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 fraction-

ation 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 *p*CO₂ 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 *p*CO₂ values, relative to the *p*CO₂ 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., Matthey 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-

ing on CO_2 derived from the decay of old carbon and elevated $\delta^{13}\text{C}_{\text{CO}_2}$ values (e.g., Noronha et al., 2015; Matthey et al., 2016). Pools in cave or subterranean river, biological productivity in the cave, and hydrothermal CO_2 can also act as additional CO_2 sources for cave air CO_2 (Fairchild and Baker, 2012). Thus, a proper understanding of the causes and dynamics of seasonality in cave air CO_2 is fundamental for climate proxies of speleothems (Fairchild and Baker, 2012).

Cave air carbon dioxide partial pressure ($p\text{CO}_2$) depends on the CO_2 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 $p\text{CO}_2$ and $\delta^{13}\text{C}$ of cave air together. Here, we present results from a one-year and monthly resolved monitoring of cave air $p\text{CO}_2$, air temperature and $\delta^{13}\text{C}$ of cave air in the Shenqi Cave System.

Study Area and Methods

Shenqi cave ($28^\circ56' \text{N}$, $103^\circ06' \text{E}$, 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 $\sim 11.7^\circ\text{C}$, slightly lower than the annual temperature outside the cave (12.8°C). Relative humidity inside the cave maintains $\sim 100\%$ 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).

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

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).

(Figure 1). 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 CO_2 concentration and $\delta^{13}\text{C}$ 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 CO_2 relative to open atmosphere. The abundance and isotopic compositions of CO_2 in cave environments are primarily controlled by the mixing between a CO_2 -rich ground air component and background atmospheric air diffused into the cave by seasonal ventilation (e.g., Fairchild and Baker, 2012; Matthey et al., 2016).

Larger $p\text{CO}_2$ differences between drip water and cave air results in faster degassing and higher calcite deposition rates. Variations in cave air CO_2 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 $p\text{CO}_2$ by changing the ventilation modes during winter and summer. We have compiled a representative collection of Shenqi cave air $p\text{CO}_2$ and carbon isotopic composition ($\delta^{13}\text{C}$) (based on 7 different sites (Figure 1)). The average CO_2 concentrations in Shenqi cave varied from ~ 550 ppm in winter to ~ 1200 ppm in summer, with their $\delta^{13}\text{C}$ 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 $p\text{CO}_2$ 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 Ca_{2+} and HCO_3^- , resulting in higher pH values in dripwaters. Consistent with previous studies (Baldini et al., 2018; Matthey et al., 2016; James et al., 2015), it suggests variable mixing of different components of CO_2 sources, e.g., one with lower $p\text{CO}_2$ and higher $\delta^{13}\text{C}$ (around ~ -11 ‰) (Figure 3d) and the other with substantially elevated $p\text{CO}_2$ and lower (but locally variable) $\delta^{13}\text{C}$ values (around ~ -19 ‰) (Figure 3a, b, and c). The first component was influenced by atmospheric CO_2 , while the second one was dominated by plant-and microbial-derived CO_2 in soil air $p\text{CO}_2$, degassing during calcite precipitation and the decay of old carbon (Matthey et al., 2016). The CH_4 concentration outside Shenqi cave is ~ 2000 ppm, which is very similar to the latest atmosphere CH_4 data (~ 1800) from the National Oceanic and Atmospheric Administration (NOAA). The CH_4 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 CO_2 concentration in unsaturated zone (Baldini et al., 2018; Matthey et al., 2016; James et al., 2015). If the second reservoir of cave air CO_2 is from soil air, the $\delta^{13}\text{C}$ would reflect photosyn-

Figure 3. Summary of $p\text{CO}_2$ monitoring and carbon isotopic composition of CO_2 collected from May 2016 to December 2016 in Shenqi caves. We only show monitoring sites 2# (a), 5# (b), 7# (c) site and 11# (outside the cave, d). The others are similar, but monitoring times are shorter.

Figure 4. Monthly total pH of drip water, pool water and underground river from April 2016 to Dec. 2016. The gray area has shown the summer half year with relatively lower pH values.

thetic pathway of the vegetation overlying different monitoring sites (e.g., between -22 and -25% VPDB for C_3 vegetation and between -10 and -15% VPDB for C_4 vegetation) (Baldini et al., 2018). The cave air $\delta^{13}C$ have values between -15 and -21% , reflecting a mixing of C_3 and C_4 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 CO_2 with lower $\delta^{13}C$ values, causing depleted $\delta^{13}C$ 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 CO_2 with higher $\delta^{13}C$ values, resulting in increased $\delta^{13}C$ of air inside Shenqi cave. In addition, enhanced ventilation during dry season may also dilute the CO_2 concentration and enhance the $\delta^{13}C$ values inside the cave (Tan et al., 2015 and reference therein).

Conclusion

Monitoring results indicate the air CH_4 concentrations change from ~ 2000 ppb outside the cave to ~ 500 ppb inside the cave. The average CO_2 concentrations varied from ~ 550 ppm in winter to ~ 1200 ppm in summer, with their $\delta^{13}C$ values from $\sim -15\%$ to $\sim -21\%$, 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.

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