Reports

Carbon-14 Content of 18th- and 19th-Century Wood: Variations Correlated with Sunspot Activity

Abstract. *A series of carbon-14 measurements of 18th- and 19-century wood revealed an excellent correlation between the variations in carbon-14 content and average sunspot activity. It seems probable, therefore, that the predominant cause of the short-term fluctuations in carbon-14 activity is the variability of solar activity.*

Since 1958, when the existence of fluctuations in the C^{14} content of tree rings was first demonstrated (*1*), the De Vries oscillations have been studied extensively. The studies essentially confirm the variability with time of the C^{14} content of tree rings, but often disagree with regard to the extent and position of maxima and minima. As the variations are of the order of only a few percent, statistical errors play an important part, and certain discrepancies can be explained statistically. The available data have been summarized by Libby (*2*).

In the study described here I concentrated on the 18th and 19th centuries, chiefly because detailed data concerning climate and other phenomena are available for these periods whereas for earlier periods such data are often lacking.

The C^{14} content of a tree ring can be measured rather accurately, but several problems arise when the result of the measurement is used to arrive at the C^{14} content in the atmosphere during the year of growth of the tree ring. The year of growth is normally determined by counting the number of rings, and the counting is valid only when all rings were formed annually. For the present study this problem is relatively unimportant because of the small number of tree rings involved, but for samples several thousands of years old the accumulation of error could become serious if other dendrochronological data were lacking.

The C^{14} content of the tree ring at the time of formation can be calculated from (i) the present C^{14} activity and (ii) the age of the ring, assuming that no C^{14} has been added to or removed from the ring since its formation. If exchange during the first few years after formation is disregarded, the probability of significant subsequent exchange seems to be low. Analyses of tree-ring samples from *Sequoia gigantea* and historically dated Egyptian samples of about the same age show approximately equal C^{14} content; consequently, the addition of C^{14} to the rings in or close to the tree center has been negligible during the growth of the tree. For rings several thousands of years old, the average carbon exchange, if it exists at all, must be less than 0.01 percent per year.

The C^{14} content of the tree ring provides an accurate indication of the atmospheric C^{14} content only if the C^{14} content of the tree ring is not influenced by local conditions. Climatic factors may also control the fractionation of the carbon isotopes, but a correction can be applied by measuring the C^{13}/C^{12} isotopic ratio. The results obtained with tree-ring measurements indicate that the influence on the C^{14} content of climatic factors is generally smaller than the standard deviation of 3 to 5 per mill involved in the analysis. As more accurate measurements are developed, these factors will certainly become more important.

A widely recognized phenomenon is the dependence of the deposition of atomic fallout on latitude; the dependence is due to the downward mixing of fallout from the stratosphere in middle latitudes via the gap in the tropopause. A similar mechanism for the distribution of cosmic-ray-produced C^{14} has been proposed by Tauber (*3*), where the extent of a possible belt of increased C^{14} concentration depends on the CO_2 exchange in the troposphere. With changing climate it is possible that the position of the belt of increased C^{14} concentration would shift, explaining the variations in C^{14} activity with time for a tree at a certain locality.

If the proposed mechanism is the principal cause of the De Vries oscillations, difference in C^{14} activity of the same order as found locally for a single tree should be found in simultaneously formed tree rings from different latitudes. To investigate this possibility, four trees were selected: a hemlock from Maine, a Douglas fir from Arizona, a fir from Colorado, and a spruce from Alaska. The results are given as the per-mill deviation of the C^{14} activity of the sample from 95 percent of the age-corrected activity of the oxalic acid standard at the National Bureau of Standards (NBS standard).

The average C^{14} content of three hemlock samples in Maine for the years 1780–1782, 1816–1818, and 1839–1841 deviates 4.1 ± 3 per mill from the age-corrected C^{14} standard, whereas the corresponding samples in Arizona deviate 3.3 ± 2 per mill. The samples from Colorado (1716–1717 and 1727–1729) deviate from the standard 7.8 ± 2 per mill and the corresponding samples in Arizona 10.8 ± 2 per mill.

The thickness of the tree-sections was limited, and it was not possible to use the same year's growth for all samples because the tree-rings often were too small to provide an adequate sample. If the Arizona tree-ring activities are taken as a base line, the Maine and Alaska samples contain, respectively, 0.8 ± 4 per mill and 2.2 ± 5 per mill more, and the Colorado sample 3.0 ± 3 per mill less than the Arizona sample. The differences in C^{14} content of trees between 32°N and 45°N is evidently extremely small and there is no indication for a greater C^{14} concentration at higher latitude than at the lower latitude. With the mechanism proposed by Tauber, a larger C^{14} content at the higher latitude is probable. Consequently, the proposed mechanism is probably not the principal cause of the De Vries oscillations.

The section most extensively analyzed is from a Douglas fir collected in the Santa Catalina mountains near Tucson, Arizona. The specimen grew at an altitude of about 1800 m, at 32° 23′N, 110°41′W, and dates from 1687 to 1951. The same section has been

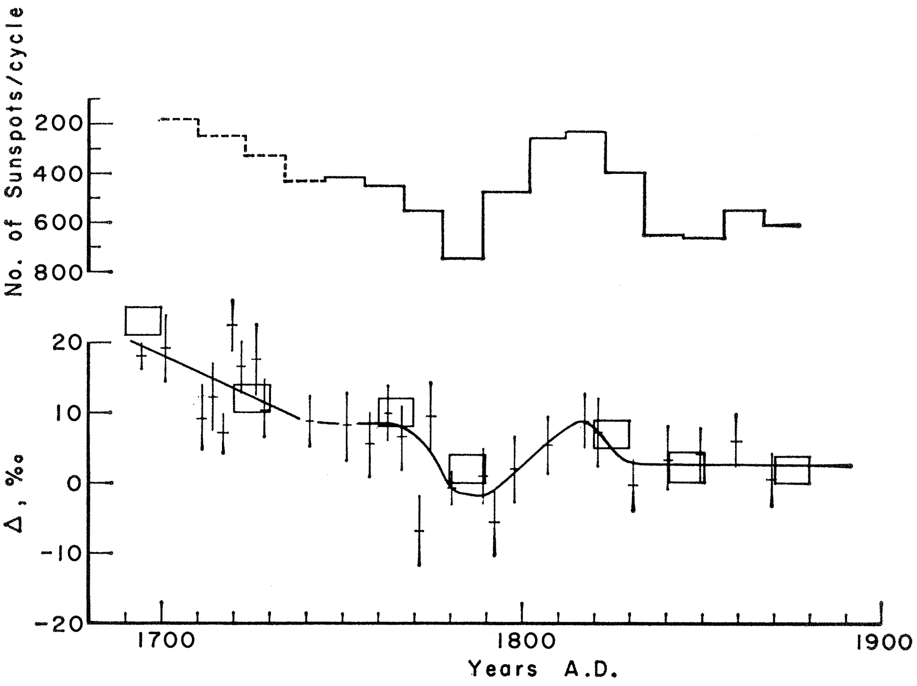

Fig. 1. Carbon-14 activity of tree rings given as per mill deviation of the activity of the samples from the age-corrected oxalic acid standard. The horizontal parts correspond with the number of tree rings used for analyses and the vertical lines correspond with the standard error. The lower curve is a visual aid only. The blocks represent older results reported by De Vries. The upper curve gives solar activity.

analyzed previously by Whitaker, Valastro, and Williams (*4*), so differences in results can only be due to differences in statistics or instruments.

All wood samples were treated in standard fashion with hydrochloric acid and dilute sodium hydroxide. The C^{13}/C^{12} isotopic ratios were determined with a mass spectrometer of the double collector type and are believed to be accurate within 0.5 per mill. The measured C^{14} activity of the sample is compared with 95 percent of the age-corrected activity of the NBS standard; the difference δC^{14} is the per mill difference in activity from the standard. No correction was applied for the C^{13}/C^{12} ratio of the NBS standard because this ratio was within 1 per mill of the recommended value of −19 per mill. The C^{14} assays are corrected for isotopic fractionation by use of the formula

$$\Delta = \delta C^{14} - (2\,\delta C^{13} + 50)\,(1 + \delta C^{14}/1000)$$

where δC^{13} is the per mill deviation of the C^{13}/C^{12} ratio of the sample from the ratio of the Chicago PDB-standard and Δ is the per mill difference in C^{14} activity of the sample and 95 percent of the oxalic acid standard; the Δ value is now corrected for isotopic fractionation. A half-life of 5730 years has been used for the age correction of the standard. The δC^{13} values of the measured samples are all within a range of -24.9 ± 1.0 per mill, resulting in a maximum correction of the average C^{14} content of $\pm$ 2.0 per mill. This correction is small when compared with the C^{14} variations actually encountered.

The data represented in Fig. 1 clearly indicate a variable but definite decrease in C^{14} content from about +20 per mill around A.D. 1700 to 0 per mill around A.D. 1790. The greatest difference in activity found between two single samples is 2.8 percent; the greatest difference found in the comparable series reported by Whitaker *et al.* is about 7.5 percent. The greater spread of the C^{14} activities reported by Whitaker *et al.* can be explained in part statistically (the standard deviation of the single measurements is about 8 per mill for the Whitaker series). In addition, the number of tree-rings used for their analysis is slightly smaller. Nevertheless, the fluctuations of up to 7.5 percent appear to be abnormally large in view of the present series of measurements of the same tree section.

Changes in production rate as well as variations in the rate of exchange between the reservoirs of carbon dioxide on earth can explain the fluctuations found in the C^{14} content of tree-rings. Large variations in neutron production in the upper atmosphere have been observed and are correlative with the sunspot cycle. Consequently, changes in C^{14} production correlated with the solar cycle certainly occur; the only problem is to determine if the solar influence is sufficiently large to explain the C^{14} variations observed. Short-term variations of a factor of 2 in neutron production have been observed, and Stuiver (*5*) calculated that for periods of the order of 100 years a change of 25 percent in production rate is sufficient to cause fluctuations in C^{14} content in the atmosphere of the order of 1 percent.

In Fig. 1, solar activity and C^{14} concentration are compared with each other. The solar activity is expressed as the total number of sunspots observed during each cycle; as the production of C^{14} is suppressed during years of maximum sunspot activity the scale for solar activity is reversed. For the construction of the curve of sunspot activity, the Zürich sunspot data of Wolff were used. The solid part of the curve is based on the continuous observations of the Zürich station; the dotted part is based on more scattered observations, and consequently there is some uncertainty with regard to this part. The curve is a visual aid only. The close relationship between sunspot activity and C^{14} content suggests that the changes in cosmic radiation are the main cause for the fluctuation in C^{14} activity in the atmosphere. Recently, Fairhall and Schell (*6*) reported a series of measurements of *Sequoia* tree-rings with C^{14} variations of only $\pm$ 1.5 percent over a period of 3000 years when a C^{14} half-life of 5830 years was used. Variations of this order of magnitude are completely compatible with those calculated from variations in sunspot activity. It is still possible that these variations are caused partly by changes in exchange rate of the earth's reservoirs.

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References and Notes

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7. The tree-ring samples from Arizona, Maine, Colorado, and Alaska were received through the courtesy of, respectively, M. A. Stokes and T. Smiley of the Laboratory of Tree-Ring Research, University of Arizona; H. E. Young of the University of Maine; E. W. Mogren of Colorado State University, and J. L. Giddings of Brown University. This research was supported by AEC under contract AT(30-1) 2652.

12 May 1965

Germanium and Silicon Disulfides: Structure and Synthesis

Abstract. *Crystal structures of the tetragonal forms of germanium and silicon disulfide are similar and consist of* $(SiS_4)^{4-}$ *and* $(GeS_4)^{4-}$ *tetrahedra which share vertices to form three-dimensional networks. These tetragonal materials, synthesized at high pressure and temperature, are different from the previously known germanium and silicon disulfides.*

Silverman and Soulen have reported on the behavior of the silicon-sulfur and germanium-sulfur binaries at high pressure (*1*). We have studied the synthesis and structure of the tetragonal germanium disulfide and the isotypic silicon disulfide prepared by the reaction of the elements at high pressure. These tetragonal phases are apparently very similar to those found by Silverman and Soulen.

When we examined the first products of the high-pressure synthesis, we found what were apparently new phases of GeS_2 and SiS_2. We could select single crystals suitable for x-ray analysis and subsequently determine the structures of both phases. These structures are similar and consist of $(GeS_4)^{4-}$ and $(SiS_4)^{4-}$ tetrahedra which share vertices to form three-dimensional networks. They are different from the structures of the low-pressure phases of GeS_2 and SiS_2 which have been known for almost 30 years. The low-pressure SiS_2 (*2*) contains parallel chains of $(SiS_4)^{4-}$ tetrahedra with the tetrahedra in each chain sharing edges. Low-pressure GeS_2, however, has a structure (*3*) in which $(GeS_4)^{4-}$ tetrahedra share vertices. For the remainder of this paper, we shall refer to the low-pressure forms as GeS_2 I and SiS_2 I and to the high-pressure forms as GeS_2 II and SiS_2 II.

Crystals selected for analysis were of irregular shape and of the following minimum and maximum dimensions: GeS_2 II, 0.04 by 0.40 mm; SiS_2 II, 0.13 by 0.50 mm. The x-ray patterns were sharp and gave no indication of twinning, disorder, or strain. The cells are tetragonal ($Z = 4$), with $a = 5.480 \pm 0.004$, $c = 9.143 \pm 0.004$ Å (GeS_2 II), and $a = 5.420 \pm 0.004$, $c = 8.718 \pm 0.004$ Å (SiS_2 II). Measured and calculated densities for SiS_2 are 2.39 and 2.37 g/cm³, respectively. The calculated density for GeS_2 is 3.30 g/cm³; we had insufficient material to measure the density. Powder patterns are given in Table 1.

Silverman and Soulen (*1*) reported a cell for their tetragonal silicon disulfide with $a = 5.43$ Å, $c = 8.67$ Å, and a measured density of 2.23 g/cm³. They did not give a cell for germanium disulfide but the powder pattern, revealed by x-ray diffraction, for this phase is similar to the one given here in Table 1. Although the apparent differences in the powder pattern are probably due to variations in composition of the reaction products, the difference in densities is larger than would be expected.

The occurrence of reflections from the body-centered tetragonal GeS_2 II and SiS_2 II obeys the following rules: $hk\ell$, $h+k+\ell = 2n$; $hh\ell$, $2h+\ell = 4n$. The diffraction symbol is $4/mmmI--d$ which includes space groups $I4_1md$ and $I\bar{4}2d$. Although both space groups are noncentrosymmetric, tests for piezoelectricity were negative.

Using chemical evidence, we selected the following trial structure in $I\bar{4}2d$, which later proved to be correct.

Atom	Equipoint	Symmetry	Cell coordinates
Ge or Si	4*a*	$\bar{4}$	0,0,0
S	8*d*	2	*x*,¼,⅛

We collected three-dimensional diffraction intensities for both crystals, using an equi-inclination diffractometer with filtered Cu*Kα* radiation, a scintillation detector, and pulse-height discrimination. A correction for absorption was applied in which the crystal shapes were approximated by a solid bounded by plane surfaces. While collecting the data for SiS_2 II, we noted that the intensities of reference reflections were diminishing with time and that the formerly clear-white crystal was becoming cloudy, indicating that the crystal was decomposing or changing state in some way. When all reflections were checked, we found that average scale factors could be applied to each reciprocal-lattice level to adjust for this error. These data, however, are not considered to be as reliable as are those for GeS_2

Table 1. X-ray patterns for GeS_2 II and SiS_2 II (I_0, intensity).

Index	GeS_2 II			SiS_2 II		
	Calc. (Å)	Obs. (Å)	I_0	Calc. (Å)	Obs. (Å)	I_0
101	4.70	4.72	80	4.60	4.61	75
112	2.96	2.96	100	2.88	2.88	100
200	2.74			2.71	2.71	40
103	2.66	2.66	35	2.56	2.55	20
211	2.37	2.38	45	2.34	2.34	30
004	2.29			2.18	2.17	20
220	1.94	1.94	40	1.92	1.92	60
213	1.91	1.91	30	1.86	1.85	40
301	1.79	1.80	15	1.77		
204	1.76	1.75	70	1.70	1.69	80
105	1.73	1.73	10	1.66	1.65	5
312	1.62	1.62	60	1.60	1.61	70
303	1.57	1.57	20	1.53	1.53	15

Table 2. Final atom parameters for GeS_2 II and SiS_2 II.

Coordinate	GeS_2 II		SiS_2 II	
	Ge	S	Si	S
x	0	0.2387 ± 0.0008	0	0.2272 ± 0.0004
y	0	.250	0	.250
z	0	.125	0	.125
*B**	0.62	.51	0.72 ± 0.16	1.31 ± 0.16
β_{11}	0.0057 ± 0.0007	0.0053 ± 0.0008		
β_{22}	0.0057	0.0033 ± 0.0008		
β_{33}	0.0015 ± 0.0005	0.0015 ± 0.0005		
β_{12}	0	0		
β_{23}	0	0.0011 ± 0.0007		
β_{13}	0	0		

* The isotropic *B's* for GeS_2 are the equivalents computed from the anisotropic values.