TAXONOMIC SUMMARY OF INORGANIC PROTECTIVE OR SUPPORTING STRUCTURES PRECIPITATED BY ANIMALS AND PLANTS

DAVID NICOL and DONALD A. EGGERT

University of Florida, Gainesville and Southern Illinois University, Carbondale

ABSTRACT.—The lower plants and animals (the broad group algae in the plants and the Protozoa among the animals) are the more heterogeneous as far as inorganic protective or supporting materials are concerned. The only exception to this is the restriction of calcium phosphate to some eumetazoans. The three main types of inorganic hard parts found in animals—calcium carbonate, the calcium phosphates, and opaline silica—are all first found in the skeletons of Early Cambrian marine invertebrates, and even the organic substance chitin is present in the skeletons of some of these animals at that time. However, this pattern of early rapid differentiation does not occur in the plant kingdom. Calcium carbonate deposition occurred in some algae well back into the Precambrian. The ability of plants to deposit opal in their tissues may not have occurred before Jurassic time with the advent of the first few diatoms.

A considerable body of scattered literature has been written about the inorganic compounds which are present in the hard parts of plants and animals. Most of it is factual with generally little attempt to interpret the data biologically. (That is our main purpose herein.) Some of the facts have been repeated in several places with little or no documentation, and some of the basic data need to be reinvestigated for accuracy.

No attempt will be made to include foreign particles which some animals pick off the ocean bottom and cement to their shells, nor, as the title implies, will organic skeletal substances be included. Minor amounts of compounds, that is, those making up 20 per cent or less of the composition of the hard parts, will be ignored. With these restrictions adhered to, it is amazing to see how little variation there is in both animal and plant kingdoms as to the kinds of inorganic compounds secreted for exo- and endo-skeletal material as well as protective and supporting structures. This is true of both fossil and living groups of organisms. At the present state of our knowledge, this short review will, of necessity, pose more questions than can be answered. It is hoped that many of these questions can be answered by more observations and research on this most interesting subject.

For the invertebrate animals, most of the basic data can be found in general systematic paleontology textbooks as, for example, Moore, Lalicker, and Fischer, 1952; and Shrock and Twenhofel, 1953.

IN THE ANIMALS

Among the animals, the most singular feature is the preponderance of calcium in their skeletons, primarily as calcium carbonate but also importantly as calcium phosphate.

No distinction will be made between calcite and aragonite in this brief survey, although calcite is generally more common and some animals, e.g. many gastropods and pelecypods, have both calcite and aragonite in their shells. Calcite and aragonite can be deposited by marine animals and plants in temperatures ranging from about −2°C to 40°C. Calcium is fairly abundant in sea water, often more so in fresh-water and soils. Calcite and aragonite are not readily soluble in water of neutral pH. All of these factors help to explain why calcite and aragonite are so common in animals and the lower plants. Members of the following groups of animals, all or in part, have calcium carbonate in their exo- or endo-skeletons: Protozoa, Porifera, Coelenterata, Pleospongia, Receptaculitida, Stromatoporoidea, Labechioidea, Sphaeractinoidea, Nidulitida, Bryozoa, Brachiopoda, Annelida, Mollusca, Echinodermata, and Arthropoda. Some of these named groups are extinct, and many of these groups have large numbers of both extinct and extant species.

The second most widespread inorganic material in the skeletons of animals is some of the minerals of the apatite group. This is primarily calcium phosphate, but fluorapatite, hydroxylapatite, or carbonate apatite occurs in some animal skeletons. Among the animals having this skeletal composition are the extinct conulariids and conodonts, some of the brachiopods and arthropods, and of course the vertebrates. One sees, however, that calcium phosphate is much less common than calcium carbonate as a skeletal material among animals, and for some reason it is confined to higher animals—the Eumetazoa. Does this indicate a phylogenetic homogeneity for the Eumetazoa? It is interesting to note, also, that calcium phosphate as a primary skeletal material appears to be completely absent in the plant kingdom.

The next most commonly occurring mineral found in animal skeletons is opal ($SiO_2 \cdot nH_2O$). It is found in some Protozoa (nearly all radiolarians) and is common in the Porifera. It has been reported in annelid worm jaws (scolecodonts). Spicules of silica are said by Nicol (1960, p. 650) to occur in the tissues of a few mollusks, and Prosser and Brown (1961, p. 72) report silica in some bryozoan skeletons.

These latter three occurrences are the only mention of silica in higher animals, and it does not comprise the main portion of the skeleton. This leads us to a most puzzling question—why do the higher animals, those above the sponges, not use silica as a main skeletal material? Again, does this indicate a phylogenetic homogeneity for the Eumetazoa?

Among the Protozoa there are a few exceptional cases in which sulphates are deposited. One small group of living radiolarians uses strontium sulphate, celestite, as a skeletal material. This occurrence is well documented and has been known for some time. One deep-sea group of rhizopods is reported by Prosser and Brown (1961, p. 72) to have a skeleton in which the inorganic part is made up of barium sulphate (barite). This latter occurrence is not well documented, and it exhausts the relatively small list of inorganic skeletal compounds found among animals.

IN THE PLANTS

The two inorganic materials most commonly deposited by plants are calcium carbonate and opaline silica. In the case of calcium carbonate, the mineral in a given species is either calcite or aragonite. This is unlike some animals in which both may be present. Information concerning the distribution of calcite and aragonite in numerous plants may be found in the papers by Lewin (1962), Lowenstam (1954), and Vinogradov (1953).

Silica is usually present as hydrated or opaline silica; however, quartz is produced in some diatoms and in the flowering plant *Ficus*, according to Roelofsen, 1959.

In addition to the inorganic materials previously mentioned as occuring in plants, a few instances of $Fe(OH)_3$ and $Mn(OH)_3$ deposition are known which appear to be a facultative feature of the physiology of the plants involved.

Inorganic cell inclusions are generally omitted from the present summary with the exception of a few examples such as the occurrence of opal in elements of wood and the occurrence of calcium carbonate in epidermal cells.

Among the various groups of algae, calcium carbonate deposition is much more widespread than is the deposition of silica. In the case of the vascular plants the two compounds are apparently about equal in occurrence.

Calcium carbonate is deposited in large amounts in the algae, including members of the Chlorophyta, Cyanophyta, Rhodophyta, Phaeophyta, and Charophyta. Among the fungi the best documented and studied case of calcium carbonate deposition occurs in the Myxomycophyta (slime molds and related forms), where the two orders Physarales and Stemonitales are partially distinguished from other orders by the presence and distribution of calcium carbonate in the fruiting structure (Alexopoulos, 1952).

It is of some interest to note that in the green algae the deposition of calcium carbonate is confined to those forms which are on the siphonine path of evolution: the orders Siphonales and Siphonocladiales. The charophytes are known to deposit calcium carbonate in both the vegetative and reproductive portions of the plant body. Large amounts of calcium carbonate in the oogonial structure probably account for the relative abundance of oogonial remains in the fossil record.

Among the blue-green algae (Cyanophyta) calcification occurs most commonly in those forms which are found in geyser pools and other bodies of relatively warm water. There appears to be no systematic pattern of calcium deposition among the taxonomic groups of the Cyanophyta; however, the following genera are important depositers of calcium carbonate: *Anabaena*, *Aphanothece*, *Chamaesiphon*, *Lithomyxa*, *Lyngbya*, *Microcoleus*, *Porocapsa*, *Petalonia*, *Phormidium*, *Rivularia*, and *Schizothrix*.

The so-called coralline red algae (Rhodophyta) are conspicuous in the formation of reefs and are for the most part members of the Cryptonemiales. These forms have a prominent fossil record. In the Nemalionales the genus *Liagora* also produces calcium carbonate, which in this case is laid down about a much simpler thallus than is the case in the cryptonemialean forms.

Only one genus of brown algae (Phaeophyta) is known to produce calcium carbonate in any large amount. This is the genus *Padina*, which is otherwise a typical member of the order Dictyotales (Fritsch, 1945). There appears to be no systematic significance to this isolated instance of calcium carbonate deposition by *Padina*.

Deposition of calcium carbonate is known to occur in the flowering plants in the families Curcurbitaceae, Cruciferae, Boraginaceae, Loasaceae, Acanthaceae, Urticaceae, Combretaceae, Moraceae, Gesneriaceae, Geraniaceae, and Cistaceae (Frey-Wyssling, 1959; Roelofsen, 1959; Uphof, 1962). This calcification occurs in epidermal cell walls, in epidermal trichomes, and in special cells of the epidermis (so-called lithocysts).

The silicification of cell walls is best known in diatoms, where it has been studied in most detail. Lewin (1962) has recently reviewed the current state of understanding of the structure of diatom walls and the physiological processes involved in silicification. In addition to diatoms, other members of the Chrysophyta are known to produce siliceous deposits in cell walls. Typically, resting spores of golden algae (class Chrysophyceae), which are sometimes referred to as statospores, have a highly silicified wall. The literature contains reports of the occurrence of silica in the cell walls of vegetative parts of some yellow-green algae (class Xanthophyceae); however, these plants have not been studied in this respect in recent years (Smith, 1955). Phycologists such as Smith have placed great significance upon the silica-metabolizing ability of the forms in the division Chrysophyta, and this feature seems to be an important one which unites the members of the three classes included in the division. Indeed, on the basis of their ability to metabolize silica, it has been suggested that the members of this division be grouped with the Choanoflagellata, Porifera, and Sarcodina into a distinct kingdom, the Silicobiota.

In vascular plants, silicification occurs in widely divergent groups: the Equisetales, which is the sole extant order of the subphylum Sphenopsida, and the class Angiospermae of the subphylum Pteropsida. In the equisetalean genus *Equisetum*, silica is deposited in the epidermal cells and forms a thick layer on the outer cell wall. Among the angiosperms, silica is deposited both in cell walls of the epidermis and within special cells of the epidermis in numerous members of the family Gramineae (grasses). In the latter instance, highly opaline silica fills the cell lumen (Esau, 1953). Among the flowering plants, silica is also found in numerous species of various taxonomic groups primarily in cells of the secondary xylem. Over four hundred timbers are listed by Amos (1952) as having siliceous cell inclusions, primarily within cells of the vascular rays. This appears to be almost pure SiO_2 and forms a vitreous layer in vessels and some other elements of wood in addition to the vascular rays. Silica is also reported as occurring in the later-formed walls of endodermal cells of *Andropogon* (Berissow, cited in Frey-Wyssling, 1959) and in hairs of members of the families Campanulaceae, Moraceae, Ulmaceae, Urticaceae, Primulaceae, Loasaceae, Crassulaceae, Compositae, Leguminosae, Haloragidaceae, and Verbenaceae. Although silicification seems to be characteristic of many members of some angiosperm families such as the Moraceae and Urticaceae, its generally scattered occurrence suggests that it does not have any special significance in determining phylogenetic relationships among the angiosperms. Both Netolitzky (1929) and Frey-Wyssling (1959) have suggested that silicification of plant parts is correlated with a warm climate in which silica would be expected to be more readily available for uptake by the plants. It is not known whether the deposition of silicates on the plant surface of submerged forms or that of iron and manganese in the cases cited here is simply accretion of the mineral or is due to an active uptake of the materials and subsequent deposition by the plant cells.

In a few cases plants are known to deposit iron and manganese in an inorganic form. Euglenoids and desmids are the most outstanding examples of this occurrence of iron and manganese, which appears to be present as $Fe(OH)_3$ and $Mn(OH)_4$ respectively (Roelofsen, 1959). In some green algae such as *Oedogonium* and *Cladophora*, the deposit of iron-containing inorganic matter forms a crystalline incrustation about the plant body. Literature cited by Frey-Wyssling suggests that the deposition of both iron and manganese hydroxides is facultative and occurs when large amounts of those two elements are present in the plant's environment.

Remarks

It is apparent that the lower plants and animals (the broad group algae in the plants and the Protozoa among the animals) are the more heterogeneous as far as inorganic skeletal materials are concerned. The only exception to this is the restriction of calcium phosphate to some eumetazoans. This seems to support the opinion that the lower animals and plants may have had a polyphyletic origin.

The three main types of inorganic hard parts found in animals — calcium carbonate, the calcium phosphates, and opal — all are found in the skeletons of Early Cambrian marine invertebrates. This has also been pointed out in a recent paper by Lowenstam (1964, p. 172). It should be added that even the organic substance chitin also occurred in some Early Cambrian invertebrate skeletons. Does this indicate little change in the chemical composition of sea water since Early Cambrian time? Here again is another example of early primary diversity or differentiation in the various major animal groups. Only minor or relatively little differentiation has appeared in major animal groups, as concerns the inorganic hard parts, since Early Cambrian time. However, this pattern of differentiation does not occur in the plant kingdom. Calcium carbonate deposition apparently arose early in the evolution of the plant kingdom, and algal limestones are known which extend well back into the Precambrian, possibly as long as 2.5 billion years ago. On the other hand, the ability of plants to deposit opal in their tissues appears to have been acquired quite late in geologic time. There is as yet no known fossil record of siliceous plants before the first few diatoms of the Jurassic, which was certainly less than 175 million years ago.

Thus we see that the number of inorganic compounds and minerals utilized by both animals and plants are amazingly few. The minerals commonly involved are calcite, aragonite, the apatite group, and opal. For all organisms, calcium carbonate is certainly the most common skeletal compound. Because of the plants, opaline silica must be ranked second most widespread, followed by the various calcium phosphates. Silica, iron hydroxide, and manganese hydroxide among the plants, and strontium sulphate and barium sulphate among the animals, are all generally rare and exceptional. Does this indicate a close phylogenetic relationship for all organisms? Because of the rarity of the elements involved, varying degrees of solubility in water, temperature of formation of the mineral (usually above that of ordinary temperatures found in the sea or on land), or some other adverse factors, the minerals present in animal or plant protective or supporting structures are perhaps about the only ones which the animals or plants could possibly find available. In other words, the minerals found in plant and animal skeletons probably represent the least soluble compounds which the animal or plant can synthesize from the elements which are available in sufficient concentrations. However, if we think of all of the minerals in sedimentary rocks, those formed at ordinary temperatures and pressures, some being quite common, we wonder why animals and plants have not used many of them as skeletal or supportive materials.

ACKNOWLEDGMENTS

This project began as a survey of the inorganic hard parts found in invertebrate animals by the senior author and two graduate students in the Geology Department at Southern Illinois University, Mr. George A. Desborough and Mr. Raymond L. Kerns, Jr., during the fall of 1959. The authors are indebted to these students for the information they each compiled on this subject. We also received helpful suggestions from Dr. Dewey H. Amos and Dr. F. Donald Bliss of the Geology Department at Southern Illinois University and Dr. Richard E. Blackwelder of the Zoology Department at Southern Illinois University.

LITERATURE CITED

ALEXOPOULOS, C. J. 1962. Introductory mycology. J. Wiley and Sons, New York. 482 pp.

AMOS, G. L. 1952. Silica in timber. Comm. Sci. Indust. Res. Australia, Bull. 267. 55 pp.

ESAU, K. 1953. Plant anatomy. J. Wiley and Sons, New York. 735 pp.

FREY-WYSSLING, A. 1959. Die Pflanzliche Zellwand. J. Springer, Berlin. 367 pp.

FRITSCH, F. E. 1935, 1945. Structure and reproduction of the algae. Macmillan, New York. Vols. I, 791 pp. II, 939 pp.

LEWIN, J. C. 1962. Physiology and biochemistry of algae. R. A. Lewin ed. Academic Press, New York. 445-455, 457-465.

Lowenstam, H. A. 1954. Factors affecting the aragonite: calcite ratios in carbonate-secreting marine organisms. J. Geol. 62: 284-322.

————. 1964. Biologic problems relating to the composition and diagenesis of sediments. The earth sciences—problems and progress in current research. T. W. Donnelly ed. Rice Univ. Semicentennial Pubs. 137-195.

Moore, R. C., C. G. Lalicker, and A. G. Fischer. 1952. Invertebrate fossils. McGraw-Hill, New York. 766 pp.

Netolitzky, F. 1929. Die Kieselkörper und Kalksalze als Zellinhaltskörper. Handbuch der Pflanzenanatomie. Bd. III. T. Ia. Borntraeger, Berlin. 130 pp.

Nicol, J. A. C. 1960. The biology of marine animals. Interscience Publishers, New York. 707 pp.

Prosser, C. L., and F. A. Brown, Jr. 1961. Comparative animal physiology. 2nd ed. W. B. Saunders, Philadelphia. 688 pp.

Roelofsen, P. A. 1959. The plant cell-wall. Handbuch der Pflanzenanatomie. 2nd ed. Bd. III. T. 4. Borntraeger, Berlin. 886 pp.

Shrock, R. R., and W. H. Twenhofel. 1953. Principles of invertebrate paleontology. McGraw-Hill, New York. 816 pp.

Smith, G. M. 1955. Cryptogamic botany. Vol. I. 2nd ed. McGraw-Hill, New York. 399 pp.

Uphof, J. C. T. 1962. Plant hairs. Handbuch der Pflanzenanatomie. 2nd ed. Bd. IV. T. 5. Borntraeger, Berlin. 206 pp.

Vinogradov, A. P. 1953. The elementary chemical composition of marine organisms. Mem. II. Sears Foundation for Marine Research, Yale Univ. New Haven. 647 pp.

Manuscript received November 9, 1965.