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A Biogeochemical Comparison of Fossil (Carboniferous) and Modern Crustose Red Algae.

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The nature of the contribution of the various types of algae to sedimentary organic matter continues to be a topic of research interest. Crustose red algae have however received less attention than other types. The fossil calcareous red algae (Rhodophyta) analyzed in this study are two relatively unrecrystallized specimens of *Parachaetetes* (Family Solenoporacea) from the lower part of the Ste. Genevieve Formation (Carboniferous, Visean) in Union County, Illinois, USA. They occurred in the patch reef phase of a small carbonate mudmound-patchreef. The three modern specimens (collected and identified by F. Collier) are the crustose algae *Lithothamnion*, *Clathromorphum* and *Phymatolithon*, (Family Corallinacea, Subfamily Melobesoidea), from a rocky intertidal area near Cape May, Massachusetts, USA.

The pyrolyzates of the three (dried, unextracted) modern algal specimens exhibited strong similarities, including a predominance of alkylbenzenes, phenols and indoles [peaks 6, 11, 13, 19, 21, 32, 35] (Fig. 1a). Polysaccharide pyrolysis products [1, 7, 8, 15, 27] are also important, as would be expected. The minor dipeptides [38, 39, 40, 42, 45] detected indicate the presence of proteins. A variety of simpler nitrogen compounds, including pyrroles [5, 9, 14] and benzonitriles [17, 23, 29] may be derived from proteins or from more resistant macromolecular structures. The long-chain alkylnitrile [44] is also noteworthy. The fossil specimens of *Parachaetetes* (pyrolyzed at 610°C after HCl digestion to remove carbonates and thermodesorption at 310° for 20 sec. to remove bitumen) yielded relatively abundant monoaromatic hydrocarbons [2, 6, 11, 13, 18, 26] and phenols [19, 21, 24, 30, 33] (Fig. 1b). While their distributions are different, the importance of monoaromatic and phenolic compounds in both the Carboniferous and modern specimens demonstrates a significant similarity. The fossil specimen's pyrolyzate also contains a variety of minor nitrogen compounds [4, 5, 9, 10, 16, 17, 32], some of which are also found in the modern samples and all of which are unusual in the pyrolyzates of such ancient (ca. 340 Ma) organic matter. The C_{16} and C_{18} alkylnitriles [44, 47] are relatively important, but normal hydrocarbons are not, except for the C_{15} and C_{17} *n*-alkanes (Fig. 1b). Coincidentally, the C_{17} *n*-alkane is the only significant normal hydrocarbon in the modern sample (Fig. 1a). In this study we have found significant chemical similarities between the pyrolyzates of specimens of modern and fossil coralline red algae. The encrustation of the organic matter of *Parachaetetes* by calcite greatly enhanced its preservation, in spite of the specimens' great geologic age.

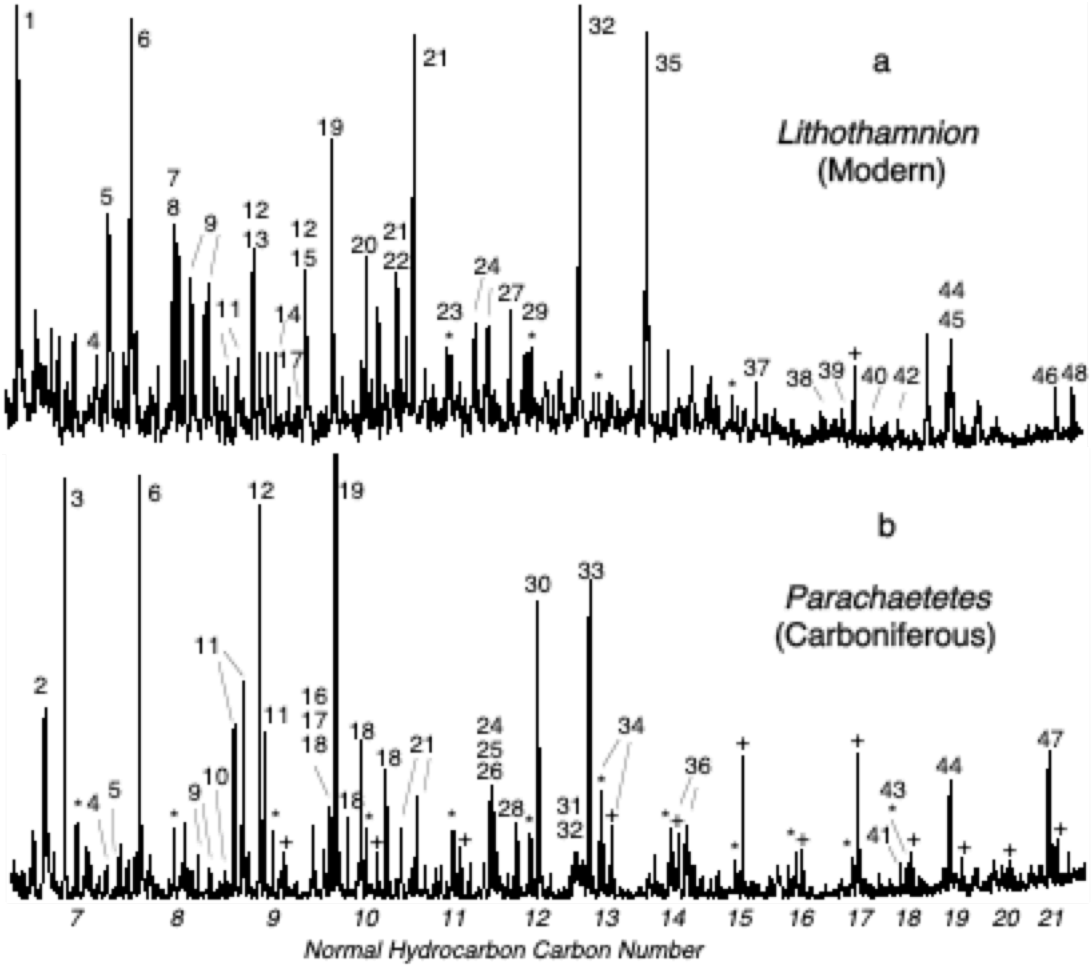

Fig. 1. Py-GC/MS total ion current chromatograms of modern and fossil specimens of crustose red algae. *: *n*-alkenes, +: *n*-alkanes, numbered peaks identified below. (CDS 120 Pyroprobe, 610°C, 20 sec.; HP 5980 GC; 50 m/0.2 mm/0.3 µm HP-1 col.; 40°C (5 min.), 40-300°/min., 300° (20 min.); HP 5780 MSD, 40-440 Da, 0.9 scans/sec.)

1 hydroxypropanone
2 benzene
3 cyclohexene
4 pyridine
5 pyrrole
6 toluene
7 cyclopentenone
8 furancarboxaldehyde
9 methylpyrrole
10 methylpyridine
11 C2-alkylbenzene
12 methylcyclopentenone
13 styrene
14 C2-pyrrole
15 methylfurancarboxaldehyde
16 benzenamine
17 benzonitrile
18 C3-alkylbenzene
19 phenol
20 methylcyclopentanedione
21 methylphenol
22 indene
23 cyanomethylbenzene
24 C2-alkylphenol
25 methylindene
26 1,2,3,4-tetramethylbenzene
27 dianhydroglucopyranose(?)
28 naphthalene
29 cyanoethylbenzene
30 phenol, 4-(1-methylethyl)
31 dimethylindene
32 indole
33 propenylphenol(?)
34 methylnaphthalene
35 methylindole
36 dimethylnaphthalene
37 methylquinoline
38 Pro-Ala
39 Pro-Gly, Pro-Lys
40 Pro-Val, Pro-Arg
41 phenanthrene
42 Pro-Val, Pro-Arg
43 anthracene
44 hexadecanenitrile
45 dipeptide
46 phytol
47 octadecanenitrile
48 alkylamide

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Abstracts
Part II

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