

# Mineralogy and Chemistry of Samples From a Drill Hole in the Southern Extension of the Land-Pebble Phosphate District, Florida

U.S. GEOLOGICAL SURVEY BULLETIN 1978





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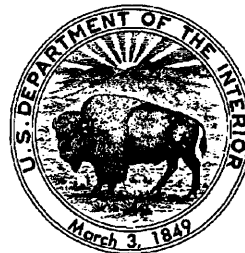
By JAMES B. CATHCART and THEODORE BOTINELLY

Economics of phosphate mineralogy and chemistry in an area of possible future mining

U.S. GEOLOGICAL SURVEY BULLETIN 1978

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# Mineralogy and Chemistry of Samples From a Drill Hole in the Southern Extension of the Land-Pebble Phosphate District, Florida

By James B. Cathcart and Theodore Botinelly

## Abstract

Although there are abundant data on the phosphate deposits of the land-pebble district of Florida (in Polk and Hillsborough Counties), data on the deposits of its southern extension (in Hardee, Manatee, and DeSoto Counties) are scarce. A core hole in the southern extension (in southern Hardee County) penetrated 5 ft (feet) of the Bone Valley Formation and about 90 ft of phosphorite of the Peace River Formation, both of the Miocene and Pliocene Hawthorn Group.

The apatite mineral of the Bone Valley and the Peace River Formations is carbonate fluorapatite (francolite), but there are distinct differences in francolite composition that are indicated by variations in the *a*-cell dimensions. The average *a*-cell dimension of the francolite in samples of the Bone Valley Formation is 9.345 Å (angstroms), but it is only 9.327 Å in samples from the Peace River Formation. Francolites with *a*-cell dimensions of less than 9.30 Å are considered to be highly substituted. The highly substituted francolites contain more MgO, Na<sub>2</sub>O, and CO<sub>2</sub>, and therefore have a lower P<sub>2</sub>O<sub>5</sub> content than the less substituted francolite. The economic implications are clear: phosphate products from the southern extension will be low in P<sub>2</sub>O<sub>5</sub> and high (>0.5 percent) in MgO.

Dolomite is the principal carbonate mineral, although some calcite in the form of "rice-grain" scalenohedrons is in the lower part of the Peace River Formation. The dolomite in the deeper part of the core hole is very close to ferroan dolomite, whereas the altered dolomite at the base of the mining pits in the land-pebble district is a nonferrous dolomite. This difference indicates that the primary dolomite of the deposits was iron rich, and the dolomites of the mine pits have been altered and iron removed.

Clay minerals of the Peace River Formation include palygorskite, sepiolite, and montmorillonite, whereas the clay mineral of the Bone Valley Formation is montmorillonite, and in the highly altered surficial parts of the Bone Valley, kaolinite is the predominant clay mineral.

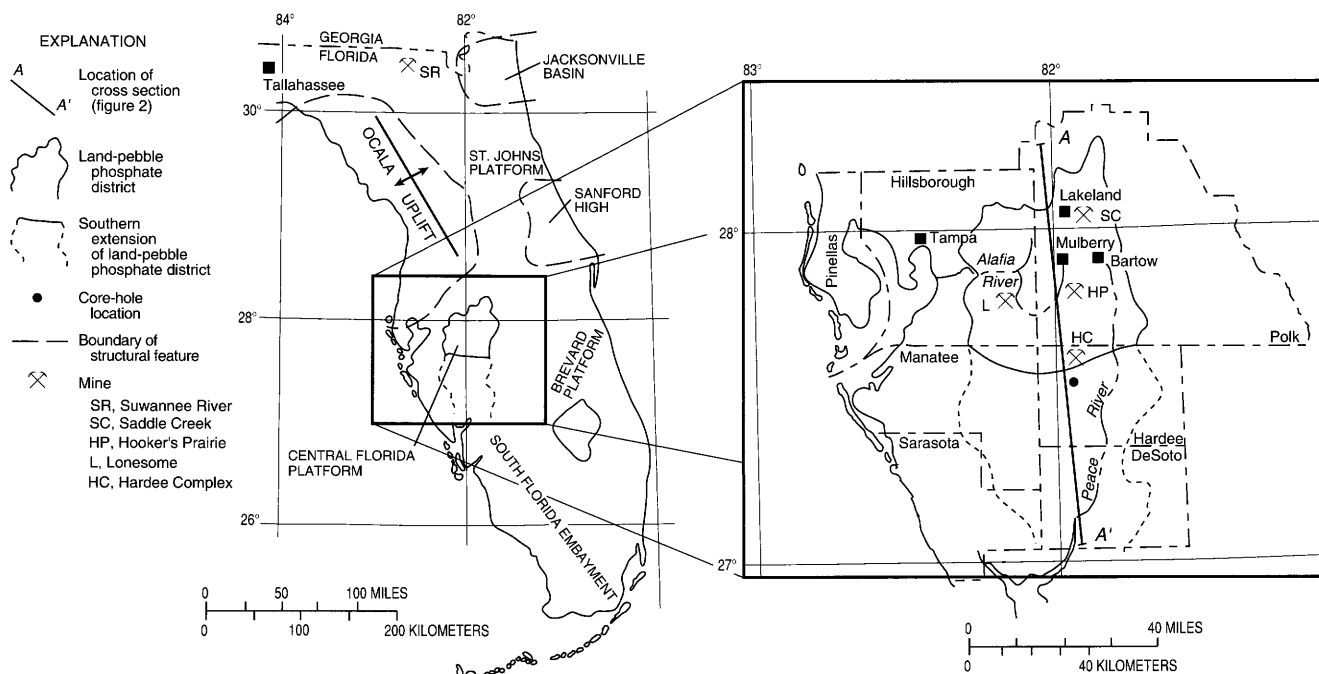
Data on trace elements are still being collected, but data on mercury and cadmium are complete. Mercury and cadmium, both toxic elements, are present in the phosphate products in both the Bone Valley Formation and Hawthorn Group but in amounts that range from 0.02 to 0.63 ppm (parts per million) (Hg) and from 2 to 15 ppm (Cd), too low to be of concern. The data show that the relations of zinc and cadmium in these samples is positive and the correlation is strong, and it seems likely that the cadmium is allied with zinc in sphalerite.

A small sphere (0.1 mm, millimeter) was found imbedded in a phosphate grain 90 ft below the surface. X-ray data show that the grain is composed mainly of native iron. Thus, this grain may be a micrometeorite (tektite?), the first found in Miocene phosphorite deposits.

## INTRODUCTION

The land-pebble phosphate district in central Florida is the most productive phosphate district in the world. About 1.1 billion metric tons of phosphate rock containing an average of about 32 percent P<sub>2</sub>O<sub>5</sub> have been produced since mining began in 1891. Almost all of the production has come from Polk and Hillsborough Counties, although there has been some mining in the northern parts of Hardee and Manatee Counties (fig. 1).

The areal extent of the land-pebble district has been known, in general, for many years. Eldridge (1893, p. 197) published a map that showed the land-pebble district in Polk and Hillsborough Counties, and Mansfield published a map of the phosphate deposits of Florida (1942, pl. 5) that showed a high-grade pebble area (equivalent to the land-pebble phosphate district) in Polk and Hillsborough Counties and a low-grade area that included much of Manatee and Hardee Counties and extended south into Sarasota and DeSoto Counties. This was the first map that indicated the presence of potentially economic phosphate to the south of the classic land-pebble district. This area was named the



**Figure 1.** Index map of Florida, showing structural features, the land-pebble phosphate district and its southern extension, and location of the core hole.

“southern extension” of the land-pebble district by Bernardi and Hall (1980), who pointed out that the phosphate rock in the southern extension differs from the rock in the land-pebble district in that it contains less  $P_2O_5$  and more  $MgO$ . Additional differences in the economic geology of the two areas were discussed by Cathcart (1985), but details of the mineralogy and chemistry of the phosphate rock in the southern extension have not been published.

Core from a drill hole in Hardee County in the northern part of the southern extension was provided for this study by John Paugh, Chief Geologist of Gardinier, Inc. The hole was drilled in sec. 7, T. 34 S., R. 24 E. The core was logged and sampled, the samples were screened, and the pebble (+1 mm), concentrate (-1 mm, +0.1 mm), and slime (-0.1 mm) fractions of each sample were analyzed by X-ray diffraction. Chemical analyses were made by D.L. Fey, P.L. Hageman, T.A. Roemer, and J.D. Sharkey, and semi-quantitative spectrographic analyses were made by B.M. Adrian and S.J. Sutley, all of the Denver laboratories of the U.S. Geological Survey.

## STRUCTURE

Peninsular Florida is in the Atlantic Coastal Plain and consists of Tertiary sediments that dip very gently (10–20 ft/mile) away from the major structural features.

The Ocala uplift (also called the Ocala arch or Ocala high) dominates the structure of the Florida peninsula. The uplift was a positive feature during the Miocene (Vernon,

1951; Olson, 1966), and Miocene sediments are thinned on the uplift and were removed from the crest of the uplift by subsequent erosion, so that Pleistocene and Holocene sediments directly overlie rocks of Eocene and Oligocene age. Similarly, Miocene sediments are not present on the Sanford high (fig. 1).

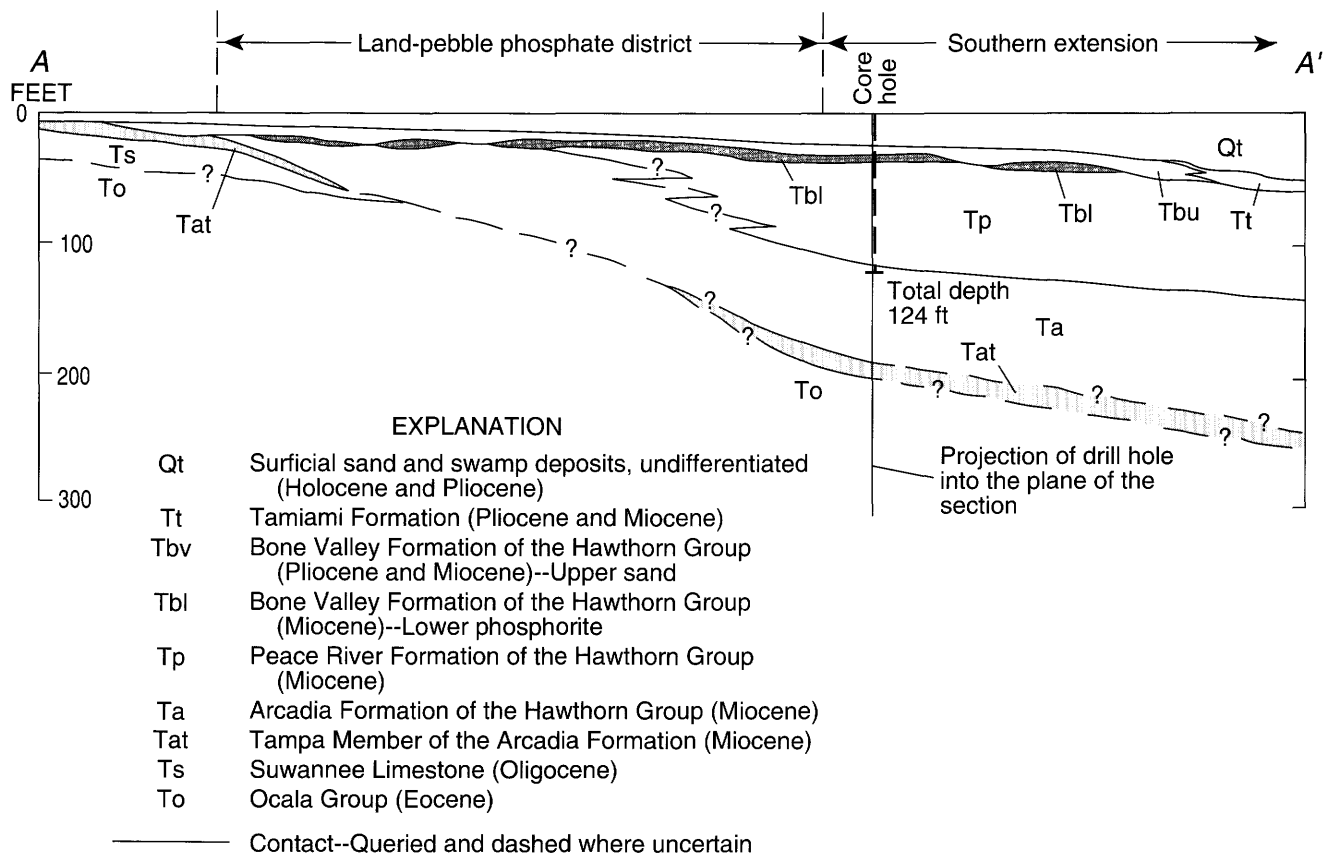
Rocks of Miocene age dip gently and thicken away from the highs. In the Jacksonville basin and the south Florida embayment (fig. 1), Miocene and post-Miocene rocks are much thicker than rocks of equivalent ages on the platforms.

The phosphate sediments of the Bone Valley Formation in the land-pebble district were deposited in a shallow basin on the south flank of the Ocala uplift. The basin was defined by both structural and topographic features on the north, west, and east, but was open to the sea to the south.

Southward thickening of Miocene and post-Miocene sediments from the land-pebble district into the south Florida embayment is clearly shown on the cross section (fig. 2).

Regional geologic structure is important in the distribution and physical characteristics of the phosphate deposits. Coarse phosphate of the land-pebble district was deposited in the shallow basin at the edge of the sea during Miocene and Pliocene time. Carbonate rock, phosphatized during an initial regression, was broken up, rolled and rounded, and deposited during transgression as beach gravel, forming the basal conglomerate of the Bone Valley Formation. Fine-grained phosphate pellets, quartz sand, and clay were deposited further offshore. This lateral facies





**Figure 2.** Diagrammatic cross section through the land-pebble phosphate district and its southern extension, Florida. Location of section shown on figure 1.

change was also repeated vertically, as the sea transgressed, so that conglomeratic phosphate is overlain by sandy phosphorite and in turn is overlain by more clayey phosphate material.

Deposits in the southern extension are thicker and are finer grained than are the deposits of the land-pebble district. Conglomeratic phosphate deposits (pebble beds) are not present except in the northernmost part of the southern extension, and the Bone Valley Formation is present only as outliers in the southern extension.

## STRATIGRAPHY

The surface of the land-pebble phosphate district is blanketed by unconsolidated sand and swamp deposits of Pleistocene and Holocene age. The only exposures of pre-Pleistocene sediments are in mining pits and where the Alafia and Peace Rivers are flowing on carbonate rock that is exposed at times of low water.

The oldest rock exposed in the mining pits is carbonate rock of the Hawthorn Group. Mining stops at this material that represents about the middle Miocene. Older rocks in the district and its southern extension are known only from a few deep drill holes.

The phosphate deposits are confined to rocks of Miocene age and to younger sediments containing phosphate derived from the Miocene rocks. The discussion of stratigraphy, therefore, is concentrated on these rocks, and older rocks, known only from drill holes, are discussed briefly. General stratigraphic relations are shown on table 1.

## Eocene

*Ocala Group.*—Limestone of the Eocene Ocala Group underlies all of Peninsular Florida. The limestone is white to cream, fossiliferous, and “\*\*\*in places contains as little as four-tenths of one percent of impurities” (Cooke, 1945, p. 54).

## Oligocene

*Suwannee Limestone.*—The Suwannee Limestone consists predominantly of calcium carbonate but contains as much as 10 percent quartz and chert. Drill-hole data show that the Suwannee is present in the northernmost and western parts of the land-pebble district. The Suwannee is missing over much of the rest of the district and its southern extension where rocks of Miocene age rest directly on rocks of the Ocala Group (fig. 2).

**Table 1.** General stratigraphic relations in the land-pebble phosphate district and its southern extension, Florida

			Land-pebble district	Southern extension	
HOLOCENE			Sand and swamp deposits (2-6 ft; 1-2 m)		
PLEISTOCENE			Bedded clayey sand. Channel deposits of pebble phosphate. (10-40 ft; 3-12 m)	Bedded slightly clayey sand. (20-70 ft; 6-20 m)	
PLIO-CENE	HAWTHORN GROUP	BONE VALLEY FORMATION	Clayey sand. Trace of phosphate, aluminum and iron phosphate when leached. (0-30 ft; 0-12 m)	Clayey sand, abundant shell, trace of phosphate. (0-75 ft; 0-23 m)	TAMIAMI FORMATION
MIOCENE			Phosphorite, sandy, clayey, pebbly. Abundant aluminum phosphate where leached. (0-50 ft; 0-15 m)		
		PEACE RIVER FORMATION	Clay and sand, dolomitic. Abundant phosphate, in part residual from underlying carbonate rock. Ranges from 10 ft (3 m) at the north edge of the district to 60 ft (18 m) at the south. Thin beds of fossiliferous dolomite are more abundant toward base.	Clay, sandy, silty, contains dolomite as lenses and fine silt to clay-size rhombs. Abundant fine-grained phosphate pellets. (60-150 ft; 18-45 m)	
		ARCADIA FORMATION	Dolomite, sandy, contains abundant phosphate pellets and some pebble. Thickness ranges from 10 ft (3 m) in the north to 100 ft (30 m) at the boundary with the southern extension. Interbeds of dolosilt and doloclay are present, particularly at the top.	Dolomite, sandy, fossiliferous. Some calcite, more abundant at depth, fine-grained phosphate pellets throughout. Clastic interbeds are more abundant near top. (100-150 ft; 30-45 m)	
TAMPA MEMBER		Sandy clay. Chert, carbonate, some phosphate. (0-20 ft; 0-6 m) (10-50 ft; 3-15 m)			
OLIGOCENE			SUWANNEE LIMESTONE		
EOCENE			OCALA GROUP		

## Miocene

The Miocene of Peninsular Florida was divided into three parts (Cooke, 1945, p. 109)—the Tampa Limestone at the base, the Hawthorn Formation in the middle, and the Duplin Marl and equivalents at the top. Data from drill holes and mine pits in the land-pebble district indicated that the Hawthorn Formation could be divided into a lower carbonate unit and an upper siliciclastic unit (Cathcart, 1985). Scott (1988) proposed that the Hawthorn be raised to group status and that the group include all of the Miocene. He proposed the name “Arcadia Formation” for the lower carbonate-rich part of the Hawthorn (about equivalent to the informal lower carbonate unit) but included the Tampa as a member at the base of the Arcadia Formation. The Peace

River Formation was proposed as a formal name for the predominantly clastic upper part of the Hawthorn (about equivalent to the upper clastic unit).

## Hawthorn Group

### Arcadia Formation

The Arcadia Formation consists primarily of sandy, gray to white fossiliferous dolomite with interbeds of gray-green dolomitic, sandy, and silty clay. All lithologic units contain varying amounts of phosphate grains. The Arcadia Formation ranges from a feather edge at the northern limit of the land-pebble district to about 100 ft at



the southern limit of the district. The formation thickens to the south and is about 150 ft thick in the southern part of DeSoto County.

The Arcadia Formation in the southern extension is similar lithologically to the formation in the land-pebble district, except that the formation contains some limestone beds near its base in southern DeSoto County.

Sample F18-87 from the core hole (121–124 ft below the surface) consists of white, sandy phosphatic dolomite (table 2) that is assigned to the Arcadia Formation. The lithology of this sample is typical of the carbonate rock of the Arcadia Formation, and the thickness (3 ft) is greater than the average thickness (0.5–1 ft) of the carbonate lenses in the Peace River Formation.

Phosphatic carbonate rock of the Hawthorn Group thickens markedly in southern Florida. For example, oil tests in Dade County have penetrated as much as 600 ft of the Hawthorn Group. Most of the thickness seems to be in the Arcadia Formation. Cuttings were reported as limestone or dolomite, but recovery of samples was poor and incomplete.

*Tampa Member.*—The Tampa Member of the Arcadia Formation in the land-pebble district consists of calcareous clayey sand and carbonate rock that contains some chert and minor phosphate nodules and pellets. The Tampa Member is present in the northernmost part and to the west of the land-pebble district, where it is as much as 10 ft in thickness (fig. 2). The Tampa Member is missing over much of the rest of the land-pebble district but is present in the southern extension where it is as much as 50 ft thick. In the southern extension, the Tampa Member consists of sandy clay and carbonate rock that contain some phosphate grains and chert fragments. The core hole that was investigated for this paper did not reach the Tampa Member.

#### Peace River Formation

The Peace River Formation of the Hawthorn Group (Scott, 1988) is about equivalent to the informal upper clastic unit of the Hawthorn (Cathcart, 1985). The unit is predominantly clastic and consists of gray-green to light-gray (white when dry) dolomitic clayey and silty sand to sandy and silty clay, and thin lenticular beds of hard dolomite. All of the beds contain black, brown, and gray phosphate pellets and nodules (pebbles). The Peace River Formation is thin or absent in the northern part of the land-pebble district, and clastic rock (called “bedclay”) may be residual from the underlying carbonate rock, and, therefore, a part of the Arcadia Formation. In the southern part of the land-pebble district, the Peace River Formation thickens to as much as 50 ft and contains thin dolomite beds that are more abundant with depth. Thus the contact of the Peace River and Arcadia Formations is difficult to locate precisely. The Arcadia Formation differs from the Peace River only in that it has much more abundant carbonate rock.

The Peace River Formation thickens markedly in the southern extension of the land-pebble district (fig. 2), and is as much as 150 ft thick in southern De Soto County. The formation is lithologically identical to the formation in the land-pebble district except that it contains less of the pebble fraction, and the concentrate fraction tends to contain more very fine grained phosphate pellets. All of the potentially economic phosphate in the southern extension is in the Peace River Formation.

#### Bone Valley Formation

The earliest publications on the phosphate deposits of the land-pebble district did not formally name the phosphate-bearing formation. Dall (1892) simply called them “pebble phosphates” and considered them to be of Pliocene age, while Eldridge (1893) referred to them as “land-pebble phosphate.” The first use of the name “Bone Valley” was by Matson and Clapp (1909, p. 138) who designated the pebble phosphate deposits then being mined as Bone Valley Gravel. They described the deposits as being largely fluvial in origin and probably of Pliocene age. Matson (1915, p. 20) was the first to indicate that the Bone Valley might be of Miocene age, although he pointed out that it has “\*\*\*generally been regarded as Pliocene and it is so classified here\*\*\*”.

Cooke (1945, p. 203) discarded the term “gravel” in favor of the more general term “Bone Valley Formation” for the phosphate deposits, because by that time, only a small part of the deposit was gravel—most of what was being mined was sand-size material. He considered the formation to be of Pliocene age.

Vertebrate fossils in the Bone Valley Formation are now thought to be of late Miocene age (Webb and Crisinger, 1983), although the uppermost part of the formation may be of Pliocene age. Scott (1988) included the Bone Valley as a member in the uppermost part of the Peace River Formation of the Hawthorn Group, but we think that the Bone Valley should be designated as a formation in the uppermost part of the Hawthorn Group, overlying the Peace River Formation.

The Bone Valley Formation was informally divided into a lower phosphorite unit and an upper clayey sand unit (Cathcart, 1963). The lower unit in the land-pebble district is a brown, gray, and white sandy and clayey phosphorite that commonly has a basal conglomerate composed of phosphate cobbles and boulders that are almost all phosphatized carbonate rock. The phosphate conglomerate was formed by the phosphatization of carbonate rock of the Peace River or Arcadia Formations that was reworked and concentrated at the base of the Bone Valley. The coarse phosphate rock in the land-pebble district is concentrated on topographic highs (ridges) that formed prior to the deposition of the Bone Valley. Submarine winnowing removed sand-size phosphate and quartz particles and the

**Table 2.** Lithologic log of core hole studied, Hardee County, Fla.

[Core hole is in sec. 7, T. 34 S., R. 24 E.; n.s., no sample]

Depth in feet below surface	Sample no.	Lithology
<b>Holocene</b>		
0–2	n.s.	Sand, dark-gray to black, organic. Surface soil.
<b>Pleistocene</b>		
2–15	n.s.	Sand, tan, unconsolidated. Very slightly clayey at base.
16–25	n.s.	Sand, gray-tan, slightly clayey.
<b>Miocene-Pliocene</b>		
<b>Bone Valley Formation of the Hawthorn Group—Upper part</b>		
25–29	F1–87	Sand, gray-tan, slightly clayey. Minor (less than 5 percent) dull-white leached phosphate grains. Trace of shiny white and tan grains. Some phosphatized shell fragments, trace of fish and shark teeth. Trace of shiny black and brown fine-grained phosphate pellets. A few fragments of tan sand cemented by aluminum phosphate minerals and apatite. Gray clay clasts in base, derived from clay below.
<b>Miocene</b>		
<b>Bone Valley Formation of the Hawthorn Group—Lower part</b>		
29–29.5	F2–87	Clay, gray, silty. Thin laminae of white sand that contain small amounts of white and tan shiny phosphate pellets.
29.5–30	F3–87	Sand, gray, slightly clayey. Contains abundant brown, gray, black, white, and cream phosphate grains, phosphatized rock fragments, and phosphatized fossils. Many of the coarser grains are broken and rounded. The sample has a higher percentage of coarse than fine phosphate.
<b>Peace River Formation of the Hawthorn Group</b>		
30–38	F4–87	Sand, yellow-gray-green, slightly clayey. Abundant brown, tan, gray, and some black phosphate pebbles, phosphatized rock fragments, and phosphatized fossils. Fine-grained phosphate is much greater in amount than coarse grained. Fine phosphate is shiny and brown, gray, tan, black, and white. Includes subangular translucent amber fragments of phosphatized shell material. Trace of white dolomite fragments.  Note: The phosphate grains in the samples from 30 to 53 ft are predominantly light-colored—gray, tan, white, cream, and only about 5–10 percent black and dark-brown grains, in sharp contrast to the samples from 53 ft to the base of the hole.
38–44.5	F5–87	Sand, gray-green, contains abundant thin green irregular and lenticular clay laminae. Most of the clay in the sample is in these laminae. Contains minor tan and cream-gray, and some black phosphate pebbles, phosphatized rock fragments, and phosphatized fossil fragments. Fine phosphate (concentrate) is much more abundant than coarse and is tan, light and dark brown, gray brown, greenish brown, white, cream, and black. All grains are shiny and are subspherical or rod shaped. Some phosphatized fossils. Trace of dolomite.
44.5–53.5	F6–87	Sand, yellow-gray-green, slightly clayey. Base sample interval is 0.5-ft green-gray clay bed. Trace of phosphate pebbles; brown, gray, green, white, and a trace of black. Some shark teeth. Concentrate size much more abundant than pebble size. Phosphate pellets, some fish teeth: brown, tan, gray-green, some black and white. Trace of white dolomite fragments.
53.5–57	F7–87	Dolomite, yellow-white, sandy, soft (or doloclay). Contains abundant phosphate grains, mostly concentrate size but with some pebble. Phosphate is black, brown, gray, and tan pellets, some phosphatized rock fragments (dolomite?), and phosphatized fossils. Black and dark-brown phosphate grains are about 70–80 percent of the total. Some quartz sand.
57–69	F8–87	Sand, gray and gray-green, clayey. Clay fraction is dolomitic. Some white, soft dolomite fragments. Phosphate (pebble and concentrate) is predominantly black and brown, very shiny, round pellets, some phosphatized rock fragments. Trace of shark teeth, and fossil molds. A few gray-green and red-brown phosphate pellets, some tan and white.



**Table 2.** Lithologic log of core hole studied, Hardee County, Fla.—Continued

[Core hole is in sec. 7, T. 34 S., R. 24 E.; n.s., no sample]

Depth in feet below surface	Sample No.	Lithology
69–73.5	F9–87	Sand, gray-green, clayey, dolomitic. Contains predominantly black and brown phosphate pellets and gray and white phosphatized dolomite rock fragments. Some compound pebbles. Some white dolomite fragments. Phosphatized fossil molds. Concentrate much more abundant than pebble.
73.5–82	F10–87	Sand, dark-gray-green, clayey, dolomitic. Grades downward into dolomite of sample F11–87. Concentrate-size phosphate pellets much more abundant than pebble size. Pellets are black and brown with lesser amounts of dark gray and green. Pellets are highly polished. Some phosphatized fossils, including shark teeth. A few white dolomite fragments more abundant with depth.
82–87	F11–87	Dolomite, yellow-white, sandy, soft (or doloclay). Interbedded with dark-gray phosphate and quartz sand. Coarse fraction (pebble) consists of dolomite fragments, partly phosphatized dolomite fragments, and shiny black and some gray phosphate grains. Fine phosphate (concentrate) is more abundant than the pebble and is predominantly black with some gray, tan, and brown very shiny grains. Some broken and rerounded shark teeth.
87–95	F12–87	Sand, dark-gray-green, clayey. Coarse fraction consists of cream-white phosphatic dolomite fragments and black, gray, and brown polished phosphate grains. One compound pebble contained a metallic sphere (about 0.1 mm) embedded in it. X-ray showed that the sphere was largely elemental iron. This may be a micrometeorite (tektite?). Concentrate-size phosphate is black with some brown and gray shiny pellets. Thin (0.5 in.) lenses of dolomite at 89.5 and 94.5 ft.
95–100	F13–87	Clay, dark-gray-green, silty, dolomitic. Irregular areas (boring fillings or bioturbation) of black phosphate and quartz sand. Contains yellow crystals (scalenohedrons) of calcite (rice-grain crystals). Fine phosphate is more abundant than coarse. Almost 80 percent of the phosphate grains are black, very shiny, structureless pellets, but there are some phosphatized rock fragments and phosphatized fossil molds.
		Note: Samples F13–87 through F17–87 contain rice-grain crystals of calcite in trace to moderate amounts.
100–104	F14–87	Sand, dark-gray-green, clayey. Pebble fraction consists of black and some brown and gray pebbles and phosphatized rock fragments, some of which are broken and rerounded, and abundant calcite scalenohedrons. Concentrate-size phosphate is more abundant and is black with some brown and gray shiny pellets and minor amounts of fossils and rock fragments.
<b>Miocene</b>		
104–108	F15–87	Sand, gray-green and white mottled, clayey, dolomitic. More clayey at base. Phosphate pebble is not abundant and is black with some brown and gray, some phosphatized rock fragments and phosphatized fossils (molds and teeth). Concentrate-size phosphate is predominantly black and more abundant than the pebble. Clay fraction is dolomitic.
108–114	F16–87	(Cuttings). Sand, light-gray-green, clayey, dolomitic, with light-gray silty doloclay lenses. Pebble fraction is black, gray, brown, and tan smooth, shiny pebbles, some phosphatized rock and phosphatized fossils. Some rice-grain calcite crystals. Concentrate fraction is mostly black with some brown, shiny phosphate pellets and is more abundant than the pebble.
114–121	F17–87	Sand, light-gray-green, clayey, dolomitic. Grades down into hard dolomite. Greenish-gray clay lenticles throughout interval. White dolomite fragments at base. Black, gray, and brown phosphate pellets and phosphatized rock fragments. Concentrate more abundant than pebble size. A few phosphatized fossils.
<b>Arcadia Formation of the Hawthorn Group</b>		
121–124	F18–87	Dolomite, white, sandy, phosphatic. Irregular areas of black phosphate and quartz sand. Phosphate is mostly black with some dark gray and brown. Concentrate fraction more abundant than pebble.

Hole bottomed at 124-ft depth in hard dolomite.

clay fraction, thus concentrating the coarse phosphate. Fine phosphate and quartz particles were deposited on the flanks of the ridges and on the flatlands adjacent to the ridges.

Pebble-size phosphate is not abundant in the southern extension, and the very coarse phosphate boulders characteristic of the Bone Valley in the land-pebble district are not present in the southern extension. The Bone Valley in the land-pebble district is as much as 50 ft thick and is thickest in sinkhole fillings. In the southern extension, the Bone Valley is thin (as much as 10 ft) and is missing over much of the area.

The upper unit of the Bone Valley is a clayey sand that contains minor to trace amounts of phosphate, most of which is present in the basal 1 or 2 ft of the unit. The unit is as much as 30 ft thick in the land-pebble district and extends as a transgressive unit to the north of the district (fig. 2). In the southern extension, the upper unit is present, but little is known of its thickness and extent. Data from a drill hole in De Soto County showed that the Bone Valley Formation was missing and in its place is a clayey, shelly sand, the Tamiami Formation (fig. 2).

## Pleistocene and Holocene

Unconsolidated sediments of Pleistocene and Holocene age gradationally overlie the Bone Valley Formation in the land-pebble district and the northern part of the southern extension. To the south, in the southern extension, where the Bone Valley is not present, Pleistocene sediments overlie the Peace River Formation or the Tamiami Formation (fig. 2). The cross section (fig. 2) also shows the thickening of these sediments to the south, from about 10 ft in the northern part of the land-pebble district to as much as 70 ft at a drill hole in DeSoto County.

Pleistocene sediments are unconsolidated sand or clayey sand that may have trace amounts of phosphate reworked from underlying Bone Valley or Peace River Formations. In the land-pebble district, lenticular channel deposits of coarse phosphate pebble and sand are present in the Pleistocene sediments and are most common at the base of the Pleistocene where they directly overlie the lower phosphorite unit of the Bone Valley. Vertebrate fossils in the channel deposits are of Pleistocene age.

Surficial deposits of wind-blown sand and swamp muck overlie the sand of Pleistocene age and are of Holocene age. Except for the swamp muck, these deposits have not been separated from the Pleistocene, and the surficial sand deposits are lumped as Pleistocene and Holocene age.

## MINERALOGY

### Apatite

The apatite mineral of the phosphate deposits of Florida is carbonate fluorapatite (francolite). Detailed work

by scientists of the Tennessee Valley Authority and the International Fertilizer Development Center (Lehr and others, 1968; McClellan and Lehr, 1969; McClellan, 1980; Van Kauwenbergh and McClellan, 1985) has shown that carbonate substitutes for phosphate in a 1:1 ratio and that the maximum amount of substitution is slightly less than 6 percent by weight (expressed as  $\text{CO}_2$ ). Both  $\text{Na}^+$  and  $\text{Mg}^{2+}$  are present in the francolite structure replacing  $\text{Ca}^{2+}$ . According to McClellan (1980), maximum MgO in the most highly substituted francolite is about 0.6 percent, whereas  $\text{Na}_2\text{O}$  may be as much as 1.1 percent. Because of these substitutions, the  $\text{P}_2\text{O}_5$  content of the most highly substituted francolite is about 35 percent, whereas fluorapatite contains about 42 percent  $\text{P}_2\text{O}_5$ .

The changes in composition of the apatite have important implications economically. In addition to lower  $\text{P}_2\text{O}_5$  content, the higher MgO and  $\text{Na}_2\text{O}$  contents can be deleterious in the manufacture of phosphate fertilizers. The contents of both  $\text{CO}_2$  and MgO in the apatite are difficult to measure because of admixtures of calcite and dolomite in the phosphate particles. McClellan (1980) showed that the dimension of the unit cell can be used to indicate the amount of substitution. Therefore, we calculated the *a*-cell dimensions from X-ray diffractograms for all phosphate samples from the drill hole (table 3). The data clearly show that the samples of weathered (altered) apatite from the Bone Valley Formation have distinctly higher *a*-cell dimensions than the apatite from the Peace River Formation, which is progressively less altered toward the bottom of the core hole.

Data from Van Kauwenbergh and others (1990) show that the apatites of the Peace River Formation have slightly lower *a*-cell dimensions than the samples from the Bone Valley. The *a*-cell dimensions of the apatite from the Bone Valley Formation as reported by Van Kauwenbergh and others (1990) are almost identical with the *a*-cell dimensions for the Bone Valley from this study (9.343 Å and 9.345 Å, respectively). However, the apatites in the samples from the Peace River Formation reported in this paper (table 3) have distinctly smaller *a*-cell dimensions than the *a*-cell dimensions reported by Van Kauwenbergh and others (9.327 Å for the core samples and 9.338 Å for the mine samples). It should be noted that the samples of the Peace River Formation used in the Van Kauwenbergh study were all taken from the mine pits in the land-pebble district and are almost certainly altered, whereas the samples from deeper in the core hole do not appear to have been altered.

Van Kauwenbergh and others (1990) shows (table 8) *a*-cell dimensions for less altered apatites from deposits around the world. Their data show that the *a*-cell dimensions of North Carolina apatite average 9.323 Å (their table 8), and are only slightly lower than the *a*-cell dimensions of apatite from the Peace River Formation. The apatite from North Carolina is one of the most highly

**Table 3.** Francolite *a*-cell dimensions from the core hole of this study compared with data from the literature and from samples of phosphorite from North Carolina

Location	a-cell dimensions (Å)	
	Range	Average
Florida (land-pebble district) <sup>1</sup> :		
Bone Valley Formation (22 samples).	9.327–9.368	9.343
Peace River Formation (24 samples).	9.328–9.357	9.338
Florida (southern extension) <sup>2</sup> :		
Bone Valley Formation (3 samples).	9.334–9.381	9.345
Peace River Formation (15 samples).	9.300–9.342	9.327
North Carolina <sup>3</sup> :		
Pungo River Formation (18 samples).	9.318–9.332	9.323
North Carolina <sup>4</sup> (Pungo River Formation):		
+20 mesh (39 samples)	9.298–9.339	9.322
–20+200 mesh (34 samples)	9.300–9.334	9.320

<sup>1</sup>Van Kauwenbergh and others (1990, table 7).

<sup>2</sup>Data from core hole, this report.

<sup>3</sup>Van Kauwenbergh and others (1990, table 8).

<sup>4</sup>J.B. Cathcart (unpub. data, 1975–90).

substituted carbonate fluorapatites known in the world today.

These data clearly indicate that the apatite of the deeper, relatively unaltered part of the Peace River Formation in the southern extension, as shown in this core hole, is highly substituted and therefore is low in P<sub>2</sub>O<sub>5</sub> content and high in CO<sub>2</sub>, MgO, and Na<sub>2</sub>O.

## Carbonate Minerals

**Dolomite.**—Dolomite is the most abundant carbonate mineral in the phosphate deposits of Florida. Soft, yellow, sandy, clayey phosphatic dolomite is present at the base of the mining pits in the land-pebble phosphate district. This is the so-called bedrock of the district, and samples of this dolomite were determined to be slightly deficient in MgO by Van Kauwenburgh and others (1990).

Dolomite is present in trace to minor amounts in analyzed samples from the core hole from 30 to 53 ft and is a major constituent from 53 ft to 124 ft. The core hole bottomed on hard white to gray, sandy, phosphatic dolomite. Gray and gray-green dolosilt and doloclay and thin lenses of hard white dolomite are present between 53 and 121 ft. The minus-150-mesh fractions of samples from 53 ft to the bottom of the core hole (samples F7–F18) contain major amounts of dolomite, and all the X-ray peaks

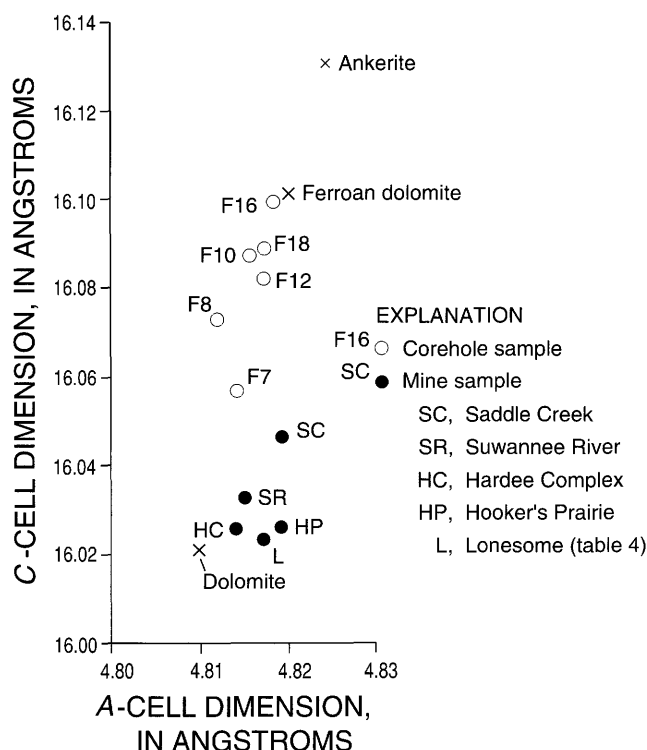
reported for dolomite were found. The X-ray diffractograms of these samples are similar, and the patterns of the dolomite differ only slightly from samples of dolomite taken from the base of the mining pits. Because the differences were so slight, it was decided to calculate the *a*- and *c*-cell dimensions for the dolomite samples from this core hole and compare them with data from the literature (table 4).

All of the samples fall between pure dolomite and ferroan dolomite (table 4) (Howie and Broadhurst, 1958), but are closer to ferroan dolomite. Cell dimensions from mine-pit samples (Van Kauwenburgh and others, 1990) are closer to pure dolomite than are the samples from the core hole. These data (fig. 3) clearly show the separation of the plots of the core-hole samples from the mine samples. The samples from the top of the core hole (F7–87 and F8–87) plot between the mine samples and the deeper core samples (F10–87, F12–87, F16–87, and F18–87, fig. 3). The deeper core samples have not been significantly altered and may represent the original composition of the dolomites in this area.

Chemical data (table 5) confirm that the dolomite from the core-hole samples contains more iron than pure dolomite. The comparison of the X-ray data from the core samples with that given by Van Kauwenburgh and others (1990) indicates that the samples from the core are slightly deficient in MgO.

**Table 4.** Unit-cell dimensions and unit-cell volumes of dolomite from the core hole of this study compared with that of dolomite from phosphate mines and with data from the literature

Sample No.	a (Å)	c (Å)	Unit-cell volume
<b>Hardee County core hole (this study)</b>			
F7-87.....	4.814	16.057	322.25
F8-87.....	4.812	16.073	322.30
F10-87.....	4.816	16.087	323.12
F12-87.....	4.817	16.082	323.16
F16-87.....	4.818	16.095	323.55
F18A-87.....	4.817	16.087	323.26
<b>Florida mine samples (Van Kauwenbergh and others, 1990)</b>			
Suwannee River mine.....	4.815	16.033	321.90
Saddle Creek mine.....	4.819	16.047	322.72
Hooker's Prairie mine.....	4.819	16.026	322.31
Hardee Complex mine.....	4.814	16.026	321.64
<b>Florida mine sample (J.B. Cathcart, unpub. data, 1980)</b>			
Lonesome mine.....	4.817	16.025	322.02
<b>Data from Howie and Broadhurst (1958)</b>			
Dolomite.....			
(JCPDS card 11-78).....	4.811	16.02	320.97
Ferroan dolomite.....			
(JCPDS card 34-517).....	4.819	16.10	323.79
Ankerite.....			
(JCPDS card 33-282).....	4.824	16.132	325.10



**Figure 3.** Relations of a- and c-cell dimensions of dolomite, ferroan dolomite, and ankerite compared with these relations in the core samples and in samples from phosphate mines, Florida.

**Table 5.** Chemical analyses of dolomite

[n.d., not determined; ---, not present; tr., trace; ppm, parts per million]

	Dolomite <sup>1</sup>	Ferroan dolomite <sup>1</sup>	F18-87 <sup>2</sup>
CaO.....	31.27	29.23	Ca (3 percent)
MgO .....	21.12	12.85	Mg (5 percent)
CO <sub>2</sub> .....	47.22	44.70	
FeO .....	.22	12.06	Fe (1 percent)
Fe <sub>2</sub> O <sub>3</sub> .....	tr.	.10	
SiO <sub>2</sub> .....	.12	.15	
Na <sub>2</sub> O.....	n.d.	.06	Na (0.2 percent)
K <sub>2</sub> O.....	n.d.	.01	
TiO <sub>2</sub> .....	---	tr.	Ti (0.05 percent)
Al <sub>2</sub> O <sub>3</sub> .....	---	.28	Al (present)
MnO .....	---	.77	Mn (500 ppm)
H <sub>2</sub> O.....	.02	.02	
Total .....	99.97	100.23	

<sup>1</sup>Howie and Broadhurst (1958).

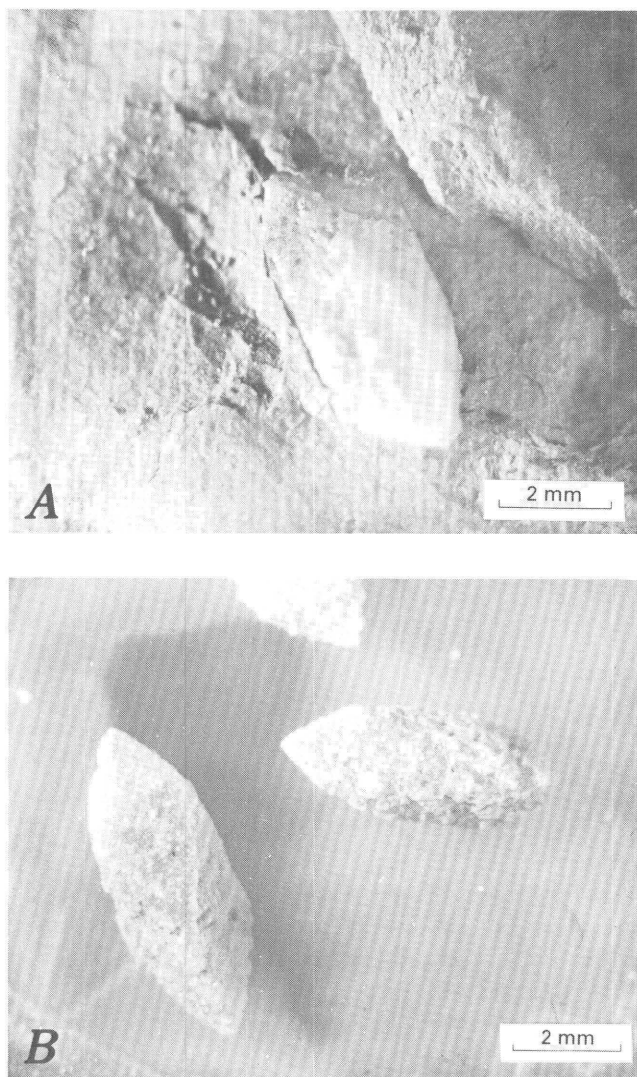
<sup>2</sup>Semiquantitative spectrographic analysis by S.J. Sutley, U.S. Geological Survey, of dolomite from the core hole of this study.

**Calcite.**—Calcite crystals (scalenohedrons) that range from 0.01 to 0.02 in. in length are present in trace amounts in samples F13-87 through F18-87 (from 95- to 124-ft depth). The crystals formed between laminae in gray-green doloclay beds as shown in the photograph of sample F14-87 (fig. 4A). Single calcite crystals, hand picked from sample F16-87, are shown on fig. 4B. X-ray data indicate that the core-hole samples contain trace amounts of calcite, about 5 percent of the +20-mesh fraction and about 1 percent or less of the total rock.

## Clay Minerals

The clay minerals in the phosphate deposits of Florida are a mixture of the common smectite, illite, and kaolinite and the less common palygorskite (attapulgite) and sepiolite. Smectite is the most abundant clay mineral in the phosphorite of the Bone Valley Formation and is present in varying amounts in the Peace River Formation. Illite is known to be present in minor amounts (Van Kauwenburgh and others, 1990), but in the samples studied for this report, only the major illite peak at about 10 Å could be detected in the X-ray diffractograms. Palygorskite and sepiolite are clay minerals with crystalline structures consisting of long double silicate chains that are parallel to the length of the mineral fibers (Carroll, 1970). In general, palygorskite occurs in samples from the bottom of the mine pits in the land-pebble district, whereas sepiolite is not present or is very rare in samples from the mine pits.





**Figure 4.** Photographs of calcite crystals from the core hole, Hardee County, Fla. A: Calcite crystal embedded in gray-green doloclay, along the bedding plane, sample F14-87. B: Hand-picked calcite crystals, sample F16-87.

Clay-mineral distribution in the minus-150-mesh fraction of samples from the core hole is shown on figure 5. Illite, although probably present in trace amounts, is not shown. Van Kauwenburgh and others (1990) concluded that illite probably was detrital in the sediments in the mine pits, and we think that the trace amounts of illite in the core samples are also detrital.

**Kaolinite.**—Kaolinite is the predominant clay mineral in the surficial samples of the land-pebble phosphate district where it formed as an alteration product of smectite during acid weathering (Altschuler and others, 1963), but detrital kaolinite has been described from a drill hole in DeSoto County (Cathcart, 1989, p. 33).

Kaolinite is present in the upper three samples (F1-87, F2-87, F3-87) from the core hole, where it is inversely correlated with smectite (fig. 5), and it is the major

clay mineral only in the uppermost sample (F1-87). Sample F1-87 contains aluminum phosphate minerals (wavellite and crandallite) that were derived from apatite during acid weathering, and the kaolinite in these samples probably was derived from smectite during this acid weathering.

**Palygorskite (attapulgite).**—Palygorskite is present in all of the samples of the Peace River Formation and is abundant in those samples that contain carbonate rock (dolomitic clay and dolomite). In these samples (fig. 5) it is inversely correlated with smectite. Palygorskite is the principal clay mineral in the middle part of the Peace River Formation (samples F7-87 to F11-87) and in the sample of the Arcadia Formation at the base of the core hole (sample F18-87).

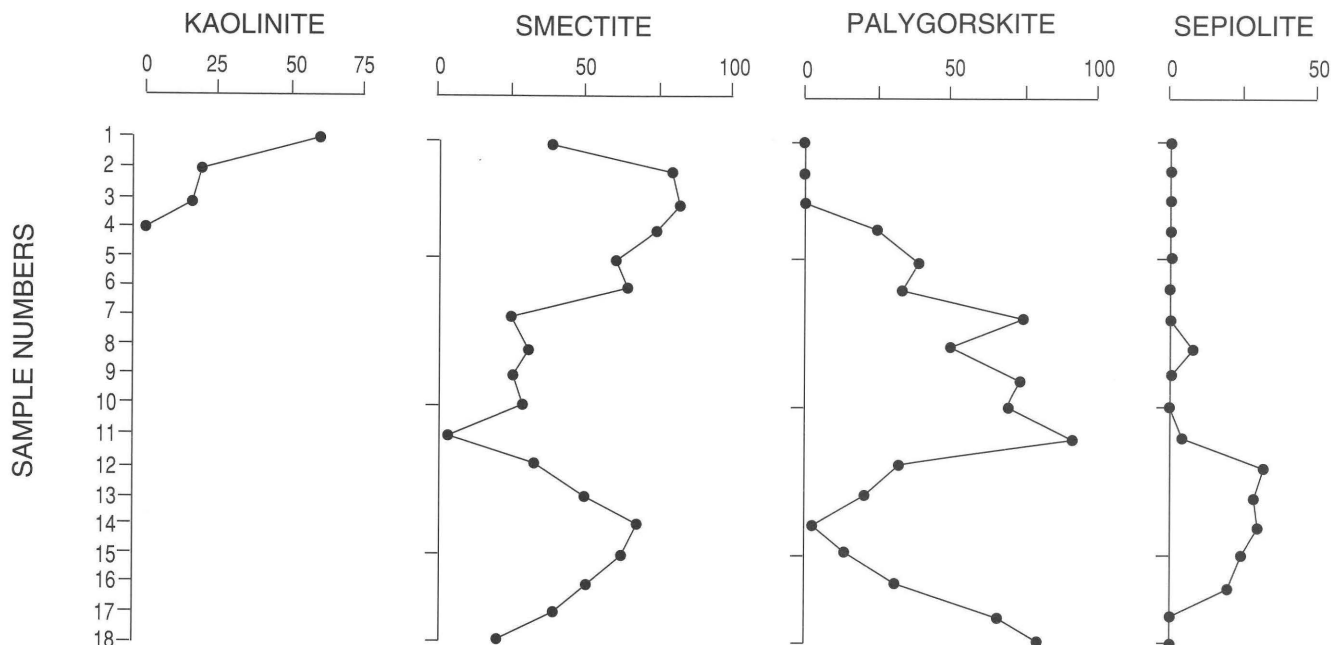
Palygorskite is mined from Miocene rocks in northern Florida and southern Georgia, is present throughout the phosphate deposits of Florida, and is also closely associated with phosphate deposits in Africa and the Middle East.

**Sepiolite.**—Sepiolite is present in the samples from the basal Peace River Formation (F12-87 to F16-87, fig. 5), where it is generally more abundant than palygorskite. Sepiolite is not present in the sample of dolomite from the Arcadia Formation (F18-87). Sepiolite is abundant only in the stratigraphically lower parts of the Arcadia Formation and may be the only clay mineral in the basal part of the Hawthorn Group, in beds of the Tampa Member (Cathcart, 1989).

It has been postulated that palygorskite and sepiolite in the phosphate deposits and clay deposits of Florida formed in a perimarine environment (Weaver, 1984) or in ephemeral lakes (Strom and Upchurch, 1985), and in the phosphate deposits of the land-pebble district by alteration of smectite (Altschuler and others, 1964). Weaver and Beck (1977) proposed that palygorskite and sepiolite in the north Florida clay deposits were deposited prior to the transgression of the Miocene sea, and, therefore, these minerals may be at least partly detrital.

Because of the wide areal and stratigraphic distribution of these clay minerals in the southern extension of the land-pebble phosphate district, it is thought that they are of detrital origin, as proposed by Weaver and Beck (1977).

**Smectite.**—Smectite is by far the most abundant clay mineral in the sediments of Miocene age in Florida. The smectites have been described as nontronitic by Altschuler and others (1964) and as iron rich by Strom and Upchurch (1985). In a detailed study of the clay mineralogy of the land-pebble phosphate deposits, Van Kauwenbergh and others (1990) concluded that the smectite-group mineral is beidellite, but they pointed out that montmorillonite also may be present. Although the X-ray diffraction studies made for this report were not detailed enough to precisely determine the nature of the smectite, we believe that it is likely that the mineral is beidellite, but some montmorillonite is probably present.



**Figure 5.** Clay-mineral distribution in samples from the core hole in sec. 7, T. 34 S., R. 24 E., Hardee County, Fla. Amounts estimated from X-ray diffractograms, recalculated to 100 percent.

The origin of the smectite in these deposits is questionable. Many writers (Grim, 1933; Mansfield, 1940; Gremillion, 1965; Heron and Johnson, 1966; and Weaver and Beck, 1977) believed that the smectite was detrital and was derived, in part, from alteration of volcanic debris. However, several authors (Kerr, 1937, Espenshade and Spencer, 1963, McClellan, 1964; and Isphording, 1973) could find no evidence of volcanic material in the sediments and argued against a volcanic origin. We found no evidence of any volcanic debris in the sediments studied for this report and do not think that the smectite formed from alteration of volcanic material.

The phosphate particles in the sediments of the land-pebble district show evidence of repeated episodes of physical reworking and chemical alteration (Altschuler, 1965). The clay minerals, therefore, must also have been reworked in the same way, and, therefore, evidence of their original nature has been thoroughly obscured.

## Aluminum phosphate minerals

*Wavellite*.—Wavellite, identified in X-ray diffraction patterns, is present only in the uppermost sample (F1–87) and only in the minus-150-mesh fraction of the sample where it occurs as very fine grained, clear needles. The total amount of wavellite is about 5 percent of the minus-150-mesh fraction and less than 1 percent of the total sample.

*Crandallite*.—Crandallite is present in trace amounts in the minus-150-mesh fraction of sample F1–87 and may be present in sample F2–87, from the thin clay bed that

separates the leached Bone Valley Formation from the underlying unleached material. The clay bed is relatively impermeable and probably acted as a seal preventing leaching of apatite in the underlying beds. The pebble fraction of sample F3–87, however, has a small percentage of white and cream-colored phosphate particles that are not as highly polished as the phosphate particles in lower samples. Sample F3–87 may be slightly leached, perhaps prior to the deposition of the clay bed of sample F2–87, or leached by lateral movement of ground water under the clay bed. Beds lower in the section show no evidence of leaching and no traces of aluminum phosphate minerals.

## Pyrite

Trace to minor amounts of pyrite were noted in the X-ray diffractograms of the concentrate fraction of samples F7–87 through F18–87. The concentrate is that part of the –1-mm fraction that sinks in bromoform (specific gravity 2.86), and pyrite is concentrated in this fraction. The amount of pyrite, calculated from the X-ray diffractograms, is between 1 and 2 percent. Pyrite was not seen in diffractograms of samples from the Bone Valley Formation or in the top samples of the Peace River Formation (samples F1–87 to F6–87), but iron oxide stains are common in these samples, indicating the possibility that pyrite may have been present in these samples prior to weathering.

Pyrite is deleterious in the manufacture of phosphoric acid because  $H_2S$  is formed in the acid treatment. Provided that the amount of pyrite present in these samples is representative of the amount in the phosphorite of the

**Table 6.** Chemical analyses of the minus 1-mm plus 0.1-mm fraction of core samples, Hardee County, Fla.

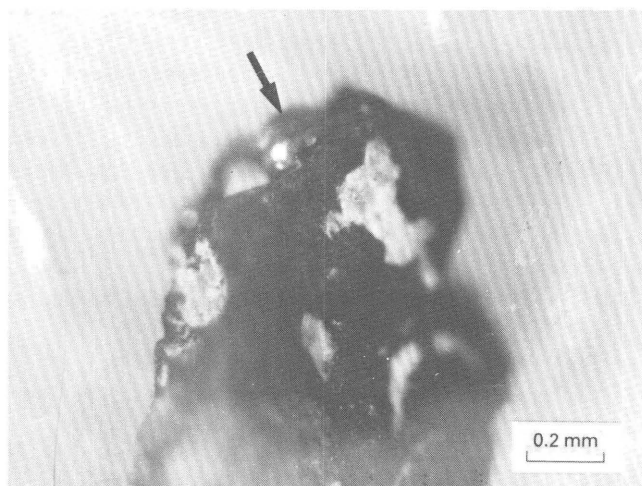
[Analyses by U.S. Geological Survey laboratories, Denver, Colo. F by ion-specific electrode by J. Sharkey; Ca and P by induction-coupled plasma atomic emission spectrography by D. Fey; Acid insoluble (percent undissolved material) by D. Fey; Mg, Na, Fe, and Ti by optical emission spectrography by B.M. Adrian. CaO and P<sub>2</sub>O<sub>5</sub> calculated from Ca and P, and the ratios were calculated by the authors]

Sample No.	Laboratory No.	Acid insoluble	Chemical analyses (in percent)									Ratios	
			F	Ca	CaO	P	P <sub>2</sub> O <sub>5</sub>	Mg	Na	Fe	Ti	CaO/P <sub>2</sub> O <sub>5</sub>	F/P <sub>2</sub> O <sub>5</sub>
F3-87	D338-192	57.4	0.82	9.12	12.76	3.80	8.71	0.1	0.2	0.15	0.05	1.465	0.094
F4-87	-193	60.7	.82	9.27	12.97	3.83	8.78	.1	.2	.15	.05	1.477	.093
F5-87	-194	58.8	.66	7.33	10.26	2.99	6.85	.05	.2	.07	.02	1.498	.096
F6-87	-195	50.0	.94	10.0	13.99	4.11	9.42	.1	.2	.1	.02	1.485	.099
F7-87	-196	43.2	1.26	15.0	20.99	5.80	13.29	1.	.7	.7	.02	1.579	.095
F8-87	-197	48.1	.94	11.3	15.81	4.47	10.24	.2	.5	.5	.05	1.544	.092
F9-87	-198	57.0	.88	9.80	13.71	3.84	8.80	.15	.5	.5	.02	1.558	.100
F10-87	-199	56.7	.76	8.88	12.42	3.47	7.95	.2	.3	.3	.03	1.562	.096
F11-87	-200	57.6	.70	8.75	12.24	3.22	7.38	1.	.5	.5	.05	1.659	.096
F12-87	-201	53.0	.88	10.3	14.41	4.05	9.28	.3	.5	.5	.05	1.553	.095
F13-87	-202	57.0	.76	9.63	13.47	3.57	8.18	.2	.3	.5	.07	1.647	.093
F14-87	-203	46.2	.94	11.1	15.53	3.86	8.84	.2	.3	.5	.05	1.757	.106
F15-87	-204	52.4	.76	7.86	11.0	3.02	6.92	.2	.2	.3	.03	1.590	.110
F16-87	-205	59.1	.70	7.61	10.65	2.93	6.71	.2	.7	.3	.01	1.587	.104
F17-87	-206	63.0	.62	6.98	9.77	2.70	6.19	.15	.3	.2	.02	1.578	.100
F18A-87	-207	51.4	1.06	13.3	18.61	5.10	11.69	.5	.7	.3	.1	1.592	.091

southern extension, H<sub>2</sub>S should not be a problem in the manufacture of phosphoric acid from the rock. However, the amounts of pyrite in the phosphate products should be carefully checked in future prospect drilling.

### Micrometeorite (Tektite?)

A very fine grained metallic sphere was found embedded in a phosphate grain (fig. 6) from sample F12-87 at about 90 ft below the surface. X-ray data show that the



**Figure 6.** Iron spherule embedded in a phosphate grain in sample F12-87 from a core hole, Hardee County, Fla.

sphere is composed of elemental iron and therefore may be a micrometeorite (tektite?). The spherule fits the definition of a tektite by Stokes and Varnes (1955, p. 149), "A glassy, rounded body thought to be of meteoric nature. Tektites usually appear to weather from sediments of Tertiary age."

The spherule was deeply imbedded in the phosphate grain; about half of the spherule was exposed on the broken surface. It seems likely that the sphere was incorporated in the phosphate grain as the grain was forming.

The chemical characteristics of the spherule are consistent with a probable meteoric origin. This is the first documentation of a micrometeorite (tektite?) in the phosphate deposits of Florida, although tektites were rumored to have been found in the material of the open-pit mines. These reports could have been about iron balls caused by welding spatter in and close to the mining pits.

### CHEMISTRY

Chemical analyses for phosphorus, calcium, and fluorine, the major elements in apatite, and for acid-insoluble material, the principal diluent, were made of the -1-mm +0.1-mm fraction of samples from the drill hole. The percentages of CaO and P<sub>2</sub>O<sub>5</sub> and the ratios of CaO/P<sub>2</sub>O<sub>5</sub> and F/P<sub>2</sub>O<sub>5</sub> were calculated by the authors (table 6).

Semiquantitative spectrographic analyses were made of the samples (table 7), and analyses for cadmium, zinc,

**Table 7.** Trace-element content of phosphate samples from a core hole in Hardee County, Fla.

[Values in parts per million. <, less than. Looked for but not detected: As, Au, Bi, Ge, Nb, Sb, Sn, Th, W.

N, not detected; N5, N10, at or just below the limit of detection. Analyses by optical emission spectrography by B.M. Adrian, U.S. Geological Survey]

Sample No.	Ag	B	Ba	Be	Co	Cr	Cu	Ga	La	Mn	Mo	Ni	Pb	Sr	V	Y	Zr
F3	<.5	30	70	1	<10	50	7	N5	50	20	N5	30	50	500	50	20	500
F4	<.5	20	150	1	<10	30	5	<5	70	50	N	5	20	500	50	50	200
F5	<.5	15	150	1	N10	15	5	<5	70	30	N	5	20	300	30	30	50
F6	<.5	15	150	1	N10	30	7	<5	70	50	N	7	15	500	30	30	50
F7	<.5	50	100	1	<10	30	10	<5	70	100	20	10	30	500	30	50	50
F8	<.5	20	150	1	<10	20	7	<5	70	150	10	5	20	500	20	50	50
F9	N	30	150	<1	<10	30	7	<5	70	30	10	5	20	500	20	50	300
F10	<.5	30	150	<1	N10	30	5	<5	70	30	5	5	20	300	20	30	70
F11	<.5	15	100	<1	N	20	7	<5	70	50	10	5	20	500	20	30	50
F12	<.5	20	100	<1	N	20	7	<5	50	50	10	5	20	500	30	50	100
F13	<.5	20	150	1	N	20	7	<5	70	50	10	5	20	300	20	50	200
F14	5 <sup>1</sup>	30	100	1	N	20	7	<5	70	50	<5	5	15	500	20	30	50
F15	<.5	30	100	<1	N	20	5	<5	50	50	N	5	15	500	20	30	100
F16	<.5	30	150	1	N	20	5	<5	50	50	N	5	20	300	20	30	150
F17	<.5	15	150	1	N	15	<5	N5	70	50	N	5	10	300	15	30	30
F18	<.5	20	150	1	N	30	7	<5	100	70	N	5	20	500	20	100	50

<sup>1</sup>A second analysis of this sample showed 2 ppm; two analyses of a second split of this sample showed 0.5 ppm.

mercury, and uranium were made of the apatite-concentrate fractions of the samples (table 8). Scatter diagrams made from the analytical data show a strong positive correlation between phosphorus and calcium and fluorine, a moderate positive correlation of phosphorus with magnesium, sodium, and yttrium, a weak positive correlation of phosphorus with the rare-earth element lanthanum, and a strong negative correlation of phosphorus with acid-insoluble material (fig. 7). Although calcium and magnesium are present in both apatite and dolomite, the strong correlation of calcium with phosphorus suggests that most of the calcium is in apatite, whereas the moderate correlation of magnesium and phosphorus suggests that much of the magnesium is in dolomite. The high magnesium contents shown on figure 7 and table 6 are caused by the presence of discrete dolomite grains in the analyzed samples. Because much of the dolomite is soft, the washing and screening disaggregated the soft dolomite and therefore, most of the dolomite is in the minus-150-mesh fraction. Grains of hard dolomite are present in the analyzed fractions of samples 7, 11, and 18, and therefore, these samples are high in magnesium content.

Ratios of CaO/P<sub>2</sub>O<sub>5</sub> (table 6) are in the range for carbonate fluorapatite (francolite) and tend to increase with depth, indicating an increase in substitution in apatite

toward the base of the drill hole. This increase in substitution in the apatite is also shown by the *a*-cell dimension of the apatite (table 3).

## Trace elements

The presence of trace elements in phosphorites has been recognized for many years. Strutt (1908) first determined the presence of uranium in phosphate rock, and Mansfield (1927) pointed out that the phosphate deposits of the western United States contain possibly significant amounts of trace elements. Jacob and others (1933) showed that many trace elements are present in phosphate rock of the United States. McKelvey and others (1951) presented data on the minor metal content of Florida phosphate rock. Krauskopf (1955) summarized data on phosphate rock, and he concluded (p. 423) that "\*\*\*\*most of the elements markedly concentrated in phosphate rocks probably owe their abundance to organic matter accompanying the phosphate rather than to the phosphate itself; only Sr, part of the Pb, As, and rare earths and possibly Be and Nb also, appear to be dependant on the phosphate." Further, he pointed out (p. 423) that "\*\*\*\*Sr, Pb, and the rare earths substitute for Ca and As for P in the apatite lattice." At the time of Krauskopf's report (1955), there were virtually no

**Table 8.** Cadmium, zinc, mercury, and uranium contents of apatite concentrate fractions of phosphate samples from a core hole, Hardee County, Fla.

[Values in parts per million. do., ditto; <, less than, Cd and Zn by optical spectroscopy, D. Fey, analyst; Hg by quantitative spectroscopy, P. Hageman, analyst; U by fluorimetric analysis, T. Roemer, analyst. Coefficients of correlation: Cd/Zn +0.89, Cd/Hg +0.82, Cd/U +0.20]

Sample No.	Cd	Zn	Hg	U	Remarks
F1-87.....	15	116	0.40	142	Leached Bone Valley Formation.
F3-87.....	7	81	.32	150	.....do.....
F4-87.....	5	32	.34	100	Weathered Peace River Formation.
F5-87.....	2	50	.08	107	.....do.....
F6-87.....	<2	48	.04	90	.....do.....
F7-87.....	2	30	.08	92	Unweathered Peace River Formation.
F8-87.....	3	43	.08	98	.....do.....
F9-87.....	2	32	.06	86	.....do.....
F10-87.....	3	36	.08	81	.....do.....
F11-87.....	2	32	.06	98	.....do.....
F12-87.....	2	42	.12	90	.....do.....
F13-87.....	2	36	.12	96	.....do.....
F14-87.....	3	33	.08	110	.....do.....
F15-87.....	3	37	.08	110	.....do.....
F16-87.....	3	34	.12	100	.....do.....
F17-87.....	3	34	.06	87	.....do.....
F18-87.....	5	55	.06	60	Top of Arcadia Formation.

data on the content of cadmium and mercury in phosphate rock.

Some of the trace elements are known to be necessary for plant nutrition; for example—boron, magnesium, and molybdenum; others are known to be toxic to plants and animals (arsenic, cadmium, mercury, and nickel); and still others are necessary for plant nutrition in small amounts but are toxic in higher concentrations (cobalt, chromium, copper, manganese, and zinc). The trace elements are present in phosphate rock in amounts that range from a few tenths to several hundred parts per million.

Variations in trace-element contents (fig. 8) show a parallelism with depth. Calcium, magnesium, and fluorine show some parallelism; phosphorus has too little variation to show much parallelism with the others. Sodium, although it is positively correlated with phosphorus, does not show the same degree of parallelism, whereas iron and titanium are nearly random in their distribution. The trace-element contents show a distinct rise in sample 7, just below the contact of weathered material with the fresh rock below. The contact of weathered and fresh material is placed between samples 6 and 7 because iron oxides occur above this level, and pyrite is present in the samples below this level.

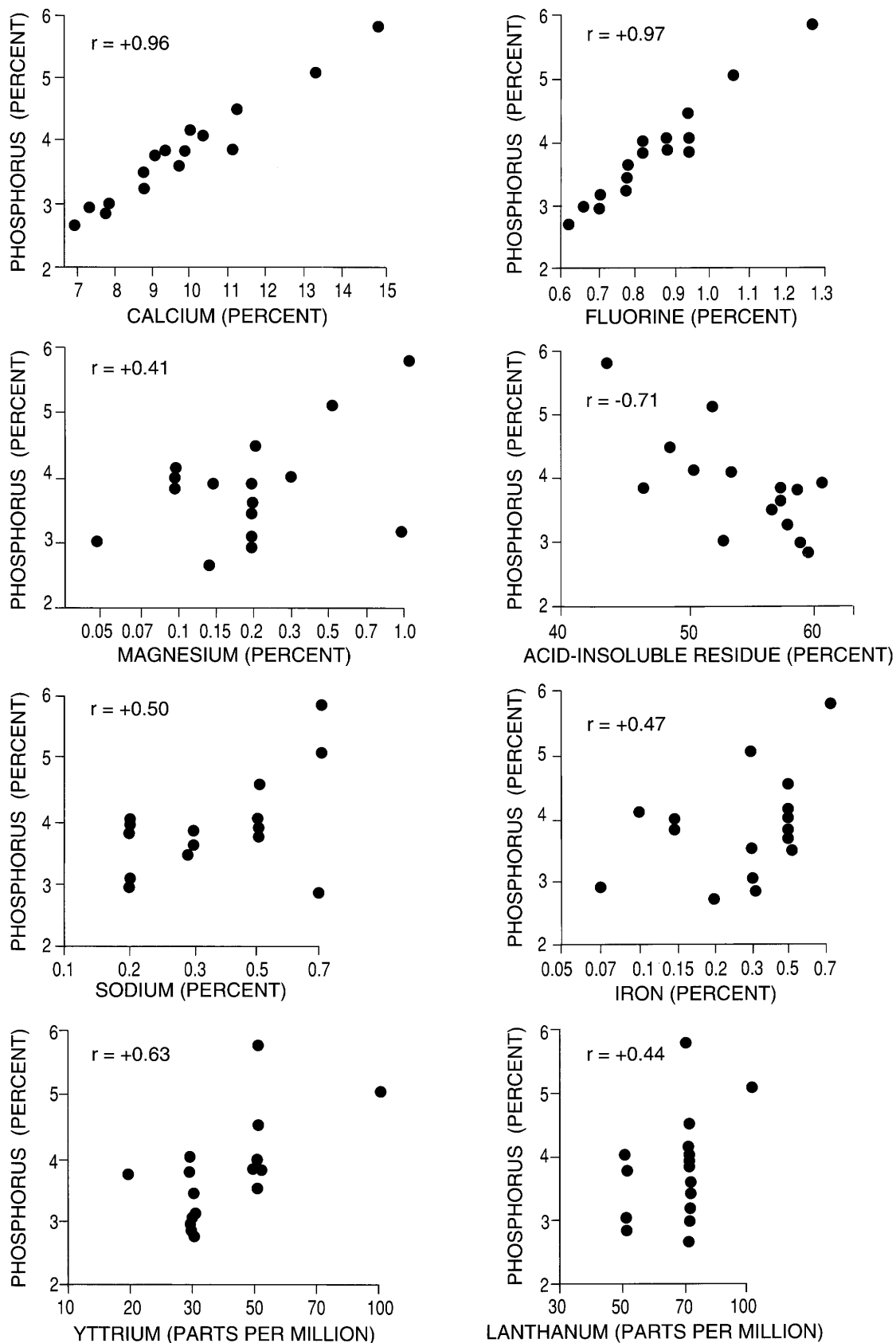
The analytical data for trace-element contents from samples of the core hole are shown in table 7; vertical distribution of elements in the core hole is shown on figure 8, and relations of the elements to one another are shown on

scatter diagrams (fig. 9). The vertical distribution (fig. 8) shows that copper, lead, molybdenum, nickel, and boron are higher in sample 7 than in sample 6. Molybdenum, titanium, zirconium, barium, and manganese are more or less random in distribution; they show little correlation with other elements.

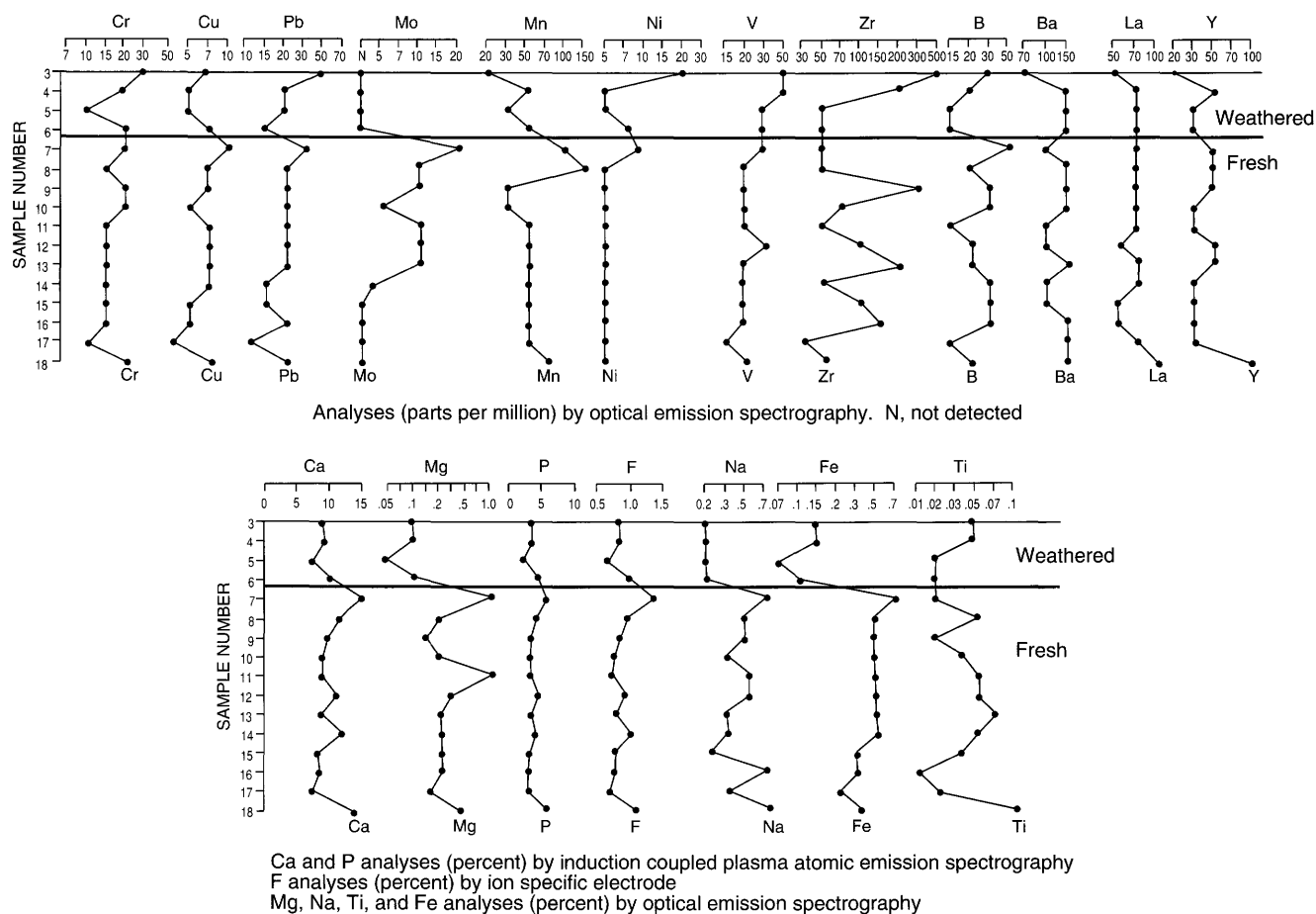
The trace elements may be present in the apatite structure, allied with the organic material, or present as discrete minerals. For example, the elements that are randomly distributed (titanium, zirconium, molybdenum, manganese, barium, and boron) probably occur as discrete mineral phases—titanium as rutile, zirconium as zircon, molybdenum as molybdenite, and so forth. All of these minerals are in amounts that are too small to be identified by X-ray diffraction.

Trace elements most likely to be present in the apatite structure include vanadium (as  $\text{VO}_4$  substituting for  $\text{PO}_4$ ), the rare earths (lanthanum and yttrium), magnesium, sodium, strontium, and perhaps a part of the lead substituting for calcium. Other trace elements (chromium, copper, nickel, and part of the lead and vanadium) are probably allied with the organic material, as indicated by Krauskopf (1955). These trace metals roughly parallel one another in vertical distribution, and they all show an increase below the zone of weathering (fig. 8). The organic fraction is depleted in the zone of weathering and is abundant in the samples below the zone of weathering.





**Figure 7.** Scatter diagrams showing relations of phosphorus to calcium, fluorine, magnesium, sodium, iron, yttrium, lanthanum, and acid-insoluble residue.  $r$ , coefficient of correlation.



**Figure 8.** Plots of the distribution of elements in the core samples, Hardee County, Fla.

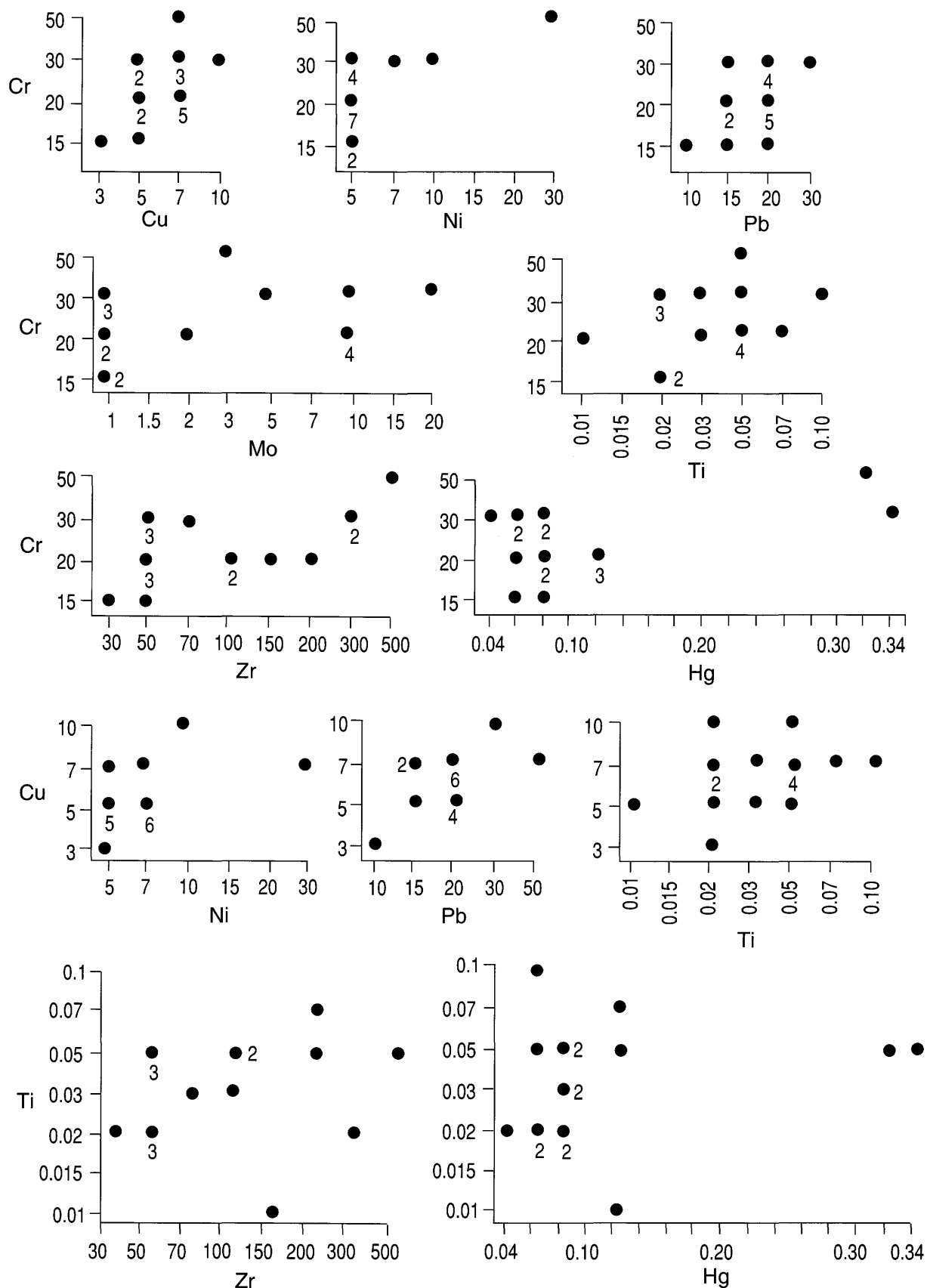
Iron is present as iron oxide (hematite?) in the weathered samples and as pyrite in the fresh samples. The fair positive correlation of iron and phosphorus (fig. 7) indicates that a part of the iron content is incorporated as either iron oxide or pyrite in the phosphate pellets, in addition to being present as discrete mineral particles.

Trace elements present in the samples in amounts that are at or just below the limits of detection include gallium, silver, beryllium, and cobalt. Gallium is known to be associated with aluminum, and the small amounts of gallium probably are present in the clay minerals of the samples. Beryllium is probably present in a beryllium mineral, not otherwise identified, and both cobalt and silver are probably allied with the organic phase. Silver is present in amounts less than 0.5 ppm except in sample F14-87, where it was 5 ppm. A second split of this sample contained 2 ppm silver, but analyses of a different split of sample F14-87 showed only 0.5 ppm silver. The anomalous amount of silver in the original split of sample F15-87 is probably caused by a random distribution of native silver in the material, the so-called nugget effect.

## Cadmium

Cadmium, a toxic element that can be absorbed by plants, is present in phosphate particles and in phosphate fertilizers in amounts that range from 1 to about 100 ppm (Baechle and Wolstein, 1984). They thought that the cadmium in phosphate rock is allied with the organic fraction of the rock. Limits on the maximum amount of cadmium that can be present in phosphate rock used to make fertilizer have been set at 20 ppm.

Semiquantitative spectrographic analyses of several hundred samples of phosphate pebble and concentrate from the land-pebble phosphate district of Florida report cadmium in most samples as being at or below the limit of detection (20 ppm), whereas the highest amounts of cadmium in these samples were 30–50 ppm (U.S. Geological Survey, unpub. data, 1960–80). Data published by Baechle and Wolstein (1984) show that Florida phosphate rock contains from 3 to 12 ppm cadmium, and they pointed out that the average cadmium content of Florida phosphate rock, reported from the literature, is 8 ppm. All of these data



**Figure 9.** Scatter diagrams showing relations of trace metals in samples from the core hole in Hardee County, Fla. Values are in parts per million, except Ti, in percent. Numbers beside dots show number of plots at that location. Plots without numbers are single samples.

are for phosphate rock from the land-pebble district, and there are no data in the literature for the cadmium content of the phosphate rock from the southern extension of the land-pebble district.

Data from samples taken from the core hole show that two samples of the Bone Valley Formation (F1-87 and F3-87) contain 15 and 7 ppm cadmium, whereas amounts in the phosphate concentrate from the Peace River Formation range from less than 2 to 5 ppm (table 8). The concentrate samples from the Bone Valley are cream, white, and gray, and probably are low in organic content, whereas the samples from the Peace River Formation are black, jet black, brown, and gray, and may be high in organic material. However, the contents of zinc are very high in the top samples of the Bone Valley Formation (115 and 81 ppm, respectively), whereas the zinc contents of the concentrate samples from the Peace River Formation range from 30 to 55 ppm. In these samples, the cadmium likely is present in the zinc sulfide mineral sphalerite rather than concentrated in the organic fraction. The coefficient of correlation for zinc and cadmium is +0.89, a very good positive correlation, as indicated in the scatter diagram (fig. 10). It should be pointed out, however, that the strong positive correlation is dependant on three samples—F1-87, F3-87, and F18-87 (fig. 10).

Most of the economic phosphate in the southern extension is in the Peace River Formation, and if the data presented herein on the cadmium content of the phosphate rock are representative, it is likely that the cadmium content of the phosphate concentrate from the southern extension

will be found to be below 20 ppm, and there should be no danger of cadmium poisoning of vegetable crops grown on land fertilized by this type of Florida phosphate. Baechle and Wolstein (1984) indicated that there is no buildup of cadmium in soils fertilized by phosphate rock with the content of 7-12 ppm cadmium.

It is evident, therefore, that the amount of cadmium in the phosphate rock from the southern extension of the Florida phosphate district is not a cause for concern. It will be necessary, however, to continue to determine the cadmium content of the phosphate deposits of the southern extension, at least until the average content can be verified.

Mercury

Mercury is present in phosphate rocks of the United States and elsewhere in the world in trace amounts. Gunnarsson (1983) stated that mercury contents of marine phosphate rock range from 0.03 to 0.33 ppm and in igneous apatite deposits from 0.01 to 0.15 ppm.

Mercury in surficial sand in peninsular Florida ranges from 0.015 to 0.05 ppm, but surface muck and swamp deposits contain as much as 0.70 ppm (Shacklette and others, 1971).

Unpublished data from the U.S. Geological Survey (J.B. Cathcart, unpub. data, 1991) indicate that surficial sand of Pleistocene and Holocene age in the land-pebble phosphate district contains an average of 0.02 ppm mercury. Samples of the pebble fraction (+20 mesh) from the land-pebble district contain from 0.02 to 0.58 ppm and average 0.075 ppm. The concentrate fraction contains from 0.03 to 0.63 ppm mercury and averages 0.17 ppm. Leached phosphate products contain somewhat higher amounts of mercury, from 0.04 to 0.75 ppm, and the average of 65 samples is 0.28 ppm.

Among the samples of phosphate concentrate analyzed for this report (table 8), the samples of leached Bone Valley contained 0.32 and 0.40 ppm mercury, whereas the samples from the Peace River Formation contain from 0.04 to 0.12 ppm mercury.

The mercury content of the samples from this core is consistent with the data from the land-pebble district and closely matches the data in Gunnarsson (1983). These data indicate that the amount of mercury in phosphate rock is too low to be of concern and confirms the statement of Gunnarsson (1983, p. 29) that "The very low content of Hg cannot possibly cause any problems."

ECONOMIC GEOLOGY

The factors that determine the economics of mining phosphate rock in Florida include, in no special order: (a) Total thickness to be mined. (b) Ratio of cubic yards that must be moved per ton of product. (c) P<sub>2</sub>O<sub>5</sub> content of the

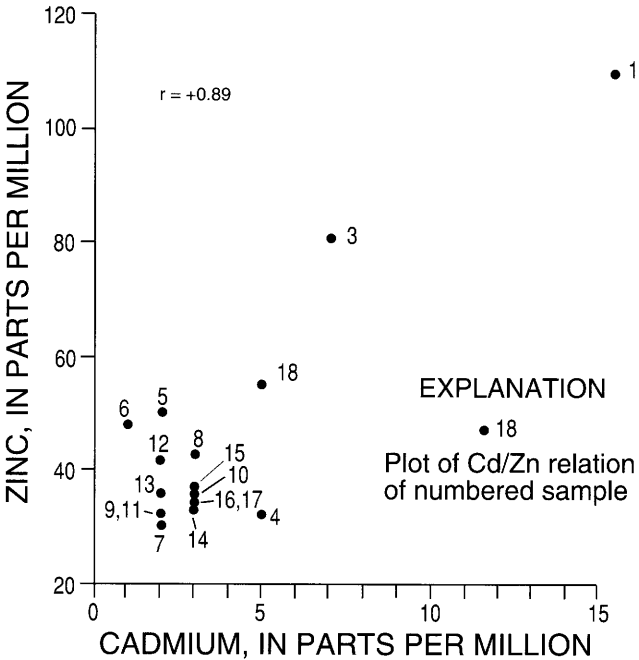
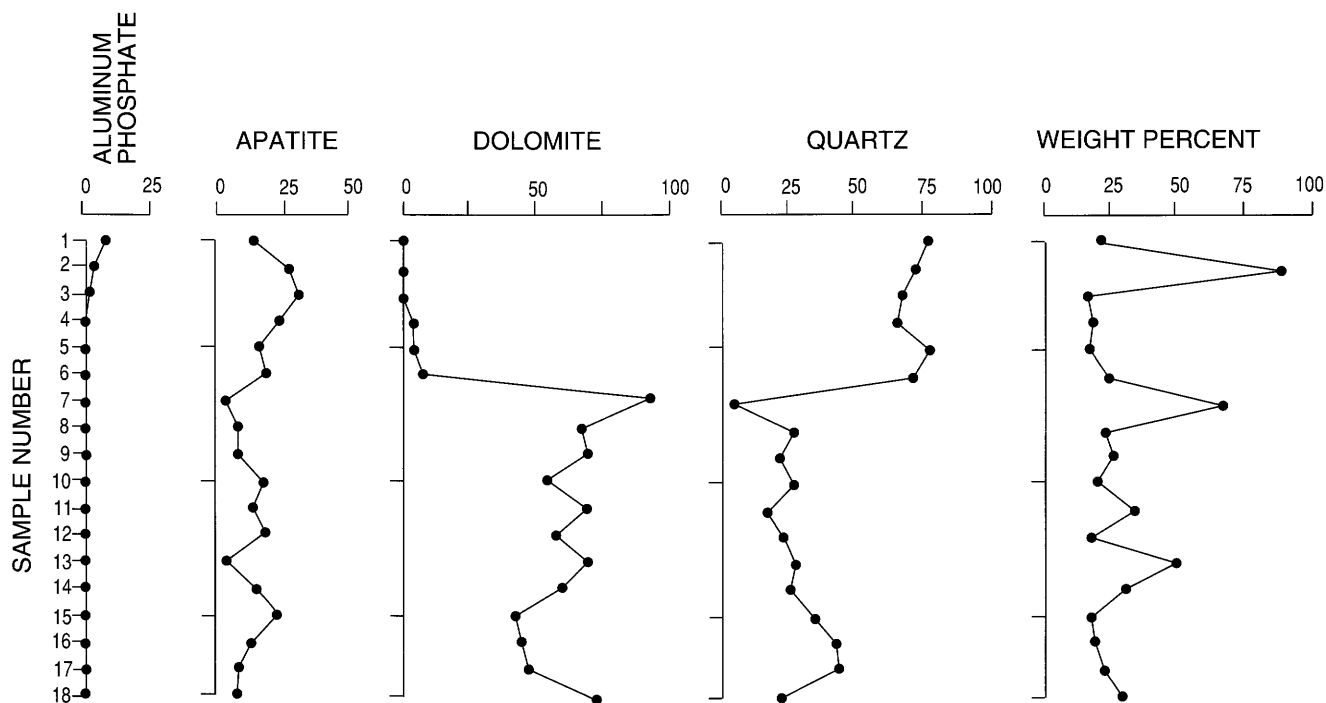


Figure 10. Scatter diagram showing relations of cadmium and zinc, in the concentrate fraction of the core samples, Hardee County, Fla. Sample data are in table 8.



**Figure 11.** Distribution of minerals (except clay) in and weight percent of -150 mesh fraction of the core samples, Hardee County, Fla. Values are in percent. Data from X-ray diffractograms, recalculated to 100 percent.

recoverable products. (d) Content of major compounds that are deleterious in making fertilizer products from the rock— $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and fluorine. (e) Content of potentially damaging trace elements, cadmium, mercury, selenium, and arsenic, for example. (f) Content of trace elements necessary for plant nutrition, manganese, boron, and molybdenum, for example. (g) Content of potentially recoverable byproduct elements, uranium, vanadium, and fluorine. (h) The amount of the -150 mesh (slime) fraction.

Economic feasibility cannot be adequately determined from a single drill hole, but data from this drill hole will indicate whether the deposit might be economic or noneconomic.

Total thickness of material that must be mined in this drill-hole area is about 120 ft, considerably greater than thicknesses in the land-pebble district. It is likely that thicknesses greater than about 100 ft will require a mining technique that involves removing a part of the overburden, forming a bench on which the dragline would then mine the remaining overburden and ore. This technique has been used successfully in North Carolina and to a lesser extent in the land-pebble district and should cause no technical problems.

The ratio of cubic yards moved per ton of product will be greater in the southern extension than in the land-pebble district.

The recoverable phosphate products in the land-pebble phosphate district include the plus 1 mm (pebble) and the minus 1 mm plus 0.1 mm (concentrate) separated by froth flotation from quartz sand.

The  $\text{P}_2\text{O}_5$  content of the recoverable product in the southern extension will be lower than in the land-pebble district. The apatite of the southern extension is more highly substituted, and the  $\text{P}_2\text{O}_5$  content of the phosphate products ranges from less than 30 to about 32 percent and averages about 31 percent (Cathcart, 1989).

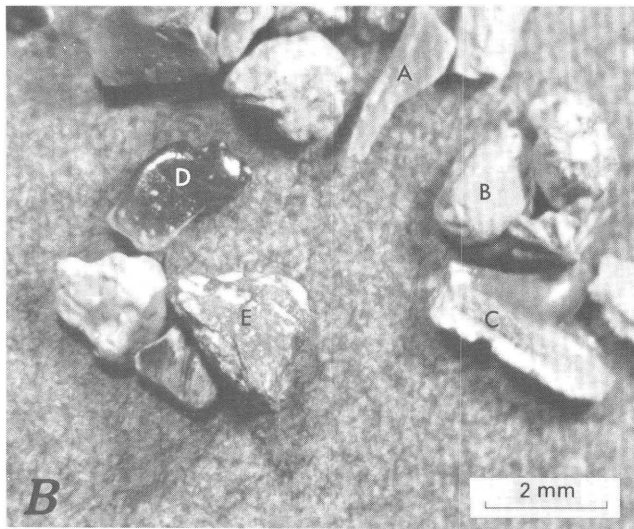
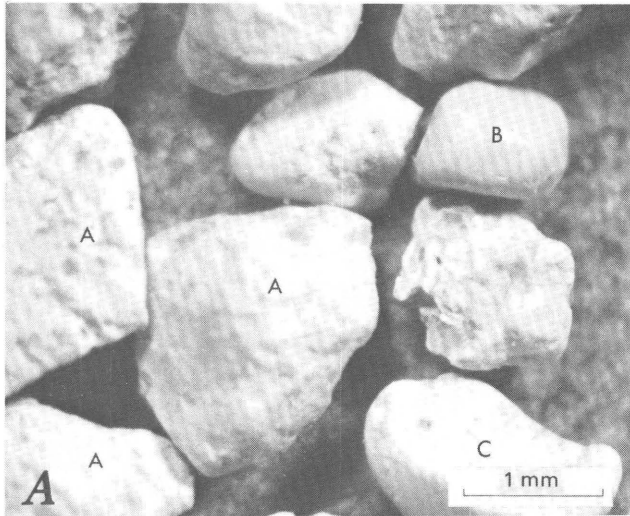
The content of major compounds that are deleterious in processing are not above the economic levels, except for  $\text{MgO}$ .

The content of the potentially damaging trace elements are within limits of phosphate products currently being mined in Florida and North Carolina, as are the trace elements needed for plant nutrition (tables 6–8).

Potentially recoverable byproducts, except for fluorine, are in lower amounts than in the land-pebble district.

The amount of the minus-150-mesh fraction in the samples from the core hole ranges from 17 to 90 percent and averages about 25 percent (fig. 11). The minus-150-mesh fraction is composed of clay minerals (fig. 5), quartz, apatite, and large amounts of dolomite that range from 3 to 90 percent, and average about 60 percent (fig. 11). The settling characteristics of this fraction will be different from





**Figure 12.** Phosphate grains (+1-mm fraction) from the Bone Valley Formation, core-hole sample F1-87, Hardee County, Fla. A: A, dull-white grains; B, shiny tan pellet; C, shiny white pellet. B: A, amber phosphatized shell fragment; B, tan shiny pellet; C, shark tooth; D, fish tooth; E, phosphatized rock fragment.

the settling characteristics in the land-pebble district. The large amount of dolomite may cause the fraction to settle quickly, but this must be determined for each mining site.

Pyrite is present in trace amounts in samples F7-87 to F13-87 and in larger amounts in samples F14-87 to F18-87. The average amount of pyrite is only about 1 percent and should not be a problem in processing.

In general, then, the economic parameters all are less favorable for the southern extension than for the land-pebble district, but it is likely that the phosphate deposits in the southern extension can be mined, although at a higher cost.

Environmental restrictions have not been considered but could be a problem when the mining companies apply for permits to mine and process the deposit.

## PHOSPHATE PARTICLES

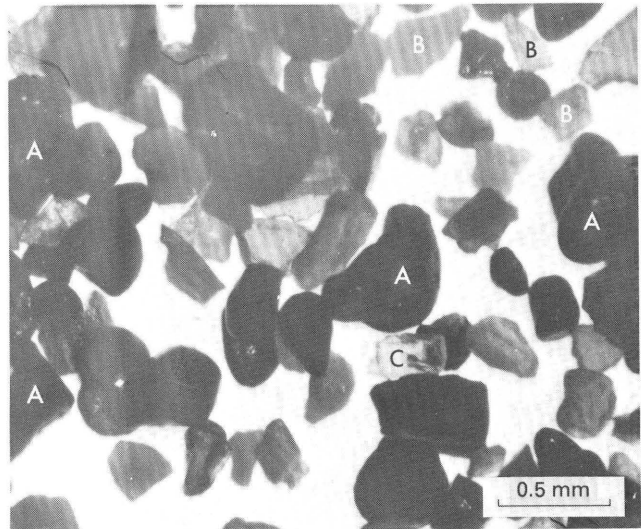
### Bone Valley Formation

Coarse phosphate particles (>1 mm) in the samples of the Bone Valley Formation (F1-87, F2-87, F3-87) are shiny, tan to light-brown, and white; there are some black as well as dull white and partly leached grains (fig. 12A). The dull-white grains are altered by weathering and contain aluminum phosphate minerals (wavellite and crandallite) as well as apatite. The phosphate grains may be structureless, phosphatized rock fragments, phosphatized shell fragments, and a few fish and shark teeth (fig. 12B). Some of the grains are broken and rerounded, and some are internal molds of fossils.

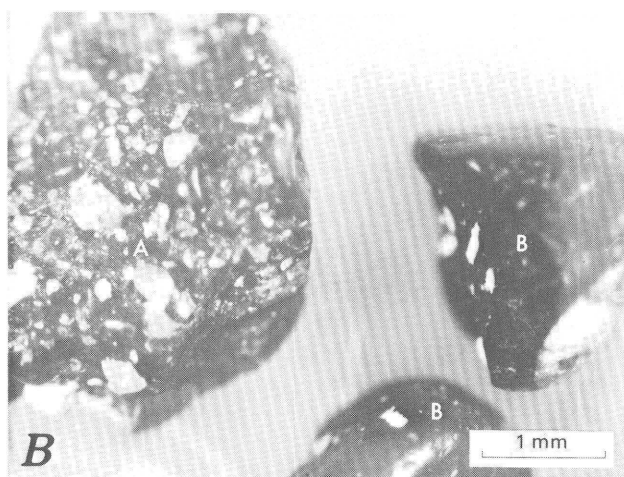
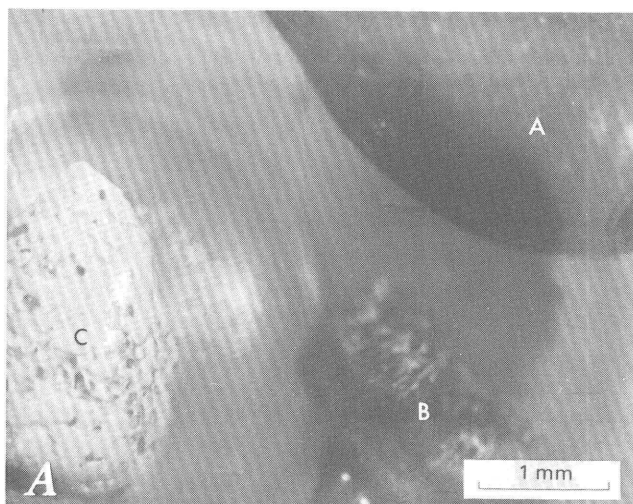
Fine phosphate particles (<1 mm, >0.1 mm; concentrate) in samples of the Bone Valley are white, gray, brown, tan, cream, and some (<5 percent) black. Most of the pellets are well rounded and structureless; broken fragments are common, and some phosphatized shell fragments and dull-white or gray pellets contain crandallite as well as apatite (fig. 13).

### Peace River Formation—Upper Part

The coarse phosphate fraction from the upper part of the Peace River Formation (samples 4-87 to 10-87)



**Figure 13.** Phosphate concentrate fraction, sample F3-87, Bone Valley Formation from a core hole, Hardee County, Fla. Black grains (A) are highly polished black and brown rounded phosphate pellets, some broken and rerounded. Gray subangular, translucent grains (B) are phosphatized fossil fragments. Clear grains (C) are quartz.



**Figure 14.** Phosphate grains from samples from a core hole in Hardee County, Fla. A: Sample F6-87. A, brown, shiny, rounded structureless pellet. B, shark tooth. C, shiny white phosphatized internal mold of gastropod, contains some quartz silt. B: Sample F7-87. A, rounded quartz grains and black and gray phosphate grains cemented by phosphate. B, shiny black rounded grains. Top grain is broken and rerounded. White areas are fine-grained dolomite plastered on grain surfaces.

consists of grains varying in color, luster, and shape. Some are shiny brown, tan, or gray; some are cream or white; and a few are black. The grains include structureless, rounded, almost spherical pebbles; phosphatized fossil teeth; phosphatized rock fragments that consist of fine sand-size quartz and phosphate cemented by apatite; and phosphatized internal molds of fossils (fig. 14). Some of the grains are broken and rerounded, and have cracks filled with secondary apatite (fig. 15).

The concentrate fraction of the upper part of the Peace River Formation contains pellets that are mostly brown, tan, or gray; some are cream and white, and a few are black. Pellets are structureless and nearly spherical or

are rod shaped. Some phosphatized dolomite grains and amber, translucent (gray in the photograph), subangular phosphatized shell fragments are present (fig. 16).

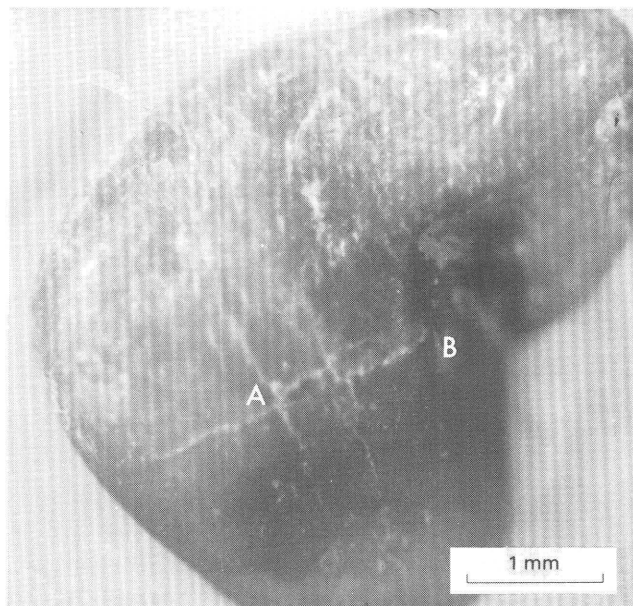
## Peace River Formation—Lower Part

The coarse fraction of the lower part of the Peace River Formation (samples F11-87 to F18-87) consists predominantly of black and brown phosphate pebbles, many of which are almost spherical (fig. 17A), some are gray and tan, and there is a trace of white grains. Phosphatized rock fragments (fig. 17B) are common in all samples; some are partly phosphatized sandy dolomite grains.

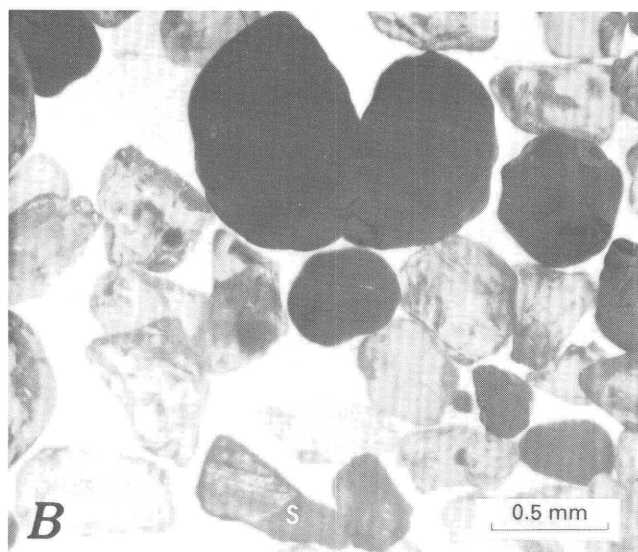
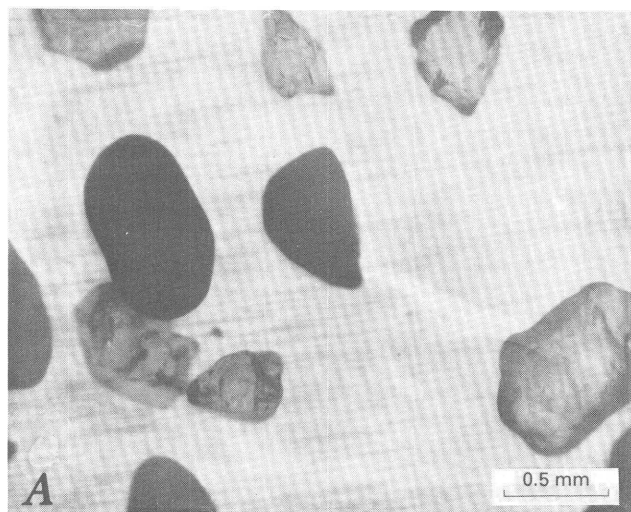
The concentrate fraction of the lower part of the Peace River Formation contains predominantly black (some jet black) and lesser amounts of dark-gray, brown, tan, gray-green, and white polished phosphate particles, some phosphatized rock fragments that are dull rather than polished, and some phosphatized fossil fragments (fig. 18), including fish and shark teeth and fossil molds.

The ratio of coarse to fine-grained phosphate in the Bone Valley samples is considerably different from the ratio in the Peace River samples. The coarse (pebble) fraction is much more abundant than the fine (concentrate) fraction in the Bone Valley Formation, where the ratio of pebble to concentrate ranges from 3.1 to 8.1 to 1 and averages 5.6 to 1.

In contrast, the samples from the Peace River Formation contain much more fine-grained than coarse-grained phosphate. Ratios of pebble to concentrate range



**Figure 15.** Gray-brown phosphate grain from sample F14-87 from a core hole in Hardee County, Fla. A, cracks filled with secondary apatite; B, broken and rerounded grain edges.

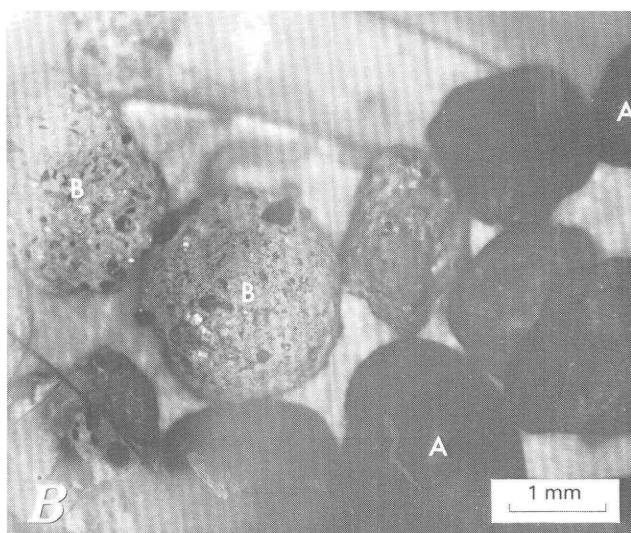
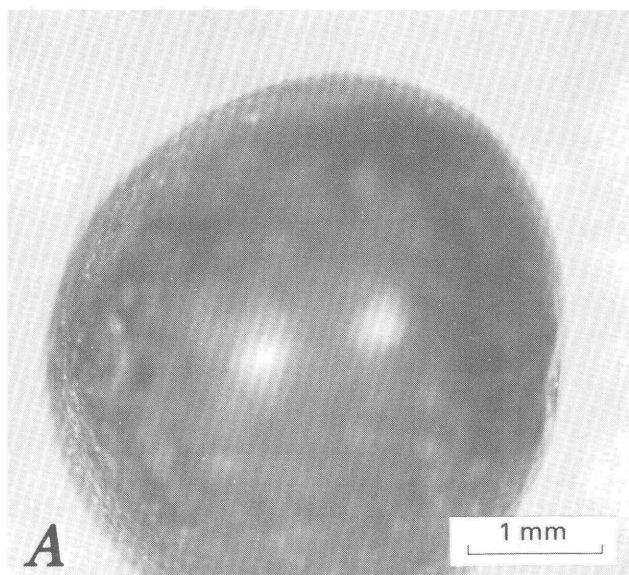


**Figure 16.** Phosphate grains ( $\sim 1$  mm  $\pm 0.1$  mm) from samples from a core hole in Hardee County, Fla. A: From sample F8–87, near the top of the Peace River Formation. Black, shiny phosphate grains are rounded; one is broken and the edges are rerounded. Clear grains are quartz. B: From sample F10–87. Phosphate grains are black and rounded. Quartz grains are clear. S, phosphatized shell fragment.

from 0.07 to 0.91 to 1 and average 0.46 to 1. However, the lowermost samples, F17–87 and F18–87, contain about equal amounts of the pebble and concentrate fractions; ratios average 0.98 to 1. The ratios do not seem to have any periodicity. Only the sharp difference between the ratios of the Bone Valley and Peace River Formations appears to be significant (fig. 19).

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**Figure 17.** Phosphate grains ( $\sim 1$  mm) from samples from a core hole in Hardee County, Fla. A: From sample F14–87. Black, spherical phosphate pellet. B: From sample F16–87. A, black, shiny phosphate grains. B, gray phosphatized rock fragments.

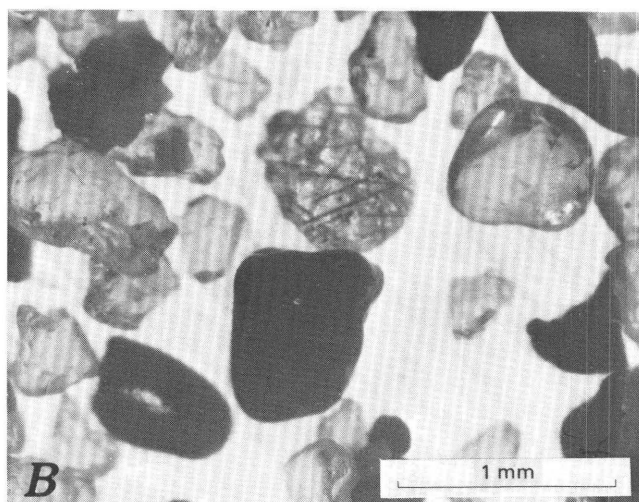
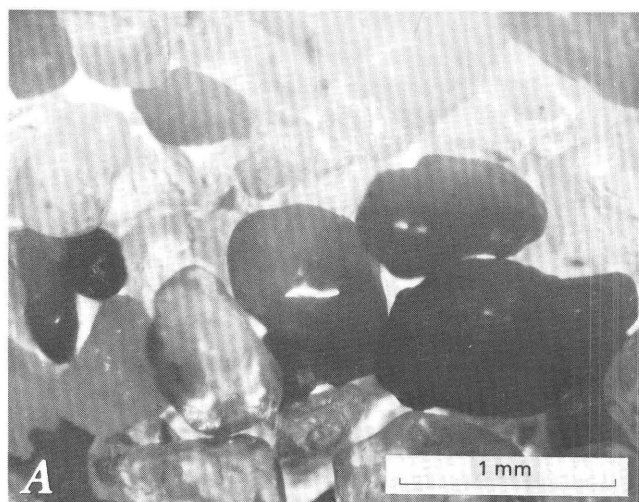
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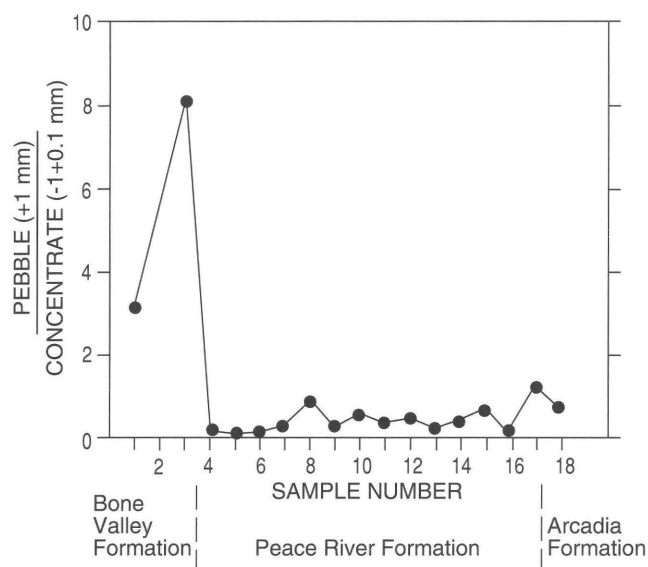
**Figure 18.** Phosphate feed fractions ( $-1\text{ mm} +0.1\text{ mm}$ ) from samples from a core hole in Hardee County, Fla. *A*: Black grains are shiny black and brown phosphate pellets. Gray grains are tan and gray phosphate pellets. Clear grains are quartz. From sample F14-87. *B*: Black grains are rounded phosphate pellets, one broken and rerounded. The irregular black grain in the upper right corner of the photograph is a fossil fragment. Clear grains are quartz; a rutiled quartz grain is in the center of the photograph. The finer quartz grains are angular. From sample F18-87.

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**Figure 19.** Ratios of coarse to fine phosphate grains in samples F1-87 through F18-87 from a core hole, Hardee County, Fla. Pebble and concentrate were not separated for sample 2.

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