Book Reviews

Paleontological Clocks

Growth Rhythms and the History of the Earth's Rotation. Papers from a conference, Newcastle upon Tyne, England, Jan. 1974. G. D. ROSENBERG and S. K. RUNCORN, Eds. Wiley-Interscience, New York, 1975. xvi, 560 pp., illus. $57.

... *every paleontologist a geochronometrist; every fossil a geochronometer.* (*1*)

In one of the most interesting presidential addresses to any scientific society, John W. Wells, in 1962, made the observation to the Paleontological Society that the number of days of ancient months and years was recorded in the daily growth lines of skeletons of fossil corals (*1*). A Devonian year had 400 Devonian days. In the past couple of years, three major summaries of paleontological clocks have appeared (*2*, *3*), and now we have this book. As the editors state in their concluding chapter,

> The palaeontological data are of central importance as they provide the only known means of directly measuring the Earth's angular momentum and moment of inertia in the distant past.

The fossil evidence has so far been less than conclusive on all but one of the important issues. As J. W. Evans remarks,

> The trouble is that counting growth lines is not easy, as anyone who has tried can testify. It is constantly necessary to make subjective decisions about whether a line is really a line or where an annual or monthly series begins or ends. As a result it is not surprising to find that counts often come out close to the hypothesized values.

This complaint is mirrored in the discussion by various authors of whether one should take as the "correct" number of lines the mean, the mode, or the maximum number counted. In fact any of these may be appropriate, depending upon the type of organism being considered. Stromatolites, for example, may suffer erosion of layers, and thus the maximum number of lines surely comes closer to their daily history than does the mean or the mode value, both of which, however, are more appropriate for accretionary growth in clams.

In the light of the technical difficulty of objectively determining growth lines, the paper by J. Dolman is outstanding. Dolman adapted an optical microdensitometer to obtain a quantitative measure of the intensity of growth lines in bivalve shells. This technical advance, attempted by several but achieved only by Dolman, is especially useful because periodicities in the strip chart record obtained can then be analyzed by various statistical means, among which Fourier analysis has proved most useful. By enhancing the melody and decreasing the noise, this paper introduces a new degree of rigor into the field, and this should allow for the resolution of patterns of growth bands among previously enigmatic specimens. In addition, daily growth increments not only are "visible" optically, they may also be evident chemically. G. D. Rosenberg and C. B. Jones examined calcium, magnesium, silicon, and sulfur variations along microprobe traverses and found enough systematic pattern to warrant future use of this method, especially in Precambrian stromatolites.

After individual bands are resolved, the important point, of course, is what do they mean? As I. Thompson states,

> So gradual have been the changes in cycle lengths that small errors in time estimation arising from misinterpretation of shell growth patterns may render conclusions from such studies meaningless. First we must know how shell growth records geophysical cycles.

Some species have band patterns composed of daily increments owing to solar-day rhythms of 24.0 hours, some to lunar-day rhythms of 24.8 hours, others to both of these independently with resulting periodic interference of bands, and still others to rhythms of as yet unknown origin (as in deep-sea bivalves [*4*]). Intertidal bivalves close their valves on exposure, and this causes cessation of carbonate deposition and the formation of an organic layer, and thus a purely tidal record, as Evans documents beautifully. Thus along the Oregon coast the bivalve *Clinocardium* has widely spaced growth bands during the 24.8-hour cycle of high spring tides and narrowly spaced bands representing the exposure twice as often during the 12.4-hour neap tides. "Innate" biological clocks also appear to control rhythms that result in periodic growth bands in bivalves. Rhythmic growth under constant environmental conditions has been documented in the quahog *Mercenaria mercenaria* by Thompson and in scallops of the genus *Pecten* by G. R. Clark. In constant light or in constant darkness, these animals maintained a solar 24-hour rhythm. But for the intertidal *Mercenaria*, this 24-hour rhythm was combined with a 23.2-hour rhythm, for reasons unknown. In the subtidal *Pecten*, the solar rhythm was the only one observed. A further complication in correctly interpreting banding patterns in larger specimens is that as each clam ages its yearly growth is represented by fewer and fewer daily growth increments, as C. A. Hall shows. Clearly, as Thompson concludes,

> Determining precisely which geophysical cycles the bivalves use to time increment deposition is not an open-and-shut matter.

In general, tropical, subtidal species appear to be the most satisfactory for geophysical purposes.

Special attention should be given to data on stromatolites because these fossils can provide the only data on day length from rocks older than about 600 million years. R. E. Mohr reports that the 2-billion-year-old Biwabik stromatolites of Minnesota have a dominant periodicity of 12.8 "microlaminations" per group (identified by him as the semimonthly period), suggesting a lunar month of 25.6 days. This contrasts with Pannella's earlier report (*3*) of 36 to 39 days for the lunar month based on subtidal stromatolites from the same general area as the intertidal (?) Biwabik collection. Obviously this must be resolved; in addition, more stromatolites from other localities must be measured.

Assuming that daily growth bands were in fact rigorously identified, and that they have been correctly partitioned into lunar and solar months, the main paleontological conclusion is that through the Phanerozoic the number of hours per day has decreased, and correspondingly the number of days per year has increased. It has not been resolved whether this relationship is linear with time, or whether there are alternating periods of rapid and slow change (as the paleontological data suggest at face value). Indeed, paleontological data indicate that for a 100-million-year interval in the Mesozoic the earth's rotation accelerated. This, of course, cannot possibly be accounted for by the dissipative mechanism of tidal friction, and demands that the paleontological data be as firmly established as possible.

All the while paleontologists have been trying to figure out what the organisms were doing, the geophysicists have been calculating variations on the theme of how much of a reduction in the earth's rotation has occurred and what are the limitations on various mechanisms of accounting for the earth's "spin-down." The traditional figure (and the one used by Wells) for the increase in length of day is about 2 percent per 100 million years (1.8 milliseconds per century). However, on the basis of presentday data, R. G. Hipkin concludes that the best value for this is about 4 percent per 100 million years, a figure that is in poor agreement with many of the paleontologic data and that is also probably too high to be explained merely by tidal friction. A lower value is also indicated by P. M. Muller and F. R. Stephenson in the longest article of the book, in which they review all the astronomical observations from 1375 B.C. onward; they conclude that for 3000 years the acceleration rate in day length due to all causes (both tidal and nontidal components) has been a constant 2.5 milliseconds per century.

Several authors examine ways in which the speed of the earth's rotation can be altered. The variety of methods indicates how much ferment there is in the field. P. S. Wesson investigates the consequences of a changing *G* (Newtonian constant of gravity) vis-à-vis global expansion on the order of several hundred kilometers, and favors the latter. K. M. Creer believes the consequences are geophysically reasonable and significant for changes in the depth of the transitional zone of the mantle, as well as for differences between the oblateness of the geoid and the hydrostatic figure, with fluctuations on a 100-million-year time scale. In yet another approach, J. A. Jacobs and K. D. Aldridge examine coupling of the core to the mantle in conjunction with Urey's idea of 1952 that changes in day length may be linked to changes in the moment of inertia related to the rate of core growth (and Runcorn's corollary of 1962 that this involves changes in the number of convection cells). O. H. Weinstein and J. Keeney discuss Hubble's law and "a cosmological drag force," and J. Gribbin focuses on the 11-year sunspot cycle and solar tides. D. H. Tarling's solution to the problem of "excess deceleration" is to deny the existence of deep oceans in the past, and thereby to increase lunar tidal torque.

It seems that, in general, even low-frequency geophysics may be no better off than this high-frequency paleontology, and that adequate paleontological data would greatly help in distinguishing among at least some of the possible mechanisms of the earth's deceleration (*5*). Indeed, as Hipkin concludes,

> Now that palaeontology has confirmed that past changes in the lengths of day and month are of the same order of magnitude as the original geophysical predictions, the role of the geophysicist can only be the reactionary one of interpreting the data given him. Its reliability is a problem for the biologists.

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References

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4. D. C. Rhoads and G. Pannella, *Lethaia* **3**, 143 (1970).
5. W. H. Munk and D. Davies, in *Isotopic and Cosmic Chemistry*, H. Craig, S. L. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1963), p. 341.

Molecular Rearrangements

Isotopes in Organic Chemistry. Vol. 1, Isotopes in Molecular Rearrangements. E. Buncel and C. C. Lee, Eds. Elsevier, New York, 1975. xvi, 302 pp., illus. $41.75.

The current revival in tracer studies, after a period of commonplace use and then a decline, is due principally to the sophistication of nuclear magnetic resonance techniques. The editors announce that this volume is the first of a series that will also include volumes on the use of isotopes in hydrogen-transfer processes, aromatic systems, and elucidation of structure and on the use of carbon-13 and isotopic sulfur in organic chemistry. The intent of the series is to bring together information from areas of organic chemistry that have in common the use of isotopes.

Only a 26-page chapter is devoted to deuterium labeling in carbonium-ion rearrangements. Its author, Deno, writes, "No great effort has been made to secure complete coverage since many deuterium studies were auxillary [sic] to other work and are of import for their bearing on mechanistic problems rather than for illustrating techniques in deuterium labeling." He describes as "ingenious" a double-labeling experiment that is now commonplace. That method is at least as old as the work of Bloch and Rittenberg, whose double-labeling experiment, reported in 1945, showed that a metabolic acetylation reaction does not involve loss of carbon-bound deuterium. Deno's treatment of protonated cyclopropanes (pages 3 and 4) leaves the reader confused by the statement that kinetic isotope effects are of the secondary type and can be neglected, since his chart (page 4) shows the making and breaking of deuterium bonds, for which a primary isotope effect is expected. The "mechanisms" he presents on page 4 are shown, surprisingly, as nonreversible carbonium-ion rearrangements.

If this chapter seems short, the chapter by Hunter on carbanion rearrangements seems unduly long, because investigators have found little use for isotopes in the study of carbanions. Consequently, some sections of the chapter contain only the barest reference to a labeled compound. The chapter does, however, provide a good and profusely illustrated up-to-date, critical review of carbanion chemistry, and it includes an excellent appendix that lists, according to type, the specific compounds referenced in the chapter.

A once-popular book on molecular rearrangements contained a chapter by Rhoads on "no mechanism" pathways. Dolbier describes some of these inscrutable reactions in a chapter that relates secondary deuterium isotope effects to pericyclic reactions and includes cycloadditions, sigmatropic rearrangements, ene reactions, and retroene reactions. His discussion of the [2 + 2] cycloaddition reaction describes only the transition state proposed by Baldwin and Kapecki and offers no comment on the later (1969 to 1971) evidence by Huisgen, Dreiding, Brook, Ghosez, and their co-workers that the reaction proceeds through a crosswise transition state.

The remainder of the book is devoted to a review, by Holmes, of the use of isotopic labeling in the determination of mass spectral fragmentation mechanisms and another, by Swenton, of the use of deuterium in organic photochemical rearrangements. Swenton emphasizes that deuterium substitution is useful not only for establishing gross molecular change but also for synthesizing specifically deuterated molecules in reactions whose course is often profoundly altered by deuterium substitution in either reactant or solvent.

The references in this volume contain several errors. Running heads would have aided the reader. In spite of being a little ragged in a few places, the book is a good beginning in what should be a worthwhile series.

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Applications of Spectroscopy

Nuclear Magnetic Resonance in Biochemistry. Principles and Applications. Thomas L. James. Academic Press, New York, 1975. xiv, 414 pp., illus. $26.50.

Nuclear magnetic resonance (NMR) spectroscopy has developed over the past 30 years into a very powerful and versatile technique in the study of molecular structures, kinetics, interactions, and mechanisms. In the last half decade or so, remarkable advances in instrument design, particularly the advent of fast Fourier transform and pulse methods, have tremendously improved the sensitivity of