Manifestations of sporopollenin, chitin and other "non-degradable plastics" in the geologic record, as evidence for major biologic events*

Alfred Traverse

Palynological Laboratories, Department of Geosciences, Pennsylvania State University, University Park, PA 16802, U.S.A.

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Robust compounds of which the walls of palynomorphs are composed have a complex natural history keying into evolutionary events in potentially significant ways. The compounds, sporopollenin and chitin, are each really "families" of related substances. 10^7-10^8 tonnes of these partial exceptions to the organic cycle are incorporated annually in the sediments of the world. Sporopollenin can be toughened and made more resistant to attack by lithification/ diagenesis, as evidenced by instances in which reworked spores/pollen are better preserved than palynomorphs produced coevally with the enclosing sediment. Some sphaeromorph acritarchs of the Precambrian are probably linked phylogenetically with land plant spore or sporelike tetrads of the mid-Ordovician, in which sporopollenin's role changed from UV/O_2 protection to desiccation-prevention and structural integrity in air. Seed plants exploited sporopollenin's elasticity (harmomegathy) and its propensity to produce "honeycomb" structures (sacci for density-reduction, columellate exine structure for recognition-compounds). Chitin is even more complex than sporopollenin, sometimes easy to lyse and at other times fully as resistant as sporopollenin. Robust-walled fungal spores do not occur until sporadically in the Permian/Triassic/Jurassic, more regularly from the Cretaceous, and abundantly in the Cenozoic. It is speculated here that melanin toughened the chitin of certain sorts of fungal spore walls beginning in the Jurassic. This variety of fungal chitin is called "euchitin."

Key-words – Acritarchs, chitin, "euchitin", fungi, harmomegathy, melanin, obligate tetrads, sporopollenin.

INTRODUCTION

"Non-recyclable organic garbage" of the geologic record

ALL organic matter (basically, C-H-O compounds, often with considerable N) can be degraded, for example, rapidly by combustion in O_2. Nevertheless, once-living structures consisting of some organic compounds are remarkably refractory to attack. These structures therefore accumulate in sediments and are found in considerable abundance in many sorts of sedimentary rocks. Indeed, the existence of robust-walled microfossils such as acritarchs and spores/pollen depends ultimately on this kind of exception to, or defiance of, the organic cycle. Here I wish to consider especially two phenomena: 1. these robust organic compounds do not always seem to display the same degree of recalcitrance, and 2. these compounds are applied by organisms, at different times, to the "solution" of quite disparate "problems." The compounds in question are a "family" of C-H-O substances called "sporopollenin" and a "class" of several "families" of C-H-O-N compounds: chitin, "pseudochitin," "scolecochitin", "scleroprotein," possibly other nitrogenous organics.

Modern human industry has, mostly in this century, synthesized a variety of organic compounds such as polystyrenes, neoprenes, polymethacrylates, that simulate natural refractory compounds. Articles made of these artificial substances are already turning up in modern sediments, and the disposition of some of the materials is becoming a major waste-disposal problem. The cellulose-resin complex of which the bodies of East German "Trabant" autos consisted is analogous to an enormous pollen exine, and is proving difficult to return to the organic cycle-bacterial lysis is even being attempted (Bal-

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ter, 1991). On the other hand, production of analogs to naturally resistant structures such as chitinous beetle wings is a frontier-development for industry (Amato, 1991), and presumably the question of recycling the substances back into the organic cycle will be dealt with later! The synthesis of sporopollenin lies still in the future and will herald a new industrial wave based on virtually indestructible pliable substances--I would guess for shoes and the like! A new crisis of disposal will follow.

It is, incidentally, interesting to contemplate what it would have meant for the organic cycles of the more refractory versions of sporopollenin and chitin had they been as predominant in biomass as is the rather easily lysed-digested cellulose. How would self-compensating "Gaia" (cf. Lovelock, 1988) have adjusted to such a situation?

THE PRODUCTION, SEDIMENTATION AND PRESERVATION OF ROBUST-WALLED ORGANIC PARTICLES

Very large amounts of ultra-resistant-walled organic particles are incorporated annually in the sediments of the world, probably about 10^7-10^8 metric tons--see discussion in Traverse (1992a). In addition to the sources cited there, extrapolations from Holland (1978) and Degens (1965) are also involved here. The calculation assumes that sporopolleninous-chitinous, etc., fossils are about 10-20% of total organic matter ("kerogen") delivered to sediment. Much of the rest of total kerogen is more-or-less structurally recognizable "palynodebris" (see Traverse, 1992b). In general, the proportion of such particles in sediments fluctuates with sedimentation rate, being greater during periods of lower sedimentation. Even the most robust-walled palynomorphs are subject to vicissitudes during the sedimentation-lithification process. Pyritization occurs in reducing environments, if the necessary iron and sulfur are present, sometimes riddling the grains with pyrite (marcasite) crystals or crystal-cast marks. On the other hand, oxidizing conditions permit abiotic and biotic lysis, producing "ghosty" or no remains. When diagenesis sets in, palynomorphs may be carbonized to the point of unrecognizability (cf. Traverse, 1988). Vicissitudes during sedimentation and lithification are often deleterious to palynomorphs. However, if O_2 is excluded, temperature is low, and if pyritization cannot occur (for lack of Fe, S and/or the requisite bacteria), the sporopollenin or chitin of palynomorph walls may actually increase in durability. Many examples are known. Plate 1, Figs 5-8, illustrate one case from current interglacial (= "post-glacial") sediment of New Jersey, in which Normapolles, *Rugubivesiculites* and many other Late Cretaceous spores and pollen, toughened by lithification/diagenesis, are better preserved on maceration of the containing Late Pleistocene (current interglacial) sediment than are the pollen and spores produced contemporaneously with the sediment. In some cases, older sporomorphs are protected during weathering and erosion by being enclosed in small shale particles. Microscopic examination of the containing mud shows that *not* to be true of the New Jersey sediment cited here. Some of the recycled forms are bisaccates which are comparable in thickness to the modern forms and are nevertheless better preserved. Traverse (1992a) reported similarly preserved reworked pollen in the water of the Trinity River, Texas, where there was also no evidence of reworked forms in shale particles. An increase in durability, a toughening, seems undoubtedly to have taken place, assuming essential identity of the original sporopollenin with that of modern sporomorphs.

"SPOROPOLLENIN"

This C-H-O substance is still not chemically characterized beyond dispute. It probably is actually a family of compounds, as I have tried to indicate by use of quotation marks in the heading. Indeed, Rowley and Claugher (1991) are convinced that even the same exine may have more than one variety of sporopollenin! Southworth (1990) diplomatically concluded that it is "...a cross-linked polymer with saturated and unsaturated hydrocarbons and phenolics." It is clearly one of nature's most adaptable products, making, for example, an animal-digestion-proof cover for fern spores (Chaloner, 1976). In fact, only a goat's digestion processes can reach it (Harris, as quoted in Traverse, 1988). It is water- repelling, elastic and leathery-rubbery. Thus, it can be and has been employed by a variety of organisms, most if not all arguably in the green-plant line, for a great variety of purposes during plant evolution.

History

Acritarchs— The oldest sporopolleninous fossils are spheromorph acritarchs, which occur in shales as old as 1.5 x 10^9 yrs. (Horodyski,1980). From 1.0 x 10^9 yrs., such aritarchs are common (Pl. 1, fig. 1), and are joined later on by an array of kinds with more diverse morphology, including giant forms that may not be strictly comparable (Vidal, 1990). It has been asserted that we can't prove that Precambrian sphaeromorph acritarch walls consist of sporopollenin. Although that is true, it seems likely that the substance of the walls was some variety of sporopollenin produced by a green alga, and that it functioned as the cover for some sort of reproductive body, or survival cyst. What was the role of the sporopollenin sheath? Not waterproofing, as the acritarchs were produced in an aquatic environment.

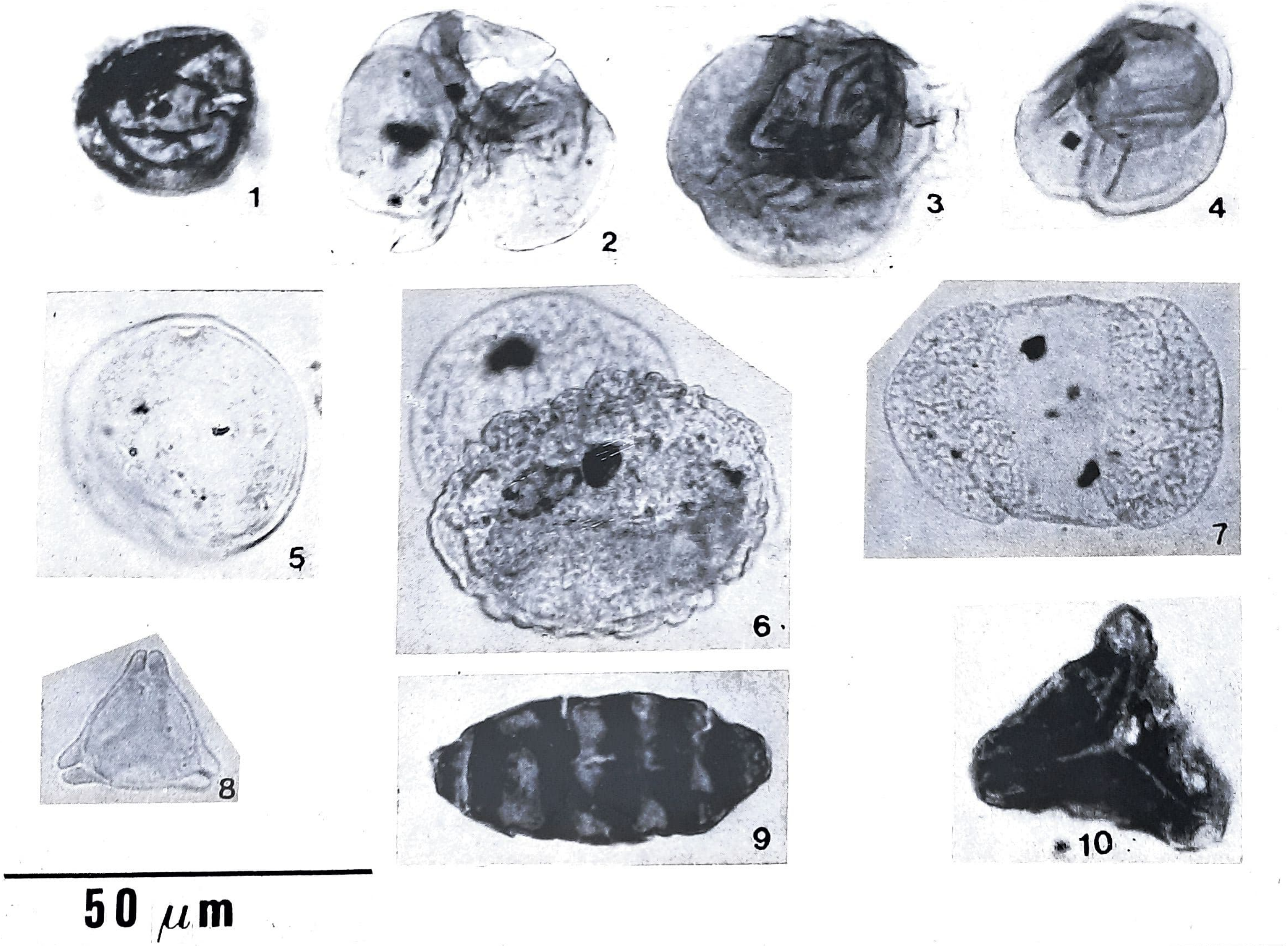


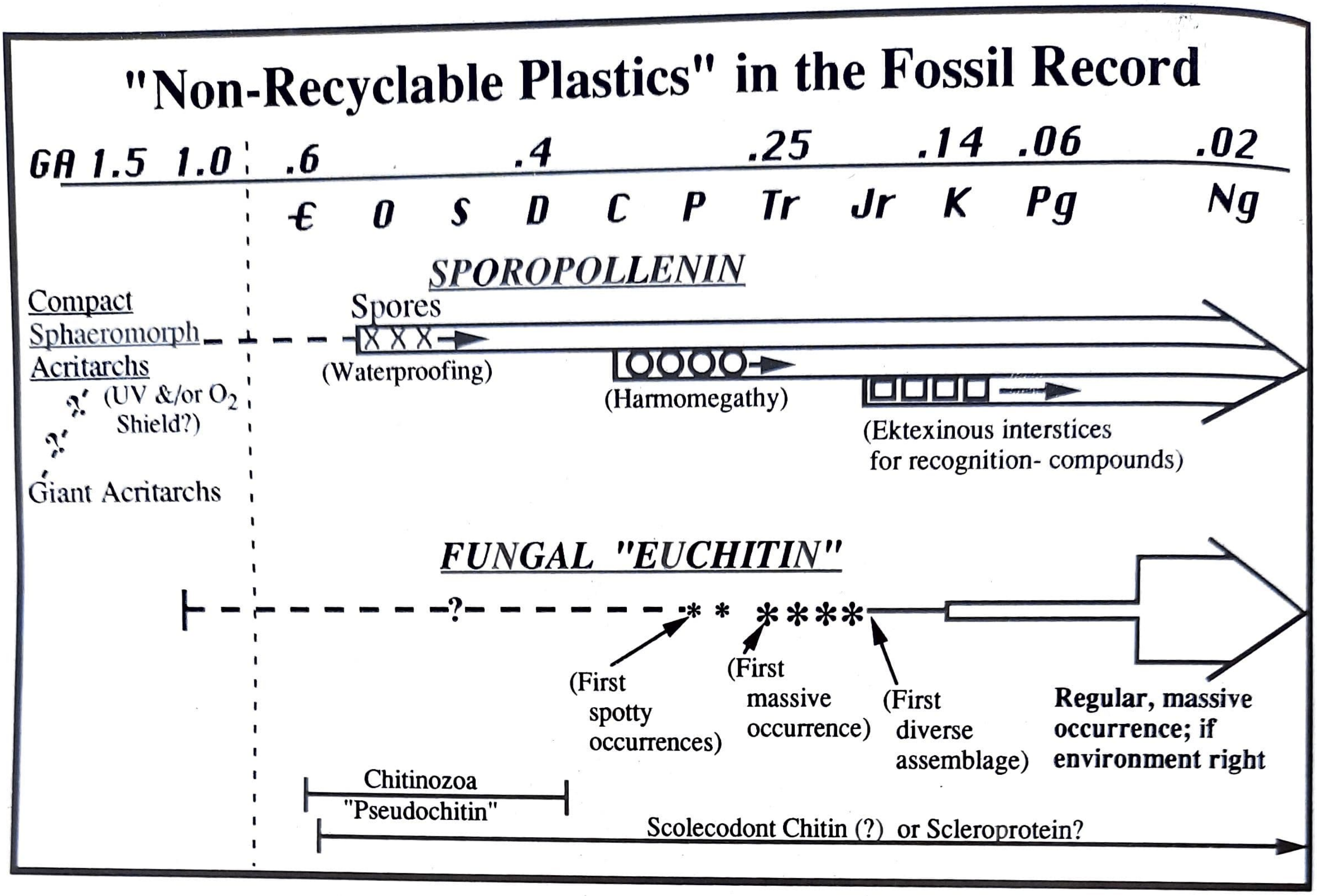
Plate 1

(Photomicrographs at magnification indicated by bar under Figure 8).

1. Sphaeromorph acritarch from Proterozoic rocks of the Wynniott Formation, Victoria Island, arctic Canada, age about 800 Ma.
2. Spore or spore-like tetrad from Hamadir Member, Qasim Formation, Llanvirnian Stage of Ordovician, Saudi Arabia.
3. As 2, a specimen showing the "ropey" contact figure typical of these tetrads.
4. As 2, more loosely organized tetrad.
5. Partially degraded *Carya* sp. pollen grain, current interglacial (= "postglacial"), Meadowlands, Bergen County, New Jersey (near New York City).
6. *Rugubivesiculites* sp., bisaccate pollen, same source as 5, but reworked from Late Cretaceous rocks.
7. *Pinus* sp. pollen, same source as 5, somewhat degraded.
8. Normapolles pollen, same source as 5, but reworked from Late Cretaceous rocks.
9. Well-preserved multicellular fungal spore, latest Early Jurassic of Hells Canyon area, Oregon-Idaho border.
10. Very degraded trilete spore, *Gleicheniidites* sp., same origin as 9.

More probably, it was a protective covering against O_2 and/or ultraviolet radiation (see Text-fig. 1). Physical toughness tending to exclude predators-parasites may have been another function, as would seem to be the case for the cysts of some dinoflagellates. It seems to me probable that some sorts of sphaeromorphs are directly connected phylogenetically to the first land plant spores (Text-fig. 1).

Earliest land plant spores—In the mid-Ordovician to Early Silurian, a likely scenario is that descendants of the Precambrian green algal complex that produced acritarchs moved onto the land. Sporopollenin, already in the "armory," assumed then a completely new role, in response to a new challenge. The substance once again assume critical importance: 1. for protection of the meiotic contents of obligate tetrads of spores such as



Text-figure 1. The fossil record of sporopollenin, fungal chitin and related substances.

Tetrahedraletes from desiccation, and 2. provision of a tough, flexible, resilient, elastic "shell" to protect the physical integrity of the protoplasts of the tetrads in a new environment--the atmosphere. These sporopolleninous tetrads are the only remains as yet discovered of the earliest land plants. Cutin and lignocellulose were at that time still in the distant future. Plate 1, figures 2-4 illustrate examples from Llanvirnian rocks of Saudi Arabia, the oldest such fossils so far discovered.

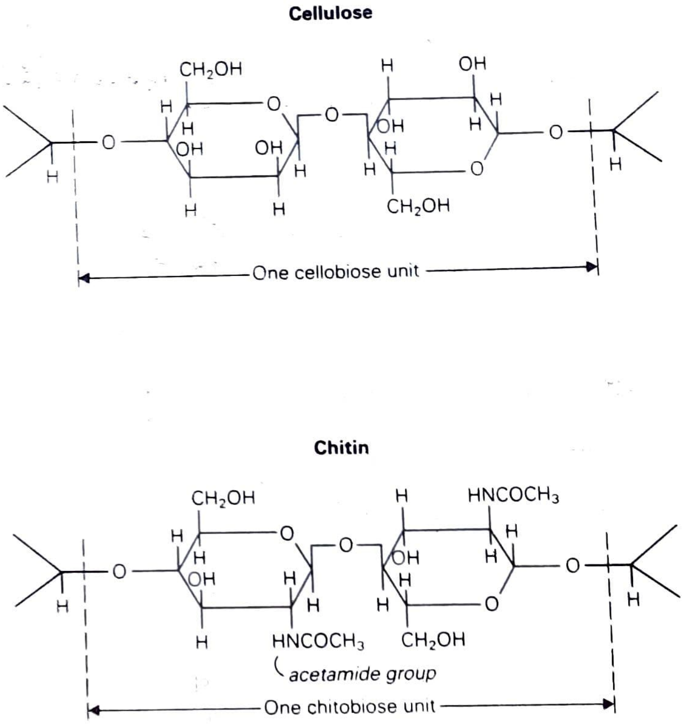
Harmomegathy and the Permian development of striate-taeniate pollen—A major "invention" by seed plants was exploitation of the elastic properties of sporopollenin for pollen walls. Many monosulcate pollen can invaginate and evaginate harmomegathically, but the earliest highly-developed expression of this design was the widespread "use" of harmomegathy in an imposing array of gymnosperm pollen in the Permian and early Triassic. The striations and straps of this sort of exine would seem clearly to have had the function of permitting "accordion-like" accommodation to volume changes in the protoplast, resulting from rapid changes in humidity. Such oscillating climatic conditions were prevalent in the Permian/Triassic over much of the world.

"Honeycombing" and harmomegathy in angiosperm exines—Sporopollenin was employed in the transition from pseudosaccate to protosaccate to truly saccate for production of varying amounts of three-dimensioal internal webbing. This capacity to be used for strong internal struts, cross-strutting, honeycombing, has appeared several times since, for example, in the sculpturing processes of chorate dinoflagellate cysts and, most significantly, in the columellate structure of angiosperm ektexines. This provides abundant locules for the storage of recognition-compounds and other substances vital to angiosperm pollination strategy.

A second large-scale application of sporopollenin's elastic properties to harmomegathy for expansion/contraction due to water-uptake/loss came with the multicolpate character of angiosperms in the Cretaceous. A few dicots in the family Acanthaceae have even reintroduced by parallel evolution the striate/taeniate character. Arens and Traverse (1989) have shown that the elastic properties of sporopollenin even permit angiosperm pollen to withstand to some extent the extreme duress of explosive pressure from microwave generated internal steam.

"CHITIN"

This substance, or better probably, family of substances, consists of the elements C-H-O-N. It is conventionally assigned the structure shown in text-figure 2, and has the formal designation poly-β-(1-4)-N-acetyl-D-glucosamine (Austin *et al.*, 1981), but it is easier to think of it as basically like cellulose, differing from it only in acetamide side-groups. "Chitin", in a broad sense, is supposed to compose the walls of some foraminiferal inner linings ("microforaminifera"), some polychaete mouth-linings (scolecodonts), arthropod exoskeleton elements in general, and walls of fungal hyphae and several disparate kinds of fungal "spores" and "fruit bodies." The robustness of chitin under some sets of conditions challenges or even exceeds that of sporopollenin. This is true, for example, of fungal spores described by Traverse and Ash (in press) from the Jurassic (better preserved than pollen and spores in the same samples), and it is often true of Cenozoic fungal spores. Yet, experiments with arthropod exoskeleton "chitin" (Allison, 1991) apparently show it to be easily biodegraded--even more so than cellulose. However Sturz and Robinson (1985) demonstrated experimentally that chitin resists degradation a bit more robustly than cellulose, but they note that although 10^{11} metric tons are produced annually in the aquatic biosphere, rather little is preserved in sediment. Briggs (1991a) emphasizes the poor preservability of chitin, meaning the sort of chitin in arthropod skeletons. On the other hand, Tegelaar *et al.* (1989) rate chitin (# 17 on their list of 36 substances) as more durable than cellulose (# 6 on the list) but not in a class with sporopollen, which is # 33. (#34 is algaenan, # 35 is cutan and #36 suberan.) Briggs (1991b), in an exchange with Traverse (1991b), asserts that the permeability of chitin is extermely variable, which is clearly right.



Text-figure 2. Structural formulas for cellulose and chitin (from Traverse, 1988).

Fungal "chitin" and "euchitin"

A further puzzling fact in the natural history of chitin is that the fungi were probably present in the Precambrian, certainly so in early Paleozic, and rather abundant in Permo-Carboniferous deposits (see discussion in Traverse & Ash, in press), yet there are no known robust-walled fungal remains before sporadic occurrences in the Permian and Triassic. Traverse and Ash (in press) report the oldest diverse assemblage of robust-walled fungal spores in late early to early Middle Jurassic rocks (Pl. 1, fig. 9) of western North America. As noted above, the fungal spores are actually better preserved than fern spores and pollen found in macerations of the same rocks. From Cretaceous onward, maceration-resistant fungal spores are common, and in the Cenozoic they are very common and often abundant. It is the chitin of these resistant-walled fungal spores that I informally refer to as "euchitin" (see Text-fig. 1). Clearly this is in some way a different substance from the chitin of shrimp exoskeletons which Allison (1991) found to lyse so readily.

As interim speculations I suggest that the sporadic occurrences of tough-walled fungal spores in Permian and Triassic and perhaps in the Jurassic are due to accidental local changes in the wall chemistry, perhaps from metal-adsorbtion, which is known to occur in chitin, or local diagenetic "maturation" occurring at just the right stage during lithification/diagenesis. These phenomena could have perhaps resulted from volcanic activity. Beginning in the Cretaceous, the regular occurrence of "euchitin" could be accounted for by incorporation in the structure for the first time of some "toughener", perhaps melanin, a derivative of tyrosine. This recalcitrant substance is a common constituent of modern fungal walls and presumably accounts for the brownish colour of most fungal spore walls in palynological preparations (in contrast to the yellowish-orange walls of spores/pollen). Melanin is known to be very resistant to biodegradation (Alexander, 1973). Part of the contribution of melanin to the durability of fungal walls is perhaps due to increasing the resistance of chitin to chitinases, therefore making the fungal walls more durable. It is tempting to speculate that introduction of melanin was a direct response to the origin of angiosperms with their chitinous-based defenses against fungi.

IMPORTANT REMAINING PROBLEMS REGARDING SUPER-RESISTANT ORGANIC COMPOUNDS

What is the fundamental nature of sporopollenin?

Answering this question requires solution of the long-standing analytical problem for the sporopollenin family of compounds. That depends in part on preparation of really pure samples. Allied with this problem is the question of what it is about sporopollenin that makes it fundamental as a unifying character for Plantae and some green algae. One can answer that question for starch, and we should be able to answer it for sporopollenin. Is the dinoflagellate cyst wall also composed of sporopollenin, as is usually assumed? If so, does this carry phylogenetic implications? In any case, how diverse is the sporopollenin "family"? Does the range of kinds tie in with phylogeny, and thus with evolutionary events? That is, is *Tetrahedraletes* sporopollenin from the Ordovician more like that of the bryophytes or that of the pteridophytes, if there is any difference? In my studies of recent sediments I have for years observed that colour and refractive properties of a variety of pollen and spore exines, after identical processing techniques, differ markedly. Is it not likely that different varieties of sporopollenin are involved?

What is the so-called "pseudochitin" of chitinozoans?

Voss-Foucout and Jeuniaux (1972) have demonstrated that the C-H-O-N compound composing the walls of chitinozoans does not pass specific enzymatic tests for chitin. In my opinion this does not at all mean that chitinozoan "pseudochitin", when synthesized in the early Paleozoic, was not some sort of chitin. I would not be surprised if the Jurassic fungal spore walls reported in this paper (P1. 1, fig.9) also were to fail the chitinase test, given that they endure even 1:1 Schulze's solution, a potent oxidant, with remarkable persistence.

What about scolecodont chemistry?

Scolecodonts are mouth linings of polychaete annelid works. Voss-Foucout *et al.* (1973) demonstrated that polychaete "jaws" (mouth- lining elements) do not pass the tests for "true chitin", and Colbath (1986) showed that they are very variable in preservation-potential, and also contain varying amounts of $CaCO_3$, in addition to the C-H-O-N component. Both Voss-Foucout and Colbath suggested that this component is a "scleroprotein" rather than chitin. Some feel that scolecodonts are organics + $CaCO_3$ "cousins" of the phosphatic conodonts. A puzzling aspect of the fossil record is that, although scolecodonts range from early Paleozoic to present, they are only sporadically preserved after the Devonian, just the reverse of the robustness phenomenon for fungal spores-- fungal spore walls become more robust in the Cenozoic. Something must have been different about the chemistry of the Early Paleozoic polychaete "scoleco-chitin", compared to that of the later forms.

RESEARCH IDEAS

The basic problem in discovering the identity or, more likely, identities of the sporopollenin family of compounds is preparation of a clean pure sample. I believe that the existence of giant, easily removable gemmae (sculptural elements), and giant ubisch bodies, in taxa such as *Ipomoea alba* (Traverse, 1991a) is an example of a range of particles that are solid sporopollenin. As such, they offer the possibility of preparing an unequivocally pure sample. Processes, elaters and the like from fossil palynomorphs could similarly be sample sources, providing analytical techniques can be applied to such tiny samples. Controlled pyrolysis with gas chromatography/mass spectrometry offers one such possibility. We are currently carrying out preliminary work of this sort at Penn State.

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