

# Stable Oxygen and Hydrogen Isotopes in Drip and Rain Waters at the Belum Cave, Andhra Pradesh, India

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**Abstract:** We report here the first  $\delta^{18}\text{O}$  and  $\delta\text{D}$  measurements of cave drip water collected during 2007–2009 and 2011 CE from the Belum Cave, peninsular India. Stalagmites found here have a great potential for providing monsoon reconstruction for hundreds of thousands of years. Rain samples were also collected from the top of the Belum Cave from May 2010 to Jan 2011 CE; their  $\delta^{18}\text{O}$  values indeed exhibit a significant negative correlation with the amount of rain recorded at a nearby (<10 km) meteorological station. Changes in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of drip water samples confirm that the cave drip water do respond to the amount-dependent isotopic changes in local precipitation. The  $d$ -excess values of the rain water samples shift from  $\sim 10\text{‰}$  during the initial phase to  $\sim 30\text{‰}$  during the final phase of the southwest monsoon, indicating varying humidity at the surface boundary layer of the Northern Indian Ocean, and also a significant mixing of evapo-transpired vapour with the incoming marine vapour in the latter phase.

**Keywords:** Belum cave; Drip water; Rainwater; Speleothem; Monsoon.

## Introduction

Much longer proxy records of temperature and precipitation than are available through instrumental records are needed to answer important questions, e.g. whether the current climate change is anthropogenic or it is a part of slow natural cycles (Hansen et al., 2012). Worldwide, numerous studies of speleothems have shown that the  $\delta^{18}\text{O}$  of these carbonate deposits serve as a proxy for variations of the local surface air temperature in the mid-to-high latitudes, and for precipitation in the tropics. The latter, the so-called ‘amount effect’ is an empirical relation (Dansgaard, 1964; Yurteswar and Gat, 1981; Rozanski et al., 1993; Frick and O’Neil, 1999) derived from a large number of

world-wide tropical precipitation samples: a significant negative correlation between the rain  $\delta^{18}\text{O}$  and the amount of monthly rain, the coefficient being  $-1.5\text{‰}$  per 100 mm of rain. However, there are a few reported exceptions, showing an absence of this effect in some places in the tropics (Breitenbach et al., 2010). Humidity at the cloud base is believed to determine the presence/absence of the amount effect (Frick and O’Neil, 1999; Lee and Fung, 2007).

Some factors could modify the amount effect present in the rain when it is recorded by speleothems. These include evaporation in the soil during recharge (Sheffer et al., 2011), prior calcite precipitation before the water drips from the roof of the cave (Oster et al., 2012; McDonald et al., 2007; Cruz et al., 2005) and natural

isotopic variations caused by seasonal differences in the oceanic moisture sources (Polk et al., 2012; Fuller et al., 2008; Matthey et al., 2008; Cobb et al., 2007; van Beynen and Febberollo, 2006). As these factors may vary geographically some sites may exhibit a weak or insignificant amount effect (Breitenbach et al., 2010). Hence, verification of the presence of amount effect in local precipitation and subsequent demonstration that such an effect is actually transferred to the cave drip water, and preserved in the speleothem carbonate, is necessary to robustly reconstruct past monsoon rainfall using speleothem (McDermott, 2004).

Generally, regions under the influence of the monsoons are those enclosed by the seasonal extreme positions of the Inter Tropical Convergence Zone from the equator. These are characterized by intense convective motion (Pant and Rupakumar, 1997) and are likely to exhibit amount effect (Dansgaard, 1964). In a typical situation where cloud masses travel inland, successive precipitation would be progressively depleted in  $^{18}\text{O}$ , and thus may show a strong regional amount effect (Polk et al., 2012; Lekshmy et al., 2014). Thickness and porosity of the overlying bedrock-soil cover above a cave and the size of hydrological pathways decide how fast each rain event percolates into the cave (Dar et al., 2014, 2011) before isotopic variations in the rain are damped due to evaporation at the soil surface and mixing.

Only a few high-resolution terrestrial monsoon proxy records from tree rings (Mangave et al., 2011) and speleothem (Yadava et al., 2004; Yadava and Ramesh, 2005; Sinha et al., 2007; Kotlia et al., 2012; Laskar et al., 2013) have been reported so far from Southern India (Ramesh et al., 2010). There has been no study of cave drip waters from anywhere in India to verify whether the drip water isotopic composition changes in consonance with that of the overhead precipitation (Williams and Fowler, 2002; Pape et al., 2010). Here we report for the first time,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of drip water collected from the Belum cave ( $15^{\circ}06'\text{N}$ ,  $78^{\circ}06'\text{E}$ ; 367 m above msl), located in the Cuddapah Basin of the Kurnool district, Andhra Pradesh, India (Figure 1); we explore if there are seasonal variations and the amount dependency in  $\delta^{18}\text{O}$  of drip water and local rain water, a pre-requisite for paleo-monsoon reconstruction. This region is well known for caves and speleothems from here are being used for past monsoon reconstruction (Narayana et al., 2014a, 2014b; Lone et al., 2014).

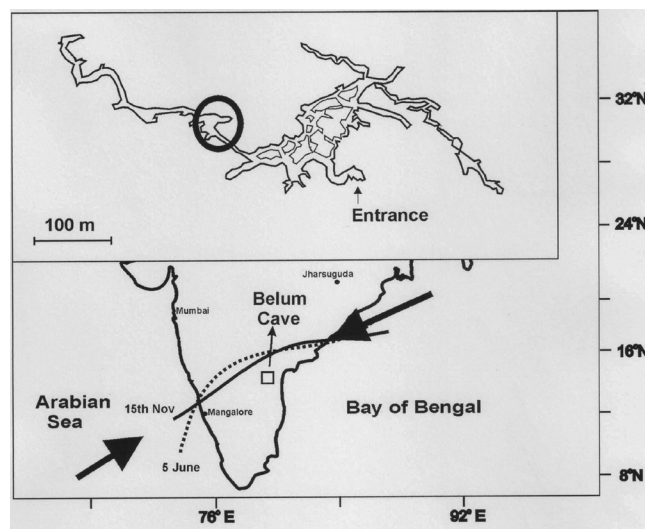
## Study Area

### The Belum Cave

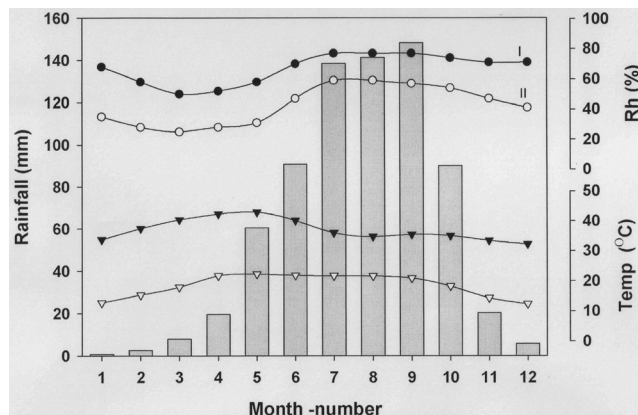
The Belum cave has several open chambers (Narayana et al., 2014a; Gebauer, 1985) and long galleries decorated with huge speleothem formation (Figure 1). The cave was declared a protected area in 2002 CE and is open to public viewing. For the convenience of the visitors, at present it is well ventilated and lit artificially. Unfortunately several stalagmites have been broken in the process. At present the land above the cave is not used for any farming and has several public utilities. However, it must have been the abode of vegetation/woods about 50 years ago.

### Climate

Based on the data from the meteorological observatories, long-term average climatological features of the Kurnool district are shown in Figure 2 (IMD, 1999). Throughout the year, Kurnool receives rains: mostly from the south-west (summer) monsoon between May and October (moisture source being the Arabian Sea) and to some extent from the north-east (winter) monsoon (moisture from the Bay of Bengal) during the remaining months.



**Figure 1:** Map showing location of the Belum Cave in peninsular India. Contours show the northern limit of monsoon rain on the approximate dates when the southwest monsoon reaches (dashed curve) and withdraws (continuous curve) from the region. A schematic of the cave galleries is shown in the inset, at the top: the circle indicates the location of drip water sampling (*Airavatham*). The arrow over the Arabian Sea indicates the usual wind direction during the southwest monsoon and the arrow over Bay of Bengal, the northeast monsoons.



**Figure 2: Long-term monthly average (from CE 1950 to 1981, IMD, 1999) of rainfall (vertical bars), the maximum (filled triangles) and minimum temperatures (open triangles) and humidity (circles). ‘I’ and ‘II’ indicate observations made at 8:30 and 17:30 Hrs Indian Standard Time (0300 and 1200 Hrs Universal Time), respectively.**

$\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses of 160 samples of summer and winter rains collected during CE 2006–2008 at Gadanki, ~200 km south of the cave site show that: (i) There are significant differences between the mean isotopic compositions of summer ( $\delta\text{D} = -15.4 \pm 2.0$ ;  $\delta^{18}\text{O} = -2.6 \pm 0.3$ ,  $n = 73$ ; uncertainties quoted are one standard error) and winter ( $\delta\text{D} = -42.7 \pm 2.0$ ;  $\delta^{18}\text{O} = -6.4 \pm 0.3$ ,  $n = 70$ ; one standard error uncertainties) rains. (ii) Summer rains show a progressive  $\delta^{18}\text{O}$  and  $\delta\text{D}$  depletion after the monsoon onset, while the isotopic compositions of winter rains fluctuate about a mean value (iii) There is no significant difference in the slopes and intercepts of the summer and winter  $\delta\text{D}$ – $\delta^{18}\text{O}$  lines, nor is there any difference between their  $d$ -excess values (Srivastava et al., 2015).

Temperature varies from ~43°C (May) to ~12°C (December) with a long-term average annual rainfall of ~726 mm. The mean annual air temperature inside the cave is 27°C (seasonal variations are less than 3°C) and the mean annual relative humidity 88%. Outside the cave the mean annual temperature is also 30°C, but the mean annual relative humidity 55%. The cave passages are located 12 m below the ground surface. The investigated site is located at about 200 m from the nearest entrance. Water drips throughout the year and the drip rate is variable at different parts of the cave. Narayana et al. (2014a, b) have described the geology of the location as the Cuddapah sedimentary basin of Proterozoic age. The cave is situated in the Precambrian Narji limestone terrain, which belongs to the Kurnool Supergroup. The limestones are bluish gray, fine-grained, and well-bedded. These limestone beds are

overlain by sandstones, quartzite, and conglomerates of the Banganapalli Group. The caves are 15 m above a 35 m escarpment, and this rules out permanent ground water contribution to speleothem formation in this cave. The caves are small and narrow, typically 0.5 m to 1.5 m wide. However, the passage is on the average ~9 m high, on two sides, and has galleries 15 m long, which narrow down to corridors less than 1.5 m wide. Soil cover above the cave is ~1 m thick.

## Samples and Methods

During the first week of March, 2007 CE, when the cave was sampled, a dripping spot was observed to be active and therefore the sampling of drip water was initiated from this spot (at *Airavatham*, Figure 1); samples were fortnightly total accumulations. Samples were collected from the end of March to the beginning of October in 2007 (number of collections,  $n = 14$ ), April to June in 2008 ( $n = 5$ ), May to July ( $n = 7$ ) in 2009 and from July 2010 to June 2011 ( $n = 21$ ). Due to the remoteness of the area and other logistic reasons, a continuous, reliable sampling of drip water could not be carried out. From May 2010 to Jan 2011, daily rainwater samples were collected in a narrow-mouthed carboy kept at the cave top attached with a known diameter funnel. Samples were transferred in storage bottles daily in the morning (8 to 10 Hrs. Indian Standard Time). Unfortunately again due to the unavailability of reliable local scientific help, while rain samples were collected, the amount of rainfall could not be ascertained.

Cave drip water samples were collected by wrapping a plastic bag around an active stalactite that had a ~200 ml capacity. As drip water samples were collected after every ~15 days; the water collected in the bag was an average representative of the previous fortnights’ drip water. Immediately after collection, all water samples were transferred in 30 ml air tight leak proof bottles (Tarson™) for storage and lab analyses.  $\delta^{18}\text{O}$  of water samples were measured using the carbon dioxide equilibration method (Gonfiantini, 1981) on WES (Water Equilibration System) attached with the GEO 20-20 mass spectrometer. Equilibration was carried out at 35°C overnight. A laboratory standard ‘NARM’ (water collected from the Narmada River, Gujarat, India) was used for inter-calibration. It was also analysed at regular interval along with sample analysis. NARM oxygen isotopic ratio,  $\delta^{18}\text{O}_{\text{VSMOW}}$  (with respect to VSMOW: Vienna Standard Mean Ocean Water) is  $-4.03\text{‰}$ . Overall reproducibility in the  $\delta^{18}\text{O}$  measurements is 0.1‰. The hydrogen isotope ratio ( $\delta\text{D}$ ) measurements

were carried out following hydrogen-water equilibration method (Hortia, 1988; Brand et al., 1996; Yadava and Ramesh, 1999) at 35°C, in presence of platinum catalyst coated on a strip of hydrophobic support, using WES in the GEO 20-20 mass spectrometer, with 1‰ overall reproducibility. The NARM hydrogen isotopic ratio,  $\delta D_{VSMOW}$  is  $-31.2‰$ .

We have participated in Fourth Inter laboratory comparison exercise for  $\delta^{18}O$  and  $\delta D$  analysis of water samples (WICO, 2011). Our  $\delta^{18}O$  and  $\delta D$  results agree very well with the IAEA reported census values (Table 1).

## Results and Discussions

### Oxygen and Hydrogen Isotopes in Rainwater

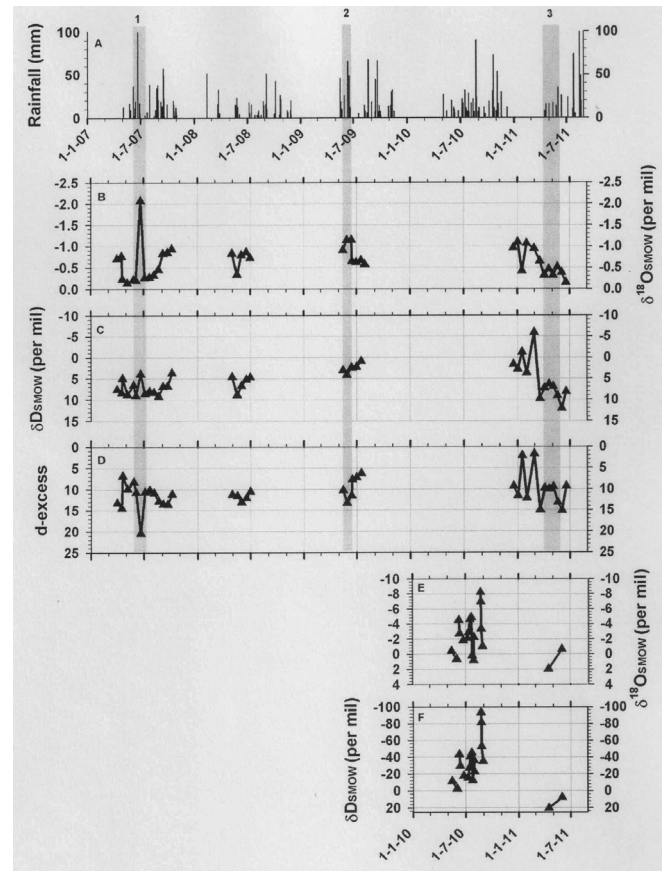
Rainfall at Kolimigundla meteorological station (located within 10 km from the cave),  $\delta^{18}O$  and  $\delta D$  of rain and cave drip water samples are presented in Figure 3. Some of the rain events registered at either of the two places (top of the cave and the meteorological station, Kolimigundla) did not occur simultaneously. This could be due to patchiness (spatial heterogeneity) inherent in rainfall distribution over land.

Daily rain events which were commonly registered at both sites (Cave top and Kolimigundla, Table 2) show a significant association between the  $\delta^{18}O$  (of rain water sample) and the amount of rain (as measured at Kolimigundla, linear correlation coefficient  $r = -0.39$ , number of samples analysed  $n = 21$ , significance level  $P < 0.1$ ) as shown in Figure 4.

Hydrogen and oxygen isotopes of rain water samples are usually together used to infer the humidity of the source region (ocean) and also evaluate kinetic fractionation during precipitation. For the Belum region rainwater  $\delta^{18}O$  and  $\delta D$  show (Figure 5) the following local meteoric water line (LMWL):

$$\delta D = (8.36 \pm 0.92) \delta^{18}O - (8.01 \pm 3.43) \quad (1)$$

$(r = 0.84, n = 36, P < 0.01)$



**Figure 3:** (A) Amount of rainfall at Kolimigundla; (B and C)  $\delta^{18}O$  and  $\delta D$ , respectively, of drip water; (D)  $d$ -excess of drip water; (E and F)  $\delta^{18}O$  and  $\delta D$ , respectively, of rainwater. Similar concurrent patterns are seen e.g., gray bands marked as '1', '2' and '3'. Open circles represent pre-monsoon; filled circles – monsoon and open triangles – winter monsoon.

The slope  $8.36 \pm 0.92$  agrees within the experimental uncertainty with the value of  $8.13 \pm 0.07$  observed for slope of the global meteoric water line-GMWL (Rozanski et al., 1993; Craig, 1961; Gat, 1996) which indicates that rain over the Belum cave is likely generated under isotopic equilibrium with the cloud vapour. The observed intercept,  $-8.01‰$ , is quite low compared to

**Table 1: Interlaboratory comparison of  $\delta^{18}O$  and  $\delta D$  values at PRL**

| Sample code | $\delta^{18}O_{VSMOW} ‰$ |                   | $\delta D_{VSMOW} ‰$ |                    |
|-------------|--------------------------|-------------------|----------------------|--------------------|
|             | PRL value                | IAEA census value | PRL value            | IAEA census value  |
| OH-13       | $-1.01 \pm 0.07$         | $-0.97 \pm 0.12$  | $-2.35 \pm 0.86$     | $-2.75 \pm 0.91$   |
| OH-14       | $-5.56 \pm 0.09$         | $-5.59 \pm 0.11$  | $-38.20 \pm 0.68$    | $-38.40 \pm 0.86$  |
| OH-15       | $-9.31 \pm 0.05$         | $-9.39 \pm 0.13$  | $-78.41 \pm 0.86$    | $-78.31 \pm 0.87$  |
| OH-16       | $-15.25 \pm 0.08$        | $-15.44 \pm 0.13$ | $-114.34 \pm 0.85$   | $-114.89 \pm 0.76$ |

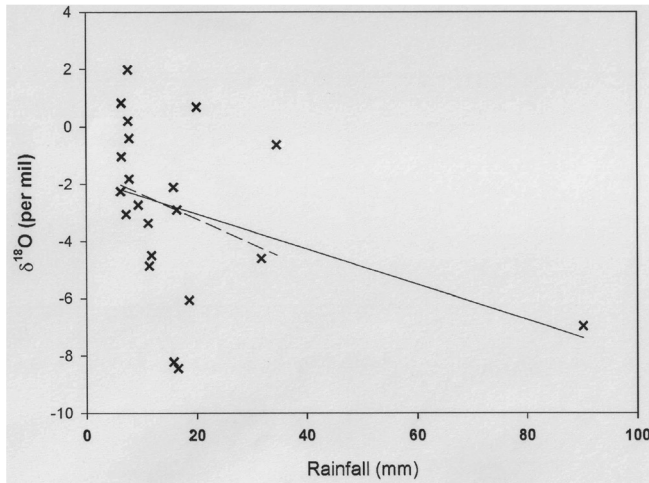


Figure 4: The  $\delta^{18}\text{O}$  (of daily rainwater above the cave) versus the amount of rainfall (recorded at Kolimigundla) for those rain events which occurred both at the cave top and at Kolimigundla. The best fit line (solid line) is:  $Y = -(0.06 \pm 0.03) X = (-1.81 \pm 0.84)$ ,  $n = 21$ ,  $r = -0.39$ ,  $P < 0.1$ . If we omit the data on the extreme right, the relation is still statistically significant (dashed line)  $Y = -(0.09 \pm 0.08) X = (-1.49 \pm 1.26)$ ,  $n = 20$ ,  $r = -0.25$ ,  $P < 0.1$ .

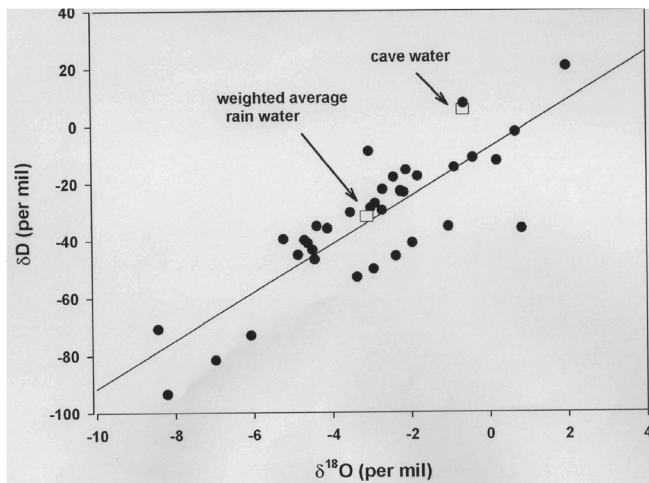


Figure 5:  $\delta\text{D}$  vs.  $\delta^{18}\text{O}$  plot for all the rain collected above the Belum cave. The observed Local Meteoric Water Line (LMWL) is:  $\delta\text{D} = (8.36 \pm 0.92) \delta^{18}\text{O} - (8.01 \pm 3.48)$ ,  $n = 36$ ,  $r = 0.84$ ,  $P < 0.01$ . Boxes show the weighted average isotopic compositions of the rain water ( $\delta^{18}\text{O} = -3.1\text{‰}$  and  $\delta\text{D} = -31.5\text{‰}$ ) and average isotopic composition of drip water ( $\delta^{18}\text{O} = -0.7\text{‰}$  and  $\delta\text{D} = 5.6\text{‰}$ ).

that of the GMWL which is generally  $\sim +10\text{‰}$  (Rozanski et al., 1993). This could be due to a significant mixture of vapour from local evapotranspiration to the cloud vapour (see discussion below).

Table 2: Time series of common dates of rain occurrence at both places: Belum cave and Kollimigundla meteorological station, less than 10 km away

| Date<br>(dd/mm/yyyy) | Rainfall<br>(mm) |
|----------------------|------------------|
| 16/5/2010            | 7.8              |
| 2/6/2010             | 20.0             |
| 9/6/2010             | 11.8             |
| 12/6/2010            | 9.4              |
| 24/6/2010            | 7.8              |
| 9/7/2010             | 15.8             |
| 13/7/2010            | 16.4             |
| 17/7/2010            | 31.8             |
| 22/7/2010            | 11.4             |
| 25/7/2010            | 7.6              |
| 30/7/2010            | 6.4              |
| 31/7/2010            | 6.2              |
| 7/8/2010             | 16.6             |
| 23/8/2010            | 15.8             |
| 24/8/2010            | 90.2             |
| 25/8/2010            | 11.2             |
| 30/8/2010            | 6.4              |
| 7/10/2010            | 18.6             |
| 7/12/2010            | 7.2              |
| 15/4/2011            | 7.6              |
| 1/6/2011             | 34.6             |

Source: Bureau of Economics & Statistics, Government of Andhra Pradesh.

### Oxygen and Hydrogen Isotopes in Drip Water

Temporal variations in the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the fortnightly drip water collection from the cave (Figure 3) show sharp changes, indicating that the cave water is responding to the isotopic variations of the local precipitation. A visual comparison between amount of rainwater (measured at Kolimigundla) and  $\delta^{18}\text{O}$  of drip water indicates that some of the sharp changes and patterns observed in the drip water have a close resemblance with the concurrent changes seen in the amount of rain (e.g. common features '1', '2' and '3' marked as vertical gray bands in Figure 3). Despite the fact that actual values of the amount of water for the rain events that occurred above the cave were not recorded, similarities in the drip  $\delta^{18}\text{O}$  and amount of rainwater (from the nearby Kolimigundla) during some events indicates that the cave is likely responding to the changes in the local rainfall. This suggests that speleothem of the Belum cave have a good potential for paleo-monsoon reconstruction using the 'amount effect'.

Effect of evaporation is difficult to see in the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of drip water. For example, the average

values of  $\delta^{18}\text{O}$  of drip water is  $-0.7 \pm 0.4\text{‰}$  which is same as that of the rainwater ( $-3.1 \pm 2.4\text{‰}$ ), within the uncertainty. Similarly  $\delta\text{D}$  values of drip water ( $5.6 \pm 3.5\text{‰}$ ) are indistinguishable from that of the rainwater ( $-31.5 \pm 23.4\text{‰}$ ). Note that the variance is considerably reduced in the cave water, because of the averaging effect.

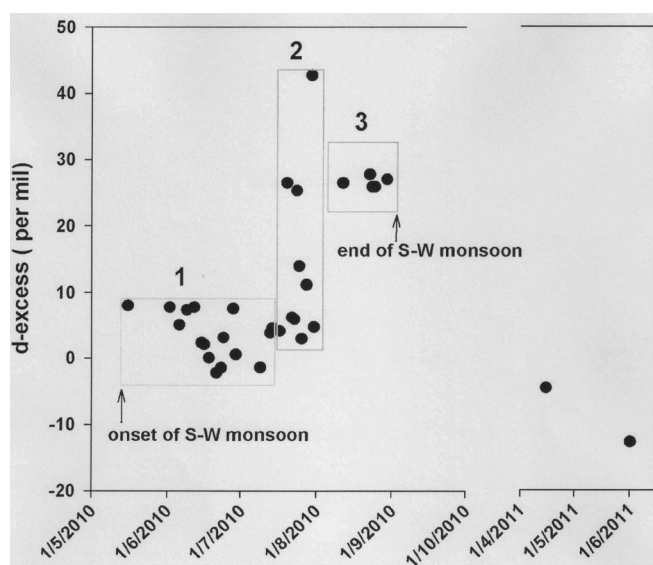
### **d-excess in Rain and Drip Water**

The deuterium excess ( $d$ ) of any water sample is defined as the difference between the measured value of  $\delta\text{D}$  and its expected value when condensation occurs under isotopic equilibrium ( $d = \delta\text{D} - 8 \times \delta^{18}\text{O}$ ). This parameter is widely used to infer the humidity, wind speed and sea surface temperature (SST) during evaporation from the ocean surface (Gonfiantini, 1981; Clark and Fritz, 1997). The  $d$ -excess values for the rainwater samples (Figure 6) show contrasting values during the beginning and the end of the south-west monsoon. At the onset of monsoon, the Arabian Sea (the source of moisture for the Belum cave region) seems to be quite humid, close to  $\sim 85\%$  for the surface boundary layer (IMD, 1999) and therefore  $d$ -excess values are within the  $+10\text{‰}$  range (box 1 in Figure 6). Withdrawal of the monsoon from northern India starts around mid-September (Pant and Rupakumar, 1997) and by the end of October it retreats completely from north of  $15^\circ\text{N}$  (approximate latitude of the Belum cave). The sea surface humidity (also wind speed and sea surface temperature) remains more or less similar until the end of July (mid-southwest monsoon) when  $d$ -excess values are highly variable (box 2 in

Figure 6), ranging from,  $\sim +4$  to  $\sim +43\text{‰}$ . Subsequently, sea surface humidity reduces further (up to  $\sim 40$  to  $60\%$ , and winds frequently become more turbulent; therefore kinetic fractionation in the boundary layer (Clark and Fritz, 1997) at the Arabian sea surface results in consistently increased  $d$ -excess (around  $+30\text{‰}$ ). Hence,  $d$ -excess values indicate the humidity at the Arabian Sea surface during the summer monsoon. Such a variation, with a trend towards higher deuterium excess may result in an intercept having negative value ( $-8\text{‰}$ ) as noticed in the LMWL.

The onset of monsoon is usually characterized by frequent storms and evaporations that may contribute to kinetic effects. Two samples collected during the onset of monsoon in CE 2011 show negative values for  $d$ -excess possibly due to mixing of vapour mass with the re-evaporated components and to some extent due to kinetic processes.

The  $d$ -excess values for all the drip water samples (shown in Figure 3) have positive values, ranging from  $+6$  to  $+20\text{‰}$ . This indicates that rain having typical  $d$ -excess values varying from  $-10\text{‰}$  to  $+40\text{‰}$ , percolates through the soil and get mixed there due to a finite residence time of the soil aquifer. As most of the rain samples have positive  $d$ -excess value, the mixing results in positive  $d$ -excess for all the drip samples. Additionally, evaporation at the soil surface reduces the  $d$ -excess of the water that percolates into the soil. This is because even during the wet months when rainwater percolates downward, humidity at the soil surface is expected to be much lower than the values usually observed at the ocean surface (average value  $\sim 85\%$ , Merilvat, 1979); therefore the evaporated vapours have higher  $d$ -excess relative to rain, resulting lower  $d$ -excess of percolating water. Alternatively, the fraction of rain that percolates into soil would have less  $d$ -excess than rain before evaporation.



**Figure 6:**  $d$ -excess values for all the rain water samples. Three phases in the values are observed, highlighted by boxes 1, 2 and 3.

### **Evolution of Isotopic Composition of Rain**

Rain falling over the soil surface of the cave, slowly percolates down and reappears as drip water inside the cave. Prior to this, it evaporates significantly at the ground level under varying ambient humidity; therefore, it could undergo non-equilibrium isotopic fractionation. When water evaporates into a static atmosphere almost saturated with water vapour, the isotopic fractionation is close to equilibrium values, whereas when water evaporates into a breezy/windy unsaturated atmosphere, the isotopic fractionation is invariably kinetic (this happens because of the different rates of diffusion of

water isotopologues, i.e.,  $\text{H}_2^{16}\text{O}$ ,  $\text{HDO}$ ,  $\text{H}_2^{18}\text{O}$  through air). In the latter case, in addition to equilibrium fractionation, a humidity dependent kinetic fractionation takes place, so that the magnitude of the overall isotopic fractionation is larger (Criss, 1999). For example, we start with a  $\delta\text{D}$  value of  $-50\text{‰}$  for water evaporating at  $20^\circ\text{C}$ , into an atmosphere containing vapour with a  $\delta\text{D}$  value of  $-100\text{‰}$ . When 80% of the water has vapourized, the  $\delta\text{D}$  of the remaining water would be  $-15\text{‰}$  if the relative humidity was 90%; and  $+55\text{‰}$  for a relative humidity of 40% (Criss, 1999).

Isotopic fractionation in the open atmosphere is a complex phenomenon (Luz et al., 2009; Cappa et al., 2003). In order to investigate isotopic changes in the water that rained and got evaporated from the cave top before it percolated, we use the approach described by (Criss, 1999). The isotopic composition ( $\delta_w$ ) of water at a time when the remaining, un-evaporated fraction of water is ' $f$ ' given as:

$$\delta_w = f^u (\delta_w^i - \delta_w^s) + \delta_w^s \quad (2)$$

where  $\delta_w$  is the isotopic composition at this instant,  $\delta_w^i$  at the initial time and  $\delta_w^s$  is the isotopic composition of the water after a long time when evaporation has gone to near completion. The values of the exponent  $u$  and  $\delta_w^s$  are given as:

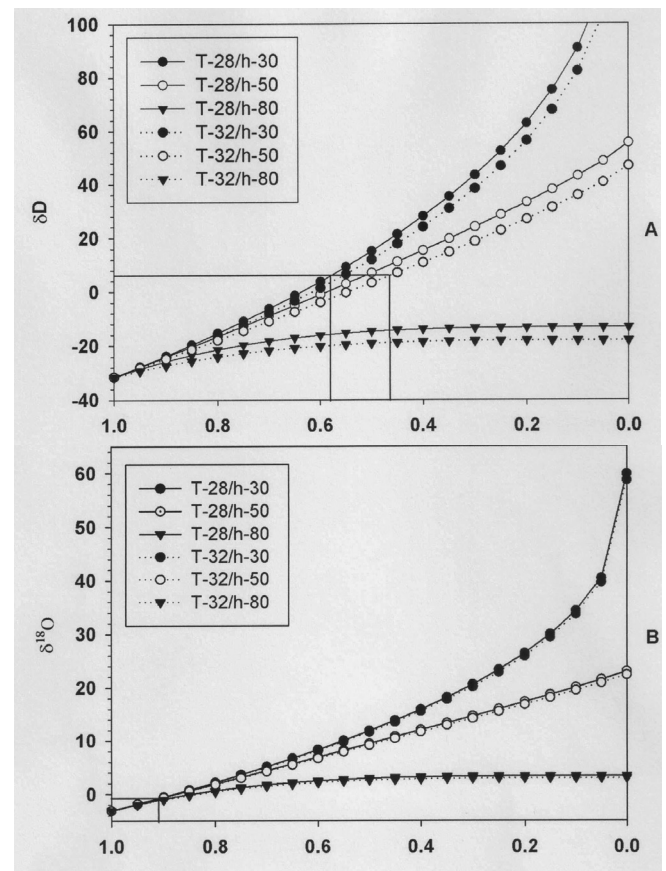
$$u = (1 - \alpha_{\text{evap}}^0)(1 - h)/\alpha_{\text{evap}}^0(1 - h) \quad (3)$$

$$\delta_w^s = (\alpha_{\text{eq}} h (\delta_v 10^{-3} + 1)/(1 - \alpha_{\text{evap}}^0(1 - h)) - 1) 10^3 \quad (4)$$

where  $h$  is the ambient humidity,  $\delta_v$  being the isotopic composition of the ambient atmospheric vapour,  $\alpha_{\text{eq}}$  the temperature dependent equilibrium isotopic fractionation factor,  $\alpha_{\text{evap}}^0$  the non-equilibrium isotopic fractionation factor and is defined as  $\alpha_{\text{evap}}^0 = \alpha_{\text{eq}} \sqrt{D}$ , where  $D$  is ratio of the diffusion coefficients for light to heavy isotopes and has values of 1.0166 and 1.0324, respectively for the case of oxygen and the hydrogen isotopes (WICO, 2011).

For Belum cave site, during the season when monsoon is most active (June to Oct) the average values of ambient temperature varies between  $28^\circ\text{C}$  and  $32^\circ\text{C}$ . Considering humidity to vary from 30% to 80%, a model was used to calculate the time evolution of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  to estimate a typical value of the fraction of rainwater ( $f$ ) that reaches the average observed value of the isotopic composition of the drip water ( $\delta\text{D} = 5.6\text{‰}$  and  $\delta^{18}\text{O} = -0.7\text{‰}$ , Figure 5). Isotopic composition of ambient vapour is estimated using the average values of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of rain, using the equilibrium isotopic

fraction factor at  $30^\circ\text{C}$  (i.e.  $\delta_v$  for oxygen  $= -3.1 - 8.9 = -12.0\text{‰}$  and for hydrogen  $= -31.5 - 71.0 = -102.5\text{‰}$ ). Results (Figure 7) show a highly variable isotopic evolution between the extreme assumed values of humidity. At high humidity, the evolved  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values reach the expected saturation levels (WICO, 2011). The value of  $f$  when  $\delta\text{D}$  reaches the observed drip water value ( $5.6\text{‰}$ ) is between 0.6 and 0.4. Contrarily, for oxygen isotope, the value of  $f$  when  $\delta^{18}\text{O}$  reaches at the drip water level (i.e.  $-0.7\text{‰}$ ) is around 0.9. Both these results indicate different values of ' $f$ ' and indicate that the evaporation is a complex process and this simple model is quite inadequate to estimate the precise fraction of rainwater that percolated into the Belum cave.



**Figure 7:** Assuming two values of ambient temperature ( $T$ ) as  $28^\circ\text{C}$  and  $32^\circ\text{C}$ , and relative humidity at ground level as 30%, 50% and 80%, a model (equations 2-4 in text) is used to calculate  $\delta\text{D}$  (A) and  $\delta^{18}\text{O}$  (B) of rain that undergoes non-equilibrium (kinetic) fractionation during evaporation at the ground surface over the cave, before percolating into the soil. The estimated fraction of water (between two vertical lines) that attains the drip water isotopic composition (horizontal line) is different in both the graphs.

## Conclusions

We present the first stable isotope measurements of cave drip waters and rain over the Belum cave, India. The slope of the local meteoric water line (i.e.  $\delta D - \delta^{18}O$  relation) is found to be quite close to 8 suggesting equilibrium condensation of vapour during precipitation around the cave region. However, the negative value of the intercept is suggestive of variable humidity at the vapour source region as evidenced by the  $d$ -excess values. Drip water shows sharp changes in the  $\delta^{18}O$  and  $\delta D$  values, indicating that the likely amount-dependent isotopic changes in precipitation are mimicked by the drip water isotopic composition. The  $d$ -excess attains values around 10‰ during initial phase of the monsoon and after a highly variable phase in between, where values vary from +4‰ to +43‰, it attains a value around +30‰ near the final phase. Effect of evaporation is difficult to observe in the average values of the  $\delta^{18}O$ ,  $\delta D$  and  $d$ -excess values of the drip water, because of the large variance associated with them. Although the sampling is unevenly spaced in time, the results clearly demonstrate the potential of speleothem in this cave for quantitative reconstruction of past monsoon rainfall.

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