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Sulfur Diagenesis in Everglades Peat and Origin of Pyrite in Coal

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Summary. The pattern of sulfur transformation in peat across the Everglades basin indicates that pyrite formation in organic-rich swamps depends on the use of organic oxysulfur compounds in dissimilatory respiration by sulfur-reducing bacteria. This paragenesis explains the primary distribution of sulfur compounds in low-sulfur coals and possibly in most coals and many organic-rich soils and sediments. It also accounts for the occurrence of framboidal pyrite bound in fossil tissue in coal and sediments.

The distribution of sulfur and its compounds in extensive contemporary peat basins bears directly on the origins of pyrite in organic-rich sediments and has particular relevence for major geologic and economic problems of sulfur in coal. The sulfur in peat and coal is fixed dominantly in three forms—as part of the organic matter, as mineral sulfide, and as mineral sulfate (*1, 2*). In most coal, sulfur is held primarily in pyrite and organic sulfur, and mineral sulfate is minor (*3*). In freshwater coastal-plain peats and many lignites, organic sulfur dominates, sulfate is important, and pyrite is minor. Thus, transformation of peat to coal appears to entrain an increase in pyrite at the expense of sulfate and organic sulfur. Total sulfur and pyrite become more prominent in peats of brackish and marine realms, and in coal derived from such peat (*4, 5*). Although traces of FeS and elemental sulfur have been reported in peat (*6, 7*) and in some coals (*8*), the sulfur analyses are conventionally presented only in terms of total sulfur and the so-called forms of sulfur: that is, sulfate, pyritic, and organic sulfur, with pyritic sulfur being assumed to embrace all metallic sulfides.

The origin of sulfur distribution in coal is obscured by postdepositional enrichment of sulfur and pyrite (*9*) and by lack of knowledge of the primary differentiation of sulfur in extensive peat beds. To find how sulfur is fixed in the first stages of coal, we have determined its forms and distribution in several regional transects of the continuous peat deposits of the Everglades freshwater basin and the mangrove-forested tidal plain of southern Florida. We will describe principally the freshwater basin.

Recent studies of iron sulfide genesis in marine and lacustrine muds reveal two general pathways for the formation of pyrite, both based on the generation of HS^- or H_2S by the bacterial reduction of aqueous sulfate (*10*). One pathway involves the initial formation of mackinawite ($FeS_{0.9}$), which is secondarily converted to pyrite by interaction with elemental sulfur:

$$HS^- + Fe^{2+} \rightarrow FeS + H^+$$

$$FeS + S^0 \rightarrow FeS_2$$

This essential sequence has been confirmed experimentally (*11, 12*) and has been shown to lead to framboidal pyrite (*13, 14*).

The second pathway is the direct precipitation of pyrite, which has been reported from coastal marshes (*15*), and requires the prior oxidation of H_2S to either elemental sulfur or polysulfide for reactions like the following (*10–12*):

$$Fe^{2+} + S^0 + H_2S \rightarrow FeS_2 + 2H^+$$

$$Fe^{2+} + S_x^{2-} + HS^- \rightarrow FeS_2 + S_{x-1} + H^+$$

The bacterial generation of H_2S, with the subsequent formation of iron sulfides, from sulfate ions in interstitial mud water is clearly established in coastal lagoons and lake or ocean basins in which salinities and sulfate contents are high and organic productivity is not dominant, as is the case in offshore basins and coastal marshes of California (*16*) and the Black Sea (*17*). However, the extrapolation of this paragenesis to extensive peat swamps, in which organic matter dominates and organic sulfur is the largest store of sulfur in the system, may be inappropriate. In the low sulfate, organic-rich bottom mud of Lake Mendota the flux of aqueous sulfate was found inadequate to account for the FeS produced (*18*). In studies of peat across the Everglades basin, we find that pyrite genesis is dependent principally on organic sulfur. It is thus of interest to document and explore the conversion of organic sulfur to pyritic sulfur and the pathways for precipitation of pyrite.

The Everglades Environment

The Everglades is one of few domestic regions of our highly uplifted and dissected Holocene world in which we may study peat of regional extent in the formative state. It comprises an exceedingly flat plain of saw grass–covered marshland and shallow sloughs, stretching for 100 miles from Lake Okeechobee to the south coast of Florida, where it merges with a brackish intertidal zone of mangrove forest (Fig. 1). The Everglades occupies a constructional basin floored and bounded on the east by a Pleistocene barrier bar of oolitic limestone, the Atlantic coastal ridge, and on the west by Big Cypress, an area of slightly elevated older limestones. Because of its low altitude and very low slope, the area is essentially at base level. Surface drainage is largely through sheet flow, by way of broad sloughs, and the area remains flooded during the wet season and several months thereafter. In the broad middle zone (Fig. 1) the water table is at the surface even during the dry season unless there is a period of excessive drought (*19*).

Unconsolidated Holocene sediments,

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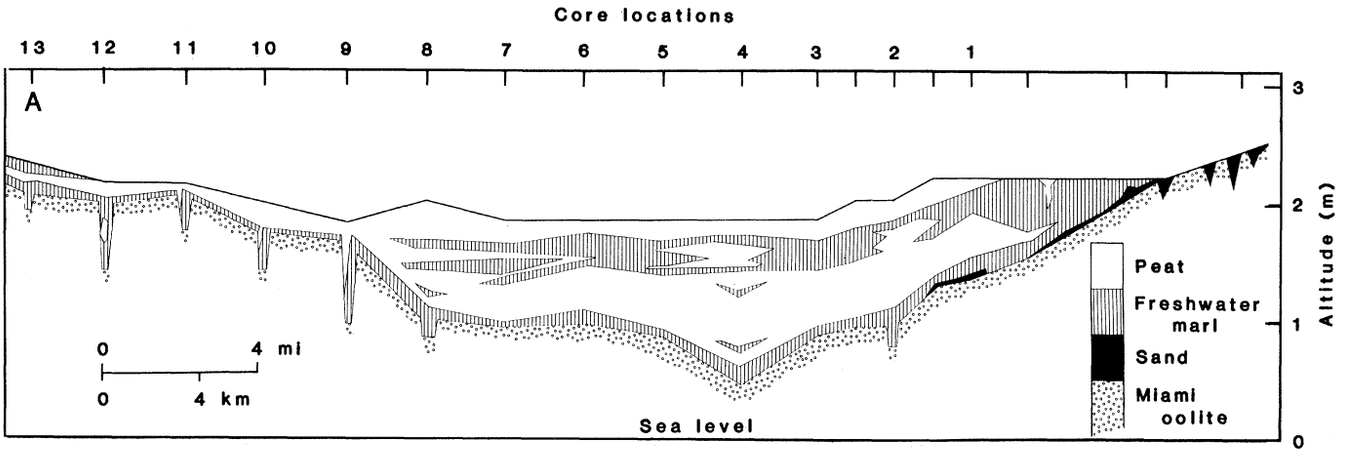

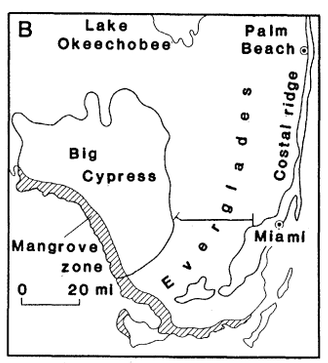

Fig. 1. (A) Core lithology and stratigraphic profile of Holocene deposits across the southern Everglades along the Tamiami Trail. Average depth to Pleistocene Miami oolite basement is shown by the general profile where cores penetrate solution pits in the basement. Thus the actual basin extends from cores 1 to 9, and major peat deposition from 1 to 8. (B) The profile in (A) follows the horizontal line through the Everglades in the area map.

dating from 5600 radiocarbon years before the present (*20*), form a meter-thick blanket over the central area. They consist dominantly of saw grass (*Mariscus jamaicensis*) and water lily (Nymphea) peat (*5, 21*) with subordinate freshwater algal limestone. Mineral detritus from the boundary areas is prominent only in the marginal zones and in the basal few inches of the deposits; it is mostly quartz sand with a few fragments of oolitic limestone. Toward the south coast, saw grass peat yields to mangrove peat, which thickens to 3 or 4 m (*5*), and the content of marine sand, clay, and biolutite increases appreciably.

The transects and coring sites shown in Fig. 1 establish a stratigraphic profile normal to the facies distribution. This profile reveals the shape and dimensions of the peat basin and shows that its Holocene fill consists of two cycles of thin, freshwater calcilutite (marl) and peat. The thin basal marl helps peat accumulate by sealing the underlying transmissive Miami oolite and minimizing infiltration of oxygenated surface water. Saw grass was the major plant at all coring sites, and saw grass litter predominates in the uppermost 5 cm of each core. None of the sites had algal mats, soils, or oxidized surface layers; all were submerged at the time of coring. The cores were taken in plastic liners within a hand-driven piston corer, at intervals of 3.2 km across the Everglades and 3.2 to 4.8 km in the mangrove zone. They were sealed and put on ice in the field and stored at 5° to 10°C.

The dissolved inorganic contents of surface water at natural sites in the southern Everglades are relatively low, a state attributable to the area's remoteness from diversified source rocks and to the filtering and fixing action of highly productive and densely covered marsh through which this surface water flows. Sulfate in rain across the area averages about 3 milligrams per liter (*22*). Sulfate in surface water is commonly from < 1 to 4 mg per liter at the end of high flow periods and from 1.5 to 15 mg per liter at the end of the dry season. Dissolved iron ranges from 20 to 300 μg per liter and averages about 100 to 150 μg per liter. Total iron ranges from 80 to 1000 μg per liter, and is commonly about 300 μg per liter in the surface water. The average *p*H of water in open marshes is about 7.5 (*22*).

The Eh (oxidation-reduction potential) and *p*H profiles, determined in situ, and the contents of SO_4, S^{2-} (essentially total dissolved sulfides), Fe^{2+}, and total iron in the ground water are shown for two coring sites in Fig. 2. In comparison with surface waters, note the two- to fivefold increase in iron content, its almost complete conversion to the ferrous state, and the substantial increase in sulfate at one coring site and at basal levels at both coring sites. The high sulfide values at the site of core 5 are probably augmented by gas streaming of volatile sulfides, an effect visible during the collection of water samples by vacuum pumping, and are untrustworthy. Nevertheless, they indicate substantial generation of sulfide in the peat. Free H_2S was not detectable by smell and is therefore not an appreciable component of the sulfides. The Eh and *p*H curves suggest the rapid downward depletion in oxygen, the maintainance of slightly reducing conditions below the upper peat zone, and a regime which is only slightly acid. Under these conditions, in a simple inorganic system, Fe^{2+} and SO_4^{2-} would be dominant species; any S^{2-} formed would tend toward aqueous H_2S which, by limited near-surface oxidation, might form polysulfide and elemental sulfur; pyrite would be supersaturated; and sulfate-reducing bacteria could fluorish (*23*). In organic-rich swamps, however, substantial dissolved polysulfide and organic sulfides might be expected from fermentative degradation of protein or interaction of hydrogen sulfide with organic matter (*24, 25*).

Sulfur Distribution Across the Everglades

Proximate and ultimate coal analyses and forms of sulfur were determined on the eight cores of the peat basin that were taken in an area 16 miles wide along the Tamiami Trail (*26*). Analyzed samples were from alternate 5-cm peat intervals, starting at the top. The major changes in carbon, nitrogen, hydrogen, and oxygen generally occur in the uppermost 15 cm. The peat approaches lignite in composition (moisture-free) and Btu content at moderate depth. Its paramount features are high moisture content

(85 to 90 percent by weight), low ash content (generally < 3 percent by weight), and an increase in carbon and decline in oxygen with depth.

As ash contents in the Tamiami Trail transect are very low, data are given on a moisture-free basis and thus comparable to coal. Total sulfur ranges from 0.4 to 1.1 percent by weight in all cores, with most samples having between 0.7 and 1.0 percent. Usually the highest values are at the top and the lowest values near the bottom of each core. Detailed data are given for cores 2, 5, and 8 in Table 1. The distribution and partitioning are shown in Fig. 3 (A and B); absolute and relative percentages by weight are used to normalize variations in total sulfur.

Sulfate sulfur, comprising aqueous and readily desorbed sulfate and any traces of gypsum, is enriched at the top of each core and declines rapidly in the upper 5 to 20 cm, as organic sulfur, but not sulfide sulfur, increases. Below the upper zone, sulfate is irregular from core to core and variable in some cores. It is generally less than 15 percent of the total sulfur. Pyritic sulfur is minimal (< 5 percent of the total) in the upper half of all cores. At mid-depth in the core it increases slightly and then progressively downward. At the base pyritic sulfur increases markedly, making up 10 to 50 percent, and averaging 20 percent of the total sulfur in the eight cores across the basin (Fig. 3B). Significantly, this increase in basal pyrite is always accompanied by a decline, of comparable magnitude, in organic sulfur, but not by a complementary decline in sulfate. In most cores, sulfate is too little changed and too limited in quantity to generate the major pyrite. Moreover, as total sulfur shows no progressive buildup, it is not reasonable to invoke continuous introduction of external sulfate as a major source of pyrite. Organic sulfur is the predominant form of sulfur throughout the profile except in the basal zone. Framboids of pyrite are found in the basal zone.

The decline in surface sulfate across the regional profile is attributed to rapid incorporation of aqueous sulfate by organic matter in the uppermost 5 to 20 cm. Incorporation of sulfur by organic matter in soils is known from experiments with labeled aqueous $-SO_4^{-2}$, which is found to be bacterially mobilized and is recovered as both ester- and carbon-bonded sulfur (*27*). Comparison of the peat data (Table 1) with analyses of fresh saw grass (Table 2) shows that the early formed peat acquires ten times the initial sulfur of the plants, dominantly as organically fixed sulfur. Only part of this is due to residual concentration (*28, 29*). The unusually high contents of sulfide sulfur and total iron in the fine rootlets of the saw grass (Table 2) may reflect incipient iron sulfide in the moribund tissue of the living plant (*30*).

Variations in total sulfur in the peat column (Fig. 3) are due mainly to variations in the amounts of organic sulfur and, to a lesser extent, of sulfate sulfur. This may be entirely primary variation caused by differences in the rate of peat

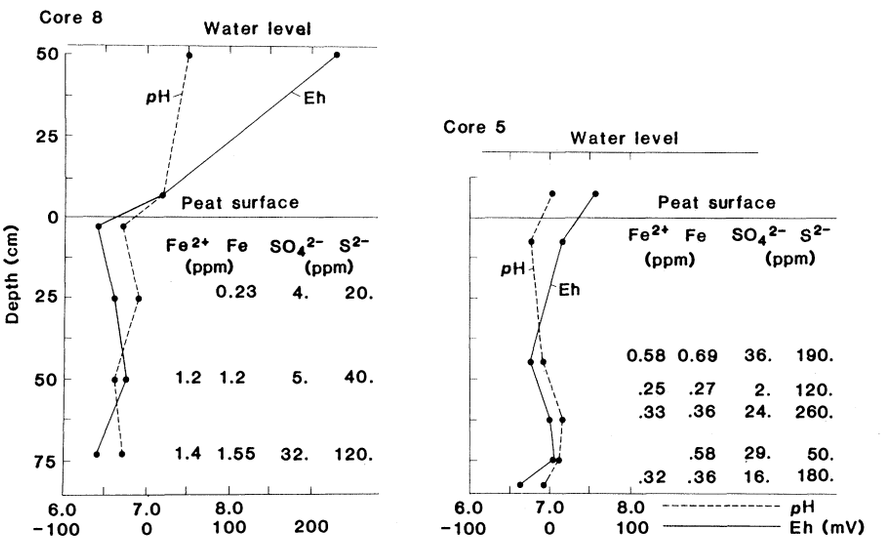

Fig. 2. Vertical distribution of Eh, *p*H, iron, and sulfur in the water column of the Everglades peat basin at the sites of cores 5 and 8.

Table 1. Distribution of iron, sulfur, and forms of sulfur in three cores taken along the profile of the Everglades freshwater peat basin shown in Fig. 1. Data are expressed as percentages by weight (moisture free) except those for FeS which are in parts per million.

Depth (cm)	Total iron	Sulfur					Reducible sulfur*	Carbon-bonded sulfide†	Reducible organic sulfur‡
		Total	in FeS	in SO_4	in FeS_2	Organic			
				Core 2					
0–5	0.7	0.84	10	0.25	0.04	0.55			
10–15	0.6	0.69	3	0.19	0.04	0.46			
20–25	0.5	0.82	0	0.12	0.02	0.68	0.39	0.43	0.25
31–36	0.9	0.71	6	0.08	0.03	0.60			
41–46	0.6	0.52	2	0.06	0.01	0.45	0.29	0.23	0.22
51–56	0.7	0.53	5	0.08	0.03	0.42			
61–66	0.6	0.56	8	0.12	0.05	0.39	0.30	0.26	0.13
71–76	0.5	0.65	8	0.17	0.08	0.40	0.33	0.32	0.08
81–86§	0.9	0.51	5	0.18	0.29	0.04	0.45	0.06	0.00 (−0.02)
Basal marl	1.0								
				Core 5					
0–5		0.86		0.26	0.01	0.59			
10–15		0.70		0.15	0.03	0.52			
41–46		0.76		0.07	0.02	0.67	0.35	0.41	0.26
51–56		0.72		0.08	0.03	0.61			
61–66		0.73		0.07	0.07	0.59	0.24	0.49	0.10
66–71		0.87		0.13	0.12	0.62	0.31	0.56	0.06
				Core 8					
0–4	1.2	0.84		0.27	0.02	0.55			
4–9	1.2	0.91	18	0.38	0.04	0.49			
14–19	1.1	0.85	12	0.23	0.03	0.59	0.41	0.44	0.15
24–29	1.4	1.08	19	0.24	0.08	0.76			
34–39	2.0	0.97	19	0.16	0.08	0.76			
45–50	2.1	0.99	22	0.11	0.08	0.80			
55–60	1.7	0.77	13	0.13	0.08	0.56	0.35	0.42	0.14
65–70	1.2	0.90	12	0.15	0.34	0.41	0.45	0.45	0.00 (−0.04)
Basal marl	2.0								

*Analysis by tin II–strong phosphoric acid leaching. †Reducible sulfur was subtracted from total sulfur. ‡Nonreducible organic sulfur was subtracted from organic sulfur; equivalent to "ester sulfur." §Corrected for 25 percent ash; ash in all other samples of core 2 is 1.0 to 2.5 percent, as received.

accumulation at the surface and hence in the duration of the period for concentrating aqueous sulfate by evapotranspiration and converting aqueous and adsorbed sulfate to organic sulfur.

The downward increase and pronounced basal development of pyrite, complemented by equivalent decreases in organic sulfur, found in all the cores show that organic sulfur is the source of pyritic sulfur on a regional scale in the Everglades. These trends also suggest that the generation of H_2S, which leads to pyrite formation by reaction with ferrous iron, is linked to bacterial mobilization of organic sulfur. This process may conceivably take one or both of two pathways: (i) indiscriminate release of all organic sulfur during anaerobic biodegradation that is not specifically linked to dissimilatory sulfate reduction and subsequent bacterial or inorganic reduction of the released oxidized sulfur species as part of the aqueous sulfate pool; and (ii) degradation of organic matter by the heterotrophic sulfur-reducing bacteria, which derive energy, nutrients, and sulfate from this same substrate and preferentially reduce organic sulfate molecules as terminal electron acceptors in dissimilatory respiration. This second pathway involves direct and specific utilization of the "ester" sulfate to produce sulfide.

Table 2. Sulfur and iron contents of composite samples of fresh saw grass at core site 4. Data are expressed as percentages by weight (moisture free).

Sample	Sulfur				Total iron
	Total	in SO_4	in FeS_2	Organic	
Leaves	0.058	0.012	0.0005	0.045	0.009
Basal leaf culm	0.049	0.012	0.0004	0.037	0.033
Rootstock	0.166	0.052	0.0004	0.114	0.042
Fine rootlets	0.072	0.017	0.001	0.054	0.15

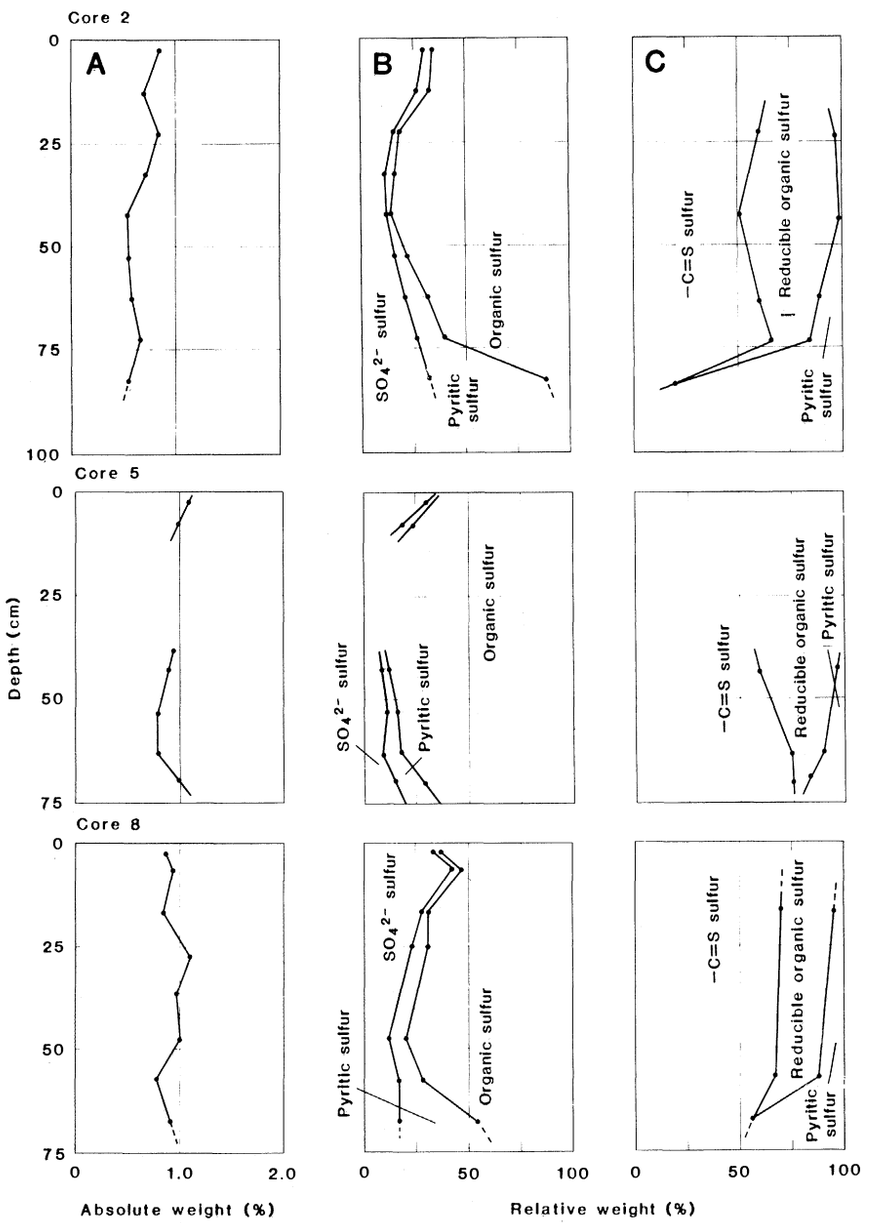

Fig. 3. Vertical distribution of (A) total sulfur and (B) its mineral and organic forms and (C) the relation of pyritic sulfur to forms of organic sulfur in Everglades peat, Tamiami Trail, core sites 2, 5, and 8.

Organic Sulfur Fractionation

There is independent and widespread evidence for a direct genetic relation between organic sulfur and pyrite. Framboidal pyrite, the dominant form of primary or early diagenetic pyrite in sediments, is most commonly bound in tissue. Framboids in plant cells, spores, protozoan tests, and animal fragments have been described as the principal form of pyrite in recent sediments and peats from a variety of environments (*31, 32*). Even loose pyrite framboids and euhedra are commonly derived from pyrite-impregnated tissue (*33*). The commonly tissue-bound state of framboidal or microglobular pyrite in coal has been repeatedly documented (*29, 34*). Figure 4 shows mangrove peat in which the vascular tissue is filled largely with framboidal pyrite.

This central fact of framboidal pyrite occurrence has had little comment in geochemical literature. Its implication is that pyrite formation in organic-rich sediment is commonly linked to H_2S formed within the organic tissues and, with our chemical data, suggests that the sulfide may derive largely from organic sulfur. The question was addressed by chemical study of the organic sulfur (*35*).

The nature of organically fixed sulfur in peat and soil is a subject of great complexity in view of the diversity of plant tissues, their undefined and transitory states of degradation, and the contributions of bacterial and fungal metabolic products. Plants and mircroorganisms fix sulfur as reduced carbon-bonded sulfide in the protein amino acids methionine, cystine, and cysteine and as sulfhydryl in glutathione; as sulfones and sulfoxides (intermediate oxidation states) in substituted amino acids and taurine; and as sulfate esters (fully oxidized) in polysaccharides, choline sul-

fate, and phenolic compounds (*24, 36–38*). Such compounds and their breakdown products may thus be expected in peats and organic-rich soils, and minor ester sulfate (*39*), cystine, cysteine, methionine, methionine sulfone, cysteic acid, and tribenzaldehyde have been recovered (*37, 40*). Nevertheless, most of the soil's organic sulfur is still uncharacterized, and soil researchers resort to broad analytical definitions of two major categories of organic sulfur compounds. One, the category of reduced sulfur, consists dominantly of carbon-bonded sulfide and sulfur radicals and is defined by Rainey nickel extraction (*41*). The second group, mainly oxysulfur radicals held in –C–O–S– or –N–O–S– linkages and thought to be mainly ester sulfate, is determined by the HI-reducible method (*42, 43*). Both carbon-bonded and ester sulfur are found to be appreciable in various soils (*43, 44*) and in peats (*7*) by these methods. However, the two methods are not completely complementary (*45*). Recent work has been based on the HI-reducible determination of ester sulfate and has defined carbon-bonded sulfur by difference from total organic sulfur.

The HI-reducible analysis is complicated by the low boiling point of hydriodic acid and the volatization of iodine. We therefore applied the tin II–strong phosphoric acid reagent, developed for quantitative reduction of insoluble sulfate, to the analysis of organic sulfur. Quantitative reduction and recovery by this reagent have been established for organic sulfate, for organosulfite (–C–SO_3–) in methyl orange, for sulfonyl (–C–SO_2–) in sulfur guanidine, and for disulfide (–C–S=S–C–) in cystine (*46*). It thus provides a clear distinction between fully carbon-bonded sulfide and all other, less reduced forms. As the HI-reducible and the tin II–strong phosphoric procedures also recover all mineral forms of sulfur (*43, 47*), these must be evaluated in the analyses (*48*).

Analyses for reducible sulfur were performed on cores 2, 5, and 8, at depths representing the upper (minimum pyrite) zone, the onset of pyrite increase, and the basal zone of maximum pyrite. The data and the calculated values for carbon-bonded sulfide and reducible organic sulfur, are given in Table 1 and plotted in Fig. 3C with pyritic sulfur, on a relative percentage basis, to normalize variations in total sulfur with depths. The notable trends are the slight but progressive decline in reducible organic sulfur as pyritic sulfur increases with depth and its pronounced decline and virtual disappearance in the basal zone where pyrite

Fig. 4. Scanning electron microscope photograph of mangrove rootlet peat with vascular columns unusually filled, distended, and ruptured by pyrite that is largely framboidal. Note loose crystallites and those impregnating inner wall of disrupted tissue from large broken framboid.

rapidly increases to maximum. Carbon-bonded sulfide may be relatively constant, or residually enriched, as its reducible organic sulfur counterpart declines, but in the basal zone it, too, is rapidly depleted after reducible organic sulfur is exhausted. These patterns parallel and explain the regional tendency of a pronounced increase of pyrite in the basal zone and the accompanying loss of organic sulfur.

Pyrite by Bacterial Reduction of Organic Sulfur

The preferential loss of reducible organic sulfur and its link to the production of pyrite must be due to its reduction in dissimilatory respiration by heterotrophic sulfur-reducing bacteria rather than to assimilatory reduction. In the latter, the reduced sulfur is utilized in protein synthesis without significant release of ambient sulfide (*49*). Although sulfate-reducing bacteria are reported to use only aqueous sulfate as a terminal electron acceptor in nature (*38*), they nevertheless are known to be facultative with respect to the presence of sulfur or its form, in vitro. *Desulfovibrio* sp. has been cultured on sulfate-free media with choline, and *Desulfotomaculum* sp. on sulfate-free pyruvate media (*50*). Moreover, *Desulfovibrio* is capable of cultured growth and sulfide production with sulfite, thiosulfate, and tetrathionate as terminal electron acceptors (*51*).

Desulfovibrio has been found throughout the peat column in cultured samples from core 8 (*52*). We propose that varieties of these or other sulfate reducers may be readily capable of dissimilatory respiration by reducing organic sulfate in their peat substrate in natural domains in which aqueous sulfate content is relatively low. In productive freshwater swamps initial sulfate is low, and biologic assimilation, as well as organic fixation, further limit the aqueous sulfate available for bacterial reduction. Although the procedure for determining oxidized sulfur also recovers carbon-bonded polysulfides, presumably only oxysulfur molecules are utilized in dis-

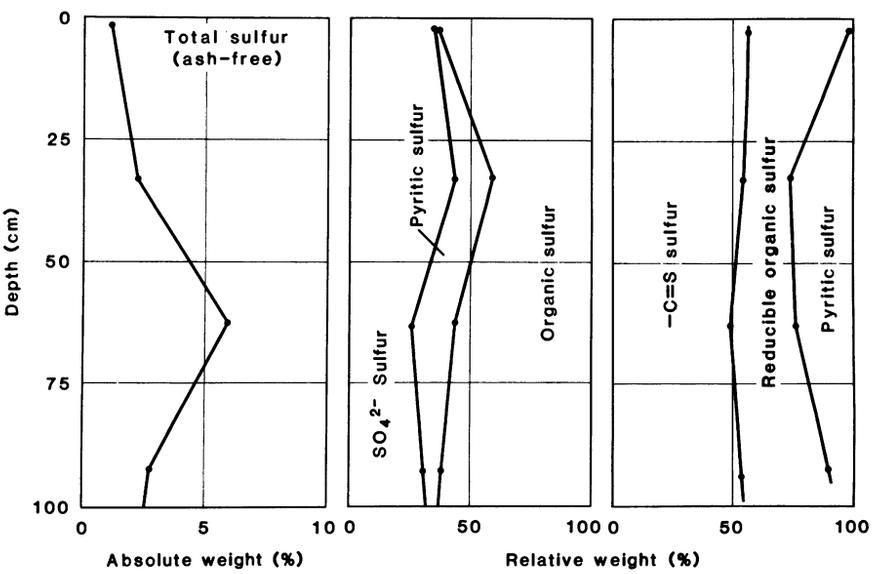

Fig. 5. Vertical distribution of total sulfur and its mineral and organic forms in mangrove peat, inner tidal zone, Harney River.

similatory respiration. However, with advanced peat degradation, at depth, carbon-bonded sulfide and polysulfides are released as HS^-, or possibly as mercaptan or dimethyl disulfide (*53*), which are further hydrolized and thus may also contribute to pyrite formation (Fig. 3C). Aqueous sulfate may also participate at all stages.

In some mangrove areas we find that appreciable pyrite formation begins close to the surface, reaches a maximum at relatively shallow depth (15 to 25 cm), and then declines rapidly. The content of reducible organic sulfur changes inversely to pyrite (Fig. 5). If the decline in reducible organic sulfur is due to bacterial hydrolysis linked to assimilatory use of sulfur (*54*) or to purely chemical hydrolysis, it should exhibit a pattern unrelated to pyrite and continue with depth. Thus, the reversal and increase of reducible organic sulfur, at a depth coincident with pyrite decrease, is further evidence that dissimilatory sulfate respiration is the major cause of ester sulfate decline and shows the importance of this process even in high sulfur peat and coal.

To determine whether pyrite forms directly or by alteration of preformed FeS in the freshwater Everglades peat, monosulfide sulfur (HCl-soluble S^{2-}) was determined in cores 2, 4, 6, and 8. Cores 2 and 8 (Table 1) display the maximum range in content. Monosulfide, as FeS, is present only in the low parts-per-million range. It is two to three orders of magnitude less than pyritic sulfur at all depths, and it displays neither the gradation with depth nor the relation to sulfate or pyrite that have been clearly shown in marine muds (*55*). Because of the insignificant amount of FeS, analyses for elemental sulfur were made only on core 4. Elemental sulfur (S^0) was not found at a 50-ppm limit of detection. Special determinations at two depths, an upper core portion and the level at which pyrite begins to increase, yielded only 0.0006 percent S^0 (*56*).

It appears that pyrite forms directly (*57*) in Everglades peat through the reduction of organic oxysulfur compounds in dissimilatory respiration, which generates HS^- or organic sulfides to react with ferrous iron in the degrading tissues. Although continuously forming and transforming intermediary FeS cannot be discounted, appreciable solid FeS is not detected. As the contents of total sulfur and the forms of sulfur in Everglades peat are like those in most low sulfur coal, the paragenesis of pyrite in the Everglades probably applies to the primary sulfur distribution of most low sulfur and continental coals, and to highly carbonaceous limnic sediments. In the saline, mangrove peats, where aqueous sulfate values approach that of seawater, we find FeS and S^0 contents of 0.001 to 0.005 percent. Thus both aqueous sulfate and reducible organic sulfur may be immediate sources of pyritic sulfur in high sulfur peats, and intermediary FeS formation may play an appreciable role.

Some elements of the sulfur cycle in large freshwater peat swamps and organic-rich waterlogged soils may be inferred from the regional tendencies in the Everglades: (i) organic fixation of aqueous sulfate in the upper peat zone, characterized by marginally oxidizing or reducing conditions and only incipient sulfide and pyrite formation; (ii) the beginning of preferential conversion of reducible organic sulfur to sulfide, and thus to pyrite, by sulfate-reducing bacteria, in the course of their use of organic matter, in the intermediate zone of consistently anaerobic environment; (iii) the pronounced or complete conversion of reducible organic sulfur to pyrite, with attendant conversion of some carbon-bonded sulfides, in the basal peat zone, where Eh values are lower and pyrite becomes more abundant; and (iv) thus the demineralization of inorganic sulfur to organic fixation at or near the surface and the progressive remineralization of organic sulfur to pyrite with depth. This paragenesis explains the tissue-bound association of framboidal pyrite. Its major implication for sulfur chemistry and sulfur-removal research in coal is that coal's organic sulfur diminishes as pyrite increases and consists increasingly of residual carbon-bonded sulfur rather than oxysulfur radicals. It also provides a specific link between organic matter diagenesis and dissimilatory respiration by sulfate-reducing bacteria and suggests a direction and limiting factors for modeling studies of this fundamental relation.

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57. This is opposed to conversion of a preexisting globule of FeS. The origin of framboids is obscure. Their architecture appears to demand crystallization of a prior gel or amorphous phase, as argued by Rickard (*12*), or a sequence from mackinawite to glubular greigite to pyrite, as noted by Sweeney and Kaplan (*14*). By urging direct fixation of pyrite in Everglades peat we do not preclude crystallization from amorphous or gel-like pyrite to form framboids. However, the presence of isolated, large octahedrons of pyrite, among the framboids, indicates some direct fixation of crystalline.
58. We thank R. A. Berner, E. C. T. Chao, M. Goldhaber, P. G. Hatcher, and J. R. Postgate for helpful comments, E. J. Dwornik for assistance in electron microscope observation, and D. Dwornik for photographic help.

The Chromosomal Basis of Human Neoplasia

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That certain chromosomal defects are consistently associated with some types of human cancer was established in the 1970's (*1*). Yet the frequency of these defects and the molecular mechanisms involved remained unknown. During the same decade, numerous data were collected on the structure and function of oncogenes of animal cancer viruses (*2*), but no definitive evidence of a viral origin of human neoplasia was presented (*3*).

In the last 2 years, the use of improved methods for culturing tumor cells and of high-banding techniques for studying human chromosomes has shown that chromosomal defects are present in most neoplasias (*4–7*). It has also been shown that active oncogenes occur in various types of human cancer and that they represent normal cellular genes of vertebrates (*8, 9*). Such genes, when taken up by certain viruses, can be used to induce neoplasia in experimental animals or to transform cells in culture (*3*).

The knowledge accumulated on chromosomal abnormalities and cellular oncogenes has just begun to merge. In Burkitt's lymphoma, for example, the human cellular oncogene *myc* (c-*myc*), normally located in chromosome 8, appears to become activated when rearranged with either the immunoglobulin heavy chain genes of chromosome 14 or the immunoglobulin light chain genes of chromosomes 2 and 22 (*9*). Such findings together suggest that chromosomal abnormalities play an important role in human malignancy and could represent, at the molecular level, mechanisms of altered oncogene activity.

Most Cancers Have a Chromosomal Defect

The malignant cells of most neoplasias show chromosomal abnormalities and in many the defects are consistent (*4–7*). The most common of the recurring defects is either a band deletion or a reciprocal translocation between two chromo-

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