13. An increase in stratospheric CH_4 would transform the active Cl radicals (Cl, ClO) into the relatively inert form HCl through the reaction $CH_4 + Cl \rightarrow CH_3 + HCl$. Conversely, an increase in CH_4 may also increase stratospheric OH, which reacts with HCl to release Cl. For a given stratospheric odd chlorine (Cl, ClO, HCl, $ClONO_2$) mixing ratio, calculations indicate that a doubling of the stratospheric CH_4 concentration would decrease stratospheric column Cl and ClO by as much as 25 percent and increase OH and HO_2 by about 2 and 10 percent, respectively.
14. The effect of increasing CH_4 and stratospheric H_2O on the global mean temperature was discussed recently by Wang *et al.* (*15*). Their calculations, based on a one-dimensional radiative-convective model, show that a doubling of the CH_4 and stratospheric H_2O concentrations might cause increases in the surface temperature of 0.3° and 1.0°K, respectively.
15. W. C. Wang, Y. L. Yung, A. A. Lacis, T. Mo, J. E. Hansen, *Science* **194**, 685 (1976).
16. The gases CH_3Cl and CH_3Br are major natural chlorine and bromine carriers. They are decomposed in the stratosphere, releasing active Cl and Br radicals, which are potent catalysts for the destruction of ozone [S. C. Wofsy, M. B. McElroy, Y. L. Yung, *Geophys. Res. Lett.* **2**, 215 (1975)].
17. U.S. Department of Health, Education, and Welfare, *Air Quality Criteria for Carbon Monoxide* (Washington, D.C., 1970).
18. The 4 percent annual increase in the rate of CO emissions in the period 1940 through 1970 was taken from (*17*). The 1971 CO emission rates were estimated from (*6*). The 5 percent annual decrease in the CO emission rate (model B) in the period 1970 through 1985 is based on the assumption that there will be a large increase in the number of vehicles equipped with emission control systems. An increase of 2 percent per year after 1985 was assumed to take into account growth of the vehicle population.

31 August 1976

Origins of Sulfur in Coal: Importance of the Ester Sulfate Content of Peat

Abstract. *The sulfur found in coal stems in large part from sulfur incorporation at the peat-forming stage. Ester sulfate (a carbon-oxygen-sulfur linkage) is a major contributor to the sulfur in peat and thus is an important determiner of the quantity and forms of sulfur eventually found in coal.*

The high sulfur content of many coals restricts their use. Although various sulfur forms in coal such as pyrite, sulfate, and total sulfur have been quantified, the organic sulfur in coal has not been characterized with respect to the type of bonding present. Organic sulfur can represent a significant portion of the total sulfur and the total dry weight of coal. It accounts for over 50 percent of the total sulfur in many cases, and in Rasa coal organic sulfur represents 11 percent of the dry weight (*1*). Sulfur in coal is difficult to characterize because of the considerable polymeric and aromatic matrix of coal.

The sequence peat → lignite → bituminous coal → anthracite coal is the primary metamorphic progression in coalification (*2*). We report here on an investigation of the incorporation of organic sulfur in the peat-forming stage. Peat-forming systems in the Okefenokee Swamp, Georgia, and the Everglades, Florida, were selected as suitable modern progenitors of coal (*3*).

A peat-forming system is a dynamic system composed of a living plant community, surface litter, water, minerals, microorganisms, burrowing animals, and peat. Peat can be thought of as a highly organic soil. Earlier studies on organic sulfur in inorganic soils have led to the characterization of two forms of organic sulfur: (i) a carbon-sulfur linkage such as that found in sulfur-containing amino acids (such as cysteine) and heterocyclics (such as thiophenes) and (ii) a carbon-oxygen-sulfur linkage (referred to as "ester sulfate") represented by chondroitin sulfate and phenolic sulfates (*4*).

Using techniques developed for inorganic soils, we have characterized organic forms of sulfur in peats and related these to events deemed important to the origins of sulfur in coal. Two areas of the Okefenokee Swamp were selected for study: (i) Chesser Prairie, a freshwater-marsh environment consisting of the plants *Nymphaea, Orontium,* and *Eleocharis* associated with 180 cm of peat (*p*H 4.0) and (ii) Minnie's Lake, a freshwater-swamp environment where *Taxodium* is the dominant plant in association with 320 cm of peat (*p*H 4.0). The marine area of the Little Shark River in the Florida Everglades was the third site selected for study; at this site *Rhizophora mangle* L. is the dominant plant species in association with 360 cm of peat (*p*H 7.0). All three sites have been more fully described elsewhere (*5*).

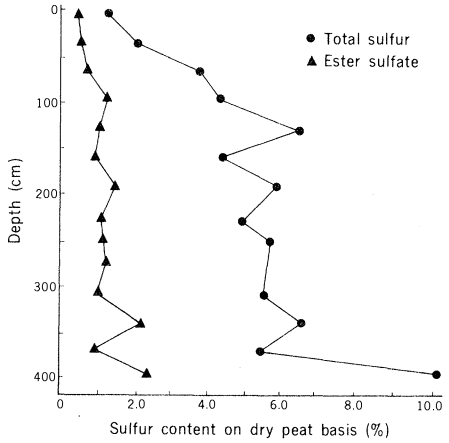


Fig. 1. Distribution of sulfur forms in peat from the mangrove environment (Little Shark River) of southern Florida.

In each of the peat profiles, samples were taken at approximately 25-cm intervals. A preliminary extraction with lithium chloride (aqueous) and then chloroform led to the removal of sulfate and elemental sulfur, respectively. We determined the total sulfur in the original sample at each level, using the Johnson-Nishita (*6*) method as modified by Tabatabai and Bremner (*7*).

The analysis of the ester sulfate content of the peat samples was carried out on samples from which the sulfate and elemental sulfur had been removed. The procedure developed by Freney was used (*8*), in which a reducing solution consisting of hydriodic acid, hypophosphorous acid, and formic acid reduces the sulfur to hydrogen sulfide (*2*). The reducing solution used here will reduce all forms of sulfur except carbon-bonded sulfur. Nitrogen, in the Johnson-Nishita apparatus, carries the hydrogen sulfide to a solution of zinc acetate and sodium acetate. The resulting zinc sulfide reacts with *p*-aminodimethylaniline and ferric ammonium sulfate to produce methylene blue, which is measured spectrophotometrically at 665 nm.

Sulfides and ester sulfate were determined by this technique. Sulfide (quantified independently by other techniques) was found to be negligible in the fraction insoluble in lithium chloride–chloroform in the samples from the two freshwater sites (two orders of magnitude lower than the ester sulfate content) (*2*). Sulfide values were significant in the samples from the marine site (at least equal to the ester sulfate content) and were subtracted from the values of sulfur reducible by hydriodic acid to give the absolute values for ester sulfate.

Table 1 shows the results of an analysis of two peat cores from the Okefenokee Swamp and one from the Everglades; the values for total sulfur represent the mean of individually determined peat levels from each profile. Figure 1 shows the ester sulfate content of peat from the Little Shark marine site as a function of sediment depth; the total sulfur content at the same site is plotted for comparison.

The data reveal a number of points: (i) the total sulfur content of the marine peat is considerably higher than that of the freshwater peats; thus, coals derived from near-marine and brackish environments would have considerably more sulfur associated with them than coals from freshwater sites; (ii) the overall differ-

Table 1. Mean values for total and ester sulfate in three peat-forming areas.

Sampling site	Percentage of sulfur (dry weight basis)		Ester sulfate as a percentage of total sulfur
	Total	Ester sulfate	
Minnie's Lake (freshwater)*	0.19	0.047	24.73
Chesser Prairie (freshwater)*	0.18	0.045	25.00
Little Shark (marine)†	5.16	1.22	23.64

*Mean of 5 samples. †Mean of 14 samples.

ences in the total sulfur content between the two freshwater peats is quite small; (iii) ester sulfate represents approximately 25 percent of the total sulfur; (iv) there is little difference between the freshwater and marine peats in the ester sulfate content as a percentage of the total sulfur; (v) the ester sulfate content increases with the depth of sample; and (vi) the ester sulfate content closely parallels the carbon-bonded sulfur and the total sulfur content as a function of depth.

It is difficult to hypothesize which naturally occurring compounds would be likely to have ester sulfate linkages. Ester sulfate linkages in substances such as choline sulfate, fucoidan, and chondroitin sulfate have been reported in various organisms and may eventually contribute ester sulfate to the sediment upon the death of the organism. Organic matter is not readily degraded in a water-logged swamp-marsh environment, and thus lignin-derived heteropolycondensates such as humic and fulvic acids can accumulate. These substances are known for their relatively high phenolic content (*9*); some of the phenolic groups may react with various sulfur forms to produce ester sulfate linkages. Sugars have been extracted from humic and fulvic acids, and these moieties may contain ester sulfate linkages (*10*). Thus ester sulfate may enter the sediment directly from the remains of certain organisms or it may be formed in situ if certain reactive chemical groups and sulfate are present.

Since peat is the first member of the coalification sequence, the relatively high values of ester sulfate in peat are significant. Ester sulfate incorporated in the peat-forming stage can be carried through the other stages of coal formation, or it can be added during subsequent stages. As far as we know, the ester sulfate content of lignites and bituminous and anthracite coals has not been investigated. Ester sulfate may be viewed as the form in which sulfate is stabilized geochemically. When a sediment is buried and becomes increasingly anaerobic, sulfate becomes an important source of oxygen for microbial metabolism. Hydrogen sulfide from the reduction of sulfate can then react with organic matter to form organic sulfur linkages. In a laboratory experiment gaseous hydrogen sulfide was shown to react with fatty aldehydes to form a variety of organic sulfur compounds (*11*). Thus, it is apparent that ester sulfate can be reworked in the sediment in such a way that it contributes to the total sulfur content in coal.

DANIEL CASAGRANDE
KRISTINE SIEFERT
College of Environmental and Applied Sciences, Governors State University, Park Forest South, Illinois 60466

References and Notes

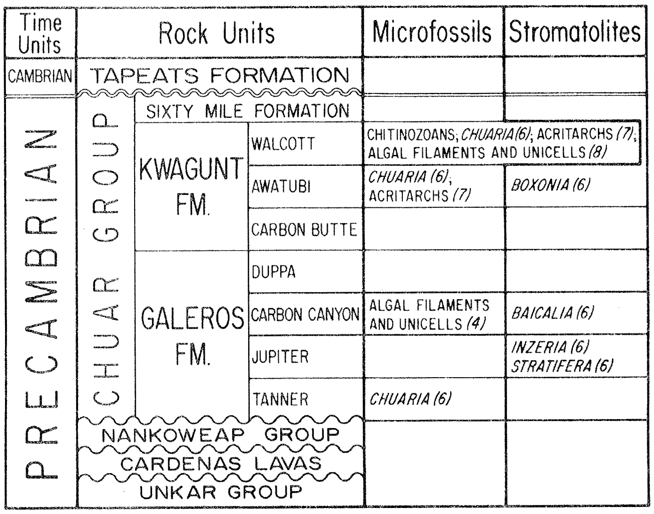
1. D. J. W. Kreulen, *Fuel* **31**, 462 (1952).
2. D. J. Casagrande, K. Siefert, C. Berschinski, N. Sutton, *Geochim. Cosmochim. Acta* **41**, 161 (1976).
3. W. Spackman, D. W. Sholl, W. H. Taft, *Field Guidebook to Environments of Coal Formation in Southern Florida* (Geological Society of America, Boulder, Colo., 1964); W. Spackman, A. D. Cohen, P. H. Given, D. J. Casagrande, *A Field Guidebook to Aid in the Comparative Study of the Okefenokee Swamp and the Everglades–Mangrove Swamp–Marsh Complex of Southern Florida* (Geological Society of America, Boulder, Colo., 1974).
4. J. R. Freney, in *Soil Biochemistry*, A. D. McLaren and G. H. Peterson, Eds. (Dekker, New York, 1967), chap. 10.
5. D. J. Casagrande and L. D. Erchull, *Geochim. Cosmochim. Acta* **40**, 387 (1975).
6. C. M. Johnson and H. Nishita, *Anal. Chem.* **24**, 736 (1952).
7. M. A. Tabatabai and J. M. Bremner, *Soil Sci.* **114**, 380 (1972).
8. J. R. Freney, *J. Agric. Res.* **12**, 424 (1961).
9. M. Schnitzer and S. U. Khan, *Humic Substances in the Environment* (Dekker, New York, 1972).
10. A. J. Lucas, thesis, Pennsylvania State University (1970).
11. M. Boelens, L. M. van der Linde, P. J. de Valois, H. M. van Dort, H. J. Takken, *J. Agric. Food Chem.* **22**, 1071 (1974).
12. We thank C. Berschinski, N. Sutton, J. M. Bremner, and M. A. Tabatabai for their assistance. This work was supported by the Earth Sciences Section of the National Science Foundation under grant DES 73-06496 A01.

17 June 1976; revised 28 September 1976

Chitinozoans from the Late Precambrian Chuar Group of the Grand Canyon, Arizona

Abstract. *Carbonaceous shales of the late Precambrian Chuar Group of the Grand Canyon, Arizona, contain abundant and well-preserved chitinozoans. The occurrence of these distinctive, tear- and flask-shaped microfossils, the oldest chitinozoans now known and the first to be reported from the Precambrian, seems to suggest that heterotrophic protists (or primitive metaozoans) were extant at least as early as about 750 ± 100 million years ago.*

One of the classic unsolved problems in paleobiology is the question of the origin of the Metazoa. In recent years, studies of megascopic fossils from strata of latest Precambrian and earliest Cambrian age have provided much new information regarding early stages of metazoan diversification (*1*). These studies suggest that megascopic invertebrates [and apparently also megascopic algae (*2, 3*)] may have first appeared about 650 million years ago. Despite this recent progress, however, and although algal microbiotas of the earlier Precambrian



Time Units	Rock Units			Microfossils	Stromatolites
CAMBRIAN	TAPEATS FORMATION				
PRECAMBRIAN	CHUAR GROUP	SIXTY MILE FORMATION			
		KWAGUNT FM.	WALCOTT	CHITINOZOANS; *CHUARIA (6)*; ACRITARCHS *(7)*; ALGAL FILAMENTS AND UNICELLS *(8)*	
			AWATUBI	*CHUARIA (6)*; ACRITARCHS *(7)*	*BOXONIA (6)*
			CARBON BUTTE		
		GALEROS FM.	DUPPA		
			CARBON CANYON	ALGAL FILAMENTS AND UNICELLS *(4)*	*BAICALIA (6)*
			JUPITER		*INZERIA (6)* *STRATIFERA (6)*
			TANNER	*CHUARIA (6)*	
	NANKOWEAP GROUP				
	CARDENAS LAVAS				
	UNKAR GROUP				

Fig. 1. Stratigraphic relationships of fossiliferous late Precambrian sediments in the Grand Canyon region of Arizona.