

# Humate in Coastal Sands of Northwest Florida

By VERNON E. SWANSON and JAMES G. PALACAS

CONTRIBUTIONS TO GEOCHEMISTRY

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GEOLOGICAL SURVEY BULLETIN 1214-B

*The distribution and probable origin of  
water-soluble organic material in  
shallow subsurface sands of the  
Florida panhandle*



**UNITED STATES DEPARTMENT OF THE INTERIOR**

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#### ABSTRACT

Layers of dune and beach sand along the north coast of the Gulf of Mexico are cemented or impregnated with a conspicuous dark-brown to black water-soluble organic substance herein called humate. The humate-cemented sand, generally 6 inches to 3 feet thick but as much as 15 feet thick in some places, forms one or several irregular layers in the subsurface of broad land areas at a depth of a few inches to 35 feet. Humate accumulates in subsurface soil layers, in and beneath marsh deposits, in shore and beach sands of bayous and bays, commonly near the mouths of tea-colored streams and near ground-water seepages, and as a type of organic sediment in bodies of brackish or saline water.

The average ash-free composition of the humate is 55.00 percent carbon, 4.4 percent hydrogen, 38.5 percent oxygen, 1.4 percent nitrogen, and 0.7 percent sulfur, which closely resembles the composition of lignin, humic acids, dopplerite, and some peat and lignite deposits. Infrared spectra, amount of benzene-extractable hydrocarbons, and spectrographic analysis for contained metals confirm this similarity.

This northwest Florida humate is derived by leaching from decaying plant material, or humus, on the land surface; surface and subsurface waters transport the soluble and colloiddally dispersed humic substances to subsurface sand environments or to brackish or saline water bodies where flocculation or precipitation of humate is triggered by various physical-chemical mechanisms. Observations and experiments in the field and in the laboratory demonstrate some of the processes of humate formation, including flocculation or precipitation by adsorption of cations, complexing with clay colloids, and lowering of pH.

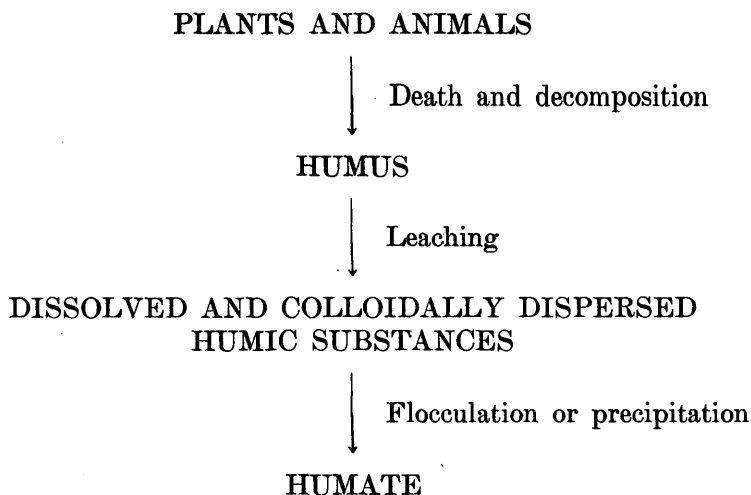
#### INTRODUCTION

A variable, but commonly large, fraction of decaying plant and animal material is removed and transported by natural waters, and is subsequently deposited to form humate. The origin, pattern of migration, deposition, and geochemical significance of humate are certainly complex and are not generally understood by geologists, though it is known that soluble organic matter composes a large part of many

soils (Waksman, 1936, p. 6); and, at least in a genetic sense, humate also may be an important constituent of coal (Hendricks, 1945, p. 11-14), black shales, and other carbonaceous sedimentary rocks (White, 1932, p. 367, 370).

A step toward learning more about the origin and chemistry of humate has been the investigation of "hasemanite" in the vicinity of Choctawhatchee Bay, Fla. This material was first reported and named by Haseman (1921, p. 75), though the continued use of the mineral-type name "hasemanite," as proposed in his paper, is unnecessary and inappropriate. Haseman (1921) titled his paper "The humic acid origin of asphalt," in the belief that the humate in Florida and elsewhere was the source material for petroleum. Similarly, Rae, in 1922 and 1923, pointed to humates as precursors of oil, as did Haseman in 1930. More recently, Corbett (1955) ascribed the origin of the asphalts of the Athabasca tar sands and the associated "McMurray oil" to humic acids and humates, and Cate (1960) suggested that the water-soluble organic materials in soils are transformed into oil (also see review by Hedberg, 1964, p. 1762-1763, 1770, and 1776-1777). Humate, however, as it now occurs in the coastal sediments of northern Florida, is genetically and chemically in the class of coal, and probably only under extremely rare and very local conditions of natural hydrogenation or pyrolysis are humates chemically altered to form fluid, gaseous, or solid hydrocarbons.

The terminology and genetic sequence involved in the formation of humate are shown below:



As used here, "humus" refers to the accumulation of plant and animal residues in an early stage of microbial and chemical decomposition found at or within several inches of the land surface, or that

complex mass of particulate organic matter being similarly decomposed and accumulating at the bottom of a body of water. Humus normally is not thought to include skeletal material such as  $\text{SiO}_2$  or  $\text{CaCO}_3$ .

Soluble and colloiddally dispersed humic substances are derived from humus on leaching by natural water, and are generally observed as the tea-colored water of many streams, lakes, bogs, swamps, bayous, and some subsurface water. This water-carried organic material, hereafter simply referred to as soluble humic substances, has been termed "water humus" by Waksman (1936, p. 304), "soluble humus" and "water humus" by Swain (1963, p. 89, 130), and "humic acids" by many authors. Further, the fractions of soluble humic substances, which are separated by some chemists and soil scientists, such as fulvic acids, crenic and apocrenic acids, hymatomelanic acids, tannins, carbohydrates, proteins and lignins, all of which may be present in the Florida organic material, are not used in this report. As adapted to use in geology and geochemistry, the term "soluble humic substances" includes all natural water extracts of peat, soil, and, particularly where undergoing weathering, coal.

"Humate" is here used as a collective term for the group of gel-like solid humic substances in sediments, coal-like in composition and appearance, that were carried in colloidal suspension or true solution by natural waters, and that were flocculated or precipitated from these waters on entering a different chemical environment. Humate is dark brown to black and is semilustrous. It generally appears as a structureless matrix filling voids and coating grains of a sediment; as such, humate may be confused with some hydrocarbons or asphaltites that fill interstices of a rock, but humate lacks the odor, viscosity, and other characteristics of oil and has distinctly different chemical composition and solubility characteristics.

In summary, humate is the product of natural flocculation or precipitation of those soluble humic substances in water that were derived by natural leaching of decaying plant and animal material, or humus. An obvious step in enhancing the genetic and environmental significance of these terms is to be able to refer to terrigenous humus and humate and to marine humus and humate. Terrigenous humate in the coastal sands of northwestern Florida is the subject of this paper.

#### FIELDWORK AND ACKNOWLEDGMENTS

The humate occurrences on Choctawhatchee Bay (fig. 1) were first examined by Swanson in 1958, in the company of and with the indispensable cooperation of Dr. L. C. Sharman of Tuscaloosa, Ala., who found the first locality that was studied and sampled and who subsequently contributed many valuable suggestions on the genesis of the

material. Many other outcrops of the humate and several water-well sites were studied in 1962 and, with Palacas, briefly in 1964.

The humate described by Haseman (1921) is the cementing material in one or several layers of sand that forms a brown (dry) to black (wet) hardpan that is generally a few inches to a few feet thick at or near the surface of beach sand. The "type locality" of this humate, the place where Haseman presumably quarried and extracted the humate for use as a stain for wood, paper pulp, and paints, is on the northeastward-trending shore of the northwestern part of Choctawhatchee Bay, Fla., about 1.8 miles east of Shalimar, due east of the center of sec. 4, T. 2 S., R. 23 W. (Fort Walton Beach quad. map, U.S. Geol. Survey, 1956, 1:62,500). Here the humate-cemented sand is clearly associated with ground-water seeps and is strikingly similar in appearance to the asphaltic sands of many oil seeps.

Reconnaissance along 150 miles of the coastal area of the Gulf of Mexico, from Pensacola to Apalachicola, Fla., resulted in locating and studying some 40 exposures of humate-cemented or humate-impregnated beach and dune sands (fig. 1). Subsurface samples of the humate-cemented sand were also collected from four water wells being drilled near the west end of Choctawhatchee Bay; the cooperation of the Echols Drilling Co. of Fort Walton Beach, Fla., in collecting these samples is much appreciated and is hereby acknowledged.

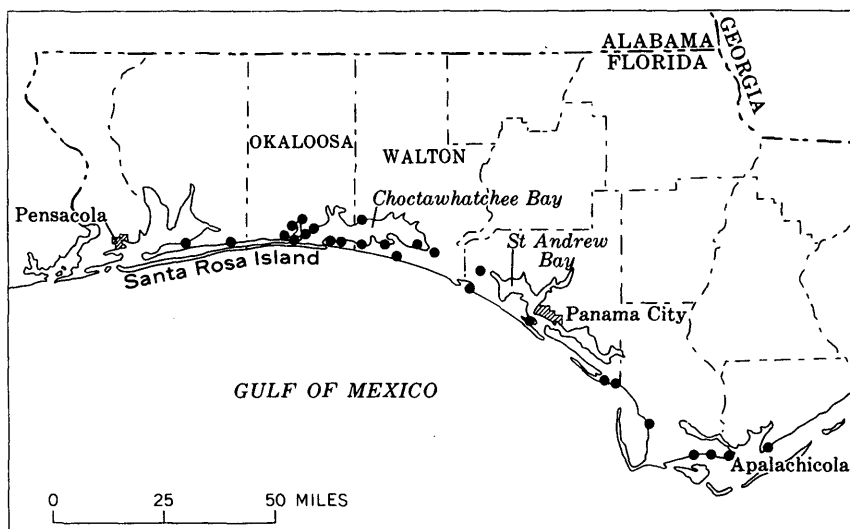


FIGURE 1.—Localities of humate-cemented beach and dune sands near the coast of the Gulf of Mexico, panhandle of Florida. Some dots represent several localities studied; four of the dots near the western end of Choctawhatchee Bay indicate locations of four water wells from which humate-cemented sand samples were collected.



For those interested, the locations of many key or representative exposures and wells are described in the body of the report, and the name, publication date, and scale of the appropriate Geological Survey topographic quadrangle map are included.

#### VARIETIES OF HUMATE-CEMENTED SAND

At least seven varieties of humate-impregnated and humate-cemented sand can be arbitrarily differentiated in this area:

1. Black, firmly cemented and relatively resistant, irregularly shaped and distributed asphaltlike masses of humate-cemented sand that is associated with ground-water seeps; observed at several places on the shores of Choctawhatchee Bay and near streams entering the Gulf of Mexico. This humate appears to be relatively recent in age but may be as old as late Pleistocene. (See fig. 2.)

Representative localities: (a) "type locality" of hasemanite (Haseman, 1921), locally known as the old dye-plant quarry (p. B4); (b) about 3 miles northeast of Destin on the south shore of Choctawhatchee Bay, about 150 yards west of Indian Bayou (Villa Tasso quad., 1956, 1:62,500). At both localities, long



FIGURE 2.—Blocks of resistant black humate-cemented sand at the edge of Choctawhatchee Bay; these blocks are eroding from irregularly shaped asphaltlike masses associated with ground-water seeps near the edge of the bay.

sinuous masses of black humate-cemented sand, 2–6 inches in diameter and as much as 10 feet long, can be observed that suggest humate precipitation around and replacing tree roots.

2. Dark-brown to black, partly cemented or loose impregnated beach sand, 1–3 feet thick, located a few to several inches below the surface of the beach, generally in the vicinity of the mouths of small streams; observed at many localities on the shore of Choctawhatchee Bay and east of Pensacola on the shores of Pensacola Bay and Santa Rosa Sound. This humate appears to be very recent and some may be accumulating today; in some places this humate may be as old as late Pleistocene. (See fig. 3.)

Representative localities: (a) 2.2 miles east of the Okaloosa-Walton County line on the south shore of Choctawhatchee Bay where a single-lane road terminates at the beach; NW $\frac{1}{4}$  sec. 28, T. 2 S., R 21 W. (Villa Tasso quad., 1956, 1:62,500); (b) about 2 miles northeast of Destin on the south shore of Choctawhatchee Bay, 0.7 mile southeast of Cobbs Point (Villa Tasso quad., 1956, 1:62,500).

3. Dark-brown or black, commonly poorly cemented sandy layer of irregular thickness, generally only a few inches thick, lying



FIGURE 3.—Dark-brown to black humate in beach sand about 3 feet from water's edge on south shore of Choctawhatchee Bay and about 10 feet from mouth of small stream.

directly beneath or a few inches beneath soil, marsh deposits; and other areas of dense vegetation; layer is at or near the water table; roots or root casts common; observed in several roadcuts and artificial drainage channels in Choctawhatchee Bay area. This humate is in some places very similar to the hardpan or ortstein described and reviewed by Waksman (1936, p. 391-392). The humate is very recent and is currently accumulating.

Representative locality: about 4 miles east-northeast of Santa Rosa Post Office (on U.S. Highway 98), on banks of U.S. Highway 330 causeway over east part of Choctawhatchee Bay, about 200 yards south of Intracoastal Waterway bridge; center sec. 20, T. 2 S., R. 19 W. (Point Washington quad., 1947, 1:62,500).

4. Generally medium- to dark-brown firmly cemented sand in a layer as much as 3 feet thick, commonly exposed as a ledge or "pavement" along shores of Choctawhatchee Bay, Apalachicola Bay, Pensacola Bay, and Santa Rosa Sound, and seen as numerous black to dark-brown rounded blocks, as much as 2 feet across, scattered along the beach and in the nearshore shallow water; contains some decomposed roots and root casts and at several localities is associated with but vertically separated from old peat beds containing tree stumps. This variety of humate is of questionable late Pleistocene or Recent age. According to Harper (1910, p. 294-297), a stratum of peatlike substance, probably the humate, was noted as long ago as 1827, and it may be an ancient swamp deposit that extended from Apalachicola Bay west to Mobile Bay in Alabama and that formed when sea level was a few feet higher than at present. (See fig. 4.)

Representative localities: (a) about 40 yards east of locality (a) described under second variety of humate; (b) 2.9 miles east of the Okaloosa-Walton County line on the north shore of Choctawhatchee Bay, NE $\frac{1}{4}$  sec. 28, T. 1 S., R. 21 W. (Villa Tasso quad., 1956, 1:62,500); (c) about 20 airline miles east of Pensacola on the north shore of Santa Rosa Sound, about 100 yards due south of the intersection of U.S. Highway 98 and Florida Highway 87, SE $\frac{1}{4}$  sec. 20, T. 2 S., R. 26 W. (Holley quad., 1936, 1:62,500); (d) about 4 airline miles west-southwest of Panama City, 0.4 mile west of the intersection of Florida Highways 392 and 392A, along a small stream on the east side of the road that terminates at the north edge of Grand Lagoon, SE $\frac{1}{4}$  sec. 9, T. 4 S., R. 15 W. (Panama City Beach quad., 1955, 1:24,000); (e) on shore of Apalachicola Bay, in Apalachicola, 1.7 miles east of intersection of U.S. Highway 98 and Apalachicola Airport Road, NW $\frac{1}{4}$  sec. 12, T. 9 S., R. 8 W. (Apalachicola quad., 1943, 1:24,000).



FIGURE 4.—Blocks of brown humate-cemented sand eroding from an old layer exposed on the south shore of Choctawhatchee Bay. Note decomposed roots and plant fragments on the upper surface of the blocks; these are scarce or absent in the lower 6 inches of the blocks.

5. Tan to dark-brown to black, generally crossbedded ancient dune sand, which is slightly to firmly cemented with humate; it is commonly exposed in 10- to 20-foot bluffs along the shoreline of Choctawhatchee Bay, and along some stream channels and in 25- to 40-foot banks of the Intracoastal Waterway between Choctawhatchee and St. Andrew Bay; the distribution and amount of humate in the sand apparently were controlled in part by variable permeability between and within crossbeds. This is an accumulation of old humate, of questionable late Pleistocene or Recent age. (See fig. 5.)

Representative localities: (a) exposure in a bank for about 200 yards on the south shore of Choctawhatchee Bay, same as locality (b) described under the first variety of humate; (b) exposure that extends about 0.5 mile in the banks of the Intracoastal Waterway, Walton County, about 2 miles east of Choctawhatchee Bay; it is reached by walking 0.3 mile north-northeast of U.S. Highway 98 along a small road 300 yards east of Destin Fire Tower; NE $\frac{1}{4}$  sec. 6, T. 3 S., R. 18 W. (Point Washington quad., 1947, 1:62,500).

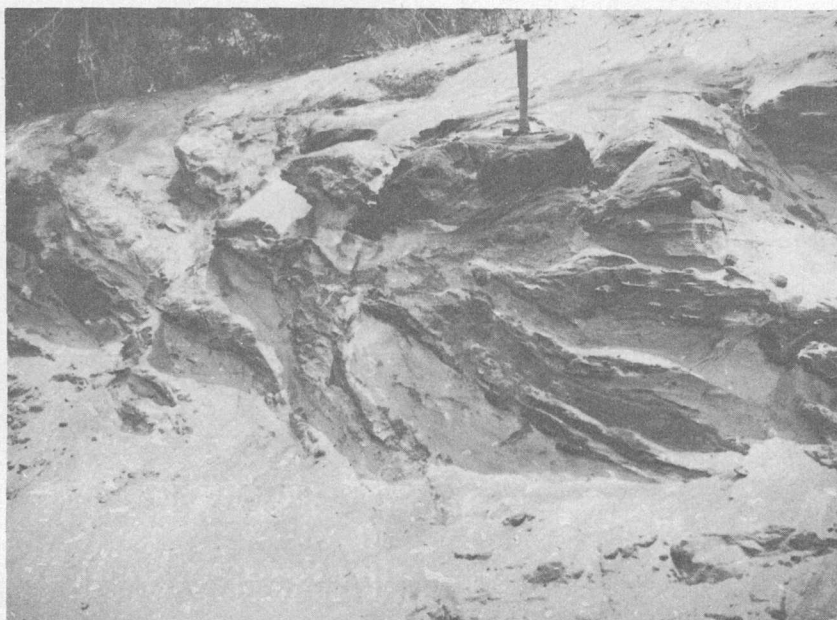


FIGURE 5.—The bluff of an old humate-cemented dune sand on south shore of Choctawhatchee Bay. The white sand is colored with humate and ranges from light tan to very dark brown; the distribution of the humate is apparently controlled by variable permeability of the dune strata.

6. Very dark brown to black humate-cemented sand is found in the subsurface at depths of a few feet to 30 feet, the "hardpan" of local water-well drillers; it is generally confined to one layer or zone, but two or three layers of the hardpan were penetrated locally; these are probably similar to those layers observed in the banks of the Intracoastal Waterway (loc. *b*, in the fifth variety of humate). According to local drillers of shallow water wells, hardpan was penetrated in about 75 percent of the wells drilled in the Choctawhatchee Bay area; and, according to Harper (1910, p. 225, 294–295), Sellards and Gunter (1910, fig. 1, p. 96), Martens (1928, p. 46, 73), and Davis (1943, p. 128), a similar hardpan is common at shallow depths in many other areas of Florida. The humate in the hardpan may be of very recent age and may be accumulating today, though, where more than one hardpan layer is present, some layers may be old humate accumulations of questionable late Pleistocene or Recent age.

Representative locality: shallow water well for house, 10 Guilder St., Fort Walton Beach, at a depth of 17 feet; NE $\frac{1}{4}$  sec. 14, T. 2 S., R. 24 W. (Fort Walton Beach quad., 1956, 1:62,500).



7. Very dark brown to black, generally fine grained humate-containing sediment accumulates in the quieter waters of bays, bayous, and lakes; the humate is disseminated in sediment because of simultaneous deposition of clay, silt, sand, and particulate organic matter; it is observed in series of bottom-sediment cores in bayous and in deeper parts of Choctawhatchee Bay and nearby lakes. The humate is accumulating today. This occurrence of humate is being investigated in a study of the distribution and types of organic matter in cored sediments in and near Choctawhatchee Bay.

Two or more of the previously described varieties of humate concentration are found at several other localities, for example: (a) about 8 miles west of Apalachicola and 0.25 mile west of the intersection of U.S. Highway 98 and Florida Highway 30; this intersection is reached by taking a small road 650 feet south to St. Vincent Sound; exposures are in the bank and on the beach of the sound, 750 feet eastward (note oyster and *Pecten*-type shells completely replaced by humate); SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 10, T. 9 S., R. 9 W. (West Pass quad., 1943, 1:24,000); (b) about 1 mile north of Port St. Joe in the south bank of the Gulf Coast Canal on the east side of the bridge on U.S. Highway 98 (Port St. Joe quad., 1943, 1:24,000); (c) about 23 airline miles southeast of Panama City and 1.2 miles northwest of the intersection of U.S. Highway 98 and Florida Highway 386 in Beacon Hill; the exposure is in the south bank of a small creek 50 feet southwest of the bridge on U.S. Highway 98 (note sawed boards projecting from humate-cemented sand; NW $\frac{1}{4}$  sec. 25, T. 6 S., R. 12 W. (Beacon Hill quad., 1956, 1:24,000); (d) about 12 airline miles east of Pensacola on the south shore of Pensacola Bay, SW $\frac{1}{4}$  sec. 24, T. 2 S., R. 28 W. (Pensacola quad., 1941, 1:62,500). Several of the varieties of humate, particularly varieties 4-6, are closely related genetically and chronologically at a single locality. However, the correlation of humate deposits from area to area and the relation of the deposits to late Pleistocene and Recent terraces and eustatic changes in sea level, particularly to the Pamlico and Silver Bluff shorelines (MacNeil, 1950), must be based on future detailed stratigraphic studies supplemented by many carbon-14 age determinations.

Once the several varieties of humate and the criteria favorable for humate accumulation are known, the finding of humate concentrations is relatively simple. The recognition of humate layers is also simplified along this part of the coast of the Gulf of Mexico because the dark-brown to black humate-rich layers are in distinct contrast to the

strikingly white quartz sand that is characteristic of the beaches and the dunes.

The humate concentrated in the sand layers is probably far more abundant and widespread than determined in this investigation, which was based largely on locating outcrops in areas of generally low relief. However, as indicated by the localities studied, it is estimated that 100,000–1,000,000 tons of humate are present per square mile at a depth of less than 35 feet, over an area of 300–500 square miles along the northern coast of the Gulf of Mexico. Thus, there may be on the order of 100 million tons of humate in this area.

#### PROCESSES LEADING TO HUMATE CONCENTRATION

The precursors of humate and the likely processes leading to humate concentration can be observed and deduced in the field. In this area of humid subtropical climate and of relatively dense vegetation, plant matter that falls on the land surface of the porous sandy soil is rapidly oxidized and decomposed by organisms (Breger, 1951, p. 205; Waksman, 1936, p. 257) to form humus. Rain, which is chemically affected by combination with the mist of sea water which is common to coast-line areas where the surf is very active (Gorham, 1955 p. 232; 1961, p. 805–807; Wilson, 1959), falls on this decaying plant matter, readily leaches out the soluble organic material, and rapidly soaks through the sandy soil to become ground water. The organic material will be transported in solution until a physical-chemical change takes place in the water, whereupon this material is precipitated or flocculated to form a humate deposit.

Many variations in the previously described sequence can be noted. For example, much of the water charged with soluble organic material accumulates in marshes, ponds, or lakes, and humate may be deposited on their bottoms or in underlying sands. Some of the tea-colored water is transported by streams into bayous and bays, and some fraction is eventually carried into the Gulf of Mexico. Part of the soluble organic matter is probably destroyed by oxidation, bacterial degradation (Waksman and Carey, 1935), or is biologically consumed (Saunders, 1957), but some is undoubtedly deposited in each environment as an integral part of peat or of the disseminated organic material in a clay, silt, or sand sediment.

Four basic steps in the geochemical sequence of humate formation in nature are postulated as follows:

1. Removal of the water-soluble fraction from humus by natural waters—generally rainwater and near-surface ground water; the more alkaline the water, the greater the amount of organic matter taken into solution.

2. Transportation of the soluble humic material in natural surface and subsurface waters over distances ranging from a fraction of an inch, as into a lower soil or peat horizon, to many miles as illustrated by the transportation of tea-colored water from its source into rivers, bayous, bays, and ultimately into the oceans.
3. Deposition of humate by precipitation or flocculation from these natural waters where they find a different physical-chemical environment, by one or probably a combination of the following mechanisms: (a) the adsorption or complexing of dissolved cations such as  $\text{Al}^{+++}$ ,  $\text{Fe}^{+++}$ , and  $\text{Mg}^{++}$ ; (b) complexing with clay colloids; and (c) a lowering of pH.
4. Redissolving, continued transportation, and redeposition of humate by repetition of cycle previously indicated.

### LABORATORY EXPERIMENTS

In order to verify and understand the several steps in the natural sequence of events leading to deposition of the humate observed in the field, the probable processes involved were duplicated in the laboratory using natural waters and dilute chemical solutions that generally simulate those found in nature. In addition, many samples of humate from the Choctawhatchee Bay area were analyzed and characterized chemically. The combination of these laboratory data and field observations also might help us to understand the distribution of carbonaceous material in ancient sediments deposited in coastal environments similar to the present Choctawhatchee Bay area.

### LEACHING OF SOIL

In general, the humus content of the soil along this part of the Florida coast is very low, even in areas of dense vegetation. The soil is sandy, very porous, and apparently well aerated throughout, and the humid subtropical climate undoubtedly favors oxidation and accelerated microbial decomposition of the plant matter. The soil consists only of a very thin decaying leaf and grass mat, commonly less than an inch thick, underlain by a light-brown sand zone a few inches to a foot thick which contains roots and some black to brown decaying woody plant fragments. Beneath this soil is light-gray to yellowish loose sand.

A core sample of soil was taken about 50 feet from the south shore of Choctawhatchee Bay in a flat area of fairly dense growth of saw-palmetto and liveoak (for description of vegetation in areas near the Florida coast see Kurz, 1942). By means of a separatory funnel having a glass-wool plug at the base, 100 g of this light-brown sandy soil, which was 0.7 foot thick, was leached for 6 days with 200 ml of distilled water having a pH of 6.0. The water that leached through



was light yellow and similar in appearance to some natural water collected from streams and lakes in the area. On addition of a small amount of a very dilute  $\text{FeCl}_3$  solution to the filtered water, conspicuous flocculation of a small amount of brown humate took place.

The same sample that had been leached with distilled water was similarly leached with 200 ml of distilled water containing a small amount of  $\text{NaHCO}_3$ , the solution having a pH of 8.3; a much darker more brownish water resulted. This indicated that rain or natural surface water that might be similarly made slightly alkaline in an area near marine water would leach even more of the soluble organic material from the soil. A brown gelatinous humate also flocculated readily from this solution upon addition of dilute  $\text{FeCl}_3$ .

### SOLUBILITY OF HUMATE

One of the unique and more intriguing aspects of the northwest Florida humate is its demonstrable mobility. Humate can be observed in the process of being deposited or of being redissolved at many places in the field, and the process can be crudely duplicated in the laboratory. It is the ease and the completeness of removal of the organic matter from the sediment by weakly alkaline to near neutral waters, only to be transported and deposited elsewhere, that suggest specific explanations for the ubiquitous distribution of organic matter as carbonaceous films, roll structures, and the like in some ancient sedimentary rocks.

The dissolution or remobilization of the humate in the Florida sands apparently takes place during ordinary physical-chemical changes in its hydrologic environment. These changes, such as an increase in pH of surface or subsurface waters or a change from brackish water to fresh water, are, in a geologic sense, common and rapid in this coastal area, which is characterized today by dynamic erosional and depositional processes and in recent geologic time by the effects of many eustatic changes in sea level (Cooke, 1945, p. 12; MacNeil, 1950).

The conditions under which humate eventually becomes immobilized or insoluble in subsurface water have not been investigated, but very probably dehydration, time, increasing depth of burial, compaction, and other diagenetic processes make the humate immune to further attack and redistribution.

To our knowledge, little study has been made of the solubility characteristics of humate in sediments under natural conditions. The method used in most laboratory studies of the water-soluble organic fractions in soils and peats is to extract humic acids with an alkaline solution such as 0.1 *N* NaOH, 2 percent NaOH, 2-8 percent  $\text{NH}_4\text{OH}$ , or 10 percent KOH, and then to precipitate the extract by addition of an acid solution such as 0.1 *N*  $\text{H}_2\text{SO}_4$  or 5 percent HCl (for ex-

ample, Waksman, 1936, p. 68; Kononova, 1961, p. 350). Methods used in studies of "regenerated humic acids" in coals and black shales involve oxidation, commonly with  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$ , and then extraction with alkaline solutions and precipitation with acids (for example, Francis, 1954, p. 428; Kinney and Schwartz, 1957, p. 1125). Though useful in fractionating and chemically characterizing naturally occurring organic materials, the strong solutions employed are extremely rare or absent in nature, and the resulting extracts, from the geologists' viewpoint, can only be considered as artifacts.

The solubility of humate can be observed in many ways in the field. For example, while collecting samples of humate-cemented sand, one's hands generally become dirty and stained a dark brown. Attempts to wash off the stain in the brackish water of the bay are fruitless, but washing in the water of a nearby fresh-water stream successfully removes the stain. Even more significant and interesting is to dig a hole into humate-cemented beach sand, which, if near the mouth of a fresh-water stream, will rapidly fill with fresh water. The fresh water dissolves or disperses some of the humate to become a very dark brown, strong coffee-colored fluid (fig. 6). If this coffee-colored



FIGURE 6.—A hole dug in the beach sand on the south shore of Choctawhatchee Bay, which rapidly filled with very dark brown, partly dissolved humate that was then swept out into the brackish water of the bay and flocculated.

water is poured into the bay, or if it washes into the bay, the humate almost immediately flocculates, or precipitates, and most, if not all, of the organic matter in the water is deposited. If the bay water along shore is relatively still, the flocculated humate slowly settles and is concentrated in the troughs of ripple marks on the bottom sand (fig. 7).

Several tests in the laboratory can display to the geologist some of the solubility characteristics of humate. Thus, humate placed in distilled water does not noticeably color the water; similarly, humate placed in Denver, Colo., tap water, which has a pH of about 5, results in only a very slightly straw-colored solution; and humate placed in other waters made very slightly acid to pH 4-6 by addition of HCl or  $\text{H}_2\text{SO}_4$ , a pH which is not uncommon in natural waters, results in extremely little or apparently no dissolution.

On the other hand, humate placed in water that is slightly alkaline rapidly dissolves, and the water becomes a dark brown, the color of very strong clear coffee. These slightly alkaline solutions can be made with reagents such as  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ , or  $\text{NH}_4\text{OH}$ , one or more of which may be present in natural slightly alkaline waters at



FIGURE 7.—Humate flocculating in shallow brackish water near the south shore of Choctawhatchee Bay. Note how the humate (dark) is concentrated in troughs of ripple marks. Crests of ripple marks are 3-5 inches apart, water is about 1 foot deep. Humate-laden water is from the hole shown in figure 6.

pH 7.5-9. Of course, the more alkaline the laboratory solution, the more rapid the dissolution of the humate; thus, a fragment of black humate-cemented sand rapidly disintegrates to loose white sand in, for example, a 0.1 *N* NaOH solution. The same result, however, has been obtained in several laboratory experiments using water made only very slightly alkaline to pH 8.3 by addition of  $\text{NaHCO}_3$ , and to pH 8.5 by addition of  $\text{Na}_2\text{CO}_3$ . The only difference between using a weakly alkaline solution and using a strongly alkaline solution is that more of the weakly alkaline water must be passed through the same material during a longer period of time in order to dissolve the humate completely.

It should also be noted that the organic matter in many of the humate-impregnated sands is largely, if not entirely, humate; particulate fragments of organic matter such as wood or root fragments are rare. The dark brown to black sand leached with slightly alkaline water is left completely white except for a few scattered detrital grains of magnetite and ilmenite, and analyses indicate that 95 percent or more of the organic matter is removed by leaching.

#### FLOCCULATION AND PRECIPITATION OF HUMATE

Preliminary laboratory tests show that humate can be readily flocculated or precipitated from slightly alkaline water containing redissolved humate and from natural tea-colored fresh water by the addition of dilute solutions of  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{BaCl}_2$ , and  $\text{KCl}$  solutions. Iron, magnesium, aluminum, calcium, barium, and potassium are elements present in solution in sea water (Sverdrup, Johnson, and Fleming, 1942, p. 176), and, as shown by some 15 spectrochemical analyses of humate and humate-containing sediment, one or several of these elements is present in sufficient amount to indicate ions responsible for humate flocculations. Aluminum, iron, and magnesium very likely are the elements that are primarily responsible for the flocculation of most of the humates in this coastal area of Florida, either in bodies of saline or brackish water or in the subsurface sands on land.

Samples of filtered Oyster Lake water and Gulf of Mexico water were mixed in the laboratory in proportions of 1:1, 1:2, 1:5, and 1:10. Oyster Lake is a few hundred feet from the Gulf of Mexico and about 10 miles east of the Walton-Okaloosa County line, SW $\frac{1}{4}$  sec. 3, T. 3. S., R. 20 W. (Point Washington quad., 1947, 1:62,500). The small stream that discharges Oyster Lake water into the Gulf of Mexico enters the pounding surf of the gulf and the dark water is so rapidly disseminated that no flocculation could be observed in the field. At the time of mixing of the waters in the laboratory, no flocculation was

observed, nor was there any apparent flocculation after the covered tubes were allowed to set for 10 days, so the experiment was set aside with the premature conclusion that no flocculation would occur. However, at some time between 10 days and 65 days after mixing, very obvious flocculation had occurred, and the amount of flocculate at the bottom of each of the glass tubes apparently was proportionate to the amount of Oyster Lake water in the mixture. No flocculation or precipitation was observed in reference tubes of "pure" Oyster Lake water or Gulf of Mexico water, which suggests that microbial action was not the cause of flocculation. Once again the factor of time was shown to be of great importance in understanding natural phenomena, particularly in geologic studies, but it is this factor of time which is so commonly ignored or underestimated in laboratory experiments designed to duplicate these natural phenomena.

Laboratory tests also have been made to observe the flocculation or precipitation of Florida humate from slightly alkaline water containing redissolved humate and from tea-colored stream waters by addition of acidic solutions. The pH of the waters was carefully lowered by the addition of dilute HCl or H<sub>2</sub>SO<sub>4</sub>, for example from pH 8.3 to 4.5 (the general range of pH of natural waters in sedimentary environments is pH 9-3; see Baas Becking and others, 1960, fig. 31). At a pH of about 5.5, slight flocculation can be observed, and at a pH of about 4.5, massive flocculation takes place, which is almost a "flash" reaction.

As indicated by the beautifully preserved "fossil" shells in the black humate-cemented sand on the beach of St. Vincent Sound (loc. a, p. B10), acid waters completely dissolved the calcareous oyster and *Pecten*-type shells and humate was subsequently deposited in the resulting voids. However, shells buried in brown humate-cemented sand at a few other localities have not been appreciably altered, which suggests that the humate-depositing waters were not acidic enough to dissolve CaCO<sub>3</sub>.

The amount of humate deposited in this coastal environment as a result of lowering of pH is not known. A few random determinations of the pH of water in sediments where humate has been deposited or is accumulating indicate an acid environment of pH 4-6. The fact, though, that some pH measurements of coffee-colored stream and lake waters are also slightly acid is puzzling, and the natural flocculation or precipitation of humate solely by pH changes is still not clear. Possibly the pH of waters below the surface of marsh areas and in the intermittently stagnant bottom waters of some lakes and bayous is in the 3-4.5 range and may account for humate deposition.

**CHEMICAL DETERMINATIONS**

To those familiar with carbonaceous rocks, the humate-cemented sand in Florida would appear to contain 15–25 percent organic matter. This estimated content might be expected because the sand is black where wet, and, in places, resembles solid blocks of asphalt. However, on close observation with a hand lens or under a microscope, the black sand is seen to be really a quartz sand whose grains are stained or coated with dark-brown organic matter—humate—that composes only a small percentage of the total sediment.

**TOTAL ORGANIC CARBON IN HUMATE-CEMENTED SAND**

The organic carbon content of the humate-cemented sand, as determined from analyses of 10 samples of several varieties, ranges from 0.57 to 5.42 percent (table 1). The organic carbon content can be crudely estimated on the basis of color, the blackest sand containing the most organic carbon. As also shown in table 1, mineral, or carbonate, carbon is negligible in these coastal sands, generally less than 0.05 percent. This indicates that carbonate minerals such as calcite are scarce or absent.

The total organic matter of the humate-cemented sands has been calculated to range from slightly less than 1 to above 8 percent (table 1). This is based on ultimate analyses of the humate, which are discussed in the following section, and on the organic carbon determinations. In comparison with some organic-rich rocks, this range is seemingly low, but it should be recalled that this organic matter consists almost completely of water-soluble organic material, or humate. Peat deposits and the black organic-rich bottom sediments from the marshes, lakes, and bays in this part of Florida, which contain abundant particulate plant matter and variable amounts of humate, contain much more total organic matter but are excluded from consideration in this paper.

**ULTIMATE ANALYSES OF EXTRACTED HUMATE**

The average composition of the humate currently being deposited in and near Choctawhatchee Bay, on a moisture- and ash-free basis, is 55.0 percent carbon, 4.4 percent hydrogen, 38.5 percent oxygen, 1.4 percent nitrogen, and 0.7 percent sulfur. This average is based on three ultimate (elemental) analyses (table 2) of two varieties of humate; samples S62-5B1 and S62-5B2, which are chemically separated humates and whose analyses were averaged, represent one variety currently accumulating in beach sand on the south shore of Choctawhatchee Bay, and sample S62-38A represents humate deposited from stream water.

TABLE 1.—Organic carbon, mineral carbon, and calculated organic-matter content of 10 samples of humate-cemented sand from near the Gulf of Mexico coast of the Florida panhandle

[Humate composes an estimated 95-99 percent of organic matter. Classification of varieties of humate given in a previous part of this paper. Organic and mineral carbon analyses by I. C. Frost; total organic matter calculated from organic carbon content using conversion factor of 1.66, based on ultimate analyses of S62-33 and S62-5 samples (table 2)]

Variety and locality (keyed to descriptions in text)	Field No.	Laboratory No.	Description	Organic carbon	Mineral carbon	Calculated total organic matter
1a.-----	S64-22C	D116576	Sand, black, humate-cemented; associated with ground-water seeps, 1-4 ft thick above and below water level of western shore of Choctawhatchee Bay (old dye plant locality).	5.42	0.01	8.46
2a.-----	S62-7	D112612	Beach sand impregnated with humate, 1 ft from edge of bay and few inches below water level on south shore of Choctawhatchee Bay.	.57	.03	.89
2a.-----	S62-5	D112611	Sand, black, has recently deposited humate; at edge of small stream about 8 ft from edge of south shore of Choctawhatchee Bay.	1.45	.03	2.26
2a.-----	S62-1	D112609	Sand, black, has recently deposited humate; at edge of small stream about 10 ft from edge of south shore of Choctawhatchee Bay.	1.07	.01	1.67
4a.-----	S60-1	D112608	Beach sand, humate-cemented, moderate-brown, oxidized; layer about 1 ft thick, 1-2 ft above water level of south shore of Choctawhatchee Bay.	.97	.16	1.51
4b.-----	S62-3	D112610	Beach sand, humate-cemented, dark-brown, slightly oxidized; layer in lower part of eroding bank, a few feet above and back from north shore of Choctawhatchee Bay.	3.10	< .01	4.84
4c.-----	S62-16	D112616	Beach sand, humate-cemented, moderate-brown, oxidized; layer in lower part of eroding bank, about 1 ft above water level of Santa Rosa Sound.	.69	< .01	1.08
5a.-----	S62-10	D112614	Dune sand, crossbedded, very light to dark brown, irregularly cemented with humate, in bluff 1-5 ft above beach on south shore of Choctawhatchee Bay.	1.55	.01	2.42
5a.-----	S62-11	D112615	Boulders of sand, black, humate-cemented, in shallow water on south shore of Choctawhatchee Bay, eroded from bluff of dune sand (S62-10).	2.63	< .01	4.10
6a.-----	S62-8	D112613	Sand, very dark brown with recently deposited humate, layer 1-2 ft thick at depth of about 17 ft in water well in Fort Walton Beach.	.71	< .01	1.11

TABLE 2.—*Ultimate analyses of humates, in percent, from Choctawhatchee Bay area*

[A, moisture-free analysis as reported; B, calculated analysis, ash free. Analyses of S62 samples are ultimate analyses by Huffman Laboratories, Wheatridge, Colo.; extraction of S60-1A by I. A. Breger; ultimate analysis by Coal Laboratory, U.S. Bur. of Mines, Pittsburgh, Pa. Other analyses of S62-5 and S60-1 in table 1.]

	S62-38 Humate- clay sediment, flocculated from stream water by bay water		S62-38A Humate extracted from S62-38 by NH <sub>4</sub> OH, flocculated with H <sub>2</sub> SO <sub>4</sub>		S62-5B1 Humate extracted from S62-5 with NaOH, flocculated with H <sub>2</sub> SO <sub>4</sub>		S62-5B2 Humate extracted from S62-5 with NaOH, flocculated with HCl		S60-1A Humate extracted from S60-1 with NaOH, flocculated by HCl	
	A	B	A	B	A	B	A	B	A	B
Carbon.....	20.19	50.15	39.53	55.57	31.69	52.49	36.60	56.46	32.6	43.7
Hydrogen.....	2.24	5.57	2.96	4.16	2.58	4.27	3.11	4.80	3.5	4.7
Oxygen.....	17.20	42.72	26.89	37.80	25.07	41.53	23.85	36.79	37.5	50.3
Nitrogen.....	.42	1.04	1.36	1.91	.53	.88	.62	.95	.7	.9
Sulfur.....	.21	.52	.40	.56	.50	.83	.65	1.00	.3	.4
Ash.....	62.38	-----	27.26	-----	43.74	-----	38.28	-----	25.4	-----
Total.....	102.64	100.00	98.40	100.00	104.11	100.00	103.11	100.00	100.0	100.0

The elemental composition of all the humate samples is very similar, as indicated by the analyses in table 2. When the analyses are compared on an ash-free basis, the few notable but minor differences in composition are readily explained by known characteristics of the individual samples. Sample S62-38, which has a slightly higher hydrogen and oxygen content and slightly lower carbon content, is a sample of the whole sediment flocculated from stream water; some nonhumate particulate organic matter of clay size undoubtedly was included in this sample. Sample S62-38A, which has a slightly higher nitrogen content, is humate extracted from the humate-rich sediment of sample S62-38 by dilute NH<sub>4</sub>OH solution; about 1 percent of a nitrogen salt undoubtedly was included with the humate recovered. Sample S60-1A, which relative to other samples has a lower carbon content and an almost exactly correspondingly higher oxygen content, is a sample of an old moderate brown humate-cemented sand layer which has been deeply weathered.

The chemical composition of the Florida humate puts it into the general class of coaly or humic material (Twenhofel, 1950, p. 463). As a recently deposited organic substance, humate is very similar in composition to humic acids derived from soils and to the soluble organic matter in streams and lakes (table 3), and the humate is compositionally not very different from lignin, a plant constituent believed by Davis (1946, p. 62), Breger (1951), and by Flaig (1964, p. 1523) to be, at least in part, a precursor of humate, as used in this paper. The Florida humate is certainly very similar, in appearance and genesis as well as composition, to both dopplerite in peat and a doppleritelike material naturally extracted by alkaline water from a Cretaceous coal



bed (table 3). The composition of humate is also generally similar to that of some peat (Davis, 1946, table 12) and lignite samples.

In general appearance, humate-cemented sand resembles asphalt-impregnated sand, but the elemental compositions of humate and petroleum substances are distinctly different (table 4). Asphalt and crude oil, which are composed predominantly of hydrocarbons, contain little or no oxygen, whereas the oxygen content of humate and humic materials is 30–50 percent (also see table 3); the carbon and hydrogen contents of the two classes of carbonaceous materials also are clearly dissimilar.

TABLE 3.—*Composition of north Florida humate*

[A, compared with that of B, the average of humic acids from seven main soil types of U.S.S.R. (Kononova, 1961, p. 90); C, "water humus," or soluble organic matter transported by streams (Waksman, 1936, p. 291); D, "humolignic acids," an ethyl acetate extract of yellow coloring matter in lake water (Shapiro, 1957, p. 167); E, fossil lignin (Francis, 1954, p. 351); F, dopplerite (analysis by Doppler, in Waksman, 1936, p. 281, recalculated to ash-free basis; also see Clarke, 1924, p. 763); G, doppleritelike material derived and transported from Cretaceous coal in Wyoming (Vine, 1959). All analyses in percent on ash-free basis]

	A Florida humate	B Humic acid	C Water humus	D Humo- lignic acids	E Fossil lignin	F Doppler- ite	G Dopplerite- like material, Wyoming
Carbon.....	55.0	60.34	45–54.....	54.56	56.7	51.1	62.2
Hydrogen.....	4.4	4.16	3.86–5.05.....	5.64	5.2	5.3	3.6
Oxygen.....	38.5	31.66	38.8–47.9.....	39.12	36.2	42.5	29.3
Nitrogen.....	1.4	4.26	1.46–4.23.....	1.23	1.9	1.1	2.2
Sulfur.....	.7	.....	Small amounts..	.....	.....	.....	2.7

TABLE 4.—*Average composition of north Florida humate compared to compositions of asphalt and of crude oil, in percent*

[Cited from Levorsen, 1954, p. 322]

	Florida humate	Asphalt	Crude oil
Carbon.....	55.0	80–85	82.2–87.1
Hydrogen.....	4.4	8.5–11	11.7–14.7
Oxygen.....	38.5	1–4 .5	.....
Nitrogen.....	1.4	0–2	1–1.5
Sulfur.....	.7	2–8	1–5.5

#### INFRARED ABSORPTION SPECTRA OF HUMATE

As another step in understanding and characterizing these humic substances, infrared absorption spectra were obtained on several samples. The humate was generally extracted from the impregnated sands with NaOH, flocculated with HCl, and evaporated to dryness. The infrared spectra were then obtained on the humate as pressed KBr pellets (J. H. Turner, analyst).

All the spectra showed similar absorption characteristics, with marked peaks at about  $3.0\mu$ ,  $5.9\mu$ ,  $6.2\mu$ , and  $7.2\mu$ . Broad bands and

minor peaks were also observed in the regions of  $8.1\mu$ ,  $9.2\mu$ ,  $9.7\mu$  and  $11\mu$ . The spectrum of humate extracted from sample S62-5 (tables 1 and 2) is shown in figure 8. Spectra of three similar substances are

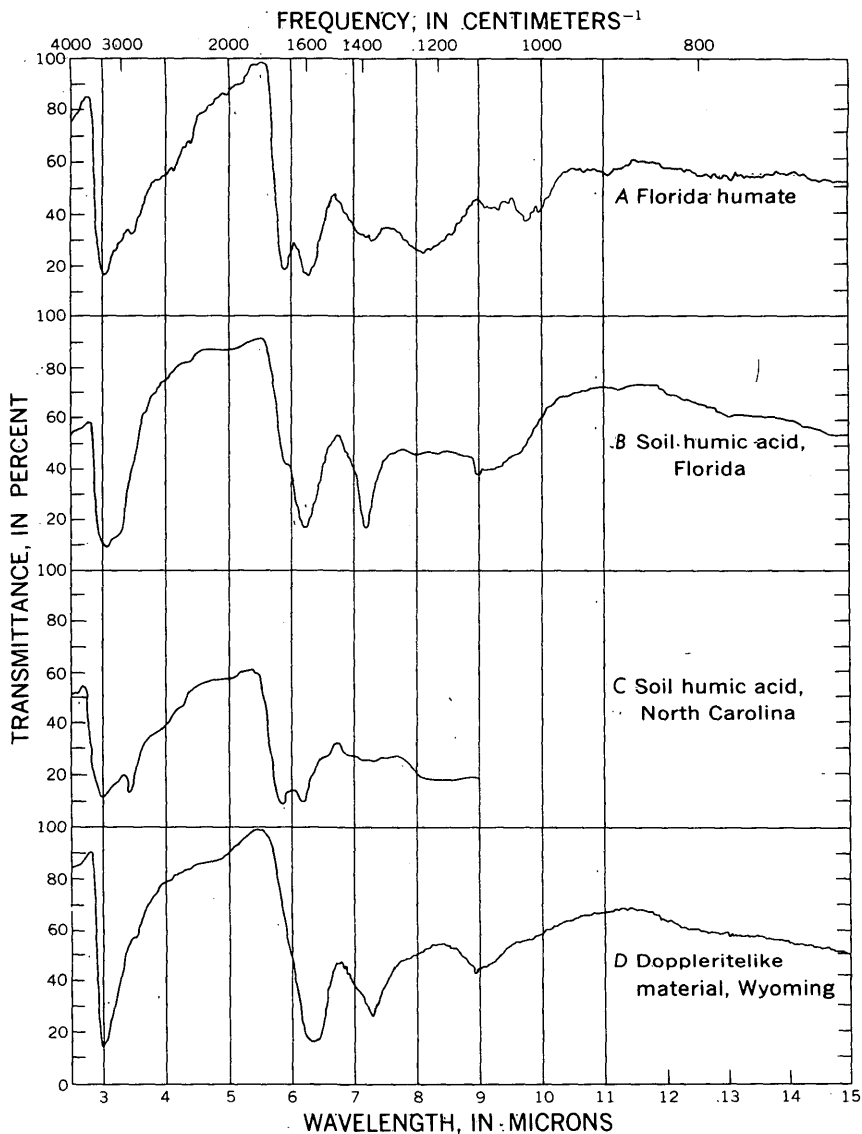


FIGURE 8.—Infrared spectrum of A, Florida humate compared with spectra of B, humic acid of soil from same area in Florida; C, humic acid of soil from North Carolina (R. L. Malcolm, 1964, unpub. Ph.D. thesis, North Carolina State Univ.); and D, a sample of doppleritelike material from same locality in Wyoming reported by Vine (1959).

included in figure 8 for purposes of comparison. Two of these spectra are of humic acids extracted from soils, and one is a spectrum of dop-pleritelike material.

The most characteristic peaks of the humate spectra are the absorption maxima at  $3.0\mu$ ,  $5.9\mu$ , and  $6.2\mu$ , which are normally attributed to hydroxyl (OH), carbonyl (C=O), and carbon-to-carbon (C=C) double-bond stretching vibrations, respectively. The inflections in the absorption region between  $7\mu$  and  $11\mu$  are generally broad and indistinct; structural interpretation at this time would be unwarranted without further chemical treatment of the samples. Comparisons of the infrared spectra, however, indicate that the chemical structure of Florida humates closely resembles the structure of humic acids, especially those derived from soils.

#### SPECTROGRAPHIC ANALYSES

Analyses by the six-step spectrographic method (concentrations of elements reported in six steps per order of magnitude, for example, 0.1, 0.15, 0.2, 0.3, 0.5, 0.7, and 1.0) of nine samples of humate-cemented sand show little variation in the number of elements detected and amount of each element. The nine samples represent all of the seven described types of humate occurrences, except bottom sediment from, for example, a bay. The following is the approximate average composition of the humate-cemented sand, given in percent, based on the nine spectrographic analyses (J. C. Hamilton, analyst):

Si -----	>10.0	Mn -----	0.0003
Al -----	.7	B -----	.001
Fe -----	.07	Ba -----	.001
Mg -----	.02	Cr -----	.0005
Ca -----	.02	Cu -----	.0003
Ti -----	.05	Zr -----	.007

Some 34 additional elements were also looked for spectrographically but were not detected.

Analyses by the six-step spectrographic method of three samples of humate, all from the south shore of Choctawhatchee Bay, are also consistent in the number of elements detected and the amount of each. The humate in these samples was extracted and air dried as described for infrared analysis and analyzed on an as-received basis. The humate, on the basis of the spectrographic analyses, which excludes such elements as the halogens and those common to organic compounds such as carbon, hydrogen, oxygen, nitrogen, and sulfur, has the following approximate average composition, given in percent (J. C. Hamilton and Barbara Tobin, analysts):

Si -----	3	Be -----	0.0005	Ni -----	0.0015
Al -----	7	Ce -----	.02	Pb -----	.003
Fe -----	.3	Co -----	.0005	Sc -----	.003
Mg -----	.07	Cr -----	.01	Sr -----	.001
Ca -----	.02	Cu -----	.002	V -----	.005
Na -----	1.5	Ga -----	.002	Y -----	.007
Ti -----	.3	La -----	.01	Yb -----	.0005
Mn -----	.0007	Nb -----	.0015	Zr -----	.005
Ba -----	.007	Nd -----	.007		

These spectrographic analyses suggest that the humates on this part of the Florida coast are predominantly organic aluminum complexes that have concentrated large parts of the available iron, titanium, cobalt, chromium, copper, lanthanum, nickel, lead, scandium, vanadium, and possibly other metals in these coastal sediments. The number and concentrations of metals, however, in either the humate-cemented sand or the humate do not differ from or exceed those commonly found in organic-rich sediments.

#### OTHER ANALYSES

Preliminary investigations indicate that the amount of hydrocarbonlike substances in the humate-rich sediment is relatively very small. A benzene Soxhlet extraction of one of the humate-impregnated beach sands, sample S62-5 (also see tables 1 and 2), yielded 200 parts per million (ppm) of extract, which is 0.02 percent of the dried sediment. The extract was yellow and waxy in appearance and fluoresced slightly under ultraviolet light. If the total organic matter of the humate-rich sediment is considered to be 2.26 percent (table 1), the hydrocarbonlike extract would compose about 0.9 percent of the organic matter. The remainder of the organic matter is presumed to be humate and is not soluble in benzene.

An X-ray analysis was made by L. G. Schultz (written commun., 1964) on the sediment derived from tea-colored stream water by natural flocculation in the brackish water of Choctawhatchee Bay. This natural flocculate (S62-38) is about 40 percent humate (table 2) and, according to Schultz, about 60 percent clay; the clay is composed of a poorly crystallized kaolin mineral which perhaps is halloysite and of dioctahedral vermiculite, in about equal amounts.

The role that natural water plays in the geochemical processes of humus leaching and the transportation and deposition of humate is extremely important, though little is known about this water at present. The chemical composition of rainwater and dew near the coast and the distribution of these chemically affected waters are probably of special significance in the initial leaching of humus, as is suggested by studies by Wilson (1959) and Blanchard (1964). Certainly the haze produced by the Gulf of Mexico surf is strikingly visible on a

clear day; it rises several hundred feet in the air and extends as much as half a mile inland. The salt in this haze actually is a driving hazard as it accumulates on the windshield of a moving vehicle.

Two samples of water were collected near the mouth of a small stream entering the south side of Choctawhatchee Bay, 2.2 miles east of the Okaloosa-Walton County line (loc. a, second variety of humate), near where samples S62-1, S62-5, S60-1 (tables 1 and 2) were collected and where abundant humate is now present. Partial chemical analyses of the stream water and of the brackish water of the bay are given in table 5. The difference in amounts of dissolved ions between the stream water and the bay water is striking; the bay water contains about a hundred times more than the stream water. For comparison, the brackish water of this part of Choctawhatchee Bay has about one-third the salinity of average sea water (table 4). Certainly, calcium, magnesium, and potassium are present in sufficient quantities in the bay water to cause some flocculation of the humate carried in by the stream; and possibly the flocculation reaction observed in the laboratory on addition of, for example,  $\text{CaCl}_2$  solution to dissolved humates closely simulates that which takes place when the tea- to coffee-colored stream water comes into contact with the bay water. These waters were not analyzed for iron and aluminum, which may also be partly or largely responsible for humate flocculation in this part of Florida, as suggested by the spectrographic analyses of the humate.

TABLE 5.—*Partial chemical analyses, in parts per million, of a stream water and brackish water from Choctawhatchee Bay that are involved in transportation and deposition of humate*

[K.A. Gardner and S. J. Rucker, analysts]

	S62-36 Water from small stream, 35 ft from south shore of Choctawhatchee Bay	S62-37 Brackish bay water, 30 ft from south shore of Choctawhatchee Bay	Average sea water <sup>1</sup>
Sodium.....	19	3, 000	10, 556
Calcium.....	1. 5	148	400
Magnesium.....	2. 1	287	1, 272
Potassium.....	1. 0	98	380
Chloride.....	32	5, 240	18, 980
Bicarbonate.....	1	61	140
Specific conductance ( $\mu\text{mhos}$ ).....	134	15, 500	-----

<sup>1</sup> Sverdrup, Johnson, and Fleming (1942, p. 173, 195).

## SUMMARY AND CONCLUSIONS

An attempt has been made in this paper to describe and define in terms useful to both the geologist and chemist an environment and

the applicable genetic processes of modern humate deposition. The primary objective has been, however, to convey to geologists the need to recognize humate as a type of carbonaceous material in the sediments and rocks of their areas of study and to consider the potential significance of humate in their interpretations of environments of deposition. Thus, in summary:

1. A large fraction of carbonaceous material in many sedimentary rocks, particularly those deposited in a coastal environment, probably was transported as dissolved or colloiddally dispersed humic substances in water.
2. These dissolved and colloidal organic materials, which are largely derived by leaching from decaying plant material at the surface, may be transported and deposited syngenetically with fine-grained sediment at the bottom of a body of water, such as a river, lake, bay, or ocean; or they may be deposited as a penecontemporaneous or epigenetic interstitial filling by downward or lateral percolation into a porous and permeable sediment such as a beach or dune sand.
3. This soluble and colloidal material, when deposited in sediment, is herein called humate.
4. Humate is formed when the soluble and colloidal humic material in surface or subsurface water enters a different physical-chemical environment and precipitation or flocculation occurs. For example, humate is deposited when it combines with waters containing dissolved ions such as aluminum, iron, and magnesium, which are common in sea and brackish waters, on complexing with clay colloids, or on combining with waters of pH less than 5.
5. Humate is abundant and is widely distributed in Quaternary sediments along the Gulf of Mexico coast of the Florida panhandle. It accumulates in and near bays and sounds of brackish water, particularly in beach and dune sands.
6. This Florida humate commonly impregnates or cements sand to form a dark brown to black layer a few feet thick, but composes only 1-8 percent of the sediment.
7. The average ash-free composition of the humate, in percent, is 55.0 carbon, 4.4 hydrogen, 38.5 oxygen, 1.4 nitrogen, and 0.7 sulfur, which is comparable to the composition of humic acids derived from soil, of yellow coloring matter in lake water, of lignin, of dopplerite, and, in a very general way, of some peat and lignite deposits.
8. The Florida humate has a larger suite and greater amount of trace metals than do the associated detrital sediments, but the metals are not in abnormally high concentrations when compared with

the content in other humates and ancient humic substances in rocks. Of interest, particularly when considering the mobility of humate, is that humate has the capacity to sorb large amounts of metals (Mortensen, 1963, p. 180; Swain, 1963, p. 133), such as iron, copper, and uranium, and potentially can form an ore deposit on final deposition (Vine, Swanson, and Bell, 1958; Cate, 1960, p. 425).

9. Humate can be compared to hydrocarbons in that both have a biologic origin and both migrate or are transported with water through sediments. However, chemically they are quite distinct—humate is a high-oxygen low-hydrogen substance, is coal-like in composition, is insoluble in benzene, and is transported in a soluble or colloidal form in water. Also, the modes and sites of accumulation of the two in a sediment greatly differ—the deposition of humate is controlled by the spatial position of a physical-chemical difference in surface or subsurface waters, commonly irrespective of sediment type or structure, whereas most hydrocarbons, being immiscible in water, are transported, physically separated, and concentrated as distinct gaseous or fluid substances in some structural or stratigraphic trap. Though these differences between humate and hydrocarbons may be oversimplified, no evidence produced during this study is construed as support for the theory that humate is a progenitor of petroleum hydrocarbons.
10. Many questions about the origin and geochemistry of humate, as a group of natural carbonaceous substances in either modern or ancient sediments, still remain unanswered. The biochemical progenitors of humate, and the processes of degradation, deposition, and diagenesis of humate are still far from being understood, but this lack should not deter geologists from recognizing humate and its significance in geologic studies.

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