# Chapter 2

Paleoclimate proxies

2.1 Speleothems

The word speleothem is derived from Greek words 'Spelaion' meaning cave and 'thema' meaning deposit[*Moore*, 1952; *Schwarcz*, 1986]. The speleothems used for paleoclimate studies are made of calcite or aragonite or a mixture of two. Speleothems are formed in karstic caves, where the water table is significantly lowered, favoring air exchange with atmosphere. A typical cross section of karstic caves can be divided to four parts, namely, soil, epikarst, vadose zone/karst and phreatic zone. A schematic representation of speleothem formation is shown in Figure 2.1. Partial pressure of carbon dioxide in rainfall is $10^{-3.5}$ bars. As rainfall percolates into the soil, it dissolves a higher amount of additional CO_2 released from microbial decay and plant root respiration. Partial pressure of CO_2 (P_{CO_2}) in soil is $10^{-1}bar$. This "corrosive" solution reacts with the host carbonate rocks in epikarst and forms HCO_3^-, CO_3^- ions [*Sasowsky and Mylroie*, 2007]. The degree of saturation of these ions depends upon the acidity of water and residence time of water in the passage. During the dissolution process, trace elements from the bedrock are also incorporated in dissolved, particulate or colloidal state. As the saturated water descends through the crevices and fractures into the karst, it comes in contact with cave air having lower P_{CO_2} ($10^{-2.5}bars$) . This leads to

degassing of CO_2 from the solution and precipitation of $CaCO_3$ in the form of calcite or aragonite.
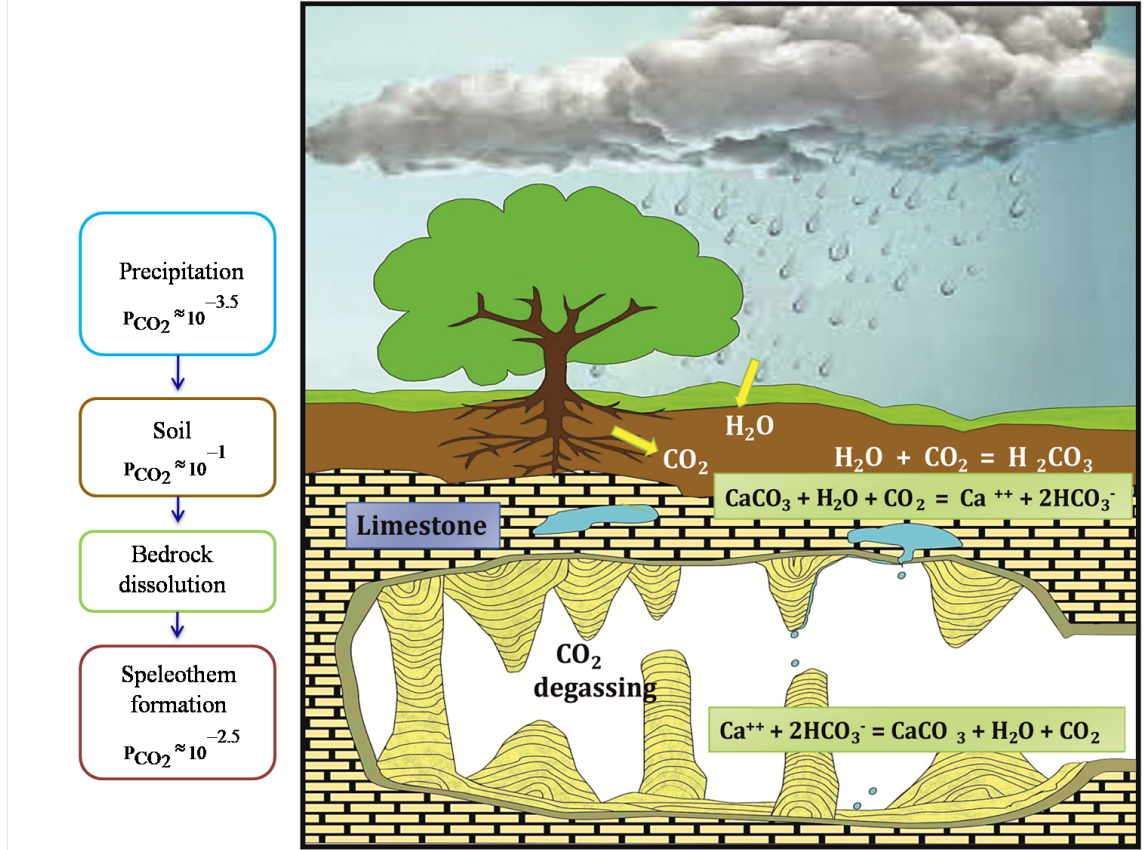
Figure 2.1: *Conceptual model explaining the formation of speleothems in a karstic cave. Partial pressures of CO_2 in rainfall, soil and cave air are typical values taken from Sasowsky and Mylroie [2007].*

At the roof of the cave, near the exposed fractures, slow dripping of water leads to the formation of hollow cylindrical tubes known as soda straws. They are among the earliest structures to form. Ceaseless dripping along soda straws leads to precipitation of calcite on its outer margin, forming a conical structure called as Stalactite. The excess water from the stalactites drips down and forms stalagmites which grow upwards. When the rate of precipitation is high, stalactites and stalagmites grow together and merge to form columns. When the rate of drip is high, the excess water is spewed on the floor, and subsequently forms layered deposits known as flow stones. Of the following morphotypes, stalactites and

stalagmites are favored for paleoclimate studies as the layers may be unperturbed and have less detrital content. Stalagmites, are preferred over stalactites, as they are cylindrical with near flat layers. This favors sub-sampling along each layer as opposed to conical growth layers of stalactites, which may also be interrupted by soda straws in the center.

2.1.1   Mineralogy

Calcite is the most abundant mineral in speleothems. However, sometimes the calcitic fabric is intertwined with aragonite. Aragonite is metastable with respect to calcite at atmospheric pressure. Trace elements play a key role in deciding the calcite-aragonite fabric [*Sasowsky and Mylroie*, 2007]. Sr^{2+} ions favor aragonite nucleation, thereby hindering the formation of calcite crystals. Aragonite precipitation is also dominant when the host rock is dolomite, with high Mg/Ca ratios. Mg^{2+}, inhibits calcite nucleation, thereby necessitating the supersaturation required for the aragonite formation [*Berner*, 1975; *Bischoff*, 1968]. Calcite-Aragonite fabric also depends upon the cave setting. In poorly ventilated caves, partial pressure of water vapor is saturated and partial pressure of CO_2 may approach that of the drip water. As a result, slow deposition of calcite crystal takes place. In a dry ventilated caves, humidity is very low and P_{CO_2} may represent the values of atmosphere background [*Bar-Matthews et al.*, 1991; *Murray*, 1954; *Railsback et al.*, 1994]. As a result, there is rapid degassing and deposition of aragonite may be favored. A speleothem from the Sai baba cave from Nepal was used to reconstruct changes in the Indian summer monsoon during the last 2300 years based on change in calcite-aragonite fabric. Aragonite crystallization was observed during the weaker/drier phases of monsoon, whereas calcite crystallization was observed during wetter conditions [*Denniston et al.*, 2000].

2.1.2 Isotope exchange in speleothems

The dissolution of bedrock and subsequent deposition of speleothem involves involved chemistry, right from the conversation of gaseous carbon oxide into dissolved aqueous state.

In the atmosphere, carbon dioxide is present as a trace species with the mixing ratio reaching up to 400 ppm. Carbon dioxide in gas phase ($CO_{2(g-soil)}$) dissolves in meteoric water to form $CO_{2(aq)}$.

$$CO_{2(g-soil)} \leftrightarrow CO_{2(aq)} \tag{2.1}$$

$CO_{2(aq)}$ then reacts with H_2O to form carbonic acid.

$$CO_{2(aq)} + H_2O \rightarrow H_2CO_3 \tag{2.2}$$

Carbonic acid, being a 'weak acid', dissociates to bicarbonate ions at higher pH.
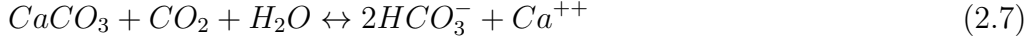
$$H_2CO_3 \rightarrow HCO_3^- + H^+ \tag{2.3}$$

The DIC pool at neutral pH values is dominant in HCO_3^- ions, but has a small proportion of CO_3^- ions for carbonate mineral stability.

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \tag{2.4}$$

The further reactions leading to speleothem formation are

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3 \tag{2.5}$$
$$H_2O \leftrightarrow OH^- + H^+ \tag{2.6}$$

Dissolution of the bedrock carbonate can be summarized as :

$$CaCO_3 + CO_2 + H_2O \leftrightarrow 2HCO_3^- + Ca^{++} \tag{2.7}$$

Speleothems can form as a result of the interplay of various subsurface processes shown in Figure 2.2 The isotopic composition of the precipitated calcite depends upon the following cave characteristics:

(1) The solution dissolving the limestone bedrock is always in contact with the soil carbon dioxide gas, known as 'open system'

(2) The solution dissolving the limestone bedrock remains isolated from the gas phase until it is exposed to cave air, known as 'closed system'.

The isotopic composition of speleothems may also be influenced by changes in the cave environment. These are:

(1) When the humidity inside the cave is very high and partial pressure of carbon dioxide in cave air is close to the saturated value, the rate of loss of carbon dioxide from the solution becomes sufficiently slow. At this rate isotopes are precipitated in isotopic equilibrium. The slowest reactions within solution are dehydration of bicarbonate ions and hydration of aqueous carbon dioxide. This is the only step where there is isotopic exchange between oxygen of water and oxygen of carbon compounds in the solution [*Hendy*, 1971]. For calcite to be precipitated under "oxygen isotopic equilibrium" with the water, equilibrium between these species is necessary.

(2) In ventilated caves, the partial pressure of cave air may be close to the atmospheric background value. In such a scenario, when the dripping water comes in contact with cave air, there is rapid degassing of carbon dioxide, prior to achieving the state of equilibrium between aqueous carbon dioxide and bicarbonate ions. This process is called "Kinetically fractionated deposition" [*Hendy*, 1971].
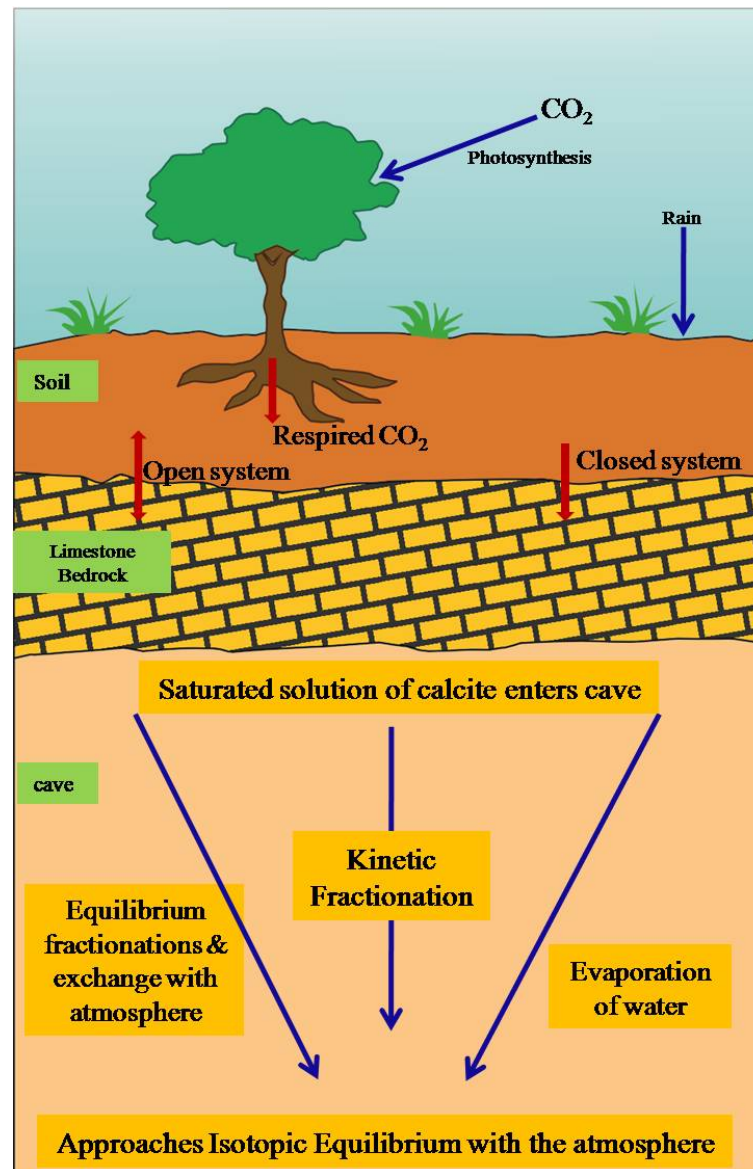
Figure 2.2: *A schematic diagram of the role of different pathways involved in speleothem formation. Figure redrawn from* Hendy [1971].

(3) The third type of deposition occurs near the cave entrance or where the cave humidity is very low. In this case, the solution becomes supersaturated through loss of water due to evaporation.

These processes play a key role in controlling the isotopic composition in speleothems, and their effects on oxygen and carbon isotopic values will be discussed in detail below.

Carbon Isotopes

The carbon in speleothems is derived from two sources (1) Soil CO_2 which is much lighter than the atmospheric carbon dioxide, with a $\delta^{13}C$ value of -9‰ [*Craig and Keeling*, 1963]. And (2) Bedrock Carbon. The evolution of carbon isotopes is a complex process and depends upon several factors [*Hendy*, 1971; *Lauritzen and Lundberg*, 1999; *Wigley et al.*, 1978] shown in Figure 2.3 . They are:

(1) The photosynthetic pathways

When carbon dioxide from atmosphere is taken by plants, it is converted to organic compound during photosynthesis, a process known as "kinetic isotopic fractionation". The plants following Calvin (normal) photosynthetic cycle (C3), produce biogenic carbon with $\delta^{13}C$ values -36‰ to -22‰ w.r.t.VPDB [*Badeck et al.*, 2005; *Cerling and Harris*, 1999]. Such type of vegetation is found in humid conditions, like tropical forests. The plants following HATCH-SLACK photosynthetic cycle (C4) on the other hand, produce carbon with $\delta^{13}C$ values of about -12‰ [*Bender*, 1968]. Grasses in semi-arid regions follow this cycle. Hence, the $\delta^{13}C$ of deposited calcite depends upon the relative contribution from these two types of vegetation. Climate driven changes can effect the type of vegetation and in turn change the $\delta^{13}C$ of speleothems [*Clark and Fritz*, 1997; *Gascoyne*, 1992; *Lauritzen*, 1995]. However, change in vegetation type in response to climate change is observed on centennial timescales scales.

(2) Biological activity

Carbon dioxide in soil is derived from two sources: plant root respiration and microbial decomposition. During the wet season, intense respiration leads to high pCO_2 and lower values of $\delta^{13}C$.

(3) Closed cave system

In closed cave systems, the carbon dioxide from the solution does not interact with the gaseous phase before coming in contact with the limestone bedrock. Thus, there are two sources of carbon: the solutions that carried carbon from the

aerated zones and the carbon released during dissolution of limestone. Here the isotopically depleted carbon species from an aqueous solution with $\delta^{13}C$ = -24‰ combine with the isotopically heavier carbon dioxide of $\delta^{13}C$ = +1‰ to form calcite. Unless variation in climate causes changes in $\delta^{13}C$ or partial pressure of carbon dioxide in the soil, there will not be significant variation in the $\delta^{13}C$ of calcite precipitated from a closed system solutions.

(4) Open cave system

In this type of cave setting, the isotopes of carbon in solution dissolving limestone are constantly interacting with the carbon dioxide from soil atmosphere, such that, a chemical and isotopic equilibrium is maintained. The isotopic composition of carbon is give by following equation
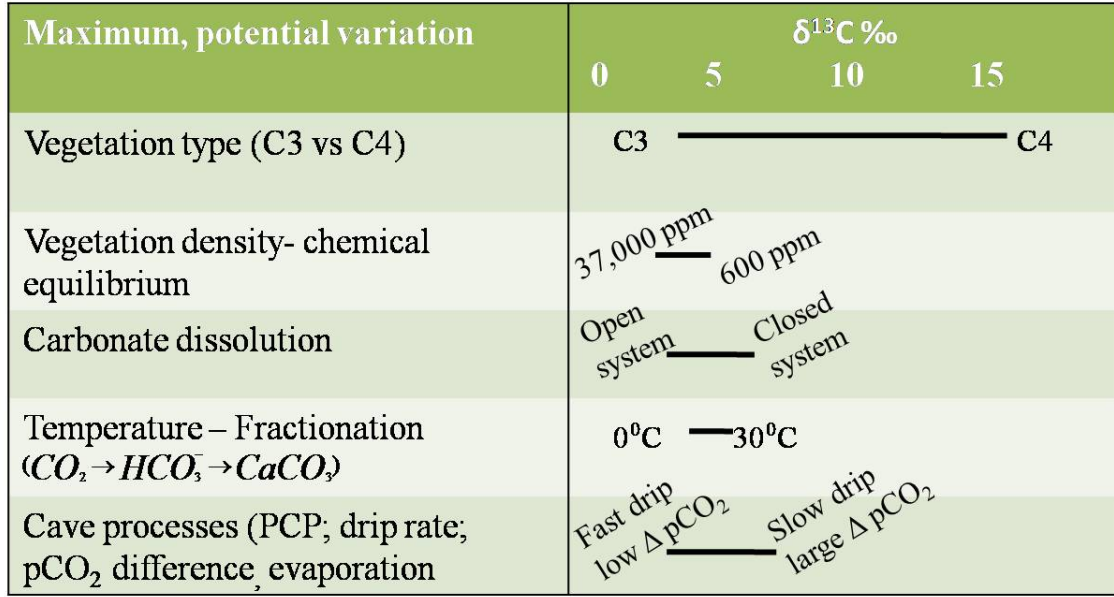
$$\delta^{13}C_{CO_{2(aq)}} \cong \delta^{13}C_{CO_{2(g)}} + \varepsilon^{13}C_{(CO_{2(aq)}-CO_{2(g)})} \tag{2.8}$$

where $\varepsilon^{13}C_{(CO_{2(aq)}-CO_{2(g)})}$ is the isotopic enrichment factor between aqueous carbon dioxide and gaseous carbon dioxide, [*Craig*, 1954; *Hendy*, 1971].

(5) Drip rate in the cave

When the saturated solution comes in contact with cave atmosphere, loss of CO_2 may take place by degassing or evaporation. If the rate of degassing is sufficiently slow then the isotopic equilibrium is maintained between degassing carbon dioxide, precipitating calcite and carbon isotopes in solution. If the equilibrium conditions are such that there is a progressive enrichment in ^{13}C of the species remaining in the solution w.r.t. carbon dioxide degassing and precipitating calcite, it is called "Rayleigh distillation" process. In this process, if rate of transport of CO_2 from the solution is close to the cave atmosphere, there will be steady exchange and isotopic equilibrium is maintained. However, $\delta^{13}C$ values may not truly represent climate variability, unless there is a systematic change in the partial pressure or $\delta^{13}C$ value of the carbon dioxide in the soil atmosphere.

Maximum, potential variation	$\delta^{13}C$ ‰			
	0	5	10	15
Vegetation type (C3 vs C4)	C3 ————————— C4			
Vegetation density- chemical equilibrium	37,000 ppm ——— 600 ppm			
Carbonate dissolution	Open system ——— Closed system			
Temperature – Fractionation ($CO_2 \rightarrow HCO_3^- \rightarrow CaCO_3$)	0⁰C ——30⁰C			
Cave processes (PCP; drip rate; pCO_2 difference, evaporation)	Fast drip low ΔpCO_2 ——— Slow drip large ΔpCO_2			

Figure 2.3: *Factors controlling $\delta^{13}C$ of speleothem. Figure redrawn from the sources of carbon is speleothems, presented at the Speleothem Summer School,2015, Oxford,Jens Fohlmeister*

Oxygen Isotopes

The use of oxygen isotopes of speleothems for paleoclimate studies was first reported in the 1960's [*Broecker et al.*, 1960; *Hendy and Wilson*, 1968]. The stable isotopes of interest are, ^{18}O and ^{16}O and their ratios are measured relative to laboratory and international standards on a mass spectrometer. And the values are expressed as

$$\delta^{18}O = \left[\frac{\left(\frac{^{18}O}{^{16}O}\right)_{Sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{Standard}} - 1 \right] \times 10^3 ‰ \tag{2.9}$$

The standard used for carbonate measurement is VPDB-Vienna Pee Dee Belemnite derived from the rostrum of Belemnitella americana from the Pee Dee Formation of South Carolina in U.S.A [*Coplen et al.*, 1983; *Gonfiantini*, 1978]. The standard is procured from IAEA (International Atomic Energy Agency, Vienna).

When the sample has higher $\delta^{18}O$ relative to a standard, it is referred as isotopically "enriched" or "heavier" and vice a versa. The fractionation factor α_{CW} is known for the calcite-water system and is given by the following equation [*O'Neil et al.*, 1969].

$$\alpha_{CW} = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{Calcite}}{\left(\frac{^{18}O}{^{16}O}\right)_{Water}} \qquad (2.10)$$

$$\Delta_{cw} = (2.78 \times 10^6/T^2)\text{--}3.39 \qquad (2.11)$$

Where, T is the ambient cave temperature in ^0K and $\Delta_{cw} = 10^3\alpha_{CW}$.

The oxygen isotopes in speleothems can be traced back to the processes controlling the hydrological cycle. Evolution of oxygen isotopes precipitating in speleothems depends upon the phase changes on its course from ocean water → vapor → prepitation → soil water → epikarst solution → karst drip water. The $\delta^{18}O$ value of the soil water is determined by the $\delta^{18}O$ value of the precipitation infiltrating the soil pores. Processes such as evaporation and transpiration play a crucial role in controlling the $\delta^{18}O$ in soil pores. In arid regions, evaporation leads to enrichment in ^{18}O , whereas in humid climates the role of evaporation is minimal [*Allison*, 1982; *Lachniet*, 2009; *Tang and Feng*, 2001]. Soil water infiltrates into the epikarst, having fissures, bedding planes and other solution features where water may get stored or mixed. Flow through the epikarst may occur through primary porosity, joints or large conduits [*Klimchouk*, 2000; *Williams*, 2008; *Yonge et al.*, 1985]. The residence time of water in the epikarst also controls the $\delta^{18}O$ of water. Longer the residence time, more are the chances of mixing with ground water. Hence, a rapid flow rate leads to less alterations in the $\delta^{18}O$, making it suitable for detecting high-frequency climatic events[*McDonald et al.*, 2007], whereas a slow residence time is useful for studying long term climate

changes. The $\delta^{18}O$ of the solution entering the caves later becomes functions of the degree of saturation of solution, humidity inside the cave etc. In ventilated caves, where the humidity is less than 100%, evaporation takes place and ^{18}O is further enriched.

In order for speleothems to track hydrological changes, it is important that the isotopic equilibrium is maintained between the drip water, degassing CO_2 and precipitating $CaCO_3$[*Hendy*, 1971]. The only factors which affect the oxygen isotopic composition are changes in the cave air temperature and change in the mean isotopic composition of water. Both these factors change with the change in climate. The temperature inside the cave remains constant throughout the year in poorly ventilated caves because of thermal inertia [*Gascoyne*, 1992; *Lauritzen*, 1995; *McDdermott et al.*, 2006; *Repinski et al.*, 1999]. Changes in the annual temperature affect the $\delta^{18}O$ of the precipitating calcite, where heavier $\delta^{18}Oc$ values imply lower temperatures. The degree on enrichment is given by equation: $d(\Delta_{cw})/dT = -0.21^0C^{-1}$at 25°C.

The temperature interpretation based on speleothem $\delta^{18}O$ is not straight forward and depends upon many parameters. The factors controlling $\delta^{18}O$ are summarized by*Lauritzen and Lundberg* [1999] in an expression

$$\delta^{18}O = \exp\{a/T_1^2 - b\}[F(T_2,t,g) + 1000] - 1000 \tag{2.12}$$

same as

$$ln\alpha = ln\Big(\frac{\delta^{18}O + 1000}{F(T_2,t,g) + 1000}\Big) = \frac{a}{T_2} - b \tag{2.13}$$

where $a = 2.78 \times 10^3$, $b = 3.39 \times 10^3$ (empirical constants), T_1 is the deep cave temperature and T_2 is the surface temperature, t is the time and g is the geographical position (latitude, longitude) of the cave. The thermodynamic frac-

tionation between calcite and water inside the cave is given by the exponential part, the drip water isotopic composition ($\delta^{18}O$) is a controlled by F(T2, t, g). In most of the cases, the cave temperature can be assumed to be equal to the surface temperature. For paleo-temperature reconstructions T derivative is expressed as

$$\mu = \frac{d\delta^{18}O_C}{dT}$$

and can be positive or negative or even zero. Hence the use of speleothem $\delta^{18}Oc$ for temperature interpretation is ambiguous [*Gascoyne*, 1992; *Lauritzen and Lundberg*, 1999]. However, $\delta^{18}Oc$ can be used to trace first order changes (glacial-interglacial events) in climate [*McDdermott et al.*, 2006].

The caves located in tropics however, show less temperature annual variability. The $\delta^{18}Oc$ of speleothems in such caves, are strongly dependent inversely on the amount of rainfall.

2.1.3 Trace elements

$CaCO_3$ while precipitating incorporates trace elements (Tr) from the solution. In the solution, various elements form divalent cations and substitute for Ca ion in the $CaCO_3$ crystal lattice [*Fairchild and Treble*, 2009]. Elements such as Mg, Sr, Ba with similar ionic radii substitute for Ca under different physical conditions [*Morse and Bender*, 1990].

$CaCO_3 + Tr^{2+} \Leftrightarrow TrCO_3 + Ca^{2+}$
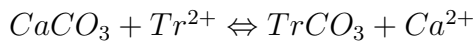
A simple equation is used to define the distribution coefficient to relate solution and mineral compositions.

$(TrCO_3/CaCO_3) = K_{Tr}(Tr/Ca)_{solution}$

Where Tr is the trace ion and K_{Tr} is the distribution coefficient that depends on precipitation, temperature, crystal morphology. Other than substitution, trace elements come through the aqueous medium where they are adsorbed on the surface of detrital particles and hence get incorporated in speleothems. Excess

Th that gets adsorbed causes trouble in dating of the speleothem. The geological setting of karst deposits plays a major role in the trace element contribution. The primary source of calcium and other major elements come from the bedrock and overlying soil. Dissolution is maximum where pCO_2 reaches its peak. Most of the P comes from minor traces of Apatite in soil[*Huang et al.*, 2001]. Trace element concentrations also depend upon residence time of drip water. When the rock has both dolomitic and limestone composition, both will dissolve in undersaturated solutions. However, in deposited calcite Mg/Ca ratio will be lower than that of the host rock composition. The two important modes of transport of trace element to karstified bedrock are chemical mobilization and through hydrological processes[*Tooth and Fairchild*, 2003]. Chemical mobilization is mediated at three different rates. At rapid rates, trace elements adsorbed on organic and inorganic surfaces, preexisting dissolved species and mobilized particles are transported. At intermediate rates, there is calcite dissolution of the host rock followed by the slow process of chemical weathering of less soluble dolomite, silicates, phosphates and oxides[*Fairchild and Treble*, 2009]. Trace element contribution is also affected by the rate at which drip water flows. If the drip rate is slow due to low-permeable soil, the interaction time increases leading to the enrichment of trace species. High flow rate on the other hand can also be associated with trace element enrichment primarily for the species that are transported as colloids.

The infiltrating water passes from the dissolution regime to the precipitation regime, when it encounters conduits with relatively lower pCO_2[*Fairchild et al.*, 2006]. The resultant degassing leads to supersaturation of water for $CaCO_3$ and calcite precipitation. As K_{Tr} values for the carbonate precipitated are less than one, there is larger reduction of Ca in solution than that of the trace element and hence an increase in the ratio of trace element to Ca in solution[*Holland et al.*, 1964]. Since there are gas filled conduits in the soil, leading to " Prior Calcite Precipitation" (PCP), it might suggest drier climatic conditions [*Fairchild et al.*, 2000; *Johnson et al.*, 2006; *McMillan et al.*, 2005]. PCP usually leads

to higher Mg/Ca and Sr/Ca ratios, which could also favor aragonite formation in speleothems[*Frisia et al.*, 2002; *McMillan et al.*, 2005]. Sr is incorporated in larger Quantities at growth rates, where it substitutes for Ca or occupies the defect sites[*Gabitov and Watson*, 2006]. Other trace elements are seen associated with colloidal medium or adsorbed on organic-inorganic substrates. The elements associated with fluorescent lamina are seen in following rank order: $Y > (Cu, Zn, Pb) > Br, P$. Y is essentially transported through an organic colloidal phase[*Borsato et al.*, 2007; *Fairchild and Treble*, 2009]. Phosphorous binds very strongly to Calcite surfaces and if present in high concentrations may inhibit calcite growth[*Huang et al.*, 2001]. Transport of colloids is likely to increase during higher precipitation conditions where the rate of infiltration is higher. Mn is transported either as a organic complex, colloidal complexes or as a particle in groundwater[*Perrette et al.*, 2000; *Richter et al.*, 2004; *Zhou et al.*, 2008]. Mn that is present as colloidal complex may get attached to the fine detrital layers in speleothem, and it may not be associated with crystal lattice.

Mg in Speleothem   Mg/Ca ratios in speleothem were considered to respond to temperature changes within caves. *Gascoyne* [1983] demonstrated a positive correlation between D_{mg} and the cave temperature. *Fairchild et al.* [2001] suggested that Mg in speleothems can be used to reconstruct hydrological changes. Mg/Ca ratios are found to be sensitive to amount of rainfall and can be used in conjunction with stable isotope values to assess monsoon variability. Mg/Ca ratio in drip water is influenced by PCP and is higher during low-flow conditions. A positive correlation is seen between $\delta^{13}C$ and Mg driven by the effect of PCP. In the case of $\delta^{18}C$ values, the Mg/Ca ratios show a negative correlation, as there are a few sites where PCP takes place. Sampling sites of speleothems are equally important.*Baldini et al.* [2006] argued that it is preferable to collect samples below active seepage flow, as the trace element contribution will respond to hydrological changes. Thickness of the overlying limestone bedrock is another factor affect-

ing the influx of trace elements. If the bedrock thickness is less, there are more chances of preserving the response of trace element to hydrological changes.

2.1.4   Speleothems as paleomonsoon proxy

Speleothems deposited in the karst formations of India are direct recorders of Indian summer monsoon as most of the annual precipitation is received in peninsular India during June to September [*Lone et al.*, 2014; *Sinha et al.*, 2007; *Yadava and Ramesh*, 1999, 2005, 2006, 2007]. Most of the speleothems studies so far studied ISM changes during part of the Holocene period. The Holocene marks the intensification of monsoon at around 11.7 ka. The monsoon variability during Holocene period, led to concomitant changes in different human civilizations spread across India.

There are several proxy records from east Asia and Oman that reconstructed the ISM during the Pleistocene. However, very few records exist from the core monsoon region of India covering this timespan[*Cai et al.*, 2015; *Yuan et al.*, 2004; *Zhisheng et al.*, 2011]. The importance of this period is recurring glacial-interglacial cycles. In tropical regions, the glacial-interglacial periods are interpreted in term of weakening or strengthening of monsoon respectively. Response of the ISM during these cycles is documented in the studies carried out over the Indian ocean [*Leuschner and Sirocko*, 2000; *Prabhu et al.*, 2004; *Schulz et al.*, 2002; *Sirocko et al.*, 1993; *Zorzi et al.*, 2015] and using various terrestrial proxies[*Agrawal et al.*, 2012; *Dutt et al.*, 2015; *Juyal et al.*, 2006; *Roy et al.*, 2012] . However, most of the terrestrial proxies which are direct recorders of monsoon focus on the last glacial maxima. Hence there is a lack of understanding regarding the effect of glacial millennial climate variability on ISM .With absolutely dated speleothems, in combination with high resolution stable isotope or trace element analyses, glacial-interglacial cycles can be studied in great detail.

The aim of the present study is to reconstruct high resolution monsoonal changes since the late Pleistocene period.

2.1.5   Sample locations

Most of the carbonate outcrops in India are karstified and host variety of speleothem formations. Some of these caves are explored extensively by geoscientists for paleoclimate studies. The caves which have been studied to understand the climate variability are shown in Figure 2.4 [*Allu et al.*, 2015; *Sinha et al.*, 2007; *Sinha and Naik*, 2004; *Yadava and Ramesh*, 2001, 2005, 2006; *Yadava et al.*, 2007]. Our present work is focused on three such caves in the Kanger valley cave complex, Chattisgarh and the Belum cave in Andhra Pradesh.

The Kanger valley cave complex

A vast cave complex is located in Kanger valley National Park, Chattisgarh of central India comprising of unexplored caves like Dandak, Kotumsar and Kailash 2.4. The caves are exposed in the north of the Kanger River[*Biswas*, 2010]. And are formed by dissolution of the Kanger limestone belonging to the Indravati group rocks of Mesoproterozoic era [*Maheshwari et al.*, 2005]. In the present study, stalagmites from all the three caves spanning different time frames are studied in detail.
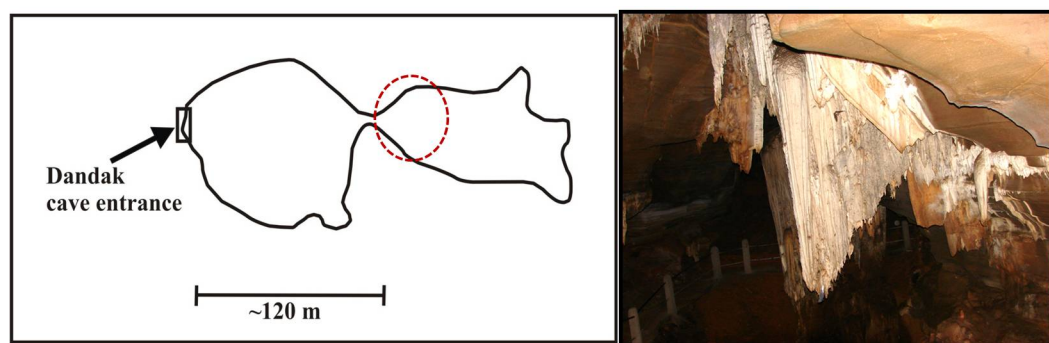
The Dandak cave   The Dandak cave (18°51'30" N; 81°57'00"E, 400 m.s.l) is one of the many caves located in the Kanger valley National Park, Chattisgarh (Figure 2.4) in Central India[*Sinha et al.*, 2007; *Yadava and Ramesh*, 2005]. The cave is situated on a hillock with scattered boulders exposed around [*Biswas and Shrotriya*, 2011]. The cave entrance located in the north-west direction opens up to a large hall, known as the outer chamber of the cave.
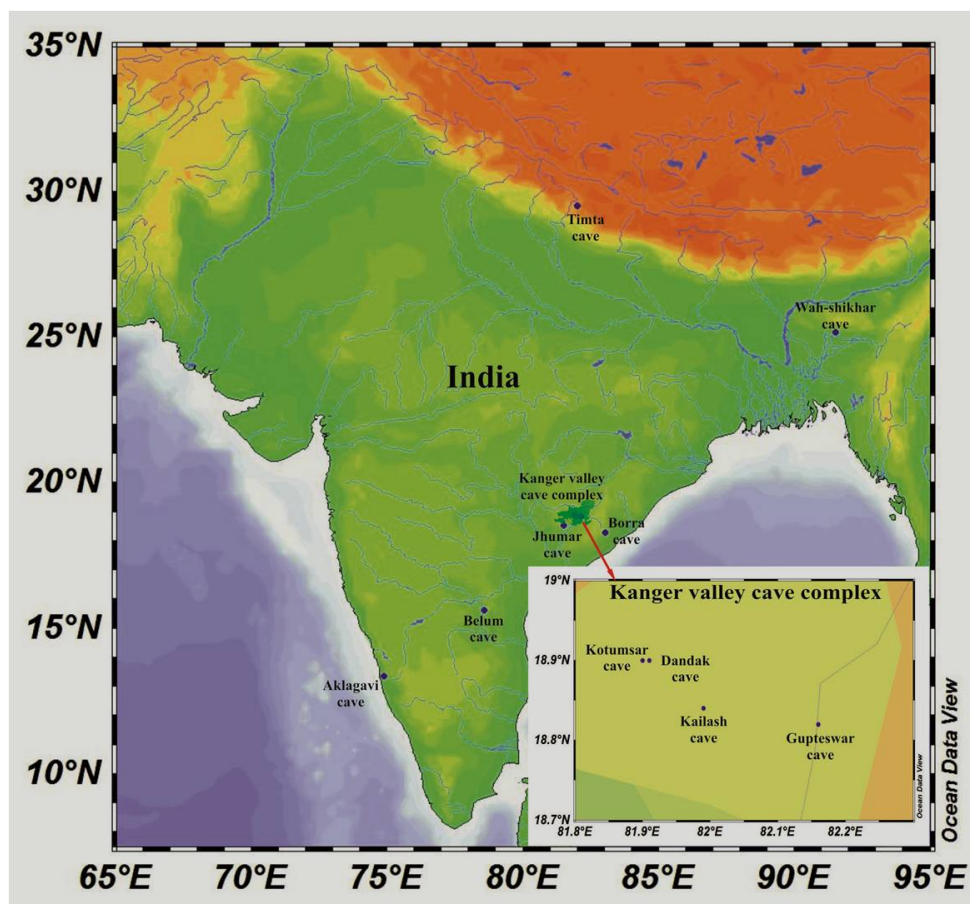
Figure 2.4: *Map of the India showing the locations of the caves explored for paleoclimate studies. The box in the lower right, zooms in onto the Kanger valley cave complex, Chattisgarh.*

The average length of the cave is 330 meters and it has two main chambers. The outer chamber is connected to the inner one through a narrow passage. The seasonal variability is found in the physical parameters of the cave such as, cave air temperature, relative humidity and water pH in both the chambers [*Biswas and Shrotriya*, 2011]. Average pH of the seepage water and drip water temperatures are (7.2-7.5) and (18-20℃), respectively, [*Biswas and Shrotriya*, 2011]. Tourism is exempted for the caves, and thus there is a good scope of undisturbed growth in the speleothem samples. The stalagmite samples were collected from the inner chamber, exhibiting high humidity and poor ventilation.

Figure 2.5: *Left: Overview of the Dandak cave, with the dashed circle indicates sampling site,Right: Photo showing Dandak stalactite.Photo source: [Biospeleologist, 2013].*

The Kotumsar cave The Kotumsar cave (19°00'N, 82°00'E, 35m below ground level) is located 5km north of the Dandak cave (Figure2.4) in Kanger valley National Park. The lateral extent of the caves is around 330 meters with several chambers and passages around 20-70 meters wide [*Yadava and Ramesh*, 2007]. Cave entrance is formed by the vertical fissure in the wall of a hill[*Biswas*, 2010]. A narrow channel of water passes through the central part of the cave galleries which is fed at the cave entrance during the ISM season (June to September), and terminates in the middle of the cave becoming a part of the underground pathways. Small ponds are seen during the dry seasons, i.e., pre-monsoon and post-monsoon (winter), which receive cave drip water and serve as a source of life for the cave biology [*Sinha and Naik*, 2004]. The average pH of the pond water is 8.04 ± 0.36. Currently the cave is open to public visit during winter. The average annual air and water temperatures within the cave are 28.25 ± 1.23 and 26.33 ± 0.96 °Crespectively[*Biswas*, 2010]. In the far interior of this cave (Figure 2.6), a few stalagmite pieces were found lying horizontally within a narrow zone (1 to 1.5 m of vertical space between the cave roof and the surface of 1m raised bedrock). A few stalagmites were recovered from this site in June, 2006 CE. Around these stalagmites, layers of fresh carbonate deposition were seen due to which these were lying intact on the surface, although the surrounding was found

to be dry at the time of collection.

The Kailash cave   Kailash cave (18°84'N, 82°00'E,40 m.s.l.) is located at $\sim$ 40 km from Jagdalpur, to the south of the Kotumsar and the Dandak caves(Figure 2.4). The cave is located on a limestone hilltop in a thickly forested area of the
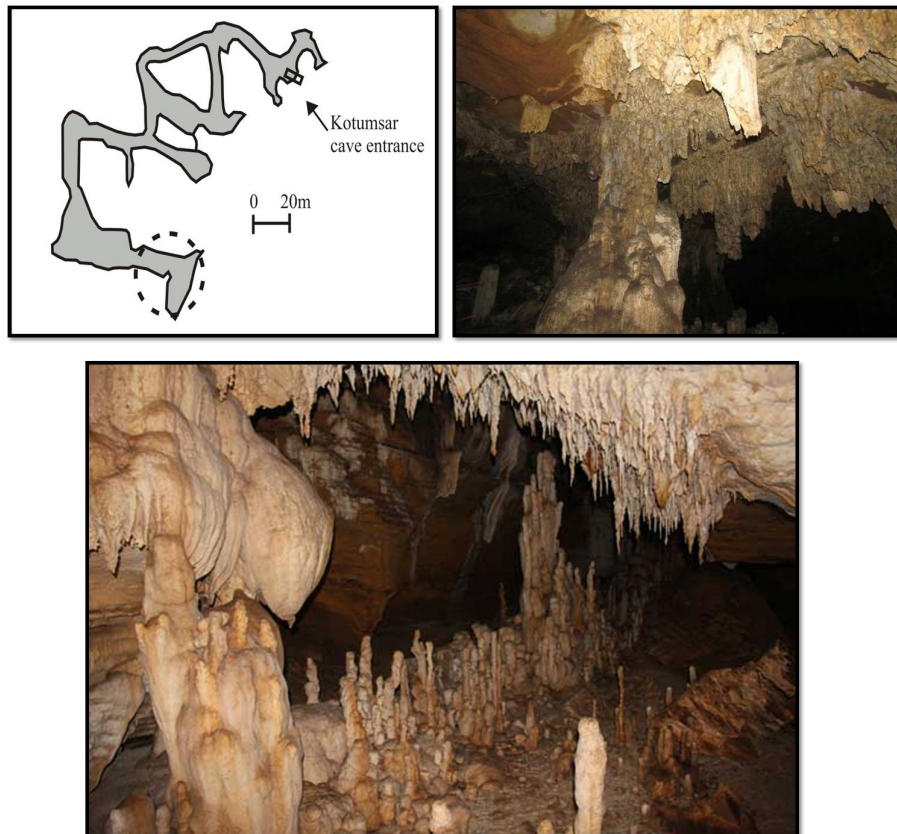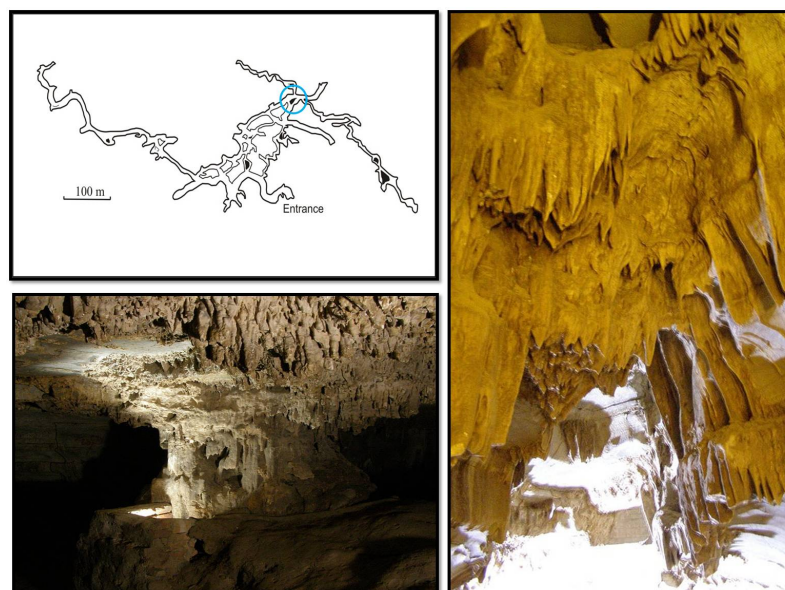

Figure 2.6: *Top left:Sketch of Horizontal cross sectional view of Kotumsar cave [Yadava and Ramesh, 2007]. Dotted circle shows the site of KOT-I speleothem. Top right and Bottom: Photos showing stalactites and stalagmites exposures in cave.Photo source:[Wikipedia, 2016a].*

Kanger National Park. The Kailash cave is 250 m long with only one narrow entrance at the top. The main hall of the cave follows the dip of the host rock with a very steep slope.

The Belum cave

The Belum cave (15^06'N, 78^06'E, 367 m above m.s.l.) is situated in the southern part of India in the Kurnool district, Andhra Pradesh. Geologically the area has outcrops representing middle to upper Proterozoic rock types of the Cuddapah Basin. The caves are formed in karstified Narji Limestone series. It is the second largest cave in the Indian subcontinent and one of the longest caves in India with its gallerias extending 825 m long(Narayana,et al., 2014). The deepest part of the cave is 80 m below the cave entrance. The caves have sixteen pathways including the main entrance. The cave is divided into many chambers colloquially referred as "hall". Each hall displays a magnificent formation of stalactites and stalagmites.The BLM-1 stalagmite was recovered from the inner gallery of cave having 100% humidity with a narrow channel to access.


Figure 2.7: *Top left: Sketch of Horizontal cross sectional view of the Belum cave.Redrawn from the sign board near the entrance of the Belum Cave. Circle over the map shows Belum stalagmite sampling site. Top right: Photo showing several stalactites famously known as "Ceiling hall of thousand hoods". Bottom:Photo showing a giant calcium carbonate column surrounded by stalactites known as "Banayan tree hall". Photo source: [Wikipedia, 2016b]*

2.2   Foraminifera

Sediments in the seas around the Indian subcontinent are excellent recorders of past monsoon variability. As southwest monsoon winds flow past the Arabian Sea, warm ocean surface water gets dragged towards the western coast of India. As a result, colder deeper waters, rich in nutrients force their way to the surface (Figure 2.8)near the Oman coast [*Anderson et al.*, 1992]. Planktons such as foraminifera bloom in such conditions and hence the abundance of certain foraminiferal species (e.g.,*G. bulloides*) is used as an indicator of upwelling/wind strength, which in turn is a proxy for the Indian monsoon. Higher abundance of this species has been interpreted as stronger monsoon winds [*Gupta et al.*, 2003].
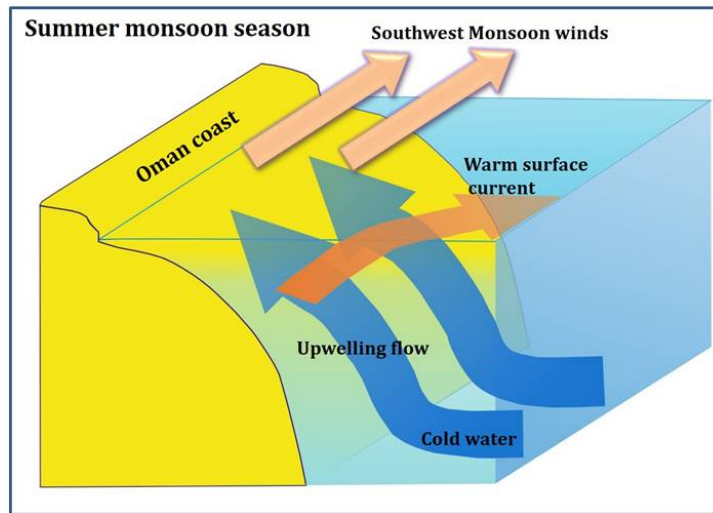

Figure 2.8: *Upwelling in the coast of Oman. Colder water from the deeper ocean rises up as the warm surface water is dragged by the south-westerly winds.*

During glaciations, Arabian Sea upwelling weakens in response to weakening in the monsoon wind strength. As a result, records show a lower abundance of *G. bulloides* during the glacial period and high abundance during interglacial period. *Urey* [1947], proposed that isotopic ratio of ^{18}O to ^{16}O (measured as deviation $[\delta^{18}O]$ in parts per mille ‰ from that of a reference, Pee Dee Belemnite) of calcitic tests of marine microfossils varies depending upon the water temperature at which the test is formed; higher ratio (i.e. more positive $\delta^{18}O$) in the test

signifies a lower temperature (i.e. a temperature coefficient of ~ -0.2 ‰$(°C)^{-1}$), as later experimentally verified by *Epstein et al.* [1953]. Marine Isotopic Stages (MISs) were first described based on a core raised from the Caribbean [*Emiliani*, 1955]. $\delta^{18}O$ fluctuations of planktonic foraminifera (marine organisms that live typically for ~ 6 weeks in the top 100 m of the ocean, on whose death, their calcareous tests settle down on the ocean floor, typically at the rate of 1 to 10 cm/ka) were used to deduce the climate variability of past ~ 280 ka as recorded by these microfossils in marine sediment. In a stratigraphic column alternate 'warm' and 'cold' stages were observed. Accordingly, the present 'warm' stage was designated by number 1 and the preceding 'cold' stage, an even number (MIS 2). Therefore, all the 'warm' and 'cold' stages are odd and even nos., respectively, giving an appearance of a sinusoidal wave where the stage boundary is marked as the midpoint between 'temperature maximum' and 'minimum'. *Shackleton and Opdyke* [1976], recognized that it is not just temperature change that contributed to the observed changes in $\delta^{18}O$ of tests of the marine microfossils, but also that changes in sea level or 'ice-volume'; thus they refined and further extended this timescale to 22 stages spanning ~ 900 ka as opposed to 16 stages originally proposed by *Emiliani* [1955]. Initially researchers used planktonic foraminiferal tests for $\delta^{18}O$ measurements. Planktonic foraminifera respond to local temperature variations and may not be a suitable proxy to record global temperature variations. Deeper oceans are more uniform in temperature and salinity than the surface ocean, therefore $\delta^{18}O$ values of benthic foraminifera (foraminifera that live and die on the ocean floor) could be more reliable, as they are believed to respond mostly to global ice volume or sea level changes. Recent reconstructions of Marine Isotopic Stages are done using $\delta^{18}O$ of benthic foraminiferal tests. Climate record was improved when stacks which were averages of $\delta^{18}O$ values of benthic foraminiferal records from multiple ocean sites were correlated. A new 5.3 Myr benthic $\delta^{18}O$ stack (called "LR04") was presented consisting of over 38,000 individual $\delta^{18}O$ measurements from 57 sites distributed globally [*Lisiecki*

and Raymo, 2005; *Shackleton*, 1987]. Most of the measurements were done on the species *Uvigerina peregrina* or *Cibicidoides wuellerstorfi*. The advantage is the elimination of "local" climate signals and generation of a smooth curve that represents "global" climate change. Two inferences are readily seen from this curve: first, a steady increasing (plotted downward) trend in the mean $\delta^{18}O$ values. This implies that the ocean water steadily became enriched in ^{18}O, signifying the formation of ice sheets (which preferentially lock in $H_2\,^{16}O$) and global cooling that appears to have commenced around 3 million years ago. Secondly, the amplitude of fluctuations has increased during the last one million years. This signifies that the $\delta^{18}O$ glacial and interglacial sea level changes have become higher in magnitude (100 m) with time. Equivalent, long and continuous monsoon proxy records are not available for the Indian region so far.
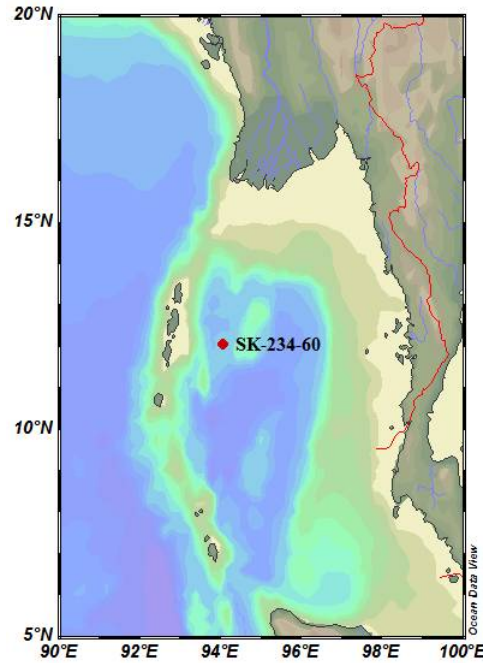
Figure 2.9: *Location of core SK-234-60 from Andaman Sea.*

The present study is based on a 4 m long sediment core (SK-234-60) raised from the Andaman Sea N 12°05'46" and E 94°05'18" at a depth of 2 km. Part of the work related to core SK-234-60(Figure 2.9) is covered in *Awasthi* [2012],

where geochemical studies on the sediments were carried out to understand the provenance of the deposits.The Present work is to interpret $\delta^{18}O$ timeseries to reconstruct ISM variability.

2.3 Tree rings

Climate change during the past 1000 years is important to reconstruct as it can be correlated with the historical archives and extent to which climate affected civilizations can be deduced.Of the several proxies used for paleoclimate (e.g. ice cores, lake sediments,corals and speleothems) reconstructions, tree rings have special advantages: they record seasonal monsoonal variability, they preserve continuous record and can be easily dated using ring-counting. An individual tree ring records contemporaneous climate changes in the year of formation over the life-span of the tree. Cross correlation and matching of ring patterns of different (dead, archived and growing) trees of the same climate regime can extend the climate reconstructions to past several thousands of years. Significant contributions to climate science within the last decade have firmly established tree-rings as valuable sources of proxy data for evaluating long-term climate variability/trends and as useful tools for developing long-term records of extreme climatic events [*Mann et al.*, 1999].

Previous monsoon reconstructions using tree rings were based on ring width. The analogy used was: trees from high latitude or altitude regions, with wider (narrower) rings correspond to higher (lower) temperature/ precipitation [*Managave and Ramesh*, 2012].However, the presumably simple relation between width and climate is rather complex and is influenced by non-climatic factors such as light availability, topography, soil type and forest thinning, ecological parameters and also genetic variability among trees of the same species (e.g. *Kress et al.* [2009], *Fritts* [1976]). On the other hand, isotopic composition (stable isotope ratios of carbon ($\delta^{13}C$), hydrogen (δD) and oxygen ($\delta^{18}O$)) of tree rings is believed

to be less effected by ecological parameters and considered to be better measures for climate reconstruction. Tree cellulose $\delta^{18}O$ is more sensitive to rainfall fluctuations as compared to ring-width and ring density [*Sano et al.*, 2010]. Several researches and reviews on tree rings isotopes by *Farquhar et al.* [1989],*Ramesh et al.* [1986], *Dawson et al.* [2002], *McCarroll and Loader* [2004] *Managave and Ramesh* [2012] highlight that oxygen and hydrogen of cellulose from individual growth rings can be used as proxies for climatic parameters such as rainfall, humidity and temperature. The oxygen isotope composition of plants is influenced by various physiological and climate processes. It is mainly controlled by $\delta^{18}O$ of the source water, the level of ^{18}O enrichment in leaf due to evaporation, biochemical fractionation of ^{18}O due to synthesis of sucrose in the leaf and the isotopic exchange between carbohydrate and xylem water during cellulose synthesis. The $\delta^{18}O$ of rainfall is inversely related to the amount of precipitation in the tropics [*Dansgaard*, 1964; *Rozanski et al.*, 1993; *Schmidt et al.*, 2007; *Yadava and Ramesh*, 2007] hence tree cellulose $\delta^{18}O$ is a powerful tool to reconstruct past monsoon rainfall.

In the present study, the available records of monsoon reconstruction from tree rings of the Indian peninsula are used to compare with speleothem based reconstructions to asses the coherence between the two proxies.