including the identification of a 22-yr cycle in a 1,000-yr δD record[12] in the bristlecone pine of the White Mountains, California. We also analysed forty trees ranging in age from 9,000–22,000 yr to obtain a most interesting record of δD of meteoric water during the Wisconsin glacial period[13].

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LEONA MARSHALL LIBBY AND LOUIS J. PANDOLFI REPLY—Long-term isotope changes in precipitation, caused by changes in climatic temperature, are well documented in polar ice caps; the heavier of the stable isotopes is depleted in ice laid down in the ice age by comparison with present-day ice. In 1970 we extended this concept to trees, suggesting that they are also thermometers. In trees which use rain to manufacture their rings, isotope variations in the rings should be climate indicators because the isotope composition in rain and $CO_2$ varies with temperature.

On May 17 1971, the Advanced Research Projects Agency funded our proposal that "temperature variations may be evaluated by measuring stable isotope ratios in natural data banks such as tree rings and varves." L.M.L. had previously calculated[1] the theoretical temperature coefficient of the isotope fractionation in manufacture of wood from $CO_2$ and $H_2O$, finding that the coefficient is small compared with that measured in rain.[2] Therefore isotope variations in rain should be dominant in trees that drink rain.

The next question is what to measure: whole wood, cellulose, lignin . . .? It may be true that the ratio of cellulose to lignin differs in spring and summer wood and over spans of decades.[3] Tentatively it seems that there is more lignin when it is warmer as in later summer, and that lignin is more enriched in the heavy isotope. We choose to regard such variations as part of the response of trees to climate variations, namely as part of the record of climate history.

Thus it is valid to measure any one of these substances, depending how faithfully it tracks local mercury thermometers. Our measurements on whole wood track for both hydrogen and oxygen. We expect the same success for cellulose and lignin, but they will track with different amplitudes because in these compounds different sets of chemical bonds are fractionating when the temperature changes.

In the development of radiocarbon dating the same question arose whether to measure wood, cellulose, or lignin, that is the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios will be different in each of these materials just as D/H is. W. F. L. chose to measure whole wood.

The next problem is what chemistry to use. There is compelling evidence that when sapwood passes into heartwood it becomes sealed against exchange with sap.[4] It is also known that isotope exchange occurs when wood is finely ground and soaked in hydrogen containing liquids[5]. So we decided to use dry chemistries. For our first tree sequence[6,7] we measured D/H by reacting sawdust with uranium to release $H^2$, 99‰ quantitatively. For the later tree sequences[4] we burned wood to water and reacted it with uranium to release $H_2$. For measurement of $^{18}O^{16}O$ we modified the method of Rittenberg and Pontecorvo[8] by carrying it out at very high temperatures, 99% quantitatively.

Our third problem was which trees to study. We could not use bristlecones because there are no lengthy temperature records for hundreds of miles near where they grow and we were determined to calibrate the trees against local mercury thermometers. Because the longest temperature records are in Europe, we obtained a German oak from the only tree laboratory then existing in Europe[4].

For measurement of the oaks, we used per force a mass spectrometer of somewhat low accuracy, and achieved the accuracy necessary to demonstrate tree thermometers by making many measurements on each sample. On the later tree sequences[4] we used high-precision machines with accuracies of ±0.1 p.p.t. for $^{18}O/^{16}O$ and ±2 p.p.t. for D/H. Whether the oxygen in tree rings comes from water or from $CO_2$ is a non-question, because Cohn and Urey[9] showed that isotopic equilibrium between the two substances is obtained in the atmosphere in a few hours.

The least square correlation of D/H against $^{18}O/^{16}O$ in the 1,800 yr sequence yielded the relation,

$$\delta D = 8.2\,\delta^{18}O + \text{constant}$$

which is the same as in worldwide rain[10] within experimental error. If both the hydrogen and the oxygen in the OH groups exchanged with water vapour there is absolutely no way that the slope can be 8, because there are twice as many hydrogens bonded to carbon as to oxygen.

The Fourier transforms[4] of our five-year samples in the 1,800 yr sequence showed ten significant periods ranging between 50 and 300 yr, the same for D/H and for $^{18}O/^{16}O$. To look for periods of less than 50 yr in a sequence of five-year samples or to look for periods of more than 300 years in a sequence of 1,800 yr is meaningless. Such periods appear in the transforms but they do not necessarily represent reality. To understand this we generated random signals of values 0 and 1, and assigned them to 10-yr intervals of a 1,000-yr hypothetical sequence, and made a Fourier transform. In three such computer experiments we always obtained periods at 10 and about 20yr which are artefacts of the sampling interval. These statements can be understood by reading carefully ref. 11, particularly pages 30–33.

Obviously ring samples integrated over 5 or 10 yr cannot give proof of the 21-yr solar cycle; instead each ring must be measured.

Nine of our ten periods[4] are equal to[12] those evidenced in the Greenland ice wells.[13] One of the periods, that at 173 yr, has also been found by Houtermans and Suess[14] in bristlecone pines.

Our isotope ratios track better with winter temperatures than with the average temperatures. Dr John Fletcher suggested that when climate deteriorates summer is brief and January, February, and March represent the longer winters.

For the cellulose component of wood, Epstein and Yapp[15] and Gray and Thompson[16] have corroborated our work.

Tree-ring thermometry promises to evaluate past climates and predict future climates.

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