

the lunar surface was below 100°C and that no diffusion losses can have occurred (5). To detect possible losses of trapped solar wind particles during exposure, return flight, and subsequent handling and treatment, several pieces of the foil which had been irradiated earlier with a known neon ion flux of solar wind energy were attached to the foil. One of these test pieces has been analyzed so far, and no losses within 10 percent have been detected. If the solar wind arrived within 10° of the mean solar wind direction and an angular spread of  $\pm 5^\circ$  or less, we calculate from the measured average  $\text{He}^4$  concentration in the foil (Table 1) a  $\text{He}^4$  flux of  $(6.3 \pm 1.2) \times 10^6/\text{cm}^2 \text{ sec}$ . This figure is in agreement with observations from satellites and space probes (4, 6) which show wide variations in the  $\text{He}^4$  flux with a most probable value of about  $7 \times 10^6/\text{cm}^2 \text{ sec}$ .

By stepwise heating of portions of the foil for 24 hours, we determined that less than 10 percent of the trapped  $\text{He}^4$  is released at 150°C, and 25 percent is released at 250°C. This heat release pattern can be compared with laboratory experiments on the release of  $\text{He}^4$  ions trapped at energies of a few kiloelectron volts (5). For an ion energy of 1 keV the corresponding figures were 10 and 59 percent; for an ion energy of 3 keV, less than 5 percent and 22 percent. The heat release pattern for the trapped solar wind  $\text{He}^4$  is thus in agreement with a solar wind velocity at the lunar surface of approximately 300 to 400 km sec<sup>-1</sup>.

Table 1. Results of  $\text{He}^4$  measurements on 17 different pieces from the upper part of the Apollo 11 solar wind composition foil (G 15-7).

| Sample No.                     | Area (cm <sup>2</sup> ) | $\text{He}^4$ (10 <sup>10</sup> atom/cm <sup>2</sup> ) |
|--------------------------------|-------------------------|--------------------------------------------------------|
| 3-1                            | 104                     | 2.27                                                   |
| 3-4                            | 12.1                    | 2.27                                                   |
| 3-7                            | 4.1                     | 2.42                                                   |
| 3-8                            | 4.0                     | 2.37                                                   |
| 3-9                            | 4.0                     | 2.24                                                   |
| 3-10                           | 3.9                     | 2.33                                                   |
| 3-11                           | 3.6                     | 2.23                                                   |
| 3-14                           | 4.0                     | 2.05                                                   |
| 3-15                           | 4.0                     | 2.37                                                   |
| 3-18                           | 4.2                     | 2.67                                                   |
| 3-19                           | 4.0                     | 2.40                                                   |
| 3-20                           | 4.4                     | 2.45                                                   |
| 3-21                           | 4.1                     | 2.39                                                   |
| 3-22                           | 1.6                     | 2.42                                                   |
| 3-31                           | 1.7                     | 2.29                                                   |
| 3-32                           | 1.7                     | 2.30                                                   |
| 3-40                           | 3.2                     | 2.16                                                   |
| Average and standard deviation |                         | $2.33 \pm 0.14$                                        |

So far the Apollo 11 Solar Wind Composition Experiment has given the following results: Although during the time of foil exposure the sun was only 15° above the horizon, the solar wind penetrated to the lunar surface in accordance with the conclusion Lyon, Bridge, and Binsack (7) obtained from their Explorer 35 observations. The influx was highly directional, and the solar wind velocity was essentially unchanged. Our measurements indicate the presence of a solar wind albedo from the lunar surface.

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## Interglacial High Sea Levels and the Control of Greenland Ice by the Precession of the Equinoxes

Abstract. *The precession of the equinoxes appears to control the occurrence of high sea levels by partial or even total melting of the Greenland ice cap during interglacial ages.*

A comparison of the generalized deep-sea core paleotemperature curve, calibrated in terms of the  $\text{Th}^{230}/\text{Pa}^{231}$  time scale, and the absolute ages obtained by uranium decay series methods for high sea level carbonates from various parts of the world, has shown that the sea level may rise to a maximum more than once during each interglacial age (1).

Figure 1 shows the relation between the paleotemperature curve and high sea levels. Table 1 shows the ages of the high sea level stands (from 1) together with the ages of coincidence of perihelion with the northern summer solstice (from 2). The fit is impressive: high sea levels appear to follow closely perihelion coincidences, with a not unexpected time delay of a few thousand years; this delay would be even smaller if perihelion coincidence with the warmest month of year were given more significance than coincidence with the summer solstice.

The observed remarkable fit suggests that the second-order oscillations which cause the high sea levels are the result of significant melting of the Greenland ice cap after interglacial conditions are

established and when northern summer solstice occurs at perihelion. The total melting would raise present sea level about 10 m. In this context, Greenland appears more critical than Antarctica, apparently because it is not centrally located with respect to the pole and because it extends to considerably lower latitudes. It also appears that precession should be given more climatic significance, as proposed by Broecker (3). Today the earth receives about 7 percent more solar energy at perihelion than at aphelion. This change is certainly not insignificant, and, moreover,

Table 1. Ages of high sea levels (from 1) and of coincidence of northern summer solstice with perihelion (from 2). The two earliest high sea level ages carry a considerable error.

| Ages of high sea levels (10 <sup>3</sup> years ago) | Ages of coincidence of northern summer solstice with perihelion (10 <sup>3</sup> years ago) |
|-----------------------------------------------------|---------------------------------------------------------------------------------------------|
| 81                                                  | 82.4                                                                                        |
| 100                                                 | 105.9                                                                                       |
| 122                                                 | 126.9                                                                                       |
| 147                                                 | 151.0                                                                                       |
| 173                                                 | 175.7                                                                                       |
| 211                                                 | 220.3                                                                                       |
| 235                                                 | 242.0                                                                                       |

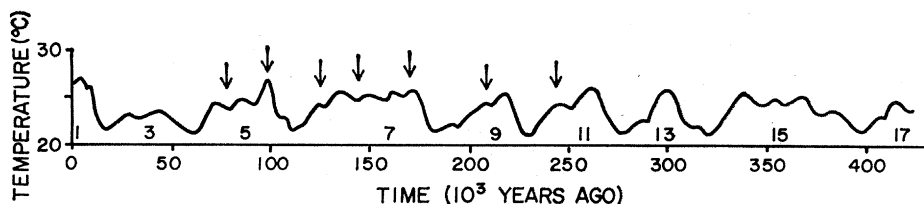


Fig. 1. Chronological relation between the generalized paleotemperature curve and high sea levels (from 1).

it would double at times of high eccentricity.

Dansgaard *et al.* (4) have shown that 85 percent of the ice now existing on Greenland dates from the postglacial while the remaining 15 percent is a residue from the last glacial age and the preceding interglacial. Incomplete or even insignificant melting of Greenland ice at the last perihelion coincidence, 11,200 years ago, probably resulted from the fact that interglacial conditions had not been established yet and that eccentricity was low (2, Fig. 1). Accelerated deglaciation, however, did take place at that time in both North America (Two Creeks) and Europe (Allerød), together with conspicuous soil formation (Brady).

The abundance of postglacial ice on Greenland demonstrates that ice ac-

cumulates there in interglacial time when the northern summer solstice occurs at aphelion. Substantial melting of Greenland ice is expected in about 10,000 years when the northern summer solstice will again occur at perihelion.

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## Phosphorus-Proton Spin-Spin Coupling and Conformation of a Dinucleoside Phosphate

**Abstract.** The phosphorus-31 nuclear magnetic resonance spectrum of  $\beta$ -adenosine-3'- $\beta$ -adenosine-5'-phosphoric acid in its aqueous solution (pH = 9.2) was studied. The signal consisted of eight peaks caused by the spin-spin coupling of the phosphorus nucleus with three protons, two on the 5' carbon, and one on the 3' carbon. The coupling constants were 3.4, 6.5, and 8.1 hertz; from these values the dihedral angles of the three P-O-C-H systems were estimated.

The conformation of a dinucleoside monophosphate in aqueous solution has been studied by Tinoco *et al.* (1, 2), Chan and Nelson (3), and Ts'o *et al.* (4). In these studies attention was directed to the intramolecular interaction of the two base residues placed at both the ends of the phosphodiester linkage. In contrast, we examined the phosphorus-proton spin-spin coupling through the phosphodiester linkage itself and we present information on the conformation of a phosphodiester linkage between two nucleosides in an aqueous solution.

A dinucleoside monophosphate has three H-C-O-P systems with the common P atom. The nuclear spin coupling in such a system depends upon the dihedral angle  $\phi$ . The coupling

constant between P and H ( $J_{PH}$ ) of an H-C-O-(PO<sub>2</sub>)<sup>-</sup> system in aqueous solution is 1.5 to 4.5 hz when C-H is *gauche* to O-P ( $\phi = 60^\circ$ ) and about 22 hz when C-H is *trans* to O-P ( $\phi = 180^\circ$ ) (5, 6). The  $J_{PH}$ - $\phi$  relation is as follows (7):  $J_{PH} = 4.5, 1.9, 22.3$ , and 23.5 hz, when  $\phi = 60^\circ, 65^\circ, 175^\circ$ , and  $180^\circ$ , respectively. It is reasonable to consider that the  $J_{PH}$ - $\phi$  relation is similar to the  $J_{HH}$ - $\phi$  relation for the H-C-C-H system (8) (Fig. 1). To apply this relation to the structural study of dinucleoside monophosphate, we observed the less complex <sup>31</sup>P nuclear magnetic resonance (NMR) spectra instead of the their proton magnetic resonance spectra.

$\beta$ -Adenosine-3'- $\beta$ -adenosine-5'-phosphoric acid [(3'-5')A<sub>p</sub>A] was prepared

by the modified Michelson's method described by Taylor and Hall (9). The (3'-5')-isomer was separated from the (2'-5')-isomer by chromatography on Dowex-1X2 (formate) ion-exchange resin. Its purity was confirmed by paper chromatography and by examination of the product after hydrolysis with ribonuclease and alkali. For the high-resolution <sup>31</sup>P NMR measurement, 25 to 30 mg of the product (ammonium salt of A<sub>p</sub>A) was dissolved in 1 ml of aqueous NH<sub>4</sub>OH (pH = 9.2), and this was placed in a thin-wall tube (4.8 mm, inner diameter). The measurement was made at room temperature with a Varian HA-100 spectrometer (Fig. 2a). To improve the ratio of signal to noise, 236 times signal accumulation was made with P<sub>4</sub>O<sub>6</sub> (in the capillary placed at the center of the sample tube) as the source of the lock signal. Curve (b) in Fig. 2 indicates our interpretation of curve (a); it was obtained from curve (a) after smoothing by visual inspection.

The <sup>31</sup>P NMR signal of (3'-5')A<sub>p</sub>A is found at +0.538 ppm (+21.8 hz/40.5 Mhz) lower frequency (higher field) than the resonance point of 85 percent H<sub>3</sub>PO<sub>4</sub>. The signal consists of eight peaks, an indication that there are three nonequivalent protons coupling with the <sup>31</sup>P nucleus in question (Fig. 2). The coupling constants  $J_{PH}$  are 3.4, 6.5, and 8.1 hz in the first-order approximation. From these values it is clear that none of the three P-O-C-H systems are fixed in the *trans* conformation. The dihedral angles ( $\phi_1$  and  $\phi_2$ ) of the two P-O-C(5')-H systems with the 5'-CH<sub>2</sub> should be given by  $60^\circ + \alpha$  and  $60^\circ - \alpha$ . For guanosine- and inosine-5'-monophosphates (in aqueous solutions), the two  $J_{PH}$ 's were both 4.5 hz, and accordingly  $\alpha$  was nearly  $0^\circ$  (6). For (3'-5')A<sub>p</sub>A,  $J_{PH}$  values corresponding to these two dihedral angles ( $\phi_1$  and  $\phi_2$ ) are probably 3.4 and 6.5 hz, because any other combination does not seem to fit the  $J_{PH}$ - $\phi$  relation given in Fig. 1. From these values,  $\alpha$  is estimated to be about  $4^\circ$ , then  $\phi_1$  equals  $64^\circ$  and  $\phi_2$  equals  $56^\circ$ . The remaining  $J_{PH}$  (8.1 hz) should be assigned to the P-O-C(3')-H system. On the basis of the  $J_{PH}$ - $\phi$  relation (Fig. 1), the dihedral angle ( $\phi_3$ ) should be about  $50^\circ$  or  $130^\circ$ . The latter possibility ( $\phi_3 = 130^\circ$ ) may be eliminated, because this corresponds to a nearly eclipsed conformation of the two atomic groups at both ends of