# External controls on $CO_2$ in Gibraltar cave air and ground air: implications for interpretation of $\delta^{13}C$ in speleothems

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Highlights

- The key $CO_2$ reservoir in karstic systems is $CO_2$-rich ground air
- Ventilation mixes external atmosphere with ground air to form cave air
- Temperature and wind drive seasonal regimes and rapid synoptic changes in cave air $CO_2$
- Ground air dynamics have implications for climatic interpretation of $\delta^{13}C$ in speleothems

**Abstract**

The principles of cave ventilation and ground air advection are outlined. $CO_2$ concentrations were monitored every 2-4 hours from 2006 to 2012 at twelve locations in two Gibraltar caves, New St. Michael's (240-275 m altitude) and Ragged Staff (0-70 m), providing detailed records of spatial distribution and temporal changes responding to transient meteorological conditions and seasonal cycles. Cave atmospheres are dynamic mixtures of external air and $CO_2$-rich ground air containing soil-respired $CO_2$ augmented by $CO_2$ derived from oxidation of organic matter washed down into the vadose fracture porosity. The dominant feature of the cave air records is seasonal alternation between high and low $CO_2$ states caused by reversals in ventilation and ground air advection into or away from the caves. The high and low $pCO_2$ states are tightly coupled between the two caves in an antiphase relationship, with rapid switching in response to temperature-controlled density differences between external air and isothermal ground air at mean annual surface temperature (18°C). The diurnal temperature cycle modulates this pattern, producing four ventilation-advection modes. Summer and winter modes occur when diurnal temperatures are respectively entirely above or below the core temperature of the Rock. During transitional modes the core temperature lies within the diurnal range and $pCO_2$ fluctuates rapidly as the flow of low-$CO_2$ external air through cave entrances alters in response. Strong easterly winds reduce $CO_2$ concentrations in ground air entering the caves and progressively lower cave air $CO_2$. The effects of the $CO_2$ regime on $\delta^{13}C$ in speleothem are restricted to variations of 2-3 ‰, suggesting that larger changes of up to 6 ‰ across major climatic transitions probably reflect changes in production, transport and oxidation rate of organic matter

in the vadose zone. Direct observations of these processes would improve future understanding of the climatic significance of $\delta^{13}C$ records in speleothems.

## 1. Introduction

Cave atmospheres are often enriched in carbon dioxide when compared with the current free atmosphere value of about 410 parts per million by volume (ppmv). Concentrations of up to several thousand ppmv are common while occasional values of several per cent have been recorded (Baldini, 2010; Carlson et al., 2018; Ek and Gewelt, 1985; James, 1977; James et al., 1975). The presence of this carbon dioxide has been ascribed in the past to various potential sources including degassing from waters entering the cave as seepage or as influent streams, decay of organic matter washed into the cave by streams or deposited as guano by troglophiles such as bats, or most commonly by transport from the $CO_2$-enriched gases found in the soil above the cave (Fairchild and Baker, 2012). Transport from the soil to the cave may be by diffusion or advection through fracture networks in the carbonate bedrock (Covington, 2016). However, Atkinson (1977) demonstrated that the supply of carbon dioxide from soil gas was apparently supplemented by a source with higher concentrations, located in the bedrock zone between the surface and a cave in the Mendip Hills, England (GB Cave). This was attributed to decay of organic matter washed into the bedrock by infiltrating water. The term *ground air* was introduced to distinguish the atmosphere of the voids in unsaturated bedrock from the soil air. Subsequent studies in many other settings confirmed the enrichment of ground air with $CO_2$, either by inference from the chemistry of vadose waters (e.g. Faimon et al., 2012a, 2012b; Gulley et al., 2014; Lang et al., 2017; Noronha et al., 2015; Peyraube et al., 2012, 2013; Riechelmann et al., 2011; see Baldini (2018) for a review), or by direct observation (e.g. Benavente et al., 2010; Vadillo et al., 2010; Wood and Petraitis,1984). Both lines of evidence were combined in a study of carbon cycling in the vadose zone of the Rock of Gibraltar by Mattey et al. (2016).

Between 2004 and 2012 we have monitored the $CO_2$ concentrations in the local atmosphere in multiple locations within two caves in the Rock of Gibraltar, New St. Michael's Cave (SM) and Ragged Staff Caves (RS) (Mattey et al., 2008, 2010, 2013, 2016). The purpose of the present paper is to analyse and as far as possible explain the influences of weather and season on the fluctuations and spatial patterns in $CO_2$ concentrations that we observed within these caves. In the first part we outline the setting of our monitoring study and the dynamic relationship between cave air and ground air, both in principle and with reference to Gibraltar. Following this we demonstrate the roles played in causing fluctuations in the $CO_2$ content of air inside the Gibraltar caves by seasonal temperature fluctuations, wind strength and direction, and diurnal variations of temperature and pressure. In the last part we consider the implications of these findings for gas transport within the unsaturated zone, for the growth of speleothems and for the interpretation of the well-dated geochemical records they can provide in terms of past climate.

## 2. Setting and methodology

### 2.1. Gibraltar physiography and climate

The Rock of Gibraltar (36°08’ N, 5°21’ W) is an isolated N-S trending ridge of dolomitic limestone 4 km long with peaks reaching over 400m above sea level. The topography of Gibraltar and the position of coastlines prior to modern development of the town and harbour and in glacial times are shown in Figure 1. The ridge has an asymmetric E-W profile and has a steep to near vertical eastern slope which is now partly banked by Pleistocene sand dune deposits derived from the coastal plain exposed by lower sea level during glacial periods and mobilized by easterly winds known today as Levanters. The western slope descends at a moderate 35° angle to sea level, truncating the generally steeper westwards dip of the bedrock. Details of the caves and geology of Gibraltar are given in publications elsewhere (Mattey et al., 2008, 2010, 2016; Rodrıguez-Vidal et al., 2004; Rose and Rosenbaum, 1991; Tratman, 1971).

Gibraltar’s climate belongs to the Mediterranean type (Strahler, 1969) and is strongly seasonal with hot dry summers and winters with a mixture of cool and wet periods. Based on records from Gibraltar Airport, 1947–2004 average for April to September is 24.3°C, October to March 13.5°C. Mean annual temperature (MAT) is 18.3°C which is similar to the present temperature in the caves. Annual average rainfall is 767 mm with >80% of precipitation in October through March. Inter-annual variability in rainfall amount is linked to the state of the North Atlantic oscillation Index (NAO) (Wheeler, 2007; Wright et al., 1994).

The Strait of Gibraltar, a sea passage 55 km long linking the Atlantic to the Western end of the Alboran Sea, is confined between two mountain ranges (the Sierra Nevada to the north and the Moroccan Rif to the south) which creates an unusual wind climatology. Low level winds are strongly channelled in an E-W direction, alternating between westerlies related to Atlantic weather systems, and easterly ‘Levanter’ winds broadly linked to the location and intensity of the Azores high (Dorman et al., 1995). Levanter wind episodes are either synoptic or mesoscale events which tend to be more common in summer months, bringing very hot and often humid conditions to Gibraltar. They may last for a few days (synoptic) up to several weeks (mesoscale). During mesoscale Levanters the easterly winds extend through the Strait into the Atlantic. Hourly wind data compiled between 2004 and 2014 show that the frequencies of E and W winds, and the percentage of annual rainfall associated with each wind direction, are approximately equal, but long-term climatological analysis shows that Levanter frequency may be correlated with the state of the NAO (Hidalgo and Gallego, 2019).

### *2.2. Principles of cave ventilation and dynamic interactions between cave air and ground air*

In this section we outline the physical principles of cave ventilation by which the $CO_2$ records discussed below may be interpreted.

The circulation of air in caves was first discussed systematically by Myers (1962) and later by Wigley and Brown (1976) and Badino (1995). Because of the huge contrast in the resistance to linear flow along a cave passage compared with the resistance to flow through the networks of narrow fractures in surrounding bedrock, subsequent accounts have tended to ignore flow through the bedrock and to treat airflow in caves as broadly analogous to fluid flow in pipes, with the walls considered as impermeable. Initially we adopt this point of view. In such a case we may distinguish between *single entrance caves* and *multi-entrance caves,* those with two or more entrances. Single entrance caves will in general have slower air circulation and be less well ventilated by outside air. If the walls are truly impermeable (which is rarely the case) then air can only exchange with the exterior via the entrance. This exchange may occur in response to changes in barometric pressure, causing the cave to exhale as external pressure falls and inhale while it rises – the phenomenon known as cave breathing. Other processes of exchange include convection driven by density differences between internal and external air. For example, in winter cold dense air may flow downwards along the floor of a descending cave entrance, displacing the warmer air within so that it flows upwards near the ceiling and out of the upper part of the same entrance. In summer the outside air is warmer and less dense than the cave air and the latter tends to be stratified, with little exchange with the external air. A seasonally reversed pattern can occur in a single entrance cave which slopes upwards from its entrance.

Density-driven air flow is much stronger in multi-entrance caves, provided that the entrances are not at the same level. For a simple two-entrance cave, if there is density difference between internal and external air, the column of air inside the cave will exert a different pressure at the lower entrance from the air column outside. The pressure difference is given by $gh(\rho_{int} – \rho_{ext})$ where g is gravitational acceleration, h is the altitude difference between the two entrances and the bracketed term is the difference in densities. This hydrostatic argument provides a measure of the force that drives a *chimney-effect wind* between the two entrances (Atkinson et al., 1983; Wigley and Brown, 1976). Chimney-effect airflow is common in multi-entrance caves and can easily be recognised as such because temperature is the dominant influence on air density, outweighing the effects of minor gaseous components such as water vapour or carbon dioxide. As air flows into a cave it exchanges heat with the walls and within a certain distance reaches a temperature little different from the wall temperature (see Wigley and Brown (1976) and Covington et al. (2012) for details). This *deep-cave temperature* is usually almost constant and close to external mean annual temperature at the same altitude (Luetscher and Jeannin, 2004). As the external air temperature varies seasonally, the chimney-effect wind in a two-entrance cave will reverse between summer and winter, and may reverse diurnally at times of year when the daily range of external air temperatures passes through the average cave air temperature. This temporal pattern is a tell-tale indicator of chimney-effect ventilation.

If we now relax the restrictive assumption that the cave walls are impermeable, we can consider situations in which there may be a coupling between within-cave airflow and a diffuse flow of air through the fracture networks in the surrounding bedrock. Consider first a single-entrance cave located within the upper part of a hill formed of air-permeable bedrock. A slow, chimney-effect circulation is possible in this situation. In summer, for example, air may be drawn into the cave and flow out into the fracture network. The relatively low permeability of this network, rather than the resistance of the conduit itself to fluid flow, will determine the volumetric flow rate into the cave entrance. The driving force in this case can be approximated by the expression given in the previous paragraph, $gH(\rho_{int} - \rho_{ext})$, with H now equal to the height of the cave entrance above the base of the hill. The main part of the resistance to flow is provided by the narrow fractures in the bedrock, including those that intersect the cave walls. It is the shape of the hill and the permeability that the fractures impart to the rock mass that determine the air flux. The cave merely provides an extremely high permeability passageway for air to flow into the interior of the hill. Furthermore, the presence of the cave is unnecessary for air to flow through the bedrock in response to the difference in density between the ground air within the hill and the external air. In summer, when the ground air is cooler than the outside air, external air will enter the ground in the upper slopes of the hill and ground air will flow out from the lower slopes. In winter it will flow in the reverse direction. The spatial pattern and rate of flow will be determined by the shape and height of the hill and the temperature of the external air compared with the ground air temperature. At depths greater than a couple of metres the latter will be close to mean annual temperature, because heat diffusion through the bedrock is slow due to its large specific heat capacity, and near-equalisation of temperature between air and bedrock takes place over a short distance as the external air flows into the network of narrow fractures (Covington et al., 2012; Covington, 2016).

For the Rock of Gibraltar, which is a ridge approximately 425 m high and 1250 m wide at its base, Mattey et al. (2016) used the Laplace Equation to model the flow lines followed by air moving through non-cavernous bedrock. They are reproduced here in Figure 2a which shows the locations of Ragged

Staff and St. Michael's Caves in relation to this pattern of flow. Although this is a theoretical model deduced from basic physical principles, it is clear from Figure 2a that the air in both caves is likely to be a mixture between ground air entering through the cave walls, floor or roof, and external air coming in through open entrances. As the flow of ground air will be downwards in summer, the Ragged Staff cave is likely to contain a relatively high proportion of ground air during that season. The St. Michaels system will likely receive some ground air that has descended through the bedrock from the surface above, but this will be mixed with a much greater proportion of external air drawn in through the cave's entrances. During winter the flow will reverse and it can be predicted that St. Michael's Cave will contain a much greater proportion of ground air in its atmosphere than in summer, while at Ragged Staff the cave air is likely to be dominantly external air drawn in via the artificial tunnel at the base of the Rock through which it was discovered.

As noted above, the carbon dioxide content of ground air is much greater than that of the free atmosphere. Mattey et al. (2016) present profiles of $CO_2$ concentrations in a borehole that penetrates the lowest 90 m of the Rock, showing values of 10,000 ppmv in winter and 15,000 ppmv in summer. Without any other direct measurements, nothing is known of the spatial variation in $CO_2$ concentrations in the ground air within the Rock, nor of their temporal variability. Nevertheless, when considering cave air, high $CO_2$ concentrations are likely to indicate a relatively large proportion of ground air in the cave atmosphere, while low $CO_2$ concentrations indicate a large fraction of external air mixed with minor amounts of ground air. Previously reported carbon isotope studies in Gibraltar and elsewhere demonstrate that cave air is generally a mix of $CO_2$-rich vadose air with low values of $\delta^{13}C$ in the range -18 to -24 ‰PDB and $CO_2$-poor background atmosphere with $\delta^{13}C$ of -7 to -8 ‰PDB, with the mixing ratio closely related to the dynamics of cave ventilation by external air (Frisia et al., 2011; Mattey et al., 2010, 2016; D.Riechelmann et al., 2011, S.Riechelmann et al., 2019; Spötl et al., 2005). Ground air mixing with external air was demonstrated semi-quantitatively in Seongryu Cave in Korea by Oh and Kim (2010), using two isotopes of radon as natural tracers of the air entering the cave from the pore spaces of the bedrock around it (Kim et al., 2010). Benavente et al. (2015) also present preliminary evidence for advective exchange between vadose ground air and the cave atmosphere of the Nerja Cave, near Malaga, but there the situation is complicated by the enormous size of the cavity, by the heat and $CO_2$ emitted by the large numbers of visitors to the touristic parts of the cave, and by the probable existence of nearby cavities detected by geophysical survey Liñán et al. (2020).

### *2.3. Airflow through Gibraltar caves*

Topographic surveys of the St. Michael's and Ragged Staff caves are shown in plan and elevation in Figure 3. The annotations classify the passages according to their ventilation regime. In St. Michael's Cave there are four entrances at different altitudes, two natural and two artificial. The lowest of the four is a tunnel constructed during the Second World War to give access to the lower part of the main cave which is known as Old St. Michael's (OSM). The highest two entrances are natural, one at the upper end and the other in the roof of the main chamber. A second artificial entrance gives tour visitors access to the middle of the main chamber. Between these four entrances there is a strong chimney-effect air circulation, with an upwards air flow from the lowest to the highest in winter and a downwards flow in summer. Thus, this part of the cave experiences an *open ventilation regime*. Leading downwards from different points in OSM are three side passages named Leonora's Cave, Lower Series and New St. Michael's Cave (NSM). All three are *single entrance branches* from OSM. Smoke tests made during monthly visits to NSM show that this segment of the cave system experiences an inward movement of air in summer and a somewhat stronger outward flow in winter. The winter flows, measured at a point between the Trap Door and Dark Rift (Figure 3) are roughly proportional to the temperature difference between external air and the cave interior where the temperature is almost constant at 17.9°C. This pattern of seasonally reversing weak airflow, combined with the absence of any other entrance than the Trap Door aperture in the floor of the above-mentioned artificial tunnel, strongly suggests that the NSM passages have a ventilation regime controlled by advective exchange of air with the fracture network in the surrounding bedrock. Figure 3 also shows the locations of $CO_2$ monitoring points. External air was monitored and a station at the Hospital was in the open ventilation regime of OSM, whereas the remaining five locations were all within the single entrance NSM branch.

In Ragged Staff System the topology of the passages and their ventilation is more complex. Figure 3 shows the directions of air flow in summer and winter. The natural cavities had no known entrances before they were discovered during construction of the Ragged Staff tunnels, to which they are connected at two points. The tunnels themselves have two entrances at different elevations; the Ragged Staff portal at 4 m above sea level and the Gardiner's Road exit at 56 m. Mattey et al. (2016, their Figure 3 caption) explain the air circulation in this cave based on observations and smoke tests at different times of year. In summary, the topology of the natural cave consists of a single passage that twists and turns in three dimensions, linking two connections to the surface that can be inferred to exist beyond the known limits of exploration on Figure 3. Under natural conditions there would have been a chimney-effect circulation between these two points, giving the inner part of cave an *open ventilation regime*. The passage from the foot of The Ramp via Akapus to Silent Pool was under natural conditions a *single entrance branch* from this loop. This topology of an openly ventilated two-entrance passage with a single-entrance branch leading off it is identical to that of St. Michael's Cave today, although the latter has three single-entrance branches rather than one. However, the natural ventilation of the Ragged Staff cave has been drastically altered by the tunnels that intersect it at Silent Pool and Hobbit Hole (Figure 3). These form a second two-entrance loop between the Ragged Staff portal and Gardiner's Road, with a very strong chimney-effect air flow between them. The former single entrance branch now acts as a cross-passage connecting with the two loops at Silent Pool and at the base of the Ramp. As explained by Mattey et al. (2016), the relative heights of the entrances can be inferred from the directions of seasonal airflow, with the external connection beyond point B (Figure 3) lying at an altitude between the Ragged Staff Portal and Gardiner's Road (i.e. between 4 and 56 m) and the external connection beyond A being at an altitude well above the Gardiner's Road entrance. Thus, under present conditions all parts of the system have an open ventilation regime in summer, when air from every part of the cave flows towards the lowest entrance. In winter, however, the cross passage is the least ventilated part of the system. Compared with the strong winter flow from the Ragged Staff Portal to Gardiner's Road, the flow from Silent Pool and Hobbit Hole to the base of the Ramp is relatively weak. There it is joined by air flowing from B via Crystal Cave, Rhino Chamber and the upper Ramp and the combined flow passes into narrow passages beneath the Ramp to reach the larger chamber at Point A where the draught leaves the explored part of the cave.

The monitoring points in Ragged Staff lie within the cross passage (Akapus and Hobbit Hole, the latter at the point where it joins the outer two-entrance loop), and within the branch of the inner two-entrance loop leading via Rhino Chamber to Crystal Cave. The extensions from Crystal Cave to Point B and from the Ramp to Point A were not discovered until after the end of the monitoring period.

### *2.4. $CO_2$ monitoring locations*

Early in the monitoring study $CO_2$ measurements were made on samples of air taken and stored in Tedlar bags prior to analysis as described by Mattey et al. (2010, 2013, 2016). These measurements along with observations of airflow made it clear that New St. Michael's cave experienced seasonal changes between high $CO_2$ concentrations in winter and low values in summer, and that the high values must reflect an outflow of $CO_2$-rich ground air from the fracture network in the bedrock into the cave (Mattey et al., 2010). In contrast, the Hospital site had low values that reflected the open ventilation regime with a dominance of external air over ground air. From 2006, $CO_2$ measurements were made with an automated system with six intakes. Five of these were placed for the whole six-year period 2006-2012 at locations designed to monitor external air, the open ventilation regime (Hospital), and the advective mixing of external air and ground air in the single entrance branch of NSM (Dark Rift, Lake and Gib04 sites). The remaining intake was deployed for shorter periods at three further locations in North Rift, just below the Trap Door and in the Bottomless Pit. The first and second of these were designed to monitor the fluctuations in the proportions of external air and ground air at the boundary between the open ventilation regime and the single entrance branch. The Bottomless Pit site was chosen to identify the inflow of ground air in the deepest part of the NSM branch. This division of ventilation regimes is reflected schematically by Figure 2c in which each is represented by a different coloured box, blue for the openly ventilated sites and pink for the sites dominated by seasonal advection of ground air into the single entrance passage of NSM.

In 2009 a second monitoring network was set up in Ragged Staff System with the aim of testing the hypothesis that high-$CO_2$ ground air was advected through the whole Rock by chimney-effect buoyancy forces, as shown by the flow lines in Figure 2a. This hypothesis predicted that the seasonal regimes of high and low $CO_2$ in Ragged Staff would be in anti-phase with those in St. Michaels, which proved to be the case (Mattey et al., 2016). However, the Ragged Staff cave is technically more difficult to traverse than St. Michaels and was incompletely explored. Without prior knowledge of the more complex ventilation, the six automated system intakes were deployed to monitor the boundary of the open ventilation regime in the tunnels (Hobbit Hole, Silent Pool), the interior of the cave (Akapus, Rhino Chamber and Crystal Cave), and the external air (Gardiner's Road). This scheme is also represented in Figures 2b and 2c, with the cave interior indicated as having a paler pink colour than for the St. Michael's cave schematic, because of its more open ventilation.

The detailed monitoring carried out in Gibraltar provides an opportunity to identify the meteorological controls on cave air $CO_2$ and in the following sections we report the results of simultaneous measurements of cave air $CO_2$ made at these locations i.e. within cave systems at different positions in the advective ground air flow within the Rock as a whole. We identify how spatial patterns of $CO_2$ respond to external changes in temperature, wind speed or direction, rainfall and atmospheric pressure. The high temporal resolution of measurements (up to 12 sets of measurements per day), carried out across six annual cycles of seasonality provide a unique opportunity to identify the impact of synoptic scale meteorology on $CO_2$ levels in caves with advective ventilation systems in both multiple-entrance and single-entrance settings.

### *2.5. Automated analysis of $CO_2$ in cave air*

Measurements were carried out between the autumn of 2006 to the summer of 2012 using two specially designed multichannel monitoring systems located in St. Michaels Cave (monitoring locations 240-275 m above sea level (ASL)) and Ragged Staff Cave, (0 m and 70 m ASL). Air for analysis was collected via a network of sampling tubes laid to cave chambers along with a reference line sampling background atmosphere outside the entrances of RS and SM. The multichannel $CO_2$ loggers are linked to star networks of six sampling lines leading to sampling points in the cave systems. These are mainly the same locations where temperature and drip-water monitoring and spot sampling have been reported elsewhere (e.g. Mattey et al., 2010, 2014, 2016). The design and operation features of both multichannel systems were broadly similar. Cave air was pumped to the logger though 6 mm OD polythene tubing using a KNF Neuburger diaphragm pump operating at 5 l/min. Gas transport time from the most distal sites (up to 250m path length) to the logger was in the order of 1 minute. The tubing network led to a multiport manifold which introduced air from the selected site to the analyser. To reduce any risk of moisture condensing in the analyser, incoming water-saturated air was passed through a 1m Nafion loop to allow equilibration with lower humidity air where the logger was situated in the open ventilated Hospital (SM) or Hobbit Hole (RS) (Figures 2c and 3) before admission to the analyser circuit. Condensation was eliminated by the warming action of the sampling pump in the insulated analyser enclosure. Since the output flow rate from the sampling pump varied according to the length of the sample tube the output from the Nafion loop leads to an open split and air analyte is drawn via a secondary low-flow rate pump at 100ml/minute through to the Licor $CO_2$ analyser at a constant pressure and flow rate.

$CO_2$ mixing ratios were measured using a Licor 820 non-dispersive infrared (NDIR) gas analyser fitted with a 14 cm optical path, dual wavelength infrared detection cell. Inlet manifold valve switching, pump operation and data collection were controlled by a Campbell Scientific CR1000 programmable data logger. The analytical cycle began by preheating the

LICOR cell to 50$^oC$. When at temperature, a sampling line was opened and flushed for 2 minutes before measuring $CO_2$ mixing ratios every 10 seconds, recorded as five one-minute averages. On completion the next sampling line was opened and the flushing-analysis process repeated. After measurements were made from each sampling line (taking about 45 minutes) the system shut down to conserve power and the cycle was repeated every two hours (St. Michaels) or four hours (Ragged Staff). With the cell heated to 50°C and pumping, the system drew around 20 watts and was powered by high capacity 12 V lead acid batteries. The St. Michaels batteries were trickle charged from the cave lighting system which was turned on each day for 8 hours. No power was available in Ragged Staff so freshly charged batteries were replaced every two weeks.

The Li-820 loggers were regularly calibrated using standard gases (air with 10044 ppmv and 0 ppmv $CO_2$). Calibration was carried out by drawing standard gases from 5 L Tedlar bags using the secondary low-flow pump. Performance was monitored using NOAA air standards at 372 and 420 ppmv measured on site, and from monthly bag samples sampled via the pumping system returned to RHUL for $CO_2$ and $CH_4$ abundance and $\delta^{13}C$ (reported in Mattey et al., 2013, 2016). Reproducibility of five measurements per cycle is typically better than ± 5 ppmv with overall accuracy better than 4% of reading.

## 3. Results

### *3.1. Seasonal patterns in cave air pCO₂*

An overview of the multichannel records for SM and RS caves is shown in Figure 4, compared to daily rainfall, diurnal temperature range and wind strength. The temporal and spatial variations of $pCO_2$ from twelve sites portray a complex data set which reveals seasonal cycles overprinted by rapid changes in the vertical and lateral spatial variability in the ground air-background atmosphere mixing ratio. The most striking property of the $CO_2$ record data are the net seasonal reversals in the direction of advective flow of ground air such that the high and low $pCO_2$ levels in St. Michaels and Ragged Staff are closely coupled on hour-day timescales in an antiphase relationship (Figure 5). Switching between these states is triggered by the temperature difference between the cave chambers and outside air, and four ventilation-advection (V-A) seasonal modes can be defined from the relationship between the surface diurnal temperature range and the core temperature of the rock (Figure 6). *Winter* and *summer* modes occur in the periods dominated by a diurnal range which is entirely below (winter) or above (summer) the rock core temperature of 18°C. The transitions between summer and winter regimes are marked by periods when the diurnal range straddles the core rock temperature. The duration of winter, transitional and summer ventilation modes vary from year to year but typically summer mode begins in early June and lasts until the end of October and winter mode begins from mid-November and persists until mid-May.

Figure 6 shows $CO_2$ variations in St. Michaels cave air for an annual cycle from August 2007, which can be compared to daily diurnal temperature range, rainfall, and wind strength and direction. The four V-A seasons (summer, autumn transitional, winter and spring transitional) are marked by the rise in $pCO_2$ at the start of the Autumn transitional season and its decline by the end of the Spring transitional period. Records for five sites are compared with background atmosphere and show behaviours in accordance with the conceptual model in Figure 2b, namely open ventilation (Hospital), ground air advection-dominated (Gib04, Lake and Dark Rift sites) and inflow-outflow switching (North Rift). The highest $pCO_2$ levels are found in the lowest regions of rifts in the floor of the main chambers, e.g. the Bottomless Pit. TheGib04 and Lake sites record $pCO_2$ in the middle and most distal points in the NSM main chamber and frequently reveal small lateral gradients in $pCO_2$ indicating the direction of incoming ventilation. Sensitivity to rapid changes in advective flux on hour-day timescales is greatest in the smaller cave chambers. Thus, sites in small rifts located in the advective region (Dark Rift, North Rift and Bottomless Pit) show rapid variability and also some of the highest $pCO_2$ levels when advection of ground air is incoming.

The situation in the main chambers of RS is more complex and the main chamber sites, Akapus, Rhino Chamber and Grotto show behaviour in $pCO_2$ which is not simply a function of increasing isolation from the modern entrance (near Silent Pool). The Grotto is the distal site with greatest apparent isolation from the Main Ragged Staff Chamber, yet Akapus can sometimes attain the highest $pCO_2$ levels in the Ragged Staff system. This is because there are additional hidden ventilation pathways, inferred from air flow tracing, entering the distal chambers of RS (Crystal Cave, see Mattey et al., 2016)

### *3.2. Changes in cave air $pCO_2$ related to synoptic time-scale patterns in temperature and wind*

Overprinting the seasonal cycles are rapid fluctuations in $pCO_2$ which operate on hour-day timescales. The forces causing rapid shifts in the ground air - background atmosphere mixing ratio are closely linked to local meteorological conditions. Some typical relationships between cave air $pCO_2$, daily temperature and wind strength and direction in winter and summer are compared in more detail in Figure 7.

*3.2.1. Winter mode ventilation*

Figure 7a compares the $pCO_2$ records from SM and RS spanning mid-January to mid-March 2011 and shows cave air $pCO_2$ trends under westerly and easterly (Levanter) winds (labelled L1 to L5) in a period with mostly stable winter temperatures plus a short warm excursion in mid-February. Advection-dominated sites (Bottomless Pit (shaded red), Dark Rift (shaded orange), Lake (blue) and Gib04a Site (red)) all have $pCO_2$ elevated by upwards advection while under westerly winds, but $pCO_2$ rapidly declines when Levanter winds blow from the east. During the strong Levanter L1 $pCO_2$ in the advective region declined by a factor of four (e.g. 5800 ppmv to 1340 ppmv at the Lake site) over 245 hours, a steady depletion of 17.5 ppmv/hr. The small lateral gradient in $pCO_2$ from the distal Lake site along the main chamber suggests that a source of ventilation exists near the Gib04 site. During this event the ground air-atmosphere mixing ratio elsewhere in the advection regime (Dark Rift and Bottomless Pit) depletes at a lower rate (8ppmv/hr).

Data for the lowest point in NSM (Bottomless Pit, shaded red) shows that rising winter advection entering through the rubble floor also declines when Levanter winds are blowing, suggesting that pathways mixing background atmosphere into the advecting column exist at deeper levels in the Rock.

The open-ventilation chamber of the Hospital shows an increase in $pCO_2$ overprinted by a strong diurnal cycle during Levanter events as $CO_2$ rich ground air is displaced out of the advection regime. The onset of westerly winds allows $pCO_2$ to rise rapidly at 39ppmv/hr to former elevated levels. This same pattern is repeated at L2, L3 and L5 and elsewhere in the record. An example of a warm spell of weather (late February in Figure 7a) coincides with transitions between a weak Levanter and westerlies. Initially the effect of a positive temperature anomaly on ventilation intensity is weak until westerly winds set in, at which point the $pCO_2$ falls very rapidly over 22 hr at 143 ppmv/hr. Then, as soon as the temperature anomaly becomes negative, the upwards advective regime instantly resumes, restoring $pCO_2$ at rate of 42ppmv/h.

The interplay of temperature versus wind control is further illustrated in Figure 7b over a period where winter temperatures are milder while winds transition from weak westerlies to strong winter Levanters (L1-3). Under moderate westerly winds the V-A system becomes very sensitive to temperature. Warm days with a positive temperature anomaly immediately inhibit winter advection. An example occurs on 6$^{th}$ Jan 2008 when $pCO_2$ dramatically falls from 5500 ppmv to <1500 ppmv in the North Rift as a temporary summer mode V-A event strengthens ventilation. $pCO_2$ in the main chamber responds more slowly. Restoration of a normal winter temperature anomaly immediately returns the V-A system to winter mode and $pCO_2$ levels rise as background atmosphere is flushed out by upward advection of ground air. Higher temperature sensitivity is maintained while westerlies prevail and periods of easterly winds only override temperature-sensitivity when wind speeds exceed 10m/s under stable colder temperatures. For example, the strong Levanter L3 promotes steady ventilation of the whole NSM system as discussed above, resulting in lowering of $pCO_2$ in chambers within the advective-dominated regime followed by declining $pCO_2$ in the Dark Rift.

Elevated $pCO_2$ in the Hospital area, modulated by strong diurnal cycles, suggests that ground air is being displaced into the open ventilation regime as outflow. This period of increased ventilation diluting the ground air $CO_2$ reservoir begins to decline when the Levanter wind speeds fall to <10ms and resumption of westerly winds allow cave $pCO_2$ return to former levels as the ground air-atmosphere mixing ratio begins to rise. A brief strong Levanter L4 temporarily strengthens ventilation but as it weakens $pCO_2$ begins to rise again.

The $pCO_2$ data for all Ragged Staff monitoring sites are close to background levels with weak evidence for brief spiked increases in $pCO_2$ towards the termination of Levanter events. The late February warm anomaly has no impact on the RS $pCO_2$ record (Fig. 7a).

### *3.2.2. Summer mode ventilation*

In summer mode the ground air flow is downwards, drawing external atmosphere into SM and raising $pCO_2$ in RS. Figure 7 (c,d) shows the $pCO_2$ records from SM and RS for periods between June and August, records which compare the impact of short duration westerly and Levanter winds under normal stable summer temperatures in 2011 (Figure 7c) with more unsettled conditions and a cool anomaly in 2010 (Figure 7d). Cave air $pCO_2$ in SM is typically less than 1000 ppmv and $pCO_2$ fluctuations in chambers within the advective regime all track each other closely. Summer mode $pCO_2$ levels are at their highest in the RS system with maximum values around 2000 ppmv measured in Akapus (orange shaded). Elsewhere $pCO_2$ values in Rhino Chamber (purple) and Crystal Cave (the most distal region of the system, blue) tend to be slightly lower. All sites in the advection-dominated regions of SM and RS are sensitive to negative temperature anomalies which quickly restore winter mode advection with elevated $pCO_2$ in SM and increased ventilation in RS (Figure 7d).

Wind speeds tend to be lower in summer and while the impact of wind direction is evident in RS, wind effects are more muted in SM. In RS, Levanter winds have the effect of lowering $pCO_2$ in the advective region and raising $pCO_2$ in the Hobbit Hole. The former suggests dilution of the ground air flux into the interior parts of RS, whereas the small rise at the Hobbit Hole is likely to be due to relatively CO2-rich air being displaced from the cave interior into the open-ventilated region of the RS tunnels (analogous to the rise in $pCO_2$ in the Hospital in SM under Levanter conditions in winter). In the SM system, summer Levanter events sometimes produce slightly elevated $pCO_2$ levels but these fluctuations are small compared with those due to other causes.

If examined at an hourly timescale over several days, parts of the records in summer show diurnal modulations of the prevailing $pCO_2$ in both caves. This appears to be related to a combination of diurnal temperature fluctuations and the small amplitude diurnal fluctuation of atmospheric pressure produced by atmospheric tides. Fuller details are provided in the Supplementary Information.

## 4. Discussion

Our main purpose in monitoring the behaviour of $CO_2$ in cave air is to provide insight into the climatic signals recorded by $\delta^{13}C$ in calcite speleothem records. The climatic significance of variation in carbon isotopes has been widely discussed in the literature but the full potential of this proxy may be underexploited because of ambiguity in identifying the climatic signals within a web of processes linked to deposition of carbonate in cave environments (for examples see discussions in Baldini et al. (2005), Fohlmeister et al. (2020), Genty et al. (2003), McDermott (2004), Meyer et al. (2014), and Peyraube et al. (2012)). The $\delta^{13}C$ of speleothem calcite deposited at any given moment is determined by three factors in the immediate environment within the cave. The first two are the $pCO_2$ and the $\delta^{13}C$ of the DIC in parent drip water as it enters the cave. The third is the $pCO_2$ of the cave air. The difference between the two $pCO_2$ values causes degassing of $CO_2$ into the cave air from the film of water on the stalagmite, progressively raising the $\delta^{13}C$ of the DIC and thereby influencing the $\delta^{13}C$ of precipitated calcite. The $pCO_2$ of cave air is a critical factor in this process and in the following sections we highlight results of this study that link local cave air $pCO_2$ to local seasonality and weather.

Extrapolating modern environments back over time requires caution as the present may not always be the key to the past in evolving karstic systems. Solution and precipitation of carbonate may enlarge or seal conduits over time, altering groundwater flow paths; cave entrances may open or be sealed by mass movement and changes in sea level over glacial-interglacial cycles will alter the position of the water table and depth of the unsaturated zone. In recent times there have also been significant changes in the configuration of entrances to the cave systems in Gibraltar. Many Gibraltar caves are now entered through man-made entrances which have altered ventilation patterns from their natural state. The picture is further complicated by the presence of other man-made tunnels which are not necessarily connected to caves but provide additional ventilation pathways that have probably altered flow lines in the advective system (Mattey et al., 2016). Nevertheless, the imprint of seasonality on modern speleothem in the form of fabric-correlated cycles in both stable isotopes and trace elements (Mattey et al, 2008)) also occurs in speleothem that grew through the Holocene and at intervals as far back as 500ka before present. This is evidence that seasonal advection permeated the Rock in its natural state prior to the historic era in a manner broadly similar to the present time. We suggest that pervasive ventilation through the 'pre-tunnels' Rock would have followed approximately the modelled airflow streamlines shown in Figure 2a. In modern times the low-level Ragged Staff caves are likely to have become strongly ventilated by the access tunnel and proximity to the major E-W and N-S tunnels penetrating the core of the Rock. In the past the Silent Pool, Akapus and Rhino chambers would have experienced a much lower ventilation flux, limited by the natural permeability of the Rock, with a seasonal ventilation regime similar to that of NSM but reversed in phase.

### 4.1. Cave air $pCO_2$, ventilation, and effects of past climate change

#### 4.1.1. Seasonal temperature

The interannual record of cave air $pCO_2$ shown in Figure 4 represents a regular succession of alternating high and low $pCO_2$ seasons, overprinted by variations at higher frequencies (hour-day). As discussed in section 3 these annual cycles of seasonally reversing advective flow are a first order response of the cave ventilation to the range in seasonal temperature.

Over multidecadal timescales the average seasonal cycle of summer and winter temperatures under the present climate is symmetrically distributed either side of the subsurface temperature of the Rock. A climatic cooling or warming episode would temporarily disturb the symmetry of temperature seasonality relative to the core temperature of the rock, such that the duration of the high and low $pCO_2$ periods become unequal. An abrupt climate change, for example a uniform drop in temperature across all seasons, would lengthen the duration of 'winter' ventilation and reduce that of the 'summer' ventilation. This would be a universal effect arising from the interaction of cave systems, the permeability of the rock around them, the enclosing topography and seasonal variations in temperature. In Gibraltar the effects are particularly clear because of the steep topography and the presence of cave systems at high and low positions in the rock. Here, as noted in section 3, Figure 5, and in Mattey et al. (2016) the seasonal ventilation and $CO_2$ patterns are in antiphase relationships in the two caves. Thus, under an abrupt climatic cooling we would expect the cave air $pCO_2$ averaged over a whole year to be reduced in NSM and increased in RS. This would be an immediate response to abrupt climate change but would gradually relax towards a restoration of symmetrical seasonality, because the core temperature of the rock would gradually adjust to the new climate. We leave aside the question of whether the dominant mechanism for this temperature adjustment would be achieved by advective heat transport by air flow or conductive transport through the mass of the rock, but in either case, the adjustment period is likely to last many decades or longer (Domínguez-Villar et al., 2013; Luetscher and Jeannin, 2004).

*4.1.2. Wind regimes*

Within the NSM system, while westerly winds do not have a significant impact on the dynamics of V-A, strong Levanter winds (>10ms$^{-1}$) systematically lower cave air $pCO_2$ at rate of 10-15 ppmv per hour. A critical observation is that declining $pCO_2$ is also recorded in the *upward* advective flux entering the Bottomless Pit and Dark Rift, implying that some ventilation pathways lie *below* the NSM system and feed into the upward flowing advective column. While accepting caveats related to the impact of man-made tunnels (see above) the secondary impact of wind direction and strength on cave air $pCO_2$ is potentially of climatic interest.

The nature of airflow across topographic relief and the effects of hills and ridges on wind speed and the atmospheric pressure field are well studied (e.g. Gallagher et al., 1988; Safaei Pirooz and Flay, 2018). Observation, numerical modelling and wind tunnel experiments show that as air flow approaches hills the wind speed increases as it rises towards the crest. Depending on the shape of the hill and atmospheric conditions, stream lines within the atmospheric boundary layer may remain attached to the lee slope, or flow separation may occur, creating down-wind turbulence (Safaei Pirooz and Flay, 2018). Bernoulli's Law requires that surface pressure will decrease with wind speed-up, creating a local field of lower pressure near the summit with fields of higher pressure at the base of the hill, both up- and down- wind. If downwind flow separation occurs then the low-pressure field will extend further down the lee slope. Thus, airflow across hills permeated by interconnected caves may stimulate ventilation driven by a pressure differential between connected cave entrances. A wind induced differential may arise where connected entrances experience different wind speed-up or are located on opposite sides of the hill with respect to airflow.

The isolated steep sided promontory of Gibraltar is exposed to winds which are mostly normal to the ridge axis. The notoriously turbulent wind conditions in the vicinity of the Rock have been closely studied with regard to air-traffic safety (Cook et al., 1978). Wind tunnel tests on scale models and aircraft observations provide a detailed picture of air flow characteristics across the rock and show that the N-S trending wedge with asymmetric slope profiles behaves very similarly to a lifting body. Air flow from the west or east becomes detached on the lee side creating a turbulent wake. The asymmetric profile of the Rock may explain why easterly winds have a greater effect on the $pCO_2$ of the V-A system. Monitoring of the vertical component of air flow by aircraft on the approach and take-off flight paths shows that turbulence created by westerly winds extends east of the Rock over the sea for 1-2 km, but under easterly Levanter conditions the field of turbulence is greatest on the westerly slope in the vicinity of entrances to the SM and RS cave systems (Cook et al., 1978, their Figure 11b). Winds from the SW sector remain attached to the lee of the rock profile, creating a powerful horizontal roll vortex with negative pressure on the east slopes of the rock. Although not frequent, these conditions have caused structural damage to the corrugated iron canopies (since dismantled) that were built as water catchments over the Quaternary sand dunes, indicating pressure differentials as large as 4 mbar (Cook et al., 1978).

Might the association between declining $pCO_2$ and Levanter winds be potentially significant as a control on nett degassing (subject to whether the effect is fully natural or partly due to the presence of man-made tunnels)? Studies of the climatological incidence of Levanter winds have been limited because of the scarcity of long wind records at daily resolution but recent compilations of historical records from sailing ships have enabled a climatological analysis extending back into the 19$^{th}$ century (Hidalgo and Gallego, 2019). The effect of Levanter episodes on cave air $pCO_2$ in the NSM system occurs only in winter. The winter Levanter frequency of 40% in our monitoring period (2006-2012) is identical with the 1849-2014 average. The $pCO_2$ in NSM on winter Levanter days averages 4474 ppmv while that on days with SW and W winds averages 4939 ppmv. The relatively small difference of less than 10% in these average values implies that even very large increases in the frequency of winter Levanter days would decrease average $pCO_2$ in winter by only a few percent from its current value. Even if major changes in wind fields arose from climatic change in the past, their influence on average cave air $pCO_2$ would have been minor. Short-term Levanter events like those in the monitoring data would not be observable unless speleothem records had time resolution of ~10 days or better.

Kowalczk and Froelich (2010) demonstrate the role of wind in reducing $CO_2$ and radon concentrations in Hollow Ridge Cave, Florida. As in Gibraltar, wind effects are small compared with the large seasonal $CO_2$ fluctuations produced by density-driven ventilation and have little effect on the annual average $CO_2$ concentration.

### *4.2. Cave air pCO2 and ground air as factors affecting the $\delta^{13}C$ of speleothem calcite across major climatic changes*

We now consider the role of cave air $pCO_2$ as well as other factors in affecting the $\delta^{13}C$ of speleothem calcite across climate change. In essence, when considering change over centennial-millennial timescales the final $\delta^{13}C$ value preserved in speleothem can be reduced to 1) the amount of degassing at the site of calcite deposition and 2) the primary $\delta^{13}C$ of bicarbonate in un-degassed drip water (Dreybrodt, 2008; Mühlinghaus et al., 2009). The amount of degassing is the product of degassing rate (controlled initially by the difference between cave air $pCO_2$ and solution $pCO_2$ but declining thereafter) and degassing time (controlled by drip interval). Hansen et al. (2013) demonstrate experimentally that the initial degassing of dissolved $CO_{2(aq)}$ occurs at a high rate and takes only a few seconds, followed by a period of up to several minutes in which degassing continues at a slower, declining rate while $HCO_3^-$ is converted to $CO_{2(aq)}$ and the pH rises. This stage produces supersaturation with respect to calcite and lasts until the solution is close to equilibrium with the $pCO_2$ of the cave atmosphere. At some point towards the end of this stage a sufficient degree of supersaturation is reached for calcite precipitation to begin, slightly lowering the pH and allowing conversion of one molecule of $HCO_3^-$ to $CO_{2(aq)}$ for every molecule of $CaCO_3$ precipitated. This prolongs the loss of $CO_2$ to the cave atmosphere, but at an even slower rate that is controlled by the rate of calcite deposition and may last for hours. This third and final stage continues until the solution reaches equilibrium with both the gas and mineral phases. At every stage in this process, carbon isotopes in the DIC are fractionated by degassing towards higher values of $\delta^{13}C$. The $\delta^{13}C$ of a sample of speleothem drilled for analysis is a time-averaged value that depends on the stages reached at the sample position by the overall degassing process as drip rate, cave air $pCO_2$ and calcite deposition rate all vary through time. It is also averaged over the calcite precipitated during the overall time interval that the sample represents.

In NSM, stalagmite Gib04a is fed by a slow drip rate of ca. 0.05 $L.d^{-1}$ with little seasonal variation, allowing a long enough interval for extensive degassing while the large seasonal shifts in $pCO_2$ of cave air create a 2-2.5 ‰ annual range in $\delta^{13}C$ of modern calcite (Mattey et al., 2008). Elsewhere in the same chamber, modern flowstone deposited under much greater discharge rates of up to 80 $L.d^{-1}$ has similar $\delta^{13}C$ to the low values of winter season calcite in Gib04a (Mattey et al., 2010). This implies that the restriction of degassing time produced by high flow rate onto the flowstone has a similar effect to the inhibition of degassing rate caused by high $pCO_2$ in winter cave air during the long drip intervals on stalagmite Gib04a.

We observe that temporal variations in $\delta^{13}C$ of speleothems across major climate transitions are often larger than the range produced by seasonal $pCO_2$ variations in Gibraltar. For example, published $\delta^{13}C$ records from West Mediterranean and Iberian speleothems show that shifts of up to

6‰ occur across climate transitions during the Holocene and Pleistocene (Budsky et al., 2019; Drysdale et al., 2004; Moreno et al., 2010, 2014; Regattieri et al., 2014; Rudzka et al., 2011). Similar ranges are seen in Pleistocene speleothem in Gibraltar (Boyd et al., 2019) and our cave monitoring suggests that it is difficult to explain this in terms of any likely change in the local degassing regime under present climatic and environmental conditions.

Other possible explanations may exist. The $\delta^{13}C$ of calcite also depends on the initial $\delta^{13}C$ of DIC in un-degassed drip water which itself reflects the mix of isotopically distinct carbon sources that have contributed to it. Conventionally, the range of $\delta^{13}C$ in DIC has been explained by alternative models of dissolution of $CaCO_3$ under conditions that are either open or closed with respect to a reservoir of gaseous $CO_2$ that dissolves to form carbonic acid (Clark and Fritz, 1997; Ford and Williams, 2007). Fohlmeister et al. (2011) expanded this model by considering intermediate cases in which a portion of the dissolution takes place under open system conditions and is followed by closed system dissolution until saturation is reached. They show that a range of ca.7‰ in the $\delta^{13}C$ of the DIC in a saturated solution of calcite can be achieved by altering the ratio of open-to-closed dissolution and varying the $pCO_2$ of the gas reservoir from 0.001 to 0.25 atm. The modelled $\delta^{13}C$ values decrease as $pCO_2$ values of the gas reservoir are increased. Given that in general $pCO_2$ of soil gas can be expected to be higher during periods of warm humid climate, the Fohlmeister model successfully predicts that $\delta^{13}C$ of speleothem calcite should rise during warm-to-cold transitions. The magnitude of this effect depends on the sensitivity of the soil gas $pCO_2$ to climate change and is greatest for large closed-to-open ratios. With the soil gas as its only source of $CO_2$, this model cannot account for the observation that in some cases the $pCO_2$ of drip water is higher than that of soil gas (Atkinson, 1977; Bergel et al., 2017; Mattey et al., 2010, 2016).

Mattey et al. (2016) present a different model whereby respired $CO_2$ in the soil contributes to an initial solution which passes deeper into the vadose zone, accompanied by organic matter (OM) which is oxidised within the enclosed spaces of the fracture porosity in the bedrock to create additional $CO_2$ and DIC. The increase in acidity dissolves more bedrock and the $\delta^{13}C$ of vadose water reflects a mix of carbon from bedrock, oxidised organic matter and respired $CO_2$ from the soil zone. The by-product of this process is a high $pCO_2$ in ground air that has equilibrated chemically and isotopically with vadose water. Mattey et al. (2016) show that the $\delta^{13}C$ values of vadose groundwater could vary by up to 5 ‰ as a function of additional OM, with lower values corresponding to greater additions of OM. The $pCO_2$ of both the vadose water and the ground air will reflect the amount of OM oxidised and this may be limited by the supply of OM from the surface (linked to vegetation productivity and soil organic matter content) or by transport in infiltrating water (recharge and water balance), both of which are related to regional climate. In this context it may be noted that the Fohlmeister models can be regarded as special cases of the ‘Gibraltar model’ (Mattey et al., 2016) in which the down-washed flux of OM is zero.

The role of OM in transporting trace metals through the vadose zone and into speleothems is well recognised (e.g. Hartland et al., 2011; Hartland and Zitoun, 2018) but its role as a key reservoir in the karst carbon cycle is often overlooked as a factor contributing to $\delta^{13}C$ variance in speleothem. A better understating of this may assist paleoclimate reconstructions from speleothem proxies in the future.

*4.2.1. The ground air component of cave atmospheres*

Cave atmospheres are a mixture of ground air and external air but the high $pCO_2$ of ground air has been comparatively little studied. Benavente et al. (2010) and Mattey et al. (2016) both present direct measurements made in boreholes, but in most cases the high $pCO_2$ of the vadose gas phase has been inferred indirectly from the fact that drip water $pCO_2$ exceeds that of soil air (e.g. Atkinson, 1977; Breecker et al., 2012; Faimon et al., 2012a; Gulley et al., 2014; Mattey et al., 2010; McDonough et al., 2016; Meyer et al., 2014; Noronha et al., 2015; Peyraube et al., 2013; Treble et al., 2015; Wood and Petraitis, 1984).

By direct measurement of air and $CO_2$ fluxes in several caves, Bourges et al. (2001, 2020) show that ground air with high $pCO_2$ enters through cracks and fissures in cave walls and is exported through cave entrances, observations that are confirmed by the present study of New St. Michael's Cave. The $pCO_2$ of ground air is largely a by-product of the oxidation of OM in vadose water followed by equilibration with vadose gas in enclosed fractures and fissures where the water-to-gas volume ratio is in the order of unity. This is a quite different setting from the equilibration of soil moisture with respired soil $CO_2$ envisaged in the Fohlmeister models, in which the gas 'reservoir' is regarded as effectively very large compared with the volume of water. The $pCO_2$ produced in ground air will depend on the $pCO_2$ of the vadose water but also on the gas-to-water ratio, with a tendency towards higher values when the ratio is reduced by influx of recharge water. It is also possible that $CO_2$ is added directly to the gas phase by decomposition of particulate organic matter or of slimes that have accumulated as coatings on fracture walls. Furthermore, seasonal and diurnal density changes in external air may cause ground air to flow at varying speeds and directions while dissolved OM is oxidised and the $pCO_2$ of the vadose water rises while the water flows downwards. All these effects are likely to make $pCO_2$ a very dynamic property of ground air, with spatial and temporal variations within the vadose zone.

The highest $pCO_2$ values observed in cave air provide a qualitative lower bound for the $CO_2$ content of ground air, but without direct measurements it is not possible to determine its true $pCO_2$ values. However, it *is* possible to deduce the $\delta^{13}C$ of ground air $CO_2$ from the $\delta^{13}C$ in cave air and external air represented on a Keeling plot of $\delta^{13}C$ vs 1/($CO_2$ concentration). A compilation of published $\delta^{13}C$ values for $CO_2$ in cave air is shown on Figure 8. Each point represents a mixture of external air with an additional source of $CO_2$ whose $\delta^{13}C$ must lie on an extrapolated straight line drawn from atmospheric air through the data point in question. The intersection with the x-axis gives the $\delta^{13}C$ of the additional $CO_2$, i.e. the $CO_2$ in ground air. A similar plot was produced by Mattey et al. (2016, their Figure 9) and the Gibraltar data from that is reproduced here, but with data from seven other cave studies added for comparison.

In soils dominated by C3 vegetation the $\delta^{13}C$ of the 'respired flux' of soil $CO_2$ should be -25 to -27.5 ‰ (Cerling et al., 1991; Davidson, 1995; Meyer et al., 2014). Isotopic analysis of gas sampled from shallow soil shows that $CO_2$ occupying pore space is a mixture of kinetically fractionated respired $CO_2$ and background atmosphere (Breecker et al., 2012; Camarda et al., 2007; Cerling et al., 1991; Mattey et al., 2016; Meyer et al., 2014) and converges towards that of the respired value with increasing depth (Cherkinsky et al., 2018). It is evident from Figure 8 that relatively few data strictly conform to the line defining mixing between atmosphere and soil respired $CO_2$. The data for Grotta di Ernesto and Obir Cave scatter around this line, but only for $CO_2$ concentrations that are less than twice that of background atmosphere. Almost all points representing higher concentrations of $CO_2$ plot to the right of the line, regardless of the site. The $\delta^{13}C$ values of ground air $CO_2$ are given by the intercepts on the x-axis of lines (not shown on Fig.8) joining each data point to atmosphere, and extrapolated down to the x-axis. The shaded triangle highlights the range from the Gibraltar caves, where the inferred $\delta^{13}C$ values for the ground air $CO_2$ source lie between -19 and -24 ‰ (see also Figure 9 in Mattey et al., 2016). Among the other six sites, the $CO_2$ concentrations that are greater than twice atmospheric at Grotta di Ernesto indicate ground air $\delta^{13}C$ values from -24 to -26 ‰. Elsewhere, the inferred ground air $\delta^{13}C$ ranges up to -18‰ with an extreme value of -16 ‰. Only at Obir Cave do the twice-atmospheric and higher $CO_2$ data suggest that respired $CO_2$ from the soil might be the sole source of $CO_2$ in the ground air. For all other sites, the additional $CO_2$ that has been mixed with atmosphere to form cave air contains an isotopically heavier component than respired $CO_2$. In locations where C4 plants may be present (such as the two Texas caves with data in Figure 8) their respired $CO_2$ might provide such a component, but for the six European sites (including Gibraltar) without C4 vegetation the only likely source is carbon derived from the dissolved bedrock with $\delta^{13}C$ ~0 ‰. This carbon has reached the ground air via equilibration with the DIC in the vadose water, which is itself composed of bedrock carbon mixed with carbon derived from soil respiration *plus* carbon oxidised from organic matter in the vadose zone.

Since the $pCO_2$ of ground air is controlled by the $pCO_2$ of vadose water, the range of inferred $\delta^{13}C$ values at each site indicates the dynamic variability of ground air values that are likely to occur under the present climate. The range in $\delta^{13}C$ of the ground air end-member for each cave can be used to derive the range of $\delta^{13}C$ in the initial DIC of drip waters in that cave, because the ground air and the vadose waters are likely to be in isotopic equilibrium. This conversion is illustrated for Gibraltar by the arcuate lines just above the x-axis labelled 'Ground air $CO_2$' and 'Groundwater $HCO_3$'. At 18$^o$C the $\delta^{13}C$ of $HCO_3$ will be 8.7 ‰ higher than the value for gaseous $CO_2$ (Clark and Fritz, 1997, Table 5-3), so the range of ground air values from -19 to -24 ‰ implies $\delta^{13}C$ values in the $HCO_3$ of vadose waters between -12.5 and -18 ‰. Similar conversions could be made for the other cave sites, using local cave temperatures for the fractionation between gaseous $CO_2$ and $HCO_3$. However, it is clear that a wide range of carbon isotope ratios can arise under present conditions, both in a single cave and between widely separated sites. This must reflect the dynamic nature of the carbon cycling in the vadose zone at each site, due to seasonal changes in ground air circulation and the rate of importation of organic matter to the vadose zone by infiltrating waters. Because speleothem deposition is a relatively slow process, much of this dynamic variation will be averaged out in the bulk composition of the calcite deposited at individual drip sites, although the fractionation of carbon isotopes caused by degassing may introduce new seasonal variations in addition to those already present in the un-degassed drip water.

*4.2.2. Climatic significance of $\delta^{13}C$ records in speleothem*

Sampling for isotopic analysis of calcite in stalagmites and flowstones only occasionally has sub-annual resolution, and most speleothem measurements record multi-annual averages for the values of $\delta^{13}C$. Changes in these averages should therefore be interpreted in terms of the factors that affect the $\delta^{13}C$ of the DIC in vadose waters, with the $\delta^{13}C$ of ground air $CO_2$ being a reflection of those factors rather than a control.

To illustrate the ambiguity which besets the interpretation of $\delta^{13}C$ in speleothem records, consider a scenario in which climate abruptly becomes colder and drier, i.e. less rainfall. Colder and/or drier climatic conditions may inhibit OM downwash either through reduced productivity of vegetation or by reducing the amount of recharge, resulting in less OM being leached from soil (e.g. Liao et al., 2018). With less OM in the vadose zone available for oxidation, the initial $\delta^{13}C$ of vadose water entering cave spaces will tend to be higher and its $pCO_2$ lower (see Mattey et al., 2016, Figure 11). This may have two effects on $\delta^{13}C$ in calcite. On one hand, higher $\delta^{13}C$ in the initial DIC will raise $\delta^{13}C$ in calcite, because this is the starting condition for degassing and calcite precipitation. On the other hand, less OM oxidation will cause lower $pCO_2$ in ground air and therefore also in cave air. The nett effect will be to reduce the force that drives degassing of $CO_2$ from the drip water, i.e. the difference between the initial $pCO_2$ of the drip as it enters the cave and the cave air $pCO_2$. This will slow the rate of degassing and *if the drip interval does not change* the fractionation of carbon isotopes caused by degassing will be reduced. Nevertheless, the value of $\delta^{13}C$ in calcite will rise as a result of the change in climate and its effect in reducing OM leaching. Complications arise if the average drip rate changes. Colder temperatures at the surface will reduce evapotranspiration, and if this shift is greater than the reduction in rainfall, nett recharge may increase, possibly offsetting the reduction in OM flux into the vadose zone induced by colder temperatures (e.g. Liao et al., 2018). An increase in recharge would reduce average drip interval and lessen the fractionation caused by degassing. A different scenario arises if the reduction in rainfall is greater than the reduction in evapotranspiration. In that case the surface water balance becomes less positive, recharge is reduced and drip intervals become longer, causing greater degassing and leading to higher $\delta^{13}C$ values in calcite. From this analysis it is clear that a reduction in OM supply to the vadose zone is likely to produce higher $\delta^{13}C$ in calcite, but that the magnitude of the shift will depend on the combined effect of temperature change on OM production with the effect of changes in the surface water balance (rainfall versus evapotranspiration) on OM leaching and transport, recharge and average drip rate. Further complications may arise from changes in the seasonal ventilation regime of the cave and its effects on cave air $pCO_2$, and on the phasing of seasonal changes in drip rates relative to the seasons of high or low cave air $pCO_2$. These may alter the effects of degassing on $\delta^{13}C$ in calcite but are unlikely to change the direction of its upward shift in response to reduced OM influx to the vadose zone.

Greater ambiguity arises in a scenario in which climate changes from cold to warm, with a resulting increase in OM availability for transport into the vadose zone. This will increase DIC and $pCO_2$ of vadose waters and ground air, and reduce initial $\delta^{13}C$ in drip waters. The reduction is likely to be offset to an unknown extent by the effect of degassing in raising $\delta^{13}C$ in calcite. If drip intervals are reduced because of a more positive water balance (i.e. increased rainfall outweighs increased evapotranspiration), then the effects of degassing will be less than before the climate change, and a nett negative shift of $\delta^{13}C$ in calcite will mark the change. But if the water balance becomes markedly drier and drip intervals increase, the effects of degassing will increase and may outweigh the reduction in initial $\delta^{13}C$ of DIC, so that $\delta^{13}C$ in calcite might actually increase following a shift to a warmer but drier climate.

*4.2.3. Concluding remarks*

To develop greater understanding of the climatic significance of $\delta^{13}C$ in speleothem calcite, it will be necessary in future to study the climatic and vegetation factors controlling the addition of OM and DIC to infiltrating waters within the epikarst and the deeper vadose zone. There are relatively few published measurements of dissolved organic matter in vadose waters, although it is known from fluorescence studies that there are seasonal and inter-annual variations in dissolved organic matter (DOM), and in the resulting fluorescence banding of fast-growing speleothem calcites (Baker and Genty, 1999; Baker et al., 1997, 1999a,b; van Beynen et al., 2000; McGarry and

Baker, 2000; Orland et al., 2012). Cave monitoring of DOM alongside inorganic carbonate chemistry in drip waters at sites distributed across climatic zones would do much to elucidate the dynamics of DOM transport and decay, as well as the production of 'added' $CO_2$ and DIC in vadose waters. By coupling such studies with monitoring of the $pCO_2$ and $\delta^{13}C$ of cave air, the controls on $\delta^{13}C$ of ground air and un-degassed vadose waters might be deduced. Only through such a future research effort are we likely to understand properly the climatic significance of the many detailed records of $\delta^{13}C$ that are being produced in well-dated speleothem calcites.

## 5. Conclusions

- The relationships between ventilation - ground air advection dynamics and local meteorology described in this study are examples of universal effects arising from the interaction of cave systems, the permeability of the rock around them, the enclosing topography and seasonal variations in temperature. The steep topography of Gibraltar karst, conducive to strong reversing seasonal advection and sensitivity to the effects of wind, highlight some of the meteorological controls on cave air $pCO_2$ which may operate elsewhere in more muted form.
- Cave atmospheres are primarily a two-component mixture of $CO_2$-rich ground air and background atmosphere introduced by ventilation. Ground air contains $CO_2$ respired from the soil zone with additional $CO_2$ derived from the oxidation of organic matter down-washed into the fracture network of the vadose zone. The

$pCO_2$ of ground air is therefore often greater than that of the soil zone and possesses a $\delta^{13}C$ shifted to values higher than normally measured in soil-respired $CO_2$.

- Fluctuations in cave air $pCO_2$ can reflect changes in the atmosphere-ground air mixing ratio or in the $pCO_2$ of ground air itself. This study details how ventilation-advection regimes respond to temperature and wind conditions and highlights the temperature sensitivity of the mixing ratio to both diurnal and seasonal temperature ranges.
- The variation in $\delta^{13}C$ values preserved in speleothem calcite is linked to cave air $pCO_2$ through the influence of the latter on the extent of degassing. Our data suggest that while both climatic cooling and warming and a change in wind regime could all potentially alter the extent of degassing, the likely variance in speleothem $\delta^{13}C$ will be similar to the range induced by the seasonally reversing ventilation-advection recorded in the modern environment (ca. 2-3 ‰ in Gibraltar).
- We argue that the larger shifts in $\delta^{13}C$ of up to 6 ‰ that have been observed in speleothems across major climate transitions may be due to changes in the initial $\delta^{13}C$ of drip water. The chemical and carbon isotopic composition of vadose waters is related to the quantity of $CO_2$ oxidised from down-washed organic matter that is available for oxidation, with the mineralised carbon being added to the Dissolved Inorganic Carbon. The $pCO_2$ and $\delta^{13}C$ of ground air are by-products of this oxidation through

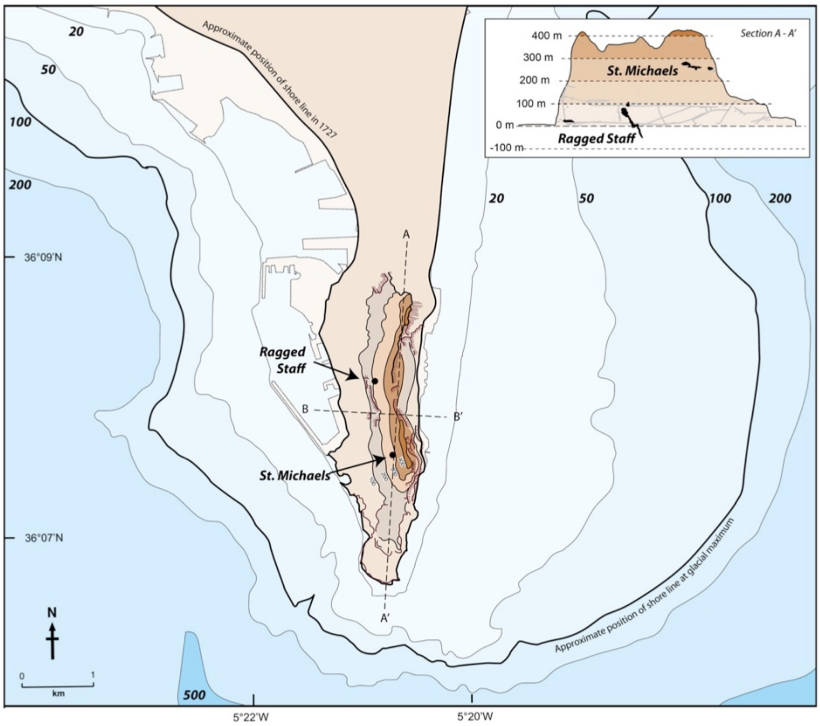
chemical and isotopic equilibration with the vadose water. The survey of cave air $CO_2$ and $\delta^{13}C$ in Figure 8 illustrates the variability of these properties and by implication the variability of initial $\delta^{13}C$ in vadose waters as they enter a cave and start to degas $CO_2$. Greater knowledge of the hydrological and vegetation factors controlling the addition of OM and DIC to infiltrating waters are needed for a better understanding of the climatic significance of $\delta^{13}C$ in speleothem calcite.

## 6. Acknowledgements

This work was supported by UK Natural Environment Research Council grants NE/G010463/1 and NE/M012689/1. We are indebted to Rebecca Fisher and Dave Lowry for calibration standards for the $CO_2$ logging systems, and colleagues, students and friends for assistance along the way. Special thanks to Hon. Prof. John Cortes and the Council of the Gibraltar Ornithological and Natural History Society for their support. Dana Riechelmann and two anonymous referees helped to improve the paper.

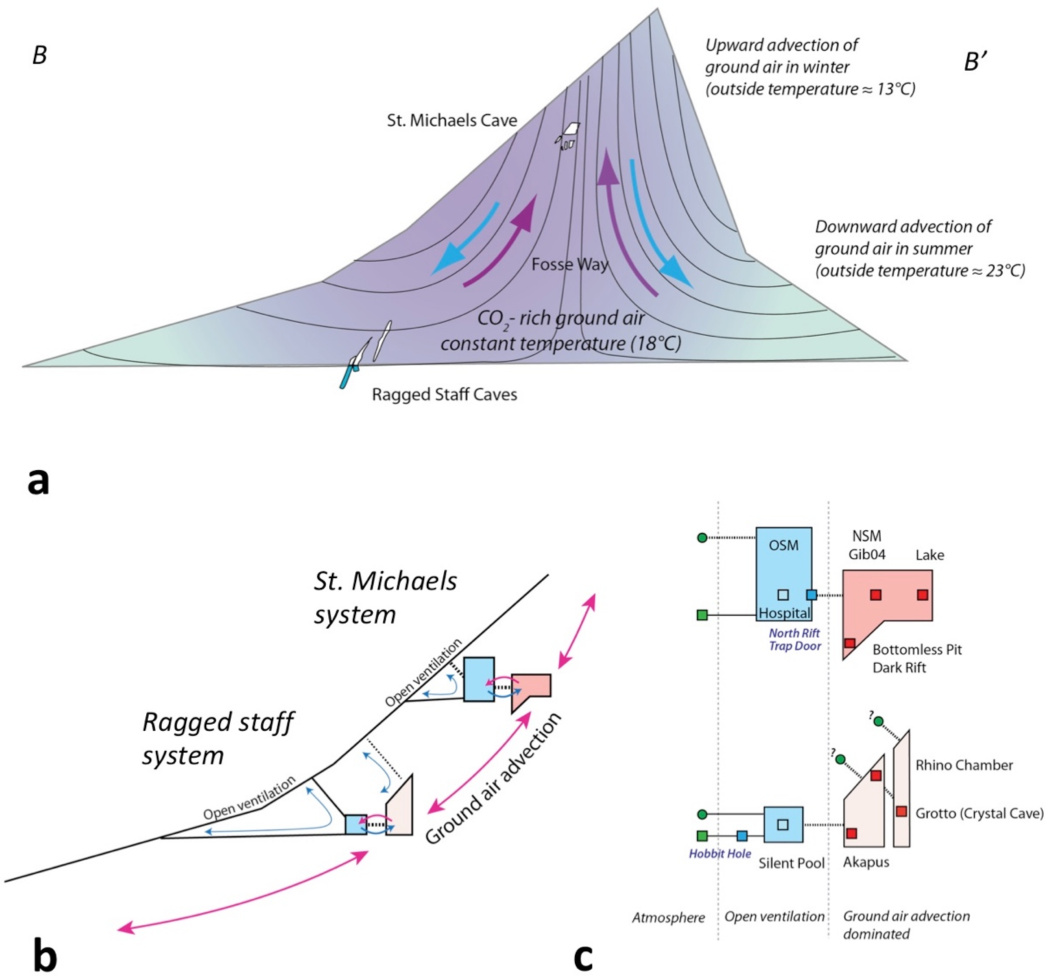
## Figures

Figure 1. The physiography of Gibraltar showing the locations of St. Michael's and Ragged Staff Caves. The plan compares the position of coastlines prior to development of the modern town and during the last glacial maximum, assumed to be near the 100 m bathymetric contour. Relative positions of major caves and man-made tunnels are also shown on the cross section (adapted from the Gibraltar 1:5000 Tunnels Survey Map, Series 984-TUN, Sheet: Gibraltar, Edition 2-GSGS, published by the DGIA, MOD, London, 2003. © UK MOD Crown Copyright 2011 and reproduced with the permission of the Controller of Her Majesty's Stationery Office)



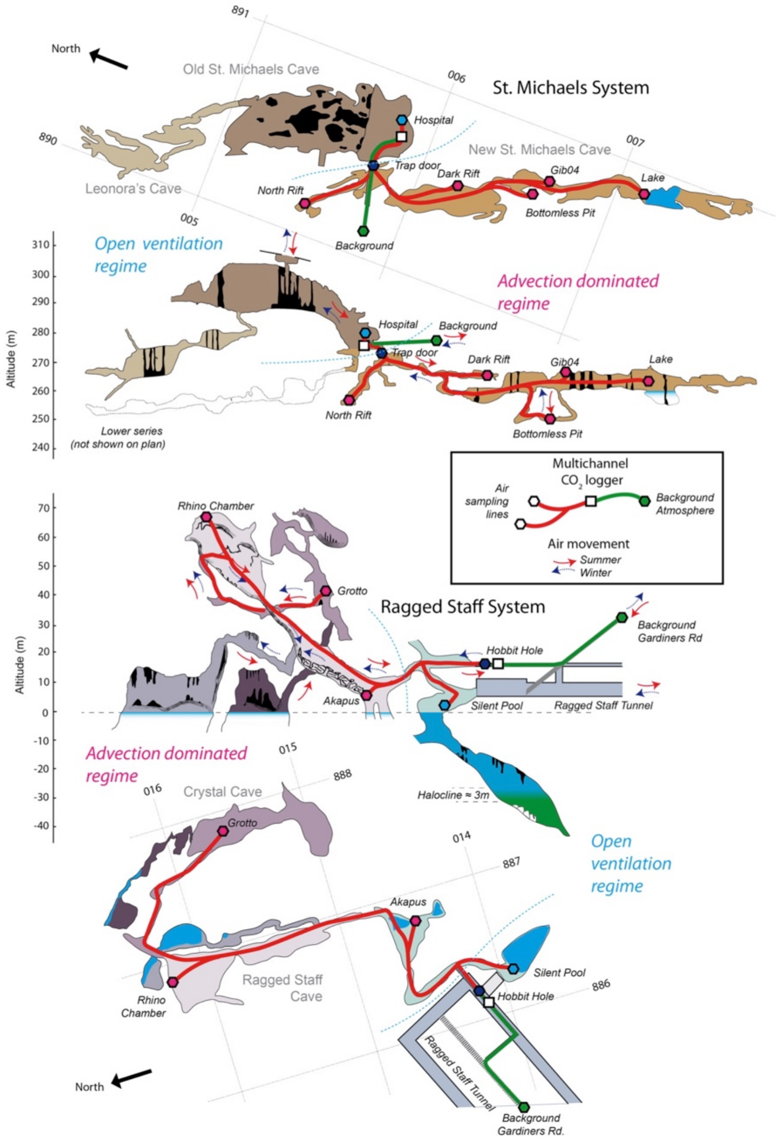

Mattey et al Figure 1

Figure 2. (a) Two-dimensional model of air circulation within the Rock of Gibraltar (from Mattey et al., 2016) showing the positions of St. Michael's and Ragged Staff caves projected onto a simplified cross section (e.g. B – B' on Figure 1) with computed stream lines for advection of ground air in the absence of man-made tunnels. For further discussion, see text. (b) Schematic representations of the St. Michael's and Ragged Staff cave systems portraying regions connected by entrances to external atmosphere and subject to open ventilation (blue), and regions which are more isolated from the effects of open ventilation and sensitive to advection of ground air (pink). (c) Enlargement of the schematic representation showing positions of sampling sites with respect to entrances and zones of open ventilation and advection dominated airflow regimes in (b). See text for discussion.




Mattey et al Figure 2

Figure 3. Plan and elevation views of the St. Michael's and Ragged Staff Cave systems showing layout of cave air sampling networks and directions of summer and winter air flow as described by Mattey et al. (2016). The cave systems are divided into two regions: chambers which have openings to the outside atmosphere and are subject to strong ventilation all year round (open ventilation regime) and chambers which are dominated by the seasonal advection of ground air (advection dominated regime). During the course of this study some sampling positions were changed. An additional sampling point was added at the "Trap Door" constriction at the top of the ladder marking the junction between the show cave and the lower New St. Michaels cave system and the sampling point in North Rift was moved to the Bottomless Pit in October 2010. Based on original cave surveys in Rose and Rosenbaum (1991), Shaw (1953a,b) and new surveying by the authors.




Mattey et al Figure 3

Figure 4. Overview of the multichannel $CO_2$ monitoring, rainfall, temperature and wind data measured between 2008 to 2012. From top: daily precipitation amount; diurnal temperature range expressed as difference from the core temperature of the rock ($T_{rock}$=18°C); multichannel data for $CO_2$ measured in St. Michaels and Ragged Staff and wind velocity. Data are colour coded as follows. Temperature anomaly: orange – diurnal range greater than $T_{rock}$; purple - diurnal range crosses $T_{rock}$; pale blue - diurnal range less than $T_{rock}$. $CO_2$ data: simultaneous measurements of background air depicted by the lowest trace. St. Michaels cave system: red - background atmosphere; green - Hospital; orange shaded - Dark Rift; red – Gib04 site; blue – lake site; pink shaded (from October 2010) – Bottomless Pit. Ragged Staff system: red – background atmosphere; green – Hobbit Hole; orange shaded – Silent Pool; purple – Rhino Chamber; blue – Crystal Cave. Wind: magenta – westerly direction; purple – easterly direction (Levanter).

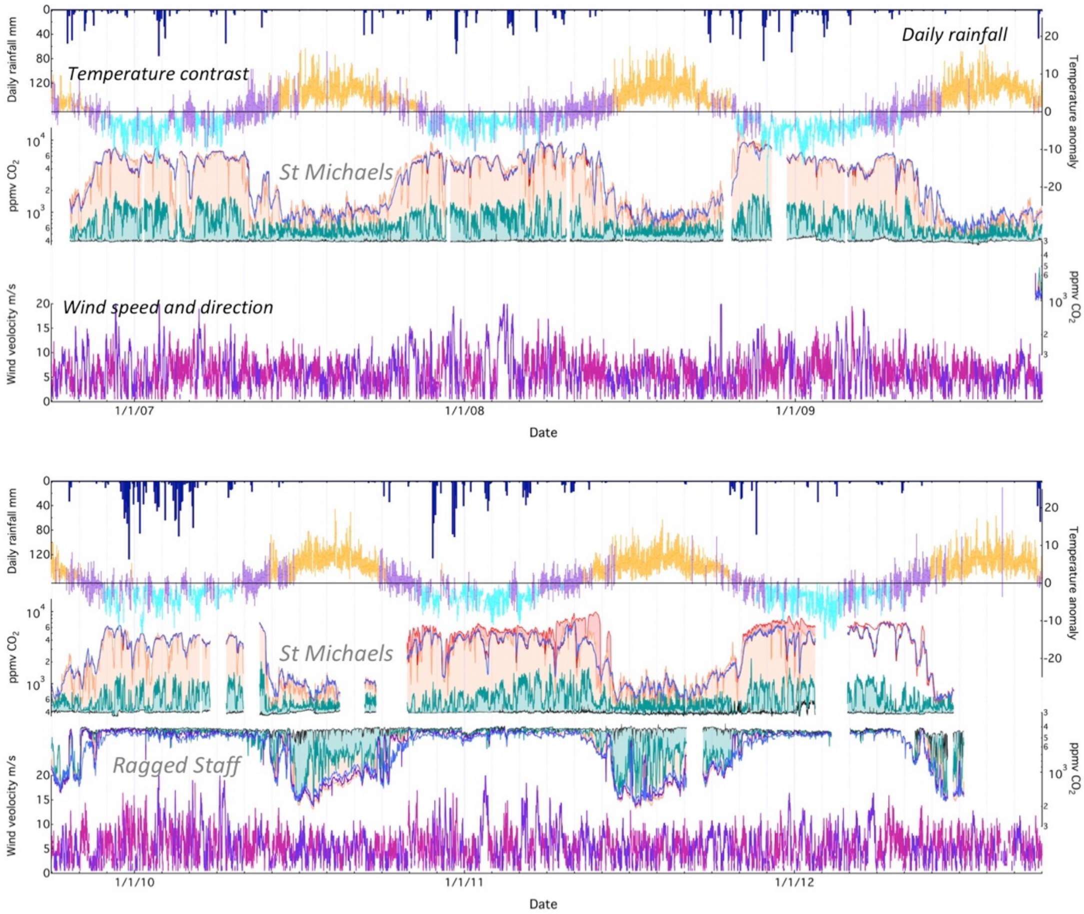
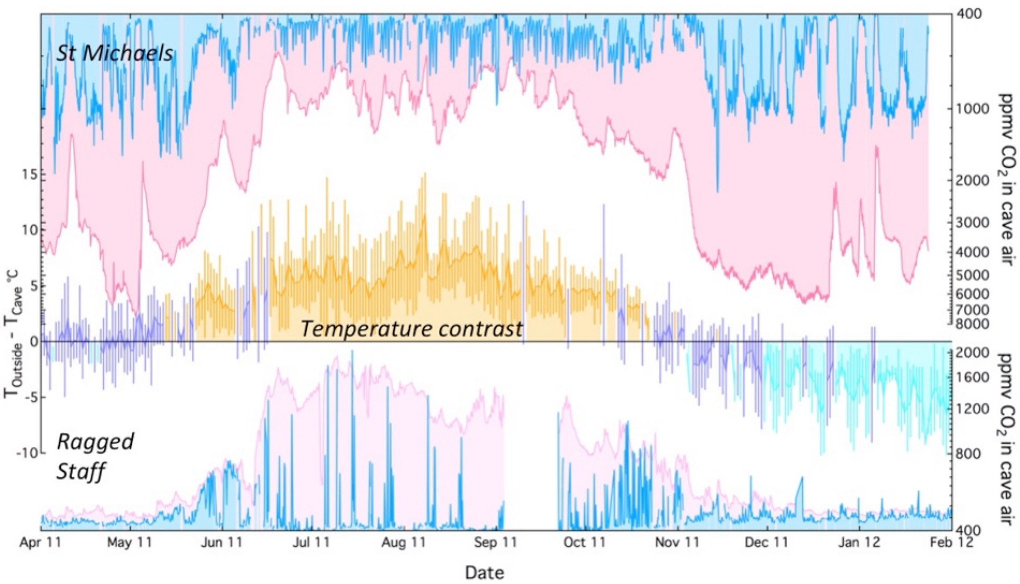
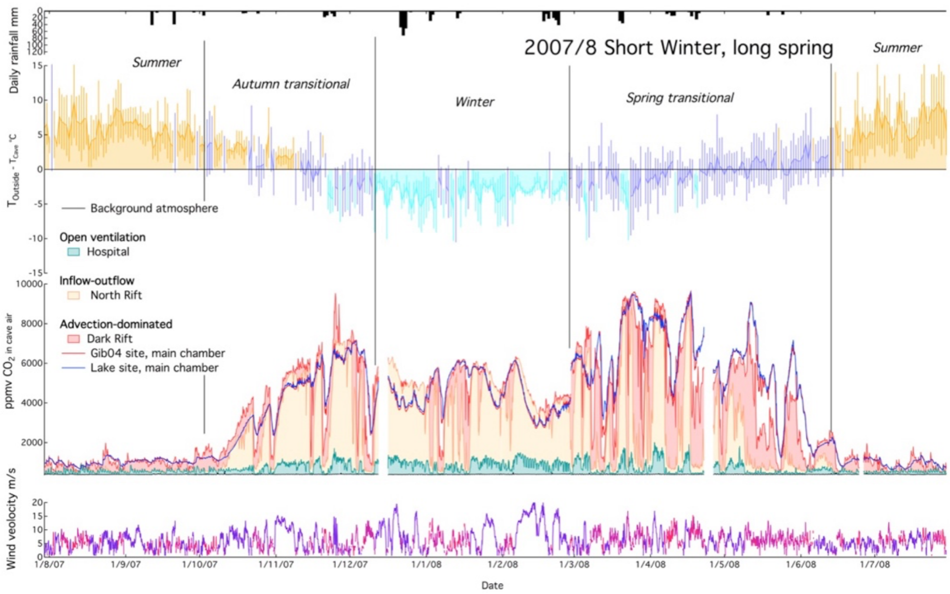


Figure 5. Enlargement of daily temperature and $CO_2$ record for April 2011 to February 2012 showing the close inverse correspondence of changes in $pCO_2$ in advective (pink) and inflow-outflow (blue) regimes of St. Michaels cave (note reversed scale) and Ragged Staff with respect to the external diurnal temperature anomaly. Temperature anomaly colour-coded as in Figure 4; $pCO_2$ records for St. Michaels are for the Lake Site (advective regime) and Trap Door (inflow-outflow) and records for Ragged Staff are for Rhino Chamber (advective regime) and the Hobbit Hole (inflow-outflow). See text for discussion.




Mattey et al Figure 5

Figure 6. Enlargement of the daily temperature, $CO_2$ and wind records for the winter of 2007/8 highlighting the sensitivity of cave air $pCO_2$ to diurnal temperature range. Summer and Winter ventilation-advection regimes are defined respectively as the periods when the diurnal range lies entirely above or entirely below the core temperature of the Rock. Transitional periods occur in spring and autumn when the diurnal range crosses the core temperature. The $pCO_2$ of cave chambers begin to rise steadily at the onset of the autumn transition, remains high through winter, then at the start of the spring transition strongly fluctuates, eventually declining to summer values at the end of this period. The colour coding for diurnal temperature range, $pCO_2$ records and wind direction are the same as in Figure 4. See text for discussion.




Mattey et al Figure 6

Figure 7. Examples of responses to diurnal temperature range, wind strength and wind direction by cave air $pCO_2$ in St. Michaels and Ragged Staff during winter and summer advective regimes. Record **a** is typical of stable cold winter conditions with a brief mild period; record **b** is for a period when temperatures are more unsettled. Record **c** is typical of stable hot summer conditions; record **d** is for a period when summer temperatures are more unsettled. Levanter events are labelled L1, L2 etc. Colour coding for all records as in Figure 4. See text for discussion.

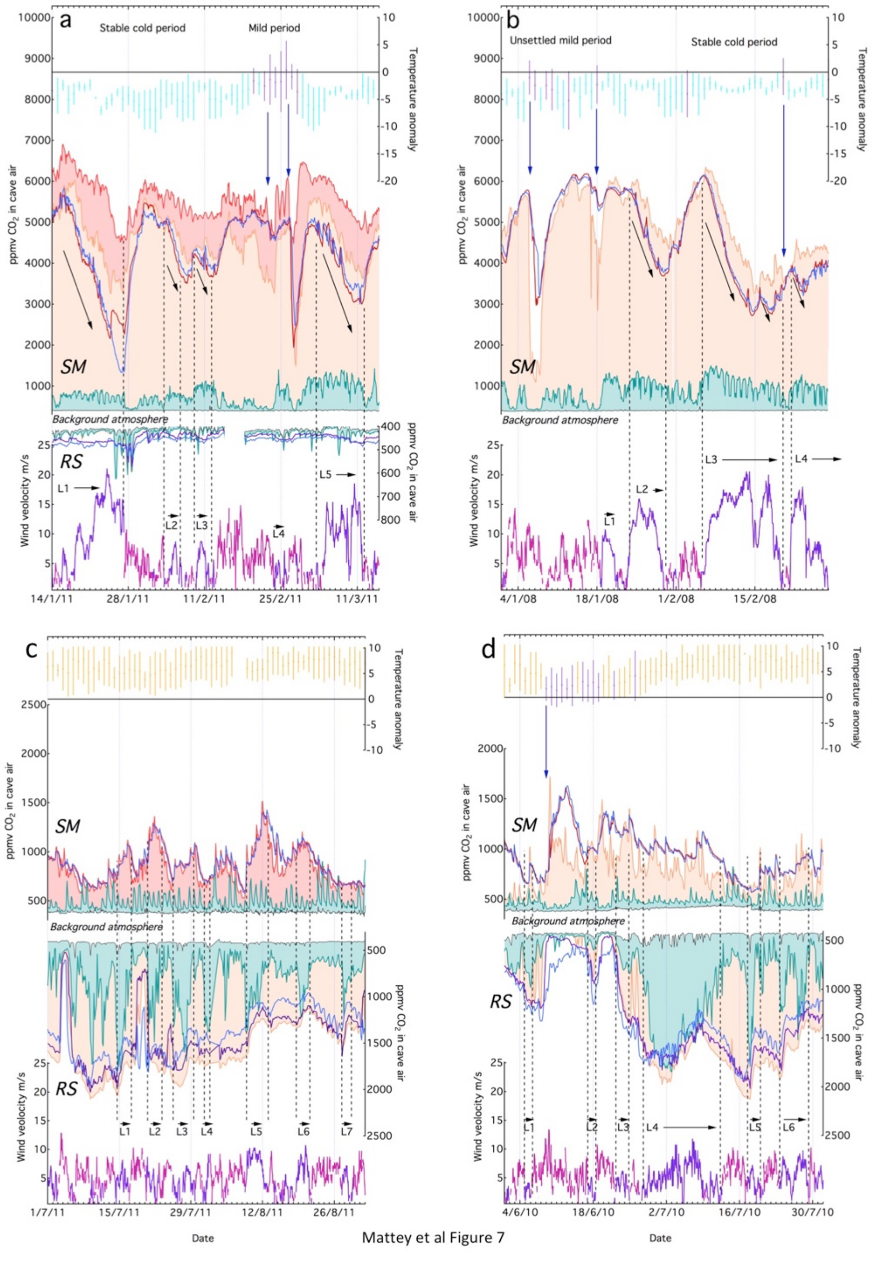
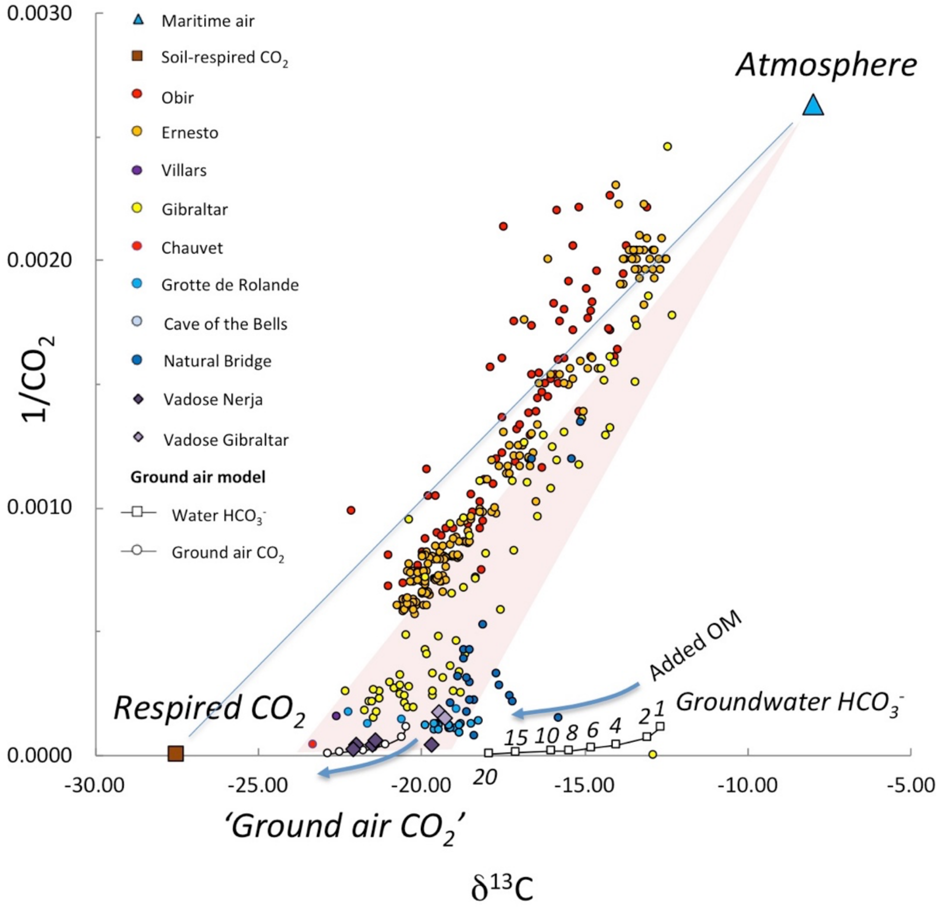


Figure 8. Keeling plot of 1/($CO_2$ concentration) vs isotopic composition of $CO_2$ in atmosphere, cave air, soil respired $CO_2$ and vadose air. The isotopic evolution of the total carbon in ground water (open squares) and gaseous $CO_2$ (open circles) as a function of amount of added organic matter are shown for comparison (from Mattey et al., 2016, Figure 11). Symbols on these curves mark the compositions created by adding $CO_2$ formed by bacterial oxidation of 1, 2, 4, 6, 8, 10, 15, and 20 micro-moles of organic matter having a $\delta^{13}C$ of -26 ‰. See text for discussion. Data sources: respired $CO_2$ (Cerling et al., 1991) ; Obir (Spötl et al., 2005) ; Ernesto (Frisia et al., 2011); Villars (Genty, 2008) ; Gibraltar sites in advection-dominated regimes (Mattey et al., 2016) ; Chauvet (Bourges et al., 2020); Grotte de Rolande (Kirk et al., 2012); Cave of the Bells and Natural Bridge (Bergel et al., 2017); Nerja (Vadillo et al., 2010).




Mattey et al Figure 8

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