Climatic significance of D/H and $^{13}C/^{12}C$ ratios in Irish oak cellulose

M G L Baillie[1], J R Pilcher[1], A M Pollard[2] and R Ramesh[3]

[1]*Palaeoecology Centre, Queen's University, Belfast, BT7 1NN, UK*
[2]*Department of Archaeological Sciences, University of Bradford, Bradford, BD7 1DP,UK*
[3]*Physical Research Laboratory, Ahmedabad 380 009, India.*
[3]*email: ramesh@prl.ernet.in*

δD and δ^{13}C analyses of cellulose nitrate from two modern Irish oak trees that form part of the 7400 year long chronology were carried out, covering a period of 123 years (1861–1983 A.D.) with a 5 year resolution so as to assess the potential of this long chronology for retrieval of palaeoenvironmental data. One of the trees (Q5293) showed significant correlations of δD, δ^{13}C and ring width with mean annual temperatures as recorded at the Armagh weather station nearby and the mean fall temperatures of Central England. The other tree (Q5296) did not exhibit any significant climatic correlations either because it grew utilizing a nearby permanent source of ground water or because the intra-ring isotopic variations in Irish oak are significant enough to mask the climatic signal. Whilst our results have given a positive indication of the usefulness of these trees for palaeoenvironmental information, more trees need to be analysed to confirm our findings.

Even though one of the trees did not exhibit climatic correlations, both trees show a significant positive correlation of δ^{13}C and a negative correlation of δD with ring width variations. Furthermore, two tree samples that grew during the 1620s B.C., when a volcano is thought to have erupted on the Aegean island of Santorini, show increased δD and decreased δ^{13}C for one to two decades following the eruption, though the magnitudes of change seem to vary with site and trees. We have proposed a possible mechanism based on tree phenology to explain both the above effects.

1. Introduction

Information on the variations of marine climate over the past several hundred thousand years has been obtained by numerous studies of the oxygen and carbon isotope ratios in marine invertebrate shells preserved in ocean sediments, with a typical resolution of a few thousand years (Shackleton and Opdyke 1973; Duplessy 1978). Similar studies on long tree ring chronologies can yield information on climatic changes on land, potentially with a resolution of one year. This is because trees that lay down annual growth rings preserve a chronological record of regional environmental changes. A large number of studies on the relationship between instrumentally measured climatic parameters (e.g., temperature, rainfall and relative humidity) on the one hand and ring width, ring density and stable isotope ratios of hydrogen, carbon and oxygen (δD, δ^{13}C and δ^{18}O respectively) on the other hand have shown that in many instances the spatial and temporal climatic variations are indeed recorded by trees (Fritts 1976; Hughes *et al* 1982; Yapp and Epstein 1982a, 1982b; Ramesh *et al* 1985, 1986a, 1986b; Pant *et al* 1988). Furthermore, specific events such as volcanic eruptions may leave their imprint on trees, thereby giving us a means to study the accompanying climatic changes (Baillie and Munro 1988).

Three long ring chronologies have so far been developed. Firstly, the bristlecone pine (*Pinus aristata* and *Pinus longaeva*) chronology from the White Mountains, California, USA, covering a period of

Keywords. Tree-rings; Irish oak; hydrogen isotopes; carbon isotopes; palaeoclimate.

Proc. Indian Acad. Sci. (Earth Planet. Sci.), **109**, No. 1, March 2000, pp. 117–127

8681 years (Ferguson and Graybill 1983). Secondly, the oak (*Quercus robur* and *Quercus petraea*) chronology for Germany, now going back approximately 9200 years (Becker and Schmidt 1989). Thirdly, the oak chronology for Northern Ireland, U.K., which now extends back approximately 7400 years before present. In addition, several shorter tree long chronologies exist. Some of them are: 1089 year chronology of Huon pine from Tasmania (Cook *et al* 1992), 800 year chronology of *Chamaecyparis obtusa* from central Japan (Sweda 1994; Sweda and Takeda 1994) and >300 year chronologies of *Cedrus deodara* from Himalaya, India (Bhattacharyya and Yadav 1990; Borgaonkar *et al* 1996; Yadav *et al* 1997).

1.1 *Previous work*

So far, stable isotopic investigations of these long chronologies are limited. Epstein and Yapp (1976) measured δD values for a 1000 year period in the bristlecone pine chronology. They demonstrated a qualitative positive correlation between the long term trends (40 year means) in the δD values and Central England winter temperatures (long temperature records are not available in the USA). δ^{13}C values were measured on the same specimens by Grinstead *et al* (1979), for the same 1000 years period. They showed a negative correlation between long term (50 year means) trends in δ^{13}C values and Central England temperatures (in both the cases, the comparison of δ values with temperature trends was for a span of 900 to 1000 years). However, the δD and δ^{13}C variations in tree cellulose were not significantly related to each other. Grinstead and Wilson (1979) also measured δ^{13}C values in a single Kauri tree (*Agathis australis*) that grew in New Zealand during the same 1000 year period. Again, they compared the long term (50 year means) trends in δ^{13}C values and Central England temperatures. In this case, they found a positive correlation. More recently, Stuiver and Braziunas (1987) reported the mean δ^{13}C values of 19 North American trees of different species collected from different latitudes, for a period of 2000 years. They compared the long term (40 to 50 years) means of δ^{13}C values with those of general Northern Hemisphere temperature indices, derived from Central England temperatures, California (White Mountains) tree ring width indices and Greenland ice sheet δ^{18}O values. They observed a positive correlation between the two variables, but only after introducing a 70 to 90 year lag in the δ^{13}C values. With a similar lag, they also found a negative correlation between δ^{13}C values and acidity peaks in Greenland ice sheets (Hammer *et al* 1980). They argued that higher acidity in the ice sheets corresponded to higher volcanic activity, which throws dust into the stratosphere and consequently cools the atmosphere, thereby reducing δ^{13}C values in tree cellulose.

Epstein and Krishnamurthy (1990) analyzed 23 trees of different species from widely differing locations for δD and δ^{13}C . One sample of bristlecone pine covered the last 1000 years, but the majority of samples spanned less than 200 years. They concluded from the δD values that the earth's temperature has risen over the last 100 years, and probably over the last 1000 years, with the rate being higher in the cooler regions. More recently, Feng and Epstein (1994) reported a 8000 year δD record from North American bristlecone pines. They found evidence for a postglacial climatic optimum 6800 years ago and a continuous cooling since then.

There are number of shortcomings associated with some of the above studies. Firstly, whilst trees can yield information with a very high resolution of one year, all the above studies deal with long term average trends. Second, since long temperature records are not available near the tree sites, tree ring data are compared with British temperature records. Obviously, British climate is very different from the arid climate of South West USA, where the bristle cone pines grow, or the climate of New Zealand, where the Kauri trees thrive. Thirdly, there are specific problems with each of the above studies. The methodology used by Epstein and Yapp (1976) for preparation of cellulose nitrate from wood for δD measurements is known to yield inconsistent results (DeNiro 1981). In Grinstead *et al*'s (1979) study the δ^{13}C of two bristlecone pine trees did not match either in their magnitude or in the general trend for the 90 year period overlap. Additionally, the bristle cone pines grow at high altitudes (~3000m above mean sea level) where relative humidities are generally low. This will result in a higher evapotranspiration rate and affect the δ^{13}C values of the tree apart from temperature (Ramesh *et al* 1986b). Grinstead and Wilson's (1979) study is not based on a well developed tree ring chronology, but a single specimen of Kauri tree. This might give rise to dating errors of a few years (this is perhaps one of the reasons why δ^{13}C values were averaged for 50 years before comparing them with temperature records). Furthermore, a single tree growing for about 1000 years will have age related physiological changes which might obliterate to some extent the climate dependence of δ^{13}C values. Also, unlike the bristle cone pine trees, the kauri tree shows a positive correlation with temperature trends. The opposite behavior of two trees (analysed by the same authors) from two hemispheres is puzzling (Ramesh 1984). The trees analysed by Stuiver and Braziunas (1987) are also not part of a standardized tree ring chronology. Additionally, δ^{13}C values of six different species growing in different periods of time were used to derive the mean δ^{13}C curve. It is known that different species have slightly different responses to changing climate (Ramesh *et al* 1986b). Two bristlecone pines (BrPn2 and BrPn3) analyzed by Feng and Epstein (1994), had an overlapping period of $\sim$1000 years, but they do not show similar variations, casting serious doubt on the validity of climatic reconstruction based on stable isotope measurements in a few trees.

Thus, although the existing work on relatively long (1000 to 2000 years) tree ring sequences has demonstrated a gross correlation between isotope ratios and temperature, there is still much scope for careful detailed investigations on long tree ring chronologies to obtain high resolution information on post-glacial climatic changes on land.

1.2 *Objectives of the present work*

The aim of the present work is two-fold. Firstly, to investigate the climatic significance of δD and δ^{13}C variations in modern Irish oak trees, which form part of the 7400 year long chronology developed by Baillie and co-workers (Pilcher *et al* 1984; Baillie and Brown 1988). Secondly, to determine the effect (if any) of the proposed major volcanic eruption of the Aegean island of Santorini in 1628 B.C. on the isotope variations in the oak trees of the Irish chronology.

The Irish oaks grow at low altitudes ($<$200m above mean sea level), where the relative humidities are more than 80% throughout the year. The trees have a life span of about 150 to 250 years, thus reducing the chances of major age-related physiological effects on isotope ratios in cellulose. Also, being ring-porous, their rings are clear and unambiguous. They do not suffer from missing or double rings (Baillie 1973). Finally, they grow relatively much closer to Central England, where long temperature records are available. However, since oaks are known to store their photosynthates of a particular year in the parenchyma cells for use in the next year's growth, it was decided to measure the isotope ratios in groups of 5 rings rather than individual rings. This, we believe, would, to some extent, reduce the autocorrelation between the isotope ratios of successive sample intervals.

2. Sample selection

We chose two healthy-looking tree samples (Q5293 and Q5296) from the collection at the Palaeoecology Centre, Queen's University, Belfast. These trees grew in Castle Coole, Co. Fermanagh, Northern Ireland, U.K. (54°20′N, 7°36′W). Q5293 was 123 years old (1861 to 1983 A.D.) and Q5296 was 273 years old (1711 to 1983 A.D.). A period of 123 years (1861 to 1983 A.D.) was chosen for stable isotopic analysis, because rainfall and temperature records for this period are available from the Armagh Weather Observatory, situated about 60 km away from the sample location (figure 1).

For determining the effect of the Santorini eruption on the isotope ratios in oaks, we selected two trees that grew during the period 1641 to 1590 B.C. One was Q5392 from Sentry Hill, Co. Antrim and the

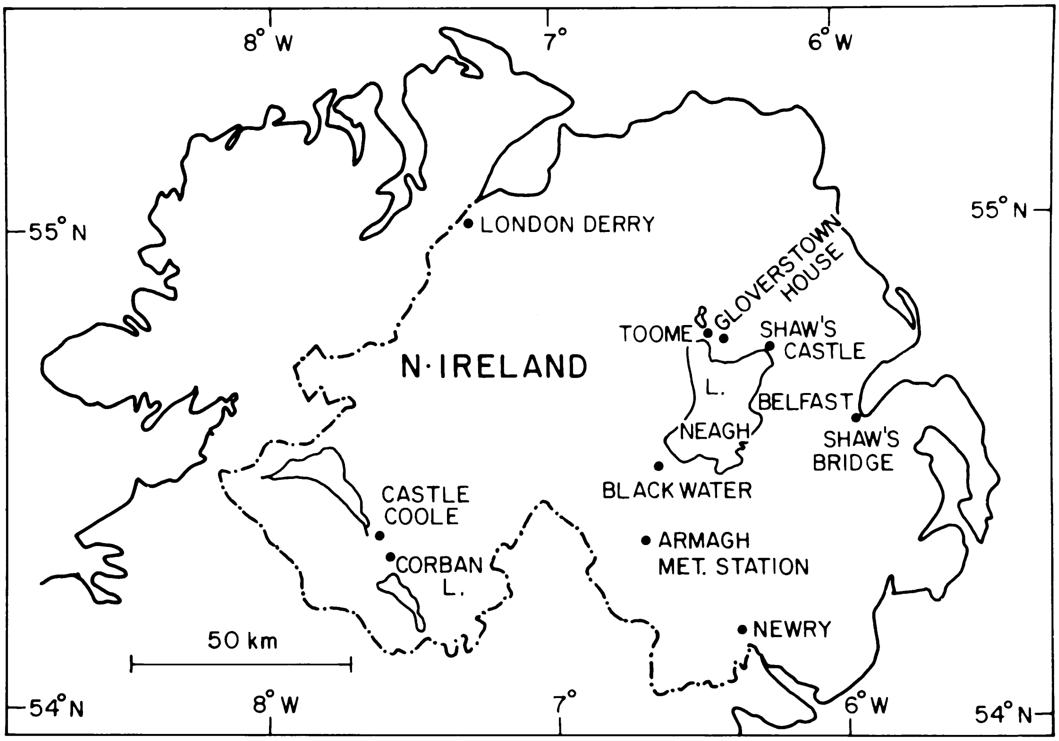

Figure 1. Map of northern Ireland showing sample locations and Armagh weather station.

other, Q1276 from Derryland, Co. Armagh. Both these trees showed very narrow rings in the 1620s B.C. Also, Q1276 showed a color change beginning 1628 B.C. and Q1276 showed anomalously small early wood vessels in the growth ring for 1625 B.C. These two trees, however, grew rooted in the peat of raised bogs (Baillie and Munro 1988), unlike the modern trees Q5293 and Q5296 which grew in normal soils; isotopic responses may therefore be different between the two periods.

3. Experimental methodology

Twenty four samples, each covering 5 year intervals from 1861–5 A.D. to 1976–80 A.D., and one sample covering 3 years, 1981–83 A.D. were cut from each of the modern trees Q5293 and Q5296.

Six samples of 10 year intervals from 1651–40 B.C. to 1600–1591 B.C. were cut from each of the prehistoric samples Q5492 and Q1276. Furthermore, the 1630–21 B.C. block of Q1276 was cut into five sub-samples, each covering a two year period from 1630–29 B.C. to 1622–21 B.C. so as to detect the effect of the proposed Santorini eruption in 1628 B.C.

All four tree samples were in the form of radial strips approximately 30mm × 30mm across. Each of the samples was powdered in a Wiley mill and the 40 to 60 mesh size fraction was recovered. Cellulose was extracted and nitrated using a mixture of nitric and phosphoric acids to remove the 30% hydrogen atoms in cellulose which might have undergone isotopic exchange with modern waters. The cellulose nitrate, which contains only the non-exchangeable carbon-bound hydrogen, was then combusted with copper oxide at 800°C and carbon dioxide was quantitatively collected for δ^{13}C measurement. The water of combustion was passed through metallic uranium at 800°C to convert it into hydrogen gas, which was then quantitatively recovered for δD measurement. Standard procedures were followed throughout and details are reported elsewhere (Ramesh *et al* 1988). The δD and δ^{13}C values were measured using two mass spectrometers (both VG Micromass 602D) with an overall precision of ±2‰ and ±0.1‰ respectively. The values are reported relative to international standards SMOW (Standard Mean Ocean Water) and PDB (Belemnitic calcium carbonate from the Pee Dee formation, South Carolina, USA) respectively.

Ring width values were measured with an optical microscope to a precision of 0.02 mm. Total ring growth (denoted here as ring width) for the 5 year (or 3 year) blocks were calculated from these data.

4. Results

The δD, δ^{13}C and ring width values for the two trees Q5293 and Q5296 are presented in table 1. δD and

Table 1. δD_{SMOW} (‰), $\delta^{13}C_{PDB}$(‰) *and ring width* (*mm*) *values for the two trees Q and Q5296. Analytical uncertainties* (1σ) *are* ± *2‰*, ± 0.1‰ *and 0.02 mm respectively.*

Years (A.D.)	Q5293			Q5296		
	δD	δ^{13}C	R.W.	δD	δ^{13}C	R.W.
1861–65	−60	−25.3	17.70	−43	−24.4	9.40
66–70	−58	−24.1	24.74	−38	−24.2	7.04
71–75	−63	−23.9	26.60	−42	−24.8	8.28
76–80	−63	−24.3	20.40	−39	−24.2	10.02
81–85	−62	−24.3	17.92	−38	−23.8	7.12
86–90	−62	−23.8	16.36	−43	−24.2	7.28
91–95	−58	−24.1	16.16	−40	−24.5	8.88
1896–1900	−61	−24.1	14.96	−40	−24.8	8.62
1901–5	−62	−25.0	6.46	−43	−24.4	7.32
06–10	−57	−24.6	7.00	−37	−24.8	6.30
11–15	−63	−24.0	11.44	−37	−24.6	6.14
16–20	−58	−24.9	11.48	−39	−25.1	6.06
21–25	−51	−25.0	8.76	−33	−25.4	4.18
26–30	−50	−25.5	5.40	−38	−24.8	4.16
31–35	−50	−25.4	6.68	−37	−24.6	5.58
36–40	−53	−25.4	6.42	−28	−24.6	4.08
41–45	−46	−25.6	6.64	−38	−24.6	7.90
46–50	−58	−25.3	8.30	−45	−24.2	13.72
51–55	−52	−26.0	7.46	−46	−24.4	10.32
56–60	−54	−25.5	6.28	−50	−24.4	9.06
61–65	−52	−25.6	7.06	−46	−25.5	4.10
66–70	−54	−25.8	6.68	−35	−25.0	5.00
71–75	−54	−26.2	6.96	−35	−24.5	4.94
76–80	−52	−26.9	6.88	−38	−24.7	5.44
81–83	−38	−26.1	3.52	−43	−24.0	6.04

Table 2. δD_{SMOW} (‰) *and* $\delta^{13}C_{PDB}$ (‰) *values for two trees, Q5392 and Q1276. Analytical uncertainties are* ±2‰ *and* ±0.1‰, *respectively.*

Q5392			Q1276		
Years (B.C.)	δD	δ^{13}C	Years (B.C.)	δD	δ^{13}C
1591–1600	−48	−27.5	1591–1600	−40	−25.5
1601–1610	−47	−28.0	1601–1610	−43	−26.1
1611–1620	−47	−28.3	1611–1620	−51	−26.7
1621–1630	−35	−28.3	1621–1622	−47	−26.7
			1623–1624	−55	−26.2
			1625–1626	−45	−25.7
			1627–1628	−47	−24.9
			1629–1630	−41	−25.5
1631–1640	−51	−28.2	1631–1640	−48	−25.2
1641–1650	−54	−27.8	1641–1650	−58	−26.1

δ^{13}C data for Q5392 and Q1276 are given in table 2. The δD values for the two trees Q5293 and Q5296 are shown in figure 2, δ^{13}C values in figure 3 and ring width values in figure 4. δD and δ^{13}C values of Q5392 and Q1276 are shown in figure 5.

5. Discussion

5.1 *Modern Trees*

The range of variation in the δD values is 25‰ for Q5293 and 22‰ for Q5296, more than ten times the experimental uncertainty of ±2‰ (1σ). For δ^{13}C , the ranges are 3.1‰ and 1.4‰ respectively, again more than ten times the uncertainty of +0.1‰ (1σ). Ranges in the ring width variations are 23.08mm and 9.64mm (5 year total ring widths) respectively. The common variance between the two trees in the δD, δ^{13}C and ring width signals are 12.3%, 12.1% and 36.4% respectively. These values were calculated using a procedure for analysis of variance outlined by Fritts (1976). The δD, δ^{13}C and ring width variations of the two trees are not similar, as is evident from figures 2, 3, and 4. The actual geographical distance between the two trees is not known. There are two conceivable reasons for the discrepancy between the signals from these two trees. First, the intra-ring isotopic variation might be so large a mask the similarity between the isotopic variations in the two trees, especially considering the measurements were carried out only along a single radial strip from each tree. Second, one of the trees could have grown near a permanent source of ground water and therefore does not reflect the variations in the δD of rainfall and consequently the climatic variations.

Straaten (1981) has measured the intra-ring isotopic variation for δD in a Dutch red oak tree (*Quercus rubra*) ring which formed in 1970 A.D. He found the magnitude to be about 16‰. Tans and Mook (1980) measured δ^{13}C values in 4 Dutch red oak trees, observing a maximum difference of 4.4‰ in the δ^{13}C values along the circumference of a single growth ring. However, while Straaten (1981) found that the

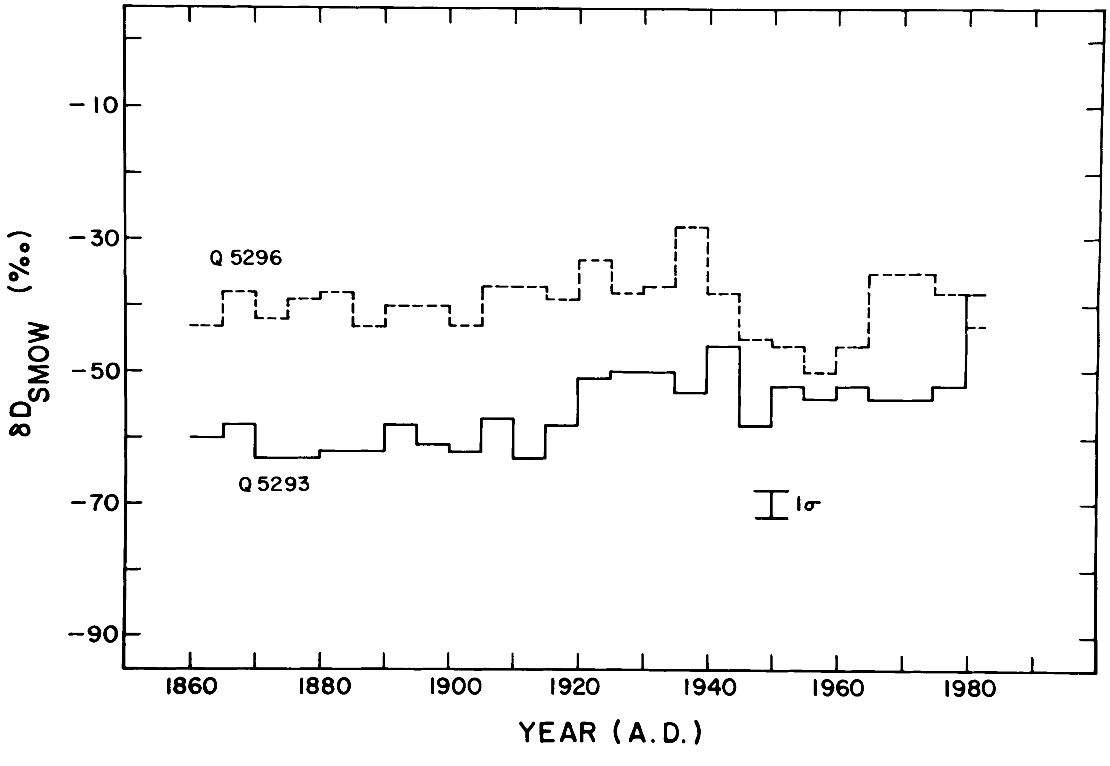

Figure 2. δD variations of two Irish oak trees (Q5293 and Q5296) from 1861 to 1983A.D.

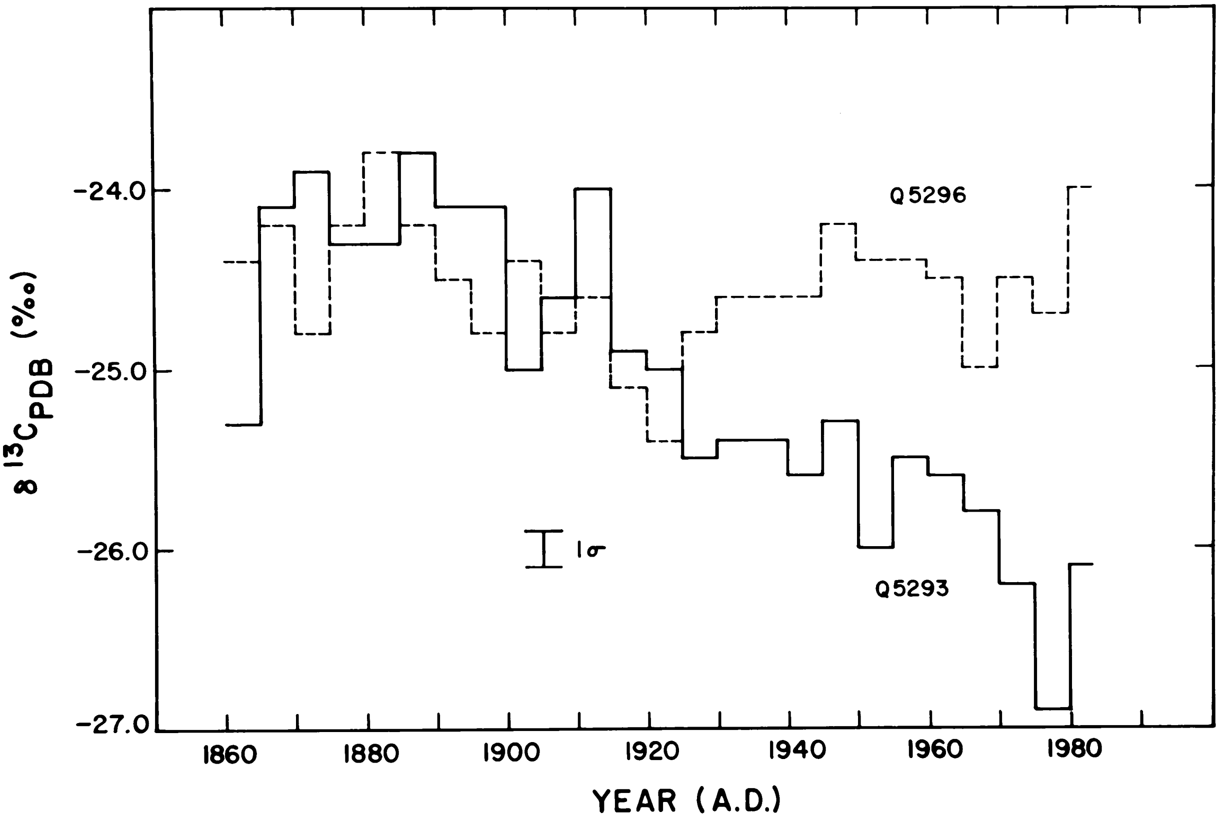

Figure 3. δ^{13}C variations of two Irish oak trees (Q5293 and Q5296) from 1861 to 1983 A.D.

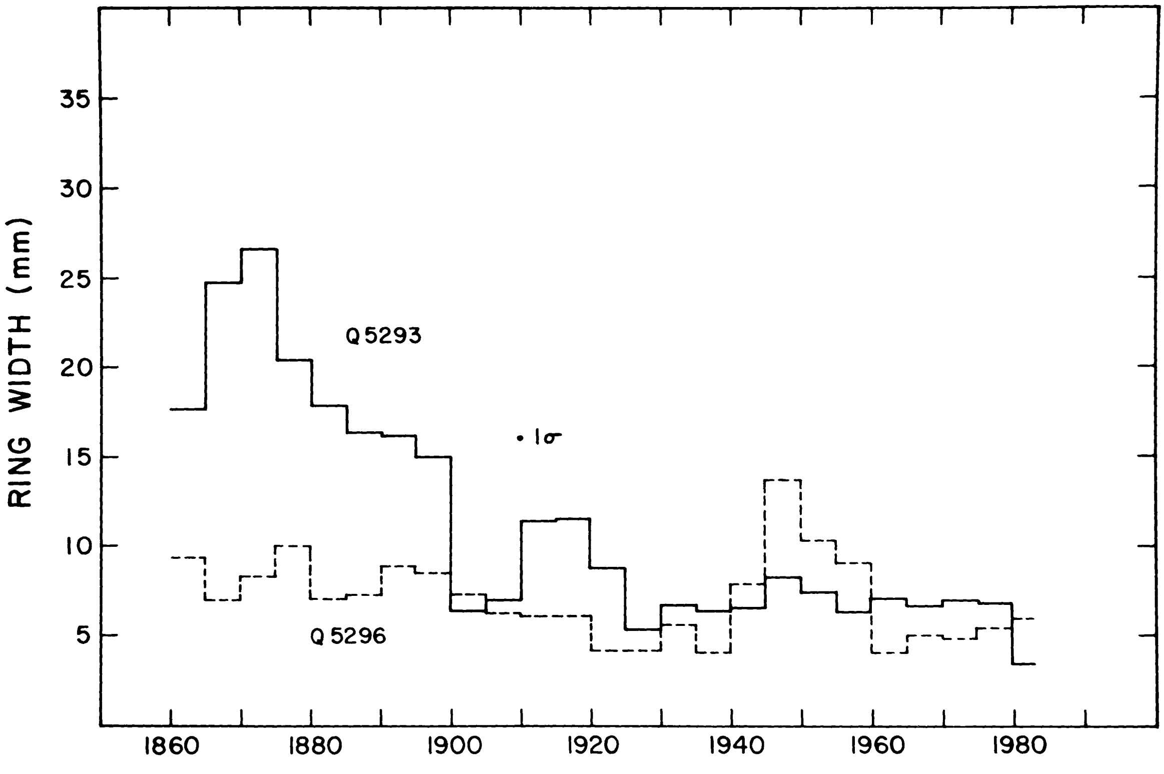

Figure 4. Ring width variations of two Irish oak trees (Q5293 and Q5296) from 1861 to 1983 A.D. (here ring width denotes five year total ring growth).

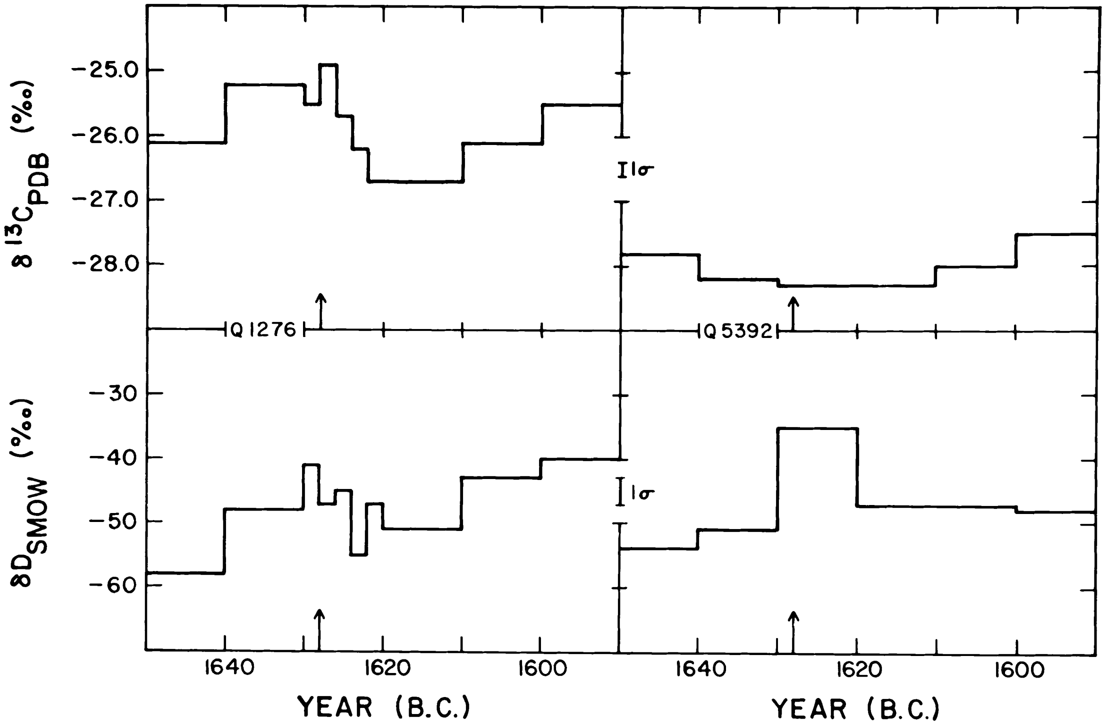

Figure 5. δD and δ^{13}C values of two Irish bog oaks (Q1276 and Q5392) for the period 1650 to 1591 B.C. Arrows denote the likely year of volcanic eruption in the Aegean island of Santorini, 1628 B.C. (Baillie & Munro 1988).

intra-ring δD variation was unsystematic for an 11 year period (1962 to 1972 A.D.), Tans and Mook observed that the year to year variations of δ^{13}C among different radial directions were more or less similar. They also state that similar results have been obtained for *Quercus robur*. If the limited data on the intra-ring isotopic variability in oak trees is indeed true, then a large number of trees in a site must be analysed and mean δD, δ^{13}C curves derived before attempting correlations with climatic parameters. Nevertheless, we computed the linear correlation coefficients between δD, δ^{13}C and ring width values of the two trees and the mean annual temperature (t), the mean annual maximum temperature ($t_{\max}$) and the total annual rainfall (r) between March and October (taken to be the growing season for Irish oaks). The climatic parameters were available from the Armagh weather observatory. These results are presented in table 3.

The tree Q5293 shows significant (at the 0.05 confidence level) positive correlations between δD and t(0.66), and δD and $t_{\max}$ (0.63); predictably, t and $t_{\max}$ are themselves highly correlated (0.89). The tree also shows significant negative correlations between δ^{13}C and t (−0.66), δ^{13}C and $t_{\max}$ (−0.59), δ^{13}C and r (−0.46), ring width and t (−0.68) and, finally, ring width and $t_{\max}$(−0.83).

The above significant correlations with climatic parameters seem to indicate that Q5293 was a tree which grew utilizing mainly rain water for its growth

Table 3. *Linear correlation matrix between* δD, δ^{13}C, *ring widths of the two trees Q5293 and Q5296* (δD$_1$, δ^{13}C$_1$, *R.W.1 and* δD$_2$, δ^{13}C$_2$ *and R.W.2 respectively) and Armagh mean annual temperature (t), mean annual maximum temperature* (t_{max}) *and March-October rainfall (r). No. of data points*= 22.

	δD$_1$	δ^{13}C$_1$	R.W.1	δD$_2$	δ^{13}C$_2$	R.W.2	t	$t_{\max}$	r
δD$_1$	1.0	$\underline{-0.77}$	$\underline{-0.67}$	0.17	−0.37	−0.36	$\underline{0.66}$	$\underline{0.63}$	0.24
δ^{13}C$_1$		1.0	$\underline{0.76}$	0.09	0.20	0.11	$\underline{-0.66}$	$\underline{-0.59}$	$\underline{-0.46}$
R.W.1			1.0	−0.06	0.32	0.29	$\underline{-0.68}$	$\underline{-0.83}$	−0.35
δD$_2$				1.0	−0.40	$\underline{-0.59}$	−0.04	+0.02	$\underline{-0.44}$
δ^{13}C$_2$					1.0	$\underline{0.50}$	−0.29	−0.36	−0.05
R.W.2						1.0	0.02	−0.06	0.12
t							1.0	$\underline{0.89}$	0.38
$t_{\max}$								1.0	0.30

Correlation coefficients $\geq$0.42, significant at 0.05 level (2 tailed Student's t-test), are underlined.

and did not have a permanent source of ground water nearby. This is also evident from the fact that the ring width of this tree shows a steady decreasing trend (figure 3) from 1860 to 1983 A.D. (figure 4), and the δ^{13}C values show a steady declining trend, probably because of fossil fuel injections into the atmosphere subsequent to the world-wide development of large scale industries after 1850 A.D., known as the Suess effect. Most normal trees analysed so far have shown these trends (Epstein and Krishnamurthy 1990).

The other tree, Q5296, appears to be an exception in that it does not show these trends. Furthermore, as evident from table 3, the δD, δ^{13}C and ring width values of this tree do not show significant correlation with climatic parameters, except for δD, which shows a barely significant negative correlation with r (-0.44). It seems likely that this tree utilized a permanent source of ground water nearby and consequently the ambient climate is not the main governing factor for its isotope or ring width variations. As suggested earlier in this section, this could perhaps be one possible reason for the absence of any similarity between the two trees in their δD, δ^{13}C and ring width time series.

It is also evident from table 3 that both trees show significant (at the 0.05 level) correlations between isotope ratios and ring width; positive in the case of δ^{13}C (0.76 for Q5293, 0.50 for Q5296) and negative in the case of δD (-0.67 and -0.59 respectively for Q5293 and Q5296). Such correlations have been reported earlier by a few workers (Ramesh *et al* 1988). This observation has led to a few speculative explanations. Of these, the most likely is that the climatic parameters have an opposing effect on the isotope ratios (δD for example) and the ring width. It has been argued that lower rainfall results generally in smaller ring width; at the same time the δD of rainfall is higher because of the 'amount effect' present in the rainfall (Dansgaard 1964). If the source water for a tree is mainly rainfall, the δD of tree cellulose would also be higher in such a condition. One would then expect a negative correlation between δD values and ring width. This explanation is not tenable in the present case because the ring width variations of neither tree show a significant correlation with rainfall. Furthermore, the δ^{13}C values are positively correlated with ring width, unlike the few earlier studies reported so far (Ramesh *et al* 1988). Temperature variations are also not responsible for this effect, because the second tree (Q5296) does not show any correlation with temperature, in δD, δ^{13}C or ring width variations.

We propose the following explanation as a likely possibility. In cases where ring width variations are not controlled by ambient climatic parameters, then a narrow ring, for example, can be produced by a relative shortfall of nutrients to a tree or because of competition among trees for nutrients. Consequently the mean assimilation rate (A) of carbon during this period of narrow ring growth will be less. This could imply that the growing season for the tree is limited to a short time, presumably to the summer months, when the ambient humidity is lower and temperature higher than the rest of the normal growing season, especially in the case of the Irish oaks under consideration. Such a condition would mean that the photosynthates produced in the shorter than normal growing season would be enriched in δD values because of the relatively higher evapotranspiration and the consequent enrichment of δD of leaf water, which is the source for synthesis of tree cellulose. Thus one would find a negative correlation between δD and ring width regardless of whether the tree used only rain water for its growth or it tapped water from a nearby permanent source of ground water. Also an "amount effect" is not necessary to be present in the regional rainfall to explain the observed negative correlation between δD ring width.

Similarly, decreased assimilation rate A (narrow ring) would result in a higher δ^{13}C value for tree cellulose, from the model of Francey and Farquhar (1982). According to this model, the δ^{13}C value of the cellulose ($\delta^{13}\mathrm{C}_p$) is related to the δ^{13}C of the atmospheric carbon dioxide ($\delta^{13}\mathrm{C}_a$), partial pressures of carbon dioxide inside and outside the leaves (C_i and C_a, respectively) through two parameters: a (the difference in the diffusivities of $^{12}\mathrm{CO}_2$ and $^{13}\mathrm{CO}_2$ in air, about 4.4‰), and b (the biochemical fractionation factor for carbon isotopes during cellulose synthesis, about 30‰).

$$\delta^{13}\mathrm{C}_p = \delta^{13}\mathrm{C}_a - a - (b - a)\mathrm{C}_i/\mathrm{C}_a \tag{1}$$

C_i and C_a are related by the assimilation rate (A) and stomatal conductance (g):

$$\mathrm{C}_i = \mathrm{C}_a - A/g. \tag{2}$$

Reduced A will increase C_i and hence decrease $\delta^{13}\mathrm{C}_p$. This would lead to a positive correlation between δ^{13}C and ring width, as has been observed by us. The stomatal conductance of carbon dioxide (g) would not perhaps change, because the trees are not water stressed.

We also performed a stepwise multiple regression analysis (Ramesh *et al* 1986b) of δD, δ^{13}C and ring width values of each of these trees with the Armagh mean annual temperature (t), mean annual minimum and maximum temperatures ($t_{\min}$, $t_{\max}$) and total rainfall during the growing season (r). Again, we found that in the case of the first tree, Q5293, δD and δ^{13}C were related only to t whilst ring widths were related to $t_{\max}$. Rainfall did not explain any significant additional variance in the δD, δ^{13}C and ring width values. In the case of the second tree, Q5296, no correlations were found, except that the δD values showed a barely significant correlation with r. The regression equations are:

For tree Q5293:

$$\delta\mathrm{D} = -\,(145 \pm 3) + (9.78 \pm 2.51)t \qquad \text{Correlation coefficient } R = 0.66 \qquad (3)$$

$$\delta^{13}\mathrm{C} = -\,(12.77 \pm 0.34) - (1.34 \pm 0.34)t \qquad R = -0.66 \qquad (4)$$

$$\text{Ring width (mm)} = (134.5 \pm 3.2) - (9.81 \pm 1.49)t_{\max} \qquad R = -0.82 \qquad (5)$$

For tree Q5296:

$$\delta\mathrm{D} = -(3.65 \pm 4.44) - (0.013 \pm 0.006)r \qquad R = -0.44 \qquad (6)$$

The autocorrelations of residuals (observed-calculated values) were not significant except in the case of equation (6). After adjusting the degrees of freedom for the autocorrelation of 0.40, the correlation R of equation (4) is not significant at the 0.05 level.

Gray and Song (1984) have reported temperature coefficients of δD in cellulose nitrate from three white spruce trees that grew in Edmonton, Canada, to be 7.3 ± 2, 13 ± 1 and 15 ± 2. Yapp and Epstein (1985) have reported a value of 14.1 ± 2 for an aspen tree that grew in Fairbanks, Alaska. Ramesh *et al* (1986b) have reported a value of 6.6 ± 2.3 for silver fir trees that grew in Kashmir, India. Within the quoted errors, our value of 9.78 ± 2.51 for the Irish oak (Q5293, equation (3)) agrees well with the above values.

Finally, we calculated the linear correlation coefficients of our tree ring data with Central England temperature and rainfall (Lamb 1977). The climate data were in the form of 3 month averages: December of the previous calendar year to February of the current year (winter); March to May (spring); June to August (summer); September to November (fall); and annual mean values for the current calendar year (January to December). The correlation coefficients are shown in table 4.

Again, the tree Q5293 shows significant correlations of δD, δ^{13}C and ring width with mean fall temperatures whilst Q5296 does not show any correlation. Q5293 also shows a significant correlation of δ^{13}C values with mean annual temperature. This confirms our earlier suggestion that the tree Q5296 must have had a local source of ground water, whilst Q5293 had used mainly rainfall for its growth. However, the tree reflects more closely the nearby Armagh temperatures rather than Central England temperatures (A seasonwise correlation with Armagh climatic parameters was not attempted because monthly mean data were not available). Neither tree shows any significant relationship with Central England rainfall values. High resolution stable isotope studies such as those of Ogle and McCormac (1994) and Loader *et al* (1995) may help to resolve this problem.

5.2 *Prehistoric samples*

Figure 5 shows that the range in the variations of δ^{13}C and δD during the period of analysis (1650–1591 B.C.) were 1.9‰ and 18‰ respectively for Q1276 and 0.8‰ and 19‰ respectively for Q5392.

In the case of δ^{13}C, compared to the decade previous to the purported Santorini eruption in 1628 B.C. (1640–1631 B.C.), both trees show a decline during the subsequent two decades (1630 to 1611 B.C.), although Q5392 shows this to a lesser degree (1.5‰ for Q1276 and 0.1‰ for Q5392). Although the decrease of 0.1‰ in Q5392 is not significant, considering the experimental error of ±0.1‰ in δ^{13}C, it is noteworthy that the 1630–1611 B.C. decades are in general lower in δ^{13}C than other decades prior and after, at least in this tree.

In the case of δD, Q5392 shows an increase of 16‰ (compared to the previous decade, 1640–31 B.C.) during 1630–1621 B.C.; Q1276 also shows a similar increase (1 to 7‰) in all the sub-samples of the 1630–1621 B.C. decade except 1624–23 B.C., where it shows a decrease of 7‰.

The lack of agreement in the magnitudes of isotopic shifts in both the above trees after the Santorini eruption is perhaps partly because of the intra-ring

Table 4. *Linear correlation matrix between δD, δ^{13}C, ring widths of the two trees Q5293 and Q5296 (notations same as in table 3) with Central England climatic parameters. No. of data points = 23.*

	δD_1	$\delta^{13}C_1$	R.W.1	δD_2	$\delta^{13}C_2$	R.W.2
Mean winter temperature	0.00	−0.07	−0.06	0.36	−0.19	−0.18
Mean spring temperature	0.32	−0.31	−0.21	−0.16	−0.02	0.19
Mean summer temperature	−0.25	0.12	0.18	0.00	0.08	0.10
Mean fall temperature	$\underline{0.54}$	$-\underline{0.62}$	$-\underline{0.62}$	−0.15	−0.06	0.10
Mean annual temperature	0.38	$-\underline{0.41}$	−0.32	0.12	−0.14	0.08
Mean winter rainfall	−0.02	0.09	0.00	0.40	−0.22	−0.15
Mean spring rainfall	−0.08	−0.15	−0.20	−0.06	−0.15	−0.13
Mean summer rainfall	−0.21	0.00	−0.02	−0.26	0.10	0.22
Mean fall rainfall	−0.01	0.01	0.32	−0.01	0.09	0.11
Mean annual rainfall	−0.07	0.03	0.03	0.16	−0.14	−0.02

Correlation coefficients ≥0.41, significant at 0.05 level (2 tailed Student's t-test), are underlined.

isotopic variability discussed earlier, considering that single radial strips of trees were analysed in the present study. However, it seems reasonable to believe that, following the volcanic eruption, the δD values tend to increase whilst the δ^{13}C values tend to decrease, the magnitude of change varying depending on the nature of the site and trees.

Stuiver and Braziunas (1987) have reported a negative correlation of tree cellulose δ^{13}C trends with Greenland ice sheet acidity peaks. Our results confirm this observation, but such an effect cannot be explained by the decreasing atmospheric temperature that generally accompanies an explosive eruption, caused by dust thrown into the stratosphere. This is because the trees in question grew on peat bogs, which provided a more or less permanent source of water. The trees, therefore, may not have utilized the rainwater directly for their growth to a significant amount. Consequently, even if the δD of precipitation decreased following the general cooling trend, the trees might not record the shifts in rainwater δD.

However, the mechanism proposed by us in the earlier section to explain the correlations between isotope ratios and ring width seems to offer an explanation for this effect as well. Baillie and Munro (1988) argue that pressure changes in the northern hemisphere months after the northern eruptions can produce a negative pressure anomaly over the British Isles. Such anomalies, associated with increased precipitation in the middle latitudes, could have resulted in flooding of the peat bogs and thereby reducing soil aeration. This will lead to a drastic reduction in the ring widths of oaks that grew on marginal bog environments. Consequently the assimilation rate of carbon (A) decreases, which will lead to a reduction of δ^{13}C in tree cellulose and an increase in δD, as explained previously. However, this result needs to be confirmed by analyzing more tree samples from this region.

6. Conclusions

We have investigated the potential of the 7400 year long Irish oak chronology for palaeoenvironmental records, by analyzing the δD and δ^{13}C of two modern trees for a period of 123 years with a 5 year resolution. We find that one tree (Q5293) shows significant correlations of δD, δ^{13}C and ring width with mean annual temperatures recorded at a nearby weather station, as well as the mean fall temperatures of Central England. The other tree (Q5296), which grew in the same general area, did not show such significant correlations. The reason could be that the latter tree had a permanent source of water nearby and did not record changes in the precipitation δD values and hence climatic temperature. However, both trees exhibited significant correlations between isotope ratios and ring widths. We have given a possible explanation for this observation. A reduction in the assimilation rate (A) during the formation of a narrow ring implies decreased δ^{13}C values for the tree cellulose according to the Francey and Farquhar (1982) model. Furthermore, the growing season is shortened, perhaps to one or two summer months, when the δD of leaf water (and hence that of cellulose) is higher due to increased evapotranspiration.

Our results on the climatic correlations of the two modern oaks indicate that the intra-ring variability in oak trees could be significant enough to prevent the derivation of a climate signal by isotopic analysis of a single radial strip from one tree. Hence, sufficiently large number of trees must be analysed to obtain a mean isotopic curve.

Our results on trees that grew during the 1620s B.C., when the Santorini volcanic eruption is thought to have taken place, show that in general δD values increased and δ^{13}C values decreased in tree cellulose following the eruption. We have explained this effect with a similar argument presented above for the isotope ratio-ring width correlations.

Acknowledgements

It is a pleasure to contribute this paper to the special issue for Prof. K. Gopalan, who, in 1978, set up the first stable isotope laboratory in India (at the Physical Research Laboratory, Ahmedabad) and initiated the programme of obtaining high resolution climate from tree rings. We thank Dave Brown for assistance in sample selection, R A Jani for help in grinding the wood samples and acid preparations. This work was made possible by a visiting fellowship granted to one of us (RR) by the Science and Engineering Research Council, U.K.

References

Baillie M G L 1973 A recently published Irish tree ring chronology; *Tree Ring Bulletin* **33** 15–28

Baillie M G L and Brown D M 1988 An overview of oak chronologies; In: *Science and Archaeology Glasgow 1987* (ed) E A Slater and J O Tate (Oxford) BAR British Series **196** 543–548

Baillie M G L and Munro M A R 1988 Irish tree rings, Santorini and Volcanic dust veils; *Nature* **332** 344–346

Becker B and Schmidt B 1989 Extension of the European oak chronology to the past 9224 years; *PACT* **29** 1–10

Bhattacharyya A and Yadav R R 1990 Growth and climate relationship in *Cedrus deodara* from Joshimath Uttar Pradesh; In: *Proceedings of the Symposium Vistas in Indian Palaeobotany, Paleobotanist* **38** 411–414

Borgaonkar H P, Pant G B and Rupakumar K R 1996 Ring-width variations in *Cedrus deodara* and its climatic response over the western Himalaya; *Int. J. Clim.* **16** 1409–1422

Cook E R, Bird T, Peterson M, Barbetti M, Buckley B, D'Arrigo R and Francey R 1992 Climate change over the last millennium in Tasmania reconstructed from tree rings; *The Holocene* **2** 205–217

Dansgaard W 1964 Stable isotopes in precipitation; *Tellus* **16** 436–468

DeNiro M J 1981 The effects of different methods of preparing cellulose nitrate on the determination of the D/H ratios of non-exchangeable hydrogen of cellulose; *Earth and Planet. Sci. Lett.* **54** 177–185

Duplessy J C 1978 Isotope studies; In: *Climate Change* (ed) J Gribbin (Cambridge: Cambridge University Press) pp. 46–67

Epstein S and Krishnamurthy R V 1990 Environmental information in the isotopic record in trees; *Philos. Trans. R. Soc. London* **330A** 427–439

Epstein S and Yapp C J 1976 Climatic implications of the D/H ratio of hydrogen in C-H groups in tree cellulose; *Earth Planet. Sci. Lett.* **30** 252–261

Feng X and Epstein S 1994 Climatic implications of an 8000-year hydrogen isotope time series from bristlecone pine trees; *Science* **265** 1079–1081

Ferguson C W and Graybill D A 1983 Dendrochronology of bristlecone pine: a progress report; *Radiocarbon* **25** 287–288

Francey R J and Farquhar G D 1982 An explanation of $^{13}C/^{12}C$ variations in tree rings; *Nature* **297** 28–31

Fritts H C 1976 *Tree Rings and Climate* (New York: Academic Press)

Gray J and Song S J 1984 Climatic implications of the natural variations of D/H ratios in tree ring cellulose; *Earth Planet. Sci. Lett.* **70** 129–138

Grinstead M J, Wilson A T and Ferguson C W 1979 $^{13}C/^{12}C$ variations in *Pinus longaeva* (Bristlecone pine) cellulose during the last millennium; *Earth Planet. Sci. Lett.* **42** 251–253

Grinstead M J and Wilson A T 1979 Variations of $^{13}C/^{12}C$ ratio in cellulose of *Agathis australis* (Kauri) and climatic change in New Zealand during the last millennium; *New Zealand J. Sci.* **22** 230–235

Hammer C U, Clausen H B and Dansgaard W 1980 Greenland ice sheet evidence of post glacial volcanism and its climatic impact; *Nature* **288** 230–235

Hughes M K, Kelly P M, Pilcher J R and LaMarche V C (Jr) 1982 *Climate from Tree Rings* (Cambridge University Press, Cambridge)

Lamb H H 1977 *Climate: Present, Past and Future* Vol. 2 (Methuen, London)

Loader N J, Switsur V R and Field E M 1995 High resolution stable isotope analysis of tree rings: implications of micro-dendroclimatology for palaeoenvironmental research; *Holocene* **5(4)** 457–460

Ogle N and McCormac 1994 High resolution $\delta^{13}C$ measurements of oak show a previously unobserved spring depletion; *Geophys. Res. Lett.* **21(22)** 2373–2375

Pant G B, Rupakumar K and Borgaonkar H P 1988 Statistical models of climate reconstruction using tree ring data; *Proc. Indian Natl. Sci. Acad.* **54(A3)** 354–364

Pilcher J R, Baillie M G L, Schmidt B and Becker B 1984 A 7272 year tree-ring chronology for western Europe; *Nature* **312** 150–152

Ramesh R 1984 *Stable Isotope Systematics in Plant Cellulose: Implications to Past Climate* PhD Thesis, University of Gujarat, India

Ramesh R, Bhattacharya S K and Gopalan K 1985 Dendroclimatological implications of isotope coherence in trees from Kashmir Valley India; *Nature* **317** 802–804

Ramesh R, Bhattacharya S K and Gopalan K 1986a Stable isotope systematics in tree cellulose as palaeoenvironmental indicators – a review; *J. Geol. Soc. India* **27** 154–167

Ramesh R, Bhattacharya S K and Gopalan K 1986b Climatic correlations in the stable isotope records of silver fir (*Abies pindrow*) trees from Kashmir India; *Earth Planet. Sci. Lett.* **79** 66–74

Ramesh R, Bhattacharya S K and Gopalan K 1988 Climatic significance of variations in the width and stable isotope ratios of tree rings; In: *Science and Archaeology Glasgow 1987* (eds) E A Slater and J O Tate (BAR Oxford) BAR British Series **196** 591–609

Shackleton N J and Opdyke N D 1973 Oxygen isotope and palaeomagnetic stratigraphy of equatorial Pacific core V 28–V 38: Oxygen isotope temperatures and ice volumes on a 105 and 106 year scale; *Quat. Res.* **3** 39–55

Straaten C M V 1981 *Deuterium in Organic Matter* PhD Thesis, University of Groningen, Netherlands

Stuiver M and Braziunas T F 1987 Tree cellulose $^{13}C/^{12}C$ isotope ratios and climatic change; *Nature* **328** 58–60

Sweda T 1994 Dendroclimatological reconstruction for the last submillenium in Central Japan; *Terrestrial Atmospheric and Ocean Sciences* **5(3)** 431–442

Sweda T and Takeda S 1994 Construction of an 800 year long *Chamaecyparis* dendrochronology for central Japan; *Dendrochronologia* **11** 79–86

Tans P P and Mook W G 1980 Past atmospheric CO_2 levels and the $^{13}C/^{12}C$ ratios in tree rings; *Tellus* **32** 268–283

Yadav R R, Park W K and Bhattacharyya A 1997 Dendroclimatic reconstruction of April May temperature fluctuations in the western Himalaya of India since AD 1698; *Quat. Res.* **48** 187–191

Yapp C J and Epstein S 1982a A re-examination of cellulose carbon bound hydrogen δD measurements and some factors affecting plant-water D/H relationships; *Geochim. Cosmochim. Acta* **46** 955–965

Yapp C J and Epstein S 1982b Climatic significance of hydrogen isotope ratios in tree cellulose; *Nature* **297** 636–639

Yapp C J and Epstein S 1985 Seasonal contributions to the climatic variations recorded in tree ring deuterium/hydrogen data; *J. Geophys. Res.* **90** 3747–3752