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SOUTHEASTERN GEOLOGY

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HUMATE, Bh SOIL HORIZONS, IN WET SANDS OF

THE NORTH CAROLINA COASTAL PLAIN[1]

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ABSTRACT

Humate accumulations 5 to 10 m thick are found in sands of the middle and lower Coastal Plain of North Carolina where the water table is at or near the surface for part of the year and the overlying soil B horizon has no more than 6 to 8 percent clay. The upper boundary of the humate may be within 20 cm of the surface or, in the drier landscapes, 1 to 2 m below the surface. The lower boundary is about 0.5 m above any less permeable underlying formation. Humate does not penetrate into gleyed, permeable, greenish gray sands because the ground water flow lines bypass these sands.

Very low pollen counts and the landscape distribution of humate indicate that it is a post-depositional feature. Humate accumulations are the Bh horizon of the modern soils formed in the sandy Coastal Plain sediments. The 3 to 40 grams of organic carbon/m^2/yr currently being added from the surface can replenish the 175 kg carbon in a 7 m^3 section every 3,500 to 28,000 years.

Humate has almost no dithionite extractable iron and very small quantities of calcium, magnesium, and potassium. Aluminum is the

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dominant cation and the exchange properties of humate are dominated by aluminum and organic carbon.

How the carbon is immobilized to form a humate or Bh horizon is open to question. One alternative explanation is that basic cations, pH changes, or other aspects of the chemical environment may have immobilized the carbon initially. If true, this suggests that humate deposition started first near the surface and moved progressively deeper until some limiting horizon was reached. The present composition of humate suggests that the factors inducing precipitation have been removed or changed through subsequent leaching. A second alternative is that humate is initially immobilized by organo-mineral bonding with silica on quartz surfaces. This mechanism requires no chemical change in the sediments such as that needed if bases are involved in the immobilization of carbon compounds.

INTRODUCTION

The term "humate" as used by geologists (Thom, 1967; Swanson and Palacas, 1965) refers to brown to black organic matter than impregnates sandy sediments. Humate is the Bh horizon of soil scientists (Soil Survey Staff, 1962). Bh horizons about 1 m or less thick and underlain by gray sand, are a major feature of the very widespread Leon (and associated soil series) soils found in wet sandy areas of the southeastern United States. Investigations near Pink Hill in Lenior County, N. C. have shown that the upper Bh and gray sand horizons commonly are underlain by another Bh horizon that reaches to depths of 8 to 10 m. Direct tracing on the local landscape shows that, in the wetter parts of the landscape, the two Bh horizons merge, the top is within 10 to 20 cm of the surface, and the Bh is continuous with depth. The subsurface relations and areal distribution were determined by use of a power auger and by standard soil mapping techniques. Laboratory analyses were based on standard procedures (Soil Survey Staff, 1972). The following is a report on the morphology, landscape, and sediment relations, chemistry, and suggested genesis of the Bh or humate horizons we have investigated in the North Carolina Coastal Plain.

MORPHOLOGY

Bh horizons near the surface are dark reddish brown (5 YR hues of the Munsell colors) but in thick sections grade down to more olive colors. Samples from the deeper horizons change color so rapidly, when exposed to air, that neither the Munsell hue nor the individual color chip can be determined accurately. Below 1 or 2 m both the red hues and the more olive colors near the base darken considerably when exposed for one-half hour or longer. In this respect, the Bh horizons

are similar to many buried peats.

A description of a typical section of the thick Bh horizons follows:

Location: Turner Woods near Pink Hill, N. C. Site is in a slight swale on the Sunderland surface, middle Coastal Plain (Point D, Figure 1; sampled section Table 3).

Bed #	Horizon	Description	Thickness m
8	A1 & A2 - B21H	Black (10YR 2/1) fine sand grading downward to gray and very dark gray (10YR 5/1 and 3/1) loamy sand; clear to	0.50
7	B22h	Black (5YR 2/1) soft, somewhat peaty feeling loamy sand; gradual to	1.70
6	B22h & A'2	Dark grayish brown (10YR 4/2) to dark gray (10YR 4/1) loamy sand; common black (N 2/0 and 7.5YR 2/1) mottles; gradual to	0.86
5	B23h	Black (5YR 2/1) soft organic-feeling sand; slightly firm; gradual to	0.53
4	B24h	Darker than dark reddish brown (5YR 2/2) loamy sand to sand; firm to slightly firm; gradual to	1.28
3	B25h	Dark reddish brown (5YR 3/3) sand grading downward to dark brown and dark reddish brown (7.5YR 3/2 and 5YR 2/2); gradual to	0.92
2		Brown (10YR 5/3) sand with common well-rounded quartz pebbles; base of Sunderland Morphostratigraphic unit; abrupt to	0.61
1		Olive (5Y 5/3) medium sand to sandy clay; partially cemented; undifferentiated Tertiary (probable Yorktown) formation	2.5+

The upper Bh horizon (Figure 2, Leon series) has the greatest range in color and consistence and many of its characteristics are closely associated with the local soil landscape. It may thin and pinch out under the better drained local high areas or thicken at the expense of the A'2 horizon in the low wet areas. The A'2 is a subsurface horizon, much like the A2 horizon, that separates the upper and lower Bh
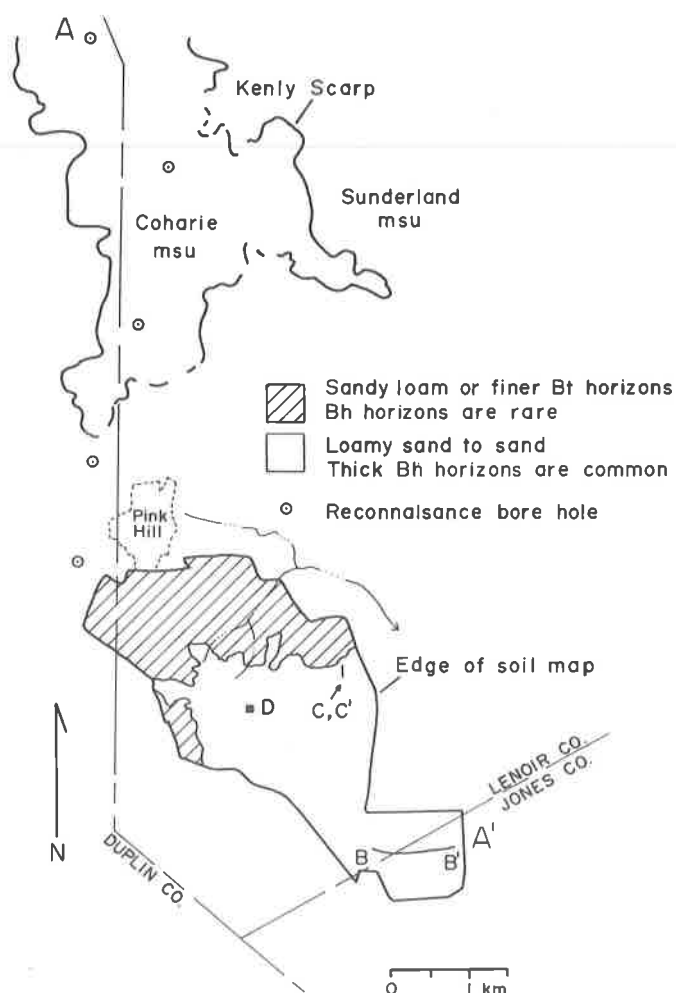
Figure 1. Areal distribution of soils with Bh
horizons in relation to B horizons texture
near Pink Hill, North Carolina.

horizons in the slightly dryer parts of the local landscape. In the wet-
test areas the two Bh's merge and the A'2 disappears (Figure 2, Mun-
ville series). Most Bh horizons have a friable consistence, but locally
the upper Bh may have a massive brittle layer a few centimeters thick
that perches water and is difficult to penetrate by hand auger (Brandon,
1975). These brittle layers are discontinuous and are not related to
any known landscape feature.

Below 2 m, the Bh horizons are remarkably uniform over large
areas. Minor variations cannot be traced even a few meters, and the
characteristics of the lower Bh appear to be determined largely by the

SOIL SERIES

Figure 2. Generalized relation between soil series, topography, and Bh horizons near Pink Hill.

permeability, grain size, and clay content of individual beds rather than anything related to the modern surface. For example, the deep Bh horizon passes nearly unchanged from beneath the Bt or (B) horizon of the Baymeade to the Murville series (Figure 2).
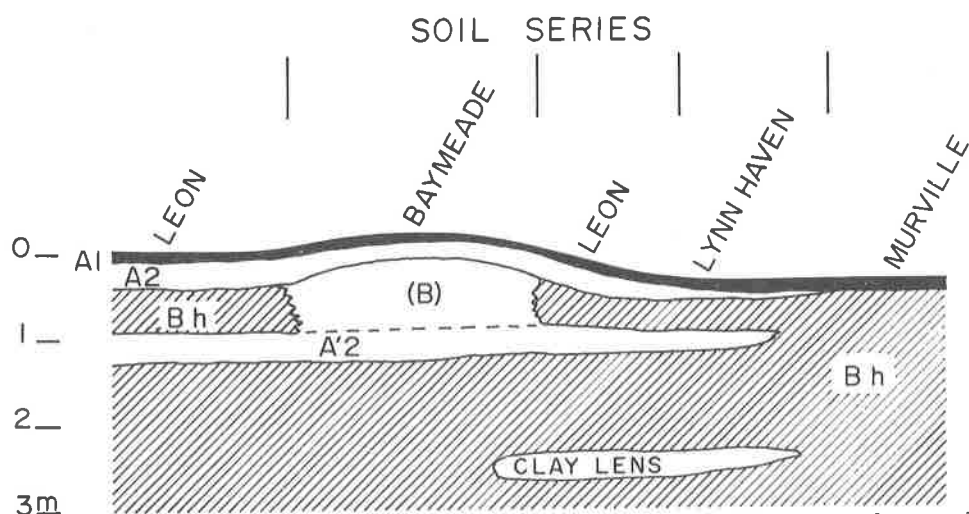
RELATION TO SEDIMENT TEXTURE

Bh horizons are found where the water table is at or near the surface sometime during the year and the soils are sands or loamy sands (Fuller et al., 1929; Righi and DeConinch, 1974). Thick (2m) Bh horizons are found where thick sand or loamy sand sediments crop out at the surface. In the Pink Hill area (Figure 1), the surficial sediments overlie fine-textured (clay to bedded silt and clays) Tertiary and Cretaceous formations (Figure 3).

From the beginning of the traverse near Pink Hill (Figure 3) to km 10, the upper part of these sediments is sandy loam to clay. Bh horizons do not occur where these surficial sediments contain a significant amount of clay. From km 10 to the end of the traverse, the upper fine-textured sediment is not present and loamy sands 10 to 30 m thick are at the surface. Where this happens, the Bh horizons are continuous under the broad divides and can be 9 to 10 m thick. Their thickness appears to be controlled in part by the thickness of the sands.

Bh horizons are continuous under the divides (Figure 4, B-B') but start to thin under the gentle slopes that lead down to small creeks on the flanks of the divide. Under narrow spur ridges, such as C-C' in Figure 4, the Bh horizons become less dark and thinner before pinching

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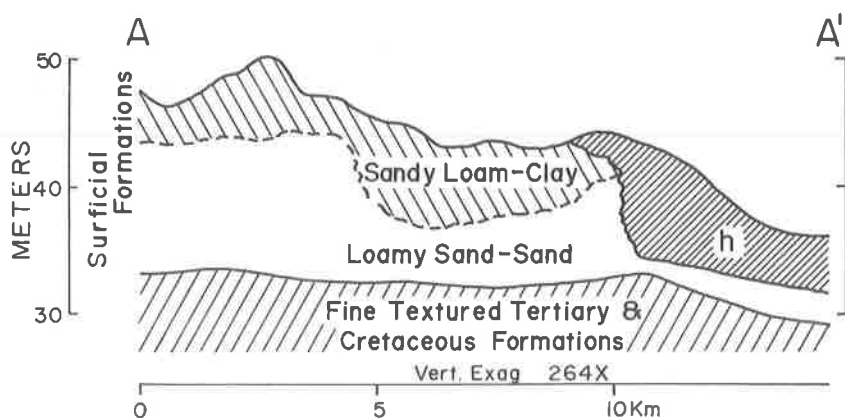Figure 3. Traverse along the Neuse-Cape Fear Divide show-
ing the relation between surface texture and thick Bh
horizons. The hachured area with an h is sand to loamy
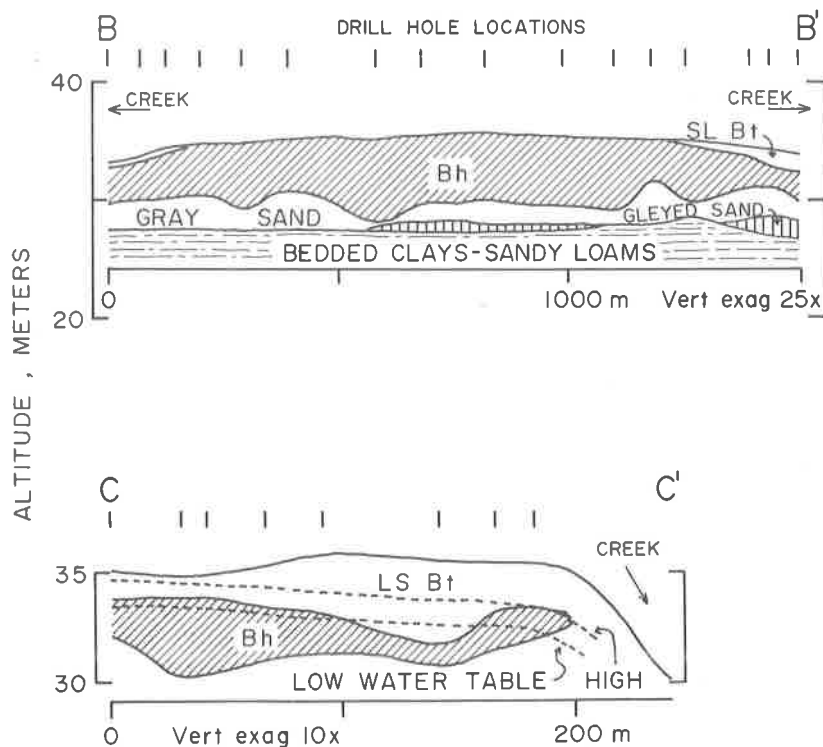sand.   Location of the traverse is shown in Figure 1.

Figure 4. Subsurface continuity of Bh (hachured) horizons
and their relation to gray and gleyed sands. Note the
discontinuous distribution of the gleyed sands. See Fig-
ure 1 for locations.

out near the convex slope that leads down to the creek.

The lower part of the Bh horizon commonly fades into a basal gray sand about a meter or less above the less permeable Tertiary and Cretaceous formations (Figure 4, B-B'). There is a 15- to 20-cm transition zone between the Bh and gray sand. In some areas under the divides and more commonly near the small creeks, the Bh and gray sands overlie gleyed greenish gray (5GY4/1 or similar) sands. There is always a transition zone of about 0.5 m, between the Bh horizon and the gleyed sands (Figure 4, B-B').

About 25 percent of New Hanover County, N. C., has soils with Bh horizons (Weaver, in press). These Bh horizons are rarely more than 4 m thick compared to 7 to 10 m at Pink Hill. In New Hanover County, the gleyed sands commonly are from 2 to 7 m below the surface and are continuous under the broad flats, rather than in small discontinuous pockets as near Pink Hill (Figure 4, B-B'). In both areas, the Bh horizons never penetrate into the gleyed sands.

WATER TABLE RELATIONS

The surficial sediments in the Pink Hill area form gently undulating plains that are truncated on the edges by stream dissection. The streams cut through the surficial sediments into the underlying Tertiary and Cretaceous formations. Small tributaries head on the valley slopes, and intermittent streamflow is common near or downstream from the contact between the surficials and the Tertiary beds.

The landscape relations of Bh horizons suggest that their distribution and formation is related to the movement of ground water through the surficial sands. If the hydraulic conductivity of the surficial sediments and the underlying Tertiary and Cretaceous materials can be estimated, it is possible to predict how the water moves within a local landscape. Hydraulic conductivity has not been measured in the Pink Hill area, but it can be estimated from similar sediments in other areas of the Coastal Plain (Table 1). The hydraulic conductivity values in Table 1 were measured in organic-free sands. The actual conductivity of sands with Bh horizons probably is somewhat less because the added organic matter reduced pore space (Brandon, 1975).

By using Figure 5 as an approximation of the Pink Hill landscape, it is possible to roughly estimate the flux from the center of the divide using the Dupuit-Forcheimer assumptions:

$$q_{1-2} = K \; \frac{(H_1^2 - H_2^2)}{2L}$$

where q is the flux from 1 to 2; K the hydraulic conductivity; L the distance from 1 to 2; and H_1 and H_2 are the hydraulic heads at 1 and 2 respectively. If we assume a water table at the surface in the divide center,

Table 1. Hydraulic Conductivity of Coastal Plain Sediments.

Texture	Range in K cm/day	Mean K	No. of test holes
Loamy sand to sand	30.72-50.8[a]	34.30	3
Loam to sandy loam	0.1533-5.647	2.45	4
Silty clay loam to clay	0.069-0.539	0.28	7

[a]Determined by the method described by Luthin and Kirkham (1949) - silty clay loam to clay, K values from greenish-gray sediments below permanent water table.

and that $H_1 = 10$ m and $H_2 = 0$; $L = 1$ km; K for sands = 0.343 m/day, K for loams = 0.0245 m/day, and K for clays = 0.0028 m/day then:

$$q_{1-2} \text{ sands} = 0.01715 \text{ m}^3/\text{day}$$
$$q_{1-2} \text{ loam} = 0.01225 \text{ m}^3/\text{day}$$
$$q_{1-2} \text{ clays} = 0.00014 \text{ m}^3/\text{day}$$

The large differences in flux between sandy and clayey sediments, even allowing for a reduction of porosity by the Bh to a K value similar to that for a loam texture, suggest that the major water flow is within the surficial sediments to outlets on the valley side, not from the surficials into the underlying bedded silts and clays and then out to the seepage areas. So long as the Tertiary and older sediments remain saturated, the streamlines within the surficial sediments should be similar to those described by Edwards (1956) for a tile line (the seepage area) placed above an impermeable layer (Figure 5). If this analysis is correct, the carbon-enriched ground water does not move through the very basal beds of the surficial sands into the underlying sediments and, consequently, the Bh horizons fade 0.5 m above the contact to the less permeable materials.

POLLEN ANALYSES

The designation of thick zones or horizons of organic carbon accumulation as Bh horizons implies that the organic matter has been translocated from the surface (Richardson, 1930). As alternatives, the carbon could have been deposited by precipitation in sea water as suggested by Swanson and Placas (1965) or it could represent surface (subaerial) buildup of carbon that more or less kept pace with sedimentation.

The hypothesis of burial of subaerial deposits can be tested because the A1 horizons of soils should be richer in pollen than organic material translocated into the lower sediments. Pollen analyses do not differentiate between deposition in the ocean and downward translocation from a subaerial surface.
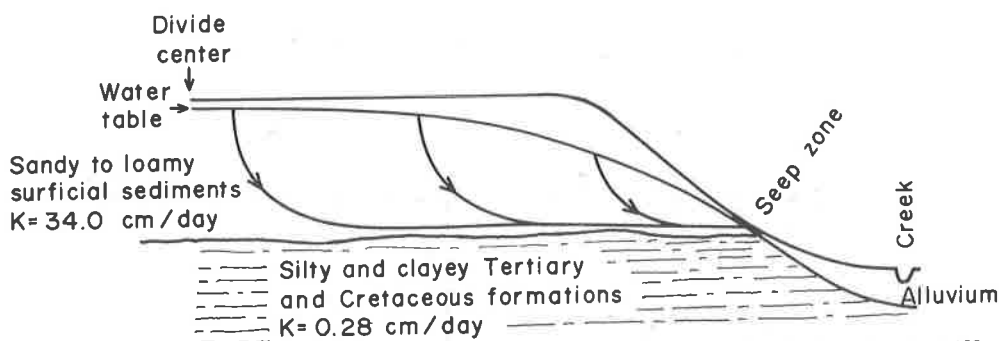
Figure 5. Suggested streamlines in surficial materials in the Pink Hill area. H_1 is at the divide center, H_2 is at the seep zone.

Samples from A1, A2, Bh, buried A1, and gyttja horizons from a large area of North Carolina have a considerable range in the amount of pollen (Table 2).   The A1 horizons with a low amount of carbon have 6 to 33 pollen grains per 100 microscopic fields, and most Bh and C horizon samples have from 0 to 8 grains per 100 fields (Table 2).

Pollen in sediments from three bore holes sampled at 30 cm intervals are shown in Figure 6 (holes 3, 8, 10).   The bore holes were within 150 m of one another and the morphology of the Bh horizon is similar.   In addition, hole no. 7 was sampled for chemical data and the thickness of the sampled horizons is variable (Table 3).

Two distinct pollen peaks of 25 grains or less are found in bore holes 3, 7, and 10, but bore hole 8 has only a small variation with depth. The distinct pollen peaks could be interpreted as representing

Table 2. Pollen grains per 100 microscopic fields. [1]

Horizon	No. of Samples	No. of Grains
AO or duff	1	20
A-1	5	206; 33; 20; 7; 6
A-2	3	0; 0; 0
Bh	13	5; 4; 2; 1; 0; 0; 0; 0; 0; 0; 0; 0; 0
Ab[2]	2	312; 81
Gyttja	2	25; 14
C	1	0

[1] Equal volumes of KOH treated samples were spread over nearly equal areas of the slide. A traverse of 100 microscopic fields were made at 480a across the slide.   For more details, see Daniels et al. , 1975.
[2] Buried A-1 horizons.

POLLEN GRAINS per 100 FIELDS
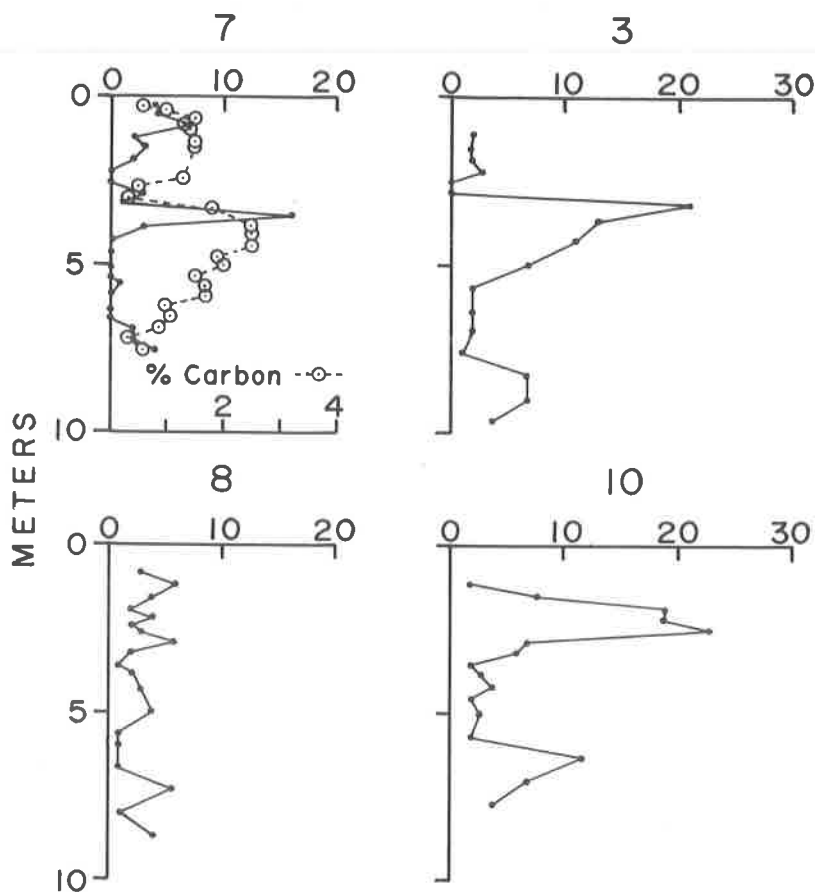
Figure 6. Vertical changes in pollen grains per 100 micro-
scopic fields in sections near Pink Hill. Bh
horizon occurs throughout to a depth of about 7
m. All sections are within 150 m of point D in
Figure 1. The hole number is above each section.

buried A-1 soil horizons since 25 grains per 100 fields are found in
some modern A-1 horizons. In hole no. 7, the pollen peak at 3.5 m
corresponds to an increase in carbon, that could represent either a
gyttja or subaerial accumulation. This accumulation of pollen is not
recognizable in hole 8 (Figure 6).

If a Bh horizon is produced by burial of soil A-1 horizons, the
pollen content should fluctuate with organic carbon content. The Bh
should be weakly expressed or absent where pollen counts are about 5

Table 3. Texture and Chemical Properties[1] of a Soil with Thick h horizon.

Depth cm	Horizon	Sand	Silt	Clay	Organic Carbon	Citrate-dithionate ext.		pH 1:1 H_2O	NH4OAc ext.		BaCl2-TEA ext. acidity	KCl ext. Al
						Al	Fe		Ca	Mg		
		---percent---							---meq/100g---			
0- 10	A1	92.1	6.4	1.5	4.0	0.04	0	3.3	tr	0.1	10.0	1.0
10- 30	A2 and Bh	94.2	4.9	0.9	0.6	0.02	0	3.6	tr	tr	2.6	0.4
30- 50	B21h	94.7	4.2	1.1	1.0	0.04	0	3.4	tr	tr	4.9	1.2
50- 77	B22h	86.9	9.9	3.2	1.5	0.16	0	4.0	tr	tr	12.9	2.9
77- 90	B22h	86.1	0.7	5.2	1.3	0.12	0	4.3	tr	tr	11.4	2.5
90-114	B22h	86.0	7.4	6.6	1.4	0.21	0	4.3	tr	tr	12.3	2.5
114-147	B22h	87.3	6.5	6.2	1.5	0.22	0	4.4	0.2	tr	12.0	2.5
147-220	B22h	90.6	4.5	4.9	1.5	0.10	0	4.2	0.2	tr	10.6	2.3
220-260	B22h	92.0	1.1	6.1	1.3	0.10	0	4.1	tr	tr	10.0	2.5
260-286	B22h	97.3	1.1	1.6	0.5	0.06	0	4.2	tr	tr	3.3	0.0
286-306	B22h	97.9	1.3	0.0	0.3	0.04	0	4.6	tr	tr	0.0	0.2
306-359	B23h	88.9	9.3	1.0	1.0	0.23	0	4.2	tr	tr	14.3	1.9
365-396	B24h	95.3	3.3	1.4	2.5	0.36	0	4.3	tr	tr	19.7	2.0
396-426	B24h	98.5	0.7	0.0	2.5	0.42	0	4.6	tr	tr	18.0	1.0
426-457	B24h	98.2	1.0	0.8	2.5	0.30	0	4.7	tr	tr	14.2	1.3
457-487	B24h	97.5	1.7	0.8	1.9	0.20	0	4.0	tr	tr	12.9	1.5
487-510	B25h	96.7	2.3	1.0	2.0	0.22	0	4.7	tr	tr	11.7	1.5
510-548	B25h	96.3	2.7	1.0	1.5	0.22	0	4.9	tr	tr	10.7	1.3
548-579	B25h	97.4	1.6	1.0	1.7	0.23	0	4.9	tr	tr	13.3	1.3
579-609	B26h	97.9	1.6	0.5	1.7	0.26	0	4.5	tr	tr	11.1	1.6
609-640	B26h	96.8	2.2	1.0	1.0	0.14	0	4.0	tr	tr	6.1	1.1
640-670	B26h	95.5	3.1	1.4	1.1	0.16	0	4.0	tr	tr	6.0	1.2
670-701	B26h	95.6	2.9	1.5	0.9	0.14	0	4.9	tr	tr	5.7	1.1
701-731	C1	99.3	0.3	0.4	0.3	0.06	0	5.7	tr	tr	1.1	0.2
731-762	C1	98.1	1.3	0.6	0.6	0.26	0	5.4	tr	tr	4.7	0.6
762-1006	IIC2	94.7	1.4	3.9	0.4	0.12	0	5.4	tr	0.1	2.0	0.4

[1] Procedures used are outlined in Soil Survey Staff, 1972. Also see Holzhey et al.,

grains per 100 fields (Table 2). But there is little relation between carbon and pollen counts and the Bh horizons are as strongly expressed morphologically where there is no pollen as where there are 25 grains per 100 fields (see section description, Figure 6 and Table 3). The Bh horizons, therefore, are independent of gyttja or subaerial accumulations of organic matter, although these horizons may be found within a thick Bh accumulation.

PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of the Bh horizon sampled at the site of the section description are given in Table 3. The mineralogy of the site is given in Table 4.

The Bh horizon has only minor amounts of silt and clay, reaching a maximum clay content of about 7 percent. The sand fraction is largely quartz with less than 3 percent weatherable minerals in most samples. The clay fraction is a mixture of aluminum interlayered vermiculite and quartz with lesser amounts of kaolinite and interstratified vermiculite/mica. The clays adhere to glassware when separated in the laboratory and are very difficult to handle. They behave much like low-charge density minerals such as gibbsite. They also have water

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Table 4. Mineralogy of fine sand, very fine sand, and clay of section characterized chemically in Table 3.

Depth	Clay Mineralogy	Sand Size	Sand Mineralogy
cm	Rel. Amt (X-ray) <0.002mm	mm	
0- 18	QZ5, KK2, VM2	0.10-0.20	QZ98, RE1, FD<1, WE1
		0.05-0.10	QZ94, RE4, FD1, WE1
18- 38		0.10-0.20	QZ97, RE2, WE1
		0.05-0.10	QZ94, RE5, WE1
38- 50	QZ5, KK2, VM2, MI2	0.10-0.20	QZ99, RE1, WE<1
		0.05-0.10	QZ96, RE4, WE<1
50- 77	QZ5, KK2, VM2, VR3, MI1	0.10-0.20	QZ98, RE1, WE1
		0.05-0.10	
90-114		0.10-0.20	QZ96, RE3, FD<1, WE1
		0.05-0.10	
147-220	QZ2, KK3, VM2, VR5, GI1	0.10-0.20	QZ99
		0.05-0.10	
260-286		0.10-0.20	QZ93, RE4, WE3
		0.05-0.10	
306-359	QZ5, KK2, VM3, MI1	0.10-0.20	QZ91, RE7, WE2
		0.05-0.10	
365-396	QZ3, KK4, VM1, VR4, MI3	0.10-0.20	QZ96, RE4, WE<1
		0.05-0.10	
427-457	QZ4, KK1, VM1, VR2	0.10-0.20	QZ91, RE7, WE2
		0.05-0.10	
457-487		0.10-0.20	QZ95, RE3, WE2
		0.05-0.10	QZ94, RE3, FD1, WE2
518-549		0.10-0.20	QZ89, RE9, WE2
		0.05-0.10	
579-609		0.10-0.20	QZ89, RE8, FD<1, WE3
		0.05-0.10	QZ75, RE20, FD1, WE4
640-670		0.10-0.20	QZ96, RE2, FD<1, WE2
		0.05-0.10	QZ84, RE15, WE1
701-731	QZ3, KK1, VM4	0.10-0.20	QZ95, RE2, FD1, WE2
		0.05-0.10	QZ55, RE12, FD20, WE13
731-762		0.10-0.20	QZ95, RE2, FD2, WE1
		0.05-0.10	QZ61, RE8, FD16, WE15
762-1006	QZ3, KK5, VR1, MI2	0.10-0.20	QZ97, RE2, FD<1, WE1
		0.05-0.10	QZ92, RE3, FD2, WE3

Legend: QZ = quartz, RE = other resistant minerals, FD = feldspar,
WE = other weatherable minerals, GI = gibbsite, KK = kaolinite,
MI = mica, VR = vermiculite, VM = interstratified vermiculite-mica

Relative amounts (X-ray): 5 = dominant, 4 = abundant, 3 = moderate,
2 = small, and 1 = trace.

repellent characteristics and several clay samples remained dark throughout the pretreatment. Many samples lost about 6 percent weight by exothermic ractions having a maximum intensity near $250^{\circ}C$. These characteristics suggest tightly bound organics that resisted the H_2O_2 pretreatment.

The ion exchange properties of the Bh horizons are dominated by organic carbon and aluminum. Aluminum is the major exchangeable cation although the amount is low. Measureable exchangeable magnesium or calcium was found in only three subhorizons. Potassium is present in only small quantities throughout the section, even in the samples that

Table 5. Constituents of percolating water collected 10 cm below the surface.

Soil Series, Classification and Site no.	Year	Soln. Collected $1/m^2$	C	Ca	Mg	Na
				--------g/m^2/yr----------		
1. Rumford Typic Hapludult	68-69 69-70	186.1 323.4	3.490 6.149	0.2999	0.1931	0.4252
2. Leon Aeric Haplaquod	68-69 69-70	161.7 580.7	5.050 14.658	0.6012	0.4381	0.8483
3. Pactolus Aquic Quartzi-psamment	68-69 69-70	273.5 476.3	5.272 11.362	0.4252	0.2787	0.8502
4. Leon Aeric Haplaquod	68-69 69-70	166.6 393.9	7.177 13.977	0.4216	0.3967	0.4838
5. Murville Typic Hallaquod	68-69 69-70	500.5 800.9	6.930 47.333	0.3066	0.2604	1.4086
6. Murville Typic Haplaquod	68-69 69-70	404.9 785.7	8.207 17.231	0.5525	0.3657	1.9154

Year 7-11-68 to 8-15-69 and 8-15-69 to 8-25-70

had some feldspar and biotite (700-760 cm) in the very fine sand fraction. There is essentially no extractable iron.

To test whether or not enough carbon was entering the sand to produce the thick Bh horizons in the Pink Hill area, water collectors were installed 10 cm below the surface of sandy soils (Holzhey et al., 1975). The amounts of carbon, cations and volume of percolating water were determined in monthly samples over a 2-year period. The results are given in Table 5. The collectors were not 100 percent efficient and for short periods they did not function at all (Holzhey et al., 1975). Thus the carbon moving through the upper 10 cm (Table 5) should be considered as a minimum although there are times where the amount of water collected exceeded rainfall.

Humic and fulvic acids were extracted from Bh horizons by standard procedures (Stevenson, 1965) that use NaOH extraction followed by separation by acid precipitation. In deeper Bh horizons, most of the organic carbon was extracted as humic and fulvic acids (Table 6). All the carbon in the water from the collectors was acid soluble, i.e., fulvic acid. Thus, fulvic acid from the surface is the material available to move deep into the sands and form the Bh horizons. The increasing humic-fulvic acid ratio with depth indicates that the fulvic acid is polymerizing to form the higher molecular weight humic acid. This increase of humic-fulvic ratio with depth is contrary to what is usually found in other soils (Table 6) (McKeague, 1968).

The amount of cations in each water sample is relatively small

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Table 6. Humic and fulvic acids in surface, B2t, and Bh horizons.

Soil	Horizon	Depth	Number of Horizons	Mean		Humic C/ fulvic C	
				Total C	Humic plus fulvic C	Mean	Range
		m		-------percent-----			
Umbraquults Wet medium textured soils without Bh horizons	02	0	1	36.3	1.12	1.0	--
	A1	0-0.3	11	4.65	0.92	1.3	0.8-1.8
	A2	0.1-0.4	3	1.27	1.80	0.6	0.4-0.8
	A3	0.2-0.3	1	2.60	0.82	0.6	--
	B2t	0.3-0.8	4	0.74	2.53	0.5	0.3-0.7
Aquods Wet sandy soils with Bh horizons	A1		1	4.99	4.51	4.5	
	A1 & A2	0-0.1	4	4.21	0.59	2.2	1.5-2.7
	Bh	0.1-0.5	4	2.17	0.62	1.4	0.9-1.73
	Bh	0.5-1.0	5	1.37	1.01	3.1	0.5-7.5
	Bh	1.0-2.5	5	1.02	1.10	3.5	1.6-8.2

[1] Humic and fulvic acids separated by using the procedure described by Stevenson (1965).

[2] (U-A) Classification according to Soil Survey Staff (1960).

but possibly highly significant because exchangeable cations in the system are so low (Table 3). Calcium and magnesium are linearly related to the amount of water moving through the upper 10 cm (Table 7). But sodium concentration increases sharply with increasing rainfall. The amount of sodium is seasonally distributed, being lowest in the summer and increasing to a maximum in the fall and winter months. Fall and winter bring frequent intrusions of maritime air over eastern North Carolina (personal communication, A. V. Hardy, State Climatologist retired), and this may be the major source of sodium.

The amount of carbon collected in water moving below 10 cm is linearly related to the amount of water (Table 7); site no 6 is an exception. In most cases, the concentration of carbon per liter decreases as the amount of water increases. Although the amount of carbon moving in the system is relatively small each year, the total amount entering the system is relatively large over a time span of 20,000 years. The section sampled (Table 3) has an average carbon content of 1.6 percent to a depth of 7 meters. This is only 175 kg of carbon in 7 m^3 or about the amount that moves into the system every 3,500 to 28,000 years at the rates recorded in Table 6. At the present time, carbon is being added at a rate of 5,000 to 30,000 kg/million years/m^2. The sediments

Table 7. Quantities of leachates related to volumes of percolating water. Y = grams of Element T/M^2, X = Liters of Water/M^2.

SITE NO.		
	CARBON	
1	Y = 23.78 + 18.03X	r = 0.89
2	Y = 96.53 + 23.25X	r = 0.68
3	Y = 46.46 + 23.83X	r = 0.78
4	Y = -27.33 + 38.62X	r = 0.60
5	Y = -399.08 + 71.26X	r = 0.87
6	Y = 709.64 + 10.65X	r = 0.33 ns.
	CALCIUM	
1	Y = 0.1 + 0.050X	r = 0.85**
2	Y = -0.29 + 0.55X	r = 0.75**
3	Y = -0.23 + 0.047X	r = 0.90**
4	Y = -0.26 + 0.059X	r = 0.96**
5	Y = 0.18 + 0.016X	r = 0.64**
6	Y = -2.35 + 0.073X	r = 0.82**
	MAGNESIUM	
1	Y = -0.12 + 0.057X	r = 0.94**
2	Y = 0.45 + 0.057X	r = 0.58*
3	Y = -0.13 + 0.049X	r = 0.48**
4	Y = -0.54 + 0.092X	r = 0.09**
5	Y = -0.76 + 0.040X	r = 0.73*
6	Y = 0.78 + 0.030X	r = ns.
	SODIUM	
1	Log Y = 0.06 + 0.837 log X	r = 0.92
2	Log Y = -1.14 + 2.374 log X	r = 0.61
3	Log Y = 0.12 + 0.802 log X	r = 0.80
4	Log Y = -0.40 + 1.082 log X	r = 0.97
5	Log Y = -1.86 + 1.957 log X	r = 0.88
6	Log Y = 0.32 + 1.554 log X	r = 0.86

at Pink Hill probably are upper Pliocene to (?) Pleistocene, or about 1.5 m years, in age (Daniels and Gamble, 1974; Daniels et al., 1972). If present additions are similar to those in the past, between 7,500 and 45,000 kg of carbon may have been available to move with the ground water. This is 40 to 250 times more carbon than is now present in the 7 m^3 section and obviously considerable carbon has been lost from the system.

The large amount of available carbon compared to that actually present suggests that an equilibrium level has been reached and is now being maintained. Most of the carbon being added is either lost by oxidation or is moving through the Bh horizon without reacting, or both. The tea colored streams of sand areas is ample evidence that much of the carbon is being flushed through the system. We do not know whether it moves through without reacting or whether a small amount of the modern carbon is exchanged for carbon in the Bh horizon.

The water-insoluble organic matter of untreated samples from

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0.6-1.0 m and 1.7-2.0 m depth of the sampled section (Table 3) gave radiocarbon dates of 11,000 and 31,000 years respectively. Trees and other plants root within the upper meter, and carbon from this source probably accounts for the average age of 11,000 years for this horizon. The 31,000 year date is for a sample below the rooting zone of most plants, but it must be interpreted with caution. A mixture of 98 to 99 percent "dead" carbon and 1 or 2 percent modern carbon will give an apparent age of 31,000 (Olson and Brocker, 1958). Thus very little carbon needs to be added to the Bh, either from roots or migrating fulvic acid, to give a datable sample. On the other hand, if the carbon in the Bh horizon is in a steady-state exchange with the fulvic acid being circulated, the 31,000 year date may truly reflect the average age of the carbon in the Bh horizon.

INTERPRETATIONS

Bh horizons are common in Pleistocene to Holocene eolian sands along the river valleys (Daniels et al., 1969). They occur in the sands of the Arapahoe Ridge (Daniels et al., 1972, Minnesott Ridge), a storm beach and eolian feature related to the Pamlico high stand of sea level. Bh horizons also are found in the upper part of marine deposits such as the Pamlico and Talbot morphostratigraphic units (DuBar and Solliday, 1963, Fallaw and Wheeler, 1969, Daniels et al., 1972) where sands are at the surface. But these Bh horizons do not penetrate into the underlying gleyed sands that probably have changed little since they were deposited. Thus, while Swanson and Palacas (1965) were able to demonstrate that soluble carbon is flocculated by sea water, this mechanism does not appear to be applicable to the production of the Bh horizon we have studied.

It is our opinion that the most likely explanation for the Bh or humate horizons we have studied in North Carolina is translocation of organic carbon from the surface and its subsequent deposition in the subsurface (see Swanson and Palacas, 1965). We suggest that water-soluble carbon, (fulvic acid) derived from surface litter and the carbon in the soil A-1 horizon, is moved downward by rainwater entering the soil. The lines of evidence suggesting this mechanism are listed below.

Large quantities of organic carbon are now entering the system (Table 6). The amount being added per square meter every year is enough to produce a 7 m^3 Bh horizon containing 175 kg of carbon in 3,500 to 28,000 years. Most of the level interstream divides of the Coastal Plain are much older, ranging from Pliocene to >30,000 year Pleistocene (Daniels and Gamble, 1974; Ward et al., 1971, Daniels et al., 1971). The amounts of time and available carbon are large enough to explain the thick Bh horizon if the carbon can be distributed and precipitated at depth.

We believe that the carbon is distributed by the ground water

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and that the factors affecting ground water movement influence the distribution of the Bh horizon. Thom (1970) believed that humate is an acquiclude and uses this property to help explain the development of Carolina Bays. Locally the top of the Bh horizon is a very dense horizon of few cm thick and in this case is an acquiclude (Brandon, 1975). The hydraulic conductivity of this dense Bh horizon can be as low as 0.5 cm/day (Unpublished report, E. E. Gamble, May 21, 1974). But this upper dense layer is broken by cracks and root channels so that wells open above and below the layer usually have the same water table elevation. Several wells near Pink Hill and in New Hanover County show little evidence of perching above the Bh with or without the dense layer, and the water table apparently fluctuates freely within or below these horizons (Daniels et al., in press).

The local distribution of Bh horizons also suggests movement of carbon by ground water. The Bh horizons do not penetrate clay lenses, the deeper finer textured Tertiary and Cretaceous beds, or the basal gleyed sands of the Sunderland morphostratigraphic unit (Fig. 4). The large differences in hydraulic conductivity between the sands and clays plus the abundant outlets for ground water in the overlying sands suggests that little water moves through these clays; consequently, they have little carbon. The gleyed sands (olive or greenish gray colors), on the other hand, are as permeable as the overlying gray sands and probably more permeable than the carbon enriched sands. The permeability of the gleyed and gray sands should be similar because the grain-size distribution is the same. The gleyed sands always have measurable amounts of ferrous and free iron whereas the gray sands have little ferrous or free iron (Daniels et al., 1961). Thus the gray sands probably are gleyed sands with the free iron removed because there is no evidence of a sedimentary discontinuity between these sands of different colors. The gleyed sands are found only at the base of the deposit in the Pink Hill area and in areas near valley side drainages where the ground-water streamlines would be rising to the local outlet. This suggests that little ground water is moving through these sands, primarily because the streamlines are not affecting these areas. The shape of the streamlines is controlled by local factors such as bed or formation hydraulic conductivity, bed configuration, and placement of outlets. Thus, wherever ground water is free to move in the wet surficial sands, Bh or humate horizons are found but they are absent where ground water movement is restricted, either by an abrupt change in hydraulic conductivity or configuration of the flow streamlines. In a landscape several meters above sea level such as that shown in Figure 5, a rise and fall of sea level will have little to do with formation of Bh horizons so long as dissection does not lower the water table either in the surficial or the underlying sediments.

The factors causing the carbon to precipitate in the sands are not fully understood. Whatever process is involved must start with fulvic acid, which is precipitated either as fulvic acids or as humic acids

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on and between sand grains. The changing humic/fulvic acid ratios with depth is evidence that polymerization is an important process in Bh formation.

Chemical precipitation of carbon by cations or changes in pH in particularly attractive because it is known to be taking place now in other places (Swanson and Palacas, 1965). The only requirement is that the factors responsible for precipitation remain in the system long enough to insure polymerization to less soluble compounds. Once this has taken place, the cations or other factors contributing to the pH changes could be removed by leaching, leaving a carbon-rich system incapable of precipitating more carbon. This condition is very much like that of the present Bh horizons near Pink Hill (Table 3).

A second method of accumulation is organo-mineral bonding, which is controlled by surface area. Possible reactants are clay minerals or broken silica bonds on quartz grain surfaces. Strong organo-mineral bonding does occur; the clay fraction of Bh horizons remains dark after several peroxide and dispersion treatments and the resulting clay is water repellent and readily adheres to glass. Organo-sesquioxides dominate the Bh horizons of northern soils (Schnitzer and Desjardins, 1969; Brydon and Shimock, 1972) where amorphous and migrating silica are found and can be supplied by weatherable minerals. But in the Pink Hill area, the soils and sediments are dominantly quartz without iron and with only small quantities of exchangeable aluminum. Organic bonding in the sediments we studied would be limited to the quartz mineral grain surface.

One problem with organo-mineral bonding is that one would expect the amount of carbon retained to be related to surface area. Clays, or permeable clayey soils should have the most carbon. This is not the relation found. Soils with more than 6-8 percent clay do not have Bh horizons. But unpublished data show that as much or more carbon in the form of fulvic acid is available in the water entering the system at 10 cm in the clayey soils as in sandy soils with thick Bh horizons. The carbon entering the system is not retained in the more clayey soils, nor is it found in the shallow or deep ground water within or under these soils. Oxidation of carbon apparently equals additions in the soils with more than about 8 percent clay, but in soils with less clay much of the carbon moves into and through the system with the ground water.

SUMMARY

The Bh or humate horizons studied in North Carolina result from post-depositional modification of wet sandy sediments by downward translocation of carbon in the form of fulvic acid from a subaerial surface supporting plants. The carbon apparently moves with the ground water and anything affecting ground water movement influences the distribution and thickness of Bh horizons. Sufficient carbon is available

to replenish the system every 3500 to 28,000 years.

The chemistry of the Bh horizon is dominated by organic carbon with aluminum as the major exchangeable cation. Iron is essentially absent and there are only very small amounts of calcium, magnesium, and potassium.

Both chemical and mineral bonding mechanisms can be responsible for precipitation of the organic carbon. If chemical precipitation is the dominant process, the cations causing the flocculation are now gone from the system. If mineral bonding is the dominant process, broken Si bonds on quartz grains and amorphous silica probably are the dominant factor. Neither idea is completely satisfactory, although either can be used to explain the apparent low reactivity of the system to modern carbon.

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EFFECTS OF WEATHERING ON THE CHEMICAL AND HEAVY

MINERAL COMPOSITION AND PHYSICAL PROPERTIES OF

PHOSPHATE PEBBLES FROM THE BONE VALLEY FORMATION

OF FLORIDA

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ABSTRACT

Differently colored pebbles of Bone Valley phosphate were separated into black, brown, gray, buff and white fractions to study chemical, mineralogical and physical variations resulting from differential weathering. Dark color fractions represent a low degree of weathering. As weathering increases, the calcium, phosphorus, aluminum, flourine, barium, uranium and zinc contents and F/P_2O_5 and U/CaO ratios rise, and decreases in iron, organic carbon, sodium, sulfate, arsenic, strontium and nickel contents and the CaO/P_2O_5 ratio occur. Carbon dioxide and magnesium show increased concentrations from partial weathering and decreased concentrations from more extensive weathering. These chemical trends are related to the mode of occurrence of the constituents in the phosphate pebbles. Weathering also resulted in replacement of pyrite and marcasite by goethite, which was then removed during more extensive weathering, as were metallic copper, garnet and epidote. Zircon, ilmenite, and kyanite-sillimanite were enriched with high degrees of weathering; tourmaline and staurolite show variable relationships to the degree of weathering. Variations in the physical properties of the pebbles--porosity, surface area, bulk density and specific gravity--are related to differential degrees of weathering.

INTRODUCTION

Sedimentary phosphates, such as those of the Bone Valley Formation of Florida, are geochemically complex mineral deposits. There are at least three basic reasons for this complexity. The structure of francolite, $(Ca_{10}(PO_4)_{6-x}(CO_3)_x(F, OH)_{2+x})$, the dominant phosphate

mineral in the deposits, allows a variety of ions to substitute in each of its principal host sites (Altschuler and all, 1967; Borneman-Starynke-vich and Belov, 1940; Gulbrandsen, 1966; Palache and all, 1951). Also the pebbles are impure, containing many phases such as clays, iron oxides, ferrous minerals, feldspars, quartz, carbonates, secondary aluminum phosphates, heavy minerals and organic carbon (Altschuler and all, 1958; Gulbrandsen, 1966; Krauskopf, 1955; Stow, 1969; Swanson and Legal, 1967). Some of these phases may concentrate trace metals.

Thirdly, weathering and secondary alteration have affected the deposits, compounding their geochemical complexity through the addition and/or removal of constituents and the replacement of apatite by secondary minerals. It is generally agreed that weathering has caused darker (black or brown) phosphate pebbles to be altered to lighter color-ed (white or buff) pebbles in the southeastern U.S. (Altschuler and all, 1958; Stow, 1969; Espenshade and Spencer, 1963; Smith and Whitlatch, 1940; Olson, 1966; Malde, 1959). Altschuler (1973) has reviewed information on weathering of phosphates; his paper contains an excellent bibliography.

The aim of this paper is to expand on the previous work and to offer additional information on the chemical, mineralogical and physical changes that accompany the weathering and color changes of the Bone Valley Formation pebbles. The greatest mineralogical emphasis has been placed on the variations in the type and abundance of heavy minerals contained in the pebbles.

The Bone Valley Formation (reworked, Pliocene) represents the weathering and transgressive reworking, with associated phosphatization, of the underlying phosphate-rich Miocene Hawthorn Formation (Altschuler and all, 1964). Weathering occurred during reworking; also since Pliocene times there has been additional weathering, increasing upward in the section which is capped by a leached zone of lateritic weathering and secondary (calcium) aluminum phosphate enrichment. Below the leached zone occurs the commercially important matrix zone from which the samples for this investigation were obtained.

Samples came from the Payne Creek Mine in southwestern Polk County, Florida (T32S, R24E, Sec. 33). The color fractions were obtained from a composite sample. This sample was taken continuously from all units from the top to the bottom of the matrix, during mining for one month. The composite sampling was chosen in order to establish general characteristics of the differently colored pebbles and to minimize variations among pebbles within a group, which might mask general differences among color groups. The particle size of the pebbles selected for study was from -6 to +14 mesh; this size corresponds to the regular grade of most phosphate producers. The results of this study may also be applicable to other commercial size fractions (concentrate, fine and coarse). The data presented herein have economic importance to the phosphoric acid industry because the wet acid

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processing behavior of phosphates is determined by the chemical, mineralogical and physical characteristics of the rock.

PROCEDURES AND RESULTS

Pebbles were washed to remove extraneous clay, sand, and carbonate and separated into five fractions on the basis of color: black (N2), brown (5YR3/4), gray (N5), buff (5Y7/2), and white (N9). Each color fraction was analyzed for calcium, phosphorus, fluorine, aluminum, magnesium, total iron, carbon as carbon dioxide and sulfate sulfur by the standard methods of the Association of Florida Phosphate Chemists (AFPC) (1960). Atomic absorption spectrophotometry was used for analysis of barium, sodium, nickel, strontium, and zinc; uranium was determined by x-ray fluorescence. Analytical procedures for arsenic and organic carbon are noted by Stow (1969). All chemical analyses were done in triplicate and figures reported represent averages of the three analyses. Analytical accuracy is within $\pm$ 3 percent except for carbon ($\pm$ 15 percent) and carbon dioxide ($\pm$ 5 percent). Standards used were NBS-120a and samples supplied by the AFPC. Upon crushing the samples for analysis, every effort was made to insure that pebbles were homogeneously colored throughout. Chemical data are presented in Figures 1-4.

Heavy minerals were recovered by dissolving about 500 grams of each color fraction in cold dilute HCl (1:10) and separating the heavy minerals from the lighter density insolubles (predominantly quartz) by use of tetrabromoethane. Examination of each suite of heavy minerals was made microscopically, aided by x-ray diffraction for the identification of some minerals. Counts for 450 grains were made for each sample; data are presented in Figure 5.

Physical properties measured for each color fraction were: percent porosity, surface area, specific gravity and bulk density. Percent porosity was determined by use of a Boyle's law porosimeter and mercury displacement. Surface area was determined by single point nitrogen absorption and specific gravity and bulk density were measured by water displacement. All measurements were made on unground pebbles (Figure 6).

The results are presented in three categories: chemical, heavy mineralogical and physical variations among the five color fractions. Based on the data presented and the previously published reports, color fractions are arranged in an order representing increased weathering. The sequence most indicative of increased weathering among the five color fractions is: black to gray to white, and brown to buff to white. The exact relationship between the two "parent" fractions--black and brown--is not entirely clear. There is evidence to indicate that black pebbles represent the most unweathered of the color fractions and to suggest that brown pebbles result from slight weathering of black pebbles.
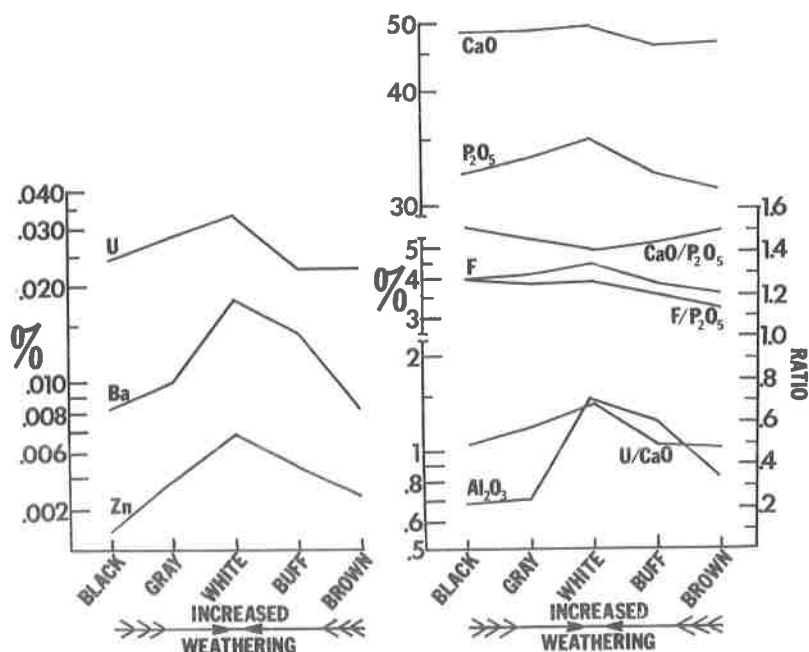
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Figure 1. Enrichment of chemical constituents during weathering of the color fractions of Bone Valley phosphate.

As weathering has progressed, brown pebbles have been altered to buff and ultimately to white pebbles, and the primary black pebbles, having not been altered to brown, were changed to gray and, also, ultimately to white pebbles. Hence both black and brown fractions are treated as "parent" fractions although it is realized that the black pebbles are less weathered than are the brown.

WEATHERING AND CHEMICAL VARIATIONS

The discussion of the variations of elements among different color fractions is divided into two groups; those elements which show an enrichment with weathering (Figures 1 and 2) and those which show a decrease (Figures 3 and 4).

Enrichment of Constituents

The three major components of francolite--calcium, phosphorus, and fluorine--increase during weathering (Figure 1), although the calcium increase is neither consistent nor well defined. Increases are expected due to the relative insolubility of the francolite, the supergene
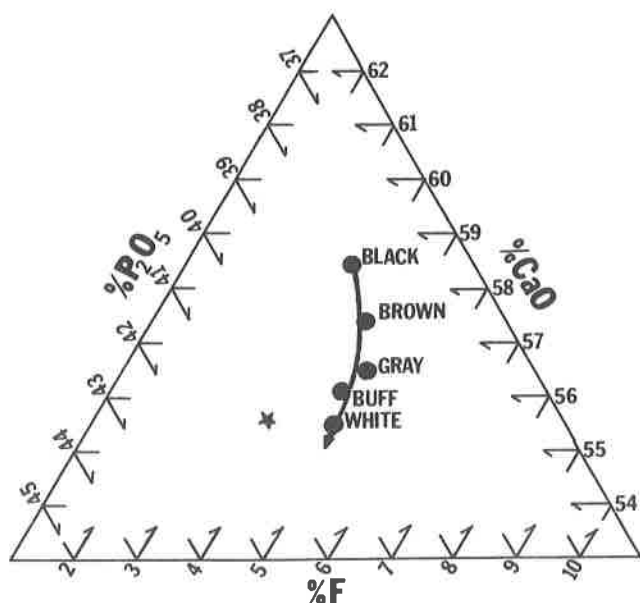
Figure 2.   Variation in P_2O_5, CaO and F contents
of the Bone Valley color fractions--
constituents have been recalculated to
equal 100 percent. Star represents
the composition of $Ca_{10}(PO_4)_6F_2$ and
the arrow shows the general direction
of increased weathering.

enrichment of secondary (calcium) aluminum phosphates, and ground-
water enrichment of fluorine. Rates of increase of the three consti-
tuents are, however, different. Fluorine is known to increase in phos-
phates due to contact with fluorine-bearing groundwaters (McConnell,
1962; Reynolds and all, 1929). The F/P_2O_5 ratio shows a slight but
consistent increase from brown to white pebbles, from 0. 114 to 0. 126,
indicating a preferential uptake of fluorine during weathering.   The
ratio is constant among the black, gray, and white fractions, indicating
that fluorine has been introduced into these fractions at the same rate
as phosphorus. This constancy, as opposed to the increase among the
brown, buff and white pebbles, may be due to the proposed different
sequences of weathering from the "parent" fractions, black and brown.
   The CaO/P_2O_5 ratio decreases from dark to light-colored peb-
bles but always remains in excess of the stoichiometric figure of 1. 31
for fluorapatite. This decrease occurs in spite of the fact that both
calcium and phosphorus increase during weathering. The relative dif-
ference in the rates of concentration of calcium and phosphorus can be
explained by secondary phosphatization associated with the formation

of highly leached phosphates. X-ray diffraction of the fractions reveal-
ed crandallite, $(CaAl_3(PO_4)_2(OH)_5 \cdot H_2O)$, and small amounts of wavel-
lite, $(Al_3(OH)_3(PO_4)_2 \cdot 5H_2O)$, in white pebbles; the dominant phosphate
was francolite. Crandallite and ultimately wavellite replace apatite
minerals and are indicative of lateritic leaching (Altschuler and all,
1964; Altschuler and all, 1956). The CaO/P_2O_5 ratio for crandallite
is only 0.40 and wavellite contains no calcium; therefore introduction
of these minerals correlates with the decrease in the CaO/P_2O_5 ratio
during weathering.

When these three constituents--calcium, phosphorus, and fluo-
rine--are plotted on a ternary graph (Figure 2), different color fractions
exhibit a trend from unweathered black to highly weathered white peb-
bles. The curved line represents the best fit for the five data points;
the stoichiometric composition of fluorapatite is marked by the star.
During weathering there is a relative increase in the phosphorus and
fluorine contents. The highest phosphorus content occurs in the highly
weathered white and buff fractions, less than the stoichiometric amount;
fluorine in excess of the stoichiometric amount is noted for all fractions
except black, the most unweathered. The fluorine content reaches a
maximum and levels off at slightly less than 5 percent. The decrease
in calcium and increases in phosphorus and fluorine exemplify the ef-
fects of weathering, which include fluoridation and the formation of
secondary calcium-poor aluminum phosphates, rich in phosphorus.

Aluminum occurs in phosphate pebbles chiefly as clays or as
secondary aluminum phosphates in the more weathered pebbles
(Altschuler and all, 1956; Swanson and Legal, 1967). Also aluminum
may substitute for calcium or phosphorus in the structure of synthetic
apatites (Fisher and McConnell, 1969). Aluminum increases during
weathering by a factor of about 2 from black (0.69% Al_2O_3) pebbles to
white (1.47% Al_2O_3) pebbles (Figure 1). The presence of crandallite
and wavellite, both rich in aluminum (36.93 and 37.11% Al_2O_3, re-
spectively),has been discussed for the white pebbles. The high enrich-
ment factor (2) for aluminum suggests introduction from outside the
pebble rather than simply a residual buildup from solution of more
soluble components. X-ray diffraction of the -325 mesh acid insoluble
portions of each color fraction showed montmorillonite (16-20% Al_2O_3)
to be the dominant clay in black, gray, and brown pebbles; kaolinite
(40% Al_2O_3) dominated in buff and white pebbles. The transformation
of montmorillonite to kaolinite by extensive weathering of the phosphates
has been fully described by Altschuler and all (1963).

Uranium occurs chiefly as a substitution for calcium in phos-
phorites (Cathcart, 1956; Davidson and Atkin, 1953). Altschuler and
all (1958) have correlated the enrichment of uranium in the leached zone
of the Bone Valley Formation with weathering; uranium replaces calcium
in the apatite structure and possibly in crandallite. In the five color
fractions the uranium content increases from 0.0225 to 0.0330 percent
from dark to white pebbles. The U/CaO ratio also increases from about
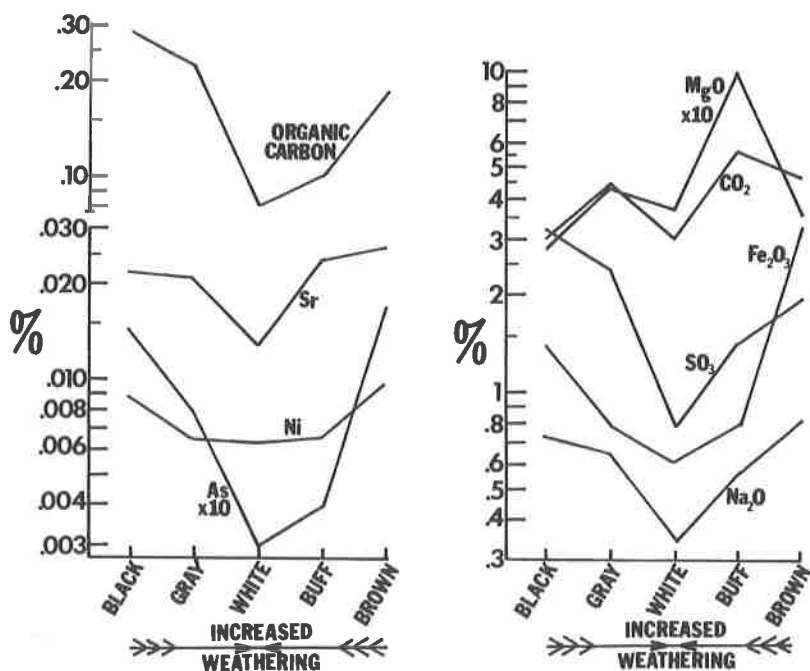
Figure 3. Depletion of chemical constituents during weather-
ing of the color fractions of Bone Valley phosphate.

0.00049 in dark fractions to 0.00068 in the white fraction, indicating
uptake of uranium relative to calcium during weathering and a preferen-
tial replacement of calcium by uranium in francolite and possibly
crandallite.

The increase of barium by a factor of 2.2 from 0.0081 (brown,
black) to 0.0180 percent (white), also indicates concentration of barium
with increased weathering compared to its possible host ion, calcium.
Barium has been noted to substitute for calcium in synthetic apatites
(Kriedler, 1967). Frondel (1958) has studied the scavenging of barium
by crandallite. Crandallite contained in white pebbles may aid in the
concentration of barium.

Zinc, as in the case of most other divalent metals, is expected
to occur in the calcium site of the apatite minerals although it is con-
centrated by organic matter in the Phosphoria Formation (Krauskopf,
1955; Gulbrandsen, 1966). The increase of zinc from darker to lighter
colored pebbles of the Bone Valley Formation is in contrast to the de-
crease in organic carbon (Figure 3); the increase does, however, cor-
relate generally with the enrichment of calcium, a possible host. Like
other cations, zinc is enriched to a greater degree than is calcium dur-
ing weathering; the enrichment is by a factor of about 2. Zinc is small-
er (0.74Å) than calcium (0.99Å) and should be more tightly bound in the

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ancolite lattice, thereby explaining its greater rate of enrichment dur-
g weathering.

Depletion of Constituents

Magnesium and carbon dioxide have multiple occurrences in apa-
tites and phosphates. Magnesium may substitute for calcium in limited
amounts (Palache and all, 1951), may occur as carbonate (Smith and
Lehr, 1966), or may be present in clay (Swanson and Legal, 1967).
Carbon dioxide may be as calcium and/or magnesium carbonate or as a
coupled substitution with fluorine for phosphate (Borneman-Starynkevich
and Belov, 1940; Smith and Lehr, 1966). The trends exhibited by mag-
nesium and carbon dioxide in the pebbles are irregular, showing partial
enrichment with partial weathering and depletion during more complete
weathering (Figure 3). Greatest enrichments occur in the buff and gray
pebbles. The similarities between magnesium and carbon dioxide data
suggest that these components may be introduced as magnesium car-
bonate, especially in the buff pebbles. No corresponding increase in
calcium (Figure 1) is noted. Because the exact modes of occurrence
are unknown, and because there may also be inclusions of carbonate
minerals within the pebbles, complete interpretation of the data is im-
possible. Data on the carbonate content of the leached zone of the Bone
Valley Formation have shown a sharp decrease upward in the section,
correlating with increasing degrees of weathering and leaching (Alt-
schuler and all, 1964).

Iron, arsenic and organic carbon are closely related and all de-
crease during weathering. Arsenic is concentrated by iron oxides in
brown and buff pebbles and appears at least partly associated with or-
ganic carbon in black and gray pebbles (Stow, 1969); brown and buff
colors are attributed to iron oxides and black and gray colors are attri-
buted to organic carbon (Stow, 1969; 1970; Swanson and Legal, 1967).
Although iron oxide is the dominant chromophore in brown pebbles
(3.22% Fe_2O_3) and organic carbon is the chromophore in black pebbles
(0.28% C), arsenic is of roughly equivalent amounts in the relatively
unweathered brown and black pebbles (0.0017 and 0.0015%, respectively).
The uniform decrease of arsenic to 0.0003 percent in the white fraction
is a result of the combined leaching of iron oxides and organic carbon.
This depletion of arsenic by a factor of slightly over 5 is in accord with
iron and organic carbon decreases, which are by factors of 5 and 4, re-
spectively.

Sodium and sulfate enter the apatite structure in coupled substi-
tution; sodium substitutes for calcium and sulfate substitutes for phos-
phate at roughly a 1:1 atomic ratio of Na:S in the Phosphoria Formation
(Gulbrandsen, 1966); McConnell (1937) reports the substitution of sul-
fate for phosphate in the apatite structure. Both components are con-
sistently leached during weathering of the Bone Valley Formation phos-
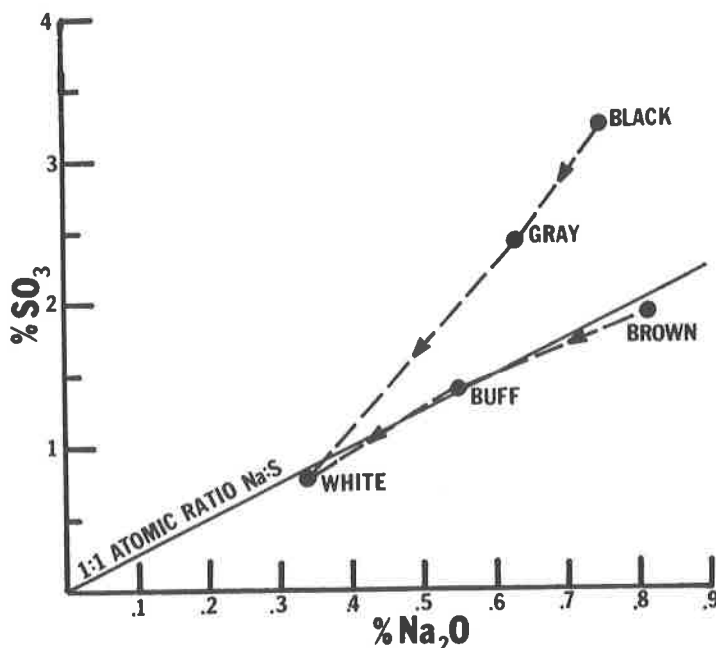phates (Figure 3). Figure 4 shows a distinct grouping of pebbles with

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Figure 4. Depletion of sodium (Na_2O) and sulfate
(SO_3) during weathering of the color fractions
of the Bone Valley phosphate.

black and gray separated from brown and buff fractions. A similar grouping was noted in the study of arsenic and carbon in the Bone Valley Formation phosphates (Stow, 1969). Brown pebbles contain sodium and sulfate at a 1:1 atomic ratio, a ratio which is retained during weathering through buff to white pebbles. In contrast, the black fraction contains sulfate in excess of this 1:1 ratio. As the pebbles are altered to gray and, ultimately, to white colors, sulfate is preferentially leached until a 1:1 ratio of Na:S is achieved. Black and gray pebbles contain iron sulfides (see following section of this paper). Partial oxidation of these sulfides may explain the relatively high amounts of sulfate in the fractions.

The occurrence of strontium in the apatite lattice is not definitely established but it is reasonable to expect that it substitutes for calcium (Palache and all, 1951). Kriedler (1967) has noted the substitution of strontium for calcium in synthetic apatites. Strontium decreases during weathering, with a large loss in the white pebbles. This depletion is not in accord with the supposed substitution for calcium, which increases in the lighter colored pebbles (Figure 1). Frondel (1958) has discussed the scavenging effect that crandallite (present in the white pebbles) has for strontium in neutral or slightly alkaline solutions; this concentration by scavenging decreases, but does not cease, below pH

6.5. The groundwaters in the Bone Valley Formation are acidic (Cathcart, 1956); scavenged strontium may be preferentially leached by these acidic waters, resulting in the decrease during weathering. Available data are not sufficient, however, to verify this hypothesis and more detailed study on stratigraphically-selected samples is needed to explore the occurrence of strontium.

Nickel is concentrated by organic matter in Phosphoria phosphates (Gulbrandsen, 1966; Krauskopf, 1955). Nickel may also be adsorbed on iron oxide, thereby explaining its high abundance in the brown pebbles (0.0098% Ni; 3.22% Fe_2O_3) of the Bone Valley Formation. Black pebbles contain the next greatest concentration of Ni (0.0090%) and are also rich in iron (1.38% Fe_2O_3) as well as organic carbon (0.28%). Nickel decreases to 0.0065 percent in lighter colored pebbles and is removed less readily than either organic carbon or iron oxide, its possible host phases. Gray, buff and white fractions contain the least nickel as well as containing the least iron and, in the case of white and buff pebbles, the lowest amounts of carbon.

WEATHERING AND HEAVY MINERAL VARIATIONS

Variations in the relative amounts of different heavy minerals in the color fractions may reflect intensity of weathering. It is assumed that prior to weathering all five color fractions contained a similar heavy mineral suite.

Six minerals--metallic copper, pyrite, marcasite, goethite, garnet and epidote--are found to decrease during weathering (Figure 5A). Metallic copper (not plotted), pyrite and marcasite have been observed visually and identified by x-ray diffraction in the acid insoluble heavy mineral fraction of black and gray pebbles. Copper, in trace amounts, occurs as flattened, elongate, hackly wires. Special care was taken to insure that its presence was not the result of laboratory contamination. Recovery of heavy minerals from two additional 300-gram samples of black pebbles was carried out after copper was noted in the first heavy mineral separate. Acid dissolution, washing, sieving with nylon mesh, etc. were carefully performed under closed conditions under a polyethylene cover; copper metal was again found in both samples; therefore, the copper is interpreted to be a constituent of the pebbles. Pyrite occurs as striated intergrown cubes and marcasite occurs as finely crystalline masses. Metallic copper, pyrite and marcasite in black pebbles are indicative of a lack of oxidative weathering for this color fraction. The decrease in the abundance of the iron sulfides from black pebbles to gray pebbles and their absence in white pebbles correlates with the increasing effects of weathering.

Goethite, identified by x-ray diffraction, also decreases during weathering but is found principally in brown pebbles. The goethite occurs as pseudomorphs after striated intergrown cubes of pyrite and
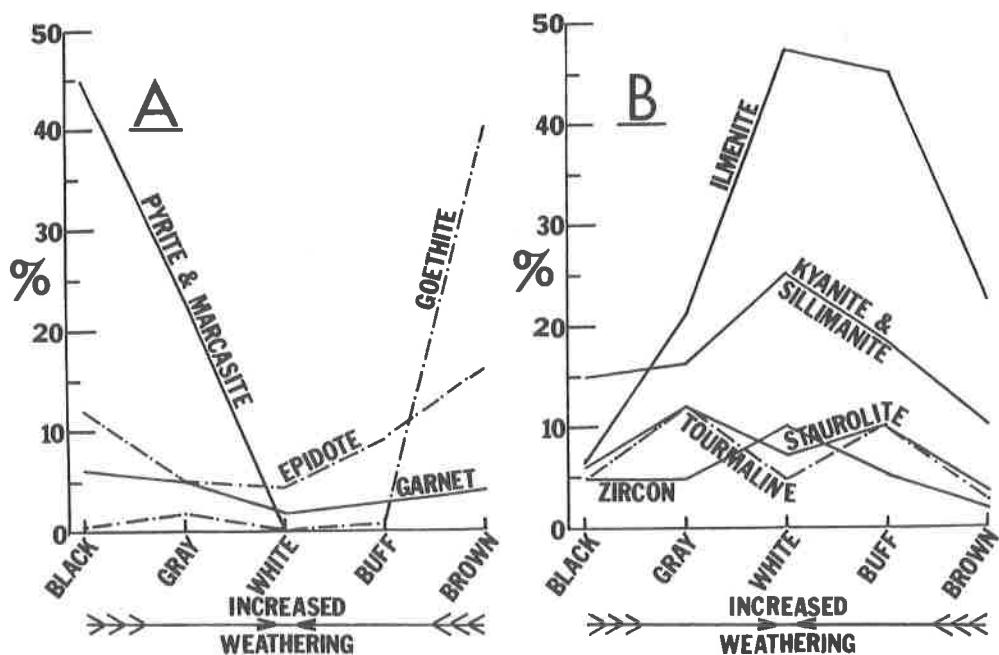
Figure 5. Depletion (A) and enrichment (B) of heavy minerals contained in the color fractions during weathering of the Bone Valley phosphate.

finely crystalline masses of iron sulfide and is morphologically identical to the iron sulfides of the black and gray pebbles. This similar morphology suggests that brown pebbles were originally black in color and have undergone oxidative weathering without removal of iron. In fact, brown pebbles contain more iron than do black (Figure 4). If brown pebbles were originally black, iron has been added with partial weathering, possibly due to the reaction of acidic groundwaters (containing iron) and francolite in a fashion similar to that noted by Altschuler and all (1956) in the lateritic weathering of the Bone Valley Formation. Garnet and epidote, both unstable under weathering conditions (Altschuler and all, 1956; Dryden and Dryden, 1946), decrease during weathering. The decrease of these six minerals correlates well with the increase in porosity (Figure 6) and the greater possibility for contact with weathering agents.

Some minerals increase in the lighter colored fractions (Figure 5B). These minerals--ilmenite, kyanite-sillimanite and zircon-- weather slowly (Dryden and Dryden, 1946; Leith and Craig, 1965) so their increases are expected. Amounts of staurolite and tourmaline increase in gray and buff pebbles, but decrease in white pebbles.
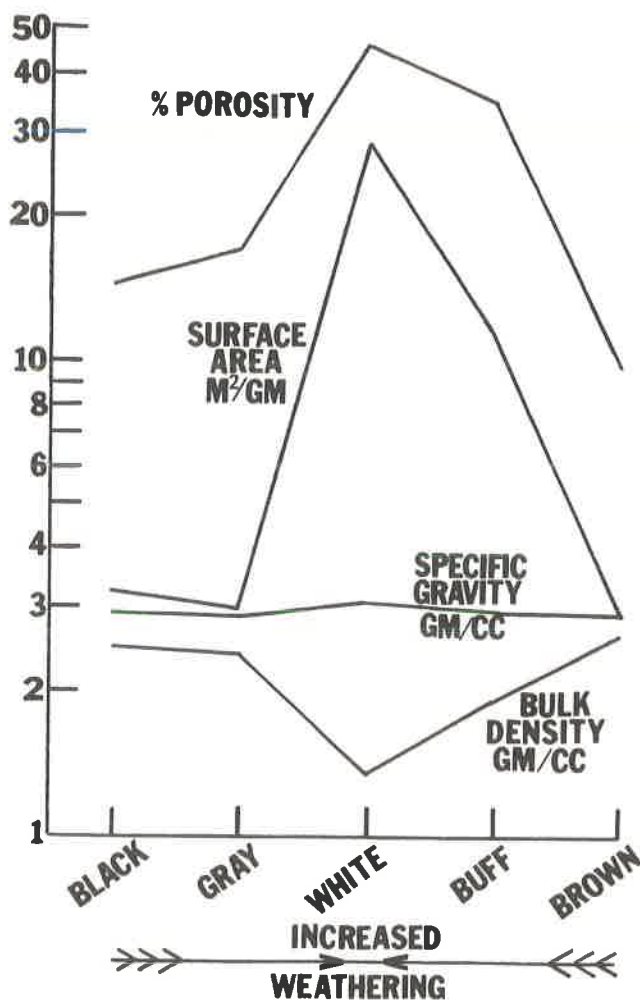
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Figure 6. Variation in the physical properties
during weathering of the Bone Valley
phosphate color fractions.

WEATHERING AND PHYSICAL PROPERTY VARIATIONS

The four physical properties measured--percent porosity, sur-
face area, bulk density, and specific gravity--exhibit consistent trends
from dark to light colored pebbles (Figure 6). Visual examination of
the pebbles verifies some of these physical data; black, brown and gray
pebbles are hard, non-porous, dense and often shiny. White pebbles
are soft, porous, less dense and have a dull, pitted appearance. Buff
pebbles are intermediate in appearance between white and brown.

The percent porosity figures reflect visual observations and verify the weathered nature of the lighter colored fractions. Note the extremely high porosity (46%) of white pebbles as compared to the 9.9 percent porosity of brown pebbles (Figure 6), which have the lowest porosity. The low porosity of brown pebbles may result from secondary introduction of iron oxides, as discussed above. Surface area varies with porosity and reflects almost a 10-fold increase from brown, gray, and black pebbles to white pebbles. These surface area data agree reasonably well with those of Hill and all (1954) for Florida phosphates. Bulk density, the density of pebbles with pore spaces filled with air, exhibits the expected trend inversely proportional to percent porosity. Changes in specific gravity among the pebbles are not large, but are significant. White pebbles, with the greatest specific gravity, are enriched in calcium fluorphosphate (Figure 1), the major constituent of the samples. The specific gravities of carbonate apatite (3.1-3.2) and crandallite (2.8-2.9) are greater than that of any other major constituent, such as the carbonates (calcite-2.72) or quartz (2.65). Therefore, the increase in specific gravity of lighter colored fractions reflects the increase in the phosphate mineral content of the pebbles and correlates with increase in calcium, phosphorus and fluorine contents (Figure 1).

SUMMARY

Weathering of Bone Valley Formation phosphates has resulted in color changes from dark (black, brown) colors to light colors, with white pebbles the most weathered of the color fractions; gray and buff represent intermediate weathering products. Inherent in the color changes have been a number of chemical, mineralogical and physical changes. The calcium, phosphorus, flourine, aluminum, uranium, barium and zinc concentrations and the F/P_2O_5 and U/CaO ratios have increased during weathering. The increases in calcium, phosphorus and fluorine correspond to the increase in the relatively insoluble francolite, the addition of fluorine to the francolite lattice and the introduction of crandallite during weathering. Secondary aluminum phosphates (dominantly crandallite) and kaolinite result in increases in aluminum; uranium appears to be preferentially concentrated in the calcium position of phosphate minerals with weathering. Barium may have been scavenged by crandallite; zinc appears to have been more slowly removed than its host, calcium, in highly weathered fractions. The concentrations of sodium, sulfate, iron, organic carbon, strontium, arsenic and nickel and the CaO/P_2O_5 ratio decrease during weathering. Sodium and sulfate have been removed at a 1:1 atomic ratio in the brown and buff pebbles, but sulfate has been preferentially removed from the black and gray pebbles in which it is present in greater than the 1:1 ratio. Strontium possibly has been leached due to the acidic pH of the

groundwaters; nickel and arsenic decrease during weathering as do their proposed host constituents, iron oxide and organic carbon. Partial weathering results in an increase in the carbon dioxide and magnesium contents, especially in buff pebbles, followed by depletion during more complete weathering.

Heavy mineral data show decreases in the amount of metallic copper, garnet and epidote during increased weathering. Unweathered pyrite and marcasite in black (and gray) fractions have been replaced by goethite in brown (and buff) fractions. Relatively slowly-weathered minerals--ilmenite, zircon and kyanite-sillimanite--increase with weathering and are most abundant in the heavy mineral suite of white pebbles.

Physical property variations correlate well with weathering and observed chemical-mineralogical changes. Porosity, surface area and specific gravity of the pebbles increase as colors become lighter and as weathering increases; bulk density, inversely proportional to porosity, decreases.

These changes show that lighter colored pebbles have resulted from weathering of the darker pebbles. Black pebbles represent the most unweathered and appear to have given rise to the other color fractions through weathering. Brown pebbles, from which the buff and white are derived, seem to have originated through oxidative weathering of black pebbles. Resulting from this oxidative weathering have been increases in the iron oxide content, replacement of pyrite and marcasite by geothite and a decrease in the percent porosity.

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HEAT FLOW AT DUCKTOWN, TENNESSEE

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ABSTRACT

Thermal gradient measurements obtained with a thermistor probe in conjunction with thermal conductivity analyses made with a divided-bar apparatus of core samples from a 290-meter deep borehole at Ducktown, Tennessee, give a heat flow of 0.69 ± 0.09 μ cal/cm^2 sec. This value represents the first determination of heat flux in the Blue Ridge and is in agreement with a postulated low heat flow anomaly in the southern Appalachians. Low heat flow values from eastern Tennessee (Blue Ridge and Valley and Ridge) and the southern Piedmont are considered indicative of a separate subprovince of the eastern United States thermal province.

INTRODUCTION

Measurements of terrestrial heat flow in the eastern United States are neither abundant nor well-dispersed. A summary of values presented by Diment et al. (1972) reveals a concentration of measurements in the northeastern United States, but only sporadic data in the southeast. Five measurements of heat flow in the southern Appalachians average less than one heat flow unit (1 hfu = μ cal/cm^2 sec). Recent work in Virginia (Reiter and Costain, 1973; Costain et al., 1976) has yielded somewhat higher values although they may be influenced by groundwater circulation.

Directly measured temperatures in a borehole (Cherokee no. 500) situated approximately 3 km south of Ducktown, Tennessee (Figure 1), and laboratory determinations of thermal conductivity on core specimens from the same borehole were used to calculate a heat flow of 0.69 hfu. This value represents the first determination of heat flow for the Blue Ridge physiographic province and is comparable to the 0.73 hfu measurement from Oak Ridge (Diment and Robertson, 1963).

The Ducktown mining district contains massive copper sulfide deposits and is located near the western boundary of the Blue Ridge in southeastern Tennessee. The geology and ore deposits of the district have been well described by Emmons and Laney (1926) and Magee (1968).
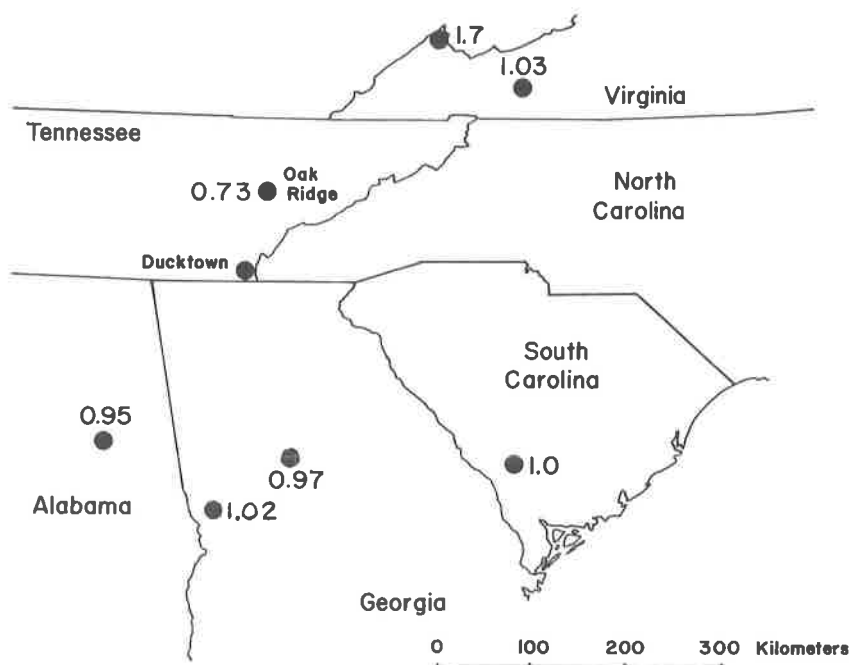
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Figure 1. Location map with heat flow values for the southern Appalachians. Data from Diment and Robertson (1963), Diment et al. (1965), Roy et al. (1968a), and Reiter and Costain (1973).

In general, the rocks are coarse, clastic metasediments of the late Precambrian Great Smokey Group, Copperhill Formation. The rock units are highly faulted and folded into broad anticlines and synclines. The core samples available for this study were primarily mica schist and gneiss. Radiometric dating of rocks from the Ducktown district (Fullagar and Bottino, 1970; Dallmeyer, 1975) suggest that metamorphism and sulfide mineralization occurred approximately 475 m. y. ago with no subsequent thermal activity.

Acknowledgments

TEMPERATURE MEASUREMENTS

Borehole temperatures were measured at discrete depths with a thermistor probe assembly coupled to a 1000 meter, four-conductor cable. A Mueller-type Wheatstone bridge, similar to that described by Roy et al. (1968a), with an Electroscientific Industries six-decade variable resistor and a Leeds and Northrup 2437 null detector was used to match thermistor resistances. The system was calibrated at $10°$ intervals from $10°$ to $40°$ C using a Hewlett-Packard quartz thermometer. The estimated accuracy of individual temperature measurements is better than $\pm 0.1°C$. The accuracy of successive temperature differentials used for gradient values is considered to be much better, perhaps $0.01°C/km$.

Figure 2 shows the borehole temperature values plotted as a function of depth below the ground surface. Surface elevation of the Cherokee no. 500 borehole (Lat. $35° 00' 15''N.$, Long. $84° 23' 20''W.$) is 510 meters. The temperature-depth profile displays temperature inversions at 180 m and 260 m which may be indicative of water flow into the hole at those depths. These phenomena tend to make the observed temperature gradient slightly lower than the actual gradient, but since the inversions are not extensive, the observed value remained a good approximation. The least squares gradient calculated for the depth interval 60-290 m is $8.17 \pm 1.27 (s^2)°C/km$, but over the 100-290 m interval for which core samples were available, the gradient is $10.29 \pm 0.17°C/km$.

Temperature gradients corrected for local topographic variations were calculated using a modification of the method developed by Birch (1950). The differences between average elevations is geographic rings (with radii totaling 1.0 km at 0.1 km intervals) and the surface elevation of the drill hole were determined from topographic maps. Topographically corrected gradients are $8.34 \pm 0.95°C/km$ for 60-290 m and $10.44 \pm 0.16°C/km$ for 100-290 m. This latter value may be compared to uncorrected gradients ranging from 9.0 to $11.6°C/km$ calculated from unpublished ten-year old temperature data from four boreholes in the Ducktown district (R. N. Diffenbach, pers. comm., 1974). Diment and Robertson (1963) measured a gradient of $11.91°C/km$ over the depth range 305-785 m at Oak Ridge, Tennessee (approximately 115 km to the northwest of Ducktown), in the Valley and Ridge Province.

THERMAL CONDUCTIVITY MEASUREMENTS

Thermal conductivity analyses of borehole core samples were made with a divided-bar apparatus similar to that described by Sass
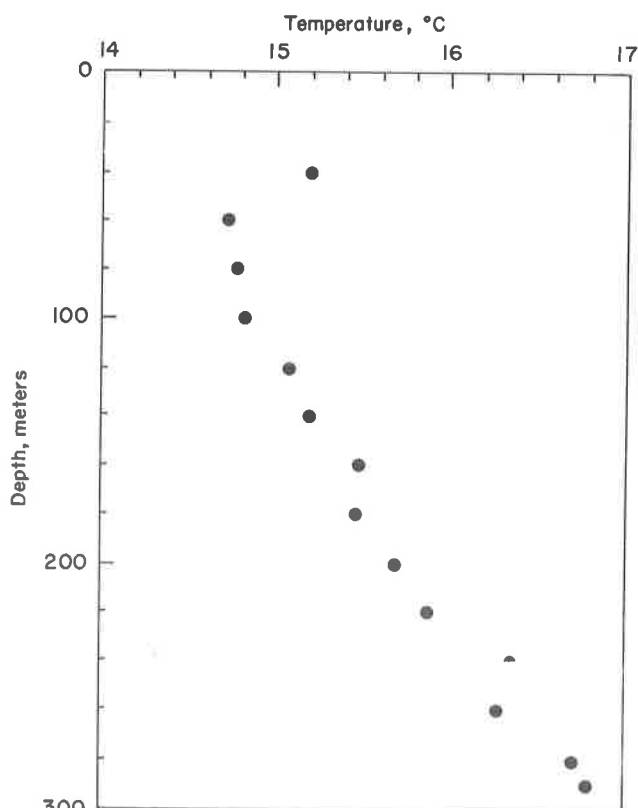
Figure 2. Temperature-depth profile for the Cherokee no. 500 borehole at Ducktown, Tennessee.

et al. (1971). The instrument consists of 3.81 cm diameter upper and lower assemblages of 0.317 cm thick copper disks enclosing 0.635 cm thick lexan disks. Circulating baths were used to establish a temperature differential of approximately 10°C across the specimen and maintain its temperature to within 10°C of its in situ value. Copper-constantan thermocouples were inserted in the copper disks to determine temperature values.

Nine disks approximately 0.5 cm thick and 1.8 cm in diameter were machined from the core samples and vacuum saturated with water. After saturation, the disks were soaked in water for at least two weeks before analyses. Measurements were made with the disks under an axial pressure of 50-100 bars. A thin coating of silicone grease or liquid household detergent was applied to the disks to facilitate thermal contact.

Individual and mean harmonic thermal conductivity values are listed in Table 1. Reproducibility of the conductivity values for

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Table 1. Thermal Conductivity Values.

Depth (m)	Rock Type	Conductivity (mcal/cm sec^{o}C)
142	mica schist	6.01
152	mica schist	7.84
166	mica schist	5.63
174	mica schist and quartz	5.17
191	mica schist	5.26
210	gneiss	11.58
245	mica schist	4.62
258	gneiss	9.89
281	gneiss	9.10
harmonic mean		6.57
stnd. dev. of mean		0.86

calibration standards of fused quartz and natural quartz as well as the borehole samples was better than 3 percent.

DISCUSSION

For a mean harmonic conductivity of 6.57 mcal/cm sec^{o}C and a temperature gradient of 10.44^{o}C/km, a heat flow of 0.69 $\pm$ 0.09 (s.d.) heat flow units is calculated for the depth range 100-290 m using

$$Q = K \, dT/dZ \tag{1}$$

where Q is heat flow, K is thermal conductivity, and dT/dZ is the thermal gradient. Although the relatively high standard deviation tends to minimize any geological interpretation, the similarity of this value to the 0.73 hfu value from Oak Ridge (Diment and Robertson, 1963) is noteworthy. However, an appreciable contrast appears to exist between the Ducktown value and the somewhat higher (1.0 hfu) heat flux determined for the southern Piedmont (Figure 1) from measurements in Alabama (Roy et al., 1968a) and South Carolina (Diment et al., 1965) and estimates in Georgia (Diment and Robertson, 1963).

A linear relationship between surface heat flow, Q, and radioactive heat generation, A, of surficial plutonic rocks has been demonstrated (Birch et al., 1968; Roy et al., 1968b; Lachenbruch, 1968) to be

$$Q = q^* + bA \tag{2}$$

where q* represents the heat flow arising from the lower crust and upper mantle. Roy et al. (1968b) described heat flow provinces as those regions in which q* and b were uniform. Small variations of surface heat flow within a thermal province could therefore be attributed to variations in the radioactive heat generation of surficial rocks.

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The definitive parameters for the Central Plains - Eastern United States thermal province are q* = 0. 8 hfu and b = 7. 5 km (Roy et al. , 1972). These data, however, are derived primarily from measurements in the northern Appalachians. Combs and Simmons (1973) have shown that these values are not consistent with measurements in the midwest and suggest that subdivisions of the originally defined province are justified. If surficial heat flow throughout the eastern United States is a uniform 0. 8 hfu from the lower crust with some variable contribution from upper crustal radioactivity, it is difficult to explain the low heat flow values from the Tennessee Blue Ridge and Valley and Ridge. Recent radioactive heat generation studies (Garvey, 1975) of plutonic rocks from the Georgia Piedmont suggest an average heat generation of about 6. 9 x 10^{-13} cal/cm^3 sec. which, in conjunction with the heat flow values calculated for the southern Piedmont, requires q* and/or b to be different from those values calculated for the eastern United States. The heat flow values from Tennessee, along with other existing data, suggest the existence of a thermal subprovince which includes the southern Blue Ridge and Valley and Ridge, or which may extend throughout the southern Appalachians.

Recent proposed descriptions of the tectonic history of the southern Appalachians (Hatcher, 1972; Odom and Fullagar, 1973) require an assemblage of different lithospheric units for that region, substantiating an expectation of inherently different thermal properties. It seems more reasonable, therefore, to associate anomalously low heat flow values from this area with a separate thermal subprovince in the southeastern United States. As additional heat flow, and particularly heat generation, measurements are made in the eastern United States, new thermal provinces and their boundaries are likely to be located and described.

CONCLUSIONS

The geothermal gradient in the depth range 100-290 m at Ducktown, Tennessee, is 10. 44°C/km after topographic correction. This value, upon combination with a mean harmonic thermal conductivity of 6. 57 mcal/cm sec°C for core samples representative of the 100-290 m depth, yields a heat flow at Ducktown of 0. 69 hfu, which is similar to a previously determined value near Oak Ridge, Tennessee. The anomalously low heat flow values seen in eastern Tennessee and other relatively low values reported for the southeastern United States are interpreted as evidence for a separate thermal province within the eastern United States. This and other provinces may reflect the composite nature proposed for the lithosphere underlying the eastern United States.

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CHARACTERISTICS OF SUSPENDED SEDIMENTS IN

ESTUARIES AND NEARSHORE WATERS OF GEORGIA

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ABSTRACT

Nearshore waters of the Georgia coast carry large concentrations of suspended sediment. The organic-inorganic ratio in these waters is approximately 30:70. Seaward of tidal inlets (in a turbid zone), the relative amount of inorganic material decreases as does the total concentration. Approximately 11 km seaward of the St. Catherine's inlet (the boundary zone) the relative amounts of organic and inorganic material are equal and the total suspended matter reaches a minimum. Further seaward the total concentration increases slightly until leveling off at approximately 30 km offshore. The amount of organic and inorganic material in suspension decreases seaward of the turbid zone, however, the relative amount of organic material increases and levels off when representing 70 percent or more of the total suspended material.

INTRODUCTION

Along the southeast coast of the United States a high density of major rivers transport large loads of suspended sediments into the nearshore waters (Meade, 1969; Meade and Trimble, 1974; Neiheisel and Weaver, 1967). These rivers drain large areas of the Coastal Plain and Piedmont Provinces (Meade, 1969; Meade and Trimble, 1974). Broad lagoonal marshes also contribute significant quantities of plant detritus to the estuarine waters. The upland and marsh sources combine to produce a large "standing load" of suspended sediment in the estuarine and nearshore waters. During stormy periods, resuspension of fine sediments by wave surge also contributes to the suspended sediment concentration. Fetch and wind velocity are important parameters

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The figure contains the following labels:

EARLY FLOOD | EARLY EBB

Marsh lagoon (appears multiple times)

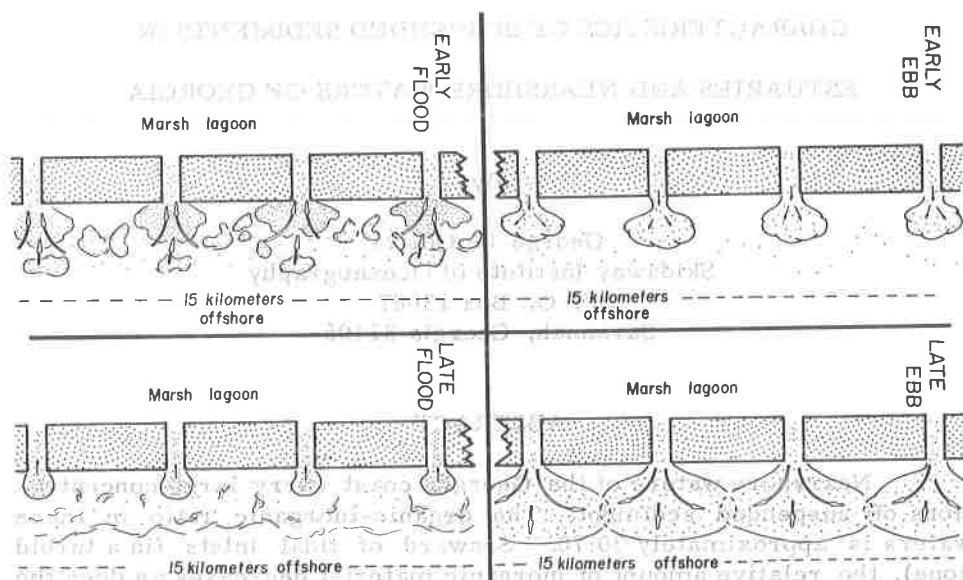15 kilometers offshore

LATE FLOOD | LATE EBB

Figure 1. Schematic maps illustrating the positions of inlet turbid plumes during early and late stages of the ebb and flood tide. A portion of the turbid plumes re-enter the inlet and a portion remains in clouds in the nearshore zone.

governing the rates and magnitudes of this resuspension (Anderson, 1972). Resuspension by the turbulent flow of shearing tidal currents is a regular phenomenon and affects the variability of the suspended concentration during mid-tides of the semi-diurnal cycle. Reduced current velocities during high and low water are generally insufficient to erode and resuspend fine-grained sediment. Resuspension is also greater during the spring tide when current speeds are higher. Tidal currents are the principal agents of transport for this material and plumes of suspended sediments are flushed out of numerous coastal inlets during each ebb tide. In nearshore zones where inlets are closely spaced, these plumes merge into a band of turbid water. This band is broadest during low and narrowest during high water when the band breaks down and forms a number of individual plumes (Figure 1).

Neiheisel and Weaver (1967) described the mineralogy of the suspended sediment in the major rivers determining that kaolinite clays were derived mainly from Piedmont formations and montmorillonite clays mainly from Coastal Plain formations. Heron, Johnson, Wilson and Michael (1964) also found that kaolinite and vermiculite are clearly of Piedmont river origin. Bigham (1973) determined that illite is the important clay minerals in the suspended sediments of inner shelf waters while montmorillonite clays dominate in nearshore and estuarine waters. The montmorillonite clays were generally associated with bands of

turbid water (Bigham, 1973). Heron, Johnson, Wilson and Micheal (1964) found that while coastal plain clays are highly montmorillonite very little gets to the ocean, and the montmorillonite clays must come from other sources.

Seaward of the nearshore turbid zone, the inner shelf waters carry .125 - 2.00 mg liter^{-1} suspended sediments with 60 to 90 percent consisting of combustible organic matter (Manheim et al., 1970). Only a small portion consists of recognizable organisms or organic remains.

The variability in concentrations of sediment suspended in water is necessarily dependent upon its source, transport and rate of deposition. Observations of distinct and different concentrations of suspended sediment have allowed identification of different water masses within estuarine environments (Levy, 1968; Oertel, 1971, 1974). The description of these water masses and the concentration gradients of suspended sediments between them, grossly illustrate a low degree of dynamic mixing between adjacent water masses in coastal areas. Contrasting zones of high and low suspended sediment concentrations in Georgia's sounds are useful in discerning water masses derived from different parts of the marsh drainage basin.

The suspended sediment in the nearshore and estuarine area comprises organic and inorganic portions that have several different sources. Inorganics come from upland runoff and resuspension from the seabed. Organics may be obtained from these two sources and from various zooplankton, phytoplankton and marsh plants. The relative amounts of organic and inorganic material in the water column is therefore an index of water-mass identification and a useful qualitative measure of dynamic mixing of river, marsh and oceanic waters.

In this study, suspended sediment analyses were made of samples from the headwaters of a marsh complex, and from numerous transects near the edge of a turbid zone and transects across the nearshore turbid zone into low-turbidity water of the middle shelf (Figure 2).

PROCEDURE

Approximately 550 water samples were taken at a variety of locales in the estuarine and nearshore waters of coastal Georgia (Figure 2). The samples were taken with a 1.7 liter Niskin Bottle and refrigerated in 500 ml polyethylene bottles until filtered through predried and preweighed 0.45 μ m Millipore filters. The filters and filtration apparatus were washed 3 to 5 times with 5 ml of distilled water to insure the retention of all sediment and to flush residual salts. The wash
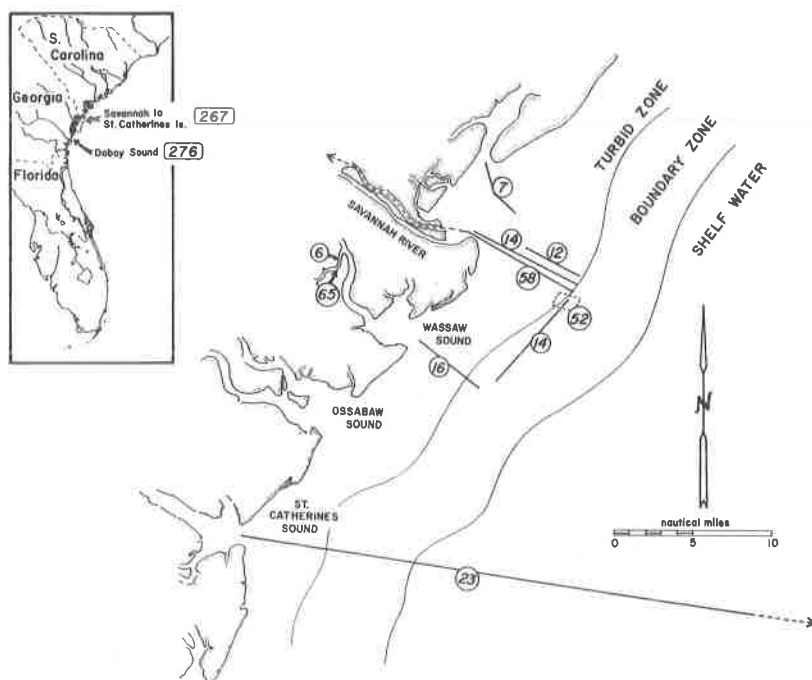
Figure 2. Location map of study areas with number of samples taken
          at each site.

water of the flushing was periodically checked with silver nitrate to in-
sure complete washing of salt from the filter.   Since all samples were
not checked, a minor increase in weight caused by residual salts may
have produced small errors in a few samples.   However, we believe
multiple   washing and the checking with silver nitrate kept errors to a
minimum.   The filter and sediments was then dried in plastic petri dish-
es for 2 h at 70°C and cooled for 15 min in a dessicator before the filter
and sediment were reweighed. These time intervals were exactly equal
to the intervals used in preweighing and predrying.   The total dry
weight of the samples was determined by the difference.

         Following gravimetric analysis the filters and sediment were
combusted at 600°C for 2 h.   The crucibles containing ash were cooled
for one hour, and reweighed to the nearest 0. 1 mg.

         The dry weight of the ash was determined by the difference bet-
ween the weight of the preweighed crucible and that of the ash plus the
crucible.   This method produces semi-quantitative measurements of
the inorganic weights because of differential losses in lattice water re-
lated to clay mineralogy.   However, the measurements obtained are
adequately precise to identify water masses and to estimate zones and
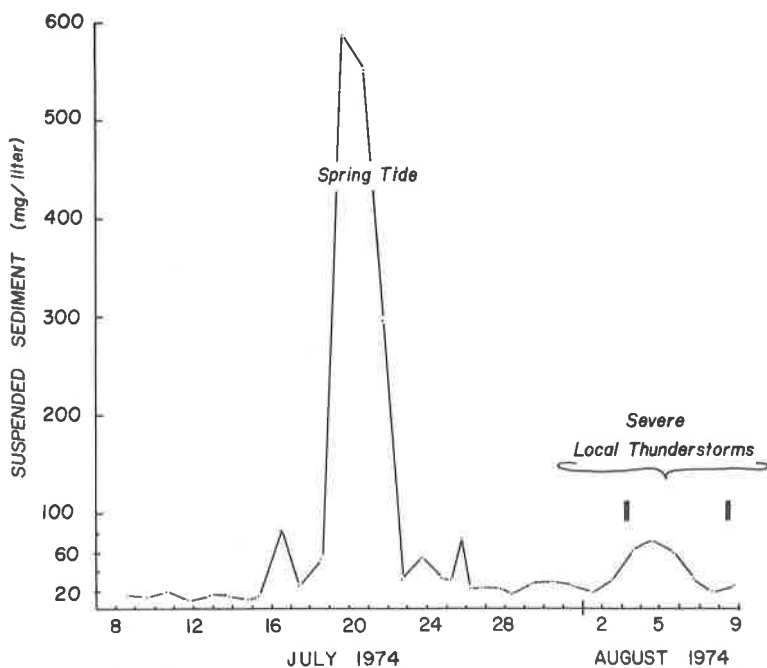gradients of mixing.

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Figure 3. Graph of the daily mean concentration of
suspended sediment in surface water taken near
the headwaters of a tidal marsh at low tides
from 8 July 1974 to 9 August 1974. Increased
turbidity is apparent at spring tide and possibly
during severe thunderstorm activity.

OBSERVATIONS

Upper Estuary (Skidaway station, Figure 2, no. 65)

During July 1974, the organic and inorganic fractions of 65 sam-
ples from the headwaters of a lagoonal-marsh complex were determined
in the laboratory. Five-hundred milliliter samples were taken daily at
low and high tide from the surface water at the margin of the tidal chan-
nel located ten miles landward of the inlet to the Wassaw Sound estuary.
The mean total concentration of these samples was 46.6 mg liter^{-1} with
individual samples ranging from 9.6 mg liter^{-1} to 585.6 mg liter^{-1}.
The high values were generally obtained during the spring portion of
the lunar cycle (Figure 3). During this period an increase in the resus-
pension of sediment was apparently produced by increased turbulent
energy of high velocity tidal currents which produce shear at the bot-
tom. During high tide the spring tide concentrations were 2 to 3 times
higher than the 9.6 mg liter^{-1} concentration, whereas, low tide con-
centrations were 30 to 50 times higher. Increased local runoff produced

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by precipitation had an unpredictable effect upon turbidity. During the study period, two intervals of rain produced increases in suspended sediment concentrations; however, during several other periods of precipitation, the variation in the suspended load was not large enough to show a similar result. It appeared that precipitation had its greatest effect on the suspended load when the marshes were exposed to rain at low tide, rather than when they were submerged at high tide. Toward the end of the sampling period intense thunderstorm activity occurred during low tide and a marked increase in the suspended load was observed. While the input of rain water was illustrated by a decrease in salinity, modest increases in the percentage of organics only hinted at a marsh rather than upland source for the increase of suspended fines (Figure 3).

The margins of the estuarine channels in Doboy Sound had relatively high concentrations of suspended sediments (Figure 4) apparently produced by the resuspension of fines by turbulent flow across shallow areas. Particularly high concentrations were observed during spring tides.

The most consistent characteristic of the suspended sediment was the organic-inorganic ratio. In the head waters of the marsh-lagoonal system the amount of inorganic material was approximately three times that of the organic portion. Based on 65 water samples, 72 percent of the suspended sediment load was composed of inorganic material, whereas, 28 percent consisted of combustible organic detritus. The standard deviation of the proportions of organic and inorganic matter was 8.7. The mean total concentration illustrates that an average sample (46.6 mg liter^{-1}) contains 13 mg liter^{-1} of combustible organic detritus.

Measurements of the upper layers of marsh mud indicated that 75 to 90 percent of these sediments are composed of inorganics and 10 to 25 percent of combustible organic material.

Inlet Zone

Inlets and their adjacent areas generally had the largest concentrations of suspended sediment (Oertel, 1971, 1974). Concentrations of over 200 mg liter^{-1} were not uncommon in Doboy Sound (Figure 4). The concentration of suspended sediments was from two to three times greater than average concentrations in areas landward or seaward of the inlet.

The highest concentrations of suspended sediment occurred during the mid-tides when the maximum ebb and flood velocities were present in the inlet. This illustrates the major influence that bottom shear and turbulent flow has upon the amount of sediment suspended in the water.

During the flooding tide, channels on the margins of the Doboy Sound inlet carry large concentrations of suspended sediment (Oertel,
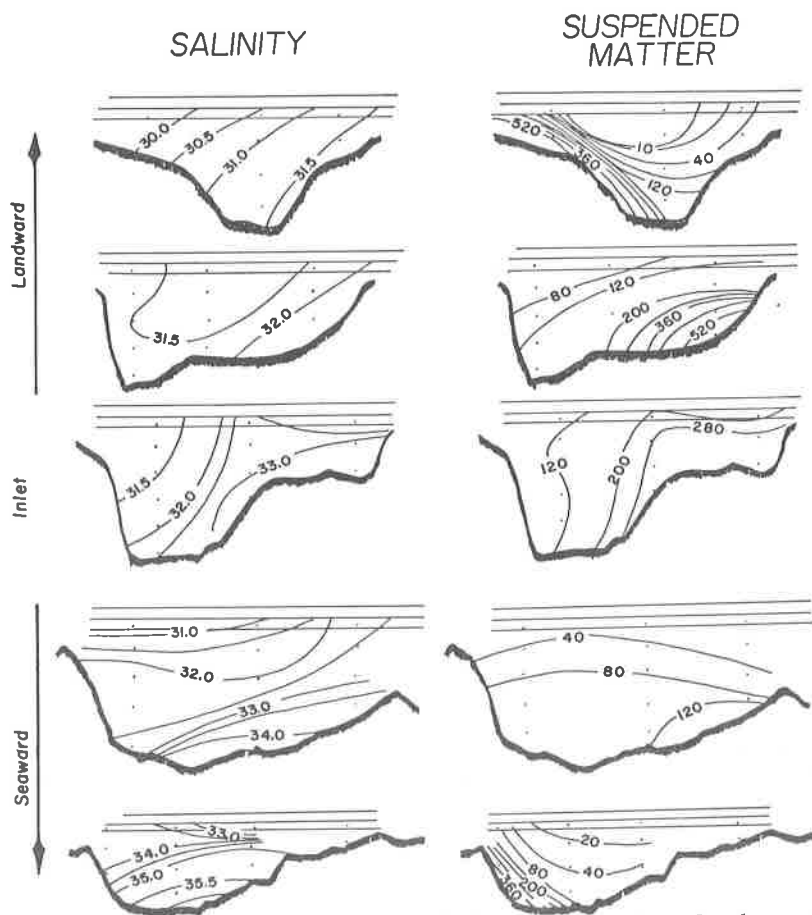
SALINITY SUSPENDED MATTER

Figure 4. Cross sections of the Doboy Sound channel
(Georgia) illustrating the distribution of salinities
and suspended matter concentrations during mid-
flood tide. Landward of the inlet, the gradient of
the suspended sediment concentration is steep and
channel margins carry suspended concentrations in
excess of 500 mg liter^{-1}. At the inlet, the turbid
water is relatively well mixed and the concentra-
tions are high (100-280 mg liter^{-1}). Samples were
taken at 2.5 m intervals beginning 1 m below the
surface.

1971, 1974). These high concentrations suggest that a portion of sus-
pended sediment that was jetted through the inlet during the falling tide
is issued back into the inlet during the flooding tide. However, the per-
centage of suspended sediment that re-enters the inlet versus that which
remains in nearshore water is not known.

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The sedimentary framework of tidal inlets is complicated. The deposition of mud results from at least four different processes (Oertel, 1973a). The areal distribution of these processes is predictable and is governed by water flow and the nature of the mud source (Oertel, 1973b). Mud pebbles from marshes and tidal flats, fecal pellets and clay-sized particles are transported and deposited differently by turbulent currents. In the inlet and turbid zones, large communities of filter-feeding organisms remove clay-sized particles from the water and deposit sand-sized fecal pellets on the shallow sea floor. These clay pellets are usually not resuspended but are reworked and moved laterally by tidal currents. During intense wave activity, however, the disruption of the shallow sea floor may cause resuspension of some of this material.

At fluvial inlets the net gains and losses of suspended matter are determined by seasonal runoff in upland areas. During periods of high runoff in spring and early summer, many of the major rivers transport relatively large quantities of fines into the nearshore waters. During periods of low runoff in the fall and winter, the quantity of fines supplied is greatly reduced.

Nearshore Turbid Zone (Savannah River entrance to

St. Catherines Inlet)

In the nearshore zone, a band of turbid water occurs between the inlets and the relatively "clean" oceanic water. The width of the band is variable depending on nearshore meteorological and tidal conditions. Low altitude aerial surveys illustrate that during low water, turbid plumes merge seaward of inlets and form a poorly mixed band running parallel to the shoreline. Aerial surveys also show turbid zones bordering shoal areas. These local turbid zones are apparently produced by the resuspension of fines by waves rather than from intrusion of water laden with suspended sediment.

During low water, the band is relatively wide as turbid water ebbs through inlets. During storms the resuspension of bottom fines in shallow water widens the band of turbid water. The characteristics of the suspended sediment in this zone illustrate areal variances. In June 1974, a transect extending from St. Catherines Inlet to a point approximately 78 km offshore, revealed some of these differences (Figures 5 and 6). The suspended sediment in the surface water of the nearshore turbid zone (0 to 11 km), had an average concentration of 28.3 mg liter^{-1} (Figure 5). This was lower than the average 46.6 mg liter^{-1} observed in the head waters of the marsh-lagoonal system.

Seasonal fluctuations were also apparent in the turbid zone. During a summer and fall sampling period (1974) the organic-inorganic ratios were 37:63. During the spring when drainage from Piedmont and Coastal Plain areas was increased, the organic-inorganic ratio at the edge of the turbid band was 9:91. Bottom samples from a late fall
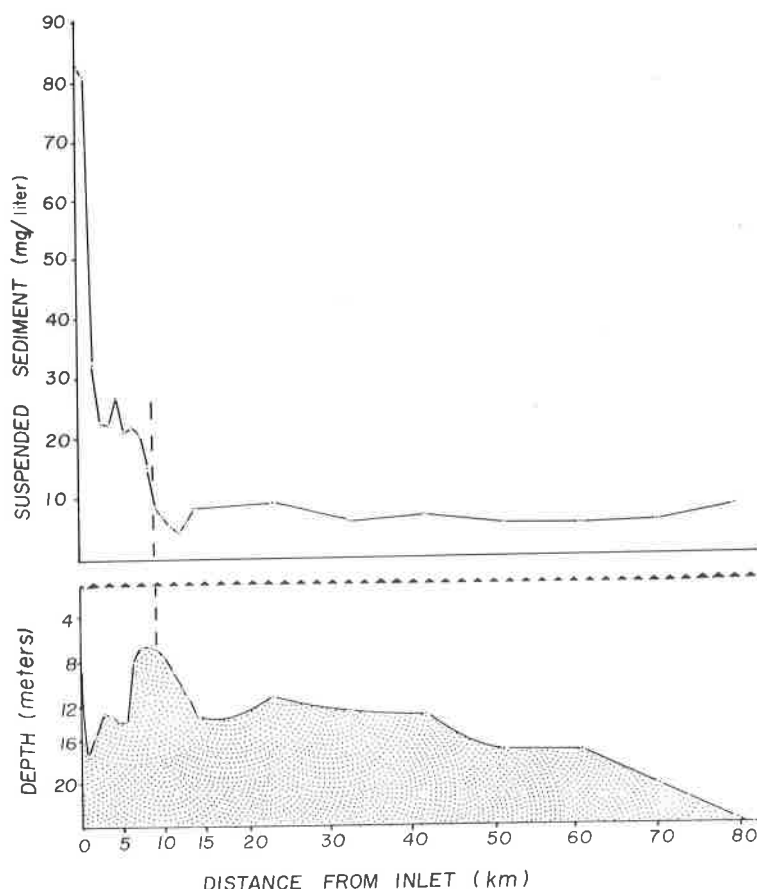
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Figure 5. Graph of the concentration of suspended matter (mg liter^{-1}) taken between St. Catherines Inlet (Georgia) and a point 78 km offshore.

sampling period during relatively high seas, also resulted in local increases in inorganic fines which accounted for over 90 percent of the sample. This was apparently produced by the resuspension of material from the bottom, and these variations were generally not transferred to the surface water.

Within 2 km seaward of the edge of the turbid zone average concentrations decreased to 4.9 mg liter^{-1}. This relatively steep suspended sediment gradient marks the edge of the turbid zone. From 13 to 23 km offshore (boundary zone) the average concentration increased to approximately 7.7 mg liter^{-1}. From 23 km to 78 km offshore (mid-shelf water) the average suspended load (1 m below the water surface) leveled off at approximately 6.1 mg liter^{-1} (Figure 5). This is considerably higher than the 1-2 mg liter^{-1} concentrations described by
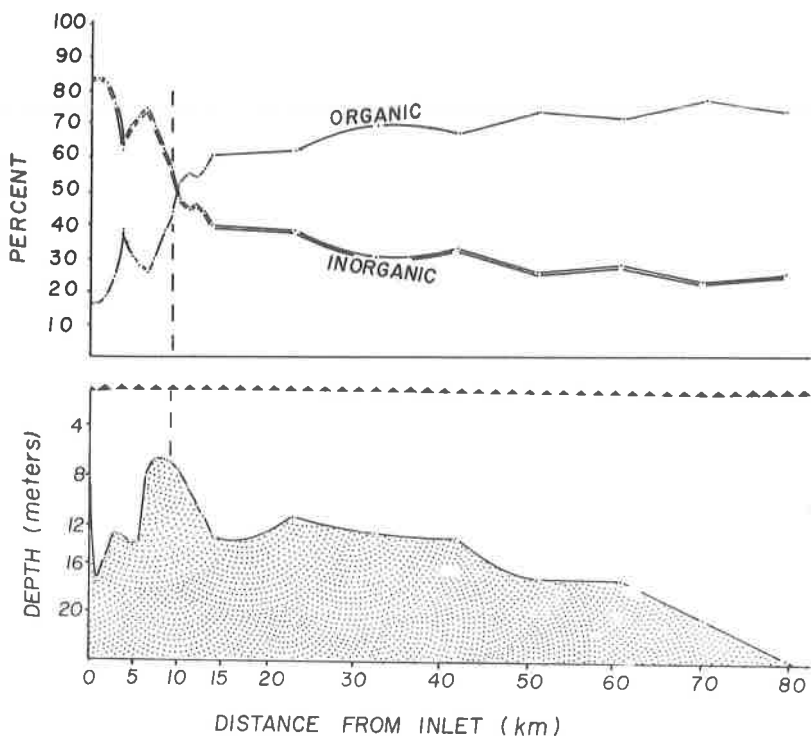
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Figure 6. Graph of the percentage of organic and inorganic material in the suspended matter of surface water taken along a transect between St. Catherines Inlet (Georgia) and a point 78 km offshore.

Manheim, Meade and Bond (1970), however, lower than the 5-20 mg liter^{-1} concentrations described by Bigham (1972). The excessively high concentrations of Bigham may be due to insufficient washing of salt from filters, the low concentrations described by Manheim et al., (1970), may have been seasonally controlled.

Organic-inorganic ratios illustrate an inversion near the edge of the turbid zone (Figure 2). Landward of this point, the percentage of inorganic material was greater than the organic. A major portion of the organic material in the turbid zone is probably derived from decomposed marsh plants. In the boundary zone the relative amount of organic material becomes greater than inorganic material, however, the total load continues to decrease. The principal contributor of organic material in this zone was probably zooplankton and phytoplankton. From approximately 13 km offshore the total load and the percentage of organic detritus increased to 23 km offshore. This may have been caused by a high productivity of zooplankton and phytoplankton. From approximately 33 km seaward of the inlet to 78 km offshore, 70 to 90

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percent of the sample was composed of conbustible organics. While this ratio is variable, a 70:30 organic-inorganic ratio is apparently of the correct magnitude and conforms with findings of Manheim et al., (1970). Although the organic portion of the total load is relatively high, the mean weight of organics in the offshore samples is approximately 4.5 mg liter^{-1} or approximately 34 percent of the total weight of organics in the nearshore and estuarine waters.

Data from transects extending seaward from the Savannah River entrance and Wassaw Sound illustrated similar distinctions between the turbid zone, the boundary zone and the shelf water zone.

CONCLUSIONS

In estuarine waters, a large temporal and areal variability exists in the concentrations of suspended sediments. Landward of tidal inlets, approximately 30 percent of the suspended load is composed of combustible organics regardless of flux in total concentrations. This percentage is similar to that of the upper layers of marsh mud. The organic-inorganic proportions (30 to 70, respectively) are relatively constant within the nearshore zone of turbid water; however, at the edge of the turbid zone (the boundary zone) there is a conspicuous decrease in the amount of inorganic material, and therefore an increase in the relative amount of organic material.

Increases in runoff and changes in turbulence caused by spring tides cause apparent changes in suspended sediment concentrations. However, concentrations are variable and quantitative predictions cannot be made between spring tides or from storm to storm. Increased runoff from Coastal Plain or Piedmont drainage basins is capable of increasing the percentage of inorganic material at the edge of the turbid zone to over 90 percent. Suspended loads seaward of the turbid zone may also be composed of over 90 percent inorganic material if storm waves are of sufficient strength to resuspend the fine-grained material from the bottom; however, resuspended particles only affect concentrations at the lower portions of the water column.

At approximately 30 km offshore (mid-shelf waters) the total suspended load remained constant and approximately 70 to 90 percent of this was composed of combustible organic material. Concentrations of suspended sediment adjacent to the Sea Island Physiographic Province are higher than in any other areas of shelf water between Cape Cod and Key West. Differences in the total suspended concentration from several sets of data (Manheim et al., 1970; Bigham, 1973) suggest that the system is quite variable.

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PREDICTION OF LITTORAL DRIFT FOR LAKES

AND BAYS FROM WIND OBSERVATIONS

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ABSTRACT

Littoral drift is a stochastic phenomenon consisting of sediment movement along the beach. The quantity of sand moved in the nearshore zone is dependent on the characteristics of breaking waves, longshore currents, and the physical characteristics of sediment in the surf zone. Other studies have shown that the longshore sediment transport on open coasts is related to the longshore flux of energy produced by the breaking waves. In many locations such as closed bays and lakes, waves are generated mainly by local winds. In these locations climatological (wind) data can be used for the prediction of sediment movement.

This study utilizes wind data for evaluation of shoreline changes that occur in Choctawhatchee Bay, Florida. The study indicates that some important features of the shore can be predicted from a knowledge of sand transport derived from wind statistics.

A conclusion of the study is that wind data can be useful for the analysis of shore processes in enclosed bays and lakes.

INTRODUCTION

Sediment located in the surf zone can be transported in the onshore-offshore direction or in the longshore direction. The longshore transport of sand is more commonly called littoral drift. The mechanisms causing sediment transport in any direction are much the same though. The sediment is moved either in suspension or as bed load. Inman and Bagnold (1963), Johnson and Eagleson (1966), Ingle (1966), Zenkovitch (1967), and Dean (1973) discuss how sediment is transported by oscillatory waves and currents.

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There are a number of methods for the calculation of littoral drift. Of these methods, two are predominant in the literature. One method is based on computations of the longshore current from wave and beach parameters. The longshore currents are then correlated with sand transport as in unidirectional sand transport formulas. The second method for calculation of littoral drift is based on computations of the "longshore energy flux" and correlates this energy flux rate with measured amounts of sand transport. This second approach has been utilized previously for the calculation of littoral drift on idealized open coast beaches of Florida (Walton, 1973).

Geologists and coastal engineers usually cannot use the wave-littoral drift correlations because wave statistics (wave heights, period, and direction) are not readily available in most locations. Wave direction is an especially difficult parameter to obtain. For this reason other methods for inferring littoral drift direction from the sediment properties were developed (Sunamura and Horikawa, 1971). Additionally, tracer studies have been used to obtain magnitudes and directions of littoral drift, (Zenkovitch, 1967; Komar, 1969). These methods, although very interesting, cannot yet predict magnitudes or directions of littoral drift for time periods of concern to the design engineer. Predictions of sand transport magnitude and direction are important for the design of beach protection and coastal structures.

The objective of this study was to develop a method for the application of readily available wind data (taken at airports) for the quantitative prediction of littoral drift.

Acknowledgments

BASIC APPROACH

Generation of water waves by winds is complicated phenomenon. Its scientific explanation is still under investigation although much progress has been made in the last two decades. Engineering approaches though, namely semi-empirical methods, have been developed by which significant wave heights and periods can be forecast from wind, fetch, and bathymetry data. A very well know set of formulas was developed by Sverdrup and Munk (1947) to forecast wind waves for deep water using wind and fetch data. The Sverdrup-Munk prediction curves were revised by Bretschneider (1952, 1958) to account for new data and also to account for the effect of depth in wave height, growth, and wave period

limitation. The revised semi-empirical wave forecasting method is often referred to as the SMB method (Sverdrup-Munk-Bretschneider). The wave height and wave period prediction formulas for fetch limited waves in "deep" water ($h > L/2$) are:

$$\frac{gH}{U^2} = 0.283 \tanh \left[.0125 \left(\frac{gF}{U^2}\right)^{0.42} \right] \tag{1}$$

$$\frac{gT}{2\pi U} = 1.20 \tanh \left[0.077 \left(\frac{gF}{U^2}\right)^{0.25} \right] \tag{2}$$

where

$\quad H$ = wave height
$\quad T$ = wave period
$\quad U$ = wind velocity
$\quad F$ = fetch
$\quad g$ = gravitational acceleration constant
$\quad h$ = water depth
$\quad L$ = wave length

As a first approximation for relatively deep short fetched bays and lakes, depth can be considered unlimited, and above equations can be used. For depth limitation, the extended equations are presented in the Shore Protection Manual (1973) as follows:

$$\frac{gH}{U^2} = 0.283 \tanh \left[0.530 \; \frac{gh}{U^2} \right]^{0.75} \tanh \left[\frac{0.0125 \left(\frac{gF}{U^2}\right)^{0.42}}{\tanh \; 0.530 \left(\frac{gh}{U^2}\right)^{0.75}} \right] \tag{3}$$

$$\frac{gT}{2\pi U} = 1.20 \tanh \left[0.833 \; \frac{gh}{U^2} \right]^{0.375} \tanh \left[\frac{0.077 \left(\frac{gF}{U^2}\right)^{0.25}}{\tanh \; 0.833 \left(\frac{gh}{U^2}\right)^{0.375}} \right] \tag{4}$$

Eqs. (3) and (4) reduce to (1) and (2) respectively as $gh/U^2 \to \infty$. The relationships between the dimensionless parameters $F = gF/U^2$, $D = gh/U^2$, $H = gH/U^2$, $T = gT/2\pi U$ are shown in Figures 1 and 2. These figures present the limits of application of the deep and shallow water formulas as well as the possibilities of finite and infinite fetchs. Infinite fetch means gF/U^2 approaches infinity.

In locations where fetches are not very large, waves are generated by local winds. Such waves in the open ocean are referred to as sea waves, as opposed to swell waves which are wind waves that have propogated away from their generating wind source. The duration required
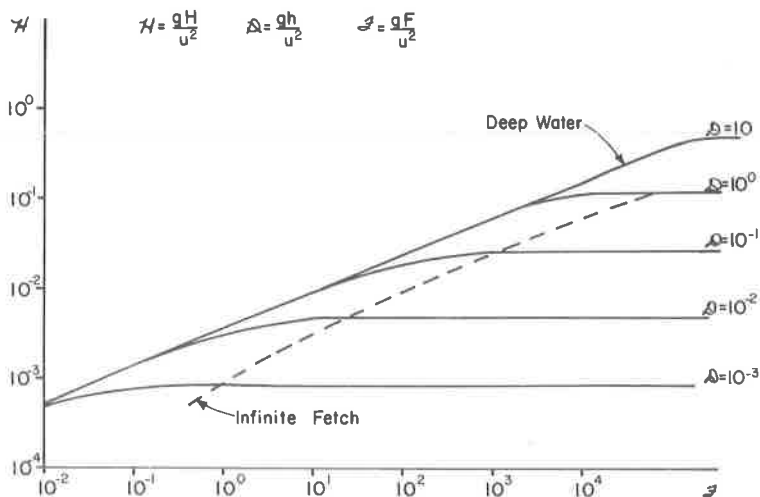
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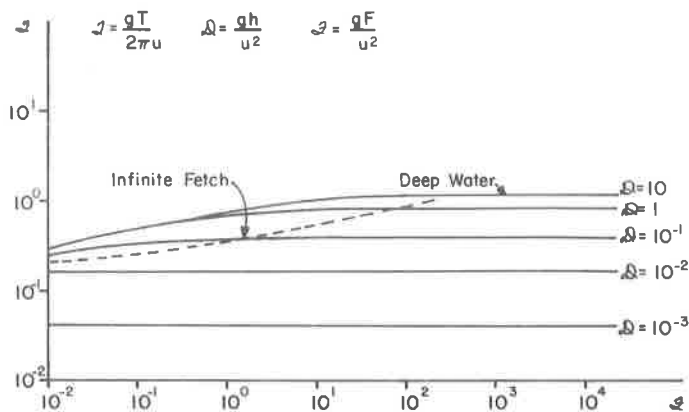Figure 1. Variation of Wave Height with Fetch and Depth
of Water.

Figure 2. Variation of Wave Period with Fetch and Depth
of Water.

for steady conditions (fully developed wind waves) is not long, there-
fore, waves in lakes and bays can be considered fetch limited to a first
approximation. These assumptions permit predictions of significant
wave heights and periods by applying equations (1) and (2) to a source of
wind direction and strength data. The production of wave data from
climatological wind data allows the application of littoral drift transport
formulas for the prediction of sediment transport along the shore. The
energy flux-sand transport formula that was used in this study is as
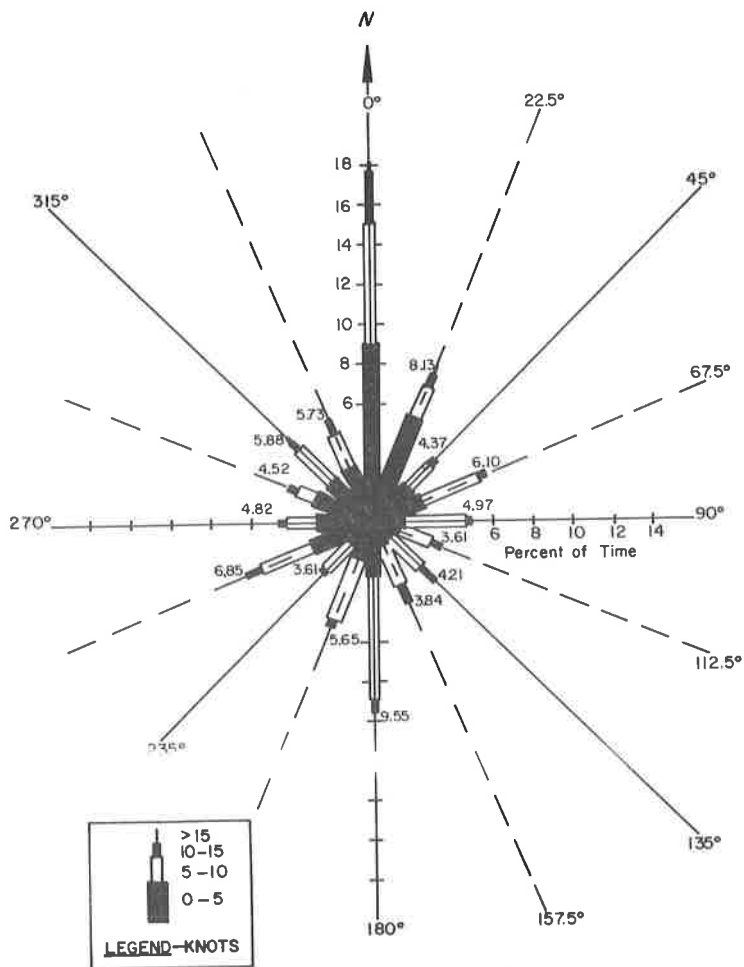follows:

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N

0°

22.5°

315°

45°

18
16
14
12
10
8   8.13
6
5.73
5.88   4.37
4.52   6.10
270°   4.82   4.97   90°
3.61 6   8   10   12   14
Percent of Time
6.85   3.61
4.21
3.84
5.65

67.5°

112.5°

9.55

135°

157.5°

180°

> 15
10–15
5–10
0–5
LEGEND—KNOTS

Figure 3.   Annual Wind Distribution at Eglin AFB, Florida.

$$Q_l = 125 \ \left(\gamma \frac{H}{8} \ C_g \ \cos \alpha_o \right) \ K^2 \ \sin \alpha_b \cdot \frac{24 \cdot 3600}{10^6} \qquad (5a)$$

or in appropriate metric units:

$$Q_l = 212 \ \left(\gamma \frac{H^2}{8} \ Cg \ \cos \alpha_o \right) \ K^2 \ \sin \alpha_b \cdot \frac{24 \cdot 3600}{10^6} \qquad (5b)$$

where

Q_l = Longshore sand transport rates in cubic yards per day (or cubic meters per day)

γ = Specific weight of seawater (64#/ft) (or 1027 Kg/m)

C_g = Deep water group velocity in feet per second (or meters per second)
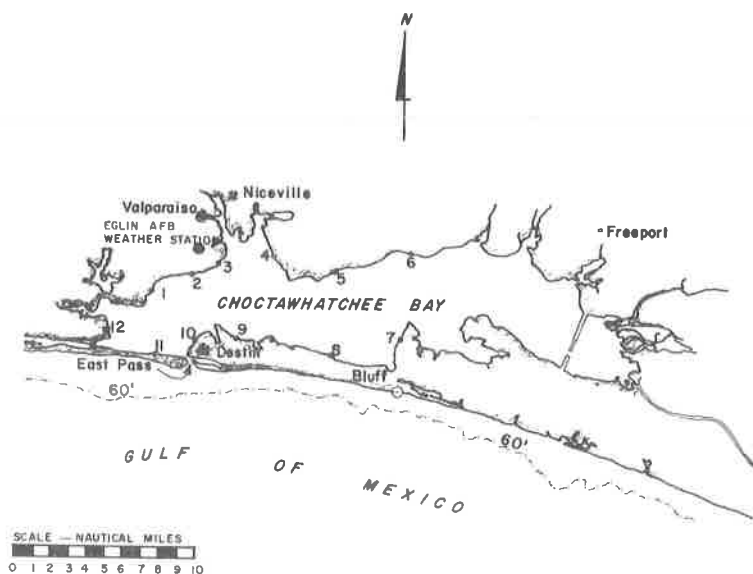
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Figure 4. Choctawhatchee Bay, Florida - Locations of Littoral Drift Computation.

H   = Wave height in feet (or meters)
α_o = Deepwater angle of wave approach to the coastline
α_b = Angle formed by breaking wave crest with the coastline
K   = Friction percolation coefficient (Bretschneider and Reid, 1954)

An extensive discussion and derivation of this formula is given by Walton (1973).

APPLICATION OF THE METHOD

The calculation of littoral drift from wind data was made for the Choctowhatchee Bay area in the panhandle section of Florida. The wind data source was the anemometer record from the weather station at Eglin AFB. The data was compiled on tape with wind speed and direction measurements at 4 - 6 hour intervals. The data source has wind recordings for a period of over 15 years.

Figure 3 presents the distribution of wind speeds and directions. These data refer to 1963. Data was compared for the periods 1959-1962 by the authors and was found to be very similar to that presented in this figure.

In the model, wave direction is assumed the same as wind direction to a first approximation.

Calculation of littoral drift at twelve different stations located along the bay shore (shown in Figure 4) was made via computor program
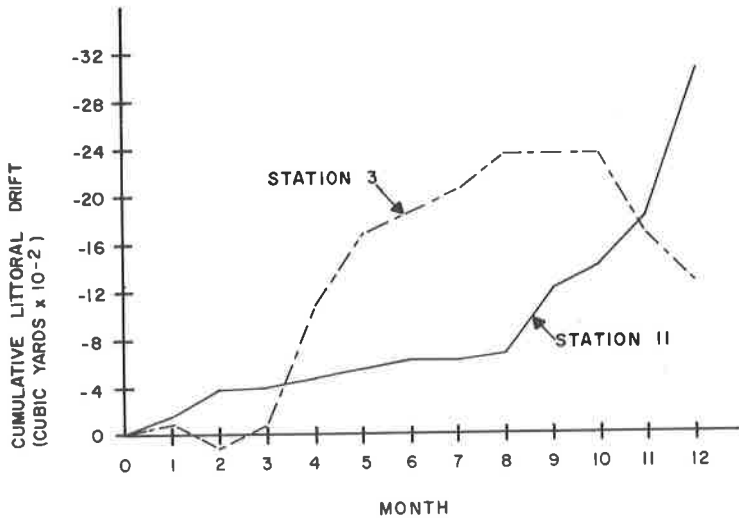
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Figure 5. Cumulative Littoral Drift at Station 3 and 11.

utilizing the wind statistics and the longshore energy flux correlation. The variation of the littoral drift at each station was computed on a monthly basis.   From a knowledge of the variation of littoral drift with direction, the long term accretion or erosion trends of the bay shore-line can be obtained.

In Figure 5 the cumulative sand transport along the bay shore at station 3 and 11 is shown.   The value of cumulative littoral drift at the twelfth month represents the annual littoral drift rate.   Most of the sediment transport at station 11 occurs between August and December as the slope of the cumulative drift plot in these months is steepest.

A measure of both positive and negative sediment transport was determined in the computer program.   Positive littoral drift refers to sand transport to the right when looking offshore and negative sand transport refers to sand moving to the left when looking offshore.   This terminology is consistent with that of Walton (1973).

On Figure 6 the annually averaged sand transport at various bay stations is shown.   Figure 6 demonstrates the littoral drift variation a-long the bay shore.   From continuity of sand considerations, areas of shoreline accretion and erosion can be found.   For example, erosion is occurring between stations 2 and 3 and accretion between stations 7 and 8.   A thorough discussion of the continuity approach is given by Walton (1973) and Walton and Dean (1975).

It is relevant at this point to answer the question as to whether the original assumption of a deep water bay was justified in the appli-cation.   Choctawhatchee Bay ranges in depth from 15-35 feet (5-10m) and is approximately 4 miles (6. 4Km) wide and 30 miles (48Km) in
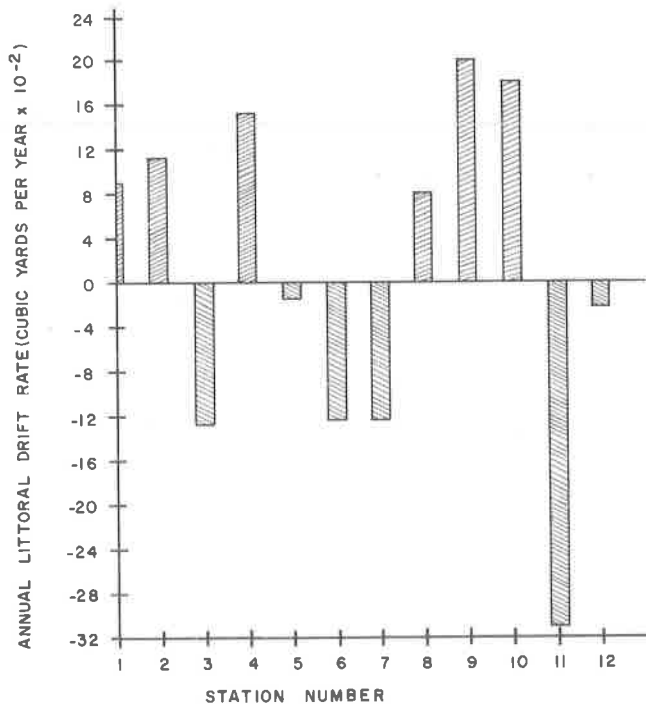
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Figure 6. Annual littoral drift rate at Station 1 - 12.

length. The dimensionless parameters become for a typical fetch of 7 miles (11Km), average depth of 20 feet (6 meters), and wind speed of 10 knots (19 kilometers per hour):

$$F \cong 7300 \qquad\qquad D \cong 4.00$$

Thus on Figure 1 it can be seen that bay depth is not yet a controlling factor in wave height growth for the fetch considered. A fetch over twice as large as considered would just begin to effect wave height for the depth considered. On Figure 2 it can be found that for the depths and fetches considered wave period modification is insignificant.

CONCLUSIONS

In locations where local climatological wind data exist, such data can be utilized for wave forecasting and consequent prediction of littoral drift. The method utilized in this paper appears to be especially encouraging when considering sediment transport in lakes and bays where waves are locally generated. The method described in this paper is especially useful where no wave data exists. Where wave height data exist a more refined regression model can be developed utilizing SMB

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modified equations for better prediction of wave heights and periods as input to the model.

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