CAVE AIR CO₂ MONITORING IN SHENQI CAVE, SOUTHWEST CHINA

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Abstract
Monthly in situ monitoring of cave air CO₂ and drip water chemistry were carried out in Shenqi Cave, Sichuan, southwest China, during a hydrological year from April 2016 to December 2016. Results indicate that the cave temperature (~11.7°C) and relative humidity (~100%) were stable during the whole year. The air CH₄ concentrations changed from ~2000ppb outside the cave to ~500ppb inside the cave. The average CO₂ concentrations varied from ~550ppm in winter to ~1200ppm in summer, with their δ¹³C values from ~ −15‰ to ~ −21‰, indicating the influences of seasonal biologic activities and cave ventilation caused by climate change.

Introduction
Over the last few decades, speleothem paleoclimate records increased significantly in number and hind-casting value (Henderson, 2006). Precise ²³⁰Th/U dating and single or multi-proxy geochemical approaches allow for detailed paleoclimate reconstructions (Fairchild and Baker, 2012; Cheng et al., 2013; Tan et al., 2019). A wide range of processes in soil, epikarst and karst zone, as well as fractionation dynamics, can alter proxy data. To gain a better and quantitative understanding of the processes involved, sophisticated monitoring programs have been established (e.g., Bögli, 1978; Fairchild and Baker, 2012). During the cave process, CO₂ plays an important role on the degree of carbonate supersaturation of the dripwater and water supply, as well as the fractionation and incorporation of isotopic and elemental signatures in speleothems (Frisia et al., 2000, 2011; Spotl et al., 2005; Lechleitner et al., 2016; Pu et al., 2016). Thus, recording cave air pCO₂ is critical for those interested in assessing speleothem precipitation behavior and proxy dynamics. However, there are few studies that trace the generation and dispersal of CO₂ in deep karst systems, e.g., as a gas and in dissolved form within a linked system comprising soil, caves and the vadose zone.

Generally, the rainwater infiltrating the soil zone absorbs plant-and microbial-derived CO₂ and constitutes a main source for CO₂ in caves. Carbonic acid is produced in the soil and subsoil, dissociates to bicarbonate, and is transported into the cave via fissures, fractures, and pore-space of the host rock. Low cave air pCO₂ values, relative to the pCO₂ of the dripwater, facilitate CO₂ degassing, with higher CO₂ gradients, leading to higher precipitation rates of calcium carbonate polymorphs (Bögli, 1978; Fairchild and Baker, 2012). Another source of cave air CO₂ is from the ground air, which exists in gaseous form in the karst vadose zone and is transported into the cave system via fissures, fractures, and pore-space of the rock. More recent studies revealed that ground air is most likely the main source of cave air CO₂ rather than soil air (e.g., Mattey et al., 2016; Baldini et al., 2018). CO₂ ground air is produced by microbial oxidation of organic matter in infiltrating water, as revealed by radiocarbon measurements, hint-
80% occurring during the monsoon season (late May to October, data from Leshan station, 95 km northeast Shenqi cave, during 1951 to 2013 AD). Modern vegetation above the cave is composed of evergreen broad-leaved shrub and forest. Spatial correlation analysis indicates that rainfall variations around the area of Shenqi cave are positively correlated with those in southwestern China, especially in the southeastern TP (Figure 1) (Tan et al., 2018).

Seven drip-site monitoring stations with glass plates were placed on the floor of the main chamber of the cave on CO₂ derived from the decay of old carbon and elevated δ¹³C CO₂ values (e.g., Noronha et al., 2015; Mattey et al., 2016). Pools in cave or subterrain river, biological productivity in the cave, and hydrothermal CO₂ can also act as additional CO₂ sources for cave air CO₂ (Fairchild and Baker, 2012). Thus, a proper understanding of the causes and dynamics of seasonality in cave air CO₂ is fundamental for climate proxies of speleothems (Fairchild and Baker, 2012).

Cave air carbon dioxide partial pressure (pCO₂) depends on the CO₂ productivity of its sources, and cave ventilation (Fairchild and Baker, 2012; Lechleitner et al., 2016), which influence speleothem isotope composition and growth dynamics as well as concentrations of carbonates. Ventilation can be influenced by very different physical mechanisms: cave breathing, with air pressure differences driving air exchange, wind-induced air flow, chimney circulation, convection, either forced or free, due to differences in air density and water-induced air flow (Fairchild and Baker, 2012). These processes can act from hourly to multi-annual timescales (Fairchild and Baker, 2012). However, microclimate monitoring in caves is rarely conducted by cave air pCO₂ and δ¹³C of cave air together. Here, we present results from a one-year and monthly resolved monitoring of cave air pCO₂, air temperature and δ¹³C of cave air in the Shenqi Cave System.

**Study Area and Methods**

Shenqi cave (28°56′ N, 103°06′ E, 1407 m above sea level) is located 37 km southwest of Ebian county, Sichuan, China on the southeast margin of the Tibetan Plateau (TP). The cave, formed in Triassic dolomitic limestone, has a small entrance of 3 by 4 meters, with its total length exceeds 400 m (Tan et al., 2018). An underground river was developed in the cave along with the main passage (Figure 1). Monitoring results during September 2014 and October 2016 show stable temperature and relative humidity inside the cave, comparing with large variations of temperature and relative humidity outside the cave on diurnal-to-seasonal-timescales (Figure 2). The temperature and relative humidity inside the cave were continuously measured every two-hours by using a HOBO U23 Pro v2 Temperature/RH data logger suspended on cave floor. The average temperature inside the cave is around ~11.7°C, slightly lower than the annual temperature outside the cave (12.8°C). Relative humidity inside the cave maintains ~100% all year around. Abundant modern and fossil speleothems formed in the cave. The annual precipitation is 1290 mm with more than

![Figure 1. Plan view of Shenqi cave. The red circles indicate monitoring sites (Tan et al., 2018).](image1)

![Figure 2. (A) Temperature and (B) relative humidity variations inside (blue) and outside (red) Shenqi cave during September 2014–October 2016. The monitoring interval is two hours. Results reveal a stable temperature and relative humidity inside the cave on diurnal-to-seasonal-timescales comparing with those outside the cave (Tan et al., 2018).](image2)
The pH and EC of the 10 ml sub-sample were measured in situ immediately, using a HACH HQ340d multi-parameter meter (±0.01 pH units). The glass tip of the pH probe is very small (micro pH meter) and sensitive to pH changes; when immersed in about 3–5 drips it can measure the pH value and record it. The 100 mL sample was immediately divided into two sub-samples of 50 mL. The drip-water and cave-air were sampled per double months in 50 ml vials and 5 L airbags, respectively. Both of the containers were completely filled and kept sealed until measuring. The CO₂ concentration and δ¹³C value of atmospheric samples in this paper were measured using a Picarro G2131-I carbon isotope analyzer with a measurement accuracy of <0.1 ‰.

**Results and Discussion**

Gases in soil, caves, and space of the vadose zone as well as atmospheric air are diffused into the cave by seasonal ventilation. Karstic vadose zone are generally enriched in CO₂ relative to open atmosphere. The abundance and isotopic compositions of CO₂ in cave environments are primarily controlled by the mixing between a CO₂-rich ground air component and background atmospheric air diffused into the cave by seasonal ventilation (e.g., Fairchild and Baker, 2012; Mattey et al., 2016).

Larger pCO₂ differences between drip water and cave air results in faster degassing and higher calcite deposition rates. Variations in cave air CO₂ concentrations are a balance of the flux from the epikarst and exchange with the outside atmosphere. Site-specific time series investigations are necessary to decipher these relationships and further the understanding of climate effects on calcite growth and isotopic compositions. Temperatures outside and inside the cave are also strongly seasonal. Monitoring results show that temperature plays a key role in controlling cave air pCO₂ by changing the ventilation modes during winter and summer. We have compiled a representative collection of Shenqi cave air pCO₂ and carbon isotopic composition (δ¹³C) (based on 7 different sites (Figure 1)). The average CO₂ concentrations in Shenqi cave varied from ~550 ppm in winter to ~1200 ppm in summer, with their δ¹³C values from ~ −15‰ to ~ −21‰ (Figure 3d), and the low pH values of cave water (including drip water and underground water) in summer confirmed this cave air pCO₂ variability (Figure 4). As shown in Figure 4, the drip water sites have higher pH value than the underground river and pool water. After dissolving limestone bedrock, the seepage water get more Ca₂⁺ and HCO₃⁻, resulting in higher pH values in drippaters. Consistent with previous studies (Baldini et al., 2018; Mattey et al., 2016; James et al., 2015), it suggests variable mixing of different components of CO₂ sources, e.g., one with lower pCO₂ and higher δ¹³C (around ~ −11‰) (Figure 3d) and the other with substantially elevated pCO₂ and lower (but locally variable) δ¹³C values (around ~ −19‰) (Figure 3a, b, and c). The first component was influenced by atmospheric CO₂, while the second one was dominated by plant-and microbial-derived CO₂ in soil air pCO₂, degassing during calcite precipitation and the decay of old carbon (Mattey et al., 2016). The CH₄ concentration outside Shenqi cave is ~2000 ppm, which is very similar to the latest atmosphere CH₄ data (~1800) from the National Oceanic and Atmospheric Administration (NOAA). The CH₄ concentration inside the cave is ~500 ppb, suggesting less influence of the atmosphere and a relative stable environment inside the cave.

Previous studies suggest high CO₂ concentration in unsaturated zone (Baldini et al., 2018; Mattey et al., 2016; James et al., 2015). If the second reservoir of cave air CO₂ is from soil air, the δ¹³C would reflect photosyn-
thetic pathway of the vegetation overlying different monitoring sites (e.g., between −22 and −25‰ VPDB for C₃ vegetation and between −10 and −15‰ VPDB for C₄ vegetation) (Baldini et al., 2018). The cave air δ¹³C have values between −15 and −21‰, reflecting a mixing of C₃ and C₄ vegetation outside the cave.

Higher temperature and monsoon rainfall during summer and autumn enhance the vegetation density and microbial activities outside the cave, producing more CO₂ with lower δ¹³C values, causing depleted δ¹³C of air inside Shenqi cave. In contrast, lower temperature and rainfall during winter and spring reduce the vegetation density and microbial activities outside the cave, producing less CO₂ with higher δ¹³C values, resulting in increased δ¹³C of air inside Shenqi cave. In addition, enhanced ventilation during dry season may also dilute the CO₂ concentration and enhance the δ¹³C values inside the cave (Tan et al., 2015 and reference therein).

**Conclusion**

Monitoring results indicate the air CH₄ concentrations change from ~2000 ppb outside the cave to ~500 ppb inside the cave. The average CO₂ concentrations varied from ~550 ppm in winter to ~1200 ppm in summer, with their δ¹³C values from ~−15‰ to ~−21‰, indicating influences of seasonal biologic activities and cave ventilation caused by climate change. In addition, the pH values were higher in winter and lower in summer.

**References**


