

tion. The reaction was not influenced markedly by the length of fixation or by pH over the range 7.5 to 9. Nor did heating the reaction mixture increase the density of the deposits, although it increases staining by uranyl salts [M. Locke, N. Krishnan, J. T. McMahon, *J. Cell Biol.* **50**, 540 (1971)]. We conclude that our procedure leads to saturation of the binding sites and that their small size reflects a correspondingly small structure. Staining on the section rather than in the tissue gave only a specificity. The nature of the bismuth binding site remains to be determined, but the reaction is not mimicked by lead or calcium, and it is therefore not due to labile phosphate groups. We have not excluded the possibility that the reaction shows exposed phosphate on DNA. If the bismuth binds to DNA (2), then the beads could be informational

- DNA [E. Bell, C. Merrill, C. B. Lawrence, *Eur. J. Biochem.* **29**, 444 (1972)] and the plaques could be membrane-bound DNA [W. Meinke, M. R. Hall, D. A. Goldstein, D. E. Kohne, R. A. Lerner, *J. Mol. Biol.* **78**, 43 (1973)], both concerned with local specific protein synthesis.
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Origin of Horizon A: Clarification of a Viewpoint

As shown in earlier studies (1), Weaver and Wise (2) report that siliceous microfossils (diatoms, sponge spicules, radiolarians) occur in some of the high-purity Tertiary opaline deposits of the Atlantic and Gulf Coastal Plain. They conclude therefore that these deposits as well as horizon A must be biogenic in origin. We wish to comment on this as it regards their interpretation of our earlier report (3) on this subject.

As a result of the JOIDES (Joint Oceanographic Institutions for Deep Earth Sampling) drilling program, a prominent and widespread oceanic seismic reflector known as horizon A has been shown to consist of hard, siliceous beds containing diatoms and radiolarians and to have a narrowly defined age from late Early to early Middle Eocene (4). A principal problem has been to explain the origin of this geographically widespread and non-linear siliceous horizon and not the other scattered and discontinuous siliceous deposits situated stratigraphically higher or lower.

Impressed by the presence of siliceous microfossils, Dietz and Holden (5), Berggren and Phillips (6), and Ramsay (7) have offered explanations based on several oceanic circulation models to explain horizon A as an entirely biogenic deposit. A major biogenic role in the formation of horizon A is undeniable. But no oceanic circulation model alone can explain the occurrences of smectites and zeolites that are found associated with almost all of the sediments correlating with this unusual horizon and found not only in the Atlantic and Gulf Coastal Plain but also on the shelf and in the Caribbean. Accordingly, Gibson and Towe (3), supported by Mattson and Pessagno (8), considered that a combined volcanic and biogenic explanation for the time-equivalent deposits was more consistent with all of the facts than a strictly biogenic explanation. The widespread distribution of horizon A in the western North Atlantic and the composition of the deposits themselves led us to a dual and

partially sequential cause: direct volcanic contributions to help explain the presence of smectite and zeolite but with accompanying increased nutrients (phosphorus, iron, and silica from dissolved fine pyroclastics) which would increase the productivity of siliceous organisms above normal background levels, providing increased contributions to the sediments. We wish to clarify that we did not state that the entire source of the relevant deposits was altered volcanic ash. We did not extend our conclusions to other siliceous deposits of different ages in the Atlantic and Gulf Coastal Plain nor did we extend them to siliceous deposits in other oceans, as Weaver and Wise have implied (2).

Silica is constantly being mobilized and deposited by diatoms in the world oceans, and few will argue about this biogenic contribution. But for horizon A, an oceanwide "chert" deposit, some mechanism is needed to raise the siliceous productivity and the deposition and preservation above the normal background level over a wide area in the Atlantic region. Changes in sediment dilution or in oceanic circulation patterns can be invoked to explain only part of the deposit, since such changes do not normally also provide a mechanism for zeolitic and smectite clays. However, wind and ocean currents can distribute soluble, fine pyroclastics and thus add potential planktonic nutrients that would contribute to the formation of the varied deposits observed. The relationship between siliceous organisms and volcanism has been noted from the time of Lyell (9) up to the present (10). In support of this concept, Lisitsyn (11) has presented consistent evidence for the indirect influences of volcanism in the active Bering Sea region on such nutrients as iron and phosphorus and the importance of these elements to plankton, notably diatoms (12). More recently, Huang *et al.* (13) have provided still further support for this viewpoint.

We noted for horizon A the consistent occurrence of correlative deposits indicative of both volcanic and biogenic ac-

tivity (3), although the degree of influence of one aspect or the other varies from place to place as might be expected. We believe this to be a noncoincidental cause-and-effect relationship, and we may be wrong; but, be that as it may, in order that any alternative explanation be correct, it must be based on all the relevant data rather than the misleading and highly selected data chosen by Weaver and Wise (2).

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11. A. P. Lisitsyn, *Recent Sedimentation in the Bering Sea* (English translation, Department of Commerce, Washington, D.C., 1969).
12. Lisitsyn (11) is, however, careful to deny any direct chemogenic relationship between major siliceous deposits and volcanism, a viewpoint popular in some earlier geologic literature.
13. T. C. Huang, R. H. Fillon, N. D. Watkins, D. M. Shaw, *Deep-Sea Res.* **21**, 377 (1974), and references therein.
14. We acknowledge advice and assistance from J. E. Hazel, R. F. Fudali, T. E. Simkin, and W. Poag.

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We are pleased that Gibson and Towe (1) accept our documentation (2) of biogenic opaline silica deposits within the Southeastern Coastal Plain but are mystified that they consider our data "misleading and highly selected" since these data cover a far broader range of evidence than they themselves are willing to consider. We have demonstrated (2, 3) a historic pattern of intermittent biogenous silica deposition in coastal plain sediments ranging from Paleocene to Eocene in age [it should be noted that, in South Carolina and elsewhere, these opaline lithologies are found well into the Miocene (for example, Coosawhatchie clay of the Hawthorne Formation)]. Until recently, practically all of these deposits have been variously classi-

fied as bentonites or altered volcanic ash deposits, a notion that we hope we have laid to rest through the presentation of fossil evidence.

We see no reason to assume that our evidence for a biogenic origin for the opaline facies of the early Middle Eocene Black Mingo, McBean, and Tallahatta formations is not compatible with the often-postulated (4) biogenic origin for the time-equivalent horizon A "cherts." Although we consider Gibson and Towe's postulation (1, 5) of a volcanic origin for this deposition interesting and encourage further research into the matter, we do not find present evidence for their speculation compelling.

Whereas various quantities of zeolite, montmorillonites, or unaltered ash indicative of volcanic activity are present in various portions of the Paleogene sequences in the areas in question, we see little extraordinary about the quantity of such materials associated with the late Early to early Middle Eocene portions of those sections. Indeed, Mattson *et al.* (6) have observed that montmorillonite occurs in the JOIDES (Joint Oceanographic Institutions for Deep Earth Sampling) cores at levels above the reflecting horizons and is less abundant in the cherty horizons than in the clays. We are impressed by the amount of biogenic silica in these sequences. For some deposits such as the Black Mingo Formation of South Carolina, zeolites indicative of ash deposition are extremely rare; however, we have demonstrated (2, 3) for the first time the presence of siliceous microfossils in that material. Opaline sediments of similar lithology and slightly younger age in Georgia (Twiggs Clay of the Barnwell Formation) contain no evidence of volcanic material but have yielded abundant siliceous microfossil remains (2). We conclude that the immediate source of silica for these high-purity opaline deposits is biogenic silica, and that contributions of silica to these deposits arising from the decomposition of volcanic ash are relatively minor or, in some cases, completely lacking. Thus the volcanic ashes are not as volumetrically important as previously assumed, and, as stated earlier (2, p. 901), "any ash deposition was apparently incidental to rather than causative of a general pattern of biogenic silica deposition."

Similar conclusions can be drawn in regard to the origin of the high-purity layer A "cherts." We have commented elsewhere (7) on the apparent low yield of chert-forming silica from deep-sea bentonites. The question of whether volcanic activity was the cause of enhanced plankton production and silica deposition during the

late Early to early Middle Eocene is, of course, a highly speculative matter. Calvert's (8) tabulations suggest that, for the present, the amounts of silica supplied annually to the oceans by submarine volcanism are insignificant by comparison with that delivered in solution by streams. After assessing data from modern ocean basins, Garrison (9) and Lisitsyn (10) strongly argue against a direct connection between volcanism and the formation of pelagic sediments, such as volcanically induced chemical precipitation or plankton blooms. For the volcanically active Bering Sea region, Lisitsyn (10, p. 117) finds that "The hydrochemical characteristics established during the last twenty years do not provide any indications of any appreciable influence of volcanism on the water masses, although in many cases investigations were performed during subaerial and submarine volcanic eruptions."

This is not to say that the supply of silica to the general reservoir of the Atlantic, Gulf, and Caribbean could not have been increased during the Early Tertiary. Frakes and Kemp (11) have summarized evidence for the Paleocene-Eocene poleward expansion of warm and humid climates. This resulted in intense weathering and laterization of soils as far north as 55°N and as far south as 45°S during the Early and Middle Eocene, and probably increased the quantitatively significant input of silica to the oceans from streams. Early Tertiary volcanism did contribute ash to the deep-sea floor, but, as noted by Riedel (12), liberation of silica into the bottom water via dissolution of any of this ash prior to burial cannot affect the production of siliceous organisms at the surface unless a circulation mechanism [for examples, see (4)] is available. In addition, a supply of nutrient is necessary. Gibson and Towe (1, 5) discount the various circulation models, reasoning (5, p. 153) that a circulation model would not explain the presence of "extensive and time-equivalent nearshore sediments of volcanic origin on the continents." We (2, 3) have shown these deposits to be biogenic rather than volcanic. Gibson and Towe instead assume dissolution of vast quantities of ash in surface waters, a fact not yet demonstrated. They further assume (5) the release of nutrient phosphorus from this ash. The efficiency of this process, however, is not clear. Recent studies by Berner (13) suggest that the reaction of iron oxides and phosphates released by submarine volcanism along the East Pacific Rise causes a net removal of phosphorus from seawater. Thus the release of iron and phosphorus from volcanogenic materials by marine waters may possibly produce a phosphorus

sink for the area in question, thereby depriving plankton of nutrient necessary for proliferation.

Gibson and Towe (1) cite studies by Huang *et al.* (14) as support for their viewpoint. Huang *et al.* (14, 15) show a correlation between maxima in the species diversity of radiolarians and intense volcanic episodes recorded in two deep-sea cores. One should realize that maxima in the species diversity are not synonymous with maxima of abundance. Huang *et al.* make clear that radiolarian abundances in their cores correlate with climatic events rather than with volcanic episodes or maxima in the species diversity. They also note judiciously (16) that changes in species diversity, which they suspect may be related to the release of volcanogenic silica and metals, could perhaps result from the selective dissolution of the radiolarians studied.

In view of the speculative and uncertain nature of present knowledge about the influences of volcanic activity on plankton productivity and chert formation, it may be premature to label anyone's contribution of data on the subject "misleading and highly selected." Perhaps, however, this uncertainty will stimulate others in the vigorous pursuit of additional data on this intriguing subject.

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