Chapter 1 Introduction

1.1 Introduction

Climate of the earth is continuously changing due to natural as well as anthropogenic reasons. For predicting future climate, it is imperative to know how climate changed in the past, especially during the past few centuries. Even though limited-span instrumental climate records are available, they are restricted to a few places and cover relatively a short period of time (e.g. about 100 years). Dearth of high resolution climatic data for longer periods necessitates finding proxies for the past climate.

Terrestrial proxies available for climate reconstruction are ice cores, lake sediments, corals, speleothems and tree rings. Among these, tree-rings have specific advantages: they have a wide geographic distribution, are annually resolved, show a continuous record, and are easily dated by ring-counting. Seasonality in the growth rate of trees driven by seasonality in the climatic factors can result in well-defined annual growth rings in trees. Individual tree-rings faithfully record contemporary climatic signatures hence provide an opportunity to decipher the variation in climatic parameters for a duration equivalent to the life-span of the tree. Using a technique called cross-dating, a procedure of matching ring patterns among trees and wood fragments in a given area (Fritz, 1976), it has been possible to stretch back tree ring record for thousands of years. Leuschner et al., (2002) and Spurk et al., (2002), for example, have constructed a tree ring record extending more than 8000 years. In the early years, only the width of the rings was used for climate reconstruction; wider (narrower) ring denoting higher (lower) temperature/precipitation. However, this simple relationship between width and climate is complicated by a variety of non-climatic factors (Fritz, 1976). For example, the site specific factors such as topography, soil type, forest thinning and ecological parameters like pest/insect infestations on trees can modify the climate- ring-width relationship. Isotopic composition (e.g., $\delta^{18}O$) of tree cellulose is believed to be less influenced by biological and ecological parameters in relation to ring-widths and can be used effectively in climate reconstruction. It has been shown by previous studies (Schiegl, 1974; Gray and Thompson, 1976; Epstein and Yapp, 1977; Burk and Stuiver, 1981;

Ramesh et al., 1985; Edwards et al., 1985; Lipp et al., 1991; Feng and Epstein, 1994) that isotopic record of oxygen and hydrogen from individual tree-rings can be successfully used as proxies to decipher climatic parameters such as rainfall, humidity and temperature.

1.2 Tropics and Teak (*Tectona grandis*)

Tropical area appears to play a crucial role in global climate through El Niño-Southern Oscillation (ENSO), a coupled atmospheric-ocean phenomenon affecting climate of tropical, subtropical and mid-latitude areas (Diaz and Markgraf Eds. 2000). In India, the relationship between ENSO and monsoonal rainfall has been established (Pant and Parthasarathy, 1981; Krishna Kumar et al., 1995). Limited time span covered by instrumental rainfall record demands finding proxies to understand past variations in ENSO. Corals have been used to reconstruct past variation in ENSO (Cole et al., 1993 and 2000; Tudhope et al., 2001). Tree rings provide excellent terrestrial archives for the past variation in ENSO related rainfall (Stahle et al., 1998; D'Arrigo et al., 2005, Christie et al., 2008). As there is no pronounced seasonality in temperature, a factor responsible for growth rings in temperate regions (Fritts, 1976), tropical trees rarely exhibit well developed annual growth rings. Nevertheless, seasonality in precipitation and relative humidity in some tropical areas does result in the development of annual growth rings in a few species. Teak is one such species with reliable growth rings and is distributed throughout tropical Asia, parts of Africa and Latin America. Several regional chronologies have been developed using teak trees (e.g. Berlage, 1931; Pumijumnong et al., 1995; Borgaonkar et al., 2007; Buckley et al., 2007).

1.3 Oxygen isotopes in tree cellulose

Stable isotope ratios of carbon ($\delta^{13}C$), hydrogen (δD) and oxygen ($\delta^{18}O$) in tree rings have been used to get information about past climate. Although $\delta^{13}C$ of the tree rings have been used to understand past variations in $\delta^{13}C$ of atmospheric CO_2 and climatic parameters such as temperature and relative humidity, its interpretation is complicated by variety of environmental effects. These effects include juvenile effect (rings corresponding to the early years of growth are depleted in ^{13}C as they ingest ^{13}C depleted CO_2 released by respiration of other plants and soil, and the degradation of organic matter) and pollution/anthropogenic effect (tree rings since the industrial era, i.e. from around AD 1850 are progressively depleted in ^{13}C due to introduction of ^{13}C depleted CO_2 in the atmosphere produced by fossil fuel burning, and a plant's response to increasing CO_2 concentration in atmosphere; also known as the 'Suess Effect'. In addition, different levels of solar radiance and nutrients available to plants, and water stress cause variations in $\delta^{13}C$ around the circumference of a ring (intra-ring variation, Francey and Farquhar, 1982). $\delta^{18}O$ of tree cellulose, on the contrary, is directly related to the oxygen isotopic ratio of the plant's source water (and hence that of precipitation) and relative humidity (e.g. Roden et al., 2000). Since oxygen isotope ratio of precipitation is directly related to temperature (Dansgard, 1964) and/or amount of precipitation (Dansgard, 1964; Rozanski et al., 1993, Yadava et al., 2007), it is conceivable that $\delta^{18}O$ signature of tree cellulose is a more powerful tool in reconstructing past climate.

1.4 Factors influencing $\delta^{18}O$ of tree ring cellulose

Oxygen isotope composition ($\delta^{18}O$) of plant material depends upon $\delta^{18}O$ of the source water, the level of evaporative enrichment of the source water in the leaf during transpiration, biochemical fractionation associated with the synthesis of sucrose in the leaf and the extent of exchange between sucrose and xylem water during cellulose synthesis. A brief description of processes that govern the above mentioned factors is discussed below.

1.4.1 Atmospheric processes

$\delta^{18}O$ of precipitation and atmospheric water vapor, and relative humidity are important in determining $\delta^{18}O$ of the cellulose. $\delta^{18}O$ of the precipitation primarily determines the $\delta^{18}O$ of the source water trees use for photosynthesis in areas of no permanent ground water, whereas $\delta^{18}O$ of water vapor and relative humidity modify the source water $\delta^{18}O$ during transpirational process. It is the transpirationally modified water that is actually used for photosynthesis. In this context, a good knowledge of what decides $\delta^{18}O$ of precipitation and atmospheric water vapor, and changes in relative humidity during growing season are necessary.

A detailed account of variation in the isotopic composition of rainfall over the world since 1961 is maintained by IAEA/WMO Global Network "Isotopes in Precipitation" (GNIP) and is available at http://isohis.iaea.org/.

On the global scale, $\delta^{18}O$ of precipitation is largely governed by ambient temperature. Decreasing temperature results in the lowering of water holding capacity of air and drives the rainout process. As a result, the progressive precipitation associated with still lower temperatures becomes increasingly depleted in ^{18}O. Dansgaard (1964) demonstrated a linear relationship between surface air temperature (T_{annual}) and $\delta^{18}O$ of mean annual precipitation ($\delta^{18}O_a$) on the global scale as

$$\delta^{18}O_a = 0.695T_{annual} - 13.6\,‰$$

In tropical areas, typical relationship between $\delta^{18}O$ of rainfall and surface air temperature is overshadowed by the amount effect, an inverse relationship between $\delta^{18}O$ of rainfall and amount of precipitation on the monthly (Dansgaard, 1964; Rozanski et al., 1993) or individual rain event (Miyake et al., 1968; Yadava et al., 2007) scale. Dansgaard (1964) explained the amount effect in terms of 1) fractional removal of heavy isotopes in the rain; 2) equilibration of light rain (smaller drops) with enriched vapor below the cloud base; and 3) high relative loss of light isotopes when raindrop evaporates below the cloud base in arid region. Yurtsever and Gat (1981) analyzed rainfall and its isotopic composition of 14 island stations in equatorial belt, and found a linear relationship (r = 0.87) between mean monthly $\delta^{18}O$ of rainfall ($\delta^{18}O_m$) and mean monthly rainfall amount (P_m)

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

The average rate of depletion in $\delta^{18}O$ of rainfall with increase in monthly rain amount was -1.5 ± 0.2 ‰ for 100 mm. Amount effect typically dominates south and south-east Asia (Araguás-Araguás et al., 1998). Yadava and Ramesh (2005) measured rainfall amount and its $\delta^{18}O$ for year 1999 at Jharsuguda (22°N, 84°E), central India and found the depletion rate of -9.2 ± 1.1 ‰ and -2.2 ± 0.8 ‰ for 100 mm rain per rain event and total monthly rain, respectively.

Rainout is another important process that determines isotopic composition of precipitation. It is a process by which moving air mass looses its water vapor through precipitation and remaining vapor becomes progressively depleted in ^{18}O. At each stage within the cloud there is isotopic equilibrium between rain and vapor. Mathematically, isotopic evolution of moving air parcel can be modeled by the Rayleigh fractionation equation

$$\delta^{18}O_{v(f)} = \delta o^{18}O_{v} + \varepsilon\, ^{18}O_{l-v} \,.\ln f$$

where $\delta^{18}O_{v(f)}$ and $\delta o^{18}O_{v}$ are the oxygen isotopic compositions of the residual fraction of water vapor at any point and isotopic composition of initial vapor, respectively; f is fraction of residual vapor remaining in cloud; and ε is the oxygen isotopic fractionation factor between the rain and vapor expressed in per mil (‰) units. $\delta^{18}O$ of accompanying rainfall is about 9 ‰ enriched than the $\delta^{18}O$ of vapor. An example of rainout effect in the Asian region is illustrated by Araguás-Araguás et al., (1998). They showed a progressive depletion of $\delta^{18}O$ of rainfall along the trajectory of Pacific monsoon from Haikou and Hong Kong (south of China) to Lhasa (Tibetan plateau) where $\delta^{18}O$ of rainwater changes from -7.2 ‰ to -18.3 ‰. This is known as 'continental' effect.

In addition to the amount and rainout (continental) effect, $\delta^{18}O$ of precipitation also changes with season. In India, the south-west and north-east monsoon have different isotopic signatures. Yadava et al., (2007) analyzed rains (2000 to 2002) at Mangalore which receives both the monsoons and showed that the NE monsoon precipitation is relatively more depleted in ^{18}O. This observation contrasts with observations elsewhere in South-East Asia, where summer rains are depleted in ^{18}O relative to winter rains (Araguás- Araguás et al., 1998).

1.4.2 δ^{18}O of atmospheric vapor

δ^{18}O of atmospheric water is one of the factors that decides the δ^{18}O of leaf water and its effectiveness increases with relative humidity (Roden et al., 2000). Higher relative humidity facilitates faster equilibration of atmospheric water vapor with leaf water. Unfortunately, in contrast to the measurement of isotopic composition of precipitation, isotopic composition of the atmospheric water vapor has not been monitored extensively. In general, atmospheric vapor is considered in equilibrium with local rainwater and its isotopic composition calculated using the corresponding equilibrium fractionation factor. It is known that δ^{18}O of atmospheric water vapor depends upon the moisture source and its interaction with the surface (Gat, 1996). In the Indian region, Srivastava et al., (2008) have found the atmospheric water vapor, in general, to be in equilibrium with ambient rain.

1.4.3 Soil hydrological processes

Isotopic composition of tree's source water is one of the important factors governing isotopic composition of tree. δ^{18}O of the rain water primarily decides δ^{18}O of the source water for plants. But various subsequent soil hydrological processes operating on the percolated rain water finally decides the δ^{18}O of water available for plant uptake. Understanding and quantification of soil hydrological processes (viz. water percolation in soil and its evaporation), however, has been largely ignored in dendroclimatological studies.

Isotopic composition of soil water primarily depends upon the isotopic composition of precipitation and ground water. In addition to this, environmental factors (viz. relative humidity, solar irradiance), through their effect on evaporation of soil water, also affect isotopic composition of soil water. Spatial and temporal heterogeneity in the isotopic composition of soil water has been reported. Barnes and Allison (1989) showed that an isotopic gradient exists in soil water due to evaporation in the upper part of the soil. The shape of this profile depends upon soil moisture content, soil texture and changing isotopic composition and amount of precipitation. They also found that the maximum heterogeneity in $\delta^{18}O$ and δD of soil water is observed at the soil surface and it gradually decreases with depth.

Tang and Feng (2001) conducted a detailed field investigation of the effect of soil hydrological processes in controlling the isotopic composition of soil water. In their study area, Hanover, NH, USA, precipitation is relatively evenly distributed throughout the year and with seasonally changing isotopic composition (isotopically enriched summer and depleted winter rainfall). They measured the temporal variation in the isotopic composition of rainwater, soils water at different depths and twig water from a maple tree. Their work demonstrated: 1) soil water isotopic composition is much less variable than that of precipitation implying mixing of various precipitation events; 2) soil water evaporation isotopically enriches the surface soil water; 3) water from summer rains gradually replaces water of winter precipitation; 4) extent of replacement of winter water with summer water depends upon intensity and frequency of summer precipitation, and its influence decreases with depth; 5) twig water samples soil water which has experienced evaporation.

Tsuji et al., (2006), in their study of oxygen isotopic composition of coexisting tree species in Hokkaido island, northern Japan, have shown the importance of rooting system of plants in controlling the plant's isotopic composition. Their work demonstrates water uptake characteristics of plants in the rhizosphere, an area of a soil affected by root system, in conjunction with the soil water processes ultimately decides tree cellulose isotopic composition. They found that shallow rooted tree species (spruce tree) respond to $\delta^{18}O$ of summer precipitation while deep rooted (oak) trees do not and explained it in terms of inability of deep rooted trees to sample summer precipitation.

Isotopic analysis of xylem water in conjunction with isotopic analysis of rain and ground water has yielded some important results in terms of water utilization by plants. White et al., (1985) have shown a single white pine (*Pinus Strobus*) tree can rapidly (within 3 days) switch its source water from shallower surface rain water to deeper groundwater. Dawson and Ehleringer (1991), on the contrary, showed that mature riparian trees growing close to perennial streams use little or no stream water, but instead prefer ground water. They explained this behavior in terms of mature trees preferring reliable ground water instead of unreliable surface or rain water. Age of the trees also decides which source water a tree samples. Dawson (1996), for example, showed older (larger) *Acer saccharum* trees have access to both shallow soil and ground water while younger (smaller) such trees depend on shallow soil water. Such results are important as different sources of water often have different isotopic compositions and decide the isotopic composition of tree ring cellulose.

1.4.4 Plant physiological processes

$\delta^{18}O$ of tree cellulose depends upon $\delta^{18}O$ of the source water, the level of evaporative enrichment of the source water in the leaf during transpiration, biochemical fractionation associated with the synthesis of sucrose in the leaf and the extent of exchange between sucrose and xylem water during cellulose synthesis. Plant physiological model for interpreting the isotopic composition of plant constituents (e.g. Flanagan et al., 1991; Saurer et al., 1997; Farquhar et al., 1998; Barbour and Farquhar, 2000; Roden et al., 2000, Barbour et al., 2004) can be used to understand the various processes outlined above.

Trees take up the soil water through roots without any isotopic fractionation (White et al., 1985) and transport it to the leaf through xylem. Analysis of xylem water/cellulose shows (Ehleringer and Dawson 1992, Lin et al., 1996, Schwinning et al., 2002, Evans and Schrag 2004) that plants record the isotopic composition of precipitation. The extent of isotopic enrichment of the leaf water depends upon temperature, relative humidity, $\delta^{18}O$ composition of atmospheric water vapor and leaf physiological parameters. Variation in isotopic composition of leaf water (and hence that of cellulose derived from it) depends upon isotopic composition of source water (therefore a function of ambient temperature or amount of precipitation) and the extent of isotopic enrichment of leaf water due to evaporation (therefore a function of relative humidity). In general, relative humidity is less effective during the peak growing season (monsoon) whereas its importance increases during the late growing season. Effect of relative humidity on the evaporative isotopic enrichment of the leaf water is lower at higher ambient humidity, a condition often characteristic of the main growing season in India. But at higher ambient humidity, isotopic composition of atmospheric water vapor through its exchange with the leaf water becomes important. During the late growing season, lower humidity creates higher vapor pressure gradients across the leaf which results in a higher evaporative isotopic enrichment of the leaf water.

Various models have been proposed to calculate isotopic composition of the leaf water. Such models are based on detailed theoretical as well as laboratory experiments. Based on the Craig and Gordon (1965)'s model describing isotopic fractionation during evaporation from an open surface and then incorporating leaf boundary layer effects and diffusion through stomata, Dongmann et al., (1974) and Flanagan et al., (1991) wrote the isotopic composition of the leaf water (R_{wl}) as

$$R_{wl} = \alpha^* \left[\alpha_k R_{wx} \left(\frac{e_i - e_s}{e_i} \right) + \alpha_{kb} R_{wx} \left(\frac{e_s - e_a}{e_i} \right) + R_a \left(\frac{e_a}{e_i} \right) \right], \qquad (1)$$

where R_{wl}, R_{wx} and R_a refer to isotopic ratios ($^{18}O/^{16}O$) of leaf water, xylem water and bulk air, respectively; water vapor pressure of intercellular leaf space is e_i, of leaf surface is e_s and of bulk air is e_a; α^*, α_k, and α_{kb} are respectively liquid-vapor equilibrium fractionation factor, kinetic fractionation factor and kinetic fractionation factor associated with leaf boundary layer.

The resultant isotopic composition of leaf water calculated using the above equation is observed to be more enriched than that of the bulk leaf water due to Péclet effect – an effect describing transpirational advection of ^{18}O depleted (xylem) water to the evaporating site opposed by the backward diffusion of ^{18}O enriched water into the leaf (Farquhar and Lloyd 1993). Barbour et al., (2004) have proposed a model considering the Péclet effect. To use this model, Péclet number for different tree species is required. This involves the measurement of effective path length; a model parameter that accounts for the discrepancy between the values predicted by the Craig-Gordon model and measured bulk leaf water measurements. In practice, detailed knowledge of the Péclet number for a given species and for a season is largely not available. Isotope dendroclimatologists circumvent this problem by either using an assumed value of the effective path length (and Péclet number) or using models (e.g. Roden et al., 2000) that ignore the Péclet effect. The results of the latter option are interpreted keeping in mind that the leaf water isotopic values obtained using such models could be more enriched in ^{18}O than the actual values. Clearly, more work needs to be done in quantifying Péclet number for each species during various times of the growing season.

Sucrose formed by photosynthesis in the leaf carries the isotopic composition of the leaf water. Complicated biochemical pathways are involved in synthesis of cellulose from sucrose, an account of which is given by Farquhar et al., (1998). Initially, it was thought (Epestein et al., 1977) that 2/3 and 1/3 of oxygen atoms of the tree ring cellulose is contributed by CO_2 and H_2O, respectively making overall enrichment of cellulose with respect to water at the evaporating site by 27 per mil. But later DeNiro and Epestein (1979) established that $\delta^{18}O$ of water determines $\delta^{18}O$ of cellulose. Sternberg (1989) based on review of available data in literature reported 27+/- 3 per mil enrichment of cellulose as compared to the water at site of synthesis. Further, it has been shown (Sternberg et al., 1986, and Saurer et al., 1997) that 45% of oxygen in cellulose is expected to exchange with (xylem) water during synthesis of cellulose from sucrose. This implies that 55% of oxygen atoms in cellulose carries the signature of evaporation processes (and hence relative humidity conditions) taking place in the leaf.

Roden et al., (2000) have outlined a mechanistic model for interpreting hydrogen and oxygen isotope ratios of tree cellulose. Their model considers exchange of oxygen atoms of sucrose with the medium (xylem) water during synthesis of cellulose. In their model, the final isotope composition of tree cellulose ($\delta^{18}O_{cx}$) is given by

$$\delta^{18}O_{cx} = fo \cdot (\delta^{18}O_{wx} + \varepsilon o) + (1 - fo) \cdot (\delta^{18}O_{wl} + \varepsilon o), \qquad (2)$$

where fo is the fraction of carbon-bound oxygen that undergoes exchange with medium water, $\delta^{18}O_{wx}$ is xylem water, $\delta^{18}O_{wl}$ refers to oxygen isotopic composition of the leaf water at the site of sucrose synthesis and εo indicates biochemical fractionation factor. The authors based on model and experimental results estimate fo to be 0.42.

It can be seen from the equations (1) and (2) that the e_a/e_i ratio, hence relative humidity plays a crucial role deciding isotopic composition of the leaf water and subsequently synthesized cellulose (Sheshshayee et al., 2005). In tropical areas, like the one in the present study, there is enough variation in relative humidity during growing season to leave its imprint on the isotopic composition of cellulose (Geeta Rajagopalan et al., 1999). Thus, by knowing relative humidity variation during entire growing season of a plant one can construct the expected tree cellulose $\delta^{18}O$ profile during that season.

1.5 A brief review of experimental isotope dendroclimatology

The components of wood viz. cellulose (~50%), lignin (~30%), hemicellulose (~15%), resin and lipids (~5%) have different isotopic ratios (Wilson and Grinsted, 1977) and their relative proportion in the ring changes with time during growing season and from year to year. In addition to this, lignin/cellulose ratios in trees are found to be climate independent (Gray, 1981). Further, resin is found to be mobile (Long et al., 1979) and lignin is shown to be deposited later than cellulose in the ring (Wilson and Grinsted, 1977). This prohibits use of isotopic composition of bulk wood for climate reconstruction and necessitates use of a specific component for climate reconstruction studies. In this context, cellulose is preferred in dendroclimatic investigations as it is durable and is a major component of wood. In addition, mechanistic models (e.g. Roden et al., 2000) used for interpreting climate are developed for the isotopic composition of cellulose. Cellulose $[(C_6H_{10}O_5)_n]$ is a long chained polysaccharide of $\beta(1\rightarrow4)$ linked D-glucose units where n can be several thousand to ten thousand units. Pure cellulose can not be extracted from the wood and always contains some traces of monosaccharides, lignin and other components (Corbett, 1963; White, 1983). Dendroclimatic investigations typically use α-cellulose, a part of cellulose that is insoluble in 17.5% NaOH, as the saponification removes some of the non-cellulosic components.

Various methods are available for extracting α-cellulose from wood samples and there is no consensus among isotope dendroclimatological community regarding use of a particular method. Moreover, investigators have modified the originally suggested methods to suite their specific needs. The extracted cellulose, as a result, often differs in its quality. Traditional techniques of extracting cellulose and measuring its isotopic composition have been laborious and time consuming leading to low sample throughput. Some recently suggested sample preparation techniques (Leavitt and Danzer, 1993; Loader et al., 1997; Brendel et al., 2000; Schulze et al., 2004; Rinne et al., 2005; Gaudinski et al., 2005) have enabled processing a large number of samples in less time leading to the analysis of number of chronologies, hitherto not considered feasible.

Traditional cellulose extraction methods (e.g. Green, 1963) involves 1) pretreatment involving extracting wood powder with organic solvent for removing components such as resins, gums and lipids; 2) bleaching stage where pretreated wood powder is delignified using glacial acetic acid and sodium chlorite; 3) purification stage where the delignified sample is immersed in 17% NaOH to obtain α-cellulose and removing wood components like mannan and xylan. As these methods are tedious and time consuming, processing of large a number of samples for isotopic measurements was difficult.

Interlaboratory comparison of different cellulose extraction methods followed by nine European stable isotope laboratories was conducted by Boettger et al., (2007). These laboratories extracted cellulose from oak and pine samples using their routine method which is either of the methods suggested by Sohn and Reiff (1942), Loader et al., (1997), Green (1963), Brenninkmijer (1983) and measured its isotopic ratio using different methods. The authors reported that the $\delta^{18}O$ values did not depend upon any specific method of cellulose extraction and recommended the elimination of a pretreatment of wood with organic solvents, inclusion of a purification step with 17% NaOH solution to produce α-cellulose, and isotopic measurements of oxygen isotopes under an argon hood.

Brendel et al., (2000)'s cellulose extraction method has become popular as it the fastest method (56 samples in 8 hours) of extracting cellulose and involves only standard laboratory chemicals and equipments. This method involves simultaneous removal of lignin and hemicellulose from the sample by treating it with a hot mixture of nitric acid and acetic acid. The other advantages of this method include the minimal use of chemicals and hence reduction of toxic waste disposal problems. Evans and Schrag (2004) scaled down the Brendel et al., (2000)'s method permitting the use of a very small amount of initial wood sample (~400 μg) and claimed α-cellulose can be extracted from 160 samples each day. Their protocol is useful to extract cellulose from tree-cores, especially when ring widths are smaller.

Gaudinski et al., (2005) pointed out that the Brendel's method adds carbon and nitrogen to the cellulose and left a residue that contains remnant lipids and waxes. In case of oxygen, the authors reported that cellulose extracted using Brendel's method is enriched in ^{18}O relative to the other methods and proposed a modification, MBrendel, involving the addition of a step to the Brendel method. This step treats the cellulose extracted by Brendel's method with 17% NaOH followed by water rinsing and acidification. The claims made by Gaudinski et al., (2005), were contested by Anchukaitis et al, (2008) who showed that the isotopic composition of cellulose extracted using the Brendel method is not statistically different from the traditional methods like Leavitte and Dansier and Gaudinski's MBrendel method.

Like traditional cellulose extraction methods, traditional techniques used for preparing gas (CO_2) from cellulose for mass-spectrometric analysis were also time consuming and laborious. These methods (Wilsen and Grinsted, 1977; Burk, 1979; Hardcastle and Friedman, 1974; Thompson and Gray, 1977) first pyrolysed the sample in presence of suitable catalyst (mercury or nickel) to produce C, CO and CO_2. The CO was then converted to CO_2 by electrical discharge and CO_2 thus recovered was used for mass-spectrometric ^{18}O analysis.

The advent of modern continuous flow IRMS (Isotope Ratio Mass Spectrometer) has revolutionized the isotopic analysis of cellulose samples; measurements today being fast and at reduced cost. Typically, the procedure involves online pyrolysis of cellulose sample in the presence of graphite and glassy carbon at ~1100°C to produce carbon monoxide (CO). In order to avoid isotopic interference of CO and nitrogen, CO is then separated from nitrogen by passing the mixture through a gas chromatograph (GC) (e.g. Farquhar et al., 1997; Saurer et al., 1998) with 5 Å sized seive. The sample gas is then introduced into the mass-spectrometer where analysis of a sample could be completed within 10 min. In this procedure a dry He gas (99.999% purity) is used as a carrier. Internal precision of the measurements is established using pure CO as a reference gas whereas external precision is measured with standards such as IAEA-C3 (32.6 ‰) and sucrose (ANU sucrose, 36.4‰). Typical reported internal and external precisions are less than 0.1‰ and 0.3‰, respectively.

1.5.1 Components of wood other than cellulose

Some pregress has been made in this direction of using oxygen atoms having specific positions in the cellulose structure rather than using all oxygen atoms for climate reconstruction. Sternberg et al., (2007) used the cellulose derived phenylglucosazone, a compound which lacks the oxygen attached to the second carbon of the cellulose-glucose moieties, instead of using bulk cellulose. These authors showed that phenylglucosazone is a better proxy for isotopic composition of the stem water and relative humidity than the bulk cellulose as the oxygen attached to the second carbon atom in cellulose can introduce isotopic 'noise' in the climate signal preserved by cellulose.

1.6 Previous isotope dendroclimatological investigations in the tropics

Relative to the extra-tropics, isotope based dendroclimatological work carried out in tropics is limited. The isotopic composition of rainfall in tropics is seldom related to temperature; it is rather affected by factors such as season, amount of rainfall and the rainout history, thus hampering meaningful interpretation of stable isotopic variations in tropical trees. To utilize tropical trees for climate reconstruction, a proper understanding of what governs isotopic composition of bulk as well as different parts of the ring is imperative. Most of the isotope dendroclimatological work being carried out in tropical area now involves high resolution/intra-ring sampling to understand driving forces that determine $\delta^{18}O$ of photosynthates produced during various times of the growing season. Recently developed models (e.g. Flanagan et al., 1991; Saurer et al., 1997; Farquhar et al., 1998; Barbour and Farquhar, 2000; Roden et al., 2000) can help in understanding parameters that govern the isotopic composition of photosynthates produced during various times of the growing season. This, coupled with newly developed cellulose extraction techniques (Brendel et al., 2000, Evans and Schrag 2004, Gaudinski et al., 2005 and Anchukaitis et al., 2008) has made intra-ring studies increasingly significant.

Ramesh et al., (1989) proposed a mechanism for using teak tree for climate reconstruction of tropical areas. They showed a positive correlation between δD of teak cellulose and amount of rainfall despite having no correlation between δD of precipitation and amount of rainfall in the area. The authors suggested increasing length of growing season as a result of higher rainfall as a possible explanation for observed positive correlation.

Evans and Schrag, (2004) demonstrated potential of tropical trees with or without growth rings in the reconstruction of past climate. Based on a protocol for rapid extraction of cellulose (Brendel et al., 2000), they extracted α-cellulose at high resolution from the sample. Based on the high resolution $\delta^{18}O$ record, they formulated an approach "tropical isotope dendrochronology" wherein seasonal cycles in (intra-ring) $\delta^{18}O$ variations are exploited to establish chronology within trees lacking annual growth rings. In their approach, wood corresponding to one seasonal cycle of $\delta^{18}O$ represents a 'ring'. Once such 'rings' are established, regular dating/counting methods can be used to assign calendar years to them. Past changes in rainfall, relative humidity and growth rate could then be reconstructed using the high resolution cellulose $\delta^{18}O$ record and a plant physiological model (Roden et al., 2000) developed for climatic interpretation of $\delta^{18}O$ of α-cellulose.

Poussart et al., (2004) studied trees from three different families from Thailand and Indonesia using an approach similar to that of Evans and Schrag (2004)'s. These authors have demonstrated reproducibility of climate signal between trees grown at the same locality as well as from wider geographical regions. Poussart and Schrag (2005) analyzed 11 different trees belonging to different families from Thailand for intra-ring $\delta^{18}O$ analysis. Their analysis of intra-ring $\delta^{18}O$ variations showed significant correlation between dry season rainfall and amplitude of intra-ring variation; and between wet season rainfall and minimum of intra-ring variation. This led them to propose a possibility of reconstructing dry and wet season rainfall using intra-ring $\delta^{18}O$ variations.

Verheyden et al., (2004) analyzed a mangrove tree *Rhizophora mucronata* Lam., for bulk wood high resolution oxygen and carbon isotope studies and found a remarkable annual cyclicity in them. Presence of ENSO related climate signal in the high resolution isotope record was also reported by them.

1.7 Rationale behind the approach

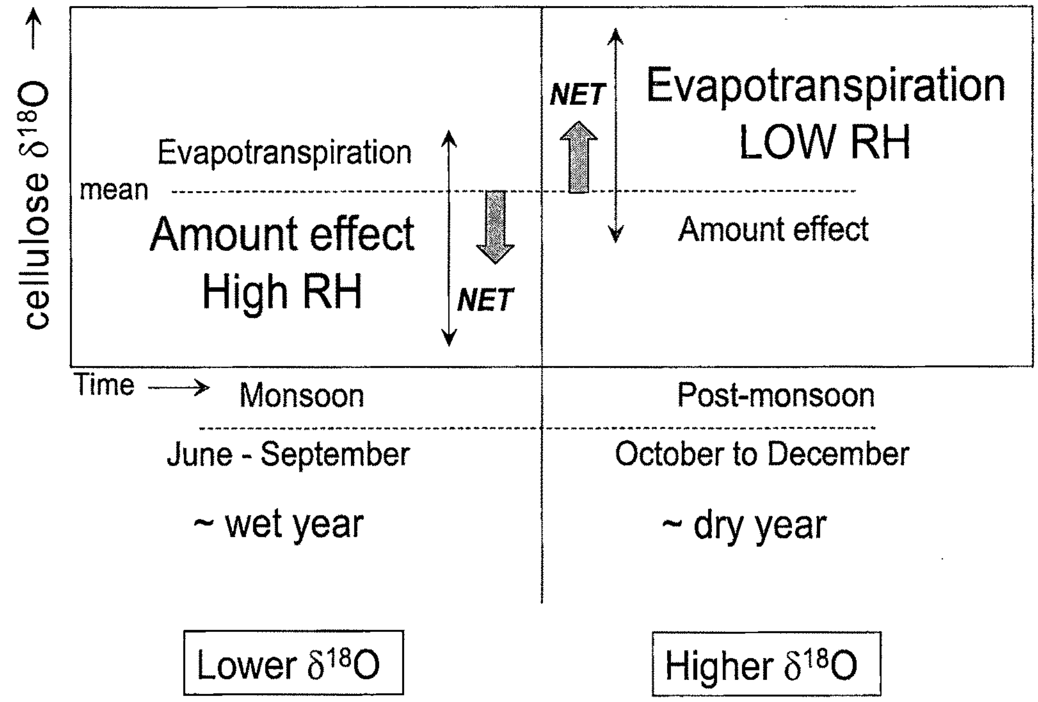

Fig.1.1. Schematic diagram showing effect of the amount effect and relative humidity on $\delta^{18}O$ of cellulose. Modified after Evans and Schrag (2004).

$\delta^{18}O$ of tree cellulose depends, among other factors, upon $\delta^{18}O$ of the tree's source water and the level of evaporative enrichment of the source water in the leaf during transpiration. The former is controlled largely by the $\delta^{18}O$ of precipitation through the amount effect while relative humidity governs the latter. Lower atmospheric humidity causes higher vapor pressure gradient between leaf interstitial space – which is saturated with water- and the leaf surroundings leading to a higher evaporative enrichment of the leaf water in ^{18}O. Interestingly, the relative influence of these 'non-biological' factors changes with season (see **Fig.1.1**). During the peak of rainy season, (e.g. peak monsoon season –June to September) higher relative humidity in the atmosphere poses less vapor pressure gradient across the leaf leading to lesser evaporative enrichment of leaf water. In addition to this, higher rainfall during this season results in rainwater depleted in ^{18}O owing to the amount effect. Photosynthates (and hence, subsequently formed cellulose) formed during the monsoon season, as a consequence, are depleted in ^{18}O.

During the post monsoon season, on the contrary, more evaporative enrichment of the leaf water due to lower relative humidity dominates the changes in source water $\delta^{18}O$ caused by amount effect leading to formation of photosynthates relatively enriched in ^{18}O. Various plant physiological models are available for quantifying the effect of these factors on $\delta^{18}O$ of cellulose. Using these models, one can decide what governs the $\delta^{18}O$ of cellulose formed during various phases of growing season, understanding of which is important in interpreting inter-annual variations in cellulose $\delta^{18}O$.

Using the same analogy, a year with higher rainfall (and higher average relative humidity) is characterized by cellulose with lower $\delta^{18}O$ values as compared to the year with lower rainfall (and lower average relative humidity). This relationship can be used to interpret variation in $\delta^{18}O$ of tree rings in terms of variation in the amount of rainfall the tree receives.

The relationship between rainfall amount and $\delta^{18}O$ of cellulose, however, is primarily complicated by two factors. Firstly, the amount effect at a given place may not be pronounced - poor correlation between the amount of rainfall and its $\delta^{18}O$ - and may vary in magnitude with time. Secondly, in case of regions which receive rainfall with seasonally changing $\delta^{18}O$, relative strength of two rains will ultimately decide the $\delta^{18}O$ of cellulose.

1.8 Statement of the problem

The proposed work aims at building past monsoon rainfall variations by using the oxygen isotopic records of teak (*Tectona grandis*) trees. Such reconstruction involves finding a relationship between comparison of observed variations in tree cellulose $\delta^{18}O$ and the actually measured rainfall of the corresponding period. The relationship is then used to reconstruct rainfall of the period for which no instrumental records are available. To use this relationship effectively, a proper understanding of what governs the isotopic ratio of tree ring is imperative.

Besides reconstructing annually resolved past rainfall, specific questions addressed in the thesis are

1. What governs the evolution of the isotopic composition of tree cellulose during growing season?
2. How do teak trees from different climatic regions of India respond to the ambient climatic setting?
3. Is it possible to reconstruct the SW and NE monsoon simultaneously using $\delta^{18}O$ studies of teak trees from southern India, a region which is under the influence of both the monsoons?

The use of stable isotopes in dendroclimatological investigations started about three decades ago while the potential of tropical trees is yet to be investigated in sufficient detail as only a few tree species in tropics exhibit distinct and clearly datable growth rings. Further, the isotopic composition of rainfall in tropics is seldom related to temperature; it is rather affected by factors such as season, amount of rainfall and the rainout history. This hampers the meaningful interpretation of stable isotopic variations in tropical trees.

Understanding of how teak (*Tectona grandis*) trees respond to changes in amount and isotopic composition of rainfall and humidity is critical for interpreting inter-annual variations in $\delta^{18}O$ of these trees, the only species available in tropical Asia for climate reconstruction. Despite some preliminary work, it is still not clear how these factors affect the $\delta^{18}O$ of teak trees. Our isotopic analysis of teak trees from carefully selected locations can shed light on issues discussed above. Teak has a widespread distribution in tropical areas of South-east Asia – Java, Sumatra, Burma and Thailand – a region important for tracking El Nino- Southern Oscillation phenomenon. The outcome of this study can also be extended to other tropical Asian regions.

In India, after successful demonstration of the usefulness of isotope dendroclimatology in reconstructing past climate by Ramesh et al., (1989), no further work has been done in this direction to obtain long isotopic records from tree-rings. This study is the first to reconstruct rainfall record for central and southern India using $\delta^{18}O$ time series of teak tree-rings. These reconstructed rainfall records can be used to test models aimed at understanding global climate change.