

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 accumulates 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 β -adenosine-3'- β -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 ϕ . The coupling constant between P and H (J_{PH}) of an $H-C-O-(PO_2)$ - 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 $J_{\rm PH}$ - ϕ relation is as follows (7): $J_{\rm PH} = 4.5$, 1.9, 22.3, and 23.5 hz, when $\phi = 60^{\circ}$, 65°, 175°, and 180°, respectively. It is reasonable to consider that the $J_{\rm PH}$ - ϕ relation is similar to the $J_{\rm HH}$ - ϕ 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 ³¹P nuclear magnetic resonance (NMR) spectra instead of the their proton magnetic resonance spectra.

 β -Adenosine-3'- β -adenosine-5'-phosphoric acid $[(3'-5')A_pA]$ was prepared by the modified Michelson's method described by Taylor and Hall (9). (3'-5')-isomer The was separated from the (2'-5')-isomer by chromatography on Dowex-1X2 (formate) ionexchange resin. Its purity was confirmed by paper chromatography and by examination of the product after hydrolysis with ribonuclease and alkali. For the high-resolution ³¹P NMR measurement, 25 to 30 mg of the product (ammonium salt of A_nA) was dissolved in 1 ml of aqueous NH_4OH (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_4O_6 (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 ³¹P NMR signal of $(3'-5')A_pA$ is found at +0.538 ppm (+21.8 hz/ 40.5 Mhz) lower frequency (higher field) than the resonance point of 85 percent H_3PO_4 . The signal consists of eight peaks, an indication that there are three nonequivalent protons coupling with the ³¹P nucleus in question (Fig. 2). The coupling constants $J_{\rm PH}$ are 3.4, 6.5, and 8.1 hz in the firstorder 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 (ϕ_1 and ϕ_2) of the two P–O–C-(5')-H systems with the 5'- CH_2 should be given by $60^\circ + \alpha$ and $60^{\circ} - \alpha$. For guanosine- and inosine-5'-monophosphates (in aqueous solutions), the two $J_{\rm PH}$'s were both 4.5 hz, and accordingly α was nearly 0° (6). For $(3'-5')A_pA$, J_{PH} values corresponding to these two dihedral angles $(\phi_1 \text{ and } \phi_2)$ are probably 3.4 and 6.5 hz, because any other combination does not seem to fit the $J_{\rm PH}$ - ϕ relation given in Fig. 1. From these values, α is estimated to be about 4° , then ϕ_1 equals 64° and ϕ_2 equals 56°. The remaining $J_{\rm PH}$ (8.1 hz) should be assigned to the P-O-C(3')-H system. On the basis of the $J_{\rm PH}$ - ϕ relation (Fig. 1), the dihedral angle (ϕ_3) should be about 50° or 130°. 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

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Fig. 1 (left). Phosphorous-proton spin-spin coupling constant $J_{\rm PH}$ plotted against the dihedral angle ϕ in the (PO₂)⁻-O-C-H system in aqueous solution. Fig. 2 (right). The ³¹P NMR spectrum (40.5 Mhz) of (3'-5')A_pA in aqueous NH₄OH (pH = 9.2). (a) Recorded curve after 236 times accumulation of the signal with P_4O_6 as the source of the lock signal. (b) Curve obtained from curve (a) after smoothing by visual inspection.

the O(3')-C(3') bond, and because such a conformation is considered unstable on the basis of what is known about internal rotation around the C-C or C-O single bond (10). Even when ϕ_3 is fixed at 50°, there are still two possible conformations: (i) C(3')-C(2') is nearly gauche to O(3')-P and C(3')-C(4') is nearly trans to O(3')-P; and (ii) C(3')-C(2') is nearly trans to O(3')-P and C(3')-C(4') is nearly gauche to O(3')-P. We choose the former conformation because this is the only one which enables the two adenine residues, each of which is considered to have the anti position with respect to the ribose ring, to come to a position having a stacking interaction; it is evident that there is an appreciable base-base stacking interaction in the $(3'-5')A_pA$ molecule in an aqueous solution of pH 8 to 9 (1-4).

For each value of the dihedral angles ϕ_1 , ϕ_2 , and ϕ_3 just shown, some



Fig. 3. Model of the $(3'-5')A_{P}A$ molecule. (a) Viewed along the O(5')-C(5') bond. (b) Viewed along the O(3')-C(3') bond. This model was constructed on the basis of the following postulates. (i) The nucleosidyl units have the anti conformation. (ii) Two adenine planes stack on each other (with a distance of about 3.5 Å) in a way similar to that shown by Ts'o et al. (4). (iii) In each ribose ring, C(1'), C(3'), C(4'), and O(1') form a coplaner structure. (iv) The dihedral angles of the two P-O-C(5')-H systems are both nearly 60° . (v) The dihedral angle of the P–O–C(3')–H system is nearly 50°, and that of the P–O–C(3')–C(4') is nearly 170°. (vi) Both of the C(3')–C(4')–C(5')–O(5') and O(1')–C(4')–C(5')–O(5') systems have nearly gauche conformations, similar to those in a Na salt crystal of inosine-5'-monophosphate (11). (vii) Both of the C(5')-O(5')-P-O(3') and O(5')-P-O(3')-C(3') systems have nearly gauche conformations, like those in a Ba salt crystal of diethylphosphate (12).

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allowance must be made because the details of the $J_{\rm PH}$ - ϕ relation (Fig. 1) are not yet fixed. In addition, what can be determined from such a relation is only a time-averaged ϕ value. We cannot eliminate the possibility, for example, that the P-O-C(3')-H group experiences the trans conformation for a small fraction of time. Beyond these ambiguities, however, we can draw the following conclusion with a high degree of certainty. In most of the $(3'-5')A_pA$ molecules in aqueous solution, the P-O-C-(5')-C(4') group has nearly trans conformation, the P-O-C(3')-C(2') group has nearly gauche conformation, and the P-O-C(3')-C(4') group has nearly trans conformation. Figure 3 illustrates one of the possible and probable models of the $(3'-5')A_pA$ molecule, which is consistent with what has been described. It should be noted here that the ³¹P magnetic resonance spectrum gives no direct information on the dihedral angles around the C(4')-C(5'), O(3')-P, and P-O(5') axes. These angles should be fixed on some other bases.

We have made a similar observation of β -uridine-3'- β -uridine-5'-phosphoric acid $[(3'-5')U_pU]$. Here, almost an equal set of $J_{\rm PH}$ values to that of $A_{\rm p}A$ was obtained: 3.4, 6.7, and 8.2 hz. The degree of stacking of A_pA is much more extensive than that of $U_{n}U$ (1-4). Therefore, the fact suggests that the rotation around the C-O bonds is not mainly responsible for the degree of stacking or destacking.

In each of the dinucleotides and trinucleoside diphosphates, the two phosphorus nuclei would have sufficiently different chemical shifts, so that the two signals do not overlap at all. If so, the method can be applied to a structure study of these molecules in their aqueous solutions.

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Molasse Facies: Records of Worldwide Crustal Stresses

Abstract. Predominantly nonmarine molasse deposits in the Tethyan and Cordilleran mobile belts record major variations in orogenic activity in latest Cretaceous to earliest Cenozoic, mid-Cenozoic, and latest Cenozoic time. During the same intervals changes in activity also occurred on the sea floor. This coincidence suggests worldwide effects of movement of crustal plates.

Current speculation about crustalplate tectonics (Fig. 1) suggests that the major variations in linear magnetic patterns and in sequences of sediments on the sea floor may record periodic readjustment of movement of the plates (1). It is useful to inquire whether these

variations correlate with marked changes in sedimentary sequences in mountain systems. Significantly, such sediments preserve abundant evidence of variations in activity.

The focus of this report is on sedimentary products of orogeny in some of those mountains deformed in the last 70 million years (Fig. 2), for that is the span of the most reliable information about the sea floor now available. The examples selected (Fig. 1) lie in the Cordilleran (2) and the Tethyan (3, 4)mobile belts.

These orogenic deposits are called molasse. As in its type area on the Swiss Plain (3), the term is applied here to thick, predominantly nonmarine sediments that followed marine geosynclinal deposition and accumulated in troughs (5) which encroached on stable cratons during completion of major deformation. Commonly, aggradation began in coastal lowlands, then alluvial plain and piedmont environments prevailed during most of the molasse phase.

Molasse began to accumulate along the continental side of the Cordilleran orogenic axes during the latest Cretaceous to earliest Cenozoic times. Uplifted crustal blocks and folded strata within the troughs and on adjacent cratons contributed considerable detritus, especially in the central Rocky Mountains where volcanism was widespread. In the Tethyan belt the marine geosynclinal phase continued.

Major deformation and the molasse phase ended in the central Rocky Mountains during the mid-Cenozoic,



Fig. 1. Aseismic crustal plates outlined by belts of shallow-focus earthquakes (17). Cordilleran mobile belt along west side of American plate-1, central Rocky Mountains; 2, Colombian Andes. Tethyan mobile belt along southern margin of Eurasian and Indonesian plates-3, northern Alps; 4, southern Himalayas.

but volcanism persisted and thin nonmarine deposits spread across the craton. Molasse sedimentation also waned in the Colombian Andes. In the northern Alps molasse began to accumulate on the continental side of the range. In the Himalayas a molasse trough developed on the oceanic side of the mountains where it lay on the Indian continental block.

Volcanism and spread of the thin plains-mantle continued in the central Rocky Mountain region in the late Cenozoic. In the Colombian Andes renewed influx of molasse was accompanied by volcanism along the central axis. Thick molasse also accumulated in the Tethyan troughs, with only minor volcanism in the northern Alpine area.

During Pliocene and Pleistocene times deformation and regional uplift affected each of the molasse sequences as well as their source areas. In the central Rocky Mountain region, rift systems and wrench faults fragmented the orogenic axis, perhaps as a result of extension of the continental crust above the east flank of the overridden East Pacific Rise (6). The Colombian Andes were broken by high-angle displacements, both vertical and lateral, as volcanism reached its climax. In the Tethyan belt nappes were thrust over molasse bordering the mountain fronts.

Do these molasse records correlate with variations in activity found in the deep sea? Apparently there were three such episodes during the last 70 million years (Fig. 3)-in latest Cretaceous to earliest Cenozoic, in mid-Cenozoic, and in early Pliocene times (7). According to a sea-floor spreading hypothesis these intervals mark times of change in rate and direction of movement of crustal plates (1). Opening of the North Atlantic Basin (8) apparently was accomplished largely during the Mesozoic era. In the course of spreading during the Cenozoic, the rate diminished markedly in late Oligocene and early Miocene times, and again in the Pliocene epoch (7, 8).

Data from the eastern Pacific Basin and the adjacent coast of California suggest that during late Cretaceous and early Cenozoic drift toward the East Pacific Rise a west-facing coastal wedge accumulated along the continental margin (9). Then mid-Cenozoic blockfaulting, volcanism, and nonmarine basin sedimentation predominated as the leading edge of the continent overran the crest of the rise (9, 10). Seaways flooded this setting in late Ceno-