ANNUAL PROGRESS REPORT ON NASA GRANT NGR-05-010-035

1 August 1972 to 31 July 1973

Summary of work performed

The tasks described below were completed or initiated during the year:

I. Studies on humic substances through geologic time were completed by Dr. Togwell Jackson, a paper on the subject by Jackson and Cloud was presented at a Symposium on Environmental Biogeochemistry (Logan, Utah, 22-24 March 1973), and a long paper on the subject by Dr. Jackson (now with the Fisheries Research Board of Canada) is in press. The main conclusion of this work is that the 43 selected samples analyzed show secular trends in the humic composition of sediments that may be correlated with other events, perhaps in biogeologic evolution, at about 3.3, 2, 1, and 0.7 billion years before the present.

II. The benzene and hexane soluble portions of the benzene-methanol extracts from the same standard suite were analyzed for hydrocarbons by Dr. Joel Leventhal using a gas chromatograph, simply as a check on previous work by others. The results confirmed our judgement that the main conclusion to be drawn from such work was that this extractable portion is probably not indigenous, and that future efforts should be concentrated on the kerogen, which offers better prospects that results obtained will reflect the properties of primary indigenous materials.

III. Experiments were iniated by Dr. Leventhal in collaboration with others in the Biogeology Clean Laboratory to find a useful pyrolytic technique and to apply it to single taxa of fossil microorganisms or even individual microorganisms. These involve the steps listed below.

A. Sample sealed in 3/16" tube under vacuum; 300°C for 5 min. with dry ice (-78°C) on one end to condense volatiles. Using packed column (1/8" Dexsil x 6 ft.)

B. Sample in pyroprobe quartz tube, pyrolyzed at 150, 250, 350, 450, 600, 900°C. Using packed column (1/8" Dexsil x 6 ft.)

C. Sample in pyroprobe quartz tube; 150, - etc. capillary column.

D. Kerogen concentrate on pyroprobe ribbon.

E. Kerogen concentrate in quartz tube.

F. Hand pick microfossils for pyrolysis on filament.

G. Analyze modern organisms related to microfossils.

The most promising procedures involve the pyroprobe quartz tube and ribbon at a range of temperatures, using a capillary column in the G. C. Preliminary results are as follows:

1. The pyrolysis analyses technique so far shows little relation to the hexane extractable material.

2. Repeat pyrolyses at 600 and 900°C give only $\leq$ 1/4 as much as is initially released, indicating that 10 sec. is enough time to give most of the products characteristic of that temperature.

3. The material released at different temperatures reflects the structure of the kerogen (which depends on source material, environment of deposition and subsequent

diagenesis). The lowest temperature (150°) material is that which is very loosely bound and may be volatilized such as hydrogen bonded, chemical or physical adsorption or absorption, or perhaps ester bonds.

4. At intermediate temperatures (250, 350, 450°), large molecules could be volatilized if they were held by only a few bonds, especially the heteroatomic (C-N, C-S, C-O) bonds. The molecules released would be large non-polymerized material. Samples giving a substantial portion of their material at these temperatures will be the most interesting since they will reflect large non-polymerized molecules (chemical fossils?).

5. At high temperatures (600° and higher) the appearance of methane and other molecules with two to six carbon atoms reflects the pyrolysis and degradation of the polymer itself. The polymer decomposition products will give information about the structure. Unsaturated and aromatic (benzene) compounds reflect the polymer nucleus, whereas methane reflects the aliphatic and methyl groups which are present.

The spectrum of results obtained by the procedures described is illustrated in Figures 1 and 2. Mr. Steven Suess, a student, has been assisting (without pay) in the above experiments.

IV. Experiments are being made to find out where the kerogen in sediments came from, particularly how and to what extent humic substances become converted to kerogen and retained in sediments. This work is being done as a project for a masters thesis by Mr. Kenneth Peters, using a variety of substances under a range of experimental conditions and analyzing products by GC. Although very preliminary, the indication is that humic substances do convert to kerogen with aging at elevated temperatures and that this process goes on without much regard to the kind of sedimentary matrix.

V. Other experiments, largely under NSF auspices, are directed toward the micromanipulation and isolation of individual minute (1 to 12 μm diameter) kerogenous fossils and monospecific fossil assemblages. Among other things we hope to be able to apply the techniques described in III to such samples so that we can begin to talk of the biogeochemistry of explicit paleobiologic taxa and not merely of rocks.

VI. In addition to the above, largely under NSF auspices but involving much of the PI's time, we have continued field work in the Mojave Desert and extended it to southeastern Newfoundland, pursued our studies of the procaryote-eucaryote transition and the Proterozoic-Phanerozoic boundary, continued our search for new pre-Phanerozoic biotas of any description, and pushed our studies of the ultramicroscopy of fossil microorganisms -- in particular the 700 m.y. old Hector microbiota and the 2000 m.y. old Pokegama microbiota. New drying and impregnating techniques are leading to limited but interesting successes which we hope with time and patience to integrate with the biogeochemistry. Preliminary paleoecological studies of the late Proterozoic Johnnie Formation of eastern California by William Benmore are nearing completion and Gary Kline is analyzing and describing a spectacular assemblage of Proterophytic-Proterozoic growth forms that are identical in detail to those of the morphologically diverse living Mn bacterium Metallogenium.

The following lists of works published, in progress, and in preparation shows in more detail what we have been doing over the past year.

Publications

1972

Cloud, Preston, response to Paleontological Society Medal Presentation: Jour. Paleont., v. 46, no. 3, p. 470-472

Germs, J. B. G., The stratigraphy and paleontology of the lower Nama Group, South West Africa: University of Capetown, Precambrian Research Unit, 250 p.

Licari, G. R. and Preston Cloud, Prokaryotic algae associated with Australian Proterozoic stromatolites: Proc. Nat. Acad. Sci. (USA), v. 69, no. 9, pp. 2500-2504, Sept. 1972

Licari, G. R. and Bennie Troxel, Fossil algae 1.3 b.y. old from eastern California rocks: Calif. Geology, 1973, p. 15-16

1973

Cloud, Preston, Possible stratotype sequences for the basal Paleozoic in North America: Amer. Jour. Sci., v. 273, p. 193-206

Cloud, Preston and Marcel Dardenne, Proterozoic Age of the Bambui Group in Brazil: Geol. Soc. Amer. Bull., v. 84, p. 1673-1676, May 1973

In press

Germs, G., A reinterpretation of _Rangea schneiderhohni_ and the discovery of a related new fossil from the Nama Group, Southwest Africa: Lethaia, _in press_

Cloud and Bever, Trace fossils from the Flathead Sandstone of Fremont County, Wyoming, compared with similar forms from California and Australia: Jour. Paleont., _in press_

McConnell, Stratigraphy, paleoecology, and paleontology of the 1.2 to 1.4 aeon-old Apache Group, Arizona, and its relation to equivalent rocks in the southwestern United States: Museum of Northern Arizona, _in press_

Allison and Moorman, A new microbiota from the late Proterozoic Tindir Formation of central Alaska: Geol. Soc. Amer., in press

Licari, Paleontology and paleoecology of the Proterozoic Beck Spring Dolomite in eastern California: Jour. Paleont., in press

Cloud, Preston, Paleoecological significance of banded iron formation: Econ. Geology, in press

Jackson, Togwell, Biochemical evolution of pre-Phanerozoic photoautotrophs -- the significance of aromatic chromophores in fossil humus: in press

Moorman, Microbiota of the late Proterozoic Hector Formation, southwestern Alberta, Canada: Jour. Paleont., in press

In preparation

Cloud, Preston, Evolution of ecosystems

Cloud, Preston, Rubey Conference on Crustal Evolution -- a conference report

Cloud and Licari, Proterozoic fungi -- new records of advanced forms.

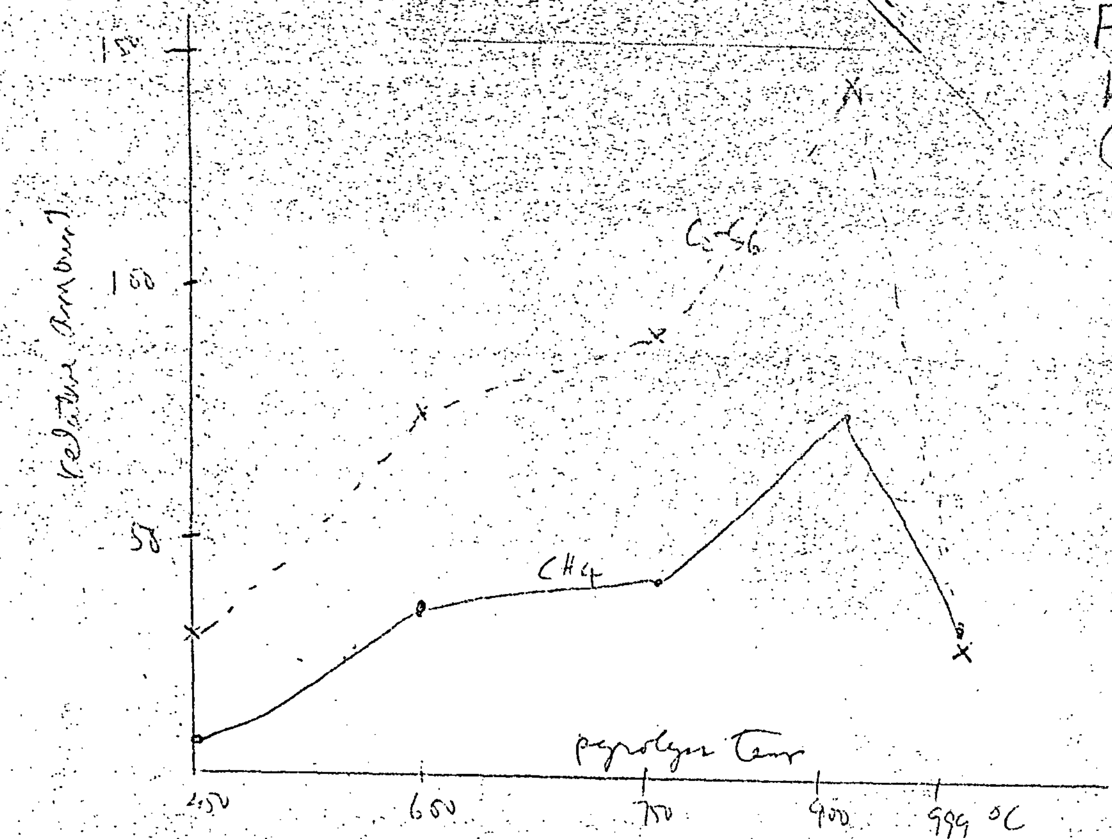
Cloud and Pierce, Further studies on the ultrastructure of pre-Phanerozoic microfossils

Kline, Gary, *Metallogenium* in the early Proterozoic and late Proterophytic

Leventhal, Joel, Stepwise pyrolysis -gas chromatography for analysis of organic materials

Leventhal and Cloud, Analysis of kerogen in pre-Phanerozoic cherts.

Fig. 1. Pyrolysis GC analyses of kerogen from 3.4 B.Y. old sediment (Onverwacht) with high thermal history



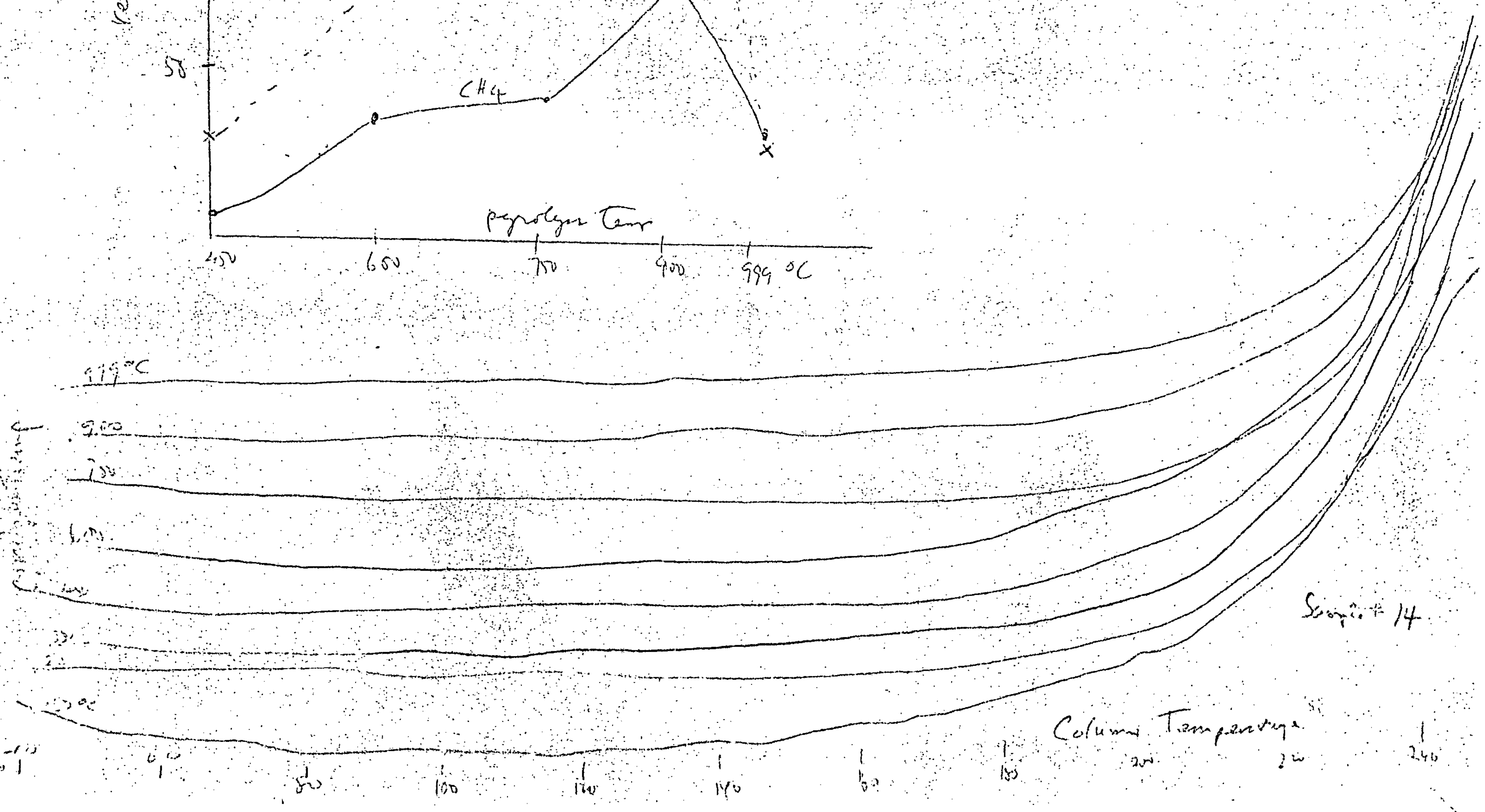


Fig. 2. Pyrolysis GC analyses of kerogen from 1.6 BY old sediment (Paradise Ck) having experienced only a low thermal history.