CHAPTER 2: SPELEOTHEMS AND CLIMATE

The Karst topography describes the dissolution of underlying soluble rocks by surface water or ground water. This is commonly found in carbonate terrain (limestone and dolomite) in mountainous regions. The rain water infiltrates through the cracks of the rocks in the vertical manner until it reaches the water table and thereafter, it moves horizontally below the surface of water table. The conditions of this process are, (1) exposure of thick limestone cover the ground surface, and (2) limestone cover overlain by non soluble rocks. The discernible character of the karst topography is simply known as caves and sinkholes.

Caves are formed by karstification where by downward percolating meteoric water interacts with the soil zone enriched in CO$_2$ content, thereby dissolving relatively soluble rocks (Bar-Matthews et al., 1996). Caves are naturally formed as underground cavity and their size ranges from few meters to several kilometres. They are formed in fractured and soluble rocks as a result of mechanical and chemical processes that continue over thousand to million years (White, 1988; Forti, 2009). The main cave types are solution caves, glacier caves and sea caves.

2.1. Cave structures

All types of depositional features in the caves are collectively called as speleothems. These are formed by mostly calcite but occasionally aragonite (Goede et al., 1998). They are precipitated slowly by degassing of meteoric water fed drips in caves. The speleothems include helictites, straws, flowstones, stalactites and stalagmites etc. (Figure 9a). The Helictites are twisted cave formations (Self and Hill, 2003) like helix shape (three dimensional smooth space curve) with pointed end. These are formed by the seeping of the ceiling water and reorientation of crystal structure of calcite. A soda straw (tubular stalactite) is a hollow cylindrical tube (mostly 1-10 cm) at the ceiling of the cave. These straws become stalactites if the hole of bottom is blocked or water begins flowing on the outside surface of hallow tube. Each successive drop of water deposits little more minerals near roof of the cave. After regular deposition, these sharp and most fragile cave structures are formed. The stalactites are formations that hang from the ceiling of a cave (Figure 9a). They have broad bases stuck to the cave ceiling (Hill and Forti, 1997) and tapering ends hanging downward from the cave ceiling.
shape and size of stalactites are controlled by the cave ceiling and drip water (Sweeting, 1972; Longman and Brownlee, 1980; Jennings, 1985). They are produced by precipitation of minerals from water dripping through the cave ceiling. If the cave ceiling is flat, stalactites are directly pointed towards the cave floor. But when the ceiling is inclined, elongated stalactites are formed.

Stalagmite is an upward-growing mineral deposit that has precipitated from water dripping onto the floor (Figures 9a,c) of a cave (Railsback et al., 1994; Genty and Quinif, 1996; Baker et al., 2008) and most stalagmites have rounded or flattened tips. They grow very slowly with isotopic equilibrium and save information in form of isotopes proxies (Dansgaard, 1964; Rozanski et al., 1993; Moerman et al., 2013). These are various processes involved in formation of cave structures (Figure 9e). The stalagmites can develop under two conditions, (i) the development under equilibrium conditions, and (ii) under disequilibrium conditions. Pillar (Figure 9a) is a calcite deposit, i.e., formed when stalactite and stalagmite meet together. Stalagmites are grouped into three categories (Frank, 1965, 1975) on the basis of morphology. (a)
uniform stalagmites are formed by constant drip rates (Curl, 1973), calcite concentrations of the feed water and the cave atmosphere, (b) the conical form is generally common in low growth rate and or high drop fall height, (c) flow sheets are generally developed during the high precipitation (Gams, 1981). Flowstones are deposits of minerals from water flowing over the floor and walls of a cave. Dripstones are calcareous deposits from dripping of water in dry limestone caves. Stalagmites long term records are used for documenting the significant changes in the frequency and magnitude of extreme climatic events (e.g., paleo-floods and droughts) and modelling of immediate future climate. They also have potential to record the palaeoclimatic changes with a range of past decade to thousand years (Hendy and Willson, 1968; Thompson et al., 1974).

The Quaternary archives such as lakes, marine cores, peat bogs and ice cores are studied by several researchers. But the strength of stalagmite is better than other on the basis of dating and resolution. Stalagmites can record continuous episodes of growth, preservation of information in the form of δ¹⁸O and δ¹³C isotopes. The excellent U/Th chronologies can be operated on stalagmites. This is far superior than other developed long records. These archives are physically and chemically robust and free from erosion and have very long potential resolution compared to other archives (Table 1).

<table>
<thead>
<tr>
<th>Archive</th>
<th>Temporal range</th>
<th>Potential resolution</th>
</tr>
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<tbody>
<tr>
<td>Stalagmites</td>
<td>0-≥500 ka</td>
<td>5-10 years</td>
</tr>
<tr>
<td>Modern lakes</td>
<td>0- ≥500 years</td>
<td>Seasonal to decadal</td>
</tr>
<tr>
<td>Palaeolakes</td>
<td>3-50 ka</td>
<td>Centennial</td>
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<td>Peats</td>
<td>0-~11 ka</td>
<td>Decadal to centennial</td>
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<tr>
<td>Tree ring</td>
<td>0-2 ka</td>
<td>Seasonal</td>
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Table 1. Comparison of various archives and their resolution.

2.2. Formation of speleothems

When the rain water hits the ground, it percolates through the soil (or weak zones) and equilibrates with surrounding carbon dioxide (CO₂). Due to high amount of CO₂, the rain drop dissolves the limestone until solution is saturated. The deposition of calcite depends upon two mechanisms (Plumer et al., 1978; Buhmann and Dreybrodt, 1985;
Baker et al., 1998; Dreybrodt et al., 1999), (i) surface reactions (ii) conversion of calcium carbonate (CaCO$_3$) into calcium bicarbonate {Ca(HCO$_3$)$_2$} (Figure 10). Each regular and continuous drop of water deposits more rings of calcite until soda straw formation occurs. The soda straw grows in length until it is filled with calcite and then water starts flowing down and outside the straw resulting in stalactite. The percolating water represents several reactions in its path. The chemical reaction of stalactite is

$$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca(HCO}_3\text{)}_2$$

Formation of stalactite and stalagmite is in chemical equilibrium (A process where a forward and reverse reaction occurs at equal rates). As water droplet falls on the floor of the cave, it spreads out in wide pattern and flat rings are formed (Hendy, 1969, 1971). The chemical reaction for the formula of stalagmite is reverse of the stalactite as

$$\text{Ca(HCO}_3\text{)}_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

Figure 10. Chemical processes of the formation of the speleothems.
2.3. Ideal stalagmites for palaeoclimatic study

The selection of ideal stalagmite is very important aspect for the palaeoclimatic research. The shape (morphology) of stalagmite depends upon the precipitation rate, nature of ceiling and shape the cave (Baker and Smart, 1995; Baker et al., 1998; Proctor et al., 2000; Kaufmann, 2003; Drysdale et al., 2005; Baldini et al., 2008). The candle or cylindrical shaped stalagmites (Figure 9c) are best because of their consistent internal growth geometry (Genty and Quinif, 1996; Frisia et al., 2000; Baldini, 2001). They have several flat rings with a constant width from centre to margin. The ideal caves are horizontal with a small entrance (Figure 9b). The small and narrow entrance supports that secondary calcite deposition typically occurs by degassing of CO$_2$ from carbonate saturated drip waters, because cave atmosphere usually have lower CO$_2$ levels (Schwarcz, 1986; Ford and Williams, 1989). If the cave is open then pco$_2$ (partial, pressure of carbon dioxide) is same as external atmosphere. On the other hand, if the cave is closed with lack of ventilation, then pco$_2$ level is high. This pco$_2$ gradient between the drop and cave air causes conversion of bicarbonate (HCO$_3^-$) in Co$_2$ within the solution.

Cave temperature remains almost constant throughout the year in poorly ventilated caves (typically±1 °C) (McDermott, 2004), reflecting thermal inertia of host rocks (Gascoyne, 1992; Lauritzen, 1995; Repinski et al., 1999). For an ideal stalagmite, the cave air humidity is characterised by high relative humidity (95-100%) (Gams, 1974; Vaupotič and Kobal, 2004; Bezek et al., 2012) that minimizes the evaporation of the drip water.

2.4. Limitations in speleothem research

The composition and morphology of stalagmites depend upon the precipitation rate, capillary supply of ions, rate of CO$_2$ out gassing and the variability of these factors (González et al., 1992; Jhones and Kahle, 1993; Kendall, 1993; Genty and Quinif, 1996). Stalagmites can provide very useful information of palaeoclimatic changes, when they are formed in isotopic equilibrium (Hendy, 1971). The evaporation effect and out gassing of CO$_2$ from droplet alters the isotopic equilibrium. This temperature and air effect of disequilibrium is known as kinetic fractionation. In equilibrium condition, candle or cylindrical shaped (Figure 9c) stalagmites are formed.
The Hendy test is widely used for assessing whether isotopic equilibrium existed during the time of stalagmite formation (Fleitmann et al., 2004; Dykoski et al., 2005; Vacco et al., 2005; Johnson et al., 2006; Spötl et al., 2006; Mangini et al., 2007; Hu et al., 2008; Zhang et al., 2008; Zhou et al., 2008). According to Hendy test, $\delta^{18}O$ values remain constant along a single growth layer. The growth rate depends on the Ca concentration (cations and anions) (Kaufmann, 2003). In stalagmites, most of the layers are thick at the central part (Figure 9d) but thin and submerged at the outer part. In the Hendy test, the isotopic equilibrium criteria is that the $\delta^{13}C$ values do not depend upon the $\delta^{18}O$ values (Hendy, 1971) but this is not possible practically. This test is not ideal for isotopic equilibrium conditions because this takes place at the same time when kinetic fractionation occurs at the outer side of stalagmite (Talma and Vogel, 1992; Spötl and Mangini, 2002; Dreybrodt, 2008). Thus, Hendy test could not explain the isotopic equilibrium conditions in all sections of a particular stalagmite. Moreover the sample resolution and error percentage are also important for the Hendy test.

2.5. High precision Uranium-series dating

Stalagmites have strong chronological control for the last 500,000 years (Edwards et al., 1987). These are ideal material for dating by U series, specially using the ‘daughter efficiency’ $^{230}\text{Th}/U$ Method. The Uranium content in calcite speleothems are (typically 0.1-10 µg/g $^{238}U$) very less and are about an order of magnitude higher in aragonite rich speleothems (McDermott et al., 1999). Uranium is incorporated into $\text{CaCO}_3$ as the uranyl ion $\text{UO}_2^+$ derives from the dominant aqueous species ($\text{UO}_2\text{CO}_3^3$)$^{4-}$. This is incorporated in speleothems only with non carbonate phases. Uranium dating in speleothems has played a significant role in Quaternary science in recent years. Thermal Ionization Mass Spectrometry (TIMS) technique for uranium series measurements (Edwards et al., 1987; Li et al., 1989) is well established for speleothems. TIMS and MC-IPMS methods are best because in these techniques, sample size (10-100 to 10-500 mg) and age error percentage (2-10% to 0.10 -0.4%) are decreased (Goldstein, 2003). Recent technological developments support new high resolution magnetic sector Multi Collector Inductive Coupled Plasma Mass Spectrometers (MC-ICP-MS) with vastly improved ionisation efficiency for elements such as thorium and protactinium (Shen et al., 2002; Richards and Dorale, 2003). The dead carbon ($^{14}C$) percentage in speleothems is in the range 10-25% (Genty and
Massault, 1999; Genty et al., 1999) and covers a time range of $10^2$-$10^3$ years with large error percentage. Therefore, several researchers limit the use of $^{14}$C as dating technique in speleothems.

2.5.1. Oxygen isotopes in speleothems

Stable isotopes of oxygen and carbon provide the main palaeo record of precipitation and vegetation. When movement of water and air in a cave is relatively slow, a thermal equilibrium is developed. The rainwater composition effect represents established empirical relationship between precipitation $\delta^{18}$O values and certain climatic parameters such as rainfall intensity (Dansgaard, 1964; Rozanski et al., 1993; Spötl and Mangini, 2002; Fleitmann et al., 2004; Harmon et al., 2004; Vollweiler et al., 2006; Wang et al., 2008; Moerman et al., 2013) and temperature (Dansgaard, 1964). The $\delta^{18}$O values decrease with increasing amount of rainfall (see Figure 9e) (Fleitmann et al., 2003). Thus, the $\delta^{18}$O values show inverse proportion to the precipitation.

On the basis of seasonal time scales, variations of $\delta^{18}$O in precipitation arise from variations in the source of rainfall. The high resolution $\delta^{18}$O series of speleothems gives evidence of solar activity influence on the ISM (Neff et al., 2001; Shindell et al., 2001; Fleitmann et al., 2003; Niggerman et al., 2003). In semi arid to arid climate, heavier $\delta^{18}$O values are observed due to high evaporation process than precipitation (Bar-Matthews et al., 1996). The $\delta^{18}$O is used to express the value of the oxygen isotope ratio ($^{18}$O/$^{16}$O) in a sample relative to that in a standard. Thus $\delta^{18}$O = ($^{18}$O/$^{16}$O)sample / ($^{18}$O/$^{16}$O)standard)−1)*1000) where s is the unknown sample and std is a standard that has been calibrated relative to the Pee Dee Belemnite (PDB) (usually expressed as Vienna Pee Dee Belemnite (VPDB)) or Vienna Standard Mean Ocean Water (VSMOW). The principle relationship between $\delta^{18}$O and temperature is approximately -24 %o °C$^{-1}$ at 25°C (O’Neil et al., 1969). But for mid-high latitudes, this relation is calculated as an average of 0.6 %o °C$^{-1}$ (Rozanski et al., 1993).

The $\delta^{18}$O composition of atmospheric precipitation becomes increasingly negative with decrease in temperature. The basic fact is that the maximum amount of precipitation that air can hold drops with decreasing temperatures (Dansgaard, 1964). When humid air cools at a point the water molecules will condensate to form precipitation. The relation
between $\delta^{18}O$ and temperature is averaged (+0.59 ±0.09‰/°C) (Dansgard, 1964; Rozanski et al., 1993) per degree celcius for mid to high latitude region (Gascoyne, 1992; Dorale et al., 1992, 1998; Mc Dermott et al., 1999, 2006; Paulsen et al., 2003).

### 2.5.2. Carbon isotopes in speleothems

Carbon isotope ratio reflects a balance between light biogenic carbon ($^{12}$C) and heavier carbon ($^{13}$C) dissolved from precipitated water. The $\delta^{13}$C values are capable of preserving vegetation signatures, such as soil organic matter (Boutton, 1996). Soil yields CO$_2$ by microbial decomposition of soil organic matter and root respiration of the plants whose intensity increases during wet periods resulting in high pCO$_2$ and depleted $\delta^{13}$C (Hesterberg and Siegenthlaer, 1991). The stalagmites are capable of recording the proportion of C$_3$ and C$_4$ plant biomass (Cerling, 1984; Deines, 1986; Cerling and Quade, 1993; Dorale et al., 1998; Hellstrom et al., 1998; Genty et al., 2006) through time and are indirectly linked to the precipitation (Richards and Dorale, 2003). The formula for $\delta^{13}$C is used to express the value of the carbon isotope ratio ($^{13}$C/$^{12}$C) in a sample relative to that in a standard. Thus $\delta^{13}$C = ($^{13}$C/$^{12}$C)sample / ($^{13}$C/$^{12}$C)standard – 1)*1000) where s is the sample (unknown) and std a standard that has been calibrated relative to the Pee Dee Belemnite (PDB).

After deposition, the secondary carbonate deposits have a range of $\delta^{13}$C between -14 to -6‰ for C$_3$ and -6 to 2 ‰ for C$_4$ plants (Cerling, 1984). Due to restricted stomata conductance, the $\delta^{13}$C of respired soil CO$_2$ of C$_3$ plants is heavier under dry conditions and lighter under humid conditions. Carbon sources in speleothems are soil CO$_2$ and bed rock carbon and depend upon three parameters such as photosynthetic pathway, biological activity and drip rate.

### 2.5.3. Trace elements and mineralogy

Speleothems are mainly composed of calcite and aragonite or both. Aragonite and calcite can precipitate regularly at the same time but they reflect separate episodes of growth rates in speleothems. The internal structure of stalagmite reflects the annual band thickness (Ayliffe, 1998; Fairchild et al., 2001; Spölt and Mangini, 2002; Duan et al., 2013). Mg rich calcite is mainly deposited in wet season and aragonite mainly in arid climate. Trace element analysis is generally related with the colour of growth rings.
(James, 1997; White, 1997). The light colour growth rings are mainly formed in high precipitation duration. But in arid time period, Mg/Ca ratio decreases and dark colour bands are formed.

Mineralogy of stalagmites is explored by XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope). Proxy records using mineralogy were first established by Fairchild et al. (2000). Recently, Duan et al. (2013) reported precipitation variation in the Indian speleothems based on mineralogy. The thickness of annual lamination thickness is directly related to amount of precipitation year, which has been proved by experimental studies (Baker and Smart, 1995; Dreybrodt et al., 1996, 1999; Baker et al. 1998) and theoretical studies (Buhnann and Dreybrodt, 1985). The growth rate in stalagmites is controlled by many physical factors (Dreybrodt, 1988, 1999; Baker et al., 1999; Kaufmann, 2003). It depends upon the mean annual temperature at the site, drip water rate and calcium concentration of drip waters (Genty et al., 2001; Polyak and Asmeron, 2001; Fleitmann et al., 2004). In some stalagmites, annual visible or luminescent bands can establish independent verification of radiometric chronologies (Wang et al., 2001; Frisia et al., 2002; Hou et al., 2003; Fleitmann et al., 2004). The drip interval is defined as the time between the two continuous drops. It depends upon the drop volume, composition and precipitation amount. Regular monitoring of caves can give information about the precipitation behaviour, growth rate and its relationship with isotopes.

2.6. Speleothem research in India

The speleothem research in India is in its early stage. Speleothem isotope records were first studied by Yadava (2002) from south Indian caves. Subsequently, Yadava et al. (2004) carried out rainfall variations on a 331-year old speleothem from Peninsular India. The work was further extended to Orissa (Gupteswar Cave) for reconstructing the rainfall data for the last about 3.5 ka BP (Yadava and Ramesh, 2005). Yadava and Ramesh (2006) studied stable oxygen and carbon isotopes in stalagmites collected from four locations viz., Gupteswar (Orissa), Dandak (Chhattisgarh), Sota (Uttar Pradesh), and Akalagavi (Karnataka) and reported various wet/dry periods within the last ~ 3.4 ka BP. Similarly, A 900 year (600 to 1500 AD) record of Dandak cave, Peninsular India (Sinha et al., 2007) reflects the Medieval Warm Period (MWP) and the earliest portion
of the Little Ice Age (LIA). Two stalagmites from Baratang Cave in Andaman Islands, covering last ∼4 ka BP documented the transition of MWP to LIA (Laskar et al., 2013). Lately, Lone et al. (2014) investigated Valmiki Cave covering a time period from 15.7 ka to 14.7 ka BP with an average sampling resolution of ∼5 years. In the Indian Himalaya, Sinha et al. (2005) studied Timta Cave from eastern part of the central Himalaya that revealed the decrease in ISM intensity during Bølling-Allerød (BA) interstadiual between 15.2 to 11.7 ka BP. A detailed study of the past precipitation from Chulerasim Cave in central Himalaya was performed by Kotlia et al. (2012) who suggested two prominent climatic phases (LIA and post-LIA) and interestingly showed that the LIA in the Himalaya was wet, while the post-LIA was drier and warmer. Duan et al. (2013) also worked on Chulerasim mineralogy and laminae counting to reconstruct the precipitation conditions for last 400 years. Stable isotope records of Dharamjali Cave (Sanwal et al., 2013) displayed the ISM variability during MWP and LIA. A cave record of ∼4 ka BP from Sainji Cave reflects precipitation behaviour of ISM and WD₅ in the Himalaya and its relation with Harappan/Indus civilization (Kotlia et al., 2015). A 2 ka BP record of Sahiya Cave shows that ISM intensity highly decreased in last 50 to 60 years perhaps due to anthropogenic activities (Sinha et al., 2015). Similarly, Mawmluh Cave (Meghalaya) has been studied for middle Holocene climate and is well correlated with Indus and Nile river civilizations (Berkelhammer et al., 2012). Another stalagmite record from 33.8 to 55 ka BP (Dutt et al., 2015) from Mawmluh Cave reveals monsoon intensity during major climatic events (YD, BA and Heinrich Event). Kathayat et al. (2016) systematically studied Bitto Cave and obtained the results for the last 280 ka BP with a relation between ISM and EASM (East Asian Summer Monsoon). More Recently, Kotlia et al. (2016a) studied a stalagmite from Jammu and Kashmir (NW Himalaya) covering the record of Last Pleistocene-Holocene transition and footprints of Older Dryas (OD), Allerød period and YD.

2.6.1. Stalagmite records from China and nearby areas

Several researchers have investigated cave records from China and nearby areas to establish a relationship among ISM, EASM and ITCZ. A study on two stalagmites from Jiuxian Cave (Central China) indicated that the EASM was not very much effective on ISM behaviour during Holocene (Cai et al., 2010). The isotopic analysis of six stalagmites of Sanbo Cave by Dong et al. (2010) indicates the climatic variation in the
last 13 ka BP and supports that the ITCZ affects ISM and EASM regularly. The $\delta^{13}$C analysis of Lianhua Cave (Cosfrod et al., 2008) reflected the vegetational record of mid to late Holocene and two intervals of warm humid and cold arid phase. Hu et al. (2008) investigated Heshang Cave and reported some major climatic events as, 8.2 ka event and LIA and showed high rainfall intensity in Holocene than today. Wang et al. (2001) reported five stalagmites from Hulu Cave and explained the importance climatic events such as YD and BA transition and their comparison with ice core records. A high resolution (1-3 year) stalagmite record of Budha cave (Paulsen et al., 2003), China covered a time span of 12.7 ka BP and reflected climatic events such as MWP and LIA.

Similarly, a more detailed study of Shigao Cave (Jiang et al., 2012) record revealed a number of wet/dry phases and their link with solar forcing effect on the ISM and
EASM. A 500 year old stalagmite from Shihua Cave reflects fourteen precipitation cycles of 30-40 years and many wet/dry phases (Ku and Li 1998). The Dongge Cave stalagmite has revealed the last 9 ka BP record with dry period (8.2 ka BP) and its relationship with Neolithic Chinese culture (Wang et al., 2005). Dykoski et al. (2005) also reported a continuous record for the last 16 ka BP from Dongge Cave and developed a relationship between Asian monsoon intensity and North Atlantic climate during glacial period to early Holocene. An important stalagmite study (Tianmen Cave) from south Tibet demonstrates the control of solar activity on the ISM and EASM behaviour during last 8.7-4.3 ka BP (Cai et al., 2012).

Similarly, an aragonite stalagmite record (Siddha Baba Cave, Nepal) shows ISM variability and aridity at 2.3-1.5 ka BP and wet period after 1.5 ka BP (Denniston et al., 2000). The Four stalagmite records (Hotti Cave) of Oman and Yemen (Fleitmann et al., 2007; Yang et al., 2010) cover a time period from early to late Holocene and explain the relation between ITCZ migration and weakening of ISM period since 4.5 ka BP. The Qunf Cave (Fleitmann et al., 2003) covers a time period of 10.4-0.4 ka BP with a high peak aridity event (8.3 ka BP). The Moomi Cave stalagmite covers a time period of 27.4 -11.1 ka BP with two peak aridity events and major global events such as YD and BA transition (Shakun et al., 2007).

2.7. Objectives of the present study

(a) Documentation of caves in selected parts of Jammu and Kashmir, Himachal Pradesh and Uttarakhand Himalaya. Detailed mapping of caves having ideal stalagmites and the selection of most ideal stalagmites for laboratory measurements.

(b) Stable isotopic ($\delta^{13}$C and $\delta^{18}$O) determination at an interval of ca. 0.8 mm along the growth axis. Dating of selected samples (at least at an interval of ca. 10cm) using Uranium series dating method through Thermal Ionisation Mass Spectrometry (TIMS).

(c) Mineralogy and trace element analysis to reconstruct the palaeoclimatic conditions in the surroundings, rainfall and other processes like intense evaporation rate etc.

(d) Reconstruction and interpretation of past precipitation on at least multi annual to decadal scale in the Indian Himalaya under various precipitation regimes.