cient to account for the entire process. Therefore, major changes such as the advance or retreat of continental ice sheets, extended tectonic activity associated with sea-floor spreading, or the alternate occurrence of reducing or oxidizing bacteria as a result of the other features are suggested as possible mechanisms. Whatever the mechanism, it seems that it must involve fluctuating temperature and salinity conditions. This suggestion has been made by Gevirtz and Friedman (*2*) to explain the soft- and hard-layer lutite couplets in the Red Sea.

The development of a lithified carbonate rock from the soft, nonlithified ooze formed on the sea bottom must involve not one, but many, periods of lithification interrupted by periods of solution. The processes involved, lithification, solution, and related chemical changes, must be random and fluctuating in intensity, duration, and location. The process of alternating lithification and solution is responsible for the removal of significant quantities of carbonate sediment at the sediment-water interface. The result is a column of carbonate strata that represents not only the net product of ocean floor deposition and erosion but also the later effects of lithification, recrystallization, and solution of the carbonate rock that follow uplift of the sea floor or regression of the sea. Thus carbonate strata presently cropping out on the continents must represent several episodes involving lithification and solution on the sea floor, lithification due to physical and chemical changes, and lithification that follows uplift into subaerial environments.

GRANT A. BARTLETT*
Atlantic Oceanographic Laboratory, Dartmouth, Nova Scotia

ROBERT G. GREGGS
Department of Geological Sciences, Queen's University, Kingston, Ontario

References and Notes

1. A. G. Fischer and R. E. Garrison, *J. Geol.* **75**, 488 (1967); G. M. Friedman, *J. Sediment. Petrol.* **34**, 777 (1964); J. D. Milliman, *Science* **153**, 994 (1966).
2. J. L. Gevirtz and G. M. Friedman, *J. Sediment. Petrol.* **36**, 143 (1966); G. A. Bartlett and R. G. Greggs, *Can. J. Earth Sci.*, in press.
3. J. Brooke and R. L. G. Gilbert, unpublished report No. 95 (Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, 1968).
4. We are grateful to Dr. B. D. Loncarevic and J. Brooke, Atlantic Oceanographic Laboratory, for material from the eastern North Atlantic and to Dr. F. Aumento, Geological Survey of Canada, for samples from the western North Atlantic. For laboratory analyses and technical assistance we are indebted to M. Gorveatt and K. Robertson, Atlantic Oceanographic Laboratory, and J. Robertson, Queen's University.
* Present address: Department of Geological Sciences, Queen's University, Kingston, Ontario.

6 May 1969

Zircon Ages of Felsic Volcanic Rocks in the Upper Precambrian of the Blue Ridge, Appalachian Mountains

Abstract. *Five zircon samples from Pennsylvania, Virginia, and North Carolina yield discordant uranium-lead ages which suggest an original age of 820 million years and an episodic lead loss at 240 million years. The indicated age of lead loss is interpreted as the age of movement of the Blue Ridge thrust sheet.*

Nonfossiliferous sedimentary and volcanic rocks, generally assigned a late Precambrian age, crop out extensively in the Blue Ridge of the Central and Southern Appalachians. These rocks are directly involved in the recurring controversy over the base of the Cambrian (*1*). They rest nonconformably upon billion-year-old plutonic rocks, and where the stratigraphic succession is preserved, they are overlain with apparent conformity by Lower Cambrian(?) clastic rocks of the Chilhowee Group. Many workers have suggested that these upper Precambrian rocks are, at least in part, correlative and not greatly different in age from those of the Chilhowee Group (*2*). Some workers, in fact, suggest that many stratified rocks here assigned a late Precambrian age should be included with the Chilhowee in the Cambrian (*3*).

We present zircon ages determined from five felsic volcanic rocks spanning a horizontal distance of about 580 km in three upper Precambrian stratigraphic units of the Blue Ridge (Fig. 1). Uranium-lead ages are discordant, but they indicate an original age of 820 million years and are interpreted to indicate episodic lead loss at 240 million years. Although the three widely separated units yield the same original age, that age is somewhat older than we had expected. The Pb/U systems in the zircons were apparently not disturbed during regional metamorphism about 350 million years ago. The suggested age of lead loss is compatible with a late Paleozoic (Appalachian) age for the major movement of the Blue Ridge thrust sheet, the probable age of thrusting in the western Valley and Ridge belt.

Because of the overprint of Paleozoic metamorphism, the radiometric technique most likely to yield meaningful original ages of the upper Precambrian rocks is the uranium-lead isotope method applied to zircons from interlayered felsic volcanic rocks. These are restricted to three areas (Fig. 1) in the Blue Ridge belt. They occur sparsely in the Grandfather Mountain Formation, form a major part of the Mount Rogers Formation, and reappear in the Catoctin Formation in Maryland and Pennsylvania where they are a significant component. At least one dated felsite sample comes from each of the above formations.

The Blue Ridge belt is essentially anticlinal with a more or less continuous core of billion-year-old granitic gneiss. Upper Precambrian stratified rocks flank the granitic gneiss for much of the length of the anticlinorium, but locally on the northwest limb Chilhowee rocks overlap onto the basement. A mid-Paleozoic metamorphism, which mineral ages date as about 350 million years old (*4, 5*), produced a gradient across the Blue Ridge from unmetamorphosed Paleozoic rocks of the Valley and Ridge on the northwest to rocks of kyanite-staurolite grade on the southeast. The ambient metamorphic grade at our sample sites is low, probably in the chlorite or biotite zone. South of Roanoke, Virginia, the Valley and Ridge belt has an imbricate structure, and, at least in northwestern North Carolina, the Blue Ridge is also allochthonous, as shown by the presence of the Grandfather Mountain window, which contains lower-grade rocks eroded through the crystalline rocks.

The Grandfather Mountain Formation (*6, 7*), present only within the Grandfather Mountain window and at least 3000 m thick, rests nonconformably upon granitic basement that has yielded two zircon samples suggesting an original age of about 1050 million years if one uses a continuous diffusion model (*8*). The top of the formation is not exposed.

The Mount Rogers Formation, present in several thrust sheets, is about 3000-m thick and contains a thick pile of rhyolite in the middle. Both the base and top of the Mount Rogers are preserved, although commonly not in the same tectonic unit. Our dated samples come from two petrographically different rhyolites in a thrust sheet that does not include the upper contact. In the next lower thrust sheet, rhyolites correlated with the dated ones are interbedded with sedimentary rocks of the Mount Rogers Formation that are in apparent conformable contact with the overlying Chilhowee (*9*).

The Catoctin Formation in Pennsylvania consists of basalt, rhyolite, and phyllite, but the internal stratigraphy has not been unraveled. No structural discordance is recognized between the Catoctin and the overlying Chilhowee (*10*). To the southwest in Frederick County, Maryland, the Catoctin nonconformably overlies granitic basement.

For each sample analyzed, approximately 75 to 100 kg of rock were crushed, and a zircon concentrate was separated. The morphology of the zircon suggests that a single population is involved for each sample. The crystals are well terminated and lack overgrowths. The results of U-Pb and Th-Pb age determinations are given in Table 1. All uranium, thorium, and lead concentrations were obtained by isotope dilution. The zircon concentrates were decomposed by sintering with borax; standard ion-exchange and dithizone extraction techniques were used for chemical purification.

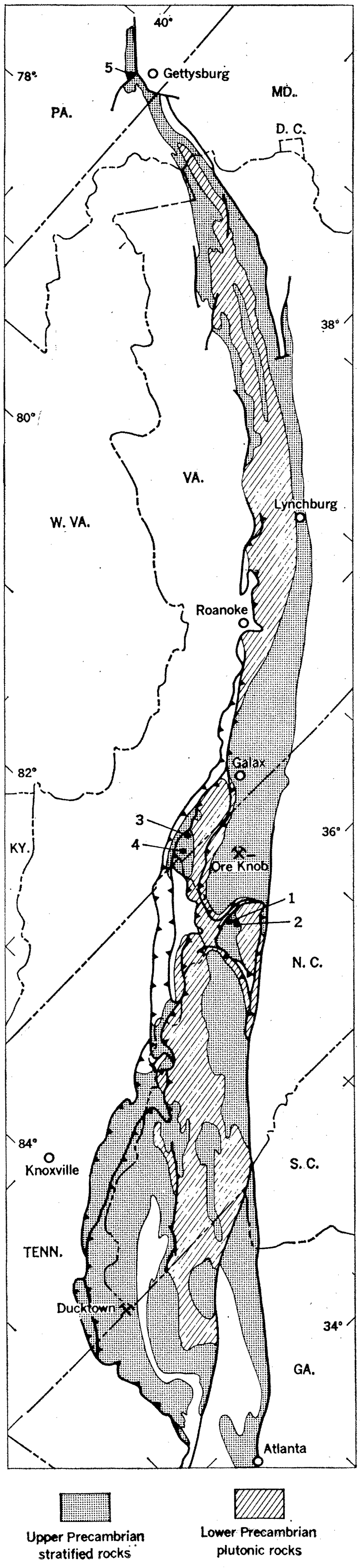
In making the common lead correction for the zircon age calculations, we assumed an isotopic composition identical with that of modern lead (*11*), which is close to the isotopic composition of lead extracted from our borax sinter. If we had used the isotopic composition of an 800-million-year model lead for the common lead correction, the calculated zircon ages would change only slightly. The original and lead-loss ages would, in turn, change by only a few million years. The accuracy of the mass spectrometric measurements of the zircon lead and the effect of these uncertainties on the original age are more difficult to evaluate. Two of the zircons analyzed contain only about 10 parts of lead per million (Table 1) and require large corrections for the nonradiogenic Pb^{207} present. Accordingly, the uncertainties in the precise plot of these two samples on the concordia diagram result in a spread of $\pm$ 30 million years for the postulated original age.

All of the zircons from the rhyolites fall very near a chord (Fig. 2, curve *A*) with lower and upper intercepts of 240 and 820 million years, respectively. Continuous-diffusion curves, assuming a fixed diffusion constant, D_0, for a primary age of 800 million years (curve *B*) and 900 million years, do not fit the experimental points as well as the episodic straight-line model. Therefore, we suggest that these zircons have an original age of 820 million years and were disturbed about 240 million years ago.

Ages from the Mount Rogers Formation are the most significant regionally because stratigraphic control is best for that unit. We initially questioned so high an age as 820 million years for the following reasons. (i) The most conspicuous hiatus in the stratigraphic section is clearly at the base of the Mount Rogers, (ii) the Mount Rogers-Chilhowee contact appears to be conformable on a local scale, and (iii) although the lowest reported Cambrian fossils are near the top of the Chilhowee (*12*), the suite of clastic rocks comprising the Chilhowee probably represents a relatively short interval of time.

Nevertheless, the isotopic data from the five zircon samples are so consistent that we are compelled to accept an older age. Such an age is compatible with new geologic evidence of an erosional interval between the Mount Rogers and the Chilhowee. Northwest of Galax, Virginia, east of the outcrop area of the Mount Rogers Formation, the Chilhowee rests directly on granitic basement. Abundant felsic and mafic dikes of probable late Precambrian age cut the granitic basement but are truncated by the nonconformity at the base of the Chilhowee.

A number of major upper Precambrian units of the Blue Ridge contain no recognized felsites, and their isotopic ages are still undetermined. These include the Ocoee Series of the Great Smoky Mountains, the recently defined Ashe Formation of northwestern North Carolina (*13*), the Lynchburg Formation of central Virginia, and the bulk of the Catoctin Formation of central and northern Virginia. All of these rest upon the billion-year-old granitic basement which places a maximum limit on their age. The Catoctin and parts of the



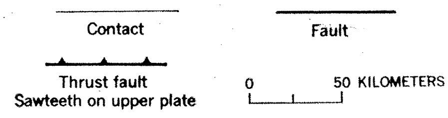
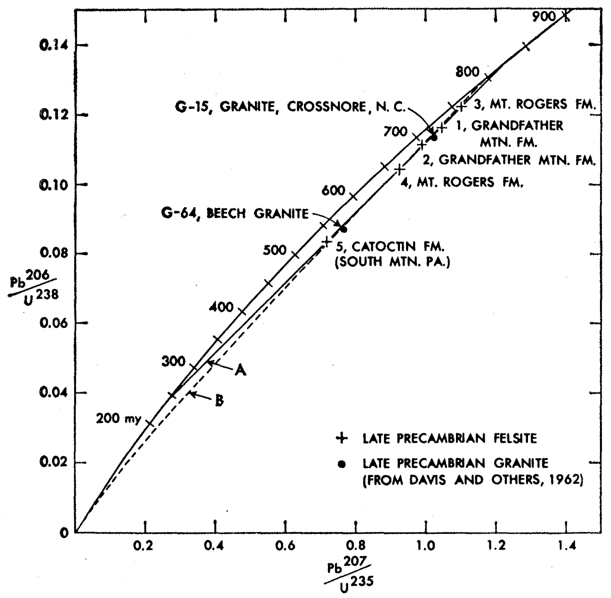


Fig. 1. Generalized geologic map of the Blue Ridge belt. Modified from Reed (*24*). The Valley and Ridge lie immediately northwest of the Blue Ridge. Numbers refer to dated upper Precambrian felsite samples. Nos. 1 and 2 are from the Grandfather Mountain Formation, Nos. 3 and 4 are from the Mount Rogers Formation, and No. 5 is from the Catoctin Formation. (See Table 1 for more detailed sample and location descriptions.)



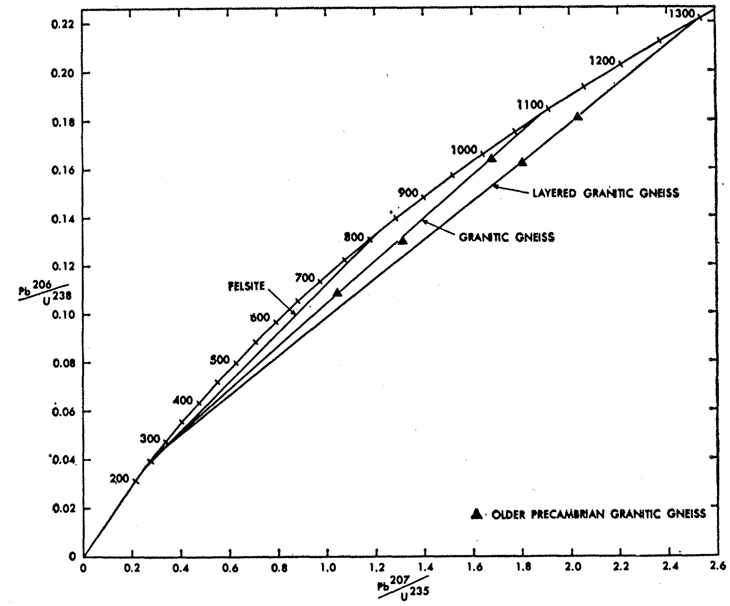


Fig. 2 (left). Daughter-parent (concordia) diagram for zircon samples. Curve *A* represents the episodic lead-loss model for the felsic volcanic zircons; curve *B* is the continuous-diffusion model for an original age of 800 million years (*m.y.*). Fig. 3 (right). Concordia diagram showing episodic lead-loss curves for Precambrian zircons of the Blue Ridge (*8*).

Ocoee are overlain by the Chilhowee and much of the Lynchburg appears to be older than the Catoctin. The minimum age for much of the Ocoee, the Ashe, and perhaps some of the Lynchburg could be early Paleozoic.

From the coherence on concordia of our samples, we suggest that felsic volcanism in the Blue Ridge is essentially coeval and that the Grandfather Mountain and Mount Rogers Formations and the Catoctin Formation north of the Potomac River are correctly included in the Precambrian rather than the Cambrian. A major hiatus is inferred between the time of felsic volcanism and deposition of the Chilhowee. We also suggest that the granitic basement of the Blue Ridge is everywhere older than 820 million years and as a corollary that all stratified units unconformab.y overlying this basement are younger than 1050 million years. Our geological interpretation that the host rocks for massive sulfide deposits at Ducktown, Tennessee, and Ore Knob, North Carolina, are upper Precambrian stratified rocks does not agree with K-Ar ages of 1045 million years and 1120 million years obtained on hornblende in ore bodies at these localities (*14*). Nor is our interpretation compatible with the pre-Mount Rogers plutonic or metamorphic event of 670 million years ago suggested by Riecken and by Dietrich, Fullagar, and Bottino (*15*) from K-Ar ages on biotite in granitic basement west of Galax, Virginia.

The zircon ages have yielded a number of dividends or at least hints of additional dividends. On geologic and petrographic evidence, Rankin (*16*) suggested that certain felsic and mafic plutonic bodies in the Blue Ridge were intrusive correlatives of volcanic rocks in the Grandfather Mountain and Mount Rogers Formations. Two of the plutonic bodies he included in this upper Precambrian volcanic-plutonic group are the Beech Granite and a small granite pluton at Crossnore, North Carolina. Published zircon ages for these two rocks (*6*) fall very close to our discordia chord for the rhyolites (Fig. 2).

Table 1. Analytical data for U-Pb and Th-Pb determinations. Sample GFM 3 is slightly sheared coarsely porphyritic felsite in the upper part of the Grandfather Mountain Formation. Roadcut along North Carolina Highway 105 along the Watauga River about 0.4 km upstream from the junction of the Watauga River and Laurel Fork, Boone 7½-minute quadrangle, North Carolina (*7*); 36°11′27″N, 81°44′46″W. Sample GFM 4 is slightly sheared felsite from near the base of the Grandfather Mountain Formation. Roadcut along the Blue Ridge Parkway about 2.1 km west of interchange with U.S. Highway 321 near Blowing Rock, Boone 7½-minute quadrangle, North Carolina (*7*); 36°8′51″N, 81°40′46″W. Sample R-TC2-14 is unsheared porphyritic rhyolite ash flow tuff from the youngest of three massive rhyolite units near the middle of the Mount Rogers Formation. Outcrop at an elevation of 10.90 m on the ridge northeast of Solomon Branch on the north slope of Stone Mountain, Trout Dale 7½-minute quadrangle, Virginia; 36°41′27″N, 81°27′45″W. Sample R-WS1-56 is unsheared phenocryst-poor, flow-banded rhyolite from median of three massive rhyolite units near the middle of the Mount Rogers Formation. Material excavated from building foundation on the summit of Whitetop Mountain, Whitetop Mountain 7½-minute quadrangle, Virginia; 36°38′20″N, 81°36′19″W. Sample 66-SO.M.-2 is unsheared phenocryst-poor rhyolite. Roadcut on north side of U.S. Highway 30, 0.8 km east of intersection with Pennsylvania Highway 234, Caledonia Park 7½-minute quadrangle, Pennsylvania (*10*, *23*); 39°53′54″N, 77°25′2″W. Concentrations are believed to be correct to within 2 percent of the reported value. The isotope ratios of the common lead used to correct for the nonradiogenic lead present in the zircons are $Pb^{206}/Pb^{204} = 18.51$, $Pb^{207}/Pb^{204} = 15.72$, and $Pb^{208}/Pb^{204} = 38.44$.

Sample		Concentration (ppm)			Atomic percent				Age (million years)*			
Lab.	Field	Pb	U	Th	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}	Pb^{206}/U^{238}	Pb^{207}/U^{235}	Pb^{207}/Pb^{206}	Pb^{208}/Th^{232}
1	GFM 3	12.8	73.3	70.2	0.328	63.21	8.89	27.57	716	736	798	620
2	GFM 4	100.7	773.2	447.3	0.104	76.10	6.41	17.39	692	710	770	680
3	R-TC2-14	19.9	118.9	104.5	0.201	66.72	7.27	25.81	750	764	798	776
4	R-WS1-56	70.4	445.3	469.8	0.304	62.33	8.44	28.92	644	674	778	586
5	66-SO.M.-2	11.2	95.2	62.5	0.329	67.31	8.99	23.37	524	558	700	434

*Constants: U^{238}, λ (decay constant) $= 1.54 \times 10^{-10}$ yr^{-1}; U^{235}, $\lambda = 9.72 \times 10^{-10}$ yr^{-1}; Th^{232}, $\lambda = 4.88 \times 10^{-11}$ yr^{-1}; $U^{238}/U^{235} = 137.7$.

Calculated continuous-diffusion curves of lead-loss for various original ages are essentially straight lines for much of their length and begin to curve perceptibly only near the origin (*17*). For rocks of the same original age and moderate lead-loss, exceptionally good analytical data are necessary to differentiate between continuous diffusion and episodic loss. Although a straight line (episodic loss) fits our data well, the near-linear part of the continuous-diffusion curve for an original age of 800 million years could be fitted within the analytical error of the experimental points.

If the near-linear part of a continuous diffusion curve is extrapolated to the concordia curve, the intercept is progressively closer to the origin for younger original ages (*18*). Published zircon ages on billion-year basement rocks from western North Carolina have been interpreted with a continuous diffusion model (*8*). If, however, the episodic lead-loss model is used, these ages define two additional chords on the concordia diagram—one for layered granitic gneisses with an original age of 1300 million years and one for granitic gneisses with an original age of 1080 million years (Fig. 3). Both of these chords intersect the concordia curve at about 260 million years. Convergence of the three independently determined chords at the concordia curve gives added weight to episodic lead loss.

Lead loss is not related to the mid-Paleozoic metamorphism. The zircon ages of older Precambrian rocks which were raised to grades as high as that of the garnet amphibolite facies by this metamorphism appear not to have been disturbed by it (*19*).

Thrust faults in this part of the Blue Ridge do not involve rocks younger than Middle Ordovician, but in the western part of the Valley and Ridge belt, imbricate thrust faults override Pennsylvanian rocks (*20*). If the imbricate structure represents one generation of thrusting, that episode must be as young as Pennsylvanian.

A single episode of thrusting is a requirement of the currently popular thin-skinned hypothesis for Appalachian structure. Cooper has attacked thin-skinned tectonics by suggesting that major thrusting which involved basement rocks at the southeast edge of the Valley and Ridge belt began in the Middle Ordovician (*21*).

Zircon ages of basement and upper Precambrian rocks show no evidence of disturbance in the Middle Ordovician nor at the time of major regional metamorphism. They do suggest an episodic lead loss at about 240 million years, an age compatible with late Paleozoic thrust faulting in the western part of the Valley and Ridge belt. We suggest, therefore, that the emplacement of the Blue Ridge thrust sheet also occurred during the late Paleozoic Appalachian orogeny and that shearing associated with the thrusting disturbed the zircon ages (*22*). Multiple episodes of thrusting are difficult to reconcile with this hypothesis.

D. W. RANKIN, T. W. STERN
J. C. REED, JR, M. F. NEWELL
U.S. Geological Survey,
Washington, D.C. 20242

References and Notes

1. P. B. King, *Amer. J. Sci.* **247**, 513, 622 (1949); J. Rodgers, in *El sistema Cambrico, su paleogeographica y el problema de su base, Symposium, Pt. 2* (20th Internat. Geol. Cong., Mexico, D. F., 1956), pp. 385–413.
2. R. O. Bloomer and H. J. Werner, *Bull. Geol. Soc. Amer.* **66**, 599 (1955); B. N. Cooper, *Grand Appalachian Excursion* (Virginia Engineering Experiment Station Extension Series, 1961), p. 15; J. C. Reed, Jr., *Bull. Geol. Soc. Amer.* **66**, 895 (1955); J. C. Whitaker, *ibid.*, p. 441.
3. R. O. Bloomer and R. R. Bloomer, *J. Geol.* **55**, 105 (1947); E. Cloos, in *The Physical Features of Washington County* (Maryland Department of Geology, Mines and Water Resources, Baltimore, 1951), p. 27; A. Keith, *U.S. Geol. Surv. Geol. Atlas*, folio 90 (1903); A. Keith, *ibid.*, folio 116 (1904).
4. W. R. Eckelmann and J. L. Kulp, *Bull. Geol. Soc. Amer.* **68**, 1117 (1957); L. E. Long, J. L. Kulp, F. D. Eckelmann, *Amer. J. Sci.* **257**, 585 (1959).
5. L. T. Aldrich, G. W. Wetherill, G. L. Davis, G. R. Tilton, *Amer. Geophys. Union Trans.*, **39**, 1124 (1958).
6. B. Bryant, *U.S. Geol. Surv. Bull. 1121-D* (1962).
7. ———, *U.S. Geol. Surv. Geol. Quad. Map GQ-243* (1963).
8. G. L. Davis, G. R. Tilton, G. W. Wetherill, *J. Geophys. Res.* **67**, 1987 (1962).
9. D. W. Rankin, *Guide to the Geology of the Mt. Rogers Area, Virginia, North Carolina, and Tennessee* (Carolina Geological Society Field Trip Guidebook, Raleigh, N.C., 1967).
10. J. L. Fauth, *Pa. Geol. Surv., 4th ser., Atlas 129a* (1968).
11. B. R. Doe, *J. Geophys. Res.* **67**, 2901 (1962).
12. R. A. Laurence and A. R. Palmer, *U.S. Geol. Surv. Prof. Pap. 475-C* (1963).
13. D. W. Rankin, in *Studies in Applalachian Geology—Central and Southern*, G. W. Fisher, F. J. Pettijohn, J. C. Reed, Jr., K. N. Weaver, Eds. (Interscience, New York, in press).
14. A. R. Kinkel, Jr., *U.S. Geol. Surv. Prof. Pap. 558*, 48 (1967).
15. C. C. Riecken, thesis, Virginia Polytechnical Institute (1966); R. V. Dietrich, P. D. Fullagar, M. L. Bottino, *Bull. Geol. Soc. Amer.* **80**, 307 (1969).
16. D. W. Rankin, *Geol. Soc. Amer. Prog. Annu. Meet.* **1967**, 181 (1967).
17. G. J. Wasserburg, *J. Geophys. Res.* **68**, 4836 (1963); E. J. Catanzaro, in *Radiometric Dating for Geologists*, E. I. Hamilton and R. M. Farquhar, Eds. (Interscience, New York, 1968), p. 232.
18. E. J. Catanzaro, *ibid.*, p. 233.
19. Sample No. M-51 of Davis *et al.* (*8*). Pelitic schists less than 2 miles away from this sample contain kyanite according to D. A. Brobst, *U.S. Geol. Surv. Bull.* **1122-A**, pl. 1 (1962).
20. P. B. King and H. W. Ferguson, *U.S. Geol. Surv. Prof. Pap. 311* (1960); Virginia Division of Mineral Resources, *Geologic Map of Virginia* (1963).
21. B. N. Cooper, *Univ. Mo. Rolla J.*, No. 1, 27 (1968).
22. This disturbance apparently affected South Mountain, Pennsylvania, also, where late Paleozoic thrusting cannot be established on direct stratigraphic evidence and the geology is not well enough understood to relate lead loss to the development of a specific structural feature.
23. G. W. Stose and F. Bascom, *U.S. Geol. Surv. Geol. Atlas*, folio 225 (1929).
24. J. C. Reed, Jr., *Tectonic Map of the Central and Southern Appalachians* (U.S. Geological Survey Open File Map, Washington, D.C., 1968).
25. We gratefully acknowledge the cooperation and interest of W. R. Shields, National Bureau of Standards, who made a high-resolution mass spectrometer available for this study. Publication authorized by the Director, U.S. Geological Survey.

21 May 1963; revised 11 August 1969

Sedimentary Phosphate Method for Estimating Paleosalinities: A Paleontological Assumption

Abstract. *Paleosalinity values in certain rocks determined by the sedimentary phosphate method differ from salinity estimates based upon contained fossil assemblages, geochemical methods, and existing stratigraphic controls. Some anomalous values are related to the abundance of fossil organisms known to be concentrators of calcium phosphate. Because of the abundance and diversity of organisms which might introduce significant errors into paleosalinity estimates, the sedimentary phosphate method seemingly is of limited applicability.*

During the course of paleoecologic investigations of the Lower Kittanning (Pennsylvanian age) rocks of western Pennsylvania, two observations proved of unusual interest. First, when compared with fossil assemblages of similar age in the midwestern states, the western Pennsylvania assemblages are impoverished, that is, characterized by the dominance (95 percent) of one or two species. Second, the maximum and mean sizes of the Lower Kittanning marine species are significantly smaller than their midwestern counterparts. Because reduced salinity could give rise to either of these effects, I examined published paleosalinity data for the Lower Kittanning rocks. Deg-