

DISCUSSION
SULFUR ISOTOPES OF IRON SULFIDES
IN DEVONIAN-MISSISSIPPIAN SHALES
OF THE APPALACHIAN BASIN: CONTROL
BY RATE OF SEDIMENTATION

KEVIN L. SHELTON

Department of Geology and Geophysics, Yale University,
P. O. Box 6666, New Haven, Connecticut 06511

The recent paper by Maynard (1980) proposed "a technique for approximating relative sedimentation rates using sulfur isotopes." He applied a relationship between $\delta^{34}\text{S}$ and sedimentation rate in recent sediments to data from ancient rocks. There are two major drawbacks to his approach: (1) sulfide nodules may not be appropriate for use as indicators of sedimentation rate, and (2) averaging of sedimentation rates obtained from ancient rocks may obscure important changes and processes within a sedimentary unit.

Maynard found that the implied sedimentation rate of Devonian-Mississippian shales, based on sulfur isotopic measurements of sulfide nodules, was "too high by a factor of about 5." The sulfur isotopic composition of the nodules was "too positive by about 10 to 20‰ for reasonable sedimentation rates." Maynard, however, found distinctly different isotopic values for "organic-bound" pyrite (Maynard, 1980, p. 782) with the difference in $\delta^{34}\text{S}$ in the correct direction for reasonable sedimentation rates. As he suggested, this "organic-bound" pyrite may more closely reflect the sedimentation rate and be more comparable to modern sediments, whereas, the sulfide nodules may represent special subenvironments ripe with organic matter in which sulfate reduction may have proceeded at a very rapid rate, having little to do with the overall sedimentation or sulfate reduction rate of the rest of the formation. A rapid rate of sulfate reduction would produce anomalously positive sulfur isotopic values similar to those found by Maynard. Thus, sulfide nodules may not be appropriate indicators of sedimentation rate.

In recent sediments instantaneous sedimentation rates can be measured, whereas in ancient rocks only average sedimentation rates can commonly be inferred. Maynard's application of sedimentation rates determined from the sulfur isotopic compositions of individual pyrite and marcasite nodules to an entire member or formation could be misleading. Even if the individual nodules could be shown to reflect instantaneous sedimentation rates, there is no reason a priori to expect these rates to be diagnostic of the entire member or formation. These inferred rates may instead reflect only local perturbations of processes of sedimentation at that point in the formation.

Maynard summarized the closed-system and open system hypotheses of Schwarcz and Burnie (1973) and cited the work of Marowsky (1969) on the Kupferschiefer as an example of a closed-system shale "whose isotopic composition is controlled by degree of contact of the basin of

deposition with open seawater." The Kupferschiefer was sampled at several localities, and the sample spacing is in centimeters. This situation was then compared to the assumed open-system shales of the Appalachian Basin. However, the sample spacing of the Appalachian shales is less controlled due to the much greater stratigraphic thickness involved.

The sample spacing in Maynard's study and his subsequent averaging of the data yield a gross difference between the inferred sedimentation rates of black and gray shales but may obscure changes in the sedimentation rate within a unit, an actual gradation and overlap of black and gray shale data, and possibly even the degree of open-system behavior of the depositional basin. The effect of such a sampling bias can be shown by considering the sulfur isotopic compositions of pyrite from Lower Devonian black shales and siltstones from the Appalachians of the Gaspé Peninsula of Quebec and comparing them to the Upper Devonian-Mississippian shale data of Maynard (1980).

The Lower Devonian black shales and siltstones near Murdochville, Quebec were sampled in both outcrop and drillcore. The drillcore data from the York Lake and Grande Greve formations are shown in figure 1. The $\delta^{34}\text{S}$ values of disseminated pyrite cubes within the York Lake Formation range from -17.1 to $+7.5$ per mil. The average of the four measurements within the formation is -4.0 per mil. This suggests a sedimentation rate of 2.1 cm/yr based on the equation of Maynard (1980), using a value of $+20.0$ per mil for Lower Devonian seawater sulfate (Holser and Kaplan, 1966). However, the individual sulfur isotopic measurements suggest sedimentation rates between 0.6 and 6.4 cm/yr. Averaging the data from the York Lake Formation obscures these possible changes in the sedimentation rate within the formation as well as preventing interpretation of possible local or limited closed-system

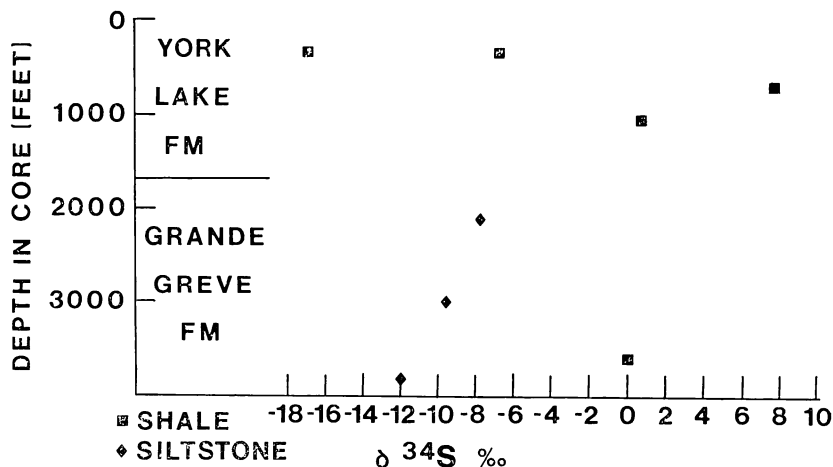


Fig. 1. Sulfur isotopic compositions of pyrite from Lower Devonian black shales and siltstones from near Murdochville, Quebec.

behavior within the depositional basin. A similar effect results if the Grande Greve data are averaged.

The Lower Devonian sequence from the Gaspé Peninsula may be reflecting changes in sedimentation rate, but the data may also suggest changes in the open-system behavior of the depositional basin. If parts of the basin are not in complete contact with open seawater, the first H_2S produced by bacterial reduction of seawater sulfate will be light (more negative $\delta^{34}\text{S}$), while later H_2S will become progressively more heavy. Such a possibility should not be quickly discounted.

Maynard's data are similar to the Gaspé Peninsula data. Most notably the Bedford Shale (the average composition of which Maynard uses as his point of comparison) and the Lower Huron Member of the Ohio Shale show sulfur isotopic ranges in $\delta^{34}\text{S}$ of -7.5 to $+20.0$ per mil and -8.7 to -0.9 per mil respectively, if data from pyrite nodules with calcite are omitted. If these data are included the isotopic ranges are even larger. Replotting Maynard's data (fig. 2) shows an overlap of black and gray shale data, if individual members and formations are not averaged. The two extremes of the Gaspé black shale data are also shown. The overlap of black and gray shales shows that Maynard's "correspondence between sulfur isotopes and inferred relative rates of sedimentation" is not clear-cut. There seems to be a gradation between black and gray shales. The black shales must also have high sedimentation rates or one of the basic assumptions, possibly complete open-system behavior, may be questioned. Maynard's application of sulfur isotopes to ancient rocks is an interesting potentially powerful tool but must be used cautiously, lest important details are overlooked in favor of generalities.

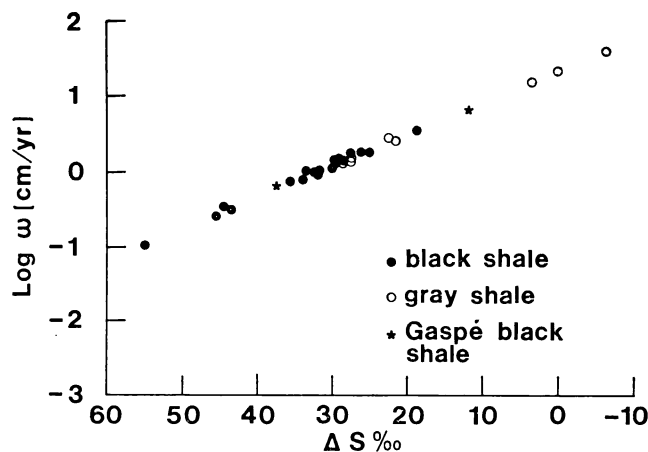


Fig. 2. $\delta^{34}\text{S}$ values from Devonian-Mississippian shales compared to the sedimentation rate, after Maynard (1980). Delta values calculated using the following values for seawater sulfate $\delta^{34}\text{S}$: Lower Devonian, $+20.0$; Upper Devonian, $+25.0$; Mississippian, $+20.0$ per mil (Holser and Kaplan, 1966). Data points are slightly offset to emphasize the overlap of black and gray shales.

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REPLY

J. BARRY MAYNARD

Department of Geology, University of Cincinnati,
Cincinnati, Ohio 45221

Shelton's discussion of my paper is a welcome contribution to our knowledge about sulfur isotopes in shales. He has pointed out a possible explanation for the discrepancy between the results for modern and ancient sediments and has presented some valuable data from another group of rocks for comparison. I would also agree with most of the cautions he presents about using this technique uncritically, but I should emphasize two points.

First, at a given locality in the Devonian shale sequence, the relationship of sulfur isotopes to lithology is striking. In table 2 (Maynard, 1980, p. 780) of the original paper samples are identified by county, which normally means a single outcrop or well. For instance, the samples from the Cleveland and Chagrin shales in Lorain County, Ohio were separated by only a few centimeters. Also the Sunbury, Bedford, and Cleveland samples from Rowen County, Ky. cover an interval of only a few meters.

Second, although averaging for whole members or formations is probably not valid for most shale deposits, in this case we are using relatively fine stratigraphic subunits. The members and beds in table 1 (Maynard, 1980, p. 778) range from less than 1 m to perhaps 30 m in thickness where sampled, although some become much thicker in the subsurface. The samples from the Wise County, Va. core are from a thicker part of the section, and the large spread in values found for the Middle Part of the Huron Member here and in other areas may reflect a stratigraphic unit that is not sufficiently homogeneous for this type of analysis. Likewise, the great spread in isotope values reported by Shelton for his stratigraphic units may be due to their much greater thickness than ours.

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DISCUSSION

SALT WEATHERING BY SODIUM CHLORIDE IN THE SAUDI ARABIAN DESERT

ERHARD M. WINKLER

Department of Earth Sciences, University of Notre Dame,
Notre Dame, Indiana 46556

Chapman's (1980) description and explanation of giant pedestal rocks in the Saudi Arabian desert with salt weathering invite some comments. The causes of decay mentioned are only in part correct; the possibilities of decay are incomplete. Halite, as the chief constituent of the soluble salts recorded, is made responsible for rock flaking and spalling. Mortensen's (1933) original account of the importance of hydration pressure as a parameter of rock decay is quoted here as an important reference. The reference, however, is misleading—halite does not hydrate at temperatures found in low latitude deserts. Hydrohalite, $\text{NaCl} \cdot 2 \text{H}_2\text{O}$, is stable only below $+ 0.1^\circ\text{C}$; hydration pressure cannot develop in the sense of true hydration when halite converts to hydrohalite incongruently by melting of halite and crystallization to hydrohalite. Correns (1949) calculated and measured the linear expansion of crystallizing halite. The calculations were extended to a variety of natural environments by Winkler and Singer (1972). Though Chapman claims halite to be by far the most common of the salts present, neither of the basic studies is mentioned by Chapman. This writer does not believe that crystallization pressure is the chief disruptive agent, since the solution-crystallization cycle does not occur often.

Halite is also very hygroscopic: it causes the surface attraction of moisture leading to clumping of the salt grains at high relative humidity. Occasional desert fog and the relative humidity in winter can attract considerable quantities of moisture by hygroscopic attraction despite only 70 mm annual precipitation for the area described. Vos and Tammes (1969) show that a halite content of 4 percent in brick can attract nearly 10 percent of moisture into the masonry from the atmosphere at a relative humidity of 80 percent. Chapman's figure of a maximum salt content of 40 percent within the rock substance at a relative humidity of 57 percent in winter may be extrapolated to a moisture content of near 50 percent. The disruptive action of moisture trapped in rock capillaries is well known. Disruption is also possible by heating-cooling cycles of moisture-saturated fine-grained rocks. The process was modeled by Winkler (1973), with the temperature-expansion pressure of entrapped water versus the expansion and may amount to as much as 250 atm when the rock is heated from 10° to 50°C ., a temperature contrast frequent in low latitude deserts. This should not distract from the proven effectiveness of crystallizing salts in rock.

Pedestal rocks are described as a desert landform, with a hard top surface and a soft, crumbling zone beneath. Despite the presentation in great detail on the mineral content of the Hofuf formation, no consideration is given to tafonis and honeycombs which are common desert

features in porous rocks. The presence of at least limited rock porosity permits the transportation of grain cement toward the surface resulting in reduced cementing material and rock strength beneath the visor-like top. The weakened rock substance may be further loosened and crumble by the effect of moisture as well as heat-moisture expansion — with or without salt action.

There appears to be a close relationship between tafonis, honeycombs, and pedestal rocks; the often overhanging hardened top resembles the strongly indurated and hardened visor of a tafoni.

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REPLY

RANDOLPH W. CHAPMAN*

University of Petroleum and Minerals,
 Dhahran, Saudi Arabia

In discussing my paper entitled "Salt weathering by sodium chloride in the Saudi Arabian desert" (Chapman, 1980), Winkler (1981) refers several times to the weathering of pedestal rocks. It should be noted that, although pedestal rocks are numerous in the Shedgum area, they are generally small features representing only a minute portion of the total bedrock, so that their weathering should not be unduly emphasized. Most of the weathering is taking place on gully walls, the edges of dissected bedrock terraces, the steep faces of erosional outliers, and the walls of deep caves.

It is true that some cavernous features such as tafoni and alveoli, which result from differential weathering, do exist in the area of investigation, but they are rare. They occur typically within or just below the tough duricrust that caps the pedestal rocks (Chapman, 1980, pl. 2-A).

Contrary to Winkler's understanding, I do not regard Mortensen's (1933) account of hydration pressure and rock decay as a pertinent and important reference in this particular situation. In fact, in the section on "Causes of rock disintegration" (Chapman, 1980, p. 127) I have specifically ruled out the development of significant stresses by salt hydration in the Shedgum area.

Winkler proposes two additional weathering mechanisms that deserve consideration here: (1) the disruptive action of moisture collected in the

* Present address: P.O. Box 785, Roswell, New Mexico 88201

rock hygroscopically by halite at high relative humidity, and (2) the disruptive action of heating-cooling cycles in moisture-saturated, fine-grained rocks. It seems that both these mechanisms, especially the first, may be involved in the weathering in the Shedgum area, but the degree of the involvement is not known.

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REVIEW

A cold-look at the warm-blooded dinosaurs (AAAS Selected Symposium 28); edited by R. D. K. THOMAS AND E. C. OLSON, P. 514. Boulder, Colo., 1980 (Westview Press, \$28.50).—The concept that dinosaurs may have been warm-blooded is one of the galvanizing ideas to emerge from the earth sciences in the past decade. So popular has the concept of warm-blooded dinosaurs become that one obliging author (J. C. McLoughlin, *Archosauria*, Viking Press, 1979), at the absolute nadir of good taste, has characterized the “conservative” “properly stodgy professor of paleontology”, “colored. . . by individual prejudice and scientific orthodoxy” who espouses a reptilian view of dinosaur physiology; in contrast to such “Grand Old Men” are “the few Young Turks” who follow “carefully liberal interpretations of dinosaur physiology”: wow! In fact, the issue of warm-bloodedness in dinosaurs is a red herring, there now being nearly universal agreement that dinosaurs, by virtue of size alone, had relatively constant (homeothermic) elevated body temperatures, a position advocated by Spotila in 1973. The debate then centers only on whether or not dinosaurs maintained body temperatures by rapid metabolism (that is, endothermy).

The book is an outgrowth of a symposium held at the American Association for the Advancement of Science meeting in Washington, February, 1978, and the 12 papers by 16 authors represent more than a doubling from the original 5 presentations. Apart from Bakker, who remains steadfast in his belief that all dinosaurs were endothermic, only four authors risk qualified support for endothermic dinosaurs. Ostrom believes some dinosaurs, especially theropods, “were probably endothermic”. Hopson observes that coelurosaurs “appear to have been metabolically as active as living birds and mammals”. Roth and Roth suggest “certain coelurosaurs. . . may have been endothermic”.

One of the interesting aspects of the debate consists of a philosophical problem: what constitutes evidence for the physiology of extinct organisms? Ricqlès, in an elegant critical essay on the significance of dinosaur bone structure, notes that evidence for dinosaur physiology is not of the *demonstrative* sort used for mathematical proofs; rather it is of the *accumulative* sort, whereby no single line of evidence can provide more than a strong inference, and a “proof” only results from a concordance of inferences. In his general review of the evidence marshalled in support of endothermy, Ostrom notes that only three lines of evidence

(posture and gait, feeding adaptations, bone histology) are direct factual observations; three others are inferences (cardiovascular considerations, high levels of activity, origin of birds); and two are ambiguous (predator/prey ratios, geographic distribution). He describes the first three as of uncertain significance and the remaining five as untestable and thus of doubtful value. Regal and Gans wryly observe, "some investigators are comfortable in drawing conclusions from evidence that other scientists regard as quite weak." These authors explicitly place the burden of proof with advocates of endothermy. However, why *should* the null hypothesis be that dinosaurs were cold blooded? T. H. Uzzell (personal commun.) points out that dinosaurs are much more closely related to living endotherms (birds) than to the vast array of living reptilian ectotherms (turtles, lizards, snakes).

A number of authors bring up-to-date their well-known positions. Farlow demonstrates that, depending on which groups of organisms are used for comparison, endotherms require from 2.3 to 9.1 times the amount of food required by ectotherms of equivalent weight; this is considerably less than the "order of magnitude difference" earlier proposed by Bakker. Bakker appears to concede the possibility of convergence of food requirements of large endotherms and ectotherms. Hopson argues unconvincingly that small brain size precluded high levels of metabolism in most dinosaurs. Spotila models body temperatures of pink elephants as well as those of white and black dinosaurs and shows that, within the confines of his model, dark skin color even for an endotherm with low (for example, elephantine) rates of metabolism would make overheating a potential problem.

Several authors are first-time contributors on this subject. Roth and Roth review evidence for the role of the parietal-pineal complex in vertebrate thermoregulation and conclude that most dinosaurs, by virtue of their loss of this complex, "retained the ectothermic strategy of ancestral thecodonts." Hotton presents a conservative but provocative view of dinosaur thermal physiology and offers water-saving uricotelic kidneys as the key adaptation for dinosaur success. He suggests that long legs and upright carriage were for stately long-distance migration, not fast running. He presents a valuable analysis of size distribution of living mammals in comparison to dinosaurs (80 percent of the former weigh less than 10 kg and only 2 percent reach the modal size of dinosaurs). Baur and Friedl, a pair of chemists, begin a complicated allometric analysis of thermal physiology with a dubious principle of evolutionary optimization: that evolution favors minimal increase in "mean animal activity rate." They correctly point out that dinosaurs were more gracile animals than are large mammals (that is, they had larger surface area to volume ratios)—but conclude from this that dinosaurs were *not* inertial homeotherms, ignoring the fact that crocodilians and large lizards are already well on the way to inertial homeothermy. They invoke a Permo-Triassic crisis in atmospheric oxygen to account for decrease in size in the therapsid-mammal lineage. At this point most readers will throw up their arms in despair.

After sitting quietly for 350 pages while 15 authors abuse him to varying degrees, Bakker appropriates the final 110 pages of text to erupt.

It is a *tour de force* of quintessential *Bakkeriana*, embodying the brilliance, imaginativeness, flamboyance, and glibness that tends to polarize his supporters and his critics. He draws skillfully on his first-hand experience from the Permian to the Tertiary. He cleverly rebuts comments on the size distribution of dinosaurs as compared with mammals by arguing that today's world is impoverished in larger mammals—and demonstrates this with data from the Chinese Miocene and the African Pliocene. He similarly argues that the modern world is depauperate in carnivores, and thus Tertiary predator/prey ratios in the 4 to 6 percent range (similar to those for dinosaurs) are more reasonable. He proposes four taphonomic tests for mammal predator/prey ratios: paired comparisons of (1) Early versus Late Cenozoic ratios, (2) sandstone versus mudstone ratios, (3) ratios in concentrated versus dispersed deposits, and (4) skeletons versus isolated materials. Although his claim that no significant differences exist in the four comparisons will not satisfy the reader, the value of his innovative approach is undeniable. He shows that across the broad range of relative brain sizes among living endotherms, no correlation with metabolic rate is to be found; thus he properly questions Hopson's suggestion that large brain size is a prerequisite for elevated metabolic rate. Bakker conveniently flags his weak points with rhetoric ("the documentation is irresistible;" "there can be no ambiguity;" without exaggeration;" "overwhelming evidence;" et cetera) that brings to mind the Nixonian "any fair-minded person would conclude. . . ." His provocative presentation will force the reader to consider whether "the Good Reptile model" has sufficient explanatory power to account for dinosaur success, but his strident insistence on the "need" for endothermy will cost him supporters.

Given that no one will ever place an oxygen mask on a dinosaur plodding on a treadmill (note that the cloacal thermocouple has been rendered unnecessary), any value this decade-long debate must have is heuristic. Indeed, there has been in the 1970's a vast increase in our knowledge of the physiology and ecology of reptiles and large mammals, as well as of our fundamental data base for dinosaurs. Victims in the '70's include stereotypes of reptile physiology and behavior and supposed thermal physiological contrasts between large reptiles and mammals. Indeed, Regal and Gans point out that, phylogenetically speaking, nearly everyone has tried endothermy (skunk cabbages, moths, bees, sharks, tunas, reptiles — even manure piles!), but because of its high inherent cost, only birds and mammals have found the expenditure justifiable. Very few scientists apparently feel a "need" for endothermic dinosaurs. The consensus is that dinosaurs were very special animals that were very probably intermediate in their metabolic characters between those of living reptiles and mammals. As no convenient stereotype comes to mind, they must be considered on their own merits.

This is a fine, stimulating, challenging book — well edited, pleasingly produced, with an excellent bibliography. It is to be recommended strongly for those interested in provocative paleobiology.

PETER DODSON