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ORIGINAL ARTICLE

Drip water Geochemistry of Niah Great Cave, NW Borneo, Malaysia: a base line study

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Abstract A base line study was conducted to understand the geochemical variations of drip waters in Niah Great Cave, Sarawak, NW Borneo of Malaysia. Drip waters were collected at three different sites within the cave (D6: SW entrance enroute to painted Cave; D5: centre of the Great Cave, and D8: west mouth Great Cave entrance). The collected samples were analysed for temperature, pH, EC, major elements, non purgeable organic carbon, $\delta^{13}C$ and $\delta^{18}O$. Mg/Ca and Sr/Ca ratios, ionic strength, partial pressure of CO_2 and saturation indices of carbonate minerals have been used to dictate the geochemical signatures of drip water compositions. The data reveal a wide range of major ion chemistry at three different sites within the cave. The $\delta^{13}C$ values in drip waters range from −10.58 to −10.09 ‰. The enriched and the depleted $\delta^{13}C$ values are noted at the entrances of the cave due to degassing of water CO_2 and warmer air results in lighter fractions of $\delta^{13}C$. The $\delta^{18}O$ values range from −6.89 to –6.16 ‰. Minor $\delta^{18}O$ deviation in the drip waters are due to the variation in drip rates as faster drip rates show depleted isotopic composition and vice versa. The spatial variability of drip water chemistry results due to water–rock interaction at various conditions of subsurface flow path. This study gives a basis for interpreting the varying controls on drip water chemistry in the cave.

Keywords Drip water · Carbonate · Log pCO_2 · Mg/Ca and Sr/Ca · Isotopes · Niah Great Cave

Introduction

Cave drip water chemistry gains its own importance for interpreting the present day cave environmental condition to regulate the paleoclimate proxy-data extracted form speleothems composition (Baker et al. 1997). In karst environment, water chemistry can vary extremely over very short distances depending on the samples collected from an actively flowing conduit or from the rock matrix (Quinlan and Ewers 1985). Water chemistry can also be modified by CO_2 outgassing, mineral dissolution and/or precipitation along the subsurface flow paths (Holland et al. 1964; Dreybrodt 1981; Herman and Lorah 1986). During low flow condition, water composition shifts towards concentrated endmembers and in the high-flow condition it appears to be diluted by rapid infiltrating fresh water endmembers (Mayer 1999). Many studies have been conducted to understand the controls on the geochemical evolution and spatial variability of cave drip waters (Tooth and Fairchild 2003; Musgrove and Banner 2004; McDonald et al. 2007).

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Carbon isotopes in the cave system may indirectly indicate the vegetative change, climatic conditions and karst processes. Carbon isotope variations arise from a variety of causes such as soil respiration, fluid–rock interaction in the host limestone, degassing of CO_2 and precipitation of calcite upflow from the speleothem drip site and calcite precipitation at the drip site (Jimenez de Cisneros and Caballero 2011). According to Li et al. (2011) the Furong Cave located in Chongqing of China shows that the $\delta^{18}O$ (−11.5 to −8.2 ‰) and $\delta^{13}C$ (−2.6 to 0.1 ‰) values of the bedrock around the Cave might be of marine biological origin during Cambrian. The variable $\delta^{13}C$ values of active speleothem deposits from −11 to 0 ‰ could have been caused by kinetically mediated CO_2 degassing processes. Carbon isotopes in drip water are affected by both Carbon isotope composition of soil air and host rock carbonate. It also strongly depends on the calcite dissolution system, i.e. open, closed and intermediate conditions (Fohlmeister et al. 2011). Li et al. (2012) found that in 54 soil samples collected from five soil profiles, $\delta^{13}C$ of soil organic matters was −22 ‰, which could be attributed to the different transportation rates of stable carbon isotopes during the decomposition of plants and organic matters in soils. The average dissolved inorganic carbon $\delta^{13}C$ value was −11 ‰, about 11 ‰ heavier than the $\delta^{13}C$ of organic matters in soils, which proved that part of dissolved inorganic carbon in cave drip water was sourced from dissolution of inorganic carbonates. In Yuncheng Basin, China, $\delta^{13}C$ values in groundwater ranging from −16.4 to −8.2 ‰ indicate that carbonate weathering is a significant source of dissolved inorganic carbon (Currell and Cartwright 2011).

Oxygen isotopes are useful as a paleoclimate proxy and the oxygen isotope composition of meteoric precipitation can exhibit systematic variation depending on various processes: (1) ambient temperature at the time of precipitation, (2) the amount of precipitation, (3) storm paths, (4) the distance of a precipitation event from its moisture source region in the ocean and (5) the ground surface elevation where precipitation occurs (Clark and Fritz 1997; Ingraham 1998). The isotopic composition of drip-waters also reflects other variables including atmospheric inputs, evaporation, soil profiles and local hydrogeology. The isotopic differences in $\delta^{18}O$ between southern (−5.9 to −5.3 ‰) and northern groundwaters (−5.7 to −3.8 ‰) in Lakhssas Plateau, Morocco, are related to elevation that induced fractionation of oxygen isotope in recharge water that originated from coastal moisture (Ettayfi et al. 2012). It is also suggested that the high salinity in groundwater from the northern margin is related to the presence of schist rocks in these areas. The isotopic contents of groundwaters in the Souss Upstream Basin, southwestern Morocco, ranging from −8 to −5.2 ‰ for $\delta^{18}O$ and from −52 to −34 ‰ for δD reveals a significant infiltration from surface water and a major recharge directly from fractures in the crystalline and limestone formations (Dindane et al. 2003).

The Great Cave of Niah in Sarawak is a famous archaeological site because they are one of the few places in south-east Asia with evidence of continuous human occupation during the late Pleistocene and early Holocene (Barker et al. 2002a, b). In the past two decades, numerous scientists have emphasized the archaeological importance of Niah Cave and human revolution in Sarawak region. Particularly, Harrisson (1958, 1959a, b, 1965, 1996) has initiated the study about the prehistory and continually concentrated on different aspects like radiocarbon dating, archaeological study, ethnological study, Stone Age culture, etc. Barker et al. (2000, 2001, 2002a, b, 2003, 2007) and Barker (2005) have discussed the archaeology at Niah Cave and also his group has done four seasons' fieldwork at Niah to study the 'human revolution' in lowland tropical Southeast Asia. Barker and his group have also done a project on geomorphology of the Great Cave of Niah, Sarawak, as a part of the Niah Caves Project.

Gilbertson et al. (2005a, b) recorded the past human activity and geomorphological change in a guano-rich tropical cave mouth: initial interpretations of the Late Quaternary succession in the Great Cave of Niah, Sarawak. According to Hunt and Rushworth (2005a, b), influx of both sediment and pollen is controlled by two major factors: proximity to external wind-blown and wash transported inputs of silt, leaves and pollen and second, the strong patterned flux of guano in the interior of the cave. Hunt et al. (2007) has described stratigraphy, sedimentary and palynological evidence for changing environments at an area known as 'Hell Trench in the west mouth of the Great Cave of Niah. Dykes (2007) studied about mass movements in cave sediments by performing a geotechnical investigation of a 42,000-year-old guano mudflow inside the Cave. The physical, hydrological and geotechnical properties of the material were determined to assess the stability of the slope which led to the conclusion that the climate had been wetter than it is at present. These findings have implications for the interpretation of sediment deposits in other relict caves.

Gillmore et al. (2005) have attempted a study on potential risk from ^{222}radon posed to archaeologists and earth scientists in the Niah cave and suggested that the level of radon concentrations at the ground surface can exceed those of the surrounding area by a factor of >2×. This study also concluded that although radon concentrations in this famous cave are low by world standards, they may pose a health risk to both excavators and cave occupants to certain extent. Cobb et al. (2007) investigated the relationship between large-scale climate variability and rainfall along with cave drip water oxygen isotopic composition from Gunung Mulu and Gunung Buda National parks on intraseasonal to interannual timescales.

According to Bird et al. (2005), during the Last Glacial Maximum (LGM) in Borneo, offshore seawater temperature was about ~2 to 3 °C lower than that today, whereas air temperature was reduced by 6–7 °C. Also the estimated annual precipitation at LGM was reduced by about 30–50 % when compared with the present due to cooler annual air temperature which was associated with the reduction of precipitation (Kershaw et al. 2001; van der Kaars et al. 2000; Bird et al. 2005). Hunt et al. (2007) have discussed about biogeographical arguments, based on modern faunal distributions, and concluded that the 'coastal' lands of north and northwest Borneo, including Niah, may have remained amply humid during the late Pleistocene for lowland rainforest. Based on the above scenarios, there has been limited attempt to study the geochemistry of drip waters in Niah Great Cave. Hence, this study is a baseline attempt to understand few controls of drip water compositions in the cave.

Study area

Niah Great Cave is one of the largest documented caves in Sarawak, NW of Borneo, Malaysia, and is the key archaeological site in Southeast Asia. The main interest in the cave has been the populations of cave swiftlets and bats (Harrisson 1959, 1996; Rabett et al. 2006). It lies in dense wet low land rainforest at the northeast corner of the Gunong Subis (N3°480; E113°470) (Fig. 1), an isolated group of tower karst massifs, located 64 km SSW of Miri and 11 km inland from the coast of South China Sea. The Gunong Subis has been developed in the algal patch reef facies of the Subis Limestone Member of the Tangap Formation, of Miocene age (Wilford 1964; Hazebroek and Morshidi 2001). This formation consists of different rock types such as calcareous shale, marl, greenish claystone and pure limestone beds (Hutchinson 2005). Near the cave mouth, sedimentation is dominated by wind-blown silt and airfall pollen, whereas the interior of the cave dominated by highly organic matters and largely composed of bird droppings (Hunt and Rushworth 2005a). Stratigraphy of Late Quaternary sedimentary sequence exposed in the West Mouth of the cave has been explained by Gilbertson et al. 2005a, b; Stephens et al. 2005. The West Mouth sediments are derived from the results of airfall, wash, fluvial, colluvial and mudflow processes, with episodic ponding and drainage (Gilbertson et al. 2005a, b). In this cave, about 3,200 m of passages have been identified which includes chambers up to 100 m in diameter and 70 m high. The morphology of the cave passages, with Scallops features, is consistent with the cave being of phreatic origin (Hunt and Rushworth 2005a, b). At the same time, the cave has been modified by subaerial processes. The west mouth of the Great Cave is a vast cave entrance (60 m high and 180 m wide) that opens about 12 m up the cliff-like side of a bedrock-floored gorge, which separates the massif containing the Great Cave from the main massif of the Gunong Subis.

Climate and rainfall

The climate of Sarawak is warm and humid throughout the year. The mean annual temperature at sea level is about 27 °C with a lapse rate of 0.5–0.7 °C/100 m elevation. The annual rainfall varies considerably both between sites and at the same site in different years. Rainfall data have been collected from January 1983 to February 2012 in the study area (Niah Forest Office). The average annual rainfall is about 2,813.5 mm per year. Higher rainfall is recorded during the month of December and lesser in June (Fig. 2). The annual rainfall is observed above average value in the south, west and interior of the State, north subcoastal lowlands and east of the Temabu Range in the northeastern uplands. Due to the variability and unpredictability of the rainfall between years, there is an underlying seasonality in rainfall patterns. However, high rainfall is expected from November to February, with a drier period from June to August. Seasonality is much more pronounced in the coastal and western parts of the State than in the northern and interior regions. Dominant moisture sources for Sarawak during the winter monsoon are the tropical western Pacific Ocean and the South China Sea, whereas during the summer monsoon it is from the Indian Ocean (Aggarwal et al. 2004).

Methods and materials

In order to assess the spatial variability, three drip water samples were collected from different sites within the cave (D6: SW entrance enroute to painted Cave; D5: center of the Great Cave; and D8: west mouth Great Cave entrance) (Fig. 1) during July 2011. Drip water samples, D6 and D8, with fast dripping rates of ~20–50 drips per minute (dpm) and for slow dripping site (~5–15 dpm), D5, were collected from the fractures of cave ceiling. pH, temperature and Electrical conductivity (EC) were determined in situ using portable pH and conductivity meter (Thermo Scientific Orion Star, 4 Star Plus Meter). The samples were collected in 250 ml polyethylene bottles and kept at a temperature of 4 °C until analysis. The collected samples were filtered using a preconditioned plastic Millipore filter unit equipped with a 0.45-μm filter membrane for further elemental analysis. HCO_3 was analysed using titrimetry, and Ca, Mg,

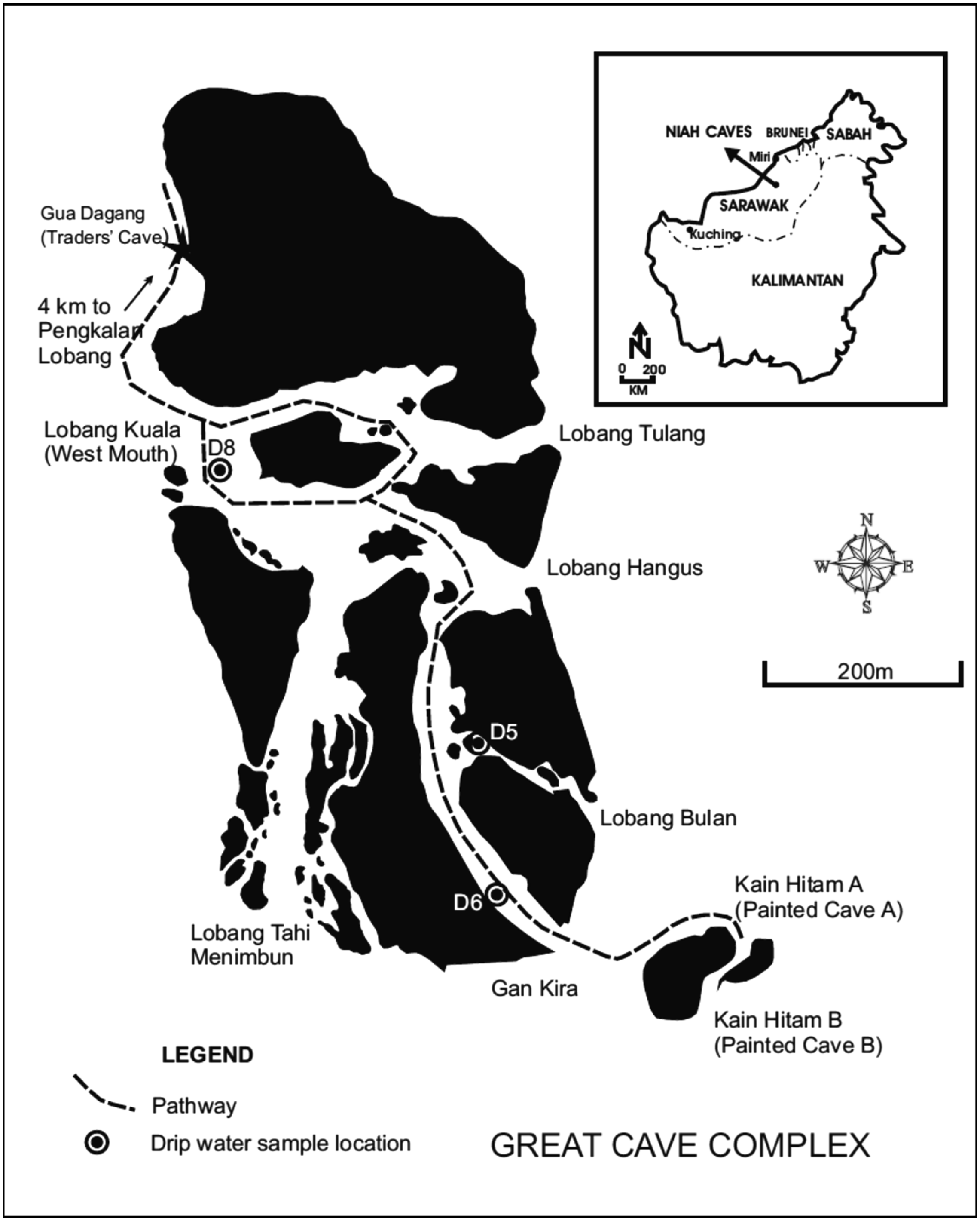


Fig. 1 Niah Great Cave with drip water sample sites

Na, K, Cl, SO_4 and Sr by the ion chromatograph (IC, Metrohm 861). Duplicate samples were analysed to check the analytical precision and it is ±5 % for all hydrogeochemical variables. Dissolved organic carbon (DOC) data were analysed as non-purgeable organic carbon (NPOC) performed by the "Total Organic Carbon Analyser TOC-VCSH" (Shimadzu Corporation). Ionic strength (IS), Carbon dioxide partial pressure (Log pCO_2) and saturation index (SI) of carbonate minerals were computed using the WATEQ4F (Hammarstrom et al. 2005).

X-ray diffraction (XRD) of the powder sample provides one of the easiest and semi- quantitative methods of identifying the minerals present in the rock samples. A representative powdered sample of bed rock (Limestone)

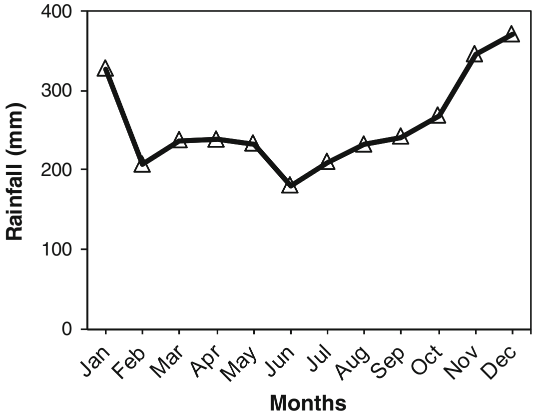


Fig. 2 Average monthly rainfall (collected from January 1983 to February 2012)

collected in the cave was subjected to X-ray diffraction with scan angle (2θ) ranging from 5 to 89°, using a Phillip X' Pert X-ray diffractometer.

For oxygen-18 isotope analysis, 25 ml of water samples were collected in airtight polyethylene bottles. The isotopic ratio was measured using Geo 20–20, Europa, mass spectrometer. For $^{18}O/^{16}O$ ratio measurement, 1 ml each of the water sample was flushed with 99.9 % pure CO_2 gas at 1 bar pressure in a 5-ml capacity vial for 1 min and equilibrated for 8 h at 50 °C temperature. The equilibrated CO_2 gas reflects the $^{18}O/^{16}O$ ratio of the water sample and the data acquisition system expresses the same ratio in permil (‰) variation with respect to an international standard, namely "Standard Mean Ocean Water" (SMOW). The results are expressed in δ values, which are in permil and are computed as follows: $\delta^{18}O = (R_{\text{sample}} - R_{\text{standard}}/R_{\text{standard}}) \times 10^3$, where $R = {}^{18}O/^{16}O$. For Carbon isotope analysis, 0.1 ml of saturated $HgCl_2$ solution was carefully added to the collected drip water samples to avoid algal growth. Then the $\delta\,^{13}C$ values were measured by isotope ratio mass spectrometer and given in ‰ with respect to PDB standard.

Results and discussion

Major ion chemistry

The concentrations of major dissolved constituents in the drip waters were quite variable at three different sampling points (Table 1). pH ranging from 6.65 to 6.92 shows near neutral in nature. EC ranges from 208 to 774 µS/cm and the higher value is noted in D8 (at the west mouth Great Cave entrance). The abundance of major ions are $Ca > Na > Mg > K = HCO_3 > SO_4 > Cl$ in D5 and D6 drip waters; $Ca > K > Na > Mg = HCO_3 > SO_4 > Cl$ in D8 drip water. In general, Ca and HCO_3 are the dominant cation and anion, respectively, in the drip water composition, which is almost similar to that of other few karst region cave waters (Langmuir 1971; Jacobson and Langmuir 1974; Poth 1977).

Nitrate in cave waters can be derived from biogenic sediments through various processes as detrital material transported from the surface, excrement or guano produced by animals inside the cave and secondary material formed inside the cave (Khanaqa and Al-Manmi 2011). In Niah Great Cave, higher concentration of nitrate (16.47 mg/L) was observed in D6, which can be derived from soil leachate by recently recharged waters. NO_3 is also derived from the degradation of organic matters present in the soil profile and also coated in the rock walls by bacterial action. This process was substantiated with the low Eh value observed in that location. Oxygen is the chief chemical species responsible for the Eh value in water. The increasing content of O_2 in water also increases the values of Eh. So the depletion of oxygen in D6 shows that oxygen was consumed by the bacteria during this process (Akinbile and Yusoff 2011).

Phosphate ranges from 0.25 to 2 mg/L and the concentration of phosphate in the drip waters may be derived from the leaching of authigenic phosphate minerals that originate from the degradation of organic matters in the cave (Hutchinson 1950; Karkanas 2001). Authigenic phosphate minerals are good indicators of prior accumulation of phosphate-rich organic matter and to identify certain activity in open-air sites (Shahack-Gross et al. 2004).

The hydrochemical data have been plotted in Piper plot (Piper 1953) and all the samples are representing in $Ca–HCO_3$ facies indicating recharged waters (Fig. 3). This type of water results from the dissolution of calcium-rich minerals such as calcite by water–rock interaction process (Freeze and Cherry 1979). The minerals present in the bed rock of Niah Cave were identified with semi-quantitative method (XRD) also reflecting the presence of large amount of Calcite with a significant high peak of Rhombohedral Calcite (Fig. 4). The other peak visible is that of Magnesite, Dolomite and Aragonite, with lesser amount of Quartz and Smithsonite. Gibbs plot (Gibbs 1970) is also used to understand and differentiate the processes control the drip water chemistry. In the plot, all the three samples fall in the water–rock interaction field suggesting that the weathering of rocks primarily controls the ion chemistry of drip waters (Fig. 5) as the bed rock is chiefly composed of carbonate minerals.

Total dissolved ion (TDI)

Total dissolved ion is used to understand the extent of reaction with bedrock minerals and thus is a rough indicator

Table 1 Drip water chemistry data

Sample no	D5	D6	D8
Location	Center of the cave	Painted cave entrance	West mouth cave entrance
T (°C)	25.4	25.3	25.1
Drip rate (dpm)	~5–15	~20–50	~20–50
pH	6.65	6.92	6.8
EC (µS/cm)	400	207.6	774
Ca (mg/L)	77.33	45.16	139.49
Mg (mg/L)	0.38	0.02	0.47
Na (mg/L)	3.05	1.30	2.93
K (mg/L)	2.73	0.43	8.45
Cl (mg/L)	4.53	2.33	5.90
HCO_3 (mg/L)	73.20	85.40	73.20
SO_4 (mg/L)	10.13	2.47	7.93
PO_4 (mg/L)	1.739	0.251	2.076
NO_3 (mg/L)	BDL	16.479	0.3
Sr (mg/L)	11.2	16.05	6.5
TDI (mg/L)	173.09	153.83	240.73
NPOC (mg/L)	4.26	1.338	1.35
$\delta^{18}O$ (‰)	−6.16	−6.89	−6.64
$\delta^{13}C$ (‰)	−10.31	−10.09	−10.58
Mg/Ca (molar)	0.008081575	0.000657233	0.005556237
Sr/Ca (molar)	0.066247148	0.16256022	0.021315162
Ionic Strength	0.0052	0.0036	0.0083
Log pCO_2	−1.79	−1.99	−1.96
SI of Calcite	−1.01	−0.88	−0.65
SI of Aragonite	−1.15	−1.02	−0.79
SI of Dolomite	−4.52	−5.35	−3.97
SI of Magnesite	−3.55	−4.51	−3.35

of residence time of water in the aquifer matrix (Mayer 1999). Drip waters range from 153.83 to 240.73 mg/L TDI. Samples collected in the three sites are inconsistent in TDI values. Higher TDI concentration was observed in D8 and significantly more concentrated ions indicate longer residence time in the rock matrix (Fig. 6). Lower TDI value was noted in D6 with less ionic concentrations except bicarbonate due to the flushing environment.

Ionic strength (IS)

Ionic strength is a measure of total concentration of ions which emphasizes increased contribution of species with charges greater than one to solution non-ideality (Domenico and Schwartz 1990):

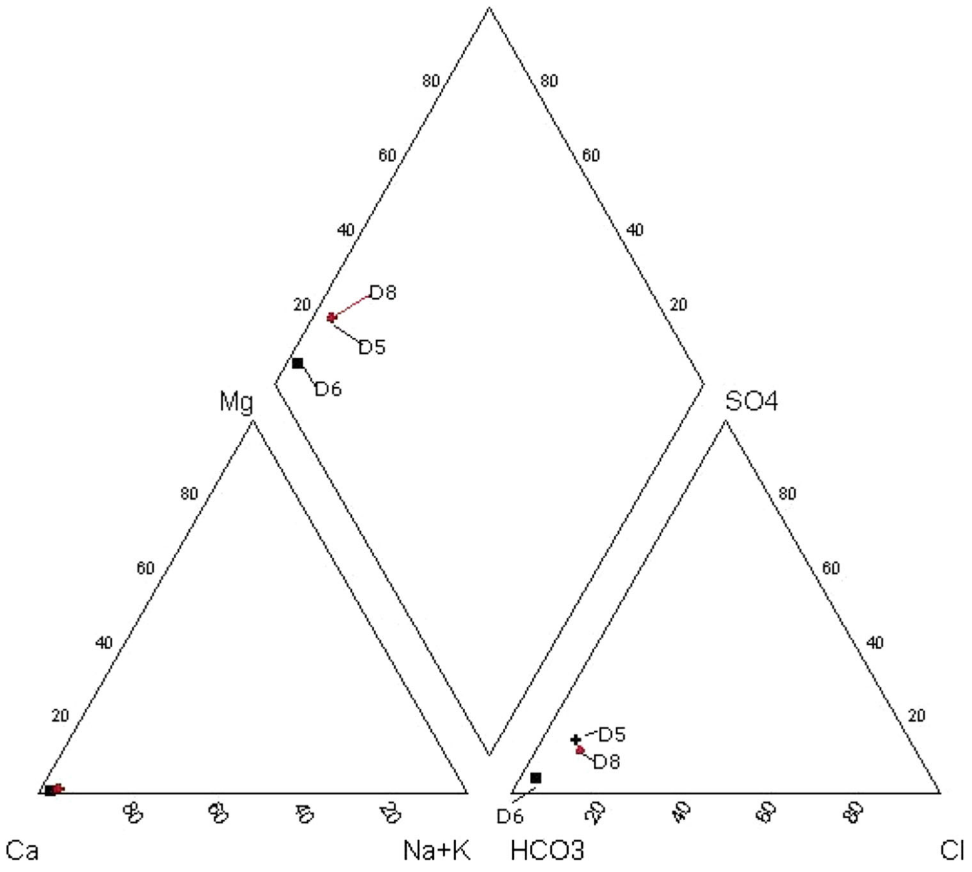
$$I = 0.5\Sigma m_1 z_1^2,$$

where m_1 is the atomic/molecular weight and z_1 is the valance of the respective ion. The approximate value of ionic strength can also be computed from the specific conductance of the solution if this has been measured (Lind 1970). Domenico and Schwartz (1990) reported that ionic strength of fresh water is <0.005. In the present study, D6 water shows lower ionic strength (Fig. 7) and indicates newly recharged water into the rock matrix, whereas D5 and D8 water has higher ionic strength and reveals longer residence time within the rock matrix with high concentration (Chidambaram et al. 2010; Prasanna et al. 2010).

Mg/Ca and Sr/Ca

The rate of water residence time states the amount of water–rock interaction that occurs, with drier intervals resulting in longer residence time, more extensive water–rock interaction and higher Mg/Ca and Sr/Ca (Musgrove and Banner 2004). There are many controls on drip water Mg/Ca and Sr/Ca which include compositional variations of soils and bedrocks, the type of flow paths, amount of water–rock interaction and variable extents of prior calcite precipitation (PCP) (Fairchild and Tremble 2009). The water–rock interaction and PCP are two different processes and the amount of water–rock interaction that occurs is largely dictated by variable water residence time, whereas prior calcite precipitation can be dominantly dictated by

Fig. 3 Piper plot for the drip waters



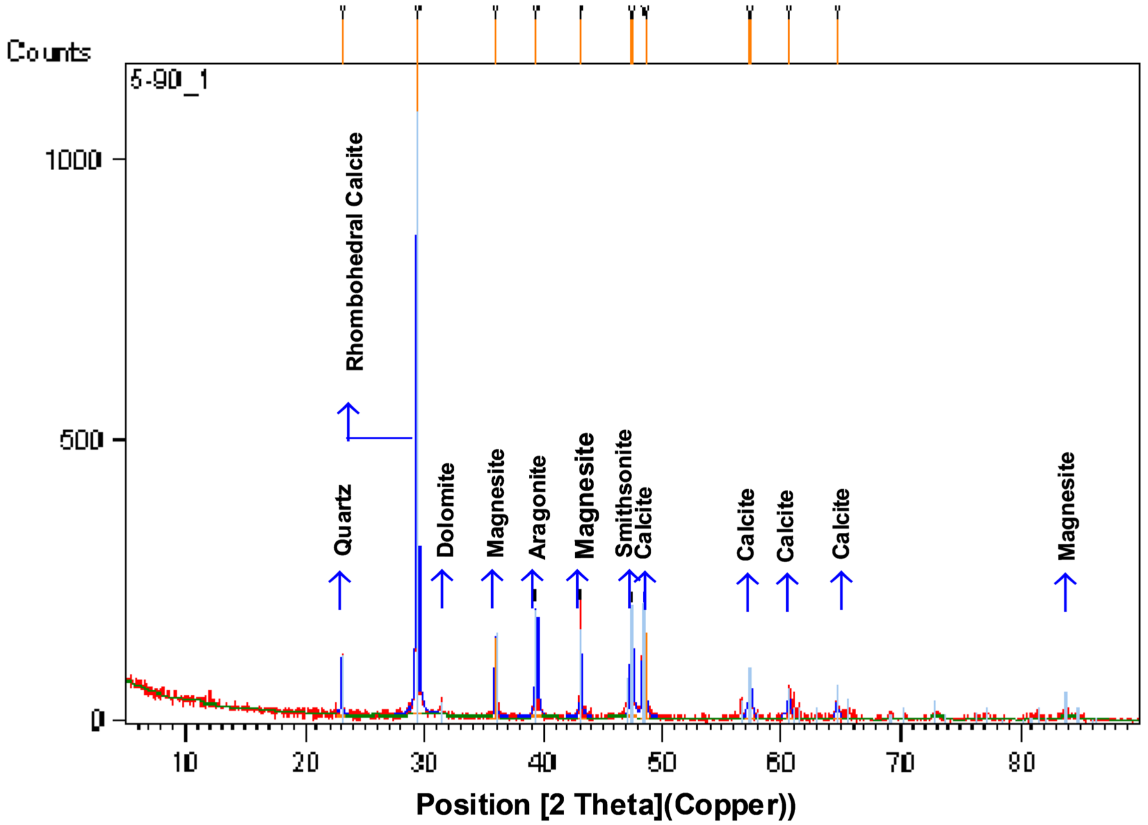


Fig. 4 XRD pattern of bed rock

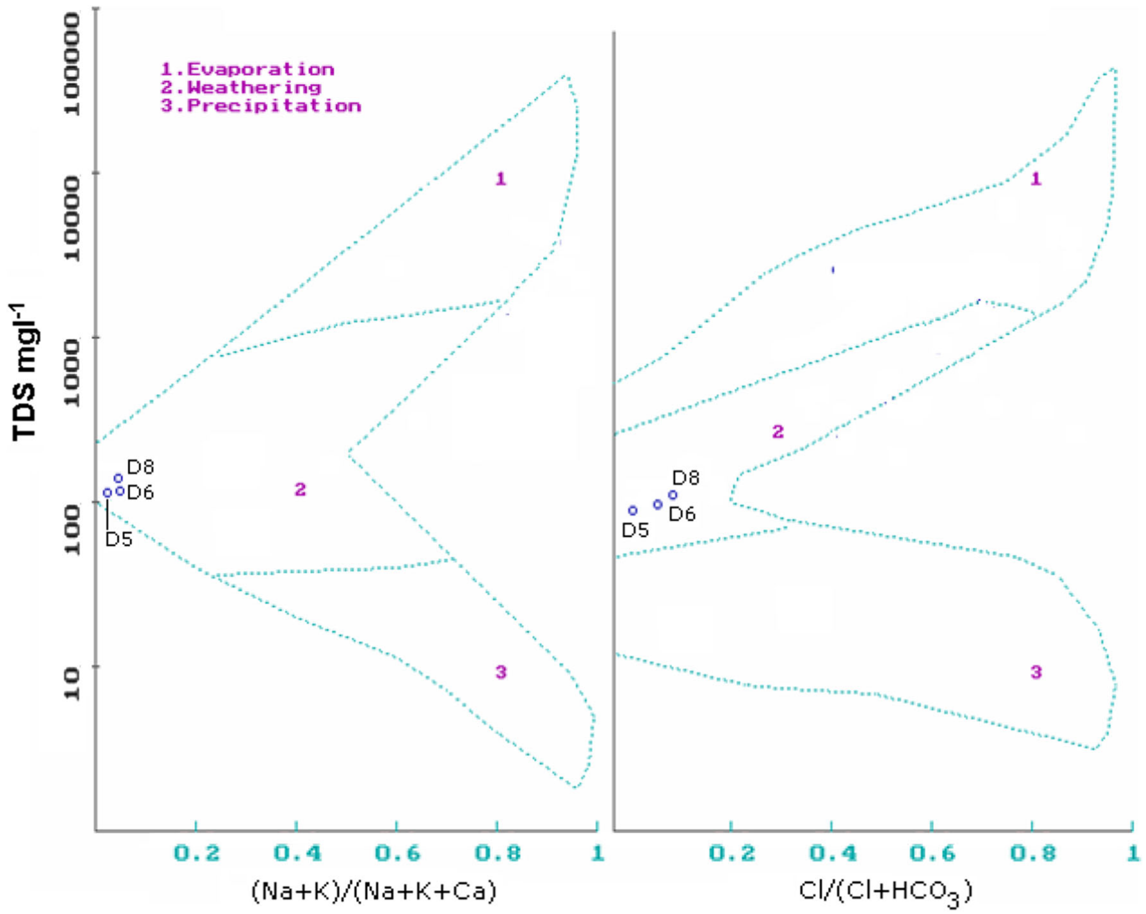


Fig. 5 Gibbs plot for the drip waters

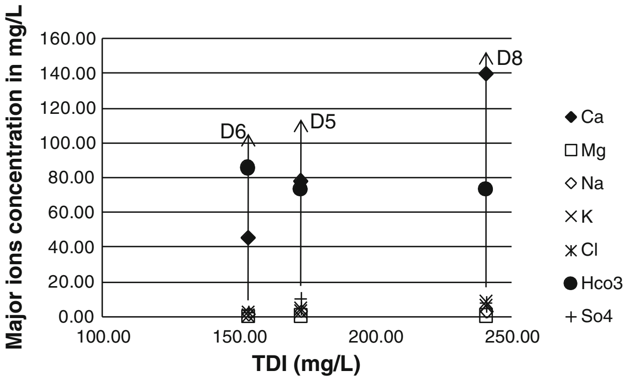


Fig. 6 Major ions vs. TDI concentrations

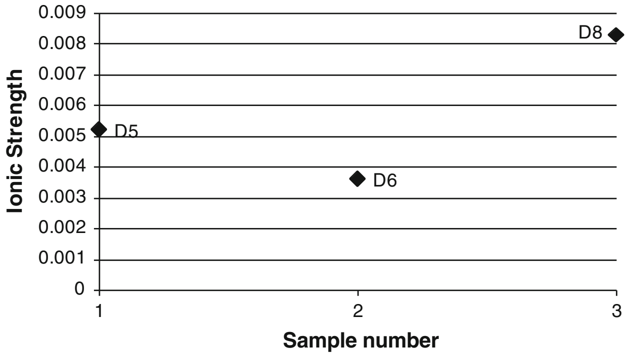


Fig. 7 Ionic strength of the drip waters

variable water residence time or ventilation of cave-air CO_2.

Drip water acquires the concentration of Mg and Sr from interaction with the soil and carbonate rocks that it moves through and attains higher Mg/Ca and Sr/Ca ratios (Musgrove and Banner 2004). Figure 8 in the present study reveals that D6 drip water has low Mg/Ca ratio and shows lesser water–rock interaction due to shorter residence time of water in the rock matrix, whereas D5 and D8 drip waters have higher Mg/Ca ratio and indicate relatively extensive water–rock interaction by longer residence time. The water–rock interaction curve in Fig. 9 demonstrating that D5, D6 and D8 drip waters experiences varying amounts of water–rock interaction. It is also shows good

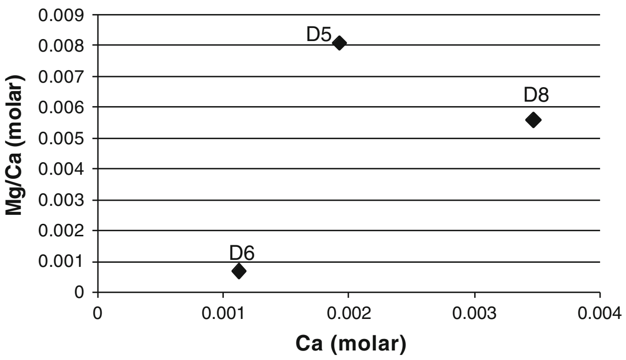


Fig. 8 Mg/Ca vs. Ca

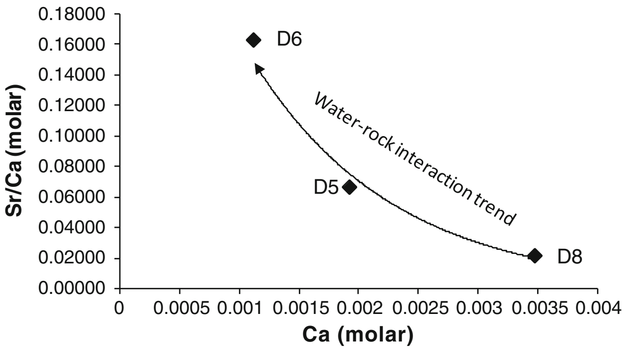


Fig. 9 Sr/Ca vs. Ca

correspondence with observed trends of increasing Sr/Ca with decreasing Ca, which is common in calcite dominant karst aquifers.

Log pCO_2

Log pCO_2 values of the waters depends on various factors: (1) primary pCO_2 of the infiltrating waters, which will be influenced by high pCO_2 in soil zones (Pitty 1971), (2) buffering of CO_2 in the aquifer (Atkinson 1977) and (3) degree of CO_2 degassing (Toran and Roman 2006). Ventilation effects may limit the pCO_2, particularly if there are large effluxes of CO_2 rich water into the cave (Barker et al. 2000). The log pCO_2 values range from −1.79 to −1.99 and individual samples show relatively significant variations in log pCO_2. These values are higher in comparison with average atmospheric log pCO_2 value of −3.5. The cave air pCO_2 values reveal the pattern of circulation and mixing in the cave. The pattern is also related to the cave ventilation. The lowest pCO_2 values were observed in D6 and D8 (Fig. 10), slightly lesser than the atmospheric value, revealing that the D6 water has just entered into the cave system or the residence time of this water in the rock matrix is considerably lesser or an open system substantiated by low TDI value. On the contrary, D8 water shows higher TDI value with lesser log pCO_2 resulting in the loss of CO_2 by degassing. The degassing possibly occurred along the fractures, cracks and fissures in the limestone leading to the near saturation of D8 water with respect to calcite.

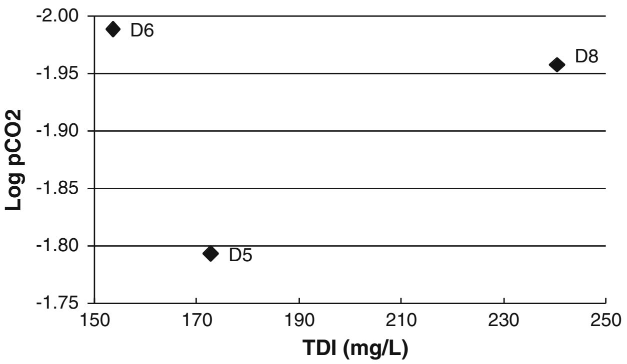


Fig. 10 Log pCO_2 vs. TDI

The fast moving conduit water would to be expected to be at under saturation, and slow moving matrix liquid is believed to be at saturation (Toran and Roman 2006). The present data give the details about the contribution of rock matrix and drip water. The possible explanation is that the recharged water (D6 and D8) picked up excess CO_2 over the atmospheric equilibrium value as it traveled through the soil profile above the cave. Subsequently, CO_2 out gassing occurred when the matrix water entered the conduit.

Higher pCO_2 value is noted in D5, the middle portion of the cave, because it is relatively shut off from the ventilation and does not experience as much air flow. This may also suggest that the additional CO_2 has been acquired from the soils/sediments caps above the cave during the process of infiltration through the fractures of the rocks.

Saturation Index of Carbonate minerals

To determine the chemical equilibrium between minerals and waters, saturation indices of carbonate minerals were calculated using the following equation (Lloyd and Heathcode 1985):

$$SI = \log(IAP/Ks),$$

where IAP is the ion activity product and Ks is the solubility product of the minerals.

The calculated values of SI for Calcite, Dolomite, Aragonite and Magnesite of the drip waters show that calcite and aragonite fall near saturation indicating precipitation (Fig. 11). The SI values of Dolomite and Magnesite fall under saturation showing dissolution effect (Prasanna et al. 2010). The out gassing of CO_2 drives the carbonates equilibrium towards more calcite precipitation (Toran and Roman 2006):

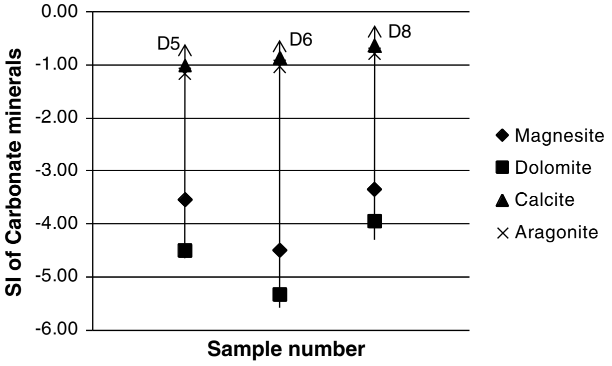


Fig. 11 SI of carbonate minerals in the drip waters

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \uparrow$$

Thus, bicarbonate is lost through the conversion of CO_2 and subsequent out gassing and pH must rise to maintain the charge balance. Another way to explain this balance is that a decrease in pCO_2 results in a decrease in H^+ [$pCO_2 = (aHCO_3 \times aH)/(K_{HCO3} \times Kco_2)$]. This pH increase further moves the reaction towards precipitation of calcite. However, out gassing occurs faster than $CaCO_3$ precipitation, which leads to oversaturation (Freeze and Cherry 1979). Particularly, precipitation of calcite does not tend to occur until the saturation index is above 0.5 (Dreybrodt et al. 1992; Lorah and Herman 1988).

The log pCO_2 versus SI of Calcite trend (Fig. 12) also supports the hypothesis that variations in out gassing are related to pathways and dissolution trends. D6 and D8 waters are closed to saturation and progressively decreasing in log pCO_2 values due to CO_2 out gassing. The out gassing exhibited a decrease in log pCO_2 value and increase in SI of Calcite, whereas D5 was under saturated condition.

The SI of Magnesite is greater than the SI of Dolomite indicating that only excess of Mg is contributed to the formation of Dolomite in association with Ca. Moreover, the XRD data show that the bed rock is chiefly represented by Calcite and the process of attaining saturation of Dolomite and Magnesite is limited due to the availability of Mg from Magnesite and Dolomite in bed rock.

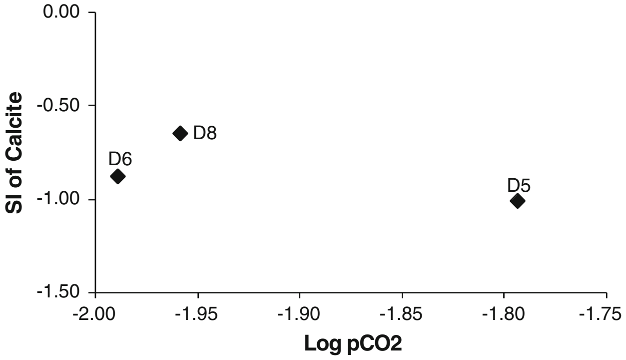


Fig. 12 Log pCO_2 vs. SI of Calcite

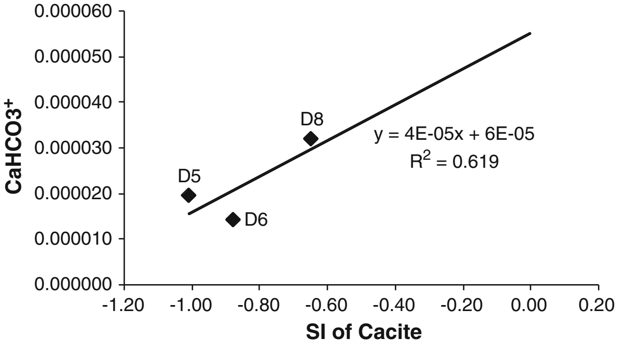


Fig. 13 $CaHCO_3^+$ vs. SI of Calcite

A mechanistic model for the precipitation of $CaCO_3$ proposed by Plummer et al. (1978) considers the reaction between bulk solution $CaHCO_3^+$ and crystal growth of Calcite. Figure 13 shows the relationship between calculated SI of Calcite and the activity of the $CaHCO_3^+$ species in solution. A linear relationship between SI of Calcite and $CaHCO_3^+$ suggests that $CaHCO_3^+$ has an active role in the precipitation of calcite.

DOC (NPOC)

The level of dissolved organic carbon (DOC), also known as non-purgeable organic carbon (NPOC), in natural environments is comparable to the inhibition of calcite precipitation (Inskeep and Bloom 1986). But most calcite precipitation models do not account for organic matter inhibition. The available model proposed by Lebron and Suarez (1996) predict the calcite precipitation rate in the presence of DOC; they found that when the DOC ≥ 0.05 mM, the precipitation rate is essentially independent of the surface area of the calcite and dependent on the DOC concentration. They also determined that the calcite crystals were coated with an amount of DOC necessary to avoid precipitation of calcite by crystal growth and added to the solutions.

In this present study, an attempt was made to know the capability of DOC in the drip waters to inhibit the calcite precipitation. Figure 14 shows a negative linear relationship between DOC and SI of Calcite suggesting that the decrease in precipitation of calcite with increasing DOC. Hence the precipitation rate of calcite as a function of the DOC in the study area as inferred in the previous studies (Lebron and Suarez 1996).

Comparison of drip-rate with speleothem growth

According to the model proposed by Dreybrodt (1988), it is complicated to link the temporal variations of pCO_2 between Ca concentration and saturation index, or between

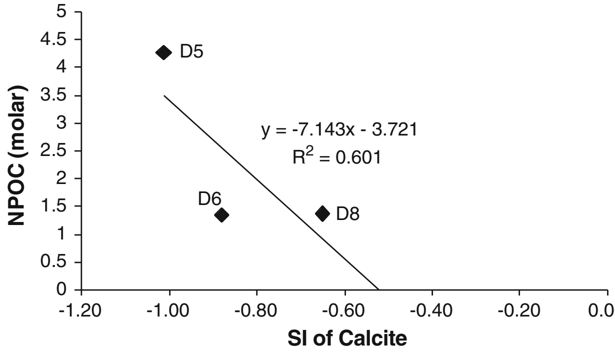


Fig. 14 NPOC vs. SI of Calcite

Ca concentration and predicted growth rate. But the effects of varying pCO_2 will enhance the variability of growth rate with time. In the present study, samples that were collected in late summer (July 2011) could be represented by relatively poorly speleothem growth, because of slow drip rates, high pCO_2 and comparatively lower Ca value observed at D5. Conversely, maximal growth rates reflecting high drip rate, low pCO_2 values and high Ca were noted in D6 and D8. This statement has also been substantiated with DOC concentration in the drip waters, where D5 has higher DOC value and indicates slow crystal growth and lower values in D6 and D8 lead to faster growth rate (Lebron and Suarez 1996).

Carbon isotope

The carbon isotopic composition in the drip waters shows only a small variation, ranging from −10.58 to −10.09 ‰ of $\delta^{13}C$. Environmental local processes such as evaporation and changes in cave air pCO_2 controlled by seasonal ventilation can influence the final $\delta^{13}C$ values. The CO_2-poor air, drawn into the cave through the entrance, enhances degassing of water CO_2 and causes concomitant $\delta^{13}C$ enriched carbonate deposition as noted in D6 (Spotl et al. 2005). D8 drip water has lighter fraction due to the reverse process as the air entering through D6 may pass through D5 and go out of the cave through D8 as observed in the field during the time of sampling. So the air coming out of the cave is warmer with slightly higher pCO_2 than D6, which results in lighter fractions of $\delta^{13}C$ (Fig. 15).

Diffuse water flow in karst aquifers would allow greater opportunity for interaction between the waters and the host limestone resulting in greater dolomite dissolution and calcite formation and there is a definite negative relationship noted between the $\delta^{13}C$ values and the SI of Dolomite. The SI increases with the decrease in $\delta^{13}C$ values. The enriched and the depleted $\delta^{13}C$ values are noted at the entrance of the caves. It is also interesting to note that the saturation index of dolomite has an inverse linear relationship to $\delta^{13}C$ (Fig. 16) than that of calcite.

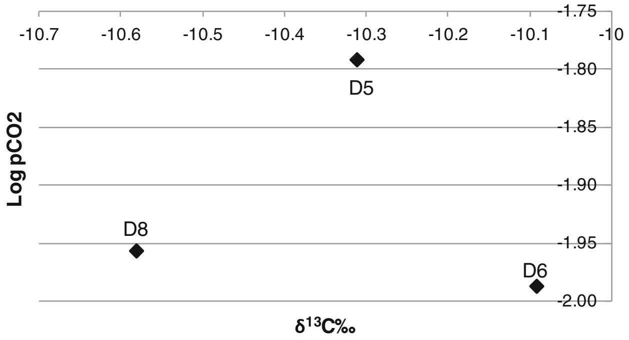


Fig. 15 $\delta^{13}C$ vs. Log pCO_2

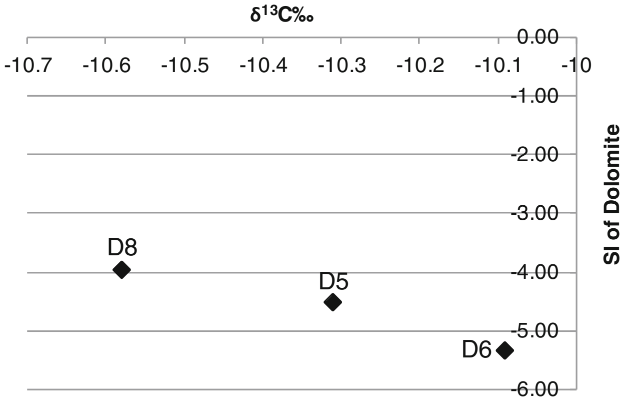


Fig. 16 $\delta^{13}C$ vs. SI of Dolomite

Oxygen isotope

The mean rainfall $\delta^{18}O$ value is −6.7 ± 2.8 ‰ in the northern Borneo region located near the study area (Cobb et al. 2007). The $\delta^{18}O$ values of drip waters in Niah Great Cave range from −6.89 to −6.16 ‰. This suggests that the oxygen isotopic composition of the supplying water into the cave reflects an average rainfall condition. Cave drip water oxygen isotope composition is interpreted here as an annual rainfall $\delta^{18}O$ signal as in Furong Cave of China (Li et al. 2011). The fact that the rainfall and drip water $\delta^{18}O$ has almost the same average value, which indirectly indicates that minimal evaporation occurs between the ground surface and the drip water site. The lighter values are noted in the entrance samples D6 and D8. The D5 may be enriched as it is located in the centre of the cave and may be due to the variation in the over burden thickness or due to water flow directions. But still minor isotopic variations are also noted due to the variation in drip rates, as faster drip rates show depleted isotopic composition and vice versa (Cobb et al. 2007).

The fast and slow drip rates were indistinguishable and match with the mean rainfall $\delta^{18}O$ value (−6.7 ± 2.8 ‰) in the nearby area (Cobb et al. 2007). The drip-rate is more responsive to specific recharge events than drip water $\delta^{18}O$, given that drip-rate is governed by instantaneous hydraulic pressure changes in the water flow pathway (Genty and Deflandre 1998; Baker and Brunsdon 2003), while drip water composition inferred to reflects a cumulative mixture of past rainfall events (Ayalon et al. 1998; Perrin et al. 2003; Cruz et al. 2005). Furthermore, the detailed investigation on drip rate, amount of rainfall, seasonal variation and humidity will help us to investigate the process responses for isotope fractionization and process governing the water chemistry of the Niah Great Cave.

Conclusions

This study reveals the geochemical variations between the drip waters collected from three different sites within the Niah Great Cave. Drip waters from the entrances of the cave shows considerably low ionic strength and lesser Log pCO_2 values indicate newly recharged water from the soil leachate, with lesser residence time in the rock matrix. Whereas the drip water collected at the center of the cave has derived from intense water–rock interaction, gets more concentrated during the low-flow condition. $CaHCO_3^+$ species in the drip waters were confirmed as the controlling mechanism of calcite precipitation. SI of Calcite and Aragonite are near saturated leading to precipitation, whereas SI of Dolomite and Magnesite are under saturation state due to dissolution. The higher concentration of DOC has also found to decrease the rate of calcite precipitation and added to the solutions. Possible geochemical processes have been identified by using the co-variation of Mg/Ca and Sr/Ca. D6 drip water composition is derived with lesser water–rock interaction, whereas D5 and D8 drip waters are dictated by extensive water–rock interaction due to longer residence time. The fractionation of drip water $\delta^{13}C$ depends on the degree of degassing of water CO_2 associated with cave air temperature. Inverse relationship between $\delta^{13}C$ and SI of Dolomite may results in greater dolomite dissolution and calcite formation due to water–rock interaction. Similar values of drip water $\delta^{18}O$ and average annual rainfall $\delta^{18}O$ indicates minimal evaporation. The lighter fractionation was observed in the entrance of the cave and enriched $\delta^{18}O$ in the centre of the cave due to the variation in the over burden thickness or due to water flow directions. Though there may be other factors controlling the drip water chemistry, which have to be studied in detail by increasing the number of parameters analysed and the number of sampling locations.

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