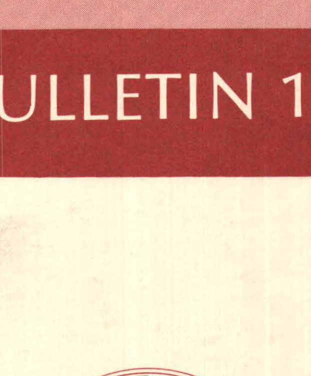
Mineralogy and Alteration of the Phosphate Deposits of Florida

U.S. GEOLOGICAL SURVEY BULLETIN 1914



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Mineralogy and Alteration of the Phosphate Deposits of Florida

By S.J. VAN KAUWENBERGH, J.B. CATHCART, and G.H. McCLELLAN

A detailed study of the mineralogy and chemistry of the phosphate deposits of Florida

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Mineralogy and Alteration of the Phosphate Deposits of Florida

By S.J. Van Kauwenbergh[1], J.B. Cathcart[2], *and* G.H. McClellan[3]

Abstract

The Neogene phosphorites of Florida were deposited in a major phosphogenic province that extended from North Carolina into the Florida Peninsula. Although phosphate is present in all areas where Miocene strata occur offshore and onshore, both in outcrop and the subsurface, economic or potentially economic Miocene and Pliocene deposits are known only from North Carolina, southern South Carolina and northern Georgia, southern Georgia and northern Florida, and central Florida. Identified resources in the phosphate province of the Atlantic Coastal Plain are estimated to be about 7 billion tons, and additional hypothetical resources are thought to be about 13 billion tons. The Florida phosphate deposits are the most productive in the world. About 1 billion tons of phosphate-rock concentrate, containing an average of about 32 percent P_2O_5, have been produced since the start of mining in 1888.

Phosphate mining in Florida was initially confined to high-grade deposits in Polk and Hillsborough Counties. This mining district is commonly called the central Florida land-pebble phosphate district. In recent years mining has progressed deeper into sections in this district and to the southern extension of the district in Hardee and Manatee Counties. In the future, mining could move even further south into DeSoto County. Two mines have been developed in north Florida.

The phosphatic sediments of the Florida deposits are unconsolidated or partly consolidated sand, clay, and carbonate rock (limestone and dolomite). The deposition of phosphate was, in part, structurally controlled. Phosphate was deposited in basins on the flanks of structural or topographic highs. The economic deposits were reworked, concentrated, and enriched after deposition. Uneconomic phosphatic carbonate rocks are abundant below mined sections and in the deeper parts of basins.

The most abundant minerals of the Florida deposits include carbonate-fluorapatite (francolite), quartz, dolomite, and clay minerals. Francolite is the only economic phosphate mineral. Iron and aluminum phosphates are characteristic of the uneconomic, highly weathered parts of the deposits. Quartz is the principal gangue mineral. Dolomite is a source of unwanted magnesium in fertilizer processing, and mining is generally terminated when indurated dolostone beds are encountered. Clays are also a source of impurities and present a significant disposal problem.

This study shows that all the Florida deposits are altered or are mixtures of more and less altered material. Changes in ore characteristics in individual sections and across the entire deposit are due to gross variations in mineralogic composition and more subtle variations in francolite and clay composition. These variations in mineralogic composition can be related to the depositional history, reworking, and weathering of the deposits.

INTRODUCTION

The Neogene phosphorite deposits of the southeastern United States were formed in a major phosphogenic province that extended along the Atlantic Coastal Plain from North Carolina to the center of the Florida Peninsula. Phosphate occurs onshore and offshore in rocks of Miocene age. Younger phosphatic strata are also present; much of this phosphate probably was derived from pre-existing Miocene rocks. Although phosphate grains are present in all areas where Miocene sedimentary rocks occur, economic or potentially economic Miocene and Pliocene deposits are present only in North Carolina, southern South Carolina and northern Georgia, southern Georgia and northern Florida, and central Florida. The identified recoverable resources of this vast deposit have been estimated by Cathcart and others (1984, p. 44) to be about 7 billion metric tons of concentrate, and additional hypothetical resources may be as much as 13 billion tons.

The initial discovery of phosphate in the United States was near Charleston, South Carolina, and

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[1] International Fertilizer Development Center, Muscle Shoals, AL 35662.

[2] U.S. Geological Survey, Denver, CO 80225.

[3] Department of Geology, University of Florida, Gainesville, FL 32611.

phosphate was first mined there in 1867. Mining of phosphate in Florida began in 1888 from phosphate-bearing gravel bars along the Peace River in Polk County and the Alafia River in Hillsborough County. These were the so-called river-pebble deposits. The dredging that began in the rivers moved onto the flood plains, and mining finally spread to the uplands adjacent to the rivers. The upland material was called, logically enough, land pebble. Ore from the higher grade and more uniform land-pebble deposits became the mainstay of the phosphate market, and river-pebble mining ceased early in the 20th century.

In the first half century of mining in Florida, only the plus 16-mesh fraction (pebble) was utilized. Flotation to separate fine-grained phosphate from quartz became technically and economically feasible in the mid-1930s. Utilizing flotation technology, the Florida phosphate-mining industry expanded; maximum production was reached in 1979 at approximately 42 million tons per year, and the total production of product (about 32 percent P_2O_5) from 1891 to 1984 approached 1 billion tons (Cathcart, 1985).

The location of the economic phosphate deposits of the southeastern United States is in part controlled by structure (Cathcart, 1968; Freas, 1968; Freas and Riggs, 1968; Riggs, 1984). Phosphate was deposited in basins on the flanks of topographic or structural highs. Although structure appears to be a prime factor in the location of the deposits, other factors such as reworking and secondary enrichment have contributed to the formation of economic deposits. Rooney and Kerr (1967) noted the extensively reworked nature of the North Carolina phosphorite and a general lack of alteration. Cathcart and Davidson (1952), Altschuler and others (1958), Altschuler and others (1964), and Altschuler (1965) have pointed out the importance of extensive reworking and secondary enrichment in the Florida deposits.

The phosphatic sediments of the economic deposits of Florida are unconsolidated or partly consolidated clay, sand, and minor carbonate rock. All the Miocene sediments of Florida contain phosphate particles (pellets, interclasts, bone fragments, and other grain types), quartz, clay minerals, and carbonate minerals (dolomite and calcite). Phosphatic carbonate rocks, some of which are well cemented, are abundant below mined sections and in the deeper parts of the basins. A major part of the total resource is this type of material. Heavy minerals are present throughout the phosphatic sediments, but they occur in minor or trace amounts. Iron and aluminum phosphate minerals are the products of weathering in the surficial parts of the deposits.

The most abundant minerals of the phosphate deposits of Florida are francolite (carbonate-fluorapatite), quartz, dolomite, and various clay minerals. Francolite is the only economic phosphate mineral. Quartz is the most abundant mineral in the deposits. The clay minerals are a major source of elemental impurities in the ore (Fe^{3+}, Al^{3+}, Mg^{2+}). The disposal of the clay minerals in the slime fraction (generally minus 150 mesh) is a serious problem in Florida. Magnesium, mostly in dolomite, is difficult and expensive to remove by beneficiation or during chemical processing. Francolite, dolomite, and the clay minerals of the deposits have variable compositions that may indicate both the environment of deposition and diagenesis, and the discussion in this paper therefore focuses primarily on these mineral groups.

Until recently, all mining of the high-grade land-pebble deposits of the central Florida phosphate district was in Polk and Hillsborough Counties, and mining was generally restricted to the coarse phosphorite at the top of the sections. These coarse high-grade deposits in the upper parts of sections in the central district are becoming depleted, and therefore mining is progressing deeper into sections in the central district and, to the south, into the southern extension in Hardee, Manatee, and DeSoto Counties (Bernardi and Hall, 1980). Two mines have been developed in northern Florida (Swift Creek and Suwannee River). The deposits of the southern extension and northern Florida are lower in grade, and the easily beneficiated pebble (plus 16-mesh) fraction is less abundant and is contaminated by dolomite grains. The phosphate grains of the feed fraction (minus 16 plus 150-mesh) are lower in P_2O_5 content and have greater amounts of mineral contaminants than the deposits in the central district. The changes in ore characteristics from the central district to the southern extension have been attributed to certain geologic factors. The southern deposits are less intensely altered, and there is a transition in the depositional environment from nearshore to offshore conditions (Riggs, 1979a, 1979b; Bernardi and Hall, 1980; Cathcart, 1985).

All the economic phosphate deposits of Florida have been altered or are mixtures of more and less altered material. Part of the change in ore characteristics from the central district to outlying areas and deeper in sections is due to systematic variations in the composition of the francolite constituent of the ore. Complex cycles of deposition, reworking, and subaerial weathering produced the deposits in their present state.

Acknowledgments

The field and laboratory studies that this paper summarizes have been part of a cooperative study between the U.S. Geological Survey (USGS) and the International Fertilizer Development Center (IFDC) under the auspices of the International Geological Correlation Program (IGCP) Project 156–Phosphorites.

This paper represents the continued commitment of these organizations to phosphorite research. The association with the IGCP enables developing countries to use this research in developing their phosphate resources.

We are indebted to many of our colleagues for their contributions to this work. T.M. Scott, Florida Geological Survey, was very helpful in unraveling stratigraphic details and assisting in some of the fieldwork. Z.S. Altschuler provided stimulating discussions on the geochemistry and mineralogy of the deposits. The following IFDC colleagues provided analyses: B.W. Biggers, M.R. Williams, B.A. Hamilton, T.C. Woodis, and D.W. Wright. M.R. Williams is particularly thanked for her efforts; much of the sample preparation and X-ray diffraction analysis was her responsibility. Marie Thompson and Marie Stribling cheerfully coordinated the artwork and word processing. Their staffs are gratefully acknowledged.

We are deeply grateful to the mining and administrative staffs of the many companies engaged in phosphate mining in Florida for their wholehearted cooperation in allowing J.B. Cathcart access to operating pits in 1984.

METHODS OF STUDY

J.B. Cathcart collected 51 samples from mines in north, central, and south Florida during 1984 (fig. 1). The samples represent currently mined economic zones (matrix). Stratigraphic correlations were made by J.B. Cathcart with the assistance of T.M. Scott of the Florida Geological Survey. Several of the samples were collected over vertical distances of tens of feet, and some were composited from sections taken from different sites at the same mine. Therefore, some of the observed variations in mineralogy may be the result of homogenization. These samples should not be construed as representative of any particular mine.

All chemical and XRD (X-ray diffraction) analyses were performed in the laboratories of IFDC. Copper radiation, at 50 kV (kilovolts) and 20 ma (milliamperes) with a graphite monochromator, was used for all XRD work. Chemical analyses were done by one or more of the standard analytical methods: X-ray fluorescence, atomic absorption, ion chromatography, gas evolution, and colorimetric and gravimetric determinations. Major-element analyses were cross-checked by two methods.

The samples were oven dried at 95°C, gently disaggregated by hand, and split to obtain representative samples for bulk chemical analyses and XRD studies. About half of each sample was placed in 1 L (liter) of distilled water containing 0.05 g (gram) of dispersant and allowed to stand overnight. Samples were wet screened on 20- and 200-mesh (Tyler) sieves to separate the plus 20-(pebble), minus 20- plus 200- (flotation feed), and minus 200-mesh (slime) fractions. The clay fraction (< 2 μm (micrometer)) was separated from the minus 200-mesh fraction by standard sedimentation techniques (Folk, 1974).

Separated size fractions (pebble, flotation feed, slime, and clay) and bulk samples were X-rayed in random powder packs to determine their mineralogy. Mineral abundances were estimated from the XRD traces as major, minor, or trace (see appendix for details). These data are qualitative and are used only to identify the mineral assemblages and compare relative proportions of the minerals in the different size fractions and at the various mine localities.

Air-dried, oriented clay samples were prepared by sedimentation onto glass slides for clay-mineral analysis. To facilitate identification of specific clay minerals, the oriented samples were glycolated and X-rayed again. These oriented samples were then heated to 350°C and X-rayed once more. Some clay samples were also treated by lithium saturation. Randomly oriented smectite samples that contained no detectable kaolinite were X-rayed to determine the d-spacings of the 060 reflections. These characteristic d-spacings were utilized to determine the smectite component.

Francolite unit-cell dimensions were determined by a high-resolution computer-assisted XRD technique, and data were reduced by an iterative hexagonal least-squares method. These unit-cell dimensions have a standard error of ±0.003 Å (angstrom). The *a*-value of the francolite unit cell shows the greatest variation and indicates isomorphic substitution in the apatite structure (McClellan and Lehr, 1969; McClellan, 1980). Thus, the *a*-value is the parameter used in this report as an indicator of francolite composition. In general, the smaller the *a*-value, the greater the amount of CO_2, SO_4, and VO_4 that are substituted for PO_4 and sodium, and magnesium for calcium in the francolite.

Grain-Size Analyses

Average grain sizes of the Bone Valley Member and the economic undifferentiated part of the Peace River Formation are given in table 1. Grain-size data for individual sections are given in figures 5–23 (appendix). Bernardi and Hall (1980) listed similar grain-size data for the land-pebble district and southern extension using slightly different mesh sizes. Obviously, the Bone Valley Member, differentiated by its pebble content, is coarser. The remaining underlying undifferentiated part of the Peace River Formation has a higher content of feed fraction, but the proportion of slime is about the same.

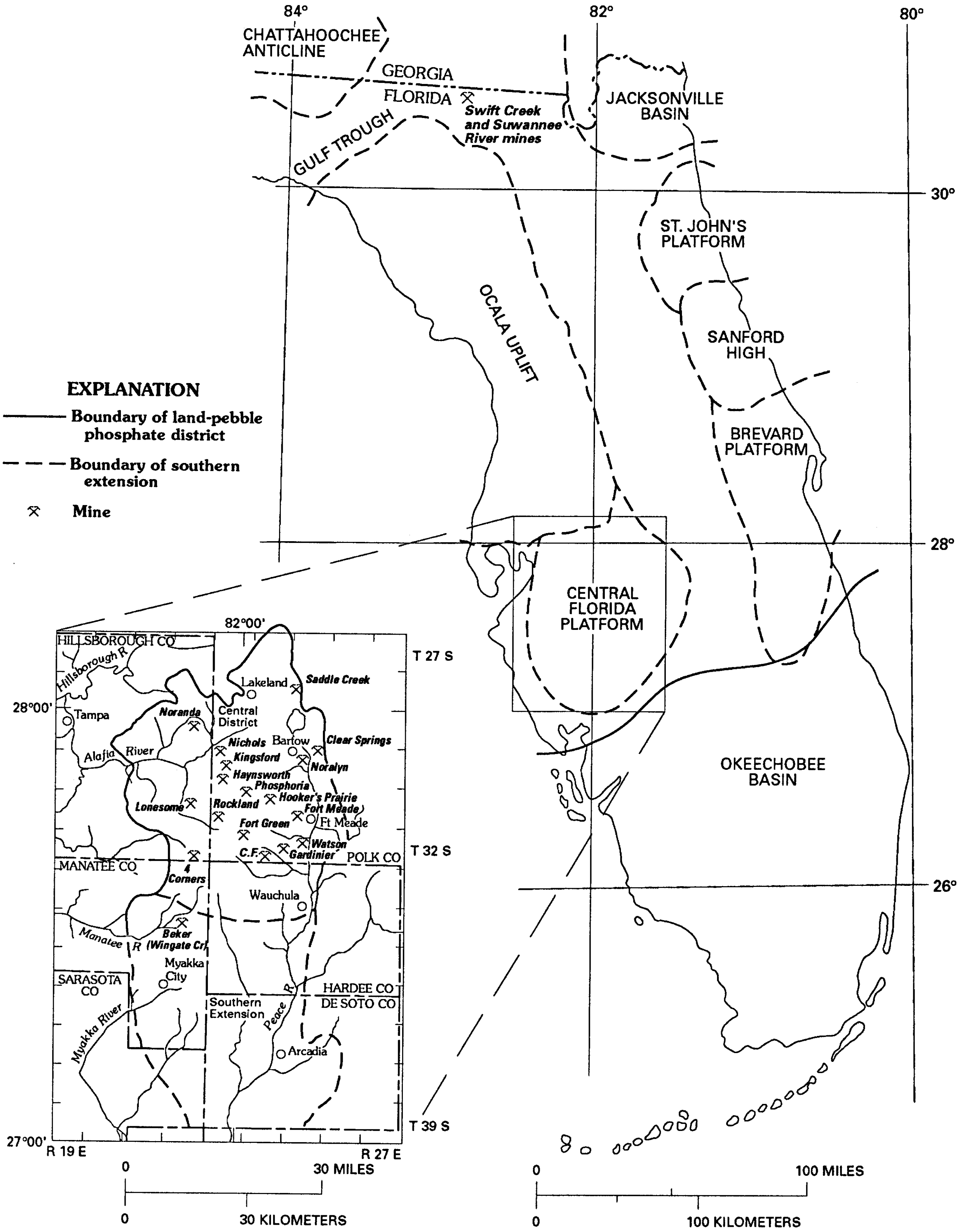


Figure 1. Sketch map of Florida showing major structural features and phosphate mines in central Florida.

Table 1. Average grain sizes of samples of the Bone Valley member of the Peace River Formation and undifferentiated Peace River Formation, Florida

[Values in percent]

	Tyler mesh sizes		
	+20	-20+200	-200
Bone Valley (22 samples)	31	50	19
Peace River (24 samples)	19	60	21

Data from this study show that the zone of overburden sand of probable Pleistocene age and noneconomic leached ore averages 5.5 m (meters) in thickness, and the ore zone (matrix) averages 4.5 m in thickness. The thicknesses of minable Bone Valley Member (2.1 m) and undifferentiated part of the Peace River Formation (2.5 m) are roughly equal.

GEOLOGY

Peninsular Floria is underlain by gently dipping sedimentary rocks that range in age from Cretaceous to Holocene. The Floridian Platform, equivalent to all of peninsular Florida, has been structurally stable, subject only to minor uplift and warping since the Cretaceous Period (Vernon, 1951).

Structure

The structure of peninsular Florida is dominated by the Ocala uplift and to a lesser extent by several positive features, including the Sanford high (fig. 1). The Ocala uplift became a positive feature as early as the late Eocene, and uplift persisted into the early Miocene (for a review, see Olson, 1966). Tertiary sediments dip gently away from these positive features into the Jacksonville basin, the Central Florida platform, and the Okeechobee basin (fig. 1). Miocene sediments thicken markedly away from these positive features and reach maximum thicknesses in the Jacksonville and the Okeechobee basins; in the center of the basins these sediments are as much as 250 m thick. Phosphatic sediments occur throughout peninsular Florida except on the Sanford high and Ocala uplift. Currently mined economic deposits are confined to the northeast edge of the Ocala uplift and the central Florida platform just off the southern end of the uplift. Potentially economic deposits occur both to the north and the south of the Sanford high on the St. Johns platform (north) and the Brevard platform (south).

Stratigraphy

According to traditional stratigraphy, sediments of Miocene age in Florida were divided into the Tampa Formation at the base, the Hawthorn Formation in the middle, and the Tamiami Formation (south Florida) and equivalents at the top. Various names, both formal and informal, have been applied to the upper Miocene sediments in north Florida and south Georgia (Patterson, 1974; Scott and Upchurch, 1982). Scott (1985, 1988) formally raised the Hawthorn Formation to group status and included most of the phosphatic sediments of Florida in this group. Details of Scott's (1985, 1988) stratigraphy and relationships to older usage are given in table 2. Scott's terminology is used on mine sections (figs. 5–23, appendix) and are followed, in general, in this work.

The Bone Valley gravels were first described by Matson and Clapp (1909) from deposits near Bartow, and the term "Bone Valley Formation" was formally applied by Cooke (1945). The original formation description appears to have been of beds derived by reworking of older sediments; these beds are present as channel deposits cutting older sediments and as blanket deposits. Webb and Crissinger (1983) described these channel deposits as unit 6. As mining expanded and processing technologies improved, more of the phosphorite section was utilized, and the term "Bone Valley" began to include coarse phosphatic sediments older than the original type material (Scott, 1985).

The Bone Valley was originally assigned to the Pliocene as was Webb and Crissinger's (1983) unit 6. The addition of older pebbly material that has faunas of middle to late Miocene age (Webb and Crissinger, 1983) widened the age limits of the Bone Valley Formation to include the Miocene and Pliocene. In the terminology of Scott (1985, 1988), the Bone Valley Formation is changed to a member of the Peace River Formation of the Hawthorn Group. The Miocene-Pliocene boundary is transgressed by the Bone Valley Member and includes all pebble beds at the top of the section.

Where well developed, the Bone Valley Member consists of two pebble beds separated by a sandy, clayey phosphorite (unit 4 of Webb and Crissinger, 1983). In the central land-pebble district, the contact between the Bone Valley Member and underlying sediments is distinct. The contacts are more subtle away from the center of the mining district. In many areas the lower pebble is missing; fine-grained sediments below an upper pebble bed may be difficult to classify. In Scott's terminology, the Bone Valley Member includes only the pebble beds at the top of the section. Fine-grained phosphorite beds below a single pebble bed are referred to as undifferentiated Peace River Formation.

In the southern extension, the lateral and time equivalent of the Bone Valley Member is the Tamiami

Table 2. Stratigraphic nomenclature and lithologic descriptions, Florida phosphate districts

<table>
<tr><th rowspan="2"></th><th colspan="2">Stratigraphy and lithology (Cathcart, 1985)</th><th colspan="2">Stratigraphic nomenclature (From Scott, 1985; 1989)</th></tr>
<tr><th>Land-pebble district</th><th>Southern extension</th><th>Southern Florida</th><th>Northern Florida</th></tr>
<tr><td>Holocene</td><td colspan="4">Loose windblown sand and black swamp muck deposits. Unnamed, or combined with named units below.</td></tr>
<tr><td>Pleistocene</td><td colspan="2">Unnamed terrace deposits
Bedded, loose to slightly clayey sand. Channel deposits of pebble phosphate at base. 10-40 ft thick.</td><td>Caloosahatchee Formation</td><td>Anastasia Formation</td></tr>
<tr><td>Pliocene</td><td>Bone Valley Formation Upper part
Clayey sand containing trace to minor amounts of phosphate grains. Aluminum and iron phosphate minerals where leached. 0-20 ft thick.</td><td rowspan="2">Tamiami Formation
Clay, sandy to sand, clayey. Contains abundant shells and a trace of phosphate grains. 0-75 ft thick.</td><td>Tamiami Formation</td><td>Citronelle and Cypresshead Formations</td></tr>
<tr><td rowspan="6">Miocene</td><td>Bone Valley Formation Lower part
Phosphorite, sandy, clayey, bedded and crossbedded. Conglomeratic at base. Contains iron and aluminum phosphate minerals where leached. 0-50 ft thick.</td><td rowspan="2">Hawthorn Group
Bone Valley Member</td><td rowspan="2">Missing
A thin, pebbly phosphate bed containing the same vertebrate fossils as the Bone Valley Member is present at the top of the ore zone at the Suwannee River mine.</td></tr>
<tr><td colspan="2">Hawthorn Formation</td></tr>
<tr><td>Northern part
Massive, yellow, fossiliferous, phosphatic dolomite. 0-10 ft thick.</td><td>Upper clastic unit
Gray-green sandy, silty clay. Contains dolomite and abundant fine phosphate. Possibly economic. 20-150 ft thick.</td><td>Peace River Formation</td><td>Statenville Formation
Coosawhatchie Formation</td></tr>
<tr><td>Central part
Interbedded dolomite, sandy clay, all with phosphate grains. 10-70 ft thick.</td><td>Lower carbonate unit
Dolomite and limestone, fossiliferous, some phosphate grains. 50-150 ft.</td><td>Arcadia Formation</td><td>Marks Head Formation</td></tr>
<tr><td colspan="2">Tampa Formation</td><td rowspan="2">Tampa Member
Nocatee Member</td><td rowspan="2">Penney Farms Formation</td></tr>
<tr><td>Clay, sandy clay, some chert and phosphate grains. 0-20 ft thick.</td><td>Dolomite and limestone at top. Gray-green clay, some phosphate at base. 0-50 ft thick.</td></tr>
</table>

Formation. The Tamiami Formation consists primarily of clayey sands and abundant shell materials with minor phosphate. Although Scott (1985, 1988) considered the Tamiami equivalent to the Pliocene part of the Bone Valley Member, Cathcart (1985) regarded the Tamiami to be synchronous with the Bone Valley section. Peck and others (1979) presented evidence that the Tamiami, similar to the redefined Bone Valley Member of Scott (1985, 1988), transgressed the Miocene-Pliocene boundary.

In northern Florida, the Citronelle and Cypresshead Formations are partly equivalent to the Tamiami Formation. Sediments having the characteristics of the Bone Valley Member are missing or not well developed. Thin pebbly phosphate beds containing vertebrate fossils similar to those in the Bone Valley Member of the central district are present at the top of the ore zone at the Suwannee River mine.

Below the pebble beds of the Bone Valley Member in the land-pebble district lie the beds previously called the Hawthorn Formation. Detailed work in the phosphate district (Cathcart, 1968) has shown that the Hawthorn Formation can be informally divided into an upper unit composed predominantly of siliciclastic material and a lower carbonate unit. This terminology has been followed by Bernardi and Hall (1980) and Cathcart (1985) and is also commonly used by mine and exploration geologists in the district. Under the stratigraphic revision, the upper clastic unit of the Hawthorn Formation is assigned to the Peace River Formation (Scott, 1985, 1988).

The Peace River Formation below the Bone Valley Member consists primarily of phosphatic, gray-green to blue clay, sand, and dolostone. Dolostone lenses are found at the base of the unit in the transition to the beds below. The undifferentiated Peace River Formation contains discontinuous pebble beds. Distinct pebble beds can be observed below indurated dolostones at the bases of many mines when water levels in drainage ditches are low.

The Statenville and Coosawhatchie Formations of north Florida are equivalent to the undifferentiated Peace River Formation. The Statenville Formation consists of phosphatic to very phosphatic interbedded and cross-bedded sand and clay with minor carbonate beds. The underlying Coosawhatchie Formation is composed of phosphatic, dolomitic sand and clay. Phosphate production in north Florida is from the Statenville Formation.

Below the Peace River Formation the carbonate unit of the Hawthorn has been renamed the Arcadia Formation (Scott, 1985, 1988, modified from Dall and Harris, 1892). The distinction between the Arcadia and Peace River Formations is the carbonate content. Where the carbonate content of the rock exceeds 50 percent and persists to depth, it is termed "Arcadia Formation". The Arcadia consists primarily of indurated dolostones. Phosphate grains and some nodules are present. It may not be possible to differentiate the Peace River and Arcadia Formations by outcrop alone; that is, if dolostone beds are found at the bottom of mining pits, they may either be carbonate lenses at the base of the Peace River or the top of the Arcadia Formation.

Equivalents of the Arcadia Formation in north Florida are the Marks Head and Penney Farms Formations. The Marks Head Formation is a complexly interbedded sequence of phosphatic carbonate, sand, and clay. The underlying Penney Farms Formation lies unconformably on Eocene carbonates and consists of interbedded phosphatic dolomites and siliciclastics. The dolomites become more abundant at the base.

The Tampa Formation has been reassigned as a member of the Arcadia Formation of the Hawthorn Group. The Tampa Member consists primarily of limestone and minor dolostone. A discontinuous dark-gray to gray-green silty dolomitic clay occurs at the base. The Tampa Member pinches out north of the central Florida phosphate district and appears to be the time equivalent of the Penney Farms Formation in north Florida.

CHEMICAL ANALYSES OF PHOSPHATE ORES

The chemical analyses of bulk samples of phosphate ore (table 3) indicate their mineralogic composition. Each chemical component is present in one or more minerals. Each mineral, especially francolite and iron and aluminum phosphates, may have variable compositions.

Beneficiation engineers and phosphate geologists commonly evaluate the chemistry of ore and phosphate concentrate in terms of major-element ratios such as CaO/P_2O_5 and F/P_2O_5. The F/P_2O_5 ratio for a stoichiometric fluorapatite is 0.09, and for the most highly substituted francolite it is about 0.15 (McClellan, 1980). Similarly, the CaO/P_2O_5 ratio is 1.32 for fluorapatite and 1.62 for francolite with maximum substitution. The presence of carbonates increases the CaO/P_2O_5 ratio above the ratio of the francolite that is present. Conversely, the presence of nonapatitic phosphates depresses this ratio.

The P_2O_5 contents of the samples are highly variable both within mines and within the entire data set; thus, general trends are not apparent. P_2O_5 is a component of francolite and of iron and aluminum phosphate minerals. The average P_2O_5 content of the Florida deposits is listed in industry reports and trade journals as 32 percent or about 70 percent bone phosphate of lime (BPL), but this figure is for concentrated phosphate particles and not for the deposit in the ground. The arithmetic average of the P_2O_5 content of all the stratigraphically correlated matrix samples in this study is 13.9 percent. Data in Pirkle and others (1967) show that 13 matrix samples from the central district averaged 15.5 percent P_2O_5. If the data from north Florida and the southern extension are excluded, the samples of this study contain an average of 14.5 percent P_2O_5. The Bone Valley Member, or equivalents, has a slightly higher P_2O_5 content (14.6 percent) than the minable undifferentiated Peace River Formation or equivalents (13.3 percent). Phosphate gravels of the Bone Valley Member are thin or absent to the south and east of the central district, and samples from north Florida and the transition to the southern extension are an indication of ore assays in the future; these samples average 9.5 percent P_2O_5.

The CaO content varies primarily with the francolite and carbonate contents but also with the clay and calcium-aluminum phosphate components. In 12 of the 17 mines examined, having both the Bone Valley Member and the undifferentiated part of the Peace River Formation in the section, the CaO/P_2O_5 ratio increases with depth. In three mines, the ratio decreases; in two, it remains the same. Samples of the Bone Valley Member and its possible equivalent in North Florida have a lower average CaO/P_2O_5 ratio (1.44) than samples of the undif-

Table 3. Chemical analyses of bulk samples of Florida phosphate ores

[Analyses in weight percent. BVE, Bone Valley Member equivalent; LBV, leached Bone Valley Member, Peace River Formation; BV, Bone Valley Member, Peace River Formation; UPR, undifferentiated Peace River Formation; S, = Statenville Formation]

		Analyses								Ratios	
Mine and sample no.	Stratigraphy	P_2O_5	CaO	F	SiO_2	Al_2O_3	Fe_2O_3	CO_2	MgO	CaO-P_2O_5	F-P_2O_5
Swift Creek-Suwannee River:											
1-84	BVE	8.0	14.8	1.3	61.1	3.6	0.7	5.6	2.5	1.85	0.16
2-84	S	7.8	11.9	1.1	63.8	6.7	1.5	1.7	1.0	1.52	.14
3-84	S	10.1	15.5	1.5	64.5	3.3	.9	1.4	.5	1.53	.15
Noralyn:											
6-84	BV	21.0	26.2	2.1	39.5	5.2	.8	1.1	.2	1.25	.10
4-84	UPR	22.5	32.6	2.7	31.3	3.6	1.5	2.6	.4	1.45	.12
5-84	UPR	11.2	17.0	1.5	51.0	2.4	8.3	1.7	.9	1.52	.13
Gardinier (Cargill):											
8-84	BV	7.3	9.9	1.1	73.9	4.2	.6	.8	.2	1.36	.15
7-84	BV	21.0	32.3	2.6	34.6	2.6	1.6	2.8	.3	1.54	.12
Nichols:											
10-84	BV	11.9	13.9	2.0	69.9	3.0	1.3	1.1	.1	1.17	.17
9-84	UPR	13.8	20.0	1.7	56.5	2.6	.6	1.4	.2	1.45	.12
Fort Meade:											
13-84	BV	16.5	24.4	2.0	46.3	3.9	.73	1.9	.3	1.48	.12
12-84	UPR	5.4	7.9	.8	73.9	5.5	1.4	.9	.3	1.46	.15
11-84	UPR	19.8	29.2	2.4	33.1	3.4	2.7	3.0	.6	1.47	.12
Clear Springs:											
16-84	BV	29.6	42.4	3.0	20.2	2.9	.27	1.7	.1	1.43	.10
15-84	UPR	15.1	21.8	1.8	51.5	3.1	.59	2.0	.2	1.44	.12
14-84	UPR	9.2	13.8	1.2	65.1	4.4	.59	1.9	.4	1.50	.13
Hardee Complex:											
17-84	BV	5.7	5.6	.6	80.5	4.0	.50	.7	.1	.98	.10
18-84	BV	19.0	31.3	2.3	43.2	1.4	.55	2.7	.2	1.65	.12
19-84	UPR	20.2	30.0	2.6	3.2	2.2	2.8	3.0	.4	1.48	.12
Fort Green:											
20-84	LBV	15.9	25.5	2.1	17.9	4.6	.52	1.9	.2	1.60	.13
21-84	BV	22.4	38.4	2.1	2.1	2.1	.7	2.6	.3	1.71	.09
22-84	UPR	15.4	21.6	1.8	1.9	1.9	1.5	1.8	.3	1.40	.12
Saddle Creek:											
25-84	BV	15.5	23.3	1.8	48.9	4.3	1.7	1.1	.3	1.50	.12
24-84	BV	15.9	26.1	1.9	47.8	3.4	1.8	1.4	.5	1.64	.12
23-84	UPR	15.6	22.6	1.9	50.0	3.3	2.1	.9	.7	1.44	.12

ferentiated Peace River Formation (1.55). The increase in CaO/P_2O_5 ratio with depth is primarily due to increases in dolomite content; however, in sections devoid of detectable carbonate, the composition of the francolite appears to change. The presence of iron and aluminum phosphate minerals in near-surface samples is indicated by CaO/P_2O_5 ratios of less than 1.32.

Francolite is the most common fluorine-bearing mineral in the deposits, although hydroxyl-bearing iron and aluminum phosphates may contain fluorine. The relatively low CaO/P_2O_5 and high F/P_2O_5 ratios in samples from the Gardinier (Cargill) and Nichols mines (table 3) suggest that other fluorine-bearing mineral phases may be present, although none has been identified. Although the average F/P_2O_5 ratio is the same (0.12) for the Bone Valley Member and the undifferentiated part of the Peace River Formation, it increases with depth in 9 of the 17 mine sections examined, remains the same in 4 sections, and decreases in 4 sections. The increase in the F/P_2O_5 ratio with depth in many mines suggests that, in general, the francolite is more highly substituted at depth.

SiO_2 occurs primarily as quartz and clay minerals and to a lesser extent as feldspar and opal. Al_2O_3 is

Table 3. Chemical analyses of bulk samples of Florida phosphate ores—Continued

		Analyses								Ratios	
Mine and sample no.	Strati-graphy	P_2O_5	CaO	F	SiO_2	Al_2O_3	Fe_2O_3	CO_2	MgO	$CaO\text{-}P_2O_5$	$F\text{-}P_2O_5$
Lonesome:											
26-84	BV	11.1	13.2	1.1	47.6	12.3	3.5	0.2	0.9	1.19	0.10
27-84	UPR	21.0	27.6	2.2	31.6	5.9	2.9	1.0	.5	1.31	.10
28-84	UPR	12.4	16.4	1.4	54.2	3.9	5.9	.6	.3	1.32	.11
Watson:											
29-84	UPR	15.0	22.2	1.8	47.3	3.4	3.1	1.9	.8	1.48	.12
Phosphoria:											
31-84	BV	11.2	14.6	1.2	62.9	5.7	.88	.9	.3	1.30	.11
30-84	UPR	12.3	16.9	1.4	55.6	5.7	1.7	1.3	.4	1.30	.11
30A-84	UPR	9.5	14.0	1.2	52.0	6.1	7.3	1.3	.9	1.47	.12
Rockland:											
32-84	BV	10.0	11.6	1.0	61.2	7.9	1.4	.9	.5	1.16	.10
33-84	UPR	7.2	10.6	1.0	47.1	2.1	17.0	7.2	1.2	1.47	.14
Haynsworth:											
34-84	BV	18.3	25.9	2.1	46.4	1.7	.87	1.2	.24	1.41	.11
35-84	UPR	17.3	24.2	1.9	47.5	2.1	.93	1.5	.25	1.39	.11
Lonesome:											
37-84	BV	12.1	18.7	1.3	57.1	5.0	1.3	1.4	.49	1.54	.11
36-84	UPR	13.3	22.6	1.7	48.1	4.5	1.8	1.2	2.0	1.70	.12
Hookers Prairie:											
41-84	LBV	20.2	28.4	2.3	37.4	4.1	.76	2.2	.29	1.40	.11
40-84	BV	13.7	23.0	1.7	50.1	4.4	1.4	2.1	.58	1.68	.12
39-84	UPR	10.6	22.0	1.4	41.0	3.6	1.7	7.5	4.2	2.07	.13
38-84	UPR	8.4	13.6	.8	66.6	3.6	1.8	1.3	.78	1.62	.09
Four Corners:											
44-84	BV	8.7	13.1	.8	74.0	1.1	.88	1.0	.2	1.50	.09
43-84	UPR	9.7	21.1	1.0	47.9	1.8	1.2	8.1	3.96	2.17	.10
42-84	UPR	9.5	14.7	.9	62.6	4.3	2.5	1.2	.59	1.54	.09
Kingsford:											
47-84	BV	12.6	18.8	1.2	53.9	5.1	1.9	1.1	.49	1.49	.09
46-84	UPR	15.4	28.6	1.8	28.6	2.7	4.4	9.1	3.59	1.86	.11
45-84	UPR	12.0	23.2	1.4	41.0	3.1	2.3	8.0	3.33	1.93	.12
Noranda-Hopewell:											
48-84	Unknown	22.8	33.2	2.4	27.4	4.6	1.6	2.2	.46	1.46	.10
Beker-Wingate Creek:[1]											
49-84	Unknown	30.3	44.7	3.4	7.9	1.2	2.1	4.0	.49	1.47	.11
50-84	Unknown	13.7	32.6	1.6	17.3	1.4	1.9	16.9	7.6	2.38	.12

[1] Sample 49-84 is a -20+200 mesh concentrate; sample 50-84 is +20 mesh pebble. Mining is under water, so stratigraphy is unknown.

present in the clay minerals, aluminophosphate minerals, and feldspar. Fe_2O_3 is highly variable and occurs as iron oxides, in iron phosphate minerals, and in clay carbonate minerals. The CO_2 content varies with the amounts of francolite and rhombic carbonate minerals. Most MgO is in dolomite, but francolite and the clay minerals also contain MgO.

The chemistry of the samples from mine to mine and within mines is highly variable, and differences are the result of both varying amounts of the mineral components and varying composition of the mineral species. The proportions of the mineral phases present may not be indicated by chemical data alone; however, changes in the CaO/P_2O_5 and F/P_2O_5 ratios can indicate variations of francolite composition both regionally and stratigraphically. The Bone Valley Member is only slightly more phosphatic than the minable zones of the undifferentiated part of the Peace River Formation.

MINERALOGY

Quartz and francolite are major components of the pebble fractions (plus 20-mesh), but potassium feldspars (both orthoclase and microcline) are in most samples in minor to trace amounts (figs. 5–23, appendix). Dolomite was commonly found at the base of many of the measured sections but is also present at the top of sections at the Swift Creek and Suwannee River mines (figs. 5, 6) in north Florida. This dolomite may have formed penecontemporaneously or may be reworked. Dolomite was present in the top sample at the Saddle Creek mine (fig. 14), but the interpretation may be confused because there is a secondary carbonate caliche in the section. The pebble fraction contains traces of smectite and palygorskite. Kaolinite was not detected in this fraction. The aluminum phosphate mineral wavellite is confined to the tops of economic zones or where shallow overburden exists.

Quartz is the major mineral in the feed fraction (minus 20- plus 200-mesh), and francolite, although present in all samples, is in minor to trace amounts in most samples. Most of the samples contain potassium feldspar, and it appears in somewhat greater abundance than in the pebble fraction. Wavellite, the only aluminum phosphate mineral detected in the feed fraction, is generally restricted to the top of sections. The only exception is at the Saddle Creek mine (fig. 14), where it is present in the bottom of the section. Clay minerals were not detected in the samples of the feed fraction.

Quartz is the major component of the minus 200-mesh (slime) fractions. Francolite shows an apparent increase in abundance with respect to quartz in both the pebble and feed fractions and is a major component of the slime fraction in the upper beds at many mines. This increase in francolite results from formation of chalky, soft, white phosphate in weathering zones. This soft phosphate is comminuted in washing and screening. Wissa and others (1982) found an average of 9.9 percent P_2O_5 in 12 phosphatic clay samples (minus 44 μm), and Bromwell (1982) found an average of 12.5 percent P_2O_5 in 16 samples of washer slimes; both studies concluded that francolite is the predominant nonclay mineral in slimes. Dolomite was commonly found at the base of most sections, although it was also present in the upper parts of some mine sections (Saddle Creek (fig. 14), Hookers Prairie (fig. 21), and Four Corners (fig. 22)). Albite is in the minus 200-mesh fraction at different levels at most mines, and potassium feldspar is abundant in this fraction. Wavellite is generally restricted to samples from the upper beds except at the Lonesome mine (fig. 15) and the Four Corners mine (fig. 22), where it is at the base. The calcium aluminum phosphate mineral crandallite is common in this fraction and can be found throughout the sections, even at the base of mines where other evidence indicates the sedimentary rocks are relatively less altered (Four Corners, fig. 22). Smectite is present from the tops to bases of economic sections. Palygorskite is generally confined to the base of sections but can be found higher in the beds of individual mines. Kaolinite is most abundant near the top of sections, although it was identified at all levels. Illite is restricted to the slime fraction. Sepiolite is rare and was detected only near the base of three of the mines. Goethite is found at the base of sections at many mines.

In the minus 2-μm fraction, quartz is nondetectable or is present in trace amounts. Francolite abundance in this size fraction varies from trace to major amounts. Albite is found throughout sections and is the predominant feldspar, although potassium feldspar is at all levels in trace to minor amounts. Wavellite, which generally is at the top of sections, was found at the base of the section at the Lonesome mine (fig. 20), where the normal sequence seems inverted. Crandallite is most common in the upper altered beds but was found throughout the deposits. Smectite is the major clay mineral, and palygorskite is generally confined to samples lower in the sections. Kaolinite is generally at the top of sections, but locally it can be found to the base of sampling. Goethite, as in the minus 200-mesh samples, is common at the base of sections.

In summary, quartz is the principal gangue mineral in the processed parts of the ore. Francolite is found in all particle-size fractions and is abundant in the slime fraction. Aluminophosphates are most common in the upper beds of individual sections. Smectite is the predominant clay mineral of the slime fraction and occurs throughout the deposits. Palygorskite generally occurs at the base of the sections, and kaolinite is generally found in the highest parts of the sections. In the coarser size fractions, potassium feldspar is the most common feldspar, and albite is the most abundant feldspar in the minus 200-mesh and clay fractions (<2 μm).

Francolite

In establishing a series of systematic relationships among francolites, Lehr and others (1967), McClellan and Lehr (1969), and McClellan (1980) used XRD, chemical analysis, and statistical methods to show that the contents of calcium, sodium, magnesium, phosphorus, CO_2, and fluorine can adequately describe most francolites. Studies of francolite in commercial concentrates of phosphate rock show that the replacement of Ca^{2+} by Na^+ and Mg^{2+} is systematic although limited. Thus, part of the Na^+ and Mg^{2+} in commercial concentrates is substituted within the francolite structure and cannot be removed by beneficiation. Similarly, carbonate substitutes for phosphate in a 1:1

ratio, with the maximum amount of substitution limited to about 6 percent CO_2. Net charge imbalances are compensated by both cation and anion substitutions. An important economic result of these substitutions is the reduction of the maximum P_2O_5 content of a 100-percent francolite concentrate from 42.2 percent in fluorapatite to 34.0 percent P_2O_5 in the most highly substituted francolite.

These substitutions have been shown to be represented adequately by a series with the following end-member empirical formulas (McClellan, 1980):

Fluorapatite $Ca_{10}(PO_4)_6F_2$
Francolite
$Ca_{10-X-Y}Na_XMg_Y(PO_4)_{6-Z}(CO_3)_ZF_{0.4Z}F_2$.

Because the unit-cell *a*-values decrease systematically with increasing carbonate substitution, the values for X, Y, and Z in the francolite model (McClellan, 1980) can be obtained by using the following formulas based on statistical models:

$$\frac{CO_3}{PO_4} = \frac{Z}{6-Z} = \frac{9.369-a_{obs}}{0.185}$$

$$(Na)X = 7.173(9.369-a_{obs}),$$

$$(Mg)Y = 2.784(9.369-a_{obs}),$$

in which

a_{obs} = *a*-value in angstroms determined by XRD,

Z = moles of CO_3^{2-} in the francolite formula,

X = moles of sodium in the francolite formula,

Y = moles of magnesium in the francolite formula.

The theoretical range of compositions between fluorapatite and francolite, based on calculations using the francolite model and empirical formulas, is shown in table 4. Francolite compositions have been computed by this method for typical concentrate samples from six well-known localities and are arranged in order of increasing substitution (table 5). Although these samples show a wide range of variability, they do not span the entire range of compositions shown by the end members.

The *a* values measured from the suite of Florida samples show a wide range (9.323–9.368 Å), both with respect to depth and within the size fractions of individual samples (table 6) and almost span the entire range of the francolite model (9.320–9.369 Å). In general, *a*-values in any particular mine decrease or remain relatively constant with depth within a given size fraction. Also, there is a trend in francolite composition from low to high *a*-values with the change from coarse to fine grain sizes, although there are exceptions.

Table 4. Comparison of the theoretical composition of fluorapatite and francolite

[Values in weight percent]

Constituent	Fluorapatite	Francolite (z/6-z≈0.30)
CaO	55.6	55.1
P_2O_5	42.2	34.0
CO_2	0	6.3
F	3.77	5.04
Na_2O	0	1.4
MgO	0	1.4
$CaO:P_2O_5$	1.318	1.621
$F:P_2O_5$	.089	.148

The changes in mean *a*-values for size fractions can be correlated with stratigraphy (table 7). The ranges and averages of P_2O_5 and CO_2 compositions were calculated from the *a*-value models; the highest grade francolites, approaching fluorapatite compositions, are present in the smaller size fractions. Histograms of *a*-values plotted according to stratigraphic position show the trends in *a*-values of francolite between size fractions and stratigraphy (figs. 2, 3). Although samples from the Bone Valley Member show slightly higher *a*-values as well as a greater range of values (standard deviation) than those from the undifferentiated part of the Peace River Formation, the data from these samples indicate that francolite compositions are not necessarily a reliable stratigraphic tool.

Previous studies of the Florida phosphorites have indicated differences in francolite composition within the deposits. Whippo and Murowchick (1967) noted compositional and crystallographic differences in francolite samples from Polk and Manatee Counties. The Manatee County samples (southern extension) were more highly substituted and contained 7 percent less P_2O_5 and 20 percent more CO_2 when calculated to an impurity-free basis. The data of Lehr and others (1967) indicated that francolites from Florida deposits have *a*-values ranging from 9.325 Å to 9.339 Å.

Studies of the pebble fractions from central Florida deposits (Stow, 1976) indicated that progressive alteration of pebbles, related to color changes (black to brown to white), resulted in decreasing CaO/P_2O_5 and lower F/P_2O_5 ratios. Williams (1971) correlated the color of concentrates from north Florida with francolite composition by chemical analysis and lattice parameter measurements. In general, dark-colored concentrates

Table 5. Calculated francolite compositions of various commercial phosphate ores

[Values in weight percent]

Source	CaO	MgO	Na_2O	P_2O_5	CO_2	F
Western United States	55.6	0.13	0.26	40.1	1.59	4.09
Tennessee	55.5	.24	.47	38.7	2.71	4.31
Florida	55.5	.36	.72	37.1	3.95	4.56
Morocco	55.4	.43	.85	36.3	4.53	4.68
North Carolina	55.3	.52	1.04	35.3	5.36	4.85
Tunisia	55.2	.60	1.20	34.7	5.70	4.93

Table 6. Unit-cell *a*-values of Florida phosphate ores

[All values in angstrom units (Å); standard error, less than 0.003 Å; NA, not available]

			a-values, Tyler Mesh			
Mine	Sample No.	Depth (feet)	Bulk	+20	-20 +200	-200
Swift Creek-Suwannee River.	[1]1-84	18-21	9.336	9.333	9.332	9.338
	[2]2-84	24-46	9.337	9.331	9.334	9.347
	[3]3-84	21-32	9.332	9.328	9.333	9.351
Noralyn	6-84	20-25	9.342	9.347	9.338	9.354
	4-84	25-34	9.337	9.336	9.347	9.345
	5-84	34-37	9.333	9.334	9.339	9.339
Gardinier	[4]8-84	27-30	9.347	9.330	9.347	9.352
	7-84	34-40	9.332	9.332	9.346	9.358
Nichols	10-84	16-22	9.355	9.352	9.356	9.352
	9-84	22-25	9.347	9.342	9.346	9.339
Fort Meade (Mobile).	13-84	19-29	9.330	9.328	9.332	9.344
	12-84	29-41	9.333	9.328	9.334	9.345
	11-84	43-50	9.334	9.328	9.332	9.343
Clear Springs	16-84	15-30	9.355	9.353	9.353	9.361
	15-84	30-38	9.338	9.337.	9.333	9.344
	14-84	42-46	9.336	9.338	9.334	9.337
Hardee Complex	17-84	16-22	9.348	9.368	9.343	9.346
	18-84	22-25	9.330	9.339	9.348	9.342
	19-84	25-29	9.335	9.332	9.350	9.350
Fort Green	[5]20-84	12-14	9.335	9.329	9.336	9.341
	21-84	14-22	9.328	9.326	9.330	9.347
	22-84	22-26	9.330	9.326	9.332	9.337
Saddle Creek	25-84	8-16	9.349	9.344	9.347	9.350
	24-84	16-19	9.340	9.338	9.341	9.347
	23-84	19-22	9.350	9.348	9.343	9.353
Lonesome	26-84	22-25	9.355	9.354	9.340	9.353
	27-84	27-30	9.341	9.345	9.342	9.353
	28-84	30-34	9.340	9.336	9.349	9.349

Table 6. Unit-cell *a*-values of Florida phosphate ores—Continued

Mine	Sample No.	Depth (feet)	*a*-values, Tyler Mesh			
			Bulk	+20	-20 +200	-200
Watson	29-84	10.5-22.5	9.338	9.336	9.335	9.342
Phosphoria	31-84	18-22	9.342	9.338	9.347	9.355
	30-84	22-31	9.345	9.345	9.347	9.352
	30A-84	31-33	9.336	9.336	9.337	9.355
Rockland	32-84	15-35	9.340	9.345	9.342	9.347
	33-84	35-37	9.335	9.328	9.337	9.345
Haynsworth	34-84	30-33	9.340	9.336	9.340	9.356
	35-84	33-36	9.345	9.337	9.339	9.357
Lonesome	37-84	16-26	9.346	9.344	9.340	9.345
	36-84	26-32	9.345	9.346	9.339	9.348
Hookers Prairie	41-84	14-17	9.334	9.332	9.336	9.343
	40-84	17-23	9.332	9.333	9.335	9.345
	39-84	23-29	9.332	9.328	9.329	9.335
	38-84	29-35	9.338	9.331	9.332	9.338
Four Corners	44-84	14-19	9.340	9.332	9.330	9.327
	43-84	23-35.5	9.336	9.324	9.332	9.333
	42-84	37-43	9.336	9.328	9.335	9.349
Kingsford	47-84	18-23	9.337	9.335	NA	9.360
	46-84	23-30	9.332	9.329	9.328	9.323
	45-84	30-42.5	9.334	9.330	9.335	9.329
Noranda-Hopewell	48-84	Unknown	9.338	9.337	9.341	9.348
Beker-Wingate[6]	49-84	Concentrate	9.336	NA	NA	NA
	50-84	Pebble	9.331	NA	NA	

[1] Combined sample.

[2] Swift Creek mine.

[3] Suwannee River mine.

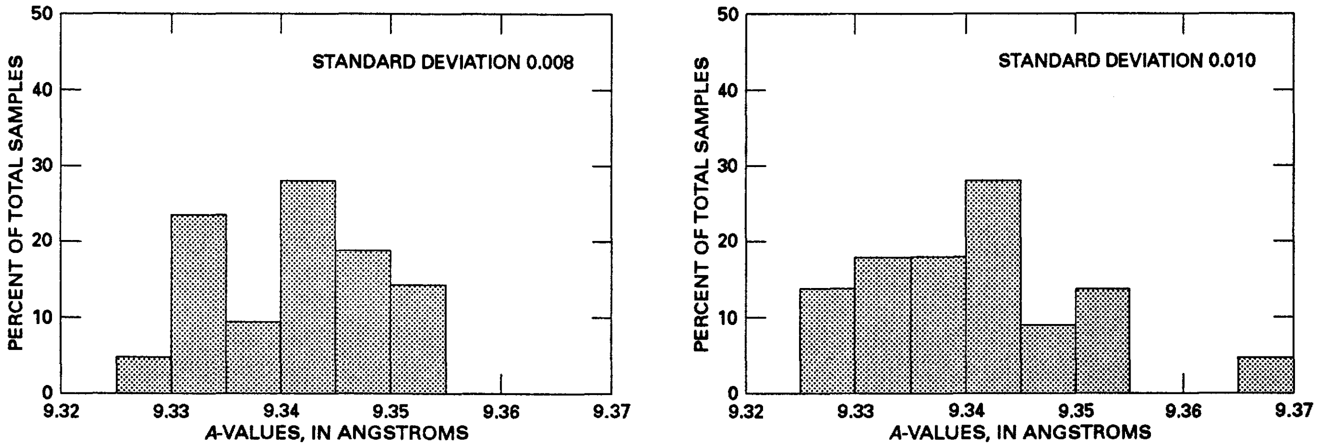
[4] Two samples from both the Bone Valley Member of the Peace River Formation and undifferentiated Peace River Formation collected 4 mi apart.

[5] One sample 20-84, leached Bone Valley Member, three samples (21-84), Bone Valley Member, three samples (22-84), undifferentiated Peace River Formation collected about 1 mi apart.

contained the most highly substituted francolites. The color of francolite grains appeared to be related to several factors including enclosing lithology, lateral and vertical stratigraphic position, postdepositional history, and possibly grain size. Williams (1971) noted the cyclicity of sedimentation and reworking of parts of the deposits as evidenced by the presence of white (altered) francolite grains in dark-colored restricted marine or basinal sediments.

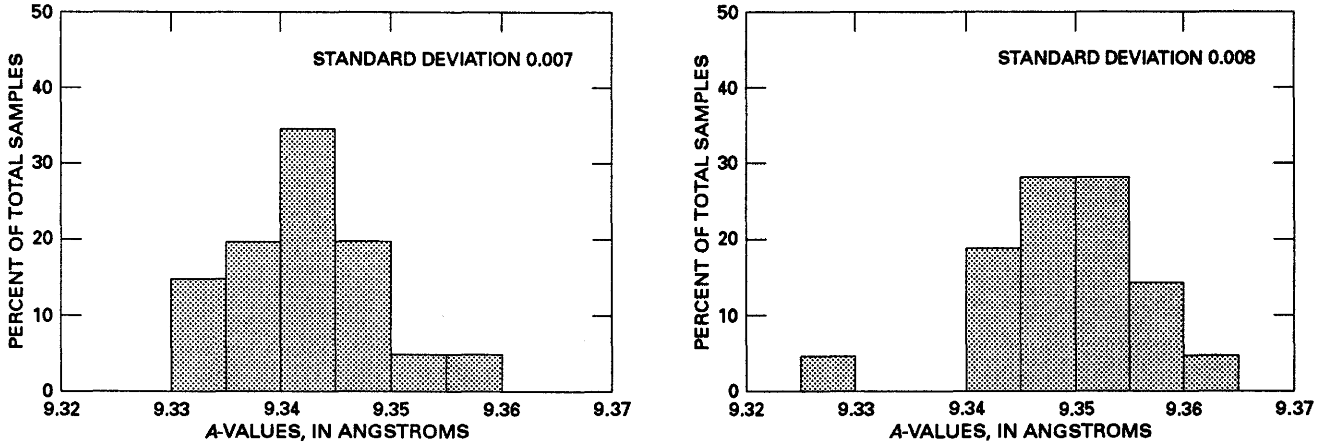
Weathering, alteration, and enrichment of phosphate deposits have been described and interpreted chemically and mineralogically at sites in Morocco (Lucas and others, 1980), Senegal (Flicoteaux and Lucas, 1984), and Togo (Flicoteaux and Lucas, 1984). For each deposit, changes in chemical ratios and francolite crystallographic properties were noted that indicated a progressive decrease in carbonate content in the weathered zones.

McArthur (1980) compared onshore and offshore Moroccan phosphorites and suggested that postdepositional weathering and interaction with ground water removes sodium, strontium, CO_3, and SO_4 from the structure of francolite. McArthur (1978) had earlier proposed the "constant composition hypothesis," according to which all primary francolites formed under similar conditions and therefore had similar compositions. McClellan (1980), working with a large sample base from deposits around the world, noted the variability of apatites in individual deposits with geologic time and proposed that through the combined effects of



BULK SAMPLES

+20 MESH SAMPLES



–20 TO 200 MESH SAMPLES

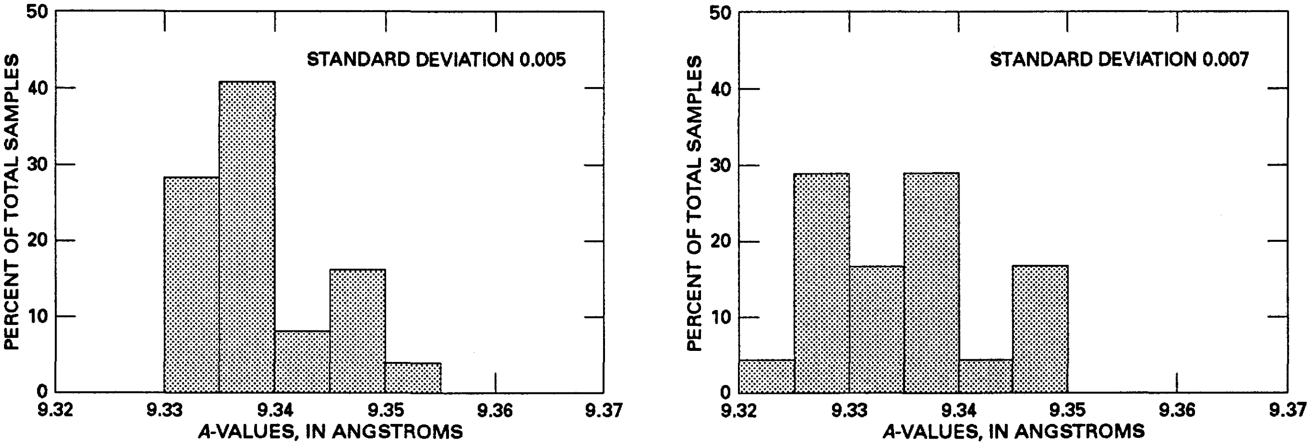
–200 MESH SAMPLES

Figure 2. Histograms showing variations in *a*-values of francolite in 22 bulk and screened samples from the Bone Valley Member of the Peace River Formation, Florida.

weathering, metamorphism, and time, francolites progressively alter from highly substituted varieties to essentially a fluorapatite composition. There are presently no known examples of reversal of this process, and thermodynamic considerations preclude this possibility (Chien and Black, 1976).

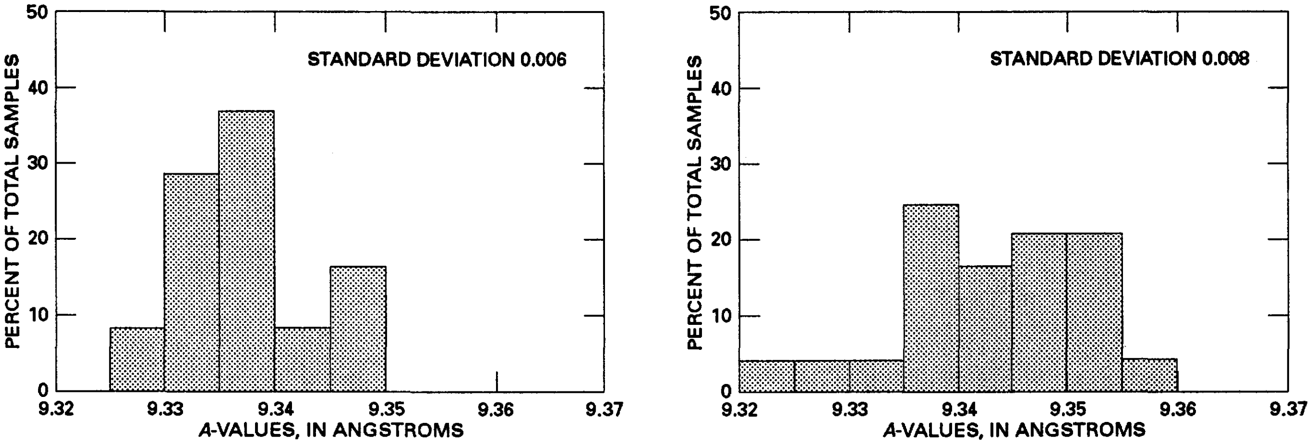
Variations in the carbonate content of francolites have also been attributed to the depositional environment. Gulbrandsen (1970) postulated that the general eastward increase in the X-ray-determined carbonate content of francolites in the Phosphoria Formation indicated a general warming of the seas as the water shallowed. Cook (1970) observed similar variations across the Phosphoria Formation and concluded that variations in temperature, pH, salinity, and depth could have caused the variations, although the complexity of dissolved inorganic carbon equilibria prevented a definitive interpretation. McArthur (1985) correlated the published CO_2 data with data on depth of burial for the Phosphoria and concluded that the diagenetic and catagenetic alteration of the francolites was related to depth of burial, presumably as a response to increased temperature and pressure.

The *a*-values of francolite from less altered deposits around the world generally are less than 9.330 Å (table 8); the *a*-value of a primary francolite, however, is not known. These deposits are considered to be less altered because they show slight or no evidence of weathering. Both the Miocene phosphorites of North Carolina (United States) and the Eocene Togo Bed 2/3 deposits of Africa (Johnson, 1987) are marine phosphorites that are now in a freshwater environment. The sample from the Congo River delta, west-central Africa, is Miocene in age and may have been subjected to freshwater in its history. The Tunisian samples are associated with calcareous marls and gypsum beds. Samples from the Miami Terrace and the West Florida Shelf are dredge samples thought to be of Miocene age. Most of these less altered francolites occur with calcite in the samples or are associated with calcite-bearing beds.



BULK SAMPLES

+20 MESH SAMPLES



–20 TO 200 MESH SAMPLES

–200 MESH SAMPLES

Figure 3. Histograms showing variations in *a*-values of francolite in 24 bulk and screened samples from the undifferentiated Peace River Formation, Florida.

The dissolution and removal of carbonates is an important process in the upgrading of phosphorite deposits. Carbonates buffer the pore water and protect the associated francolite by increasing the field of stability of francolite (Nathan and Sass, 1981). It is only after the carbonates are minimized or disappear that the francolite begins to alter towards low-carbonate varieties or to iron and aluminum phosphates (Altschuler, 1973; Lucas and others, 1980). This important constraint on the geochemical system limits changes in the composition of the bulk sediment through a series of complex steps. The alteration of carbonate-bearing phosphatic sediments would progress from dissolution of calcite to dissolution of dolomite (if present) and, at some time in the latter stages of carbonate dissolution, the alteration of highly carbonate substituted francolites to low-carbonate varieties. The actual mechanism of the latter process is not understood, but the process clearly results in the removal of some constituents from the francolite structure, in addition to CO_3. Solution and reprecipitation probably occur, although the scale of the process is not known.

The *a*-value data for least altered francolites in Florida (less than 9.330 Å, table 9) indicate that the highly carbonate substituted varieties are associated with the coarser fractions and with samples that contain dolomite or calcite. However, the presence of dolomite does not assure low *a*-values. For example, samples from the Saddle Creek (fig. 14) and Clear Springs (fig. 11) mines contain dolomite, but the *a*-values of the francolites are more than 9.340 Å. These values suggest that the alteration of the francolite may have occurred before dolomitization in these beds or that mixing has occurred.

The size fractions in only three samples (from Four Corners (fig. 22) and Kingsford (fig. 23) mines) deviate significantly from the typical sequence of increasing *a*-values with decreasing particle size (samples 47–84,

Table 7. Variations of francolite *a*-values and composition with stratigraphy, Florida phosphate ores

[X-ray P_2O_5 and CO_2 values, in weight percent, calculated by procedures from McClellan (1980)]

Sample group (Tyler mesh)	Range *a*-values (Å±0.003)	Mean *a*-value (Å±0.003)	Range X-ray P_2O_5	Average X-ray P_2O_5	Range X-ray CO_2	Average X-ray CO_2
Bone Valley Member of the Peace River Formation (22 samples)						
Bulk	9.328-9.355	9.341	35.86-39.14	37.65	4.93-1.87	3.53
+20	9.328-9.368	9.340	35.86-39.31	37.50	4.93-0.14	3.64
-20 to +200	9.330-9.356	9.341	36.12-36.94	37.65	4.72-1.74	3.53
-200	9.327-9.361	9.349	35.73-40.08	38.84	5.03-1.04	2.60
Undifferentiated Peace River Formation (24 samples)						
Bulk	9.330-9.350	9.338	26.12-39.00	37.22	4.72-2.48	3.87
+20	9.324-9.348	9.334	35.35-38.69	36.66	5.33-2.72	4.30
-20 to +200	9.328-9.346	9.337	35.86-38.84	37.08	4.93-2.60	3.98
-200	9.323-9.357	9.343	35.22-40.12	37.94	5.43-1.61	3.31

Table 8. Examples of *a*-values of less-altered francolite from various localities throughout the world

[Values are in angstrom units (Å)]

Sample locality	No. of samples	Range (Å±0.0001)	Average (Å±0.0001)
Congo, Africa (offshore)	5	9.320-9.327	9.324
Togo, Africa (Bed 2/3)	5	9.325-9.333	9.329
Tunisia	5	9.320-9.331	9.327
North Carolina	18	9.318-9.332	9.323
Miami Terrace	1	None	9.326
West Florida Shelf	1	None	9.319

Table 9. Francolite samples from Florida with *a*-values less than 9.330 (±0.003 Å)

Mine	Sample No.	Size fraction (Tyler mesh)	*a*-value	Carbonates All size fractions
Suwannee River	3-84	+20	9.328	Dolomite, calcite.
Fort Meade	13-84	+20	9.328	Not detected.
	12-84	+20	9.328	Dolomite.
	11-84	+20	9.328	Dolomite.
Fort Green	20-84	+20	9.329	Not detected.
	21-84	+20	9.326	Not detected.
	22-84	+20	9.326	Dolomite.
Rockland	33-84	+20	9.328	Dolomite.
Hookers Prairie	39-84	+20	9.328	Dolomite.
	39-84	-20-200	9.329	Dolomite.
Four Corners	44-84	-200	9.327	Dolomite.
	43-84	+20	9.324	Dolomite.
	42-84	+20	9.328	Dolomite.
Kingsford	46-84	+20	9.329	Dolomite.
	46-84	-20-200	9.328	Dolomite.
	46-84	-200	9.323	Dolomite.
	45-84	-200	9.329	Dolomite.

46–84, 45–84). At the Four Corners mine (fig. 22), the beds below sample set 44–84 show a normal progression to higher *a*-values with decreasing particle size. In two of these three samples (44–84 and 47–84) as well as in sample 13–84 (fig. 10), aluminophosphates occur with less altered francolites in the pebble fraction. This unusual association may result from mixing of materials from different sources or may indicate that francolites do not have to progress to low-carbonate-substituted varieties before conversion to aluminophosphates can occur.

The variability in francolite composition may result from many factors. Original composition, presence of carbonates, mixing of altered francolite with unaltered francolite, stratigraphic position or depth, degree and depth of weathering, depth and character of overburden, size of phosphate particles, possible sheltering effects of impermeable clay beds or indurated dolomite layers, hydrologic controls, and paleotopography all may have contributed to producing the francolite compositions of today.

The general increase in *a*-values from coarser to finer size fractions may be due to preferential alteration of the fine sizes because of their greater relative surface area. Mixing of altered and primary or less altered francolites in various particle sizes may have occurred during subaerial or subaqueous exposure and erosion of the phosphorites. The fine-grained altered francolite could have been preferentially moved offshore to be mixed with primary or less altered francolites, and the resultant *a*-values of such samples would then vary in proportion to the composition of the constituents.

On the basis of francolite compositions, every section examined in this study shows some degree of alteration, even in the lowermost beds of the downdip facies in the southern extension of the central district. The precise stratigraphic position of the samples from the Wingate Creek mine cannot be ascertained because the section is mined by dredge; however, the samples show enough variation to indicate that they were from a zone of detectable alteration. The lowermost beds of the Kingsford mine (fig. 23) appear to be the least altered of the sections studied.

In deeper sections, downdip to the south, and in the north where the phosphatic Miocene sediments of Florida are less altered, the francolites change in composition to more highly substituted varieties with decreasing P_2O_5 content and increasing impurity content. In general, the finer size fractions contain francolite with the lowest carbonate substitution, lowest impurity content, and greatest P_2O_5 concentration. Based on an average of 12.5 percent P_2O_5 in washer tailings (Bromwell, 1982) and an average *a*-value of 9.346 Å for combined beds of the Bone Valley Member and the undifferentiated part of the Peace River Formation, the francolite content of an aluminophosphate-free sample slime would be about 33 weight percent. Because most slime samples contain appreciable amounts of aluminophosphates, this is a maximum value. Deviations from the typical occurrence of most altered francolite at the top of the sections and in the finer size fractions indicate the complex nature of the formation of the deposits.

Clays

The clay minerals in the phosphate deposits of Florida are a mixture of common (smectite, illite, and kaolinite) and less common (palygorskite and sepiolite) minerals. The general sequence of clay minerals in economic zones is, from top to base, kaolinite to smectite to smectite plus palygorskite (Altschuler and others, 1964). Smectite is the most abundant clay mineral in the Florida Miocene sediments (McClellan, 1962; Weaver and Beck, 1977; Reik, 1982). The smectite may be original detrital material (Weaver and Beck, 1977), the result of diagenesis, or a mixture of the two. The kaolinite is thought to be a mixture of detrital material (Weaver and Beck, 1977) and material derived from the alteration of smectite (Altschuler and others, 1963). The illite in these sediments is considered to be detrital and is only a minor phase.

Palygorskite (attapulgite) and sepiolite, clay minerals with chain-type molecular structures similar to amphiboles, tend to be fibrous and range in size from less than 2 μm to about 10 μm. Sepiolite is rare and is generally restricted to the very base of sections. Commercially important deposits of palygorskite occur interbedded with the Miocene sediments of northwestern Florida and southwestern Georgia. The association of phosphorite and palygorskite is not unique to the Florida deposits; palygorskite is interbedded or closely associated with many phosphorite deposits in Africa and the Middle East. In general, palygorskite occurs at the base of the phosphate mines in Florida and higher in the sections where carbonates are present. It is also associated with endogangue in phosphate pebble and can be found high in sections where protected by relatively impermeable smectite beds. One occurrence of massive-bedded palygorskite in peninsular Florida is at the Clear Springs mine (Upchurch and others, 1982; Strom and Upchurch, 1983, 1985).

Chemical analyses of two nearly pure palygorskite samples from north and central Florida phosphorite deposits (table 10) are typical of palygorskite from deposits in the region (Weaver and Pollard, 1973). XRD patterns of the samples indicate a minor amount of intimately associated smectite, and a separation of the (121) and ($12\bar{1}$) reflections indicates the monoclinic polymorph. Both samples proved to be the long-fiber variety (fiber lengths greater than 2 μm) under scanning electron microscope observation. Weaver and Pollard (1973) and Weaver and Beck (1977) reported that the short-fiber variety (fibers averaging approximately 1 μm in length) is the predominant type from commercial deposits in south Georgia and north Florida and interpreted their palygorskite XRD data to indicate orthorhombic symmetry.

Palygorskite is known to form by hydrothermal alteration of mafic rocks, in soil zones under arid conditions, in deep-sea sediments, and in hypersaline playa lakes, and it is thought to form in restricted schizohaline lagoons or ephemeral lakes (for a review, see Singer, 1979). There is little evidence that palygorskite forms under normal marine conditions. Palygorskite-sepiolite in the Florida deposits has most recently been postulated to have formed in a perimarine environment (Weaver, 1984; Weaver and Beck, 1977) or in ephemeral lakes (Strom and Upchurch, 1983, 1985; Upchurch and others, 1982). Weaver and Beck (1977) proposed that primary deposition of the palygorskite and sepiolite in north Florida occurred prior to the transgression of the middle Miocene seas and that the association with the middle Miocene phosphates may largely be detrital, although some diagenetic palygorskite also is present in the deposits. The palygorskite in the

Table 10. Chemical analyses of palygorskite samples from Florida phosphate deposits

[Values in weight percent]

Constituent	Clear Springs mine	Suwanne River mine
SiO_2	60.04	58.65
Al_2O_3	9.76	10.32
Fe_2O_3	3.46	4.94
MgO	12.15	10.51
K_2O	.57	.39
Na_2O	.18	.37
CaO	.00	.02
TiO_2	.41	.28
MnO	.03	.02
$^*H_2O^+$	12.60	12.93
Total	99.20	98.43
Octahedral Al/Mg	.59	.71

*Water retained above 105°C.

phosphate deposits of Florida may have resulted from the transformation of smectites by the addition of magnesium (Altschuler and others, 1956; Altschuler and others, 1964).

The smectites of the Florida phosphorite deposits have been described as nontronitic (Altschuler and others, 1963) and iron rich (Strom and Upchurch, 1985; Bromwell, 1982). XRD analysis of clays from cores of phosphorites in northeastern Florida shows broad smectite peaks, which were interpreted by Reik (1982) as indicating mixed-layer types.

Chemical, XRD, and thermal techniques were used in this study to investigate the nature of smectite-rich clay samples. Several kaolinite-free smectite samples were X-rayed to determine their characteristic d-spacings (table 11). The measurement of 060 reflections indicates an average value of 1.501 Å, which nearly agrees with the 1.495-Å value reported by Altschuler and others (1963) for their nontronitic montmorillonite. Brindley (1980) reported 060 values of 1.504–1.492 for various types of montmorillonites. Weir and Greene-Kelley (1962) and Brindley (1980) report 060 values of 1.498 Å and 1.497 Å, respectively, for beidellite. Nontronites have slightly larger 060 values of 1.522–1.525 (Schneideröhn, 1964; Carroll, 1970; Chen, 1977). These data indicate that the smectite in the samples studied is beidellite or montmorillonite rather than nontronite.

Lithium saturation, heat, and glycolation treatments, according to the method of Brusewitz (1975), were performed on clay samples 26–84, 38–84, and 42–84 (table 11). Using these treatments, montmorillonite may be distinguished from beidellite and nontronite. Changes in the observed 001 reflection also

Table 11. Characteristic d-spacings of smectite from Florida phosphate deposits

[Values in angstrom units. BV, Bone Valley Member of the Peace River Formation; UPR, undifferentiated Peace River Formation]

Mine and sample no.	Stratigraphy	d-spacing Air dried (001)	Glycolated (001)	Heated (001)[1]	Randomly oriented(060)[2]
Lonesome 26-84	BV	14.66	17.36	10.08	1.500
Phosphoria: 30a-84	UPR	14.93	17.03	10.15	1.502
Hookers Prairie: 38-84	UPR	15.08	17.26	10.40	1.502
Four Corners: 42-84	UPR	14.54	17.30	10.30	1.505
Kingsford: 45-84	UPR	14.72	17.14	10.10	1.502
Hookers Prairie: 1985-1	UPR	15.43	17.55	10.15	1.498

[1] Heated at 350°C for 24 hours.

[2] No kaolinite detectable by X-ray diffraction.

indicate that the smectites associated with kaolinite-free samples are beidellite. These lithium- and heat-treated samples re-expanded with glycolation.

Structural formulas derived from the chemical analyses of the clay samples confirm this interpretation. When the chemical data for some of these smectites (table 12) and that of Altschuler and others (1963) are converted to structural formulas using the methods of Marshall (1949) and Ross and Hendricks (1945), the results indicate that most of the charge occurs in the tetrahedral layer. This characteristic separates beidellite from montmorillonite (Greene-Kelly, 1955; Weir and Greene-Kelly, 1962). The charge division between the octahedral and tetrahedral layers of sample 26–84 (Lonesome mine, Bone Valley Member of the Peace River Formation (fig. 15) is approximately equal; however, the sample reacted positively to the lithium-saturation test. These structural formulas and layer-charge calculations are not inerrant, but they may be useful data transformations when used in conjunction with other data. For a more complete discussion of the errors and limitations in the interpretation of such chemical data and structural formulas, see Schultz (1969).

The high iron oxide contents in Florida smectite samples complicate the interpretation of the chemical data. Field and microscopic evidence indicate that some of the iron occurs as discrete clay-size iron oxide particles and surface coatings. Although routine chemical extraction of clay minerals should be avoided because of possible mineralogic changes, samples 26–84 and 42–84 (table 12) were extracted with sodium dithionite (Mehra and Jackson, 1960). A reduction of 40–50 percent in the Fe_2O_3 content of these samples resulted in analyses very similar to those of the average montmorillonite-beidellite of Weaver and Pollard (1973, p. 56). XRD analyses before and after iron oxide extractions indicated no significant change in the smectite. The molar Mg/Fe ratio of unextracted samples is essentially 1, but the ratio of extracted samples is about 2. The contents of MgO in the samples suggest that these smectites are members of a beidellite-montmorillonite series rather than a beidellite-nontronite series.

Thermal analyses also confirm that these smectites are beidellites. Trauth and Lucas (1967) reported that nontronite dehydroxylates at approximately 500°C, whereas beidellite dehydrated at 550°C. Thermal analyses of the central Florida smectites indicate endotherms between 540 and 560°C. Schultz (1969) classified montmorillonites and beidellites into seven groups based on their composition, amount and distribution of their layer charge, thermal behavior, and properties that are revealed by Li^+ and K^+ treatments. Nonideal montmorillonites and nonideal beidellites can be distinguished from their ideal counterparts by their characteristic dehydroxalation endotherms (550–590°C for nonideal types versus 665–730°C for all other types). On the basis of thermal analyses and other data, the Florida smectites may be more appropriately termed nonideal beidellites.

Table 12. Chemical and layer-charge analyses of selected Florida smectite samples

[Analyses, in weight percent, corrected for identified apatite, dolomite, crandallite, and wavellite after chemical determination of P_2O_5, CaO, MgO, CO_2, and Al_2O_3. NA, no analysis]

	Sample no., location, and stratigraphic unit			
Constituent	26-84[1]	SC1[2]	FHPC	42-84
SiO_2	57.25	56.91	53.38	55.46
Al_2O_3	21.54	22.65	22.89	20.95
Fe_2O_3	3.13	6.29	6.48	4.75
FeO	None	.11	NA	NA
MgO	3.28	3.62	2.59	3.90
K_2O	1.64	.74	1.32	1.41
Na_2O	.21	.18	.87	0.06
CaO	.75	1.47	.67	.27
TiO_2	.95	.65	.76	.64
MnO	.03	NA	.02	.04
[3]H_2O^+	11.21	7.34	10.87	11.54
Total	99.99	99.96	99.85	99.02
Octahedral charge	-.18	-.05	+.01	-.10
Tetrahedral charge	-.15	-.30	-.35	-.22
Total charge	-.33	-.35	-.34	-.32

[1] Sodium dithionite extracted, original Fe_2O_3 analyses: 26-84, 5.1 weight percent; 42-84, 10.6 weight percent.

[2] From Altschuler and others (1963).

[3] Water present above 105°C.

SAMPLE SOURCES

26-84: Lonesome mine, Bone Valley Member of the Peace River Formation.
SC1: Silver City mine, Bone Valley Member of the Peace River Formation.
1985-1: Hookers Prairie mine, undifferentiated Peace River Formation.
42-84: Four Corners mine, undifferentiated Peace River Formation.

Wissa and others (1982) also performed lithium-saturation tests on mixed slime samples and noted incomplete expansion with glycolation, which indicated the presence of a minor montmorillonite component and an undefined smectite. Montmorillonite may be present in the Florida phosphate deposits, and further studies are needed to define its relationship to the other clays of the deposit.

XRD analysis of smectite-kaolinite mixtures from the upper, more weathered levels of the mines show 001 smectite peaks that are broad and that contain multiple maxima, which suggest mixed-layer effects. Wissa and others (1982) and Bromwell (1982) studied washer and pond slimes and concluded that most of their samples contained a mixed-layer smectite of an unspecified nature. These samples represented mixtures of clays from many different areas undergoing active mining. The apparent mixed-layer effect in smectite-kaolinite mixtures may be due to transitional phases that form as smectites alter to kaolinite (Altschuler and others, 1963). The broad, diffuse nature of the 001 peaks of the smectite and responses to various treatments may be a function of the crystallinity of these phases rather than discrete mixed-layer conditions.

The origins of the smectites in the Florida phosphate deposits are a matter of speculation. Weaver and Beck (1977) referred to the smectites as detrital material and suggested a volcanic origin (p. 186). Grim (1933), on the basis of the identification of isotropic fragments as glass shards, proposed that the clays of the Miocene deposits in the southeastern United States might be the result of alteration of volcanic debris. Mansfield (1940), Gremillion (1965), and Heron and Johnson (1966) all supported the interpretation that these clays, or parts of them, were derived from volcanogenic material. Kerr (1937), Espenshade and Spencer (1963), and McClellan (1964), however, did not find evidence of volcanic material in these sediments. Heron and Johnson (1966) believed the absence of glass shards to be inconclusive; vitreous volcanic material would probably be destroyed or altered by subsequent weathering or diagenetic alteration. Based on province studies using heavy and clay-mineral suites from the western, central, and eastern Gulf Coast Miocene sediments, Isphording (1973) argued against a volcanic origin for these clays. Just as Altschuler (1965) interpreted the phosphate in the central Florida deposits to have been repeatedly physically and chemically recycled, these smectites may have been similarly recycled and their original character obscured.

Carbonates

Dolomite is the most abundant carbonate mineral in the Florida phosphate deposits. Dolomite may be present as mineral grains dispersed in the phosphate sediments or as nearly pure indurated lenses. Dolomite is generally found in the lower beds of the minable ore in the central Florida phosphate district, and mining commonly ends at the occurrence of indurated dolostones or bed clays immediately above dolostone beds. In the south and north Florida districts, dolomite is more prevalent and occurs throughout the minable horizons. Much further downdip, and at depth, in the transition from the Arcadia Formation to its underlying Tampa Member, calcite is the predominant mineral (T.M. Scott, Florida Geological Survey, oral communications; Berman, 1953). Siderite has been observed in the minus 200-mesh (Tyler) fraction of the bed clay in the Noralyn mine (this study) and associated with vivianite at the Clear Springs mine (Barwood and others, 1983).

Table 13. X-ray analyses of Florida dolomite samples

[$CaCO_3$ estimated graphically from diagrams based on iron-free dolomite (Reeder, 1983); the exact chemical compositions of the Florida samples are unknown]

Mine	*a*-value (±0.002) (angstroms)	c-value (±0.007) (angstroms)	X-ray $CaCO_3$ by *a*-value (percent)	X-ray $CaCO_3$ by c-value (percent)
Hardee Complex	4.814	16.026	51.8	51.1
Hookers Prairie	4.819	16.026	53.2	51.1
Saddle Creek	4.819	16.047	53.2	52.0
Suwannee River	4.815	16.033	52.2	51.3

XRD analyses of indurated dolostones that occur at the base of several mine sections (table 13) indicate that these carbonates are well crystallized and slightly magnesium deficient (1–3 percent mol $MgCO_3$). Such calcium-rich, magnesium-deficient dolomites have been noted in northern Florida and southern Georgia in Miocene sediments and were interpreted to have formed penecontemporaneously under schizohaline conditions (Weaver and Beck, 1977). Replacement of preexisting calcite by dolomite has been proposed (Altschuler and others, 1964). Hanshaw and others (1971) also noted replacement dolomites in Tertiary rocks of Florida but explained this extensive dolomitization by ground-water circulation.

Although seawater is the most logical source of Mg^{2+} for dolomitizing solutions, the breakdown of mineral components may also provide Mg^{2+}. One mineral source for dolomitizing constituents within the sediments is the degradation of smectite that releases Mg^{2+} into the environment (Altschuler and others, 1963). Another possible source of Mg^{2+} and CO_2 for dolomitization is the alteration of francolite in the deposits (this study). A maximum substituted francolite (McClellan, 1980) contains about 5.72 weight percent CO_2 and 0.57 weight percent MgO as an integral part of its structure. As the francolite is altered, these constituents are removed and released into the pore fluids. Interaction with other magnesium-rich minerals undergoing alteration (palygorskite and sepiolite) could result in the formation of dolomite.

Carbonates may have been precursors of the Florida deposits. One origin suggested for the phosphate in the Bone Valley Member of the Peace River Formation is the weathering of a source limestone or marl, removing carbonate and thereby concentrating phosphate (Altschuler and others, 1964). Riggs (1979a, 1979b, 1984) stressed the primary nature of phosphorite formation in the deposits of the southeastern United States. Riggs (1979a) did not believe that the replacement of calcite by phosphate was significant in forming the phosphate deposits, although evidence suggests that this process has occurred. Gilliland (1976) provided an interesting model of the formation of the Florida deposits. This computer simulation is based on an energy-circuit model utilizing chemical reactions, reaction pathways, and mass balancing. Although the model is based on many assumptions, it attributes the occurrence of phosphate deposits in Florida to a combination of primary low-level deposition by the upwelling of deep ocean water to the surface and enrichment by the selective removal of carbonate from phosphatic carbonate source rocks since Miocene time.

Other Minerals

Reported heavy minerals from tailings sands (Stow, 1968) include ilmenite, rutile, zircon, monazite, garnet, kyanite, sillimanite, tourmaline, epidote, and gahnite. Because these detrital heavy minerals are a very minor component of the deposits, they are not discussed in this paper other than to note their presence.

Opal-CT also occurs in variable quantities in the Hawthorn Group (Strom and Upchurch, 1985), although it was not detected as a major component in the samples in this study. Its significance is unknown; does the dissolution of opal-CT contribute to the development of authigenic clays, or does the dissolution of clays lead to the formation of authigenic opal-CT?

Both aluminophosphates and iron phosphates are common in the mining districts of Florida. Because the samples for this study were taken from producing horizons and excluded the leached uppermost zones of the mines, no iron phosphates were noted. Crandallite and wavellite (aluminophosphates) were common components of the samples, particularly at the upper levels of mines. Altschuler and others (1956) first noted the progression: crandallite plus millisite (if conditions are correct) to wavellite. This sequence was generally observed in the sections used in this study. Wavellite appears in all size fractions of the ore, whereas crandallite appears only in the slimes and minus 2-μm fraction.

The presence of aluminophosphates throughout sections of individual mines confirms the extensive weathering these phosphorites have undergone. Wavellite and crandallite can occur deep in sections with minerals that represent less altered phosphorite (dolomite, low *a*-value francolites, and palygorskite) and are evidence for mixing of materials with differing origins (Hookers Prairie (fig. 21), Four Corners (fig. 22), and Kingsford (fig. 23) mines). These minerals are detrital where they occur with less altered phosphorite in that they are derived from local reworking of preexisting altered phosphorite. Little information exists on the stability of these minerals in various environments.

Feldspars are a minor component of all the phosphorite sections at all levels of the mines. The interesting characteristic of the feldspar mineralogy is that albite is found in the slimes and clay fractions, whereas potassium feldspar predominates in the coarser size fractions. Albite has been noted in less altered phosphorites in North Carolina (Rooney and Kerr, 1967) and in the finer size fractions of palygorskite-sepiolite deposits in northern Florida (Weaver and Beck, 1977). Weaver and Beck attributed the presence and mixed mineralogy of the feldspars to detrital particles from differing source areas.

DISCUSSION AND CONCLUSIONS

The observed variations in mineralogy through the Florida phosphate districts result from primary depositional and compositional differences as well as superimposed postdepositional alteration. Primary compositional differences may result from mixing or changing of the source areas, mixing of primary minerals with altered, recycled minerals, winnowing and resultant lag deposits of larger and(or) heavier minerals (that is, apatite), and the result of the effects of changing climatic and environmental conditions. Postdepositional alteration is the result of all the changes in physical and chemical factors that have modified the sediment since deposition.

Altschuler (1965) stressed the precipitated and recycled nature of the phosphate in the Florida land-pebble deposits. Altschuler's cyclic model, based primarily on petrographic and field evidence, equated the reworked character of the phosphorite deposit with periods of submergence and emergence and associated wave activity. These numerous cyclic episodes of reworking and weathering left multiple imprints upon the Florida deposit. The multiplicity of these episodes and the contrasting depositional and postdepositional histories of the North Carolina and Florida deposits are made apparent by combining the data of Webb and Crissinger (1983) with that of Riggs (1984), based on the sea-level curves of Vail and Mitchum (1979) (fig. 4).

At the northern end of the phosphogenic province, the North Carolina phosphorites appear to have been continually deposited in a marine environment. The deposits have been essentially preserved in their original state. The deposits in Florida, however, were subjected to many episodes of subaerial exposure and nearshore sedimentary processes. Deposition of the lower undifferentiated part of the Peace River Formation (units 1 and 0 of Webb and Crissinger, 1983 (fig.4)) corresponds to a general rising in sea level in the early to middle Miocene.

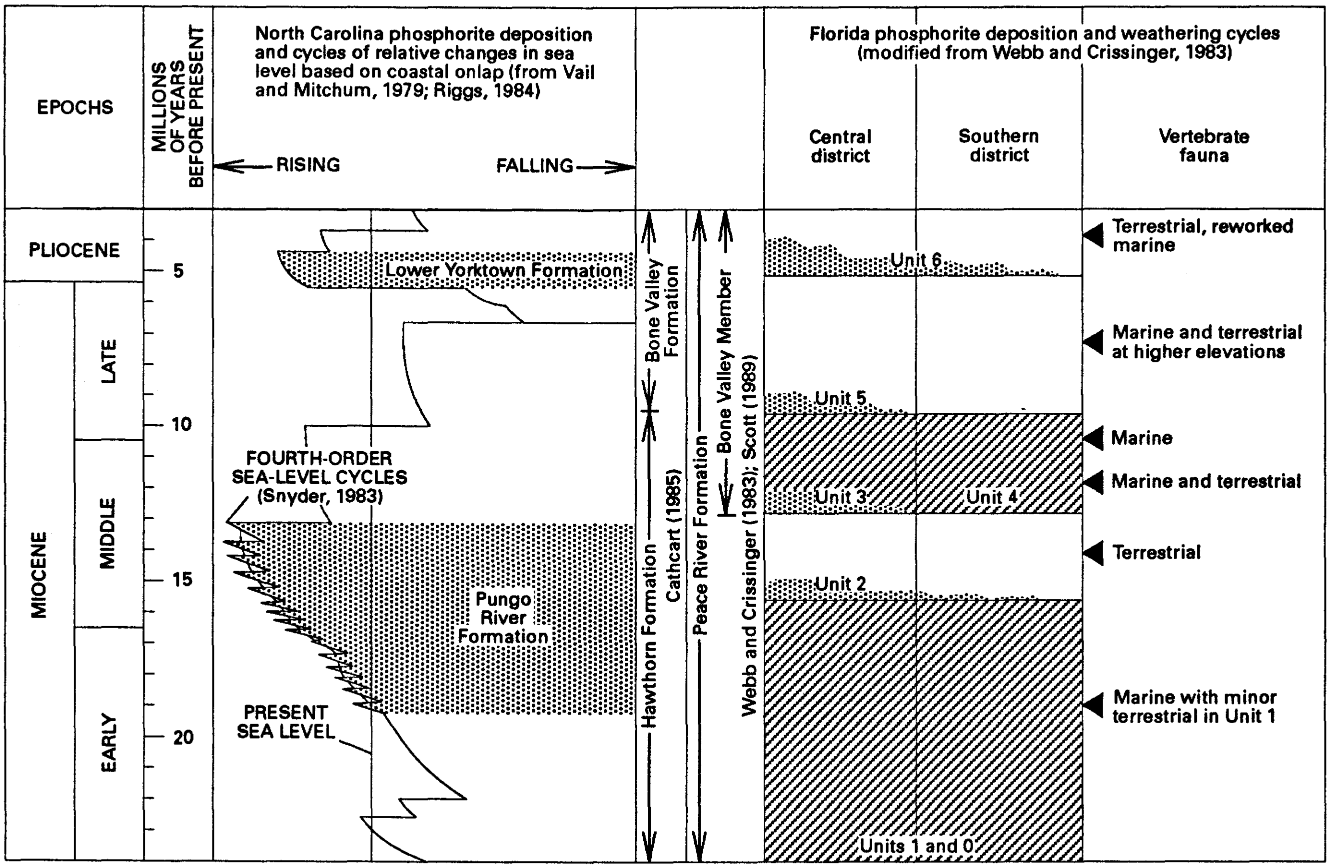


Figure 4. Contrasts in the depositional and postdepositional histories of the North Carolina and Florida phosphorite deposits. Dotted pattern shows major phosphate deposition; diagonal-line pattern shows some phosphate deposition.

Similarities to North Carolina phosphorite deposition and global sea-level curves end with the apparent regression of the sea and the occurrence of vertebrate terrestrial fauna in the Peace River Formation (unit 2) near the middle of the time of deposition of the Pungo River Formation (fig. 4). Although deposition of the Pungo River Formation continued under rising sea level, a hiatus is seen in central Florida after the deposition of unit 2. At the end of Pungo River Formation deposition, sea level fell, and unit 3 was deposited in Florida. Unit 4 appears to have been deposited under rising sea-level conditions. Unit 5 (lower and middle part of the Bone Valley Member or its time equivalent) is apparently associated with another major lowering of sea level. Time of deposition of unit 6 (upper part of the Bone Valley Member or its time equivalent) is enigmatic, similar to that of unit 2, in that terrestial fauna are present during interpreted conditions of rising global sea level concurrent with the deposition of phosphorite in North Carolina.

There is a narrow range in composition for the highly carbonate substituted francolites from the relatively unaltered North Carolina deposit at the northern extremity of the phosphogenic province and other unaltered deposits around the world. In contrast, francolites in the Florida phosphorite deposits range from highly substituted varieties, indicating primary formation, to altered varieties approaching a fluorapatite composition. Because the Florida deposits have never been subjected to deep burial or intense heat, these compositional variations must be attributed to repeated subaerial exposure and weathering. Altered francolites found in beds below less altered francolite point out the complexity of sedimentation, weathering, reworking, and primary phosphorite formation.

The dissolution and removal of carbonates is an important process in the upgrading of phosphorite deposits, and francolites cannot be altered to low-carbonate-substituted varieties until the buffering influence of carbonates is minimized. Before the cyclic episodes of emergence and submergence, deposition was in a marine environment; dolomite is a common constituent of the lowermost beds of the Peace River Formation. Relicts of dolomite and palygorskite found with less altered francolites in the coarser fractions in the reworked parts of the deposit suggest an origin similar to the noneconomic carbonate-rich beds deeper in sections and downdip. With each period of emergence, freshwater conditions would have removed carbonates, and alteration of the francolites would have occurred.

Dolomite within and below phosphorite beds indicates diagenetic influences. These sediments have been exposed to the repetitive influence of freshwater, seawater, and mixed waters under both phreatic and vadose conditions. Mixed-water conditions may be conducive to the formation of dolomite (Folk and Land, 1975).

The effects of weathering are also indicated by the variations in clay mineralogy with depth. Aluminophosphates and kaolinite formed at the top of the deposits, but unstable palygorskite and sepiolite are preserved at the base. The presence of aluminum-rich smectites (beidellites) also may indicate the overall degree of weathering of the deposits.

It is difficult to decide what aspects of the mineralogy and chemistry of the deposits are cumulative or are the result of the last weathering overprint. Every section examined in this study showed some degree of alteration even in the lowermost beds of the downdip facies in the southern extension. The significant trends of francolite composition suggest that the most recent weathering cycle overshadowed all other events. However, the extent and degree of alteration caused by early weathering cycles are masked by successive weathering cycles. Although most of the major periods of sedimentation and subaerial exposure can be documented (fig. 4), the shorter term effects of minor sea-level fluctuations and possibly changing paleoclimatic conditions are unknown.

As mining progresses into leaner, less altered parts of the deposits, changes in ore characteristics will vary with the degree of weathering of specific parts of the deposit or with proportions of unaltered and altered material. The transition from mining altered ores to less altered ores will result in the processing of phosphate containing greater amounts of endogange contamination and more highly carbonate substituted francolites. The inevitable depletion of high-grade phosphate ores must be accompanied by the development and refinement of processing technology if the Florida phosphate industry is to remain economically viable.

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APPENDIX

Figures 5–23

Lithologic, stratigraphic, mineralogic, and grain-size analyses of sections from Florida phosphate mines

Samples 1–84 to 47–84

Figures 5–23 contain lithologic notes, stratigraphic interpretations, mineralogy, francolite *a*-values, and screen data for the samples used in this study. In the mineralogy section, major minerals (in capital letters) have a most intense peak ($I/I_1 = 100$) greater than 50 percent of the most intense peak determined. Mineral components with a most intense peak less than 50 percent and greater than 10 percent are termed minor (m). Trace minerals (tr.) have a $I/I_1 = 100$ peak that is less than 10 percent of the most intense peak. Analyses by X-ray diffraction by the authors. Screen data are in Tyler mesh. Names in capital letters in the Lithology column are local terminology. K, potassium.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Swamp muck. Muck is absent 3½ mi northeast, but there is 2 ft of black, organic sand.	Terrace Deposits	HOLOCENE
2-8	None	Sand, brown, iron stained. Only 3 ft of white sand 3½ mi northeast.		PLIOCENE–PLEISTOCENE Undifferentiated
8-18	None	Sand, clayey, gray green. Unit is 8 ft thick 3½ mi northeast. Gradational contact.		
		MATRIX		
18-24	1-84	Sand, brown, pebbly, clayey. Unit is 3 ft thick, 3½ mi northeast. Sharp, irregular contact.	Hawthorn Group	MIOCENE-PLIOCENE Unnamed equivalent to Bone Valley Member, Peace River Formation
24-46	2-84	Sand, tan and gray, slightly clayey. Bedded and cross bedded. Abundant fine-grained phosphate pellets. Thin green clay lenticles.		MIOCENE Statenville Formation

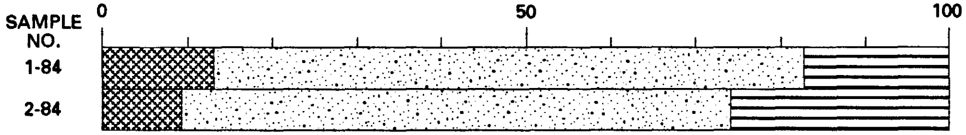
Mineralogy
(Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 1-84	FRANCOLITE QUARTZ DOLOMITE Palygorskite (tr.)	QUARTZ Francolite } (tr.) Dolomite	QUARTZ DOLOMITE Smectite Francolite } (m) Albite K feldspar Wavellite } (tr.) Crandallite Palygorskite	SMECTITE PALYGORSKITE Kaolinite (m) Francolite Illite Albite } (tr.) Wavellite Crandallite
SAMPLE 2-84	FRANCOLITE QUARTZ K feldspar Palygorskite } (m)	FRANCOLITE QUARTZ K feldspar (m)	QUARTZ Kaolinite Francolite } (m) Dolomite Albite K feldspar } (tr.) Crandallite Palygorskite	SMECTITE PALYGORSKITE KAOLINITE Albite (m) Francolite (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
1-84	9.336	9.333	9.332	9.338
2-84	9.337	9.331	9.344	9.347

SCREEN DATA (IN PERCENT)



EXPLANATION

▩ **Plus 20-mesh**

░ **Minus 20- plus 200-mesh**

☰ **Minus 200-mesh**

Figure 5. Swift Creek mine. SW¼NW¼ sec. 36, T. 1 N., R. 14 E., Hamilton County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Sand, black, organic.	Terrace Deposits	HOLOCENE
2-10	None	Sand, red brown, iron stained. Unit is gray and 8 ft thick 2 mi northeast.		PLEISTOCENE
			Hawthorn Group	Irregular, sharp contact
10-18	None	Sand, clayey, yellow. Unit is 3 ft thick 2 mi northeast.		MIOCENE–PLIOCENE Unnamed equivalent to Bone Valley Member, Peace River Formation
		MATRIX		
18-21	1-84	Sand, clayey, leached; some white and brown phosphate.		
21-32	3-84	Sand, clayey, mottled rust and blue gray. Thin green clay lenses. Unit is 6 ft thick 2 mi northeast and is underlain by 6 ft of interbedded hard, thin dolomite and gray-brown phosphatic sand. These units are bedded and cross bedded. Underlain by yellow bedded dolomite.		MIOCENE Statenville Formation

Mineralogy (Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 1-84	FRANCOLITE QUARTZ DOLOMITE Palygorskite (tr.)	QUARTZ Francolite Dolomite } (tr.)	QUARTZ DOLOMITE Smectite Francolite } (m) Albite K feldspar Wavellite Crandallite Palygorskite } (tr.)	SMECTITE PALYGORSKITE Kaolinite (m) Francolite Illite Albite Wavellite Crandallite } (tr.)
SAMPLE 3-84	FRANCOLITE QUARTZ K feldspar Palygorskite Calcite } (tr.)	QUARTZ Francolite Dolomite K feldspar } (tr.)	QUARTZ Smectite Palygorskite Francolite Albite } (m) K feldspar Crandallite } (tr.)	SMECTITE Palygorskite Albite } (m) Francolite Dolomite Crandallite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
1-84	9.336	9.333	9.332	9.338
3-84	9.332	9.328	9.333	9.351

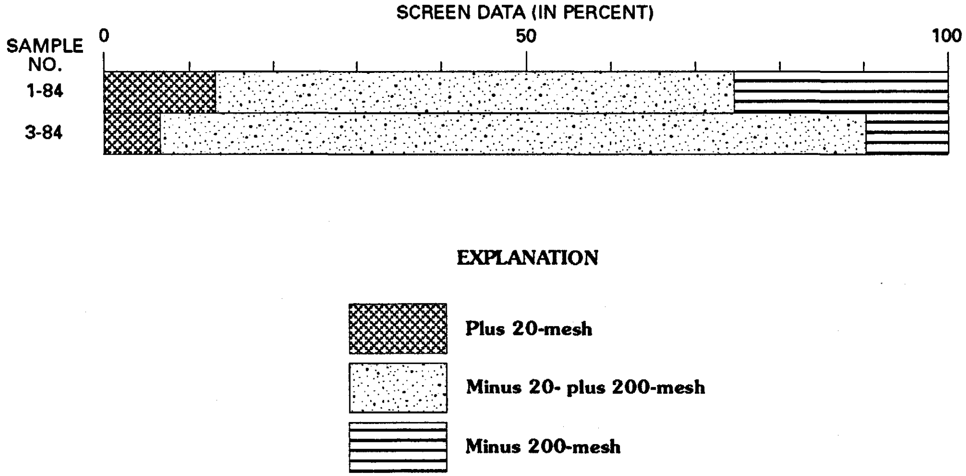


Figure 6. Suwannee River mine. SW¼NW¼ sec. 30, T. 1 S., R. 16 E., Hamilton County.

Depth (feet)	Sample No.	Lithology		Age and Stratigraphy
		OVERBURDEN		
0-11	None	Sand, white, loose at top, slightly clayey at base.		HOLOCENE and PLEISTOCENE, undifferentiated
11-20	None	Sand, clayey, white beds of coarsely vesicular textured sandstone.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
20-25	6-84	Sand, clayey, white, contains pebbles of soft, white phosphate.		Bone Valley Member
		MATRIX		MIOCENE Undifferentiated Peace River Formation
25-34	4-84	Sand, clayey, gray-brown, mottled white, bioturbated. Clayey and laminated at base.		
		RESIDUUM		
34-37	5-84	Clay, sandy, red brown and yellow brown.		
		Base exposure. Yellow dolomite exposed in pit bottom.		

Mineralogy
(Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 6-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ Francolite K feldspar } (m)	QUARTZ FRANCOLITE Crandallite Goethite } (m) K feldspar (tr.)	SMECTITE FRANCOLITE ILLITE Kaolinite Albite } (m) Wavellite (tr.)
SAMPLE 4-84	FRANCOLITE Quartz (m) K feldspar (tr.)	FRANCOLITE QUARTZ Wavellite K feldspar } (tr.)	QUARTZ FRANCOLITE Smectite (m) Wavellite (tr.)	No clay fraction available
SAMPLE 5-84	FRANCOLITE QUARTZ K feldspar Goethite } (m) Dolomite (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Palygorskite Albite Siderite } (m)	PALYGORSKITE K FELDSPAR Francolite Goethite Albite } (m) Smectite (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
6-84	9.342	9.347	9.338	9.354
4-84	9.337	9.336	9.347	9.345
5-84	9.333	9.334	9.339	9.339

SCREEN DATA (IN PERCENT)

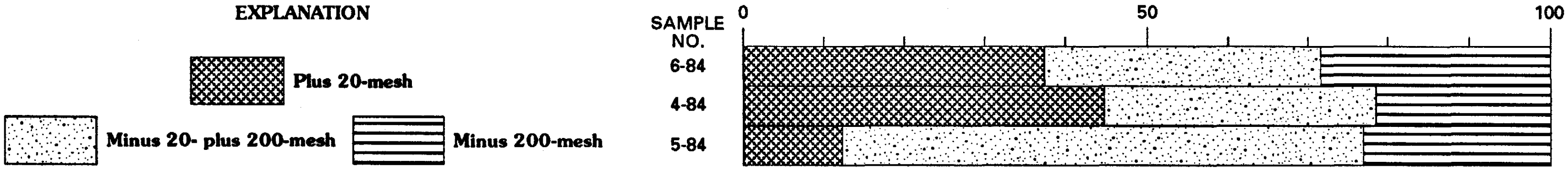


Figure 7. Noralyn mine. NE¼SE¼ sec. 22, T. 30 S., R. 24 E., Polk County.

Depth (feet)	Sample No.	Lithology		Age and Stratigraphy
		OVERBURDEN	Terrace Deposits	
0-2	None	Sand, loose, white, wind blown.		HOLOCENE
2-13	None	Sand, brown and light gray.		PLEISTOCENE
13-27	None	Sand, gray, clayey. Unit is 10 ft thick 7 mi southwest.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
27-30	8-84	Sand, clayey, gray, leached. Contains soft white phosphate pebbles.		Bone Valley Member
30-34	Not sampled	Clay, sandy, gray, green, and red mottled. Minor black and brown phosphate.		
		MATRIX		
34-40	7-84	Sand, slightly clayey, gray. Graded bedding. Very coarse pebbles at base, finer grained, more clayey at top. Unit is 4 ft thick 7 mi southwest and rests directly on hard yellow dolomite.		
40-43	None	Clay, green, laminated, slightly sandy, minor phosphate.		MIOCENE Undifferentiated

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 8-84	FRANCOLITE QUARTZ	QUARTZ Francolite K feldspar } (tr.)	QUARTZ Smectite Francolite } (m) Albite K feldspar Wavellite Crandallite Kaolinite } (tr.)	SMECTITE Kaolinite (m) Francolite Dolomite Albite Wavellite Crandallite Illite } (tr.)
SAMPLE 7-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ Semectite Francolite } (m) Albite Crandallite } (tr.)	SMECTITE Francolite Albite Crandallite Kaolinite Illite Palygorskite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
8-84	9.347	9.330	9.347	9.352
7-84	9.332	9.332	9.346	9.358

SCREEN DATA (IN PERCENT)

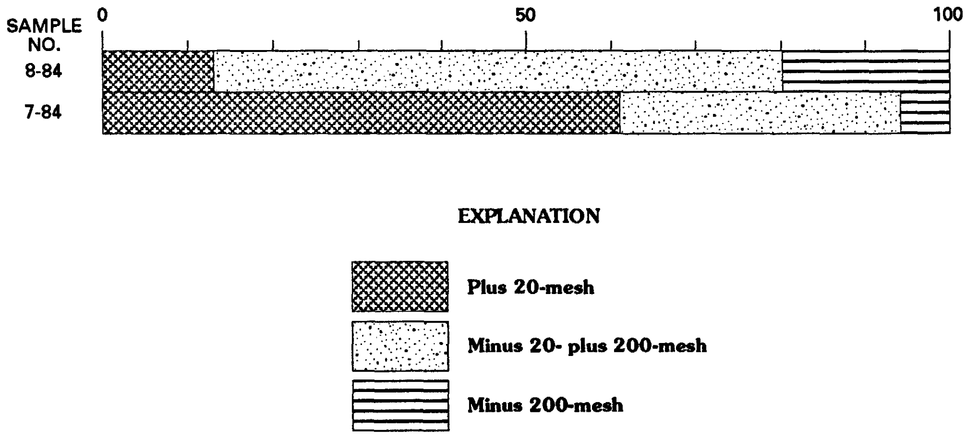


Figure 8. Gardinier (Cargill) mine. NW¼NE¼ sec. 9, T. 32 S., R. 25 E., Polk County.

Depth (feet)	Sample No.	Lithology		Age and Stratigraphy
		OVERBURDEN		
0-2	None	Sand, black, organic.	Terrace Deposits	HOLOCENE
2-6	None	Sand, brown, unconsolidated, iron stained.		PLEISTOCENE
6-10	None	Sand, clayey, white. A few fragments of vesicular-textured aluminum phosphate-cemented sandstone.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
10-16	None	Same as above, but yellow brown, iron stained.		
		MATRIX		
16-22	10-84	Sand, red brown, clayey. Phosphate, pebble and sand size, brown, black, gray.		Bone Valley Member
22-25	9-84	Sand, clayey, blue gray, tan, yellow mottled, bioturbated. Sand size phosphate is abundant. Total depth 36 ft, could only sample top 3 ft. Yellow dolomite in pit bottom.		MIOCENE Undifferentiated

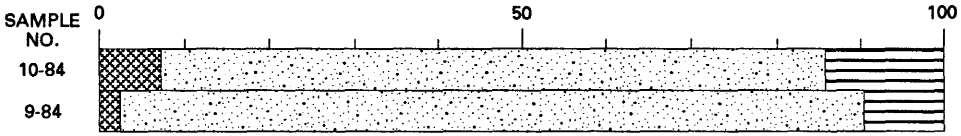
Mineralogy
(Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 10-84	QUARTZ Francolite (m) Wavellite } Crandallite } (tr.) K feldspar }	QUARTZ Francolite (tr.)	QUARTZ CRANDALLITE FRANCOLITE Wavellite (tr.)	KAOLINITE ILLITE CRANDALLITE FRANCOLITE ALBITE
SAMPLE 9-84	FRANCOLITE QUARTZ Dolomite } (m) Goethite } (tr.) Palygorskite }	QUARTZ Francolite (m) K feldspar (tr.)	QUARTZ SMECTITE FRANCOLITE K FELDSPAR	SMECTITE PALYGORSKITE Quartz } Francolite } Albite } (tr.) Crandallite }

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
10-84	9.355	9.352	9.356	9.352
9-84	9.347	9.342	9.346	9.339

SCREEN DATA (IN PERCENT)



EXPLANATION

▩ **Plus 20-mesh**

░ **Minus 20- plus 200-mesh**

☰ **Minus 200-mesh**

Figure 9. Nichols mine. SE¼NE¼ sec. 21, T. 30 S., R. 23 E., Polk County.

Depth (feet)	Sample No.	Lithology	Formation	Age and Stratigraphy
		OVERBURDEN		
0-2	None	Sand, black, organic.	Terrace Deposits	HOLOCENE
2-9	None	Sand, white and tan, unconsolidated.		PLEISTOCENE
9-15	None	Sand, clayey, gray, leached. Boulders of sand cemented by aluminum phosphate.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
15-19	None	Sand, clayey, gray green. Leached. Soft white phosphate.		Bone Valley Member
		MATRIX		
19-29	13-84	Sand, gray green, pebbly. Graded bedding.		
29-41	12-84	Sand, clayey, yellow and gray green. Fine-grained phosphate pellets abundant.		MIOCENE Undifferentiated
41-43	Not sampled	Clay, sandy, yellow green with some phosphate pellets.		
43-50	11-84	Sand, clayey, mottled brown and gray. Phosphate pebble and pellets. Graded. Blue clay clasts abundant at base.		
		Yellow dolomite in pit bottom.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 13-84	FRANCOLITE QUARTZ Wavellite K feldspar (tr.)	QUARTZ Wavellite Francolite K feldspar (tr.)	QUARTZ FRANCOLITE Smectite Albite Wavellite (m) Kaolinite Palygorskite (tr.)	SMECTITE FRANCOLITE Illite Wavellite (m) Kaolinite (tr.)
SAMPLE 12-84	FRANCOLITE QUARTZ K feldspar (m)	QUARTZ Francolite Dolomite K feldspar (tr.)	QUARTZ Smectite Francolite K feldspar (m) Crandallite Illite (tr.)	SMECTITE Illite K feldspar (m) Quartz Francolite (tr.)
SAMPLE 11-84	FRANCOLITE Quartz (m) Goethite (tr.)	QUARTZ Francolite (m) K feldspar (tr.)	QUARTZ FRANCOLITE Albite K feldspar Palygorskite Kaolinite (m) Crandallite Dolomite(?) (tr.)	PALYGORSKITE SMECTITE ALBITE Francolite Dolomite K feldspar (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
13-84	9.330	9.328	9.332	9.344
12-84	9.333	9.328	9.334	9.345
11-84	9.334	9.328	9.332	9.344

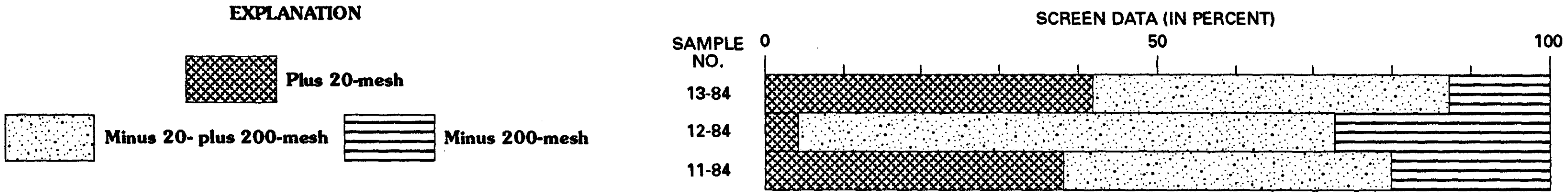


Figure 10. Ft. Meade mine. NW¼NW¼ sec. 28, T. 31 S., R. 25 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Sand, gray-black, organic.	Terrace Deposits	HOLOCENE
2-15	None	Sand, white, loose at top, tan-brown and slightly clayey at base.		PLEISTOCENE
15-30	16-84	Sand, clayey, irregular bedding, phosphatized crusts throughout and abundant white-cream clay-size francolite.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Bone Valley Member
		MATRIX		
30-38	15-84	Clay, sandy, gray-green, bedded, crust of secondary precipitated francolite in middle of unit. Black phosphate pellets abundant. Sharp contact at base.		MIOCENE Undifferentiated
		BEDROCK		
38-42	Not sampled	Dolomite, hard, yellow, phosphate bearing. Irregular gradational contact.		
42-46	14-84	Clay, dolomitic, soft with some phosphate and quartz sand.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 16-84	FRANCOLITE Quartz (m) Wavellite (tr.)	QUARTZ Francolite (m) Wavellite (tr.)	QUARTZ FRANCOLITE Wavellite } Crandallite } (tr.)	FRANCOLITE Kaolinite (m) Crandallite (tr.)
SAMPLE 15-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ Francolite } Dolomite } (tr.) K feldspar }	SMECTITE QUARTZ FRANCOLITE Albite } K feldspar } (tr.)	SMECTITE Francolite (m) Kaolinite (tr.)
SAMPLE 14-84	QUARTZ Francolite (m) Dolomite (tr.)	QUARTZ Francolite } Dolomite } (tr.)	SMECTITE QUARTZ FRANCOLITE K feldspar (m) Albite (tr.)	SMECTITE Illite (m) Francolite } Sepiolite } (tr.)

FRANCOLITE *A*-VALUES (±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
16-84	9.355	9.353	9.353	9.361
15-84	9.338	9.337	9.333	9.344
14-84	9.336	9.338	9.334	9.337

EXPLANATION

▩ **Plus 20-mesh**

░ **Minus 20- plus 200-mesh**

▤ **Minus 200-mesh**

SCREEN DATA (IN PERCENT)

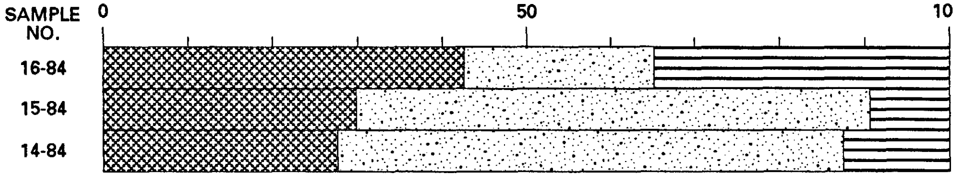


Figure 11. Clear Springs mine. Sec. 11, T. 30 S., R. 25 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN	Terrace Deposits	
0-2	None	Sand, gray, organic.		HOLOCENE
2-15	None	Sand, white, unconsolidated. Tan and slightly clayey at base.		PLEISTOCENE
		Sharp, irregular contact.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Bone Valley Member
15-16	None	Clay, gray green, leached. Some fragments of cemented sand.		
		MATRIX		
16-22	17-84	Sand, slightly clayey, tan gray, leached with soft white phosphate.		
22-25	18-84	Sand, gray, pebbly, slightly clayey. Phosphate is mostly black.		
		Sharp contact.		MIOCENE Undifferentiated
25-29	19-84	Sand, clayey, gray green, bedded with some pebble. Yellow dolomite in pit bottom.		

	Mineralogy (Screen size)			
	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 17-84	QUARTZ Francolite Wavellite } (m)	QUARTZ Francolite Wavellite } (tr.)	QUARTZ Francolite (m) Smectite Wavellite Crandallite } (tr.)	SMECTITE WAVELLITE QUARTZ Kaolinite Illite } (m) Francolite K feldspar } (tr.)
SAMPLE 18-84	FRANCOLITE QUARTZ	QUARTZ Francolite K feldspar } (tr.)	SMECTITE QUARTZ Francolite K feldspar } (m) Crandallite (tr.)	SMECTITE Illite (m) Kaolinite Francolite } (tr.)
SAMPLE 19-84	FRANCOLITE Quartz (m) Dolomite K feldspar } (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ Smectite Francolite K feldspar } (m) Kaolinite (tr.)	SMECTITE Kaolinite Illite } (m) Albite (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
17-84	9.348	9.368	9.343	9.346
18-84	9.330	9.339	9.348	9.342
19-84	9.335	9.332	9.350	9.350

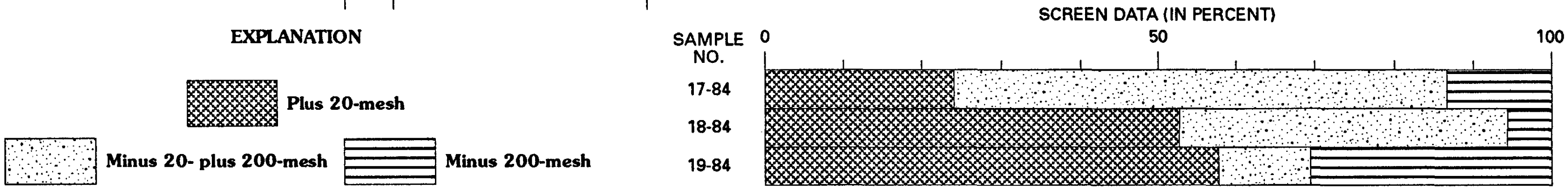


Figure 12. C.F. Hardee complex. SE¼NW¼ sec. 5, T. 33 S., R. 24 E., Polk and Hardee Counties.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN	Terrace Deposits	HOLOCENE
0-1	None	Sand, black and gray, organic.		
1-3	None	Sand, white, unconsolidated, windblown.		PLEISTOCENE
3-8	None	Sand, white, unconsolidated, fine to medium grained.		
8-12	None	Sand, gray tan to yellow tan, clayey at base. Unit is 15 ft thick ½ mi southeast, and 12 ft thick 2 mi southwest.	Hawthorn Group–Peace River Formation	PLIOCENE–PLEISTOCENE Bone Valley Member(?)
		Gradational contact.		
12-14	20-84	Sand, clayey, white, leached. Soft white phosphate. Unit thickens to 6 ft to southeast but is absent to the southwest.		MIOCENE–PLIOCENE Leached Bone Valley Member
		MATRIX		
14-22	21-84	Sand, gray white, graded bedding. Bottom 3 ft very pebbly. Unit is 5 ft thick to the southeast and is14 ft thick 2 mi to the southwest.		Bone Valley Member
22-26	22-84	Sand, clayey, brown. Bedded. Fine sand-size phosphate unit is 14 ft thick to the southeast, but thins to only 1 ft 2 mi to the southwest.		MIOCENE Undifferentiated
		Yellow dolomite in bottom of the pit.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 20-84	FRANCOLITE QUARTZ	QUARTZ Francolite Wavellite } (tr.)	QUARTZ FRANCOLITE Kaolinite Wavellite Crandallite } (m) Albite (tr.)	KAOLINITE FRANCOLITE Illite (m) Wavellite (tr.)
SAMPLE 21-84	FRANCOLITE QUARTZ	QUARTZ Francolite (m) Wavellite (tr.)	QUARTZ FRANCOLITE Kaolinite K feldspar } (tr.)	SMECTITE FRANCOLITE Kaolinite K feldspar } (m) Illite Albite } (tr.)
SAMPLE 22-84	FRANCOLITE Quartz K feldspar } (m)	QUARTZ Francolite (m) K feldspar (tr.)	SMECTITE QUARTZ FRANCOLITE Albite (m) Dolomite Illite K feldspar } (tr.)	SMECTITE Illite (m) Kaolinite Francolite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
20-84	9.335	9.329	9.336	9.341
21-84	9.328	9.326	9.330	9.347
22-84	9.330	9.326	9.332	9.337

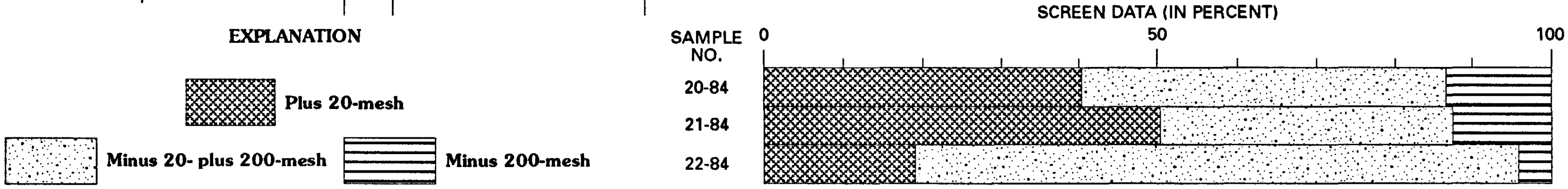


Figure 13. Ft. Green mine. NW¼NW¼ sec. 25, T. 32 S., R. 23 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Sand, unconsolidated, gray, organic rich.	Terrace Deposits	HOLOCENE
2-8	None	Sand, unconsolidated, tan. Fragmental horse teeth (*Equus* sp.).		PLEISTOCENE
		Sharp contact.		
		MATRIX	Hawthorn Group–Peace River Formation	
8-16	25-84	Sand, light gray, slightly clayey. Abundant white phosphate pebble in three distinct beds in top, middle, and base of this bed.		PLIOCENE-PLEISTOCENE Channel deposit Bone Valley Member
		Sharp, irregular contact.		
16-19	24-84	Sand, brown, clayey, pebbly. Pebble is brown, some white, and finer than in bed above.		MIOCENE–PLIOCENE Bone Valley Member
		Irregular contact.		
19-22	23-84	Sand, clayey brown. Abundant fine sand-size phosphate. Minor pebble.		MIOCENE Undifferentiated

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 25-84	FRANCOLITE QUARTZ Dolomite (m) Smectite (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Crandallite (m) Kaolinite (tr.)	SMECTITE Kaolinite Crandallite Francolite Albite K feldspar } (tr.)
SAMPLE 24-84	FRANCOLITE QUARTZ Dolomite Smectite } (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Crandallite Palygorskite } (m) Albite K feldspar Dolomite(?) } (tr.)	Kaolinite Palygorskite } (m) Smectite Francolite Crandallite K feldspar Albite } (tr.)
SAMPLE 23-84	FRANCOLITE QUARTZ Wavellite (m) K feldspar (tr.)	QUARTZ Francolite (m) K feldspar Wavellite } (tr.)	QUARTZ FRANCOLITE CRANDALLITE K FELDSPAR Palygorskite (tr.)	SMECTITE FRANCOLITE PALYGORSKITE Quartz Crandallite Albite K feldspar } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
25-84	9.349	9.344	9.347	9.350
24-84	9.340	9.338	9.341	9.347
23-84	9.350	9.348	9.343	9.353

EXPLANATION

- ▩ **Plus 20-mesh**
- ░ **Minus 20- plus 200-mesh**
- ☰ **Minus 200-mesh**

SCREEN DATA (IN PERCENT)

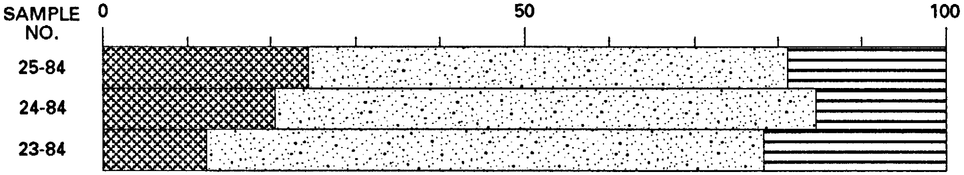


Figure 14. Saddle Creek mine. SW¼ sec. 19, T. 28 S., R. 25 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Sand, unconsolidated, gray, organic.	Terrace Deposits	HOLOCENE
2-10	None	Sand, unconsolidated, brown and white.		PLEISTOCENE
10-22	None	Sand, unconsolidated to slightly clayey, brown and gray.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Bone Valley Member
		MATRIX		
22-25	26-84	Sand, clayey, white, yellow, and red mottled. Leached. Soft white phosphate.		
25-27	Not sampled	Clay, sandy, green and red mottled. Minor phosphate.		
27-30	27-84	Sand, clayey, white. Phosphate pellets and pebbles. Gradational contact.		MIOCENE Undifferentiated
30-34	28-84	Sand, clayey, cream and yellow brown mottled. Fine-grained phosphate pellets, less abundant at base. Pit bottom at 34 ft.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 26-84	QUARTZ Francolite Wavellite } (m) Smectite K feldspar } (tr.)	QUARTZ Francolite Wavellite K feldspar } (tr.)	QUARTZ Francolite Smectite } (m) Goethite (tr.)	SMECTITE Francolite Illite Wavellite } (tr.)
SAMPLE 27-84	FRANCOLITE QUARTZ Wavellite K feldspar } (tr.)	QUARTZ Francolite (m) Wavellite K feldspar } (tr.)	QUARTZ FRANCOLITE Smectite (m) Wavellite Crandallite } (tr.)	SMECTITE Francolite Wavellite K feldspar } (m) Illite Crandallite Quartz Dolomite } (tr.)
SAMPLE 28-84	FRANCOLITE QUARTZ Goethite (m)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Wavellite (m) Kaolinite Crandallite K feldspar } (tr.)	SMECTITE WAVELLITE Francolite (m) Illite Goethite Crandallite Dolomite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
26-84	9.355	9.354	9.340	9.353
27-84	9.341	9.345	9.342	9.353
28-84	9.340	9.336	9.349	9.349

EXPLANATION

▩ **Plus 20-mesh**

░ **Minus 20- plus 200-mesh**

▤ **Minus 200-mesh**

SCREEN DATA (IN PERCENT)

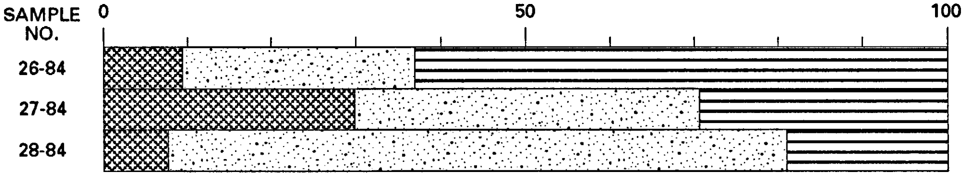


Figure 15. Lonesome mine. Sec. 16, T. 31 S., R. 22 E., Hillsborough County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-1	None	Sand, gray, organic.	Terrace Deposits	HOLOCENE
1-4	None	Sand, white, unconsolidated. Windblown.		PLIOCENE(?)–PLEISTOCENE
4-10½	None	Sand, brown, iron stained, slightly clayey at base. Sharp contact.		
		MATRIX		
10½-22½	29-84	Sand, clayey, green, yellow green, and gray. Bioturbated. Beds of more and less clay and pebble. Bedding is not distinct.	Hawthorn Group–Peace River Formation	MIOCENE Undifferentiated
		RESIDUUM		
22½-24	None	Gray, sandy, dark red-brown, dolomitic. Minor phosphate.		
		Yellow dolomite in pit bottom.		

Mineralogy (Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 29-84	FRANCOLITE QUARTZ Crandallite K feldspar } (tr.)	QUARTZ Francolite K feldspar } (tr.)	SEPIOLITE QUARTZ FRANCOLITE Goethite Palygorskite K feldspar } (m) Dolomite Crandallite } (tr.)	SMECTITE PALYGORSKITE SEPIOLITE Kaolinite K feldspar Francolite } (m) Crandallite Dolomite } (tr.)

FRANCOLITE *A*-VALUES (±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
29-84	9.338	9.336	9.335	9.342

SCREEN DATA (IN PERCENT)

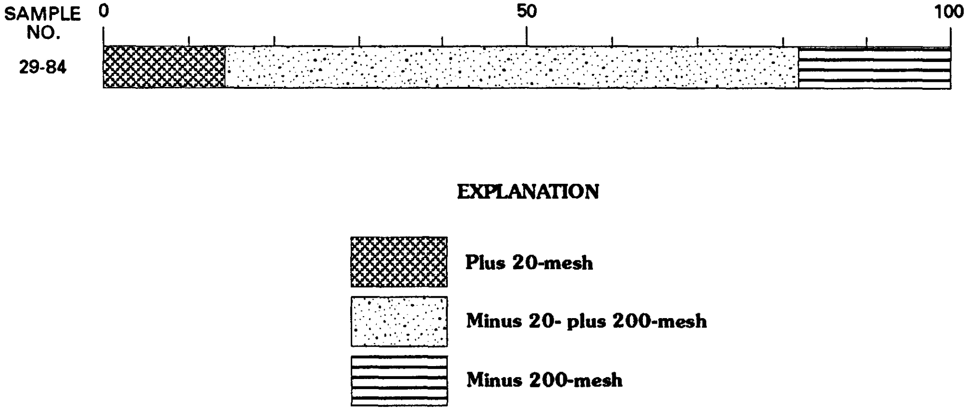


Figure 16. Watson mine. Sec. 11, T. 32 S., R. 25 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN	Terrace Deposits	PLEISTOCENE and HOLOCENE
0-4	None	Sand, gray, and white, unconsolidated. Top 1 ft of sand is black and highly organic 1 mi northeast.		
4-11	None	Sand, clayey white, contains abundant round, vesicular boulders of sandstone cemented by aluminum phosphates. Bed is missing 1 mi northeast and is a gray clayey sand.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
11-18	None	Sand, gray, clayey, leached. Zone is 4 ft of vesicular aluminum phosphate 1 mi northeast. Zone is underlain by 2-ft intervals that contain soft white phosphate pebbles.		
		MATRIX		Bone Valley Member
18-22	31-84	Sand, gray and white, pebbly. Zone is 2 ft thick 1 mi northeast.		
22-31	30-84	Sand, clayey, gray-green and rust mottled. Fine-grained phosphate pellets. Bed is 10 ft thick 1 mi northeast and rests on yellow dolomite.		MIOCENE Undifferentiated
		RESIDUUM		
31-33	30A-84	Clay, very sandy, brown. Some fine-grained phosphate pellets. Absent 1 mi northeast.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 31-84	FRANCOLITE QUARTZ	QUARTZ FRANCOLITE	QUARTZ FRANCOLITE Smectite Crandallite } (m) Kaolinite K feldspar } (tr.)	Smectite Francolite } (m) Albite Wavellite } (tr.) Illite
SAMPLE 30-84	FRANCOLITE Quartz (m) K feldspar (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ Smectite Francolite } (m) K feldspar Crandallite } (tr.)	SMECTITE Kaolinite Illite Crandallite Francolite } (tr.) Albite K feldspar Dolomite
SAMPLE 30A-84	FRANCOLITE Quartz (m) Smectite Palygorskite } (m)	QUARTZ FRANCOLITE K feldspar (m) Dolomite (tr.)	QUARTZ Smectite Albite } (m) Francolite Crandallite Palygorskite } (tr.)	SMECTITE Illite Palyorskite Goethite } (tr.) Francolite Albite

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
31-84	9.342	9.338	9.347	9.355
30-84	9.345	9.345	9.347	9.352
30A-84	9.336	9.336	9.337	9.355

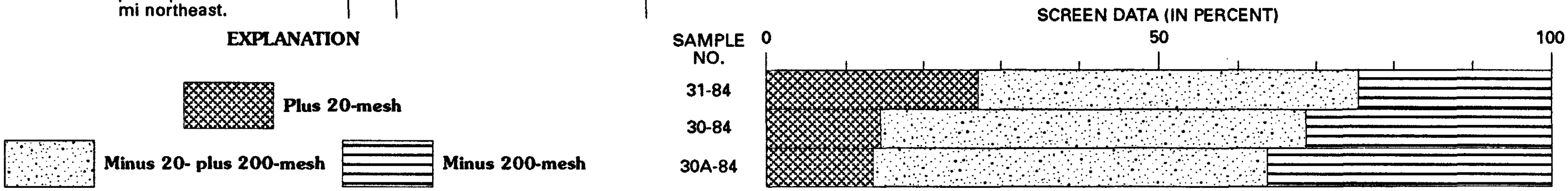


Figure 17. Phosphoria mine. SE¼ sec. 12, T. 31 S., R. 23 E., Polk County.

Depth (feet)	Sample No.	Lithology		Age and Stratigraphy
		OVERBURDEN	Terrace Deposits	
0-2	None	Sand, gray, unconsolidated, organic.		HOLOCENE
2-12	None	Sand, brown and tan. Slightly clayey at base.		PLEISTOCENE
12-15	None	Sand, clayey white. Some soft, white phosphate and vesicular boulders.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
		MATRIX		
15-35	32-84	Sand, clayey, gray green. Interbedded clay lenses and pebbly sand beds.		Bone Valley Member
		RESIDUUM		
35-37	33-84	Clay, very sandy, red brown. Abundant brown phosphate pellets.		MIOCENE Undifferentiated
		Yellow dolomite in pit bottom.		

Mineralogy
(Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 32-84	FRANCOLITE QUARTZ Wavellite (m) Dolomite K feldspar } (tr.)	QUARTZ Francolite Wavellite K feldspar } (tr.)	QUARTZ Smectite Francolite } (m) K feldspar Wavellite Illite } (tr.)	SMECTITE Kaolinite Illite Crandallite Wavellite Francolite K feldspar Albite Quartz } (tr.)
SAMPLE 33-84	FRANCOLITE QUARTZ K feldspar (m) Dolomite Palygorskite } (tr.)	QUARTZ K feldspar (m) Francolite (tr.)	SEPIOLITE Palygorskite Goethite } (m) Quartz Francolite K feldspar } (tr.)	PALYGORSKITE Smectite Albite Francolite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
32-84	9.340	9.345	9.342	9.347
33-84	9.335	9.328	9.337	9.343

SCREEN DATA (IN PERCENT)

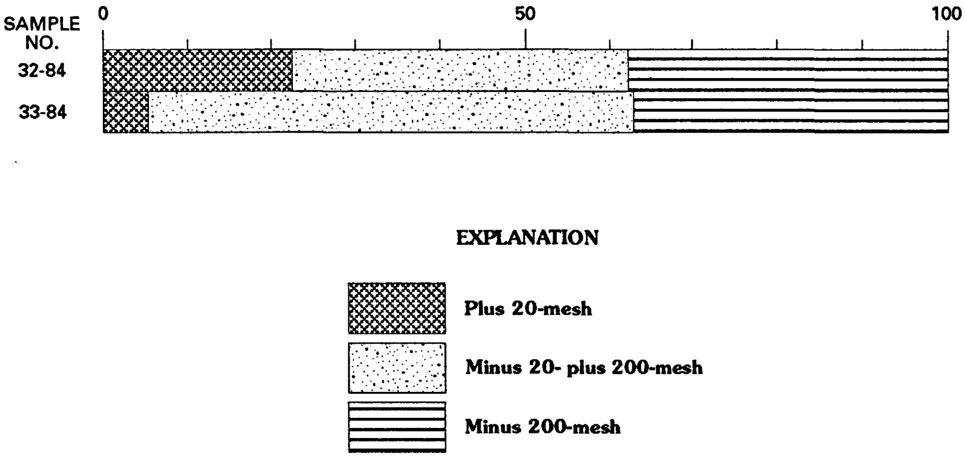


Figure 18. Rockland mine. NW¼ sec. 30, T. 31 S., R. 23 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-2	None	Sand, gray, organic rich.	Terrace Deposits	HOLOCENE
2-13	None	Sand, unconsolidated, brown, iron stained.		PLIOCENE–PLEISTOCENE
13-30	None	Sand, unconsolidated, white. Slightly clayey at base.		
		MATRIX	Hawthorn Group–Peace River Formation	
30-33	34-84	Sand, black, pebbly. Graded bedding. Coarse black phosphate conglomerate at base. Sharp contact.		MIOCENE–PLIOCENE Bone Valley Member
33-36	35-84	Bioturbated. Fine sand-size phosphate abundant. Water level in pit is 36 ft. Prospecting indicates this unit extends to 65 ft below surface.		MIOCENE Undifferentiated

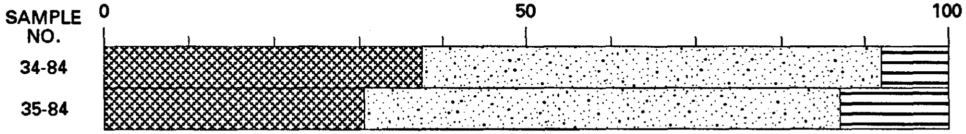
Mineralogy (Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 34-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Wavellite Crandallite Smectite } (m) Albite Kaolinite Illite } (tr.)	SMECTITE Kaolinite Illite Francolite } (m) Wavellite Crandallite K feldspar Sepiolite } (tr.)
SAMPLE 35-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ Francolite K feldspar } (tr.)	QUARTZ FRANCOLITE Smectite Crandallite K feldspar } (m) Kaolinite (tr.)	SMECTITE Francolite (m) Kaolinite Illite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
34-84	9.340	9.336	9.340	9.356
35-84	9.345	9.337	9.339	9.358

SCREEN DATA (IN PERCENT)



EXPLANATION

▩ **Plus 20-mesh**
░ **Minus 20- plus 200-mesh**
☰ **Minus 200-mesh**

Figure 19. Haynsworth mine. SE¼SW¼ sec. 8, T. 31 S., R. 23 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		
0-16	None	Sand, unconsolidated, gray at top, white and brown below. Slightly clayey at base.	Terrace Deposits	PLEISTOCENE and HOLOCENE
		MATRIX		
16-26	37-84	Sand, clayey, brown and gray. Abundant sand-size, brown, cream, and gray phosphate pellets. Some pebble. Unit is missing 1 mi southwest. Top is leached.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Bone Valley Member
26-32	36-84	Clay, sandy, red and green mottled, some pebble. Yellow and dolomitic at base. Unit is tan, brown, and red, and is bioturbated 1 mi southwest. Rests on hard yellow dolomite.		MIOCENE Undifferentiated

Mineralogy (Screen size)

	+20 mesh	–20 +200 mesh	–200 mesh	–2 µm
SAMPLE 37-84	QUARTZ Francolite (m) Wavellite, K feldspar, Palygorskite (tr.)	QUARTZ Francolite (m) K feldspar (tr.)	QUARTZ FRANCOLITE Crandallite, Albite (m) Kaolinite, Smectite, Wavellite (tr.)	SMECTITE Palygorskite, Albite, Francolite (m) K feldspar, Crandallite (tr.)
SAMPLE 36-84	FRANCOLITE QUARTZ K feldspar (tr.)	QUARTZ K FELDSPAR Francolite (m)	QUARTZ FRANCOLITE PALYGORSKITE Smectite, Goethite (m) Dolomite, K feldspar, Wavellite, Sepiolite (tr.)	SMECTITE PALYGORSKITE Sepiolite (m) Dolomite, Francolite, Crandallite (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	–20 +200 mesh	–200 mesh
37-84	9.346	9.344	9.340	9.345
36-84	9.345	9.346	9.339	9.348

SCREEN DATA (IN PERCENT)

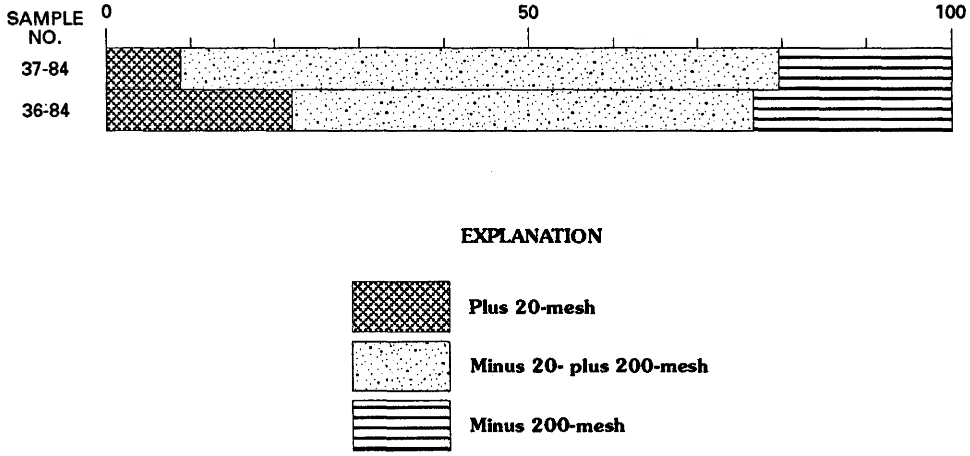
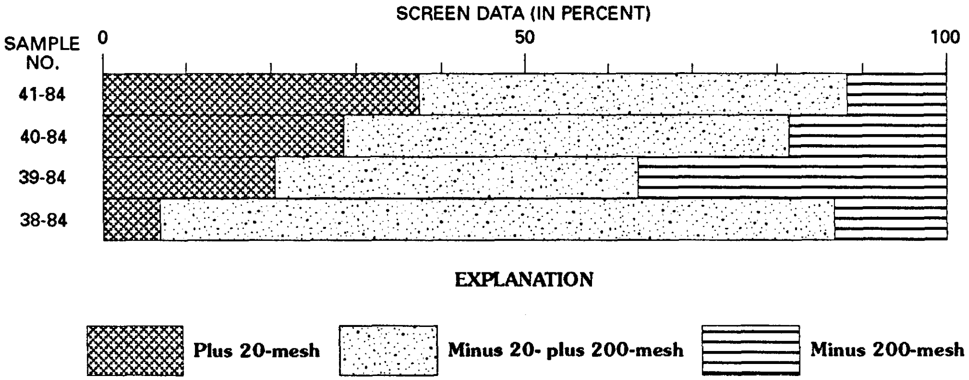


Figure 20. Lonesome mine. NE¼ sec. 16, T. 31 S., R. 22 E., Hillsborough County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN		HOLOCENE Swamp deposit
0-14	None	Sand, white, unconsolidated. Sand is only 3 ft thick 1 mi east and is overlain by 4 ft of swamp muck.		PLEISTOCENE Terrace sands
		MATRIX	Hawthorn Group–Peace River Formation	
14-17	41-84	White pebbly sand, slightly clayey. Unit not present at section 1 mi east.		MIOCENE–PLIOCENE Leached Bone Valley Member
17-23	40-84	Sand, pebbly, gray-green, clayey. Coarse phosphate at base. A graded bed is same thickness and lithology at the mine section 1 mi east. Sample 40-84 is a composite from both localities.		Bone Valley Member (Graded bedding)
23-29	39-84	Sand, clayey mottled gray and red-brown. Dolomitic. Fine-sand size phosphate more abundant than coarse phosphate. Upper contact sharp and irregular. Unit 4 ft thick at section 1 mi east.		MIOCENE Undifferentiated
29-35	38-84	Clay, very sandy, brown. Sand-size brown phosphate. Minor fine pebble size. Unit not present at section 1 mi east.		
		Yellow dolomite in pit bottom.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 41-84	FRANCOLITE QUARTZ K feldspar (m)	QUARTZ Francolite (m) K feldspar (tr.)	FRANCOLITE QUARTZ Smectite, K feldspar (m) Wavellite, Crandallite, Kaolinite, Illite, Palygorskite (tr.)	SMECTITE KAOLINITE ILLITE FRANCOLITE Albite (tr.)
SAMPLE 40-84	FRANCOLITE Quartz (m) K feldspar, Palygorskite (tr.)	QUARTZ Francolite, K feldspar, Palygorskite (tr.)	QUARTZ SMECTITE FRANCOLITE CRANDALLITE K FELDSPAR Albite, Palygorskite (tr.)	SMECTITE Dolomite, Kaolinite, Illite, Crandallite, Francolite, Albite, K feldspar (tr.)
SAMPLE 39-84	FRANCOLITE Quartz, K feldspar, Dolomite (m) Palygorskite (tr.)	QUARTZ Francolite (m) K feldspar (tr.)	QUARTZ DOLOMITE Francolite, Smectite, Palygorskite, Goethite, K feldspar (tr.)	No clay sample
SAMPLE 38-84	QUARTZ Francolite (m) K feldspar, Smectite (tr.)	QUARTZ Francolite, K feldspar, Smectite (tr.)	QUARTZ K FELDSPAR Smectite (m) Palygorskite, Francolite (tr.)	SMECTITE Palygorskite, Goethite, Quartz, Francolite, Albite, Wavellite (tr.)



FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
41-84	9.334	9.332	9.336	9.343
40-84	9.332	9.333	9.335	9.345
39-84	9.332	9.328	9.329	9.335
38-84	9.338	9.332	9.332	9.338

Figure 21. Hookers Prairie mine. SE¼NE¼ sec. 7, T. 31 S., R. 24 E., Polk County.

Depth (feet)	Sample No.	Lithology	Age and Stratigraphy	
		OVERBURDEN	Terrace Sands	PLEISTOCENE and HOLOCENE
0-14	None	Sand, black at top, gray, white, and brown below and slightly clayey at base.		
		MATRIX	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Bone Valley Member
14-19	44-84	Sand, pebbly, dark gray to black. Phosphate pellets and pebbles, most black, some gray and brown.		
		BEDROCK		MIOCENE Undifferentiated
19-23	Not sampled	Hard, fossiliferous, yellow dolomite. Pebbles and grains of phosphate. Upper contact sharp and irregular.		
23-35½	43-84	Sand, clayey, gray-green and blue. Laminated. Sand-size phosphate pellets. Pebbly sand near middle. Rubble zone of partly phosphatized dolomite nodules at base.		
		Very, sharp, irregular contact.		
35½-37	Not sampled	Yellow phosphatic dolomite.		
37-43	42-84	Sand, gray brown. Fine sand-size phosphate pellets. Water level at 43 ft.		

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 44-84	QUARTZ Francolite (m) K feldspar (tr.)	QUARTZ Francolite, K feldspar (tr.)	QUARTZ SMECTITE FRANCOLITE Crandallite, K feldspar, Dolomite (tr.)	SMECTITE KAOLINITE FRANCOLITE Illite (m)
SAMPLE 43-84	FRANCOLITE DOLOMITE Quartz (m) K feldspar (tr.)	QUARTZ Francolite (m) Dolomite, K feldspar (tr.)	DOLOMITE Smectite, Quartz, Goethite, Francolite (tr.)	SMECTITE Illite, Dolomite (m) Kaolinite (tr.)
SAMPLE 42-84	FRANCOLITE K FELDSPAR Quartz (m) Wavellite (tr.)	QUARTZ Francolite, K feldspar (tr.)	SMECTITE QUARTZ Palygorskite, Francolite, Goethite (m) Dolomite, K feldspar, Wavellite, Crandallite (tr.)	SMECTITE Francolite, Albite, K feldspar, Palygorskite, Illite, Goethite (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
44-84	9.340	9.332	9.330	9.327
43-84	9.336	9.324	9.332	9.333
42-84	9.336	9.328	9.335	9.349

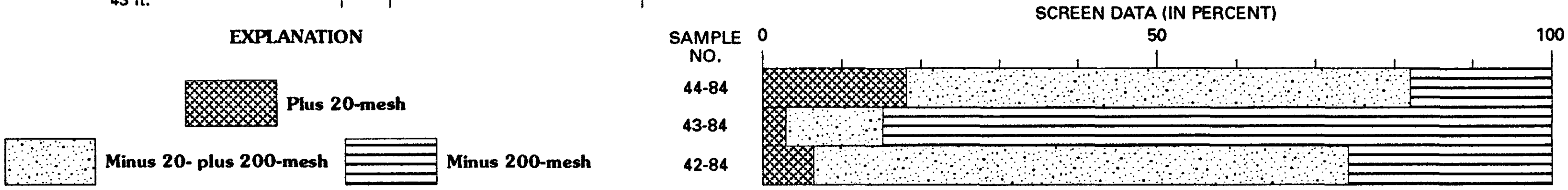


Figure 22. Four Corners mine. NW¼NW¼ sec. 2, T. 33 S., R. 22 E., Hillsborough County.

Depth (feet)	Sample No.	Lithology		Age and Stratigraphy
0-14	None	OVERBURDEN Sand, unconsolidated, gray and organic in top 2 ft, white below. Bottom 6 ft is red brown, iron stained.	Terrace Sands	PLEISTOCENE and HOLOCENE
14-18	None	RUBBLE ZONE Sand, gray white, slightly clayey. Contains abundant boulders of vesicular leached rock.	Hawthorn Group–Peace River Formation	MIOCENE–PLIOCENE Leached Bone Valley Member
18-23	47-84	MATRIX Sand, clayey to sandy clay, mottled yellow and gray green. Abundant sand-size phosphate pellets, some pebbles. Unit is 24½ ft thick 100 ft east.		Bone Valley Member
23-30	46-84	BEDROCK Interbedded, thin, hard yellow dolomite and pebbly, clayey sand containing abundant coarse phosphate pebble. Pit base at 42½ ft.		MIOCENE Undifferentiated
30-42½	45-84			

Mineralogy (Screen size)

	+20 mesh	−20 +200 mesh	−200 mesh	−2 µm
SAMPLE 47-84	FRANCOLITE QUARTZ Wavellite K feldspar } (tr.)	QUARTZ Francolite K feldspar } (tr.)	SMECTITE QUARTZ FRANCOLITE	SMECTITE Illite Quartz Francolite K feldspar Crandallite } (tr.)
SAMPLE 46-84	FRANCOLITE QUARTZ Dolomite (m) K feldspar (tr.)	QUARTZ K feldspar (m) Francolite (tr.)	SMECTITE DOLOMITE Francolite Quartz } (m) Palygorskite (tr.)	SMECTITE Dolomite (m) Quartz Francolite Albite K feldspar Crandallite Illite Palygorskite Sepiolite } (tr.)
SAMPLE 45-84	FRANCOLITE Quartz Dolomite } (m) K feldspar (tr.)	QUARTZ K feldspar (m) Francolite (tr.)	DOLOMITE Quartz Francolite K feldspar Smectite Palygorskite Kaolinite } (tr.)	SMECTITE Albite (m) Quartz Francolite Dolomite K feldspar Palygorskite Illite } (tr.)

FRANCOLITE *A*-VALUES
(±0.003 ANGSTROMS)

SAMPLE NO.	Bulk Sample	+20 mesh	−20 +200 mesh	−200 mesh
47-84	9.337	9.335	N.A.	9.360
46-84	9.332	9.329	9.328	9.324
45-84	9.334	9.330	9.335	9.329

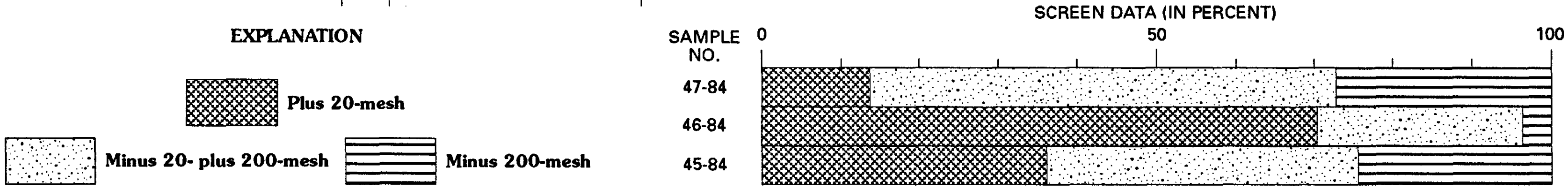


Figure 23. Kingsford mine. NE¼NE¼ sec. 30, T. 30 S., R. 23 E., Polk County.

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