STABLE ISOTOPE SYSTEMATICS IN CAVE CALCITES: IMPLICATIONS TO PAST CLIMATIC CHANGES IN TROPICAL INDIA

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March 2002

Dedicated To

Bauji and Ammaji

CERTIFICATE

I hereby declare that to the best of my knowledge this thesis does not contain any part of any work which has been submitted for the award of any degree or diploma either in this university or in any other university or institution.

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Plan of the thesis

This thesis is divided in to five chapters and it presents the first detailed study of speleothems (cave deposits) from India with an aim to test its applicability as a Samples from four caves have been assessed for changes in the palaeoclimate proxy. stable isotope ratios of oxygen (δ^{18} O) and carbon (δ^{13} C) and one of them has been studied for trace element variations. Several types of water samples have also been analyzed for their stable isotope compositions. Chapter-1 gives a brief summary of speleothem evolution and factors controlling the stable isotope ratios of oxygen and carbon in them. The purpose of the study and details of the samples collected are also presented. Chapter-2 discusses briefly an overview of the climate scenario in India over the Holocene period. Present status of climate reconstruction using speleothems based on the earlier work carried out by several workers on caves located in other countries is also presented. In Chapter-3 details of the experimental work carried out for this thesis is presented. A brief account of the stable isotope measurements of carbonate and water samples is given. Carbon dioxide was obtained from carbonate samples in a vacuum line and was introduced in to a mass spectrometer. For water samples, the CO_2 equilibration method was adopted. The vacuum lines, their operations and other related procedures to get δ^{18} O, δ^{13} C and δ D are explained in this chapter. Radiocarbon dating method was applied to assign an approximate chronology to the speleothems. From speleothem carbonates, benzene was synthesized and its radioactivity was measured using a liquid scintillation counter. A brief account of the method followed is given in this chapter. Elements Mg, Sr and Ba have properties very similar to the Ca and hence they enter into the speleothem carbonate in trace amounts. A speleothem was sampled at regular intervals and the concentration of trace elements was measured using ICP-AES method. A brief discussion on related aspects is also presented. Speleothems were also checked for mineral composition at the spots where extreme variations in the stable isotope ratios of the oxygen and carbon were found. One of the deposits has been investigated further as it showed correlation between aragonite content with speleothem δ^{18} O. Distinct laminations in one of the speleothems have provided a unique opportunity to investigate changes in the δ^{18} O and δ^{13} C at a finer (annual) scale. Gray levels and thickness measurements of annual laminations have been carried out to check for climate control on these parameters. It is speculated that the water drip rate

variation may be the primary factor controlling the speleothem δ^{13} C. To support this speculation, samples of cave water were collected and their $\delta^{13}C$ analyzed. The methodology is discussed briefly. In the Chapter-4, all the results and related discussions are presented. Dead carbon is contributed from bedrock dissolution and hence, ¹⁴C ages obtained in speleothem layers are usually older. Corrections for the dead carbon is made by assuming that throughout the past 3400 years, the dead carbon proportion in speleothem has remained constant. Bomb ¹⁴C present in a speleothem showing distinct laminations suggests that it may have annual resolution. The magnitude of temporal variations in δ^{18} O and $\delta^{13}C$ are large and can not be explained by mere consideration of the past temperature fluctuations. This is because temperature reconstructions are unrealistic and speleothem δ^{18} O and δ^{13} C are primarily controlled by the amount of rainfall in tropical regions. Using empirical relations between δ^{18} O and amount of rainfall (based on modern observations), speleothem δ^{18} O has been converted into past rainfall variations. The most important outcome of this thesis is that quantitative rainfall reconstruction for different cave locations are now available. The maximum time span covered is up to last 3400 years (with ~15 yr resolution) from a cave in Chattisgarh. Rainfall reconstruction with an yearly resolution is made available for the past 330 years from Karnataka. In this sample, low/high rainfall years observed by instrumental weather records are shown as enriched/depleted δ^{18} O levels, thus giving a direct proof of the rainfall reconstruction, which assumes that δ^{18} O variations are dominantly controlled by the rainfall. Comparisons between average values of δ^{18} O and δ^{13} C for all speleothems have been carried out and various possible processes occurring in a cave system leading to such values are discussed. The prime control on the average values of speleothem δ^{13} C is by the soil thickness and size of pathways. Significant correlation between temporal profiles in $\delta^{13}C$ and $\delta^{18}O$ suggests that rainfall is also one of the controlling factors for δ^{13} C. Continental effect is also found in the speleothem δ^{18} O. This also suggests that speleothem δ^{18} O values are strongly dependent upon the δ^{18} O of precipitation in tropical regions. Using d-excess values, evaporation conditions of several types of water samples have been discussed. Seepage water is generally found to be more enriched compared to the ground and river waters from locations surrounding the cave area. Rainfall reconstructions from speleothems have been compared with the available data covering recent (from meteorological stations) and older periods (from ocean sediments).

Some of the famine years documented in the history are indicated in the rainfall reconstruction. Speleothems are usually found to have pure calcite type mineral structure. However, in the four speleothems studied, two are mixtures of calcite and aragonite. In one of the sample covariance of aragonite content with δ^{18} O suggests that the mineralogy is also possibly controlled by rainfall. Though the observed variations in the speleothem δ^{18} O are due to fluctuations in both the past temperature and rainfall, the relative contribution of temperature seems to be small and negligible in tropics. Therefore, past rainfall profile of the respective cave locations have been reconstructed. However, using speleothem δ^{18} O, past temperature variations could not be reconstructed. It is known that Sr incorporation in carbonates doesn't depend upon temperature while Mg incorporation depends upon temperature. This differing property has been applied in speleothems to reconstruct past Temporal variation in Mg, Sr and Ba content in one of the temperature changes. speleothems was measured. However, the estimate of the magnitude of past temperature fluctuations are unrealistic and like stable oxygen and carbon isotopes the trace elements are also found to be dominantly controlled by rainfall in tropics. Various hidden processes that may control the chemistry of trace elements are discussed in this chapter. Chapter-5 gives a brief summary and conclusions based on data obtained in this thesis work. The scope for future research is presented at the end.

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Introduction

Limestone is a sedimentary rock consisting essentially of carbonates. These may be fresh water or marine and usually indicate deposition in a warm, clear water environment. Mostly their origin is either by organic secretion or by chemical precipitation (Faure 1991). These were part of the sea bed in ancient times and were exposed as earth's crust shifted subsequently. Uplifting of a limestone surface initiates cave formation. Rain water while seeping through the tiny cracks in the limestone bedrock, gradually enlarges them hollowing out to form complex labyrinths of interconnected chambers and galleries. This is how limestone caves are formed. Seeping water is also the agent that decorates the caves with deposits (called speleothem) of various shapes and colours.

1.1 Speleothems

The word 'speleothem' describes any mineral precipitated in a cave environment. It is derived from the Greek words *spelaion*, meaning cave, and *thema*, meaning deposit (Schwarcz 1986). They are secondary mineral deposits formed in caves in karst regions. They are mostly calcium carbonates (and rarely gypsum and halite-Goede et al 1990) and are formed by the action of rain water which percolates through the cave surface and drips from the ceiling or walls of a cave. Evolution of speleothem is shown by a schematic diagram in the Fig.1-1. As soils have high pCO₂ (due to root respiration and bacterial they become acidic. The seeping water flowing decomposition of organic matter) through cracks and fissures dissolves carbonates in the bedrock strata and is laden with HCO_3^{-1} , $CO_3^{2^-}$, Ca^{2^+} and several other soluble components. Due to ventilation, the air in the cave chamber has a lower pCO_2 (same as atmosphere outside the cave) than the water and so automatic degassing of CO₂ takes place, leading to super-saturation and then precipitation of carbonate. Ceaseless dripping forms successive growth layers of CaCO₃ at the dripping spot in the form of tubes or 'soda –straw' (growing downward). Blockage of the tube or flow over the outside will cause it to thicken near the ceiling and assume a conical shape, called stalactite. When dripping rate is high so that the solution does not



Fig.1-1: A schematic diagram showing speleothem evolution. Rain water, high pCO_2 in the soils and the limestone bedrocks cause the speleothem formation. Stalactites are the deposits hanging on the roof, stalagmites grow on the floor while flowstones are those depositing on the wall or the floor.

reach equilibrium on the roof of the cavern, additional calcite may precipitate on the floor forming stalagmite (growing upward) and flowstones (thin carbonate layers on the floors or on the cave walls). Ultimately stalactites and stalagmites may join to form pillars or curtains of carbonates (Faure 1991; Ivanovich and Harmon 1995; Lowe and Walker 1998). The seepage water acts as a transferring medium, carbonate in the bedrock strata is redeposited as speleothem in the cave gallery.

Major speleothem formations occur during the wet season when the seepage is more. A process of speleothem deposition by slow outgassing of the seepage water with no evaporation gives rise to a very slow speleothem growth, and enables the deposit to be used for palaeoclimate determination through analysis of the variations in stable isotopic content of the carbonates (Hendy 1969). Speleothems growing over centuries are very important proxies for continental palaeoclimate. A general account of their physical properties is given in Dreybrodt (1980). Generally, stalagmites are thicker as drip water splashes and flows outward causing more lateral deposition. In a vertical section view, a series of superimposed growth bands can be distinguished from each other on the basis of colour, texture, impurity content, and the density of fluid inclusions. Different colours arise largely due to varying amounts of organic content and in some cases due to high concentrations of certain trace elements (Beynen et al 2001).

1.2 Basis of isotopic exchange

Speleothems are inorganic precipitates of calcium carbonate, generally calcite, formed from dilute aqueous solutions. The chemistry involved is given below.

$CO_{2(g\text{-soil})} \leftrightarrow CO_{2(aq)}$	(1-1)
$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$	(1-2)
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	(1-3)
$\text{CO}_3^{2-} + \text{Ca}^{2+} \leftrightarrow \text{CaCO}_3$	(1-4)
$H_2O \leftrightarrow OH^- + H^+$	(1-5)

Dissolution of bedrock carbonate can be summarized as:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^{-}$$
(1-6)

The above reaction shows that when the CO_2 degasses out from the seepage water in the cave environment, $CaCO_3$ precipitates forming speleothem layers. Through the above

mentioned reactions stable isotopes of oxygen and carbon are exchanged among the different ionic species. If CO_2 loss is slow then isotopic equilibrium is maintained between freshly precipitated carbonates and the solution. Estimation of the time required (Hendy 1971) has shown that if about half of bicarbonate in solution is converted to CO_2 and $CaCO_3$ in ~2000 sec, then oxygen of the carbonate will be in isotopic equilibrium with the oxygen of the water. Time required for the equilibration of carbon isotopes of the carbonate and the solution is relatively much less. In a pioneering study of isotopic geochemistry of speleothems, Hendy (1969, 1971) observed that some speleothems are deposited in oxygen isotopic equilibrium, and that they can be recognized by the fact that the oxygen isotopic composition measured along a single growth layer is constant (any slight change which is observed must not be correlated with the change in the isotopic composition of carbon). Such samples deposited in isotopic equilibrium are found in the poorly ventilated sections of caves where humidity is very high (close to 100%).

Oxygen isotopes

During CaCO₃ precipitation stable isotope ratios of oxygen (¹⁸O/¹⁶O) and carbon (¹³C/¹²C) in the HCO₃⁻ ions in the dripping water are affected by the cave environment. These ratios are preserved in the CaCO₃ laminae and are used to decipher the past cave environment. The ratios are measured relative to a laboratory standard on a mass spectrometer and expressed as δ^{18} O and δ^{13} C where,

 $\delta^{18}O = [(({^{18}O}/{^{16}O})_{sample}/({^{18}O}/{^{16}O})_{standard})-1] \times 1000 \text{ permil}$ (1-7) similarly,

$$\delta^{13}C = [((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard})-1] \times 1000 \text{ permil}$$
(1-8)

The standard used is V-PDB supplied by IAEA (International Atomic Energy Agency, Vienna). PDB is a CaCO₃ standard derived from the rostrum of *Belemnitella americana* from the Pee Dee Formation of South Carolina in U.S.A. (Gonfiantini 1981). The fractionation factor α_{cw} is known for the calcite-water system and is given by the following equation (O'Neil et al 1969).

$$\alpha_{cw} = ({}^{18}\text{O}/{}^{16}\text{O})_{\text{calcite}} / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{water}}$$
$$\Delta_{cw} = (2.78 \text{ x } 10^6/\text{ T}^2) - 3.39 \qquad (1-9)$$

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

It can be shown that the isotopic composition of seepage water in caves reflects the average value for the meteoric water falling on the soil above the cave (e.g. Schwarcz 1986; Ivanovich and Harmon 1995) and the temperature in the cave is equal to the average annual surface temperature outside the cave (Gascoyne 1992; Lauritzen 1995 and Repinski et al 1999). This is because the air in the cave is warmer than outside air in winter and cooler than outside air in summer. Any change in the annual temperature will affect the calcite $\delta^{18}O_c$ whereby heavier $\delta^{18}O_c$ values imply lower temperature ($d(\Delta_{cw}) / dT = -0.21$ ‰ °C⁻¹ at 25°C, from eq.1-9). Additional accounting for the temperature dependent changes in the oxygen isotopic composition of meteoric water ($\delta^{18}O_w$) is also required. For example at high latitudes $\delta^{18}O_w = 0.695(t) - 13.6$ (i.e. $d(\delta^{18}O)/dT = 0.69$ ‰ °C⁻¹; Dansgaard 1964). At tropical locations $\delta^{18}O_w$ is dominantly controlled by the amount of rain and temperature dependence is not observed.

Lauritzen and Lundberg (1999) have given an expression for $\delta^{18}O_c$ (as speleothem delta value);

 $\delta^{18}O_c = \exp\{a/T_1^2 - b\}[F(T_2, t, g) + 1000] - 1000$ (1-10)

where $a=2.78*10^3$, $b=3.39*10^{-3}$, 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 site. Exponential part gives thermodynamic fractionation between calcite and water inside the cave and $F(T_2, t, g)$ is the drip water isotopic composition ($\delta^{18}O_w$). In most of the cases T_1 can be assumed equal to the T_2 . $F(T_2, t, g)$ may respond either positively or negatively, depending on regional meteorology (Gascoyne 1992; Lauritzen 1995). The T-derivative defined (Lauritzen 1995) as,

$$\mu = \partial(\delta^{18}O_c) / \partial T \qquad (1-11)$$

can be positive negative or zero depending upon the cave site. The temperature sensitivity and therefore the interpretation of speleothem $\delta^{18}O_c$ is by no means straightforward and often ambiguous (Lauritzen and Lundberg 1999). The problems however may be overcome by 1) estimating F(T₂,t,g) by analyzing δD of fluid inclusions and 2) by comparing the $\delta^{18}O_c$ trends with the known past climate changes, the sign of μ can be judged and can be used for climatic interpretation.

In the tropical speleothems studied in this thesis, large changes in the $\delta^{18}O_c$ are observed and it is inferred that the temperature dependence is relatively negligible. The

 $F(T_2,t,g)$ is found to be strongly dependent upon the amount of rainfall. Moreover, due to dominant control of rainfall on $F(T_2, t, g)$ it is difficult to recover the small, past temperature variations from $\delta^{18}O_c$.

Carbon isotopes

The carbon in the speleothem $CaCO_3$ is incorporated from two sources 1) soil CO_2 which is isotopically lighter than the atmospheric CO_2 and; 2) bedrock carbon. The carbon isotopic evolution of speleothems is a complex process that depends upon several factors (Hendy 1971; Wigley et al 1978; Lauritzen and Lundberg 1999) mainly on,

1) the photosynthetic pathways (i.e. C3/C4 pathways)

Plants using the C4 (Hatch-Slack) cycle of photosynthesis abound in semi-arid environments and synthesize cellulose which has δ^{13} C lower by about 5‰ (they have δ^{13} C values between ~ -10 to -16‰, mean value of about -12.5‰) relative to the atmospheric CO₂ (~-7‰), whereas C3 (Calvin cycle) plants which live in humid environments produce carbon compounds which are depleted by about 19‰ (they have δ^{13} C between ~ -24 to -30‰, mean value of about -27‰) with respect to the atmospheric CO₂. As δ^{13} C_c (suffix denotes calcite) will depend upon CO₂ contributed from both type of plants, any change in their relative proportions caused by climatic change may alter the C3/C4 ratio and hence the relative contribution to the δ^{13} C_c (Clark and Fritz 1997; Lauritzen 1995; Gascoyne 1992).

2) biological activity

Carbon dioxide in the soil is derived from two sources: microbial decomposition of the soil organic matter and root respiration of the plants (this has relatively more negative δ^{13} C). During wet periods intense respiration process might result in high pCO₂ and depleted δ^{13} C (Hesterberg and Siegenthlaer 1991).

3) bedrock proportion

Limestone dissolution may proceed (Hendy 1971; Dulinski and Rozanski 1990; Clark and Fritz 1997) along two extreme routes:

a) under open system condition, the seepage water is always in contact with the reservoir of gaseous CO₂. In this case the isotopic composition of all carbonic

compounds present in the solution is controlled by the isotopic composition of the gaseous CO₂.

- b) under closed-system condition the seepage water is isolated from the reservoir of gaseous CO₂ before bedrock dissolution begins. In this situation carbon atoms in the solution originate from two sources, the soil CO₂ and dissolved limestone. In nature, the dissolution process mostly should be considered as a mixture of these extreme situations.
- 4) drip rate in the cave

There is progressive enrichment in the successive (time variation) CaCO₃ deposits (Hendy 1971; Wigley et al 1978; Dulinski and Rozanski 1990; Hellstrom et al 1998) even when oxygen isotope equilibrium is observed. At 5^oC temperature which is typical for most mid-latitude caves, model calculation by Dulinski and Rozanski (1990) shows that $\delta^{13}C_c$ of the total calcite precipitated from a thin film of seepage water, varies as a function of time from ~-16‰ to ~ 0‰ (between 0 to ~1.5 hr time period), depending upon the particular condition under which the precipitation occurs. Also, large changes in the $\delta^{13}C_c$ are found in the initial periods (within first 30 min. it varies from ~-16‰ to -2.5‰). Due to this effect, higher drip rate results in depleted $\delta^{13}C_c$. As the drip rate is directly proportional to the rainfall in a crude way, this may result in dependence of $\delta^{13}C_c$ on the amount of rainfall.

Although, fractionation of various carbon isotopic species is temperature dependent (Hendy 1971), changes in the equilibrium fractionation factors with temperature are compensated by parallel changes in the molar ratios of carbonic molecules in the solution (Hendy 1971; Dulinski and Rozanski 1990). Hence, use of $\delta^{13}C_c$ for temperature reconstruction is impossible in practice but, it can be used to get some information about the history of the cave and the climate above it (Schwarcz 1986). The interpretation of $\delta^{13}C_c$ depends upon the settings of the cave environment where one of the these processes may be dominant and others may be assumed invariant (Lauritzen and Lundberg 1999).

Trace elements and mineralogy

Use of trace elements (<0.1% amount by weight) in biogenic carbonates such as foraminifera and corals for reconstruction of past ocean condition is well established. Their systematics in speleothems is yet to be understood critically for using them to recover past terrestrial environmental data (Fairchild et al 2000). Mineralogy of speleothems (calcite/aragonite) is also a possible climate proxy (Deninston et al 2000).

1.3 Purpose of the study

Current attention of the climate science is on the role of tropics during major climate changes such as glacial periods that occurred in the past. Earlier results based on shells from the ocean indicate the tropical temperature reduction to be within 1 to 2°C during LGM (CLIMAP 1976-Last Glacial Maximum, during 18-20 kyr ago). Results based on corals (Beck et al 1992) using advanced techniques and amount of dissolved noble gases in the ground waters (Stute et al 1995) have shown that tropics cooled by about 5 °C during LGM, contradicting the older results. Some new data from tropical regions can throw light on this controversial issue. Hence, it has become important to reconstruct past climate of the Indian tropics with high resolution to understand climate in a better way.

It is important to understand past climatic variations firstly, to understand various mechanisms responsible for the natural variability and secondly to provide a data base to serve as boundary conditions for climate models meant for long term predictions. In India meteorological observations such as temperature and rainfall are available since last century. For older periods one has to look for climate proxies such as tree-rings, corals, glaciers and varve deposits which have annual resolution, whereas, sediments from lakes and oceans, peat deposits, palaeo-soils, sand dunes etc. provide resolutions of decadal, century scale or more. So far, the potentials of all these archives in India have been examined by many workers, however, cave deposits occurring in limestone terrain have not been explored for using them as a record of past climate conditions using stable isotopes of oxygen and carbon. This has been attempted in the present study.

Aim of the present study is:

- 1) to explore various caves in the tropical India for suitable speleothems.
- to evaluate the potential of stable isotopes of oxygen and carbon of speleothems in palaeoclimatic reconstruction.

1.4 Sample locations

Speleothems

Cave exploration was carried out in the four districts (Fig.1-2) viz. Koraput (Orissa), Jagdalpur (earlier Madhya Pradesh, now Chattisgarh), Chitrakoot (Uttar Pradesh) and Uttar Kannada District (Karnataka). Caves which are least disturbed by human activity are the most suitable for palaeoclimatic studies as the samples are in pristine condition, preserving each and every layer formed earlier. Speleothems which are in the deeper parts where humidity is very high and ventilation is very poor are best suited for palaeoclimatic studies as isotopic equilibrium condition is known to occur at such places (see Sec. 1.2). The following are the four caves which were explored in detail and samples were collected for further studies (Fig.1-2):

- Gupteswar cave, Koraput district, Orissa. An actively growing stalactite was collected on Feb. 7, 1996. Sketch showing cave and the stalactite before collection is shown in the Fig.1-3 and Fig.1-4, respectively. This cave is occasionally visited by village people, but, being at height (tip part at ~6ft above ground) it is well preserved. Total length of the stalactite is ~128 cms, however, due to its large weight only ~70 cm part from the tip was collected. Presently the vegetation is densely forested and is C3 type (Fig.1-5).
- 2. Dandak cave in the Jagdalpur district, (earlier Madhya Pradesh, now Chattisgarh state). The cave is within ~30 km distance from the Gupteswar cave and is prohibited by the forest department for public visit. There are huge stalactites and stalagmites in the deeper parts (see the cave sketch in the Fig.1-6). An active stalagmite growing just below a huge stalactite was collected on Feb. 8, 1996. Photo of the stalagmite after collection is shown in the Fig.1-7. A photograph of the surrounding dense forest which is C3 type is presented in the Fig.1-8.



Fig.1-2: Map showing the geographical locations of the four caves. Thin lines show the boundaries of the meteorological subdivisions in which these caves are located.



Fig. 1-3: Sketch showing the Gupteswar cave and the stalactite location inside. (A) Vertical cross sectional view of the cave, (B) horizontal cross sectional view of the cave and (C) the stalactite view.



Fig.1-4: Photo shows Gupteswar stalactite before collection.



Fig.1-5: Photo showing vegetation in the Gupteswar cave area.



the cave and (C) the stalagmite location.



Fig.1-7: Photo of the Dandak stalagmite after collection.



Fig.1-8: Photo showing vegetation in the Dandak cave area.

- 3. Akalagavi cave (Uttar Kannada District, Karnataka). This cave has a small size (sketch given in the Fig.1-9). The cave is located in the tropical dense forest (C3 type; Fig.1-11). A photo of the sample before collection is shown in the Fig.1-10. A stalagmite was collected on April 4, 1997. The cave is often visited by tourists, however, the stalagmite was growing in a narrow section at a height of ~ 15 ft. and hence may not have been disturbed by anybody.
- 4. Sota cave (Uttar Pradesh). This cave is located in the Karwi Taluk, in the Banda District of Uttar Pradesh. The cave is small in size (cave sketch given in the Fig.1-12) and is not a tourist place, also it is rarely visited by village people. A stalactite from a narrow chamber in the interior part (Fig.1-13) and several straw samples (Fig. 14) growing near the cave entrance were collected from this cave on October 10, 1997. During sample collection the cave was found dry. The area surrounding the cave is not a dense forest unlike the other caves mentioned above, however, the vegetation is C3 type.

From each cave, representative samples of bedrock and leaves were also collected for δ^{13} C studies. Another cave Kotamsar (Fig.1-15) is located within ~5km distance from the Dandak cave. This cave is very big in size (~500m in length). As it is a tourist place, most of the speleothems have been broken down. Only water samples have been collected from this cave.

Samples of cave seepage water, rain water, ground water and open surface water.

Cave seepage water, ground and surface water (from rivers , falls and ponds) samples were collected from several locations (sites shown in the Fig.1-15 (A) & (B)) to compare the δ^{18} O and δ D values. For water samples δ^{18} O is defined by eq.(1-7) and δ D is defined as,

 $\delta D = [((D/H)_{sample} / (D/H)_{standard}) -1] \times 1000 \text{ (permil)} (1-12)$ For water samples, the standard used is V-SMOW supplied by IAEA. V-SMOW (Vienna-Standard Mean Ocean Water) is a water standard the isotopic composition of which is close to the average ocean water (Gonfiantini 1981).





Fig.1-10: Photo showing the Akalagavi stalagmite before collection.



Fig.1-11: Photo showing vegetation in the Akalagavi cave area.



Fig.1-12: Sketch showing the Sota cave and the stalactites and straws inside. (A) Vertical cross sectional view of the cave, (B) horizontal cross sectional view of the cave and (C) the locations of the straws, (D) locations of the stalactite.



Fig. 1-13: Photo showing the stalactite before collection.



Fig.1-14: Photo shows straws before collection.



Fig.1-15: Maps show sites from where water samples were collected. (A) Transects-I and –II are the routes followed for collection of ground water samples (from tube wells). Rain water was collected at the site no.1. (B) Expanded view of the cave locations.

Cave seepage water samples were collected from Dandak (site no.-21), Gupteswar (site no. 22; Fig.1-15 (8)) and Kotamsar caves (site no. 8; Fig.1-15(B)) during different periods. Ground water (from hand operated tube wells) and open surface waters (rivers and ponds) were collected from the area surrounding the caves in the Jagdalpur district (site no.24, Fig.1- 15(B)). Two separate field trips were carried out by road on the routes marked as transect-I and transect-II, to collect ground water samples from locations far from the cave area as shown in the Fig.1-15(A). Rain water samples were collected for each rain spell during the monsoon seasons of 1999 (for three months July, Aug and Sept) at Jharsuguda; site no. 1 in the Fig.1-15 (A). A severe cyclone appeared in the Bay of Bengal and it hit Bhubaneswar (site no. 7, transect-I) on 29th Oct., 1999 (Kalasi and Ray 2000). Five samples of cyclone waters were collected at regular intervals of 1 hr. from site no.7. All the water samples were analyzed for δ^{18} O and some were also analyzed for δ D.

Past climate and its reconstruction from speleothems

2.1 Past climate from other proxies

2.1.1 Present Global Scenario

Palaeoclimate research has mainly focussed on deciphering; 1) temperature, precipitation, humidity, dustiness and plant cover conditions on the Earth during the past and 2) The geographic pattern of these changes. Climate data for the past 5 million years recovered from ocean sediments using faunal abundance (CLIMAP 1976) and δ^{18} O variations (Broecker and Denton 1990) and ice cores (Hammer et al 1997) have shown rhythmic variations, having strong frequencies of 41kyr and 23kyr due to changes in the axial tilt and orbital precession of the earth respectively. The dominant cycle has been , however, a 100kyr component which is related to earth's orbital eccentricity variation.

Based on faunal abundance in the ocean sediments it was earlier believed that during glacial periods the tropical temperature decreased only by 1-2 °C. However, Guilderson et al (1994) showed that the Sr/Ca ratio and δ^{18} O in corals from Barbados indicate a significant temperature drop, up to 5 °C during LGM (Last Glacial Maximum, around ~18kyr ago). Noble gases dissolve in the ground water during recharging. Their solubility explicitly depends upon the temperature. Stute et al (1995) based on the concentration of noble gases dissolved in the Brazilian water acquifers of glacial periods, have shown that during glacial periods tropical temperature was lower by 5°C. δ^{18} O variations in the tropical ice cores from Peru (Thompson et al 1995) and Bolivia (Thompson et al 1998) have also indicated cooling up to 5°C during LGM. However, pollen species from peat bogs (Bonnefille et al 1990) indicate 2-4°C cooling in the equatorial Africa during glacial conditions. Tropical sea-surface temperature during LGM based on alkenone studies in which the ratio of di-and tri-unsaturated 37-carbon methyl ketones in the sediment is measured and converted to SST with an empirical calibration, have suggested that Indian ocean tropical temperature remained an average within 1.5 to 2.5 °C of the present values during LGM (Sonzogni et al 1998).

Hence, quantification of tropical temperature during the last glacial cycle (0-150kyr) is a controversial issue since different proxies seem to provide conflicting information. Several of the observed temperature differences could be due to regional response to global cooling linked to circulation changes in the atmosphere or oceans. A cooling of about 5°C can not be explained by reduction in the Sun's energy output (due to orbital eccentricity variations); changes in the inventory of the atmospheric water vapour is proposed to be the chief suspect (Broecker 1997). Short scale (decadal to centennial) variability may be linked to the solar irradiance, volcanism and internal variations in the ocean atmosphere system (Crowley and Kwang-Yul 1993).

Hence, to improve our understanding of the climate system it is utmost important to reconstruct tropical palaeoclimate with a large spatial coverage using different climate proxies.

Mann et al (1998) have reconstructed global annual surface temperature pattern for the past 600 years. This is based on multiple regression of multi-proxy data from tree rings, varve sediments, ice cores, corals, available instrument and historical records. Greater weight is placed on specific proxy series that exhibits greatest affinity with the modern large scale instrumental record. It has been further extended to cover last 1000 years using some more additional data from tree rings and ice cores (Mann et al 1999). Eurasian tree-ring widths indicate that global temperature changes in the last 2000 years remained within 0.5°C or less (Briffa and Osborn 1999).

Ice and ocean sediment cores have provided a detailed picture of the temporal characteristics of climate over the past 100,000 years. However, except for the past 600 years (Mann et al 1998), the spatial pattern of the climate changes remain virtually unknown. Because most of the data come from just a few locations: the Greenland Ice Sheet, the Antarctic Ice Sheet and the North Atlantic Ocean (Steig 2001).

2.1.2 Holocene climate in India

In India palaeo-climate data is scant. Some work has been carried out to reconstruct Holocene climate using proxies such as tree rings, corals, lake sediments, peat deposits,
pollen studies and ocean sediments. Tree ring-width studies have reconstructed temperature record of the western Himalaya back to the 1390 AD (Borgaonkar et al 1999; Yadav et al 1997). No anomalies indicating the so called "Little Ice Age" is observed in the temperature reconstruction. Trees in the Kashmir have shown sensitivity to the summer precipitation which has helped in reconstructing the precipitation back to the 18th century (Borgaonkar et al 1994). In some of the tropical trees the ring width is found to be significantly influenced by the precipitation. For tropical trees, ring-width index data has been recently reconstructed by Bhattacharyya and Yadav (1999) back to 1150 AD.

Ramesh et al (1985) showed that the δD in the cellulose of the teak wood (covering ~50 yrs.) recorded the monsoon rainfall. Chakraborty et al (1994) and Chakraborty and Ramesh (1998) found that in the Indian corals, $\delta^{18}O$ (covering ~50 yrs.) is influenced by the sea surface temperature and also bomb ¹⁴C activity variations is preserved in the successive growth layers. Using $\delta^{13}C$ in the peat samples from southern India it is observed that there was arid climate from 6 to 3.5 kyr ago and a short wet phase about 600 yrs ago (Sukumar et al 1993).

Based on pollen studies, monsoon condition in Rajasthan (North-West part of India) has been reconstructed for the last 10 kyr from two lakes Didwana and Lunkaransar (Bryson and Swain 1981). These records show maximum monsoon in the early part of the Holocene (between 10-4 kyr BP).

Sedimentological, mineralogical and δ^{13} C study of sediment cores collected from Mansar lake in Jammu, northern India shows that precipitation during 2500-1600 was similar to present and during 1600-500 BP it was somewhat subdued (Kusumgar et al 1995). Pollen study from Himalayan lake sediment have revealed that between 2-1kyr BP the climate was cold and dry. Onset of warm and moist phase is observed between 1kyr to 400 yr BP (Mazari et al 1995).

Palaeomonsoon data from other parts of India are available from ocean sediments. Sirocko et al (1993) based on δ^{18} O of foraminifera shells, % of CaCO₃ and dolomite content in a sediment core covering last ~24kyr found that there was a major transition between glacial and Holocene at ~13 kyr BP. Sediment cores collected from Indian ocean reveal that ~18kyr ago there was weaker summer monsoon (Duplessy 1982; Sarkar et al 1990). Foraminifera abundance in a sediment core from western Arabian sea (Naidu 1996)

have shown that summer monsoon was stronger between 6 to 9 kyr and aridity started from ~3.5 kyr. δ^{18} O and δ^{13} C of foraminifera shells from sediment core collected from eastern Arabian sea show increasing trend in the summer monsoon since last 10 kyr to ~ 2kyr (Sarkar et al 2000).

Based on pollen and δ^{13} C study in a sediment core from marine cores from Karwar, western India, Caratini et al (1994) have shown that present day climate was established in the western India around 2200 yr BP and has remained stable. Before 3500 kyr BP it was more humid. Onset of a less humid condition in the coastal part Karnataka (southern India) started at ~ 2000 yr BP (Nigam and Khare 1994).

The data so far available reveals that past monsoon rainfall was significantly different from the present day monsoon.

2.2 Climate reconstruction from speleothems

During the last two decades the interest in speleothem as a climate proxy has grown, due to the fact that now better chronology can be tied to them using U-Th dating by thermal ionization mass spectrometry (TIMS) and they can be used as terrestrial complement of the ice core and deep ocean sediment records.

It was first demonstrated by Hendy and Wilson (1968) that isotopic geo-thermometry may be applied to speleothems. Detailed theoretical investigation of the stable isotopes in speleothem and their potential in palaeoclimate was later presented by Hendy (1969, 1971). Schwarcz et al (1976) showed that it is possible not only to determine relative shifts in the past cave temperature variations but also the absolute magnitudes using δ^{18} O of speleothem calcite and δ D of fluids trapped as inclusions in it. Subsequently, cave calcite from West Virginia, Canada, north American locations, the Bahamas, Jamaica and England were analyzed. In most of the earlier studies, Uranium-Thorium Dating by alpha spectrometric method was applied. Li et al (1989), first showed application of massspectrometry in uranium-series dating. Due to this, precision in the U-series ages were improved extending the dating limit beyond ~300ka and at the same time sample quantity required for analysis reduced to ~1gm calcite unlike 10 to 40 g in the counting method. Samples as old as ~300ka were investigated and possible past temperature conditions were inferred. Inorganic calcite precipitation under laboratory conditions have shown that Mg content increased with increasing temperature. This property was investigated in the cave deposits from different natural conditions and it was found that there is indeed temperature dependence in the speleothem Mg content (Gascoyne 1983). A review of previous work on speleothems for retrieving palaeoclimate and related references are given in Gascoyne (1992). Fossil speleothems from Botswana, South Africa have also been used to reconstruct Pleistocene environment (Holmgren et al 1994).

High resolution climate reconstruction (based on U-Th TIMS ages) of the Holocene period using speleothem δ^{18} O and δ^{13} C have been carried out using speleothems e.g. from Cold Water cave, northeast Iowa, United states (Dorale et al, 1992), Hoti cave in northern Oman (Burns et al 1998), Nahal Qanah Cave in Israel (Frumkin et al 1999) and caves in northern Norway (Lauritzen and Lundberg 1999; Linge et al 2001). As use of δ D of fluid inclusions is based on an assumption that local meteoric water relationship holds in the past, which often gives ambiguous results (Gascoyne 1992) and hence, most of the recent studies are based on the analysis of speleothem δ^{18} O and δ^{13} C only, except that of Matthews et al (2000).

Detailed isotopic and chemical studies was initiated in the Soreq Cave which is located in the semi-arid zone in Israel in the last decade. Climate reconstruction is now available from speleothems of Soreq cave for the last 60 ka BP. Variations in the δ^{18} O and δ^{13} C of the speleothems and cave waters have shown prominent control of the rainfall and temperature cave (Bar-Matthews et al 1996, 1999; Bar-Matthews and Aylon, 1997). Variations in the trace elements Mg, Sr and U and isotope variations ⁸⁷Sr/⁸⁶Sr and ²³⁴U/²³⁸U have shown climate control on the geochemistry of the speleothem (Kaufman et al 1998; Bar-Matthews et al 1999). Fluid inclusion studies have suggested that $\delta D - \delta^{18}O$ had relationship similar to the global Meteoric water line during glacial periods (Matthews et al 2000).

Trace elements specially Mg, Sr and Ba are found to be promising climate proxies; however, their control mechanism is yet to be understood. Gascoyne (1983) first investigated the potential of trace elements in temperature reconstruction. In the last couple of years several papers have presented high resolution trace element studies by SIMS (secondary ionization mass spectrometry) analysis. High resolution (annual and subannual scale) studies on speleothems from England have suggested potential of trace impurities as climate proxy (Roberts et al 1998). Based on systematic collection and chemical studies of cave seepage water, Fairchild et al (2000) have shown that the trace element chemistry is interpretable in terms of past hydrology of a cave system. Water residence time is found to be controlling the Mg/Ca, Sr/Ca and ⁸⁷Sr/⁸⁶Sr ratios in a Holocene Belgium speleothem (Verheyden et al 2000). Trace element studies at annual to sub-annual scale in a speleothem from Cold Air cave , Southern Africa have suggested the rainfall as possible control factor on the chemistry of Sr and Ba (Finch et al 2001). Huang et al (2001) have proposed that multiple trace element profile in speleothem should be calibrated against weather records to establish palaeo-climatological meaning.

Denniston et al (2000) have reported the rainfall induced mineralogical changes over the ~2300 years from a cave in the central Nepal. This study has shown that during ~2300 to 1500 yr BP, climate was arid and around 450 yr BP the climate was cool and/moist. Ku and Li (1998) have shown precipitation temperature and type of vegetation for the northeastern China for the last 3 kyr using stable isotope and trace element measurements in a stalagmite from Shihua Cave near Beijing, China. It has shown a periodicity of 30-40 years in the East Asian summer monsoon.

Laminated stalagmites have shown dependence of thickness of annual layers on the rainfall (Genty and Quinif 1996). Annual laminations in speleothem from SW France have recorded the ¹⁴C activity history and atmospheric δ^{13} C pattern (Genty and Massault 1997, 1999). Stalagmite growth rate is experimentally observed to be dependent on local cave factors such as temperature and Ca content in the seepage water (Baker et al 1998; Genty et al 1998, Genty et al 2001).

Speleothems fluoresce when illuminated with UV light and this has been a matter of investigation. Some work has been carried out recently to use this property for setting up the speleothem chronology and its application in the palaeo-environment reconstruction (e.g. Shopov et al 1994 and Beynen et al 2001).

Caves near coastal locations are flooded when sea level is high, thereby ceasing the deposition process. Therefore, carbonate layers show sea level, lower than the cave and depositional hiatuses show the period when it was high. Using U-series dating of speleothems, sea-level changes in the Late Pleistocene period have been estimated (e.g. Vesica et al 2000).

Stalagmites and flowstones from England, Vancouver Island , the Canadian Rocky Mountains, and Mexico, have been used to find the temporal and spatial changes in the earth's magnetic field (Gascoyne 1992). Fossil speleothem age and their frequency variation has been used to determine palaeoclimate at global scale (Gascoyne 1992) . Speleothems have also been used to monitor 14 C variations which suggests large deviations in the 14 C and absolute chronology between 35-40kyr (Holmgren et al 1994, Goslar et al 2000).

In India , first stable isotope measurements ($\delta^{18}O$, $\delta^{13}C$ in speleothem carbonate and δD in fluid inclusion) were carried by Padia and Ramesh (unpublished work 1994) on speleothems from caves in Jammu, northern India. Petrological studies of calcite speleothems from Deccan-trap basalts, Maharashtra, have been recently reported by Sarkar et al (1998). This thesis work is the first detailed isotopic study on the Indian speleothems.

Experimental techniques

3.1 Sampling

Preparation of subsamples for stable isotopes analysis and Radiocarbon dating

The Gupteswar stalactite being bigger in size (\sim 35 cm in length and 16-20 cm in diameter) was cut into slices of \sim 1.5 cm thickness using a high speed steel saw-tooth blade. Other speleothem samples were cut along the length using a motorized diamond cutter (blade diameter \sim 12 inches). Heating of carbonates might alter the isotopic signatures of the carbonate layers and hence, cutter and fresh speleothem surfaces were kept cooled using normal flow of water. Photographs showing cross sectional view of all the speleothems are shown in the Figs. 3-1(A to D).

For stable isotope analysis subsamples amounting about 5 mg were recovered from each visible layers, using a hand operated and a slow speed portable electric drill fitted with stainless steel bits (diameter between 0.4 to 1.1mm). The Growth layers and subsampling points are shown in the Figs.3-2(A to D).

For radiocarbon dating about 3 to 7gm of carbonate powder was recovered from different slices using a drill machine and carborundum files. In the Figs.3-2 (A to D) patches indicate the part of layers selected for the radiocarbon dating. The exact amounts of sample and their radiocarbon ages are listed in the Tables 4-1 to 4-4 (Sect. 4.1).

3.2 δ^{18} O and δ^{13} C measurements of carbonate samples

Stable isotope ratios of oxygen and carbon for the subsamples from the Gupteswar and the Dandak caves were measured on the 'VG 903' mass spectrometer; samples from the Akalagavi and the Sota cave were measured on the 'Geo 20-20' mass





Fig. 3-1: Cross sectional view of speleothems. (A) Stalactite from Gupteswar cave is shown in two parts. (B) Stalagmite from Dandak cave; (C) Stalagmite from Akalagavi cave; (D) Two half sections of the stalactite from Sota cave.









Fig.3-2: Sketch showing sampling spots for the sub-samples for the stable isotope studies (by dots) and for the radiocarbon dating (by patches) for (A) the stalactite from Gupteswar cave; (B) the stalagmite from Dandak cave; (C) the stalagmite from Akalagavi cave; other details are discussed in the chapter-4. (D) the stalactite from Sota cave.

spectrometer (Europa-PDZ). The carbon dioxide preparation lines and the procedures followed are discussed below separately for the two machines.

On-line measurement is very fast, as in an hour, 2-3 samples in sequence can be analyzed and, hence, large numbers of measurements can be carried out for high resolution studies. 100% H₃PO₄ with the density around 1.90 to 1.92 (Coplen et al 1983) was used in the present study.

On-line CO₂ preparation in the VG 903 mass spectrometer

Carbon dioxide was prepared from the subsamples from the Gupteswar and Dandak speleothems, in the on-line extraction system connected to a VG 903 mass spectrometer (line diagram shown in Fig.3-3, Sarkar 1989). About 5 mg powder was taken in the reaction vial and after evacuation slowly drops of ~100% orthophosphoric acid (McCrea 1950) was added to get CO₂. The chamber temperature is set at 50°C to enhance the reaction rate and is precisely controlled ($\pm 0.1^{\circ}$ C). Although most of the reaction was over within a few minutes, 10 min duration was fixed so that complete reaction of the carbonate sample is achieved. All the reaction conditions such as the chamber temperature (50°C), reaction time (10 min.), CO_2 handling procedures in the preparation line etc. were kept same so that any fractionation contributed due to procedures (although insignificant) remains same for each subsample. CO_2 was quickly trapped in the cold finger at -196°C(LN₂) between SC(stopcock) 8 and 9. Water produced in the reaction was collected into cold finger between SC-8 and 4. CO₂ was further transferred in to the cold finger between SC-9 and 10 while maintaining the temperature at -100°C to retain any traces of H₂O in the cold finger. Care was taken to maintain -100°C of the alcohol slush by frequently adding liquid nitrogen to the dewar flasks when they were not being used. The major ion current (associated with mass 44) was maintained between $3x10^{-9}$ to $5x10^{-9}$ amp by adjusting the reservoir volume of the mass spectrometer. The inlet part of the VG 903 mass spectrometer is very similar to that of the GEO 20-20 which is discussed in Sect. 3.2.

Reference CO_2 gas for the mass spectrometer was obtained from modern forams (labeled as Foram-1295) collected from the ocean sediments (Sarkar 1989). This is prepared and stored in the storage flask. The isotopic value of the foram CO_2 is calibrated with respect to the PDB (PeeDee Belemnite, a carbonate material used as International



Fig.3-3: CO₂ preparation line connected to VG 903 mass spectrometer.

Standard for reporting isotopic ratios of oxygen and carbon, Craig 1957). The δ (δ^{18} O and δ^{13} C) values with reference to Foram-1295 was converted in to δ values wrt PDB by using following equation:

$$(\delta_{\text{SAM}})_{\text{PDB}} = (\delta_{\text{SAM}})_{1295} + (\delta_{1295})_{\text{PDB}} + (\delta_{\text{SAM}})_{1295} \cdot (\delta_{1295})_{\text{PDB}} \cdot 10^{-3}$$
(3-1)

Inside the mass spectrometer the sample CO_2 is positively ionized by a heated electron source (generally tungsten or rhenium filament). By applying appropriate electric field the ions are collimated and are exposed to constant magnetic field where they follow a circular orbit, the radius of which depends upon the masses of the singly charged ions.

In a triple collector type mass spectrometer such as VG 903 and GEO 20-20 simultaneous measurement of δ^{18} O and δ^{13} C is carried out in the same focussing condition. The ion beams corresponding to species 44, 45 and 46 are collected separately in three different collectors. The current ratios δ_{45} and δ_{46} are estimated by using appropriate electronic circuits. Here, $\delta_{45} = [(I_{45}/I_{44})_{sam} / (I_{45}/I_{44})_{ref} -1] \times 10^3$ and $\delta_{46} = [(I_{46}/I_{44})_{sam} / (I_{46}/I_{44})_{ref} -1] \times 10^3$; where, I_{44} , I_{45} and I_{46} are currents at the three collector due to ionic species 44, 45 and δ^{18} O by applying following Craig corrections (Craig 1957).

$$\delta^{13}C = 1.067675 \,\delta_{45} - 0.033836 \,\delta_{46} \tag{3-2}$$

$$\delta^{18}O = -0.00224 \,\delta_{45} + 1.00107 \,\delta_{46} \tag{3-3}$$

In order to check the precision and reproducibility of the measurements a laboratory carbonate standard 'MAKMARB or MMB' (crushed and thoroughly mixed Makrana Marble of Rajasthan, Sarkar 1989), was analyzed twice in the beginning and at the end of daily measurements. Routinely about 10-18 samples were analyzed on the online extraction system. In the Table 3-1 list of all the measurements are given along with the mean and standard deviation at 1σ level. Values analyzed at the Godwin Laboratory, U.K., are also given which show quite a good agreement between values from both the laboratories. Results of the stable isotope analysis of the subsamples from the Dandak and Gupteswar cave are discussed in the chapter-4.

δ ¹³ C (‰)	δ ¹⁸ O(‰)	δ ¹³ C(‰)	δ ¹⁸ O(‰)
3.726	-10.394	3.843	-10.690
4.078	-10.320	3.770	-10.730
3.827	-10.710	3.740	-10.790
3.830	-10.764	3.801	-10.608
3.817	-10.824	3.812	-10.718
3.889	-10.591	3.687	-10.676
3.935	-10.417	3.667	-10.922
3.870	-10.974	3.723	-10.838
4.027	-10.460	3.616	-10.809
3.903	-10.741	3.704	-10.765
3.852	-10.769	3.648	-10.545
3.825	-10.575	3.662	-10.512
4.011	-10.538	3.706	-10.692
3.847	-10.758	3.709	-10.791
3.878	-10.712	3.588	-10.738
3.785	-10.731	3.644	-10.786
3.851	-10.530	3.629	-10.759
3 788	-10 605	3 694	-10 593
3 860	-10 342	3 793	-10 710
3 777	-10 581	3 853	-10 533
3 860	-10 538	3 834	-10 514
3 847	-10 550	3 798	-10.627
3 663	-10.882	3 462	-10.368
3 922	-10.447	3 820	-10.500
3.806	-10.447	3.671	-10.614
3.800	-10.075	3.071	-10.014
3.774	-10.855	3 754	-10.495
3.798	-10.505	3.734	-10.718
3.734	-10.347	3.729	-10.025
2.724	-10.550	5.020 2.705	-10.301
3.724	-10.510	5.795 2.945	-10.556
5.004 2.670	-10.307	5.845 2 700	-10.0//
5.079	-10.0/2	5.788	-10.509
3.674	-10.314	3.721	-10.5/3
3.790	-10.60/	3.112	-10.612
3.769	-10.590	3.686	-10.397
3.738	-10.574	3.820	-10.737
3.486	-10.500	3.792	-10.62/
3.645	-10.545	3.776	-10.481
3.328	-10.344	3.838	-10.441
3.549	-10.400	3.775	-10.681
3.777	-10.773	3.659	-10.721
3.689	-10.718	3.749	-10.605
3.770	-10.610	3.757	-10.682
Mean δ^{13} C 3 76	6+0.12 (86)*		3.9+0.1(28)**
Mean δ^{18} O 10.67	2 ± 0.12 (00)		$-10.5\pm0.2(28)**$
ivican o O -10.0.	$2\pm0.13(80)^{\circ}$		$-10.3\pm0.2(28)$

Table 3-1: $\delta^{13}C$ and $\delta^{18}O$ (relative to PDB) of MAKMARB values measured at PRL during 26-6-96 to 18-10-96.

Values in the parentheses are the numbers of measurements. * values obtained at PRL . ** analyzed at the Godwin Laboratory, Cambridge, U.K.

On-line CO₂ preparation for the GEO 20-20 mass spectrometer

Another mass spectrometer "GEO 20-20 was installed in 1998. This mass spectrometer has an attached on-line CO_2 preparation system (CAPS) and water equilibration system (WES) which are designed for fully automatic operations controlled by pre-written software commands (Macro's). The GEO 20-20 mass spectrometer is more sensitive i.e. the major current achieved is more compared to the VG 903 for the same amount of CO_2 . Also, the performance remains stable for a wide range of current values due to the variable sample amount.

Speleothem samples from the Akalagavi cave (Karnataka) and the Sota cave (Uttar Pradesh) were analyzed in the new mass spectrometer during April to July 2000. For reference purpose carbon dioxide prepared from another set of forams collected from ocean sediments and labeled as CD-forams (Sarkar 1989), was used. As its δ^{18} O and δ^{13} C values wrt. PDB is calibrated, hence, $(\delta_{SAM})_{PDB}$ is obtained by using following expression:

 $(\delta_{\text{SAM}})_{\text{PDB}} = (\delta_{\text{SAM}})_{\text{CD-std.}} + (\delta_{\text{CD-std.}})_{\text{PDB}} + (\delta_{\text{SAM}})_{\text{CD-std.}} (\delta_{\text{CD-std.}})_{\text{PDB}} . 10^{-3}$ (3-4)

A line diagram showing the on-line CO₂ preparation system of the CAPS system is given in the Fig.3-4 (from the manual of CAPS). In the CAPS system there is an arrangement of a carousel (a circular aluminum holder not shown in the sketch) with a provision to accommodate 24 glass vials containing carbonate subsamples. All the valves shown in the line diagram are pneumatically controlled by computer commands. As there was a mechanical problem in the automatic advancing and lifting mechanism in the carousel all the glass vials were manually moved in sequence at the appropriate reaction part, position, near V(valve)-4. It was slowly evacuated by opening V-6,7 and 9, while keeping V-8 closed. Air is allowed to enter the acid reservoir which is otherwise kept in vacuum condition, by opening V-1 and 2. About 0.5ml acid is released through acid dosing valve '5'. The carbon dioxide and moisture evolved immediately passes through a moisture trap $(at - 80^{\circ}C)$ between V-6 and 7, whereby all the water molecules are frozen. Pure CO₂ is trapped in a cold finger near V-8 for smaller gas volumes or near V-10 for bigger volumes. The gas is subsequently introduced in the sample reservoir of the mass-spectrometer

through V-11 . The acid dosing system is kept at 80° C to enhance the reaction rate. Same reaction time (10 min.) and same procedure was followed every time for all subsamples.

Mass-spectrometer inlet system in the GEO 20-20

A schematic diagram of inlet system of the GEO 20-20 mass-spectrometer is shown in the Fig.3-5 (GEO 20-20 User's Manual 1999). The sample CO₂ is introduced through inlet near V-11, while V-22 and 14 are kept closed. The CO₂ is allowed to equilibrate for 1min. duration after which V-12 is closed and V-14 is opened which allows the CO₂ to enter in to the mass spectrometer. Reference CO₂ gas (CD-foram) was taken in the reference reservoir through the inlet near V-18. The procedures are exactly similar to those followed in the sample side. Through the change-over valve system, CO₂ either from the sample or reference side periodically enters in to the mass spectrometer while the other is continuously being pumped and goes to waste. The variable volume reservoir was adjusted to provide major current (associated with mass 44) to be between 10 to 12 nano-Amperes. As discussed in (Sect. 3.2), by applying Craig corrections (eqn. 3-2 & 3-3), δ_{45} and δ_{46} were converted in to δ^{18} O and δ^{13} C respectively. Routinely about 16 to 22 samples were run on the CAPS system per day. A secondary laboratory reference material Z-Carrara (less than 63µ fine powder from a marble piece provided by Prof. N. J. Shackleton) was run before daily measurements and after each sequence of about 10 measurements. Table 3-2 gives list of all the results along with their statistical mean. As in the last phase of the measurements, the aliquot of Z-Carrara was found to be contaminated due to unknown reasons, another secondary reference Marble-V (a fine powder made from a marble piece, Sarkar (1989)) was used. However, statistical mean shown in the Table 3-3 has large fluctuations in the δ^{18} O values (±0.44). The aliquot of Marble-5 was also discontinued and finally precision of the measurements were checked using the primary standard NBS-19. In Table 3-4 results for NBS-19 measurements show quite a good reproducibility and agreement with the values quoted by IAEA (International Atomic Energy Agency). Results of the stable isotope analysis of the carbonate subsamples from the Akalagavi and the Sota caves are discussed in the chapter-4.



Fig.3-4: CO₂ preparation line connected to GEO 20-20 mass spectrometer.



Fig. 3-5: Inlet part of the GEO 20-20 mass spectrometer.

$\delta^{13}C$ (‰)	$\delta^{18}O(\%)$	$\delta^{13}C(\infty)$	$\delta^{18}O(\%)$
2.25	-1.80	2.25	-0.96
2.26	-1.54	2.29	-1.08
2.18	-1.70	2.05	-1.53
2.27	-1.57	2.24	-1.41
2.14	-1.79	2.35	-1.01
2.23	-1.78	2.34	-1.01
2.27	-1.74	2.28	-1.22
2.14	-1.63	2.32	-1.08
2.29	-1.77	2.29	-1.23
2.32	-1.12	2.05	-1.08
2.33	-1.11	2.04	-1.25
2.27	-1.63	2.26	-0.89
2.32	-1.22	2.19	-1.25
2.26	-1.80	2.22	-1.26
2.36	-1.12	2.07	-1.36
2.28	-1.74	1.84	-1.14
2.33	-1.22	1.70	-2.41
2.35	-1.12	1.95	-1.78
2.36	-1.02	2.30	-1.21
2 36	-1.01	2.32	-1 21
2.29	-1.25	2.33	-1.01
2 30	-0.88	2.36	-1 12
2.34	-1.16	2 34	-1.03
2.34	-1.12	2.25	-1.14
2.33	-1.15	2.24	-1.33
2.31	-1.44	2.33	-1.00
2.32	-1.16	2.21	-0.94
2.34	-0.99	2.31	-1.00
2.30	-1.18	2.30	-1.02
2.31	-0.93	2.30	-1.03
2.33	-1.09	2.21	-1.21
2.26	-1.76	2.24	-1 27
2.30	-0.91	2.26	-1.27
2 31	-1.18	2.27	-1.15
2.32	-0.99	2.33	-1 13
2.29	-1.12	2.22	-1.32
2.35	-0.97	2.23	-1.26
2.33	-1.12	2.21	-0.95
2.33	-1.11	2.25	-1.21
2.31	-0.95	2.07	-1.43
2.31	-1.13	2.26	-1.14
2.30	-1.13	2.09	-0.89
2.30	-1.12	2.12	-0.92
2.33	-0.95	2.32	-1.17
2.32	-1.11	2.06	-0.90
2 32	-0.98	2.22	-1 34
2.31	-1 17	2 29	-0.91
2.30	-1 03	2.21	-1 48
2.32	-1.15	2.07	-1.67
2.52	1.10	2.51	-0.93
Mean δ^{13} C 2.257+0	113 (99) · Mean δ^{18} O -1	$223\pm0.281(99)$	

Table 3-2: δ^{13} C and δ^{18} O (relative to PDB) of Z-carrara values measured at PRL during 27-4-2000 to 18-7-2000.

Values in the parentheses are the numbers of measurements.

Table 3-3: δ^{13} C and δ^{18} O (relative to PDB) values of Marble-V measured at PRL during 6-7-2000 to 12-7-2000.

$\delta^{13}C(\%)$	δ ¹⁸ O(‰)
2.49	-0.55
2.33	-0.78
2.30	-0.94
2.45	-0.48
2.10	-1.15
2.03	-1.17
2.25	-1.05
2.15	-1.27
1.79	-1.84
2.45	-0.70
2.36	-1.20
2.42	-0.85
2.42	-0.85
2.38	-0.56
1.98	-2.08
2.60	-0.90

Mean δ^{13} C 2.283±0.217 (16) Mean δ^{18} O $-1.023\pm0.439(16)$

Table 3-4: δ^{13} C and δ^{18} O (relative to PDB) of NBS-19 measured at PRL during 16-7-2000 to 20-7-2000.

$\delta^{13}C(\%)$	$\delta^{18}O(\%)$	
2.06	-1.93	
2.08	-1.89	
2.06	-2.07	
2.10	-2.03	
2.11	-2.04	
2.04	-2.09	
2.06	-1.90	
2.15	-2.26	
2.26	-2.06	
2.04	-2.25	
2.04	-2.07	
Mean $\delta^{13}C$	2.09±0.07 (11)	$\delta^{13}C^* = 2.00$
Mean $\delta^{18}O$	-2.05±0.12 (11)	$\delta^{18}O^* = 2.20$
* Values quo	ted by IAEA	

Values quoted by IAEA.

3.3 $\delta^{18}O$ measurements of water samples

The CO₂ equilibration method

Measurement of the oxygen isotope composition in the water sample can be done by three methods (Gonfiantini 1981; Brand et al 1996). In the first method called equilibration method, CO₂ gas (from any reference reservoir) is allowed to exchange oxygen isotopes with the sample water at constant temperature. In the second method,

oxygen of the water is extracted by reduction and converted into CO₂. The carbon dioxide is then introduced in the mass spectrometer. In the third method water vapour are directly let into the mass spectrometer. For practical reasons the equilibration method is simpler to follow in the machines which are automated. In the present study, the CO_2 equilibration method (Gonfiantini 1981) was followed. Equilibration was carried out on WES (Water Equilibration System) attached with the GEO 20-20 mass spectrometer. The operation of the of the WES is fully automated, controlled by software. A schematic diagram of the WES is shown in the Fig.3-6 (A) & (B). Water sample (each 1ml) is filled in a 6.8ml standard glass bottle. A threaded cap having a neoprene septum seals the bottle preventing any leakage. About 40 such bottles filled with water samples are kept in sequence in a rack. A secondary laboratory reference 'NRM' (taken from the river Narmada) was also filled in similar glass bottles and one each placed after a batch of 10 samples. Its oxygen isotopic ratio with respect to VSMOW (Vienna Standard Mean Ocean Water, which is the international water standard used as a primary reference for the δ^{18} O and δD measurements of the water samples (Baertschi 1976; Hageman et al 1970). The measurement of oxygen isotopes is carried out in three steps.

1) Flushing of the air: A sharp needle with double holes (shown in the Fig.3-6: (A) & (B)) which can move up and down in to the sample bottle, pierces the neoprene septum from the top of the cap so that both holes are inside the bottle. Carbon dioxide from a cylinder (obtained from Vadilal Gas Company and labeled as $-VDCO_2$) is let into the sample bottle by opening the V-1. For 1 min duration the cylinder CO₂ flushes the air through vent (V-3 remains open and V-4 closed). After this only pure CO₂ remains inside the sample bottles. During flushing some water vapour may be flushed out. But, the amount is too small to fractionate the sample significantly, or else it is uniform for all samples and standards.

2) CO_2 equilibration: The needle moves up and the holes in the neoprene septum get immediately closed by the elastic nature. The carbon dioxide and water are left overnight (~12 hrs) in the fully sealed and isolated condition for complete equilibration to occur. The rack carrying all the sample glass bottles is kept at 35°C to enhance the isotopic exchange and to reduce the equilibration period.





Fig. 3-6: (A) WES system: Hydrogen and carbon dioxide equilibration line of the GEO 20-20 mass spectrometer. (B) Sample bottle and Gilson needle.

Isotopic exchange takes place due to the following reactions:

$$CO_2(g) \leftrightarrow CO_2(aq)$$
 (3-5)

$$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$$
 (3-6)

The isotopic exchange reaction is written as

$$C^{16}O_2 + H_2^{18}O \leftrightarrow C^{16}O^{18}O + H_2^{16}O$$
 (3-7)

After some time (e.g. 12hrs at 35° C in the present case) the reaction reaches equilibrium condition and the ratios (18 O/ 16 O) in the water and carbon dioxide is related by a temperature dependent fractionation factor α :

(3-9)

$$({}^{18}\text{O}/{}^{16}\text{O})_{\text{CO}_2} = \alpha \cdot ({}^{18}\text{O}/{}^{16}\text{O})_{\text{H}_2\text{O}}$$
 (3-8)

 $1000 + \delta^{18}O_{CO_2} = (1000 + \delta^{18}O_{H_2O}) . α$ Value of α at 35°C is 1.0393 (Criss 1999)

3) δ^{18} O measurement: The equilibrated CO₂ is passed through a moisture trap at -100^oC (before V-4) whereby all the water vapour is trapped and the pure CO₂ is passed into the sample reservoir of the mass spectrometer. The reference reservoir is filled with the VDCO₂ gas and the measurement procedures are similar to those discussed earlier in the (Sect. 3.2). The flushing and measurements were carried out in automatic mode.

The $\delta^{18}O_{CO_2}^{0}$ which is the oxygen isotope composition of the CO₂ gas equilibrated to the water sample assuming that the amount of water is infinite and hence it doesn't change the original isotope signature of water during equilibration is given (Craig 1957, Gonfiantini 1981) as:

$$δ^{18}O_{CO_2}^{o} = (1 + α.(n/N)). \delta^{18}O_{CO_2} - α.(n/N). \delta^{18}O_{CO_2}^{i}$$
 (3-10)

where, $\delta^{18}O_{CO_2}$ = oxygen isotope composition of the equilibrated CO₂

 $\delta^{18}O_{CO_2}^{i}$ = initial oxygen isotope composition before equilibration, which is 0‰ as the same gas (VDCO₂) has been used as reference gas.

N= gram-atoms of oxygen present in the water sample and n in CO_2 .

As the amount of oxygen in the CO₂ gas (5.8ml at 1atm pressure) in the 6.8ml glass bottle is insignificant compared to that in the water phase (1ml), hence, n/N \approx 0, this means that for practical purposes $\delta^{18}O_{CO_2}^{0}$ and $\delta^{18}O_{CO_2}$ are same and oxygen isotope composition of the water ($\delta^{18}O_W$) sample can be obtained using equation (3-8):

 $({}^{18}O/{}^{16}O)_{CO_2} = \alpha . ({}^{18}O/{}^{16}O)_{H^2O}$

During measurements NRM water, which is a secondary laboratory standard, is placed after each batch of 10 samples and is also equilibrated with the same CO₂ (VDCO₂).

If the CO₂ measurements for NRM are represented as $\delta^{18}O_{NRM-VDCO2}$ and for the sample as $\delta^{18}O_{SAM-VDCO2}$ then oxygen isotope composition of the <u>water</u> sample relative to NRM <u>water</u> i.e. $\delta^{18}O_{SAM-NRM}$ is:

 $1000 + \delta^{18}O_{SAM^{-}NRM} = (1000 + \delta_{SAM^{-}VDCO_{2}}) / (1000 + \delta_{NRM^{-}VDCO_{2}})$ (3-11)

As the temperature of equilibration for the water samples as well as the NRM standard is same (35°C), hence, value of α is same in both the cases and is cancelled out in the above expression.

Values with respect to SMOW standard is given as: $\delta^{18}O_{SAM-SMOW} = \delta^{18}O_{SAM-NRM} + \delta^{18}O_{NRM-SMOW} + \delta^{18}O_{SAM-NRM} \cdot \delta^{18}O_{NRM-SMOW} \cdot 10^{-3}$ (3-12)

Results of analysis on the NRM water and the associated precision are given in the Table 3-5. Results of water sample analysis will be discussed in chapter-4. Table 3-5: δ^{18} O of the NRM (Narmada water) wrt. VSMOW measured during different periods.

$\delta^{18}O_{\text{NRM-VSMOW}}$ (%)
Dec. 1999 measurements
-4.59
-4.64
-4.69
-4.72
June 2000 measurements
-4.40
-4.43
-4.44
-4.55
-4.61
-4.62
$Av. = -4.57 \pm 0.11$

3.4 δ **D** measurements of water samples

The measurement of D/H ratio in the water sample is done by two methods (Brand et al 1996; Gonfiantini 1981). In the first method water is completely reduced to hydrogen gas. This is generally carried out manually by using platinum and zinc as reagents and automatically by using hot chromium. In the second method hydrogen gas is equilibrated with H_2O along with a catalyst (platinum on a hydrophobic support). The WES (Water Equilibration System) in the GEO 20-20 mass spectrometer can also be used for hydrogen - water equilibration.

In the hydrogen-water equilibration, sample filling procedures are exactly same (see Fig.3-6: (A) & (B)) as discussed in the (Sect. 3.3) except that platinum catalyst pellets are

put inside the bottles. Instead of CO₂, hydrogen from a cylinder (labeled as BOC-H₂) is used to flush the air in the glass bottle (by opening V-2 while keeping the V-1 closed) for 1min duration. Equilibration is generally complete within half an hour, but, in the present case all the measurements were carried out after about 20 hrs. (next day). The sample glass bottles in the rack were kept at 35^{0} C. Hydrogen gas, free of water vapour, is obtained by following steps similar to those discussed in the (Sect. 3.3). The hydrogen gas is further ionized to H₂⁺ and DH⁺ ions from electron impact in the mass spectrometer and the ratio of mass-3 to mass-2 i.e. DH⁺/H₂⁺ is measured. An automatic correction is made for H₃⁺ contribution (see next section). The reference H₂ is the same which has been used for the equilibration purpose. If the Hydrogen isotope composition of the H₂ gas equilibrated to the water samples is:

$$\delta D_{\text{sam-H}^2} = ((DH^+/H_2^+)_{\text{sam-H}^2} / (DH^+/H_2^+)_{\text{ref-H}^2} - 1). \ 10^3$$
(3-13)

Then the δD of the sample water($\delta D_{sam-wat}$) can be obtained by using the expression below:

$$(DH/H_2)_{sam-H_2} = \alpha_{H_2-H_2O} \cdot (DH/H_2)_{sam-wat}$$
 (3-14)

As the amount of hydrogen atoms in the gas phase (5.8ml-gas) in the 6.8ml bottle is negligible compared to the amount of atoms in the water phase (n/N \approx 0), the volume corrections are not applied (correction is similar to expression 3-10). Along with the samples, standard water (NRM) is also filled in the sample rack after each batch of 10 samples. If δD_{SAM} is the δD of H₂ equilibrated with the sample water and δD_{NRM} is the δD of the H₂ equilibrated to the NRM water then $\delta D_{SAM-NRM}$ is given as :

 $1000 + \delta D_{SAM-NRM} = (1000 + \delta D_{SAM}) / (1000 + \delta D_{NRM})$ (3-15)

As in both the gases $\alpha_{H_2-H_2O}$ involved is same hence, the same expression gives δD of the sample <u>water</u> relative to the NRM <u>water</u>. Relative to SMOW it was converted using the following expression:

 $\delta D_{SAM-SMOW} = \delta D_{SAM-NRM} + \delta D_{NRM-SMOW} + \delta D_{SAM-NRM} \cdot \delta D_{NRM-SMOW} \cdot 10^{-3} \quad (3-16)$

Results of different runs of the NRM water and its precision is given in the Table 3-6. Hydrogen isotope compositions of the water samples analyzed are discussed in chapter-4.

Table 3-6: δD of the NRM	(Narmada water) wr	. VSMOW measure	ed during different	periods.
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$\delta D_{\text{NRM-VSMOW}}$ (‰)
measurements made on 18 and 19
Dec 1999
-38.46
-38.46
-38.61
-38.95
-38.41
-37.03
$Av. = -38.22 \pm 0.66$

Corrections required in the H₂ isotope analysis

Hydrogen ions and hydrogen molecules interact in the source of the mass spectrometer to produce H^{3+} ions by the following reaction

 $\mathrm{H_2}^+ + \mathrm{H_2} \longrightarrow \mathrm{H_3}^+ + \mathrm{H}$

(3-17)

This means that there is another ion of mass-3 which interferes with the DH⁺ ions at the collector. Concentration of these H_3^+ ions is proportional to the concentration of the major ion H_2^+ . Hence, current ratio estimated i.e. mass-3/mass-2 is $(DH^+ + H_3^+)/H_2^+$. However, an appropriate correction (called H_3^+ correction) for this can be empirically obtained (Gonfiantini 1981) and actual required ratio (DH^+ / H^+) can be obtained. This correction is estimated by the GEO 20-20 using a linearity routine which is run (before measurements are started) at different concentrations of the major beam (H_2^+) using the reference H_2 gas. The correction is then applied to all the HD analyses. Contribution from H_3^+ ions was around 4.2 %. External precisions in the $\delta^{18}O$, $\delta^{13}C$ and δD measurements are within $\pm 0.15\%_0$, $\pm 0.15\%_0$ and $0.66\%_0$, respectively.

3.5 Radiocarbon dating of speleothems

Radiocarbon dating was used to assign chronology to the speleothems. Benzene was synthesized in three steps from speleothem subsamples (shown by patches in the Figs.3-2(A to D)) and liquid scintillation spectrometry was used to estimate the residual specific ¹⁴C activity. In the first step powdered carbonate covering several laminae weighing from 3 to 7g was taken in a round bottom flask connected to a vacuum line as shown in the line diagram (Fig.3-7(A)). It was wetted with distilled water and after evacuating the flask, concentrated H₃PO₄ was added slowly to liberate CO₂ (Gupta and Polach 1985; Agrawal and Yadava 1995 and Yadava and Ramesh 1999b). Water vapour was condensed by two



moisture traps cooled using alcohol slush at -100°C. Carbon dioxide was collected in traps cooled at LN₂ (liquid nitrogen) temperature. In the second step, the CO₂ from the sample carbon was converted in to acetylene (Polach and Stipp 1967, Tamers 1975). For this purpose CO₂ is allowed to react at a controlled rate with pure lithium metal melted in a specially designed reaction chamber (Fig.3-8 (A)). The reaction temperature is set at 550°C. About 6 g of lithium is taken for CO₂ equivalent to 1 g carbon. The reaction product is the lithium carbide (Li₂C₂) which is cooled at room temperature and further hydrolysis using distilled water produces C₂H₂ apart from some trace gases and water vapour. Distilled ground water is used at this stage so that there is no tritium activity and hence no beta interference at counting stage. Moisture traps at -100°C are again used to remove water vapour. Two traps as shown in Fig.3-8 (A) filled with glass beads coated with NaOH and H₃PO₄ and a third one filled with sodalime are used to remove trace gases from acetylene which may generate quenching at the ¹⁴C counting stage. The acetylene is collected using two traps cooled at liquid nitrogen temperature. In the third and final step the acetylene is absorbed and is polymerized into benzene by catalyst (V_2O_5) pellets in a column as shown in the Fig.3-8 (B). The sample carbon converted into benzene (Polach et al 1972) is recovered by heating the catalyst column at 110°C and the benzene vapour is condensed (Fig.3-7 (B)) again at liquid nitrogen temperature. The catalyst is reactivated at about 300°C by periodically passing dry air (through molecular sieve) into the column. The overall chemical yield is between 90-94%.

Old coal (a laboratory batch labeled as anthracite-II) is used to prepare benzene for background measurements of the overall procedure. For modern reference activity, OXALIC ACID-I (Olsson 1970) and OXALIC ACID-II (Stuiver 1983) availed from U.S. National Bureau of Standards) are periodically used to prepare benzene using the above mentioned procedure. The CO₂ preparation differs for these materials. The background and reference materials were heated in a quartz tube to produce carbon dioxide under continuous flow of oxygen (Fig.3-6 (B)). Traces of carbon monoxide are oxidized by using CuO mesh heated at 550°C. Carbon dioxide was purified by passing it through chemical traps filled with dilute solutions of KI/I₂, AgNO₃ and H₂SO₄/K₂Cr₂O₇. Acetylene and benzene preparation is common both for background and reference materials.

An organic scintillator (Butyl-PBD) was mixed (0.015 g per ml) with the sample benzene prior to decay measurements. 14 C decays were counted in a low background teflon



vial in the ultra low background detector "LKB-QUANTULUS". The overall procedure is standardized to 1 ml of benzene volume. The counting period is set to 85 min duration with 30 repeat measurements to statistically check the data fluctuations. The average background for 1 ml of benzene is 0.30+0.03cpm and the modern reference is 9.36+0.13cpm per ml of benzene over a period of a year with an overall precision of 1.5% Modern. The figure of merit obtained is 23,800 and the laboratory dating limit is 40kyr. The ages estimated on the speleothems have an error between 80 to 100 years. Isotopic fractionation during benzene synthesis is minimal when CO₂ to C₆H₆ conversion is high (greater than 80%); a depletion of δ^{13} C in benzene by 1.7± 1‰ is observed (Panarello et al 1983), due to this the ages will be overestimated only by 10 to 45 yr. Unless precise age estimation was required, $\delta^{13}C$ corrections due to laboratory fractionation and due to δ^{13} C variations in natural reservoirs (Stuiver and Polach 1977; Mook and van der Plicht 1999), were not applied. As shown in the Table 3-7 for most of the samples provided at the second stage of the TIRI (Third International Radiocarbon Inter-comparison) assessed using "Quantulus-liquid Scintillation counter", the estimated ages agree well with the consensus values (Marian et al 1997). The teflon counting vials have different transmission efficiencies and each synthesized benzene has variable quenching level. Recently, a correction (Forest and Strydonck 1995) for these is being applied by using SQP measurements (Spectrum Quench Parameter- end point in the

compton energy spectrum using 226 Ra as external standard, recorded in the Multi Channel Analyser). Radiocarbon age (T) equation is given as:

 $T=(1/\lambda).\ln(A_{abs}/A)$

(3-18)

A = net activity of the sample

 A_{abs} = original equilibrium ¹⁴C activity of the reservoir that supplied the sample. This is obtained using reference materials e.g. oxalic-I and oxalic-II.

 $\lambda = 1.21 \times 10^{-4} \text{ yr}^{-1}$, ¹⁴C decay constant (half-life of 5730 years)

Age estimations of various subsamples are discussed in Chapter-4.

Table 3-7: Radiocarbon ages of TIRI samples

Sample	PRL value	Consensus value	
Fuglaness wood	50,510±3480	39,784 <u>+</u> 620	
Ellanmore whole peat	$11,130\pm90$	$11,152\pm23$	
Travertine	11,540 <u>+</u> 90	11,060 <u>+</u> 17	
Crannog wood	1,550+50	1,605+8	

3.6 Measurement of trace element concentrations

Subsample dissolution

Variations in the concentrations of trace elements Mg, Sr and Ba were studied in the Dandak stalagmite following ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) method. As shown in Fig.3-9, 105 subsamples weighing between 30 to 100mg were recovered from stalagmite along the main growth direction.

In the present study all subsamples were dissolved by $1N \text{ HNO}_3$. All the carbonates dissolved immediately, but, to ensure complete dissolution they were heated at 50°C for about an hour to completely dissolve the carbonates. The solution volume was later made to precisely 25ml by adding $1NHNO_3$ in a volumetric flask. After dissolution the solution doesn't show any particulate matter (except in the hiatus layer discussed later), which suggests that the TE (trace elements) in calcite are totally derived from seepage water and not from any detrital material.

Measurements

The Inductively Coupled Plasma of argon gas has very high temperature between 6000 to 8000°K. Under these conditions any dissolved solution introduced in to the argon plasma in the form of aerosols using appropriate nebulizer gets efficiently atomized. Ionic and atomic line spectra are generated, which can be used to measure concentrations of major and trace elements, using a suitable spectrometer (Potts 1995). Emission lines selected for the TE measurements are 279.806nm for Mg, 421.552nm for Sr and 455.403nm for Ba. Measurements were carried out on ICPAES-JY-38S (Jobin Yvan-38S) machine at PRL, Ahmedabad. A calibration line i.e. emission line intensity vs. concentration (µg/ml) for Mg was generated using 1, 5 and 10 µg/ml Mg standards. Similarly, both for Sr and Ba 1, 2 and 5 μ g/ml standards were used to generate calibration lines. For samples of unknown concentrations, first, specific emission line intensity was measured on ICP-AES and then from the calibration line, its solution concentration (µg/ml) was estimated. This value was later converted in to TE concentration in the subsamples.

TE concentration (μ g/gm or ppm) = solution concentration (μ g/ml) x (25/w) (3-19) where, w is the weight (in grams) of the sample dissolved in 25 ml 1N HNO₃.

Carbonate matrix problem

The dissolved subsample solution has many ionic species particularly the calcium ions. The carbonate matrix may either enhance or suppress the emission line intensities of specific interest. Calibration for Mg, Sr and Ba lines are generated using standards prepared from pure 1N HNO₃ where carbonate matrix is not present. If the matrix effect is dominant then it may not be possible to estimate absolute concentrations of TE using the method of calibration discussed above. Method of addition which can estimate absolute concentrations was applied for a few subsamples and then the results were compared with those obtained using method of calibration. For this three separate aliquots were taken from the 25ml volume subsample solution. Known (μ g/ml) amount of TE was added to two of the aliquots. After measuring the respective line intensities absolute concentration of TE is estimated from the abscissa cut on emission line intensity vs. μ g/ml plot. Results obtained for one of the subsamples is given in the Table 3-8.

Table 3-8: Met	hod of a	iddition	for absolute	Mg	conc	centra	tion	measure	emen	t for a	typica	il spe	leother	n sam	ple.
A 1 * .		11 1/	(1)	1		1.	• .	• . •		1.4	•		1	1	

. . . .

Aliquot	Mg added (µg/ml)	relative line intensities at 279.806 nm	Mg in the subsample solution (μ g/ml)
1	0	4725.8 ± 70.9	28.4±0.6/0.9998*
			$26.4 \pm 0.5^{**}$
2	20	7932.1 ± 119.0	
3	40	11368.6 ± 132.8	

* correlation coefficient for the best fit line (emission line intensity (column-3) vs. µg/ml (column-2) plot). ** values obtained using calibration method.

Aliquot	Sr added (µg/ml)	relative line intensities at 421.552 nm	Sr in the subsample solution ($\mu g/ml$)
1	0	6304.5 ± 94.6	0.5659±0.0106 0.9998* 0.6018±0.0141 **
2	0.465	11157 ± 36.8	
3	0.929	16444.1 ± 106.9	

Table 3-9: Method of addition for absolute Sr concentration measurement for a typical speleothem sample.

* correlation coefficient for the best fit line (emission line intensity (column-3) vs. µg/ml (column-2) plot). ** values obtained using calibration method.

Aliquot	Mg added (µg/ml)	relative line intensities at	Ba in the subsample
		455.403 nm	solution (µg/ml)
1	0	11424.1 ± 51.4	1.0166±0.0132 0.9998*
			1.131±0.0142 **
2	20	22126.1 ± 143.8	
3	40	31271.3 ± 437.8	

* correlation coefficient for the best fit line (emission line intensity (column-3) vs. µg/ml (column-2) plot). ** values obtained using calibration method. As shown in Table 3-8 the solution concentration values 28.4 ± 0.6 obtained from method of addition and 26.4 ± 0.5 from method of calibration agree at 3 sigma level. Similarly, in Table 3-9 and 3-10 results obtained for Sr and Ba are given. The difference between results obtained both for Sr and Ba using the methods of addition and calibration are insignificant at 3 sigma level.

This proves that concentration values can be generated using calibration lines without any significant deviation from the absolute values. Subsequently, TE concentrations in all the subsamples were measured using the calibration method. The Mg, Sr and Ba concentrations with depth from tip to base part are shown in chapter-4.

3.7 Mineralogical studies

Speleothem mineralogy was checked using XRD method. Fine homogeneous powder was prepared by gentle drilling and slow grinding of speleothem layers at selected spots and later passed through a 350-mesh (45μ) sieve. Diffraction spectrum of samples were checked for the presence of calcite and aragonite. Line intensity different at d value 3.02 Å was taken as reference for the calcite and at 3.40 Å for the aragonite. The powdered samples of speleothems were scanned at a rate of 1° per minute using Philips instrument having a copper target, in the scanning range of 21 to 51° (20). All the subsamples prepared from the Dandak stalagmite turned out to be pure calcite. In order to obtain quantitative assessment of mineralogy (Hardy and Tucker 1988) several mixtures of different proportions of calcite and aragonite were prepared. For pure aragonite a piece of coral (corals are 100% aragonite) and for calcite a piece from the Dandak stalagmite (found to be pure calcite)was used. Peak area was estimated for the lines associated d values 3.02 and 3.40 Å. A calibration line obtained by the best fit of the different measurements is shown in the Fig.3-10. The calibration equation obtained is

$$Y = a.(1-e^{-0X});$$
 (3-20)

where Y=% aragonite,

X= area of aragonite peak / (area of aragonite peak + area of calcite peak)

 $a = 100.00 \pm 7.18$ and $b = 4.77 \pm 0.91$.

Using the above relationship aragonite fraction in the carbonate layers from different speleothems have been estimated and is reported in Chapter-4.
3.8 Measurement of thickness and gray levels

Distinct layers alternatively compact and coarse are observed in the stalagmite from Akalagavi cave, Karnataka. One of the half section was polished further and thickness of each compact layer was measured on a tree ring thickness measurement machine at IITM (Indian Institute of tropical Meteorology, Pune). The machine was fitted with a microscope having an amplification of 5 to 20 times and a linear movement platform with a resolution of 0.01cm (0.001mm). The results are presented in Chapter-4.

In the same deposit compact layers are whitish whereas coarse layers appear dark due to trapped detrital particles. Gray level of one of the half section surface was examined to understand if the degree of detrital content can be used as a proxy for past rainfall changes. Images of cross sectioned pieces were scanned with a high density scanner attached to a personal computer and then using an image analysis program, its gray level was generated along the growth direction. Results are discussed in chapter-4.

3.9 δ^{13} C of seepage water

For the Dandak cave, dripping water was collected from different stalactite tips firstly by sucking the water from wet surfaces of the stalactites using a sterilized syringe and secondly by directly accumulating them in a small beakers. Later, they were all transferred in a 15 ml cylindrical glass tube up to the maximum level. It was tightly sealed using a special type of neoprene rubber cork so that there is no air inside. The tube was then covered using aluminum foil so that the light doesn't enter the glass tube and hence there are no chances of bacterial photosynthesis which may change the original $\delta^{13}C$ of the seepage water. The water was collected quickly from each dripping spot hence, significant CO₂ degassing is not expected. After about 15 days few drops of MgCl₂ was added to avoid any bacterial photosynthesis. Measurements of δ^{13} C of the dissolved carbon were carried out by adding 1ml H₃PO₄ and about 5ml of the water sample in an evacuated reaction bottle through a neoprene rubber cork. Evolved CO₂ gas was trapped under liquid nitrogen temperature after passing it through a moisture trap. Water and acid mixture were stirred for about 1 hour for complete reaction to occur. Trapped CO₂ was further passed through a moisture trap and was measured for the $\delta^{13}C$. The results are discussed in chapter-4.



Fig.3-10: A calibration curve (dotted) generated from the mixtures of calcite and aragonite in varying proportions. Y axis shows aragonite percentage in the mixture prepared from pure aragonite and calcite powders. X axis shows area of aragonite peak / (area of aragonite + area of calcite peak): aA and aC are the pulse heights observed at the d values 3.40 Å (for aragonite) and 3.02 Å (for calcite), wA and wC are the corresponding pulse widths at the base.

Results and discussions

4.1 Speleothem chronology

Radiocarbon ages obtained on the subsamples shown by patches in the Figs.3-2 (a-d) are listed in Tables 4-1 to 4-4.

4.1.1 Fractionation correction

Due to the fractionations arising by various physical and chemical processes, different contemporary materials have δ^{13} C values varying from about +2‰ to -27‰ (Stuiver and Polach 1977) and the specific radiocarbon activity (activity per gm of carbon) in these materials also differ from each other. However, their specific activities become same if they are normalized to the same δ^{13} C value. As the standard for the radiocarbon age estimation is the wood material grown in the year 1890 (its activity represents A_{abs}) which has δ^{13} C = -25‰, hence, all the measured sample activities (A_{meas}) are corrected to -25‰ by using the following relation (Stuiver and Polach 1977):

A= A_{meas} .[1-2.(25 +
$$\delta^{13}C_{meas}) / 10^3$$
] (4-1)

Where, $\delta^{13}C_{meas}$ is the carbon isotopic composition of the carbonate from the speleothem layers which is estimated by taking an aliquot of CO₂ prepared at the initial stage of the benzene preparation (Sect. 3.5) and measured in the mass spectrometer.

The above corrections were applied to all measurements carried out for the Akalagavi (Table 4-3) and Sota cave (Table 4-4). However, for the subsamples taken from Gupteswar and Dandak cave the CO₂ aliquots were not available for the δ^{13} C estimation. At a later stage when stable isotopic compositions of carbon were available (Sect. 4.2), the average δ^{13} C values of the subsamples covering the dating zone (patches in the Fig.3-2 (A) & (B)) were assumed as δ^{13} C_{meas} for the correction purpose. This assumption doesn't generate any significant error. For example, for PRL-2112 in the Table 4-4, the δ^{13} C for the

 CO_2 aliquot used for benzene preparation is -12.75% where as average value for the associated subsamples taken for stable isotope analysis is -13.22%. The difference being 0.46‰ which introduces an error of about 8 yrs, is negligible compared to the uncertainty in the ages (about ±80 to 130 yrs; Table 4-1 to 4-2).

The modern primary reference materials OXALIC-I (Olsson 1970) and OXALIC-II (Stuiver 1983) were taken for the estimation of A_{abs} by preparing benzene (Sect. 3.5) and following corrections were applied to get A_{abs} :

$$A_{abs} = 0.95.A_{OX-I} [1-2.(19 + \delta^{13}C)/10^{3}]$$
(4-2)

$$= 0.7459.A_{OX-II} [1-2.(25+\delta^{13}C)/10^{3}]$$
(4-3)

Where, A_{OX-I} and A_{OX-II} are the measured ${}^{14}C$ activity of the benzene prepared from OXALIC-I and OXALIC-II respectively. $\delta^{13}C$ is the stable carbon isotope composition of the respective CO₂ aliquots.

The permil deviation of the sample ¹⁴C activity from the A_{abs} is given as

$$\Delta^{14}C = [A/A_{abs} - 1].10^3 \%$$
(4-4)

And percent modern or percent modern carbon is defined as,

pM or pMC =
$$(A/A_{abs}).100$$
 % (4-5)

All the quoted errors in the Table 4-1 to 4-4 are based on the no. of accumulated counts of the sample, reference and background plus additional errors caused by the dilution (Stuiver and Polach 1977). The ages reported are rounded to the nearest multiple of ten as per the convention of reporting radiocarbon ages (Stuiver and Polach 1977)

Table 4-1: Details of the subsamples from Gupteswar stalactite and their ¹⁴C ages.

Sample code	Depth from tip part	Sample total	Apparent age	Corrected age
	(mm)	weight (g)	(years BP)	(years BP)
PRL-1969	483.5-480.5	3.8	880 ± 100	0 ± 100
PRL-2001	456.0-458.0	7.0	1370 ± 90	490 ± 130
PRL-2000	390.3-392.8	7.5	2430 ± 90	1550 ± 130
PRL-1999	260.8-270.5	4.0	3800 ± 90	2920 ± 130
PRL-1992	112.8-156.0	7.6	3780 ± 90	2900 ± 130
PRL-1998	2.5-10.8	7.7	4270 ± 90	3390 ± 130

Sample code	Depth from tip (mm)	Sample total weight (g)	Apparent age (years BP)	Corrected age (years BP)
PRL-1995	12.5-22.3	3.2	1310 ± 80	0 ± 80
PRL-1996	72.3-79.0	4.4	1640 ± 80	410 ± 110
PRL-1993	127.5-135.8	4.6	1970 ± 80	740 ± 110
PRL-1997	176.8-185.3	4.1	1940 ± 80	710 ± 110
PRL-1994	267.3-278.8	5.0	4770 ± 100	3540 ± 130

Table 4-2: Details of the subsamples from Dandak Stalagmite and their ¹⁴C ages.

Table 4-3: Details of the subsamples from Akalagavi stalagmite and their ${}^{14}C$ ages. RC-1 ,2 &3 are patches shown in the Fig.3-2.

Patches	Depth from the Tip part	Sample total weight (g)	¹⁴ C age (years BP)
			$(t_{1/2}=5730 \text{ yrs})$
RC-1/PRL-2018	~ 0.2 to 0.3cm	9.0361	$108.62 \pm 1.09\%$ M
			Δ^{14} C= 86.2 %o
RC-2 / PRL-2019	~ 2 to 2.9 cm	3.5089	123 01 + 1 49%M
			Δ^{14} C=230.1±14.9 ‰
RC-3 / PRL-2020	~43.5 to 44.3 cm	4.5753	$210 \pm 100 \text{ yr BP}$

Table 4-4: Details of the subsamples from Chitrakoot stalactite and their ¹⁴C ages.

Sample code	Depth from tip part (mm)	Sample total weight (g)	Apparent age
PRL-2113	0-21.2	3.5	$117.69 \pm 1.46\%$ M Δ^{14} C = 176.9 ± 14.6 ‰
PRL-2112	235.8-244.6	4.0	$1100 \pm 120 \text{ yr BP}$

4.1.2 Dilution of ¹⁴C activity

The ¹⁴C age of the speleothem is greater than that of organisms deriving carbon from the atmosphere. This is due to contribution of ¹⁴C free carbon from the leached carbonate bedrock (reservoir effect).

Radiocarbon activity of the soil CO_2 enters in to the seepage water through following equilibrium reaction:

$$CO_2 + H_2O = H^+ + HCO_3^-$$
 (4-6)

Subsequently, limestone bedrock (which is free of any ${}^{14}C$ activity as generally it is millions of year old) through the following reaction (this is same as equation 1-6), dilutes the ${}^{14}C$ activity in the seepage water:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^{-}$$
 (4-7)

The extent of dilution depends upon various local factors of the cave system such as open system or closed system dissolution condition (Hendy 1971; Clark and Fritz 1997). If the seepage water is diluted by a factor 'D' then the age equation (3-18) is modified as (Mook 1980):

$$t_{corr} = -8267.\ln (A/D.A_{abs})$$

or
$$= -8267.\ln (A/A_{abs}) + 8267.\ln D$$

$$= t_{app} + 8267.\ln D$$
 (4-8)

Here, t_{corr} is the dilution corrected age (i.e. real age) and t_{app} is the apparent age which is obtained experimentally by using equation (3-18).

In the case of an actively growing speleothem at the tip part, $t_{act} = 0$ and hence, the measured age $t_{app} = -8267.$ lnD gives the value of the factor-D. Assuming that during the past periods the dilution factor 'D' remained constant, the actual ages of the speleothem layers are obtained by simply subtracting the tip age from the apparent ages (Table 4-1 and 4-2). The best test for the application of a dating method is the stratigraphic order. All the ages listed in the tables 4-1 to 4-4, increase from the tip to the base part. There are some exceptions such as in the Gupteswar stalactite (Table 4-1) ages for the PRL-1993 and PRL-1997, for the Dandak stalagmite (Table 4-2) ages for the PRL-1999 and PRL-1992 are indistinguishable. The reasons could be that, firstly, the dilution factor for the associated layers may not be same, secondly, the growth rate could have been very high so that the two dated patches are deposited within the period equivalent to the age uncertainty (~ ±130 yrs). Further details of the chronology of speleothems is discussed below separately for different caves.

Following abbreviations are used further during discussion,

GUP - Gupteswar stalactite

DAN - Dandak stalagmite

AKG - Akalagavi stalagmite

SOT - Sota stalactite.

4.1.3 Radiocarbon ages

GUP

Assuming that during the growth of the stalactite the dead carbon contribution from the bedrock strata was constant, all the radiocarbon ages (Table 4-1) are corrected by subtracting the surface age (880 ± 100 yr). Depth vs. age is presented in the Fig.4-1.



Fig. 4-1: Depth vs. ¹⁴*Cage in the Gupteswar stalactite (GUP). Actual age (dotted line) has been obtained by subtracting 880yr (tip age) from each apparent age (dark line).*

By considering constant deposition rate between two consecutive dating patches (center of the laminae analyzed), successive growth layers were assigned with equivalent ages without considering the associated uncertainties. All the ages are in the stratigraphic order except PRL-1992 (2900 \pm 130) and PRL-1999 (2920 \pm 130) which are within errors. From the ¹⁴C calibration curve (Stuiver and Becker 1998) for 2900 \pm 130 yr BP, the associated calendar age range is 2750 to 3230 yr BP. The actual age of PRL-1992 and

PRL-1999 could be between the above range. To simplify the calculation of deposition rate in this area, we have assumed all the growth layers between the two dated patches deposited in the duration of 130yr (error in the apparent ages of PRL-1992 and 1999). Ages to the subsamples taken for the stable isotope study have been assigned accordingly. The average deposition rate is 0.14mm/yr for the stalactite. Near the tip, tapered part of the some of the layers inside were missing during collection. The cave gallery in which the stalactite grew is inclined by about 45 degrees (Fig.3a, Chap. 1). Therefore, any cave material such as broken pieces of bedrock which collapses from the top of the gallery might have hit the stalactite base while slipping down. The collapsing might have occurred due to random non-climatic processes. However, as the side or flank part of the layers are intact (see tip part in Fig.3-2), subsamples were drilled from there for ¹⁴C and stable isotope analysis. This will not introduce any error as the ¹⁴C content in the tip and side part of any layer is same and also the stable isotope values do not differ significantly along a single layer (Sect. 4.2).

DAN

Fig.4-2 (depth vs apparent age) plot clearly shows deviation of the stratigraphic trend at about 20 cm depth. Considering only the recent first three ages i.e. 1310, 1640 & 1970 yr, an extrapolation line gives the surface age as 1230 yr. As discussed previously a similar approach is followed here and surface age has been subtracted from other measured ages to give corrected ages (Table 4-2) for the stalagmite. Radiocarbon ages increase in the older layers except PRL-1993 (740 yr) and PRL-1997 (710 yr) which are the same within associated uncertainties. This is possible due to a higher growth rate during the period. However, as there is no other date between hiatus and PRL-1997, ages can't be assigned assuming uniform growth rate between two dating spots (as it was done for GUP). Average growth rate estimated based on best fit line passing through first three ages (viz. 0, 410 and 740 years) is 0.18 mm/yr. Assuming this average growth rate, depth of each stable isotope subsample is converted into age. The texture of the layers observed along the growth direction shows a sudden change in the lower part due to the hiatus (depth 214mm) in the growth of the stalagmite. Also above the hiatus layer, coarse detrital



Fig. 4-2: Depth vs. ¹⁴*Cage in the Dandak stalagmite (DAN). Actual age is obtained by subtracting tip age (1230 yr) from each apparent age.*

material is present. Hiatus was initiated probably by aridity or change in the nature of flow pattern of the seepage water which after bringing detrital material might have clogged the opening. All subsampling points for stable isotope measurement beginning from the modern surface (tip) have been assigned ages assuming a uniform growth rate between two dating spots in the sample. Assuming a uniform growth rate (0.18 mm/yr) and using the age of PRL-1994 (3540yr), the beginning of the hiatus is estimated to be 3200 yr BP and this continued till 1230 yr BP. Hence, the hiatus period prevailed for about 2000 yr. This may not have a climatic significance if this is due to a change in the micro-environment.

AKG

This sample shows laminations throughout the length. These laminations seem annual (this will be discussed in the Sect. 4.3) and their total number is 331 which means the sample is 331 years old. The sample was collected in 1997 AD in active condition, therefore, the base part should be 1666 AD. As total thickness of layers (along the maximum growth direction; see Sect. 4.3.2) is 44.25 cm the growth rate is 1.34mm/yr.

RC-1 (Table 4-3 and Fig.3-2(c)) which corresponds to about 2-3mm Sample thickness of the tip part should cover compact layers between 1995 and 1997 (as growth rate is 1.34mm/yr), has bomb ¹⁴C; Δ^{14} C= 86.2 ‰. Single yearly Δ^{14} C data generated from the yearly measurements of atmospheric CO₂ activity (Fig.4-3) from tropical locations suggests that the estimated average Δ^{14} C in the soil CO₂ for the years 1995 to 1997 should be 101.7 ‰. This means that the tip layers are diluted by dead carbon contributed from the bedrock only to about 1.4%. Assuming that the dilution factor has remained constant throughout the 331 years of deposition, the estimated Δ^{14} C for the RC-2 (covering layers between 2.0 to 2.9cm; Table 4-3 and Fig.3-2(c)) is 247.7‰ which corresponds to Δ^{14} C of the atmospheric CO₂ of the year 1982 (Nydal and Lovseth 1996, Fig.4-3). At 2.0cm depth, chronology by layer counting is 1978 AD which shows that there is good agreement between the ages generated by bomb ¹⁴C measurements and counting of compact layers, considering the uncertainties involved in the radiocarbon measurements. The dilution corrected age (assuming 1.4% dilution) for the base part (RC-3, Fig.3-2(c)) is 90 ± 100 yrs. Corresponding calibrated ages at 1 sigma level are between cal AD 1668 to 1955 (Stuiver and Becker 1998). The older part of the calibrated age range (i.e. Cal AD 1668) is very close to the age of the oldest layer which is 1666 AD by layer counting. From the above discussion, it can be concluded that the compact layers are annual.

Earlier studies have shown bomb ${}^{14}C$ (by Accelerator Mass Spectrometry) distribution in stalagmites to follow the atmospheric ${}^{14}C$ distribution pattern with damped amplitude depending upon the turnover period of different soil components (Genty and Massault 1999). Dilution of ${}^{14}C$ activity by dead carbon contributed from the bedrock (dead carbon proportion) is found to vary from 9.2 to 21.9% in several laminated



Fig. 4-3: $\Delta^{14}C$ curve for the atmosphere. The data is based on ${}^{14}C$ measurements in the CO₂ by various groups (Nydal and Lovseth, 1996). See fig. for comments.

stalagmites (Genty and Massault 1997). Whereas in our case it is 1.4%. This means that the dissolution of bedrock is very close to the open system dissolution (Hendy 1971). Fast growth rate (1.34mm/yr) and dissolution very close to open system condition (1.4% dilution at the tip) suggests that the seepage water resides for less period of time in the soil bedrock zone before dripping on the stalagmite surface. In one of the stalagmite studied by Baker et al 1993, ¹⁴C age obtained at the base level of the laminated stalagmite is 210 \pm 120 yr BP (dilution corrected and uncalibrated), which is statically equal to the number of laminations (a total 198).

SOT

The procedures of the routine radiocarbon dating method are standardized to preparation and counting of 1ml of benzene. For this about 9 g of calcium carbonate is required to prepare 1ml of benzene with high chemical yield. If the subsample amount is small then age uncertainty becomes large. However, if the amount of the sample is increased by taking more stalagmite layers the age resolution becomes poor. This limits the sampling amount and the number of samples dated for each speleothem. The stalactite

from Sota cave is relatively smaller in size (Fig.3-2 (D)) and hence due to the reasons given above only two samples have been dated. The tip part shows presence of bomb ¹⁴C and the base level is dated to 1100 ± 120 yr BP.

The Sota stalactite was collected during October, 1997 (winter season) and the cave was found to be totally dry. There is bomb ¹⁴C in the tip part (Table-4-4) which proves that the stalactite is active, growth is mainly during wet periods. The cave entrance is narrow and the length of the passage is about 10 m. However, the surrounding vegetation is C3 type and the soil cover seems to be reasonably thick. Thickness of the soil plus bedrock above the cave is \sim 3-5 m. Therefore, the bedrock part seems to be very shallow. This means that the cave is very shallow and hence, during dissolution of the bedrock it is highly likely that the seepage water is well mixed with the soil CO_2 phase. In such a situation open system dissolution (Clark and Fritz 1997) takes place and we can assume that the dead carbon contribution is negligible (dilution factor $D\approx 1$ or $\ln D\approx 0$). The tip layer is assigned 0 yr BP as the conventional ¹⁴C age (precisely it is associated with the year 1996, the year of collection) and the base is assumed to be 1100 ± 120 yr BP. The total length being 24.46 cm, the estimated growth rate is 0.22mm/yr. All the layers selected for subsampling for the stable isotope (Fig.3-2 (D)) studies are assigned ages using the above growth rate. Validity of the assumption that there is negligible dilution by the bedrock (and hence $D\sim1$) is checked by the following approach.

The sample (PRL –2113, Table 4-4) covers stalactite layers up to 2.1cm from the tip surface. Average value of radiocarbon activity in the atmosphere during 1954 (initiation of artificial ¹⁴C injection in to the atmosphere, Fig.4-3) to 1996 is

 $A_{av} = (1/n) \sum Ai$

or

$$\Delta^{14}C_{av} = [\{(1/n)\sum (\Delta^{14}Ci.10^{-3}+1)\} -1].10^{-3}$$
(4-9)

where, Ai (dpm/gm) and Δ^{14} Ci (permil) are the atmospheric 14 C activity of the ith year, i = 1954 to 1997 and n = 43.

As it is assumed that there is negligible dilution by dead carbon from bedrock, hence, the same activity should be observed even in the yearly layers of the SOT. Using yearly Δ^{14} Ci data from (Nydal and Lovseth 1996), this equals to 290.6 pMC (percent modern carbon). As the average value of the δ^{13} C in this period is around -7.5% and δ^{13} C of the CO₂ aliquot used for benzene preparation is -13.9%, A_{av} in the stalactite should have been,

$A_{av} = 290.6[1-2(13.9-7.5) / 10^3] = 286.9 \%$

If it is assumed that there is no dilution by bedrock and the same atmospheric activity level is introduced in the speleothem layers then in order to get $\Delta^{14}C = 176.9 \pm 14.6 \%$ or $117.7 \pm 1.5 \%$ pMC in the dated sample, there should be contribution from additional layers older than 1954 which have 100pMC and will dilute the average activity from 290.6pMC to 117.7 pMC. The estimated number of additional years required are 28. Therefore, it can be stated that the first 2.1cm of the tip part was deposited in the past 71 years. With this estimate of the growth rate, the base part (24.46cm) should have been deposited before 827 years. At two sigma levels of error, $\Delta^{14}C = 176.9 - 2 \times 14.6 = 133.1 \%$ and to get this value a total of last 93 years of deposition is required. This estimate results in to the base age as 1083 years which agrees well with the measured ¹⁴C age (i.e. 1100 ± 120). In the above approach the estimation of duration to form the tip part satisfies the base age, therefore, the assumption that D=1 (i.e. no dilution) is validated.

4.2 Speleothems from Gupteswar and Dandak caves

As the two caves GUP and DAN are very close (~30 km from each other, Yadava and Ramesh 1999a) their results will be discussed together. For the AKG and SOT the discussion will be presented in Sect. 4.3 and 4.4 respectively.

GUP

Gupteswar cave (18°45'N, 82°10'S) is located on the bank of river Kolab in the southwest Orissa (Fig.4-4). The cave is located at 457 to 518 m above m.s.l. and is a part of the



western foothills of northeast-southwest trending hill ranges. A stalactite hanging in the passage at about 100 m distance from the cave entrance was collected from this cave in the month of February 1996 (Fig.4-4). During collection the inside temperature was 20°C and relative humidity was recorded as 66%. The length of the stalactite was 36 cm and in the middle part the diameter was 16 cm. A total of 233 stable isotope measurements were carried out on the Gupteswar stalactite (shown by dots in the Fig.3-2(A)). Four laminae representing the sample growth were taken to test for isotopic equilibrium deposition Fig.4-5 (discussed later). δ^{18} O and δ^{13} C relative to PDB are shown in Fig.4-6 as a function of depth. The average fluctuation observed from the modern value is about 1.5‰ for δ^{18} O and 3.5‰ for δ^{13} C.



Fig.4-5 (A, B, C & D): $\delta^{18}O$ and $\delta^{13}C$ (relative to PDB) vs. depth and $\delta^{18}O$ vs. $\delta^{13}C$ for four layers (positions shown in the Fig 3-2(A)) selected to test isotopic equilibrium condition during stalactite (GUP) growth in the Gupteswar cave.



Fig. 4-6: $\delta^{18}O$ and $\delta^{13}C$ (relative to PDB) vs. depth for measurements along the growth direction for the GUP. Boxes show corrected radiocarbon ages.

DAN

Dandak cave (19°00'N, 82°00'S) which is located at about 30 km from Gupteswar, is in the Kanger Ghati National Park to the west of the Gupteswar cave. The altitude of this forest area is between 261 to 604 m. These caves are within 30 km distance from Jagdalpur. Based on meteorological observations between 1931 and 1960 (Climatological Tables 1960), the annual average rainfall for the Jagdalpur is about 1534 mm and the mean annual temperature 25° C. The important rock types in the area covering both the caves are purple shale, quartzite and limestone. The limestone is found to be light gray and cream colored and varies in thickness from 3 m to 6 m (GSI, Publication No.30,1974).

A stalagmite was collected from Dandak cave in the February 1996, at a distance of about 220 m from the cave mouth (Fig.1-6(A)). The temperature at the sample location was 27°C and relative humidity was 92%. The stalagmite was about 28 cm long and the diameter was about 9 cm.

For stable isotope measurement 117 subsamples were prepared from the Dandak stalagmite. Three representative layers were taken for test to isotopic equilibrium deposition (discussed later) and δ^{13} C, δ^{18} O values relative to PDB are shown in Fig.4-7.

 δ^{18} O and δ^{13} C as a function of depth is shown in Fig.4-8. About 1‰ variation in δ^{18} O and up to about 4‰ in δ^{13} C relative to modern value are observed in the stalagmite.

Stable oxygen isotopes in speleothems

a) Effect of cave temperature

In deeper parts of a cave the growth of a speleothem is in isotopic equilibrium i.e. the degassing of CO₂ is very slow so that ionic species in the dripping water have enough time for exchange of isotopes to attain isotopic equilibrium before calcite precipitation. In such a situation if temperature inside the cave increases, then less of ¹⁸O gets incorporated into the precipitated calcite. From experiments with inorganically precipitated carbonates (O'Neil et al 1969) the changes in δ^{18} O of calcite has been found to be -0.21‰/°C at 25 °C, -0.22‰/ °C at 20 °C and -0.24‰ at 10 °C. In most of the deep caves, the inside temperature is the annual average of the ambient temperature at the site. Hence, using δ^{18} O of growth layers palaeo-temperature reconstruction of the cave site is possible (Lauritzen 1995; Gascoyne 1992; Schwarcz 1986). The speleothem sample collected is first checked for isotopic equilibrium, indicated by 1) same values of δ^{18} O along a single layer (an enrichment indicates precipitation due to evaporation of water, 2) there is no correlation between $\delta^{18}O$ and $\delta^{13}C$; (otherwise it is an indication of fast CO₂ degassing and hence kinetic fractionation (Hendy 1971; Gascoyne 1992). The plot of $\delta^{18}O_c$ and $\delta^{13}C_c$ vs. layer depth and $\delta^{18}O_c$ vs $\delta^{13}C_c$ shows no linear correlation for either Gupteswar (Fig.4-5) or Dandak cave (Fig.4-7). This proves that during the growth of calcite layers cave humidity was very high and, the degassing rate of CO₂ from the dripping water was quite slow leading to isotopic equilibrium deposition. If speleothem is pure aragonite type then the absolute value of $\delta^{18}O_c$ is enriched by 0.6‰ at 25°C (Tarutani et al 1969), however, the temperature coefficient ($d\delta^{18}O_c/dT$) remains indistinguishable from the values obtained for the calcite (Faure 1991).



layer1



Fig.4-7 (A, B & C): $\delta^{18}O$ and $\delta^{13}C$ (relative to PDB) vs. depth and $\delta^{18}O$ vs. $\delta^{13}C$ for three layers (positions shown in the Fig. 3-1(c)) selected to test isotopic equilibrium condition during stalagmite (DAN) growth in the Dandak cave.



Fig. 4-8: $\delta^{18}O$ and $\delta^{13}C$ (relative to PDB) vs. depth for measurements along the growth direction for the DAN. Boxes show corrected radiocarbon ages.

b) Factors affecting the oxygen isotopic composition of cave drip water

The isotopic composition of the cave drip water $\delta^{18}O_w$ is a function of (1) temperature at the cave site as the $\delta^{18}O$ of rainfall is found to be temperature dependent (Dansgard 1964; Yurtsewar and Gat 1981; Fricke and O'Neil 1999) and is about 0.7%o/°C for subtropical and high latitude regions. This is based on worldwide data on modern rain water collected from sites at different temperatures. However, in tropical locations, the temperature dependence is mostly absent; in such cases $\delta^{18}O_w$ depends on the amount of rainfall (amount effect, Dansgaard 1964) (2) the geographical position; the altitude and latitude effects on the precipitation vary from place to place and (3) time; the ice-volume effect contributed 1.2‰ to 1.8‰ during glacial to interglacial periods in past (Harmon and Thomson 1978; Gascoyne 1992; Lauritzen 1995).

The overall temperature dependence of $\delta^{18}O_c$ at a cave site in equation (4-12) is a positive , zero or negative function depending upon the $\delta^{18}O_w$ and its T-derivative (given

by equation 1-11). In most of the cases $\delta^{18}O_w$ is not known and $\delta^{18}O_c$ is used as relative indicator of temperature variations (Lauritzen 1995).

c) Climatic effects on cave deposits in tropical and mid latitudes

 $\delta^{18}O_c$ is related to temperature as described in equation (1-10) due to temperature dependent fractionation (α_{c-w} ; about $\delta^{18}O_c/dT \approx -0.21$ % o/ °C at 25°C, O'Neil et al, 1969) and dependence of $\delta^{18}O_w$ on condensation temperature which is 0.5 to 0.9% / C between 40° N to 60° N (Rozanski et al 1993). Temperature- δ^{18} O relationship is empirically known for the high latitudes and can be used in some cases to retrieve the past temperature variations. For mid latitude and semiarid climatic zones $\delta^{18}O_w$ decreases with increasing rain amount (Dansgaard 1964; Bar-Matthews et al 1996; Bar-Matthews and Ayalon 1997; Fricke and O'Neil 1999). In tropical locations any obvious temperature correlation is not observed for the modern rainfall (Dansgaard 1964; Yurtsever and Gat 1981; Bar-Matthews and Ayalon 1997; Fricke and O'Neil 1999). The $\delta^{18}O_w$ is rather dependent on the amount of rainfall. In tropics it is found that δ^{18} O content of precipitation is related to the amount of rainfall (Yurtesever and Gat 1981). More rainfall is associated with less of ¹⁸O content in the precipitation. In tropics $d\delta^{18}O/dP = -1.5\%/100$ mm, where P is the monthly precipitation in mm (discussed in Sect. 4.2 and 4.6.2). Hence, in tropical caves the δ^{18} O of freshly deposited calcite layers on a growing speleothem is depleted with increasing precipitation and temperature. Usually, the ambient temperature of a cave is the mean annual surface air temperature and hence $\delta^{18}O$ of the speleothem layers are a proxy for the past variations of δ^{18} O of meteoric water and thus of mean annual surface air temperature in high latitudes. In mid latitude and tropical caves the $\delta^{18}O_c$ will be depleted with increase in temperature and precipitation.

Past variations in $\delta^{18}O$ and $\delta^{13}C$

A combined plot of $\delta^{18}O_c$ and $\delta^{13}C_c$ vs age for Gupteswar and Dandak cave is shown in Fig.4-9. For the recent 1200 year period $\delta^{18}O$ in both caves show concordant variations (any apparent discordance is mainly due to the different sampling resolutions in the two samples). This is expected as the two caves are within 30 km distance and hence



Fig. 4-9: A combined plot of $\delta^{18}O$ and $\delta^{13}C$ (relative to PDB) vs. age for GUP (black line) and DAN (red line). From the present time to ~1200 yr BP there is a good similarity in the $\delta^{18}O$. $\delta^{13}C$ variations are similar only between 1200 to 600 yr BP. Beyond 3200 yr BP both records differ significantly.

changes in surface air temperature or isotopic composition in the precipitation above the caves should have affected both the caves in a similar way.

If the changes in $\delta^{18}O_{c}$, which are up to 1.5‰ for Gupteswar and 1% for Dandak excluding few high amplitude sharp peaks (about 2.5‰), are considered to reflect only fluctuations in the past temperature then the estimate (fractionation in the precipitated calcite due merely to temperature changes is -0.21‰ /°C at 25°C) for the amplitude of variation would be about 7°C. The $\delta^{18}O_c$ variations in these speleothems are quite high and are unlike the high latitude speleothem deposits (Talma and Vogel 1992; Dorale et al 1992) where such large changes are not observed. As during past 3400 yr period temperature fluctuations of more than 1°C are highly unlikely, (including the recent historical period,

Mann et al 1998), the varying δ^{18} O of past precipitation should have been by and large responsible for the variations in calcite δ^{18} O_c.

4.2.1 Rainfall reconstruction

Amount Effect in rainfall

From the data on the modern precipitation collected from sites in mid to high latitude regions at different temperatures, it is observed that mean annual temperature and oxygen isotope composition (amount weighted) show correlation, whereby higher temperature corresponds to higher $\delta^{18}O$ values (Dansgaard 1964; Yurtsever and Gat 1981; Rozanski et al 1993). Such correlations have been applied to speleothem $\delta^{18}O$ to reconstruct past temperature conditions. In tropical regions such correlations are not observed (Dansgard 1964; Yurtsever and Gat 1981). However, a negative correlation between δ^{18} O of precipitation and amount of rainfall is observed in tropics which is termed as the "amount effect" (Dansgaard 1964). The effect is manifestation of gradual saturation of air masses below the cloud base as rainout continues and also, due to preferential removal of ¹⁸O as rainout continues. Initially, the air mass is undersaturated and this leads to evaporations of water droplets and consequently they are enriched in $\delta^{18}O$. As precipitation proceeds air masses become saturated and in turn the enrichment due to evaporation gradually diminishes (Dansgaard 1964; Rozanski et al 1993; Fricke and O'Neil 1999).

Word wide modern precipitation data available from island stations in the equatorial belt (collected by IAEA) have shown a linear relationship (Yurtsever and Gat 1981) between the mean monthly $\delta^{18}O_m$ of precipitation and the mean monthly rainfall (Fig.4-10),

$$\delta^{18}O_m = (-0.015 \pm 0.002)^*P_m - (0.47 \pm 0.42)$$
 (4-10)

where, P_m is mean monthly rainfall in mm, with r=0.874 for 14 island stations (each has at least 40 monthly observations). As these stations are near the equator, seasonal temperature variations are small. Average rate of depletion is found to b e -1.5 ± 0.2 ‰ for a 100mm increase in the mean monthly rainfall.



 $\delta^{18}O = -(0.015 \pm 0.002) P - (0.47 \pm 0.42)$

AVERAGE MONTHLY RAINFALL AMOUNT (mm)

Fig. 4-10: $\delta^{18}O$ vs. monthly rainfall observed for the island stations in the equatorial zone. There is an amount effect whereby $\delta^{18}O$ depletes by 1.5‰ with an increase of 100m in the monthly rainfall (source: IAEA Technical Report Series 210, 1981).

Meteorological data from Jagdalpur district for the period 1931 to 1960 show that the average *monthly* rainfall during wet season (June to October) is 270.4 mm (Climatological Tables 1960). Average annual rainfall is recorded as 1534.1 mm. A ratio of average annual and monthly rainfall during the monsoon season is 5.7 (1534.1/270.4). This has been used to get a relation between amount of annual rainfall (Pa, mm) and the δ^{18} O of speleothem carbonate,

Pa =
$$(100/1.5)^* 5.7^* (\delta^{18} \text{Otip} - \delta^{18} \text{Oi}) + 1534.1$$

or
Pa = $380.0^* (\delta^{18} \text{Otip} - \delta^{18} \text{Oi}) + 1534.1$ (4-11)

Where, δ^{18} Oi and δ^{18} Otip are the oxygen isotope composition of the speleothem carbonate with depth and at the tip, respectively.

Using above equation we have reconstructed annual rainfall (Fig.4-11) of the area GUP/DAN area with the assumption that all the variation in calcite δ^{18} O is due only to



Fig. 4-11: Rain reconstruction from the GUP for the last 3400 yr period. $\delta^{18}O$ is converted in to rainfall by using equation (4-14). Rain reconstruction from DAN is very similar with GUP. For comparison, $\delta^{13}C$ values are also shown. Maximum reduction in the rainfall amplitude due to corrections required by the mixture of aragonite and calcite is given by black rectangle (see text in Sect. 4.8).

changes in the δ^{18} O of dripping water. About 500mm/yr (33%) average variation relative to modern value (1534mm/yr) is observed in the reconstruction during the 3400 yr period. Several periods with sharp changes in precipitation are observed. If the variation in the past temperature for the last 3400 yr is assumed to be within 1°C then the average rainfall fluctuation will be still up to 22%. Based on the radiocarbon ages, the layers in the subsamples in GUP average about 14 yr period with a resolution of about 40 yr between modern to approx. 2900yr. From 3000 yr to the base of the deposit i.e. ca. 3400 yr, layers in the subsamples average about 3yr period while the sampling resolution is about 11 yr.

There is a higher growth rate in the GUP between 2900 to 3000 yr period as observed from the increased density of data points. But, a contradiction arises as during this period the mean $\delta^{18}O_c$ has shifted by +1% and $\delta^{13}C$ simultaneously shows a 4‰ enrichment (Fig.4-9) which means a low precipitation regime and hence a slower growth of the stalactite. It is speculated that the low precipitation event recorded both by $\delta^{18}O_c$ and $\delta^{13}C_c$ is genuine. The increased residence time of the seepage water because of less rainfall might enhance the exchange of soil CO₂ (relative molar proportion of water being less) which will apparently reduce the dead carbon content in the seepage water before calcite is precipitated. Hence, at this point because of low precipitation and hence increased residence time of water the ages are underestimated. The real age of PRL-1992 should have been older.

The period between 3400 to 3000 yr is characterized with rainfall more than or comparable with present day values. This led to favorable conditions for the increase in C₃ type vegetation as shown by the depletion in the δ^{13} C trend. The depletion trend could also be due to higher mean drip rate. Between 2900 -1200yr rainfall was comparatively lower with several short dry and wet phases. There are two extremely low rainfall events recorded at 2020 and 1730 B.P. As subsamples at these points cover about 14 yr period, these may indicate aridity for a short duration. The associated δ^{13} C values are also higher, indicating either increased C4 abundance or reduction in the average drip rate. The associated errors in the equation (4-11) and analytical errors in the measurement contribute ~15% uncertainty in the reconstructed rainfall amount.

As both δ^{18} O and δ^{13} C do not co-vary, this means that the age estimates in both the speleothems may not be correct in the 3200-3400 yr BP period. This is because we have assumed that for all past periods dead carbon proportion to be same as observed at the tip part. This may not be valid during this period of time.

4.2.2 Comparison with other palaeoclimatic results

Palaeomonsoon variability has been documented from marine cores earlier (Sect. 2.1.2). A sharp change in vegetation was observed in the west coast of India at ca. 3500 B.P. indicating less humidity and it continued till ca 2200 yr B.P. (Caratini et al 1994). Weakening of monsoon was also observed based on fluxes of total planktonic foraminiferal shells and *Globigerina bulloides* (Naidu 1996), from the western Arabian sea at ca. 5000 B.P., which continued till ca 1000 B.P. An arid phase is observed in Southern India between 6000 to 3500 B.P. with a short humid phase and around 600 yr ago (Sukumar et al 1993). More recent work on peat samples (Geeta Rajagopalan et al 1997) shows an arid phase during 2000-5000 BP. Compared to the above available climatic data, time resolution in the present study is higher and hence only coarse trends in the published climatic reconstructions changes can be compared.

As our record up to ca. 1200 B.P. shows a good concordance between the isotopic compositions of the two caves, this implies that radiocarbon dating and rainfall reconstruction are a valid outcome of our study. Within this period the beginning of humid phase starts at ca 1000 B.P. and attains a maximum between 500 -750 B.P. There is a trend towards aridity reaching the peak value around 125 B.P., which considering the dating uncertainty (\pm 90yrs), coincides with the drought events recorded in the beginning of the 1900 A.D. (Singh et al 1991).

There is a striking difference in the isotopic composition of the two caves in the initial part of the speleothem growth. The Dandak sample shows an arid phase between ca 3700 to 3200 B.P., which agrees with the other palaeoclimatic results. While the Gupteswar sample shows higher rainfall between ca 3400 to 3000 B.P. in contrast to other observations. It seems at this stage that the constant dead carbon assumption is invalid in this part of the speleothem. The concordance of variations in the stable isotopic compositions from both caves breaks down beyond 3200 B.P. The δ^{18} O and δ^{13} C values of the Dandak sample indicate reduced precipitation whereas the Gupteswar stalactite points to enhanced rainfall. At this stage we feel that the assumption of constant dead carbon contribution may not be valid for the older growth layers in these cave deposits and hence due to different real ages the problem of concordance arises beyond 3200 BP

4.3 Caves in the Uttar Kannada District of Karnataka

Several Karst formations are known to exist in the Uttar Kannada District of Karnataka (Fig.4-12). In 1997, we conducted a field expedition in this district to explore caves and their suitability for palaeoclimate studies. Karst topography is widespread in the Yana village of Kumta Taluk, mainly consisting of barren bedrocks in the dense forest,



Fig: 4-12: Map showing the location of the Akalagavi cave in the Ulvi village, Karnataka.

looking like stalactites. However, we did not find any speleothem deposit as described by Radhakrishna (1996). Precipitated silica stalactites of 2-3 cm size are seen in the cave 'Bavalihakki' in the Yellapur Taluk. Another cave 'Halesidda' in the Wadehakli village is about 20ft in length and has huge columnar stalactite and stalagmite deposits but are unsuitable for palaeoclimate studies as there is a wide opening of the mouth area. Due to this fact evaporation of drip water is always expected which might have modified the environmental signals registered by the oxygen isotopes in an unpredictable manner. In the Kavala cave in the Halyal Taluk there are many good stalagmite deposits but it's collection is not allowed as they are all part of a temple premises.

4.3.1 Stalagmite from Akalagavi cave

In the Ulvi village of the Joida Taluk , none of the small caves viz. Akkanagamma, Vibhutikanaja, Panchalingheswara had suitable speleothems. However, in the same village we found an actively growing stalagmite in another cave 'Akalagavi' in a small narrow chamber (Fig.1-9 (A,B &C)). The sample was collected by applying light hammering at the base in April, 1997. This month being summer and hence

rains are only due to local convection. During sample collection the relative humidity and temperature recorded were respectively 64% and 29.3°C.

Using a diamond cutter stalagmite was cut along the length to get a 1cm thick slice from the central part and two other remaining pieces. Distinct layers are seen on the surface of these different sections (Fig.3-2(c)). Under a microscope, sequences of two types of layers (a couplet) are seen: one compact layer and another coarse layer. These layers are very clearly seen throughout the sample. The coarse layers are having needle like structures and the pores are filled with fine brownish detrital particles due to this the coarse layers appear dark compared to the compact ones. As seen in Fig.3-2(c) the growth direction had changed with time.

4.3.2 Thickness measurements

One of the half sections was polished further and thickness (or width) of each compact layer was measured under a travelling microscope, used for tree-ring width measurements at IITM (Indian Institute of Tropical Meteorology, Pune). The results are presented in Fig.4-13. The microscope had a magnification of 5 to 20 and a linear movement platform with a resolution of 0.01cm (0.001mm).

During collection, the speleothem fell down breaking into two half pieces. A few layers just below the tip part were also lost. Missing layers were estimated to be three based on their remaining flank part. However, the tip layer associated with the year of collection (April, 1997) is preserved as confirmed from the continuity of the outermost

surface and the texture. Total number of couplets (including 3 layers estimated for the missing part near the tip) counted under the microscope are 331. As all the distinct compact layers, some of which are very thin were counted, the error in the total number of





Fig. 4-13: (A) Thickness of each couplet in the AKG. Rainfall data from the nearest meteorological station, Karwar is shown on top. (B) The same curve expanded for the period 1960 to 1997.

layers is assumed to be zero. However, at the places where the layers are very thin or dust content is very low; some of the layers diffuse in to each other and at such places: judgement ability of the observer is involved which may introduce an error of a few layers (a total of 7 yrs. only).

As the tip layer which is coarse corresponds to 1997 it means that the first compact layer is associated with the year 1996 and the oldest compact layer (331st) should represent 1666 AD. Along the maximum growth direction total length of the sample is 44.25cm (vertical height is 42.5cm, Fig.3-2 (C)) for the 331 couplet of compact and coarse layers. As each layer corresponds to a single year, the average growth rate is estimated to be 1.34mm/yr.

Thickness of each layer is not uniform all along. It is maximum at the point of dripping. In an ideal case when drip spot on the roof doesn't change with time then maximum growth occurs in the vertical direction.

In the Akalagavi stalagmite, however, the maximum growth point varies along the length (Fig.3-2(C)). Orientation and nature of growth layer in all the sectional pieces of the stalagmite indicates that the drip position has varied in past by about 2-3 cm around the tip.

Inspection under microscope reveals that major changes in the drip position occurred at layers marked by numbers 4/5 (4 and 5 stand for the same layer but at different points as shown in the Fig.3-2(C)), 6/7, 8/9 and 10/11 are always associated with dark layers. The sequence of layer formation observed under microscope are as follows.

- Growth started at point '1' at 1666 AD. Laminations are added continuously without any break with a tendency of growth direction towards right (in the cross sectional view of Fig.3-2(C)).
- '2' shows boundary of the two broken half pieces.
- It continues up to '3' after which there is a little tilting towards left and then continues further up to '4'.
- Growth in vertical direction stops and then next layer forms on the side part of the layer marked by '4' at '5'.

Prior to '4' several layers are seen which are filled with detrital particles.

- The growth initiated at '5' continued up to '6'.
- Next growth starts at '7' and continues up to '8'. However, in the other sections i.e. 1cm slice, , the drip position at '6' doesn't change much which means that there was

shifting of the drip position in the radial directions (i.e. perpendicular to the plane of the speleothem sections). There are very thin layers observed in the segment '7-8'. Some of the thin layers which may indicate low drip rates are not dark colored.

- Next layer is added at '9' and continues up to '10'.
- Drip position changes to '11' and then it continues up to '12' which corresponds to the year of collection. The tip surface is coarse which supports that only during non-monsoon seasons coarse layers are formed.

For the ease in discussing the data all the growth layers are grouped in the following segments : 1-2, 2-3, 3-4/5, 4/5 - 6/7, 6/7 - 8/9, 8/9-10/11, 10/11-12 (Fig.3-2(c)).

It is assumed that there was no hiatus in the layer formation. This is validated because of following reasons. Unless rain amount is very low or flow pathways in the unsaturated zone (just below the soil layers) is changed, hiatus is not expected to occur. Also, in none of the years rainfall recorded by the nearest meteorological stations (e.g. Fig.4-13) is zero or extremely low. This means that layer formation had never stopped.

Thickness data and actual rainfall available from meteorological station at Karwar is shown in Fig.4-13 (A & B). Following are the observations.

- 1) Thickness data and actual rain occurred in the Karwar agree very well for period between 1992 to 1996 and for the year 1970.
- 2) for other periods the variations differ.

As seen in the thickness data (Fig.4-13) not all the thickness levels correlate very well with the Karwar rainfall data. This could be due to two reasons firstly width may not be purely proportional (Dreybrodt 1999) to the actual rain or actual rain occurred in the cave area had been different from what occurred in the Karwar due to spatial variations. The distance between Karwar and cave site (Ulvi) is about 50km, but the Karwar station is located in the coastal area. Whereas the cave site is located in the hilly area of Western Ghats. These could be the reasons for less similarity of the width and the Karwar rain data.

4.3.3 $\delta^{18}O$ and $\delta^{13}C$ variations in AKG

As shown in Fig.4-14 there is very poor correlation between $\delta^{13}C$ and $\delta^{18}O$ and also there is no significant enrichment in $\delta^{18}O$ along layers B and C. This proves that there was no water evaporation and deposition of carbonate was very slow process



Fig. 4-14: $\delta^{18}O$ and $\delta^{13}C$ vs. depth and $\delta^{18}O$ vs. $\delta^{13}C$ for the two layers selected for the isotopic equilibrium test.

(deposition under isotopic equilibrium condition). However, during sample collection observed R. H. was 64%; this indicates that major growth occurred during monsoon when relative humidity inside a cave is generally very high (close to 100%). Using $\delta^{18}O$ and $\delta^{13}C$ of such samples, past cave climate can be reconstructed (Hendy 1971). Along the flanks the thickness of the layers are either very small or simply disappear. Also, there are large yearly fluctuations in the $\delta^{13}C$ values. Due to this there are always chances that the sampling is done on some other neighboring layers which have quite different delta values and hence for layer B (Fig.3-2(c)) there are large changes in the $\delta^{13}C$ and $\delta^{18}O$ values after a distance of ~3cm which is generally length of most of the growth layers.

Stable isotope data obtained is presented in the Fig.4-15. The chronology is based on counting of each annual layer and assigning ages to the stable isotope sampling spots.

Fast changes in the δ^{13} C values with an order of 1yr can't be triggered due to changes in C3 or C4 vegetation as switching to C3 or C4 takes place after several years depending upon the turnover time and kind of the vegetation system (Claussen et al 1999; Genty and Massault 1999). A high correlation (r=0.6) between δ^{13} C and δ^{18} O is an indirect evidence that Rayleigh type calcite precipitation plays important role in deciding the δ^{13} C of the tropical speleothems, and the dripping rate of the seepage water is affecting the short (yearly) fluctuation in the δ^{13} C. Long term (more than years) fluctuations are controlled; 1) by soil components having different residence times (Genty and Massault 1999); 2) by climate changes affecting C3/C4 ratios.

4.3.4 Rainfall reconstruction from AKG

Nearest meteorological station (to the Akalagavi cave site) is Karwar (Fig.4-12). Annual rain in 1997 (the year of AKG collection) was 3257.2mm. Wet season in the cave area is between June to October. The ratio of annual rainfall to the average monthly rainfall during wet season is 5.3 (Climatological Tables 1970). Hence, rainfall equation can be written as,

Pa =
$$(100/1.5)$$
* 5.3* $(\delta^{18}$ Otip - δ^{18} Oi) + 3257.2
or

 $Pa = 353.3*(\delta^{18}Otip - \delta^{18}Oti) + 3257.2$ (4-12)

Where, δ^{18} Oi and δ^{18} Otip are the oxygen isotope composition of the calcite with depth and at the tip respectively. Using the above equation oxygen isotope composition is converted in to rainfall variations and is presented in the Fig.4-15.

Southwest monsoon (summer monsoon) during June to September accounts for most of the rainfall (70-90%) over India. Northeast monsoon (winter monsoon) during months of October to December affects mainly states of Indian peninsula (Tamil Nadu and Kerala). Based on meteorological data available from area weighted average of 306 stations, all-India summer monsoon rainfall time series is available from 1871 to 1995 (Pant and Rupa kumar 1997 and references therein). Summer monsoon rainfall is found to



Fig. 4-15: $\delta^{18}O$ vs. age for the AKG. Rainfall reconstruction from AKG is obtained by converting the $\delta^{18}O$ in to appropriate rain amount using global depletion rate (eqn. 4-12). Rainfall scale is shown in the right side. Years labeled in the curve are the excess rainfall (depleted $\delta^{18}O$ values) and deficient rainfall (enriched $\delta^{18}O$ values) years observed in the all India rainfall data based on instrumental data. Beyond instrumental record such years are identified as ER and DR.

be trendless (over a period of 100 years or more) and is random in nature over a long period of time on all India scale (Mooley and Parthasarathy 1984), but, it is dominated by inter annual variability. The inter annual variability is generally caused by changes in the slowly varying boundary conditions of sea surface temperature, soil moisture and snow cover over the land surface. It has been found that there is close association between the ENSO phenomenon and summer monsoon. Majority of the El-Niño events (warm phase of ENSO) are associated with drought years over India. While the La-Niña events (cold Phase of ENSO) are associated with flood years, though this relationship might have broken down in the recent years.

Rainfall reconstruction for the period 1997 to 1870 AD

The Akalagavi is a very shallow cave. This means that there is no big water reserves above and hence the residence time of the water should be very less, probably less than a month. In such a case the mixing of older water is expected to be negligible and the original amount-dependent oxygen isotopic signature of the rain water will be recorded in

the yearly laminations. Using the global depletion rate (-1.5%) per 100 mm monthly rain) we have reconstructed annual rainfall offset (Fig.4-15) of the cave area assuming that the annual rainfall of the cave area in the year 1997 is the same as for the Karwar station which is 3257mm. As the total measurement made for stable isotopes is 301 and there are 331 layers it shows that the sampling/data resolution is ~ 1.1 year. Many of the severely deficient rain fall events which occurred around years 1979, 1982, 1928, 1918, 1920, 1905, 1899 and 1877, 1854 and 1815 (Pant and Rupa Kumar 1997) observed in the all India deficient rainfall time series are also seen in the rainfall reconstruction from AKG. Deficient rainfall signal which occurred in 1987 is not shown in the reconstruction and is probably due to the missing layers, which coincide during this period. Some of the excess rainfall years such as years 1988, 1975, 1961, 1956, 1953, 1925, 1917, 1910 and 1892 (Pant and Rupa Kumar 1997) are also seen in the AKG reconstruction. Hence, most of the prominent excess and deficient rainfall signals recorded by meteorological observations are seen in the AKG rainfall reconstruction. As observed by Krishnan (1984) that there is an increasing trend in the annual rainfall over coastal and north-interior Karnataka during 1901-75 is also shown by AKG rainfall reconstruction (Fig.4-15). Dry epochal period between 1901-30 in the epochal patterns of all India summer rainfall is very well shown as low layer thickness and also enriched δ^{18} O during 1890 to 1930 Fig.4-15. Similarly, wet epoch 1931-60 is very well shown by in AKG reconstruction. The dry epoch 1961-90 is marked by persistent deficient rainfall conditions in our reconstruction. However, not all the deficient or excess (moderate level) rainfall events shown by all India rainfall time series are registered in the Akalagavi stalagmite. The reasons could be due to large spatial variability in the rainfall. There are occasions when some part of the country receives excess rain where as other part has serious deficient conditions. Rainfall comparison for two stations in Karnataka, at Chikamagalur (at a distance of ~240km from the cave site; Fig.4-12) and Karwar (~ 50km from the cave site; Fig.4-12) are shown in the Fig.4-16. There is poor correlation coefficient (r=0.167). As the distance between Chikamagalur and Karwar is also ~ 240 km, spatial monsoon variations is the obvious reason for the poor correlation coefficient.


Fig. 4-16: Modern rainfall data from two stations Karwar and Chikmagalur. There is poor correlation (r=0.167) between yearly values.

Rainfall before 1870

- Before 1970 only fewer meteorological stations existed (which covers period from 1813), based on adequate representative index, rainfall data series has been extended up to 1813 (Sontakke et al 1992; Pant and Rupa Kumar 1997). In the 1813-1994 data series, around 1815 there is a severe deficient rainfall year which is shown in the AKG reconstruction.
- Low rainfall events shown at 27.2 cm and 28.9cm depth (i.e. DR7 and DR8 in the Fig.4-15) may coincide with the historically recorded devastating droughts during 1777 and 1796. Other events such as DR1 to DR6 (Fig.4-15) should indicate the major deficient years.
- At 28.5cm , 42.9cm and at the base at 44.5cm (marked by ER4, ER3, ER2 and ER1 respectively, in the Fig.4-15) the major excess rainfall conditions are recorded. Excess rainfall at 44.5cm (1666 AD by layer counting) is also shown by maximum depleted δ¹⁸O levels. Probably, the stalagmite growth originated during high rainfall conditions.

 Peculiar feature of the rainfall reconstruction is that none of the deficient rainfall events observed before 1772 are comparable in magnitude to the deficient years that occurred around 1900. However, average rainfall conditions before 1927 has remained lower than the rainfall during 1927 –97.

Most of the extreme rainfall events (deficient or excess) from 1870 till today in the all–India rainfall data, is shown in the stalagmite-based rainfall reconstruction and hence, it is quite possible that extreme events shown by ER1 to ER4 and DR1 to DR8 are applicable on all-India scale.

4.3.5 Gray level measurements from AKG

Gray level was examined to understand any relationship between detrital content and the past rainfall. The gray level variation along the growth direction in AKG is shown in Fig.4-17(A). The range of variations in the gray levels vary between 14 (for very dark layer) and 255 (for very bright layer). The image analysis program shows '>256' level for a pure white background. Each measurement number is approximately equivalent to 0.3mm distance. This means that gray level measurement has a resolution of less than a year (assuming a growth rate of 1.34mm/yr).

A possible explanation for the occurrence of coarse layers is as follows. Along with the seeping water fine detrital particles, either derived from soil zone or from bedrock fissures, are carried to the dripping spot. These detrital particles fall on the tip of a stalagmite, and are trapped in the growing carbonate layers, provided they remain on the growing surface for sufficient time. When drip rate is high during monsoon seasons, before these are trapped they are removed by the splashing of next drip. This plausible mechanism is probably responsible for the seasonal contrast. During rainy season when the drip rate is quite high most of the detrital particles are removed from the growing surface and hence the compact (whitish or high gray level) carbonate layer is formed. When there is non-monsoonal seasons not all the detrital particles are removed and some of them are trapped. Between these trapped particles, CaCO₃ precipitation continues, forming needle like coarse structures (as shown in the Fig.4-18). Genty and Quinif (1996) have argued that annual



Fig. 4-17: (A) Gray level (B) $\delta^{13}C$, (C) $\delta^{18}O$ and (D) width record for the AKG measured along the growth direction.

variations of dripping flow rate and super-saturation which is due to seasonality in the seepage water may produce degree of crystalline coalescence and thus forming compact vs. porous layers. Such argument in this case, however, does not explain annual variations in the detrital content.



Fig. 4-18: Photo showing the nature of laminations. The compact layer is associated with the coarse layer filled with clay particles in the voids shown in the photograph.

As the detrital particles are filled, layers appear dark resulting in to low gray levels or low pixel values. Horizontal inclination of the growth layers may also affect the trapping of detrital particles. In a flat or horizontal layer chances of trapping detrital particles are more compared to tilted layers. In an ideal case when growth direction doesn't change, the pixel values or gray levels can be used as a parameter for the water availability in the bedrock zone and indirectly as an indicator of the past rainfall conditions.

Gray level and δ^{18} O comparison

Gray level and δ^{18} O data comparison in Fig.4-17. shows following observations.

• Between segment '1' and '2' (numbers shown in Fig.4-17(D) and Fig.3-2(C)) initial trends of enrichment in δ^{18} O and lowering of pixel values are very similar. But a

plateau like saturation in gray level data (near measurement no. 800) is not seen in the δ^{18} O profile.

- Between '2' to '3' variations are quite similar. Number of peaks in gray level and δ^{18} O data are nearly the same.
- Between '6/7' and '8/9': gray levels show variations very similar to δ^{18} O data.
- Between 8/9 to 10/11: Gray level values don't change much like δ^{18} O in this segment.
- Between 10/11 to tip part: An enriched δ^{13} O and δ^{13} C spike which occurred at 1.55 to 1.70 cm depth is associated with low gray levels.

The conclusion of this comparison is that the gray levels follow trends of variation in δ^{18} O in some of the segments. Higher gray levels correspond to depleted δ^{18} O or higher rainfall. Hence, there is possibility of using gray levels as a crude indicator of the past rainfall. Very low pixel values in each section could be due to very low rainfall events whereby fine detrital particles are trapped in the coarse layers.

At major drip position changes such as '3','4/5','6/7','8/9' and '10/11', the gray level is low and δ^{13} C and δ^{18} O are enriched compared to surrounding layers. This could be due to low rainfall events which will give an enriched δ^{18} O and δ^{13} C values. Major change in the drip positions suggests that during low rainfall years the soil zone, due to low water content or dryness got reworked at micro level (possibly due to bacterial activity). Therefore, finer particles were released during next wet season giving rise to dark layers or low gray levels and also enriched associated ' δ ' values.

However, 1) not all the low rainfall events (i.e. enriched δ^{18} O) and 2) not all the dark layers are associated with the changes in drip position. The minor changes in the drip position could occur because of the irregular structure of the associated stalactite (see Fig.1-10).

Gray level and thickness comparison

Comparison between the pixel and width data (in the Fig.4-17 (A & D)) shows that in segments 2-3 and 3-4/5, pixel and width data have trends of variations very similar, whereas there is less similarity in 1-2 and 6/7-8/9 segments.

Thickness of annual layers and $\delta^{18}O$ comparison

A few events with extreme depletion or enrichment in δ^{18} O record can be correlated very well with the width record. For example,

- at '1' very depleted level of δ^{18} O coincides with large thickness value
- between 6/7 and 8/9 most of the layers have enriched δ^{18} O and also low thickness.
- A sharp enrichment event which occurred between 1.55 to 1.70 cm is also associated with low layer thickness.

In a broad sense δ^{18} O and thickness data have quite a good similarity in different segments (Fig.4-17 (C & D). It is remarkable that enriched δ^{18} O signal recorded in 6/7-8/9 segment is also recorded by the width data. In the present study, however, thickness record and the δ^{18} O (which represents the rainfall) do not show a very good similarity at the annual scale. The obvious reason could be that the drip position has changed with time in a horizontal (x-y plane: parallel to the cave floor) direction and hence the thickness of



Fig. 4-19: $\delta^{18}O$ vs. $\delta^{13}C$ for the AKG plotted for all the measurements along the growth direction.

layers in a cross sectional surface (e.g. polished surface which has been used for thickness measurement) may not represent the actual thickness in the maximum growth direction. As $\delta^{18}O$ and $\delta^{13}C$ co-vary in most of the subsamples (Fig.4-19, r=0.604), in different segments, behavior of $\delta^{13}C$ is very similar to $\delta^{18}O$. Atmospheric $\delta^{13}C$ variations due to fossil fuel burning (i.e. the Suess Effect) has been observed in the annual layers of stalagmites at higher latitudes (Genty and Massault 1999). Probably, in these caves the rainfall over many years has not changed much and hence, the average drip rate had remained constant. In the absence of such variations atmospheric $\delta^{13}C$ trend is very well recorded. Further investigation of effect of rainfall amount on the $\delta^{13}C$ values in such caves is required.

Laminated stalagmite has been reported for the first time from tropical India. These laminations are annual as confirmed from the overall nature, presence of bomb ¹⁴C and similarity between ages by layer counting and ¹⁴C method at the base level Parameters such as thickness and gray levels of annual layers can be used to indicate broad (decadal order) changes in the rainfall. A good correlation between $\delta^{18}O$ and $\delta^{13}C$ indicates that 1) it is the changes in the drip rate of the seepage water (proportional to the annual rainfall) which is responsible for the changes in both $\delta^{18}O$ and $\delta^{13}C$; 2) $\delta^{13}C$ of annual laminations can also be used as an indicator of past rainfall.

4.4 Stalactite from Sota cave

Sota is a small cave located in the foothills of the Vindhyan ranges. It is part of a pilgrim center 'Chitrakoot' in the Uttar Pradesh (Northern State of India). Two caves viz. 'Gupt Godavari' and 'Sota' exist in the two hillocks which are within half a km distance from each other. In the Gupt Godavari cave, a stream of water flows inside the cave gallery. The source of the stream is known to be the stored rain water in the nearby reservoirs consisting of soils and rocky terrain. However, as it is frequented by devotees most of the speleothem deposits have been destroyed . Another cave 'Sota' is very shallow (roof thickness less than 3m) and as the entrance is very narrow, it is rarely visited by anybody. Due to this, the deposits are least disturbed by human activity and most of them growing in the narrow chambers were found undisturbed. The cave is above the ground level and this ensures that the drip water is originated from monsoonal precipitation.

October marks the end of the summer monsoon in this area (Climatological Tables 1970). However, occasional rain spells are experienced in this month. There were no recent rain spells in the region within the preceding week of sampling. During sample collection, the inside part of the cave and the stalactite's outer surface were found dry. This means that the stalactite collected has either stopped growing or all the rain water received during the previous rain spells has fully percolated within a short period (probably less than a month) and the cave surfaces dried up. However, we infer that the stalactite was an actively growing during collection due to two reasons: First, the tip part of the stalactite has bomb carbon which means that the growth has not stopped at least prior to 1957 (the initial year when bomb carbon appeared in the atmosphere, Nydal and Lovseth 1996). Second, as the thickness of the soil and bedrock above the stalactite is less (~3m) this suggests the possibility of fast passage of rain water from the cave surface to the dripping spots. Due to this wetness in the cave lasts for a very short duration and it dries up after a few days of the rainy season. And hence most of the growth of the cave deposits occur during few days after rains occur in the region. During the sample collection relative humidity and the ambient temperature were 64% and 27° C respectively.

Porosity and fissure size of the bedrock and the overlying soil thickness is such that there is very less resistance to the seepage water. This can be checked by measuring δ^{18} O composition of the rain and drip water. If δ^{18} O of rain water is not enriched significantly compared to the rain water then this can be used as an evidence of shallow thickness of the cave. However, during the visit the cave was found to be dry and hence samples of seepage water were not available and therefore, it can not be proved at this stage.

4.4.1 $\delta^{18}O$ and $\delta^{13}C$ variations in SOT

In the Fig.4-20, δ^{18} O and δ^{13} C variations along the growth direction of SOT is presented. As discussed in Sect. (4.1.3) it is reasonable to assume insignificant dilution (D=1, in equation 4-8) by the dead carbon contributed from the bedrock and hence apparent ages at the tip and base part can be assumed as the actual ages. The age of the base is



Fig. 4-20: $\delta^{18}O$ and $\delta^{13}C$ vs. age for the Sota stalactite (SOT). ¹⁴C measurements were carried out for the layers covered by the rectangles.

assigned 1100 yr BP and the tip part is assumed to be 0 yr BP (the tip is precisely associated with the 1997 AD which is the collection year). Each subsampling spot for the stable isotope analysis is assigned age by a linear interpolation between the tip and the base ages. Growth rate of the stalactite is 0.22 cm/yr which is higher than those of the Gupteswar and the Dandak speleothems. The striking observation in the profile is the most enriched value of δ^{18} O and δ^{13} C is observed during the recent period (depth 0.82cm). Each stable isotope subsample is about 1mm in size which is equivalent to ~5 yr time span. And the sampling interval is ~1mm (equivalent to) ~5 year.

Test for the isotopic equilibrium deposition in the Sota cave

Stalactite from Sota cave is light brown colored. Laminations are not seen very distinctly. Hence, only one layer which could be tracked, was sampled for the Hendy's test. Isotopic variations in O and C are presented in the Fig.4-21. The δ^{18} O and δ^{13} C do not show any correlation and also enrichment as one moves towards tip (for stalagmite enrichment should not be observed as one moves away from the tip). This probably means that in the past periods the stalactite grew in isotopic equilibrium.

4.4.2 Rainfall reconstruction from SOT

At Chitrakoot there is no rain-gauge station and hence for monthly rainfall data we selected nearby stations, Allahabad (at ~100kms), Satna (~72kms) and Banda (~65kms). An important observation is that there is a large regional variation in the rainfall within 100km distance. The physical and geographical causative factors and their relation with the Indian monsoon system is yet to be understood (Gadgil et al 1993). The average annual rainfall for these stations, based on instrumental observations from 1931 to 1960 (Climatological Tables 1970) is listed in the Table 4-5. Most rainfall is received in the area during June to September (Summer rain). There are rain spells in other months which contribute the rest of the components (12-14%). As each subsample for ¹⁴C analysis is about 5 yr time span, 5 point moving average of annual rainfall data from 1901 to 1950 is plotted for the nearest station 'Banda' in the Fig.4-22. Low rainfall event is observed at Banda near 1940 AD. Such low rainfall event may coincide with the cave area giving most enriched δ^{18} O and δ^{13} C at depth 0.82cm.

Tuble 1 5. Clillate data of	Tuble 1 5. Childred dud of the three stations hear Sola dave (Childred Stations 1970).					
Stations/distance from	Banda	Allahabad	Satna	Average of three		
cave(km)	~65	~100	~72	stations		
Annual rain (mm)	1003.6	1026.8	1137.1	1056.0		
Summer rain (mm) June-Sept.	872.9 (87%)	904.7% (88%)	978.1 (86%)	918.6 229.6*		
Annual av. Temp. (°C)	26.1	25.4	26.4	26.0		

Table 4-5: Climate data of the three stations near Sota cave (Climatological Tables 1970).

* average monthly rain during wet season (June-Sept.)

The average annual rainfall of the three stations (Banda, Allahabad and Satna) is 1056 mm (Table 4-5). During summer monsoon (June to Sept.) average value is 230 mm.

And hence annual rain is 4.6 (1056/230) times the mean monthly rain during summer season. It should be noted that for Jagdalpur and Karwar stations there is significant rain even in the Oct. months (Climatological Tables 1970). Whereas in the stations near Sota cave area, rainfall in the Oct. month is comparatively little. Assuming that all the variations in the stalactite δ^{18} O are due to the past variations in the amount of rainfall (because of amount effect), the rainfall equation for the Sota cave is:

 $Pa = (100/1.5)^* 4.6^* (\delta^{18} Otip - \delta^{18} Oi) + 1056.0$

or $Pa = 306.6*(\delta^{18}Otip - \delta^{18}Oi) + 1056.0$ (4-13)

Where, δ^{18} Oi and δ^{18} Otip are the oxygen isotope composition of the calcite with depth and at the tip respectively.

Using the above equation oxygen isotope composition is converted into rainfall variations and is presented in the Fig.4-20.

4.4.3 $\delta^{18}O$ and $\delta^{13}C$ variations in straws from Sota cave

Straw formations

Origin of stalactite or straw is decided by the movement of seepage water on the roof surface. As seepage water seeps out of the bedrock fissures, depending upon the curvature /slope of the roof surface it drips either from the fissure opening or at some other point along the roof surface. If it drips directly at the opening then calcite is precipitated on the outer side of a drop (see Fig.1-14) and deposits look like hollow straw in due course of time. In such a sample the successive precipitation occurs on the tip part. However, if the fissure opening is on a tilted part of the roof, then stalactites are more probable to form. Hendy's test is not applicable on the straws as laminations of large size similar to stalactite and stalagmite do not occur in them. In the Sota cave near the entrance, straw deposits were seen to grow in the cracks (size ~ 100 cm) inside bedrocks. Some of them were collected and their outer part was sampled for the stable isotope analysis. The result is presented in the Fig.4-23. There is wide range of variation in $\delta^{18}O$, from –6 to-8‰and for $\delta^{13}C$ from –14 to -7%. Such a large variation in the contemporary straws may be due to their proximity to the cave entrance which may generate kinetic fractionation as fast degassing and evaporation both are expected in such a situation. These straws can not be used for past climate reconstruction.



Fig. 4-21: Hendy's test for one of the layers which was possible to track in the SOT.

Fig. 4-22: Rainfall recordfromBandameteorologicalstation.Five pt. running mean isshown to indicate lowvalue of the rainfallobservedduring 1940AD.



Fig. 4-23: $\delta^{18}O$ and $\delta^{13}C$ for modern straws and stalactites collected near the cave entrance.

4.5 Comparison of speleothem δ^{13} C and δ^{18} O

4.5.1 Dependence of the mean $\delta^{13}C$ values

Temperature effect on the carbon isotopic enrichment of calcite, which is precipitated in isotopic equilibrium with the seepage water, is negligible (Bottinga 1968; Hendy 1971; Clark and Fritz 1997). The δ^{13} C of carbon depends upon pCO₂ of the water, temperature of calcite precipitation, type of overhead vegetation (C3 or C4) and the dripping rate of water in a complex fashion. Broadly, the slow changes occurring in δ^{13} C at decadal scale or more are ascribed to variations in the abundance of C3 or C4 plants. At shorter time scales (e.g. yearly) the fast changes are due to varying dripping rate which finally depends upon the amount of rainfall in the cave region.

The δ^{13} C of leaves from the vegetation growing atop the two caves (GUP/ DAN) was measured. The mean values are -28.3 and -27.8 per mil respectively for DAN and GUP, showing predominance of C3 type of vegetation currently. δ^{13} C vs. age for all the

four speleothems is presented in the Fig.4-24. Average δ^{13} C values are given in the Table 4-6 and 4-7. Sota has the most depleted δ^{13} C value compared to all others. The δ^{13} C values are primarily controlled by the dripping rate (Dulinski and Rozanski 1990; Hendy 1971; Sect. 1.2), which essentially depends upon,

- 1) thickness of roof (more the thickness, lesser the drip rate)
- fissure size (more the size, lesser resistance provided to seepage water and hence higher the drip rate)
- 3) the water available above the cave roof.

Thickness of the roof and fissure size will decide the average level of dripping and hence average δ^{13} C, this will be further modulated by the drip rate variations contributed by the varying rainfall. As the thickness of the roof (bedrock +soil cover) is least (~3m) for the Sota cave which means average drip rate is relatively high. Therefore, this gives maximum depleted levels in the δ^{13} C values.

There is systematic depletion in the Sota δ^{13} C value (δ^{13} C vs. time) Fig.4-24. This can be explained by the following process: As in the Sota cave the δ^{13} C has the most

		10	10	
Cave/location	Type of sample	$\delta^{18}O(\%)$	$\delta^{13}C(\%)$	Time span covered
	/mineralogy	max./ min.	max/ min.	Length (cm)
		mean	mean	Mean growth rate (mm/yr)
		size	size	
		tip value	tip value	
Gupteswar	Stalactite	-0.39/-6.79	-6.71/-13.17	~3400 yr BP to 1996 AD
(Orissa)	Calcite/aragoni	-3.90 ± 0.80	-10.19 ± 1.41	36cm
	te	(n=198)	(n=198)	0.14mm/yr
		-4.66	-11.42	-
Dandak	Stalagmite	-2.85/-6.18	-5.41/-11.04	~3700 to 3200 yr BP, with a
(Madhya	Pure calcite	-3.99±0.57	-8.68±1.28	hiatus and then from 1200 yr BP
Pradesh)		(n=103)	(n=103)	to 1996 AD.
,		-4.23	-9.43	28cm
				0.18mm/yr
Akalagavi	Stalagmite	+1.60/-2.69	-7.95/-13.56	~1666 AD to 1996 AD
(Karnataka)	Calcite/aragoni	-0.84±0.57	-11.11±1.27	42cm
	te	(n=301)	(n=301)	1.34mm/yr
		-1.01	-11.46	
Sota	Stalactite/	-6.37/-9.71	-12.59/-15.23	~1100 yr BP to 1996 AD
(Uttar	Pure calcite	-8.12±0.63	-3.73 ± 0.56	24cm
Pradesh)		(n=124)	(n=124)	0.22mm/yr
, í		-8.86	-14.22	

Table 4-6: Average values of stable isotopes of oxygen and carbon (relative to PDB) and their minimum, maximum and tip values (from measurements along the growth direction).

Cave	$\delta^{18}O(\%)$	$\delta^{13}C(\%)$
	max./ min.	max./ min.
	mean	mean
	size	size
Gupteswar	-2.55/-5.66	-7.75/-11.62
	-3.97 ± 0.75	-9.83 ± 1.13
	(n=31)	(n=31)
Dandak	-3.10/-6.18	-6.85/-11.04
	-4.21 ± 0.49	-9.13 ± 0.88
	(n=72)	(n=72)

Table 4-7: $\delta^{18}O$ (‰) and $\delta^{13}C$ (‰) values compared for 0 to ~1200 yr BP period for Gupteswar and Dandak cave.

depleted values it means that the average drip rate is high compared to other caves. The fissures through which the seepage water flows is being broadened in due coarse of time due to acid attack (carbonic acid) and also the fast flow of the seepage water (physical erosion). This systematically increases the mean drip rate level which depletes the average δ^{13} C value. However, the broadening of the fissures is also occurring in other deep caves but as the roof thickness is comparatively very large and the mean drip rate (based on average δ^{13} C level) is comparatively less the acid broadening takes place in the upper parts and erosion is less due to slower flow of seepage water. Changes in the drip rates due to broadening in these caves however are very less and such effects have not been observed.

$\delta^{13}C$ values of SOT

Annual average temperature based on daily max. and min. temperature observations from Allahabad, Bombay and Satna stations is 26^oC (Climatological Tables 1970). The present day vegetation is mainly C3 type and as δ^{13} C values for surrounding vegetation is not available, hence, it is assumed to be ~-28‰ (values obtained for the vegetation in the Dandak and Gupteswar cave area). Soil CO₂ is enriched by about 4.4‰ due to diffusion occurring at the soil-air interface (Cerling et al 1991). Hence, the CO₂ for such soils should have δ^{13} C = ~-23.6‰. At 26^oC calcite precipitated in isotopic equilibrium with the solution is enriched by 10.2‰ (Clark and Fritz 1997). Hence, calcite at the tip part should have a δ^{13} C value of -13.4‰. If the mean temperature of only wet season is considered (which is 28.9°C) then at this temperature the enrichment is 9.9‰, which will result in to calcite with δ^{13} C = -13.7‰. The average δ^{13} C of the Sota stalactite is -13.73 ± 0.56 ‰ and at the tip it has -14.22‰ value. The range of δ^{13} C values obtained is from -

15.23 to -12.59‰. Lower dripping rates may result in to higher values (-12.59%). However, in order to get most depleted value (-15.23‰), it is the δ^{13} C of the soil CO₂ which should have values close to -30%. More depletion of δ^{13} C is expected if the rainfall is enhanced which may increase more of C3 abundance. This is observed here as the value of δ^{18} O is also guite depleted (- 8.26‰). However, the most depleted value of δ^{18} O is not associated with the most depleted δ^{13} C. It is worth mentioning here that each subsample covers ~5yr time span and hence it is the major change in the precipitation pattern which can lead to such extreme values in the δ^{13} C and δ^{18} O. The δ^{13} C of the C3 type plants and humus material have a wide range of between -20 to -31‰ (Vogel 1993; Stuiver and Polach 1977; Clark and Fritz 1997). If % of C3 plants and the species vary and contribute a very depleted levels of δ^{13} C such as -30%, then the most depleted value (-15.23‰) can be obtained. If the enrichment by diffusion is less efficient then also most depleted value of δ^{13} C (i.e. -15.23‰) is possible. However, there are various possible explanations and in order to understand the exact process one has to do a rigorous study in which in situ soil CO₂ is collected from the cave surface, % of C3 and C4 plants are established and their temporal variations studied.

δ^{13} C values of AKG

Average value of δ^{13} C and maximum and minimum values are given in the Table 4-6 and 4-7. As the present day vegetation is dominantly C3 type and hence, we can assume δ^{13} C = -28‰ . The CO₂ in the soil should have values close to -23.6‰. The nearest meteorological station from the cave area is Karwar, for which the mean of daily highest and lowest temperature from 1960 to 1997 is 27^oC. At this temperature the calcite precipitating in isotopic equilibrium with the ions in the drip water should have enrichment by -10‰ (Vogel 1993; Clark and Fritz 1999). Hence calcite at the tip part should have values close to -13.5‰. Observed δ^{13} C value at the tip part is -11.46‰ (Table 4-6). The observed value (-11.46‰) is enriched as compared to the estimated values (-13.5‰). Such enrichment is possible due to slow dripping rate (Dulinski and Rozanski 1990).

As the roof (soil + bedrock) thickness of the Akalagavi cave is more (~30m) compared to the Sota cave (~3m), the mean drip rate in this cave is expected to be relatively less. Possibly, due to this the relative δ^{13} C values (Table 4-6) are enriched in the Akalagavi cave.

$\delta^{13}C$ values of GUP and DAN

The soil layer above Dandak and Gupteswar caves are bigger in size compared to Sota and Akalagavi caves. Due to this the rainwater resides comparatively for longer period of time in the former. Hence, the mean drip rate of the caves (Dandak and Gupteswar) are expected to be less which results in to relatively enriched δ^{13} C levels compared to Sota and Akalagavi speleothems. δ^{13} C of the representative leaves collected from the Gupteswar and Dandak caves have δ^{13} C values are close to -28.0‰. Considering average δ^{13} C of the soil CO₂ to be -28.0‰ , enrichment due to diffusion (by -4.4‰; Cerling et al 1991) will result in to soil CO₂ environment labeled as δ^{13} C = -23.6‰.

Daily max. and min. temperature recorded at Jagdalpur met. Observatory over a period of 1931 to 1910 (Climatological Tables 1970) shows that mean value is 25° C. At this temperature, enrichment in the calcite which is precipitated in isotopic equilibrium with the CO₂(aq), HCO₃⁻, CO₃²⁻ in the seepage water is enriched by 10.4‰ (Clark and Fritz 1997). Hence, at the tip part the δ^{13} C should be -13.2%. However, this is the value for the first calcite precipitated from the drip water and successive calcite is further enriched as shown by the values of the tip layers, δ^{13} C = -11.42% and -9.43% for the Gupteswar and the Dandak caves respectively. The question arises that why the δ^{13} C values at the tip are different for GUP and DAN. This again can be explained based on the average drip rate in the cave which depends on the roof size. Roof thickness of the Gupteswar is comparatively less than that of the Dandak . Due to this the average drip rate should be more in the Gupteswar cave compared with the Dandak cave and hence, the Gupteswar values are relatively depleted (-11.42‰).

The δ^{13} C matches well only between 600 to ~1200 yr BP and then the similarity breaks down between 600 to 0 yr BP (Fig.4-24). Between 600 to 0 yr BP δ^{13} C values of GUP are generally higher than the values in the Dandak cave. Possible reason for this may be the internal changes in the flow pathways in either of the caves due to which the mean drip rate might have changed. Between 1250-600 yr BP the mean drip rate of the two caves were probably almost same hence there is a good similarity in the δ^{13} C profile.



Fig. 4-24: $\delta^{13}C$ comparison of all the speleothems. DAN and SOT have been smoothed by a 2 point running mean. AKG data is smoothed by a 13 point running mean.

4.5.2 δ^{13} C vs. δ^{18} O in speleothems

 δ^{13} C vs. δ^{18} O for all the four speleothems are plotted in the Fig.4-25. For the regression equation δ^{13} C = m. δ^{18} O + c, m and c values are listed in the Table 4-8. Significant correlations of δ^{13} C with δ^{18} O (r=0.5428 to 0.7201) shows that δ^{13} C is also dominantly controlled by rainfall variations (through varying drip rate). This fact is more evident from the observation in the AKG, where for yearly deposition there is significant positive correlation between δ^{18} O and δ^{13} C (r=0.6147). At yearly scale C3 type of plants do not switch over to C4 (Claussen et al 1999). And hence, it is rainfall dependence of δ^{18} O and δ^{13} C which causes changes in both of them showing a high positive correlation in the



Fig. 4-25: $\delta^{13}C$ vs. $\delta^{18}O$ measured along the growth direction for all the speleothems.

annual data. There are other processes which are not rainfall dependent: such as, proportion of bedrock carbon contributing dead carbon to the seepage water, random fluctuations in the seepage pathways, changes in the biological activity etc. These may contribute to the natural variability and may be responsible for the scatter in the data (responsible for lowering down the value of r from unit value to value such as r=0.6147 for AKG).

Three inferences can be drawn from the $\delta^{13}C$ data:

- 1) The mean drip rate varies with the roof thickness and size of the pathways.
- δ¹³C is dominantly controlled by rainfall as evident from high +ve corr. coeff. (Table 4-8) between δ¹⁸O and δ¹³C.

3) δ^{13} C vs. time plot for all the caves (Fig.4-24) do not show very good similarity as other local factors (mainly changes in the pathways) contribute to the fluctuations in the δ^{13} C.

Cave	Equation	Correlation coefficient & no. of data points
Gupteswar	$\delta^{13}C = (1.28 \pm 0.09) * \delta^{18}O - (5.21 \pm 0.35)$	0.7201 198
Dandak	$\delta^{13}C = (1.31 \pm 0.17) * \delta^{18}O - (3.45 \pm 0.72)$	0.5870 103
Akalagavi	$\delta^{13}C = (1.36 \pm 0.10) * \delta^{18}O - (9.97 \pm 0.10)$	0.6147 301
Sota	$\delta^{13}C = (0.48 \pm 0.07) * \delta^{18}O - (9.81 \pm 0.55)$	0.5428 124

Table 4-8: Regression equations relating δ^{13} C with the δ^{18} O

4.5.3 Bedrock δ^{13} C values and their significance

Carbon isotope composition of the representative bedrock sample from each cave is listed in the Table 4-9. Dead carbon percentage (presented in Table 4-9) is defined as (1-D)*100, where D is the dilution factor given by equation (4-8). Dilution factor of each actively growing speleothem can be calculated using equation (4-8); for the tip part, t_{corr}=0 yr and t_{app} is the experimentally estimated ¹⁴C age (Sect. 4.1.2)). These bedrock samples are enriched in δ^{13} C compared to the respective speleothems (Table 4-6 & 4-7). These bedrocks are stratified and were part of marine sediment in the past. The present day marine HCO₃⁻ and CO₃²⁻ have δ^{13} C values ranging between +4 to -2 ‰ (Stuiver and Polach 1977). The speleothems evolve from the respired CO₂ which have much depleted level of δ^{13} C (-28‰) and the HCO₃⁻ shows values around (-15‰, discussed later). This is the reason why the speleothems are comparatively depleted relative to bedrocks in δ^{13} C.

When the seepage water (which is mild carbonic acid) percolates in the bedrock fissures, depending upon the local settings, carbonate dissolution takes place which is between open or closed type of dissolution (Sect. 1.2). In the caves which were investigated, the AKG is the most open type dissolution system, as the dead carbon

contribution is only 1.4% (Table 4-1 to 4-4). This means that in the $\delta^{13}C$ of DIC of the drip water there is 1.4% contribution from the bedrock ($\delta^{13}C=0.08\%$) and the rest is from the soil CO₂ (δ^{13} C close to -23‰). In the beginning of dissolution 50% of the carbon is contributed each from limestone bedrock and the soil CO₂ (equation (4-7)). While it appears in the form of drip water, the contribution reduces to 1.4%. This is due to continuous exchange of carbon between the dissolved carbon species $(CO_{2(aq)}, HCO_{3},$ CO_3^{2-}) and the gas phase of the soil CO_2 (in the fissures the water and gas phase exist together) during downward flow whereby the imprint of the bedrock carbon is slowly lost in the large reservoir of the soil CO_2 . A contribution of 13.8 % bedrock carbon is found in the DAN. During the bedrock dissolution and subsequent downward flow, the degree of exposure of the seepage water to the soil CO₂ decides the value of 'D' and, therefore, contribution of bedrock δ^{13} C to the speleothem δ^{13} C (Genty et al 1999). If it is assumed that the there are no changes in the contribution from the bedrock then, the variations in the δ^{13} C of speleothem purely reflects climate change. However, the amplitude of variations brought out by climate change will appear damped in the speleothem $\delta^{13}C$ if the bedrock contribution is more.

Cave	δ^{13} C of representative	Dead carbon content
	bedrock (%)	(%)
GUP	4.24	10 %
DAN	2.27	14.6%
AKG	0.08	1.4 %
SOT	-0.46	0 % (assumed)

Table 4-9: δ^{13} C (relative to PDB) of bedrocks from different caves.

4.5.4 δ^{13} C value of the seepage water from DAN

 δ^{13} C value obtained for the drip water sample collected from the Dandak cave is – 15.76‰. This value can be correlated to the δ^{13} C of the plant and the modern value of the cave calcite using known enrichment factors (Clark and Fritz 1997) for the CO₂(g), CO_{2(aq)}, HCO₃⁻, CO₃⁻² and CaCO₃. As the present day pH of the drip water is 7.4 (discussed further in Sect.4.8) which means that inorganic carbon in the dissolved ionic form is mainly abundant in HCO₃⁻. Average temperature for DAN is 25°C and hence the CO₂ in the soil is expected to be depleted by 7.9‰ relative to δ^{13} C of HCO₃⁻ (Clark and Fritz 1997). This yields δ^{13} C of the soil CO₂ to be -23.7 ‰. The CO₂ released by the plant respiration is actually depleted by ~4.4‰ (Cerling et al 1991), therefore, the plants should have δ^{13} C

value -28.1‰. The measured δ^{13} C values for the vegetation above the DAN cave is – 28.3‰. This confirms that the carbon isotope deposition is equilibrium type. The first calcite which precipitates (from the seepage water in isotopic equilibrium) should be enriched by 2.4‰ (at 25°C). Hence, calcite at the tip of the speleothem should have value equal to -13.4‰. Whereas actual value of δ^{13} C at the tip is -9.43‰. The further enrichment observed here is due to Rayleigh type δ^{13} C enrichment observed in the calcite precipitation (Dulinski and Rozanski 1990; Hendy 1971) and it is related to the drip rate variations in the cave. At various steps the evolution of δ^{13} C is shown in the schematic diagram (Fig.4-26).



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4.5.5 Growth rate dependence

The calcite deposition Growth rate depends upon several factors such as Ca^{++} concentration in the drip water, cave temperature, drip rate and pCO₂ level in the drip water.

Growth rate for a surface of unit area per second from a film of seepage water is given by Dreybrodt (1999) as

 $F = \alpha . (c - c_{eq}) \qquad mol/(cm^2 s)$ (4-14)

Here, α is the constant of the chemical kinetics and c and c_{eq} are the concentrations of Ca⁺⁺ (mol/litre) in the supersaturated and equilibrium conditions respectively. The α increase with increase in temperature or thickness of water film (Dreybrodt 1999).

Speleothem growth rate (cm/yr) at the drip position is given by Dreybrodt (1999) as

 $R_0 = 1.17.10^{6} (c-c_{eq}) . \delta / \Delta T . [1-exp(-\alpha \Delta T / \delta)] \quad (cm/yr)$ (4-15)

Speleothem growth rate (cm/yr) is maximum at the center (the spot where drip water falls) and decreases very fast at the edges. An exponential decay function has been applied by Dreybrodt (1999) to discuss the morphology of stalagmites. Hence, growth rate depends on degree of supersaturation (c-c_{eq}), the seepage water film thickness δ , constant of the chemical kinetics α and time ' Δ T' between two successive drops. Constant of the chemical kinetics is also function of temperature and thickness of water layer- δ . The climatic fluctuations in temperature, rainfall and pCO₂ may induce changes in these parameters which may counter-balance each other. If rainfall is more then drip rate inside the cave will be large, in that case Δ T will be less and also thickness of water film will be more due to increased flow rate and hence, more thickness of annual growth layers are expected. Increase in temperature however reduces the carbonate solubility, while increases the calcite precipitation rate.

Genty and Quinif (1996) analyzed the laminations by using a CCD camera, the thickness of laminations were measured using an image analysis program. They have found very good correlation between water excess (net amount of water which percolates) and thickness of annual layers. In our study thickness of layers vary from 0.09mm to 2.8mm. The thickness of layers observed by other authors vary from 0.043mm to 1.8mm for visible layers and from 0.0016mm to 0.05mm for luminescent layers (Genty and Quinif 1996). A very high growth rate (~5mm/yr) of stalagmite deposition has been reported by Böglie (1980).

As mentioned above the growth rate of speleothem depends upon several factors. However, certain things are observed in this study.

- a) Growth rate of stalagmite-AKG (1.34 mm/yr) is higher compared to the DAN (0.18mm/yr). This may be due to,
- 1) higher average drip rate in the AKG relative to DAN. This is evident from average δ^{13} C value which is more depleted in the AKG relative to the DAN (Table 4-6, 4-7; Fig.4-24).
- higher average rainfall in the AKG cave area (~3500mm/yr) compared to DAN cave area may also be responsible for higher drip rate inside and hence, relatively higher growth of AKG.
- b) Growth rate of stalactite-SOT (0.22mm/yr) is higher compared to that of GUP (0.14mm/yr). This may be due to,

1) relatively higher drip rate in SOT. This is evident by the fact that average δ^{13} C in SOT is depleted compared to GUP (Table 4-6, 4-7; Fig.4-24).

2) although, the rainfall in GUP (~1500mm/yr) is higher compared to SOT (~1100 mm/yr), this does not increase the average drip rate in GUP, possibly due to less roof thickness of SOT (~3m) compared to GUP (~6m) which may provide less resistance to the seepage water, the average drip rate in SOT is relatively more and hence, the growth rate is higher compared to GUP. Effect of higher rainfall on the drip rate is counter balanced by the roof thickness.

The growth rate may not be the same for all speleothems in a cave, as it depends upon the drip rate from the fissures which may vary with the fissure size. This has been observed by me in the year 1999. The drip rates varied from 5 sec per drop to 5 min. per drop (Sect. 4.6.1). In such a situation even in a same cave the growth rate may vary significantly. However, all the fast (some are very fast: 1sec per drop) drip sources were not associated with huge speleothems which means that the drip water was not loaded with much of dissolved ions (HCO₃⁻, CO₃⁻, Ca⁺⁺ and CO₂ (aq)). This may happen only if the rain water passes through fissures which may have bigger size and opens directly in to the less thick soil layer. In such a case the rain water percolates in to it with very less resistance to the flow. There is not much of dissolved soil CO₂ as the soil thickness is less and movement of water is fast. This means that subsequent dissolution of the bedrock will be less and the growth rate of speleothem will be slow even though the drip rate is high.

4.5.6 Comparative study of speleothem δ^{18} O

I. Mean δ^{18} O values of each cave

Caves have δ^{18} O values which is characteristic value due to:

- 1) Extent of evaporation is different due to differences in the pathways such as thickness of bedrock+soil, porosity, fissure size etc.
- 2) The source of water vapors are different. Such as the AKG receives water from the Arabian sea branch of the S-W monsoon, whereas others caves DAN, GUPT and SOTA receives from the Bay of Bengal branch (Fig.1-2). Average value of δ^{18} O of rain received by the caves GUP and DAN are same as the distance between them is about 30km and the areal extent of a cloud mass during monsoon season is usually ~100km or more. Due to this there is a very good similarity in the present day δ^{18} O values (at the tip) of GUP and DAN (Table 4-6 and 4-7).

II. Spatial variations in different caves

Low rainfall event ~1900 AD is shown by line 'l₁' and is commonly recorded in all speleothems (Fig. 4-27). The AKG is precisely dated by counting of each distinct layer and is having highest resolution (annual). Other speleothems have been dated by ¹⁴C method and ages have generally uncertainty up to ± 130 years and it has been assumed that the dead carbon contribution from bedrock has remained constant throughout their growth. Hence, positions of event 'l₁' in DAN, GUPT and SOT may have certain age uncertainty. Similarly, another enriched δ^{18} O event is shown by line 'l₂' in DAN, GUP and SOT. Between 'l₁' and 'l₂' there is a trend of increasing rainfall this is clearly observed in GUP, DAN and SOT. In Sota the rainfall increase is very prominent. Possible reason could be relatively very high rainfall in the SOT cave during the past (between l₁ and l₂).

In DAN, amplitude variation in δ^{18} O (between l_1 and l_2) is relatively less compared to GUP. This appears to be due to different degrees of evaporation in GUP and DAN. Present day δ^{18} O of seepage water shows that there is more evaporation in the DAN cave surface (δ^{18} O = -1.84 ‰) than GUP (δ^{18} O = -2.80 ‰). It can happen if the percolation rate is different in the top soil surface due to different physical properties. Rain water percolates slowly in the DAN and hence there is more enrichment in δ^{18} O due to evaporation at the cave surface (relative to GUP). When rainfall is more (its δ^{18} O is depleted), excess rain water on the cave surface goes as runoff and remaining evaporates. This reduces the amplitude of δ^{18} O depletion (which was brought due to increase in the rainfall). The reduction in the amplitude doesn't happen in the cave with fast percolation such as GUP. When rainfall is less (its δ^{18} O is enriched), there is no runoff of rain water at the cave surface as the water availability is less. The enrichment due to evaporation is same in both caves (DAN and GUP). This may be responsible for the less magnitude of δ^{18} O variation of DAN relative to GUP between l_1 and l_2 .

Between l_2 and l_3 (Fig.4-27), rainfall has attained high values which are shown by DAN, GUP and SOTA caves. A low rainfall event ' l_3 ' is observed in all these caves.



Fig. 4-27: $\delta^{18}O$ comparison of all the speleothems. DAN and SOT have been smoothed by a 2 point running mean. AKG data is smoothened by a 13 point running mean.

Mean values of δ^{18} O for all the speleothems are given in the Table-4-7. Rain water after percolating through the soil+bedrock zone is enriched to a characteristic value. Gupteswar and Dandak caves are geographically very close and they receive rain water from the same cloud source. Hence, the mean value of the rain water which falls on the cave surface should be same. However, due to differences in the soil + bedrock properties such as the porosity, fissure size, length of the pathways etc., the extent of evaporation differs in each cave. For example, if the water percolates fast in the soil zone (hence less evaporation at the cave surface) and then remains locked in the saturated zone then it will be less enriched compared to the case where it percolates slowly and hence there is more evaporation (at the cave surface) before it goes to the deeper parts of the bedrock strata. The present day seepage waters have slightly different values e.g. $\delta^{18}O = -1.84$ ‰ and -2.80 ‰ respectively for the Gupteswar and Dandak caves.

The δ^{13} C value at the tip in GUP and DAN have shown (Sect. 4.2) that, the drip rate is more in the GUP compared to DAN. It appears that in Gupteswar cave (rain water percolates fast (therefore less evaporation at the cave surface) and also drips fast inside the cave, relative to DAN. This results in

- 1) depleted tip values of speleothem δ^{13} C (-11.42 ‰) compared to DAN (-9.43 ‰ ; Table 4-7),
- 2) depleted δ^{18} O of seepage water (-2.80 ‰) compared to DAN (-1.84 ‰, Table 4-10 and 4-11, see Sect.4.6).

Between GUP and DAN, δ^{18} O comparison shows that,

- 0-1250 yr: δ^{18} O of both caves are very similar
- *3200-3400: δ^{18} O of both the caves (DAN and GUP) differ possibly due to invalid assumption of constant dead carbon contribution during this period.

4.5.7 Continental effect in speleothems

Sota cave has average $\delta^{18}O = -8.12 \pm 0.63\%$ (n=124). The tip value is -8.86%, which is more than 4‰ depleted compared to the Gupteswar (-4.66%) and the Dandak (-4.23‰) cave. Rainfall received by the three caves viz. Gupteswar, Dandak and Sota are from the Bay of Bengal branch of the S-W monsoon. Clouds originate in the Bay of Bengal and then as they move inland, there is progressive depletion in the precipitation. This is due to preferential removal of ¹⁸O. Such progressive depletion is known as continental effect (Clark and Fritz 1997). The progressive depletion in rains occurring over the land area can be explained by considering Rayleigh process, whereby a given amount of moisture forming cloud enters a continent through coast and rains successively as it

moves farther. The rain-out is accompanied by isotopic fractionation where condensate is enriched relative to vapor. Due to preferential removal of the heavy isotope in the liquid phase the remaining vapor becomes depleted in it and consequently each stage of precipitation is lower in ¹⁸O than the preceding one (Rozanski and Sonntag 1982, Clark and Fritz 1997). The tip δ^{18} O value of Sota stalactite is –8.86‰ and mean tip δ^{18} O value of the speleothems from Gupteswar / Dandak cave is -4.45‰. The cloud mass covers a linear distance of about 650km. It shows that as the cloud moves ~650km distance from Gupteswar/Dandak to Sota site there is 4.42‰ depletion in the rain. This means that there is continental effect: -6.5‰ depletion for 1000km distance. This result is very close to the values shown by earlier work which is –6‰/1000km, based on stable isotope studies of North Indian ground water (Bhattacharya et al 1985).

Akalagavi cave

Average values of the δ^{18} O for the Akalagavi stalagmite is $-0.84 \pm 0.57\%$ (n=301), which is about 8‰ enriched compared to Sota cave and about 3.5‰ enriched compared to the Dandak and Gupteswar caves. Spatial distribution of δ^{18} O values in the speleothems are manifestation of the pattern of δ^{18} O in the monsoon rainwater.

On the western Ghats monsoon precipitation occurs due to cloud formations in the Arabian Sea. Most of the rains occur on the sea facing side (south-west). Due to this all the clouds precipitate without preferential removal of δ^{18} O as it occurs on the land (continental effect). Therefore, enriched δ^{18} O is observed for AKG (Fig.4-27).

4.6 δ^{18} **O** and δ **D** of water samples

4.6.1 Cave drip waters

a) Dandak cave

Cave waters were collected from different seasons in order to understand its seasonal and geographical variations and its relation with the speleothem δ^{18} O. They were collected from DAN, GUP and Kotamsar (a cave within 5 km distance from DAN (site no.8 in Fig.1-15 (B)).

To accumulate enough seepage waters, pre-cleaned plastic bottles and polythene bags were hung just below the dripping spots for 1-2 days, after that they were tightly closed and teflon tapes were wrapped to avoid any evaporation before analysis. Seepage water samples were collected from the Dandak cave during July'99, Sept'99 and June 2000. During July'99 when already there were few rain spells, still most of the stalactites were found dry. However, some of the stalactites inside were wet and the dripping was very slow (~10min per drop). During Sept.'99 (after ~2 months) all the stalactites were found wet and also the drip rate was found to be more (~ 5sec per drop to ~5min per drop). During June 2000 the cave was found again dry like it was during July'99 only some of the stalactites were found to be active. This shows that the transit time for the rain water from the surface to the Dandak cave interior is less than 2 months.

It shows that the most of the water percolated during monsoon seasons is stored in the saturated zone of the cave system and is drained out before next monsoon season starts. Only a little fraction is left which continues to drip even during the end of the dry seasons (i.e. June month, first month prior to the onset of summer monsoon). The transit time i.e. the average passage time the rain water takes in percolating from the soil zones to the dripping spot is possibly less than two months. Isotopic signature of seepage water collected from Dandak cave is shown in the Fig.4-28(A). It shows statistically insignificant differences in the isotopic compositions collected during different months.

For each rain out event above the cave surface (Fig.4-29) there is net percolation in the soil zone. The δ^{18} O of rain water is systematically enriched due to evaporation occurring at the cave surface. Old water residing in the saturated zone, will modify the δ^{18} O of seepage water if its amount is significant compared to the percolated water. Seasonal variations in the rain water- δ^{18} O and its appearance in the seepage water depends upon the transit time which in turn depends upon the roof thickness (bedrock +soil) and size of pathways. If transit time is less then any change in the δ^{18} O of rain appears in the drip water with least damping (Clark and Fritz 1997). Whereas in the deeper caves, the transit time is more which means any change in the rain δ^{18} O is damped in the δ^{18} O_c (Clark and Fritz 1997). However, all the transit times are less than a year as observed from the drip rate variations, which increase within a week to about two months from the onset



Fig. 4-28: $\delta^{18}O$ plotted for the cave drip water samples collected during different periods for the DAN (A), Kotamsar cave (B) and GUP (C). Ground and river samples near the cave area and for the transect-1 and transect-2 are shown in (D).



Fig. 4-29: A sketch showing percolation of rain water and its subsequent evaporation in the unsaturated and partly from the upper part of saturated zone. Net δ is enriched and has a characteristic value. of S-W monsoon and after the wet season is over they become partially (DAN, GUPT and AKG) or fully dry (SOT).

Net isotopic signature of rain water (considering mass balance) collected in Jharsuguda (site no. 1 in Fig.1-15(A)) in 1999 is found to be -8.5 ‰ (discussed later). Evaporation occurs on the soil surface and in the unsaturated zone which enriches the stable isotopes. The degree of evaporation is dependent upon 1) the ambient humidity at the soil surface above the cave and 2) physical parameters such as porosity in the soil and thickness of soil layer. The physical parameters may not have changed significantly during the past(such as last 3500 yr), implying that the degree of evaporation may remain approximately constant if the ambient humidity remains more or less constant. Finally, in the saturated zone there will be mixing of old waters, this component may be negligible as observed drip rates, during dry seasons are less. Hence, during each rain event, rain waters with net δ^{18} O signature (after systematic evaporation in the unsaturated zone) and mixing with old waters in the saturated zone drips in the cave system. Depending upon the cave ambient temperature there is further enrichment in the δ^{18} O in the freshly growing carbonate layers and further it remains preserved for ever.

Amount effect in rain water and evaporations at the soil surface

The question which arises here is that if there is evaporation at the soil surface above the cave, then will it modify the amount effect (-1.5%/100mm for the monthly rain) observed in the rain water? As mentioned earlier the evaporation which is related to physical parameters of the soil layer may not have changed significantly with time and hence they may contribute a constant enrichment factor to the rain water δ^{18} O. However, at the soil surface the evaporation is also related to humidity and hence the ambient rainfall. There is more evaporation when humidity is less (in low rainfall years when rain δ^{18} O is already enriched). The evaporation at the cave surface reduces when ambient humidity is higher (due to higher rainfall when rain δ^{18} O is already depleted). Thus, qualitatively the evaporation at the cave surface is also dependent upon the amount of rainfall. Hence, δ^{18} O of cave seepage water is characterized by; 1) δ^{18} O of rainwater; 2) evaporation at the soil surface, both the factors are dependent upon the amount of rainfall and *act in the same direction*. In absence of any systematic observation of long term temporal variation in the δ^{18} O of cave seepage water and amount of rainfall, we assume that the depletion rate observed in the rain water is also applicable in the cave seepage water and hence the speleothem $\delta^{18}O_c$. A direct support to the validity of this assumption is given by the AKG-rainfall reconstruction where depleted $\delta^{18}O_c$ is related to excess rainfall years and enriched $\delta^{18}O_c$ are related to the deficient rainfall years observed in the all India rainfall time series (Sect. 4.3.4). As during low rainfall years there is more evaporation which progressively reduces as rainfall increases, the actual depletion rate in the cave seepage water could be more. Thus, if at all, in fact we may be underestimating the amplitude of rainfall variations in all the speleothem based reconstructions.

An empirical relation relating oxygen isotopic composition of the calcite layer $(\delta^{18}O_{cal-PDB})$ and the supersaturated water $(\delta^{18}O_{water-PDB})$ from which calcite precipitates at an ambient temperature (T), is given (O'Neil et al 1969) by equation (1-9). This can be rewritten as,

$$\delta^{18}O_{cal-PDB} - \delta^{18}O_{water-PDB} = (2.78 \times 10^6/T^2) - 3.39$$
(4-16)

For Dandak speleothem the recent layers near tip part have average $\delta^{18}O_{cal-PDB}$ (first three measurements) -4.42‰, the average drip water $\delta^{18}O_{water-SMOW}$ for seasonal observation is -1.84‰ (Table 4-10). For Jagdalpur district the mean annual temperature for the period 1931 to 1960 is 25.5°C (Climatological Tables 1960). The mean temperature 25.5°C should enrich the calcite relative to drip water by 27.8‰ ((2.78×10⁶/T²) - 3.39=27.8; where T=273+25.5) in PDB scale. The observed enrichment is ($\delta^{18}O_{cal-PDB} - \delta^{18}O_{water-PDB}$) 27.3‰. The observed and estimated values are in good agreement, which proves that there is equilibrium deposition of the calcite precipitating in Dandak cave.

For the recent growth layers in the Gupteswar stalactite the mean of δ^{18} O is -4.3‰. The estimated cave temperature is 25.17°C, if the isotopic composition of the precipitation is assumed to be -2.5‰ (SMOW). This temperature estimate is very close to the annual temperature of the cave area (25.5°C, annual temperature of Jagdalpur). A few samples of cave water from Gupteswar have shown δ^{18} O =-2.80‰ (very close to the assumed value). It means that there is likely equilibrium type precipitation of the carbonates in the Gupteswar cave.

Sample no.	Collection	$\delta^{18}O_{\text{SMOW}}(\%)$	$\delta D_{SMOW}(\%) / d$ -excess
_	period		
14/7/2	July'99	-1.63	-8.92 / 4.12
14/7/3	-do-	-1.90	-8.77 / 6.43
14/7/4	-do-	-1.61	-8.69 / 4.19
14/7/5	-do-	-1.48	-
14/7/6	-do-	-1.73	-7.78 / 6.06
14/7/7	-do-	-1.77	-
14/7/8	-do-	-1.31	-
14/7/9	-do-	-2.08	-10.70 / 5.94
		Av.=-1.69±0.24	Av.=-8.97±1.07
			/ 5.35±1.10
14/7/prl1	July-Sept. 1999	-1.92	-9.63 / 5.73
14/7/prl2	-do-	-1.86	-9.25 / 5.63
, p	u o		
		$A_{V} = -1.89 \pm 0.01$	$Av = -9.44 \pm 0.27$
		1100 1000 0001	/5 68±0 07
			70.00-0.07
12-9-04	Sent 1999	-1.83	-7 34 / 7 30
12-9-03	-do-	-1.96	-8 57 / 7 11
12-9-05	-do-	-2.05	-10.25 / 6.15
12-9-05	-00-	-2.05	-10.237 0.13
		$A_{\rm V} = 1.95 \pm 0.11$	$A_{\rm V} = -8.72 + 1.46$
		AV1.75±0.11	$/6.85\pm0.62$
Fast drip source			70.85±0.02
	-do-	-2.76	17 79 / 1 29
12 0 06	-do-	2.70	17.79 / 4.29
12-9-00	-00-	-3.03	-17.797 0.43
		$\Lambda_{\rm W} = 2.80\pm0.10$	$\Delta x = 17.79 \pm 0.01$
		Av2.09±0.19	$Av 1/./9 \pm 0.01$
			/3.3/±1.33
1 11 6 00	Juna 2000	1.02	
1-11-0-00	Julie-2000	-1.92	-
2-11-0-00	-d0-	-1.95	-
3-11-0-00	-00-	-1./5	-
4-11-0-00	-uu-	-1.07	-
5-11-0-00	-00-	-1.08	-
	-00-	-2.00	-
/-11-0-00	-uo-	-1.85	-
$\delta - 11 - 0 - 00$	-00-	-1.95	-
9-11-6-00	-00-	-1.84	-
10-11-6-00	-do-	-1.68	-
11-11-6-00	-do-	-1.82	-
		Av.=-1.83±0.11	

Table 4-10: Dandak cave (site no. 21 in the Fig. 1-15(B)) seepage water.

On annual scale the following processes may be realized;

- 1) Due to the amount effect, variations in the annual rainfall leads to changes in the net δ^{18} O of total rain water. Subsequently this change is reflected in the total water, which dripped in the cave.
- 2) Net δ^{18} O of the calcite precipitated in a single year (major growth during monsoon season) is a function of δ^{18} O of drip water and ambient cave temperature.
- Hence, in a year when there is more rain the calcite layers will be depleted and vise versa.

At monthly scale, rain waters with net δ^{18} O signature after systematic evaporation in the unsaturated zone and mixing with old waters in the saturated zone drips in the cave system. The freshly growing carbonate layers preserve the drip water δ^{18} O signal.

In the Dandak cave there are some fast dripping sources which were found active during monsoon seasons, δ^{18} O values for these sources (-2.89 ± 0.19 ‰; n= 2, Table 4-10, Fig.4-28(A)) are depleted compared to slow dripping sources. This means that there are some direct pathways from which the rain water is directly drained inside. Also, there are only small speleothem structures on such associated dripping spots, which is possible when rain water passes through channels in the overlying strata which have openings in the cave surface. Such waters have less exposure to high pCO₂ soil environment and therefore the dissolution of limestone bedrock strata and subsequent calcite precipitation is less effective.

b) Kotamsar and Gupteswar cave

Stable isotope signature of the seepage water samples collected from Kotamsar and Gupteswar are shown in the Fig.4-28(B and C). These caves are having different characteristic δ^{18} O values. For Kotamsar cave it is -2.63 ± 0.38 ‰ (Table 4-12; n= 4) and for Gupteswar it is -2.80 ± 0.33 ‰ (Table 4-11; n=5). These values are depleted compared to the δ^{18} O value in the Dandak cave. It should be due to a shallow bedrock and openings of the pathways in the unsaturated zone due to which the extent to which evaporations occur in the unsaturated zone in these caves is less compared to the δ^{18} O is –

Sample no.	Collection period	$\delta^{18}O_{\rm SMOW}$ (‰)	$\delta D_{\text{SMOW}}(\%)$
GUP1996	Feb. 1996	-3.07	-
1-9-6-00	June 2000	-2.77	-
2-9-6-00	-do-	-2.27	-
1-10-6-00	-do-	-3.08	-
2-10-6-00	-do-	-2.83	-
		Av.=-2.80±0.33	

Table 4-11. Gupteswar cave (site no.22, Fig. 1-15(B)): seepage water details.

Table 4-12: Kotamsar cave (site no. 8, Fig. 1-15(B)): seepage water details.

Sample no.	Collection period	$\delta^{18}O_{\rm SMOW}$ (%)	$\delta D_{SMOW}(\%) / d$ -excess
13/7/11	July 1999	-2.78	-11.77 / 10.47
13/7/12	-do-	-2.78	-11.64 / 10.6
13/7/13	-do-	-2.89	-
13/7/14	-do-	-2.07	-
		Av.=-2.63±0.38	Av.=-11.71±0.09
Pool water			/10.53±0.09
13/7/10	-do	-3.16	-18.39 / 6.89

3.16‰ which is a little depleted compared to the average seepage water value -2.63 ± 0.38 ‰. This shows that pool water is accumulated during monsoon seasons when floors in the Kotamsar cave are flooded with direct rain water. Such flooding was observed during a field visit in September 1999 (monsoon season). For Gupteswar cave, seepage water samples collected in two different years i.e. Feb, 1996 and June 1999 do not show any significant difference in the δ^{18} O values. As the cave regions have received good rains during past few years and there were no deficient rainfall years, hence, there are no significant differences in the δ^{18} O values of the seepage waters collected during these years.

4.6.2 Water from surface, ground and cyclone system

a) Near cave area

River water, pool waters and tube-well (ground water) waters were collected during September, 1999 from different locations as shown in the Fig.1-15, stable isotope data is listed in the Table 4-13 and 4-14. The mean values for river and ground water samples are shown in the Fig.4-28(D). Oxygen isotopic composition of all the seepage water samples collected from the three caves discussed above range between -3.08 to -1.31% (mean value -2.06 ± 0.47 ; n=33, Table 4-10, 11 & 12), whereas values for the river and

Sample Id.	Site name	Site no.	$\delta^{18}O_{\text{SMOW}}(\%)$	δD _{SMOW} (‰) / d-excess
TRANSECT-1				
(Oct. 1999)				
t1	IB power plant	1	-4.15	-30.19 / 3.01
14/9/1	Jharsuguda	20	-4.20	-31.58/2.02
t2	Bhawanipalli	$\frac{1}{2}$	-3.96	-29.08/2.60
t3	Angul	$\frac{1}{3}$	-4 55	-30 44 / 5 96
t3 t4	Dhenkanal		-5 30	-35 74 / 6 66
+5	Nakahi	т 5	6.09	40.76 / 7.88
+4	Dhubraguar	5	-0.08	-40.7077.88
	Diublieswai	0 7	-4.12	-29.24 / 5.72
ι/	Pull	/	-3.12	-33.30 / 3.40
			Av.=-4./8±0./8	Av.=-32.99±4.43
				/4.66±2.12
NEAR THE				
CAVE AREA				
(July 1999)				
9-9-02	Kotamsar village	9	-3.81	-25.42 / 5.06
9-9-06	Lohandigarh	13	-2.78	-20.79 / 1.45
9-9-07	Karanji	14	-3.77	-24.96 / 5.20
11-9-01	Banzarighat	15	-2.00	-11.91 / 4.09
11-9-02	Danteswari	16	-3.30	-25.33 / 1.07
11-9-03	Barsoor	17	-2.93	-28.59 / -5.15
11-9-05	Gidam	19	-2.78	-20.15/2.09
11 9 00	Gruum	17	2.70	
			$A_{\rm V} = -3.05 \pm 0.64$	$A_{\rm V} = -22.45 \pm 5.48$
TRANSECT_II			111. 5.05-0.01	/ 1 97+3 57
(Jupe 2000)				1.97=5.57
(June 2000)	Iagdalpur	22	3 83	
2	Vandagaan	23	-3.05	
2	Kondagaon	24	-4.40	
3	Keshkai	25	-0.19	
4	Laknnapuri	26	-4.10	
5	Dhamtari	27	-1.85	
6	Raipur-i	28	-3.06	-20.07 / 4.41
13/9/1	Raipur-ii	28	-2.54	
7	Rajnandgaon	29	-3.26	
8t	Khairagarh	30	-3.83	
9	Langi	31	-2.52	
10t	Seoni	32	-2.83	
11	Lakhanadon	33	-3.23	
12	Kothotiya	34	-3.61	
13	KondaJamuniya	35	-2.58	
14	Dehgon	36	-3.48	
15b	Bhopal	37	-2.83	
15t	Indore	38	-3.87	
16	Sonagarh	39	-2.66	
17	Dahod	40	-2.95	
			$A_{\rm V} = -3.34 + 0.80$	
			111. J.J (±0.00	

Table 4-13: Ground water (taken from tube wells) samples. Site details shown in the Fig. 1-15 (A & B).
Sample Id.	Site name	Site no.	$\delta^{18}O_{\rm SMOW}$ (‰)	$\delta D_{SMOW}(\%) / d$ -excess
9-9-1	Kotamsar Gate	9	-3.16	-17.58 / 7.70
9-9-3	Tirathgarh	13	-3.54	-22.61 / 5.71
9-9-4	Chitrakoot fall	5	-4.00	-26.37 / 5.63
9-9-5	Small stream	4	-3.57	-24.50 / 4.06
11-9-4	Shankini-Dankini	7	-4.78	-35.91 / 2.33
			Av.=-3.81±0.62	Av.=-25.40±6.73
				/5.08±2.01

Table 4-14. Surface (rivers, falls and ponds) water collected during Sept. 1999 near the cave site. Details given in Fig. 1-15 (B).

open reservoir waters are between -3.16 to -4.78 ‰ (-3.81 ± 0.62 , n=5, Table 4-14) and for tube-well waters (ground water) are between -2.00 to -3.81 ‰ (mean value -3.05 ± 0.64 ; n=7, Table 4-13). This shows that karst waters studied are generally more enriched compared to the shallow ground waters and also river waters. This is possibly because all the caves studied are above the ground level and are part of hillocks. The catchment area generally has a mound kind of structure where rain water continuously flows and can not stay once the rain spell is over. In such a situation evaporation is more dominant compared to the plains where depleted rain water stays in rivers, ponds etc. for longer periods of time and recharges the shallow acquifers.

b) Ground water samples from other locations

Oxygen isotopic compositions for tube-well water samples collected from different locations as shown in the Fig.1-15 are listed in the Table 4-13. Samples collected in the Transect-1 (Fig.1-15) have mean values $-4.78 \pm 0.78\%$ (n= 7). For samples in Transect-2 (Fig.1-15) mean value of δ^{18} O is -3.34 ± 0.800 (n=19). Comparing δ^{18} O of all the water samples collected from tube-wells with the cave δ^{18} O values which range from -1.31 to -3.08%, we find that the cave water is relatively enriched.

c) Cyclonic water

A super cyclone storm appeared on 29th of October 1999 (Kalasi and Ray, 2000) in the coastal Orissa. Five rain water samples were collected at an interval of 1hr. at an average temperature of ~25°C and relative humidiy ~90% between 15:45hrs to 19:45hrs. Mean δ^{18} O of these samples is -18.50 ± 0.82 ‰ (Fig.4-28(C)) and δ D is -137.34 ± 6.27 ‰ (Table 4-15, n=5). In comparison with the river , ground and karst seepage waters

Sample no	$\delta^{18}O_{\text{SMOW}}(\%)$	δD _{SMOW} (‰) / d-excess
c1	-18.07	-135.02 / 9.54
c2	-19.91	-148.16 / 11.12
c3	-18.36	-136.43 / 10.45
c4	-18.29	-135.17 / 11.15
c5	-17.84	-131.94 / 10.78
	Av.=-18.45±0.82	Av.=-137.34±6.27/10.61±0.66

Table 4-15: Cyclone water collection at site no.7 shown in Fig.15 (A), on Oct. 29, 1999.

the cyclone waters are highly depleted. A plausible mechanism responsible for such high depletion is the continuous precipitation and evaporation during cyclone formation over the sea surface which acts as a distillation column where by light molecules of water are preferentially carried in the moist air and cloud phase. Hence, as the cyclones reach the coastal land area, already their cloud masses are highly depleted in comparison to the monsoon clouds (unpublished Ph. D. Thesis of Geeta Rajagopalan, 1997).

4.6.3 Amount effect observed in the south-west monsoon

In order to verify the presence of amount effect in the monsoon rain water, water samples from each major rainout spell between July to October season (year 1999) were collected at Jharsuguda ($22^{\circ}N$, $84^{\circ}E$,), about 400 km in the north-east direction from GUP site. Rain water was collected in a plastic carboy (20 lit) attached with a plastic funnel of known (20cm) diameter. It had a small neck so that evaporation is insignificant. Water was removed from the container once daily around 8 a.m. Its amount was measured in a graduated cylinder and part of the water was filled in a 25ml air tight plastic bottle for isotopic measurements. The isotopic results are given in Table 4-16 and plotted in Fig.4-30. For the amount of water and $\delta^{18}O_m$ the least square fit obtained is:

 $\delta^{18}O_i = -(0.092 \pm 0.011)*P_i -(3.368 \pm 0.413)$ (4-17)

where, P_i is the amount of each daily rain in mm

r=0.8699 (n=24)

Average rate of depletion is: -9.2 ± 1.1 ‰ per 100mm.

The above rain data has been converted in to monthly $\delta^{18}O$ and amount by simple isotopic mass balance of all the collections in each month. Expression for the best fit line

obtained from three data point for the July, Aug. and Sept. month (shown in the Fig.4-30) is given below

$$\delta^{18}$$
O = -(0.0223 ± 0.0082)*R_m - (2.513 ± 1.891) (4-18)
n=3, r = 0.939



Fig. 4-30: $\delta^{18}O$ vs. rainfall plotted for the rain water samples (solid circles) collected from Jharsuguda. Rainfall of each month is added to get the monthly rainfall for July, Aug and Sept (solid triangles). A best fit line shows depletion rate agreeing with global values (see text).

This shows that there is 2.2 ‰ depletion per 100mm increase in the monthly rain amount. Net δ^{18} O of all the rain water (considering isotopic mass balance) collected at Jharsuguda is -8.5‰.

The observed value (2.2 ‰ depletion per 100mm in monthly rain) agrees very well with the value (1.5 ‰ depletion per 100mm monthly rain) as shown by the IAEA stations. Equation (4-17) is based on the three data points and samples collected over three months of the wet season –1999, whereas, equation 4-10 is based on samples collected over several years (more than 10 years; Yurtsever and Gat 1981). Hence, in all rainfall reconstructions, depletion rate based on IAEA observations (1.5 ‰ depletion per 100mm monthly rain) has been applied.

Date of collection	Sample no.	Rain (mm)	$\delta^{18}O_{\rm SMOW}$ (‰)	$\delta D_{SMOW}(\%)$ d-excess
10-7-99	R1	5.73	-3.13	-23.24 / 1.8
11-7-99	R2	1.91	-3.85	-27.22 / 3.58
12-7-99	R3	0.32	-0.64	-6.49 / -1.37
14-7-99	R4	22.92	-3.34	-19.00 / 7.72
15-7-99	R5	9.23	-2.84	-14.82 / 7.90
29-7-99	R6	6.37	-2.47	-13.53 / 6.23
3-8-99	R7	35.01	-8.25	-59.56 / 6.44
4-8-99	R8	81.17	-9.91	-73.19 / 6.09
21-8-99	R9	11.14	-3.83	-28.44 / 2.20
24-8-99	R10	24.83	-5.23	-37.11 / 4.73
29-8-99	R11	4.77	-2.96	-13.50 / 10.18
1-9-99	R12/13	71.94	-10.62	-77.72 / 7.24
2-9-99	R14	37.24	-8.19	-59.46 / 6.04
3-9-99	R15	4.14	-4.51	-30.21 / 5.87
5-9-99	R16	8.28	-2.90	-15.00 / 8.20
7-9-99	R17	10.82	-4.09	-22.85 / 9.87
9-9-99	R18	2.71	-5.64	-34.55 / 10.57
13-9-99	R19/20	49.34	-10.64	-77.74 / 7.38
15-9-99	R21/22	37.24	-7.76	-54.04 / 8.04
16-9-99	R23	8.28	-5.09	-39.81 / 0.91
17-9-99	R24	6.37	-5.19	-35.91 / 5.61
18-9-99	R25	2.01	-4.99	-51.46 / -11.54
23-9-99	R26/27	98.36	-10.12	-75.52 / 5.44
28-9-99	R28/29	59.39	-9.70	-68.18 / 9.42
			Av.=-5.66±2.97	Av.=-39.94±23.16
				/5.37±4.67

Table 4-16: Rain water samples: Collected at the site no.1 (Fig. 1-15 (A)).

4.6.4 General rainfall equation based on amount effect

Annual rain R_{an} can be given in terms of stable oxygen compositions of each daily rain collection (δ_i) as;

 $R_{an} = (1/(\delta_{an}. m)) [\sum (\delta_i^2) - c\sum(\delta_i)]$ (4-19) n= no. of rainy days; i=1 to n

Where, m (= -0.092) is the slope and c (= -3.368) is the intercept in the above fit.

(If the best fit line for the above measurements is δi = m. Ri + c

Then , $Ri = (\delta i - c)/m$, and

 $\sum \delta i.Ri = \delta_{an}.R_{an}; R_{an} = \sum Ri; i=1$ to n where n= number of rainy days in a year.

Hence, $\sum (\delta i^2/m) - (c/m)$. $\sum (\delta i) = R_{an} \cdot \delta_{an}$

This gives, $R_{an} = (1/(\delta_{an} \cdot m \cdot)) \cdot [\sum (\delta_i^2) - c \sum (\delta_i)]$).

It is assumed that the same depletion rate is applicable to the $\delta^{18}O_c$ of the speleothem. If calcite layers in speleothems are sampled at annual scale then using their $\delta^{18}O$ values we can estimate the oxygen isotopic composition of annual rain (i.e. δ_{an}) using suitable expression. The range of variations in the number of rainy days per year for a typical site such as Jagdalpur has been found to vary between 61 to 110 (during 1910 to 1950 AD) which is highly variable. Isotopic compositions (δ_i) for the daily water collections and no. of rainy days (n) for the past years are not known and hence in such cases we can not use the equation (4-18) to reconstruct past rainfall using $\delta^{18}O$ of speleothem calcite.

South-west monsoon which is active during June to October a contributes maximum (88 to 94 %) to the annual rainfall R_{an} in the regions studied. If we assume that this percent contribution remains essentially constant in time then,

 $R_{monsoon} = (\sum \delta i.Ri) / \delta_{monsoon}$ where i =1 to 5 stands for each month during monsoon season. Again in this case we do not know the monthly δi . and Ri for the past periods. If we assume that mean monthly rain in the wet season is R_m and the mean monthly isotopic composition is δ_m , then $R_{monsoon}$ can be approximated to,

$$R_{\text{monsoon}} = 5.R_{\text{m}} \tag{4-20}$$

Also, $R_{an} = R_{monsoon} (1 + f)$; where f is the fractional part contributed by the rest of the months except June to October when the south-west monsoon is active.

Hence,

$$R_{an} = 5.(1+ f). R_{m}$$
or
$$R_{an} = F. R_{m}$$
(4-21)
where,
$$F = 5.(1+f) \text{ or } = R_{an} / R_{m}$$

If $\delta_m = a.R_m + b$, then from equation (4-17),

a = -0.0223 and b = -2.513

Equation (4-20) can be rewritten as

$$R_{an} = F.(\delta_m - b)/a$$
 (4-22)

From eq.(4-15), drip water stable isotope ratio is

$$\delta_{\text{water-PDB}} = \delta_{\text{cal-PDB}} - d$$
, where $d = 2.78 \times 10^6 \times T^{-2} - 3.39$,

T = ambient temperature of a cave site which is assumed constant for all past.

When this rain water percolates in a cave system, drip water is systematically enriched compared to rain water. Hence, to account for that, a positive enrichment factor (ϵ) has to be added, i.e. $\delta_{water-PDB} = \delta_m + \epsilon$

or, $\delta_{\rm m} = \delta_{\rm water-PDB} - \epsilon$, (4-23)

 ε = enrichment factor relating the mean isotopic compositions of monthly rain water to the drip water. This factor is dependent upon the nature of soil and bedrock strata and can be assumed to remain constant for the past periods.

Hence, $R_{an} = F.[(\delta_{cal-PDB} - \epsilon - d) - b]/a$ (4-24)

The above expression directly gives annual rain using δ^{18} O of speleothem. The expression is based on assumption that annual rain and monthly rain are related by definite relation (by equation 4-20) and that it holds true for the past periods. The assumption is relatively valid as compared to the case where no. of rainy days appear in the expression (equation 4-18), which are highly variable and can't be assumed as constant for the past periods.

If annual rainfall associated with the tip part of speleothem is known then the above expression reduces to,

$$R_{an}(x) = (F/a) \cdot (\delta_{cal-PDB}(x) - \delta^{0}_{cal-PDB}) + R^{0}$$
 (4-25)

where, R^0 is the rainfall at the tip part of a speleothem which have oxygen isotopic composition $\delta^0_{cal-PDB}$ and $R_{an}(x)$ and $\delta_{cal-PDB}(x)$ are the annual rainfall and oxygen isotopic composition at the sample depth-x.

4.6.5 δD of water samples

As evaporation occurs at the ocean surface there are several events of rainout and reevaporation before it rains on land. During each event the ¹⁸O and ²H(or D) are fractionated. For worldwide fresh surface waters, Craig (1961) found that δ^{18} O and δ D have linear correlation, the line called meteoric water line:

$$\delta D = 8 \,\delta^{18} O + 10 \,\% \tag{4-26}$$

Later, for the precipitation samples from the stations in the IAEA global network, the average annual values (Rozanski et al 1993) show that,

$$\delta D = 8.13 \ \delta^{18} O + 10.8 \ \% \tag{4-27}$$

This line is known as true global meteoric water line as it is based on true precipitation sample and not from the surface water samples. However, the local meteoric water line (LMWL) may differ in the slope as well as the intercept depending upon the local meteorological conditions. The global meteoric water line is an average of all such regional lines. There are two types of fractionation processes which control the slope and intercept values of such lines. The equilibrium type evaporation or condensation for which the fractionation factor is less for oxygen than hydrogen, the other one is the kinetic effects which has greater effects on the oxygen isotopic ratios.

Slope of the meteoric water line

The slope value close to 8 indicates that it was equilibrium condensation of cloud vapor and there were no subsequent evaporation. The slope is 8 because this is approximately the value produced by equilibrium Rayleigh condensation of rain at about 100% humidity. The value of 8 is also close to the ratio of the equilibrium fractionation factors for H and O isotopes at 25-30°C (Carol and McDonnell 1998; Clark and Fritz 1997; Gonfiantini 1981). Slope reduces to less than 8 due to two processes, 1) primary evaporation controlled by humidity variation (due to diffusion through the water vapor boundary layer) at the ocean surface and 2) secondary evaporation which occurs during arid conditions whereby the evaporation of rain imparts kinetic fractionation (Gonfiantini 1981; Clark and Fritz 1997) to a falling drop. Higher slope (>8) is indicative of exchange of light rain with fast evaporated fresh waters (which have high deuterium excess in accordance with the kinetic effects) to a higher degree than heavy rain (Dansgaard 1964).

Intercept of the global meteoric water line

The intercept value (~10‰) in the global meteoric water line, indicates that the global atmospheric water vapor forms with an average humidity in the vapor source region just greater than 85% and produces precipitation on a line that is displaced from seawater by 10‰ for δD (Gonfiantini 1981; Clark and Fritz 1997). Alternatively, this means that the ocean vapors have evaporated fast enough to give a surplus of deuterium by +10 ‰ (Dansgaard 1964).

For any precipitation sample the deuterium excess (Dansgaard 1964) is defined as:

$$d = \delta D - 8 \delta^{18} O \qquad (4-28)$$

The d values and intercepts become same for $\delta^{18}O = 0$ ‰. Also, the d values are dependent upon the $\delta^{18}O$ if the slope of the LMW line differs from 8. The value of deuterium excess is decided primarily by the humidity conditions in the vapor source region (Clark and Fritz 1997). Secondary evaporation also decreases the deuterium excess and the intercept.

A local line can reflect the origin of the water vapor and subsequent modification by secondary processes of re-evaporation and mixing. In general, following the possible interpretation can be obtained from slope and intercept of local meteoric water line (δD vs. $\delta^{18}O$ line) and d-excess values of precipitation samples, provided there are no mixing with water reservoirs having different isotopic signatures:

Slope:

- = 8, equilibrium condensation of the rain (slow condensation)
- < 8, re-evaporation during rainout
 - or kinetic effects (diffusion process) during vapor formation
- > 8, mixing of light rain with fast evaporated fresh water

Intercept of the LMW line and d-excess of water samples

=10, kinetic fractionation due to \sim 85% humidity condition at the vapor source region

- <10, high humidity (>85%) condition at the vapor source region or secondary evaporation may also reduce it
- >10, less humid (<85%) conditions in the vapor source region.

In Table 4-13, the slope (m) and intercept(c) values in $\delta D=m\delta^{18}O + c$ relationship for various types of water samples is listed.

Rain water from Jharsuguda

The local meteoric water line at Jharsuguda has a slope of 7.65 and intercept 3.37. This shows that equilibrium type condensation occurs during rains and there is a little evaporation during rain. Also, the intercept 3.37 suggests that the vapor source originated (from Bay of Bengal) in high humidity, so that the kinetic evaporation is less (Gonfiantini 1981; Clark and Fritz 1997). In Table (4-16) values of d-excess for each rain sample is listed. The Fig.4-31 shows that the d-excess vs. rain amount for the rain samples collected at Jharsuguda. It is obvious that for small amounts of rain (less than 10mm) there is scatter



Fig. 4-31: *d*-excess for rain water samples; *d*-values scatter for small amount of rain probably due to significant evaporation.

in the d-excess values ranging from -11.54 to 10.18 ‰. This is due to secondary evaporation (kinetic fractionation) of the rain drop during the initial phase of the rain and is

dominant if the rain amount is less. If the rain amount is more, then the ambient high humidity suppresses the secondary evaporation and the d-excess attains a consistent value between ~5 to 6 ‰. The rain water samples have d values ranging from -11.54 to 10.57 ‰. For low rain samples the d values are highly variable. When there is low rain, there is enough chance that the vapors from kinetic evaporation of the local moisture from the land area (which have high d values) will mix up with the vapor source originating from the ocean surface (with low d values). Very negative d values are obtained for the rain water samples (-1.37 and -11.54 ‰) for a very low amount of rain. A possible reason could be the evaporation of the local surface water or moisture in the soils which have very small size. Initial kinetic evaporation of such bodies will lead to vapors with high d values. However, as the water which is left is depleted in the d values due to small reservoir size, subsequent vapors will have d values which will be highly depleted.

Cyclone water samples

The slope (m) and intercept (c) value (Table 4-17) for the cyclone water samples collected at Bhubaneswar (Sect. 1.4) is 7.64 and 3.85 respectively. Hence, the meteoric water line based on the cyclone water samples from Bhubaneswar (initial part of the continent encountered by the vapor mass) matches very well with rain water samples collected at Jharsuguda (inland part of the continent) and can be considered as the representative meteoric water line for the Bay of Bengal branch of the S-W monsoon. The d-excess values for the cyclone water samples are between 9.54 to 11.15‰ (average 10.61‰). These values indicate that during cyclone formation the vapor source region had ~85% humidity level. The differences in the average values of the d-excess of the rain and cyclone water samples may be due to geographical differences and local parameters such as temperature and wind effects also the temporal variations in the humidity in the source region. The duration of rain water collection was 24 hrs. whereas each of the cyclone water samples were collected within 1 hr period. Short term fluctuations in the d values are averaged out in the rain samples.

Dandak cave drip water

The slope is 7.81 and intercept is 5.40 whereas the average d value is 5.86‰. This shows that the Dandak cave water has faithfully recorded the LMW signature (shown by rain and cyclone water) with a little difference in the slope and intercept values which may be due to local geographical factors. Secondary kinetic fractionation is very small.

Table 4-17 : Show	ws values of slopes (n	n) and intercepts	(c) for the best fit	lines ($\delta D = m \delta^{18} O =$	- c) for different
kinds of water sam	ples.				

Samples	m	с	r (correlation	no. of samples
-	(slope)	(intercept)	coefficient)	-
Rain water	7.65±0.33	3.37±2.01	r=0.9805	n=24
Seepage water	7.81±0.78	5.40±1.62	r=0.9533	n=12
Dandak cave				
Seepage water	17.61±0.30	37.2±0.86	r=0.9999	n=3
Kotamsar cave				
Ground water	6.13±0.57	-3.96±2.25	r=0.9451	n=8
(transect-I)				
Surface water	10.7±1.01	15.52±3.89	r=0.9870	n=5
Cyclone water	7.64±0.42	3.85±7.72	r=0.9956	n=5

Variations in the d values of different cave water samples

The d values of each sample collected from different stalactites vary from 4.12 to 7.30 % (Table 4-10). The associated δ^{18} O values vary from -1.61 to -2.08 %. Possible reason could be that the drip water passes through different pathways. Each pathway has different flow rates and input characteristics. In the Fig.4-32, the d value vs. δ^{18} O is plotted for various drip water samples collected from different stalactites and during different periods from the Dandak cave (Table 4-10). In general, it is observed that more depletion in the δ^{18} O values are associated with lesser d values. This is possible if degree of kinetic evaporation (although small) from the unsaturated part of the pathways is different for different fissures. In the case of higher evaporation, the vapor will have higher d values and the leftover water will have less d values.

Ground water from Transect-1

Ground water samples collected for the transect-I have slope 6.13 and intercept – 3.96 (Table 4-17). The LMWL for the sampling site is same as shown by the rain and cyclone water samples as the source of rain water for all the ground water aquifers are the monsoon depressions originating from Bay of Bengal. The slope less than 8 shows that there is a significant evaporation of the ground water. In the unsaturated zone the thickness

of the boundary layer through which diffusion occurs may be quite large compared to surface evaporation and hence evaporation effect is sometimes very dominant bringing the slope down to ~ 2 (Clark and Fritz 1997). However, the slope in this case suggests that



Fig. 4-32: d-excess vs. $\delta^{18}O$ (wrt SMOW) plotted for the seepage water samples collected during different months from DAN.

effects have not occurred to such a high degree which implies that the secondary evaporation is not very high. The average d value is 4.66‰ (Table 4-13) which means that during vapor formation the humidity was quite high, however due to secondary evaporation in the unsaturated zone, the slope has come down to 6.13. The negative intercept (-3.96) could possibly be due to mixing of probably older water (with a negative d value).

Surface waters

Surface waters (from rivers, falls and ponds) collected near caves DAN and GUP have shown a slope of 10.7 and an intercept value of 15.52. The d values range from 7.7 to 2.33‰ for five samples (Table 4-14). The reason could be the local meteorological factors. The surface water samples were collected during the summer monsoon season in September 1999. The no. of samples are small (only 5) and the samples were collected during different days. Apart from kinetic evaporations and mixing effects each surface

water sample may have different precipitation source with different d values (see Table 4-16). Here we see that the depleted δD and $\delta^{18}O$ are associated with low d values and vice versa. This is the reason for the high slope and intercept values. It seems that when there is high amount of rain, due to amount effect low δD and $\delta^{18}O$ values are obtained. In such a case probably the vapor source region has very high humidity and hence low d values. When the rain amount is less, δD and $\delta^{18}O$ are high and the vapor source region has low humidity and consequently high d values.

Kotamsar cave

As the number of samples analyzed for δD are only two (Table 4-12)and hence the nature of the evaporation is not clear for this cave. However, the d values of the two seepage water samples are ~10. This is different from the d values in the DAN (av. value 5.86‰: Table 4-10). The cave water samples were collected during July '99, the month being part of the monsoon season. However, there were not many spells of rain before sample collection day. This means that the rain derived from local convection may have contributed significantly to the cave seepage water and hence has high d value. Water from the surface near the cave area may evaporate fast (kinetic) contributing high d values to the vapor.

$\delta^{18}O$ of water samples collected from the transect-II

For the ground water samples collected for the transect-II, the δ^{18} O vs. distance from the cave area (shown by site no. '23' in the Fig.1-15 (A)) is presented in the Fig.4-33. The δ^{18} O of the ground water samples is a long term average of the regional δ^{18} O of the rain water and also the evaporation effect. The mean δ^{18} O of the rain water collected at Jharsuguda is -8.5‰ (Sect. 4.6.2). However, most of the ground water samples are quite enriched in ¹⁸O. This could be due to evaporation occurring at the ground surface. Except for the site no. '25' (Keshkal, Fig.1-15(A) & Table 4-13) which is very depleted in ¹⁸O (-5.19‰) all other samples have values between -2.5 to -4 ‰ and there is no systematic trend observed with distance. The reason for the depleted values of the δ^{18} O at 'Keshkal' is probably the high altitude (790m. above m.s.l.) due to which the annual temperature is low and hence the average evaporation may be relatively less compared to other places (such as Jagdalpur which is at ~553m above m.s.l.).



Fig.4-33: $\delta^{18}O$ (wrt SMOW) vs. distance from Jagdalpur for various ground water samples collected from places in the transect-II. Exact location shown in the Fig.1-15(A).

Similarly, the for the site no. '24' (Kondagaon, Fig.1-15(A) & Table 4-13) the height is 657 m. above m.s.l., which means relatively low temperature and hence less evaporation which results in to depleted δ^{18} O value (-4.46‰).

Stable isotope data for the ground water samples collected in 1983 from some of the sites in transect-II (e.g. Bhopal and Dahod) have been reported earlier by Bhattacharya et al (1985). Their δ^{18} O values for the Bhopal and Dahod are -2.4‰ and -2.9‰ respectively For these sites the values obtained in the present work is given in the Table 4-13 (-2.8‰ and -2.9‰, respectively). The values are in reasonable agreement.

4.7 Comparison with other records

4.7.1 Comparison with the tree/varve data

a) Tree ring indices have been available recently reported by Bhattacharyya and Yadav (1999) from southern India. Around 1660 AD, tree ring width indices shows a very high value, which coincides with the highly depleted δ^{18} O signal around 1666 AD in AKG (Fig.4-15).

b) High resolution (comparable with the speleothems; i.e. -1yr to -15 yr) climatic record from Indian landmass spanning last 3400 yrs is not available other than ours. Recently, a high resolution (~7yr) record has been reconstructed by von Rad et al (1999), using thickness variation in the varved sediments collected from the west of Karachi (northeastern Arabian Sea, off Pakistan). Monsoon reconstruction from varved sediments and GUP has been compared below. According to von Rad et al (1999) precipitation and hence, river run off are assumed to control varve thickness. The precipitation at the sampling site (von Rad et. al 1999) is contributed both during summer monsoon (June-Sept: from south-west monsoonal currents) and winter monsoon (Nov to March: linked to storms in the Mediterranean sea). These derive alternatively dark and light colored sediment sequences which form an annual couplet. The precipitation may have fluctuated (Lückge et. al 2001) due to variations in the extreme positions of the ITCZ (inter-tropical convergence zone) and hence, the variability in varve thickness was interpreted as a proxy for past rainfall variations. The figure showing thickness variation of the varve sediments is presented in the Fig.4-34. The thickness diagram from von Rad et al (1999) paper was first scanned and then the peak heights were read using image analysis software. Stable isotope analysis of Gupteswar stalactite has a different time resolution in different periods (Table 4-18). The varve thickness data shown by von Rad et al (1999) is a 7 point moving average of annual thickness data and hence our data values were smoothed out by using appropriate running mean during different time periods (Table 4-18). Fig.4-34 shows comparison of varve thickness data and rainfall reconstructed from the Gupteswar stalactite. Following are the observations:

1) From 0-1000 yr BP: The initial trends are quite similar. Later during 500 to 1000 yr BP there is an opposite trend in both records. The stalactite shows high rainfall around 600 yr BP whereas thickness data shows low rainfall. Pollen records from different lakes in Rajasthan (Singh et al 1974; Bryson and Swain 1981; Swain et al 1983) show high monsoon rainfall similar to our observations. Nitrogen content which is an indicator of marine productivity is strongly related to the upwelling of the surface water. If it can be used as a proxy of past rainfall, the recently reconstructed data from the Indian coastal area in the Arabian sea for the last 1kyr from a ocean sediment core (unpublished data), shows a reduced level of productivity and hence a low level of rainfall around 600yr. These observations suggest that the Arabian branch of the S-W



Fig. 4-34: Comparison of rainfall record from the GUP and the varve sediments from east Arabian sea (von Rad et al 1999).

monsoon (source of rain for coastal India and Pakistan) was subdued whereas the Bay branch was active during 600 yr BP. A possible mechanism can be envisaged where by the extreme ITCZ positions either moves north-east or north-west wards. This may cause weakening of the Arabian sea branch and strengthening of the Bay of Bengal branch and *vice versa*.

2) From 1000 to 2000 yr BP speleothem shows arid condition with two high arid durations around 1700 and 2000 yr BP. The varve data show increasing trend of rainfall

Table 4-18: Time resolution in the rainfall record from Gupteswar stalactite and varve thickness record from von Rad et al.,1999. Appropriate running means have been calculated to make the time resolutions to same level.

Period	Rainfall record from Gupteswar		Varve thickness recor al,1999	rd from von Rad et.
	Time resolution(yr)	Running mean applied	Time resolution(yr)	Running mean applied
0-2920	13.36	-none-	7	2pt.
2920-2980	0.45	16pt.	7	-none-
2980-3400	3	2pt.	7	-none-

starting at 1000 yr BP and then after attaining high values again decreases with sharp low rainfall events around 1900 and 2000 yr BP. The low thickness event during 2000

yr BP is also shown by our rainfall reconstruction. Lückge et. al (2001) have recently reported lowest Ti/Al ratio (terrigenous origin) in the same core during this period.

3) From 2000 to 3400 yr BP: The trends of increasing rainfall is very similar in both the records.

Correlation of rainfall at Karachi with other stations in tropical India:

The extent to which similarity is expected in the rainfall reconstruction from GUP and varved sediment data can be judged based on the similarity in the present day rainfall record (instrumental observations). Correlation coefficients (r) between rainfall time series at Karachi and some of other stations given in the Table 4-19. The annual rainfall record of different stations has been downloaded from CDIAC's (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, USA) anonymous FTP area (ftp://cdiac.esd.ornl.gov/pub/tr051) via the internet.

It is obvious from values of 'r' given in the Table 4-19 that the present day annual rainfall at Karachi and Jagdalpur are not correlated. When 6 pt. running mean (Dandak stable isotope samples cover ~6yr time span) is applied to annual rainfall data then it results in to significant correlation (0.347). However, for the 14 pt. running mean (Gupteswar S.I. samples between modern to 2900 yr BP cover ~14 yr time span) the 'r' becomes insignificant. Annual rainfall at most of other stations do not correlate significantly with the Karachi rainfall (Table 4-19).

Stations	Correlation (r) with the Karachi rainfall	Period / no. of data points (n).
Calcutta	+ 0.006	1856-1969/ (108)
(22.34N 88.24E)	+ 0.201 (6 pt. mov. Av.)	
	+ 0.191 (14 pt. mov. Av.)	
Jagdalpur	+0.002	1910-1969 / (57)
(19.05N 82.04E)	+ 0.347 (for 6 pt. mov. Av.)	
	+ 0.248 (for 14 pt. mov. Av.)	
Madras (13.04N 80.17E)	-0.095	1856-1969 / (108)
Mangalore (12.52N 74.53E)	+0.081	1856-1969 / (102)
Bangalore (12.58N 77.38E)	+0.130	1856-1969 / (107)
New Delhi	+0.263	1856 - 1969 / (91)
(28.38N 77.12E)		
Bombay	+ 0.323	1856-1969 / (108)
(18.55N 72.54E)	+0.069 (6pt. run. Av.)	
	-0.142 (14 pt. run. Av.)	
Ahmedabad	+0.432	1869-1969 / (97)
(23.03N 72.40E)		

Table 4-19: Correlation of annual rainfall at Karachi with other stations in tropical India. Correlation coefficients (r) significant at 0.05 level are shown by bold numbers.

For, Ahmedabad, Bombay and New Delhi the rainfall at Karachi correlates significantly, but with low 'r' values. The reason could be the relative proximity of the locations (within ~1100km) compared to east west stations. It is clear that the rainfall variation occurring at the cave site (Jagdalpur) and at the varve sediment site (Karachi, von Rad et al 1999) are different in the present period. However, as there are similarities in the rainfall reconstruction in different time periods, it suggests that an overall weakening or strengthening of the S-W monsoon would have contributed to such changes in the cave and varve sites during the past. The variations in some periods are not similar, which may be due to regional fluctuations in the extreme positions of the ITCZ.

4.7.2 Comparison with meteorological data

Based on the statistical analysis of annual rainfall data available for the period 1871-1994 from different rain gauge stations, the Indian landmass area has been divided in to five homogeneous regions and 29 meteorological subdivisions (Parthasarathy et al 1995). Summer monsoon rainfall time series for each subdivision is the average (district area used as weight) of the rainfall from different stations. The rainfall time series is limited only up to 1871 AD when observations from rain gauge stations started.

The most recent part of the rainfall reconstruction has been compared below with the rainfall time series of nearby stations or the corresponding subdivisions to check for similarities in the variations.

GUP and DAN

These caves are located in the Jagdalpur district which is part of subdivision 20 (East Madhya Pradesh, now Chattisgarh, Fig.1-2). In Fig.4-35 the δ^{18} O of GUP and DAN is compared with the rainfall time series of Jagdalpur. The age is shown relative to the 1996 AD which is the year of sample collection and is represented by the stable isotope subsample at the tip of the sample. Sample resolution is better in the DAN cave (~6yr) compared with the GUP (~14 yr). Also, the sampling frequency is more in the DAN (every ~17yr) than GUP (~40 yr). Therefore, variations in the rainfall will be better reconstructed by the DAN. In Fig.4-35 the possible similarities are shown by the arrows marked by 'A' and 'B'. In Fig.4-36, the δ^{18} O of GUP and DAN is compared with the annual rainfall of the subdivision-20. The variations in the δ^{18} O and rainfall are not very similar, except some possible associations marked by arrows in Fig.4-36. This shows that the cave oxygen isotope record of GUP/DAN is a reasonably good proxy for only the low frequency variations in the local rainfall.

SOT

Sota cave is part of subdivision-10 (East Uttar Pradesh, Fig.1-2). As each stable isotope subsample in SOT is equivalent to ~5yr. time span, in the Fig.4-37, 5 pt. running mean of the annual rainfall time series for the subdivision-10 is compared with the δ^{18} O data of the SOT. The age is shown before 1997 which is the year when the SOT was collected. A possible association is marked by the arrows 'A', 'B' & 'C'. A very enriched value in δ^{18} O may be due to very low rain phase (shown by 'B'). As the SOT site is also near to the subdivisions 20 and 11, their rainfall time series is also presented in Fig.4-37 with possible association of the low rainfall periods marked by arrows. It is clear from Fig.4-37 that some of the rainfall events indicated by the δ^{18} O levels of the SOT had occurred on a wider scale (shown by subdivisions 10, 20 & 19, Fig.1-2).

AKG

Akalagavi cave is located very near to the boundaries of the subdivisions-31 (coastal Karnataka, Fig.1-2) and subdivision-32 (north Karnataka, Fig.1-2). In the Fig.4-38, comparison between δ^{18} O and annual rainfall of the subdivision-31 & 32 is presented. Some of the prominent rainfall events experienced in the subdivision-31 & 32 can be associated with the δ^{18} Ovalues (marked by lines in Fig.4-38). Akalagavi cave is within the western Ghat sections which have heights between 500 to 1000m. The rainfall pattern depends upon the orography of any location. The rainfall on the western Ghats facing the coast is very high as shown by the average rain of the subdivision -31 whereas the other side experiences less rainfall (shown by comparatively less rain in the subdivision-32). Variations in the rainfall events observed in the two subdivisions may not have the same magnitude. Only changes which are commonly experienced in the two subdivisions with significant magnitude have a high possibility to be seen by the AKG reconstructed record. This has been shown by the fact that the low and high rainfall years observed in the all India rainfall time series (which means that such events were observed in most of the subdivisions) are registered in the AKG (Sect.4.3.4).



Year before 1996

Fig.4-35: $\delta^{18}O$ of GUP/DAN is compared with the rain gauge record of the Jagdalpur. In the x-axis chronology is shown in years before 1996 (year assigned to the tip surface). Black, red and green lines show yearly, 6 point running mean and 14 point running mean data for appropriate comparison with the GUP (~14 yr time span) and DAN (~6yr time span). Arrows indicate possible associations.



Fig. 4-36: Possible association of the $\delta^{18}O$ of GUP/DAN with the rainfall time series of sdiv-20 which includes the cave site. Red and black lines are for the 6pt. and 14 point running means of the yearly rainfall data. Years are given in before 1996.



Fig.4-37: Possible association of the $\delta^{18}O$ of SOT with rainfall time series of subdivs-10, 19 and 20. Years are given in before 1997 (tip age).



Fig. 4-38: Possible association of the $\delta^{18}O$ of AKG with the rainfall time series of the sdivs-31 and 32 is shown by dark guiding lines. Years are given as before 1996 (age of the first compact layer).

Correlation: AKG rainfall reconstruction and rainfall time series of sdiv-31

Stable isotope sampling in AKG has been carried out possibly from each distinct layer; hence, the resolution of stable isotope measurements is very near to annual and it gives an opportunity to compare annual rainfall and stable isotope values. Annual rainfall data available (Parthasarathy et al 1995) for the sdiv-31 ranges from 1871 to 1994 (123 yr duration). However, there are only 102 stable isotope subsamples during this time interval. This is because some of the subsamples cover more than one layer when layers are very thin (smaller than the drill bit diameter; see Fig.4-13(A)). In order to find the correlation coefficient, the rainfall data from sdiv-31 has been compressed (to make same no. of data points) by taking average of rainfall for those years which correspond to single stable isotope measurements. After appropriate corrections the correlation coefficient (r) is found to be -0.15 (n=89) which is insignificant. However, when a running mean is applied to the data, then 'r' attains negative but significant low value. The magnitude of 'r' increases with the size of the moving average (see the Table 4-20). As one yearly correlation coefficient is insignificant, probably the yearly rainfall was different in the cave compared to the subdivision-31. Insignificant correlation may also be due to the fact that some of the thin layers were missed during the measurement of the number of layers and their thickness (see Sect. 4.3.2). This might had introduced unpredictable errors (by few years) in the chronology of the δ^{18} O and , therefore, the cross correlation will give 'r' value which may not be meaningful. But, as the 'r' increases with the size of the moving average, this means

Table 4-20: Correlation coefficient between for the rainfall of subdivision-31 and AKG reconstruction (n=89). Bold numbers are significant at 0.05 level.

corr. coeff.(r)	Size of moving average
-0.15	1
-0.23	2
-0.30	3
-0.35	4
-0.38	5
-0.44	6
-0.65	10

that the rainfall and δ^{18} O are significantly correlated for variations more than two years. Slow changes in the cave and subdivision-31 are highly correlated (Table 4-20). Comparison of the speleothem rainfall reconstruction with the regional rainfall time series suggests that δ^{18} O of cave deposits are very good proxies of the local rainfall.

4.7.3 Comparison with the historical famine years

History of famines in India from 298 BC have been compiled by Srivastva (1968). Several years of famine were observed due to mainly lack of enough rain. Other factors for famine were high rainfall leading to floods and purely man-made such as wars, trade-depressions, heavy taxation and financial crisis. The famine years due to deficient rain observed in the recent periods are fairly accurately recorded. The failure of rainfall in large parts of country is occasionally observed (e.g. failure of S-W monsoon in 1899 AD), otherwise, it occurred only in small parts of the country. Therefore, speleothems located in different parts will show <u>low</u> rainfall events only for those events which occurred in the respective cave areas.

GUP/DAN

In the area covering GUP/DAN locations, several low rainfall years in the 19th century leading to famine have been reported (Srivastva 1968). Some of them are 1832-1834, 1854, 1865-1867, 1868-1870. Enriched levels of δ^{18} O which occurred around 150 yrs. before 1996 (Fig.4-11) may coincide with these low rainfall events. Around 298 BC (2248 BP) there was a low rainfall event for 12 years which caused famine in Bihar (eastern India). The same event might have appeared even in the GUP, however, not mentioned in the history, probably due to lack of civilization in the cave area, being very dense forest even in the present period. Considering the ¹⁴C age errors and assumption of constant dead carbon contribution, this may coincide with the low rainfall event around 2000 yr BP (Fig.4-11).

SOT

Several years of rainfall failure are reported from the SOT cave area. In the Fig.4-20, events marked by 'A', 'B', 'C' and 'D' are compared with the meteorological data and are discussed in the Sect. 4.4. The other events marked by 'E', 'F', 'G' and 'H' may coincide with the famine years AD 1860-61, 1837-38, 1555-56 and 1326-27 respectively. In the SOT reconstruction during 400 to 200 yr BP, average rainfall is high, whereas such a high rainfall is not observed in GUP and DAN (see Fig.4-27). This is a major difference between reconstruction of SOT and GUP/DAN. During AD 1641, historical records

(Srivastva 1968) have shown heavy rainfall in Kashmir and in Punjab during 1646 AD, which caused famine in these regions, whereas at other places such heavy rainfall event is not reported. It means that during this period the northern part of India and, therefore, possibly SOT were having a comparatively wetter phase than GUP/DAN. This could have been caused by the extreme position of the ITCZ that remained stationary or relatively farther from the cave area during this period. Between ~900 to ~400 yr BP rainfall in the SOT and GUP/DAN increased at ~600 yr BP. During this period not many famine events are recorded in the historical documents. Between 900 yr BP (1050 AD) to 400 BP (1550 AD) i.e. within 500 yr duration, ~7 famine years due to low rainfall have occurred. Whereas, after 1550 to 1920 (i.e. 370 yr) more than 30 low rainfall events scattered over various parts in the country are observed. If the historical documentation is believed to be complete and reliable then this means that the earlier duration i.e. 900 to 400 was comparatively wetter, as observed in the speleothem based reconstruction.

KAR

Low rainfall year 'DR7' shown in the AKG rainfall reconstruction (Fig.4-15) correlates with the severe famine year which appeared in the north western provinces during 1783. There are other low rainfall events marked by DR 1-7 in the earlier periods. In the historical records these events are not mentioned. As AKG has shown to record the extreme deficient and excess rainfall years observed in all India rainfall it can be inferred that DR1-7 were moderate low rainfall years which did not bring out severe famine but were experienced by many subdivisions. It can be concluded that the AKG is sensitive to the local rainfall conditions. Being very near to the coastal area, AKG will face all primary changes (weakening or strengthening) in the S-W monsoon. Hence, ER1-4 and DR1-8 (Fig.4-15) are the events which are definitely local (size of the subdivision-31) and with high possibility they occurred at large scale (large part of the country).

4.8 Mineralogy of speleothems

Inorganic precipitation of carbonate and aragonite under controlled laboratory conditions has shown that the oxygen in aragonite is isotopically enriched compared to calcite by 0.6‰ at 25°C (Tarutani et al 1969) whereas the carbon isotopes are enriched by 1.8‰ at 25°C (Rubinson and Clayton 1969). This means that more ¹⁸O and ¹³C gets

incorporated in the aragonite compared with the calcite. All the speleothem samples were analyzed for the mineralogy i.e. if they are calcite (hexagonal CaCO₃) or aragonite (orthorhombic CaCO₃) or mixture of both. The aim is to 1) observe if there is any climatic link with the mineralogy, 2) if there is mixture of the aragonite and calcite then appropriate correction to the δ values (oxygen and carbon both) should be applied. This is necessary as there may be under or overestimation of past rainfall.

With an aim to find out any relation between δ^{18} O (hence climate) and mineralogy, samples of speleothems were analyzed from parts where most depleted and enriched isotope values are obtained.

Two samples for XRD analysis were taken from AKG, one from the base part where δ^{18} O is most depleted (~1666 AD, Fig.4-15) and another from the part where δ^{18} O shows enriched values (~1900 AD, Fig.4-15).

Two samples for XRD analysis were prepared from SOT, one from the part where δ^{18} O is very depleted (between ~600 to 800 yr BP, Fig.4-20) and another from the part where most enriched value of δ^{18} O is obtained (i.e. near tip part; ~1950 AD, Fig.4-20).

Similarly, from DAN speleothem powder was taken from three spots where there are large variations in the δ^{18} O and δ^{13} C (Fig.4-39). Results are listed in the Table 4-15. DAN and SOTA are found to be pure calcite. The two samples from AKG (position shown in the Fig.3-2(c)) show that there is 96.4 to 98.5 % aragonite. Two samples from GUP taken from zones of extreme value of δ^{18} O shows large variations in the % of aragonite and hence more samples were checked for mineralogy in GUP. Later it showed quite a large amount of change in the % aragonite from ~7 to 98% (Fig.4-40 and Table 4-21). Summary of the results are given in the Table 4-22.

4.8.1 Stable isotopes and aragonite percentage

Correction required in a mixture of calcite and aragonite

The annual rain is either depleted or enriched depending upon the amount of precipitation, the depletion rate assumed is 1.5 % for 100mm increase in the monthly rain (Sect. 4.2.1, 4.3.4, 4.4.2 & 4.6.2). The same depletion rate has been assumed to hold in the seepage or drip water and also in the speleothem δ 180. If the speleothem is pure calcite or pure aragonite then by applying the same depletion rate (1.5%/100mm) rainfall can be



Fig. 4-39: XRD sample location for the DAN. Samples were selected from layers showing extreme values of $\delta^{18}O$ and $\delta^{13}C$.



Fig. 4-40: XRD sample location for GUP. Samples were selected from layers showing extreme values of $\delta^{18}O$ and $\delta^{13}C$.

Sample	Depth (mm)	Depth (mm) % Aragonite Corrections required		red
			(* for pure aragor	nite)
			$\delta^{18}O(\%)_{PDB}$	δ^{13} C(‰) _{PDB}
GUP	16.25	79.61	0.44	1.31
	134.38	40.57	0.25	0.74
	171.63	7.48	0.08	0.25
	191.50	92.43	0.52	1.55
	347.75	88.44	0.50	1.49
	373.75	91.23	0.49	1.46
	398.75	98.07	0.56	1.67
	483.50	23.64	0.22	0.67
DAN	26.25	0.0	0.0	0.0
	118.13	0.0	0.0	0.0
	298.75	0.0	0.0	0.0
AKG	-	96.44	0.02*	0.06*
	-	98.53	0.01*	0.03*
SOTA	-	0.0	0.0	0.0
	-	0.0	0.0	0.0

Table 4-21: shows amount of aragonite and the appropriate corrections required.

Table 4-22: Summary of mineral studies for different speleothems.

Sample	Mineral type	Present day pH of drip water.
Gupteswar stalactite (GUP)	 a) Mixture of calcite and aragonite (7.5 to 98.0%). a) possible relation with stable isotopes. b) variation found with depth. (n=8) 	8.0
Dandak stalagmite (DAN)	 a) pure calcite c) no relation with stable isotopes. b) no variation with depth (n=3) 	7.4
Akalagavi stalagmite (AKG)	 a) 98% aragonite. b) no variation found with depth (n=2) 	Not available
Sota stalactite (SOTA)	 a) pure calcite b) no variation with depth (n=2) 	Not available

reconstructed. However, if speleothem is a mixture of both calcite and aragonite then the speleothem delta value will be a weighted mean of calcite-delta and aragonitedelta. In the case of pure calcite precipitation, if due to environmental changes the crystal structure partially switches over to aragonite then there will be an enrichment in the delta value depending upon the % of aragonite. In such a situation there will be an under estimation of the rainfall. This can be accounted by decreasing the delta values by an amount proportional to the % of aragonite. Thus a speleothem with a mixture of calcite and aragonite will be treated as an equivalent calcite speleothem.

For the small amount of calcite present in the AKG the amount of correction in δ^{18} O and δ^{13} C is insignificant (Table 4-21). Due to this reason no correction to the stable isotope profiles in the AKG sample was applied.

Corrections in the GUP sample (assuming to be pure calcite) are significant (Table 4-21). The magnitude of corrections in δ^{18} O and δ^{13} C for the eight XRD samples for GUP is shown in the Fig.4-41. Effect of correction will be reduction of enrichment levels. This means that the magnitude of fluctuations in the δ^{18} O and δ^{13} C will reduce. Maximum correction in the δ^{18} O would be 0.6‰ (for occurrence of 100% aragonite). This is equivalent to 226mm of correction in the rain amount (as $\Delta Pa = -378.08*\Delta\delta^{18}$ O; equation 4-11), which is the maximum limit of reduction in the magnitude of fluctuations in the rainfall reconstruction (Fig.4-11). The important fact is that even by applying maximum corrections to the rainfall reconstruction (Fig.4-11) the variations remain still quite large. This shows that the rainfall reconstruction from GUP (Fig.4-11) is likely genuine.

Aragonite percentage

In Fig.4-42 (S.I. and % aragonite) the δ^{18} O and δ^{13} C values of the subsamples and % of aragonite is presented for the GUP. It is observed from the plot that most of the relatively enriched δ^{18} O and δ^{13} C values coincide with high % of aragonite. It has been observed that the enriched δ^{18} O and δ^{13} C levels are indicative of less rainfall , which suggests that during reduced rainfall conditions aragonite formation is preferred. However, our data points are only a few, and in order to understand the process, high resolution XRD measurements are required. The question arises that 1) what controls aragonite formation so that in GUP and AKG mixture of calcite and aragonite is found and in other caves (DAN and SOTA) pure calcite is found ? ; 2) why % of aragonite and S.I values are related (Fig.4-42)?. Given and Wilkinson (1985), based on the occurrences of various types of sedimentary carbonates found in different kinds of environmental settings have indicated the kinetics of surface nucleation and the rates of reactants, principally carbonate ions at the growth site decides the mineralogy. They find that aragonite precipitation is favored



Fig.4-41: Amount of corrections (equal to the rectangle height) required in the $\delta^{18}O$ and $\delta^{13}C$ if the GUP is assumed to be pure calcite.



Fig. 4-42: $\delta^{18}O$ and $\delta^{13}C$ vs. % aragonite for GUP. Clustering of the values show possible relation between the parameters.

when rates of reactant supply (CO₃⁻⁻), are high; calcite is formed when rates are low. Crystallization of calcium carbonate under controlled conditions also shows that crystal formation depends upon availability of carbonate ions (Fernandez-Diaz et al 1996). It is found that the mineral composition of calcium carbonate is influenced by the precipitation rate. The growth rate of a precipitation depends directly on the super-saturation of the drip water with respect to the dissolved CaCO₃. Different rates of CO₃⁻²⁻ supply means different degree of super-saturation. Higher degree of super-saturation favors aragonite precipitation. Mg/Ca ratios also decides the mineral structure (Given and Wilkinson 1985; Fernandez-Diaz et al 1996). Presence of Mg affects the crystallization in two ways (Fernandez-Diaz et al 1996): it affects the nucleation kinetics and it disturbs crystal growth. Higher degree of super-saturation is achieved in the presence of Mg , in such a case aragonite is precipitated. More the ratio, aragonite occurrence is favored.

What is realized is that lower degree of super-saturation (low supply of $CO_3^{2^2}$, low Mg content, slow growth rate) favors calcite precipitation. In the case of speleothem formation, this can be achieved when the soil pCO₂ is relatively high, due to which HCO3⁻ ions are more than the $CO_3^{2^2}$ ions. The supply of $CO_3^{2^2}$ is less and conversion of HCO₃. to $CO_3^{2^2}$ ions is involved before Ca^{2^+} and $CO_3^{2^-}$ ions are precipitated. The carbonate precipitation is favorably calcite. This may happen in caves such as Dandak and Sota where soil thickness seems to be more (bedrock thickness is relatively less in Sota cave) due to which soil pCO₂ could be very high and the resulting alkalinity of the drip water might be less. Aragonite precipitation may occur where $CO_3^{2^-}$ supply is more, such as high alkalinity drip water which may originate when the soil pCO₂ is relatively less due to low soil thickness and size of the pathways (fissures) decide the drip rate in the caves whereas the soil thickness will decide the pCO₂ level. There are other factors as well, which may alter the pCO₂ level, such as vegetation activity, water availability, climate etc.

Speleothems having alternate layers of calcite and aragonite have been reported by Railsback et al (1994). The aragonite layer is found to occur during drier conditions when due to seasonal temperature rise Mg/Ca increases. Also, when there is evaporation of water the solution is more saturated which increases the carbonate precipitation rate, enhancing the supply of carbonate ions. Subsequently, this also favors aragonite precipitation.

Speleothem from Nepal (Deninston et al 2000) has shown calcite and aragonite occurrence controlled by changes in the monsoon precipitation.

Based on the observation that the carbonate ion supply is one of the factors which controls the mineralogy, a process can be speculated for the caves studied to explain their mineralogy. The carbonate ion concentration in the seepage water depends primarily upon the pCO_2 level of the soil zone. If the soil thickness is more then the vegetation activity will be more (in humid climate) and this will give high pCO₂ conditions. In the caves such as DAN and SOTA (although shallow, but soil thickness seems to be more) the pCO₂ is expected to be high and hence, the concentration of the CO_3^{2-} is relatively less (Drever 1997); this might favor calcite precipitation. Whereas, the caves such as AKG and GUP with relatively less soil thickness, resulting in less of pCO₂, might favor aragonite formation. In AKG it is more than 96% aragonite. We don't have pCO₂ of the soil and their thickness data; however, the speculation can be checked by actually measuring the pCO₂ level in the soils and their thickness for these caves. For the two caves DAN and GUP the pH of the modern drip water was measured (using both a pH paper and electronic portable hand held pH meter) during the summer season of 2000. It was found that the DAN (pure calcite) has pH=7.4 which means less CO_3^{2-1} ions concentration, whereas GUP (mixture of calcite and aragonite) has pH 8.0 or relatively more CO_3^{2-} ion concentration. This difference in the modern pH level of the drip waters supports the explanation that the CO_3^{2-} ion supply decides the mineral composition.

Climate control on the mineral composition

Stable isotopes (δ^{18} O) are controlled by the water availability proportional to the rain amount. Mineral type which has been explained to be controlled by CO₃²⁻supply (proportional to the pCO₂ level in the soil) is also indirectly controlled by the rain amount. If the rain is enhanced then it will lead to more vegetation activity this will increase the pCO₂ level and hence calcite precipitation will be favored. If the rainfall is reduced then arid conditions will reduce the vegetation activity and hence the pCO₂ level, favoring aragonite precipitation.

4.9 Trace elements in speleothems

The seepage water contains dissolved organic compounds and several ions at trace levels (Gascoyne 1983; Goede 1994). While calcite is precipitated they are

incorporated in the speleothem. As their chemical properties are similar and ionic radii are comparable (Table 4-23), substitution of Ca^{++} ion is possible in the growing speleothem (Tesoriero and Pankow 1996).

ELEMENT	IONIC RADIUS A° (M ⁺⁺)
Mg	0.72
Ca	1.00
Sr	1.16
Ba	1.36
Cd	0.95
Mn	0.67
Со	0.65

Table 4-23: Several divalent ions and their radii from Rimstidt et al. 1998.

As ionic radius of Mg is (0.72A°) less than that of Ca (1.00 A°), it is very likely to be substituted for Ca in the calcite lattice. Also, being smaller in size, the temperature increase may raise the rate of diffusion. This may enhance the substitution of Ca by Mg in the calcite precipitated. Sr and Ba have larger but comparable radii relative to the Ca ion and hence non-lattice substitution may be possible for them (Tesoriero and Pankow 1996). These effects should be observed in controlled laboratory experiments and also in natural calcite samples.

A summary of trace metals in speleothems and their temperature dependence is given by Gascoyne (1983). Following are the main sources of contribution of TE (trace elements) in cave seepage water .

1) The bedrock will contribute mainly to TE content in the seepage water during dissolution process. It is expected that the contribution from bedrock will remain constant over a large period of time unless seepage water pathways have changed in the course of time.

2) Dissolved organic complexes are also a source of TE. This dissolved organic material originate from different kinds of vegetation in the overlying soil zone

Presence of trace elements in speleothem calcite may be due to the following processes.

1) Drip water may contain particulate material which is trapped during calcite formation.

2) TE may be adsorbed on the growing surface of the calcite.

3) Direct substitution of the Ca^{++} by trace elements.

Speleothems free from particulate materials will incorporate TE by processes no. 2 and 3. Adsorption process is expected to be temperature dependent and increase in temperature should result in less adsorption. At the same time the diffusion process will enhance substitution for the Ca^{++} ion (process no.3). For a pure substitution process degree of incorporation is defined (Gascoyne 1983) as

k=[conc. of TE in solid phase]/[conc. of TE in co-existing liquid phase]

For a very dilute and infinite volume system the homogeneous distribution coefficient is defined as

(4-29)

D_{TE}=[TE/Ca]_{solid}/[TE/Ca]_{liquid}

Because free energies may differ in different phases the D_{TE} may be temperature dependent. This property can be utilized for palaeo-temperature reconstruction.

Although the real solution may not be dilute and the TE ions precipitated in calcite may not be insignificant compared to ions in leftover seepage water, activity term should be used for the concentration. In reality the heterogeneous distribution coefficient will obviously differ from D_{TE} .

But, for simplicity it is assumed that the seepage water is a dilute system and the amount of precipitated calcite is insignificant compared to the ionic content of the coexisting liquid and hence, properties of TE are considered only in terms of D_{TE} .

4.9.1 Causes of variations

During the deposition of calcite TE concentration may vary because of the temperature dependence of D_{TE} . Changed water pathways may also contribute to the different TE/Ca ratio. Varying residence time of seepage water in the soil and bedrock will change the degree of saturation and hence calcite TE/Ca. It seems that the residence time of seepage water in overlying strata affects the concentration of trace elements. Generally, dolomites have lower Sr and Ba compared to calcite. Also, they dissolve slowly compared to calcite. Increased residence time of water in bedrock strata will dissolve more of dolomites. However, varying TE/Ca of the seepage water may interfere with the temperature induced component.

4.9.2 Application of trace elements in speleothems

Behavior of trace elements in cave deposits and their potential in palaeoclimate is still under investigation and this is an expanding geochemical field. Only a little work is reported in the literature and so far the Indian speleothems have not been studied.

Gascoyne (1983) measured TE/Ca ratio in modern seepage water and calcite deposited in different caves which had different ambient temperatures. It was found that the Mg/Ca ratio in speleothems deposited at different temperatures are correlated with ambient temperature of a cave. Between temperatures ranging from 7 to 24° C , D_{Mg} = +0.0017/ °C. Also, D_{Mg} has not shown any clear dependency on the seepage water conditions i.e. different Mg/Ca ratios. In the same study the D_{Sr} was found not to have any clearly observed temperature dependency, although it showed sensitivity to the seepage water conditions. Based on such observations it was proposed that Mg and Sr concentrations could be utilized for past temperature reconstruction.

Four elements Mg, Sr, Ba and Br among thirteen studied in a speleothem by Goede and Vogel (1991) were shown to be potential palaeoclimatic indicators.

Further work on a fossil flowstone deposit from Ingleborough cave, northern England (Gascoyne 1992) showed no correlation between trends in δ^{18} O and Mg content, possibly as the Mg in the feed water content varied in the past.

Magnesium content showed significant correlation with $\delta^{13}C$ and little correlation with $\delta^{18}O$ in a study on stalagmite from Tasmania by Goede (1994). In the same study Sr content and $\delta^{18}O$ showed significant correlation and virtually no correlation with $\delta^{13}C$. It was suggested that the Mg content in speleothems may not be suitable for palaeotemperature reconstruction.

High resolution analysis by SIMS (secondary ionization mass spectrometry) on a Holocene stalagmite from Tartair cave in north-west Scotland (Roberts et al 1998) reveals annual cyclically in the Mg/Ca, Sr/Ca and Ba/Ca. High frequency oscillations show anti correlations between Mg/Ca and Sr/Ca and positive correlation between Sr/Ca and Ba/Ca. Investigations of Sr and Mg in the speleothems from GB cave, UK suggests that Sr is more useful environmental proxy compared to Mg (Roberts et al 1998). At micron scale trace elements (Sr and Ba) have been investigated by SIMS in a speleothem from Southern Africa and the chemical complexities have been explored at small levels (Finch et al 2001).
Behavior of Mg, Sr and Ba in marine environment

Oxygen isotopes and Mg/Ca in marine organisms such as bivalve mollusks and corals have been used to infer palaeo-temperature and Sr/Ca for palaeosalinity during their growth (Klein et al 1996a). For ocean water, palaeotemperature is derived from skeletal δ^{18} O, provided δ^{18} O of precipitating fluid is known. If an assumption of constant δ^{18} O of ocean water is made then the temperature reconstruction is inconsistent with those obtained using Mg/Ca variations. Lowest (depleted) δ^{18} O is possible during summer (oxygen will be more enriched at lower temperatures as fractionation will be more at reduced temperature due to temperature dependent calcite-water fractionation factor) or when the salinity is low. High δ^{18} O values are indicative of low temperatures or increased salinity. The inverse follows for Mg/Ca ratio, high ratio is associated with increased temperature and low with reduced temperature. Mg/Ca ratio is relatively insensitive to salinity variations. Empirically Mg/Ca ratio is calibrated to sea-water temperature (Chivas et al1986, Klein et. al, 1996a). Sr/Ca ratio in the skeleton varies with salinity and can be used as an accurate proxy of sea-water salinity (Klein 1996b). Salinity effect on δ^{18} O of palaeo ocean water can be removed by using empirical relation of Sr/Ca and salinity. Thus accurate temperature reconstruction is possible using Mg/Ca and Sr/Ca ratio.

Mg content of benthic foraminifera is primarily controlled by temperature (Rosenthal et al 1997). The overall variation in Mg/Ca is more than expected by inorganic precipitation experiments and thermodynamic considerations. The additional fluctuation is derived by temperature related physiological processes. As there are large intergenic and interspecific differences both in planktonic and benthic foraminifera, only using a singlespecies calibration may yield the best precision for seawater palaeothermometry. Exponential relation between temperature and Mg/Ca ratio and application to thermocline palaeo-oceanography is discussed by Rosenthal et al 1997. Strontium distribution coefficient is negatively correlated with temperature by thermodynamic considerations. But, the only data of inorganic precipitation experiments (Katz et al 1972) shows negligible effect of temperature on the distribution coefficient of Sr in calcite. In some of the foraminiferal shells (e.g. ocean wide *Cibicidoides*) there is a linear decrease of Sr/Ca with depth with no correlation with temperature. Probably, pressure related effects control the Sr content which needs further investigation. Whereas in H. elegans there is positive covariance between Sr/Ca and temperature. This in contrast to corals (Beck et al 1992; De

Villiers et al 1995) and inorganic precipitation experiments. Probably depth dependent factors other than temperature are playing the roll.

Calcareous skeleton is secreted as the corals grow and trace elements are partitioned from the ambient sea water depending upon the environmental condition, physiology and incorporating mechanisms. In Corals Sr/Ca ratio has been found to vary inversely with temperature changes (Beck et al 1992; De Villers et al 1995). REE elements are incorporated in the coral in proportion to the sea water concentrations. REE/Ca can be used as proxy of the river water discharge in tropical regions which can be correlated to past rainfall, climatic variation etc. (Sholkovitz and Shen 1995). B/Ca, Mg/Ca, Sr/Ca and U/Ca have been found to be correlated with the SST whereas Ba/Ca is not found to show any temperature dependence in corals (Sinclair et al 1998). However, detailed studies on coral aragonite at micron scale measurements have shown that there is very variable trace element distributions even at micron scales measurements (Allison 1996; Hart and Cohen 1996). These suggest that the growth and incorporation of TE in such materials may be complex and it is necessary to understand at finer scales and also investigate samples from different environments.

4.9.3 Mg, Sr and Ba concentration variations in DAN

The Mg, Sr and Ba concentrations with depth from tip to base part are shown in Fig.4-43 (A, B and C). During the growth period more than 100% fluctuation is observed in the TE concentration. The overall uncertainty in the concentration value is 10%. The δ^{18} O and δ^{13} C taken from section (4.2) is shown in the Fig.4-43 (D and E) respectively.

a) Correlations between different parameters

To see any similarity in the behavior of trace elements and stable isotopes, correlation coefficients between different parameters are calculated The amplitude of variations in trace element content is more than 100% compared to the present level (Fig.4-43). To suppress high frequency components a, five-pt. moving average was taken. As the central points of the sampling spots for stable isotopes (Sect.4.2) and trace elements are at about 20 yr intervals, this moving average will yield components of 100 yr period and above. High frequency (less than 100 yr) components are obtained by



Fig.4-43: Trace elements Mg, Sr and Ba along with the $\delta^{18}O$ and $\delta^{13}C$ for the DAN.

subtracting smoothed data from the originals. Correlation coefficients for the high and low (bold numbers) frequency components are given in Table 4-24.

Table 4-24: Correlation coefficients significant at 0.05 level are listed for low (bold font) and high (normal font) frequency variations for different parameters (for the last \sim 1200 yrs). Bold numbers within brackets are for data points smoothened by a 10 pt. moving average. (The diagonals have a correlation coefficient of unity and are not shown)

	Mg	Sr	Ва	$\delta^{18}O$	$\delta^{13}C$
Mg			0.27		
Sr	0.73 (0.88)		0.83		
Ba	0.75 (0.85)	0.92 (0.93)			
$\delta^{18}O$	-0.27 (-0.28)	(-0.38)	-0.25 (-0.41)		0.45
$\delta^{13}C$	-0.73 (-0.75)	-0.43 (-0.65)	-0.53 (-0.71)	0.72 (0.75)	

b) Low frequency changes

At low frequencies, changes are brought out by slowly varying precipitation. This is confirmed by the values of correlation coefficient for different pairs discussed later, between $\delta^{13}C$ and Mg it is -0.73, between $\delta^{13}C$ and Sr it is 0.43 and between $\delta^{13}C$ and Ba it is -0.53 (correlations significant at 0.05 level, after adjusting for autocorrelations). Correlation coefficients for Mg and Sr is 0.73, between Mg and Ba is 0.75 and Ba and Sr it is 0.92. As D_{Mg} depends only on temperature whereas D_{Ba} and D_{Sr} are dependent on source conditions and not on temperature, the Sr and Ba contents are significantly correlated. Oxygen isotopic composition may vary with temperature and amount of rainfall. There is a weak negative correlation between $\delta^{18}O$ and concentrations of trace elements. For $\delta^{18}O$ and Mg, r is -0.27, with Ba it is -0.25. No significant correlation between TE and $\delta^{18}O$ and $\delta^{13}C$ are proportional to the mean concentration of an element (Table 4-24). This could be due to some kind of concentration dependent geochemical process.

c) High frequency changes

The linear correlation coefficient between Mg and Ba concentrations is 0.27. Sr and Ba are significantly (r = 0.83) correlated . Oxygen and carbon isotope ratios have positive significant positive correlation (r=0.45). For other pairs r is insignificant.

d) Better correlation between $\delta^{13}C$ and TE as compared to $\delta^{18}O$

As measurements of TE and SI were made on different samples, although with very little spatial separation, correlation coefficient (r) for changes occurring at ~6yr time span (resolution of SI sampling in the DAN sample) could not be assessed. Fast changes (> ~6yr and <100yrs) in δ^{18} O and δ^{13} C have r=0.45. This improves for slower changes (>100yrs, r = 0.72). A further smoothing of the data by a 10 pt. moving average results in to better correlation in the 'r' values (Table 4-24). A possible reason for such improvement could be that there are soil organic compounds that degrade slowly. Due to this any change in the rainfall will not affect the C3/C4 ratio immediately and hence the δ^{13} C. The older components may continue to contribute to the soil CO₂ by virtue of bacterial decomposition. This kind of memory effect (of older climate) damps fast changes in δ^{13} C due to rainfall fluctuations and it subsides in due coarse of time. Therefore, fast changes in the rainfall is reflected in δ^{18} O but may not be seen in the δ^{13} C resulting in to less 'r' value.

It has been found that δ^{18} O in speleothem varies with the rainfall (due to amount effect) and thus δ^{18} O can be used as proxy of the past rainfall. Any other parameter which is significantly correlated with speleothem δ^{18} O shows that one of the effective controlling parameter for them is the rainfall. In the Table 4-24, 'r' values for the 10 point moving average data which is equivalent to suppressing any variation less than 200 year period are shown (by bold numbers in the bracket). It is seen that TE and δ^{13} C are highly correlated whereas δ^{18} O and TE are relatively less (but significantly) correlated. This suggests that δ^{13} C and TE have more common systematics in a cave system. The question arises that why δ^{13} C and TE are more strongly correlated than δ^{18} O, when the controlling factor is common? A possible explanation is given below:

Increase in annual rainfall results in an increased drip rate in a cave. Soil pCO₂ is also found to enhance due to increase in the vegetation activity as water is more abundant. High pCO₂ is also observed to be associated with depletion of δ^{13} C levels (Hesterberg and Siegenthlaer 1991). As the precipitation rate increases the TE incorporation into growing carbonates is also intensified. TE are mainly contributed from the dissolution of the bedrock. However, dissolved organic complexes may also contribute to the TE. Whenever there is high water availability the pCO₂ increases and also the bacterial decomposition of organic material which may contribute more to the TE in the seepage water and hence to the speleothem. These processes may cause a high correlation between δ^{13} C and TE.

Significant negative 'r' value (although, relatively lower) between $\delta^{18}O$ and TE are again due to rainfall dependence. During monsoon season no. of rainy days are found to vary widely (e.g. for Jagdalpur 61 to 110, between 1910 to 1950 AD (Climatological Tables 1970). Large no. of rain spells each with low rainfall amount (hence enriched $\delta^{18}O$) may also result in enriched $\delta^{18}O$, depleted $\delta^{13}C$ and increased TE for high annual rainfall. Also, less no. of rain spells with high rainfall amount (hence depleted $\delta^{18}O$) may contribute depleted $\delta^{18}O$, enriched $\delta^{13}C$ and less TE in the seepage water with low rainfall. Such opposite behavior of $\delta^{18}O$ with $\delta^{13}C$ and TE may be the natural variability and is expected in the monsoon system. This may also be the reason for less 'r' values between $\delta^{18}O$ and TE. This may also be the cause for less 'r' between $\delta^{18}O$ and $\delta^{13}C$ (r=0.45 for slow changes, however, if rainfall is the dominant controlling factor then 'r' should be very high i.e. near unity). This puts forward a possibility that if there are no internal changes in the pathways and bedrocks then $\delta^{13}C$ and TE are more sensitive rainfall proxies than $\delta^{18}O$ in tropical caves, although the quantification of this relationship is more difficult.

4.9.4 Temperature reconstruction

In Fig.4-44 ratios of Mg/Sr, Mg/Ba and Ba/Sr are shown. It is clear that the Ba/Sr has remained essentially constant during growth of stalagmite. This proves that the bedrock constituents and seepage water pathways have not changed significantly during growth except a changed Ba/Sr ratio around 3450 yrBP (Fig.4-44) for which the reason is not clear. Hence, it can be argued that Mg/Ca in seepage water remained constant throughout the growth period and all the variations (Fig.4-44 (A, B and C)) are derived due to past environmental changes.

We do not have the value of present day (Mg/Ca)_{water} of the Dandak cave. Its value is estimated by taking D_{Mg} at 25°C from Gascoyne (1983) and using present day (Mg/Ca)_{calcite} value of the tip part of the Dandak stalagmite. Using $\Delta D_{Mg}/\Delta T = 0.0017$, from Gascoyne (1983), the estimated change in Mg concentration in calcite deposited for 1 °C change in ambient cave temperature is 173.4 ppm (Table 4-25). We have further used this value for the temperature reconstruction.

Reference	$\Delta D_{Mg} / \Delta T$	$\Delta Mg/\Delta T$
1-Katz, 1973	0.0009	91.8
2-Gascoyne, 1983*	0.0017	173.4
3-Oomori et al. 1987	0.007	71.4
4-Mucci, 1987	0.00042	42.8
5-Burton and Walter, 1991	0.00043	43.9

Table 4-25: Temperature and D_{Mg} relations obtained from inorganic calcite precipitation experiments (nos. 1, 3, 4 and 5) and from cave systems (no. 2). Third column represents estimated $\Delta Mg/\Delta T$ (ppm / °C).

* Derived from cave seepage water, speleothems and ambient cave temperature.

Annual average temperature for the cave area is 25° C and Mg. conc. for the tip part is 1955.5ppm. Cave temperature T(t) was reconstructed by assuming that all variations in Mg concentration are due to solely temperature (Fig.4-45)

T(t)=25+[Mg(t)-1955.5]/173.4

(4-30)

Part of large variations in Mg, Sr and Ba concentrations have originated presumably due to changes in rainfall above the cave area. Concentration of trace elements in dripping water is constant as shown by consistent ratio of Ba/Sr (Fig.4-44). The drip rate varies with the amount of water available in the seepage zone or bedrock which essentially is directly related to the amount of rainfall above cave area. The original Mg data is a resultant of both past temperature and rainfall variation above the cave area . As D_{Ba} and D_{Sr} depend primarily on source conditions and not on the temperature variations (Gascoyne 1983 and Roberts et al 1998) their past changes are expected due solely to rainfall fluctuations. To decouple the two we have taken the modern value of Mg/Sr=11.6956 and Mg/Sr=3.7376 at 25°C from tip part and reconstructed the Mg profile Mg_{Sr} and Mg_{Ba} from past Sr and Ba data. Mg_{Sr} and Mg_{Ba} represent purely temperature induced variations in Mg concentration.

$Mg_{Sr}(t)=Mg(t) - Sr(t) \times 11.6956$	(4-31)
$Mg_{Ba}(t)=Mg(t) - Ba(t) \ge 3.7376$	(4-32)

Temperatures reconstructed from Mg_{Sr} and Mg_{Ba} are also shown in Fig.4-45. Table 4-25 shows wide uncertainty in the estimated $\Delta D_{Mg}/\Delta T$ from a cave system and inorganic precipitation experiments. Considering different $\Delta D_{Mg}/\Delta T$ values given, change in speleothem Mg content for 1°C change in ambient cave temperature varies from 173.4 to 42.8 ppm (see Table 4-25).



Fig.4-44: Variations in the ratio of trace elements along the growth direction in DAN sample.



Fig.4-45: Temperature reconstruction using Mg and Mg amount corrected for the source variation by Sr and Ba.

4.9.5 Effect of environmental changes

a) Temperature fluctuation

Partitioning of Mg between water and calcite is found to be temperature dependent and experimental studies have attempted to quantify this temperature dependence (Table 4-25). Sr and Ba incorporation is found to be temperature independent (Katz et al. 1972; Mucci and Morse 1990; Roberts et al 1998). Temperature reconstruction based on Mg concentration variation have given unrealistic amplitudes (up to 40° C, Fig.4-45) in the past fluctuations. But global temperatures for last 2000 yr have not changed more than 0.5°C from the present level (Briffa and Osborn 1999). However, temperature could be indirectly involved in controlling the partitioning of trace elements as suggested bv Roberts et al. 1998. As temperature increases D_{Mg} increases raising Mg concentration in calcite subsequently precipitated. Temperature also increases the calcite precipitation rate and hence indirectly increases the D_{Sr} and D_{Ba} (Roberts et al 1998) raising Ba and Sr. This is observed in our data indicating high correlations between slow changes in Mg, Sr and Ba (Table 4-24). Hence, it can be conclude that part of the fluctuations experienced are due to past temperature changes.

b) Effect of rainfall amount

Stable isotopes

Rate of dripping is directly related to the annual intensity of rainfall in the karst area. Stable isotopes of C and concentration of trace elements are affected by the dripping rate. δ^{13} C of calcite precipitated from a single droplet is found to be a function of time: with time, loss of CO₂ increases, which will continuously enrich the calcite (in δ^{13} C), precipitated in isotopic equilibrium with the ionic species. This follows Rayleigh type loss (Dulinski and Rozanski 1990). Oxygen isotopes in the calcite will not be affected with time as ionic species remaining in the drop immediately exchange with oxygen of bulk H₂O. However, δ^{18} O is depleted as amount of rainfall increases, an effect observed in many regions and called amount effect (e.g. Bar-Matthews et al 1996).

Trace elements

Concentration of trace elements are also function of time. Calcite precipitation rate increases due to enhanced rainfall. This leads to increase in D_{Sr} and D_{Ba} (Lorens 1981; Tesoriero and Pankow 1996). Hence, the successive calcite lot will have more Ba/Ca and Sr/Ca ratio. Calcite precipitation rate dependence of $Cd^{2+}(0.95A^{\circ})$, $Mn^{2+}(0.67A^{\circ})$ and $Co^{2+}(0.65A^{\circ})$ all having lower effective ionic radii compared with Ca^{2+} , have shown inverse relations in the inorganic precipitation experiments (Lorens 1981 and Tesoriero and Pankow 1996). A review of factors affecting Mg^{2+} partitioning when calcite is precipitated from sea water is given by Hartley and Mucci (1996). The literature is abundant but frequently marked by controversy. The Mg^{2+} partitioning is found to be independent of calcite precipitation rate from the sea water (Mucci and Morse 1983). But, as seen in the Table 4-24 slow changes in the Mg, Sr and Ba have high correlations which means that behavior of Mg is very similar to Sr and Ba when calcite precipitation rate is changing in a cave system. Presumably, the sea water based results where high concentrations of elements are involved is not applicable to seepage water -calcite system in a cave.

Recently, Rimstidt et al (1998) have proposed that both set of divalent ions, having larger and smaller radii compared with Ca and with equilibrium distribution coefficients $D_{TE} < 1$ (e.g. for Mg, Sr and Ba) are affected by the calcite precipitation rate in the same way. It has been shown that due to the kinetics related processes occurring at the solutioncalcite boundary, the distribution coefficient D_{TE} measured for such divalent ions in an experiment are systematically increased by increasing calcite precipitation rate. This means that distribution coefficients of Mg should also increase with increasing calcite precipitation rate in a cave system similar to Sr and Ba.

In the light of such observations it can be inferred that

(1) only part of the changes in the trace element and stable isotope data are due to temperature fluctuations, major changes are due to the amount of water received by the surface area.

(2) changes in δ^{18} O of speleothem are due to the amount effect.

(3) change in δ^{13} C , Mg, Sr and Ba are derived by fluctuating drip rate inside the cave which is indirectly related to the rainfall above the cave.

The following explanation of the cave data can be given. When rainfall received by the catchment area increases, the dripping rate from the fissures increases, this also increases

calcite precipitation rate. Each drop will stay for shorter period of time, on the tip of an actively growing speleothem as it is splashed away by a new drop. The δ^{13} C of the calcite depletes due to Rayleigh type loss (Dulinski and Rozanski 1990), while Mg, Sr and Ba concentration increases due to increased D_{TE}. Increase in the rainfall is also shown by depletion trend in the δ^{13} C and δ^{18} O data (Fig.4-43). When rainfall decreases, dripping rate is reduced. The drop stays for longer period of time, speleothem will have more enriched δ^{13} C and less of Mg/Ca, Ba/Ca and Sr/Ca ratios. The δ^{18} O and δ^{13} C and reduced Mg/Ca, Ba/Ca and Sr/Ca.

All these processes leads to significant correlation between slow changes in Mg, Sr , Ba, δ^{18} O and δ^{13} C as shown by bold numbers in the Table 4-24.

c) Effect of residence time on trace element concentrations

The residence time of seepage water in overlying strata affects concentration of trace elements. Generally, dolomites have lower Sr and Ba compared to calcite but higher Mg content. Also, they dissolve slowly compared to calcite and hence saturation with respect to calcite or dolomite is a time dependent process. Increased residence time of water in bedrock strata will dissolve more of dolomites. (Roberts et al. 1998). If residence time is affecting the trace element concentrations then the Ba and Sr together should show inverse correlations with Mg concentration data. This is not observed in our study hence we rule out the possibility of differential calcite / dolomite dissolution to be playing any role.

4.9.6 Rainfall reconstruction

As the temperature reconstruction is unrealistic and considering the significant correlation coefficients of the slow changes among all the parameters studied we infer that major changes in TE concentration are driven by the past rainfall variations. Based on characteristic changes in Mg, Sr and Ba and δ^{18} O and δ^{13} C compared in Fig.4-43 (A , B, C, D and E) the deposit can be divided in to five different zones (Fig.4-43).

Period 3700 to 3350 yr BP: Arid phase

Growth of speleothem originated at ~3700 yr BP when rainfall was comparatively lower than present level as Sr, Ba and Mg contents are all low. High aridity makes δ^{13} C 186

enriched due to reduced rate of dripping in cave environment and due to increased abundance of C₄ type plants. δ^{18} O is enriched due to amount effect.

Period 3350 - 3200 yrBP : High rainfall

Rainfall started increasing from 3350 yr BP as Mg, Sr and Ba all have increasing trend. δ^{13} C is having depletion trend due to 'Rayleigh Distillation' loss of CO₂ and increasing C₃ type plant abundance. The change in δ^{18} O is ~1%₀ which is equivalent to increase of 378mm of rain per year.

This high rainfall phase presumably, disturbed the inlet of water into the cave and at about 3200 yr BP, the stalagmite experienced a formation break in growth. The high flow conditions might have eventually filled the seepage path and due to choking the dripping stopped. The hiatus layer is associated with fine clay particles which supports this argument.

1200 to 400 Yr BP : Increasing trend in the rainfall

Between this period rainfall was high with peak values around 650 yr BP. This is indicated by increasing trends in Mg, Sr and Ba concentrations and depletion trends in δ^{18} O and δ^{13} C, all attain peak levels around 650 yr BP. Already existing aridity during this period is confirmed. In the Gupteswar cave, humid phase starts around 1.2ka. Probably, the Dandak stalagmite formation restarted due to increased precipitation ~1200 yr BP. The δ^{18} O shows high precipitation around this period due to amount effect.

400 yr BP to present day : Short arid and enhanced rainfall events.

After a little enhanced rainfall phase around 200 yr BP again low rainfall event near 90 yr BP is observed.

Through this study it is observed that both changes in temperature and rainfall affect the stable isotopes and trace element concentration in the same way. However, the temperature induced component is very little and major variations are derived by fluctuating intensity of the past rainfall. This study has shown that trace elements can be used for understand high resolution hydrological changes in the karstic area. Further calibration studies in a cave environment and laboratory experiments are required for quantitative assessment of precipitation record.

Summary, conclusions and suggestions for research

5.1 Summary

The summary of results from radiocarbon dating of speleothems, $\delta^{18}O$ and $\delta^{13}C$ analysis of speleothems, $\delta^{18}O$ and δD analysis of rain water, seepage water and ground water samples is given below:

- i) Assuming a constant dead carbon contribution from parent bedrock throughout the past, ages have been assigned to each speleothem. Longest duration (0-3400) yr BP is shown by the stalactite (GUP) from the Gupteswar cave. Growth of Dandak stalagmite (DAN) started at ~3700 yr BP and continued up to 3200 yr BP. After a hiatus of ~2000 yr, the growth again started from ~1200 yr BP and continued till the present. Akalagavi (AKG) stalagmite is a unique deposit as growth layers are distinctly observed. Radiocarbon activity at the tip and at the base support the annual nature of the distinct layers. The chronology to the AKG is based on the counting of annual layers (total ~330). Sota stalactite (SOT) covers last ~1100 yr duration and dilution due to dead carbon is found to be negligible (D~1). It is found that if the thickness of the roof (bedrock + soil) is higher, then the dissolution of limestone is of closed system type. Radiocarbon dilution factors in the speleothems from Gupteswar, Dandak and Akalagavi is estimated to be 13.8, 10.0 & 1.4% respectively.
- Hendy's test suggests that samples DAN, GUP, AKG and SOT have been deposited under isotopic equilibrium. Therefore, it is likely that there is stable isotope systematics controlled by the ambient climate.
- iii) Large variations (>1.5‰) in δ^{18} O of samples GUP and DAN along the growth direction are seen. If only temperature variation is assumed to have caused δ^{18} O changes in these speleothems, then the estimation of the palaeo temperature results in unrealistic amplitudes (up to 7⁰C). Using the relation between δ^{18} O of monthly rain and its amount, observed at tropical island stations (which is -1.5‰ depleted per 100m increase in the rain), speleothem δ^{18} O values have been transformed to amount of rainfall, resulting in the reconstruction of the rainfall history of the cave

area. The longest high resolution rainfall reconstruction up to last ~3400 years is obtained from GUP. DAN and GUP have similar δ^{18} O variations for the 0-1200 yr BP period. This indicates that: 1) ¹⁴C dates are reasonably valid; 2) δ^{18} O is influenced by the common atmospheric forcing factors e.g. rainfall and temperature.

- iv) Large variations in δ^{18} O (2.5‰) are observed in the AKG sample. Depletion and enrichment peaks coincide respectively with the excess and deficient rain years observed in the all India rainfall time series. Biennial average of δ^{18} O and rainfall time series of the subdivision-31 (near the cave) are significantly correlated. The increasing trend in rainfall during 1901-75 A.D. is shown by δ^{18} O of the AKG sample. Around 1666 AD high rainfall is indicated by the highly depleted ¹⁸O signal. Prior to 1850 AD, average δ^{18} O is relatively lighter compared to the values after 1850 AD, indicating the prevalence of generally low rainfall. Several deficient and excess rainfall events are shown by the AKG for the period before 1813 A.D., for which rain-gauge records are not available. These may represent excess and deficient rainfall years for the all India rainfall, in all probability.
- v) More than 2‰ variations in the δ^{18} O is seen in the SOT sample. The most depleted δ^{18} O is observed within the recent past near around 1960 A.D., coinciding with the low rainfall observed around 1965 A.D. by the nearby meteorological subdivisions 10, 20 & 19. Rainfall reconstruction is similar to what is shown by GUP/DAN for the 1000 to ~ 400 yr BP period. Between 400 to 200 yrs it shows higher rainfall unlike the GUP/DAN samples. Kinetic fractionations are observed in the modern straw samples (from Sota cave) resulting in wide ranges in δ^{18} O and δ^{13} C values.
- vi) Speleothem δ^{18} O is found to be primarily controlled by the δ^{18} O of the local precipitation. This is observed from the tip δ^{18} O values of each speleothem. Between GUP and DAN there is only a minor difference as the rain water source is the same. Whereas the SOT sample differs significantly from the DAN/GUP samples as the source of rain water is quite depleted (due to the continental effect).
- vii) Rain water samples collected during 1999 A.D. monsoon period manifests the amount effect. The observed depletion rate ($-2.2 \pm 0.8\%$ / 100mm) agrees very well with the globally observed depletion rate ($-1.5 \pm 0.2\%$ / 100mm). As the number of monthly data points in our data set are only three, the global depletion rate has been used for the rainfall reconstruction.

- viii) There is a systematic evaporation during precipitation, and the degree of evaporation is site dependent. It gives a characteristic δ^{18} O value to the seepage water. This characteristic value is presumed to vary with the change in the annual rainfall and it is assumed that the depletion rate observed in the rain water is also applicable to the δ^{18} O of speleothem carbonates. Validity of the assumption is supported by the fact that for the AKG sample during the recent period there is a good correlation between speleothem δ^{18} O and annual rain in the cave area. Pixel values and thickness can be used as broad indicators of the past rainfall condition in the AKG site.
- ix) The slope of the local meteoric water line (LMW in δD $\delta^{18}O$ plot) near the cave area has been observed to be 7.65 ± 0.33. Seepage water from the DAN cave has signatures very similar to the LMW line. It means that kinetic fractionation is very small and evaporation in the cave soil pores is very slow (hence of equilibrium type) but significant. Seepage waters are generally found to be relatively more enriched compared to the river and ground waters nearby.
- x) A significant correlation between δ^{18} O and δ^{13} C (for all the speleothems) indicates that the drip rate inside the cave controls the δ^{13} C value of the speleothem carbonate. Hence, it is the rainfall which dominantly controls even the δ^{13} C variations. Average δ^{13} C values are found to be dependent upon the thickness of cave roof and it is further modulated by the varying drip rates caused by overhead rainfall variations.
- xi) Due to Rayleigh type carbonate precipitation δ^{13} C of DIC (Dissolved Inorganic Carbon) in a drip water sample (from DAN) is found to be more enriched than the expected value suggesting that drip rate is the effective factor controlling δ^{13} C of the speleothem.
- xii) Continental effect is observed in the speleothem δ^{18} O values and the observed depletion rate due to this effect agrees well with the values obtained from earlier studies on ground water from this region. Cyclone precipitation is found to be the most depleted due to continuous distillation during its formation and movement over the sea surface.
- xiii) DAN and SOT samples are found to have a rather pure calcite structure, AKG samples has a high aragonite content (96%) whereas GUP samples is a mixture of

aragonite (7 to 98%) and calcite. The percentage of aragonite is observed to be more when δ^{18} O and δ^{13} C are relatively enriched. It is inferred that due to fluctuations in the pCO₂ level (rainfall dependent) decides the mineralogy of the speleothem.

- xiv) Trace element (TE, such as Mg, Sr and Ba) concentrations have been measured in the DAN sample to separate temperature and rainfall effects on the speleothem δ^{18} O. Palaeo temperature reconstruction may result in unrealistic high values (up to 40°C). Due to the dependence of trace element distribution coefficient on the calcite precipitation rate, TE incorporation in the speleothem is found to be dominantly controlled by the amount of rainfall. The low frequency components of stable isotope and TE are significantly correlated indicating rainfall to be the controlling factor. TE variations are better correlated with δ^{13} C than with δ^{18} O. Significant correlation (for the low frequency component) with δ^{18} O of Mg, Sr and Ba suggests that the TE changes (>100 yr) are mainly due to the variation in the rainfall. The possibility of a small temperature contribution to these variations cannot be ruled out. Rainfall reconstruction from TE (more rainfall indicates more TE) is qualitative and agrees well with the rainfall reconstruction using the δ^{18} O of the DAN sample.
- xv) Comparison of rainfall reconstruction with the local meteorological data shows that the DAN sample has recorded some of the high and low rainfall events observed at the nearest meteorological station. The SOT sample also shows high and low rainfall events observed in the corresponding subdivision rainfall time series. The AKG sample also shows a high correlation with the associated subdivision rainfall time series (biennial average).
- xvi) Some of the low rainfall years recorded as famine years in the historical documents can be linked to the low rainfall periods inferred from the speleothem data.
- xvii) Based on the behaviour of δ^{18} O, δ^{13} C and concentration of trace elements, the following rainfall conditions are inferred during the past,
 - 3400-2900 yr BP: high rainfall (from GUP)
 - 2900-1200 yr BP: low rainfall with events indicating very low rain (from GUP).
 - 1200-0 yr BP: rainfall high compared to previous periods with the highest level around 600 yr BP (from GUP, DAN and SOT).

- 400 yr to 200 yr BP: high rainfall (from SOT).
- High rainfall around 1666 AD by AKG.

Rainfall reconstruction from speleothems agrees well with the earlier observations using other proxies e.g.1) Before ~1200 yr BP arid phase is indicated by the GUP, which is observed by the sediment cores in the western Arabian sea (Naidu, 1996). 2) Sharp (~14 yr time span) arid events observed around 2000 yr BP may have been due to large scale weakening of S-W monsoon system as similar events are observed in the varved sediments collected from northeastern Arabian sea (von Rad et al 1999). High rainfall during ~1666 AD by AKG agrees with the tree-ring width index (Bhattacharyya and Yadav 1999) around this period.

5.2 Conclusions

The potential of speleothems as climate proxy has been investigated for the first time in India. Several caves in Madhya Pradesh, Karnataka and Orissa were explored and appropriate samples were collected to assess their potential for climate reconstruction. So far, four speleothem samples from different caves have been analyzed for variations in the ratios of stable isotopes of oxygen (δ^{18} O) and carbon (δ^{13} C). The amplitude of δ^{18} O and δ^{13} C variations are quite large and is likely to be primarily controlled by past rainfall. Contribution from past temperature variations seems to be relatively small. Amount effect in rainfall has been quantified by analyzing rainwater samples collected during the monsoon season. Assuming that the variations in the δ^{18} O of cave carbonates are solely due to the past variations in rainfall, history of the latter has been reconstructed from each cave area. The longest, high resolution, rainfall reconstruction up to the last ~3400 year is now available from Gupteswar cave, Orissa. The δ^{18} O in annual layers of a speleothem from Karnataka is found to retain the yearly excess and deficient rainfall signals which coincide very well with the all-India rainfall time series. It is observed that in a tropical speleothem δ^{13} C is dominantly controlled by the drip rate of the seepage water.

Some of the elements like Mg, Sr and Ba have properties similar to Ca and are found in speleothems in trace amounts and their occurrence is known to be dependent on the specific cave environment. Concentration of these elements measured in one of the speleothems has indicated the dominant control of rainfall on the incorporation of these elements while the speleothem grew. Mineral composition (calcite / aragonite) is observed to be related to past rainfall conditions, as well as to the pH of cave waters. Cave seepage waters were collected during different months to study monthly variations. It is observed that rain water δ^{18} O is systematically enriched and attains a characteristic δ^{18} O value which is dependent upon the amount of rainfall. Also monthly variations are small. The δ D measurements of water samples have further helped in understanding the evaporation occurring in the cave system. Comparison of the rainfall reconstruction with the nearest rain gauge data, indicates reasonable similarity. Based on the behaviour of δ^{18} O, δ^{13} C and concentration of trace elements, past rainfall has been reconstructed.

The study has shown that tropical speleothems faithfully record the annual rainfall in the cave site.

5.3 Scope for the future work

- In the present study, the chronology is based on ¹⁴C dating assuming constant dead carbon contribution in the past from the bedrock. Although this has given a fairly good chronological control over last ~1000 year for DAN and GUP, they should be confirmed using U-Th (TIMS) dating method. SOT ages are also based on the assumption of zero dilution from bedrock, therefore, U-Th dating (TIMS) is required for this sample. Fluorescent patterns and possibility of their use for the chronology is yet to be assessed.
- Data in this study is sufficient to conclude that the speleothems within tropical parts of India are a good proxy for past rainfall. Further study of caves in other geographical locations are required to understand the spatial distribution of past rainfall and its variation with time.
- 3. Stable isotope and trace element studies on the same sample is necessary to understand high frequency variations in δ¹⁸O, δ¹³C and TE. TE studies on GUP, SOT and AKG may be carried out to establish that their variation is dominantly controlled by rainfall. Also, TE studies in AKG may help to understand annual and even subannual (using SIMS) changes in the TE. More work is required to understand why δ¹³C is better correlated with δ¹³C than δ¹⁸O.

- 4. Periodic sampling of the seepage water, rain water above the same cave, pCO_2 variations and CO_2 sampling in the soil zone over a few years will give very good understanding of the $\delta^{18}O$, δD and $\delta^{13}C$ systematics.
- 5. Soil thickness and pH of the seepage water can be studied in detail to establish the exact cause for the variations in the mineralogy.
- 6. Fluid inclusions are yet to be studied in these speleothems. It may help in providing the past δD variations. As there is amount effect in the δD , it may work as an additional rainfall proxy.

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