Examining the Spatial and Temporal Variations in CO2 Partial Pressure in the Deep Vadose Zone Above Jinapsan Cave, Guam

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Examining the Spatial and Temporal Variations in CO₂ Partial Pressure in the Deep
Vadose Zone Above Jinapsan Cave, Guam

by

Jamar Regis

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of Geology
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Carbon dioxide is the primary driver of dissolution and precipitation reactions in epigene limestone caves. While much work has been conducted on CO$_2$ dynamics involved in dissolution in the phreatic zone, less research has been conducted on vadose CO$_2$ dynamics, especially in tropical caves developed in eogenetic limestones. In this study, we investigate spatial and temporal variation in pCO$_2$ in the deep vadose zone of eogenetic limestone above Jinapsan Cave, located in northern Guam. Five years of carbonate chemistry data from three dripwater sites in Jinapsan Cave (Flatman, Station1, and Trinity) were used to model the theoretical pCO$_2$ with which infiltrating waters had likely equilibrated along flow paths between the soil and the cave. Theoretical pCO$_2$ essentially models the amount of CO$_2$ that would need to be added to dripwaters that have degassed and become supersaturated with respect to calcite upon entering a lower CO$_2$ cave void in order to return the water to equilibrium. Theoretical pCO$_2$ values range from $10^{-2.8}$ to $10^{-1.8}$ atm among the three sites examined. These results were generally lower compared to similar studies in telogenetic and continental karst, which range from $10^{-3.7}$ to $10^{-0.96}$ atm. Theoretical pCO$_2$ data from Jinapsan Cave have significant differences among the three drip sites, with the site closest to the entrance (Flatman)
having the highest values and the farthest from the entrance (Trinity) having the lowest values; in addition, the values also have a great seasonal variability. Low theoretical pCO2 values in Jinapsan Cave’s dripwaters indicate that vadose zones in eogenetic limestone may be better ventilated, and hence have lower pCO2, than those in telogenetic limestone. The ventilation of the vadose zone is facilitated by high matrix porosity and permeability of eogenetic limestone and may be driven by barometric pressure changes or wind.
CO₂ respiration in the vadose zone of carbonate terrains has been proposed to play a significant role in the formation of caves through dissolution (Wood et al., 1985; Gulley et al., 2014) and in the precipitation of speleothems through dissolution and degassing (Faimon et al., 2012). Because caves, and the deposits found within them, are used for paleoenvironmental reconstruction (Fairchild et al., 2000, 2006; Mylroie 2008; Faimon et al., 2012; Hansen et al., 2013; Meyer et al., 2014), understanding the role of CO₂ in their formation is fundamental to proper interpretation of these paleo records. Most canonical models suggest CO₂ involved in cave and speleothem formation is derived from respiration in soil and is later transported into the deeper vadose and phreatic zones as a dissolved component of recharge (White, 1988). A growing body of literature, however, suggests that this CO₂ may be derived from root respiration (Keller et al., 1998; Breecker et al., 2012) and microbial oxidation of organic matter (Wood et al., 1993; Hendry et al., 1993; Benavente et al., 2010) in deeper, subsoil portions of the vadose zone. Consequently, CO₂ involved in cave and speleothem forming processes may be decoupled from soil processes. Hitherto, however, most studies on CO₂ production in vadose zones have emphasized continental settings, temperate climates, and telogenetic
limestones that have had their primarily porosity occluded by burial, compaction, and cementation (Choquette & Pray, 1970). Far fewer studies have investigated CO$_2$ production in vadose zones in tropical climates that are developed in eogenetic limestone which has not been subject to porosity occlusion through burial and diagenesis (Choquette & Pray, 1970).

Studies of carbonate landscapes around the world have found that CO$_2$ concentrations tend to increase with depth below the soil zone in non-cavernous regions of the epikarst. Because CO$_2$ cannot diffuse against a concentration gradient, the soil cannot be the source of this deeper CO$_2$. For example, studies measuring pCO$_2$ in boreholes in the Mediterranean region near the Nerja Cave (Spain) found pCO$_2$ increased from the soil’s surface, where pCO$_2$ averaged $\sim$10$^{-2.9}$ atm, to a maximum of $\sim$10$^{-1.3}$ atm at depths of $\sim$ 60 m (Benavente et al., 2010). Other studies that measured pCO$_2$ in boreholes drilled into the vadose zone, such as Wood & Petraitis (1984) in Southern High Plains of Texas, found pCO$_2$ below the surface increased from an average $\sim$10$^{-2.9}$ atm at a depth of 0.6 m to $10^{-2.1}$ atm at 36.6 m; the highest pCO$_2$ recorded in their study was $\sim$10$^{-1.6}$ atm at depth of 21.6 m below the surface. Similarly, the Sánchez-Cañete et al. (2016) study in Llano de Los Juanes (southeast Spain) also found pCO$_2$ increased from $\sim$10$^{-2.8}$ atm to $10^{-1.7}$ atm from depths of 0.15 m to 7 m below the surface, respectively.

In cavernous portions of the vadose zone, caves provide efficient links between the outside atmosphere and epikarst, facilitating ventilation and air exchange (Gulley et al., 2014). Flux of CO$_2$ from the unsaturated zone into caves tends to elevate the partial pressure of CO$_2$ in the latter relative to the outside atmosphere; ventilation of caves by atmospheric air through cave entrances, however, typically keeps cave pCO$_2$ lower than
in non-cavernous portions of the vadose zone (Gulley et al., 2014). The major processes causing ventilation and airflow movement in caves have been largely attributed to factors such as chimney effect, convection, barometric airflow (barometric pressure differences), temperature differences (Figure 1), and entrainment by flowing water (Figure 2) (Denis et al., 2005; Palmer 2007; Kowalczk & Froelich, 2010; Gulley et al., 2014; Covington & Perne, 2015). Additionally, the cave's geometry, orientation, interconnected chambers and openings will likewise impact the airflow and thus ventilation mechanisms (Palmer, 2007; Covington & Perne, 2015).

![Figure 1. Major air ventilation mechanisms in caves. (a-b) Chimney effect showing airflow in caves with multiple entrances. During the summer (a), the cold air moves out from the cave through the lower entrance due to chimney effect while during the winter (b) the warm air moves out through the upper openings. The movement of air through these caves is complex because of the geometry, thus, it can enter and leave at different openings. (c-d) Barometric airflow effect: When the outside air pressure is low (c), ventilation results in movement of air outside of the cave, whereas when the outside air pressure is high, the opposite of (c) occurs with ventilation resulting in movement of denser air into the cave (as seen in (d)). (e) Summer driven convection airflow. There is no air flow in the summer because the cave air will become density stratified and (f) Winter driven convection airflow causes air circulation as indicated by the black arrows (created with reference to Palmer 2007; Covington & Perne, 2015).]
For example, in caves with a single entrance located at a higher elevation than the rest of the passages, cave air can become density stratified in late summer, when outside air temperatures do not decrease below cave air temperature (Figure 1d). Because cooler cave air is more dense than the warmer outside air, little exchange occurs between caves and the atmosphere during these times; pCO$_2$ in the cave increases and may eventually approach pCO$_2$ in non-cave portions of the vadose zone (Gulley et al., 2014). As air temperatures decrease below cave temperature at night during autumn and winter, cooler outside air sinks into the cave (Figure 1e) to drive ventilation and lower cave pCO$_2$ values (Baldini et al., 2008; Kowalczk & Froelich, 2010; Gulley et al., 2014; Pu et al., 2017).

Seasonal fluctuations in ventilation and cave air pCO$_2$ are well documented. The pCO$_2$ in the Signature Room in Hollow Ridge Cave (Florida) fluctuated diurnally between 10$^{-3.3}$ to 10$^{-2.7}$ atm during the autumn, from 10$^{-3.3}$ to 10$^{-3.0}$ atm in the cold season and 10$^{-3.3}$ to 10$^{-2.4}$ atm at the peak of the warm season (Kowalczk & Froelich, 2010). Similarly, in Crag Cave (Ireland) (Baldini et al., 2008), Ascunsă Cave (Drăgușin et al. (2017), and
Cova De Sa Font (Spain) (Gines et al., 2017), pCO$_2$ fluctuated from $10^{-3.0}$ to $10^{-2.1}$ atm, $10^{-2.55}$ to $10^{-2.04}$ atm, and $10^{-3.4}$ to $10^{-1.0}$ atm from the cold to the warm season, respectively.

While variability in daily and seasonal temperatures has been proposed to be the main driver of ventilation (Kowalczk & Froelich, 2010; James et al., 2015), recent work has suggested wind-driven ventilation is also important in lowering pCO$_2$ values in caves (Covington, 2016). For example, seasonal fluctuations of pCO$_2$ (~$10^{-3.3}$ to $10^{-2.3}$ atm) logged at Jinapsan Cave in Guam were correlated with windy conditions associated with the onset of the dry season rather than temperature variability (Noronha et al., 2017).

Regardless of mechanism, ventilation lowers cave pCO$_2$ relative to the soil and vadose zone, which drives degassing of vadose infiltration that intersects caves and the precipitation of calcite speleothems (Baldini et al., 2006; Casteel et al., 2015). Vadose infiltration dissolves carbonate bedrock and dissolution proceeds until equilibrium is reached with respect to the carbonate minerals for that pCO$_2$. Flow from regions of higher to lower pCO$_2$, such as from the inside of a fracture or bedrock matrix into a cave connected to the surface, leads to degassing of CO$_2$ and the precipitation of calcite (Baldini et al., 2006; Kowalczk and Froelich, 2010; Gulley et al., 2014). Consequently, most drip waters are supersaturated with respect to calcite. Assuming that drip waters were at equilibrium with respect to calcite prior to entering the cave, a theoretical pCO$_2$ can be calculated by determining what pCO$_2$ would be required to be at equilibrium with respect to calcite (Fairchild et al., 2000; Dreybrodt, 2011; Faimon et al., 2012; Hansen et al., 2013). Studies using cave waters to calculate theoretical pCO$_2$ revealed the following range of values: $10^{-2.6}$ to $10^{-1.9}$ atm in caves from SW England (Atkinson, 1977), $10^{-1.9}$ to $10^{-0.96}$ atm in the Moravian karst (Faimon et al., 2012), $10^{-1.9}$ to $10^{-1.4}$ atm in Briar Cave,
Florida (Gulley et al., 2014), $10^{-1.8}$ to $10^{-1.6}$ atm in Srednja Bijambarska Cave, Bosnia and Herzegovina (Milanolo & Gabrovšek, 2015), $10^{-2.4}$ to $10^{-1.9}$ atm in Golgotha Cave, Australia (Treble et al., 2015), $10^{-2.39}$ to $10^{-1.58}$ atm in Ascunsă Cave, Romania (Drăgușin et al., 2017) and $10^{-3.22}$ to $10^{-1.66}$ atm in Xueyu Cave, SW China (Pu et al., 2017).

The majority of research which focuses on investigating CO$_2$ in carbonate rock within the vadose zone has mainly been in telogenetic limestone, where the low matrix porosity and permeability limit flow of water and air through fractures and conduits (Baldini et al., 2006; Faimon et al., 2012; Milanolo & Gabrovšek 2015; Treble et al., 2015). Comparatively, little is known about CO$_2$ dynamics in vadose zones of eogenetic limestones, where high matrix porosity and permeability allow water and air to flow through interparticle and vuggy porosity as well as through fractures and caverns. The tropical location of eogenetic limestones has typically been interpreted to indicate soil pCO$_2$ which should be much higher as compared in the temperate climates that are more characteristic of telogenetic limestone (Brook et al., 1983; Borsato et al., 2015). If this hypothesis is correct, we might expect the pCO$_2$ in the vadose zones of eogenetic limestone to be greater than in telogenetic limestone. Alternatively, the increased connectivity among caves, matrix porosity and the atmosphere in the vadose zones of eogenetic limestone may result in greater ventilation, and perhaps lower vadose pCO$_2$, relative to telogenetic limestones. The objective of this study is to use geochemical modeling to calculate and assess theoretical pCO$_2$ of dripwater in the deep vadose zone. Using data collected from Jinapsan Cave developed in the tropical island of Guam, the study seeks to understand the CO$_2$ dynamics in the formation of caves and speleothems precipitation in eogenetic limestone.
DESCRIPTION OF STUDY AREA

Geology of Guam

The island of Guam and the Northern Mariana Islands chain overlie the subduction zone that bounds the Pacific and Philippine Plate (Whitaker et al., 2006). The Northern Mariana Islands have a complex geologic history because they were formed in a tectonically active area. The island of Guam is the largest in Micronesia and has two main geological divisions separated by the Pago Adelup Fault which is oriented to the NW to SE (Taboroši et al., 2003). The northern half of the island is predominately a limestone province overlying a volcanic basement unit. In the south, it is dominated by volcanic terrain with sectors of uplifted limestone units occurring in the south east (Tracey et al., 1964).

Northern Guam is comprised of an elevated (60 to 80 m above sea level) limestone plateau (Whitaker et al., 2006). The Miocene-Pliocene Barrigada Limestone is the principle aquifer unit, consisting of a well-lithified limestone deposited in a deep-water environment (Whitaker et al., 2006). This unit is highly permeable, covers approximately 9% of Guam’s surface area and has a thickness greater than 165 m (Tracey et al., 1964; Gingerich, 2003; Whitaker et al., 2006). The Barrigada Limestone unit grades laterally
and upwards to the Pliocene to Pleistocene Mariana Limestone, deposited in a lagoonal reef setting (Taboroši et al., 2005). The Mariana Limestone is the most extensive unit that occupies a surface area of about 45% of all of Guam (Gingerich, 2003) and about 75% of the surface of Northern Guam (Tracey et al., 1964; Gingerich, 2003). The unit is highly permeable due to dense networks of fissures and joints (Gingerich, 2003). These limestone units overlay the Oligocene age Alutom Formation which is the volcanic basement unit (Taboroši et al., 2003).

The Southern Guam volcanic units of the Alutom Formation (Eocene and Oligocene) are the oldest, have low permeability, and consist of basalt flows, pillow basalts, and tuffaceous shale (Gingerich, 2003). These volcanic rocks are overlain by the Miocene to Pliocene age Bonya Limestone (in the interior) and the Alifan Limestone (in upland areas) units (Tracey et al., 1964; Gingerich, 2003). The Bonya Limestone is a permeable jointed and fractured detrital rock whereas the Alifan consists of a detrital limestone and conglomeratic clay marl deposited in a shallow reef margin (Gingerich, 2003), thus moderate to highly permeable (Tracey et al., 1964; Johnson, 2012).

Guam is widely cited as an example of eogenetic karst (Mylroie et al., 2001), however, the carbonate landscape developed in the limestones of northern and southern parts are fundamentally different (Taboroši et al., 2005). The karst in northern Guam is younger and is mostly eogenetic, characteristic of a young carbonate islands. In contrast, the karst in the southern Guam is developed in older limestone and has features more consistent with continental telogenetic karst (Taboroši et al., 2005).
**Climate, Recharge, and Runoff**

Guam’s climate is tropical with two different seasons, wet and dry. The rainfall is strongly seasonal with most of the precipitation occurring during the wet season, between July and December and usually associated with typhoons (Whitaker et al., 2006). The mean average rainfall is ~2580 (mm/yr), with 70% in the wet-season and 30% in the dry-season (January through June) (Lander & Guard, 2003). The average daily temperature is 26.6-28.3°C, resulting in a mean annual recharge (precipitation minus evapotranspiration) of ~1006 mm/yr (Johnson, 2012).

Recharge is highest in the karst regions and can reach 40 to 60% of rainfall (Johnson, 2012). In northern Guam, where exposed limestone and heavy rainfall has resulted in extensive karstification, runoff is nearly absent due to fast infiltration via pits and enlarged fractures (Taboroši et al., 2005). Karstic, fast-flow routes contribute to about 30% of the recharge to the aquifer, with the remainder occurring via slower matrix porosity (Contractor & Jenson, 2000). Water flowing along faster routes can also transport organic matter rapidly through Guam’s thick vadose zone (>100 m) into the freshwater lens, where subsequent oxidation may drive active phreatic diagenesis (Whitaker et al., 2006).

**Caves in Guam**

Caves are common in the limestone regions of Guam. The classification of these caves includes two fundamental categories, vadose and phreatic (Taboroši et al., 2005). The first type form above the water table by dissolving water in the bedrock, whereas the latter originate at or below the water table. In northern Guam, most caves appear to be phreatic in origin and have been interpreted to form by dissolution resulting from the
mixing of fresh and marine groundwater (Taboroši et al., 2005). In southern Guam, caves are primarily vadose in origin (Mylroie et al., 1999).

Jinapsan Cave Site Description

Our research is based on data collected from Jinapsan Cave, which is located along the coastline at the northern tip of Guam in a heavily vegetated area at the base of a talus slope (13°38’24.3” N, 144°52’42.3” E; Figure 3).

There have been several other studies at Jinapsan Cave including: the investigation of paleoclimate records in speleothems (Moore et al., 2011), analysis of rainfall variability on stalagmite geochemistry (Partin et al., 2012), investigation of atmospheric influence on cave meteorology (McCann, 2013), and most recently an analysis of vadose hydrology (Bautista et al., 2018).

Figure 3. Map of Guam showing the location of the Jinapsan Cave. (A) A map of the island of Guam. (created using ArcMap version10.5). (B) A zoomed in satellite image showing the location of Jinapsan Cave in Northern Guam. (created from Google Maps/Google Earth, retrieved 3/11/ 2019).
Jinapsan Cave is interpreted to be of phreatic origin. The initial void formed in the Mariana Limestone by mixing dissolution, with later enlargement through progradational collapse (Taboroši et al., 2005; Miklavič, 2011). The cave entrance (dimensions ~0.7 x 1.05 m wide) is situated 25 m above the present sea level. Heavy vegetation near the entrance shelters the cave from direct sunlight and wind. The cave has a sloping profile and a complex interior (Figure 4). Multiple rooms extend downslope, approximately 48 m, before terminating in a tidal pool at the deepest point of the cave (McCann, 2013). The overlying vadose zone ranges from 2 to 46 m thick and beneath it is the distal margin of the Northern Guam Lens Aquifer, which is very thin in the vicinity of the cave. The drip sites investigated are: Flatman (FM), Station 1 (S1), and Trinity (TR), which are located within the following rooms of the cave: Big Room, Shakey Room, and Midslide listed from farthest proximity to the cave's entrance (Figure 4).
Figure 4. Cave map showing the plan and profile view of Jinapsan Cave. The monitored sites are shown: Flatman (FM), Station 1 (S1), and Trinity (TR) (created with reference to Partin et al., 2012; Bautista et al., 2017).
MATERIALS AND METHODS

Cave Data Collection and Monitoring

We analyzed water samples that were collected at approximately monthly intervals from three drip sites (Trinity, Flatman, and Station 1) in Jinapsan Cave over a five-year period (from June 2009 to August 2014). The Trinity drip site is located within the Big Room, Flatman in Midslide, and Station 1 in Shakey Room (Figure 4).

Dripwater samples were collected over ~24 hours; bottles were placed below drip sites and then collected one day later (Noronha et al., 2016). Further analyses of dripwater pH, conductivity, and temperature were conducted on site using Myron Ultrameter II-6P meter. The drip rates were measured with a chronometer and cave air CO₂ gas concentrations were recorded initially using Vaisala GM70 CO₂ probe (0-5000 ppm range) and a Vaisala M170 data logger at the time of water sampling (Noronha et al., 2016). Alkalinity was measured on site using a Hach digital titrator with a concentration of 0.16 N sulfuric acid to a pH endpoint of 4.00, with the starting and ending temperature of all titrations being logged. Subsamples of dripwater were analyzed for anions using a Dionex ion chromatograph, and for major cation concentrations, either an Optima 4300
inductively coupled plasma optical emission spectrometer or an Agilent 7500ce quadrupole ICP-mass spectrometer at the University of Texas at Austin (Noronha et al., 2016).

**Geochemical Data Modeling & Calculations**

We used geochemical data from dripwater samples and geochemical modeling software to calculate the theoretical pCO₂ of dripwater samples using the techniques described by Faimon et al. (2012). All modeling was conducted with PHREEQC (version 3.3.10.12220) and the PHREEQC database (Charlton & Parkhurst, 2002).

A total of 733 samples were collected, however, not all dripwater samples had sufficient water volumes to conduct all the chemical analyses needed to characterize cations (Ca²⁺, Mg²⁺, Na⁺), anions (Cl⁻, SO₄²⁻), and alkalinity. In all, 119 samples collected from three dripwater sites had enough water and sufficient geochemical data to fully characterize the carbonate chemistry: Flatman (n = 48), Station 1 (n = 20), and Trinity (n = 51). Of these, only 94 samples had charge balance errors less than 10% and were used in our study (Table 1).

Table 1. Number of drip samples used before and after charge balance error calculations.

<table>
<thead>
<tr>
<th>Drip Site</th>
<th>Before modeling</th>
<th>Samples accepted after charge balance calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinity</td>
<td>51</td>
<td>44</td>
</tr>
<tr>
<td>Flatman</td>
<td>48</td>
<td>33</td>
</tr>
<tr>
<td>Station 1</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>Total</td>
<td>119</td>
<td>94</td>
</tr>
</tbody>
</table>
Because we are interested in investigating the pCO$_2$ within the vadose zone, and because degassing in the cave atmosphere can increase the carbonate mineral saturation state and decrease pCO$_2$ of drip waters, we reduced the pH values of each sample in PHREEQC in increments of 0.1 until the sample reached equilibrium with respect to calcite. The pH values at equilibrium for the 3 drip sites ranged from 7.2 to 7.8 (Table 2).

Table 2. The pH of samples recorded to be at equilibrium with calcite.

<table>
<thead>
<tr>
<th>Drip Sites</th>
<th>Category 1: pH range</th>
<th>Category 2; pH range (charge balance on Ca$^{2+}$)</th>
<th>Category 3; pH range (charge balance on alkalinity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinity</td>
<td>7.5-7.8</td>
<td>7.1-8.0</td>
<td>7.3-7.7</td>
</tr>
<tr>
<td>Flatman</td>
<td>7.2-7.3</td>
<td>7.2-7.8</td>
<td>7.1-7.3</td>
</tr>
<tr>
<td>Station 1</td>
<td>7.3-7.6</td>
<td>7.3-7.8</td>
<td>7.3-7.6</td>
</tr>
</tbody>
</table>

Physically, this approach equates adding CO$_2$ back into each dripwater, until the solution returns to equilibrium with respect to calcite. Assuming that degassing primarily occurs within the well-ventilated cave atmosphere, and minimal Ca$^{2+}$ and HCO$_3^-$ is deposited prior to dripping, then this theoretical pCO$_2$ should be roughly equivalent to the pCO$_2$ of the less well-ventilated flow paths within the non-cave portions of the epikarst (Fairchild et al., 2000; Dreybrodt, 2011; Faimon et al., 2012; Hansen et al., 2013). We assessed the potential impact of ion measurement errors on theoretical pCO$_2$ by alternatively forcing charge balance on Ca$^{2+}$ (modeling Category 2) and alkalinity (modeling Category 3), which are the dominant cation and “anion” in solution, respectively. The theoretical pCO$_2$ ranges in category 2 and 3 were further computed by calculating the difference from that of category 1. The differences represented the data variability and plausible ranges of theoretical pCO$_2$. 
RESULTS

Geochemical Results

Theoretical pCO₂ ranged from $10^{-2.8}$ to $10^{-1.8}$ atm, with the highest concentration occurring at the Flatman site on July 30, 2013 and the lowest at the Trinity site on May 4, 2010 (Figures 5, 6, and 8). The dripwater theoretical pCO₂ was always significantly greater than the recorded cave pCO₂ (Figure 5). Additionally, there is an inverse correlation between theoretical pCO₂ and the distance of the drip sites from the cave entrance. The Trinity site, which is the farthest from the entrance, has the lowest theoretical pCO₂ whereas Flatman, which is located closest to the entrance has the highest. The theoretical pCO₂ time-series is more variable at Trinity and Station 1 compared to the Flatman drip site (Figure 5). The general trends for the theoretical pCO₂ at each site are described below.
Figure 5. Temporal variation of dripwater theoretical pCO$_2$ for all three sites and recorded cave pCO$_2$. 
Flatman

Drip rates at Flatman ranged from 0.097 to 0.37 mL/min (average 0.23 mL/min) with the highest value recorded during the wet season. The theoretical pCO₂ fluctuates between $10^{-2.0}$ and $10^{-1.8}$ atm (Figure 6). The five-year average was $10^{-1.9}$ atm and there was a weak positive correlation between theoretical pCO₂ and drip rate (Figure 9).

![Figure 6. Drip rate and temporal variation of dripwater theoretical pCO₂ in Flatman.](image)

Station 1

Drip rates at Station 1 were generally constant and ranged from 0.076 to 0.16 mL/min, averaging 0.11 mL/min over the period of study. Theoretical pCO₂ varied from $10^{-2.44}$ to $10^{-1.96}$ atm and were generally lower in the dry season (e.g. January to February 2012) and higher during the wet season (e.g. August 2011). The average theoretical pCO₂ over the four-year interval was $10^{-2.2}$ atm (Figure 7). Unlike Flatman, there is a strong positive correlation between theoretical pCO₂ and drip rates at Station 1 (Figure 9).
Trinity

Drip rates at Trinity ranged from 0 to 9.1 mL/min and averaged 2.6 mL/min over the period of study. Theoretical pCO₂ fluctuated between $10^{-2.8}$ and $10^{-2.3}$ atm being lower in the dry season and higher in the wet season. The average over five years was $10^{-2.5}$ atm (Figure 8). Like Flatman, there is a weak positive correlation at Trinity site between theoretical pCO₂ and drip rate (Figure 9).
Figure 8. Drip rate and temporal variation of dripwater theoretical pCO₂ in Trinity.(N.B. the zero-drip rate indicates there were no data available).
Figure 9. Temporal variation of dripwater theoretical pCO$_2$ and drip rates (log scale) for all three sites.
DISCUSSION

The purpose of this study was to investigate the spatial and temporal dynamics of CO₂ in the vadose zone developed in eogenetic limestone above Jinapsan Cave. My results suggest that the pCO₂ of the vadose zone in Guam’s eogenetic limestone is comparable to, but with maximum values somewhat lower than, the pCO₂ recorded in the vadose zones of other carbonate areas, especially those in telogenetic limestones (Table 3 & Figure 10). Theoretical pCO₂ in Jinapsan Cave ranged from 10⁻².₈ to 10⁻¹.₈ atm, whereas pCO₂ values between 10⁻³.₇ and 10⁻⁰.₉₆ atm have been reported from cave, borehole and dripwater studies in other carbonate regions (Table 3 and Figure 10). The finding that maximum theoretical pCO₂ values are generally higher in telogenetic karst areas, which typically develop in colder climates, is somewhat surprising because soil CO₂ production rates and concentrations are higher in warmer, tropical climates (Brook et al., 1983) similar to what Guam experiences.

In the following paragraphs, I describe possible controls on the spatial and temporal variability of pCO₂ in Jinapsan Cave. I then postulate why the maximum values in Jinapsan Cave’s drip waters may be lower than maximum pCO₂ values from other
similar studies (Table 3 & Figure 10), which have mainly been conducted in telogenetic karst areas.

Table 3. Summary of published pCO₂ values from caves, boreholes, and dripwaters.

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Measurement Type (borehole, cave, dripwater)</th>
<th>log pCO₂ range (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood &amp; Petraitis, 1984</td>
<td>Southern High Plains of Texas</td>
<td>Borehole</td>
<td>-2.9 to -1.6</td>
</tr>
<tr>
<td>Benavente et al., 2010</td>
<td>Mediterranean region near the Nerja Cave (Southern Spain)</td>
<td>Borehole</td>
<td>-2.9 to -1.3</td>
</tr>
<tr>
<td>Sánchez-Cañete et al., 2016</td>
<td>Llano de Los Juanes (SE Spain)</td>
<td>Borehole</td>
<td>-2.8 to -1.7</td>
</tr>
<tr>
<td>Mattey et al., 2016</td>
<td>Fosse Way Tunnel and Lathbury Barracks (Gibraltar)</td>
<td>Borehole</td>
<td>-2.40 to -2.00</td>
</tr>
<tr>
<td>Atkinson, 1977</td>
<td>G.B. Cave within Cheddar drainage area (SW England)</td>
<td>Cave (from joints and fissures)</td>
<td>~-2.09 (mean)</td>
</tr>
<tr>
<td>Spötl et al., 2005</td>
<td>Obir Cave (Austria)</td>
<td>Cave</td>
<td>-3.35 to -2.83</td>
</tr>
<tr>
<td>Baldini et al., 2008</td>
<td>Crag Cave (Ireland)</td>
<td>Cave</td>
<td>-3.00 to -2.10</td>
</tr>
<tr>
<td>Baldini et al., 2008</td>
<td>Ballynaminta Cave (Ireland)</td>
<td>Cave</td>
<td>-3.70 to -2.20</td>
</tr>
<tr>
<td>Kowalczk &amp; Froelich, 2010</td>
<td>Signature Room Hollow Ridge Cave (Florida)</td>
<td>Cave</td>
<td>-3.30 to -2.40</td>
</tr>
<tr>
<td>Frisia et al., 2011</td>
<td>Grotta di Ernesto (NE Italy)</td>
<td>Cave</td>
<td>-3.30 to -2.80</td>
</tr>
<tr>
<td>Riehlemann et al., 2011</td>
<td>Bunker Cave (Western Germany)</td>
<td>Cave</td>
<td>-3.10 to -2.90</td>
</tr>
<tr>
<td>Wong et al., 2011</td>
<td>Natural Bridge Caverns (Central Texas)</td>
<td>Cave</td>
<td>-3.40 to -1.40</td>
</tr>
<tr>
<td>Denis et al., 2012</td>
<td>Lascaux Cave (Dordogne, France)</td>
<td>Cave</td>
<td>-2.00 to -1.20</td>
</tr>
<tr>
<td>Peyraube et al., 2012</td>
<td>Cussac Cave (Dordogne, France)</td>
<td>Cave</td>
<td>-2.50 to -1.50</td>
</tr>
<tr>
<td>Smith et al., 2015</td>
<td>Cueva de Asiul (Northern Spain)</td>
<td>Cave</td>
<td>-3.40 to -2.70</td>
</tr>
<tr>
<td>Mattey et al., 2016</td>
<td>St. Michaels, New St. Micheals and Ragged Staff caves (Gibraltar)</td>
<td>Cave</td>
<td>-3.30 to -2.10</td>
</tr>
<tr>
<td>Drăgușin et al., 2017</td>
<td>Ascunsă Cave (Romania) (3 sites POM A, POM 2, and POM B)</td>
<td>Cave</td>
<td>-2.55 to -2.04</td>
</tr>
<tr>
<td>Study</td>
<td>Location</td>
<td>Measurement Type (borehole, cave, dripwater)</td>
<td>log pCO₂ range (atm)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------------------------------------------</td>
<td>---------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Ginés et al., 2017</td>
<td>Cova De Sa Font (Sa Dragonera, Balearic Islands, Spain)</td>
<td>Cave</td>
<td>-3.40 to -1.04</td>
</tr>
<tr>
<td>Noronha et al., 2017</td>
<td>Jinapsan Cave (Guam)</td>
<td>Cave</td>
<td>~ -3.3 to -2.3</td>
</tr>
<tr>
<td>Pérez-Mejías et al., 2018</td>
<td>Ejulve Cave (Spain)</td>
<td>Cave</td>
<td>-3.34 to -2.67</td>
</tr>
<tr>
<td>Atkinson, 1977</td>
<td>Swildons Hole (SW England)</td>
<td>Dripwater</td>
<td>~ -1.9 to -1.4</td>
</tr>
<tr>
<td></td>
<td>Reservoir Hole (SW England)</td>
<td></td>
<td>~ -2.1 to -1.8</td>
</tr>
<tr>
<td></td>
<td>Contour Cavern (SW England)</td>
<td></td>
<td>~ -2.6 to -2.0</td>
</tr>
<tr>
<td>Mayer, 1999</td>
<td>Pettyjohns Cave (Georgia)</td>
<td>Dripwater</td>
<td>-3.15 to -2.08</td>
</tr>
<tr>
<td>Karmann et al., 2007</td>
<td>Santana-Perolas Cave system (SE Brazil)</td>
<td>Dripwater</td>
<td>-2.77 to -1.94</td>
</tr>
<tr>
<td>McDonald et al., 2007</td>
<td>Wombeyan Caves (SW Sydney)</td>
<td>Dripwater</td>
<td>-2.57 to -1.99</td>
</tr>
<tr>
<td>Faimon et al., 2012</td>
<td>Moravian Karst</td>
<td>Dripwater</td>
<td>-1.9 to -0.96</td>
</tr>
<tr>
<td>Milanolo &amp; Gabrovšek, 2015</td>
<td>Srednja Bijambarska Cave (Bosnia and Herzegovina)</td>
<td>Dripwater</td>
<td>-1.8 to -1.6</td>
</tr>
<tr>
<td>Treble et al., 2015</td>
<td>Golgotha Cave (SW Australia)</td>
<td>Dripwater</td>
<td>-2.4 to -1.9</td>
</tr>
<tr>
<td>Bergel et al., 2017</td>
<td>Natural Bridge Caverns and Inner Space Cavern</td>
<td>Dripwater</td>
<td>~2.0 to -1.2</td>
</tr>
<tr>
<td>Drăgușin et al., 2017</td>
<td>Ascunsâ Cave (Romania) (3 sites POM A, POM 2, and POM B)</td>
<td>Dripwater</td>
<td>-2.39 to -1.56</td>
</tr>
<tr>
<td>Pu et al., 2017</td>
<td>Xueyu Cave (China) (3 sites D1, D2, and D3)</td>
<td>Dripwater</td>
<td>-3.22 to -1.66</td>
</tr>
<tr>
<td>This study</td>
<td>Jinapsan Cave (Guam)</td>
<td>Dripwater</td>
<td>~2.0 to -1.8</td>
</tr>
<tr>
<td></td>
<td>Flatman Station 1</td>
<td></td>
<td>~2.44 to -1.96</td>
</tr>
<tr>
<td></td>
<td>Trinity</td>
<td></td>
<td>~2.8 to -2.3</td>
</tr>
</tbody>
</table>
Figure 10. Bar graph of published pCO$_2$ values from caves, boreholes, and dripwaters.
**Spatial pCO₂ Variability**

Spatial variability in theoretical pCO₂ in Jinapsan Cave indicates that ventilation through the small cave entrance is unlikely to be the primary driver of differences in pCO₂ among the sites. Flatman, which is the closest to the entrance, had the highest average theoretical pCO₂ values (10⁻¹.⁹ atm), whereas Trinity, located farthest from the entrance, had the lowest (~0.25 times less than Flatman). Station 1, which is situated halfway between the two sites, had values ~0.50 times less than Flatman. If pCO₂ was controlled solely by cave ventilation (such as convective airflow) through the only entrance, Flatman should have the lowest theoretical pCO₂ and Trinity the highest. However, our findings show otherwise, prompting us to search for other possible explanations that cause pCO₂ values to vary among the drip sites.

One possible reason why theoretical pCO₂ is higher in drip waters nearer the entrance of the cave is that the flow path type, rather than entrance ventilation, controls theoretical pCO₂. In their vadose hydrology analysis, Bautista et al. (2018) note differences in ceiling fracture size and density among the various rooms. A major fracture was observed in the Big Room (location of Trinity drip site) whereas fewer fissures were noticeable in the other rooms. Bautista et al. (2018), interpreted the hydrologic pathway for Trinity as predominately fracture flow, Flatman as a fracture-fissure flow, and Station 1 as predominately fissure flow. These various flow pathways are also reflected in differences in drip rates. Specifically, the Trinity site has the fastest drip rate and lowest pCO₂. Fractures delivering water to Trinity may facilitate ventilation of vadose flow paths and lower pCO₂ relative to the other drip sites. Flatman and Station 1 have reduced drip
rates and higher theoretical pCO₂. Slower flow rates indicate less efficient flow paths that may have less air space in contact with water to facilitate degassing or ventilation.

Differences in limestone thickness above the cave may also account for pCO₂ variation among sites. In Jinapsan Cave, shallower drip sites had higher theoretical pCO₂ than deeper sites (Figure 11). These findings are similar to Pu et al. (2017), who found CO₂ concentrations were higher at drip sites under thinner limestone cover near the cave entrance and lower where the vadose zone is thicker. Pu et al. (2017) suggested the following explanation for this inverse relationship between pCO₂ and carbonate rock thickness: shorter flow paths traversing thinner vadose zones allow less time for degassing, whereas longer flow paths towards deeper cave sites may increase time available for degassing. However, these findings are contrary to Sanchez-Cañete et al. (2016), who report higher CO₂ concentrations in the deeper boreholes suggesting there is a deeper source of CO₂.

Other possible causes of spatial variability in theoretical pCO₂ in Jinapsan Cave include differences in the amount of labile organic carbon at depth and/or density of tree roots which respire CO₂. Intuitively, higher pCO₂ is expected to be associated with regions of higher labile organic carbon and tree root densities, but testing these hypotheses is difficult due to limited access to the vadose zone (Hesterberg & Siegenthaler, 1991; Bacon & Keller, 1998). Prior work suggests that root respiration can be an important source of CO₂. For example, at least half of the CO₂ in the Natural Bridges Caverns, central Texas, may have been derived from root respiration, as the clear-cutting of trees above the cave in that study showed a nearly 55% decline in CO₂ in the cave (Wong & Banner, 2010).
Temporal pCO₂ Variability

In our study, Trinity and Station 1 sites show clear seasonal variability in theoretical pCO₂ whereas Flatman has less variability. This observation is similar to prior studies showing seasonal variability of CO₂ values between deep and shallow sites (Sánchez-Cañete et al., 2016; Pu et al., 2017). At the Trinity site, theoretical pCO₂ and drip rate are generally higher and reach peak values during the wet season (July - December), whereas they are lower and achieve minimum values in the dry season (January - June) (Figure 5). Seasonal variability in pCO₂ may result from changes in residence time, or, more likely, episodes of wetting and drying of the vadose zone. During the wet season, a more saturated vadose zone would limit ventilation and degassing whereas drawdown of
porewater in the dry season could promote airflow through fracture or vug systems, thus increasing ventilation and degassing.

At Flatman and Station,1 recharge events during the wet season correspond to moderate increases in theoretical pCO₂. This positive correlation between drip rates and increased pCO₂ can possibly be explained by increased transportation of decaying of organic matter into the vadose zone or increased rates of root respiration during the wet season. The less-efficient, smaller flow paths (whether being fracture-fissure or fissure network dominated) are more likely to fill easily in the wet season to decrease the effects of ventilation, limit degassing, and facilitate higher dripwater pCO₂ than in the dry season. Furthermore, the lower and reduced seasonal variability in drip rates at Flatman and Station 1 essentially suggest they are recharged by less-efficient flow paths, which may also be less susceptible to the air exchange and the transitions between the wetting and drying cycles.

**Controls on Ventilation**

There are many mechanisms that drive ventilation in caves and connected air-filled pore spaces in the vadose zone. Ventilation of Jinapsan Cave occurs primarily via barometric wind-induced ventilation. As noted by Noronha et al. (2017), changes in the carbonate chemistry appear to relate to the seasonal trade winds. The drop-in cave air pCO₂ was related to windy conditions, which in turn are strongly correlated to variations of Ca^{2+} within the dripwaters. Similar wind-driven cave air exchange has been reported by Kowalczk & Froelich (2010).
Gradients in barometric pressure associated with temperature changes can also drive ventilation of single entrance caves (James et al., 2015). As surface temperature drops, outside air becomes denser than warmer air in the cave, causing outside air to flow into the cave (Figure 12A); the opposite occurs when the temperature increases and there is no exchange of air with the atmosphere (Figure 12B) (Kowalczk & Froelich, 2010; James et al., 2015). For example, in temperate and subtropical climates the temperature changes occurring during the various seasons (winter, spring, fall, and summer) are the main cause for seasonal density stratification or ventilation of single-entrance cave. However, in the tropics there is no seasonal cycle because the diurnal temperature and air density differences are generally about the same magnitude as seasonal variability, resulting in diurnal ventilation (James et al., 2015). Nonetheless, if there are periods of time when temperature does not change, one would expect air stagnation to occur.
Figure 12. Simplified model representing the differences in air densities between the atmosphere and single entrance cave. (A) When the outside temperature decreases, the air density will increase as compared to the cave and there is the exchange of cave air with the atmosphere. The black arrows show outside air flowing into the cave and the red arrows depict the air leaving the cave. The flux of denser air will dilute the CO$_2$ in the cave. (B) When the outside temperature increases, the air density will decrease as compared to the cave and there is no exchange between the atmosphere and cave air. CO$_2$ concentrations will increase as gas from non-cave portions accumulates in the cave (as depicted by blue arrows).
Differences in pCO2 between Telogenetic and Eogenetic Karst Aquifers

The high temperatures of the tropics, dense vegetation, and high flux of carbon into the soil and vadose zone are expected to produce higher pCO2 compared to colder and temperate regions (Brook et al., 1983). However, in Jinapsan Cave, the theoretical pCO2 of dripwaters is comparable to, and/or lower than, pCO2 in telogenetic karst aquifers, which are mostly in colder climates (Figure 10). I propose that the cause of this surprisingly lower theoretical pCO2 is due to differences in porosity structure of telogenetic and eogenetic limestone. Telogenetic limestone has low matrix porosity and permeability. Consequently, flow of water and air through the epikarst and vadose zone is limited to a few dominant fractures and conduits (Vacher & Mylroie, 2002). In contrast, eogenetic limestone has high matrix porosity and permeability and consequently, water and air can flow through primary porosity, touching-vugs, fractures, and conduits (Vacher & Mylroie, 2002). Differences in porosity structure may affect vadose pCO2 because of volumetric disparities between the two limestones. In telogenetic limestone, respired CO2 can only accumulate in a reservoir within the dimensions of the fracture (Figure 13A). Therefore, the dispersal of dissolved organic matter and subsequent oxidation may be limited and more concentrated through fewer fractures. In contrast, the flux of DOC and CO2 gas can accumulate in both fracture and matrix porosity in eogenetic limestone, which creates a much larger reservoir (Figure 13B). Therefore, if an equivalent amount of DOC is oxidized in both systems, the resulting pCO2 would be higher in telogenetic limestone because the system volume is lower relative to eogenetic limestone.
Figure 13. Diagram showing different scenarios under which meteoric water flow through distinct matrix porosities. (A) Percolating water moving through a telogenetic aquifer. Fractures (depicted in black) facilitate the transfer of water from the surface into the cave, and dripwater into the cave are depicted by the blue arrows (B) Dripwater originating from eogenetic aquifer. Higher matrix porosity and permeability resulting in lower pCO₂.
CONCLUSIONS

This study examines dynamics of CO₂ in the deep vadose zone of Jinapsan Cave, Guam. Theoretical pCO₂ of dripwater ranged from 10⁻².8 to 10⁻¹.8 atm at three drip sites, with theoretical pCO₂ decreasing with distance from the cave only entrance. The lower theoretical pCO₂ values farther away from the opening suggest that ventilation of the cave via the entrance is not the primary control on pCO₂. Differences in theoretical pCO₂ and seasonality are caused by variations of flow paths through the vadose zone, recharge response, and residence times in the matrix.

The theoretical pCO₂ values from Jinapsan Cave drip sites are significantly less compared to other studies of pCO₂ in telogenetic limestone environments. The lower theoretical pCO₂ values suggest that the vadose CO₂ in eogenetic limestone is more easily ventilated.

Future studies can examine the pCO₂ from the other drip sites within the multiple rooms of the cave to better understand the flow routes, sources and variation of pCO₂ within this complex cave.
REFERENCES


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APPENDIX B:

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Sketch showing the location, estimated talus and bedrock thickness above the drip sites and the average theoretical pCO₂ for 3 drip sites in Jinapsan Cave (From “Vadose Hydrology at Jinapsan Cave, Northern Guam. Water and Environmental Research Institute. Technical Report 163”, Bautista et al., 2018).

Kaylyn K. Bautista <kaylynk@gmail.com>  Mon, Mar 11, 2019 at 8:33 PM
To: Jamar Regis <jregis@mail.usf.edu>
Hi Jamar,
Thanks for your email. Sure, feel free to use the figures from my tech report. Best of luck!
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