcite dissolution. This phenomenon is termed condensation corrosion, and the rates are dependent on cave atmosphere P_{CO_2}. Previous research has demonstrated that although condensation corrosion is most prevalent in hydrothermal caves (Bakalowicz *et al*., 1987; Cigna and Forti, 1986), it can occur in non-thermal caves (De Freitas and Schmekal, 2003; Dublyanski and Dublyanski, 1998; Jameson, 1991; Sarbu and Lascu, 1997; Tarhule-Lips and Ford, 1998). Opinions on the speleogenetic importance of condensation corrosion vary, but the potential risks to speleothems and cave pictographs are well-documented (Carrasco *et al*., 2002; Pulido-Bosch *et al*., 1997). Understanding the behavior of CO_2 in caves is therefore critical for the preservation of cultural heritage sites and heavily visited commercial caves, and may also affect the vadose modification rate of existing cave passage.

Many researchers have measured P_{CO_2} in caves, but very few high-spatial resolution datasets of P_{CO_2} exist. Gewelt and Ek (1983) published a comparison of the spatial P_{CO_2} variability in two Belgian caves where respired CO_2 was absorbed by a breathing apparatus filled with sodium carbonate. A linear relationship existed between the distance from the cave entrances and cave air P_{CO_2}. Based on the CO_2 distribution in the caves, the soil zone and an underground stream flowing through one of the caves were inferred as CO_2 sources.

Another study presented data from Belgium and numerous other countries, and demonstrated that P_{CO_2} is positively correlated with above-ground temperature (Ek and Gewelt, 1985) and that P_{CO_2} concentrations are higher near the ceiling of passages. A study of the Aven d'Orgnac in France suggested that air enriched with biogenic CO_2 moved through bedrock fissures into the cave (Bourges *et al*., 2001).

The P_{CO_2} data presented here are used to develop a high spatial resolution survey of carbon dioxide concentrations for Ballynamintra Cave, Ireland. Whereas previous research on spatial variability of cave atmosphere CO_2 [*e.g.*, (Ek and Gewelt, 1985; Gewelt and Ek, 1983)] was conducted using chemical pump detectors that were relatively imprecise and cumbersome, the current research was conducted using an infrared CO_2 probe, greatly increasing the precision and decreasing the time necessary per measurement. Consequently, the entire cave was surveyed with a spatial resolution better than one point per five meters, both horizontally and vertically. This high resolution also facilitates the development of air circulation models that identify sources and sinks. To our knowledge, this is the first cave air P_{CO_2} survey created using high-precision CO_2 loggers coupled with breathing apparatuses to minimize the effects of operator-respired CO_2.

Site Description

Ballynamintra Cave is located approximately 11 km NW of Dungarvan, County Waterford, Ireland, and is developed in lower Carboniferous (Mississipian) limestone strata (Fig. 1). It is a very short cave, with only 95 m of surveyed passage and a depth of 14 m (Ryder, 1989), but is divided by slopes and constrictions into three distinct sections. The large (~3 m diameter) entrance leads immediately to the first section, a relict phreatic tube approximately 3 m in diameter that also has a smaller entrance near the far end via a collapse skylight. A narrow, excavated passage leads 3 m downwards from here into the cave's main section, which consists of a large chamber 12 m long, 3 m high, and 3 m wide. This chamber continues south until a large (6 m long, 2 m wide, and 4 m high) accumulation of soil. A vertical passage (called The Hole) at the accumulation's base leads through very narrow passages to the lowest point in the cave, which terminates at a sump. This is the only small area that was not included in the CO_2 survey, because the extremely tight nature of these tunnels prevented passage of the operators and breathing apparatuses. The top of the soil accumulation is approximately 2 m below the ground surface, and plant roots are observable extending into the cave at this point. A very tight (0.25 m high, 1 m wide), excavated passage leads downwards to the cave's third distinct section, a very well decorated chamber 10 m long, 3 m wide, and 2 m high at approximately the same level as the main chamber.

The cave is developed in the side of an escarpment overlain by a small, well-developed mixed beech and oak wood with substantial undergrowth, though pasture surrounds the escarpment in all directions. The soil is well-developed with distinct O and A horizons. The epikarstic zone is reached after approximately 50 cm, but depth varies considerably at different locations on the escarpment.

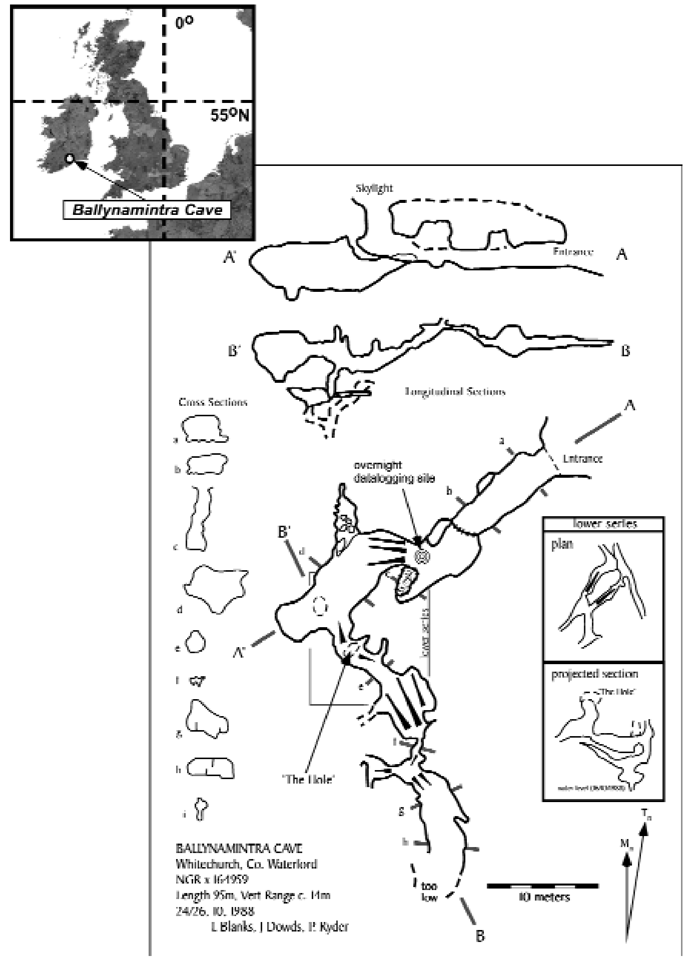

Figure 1. Map and location of Ballynamintra Cave, County Waterford, Ireland. The concentric circles indicate the overnight logging site. Adapted from the original survey by L. Blanks, J. Dowds, and P. Ryder (Ryder, 1989).

Mean annual surface temperature at Cork Airport (50 km to the SW) is 10.1 ºC and mean annual rainfall is 1,191.7 mm.

Methods

Temperature and CO_2 concentrations were determined using a calibrated Vaisala GM70 CO_2 meter, which calculates P_{CO_2} by measuring the absorption of an infrared beam by CO_2 molecules. The precision for the P_{CO_2} measurements is better than ±30 ppm (2σ), and the temperature measurement precision is ±0.02 ºC (2σ). All P_{CO_2} values are presented as ppm (volume) and were corrected for barometric pressure. Measurements for the survey were made on September 9, 2005.

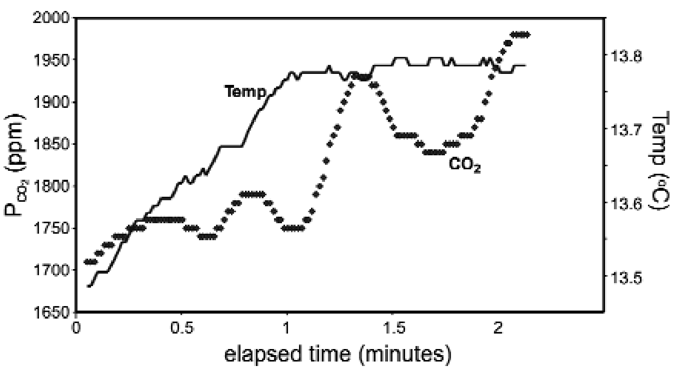

Figure 2. Time-series dataset of P_{CO_2} and temperature obtained after removal of breathing apparatus. Solid line represents temperature data and filled diamonds represent P_{CO_2} measurements.

Error due to respired CO_2 contributions into the cave atmosphere was minimized by using a breathing apparatus that allowed normal breathing but expelled respired air through a 20 m long flexible tube and into the atmosphere in previously surveyed portions of the cave. Because of the measurement rapidity (less than 2 minutes in most cases), the respired air did not have sufficient time to diffuse into the sections of the cave where measurements were actively being taken. Electric lights were used exclusively.

P_{CO_2} and temperature measurements (n = 137) were taken along short transects in the cave, and the location of each measurement relative to datum measured with a compass, clinometer, and calibrated tape. P_{CO_2} measurements were often taken in vertical profiles; the mean of these points was determined to create a single point in an x–y grid. These points were then used to create horizontal two-dimensional contour maps. All contour maps were created using Surfer 8®. Data were also logged overnight every 15 minutes in the phreatic tube section of cave near the entrance to the more poorly ventilated section of cave (see Fig. 1 for location) to observe whether any shifts associated with colder nighttime temperatures occurred.

RESULTS AND DISCUSSION

IMPACTS OF RESPIRATION

Removal of the breathing apparatus near the furthest point away from the cave entrance after completion of the survey (in a small tunnel approximately 2 m high and 2 m wide) demonstrated that respiration immediately caused CO_2 levels to rise from 1,700 ppm to 1,980 ppm, an increase of 16% in just over 2 minutes (Fig. 2). This is broadly consistent with previous studies that suggest increases of 32% after 5 minutes respiration from 3,800 to 5,000 ppm (Ek and Gewelt, 1985; Gewelt and Ek, 1983). The increase was punctuated with minima and maxima, suggesting that direct, high-P_{CO_2} respiration reached the CO_2 meter only occasionally, depending on the breathing direction of the operators. A human breath contains approximately 40,000 ppm CO_2 (Miotke, 1974), considerably higher than atmospheric values (380 ppm) and cave air values (mean value in Ballynamintra Cave 1,050 ppm), and therefore can significantly alter cave air concentrations. When long measurement times are necessary, as with CO_2 meters dependent on chemical pump detectors, significant error is introduced. Studies not using techniques to mitigate the effects of respired CO_2 will likely report erroneously high P_{CO_2} values.

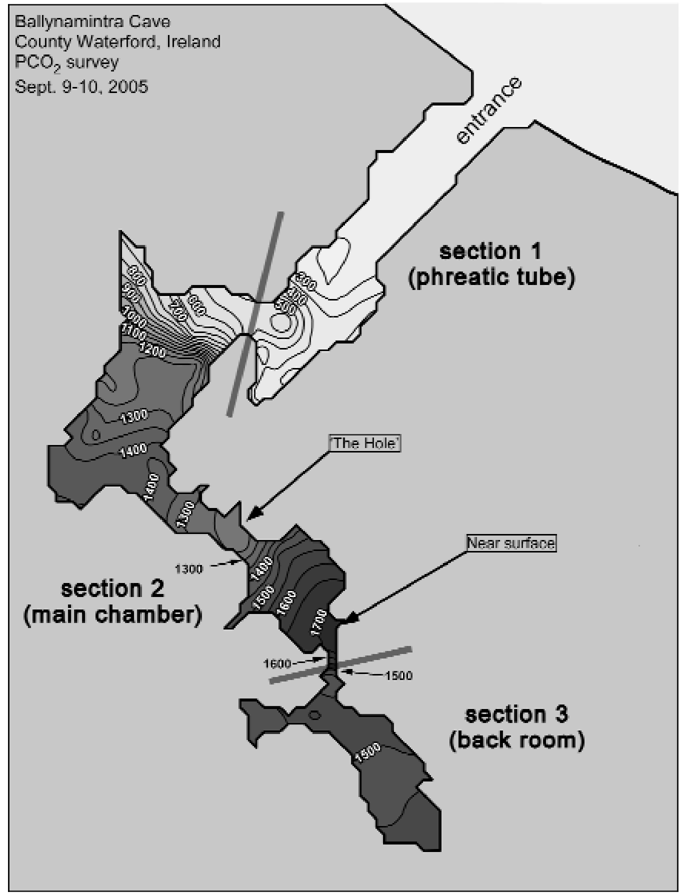

Figure 3. Contour map of CO_2 concentrations throughout Ballynamintra Cave. Contour interval is 50 ppm. Points used to construct contour map are shown as black circles.

The temperature measurements taken simultaneously with the P_{CO_2} measurements suggest that the presence of two people raised the temperature of the small chamber by at least 0.3 °C in two minutes, though because the operators were present in the room before logging began, the effect likely exceeds this estimate. Because of this potential error, temperature measurements are not precise enough to create a detailed temperatures contour map; however, general spatial trends in temperature are apparent and will be discussed below.

CAVE AIR CO_2 DISTRIBUTION

Ventilation caused by the large entrance combined with the smaller skylight entrance results in considerably lower P_{CO_2} in the phreatic tube section of cave than in the other sections (Fig.

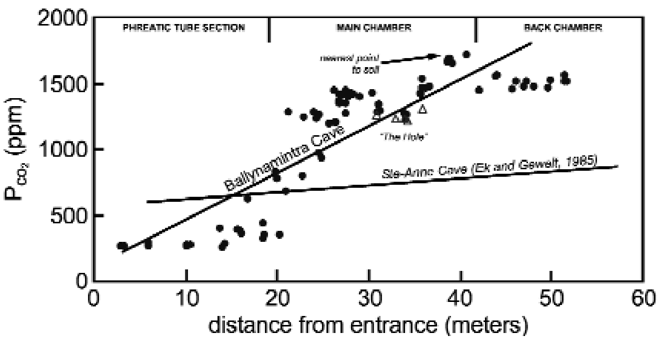

Figure 4. CO_2 concentrations plotted against distance from the entrance of Ballynamintra Cave. Unfilled triangles represent data points obtained in the lower level of the cave ('The Hole') that were not included in the survey shown in figure 3. Regression lines describing the data from this study and from a previous study (Ek and Gewelt, 1985) in Ste-Anne Cave, Belgium, are shown. The slope for the regression line describing the data obtained in the current study (*m* = 34.29) is greater than that for the older study (*m* = 5.3) because the small passages and constrictions present in Ballynamintra Cave inhibit air circulation more effectively than the larger passages in Ste-Anne Cave.

3). P_{CO_2} values reach a local maximum (550 ppm) directly adjacent to the narrow, inclined constriction leading to the deeper main section of cave. A plume of CO_2 rich air exists protruding from this constriction into the phreatic tube section, where advection likely prevents accumulation to more elevated P_{CO_2} values. Values increase very steeply from the well-ventilated phreatic tube entrance passage into the cave's second, main section, reaching local peak concentrations of 1,450 ppm before decreasing gradually to values of 1,250 ppm towards the extremely tight passage known as The Hole that leads downwards towards a sump. Values obtained within this tight vertical passage are the lowest of the entire cave (1,230 ppm), with the exception of the phreatic tube section closest to the entrance. Carbon dioxide partial pressure values increase again as the cave ceiling approaches the ground surface, eventually reaching the most elevated values in the entire cave (1,720 ppm). The passage here is developed at the top of a large accumulation of sediment, and roots growing in roof fissures indicate the close proximity of the soil. This was confirmed by comparing the survey to a GPS measurement of surface altitude, suggesting that this section of cave is less than two meters below the surface. P_{CO_2} values gradually decrease downward through a tight constriction into the third section of the cave (Fig. 3). Values in this isolated chamber are approximately 1,500 ppm and do not vary considerably, suggesting that the single small entrance to the chamber prevents significant air exchange.

CONTROLS ON CAVE AIR P_{CO_2}

The trend towards more elevated P_{CO_2} values with distance from the entrance (Fig. 4) suggests that air circulation is the most important control governing CO_2 distributions, and that physical constrictions in the cave impede air movement. Diffusion of CO_2 out of the highest P_{CO_2} area was calculated using an equation derived from Fick's First Law:

$$J = -D\frac{dC}{dx} \quad (1)$$

where:
- J = flux [(kg m^{-2} s^{-1})]
- D = diffusion coefficient of CO_2 in air (m^2 s^{-1})
- dC = concentration change (g m^{-3})
- dx = distance (m)

Using values of $D = 3.0 \times 10^{-6}$ (m^2 s^{-1}), $\Delta C = 1{,}500$ (g m^{-3}) (concentration change between high concentration area to phreatic tube area), and $\Delta x = 50$ m (approximate distance from high concentration area to phreatic tube area), the flux (J) out of the high P_{CO_2} area is calculated as -1.989×10^{-10} (kg m^{-2} s^{-1}). The amount of CO_2 contained within the high P_{CO_2} region of cave at the back of the main chamber is 0.11 kg, assuming the volume of the high P_{CO_2} area of cave is 33.3 m^3 and the P_{CO_2} is 2,000 ppm. Using a cross-sectional area value for the passage of 6.0 m^2, diffusion will homogenize CO_2 concentrations throughout the cave in approximately 3 years. This time period is long compared to the probable time required to ventilate the cave via differential pressures caused by changes in surface atmospheric barometric pressure, and is thus probably not an important mechanism for CO_2 transport in Ballynamintra Cave.

The steepest gradients in P_{CO_2} occur immediately after tight passages separating different sections of Ballynamintra Cave (Fig. 4). The regression line between P_{CO_2} and the distance from the entrance in Ballynamintra Cave has a steeper slope (m = 34.29) than the regression line calculated by Ek and Gewelt (1985) for Ste-Anne Cave, Belgium, (m = 5.3) and probably results from the difference in cave morphologies. Ballynamintra Cave is small with several tight constrictions, while Ste-Anne Cave is larger with wider passages, allowing more ventilation and air exchange. Although the maximum P_{CO_2} reached in the main passage of Ste-Anne Cave is much greater than that reached in Ballynamintra Cave (3,200 ppm versus 1,720 ppm), the value reached after 50 m (the maximum distance from the entrance, Ballynamintra Cave) is much lower (800 ppm compared with 1,720 ppm), supporting the hypothesis that the differences in the slopes of the regression lines results from more air circulation in Ste-Anne Cave. This interpretation is also supported by evidence from other caves with very large dimensions that have very low P_{CO_2} values (Ek *et al*., 1989).

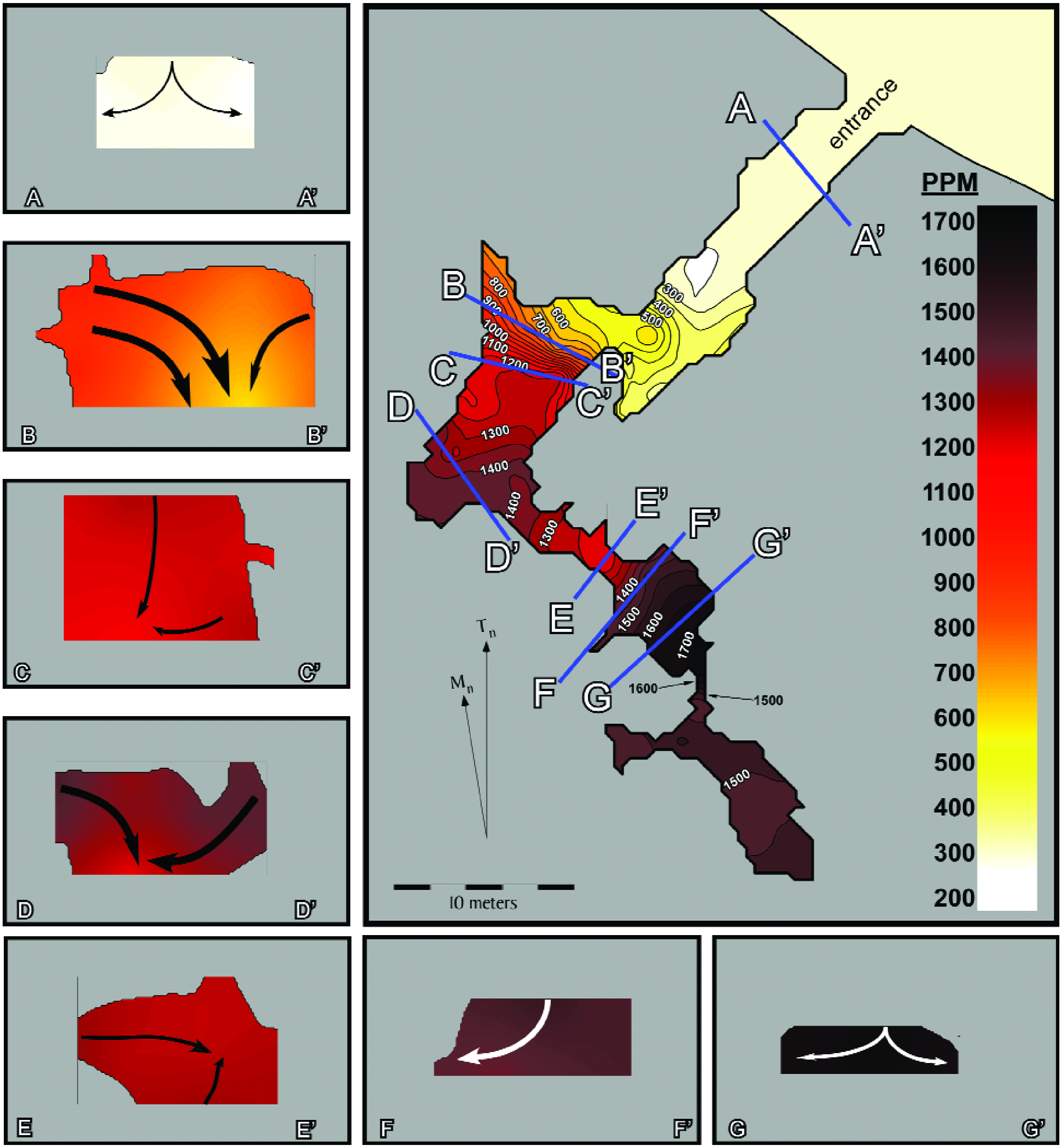

Figure 5. Contour maps of P_{CO_2} values (ppm) at various cross-sections of passages in Ballynamintra Cave. All values use the same contour interval (10 ppm). Arrows indicate inferred direction of CO_2 flux, from high P_{CO_2} to low P_{CO_2}. The gradient strength is reflected schematically by the size of the arrows; larger arrows indicate a stronger P_{CO_2} gradient. Solid grey indicates rock.

A widespread misconception is that because CO_2 is approximately 1.5 times heavier than typical air, it sinks to deeper sections of cave. This mechanism will only affect caves with temperatures near absolute zero, when gas molecules lose nearly all their vibrational energy, and so is not an important factor anywhere (Smith, 1999). Several other mechanisms may increase cave atmosphere P_{CO_2} (James, 1977): 1) degassing of dissolved CO_2 from cave waters that generally obtain elevated CO_2 contents from the soil, 2) production of CO_2 from the respiration of micro-organisms in the cave, usually associated with decaying organic matter, 3) CO_2 flow through fractures connected to the soil, and 4) deep-seated CO_2 seepage from porous reservoirs, usually igneous in origin. Only the first three mechanisms are relevant in Ballynamintra Cave.

The first mechanism (CO_2 degassing) is identifiable by a vertical gradient in P_{CO_2} concentrations in a passage with no organic matter accumulation. The high P_{CO_2} locus depends on the drip rate of the degassing water. If drips are very rapid, water does not have sufficient time to degas on the cave ceiling but instead degasses near the floor, creating locally high concentrations near the base of a passage. Conversely, slow drips will degas on the ceiling and will result in locally high P_{CO_2} values at the top of passages. In both cases, degassing rates must exceed gas diffusion and advection rates; otherwise the CO_2 will spread evenly throughout the chamber. The second mechanism (CO_2 flux from fissures) also results in elevated P_{CO_2} values near the ceiling, but is distinguished from the degassing mechanism by the lack of active drips and the presence of vertical cracks or fissures. The third mechanism (microbially-produced CO_2) is generally associated with the presence of organic material.

In Ballynamintra Cave, most passage cross-sections demonstrate higher CO_2 concentrations near the ceiling or fractures (Fig. 5), suggesting that the dominant mechanisms involve CO_2 degassing from drip waters or CO_2 fluxes from fissures. A major exception occurs in the cross-section of the passage at the top of the sediment accumulation (Fig. 5f). Carbon dioxide concentrations are greatest near the passage base, suggesting that this localized CO_2 maximum reflects microbially-induced organic matter decay in the sediment. Sheltered areas typically have elevated P_{CO_2} values (Fig. 5), suggesting reduced advective CO_2 dispersion. This suggests that air movement through the cave is analogous to water movement in streams, with a central zone of greatest flow (the thalweg in surface streams) and lateral zones of reduced velocity due to either friction or physical sheltering.

The distribution of CO_2 in Ballynamintra Cave and the association of locally elevated concentrations with ceiling fissures strongly suggest that the gas originates predominantly from the soil. A soil P_{CO_2} logger permanently installed directly above the cave indicates that P_{CO_2} values greater than 5,000 ppm are typical during the summer. This soil gas is dissolved in percolation water, transported into the subsurface, and degassed in the cave. Additionally, soil gas may also diffuse downward through fissures into the cave. Downward soil gas diffusion is probably the dominant source of CO_2 to Ballynamintra Cave because of its proximity to the soil zone and lack of high discharge drips. Calculations based on the P_{CO_2} of cave waters and estimated number of drips suggest that if drips were the only source of CO_2 into the cave, it would take at least 50 years to produce the accumulation of CO_2 observed in the high P_{CO_2} sections, assuming the complete absence of any CO_2 sinks. This calculation and the association of high P_{CO_2} areas with fissures therefore suggest that downward soil gas diffusion, rather than degassing from drips, is the dominant source of CO_2 to Ballynamintra Cave. However, because fracture frequency and width in karst areas decreases with depth (Baker *et al*., 1997), downward diffusion of gaseous CO_2 is probably a more important source at Ballynamintra Cave than at deeper caves.

A CO_2 sink is inferred to exist in The Hole because of anomalously low concentrations present in and around the vertical passage. The presence of water at the passage base suggests that the water P_{CO_2} is lower than the cave atmosphere P_{CO_2}, and is actively absorbing CO_2 from the atmosphere. Unfortunately, the very tight passages prevented the researchers from reaching the water to obtain any measurements.

Temperature Distribution

The temperature above-ground on the day of the survey was measured as 17 ºC and was only slightly lower in the phreatic tube section, with a mean measurement of 15.5 ºC. Once past the constriction leading into the main chamber, the recorded temperature decreased to approximately 12.5 ºC and remained stable until The Hole when temperatures dropped noticeably to 11.5 ºC. This is the deepest section of cave and probably has the least exchange with the external atmosphere. The presence of water may also have contributed to the lower temperature. Temperatures increased dramatically near the top of the sediment accumulation to almost 14 ºC, but this may partially result from the presence of two cavers in a small space for a prolonged period of time (as mentioned above). However, it may also reflect the proximity of warmer 17.0 ºC above-ground air two meters away through the overburden. The temperature in the deeper back chamber was approximately 12.5 ºC and stable throughout.

Temporal CO_2 Variability

Carbon dioxide and temperature measurements were logged every 15 minutes between 8:39 p.m. and 11:39 a.m., September 8–9, at the top of the steep passage connecting the phreatic tube section to the main chamber (Fig. 6). The measurements vary from very low (200 ppm, value below atmospheric probably because of forest photosynthetic effects) late in the logging interval to a maximum of 1,390 ppm occurring at 1:39 a.m., suggesting that CO_2 rich air was expelled from the

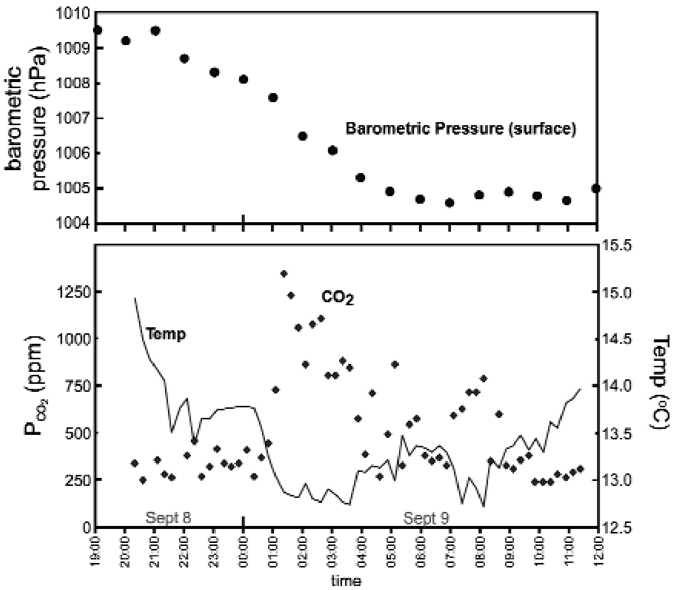

Figure 6. Temperature (solid line) and P_{CO_2} variations (filled diamonds) measured every fifteen minutes between 8:39 p.m. and 11:39 a.m., September 8–9, at the top of the steep passage connecting the phreatic tube section to the main chamber. Maximum P_{CO_2} values were recorded at 1:39 a.m. (1390 ppm). The top panel displays the hourly barometric pressure at Cork Airport (closest meteorological station to cave, 40 km to the west) during the measurement period.

cave during the night. The maximum concentration recorded is comparable to the concentrations characteristic of the rest of the cave; therefore a barometric pressure reduction that occurred on the surface overnight may have caused the cave to exhale, resulting in an extension of the high-P_{CO_2} plume (Fig. 3). The interpretation is supported by the temperature data, which reach their lowest values (12.8 ºC) coincident with the highest P_{CO_2} values. The similarity between this temperature value and typical cave air temperature (12.5 ºC) suggests that both the high P_{CO_2} and the low temperature values reflect advection of air from deeper in the cave. Longer term CO_2 concentration datalogging in the main chamber of Ballynamintra Cave demonstrates the presence of quasi-periodic, large P_{CO_2} spikes reaching maximum values of over 3,000 ppm. These may correspond to periods of decreased barometric pressure on the surface, which cause the extraction of CO_2 rich air from fissures (Baldini *et al.*, in prep.). Conversely, high external barometric pressure pushes in atmospheric air, reducing cave air P_{CO_2}.

IMPLICATIONS

The distribution of CO_2 in Ballynamintra Cave implies that the elevated P_{CO_2} values found deeper in caves will result in reduced degassing from dripwater, consequently reducing calcite deposition rates. This study therefore suggests that stalagmite calcite precipitation rates must vary spatially throughout a cave, even if all other parameters affecting precipitation remain unchanged. Furthermore, a large overnight P_{CO_2} shift suggests that calcite precipitation may vary temporally as well as spatially in response to the P_{CO_2} variations induced by external barometric changes. The hypothetical creation of an entrance (either naturally through erosion or artificially) to a cave previously with no entrance will ventilate the cave and produce a rapid P_{CO_2} drop. This phenomenon would result in a rapid stalagmite growth rate increase that may resemble the effects of a climatic amelioration (Baldini *et al.*, 2002; Genty *et al.*, 2003). Paleoclimate studies using stalagmite growth rate or isotopic proxies must consider the possibility of rapid ventilation in relevant situations. A comparison of stalagmite $\delta^{13}C$ and growth rates could distinguish between the two effects (ventilation and climatic amelioration). Both effects would result in increased calcite deposition rates, but ventilation would raise $\delta^{13}C$ values while a climatic amelioration would reduce stalagmite $\delta^{13}C$ (because of increased surface bioproductivity).

Because the research presented here indicates that concentrations of CO_2 are not homogenous throughout caves, heterogeneities must also exist in the rates of speleogenetic processes that are affected by P_{CO_2}. Condensation corrosion will affect areas of elevated P_{CO_2} preferentially over other areas of lower P_{CO_2}, particularly when associated with high humidity (Dublyanski and Dublyanski, 1998). The heterogeneous spatial and temporal distribution of CO_2 concentrations also affects gypsum deposition in caves via the Palmer Model, where low P_{CO_2} drip water containing sulphate ions absorbs CO_2 from the cave atmosphere, dissolves the surrounding limestone, and redeposits gypsum (Palmer, 1986). Because gypsum has a higher molar volume than calcite, this replacement can lead to the formation of breakdown and cavern enlargement (White and White, 2003). This chemical model is highly sensitive to the cave air P_{CO_2}, and relatively small variations may either initiate or inhibit gypsum deposition.

CONCLUSIONS

The CO_2 distribution in Ballynamintra Cave demonstrates that CO_2 concentrations generally increased with distance from the entrance, but that local sources and sinks countered this trend. Constrictions in the cave compartmentalized areas with distinct P_{CO_2} signatures. In this cave, most CO_2 apparently enters the cave through the ceiling; either dissolved in dripwater or more likely by seeping in the gas phase from the soil to the cave through fractures, though a combination of both mechanisms is probable. Transport throughout the cave occurs by advection induced by barometric pressure differences between the surface and cave. Concentrations in fissures, cracks, and adjacent to walls were higher than those in the centers of passages, suggesting that these locations partially shelter CO_2 gas from advection. Cave air P_{CO_2} may also increase locally due to microbially produced CO_2 originating from a soil accumulation near the end of the cave. A sump located at the cave's lowest point may act as a CO_2 sink.

These data indicate that one P_{CO_2} measurement will not accurately characterize cave air P_{CO_2}. Because of the importance of CO_2 on calcite deposition, condensation corrosion, speleogenetic processes, and the preservation of cave pictographs, the distribution of CO_2 in caves should be researched further. The simple, efficient technology involved permits the construction of high-resolution surveys of larger caves, testing whether the relationships observed in Ballynamintra Cave are applicable on larger scales. Future studies in deeper caves, caves containing active rivers, and commercial caves would provide interesting supplements to the results reported here. Additionally, future research should apply natural or artificial tracers to more positively identify sources and sinks of CO_2. Isotopic studies would help identify potential CO_2 sources, and would also evaluate the response of stalagmite calcite carbon isotopic ratios to P_{CO_2} variations.

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