# GEOLOGIC HISTORY OF CARBOHYDRATES: I. PRECAMBRIAN

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## Summary

The organic residues in rocks of all ages have been studied most extensively for hydrocarbons, particularly biomarkers, less extensively for amino acids and pigments in younger rocks, but very little for carbohydrates. In biochemistry, significant strides have been made in carbohydrate composition, especially in the synthesis and knowledge of sugar nucleotides and associated enzymes. Ginsburg has noted that the sugar nucleotide UDPGlc (uridine–5'-*alpha*–D–glucanopyrosyl pyrophosphate) is a likely precursor of most of the monosaccharide moieties found in nature, and may have formed in abiotic or early biotic evolution. Furthermore, the enzyme UDP-D-glucose 4-epimerase may have been the first (by being the simplest) UDPGlc modifying protein catalyst to have participated in monosaccharide synthesis.

Carbohydrates have played a major role in the composition of all three Domains of living things, especially in their conservative cell-wall composition, based on study of their sugar nucleotides and associated enzymes. The Domain ARCHAEA have cell walls composed of either protein or "pseudopeptidoglycan". The Domain BACTERIA have cell walls of teichoic acid, peptidoglycan (in thick-walled Gram (+) forms), or these components, plus lipopolysaccharides and short-chain bacterial cellulose (in thin-walled Gram (-)forms). The Domain EUKARYOTA have cell walls of long-chain cellulose (green algae, plants, some Fungi), chitin, chitosan (Fungi) or no carbohydrates (animals). Assuming that these conservative components have persisted from their earliest origins to the present time, the geologic history of the fossil carbohydrate residues can be inferred, despite the rarity or absence of their residues in the rocks.

Photosynthetic (or other light sensitive pigment) activity may have begun in the Archean Era of Australia and South Africa between 3800 and 3500 Ma ago (Knoll, Barghoorn, Schopf). Some of the Australian records are under dispute as to their biogenicity (Brasier). Other recent data support the antiquity of the 3500 MS Australian records (Grambling). For this reason, the earlier Archean ranges in Table 1 are shown as questionable. Ribose, from DNA/RNA would have been one of the earliest, if not the earliest, monosaccharide residues to be produced in the Archaea of thermophilic or methanogenic type. During that time interval glucose and glucosamine would have been produced from "pseudopeptidoglycan" (peptides with L-amino acids) also of Archaea. Between 3500 and 3000 Ma ago, the stromatolite record (questioned by Brasier) suggests that the Cyanobacteria (blue-green algae) were in existence and their teichoic acid and peptidoglycan (peptides with D-amino acids) cell-wall components are inferred to have yielded glucose and glucosamine. Some iron-formations (ie. Soudan) of that time interval show that oxygen was increasing to provide a slight surplus in the atmosphere, over

that consumed by oxidation of minerals. Photosynthetic production of sucrose, yielding glucose and fructose may have accompanied these phenomena (Table 1).

In the early Proterozoic Era (2500-500 Ma) an extensive microbiota is preserved in the Gunflint Formation (~2000 Ma ago) of Ontario and Minnesota (Barghoorn, Tyler); in the Duck Creek Dolomite (~2000 Ma ago) of Antarctica (Knoll); and petroliferous schists in the Onega Basin of northern Russia (2502-1970 Ma ago) (Melezhik). The presence of peptidoglycan, bacterial polysaccharides and teichoic acid is inferred in the first two deposits by their microbiota; the presence of lipopolysaccharides in the Onega Basin deposits is suggested, as well as saccharide residues arabinose, galactose, mannose, rhamnose, ribose and glucose, glucosamine, sugar alcohol ribotol and glycerol in advanced Cyanobacteria. The main iron formations of the Precambrian and petroliferous deposits in Russia and elsewhere formed in this time interval. (An example of graphite schist occurs in the Homestake Mine, South Dakota)

The Middle Proterozoic Skillogalee Group of South Australia (1900-1050 Ma ago) (Schopf, Barghoorn), in addition to the preceding types, has yielded examples of Domain EUKARYOTA in the form of fungal hyphae, sporangia and of Chitinozoa, Saccharides of these forms include chitin, chitosan? and chitobiose, with residues of glucosamine, mannose and glucose.

The late Proterozoic Svanbergfigellet Shale of Spitzbergen (800-700 Ma old) (Knoll) and the Bitter Springs Chert of Australia (lacustrine—about 850 Ma old) (Schopf) have yielded rich microbiotas of blue-green algae, bacteria including heterotrophic types and eukaryotic green algae (Chlorophyta,), acritarchs, a possible dinoflagellate, and possible red algae (Rhodophyta). The polymeric carbohydrates in these organisms are inferred to include long-chain cellulose, complex galactans (arabinogalactan that may have attached sulfate ester groups (agar)) and pectins. These yield residues of D-xylose, L-rhamnose, glucose and glucuronic acid. Records of the red algae are sparse in the Precambrian, but become more definite in the early Paleozoic. The Spitzbergen microbiota offers support to the concept that green land plants evolved from green algae in the early Paleozoic (Stewart, Rothwell).

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