

FIELD GUIDEBOOK  
GEOLOGY AND GEOCHEMISTRY OF  
THE BONE VALLEY FORMATION AND ITS PHOSPHATE DEPOSITS,  
WEST CENTRAL FLORIDA

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## INTRODUCTION

The Bone Valley Formation is a shallow-water, marine and estuarine phosphorite of Pliocene age. It underlies about 2000 square miles of the coastal plain, inland from Tampa Bay, Florida, and is one of the world's most important sources of phosphate. The formation occurs on the southern flank of the Ocala uplift as a thin blanket of pebbly and clayey sands composed of quartz and clastic phosphate. This deposit is an excellent example of marine transgression during which the phosphate was derived, by reworking, from the underlying, weathered, Hawthorn Formation.

The southeastern coastal plain has been traditionally viewed as a very stable and undisturbed domain of shelf sedimentation. Study of the Bone Valley Formation, however, shows the Florida shelf to be a region of both tectonic and geochemical instability. Linear belts of structural uplift have been active in the region since the mid-Tertiary. This uplift has influenced the scenic present-day karst topography and has determined the Bone Valley's lithologic and faunal facies differentiation.

Weathering has transformed phosphatic clays and clayey sands of the Bone Valley Formation to lateritic aluminum phosphates, has created zones of supergene uranium enrichment, and also has caused a regional transformation of montmorillonite to kaolinite. Prolonged weathering leads to breakdown and removal of clay, and ultimately creates apparently unconformable mantles of residual quartz sand, which have been regarded as Pleistocene terraces. Geologic study in this area is characteristically plagued and enlivened by weathering which has destroyed real unconformities and created apparent ones.

Trips into the open-pit phosphate mines of the region will review recent studies of the U. S. Geological Survey, emphasizing the above aspects of the geology. It is pertinent to note that many of the interrelations and problems reviewed, however fundamental and interesting in themselves, were disclosed in the course of Geological Survey investigations of phosphorites as radioactive raw materials. These studies of phosphorite were motivated, in turn, solely by the occurrence of uranium as a trace substituent in the structure of apatite!

Many geologic studies pertinent to the area are cited in the following pages. A number of these, however, warrant special notice as synoptic or regional studies. Cooke (1945) in a classic and indispensable treatise covering the entire state; Vernon (1951) presents a cogent regional study of the Ocala uplift; and important data and observations on an area of comparable lithology and problems in the "hardrock" belt to the north, are presented in Espenshade and Spenser (1963).

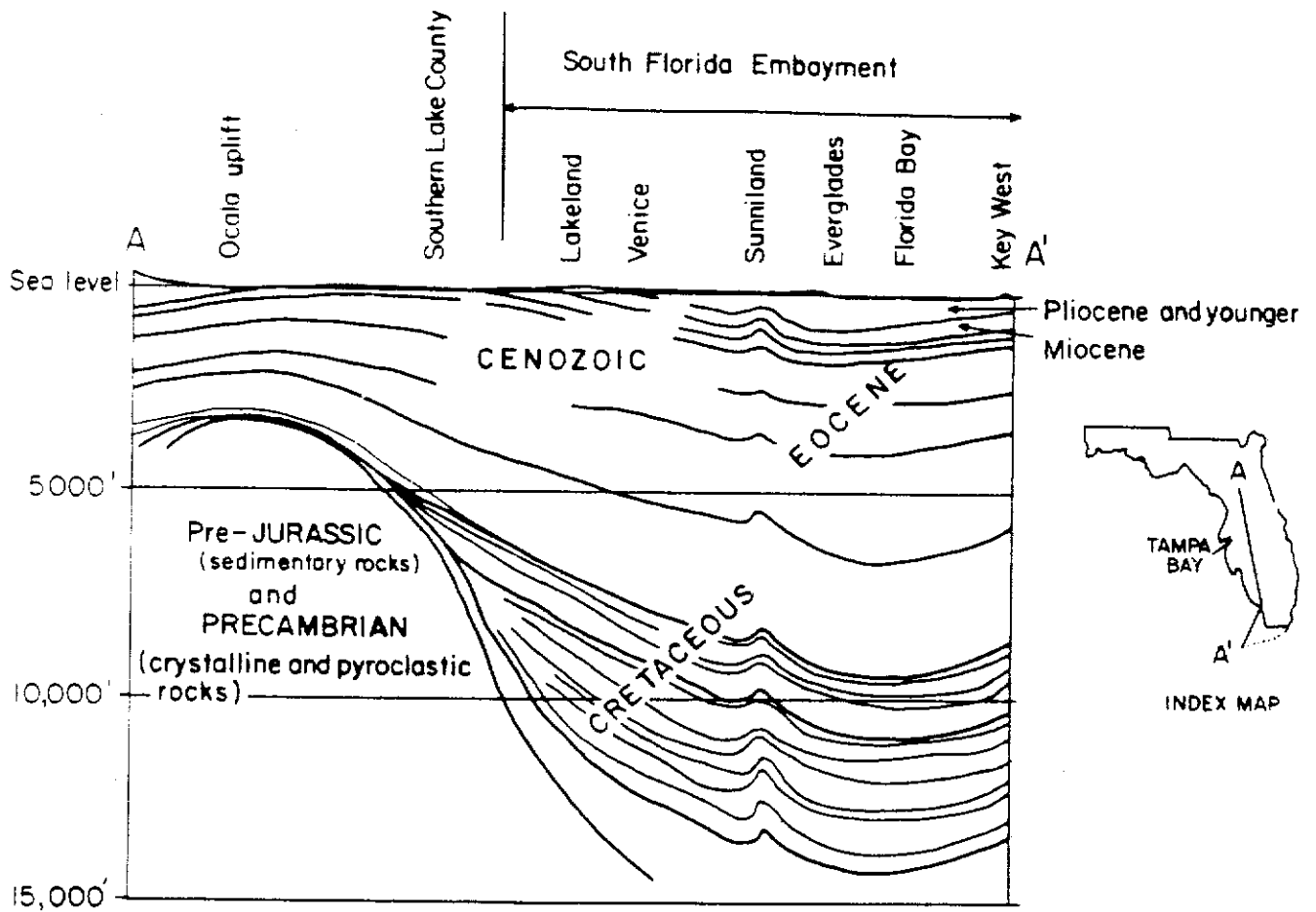


Figure 1. Cross-section through central peninsular Florida. Modified from Pressler (1947, fig. 2).

## GENERAL GEOLOGY

### Regional Structure

Peninsular Florida is strikingly subdivided across the middle into a northern clastic platform and a southern basin mainly of carbonate deposition, the South Florida Embayment of Pressler (1947). The slope between these two major provinces is, in effect, an immense monoclinical flexure, roughly coinciding, perhaps significantly, with a line joining the Canaveral coastal salient with the coastal indentation of Tampa Bay (figure 1).

Although limestone, clay, and sand are common throughout the subsurface of Florida, the essential contrast between the northern and southern provinces is that of a thin clastic platform and a thick carbonate basin. For example, beds of Austin age are differentiated into a sand and shale facies in northern Florida, an intermediate marly facies in central Florida, and a limestone facies in southern Florida (Applin and Applin, 1944). As another example, clastic beds of Wilcox age in northern Florida grade, both east and south, into an appreciably thicker carbonate facies, the Oldsmar Limestone (Applin and Applin, 1944). These relations are clearly shown by the regional stratigraphic cross sections of Furi and Vernon (1959) and Goodell and Yon (1960).

A number of large structural domes have been superimposed upon the northern platform. Florida geology is often discussed in terms of the contrast between the largest of these, the Peninsular arch of Applin (1951), and the South Florida Embayment. However, we feel it more proper to consider the entire platform as a province, adjoined by the embayment province, much as a stable shelf region adjoined by a marginal basin. Although the Peninsular arch determined the distribution of Cretaceous sediments in the northern province, the arch was covered during the Late Cretaceous by Austin-age beds (Applin, 1951). During Tertiary time Central Florida structure and stratigraphy were strongly influenced by another structure, the Ocala uplift, in the southwestern quarter of the clastic platform.

## Stratigraphy and Structural History of West Central Florida

The Ocala uplift is a broad, elongate dome composed of the Tertiary and Quaternary rocks of the Floridan plateau and underlain by a core of Precambrian and lower Paleozoic rocks. This dome trends southeasterly and plunges to the southeast. On the crest, the top of the Ocala Limestone has an altitude of 150 feet. In the vicinity of Clearwater it drops to 450 feet below sea level, and in Monroe County (southernmost) it is 1200 feet below sea level, an apparent average dip of about 5 feet per mile over the entire region (Parker and others, 1955). Near the crest of the arch the dip of the Ocala Limestone exceeds 8 - 10 feet per mile (Vernon, 1951). These stratigraphic dips may not reflect the actual structural steepness, however, as the slope of the "basement" underlying the South Florida Embayment is thought to exceed 100 feet per mile (see Murray, 1961, for review and references).

Formations of Oligocene and Miocene age flank the Ocala uplift, dip away from it in all directions, and thicken to the south and east. Formations of Pliocene and younger age, in contrast with Hawthorn (Miocene) and older strata, are almost all thin and flat-lying blankets of transgressive clastics in the lowland areas of central and northern peninsular Florida.

The Bone Valley Formation and a number of other phosphate deposits are a part of, or immediately underlie, this upper Tertiary blanket. These deposits occur:

1. wherever subaerial weathering has leached the underlying sparsely phosphatic Hawthorn limestone to produce sinks, with pinnacles of limestone (karrenfels) and residual pockets of the less soluble phosphate nodules;
2. where fluvial reworking has further concentrated weathering residues to form "river pebble" deposits;
3. where marine transgression has reworked residuum into extensive bedded deposits known as "land-pebble" phosphate; or
4. where leaching through a thin cover of Hawthorn has phosphatized subjacent limestone, to form "hardrock" phosphate.

The phosphates of the Bone Valley Formation, together with small amounts of underlying residuum, comprise the land-pebble deposits. The reserves and characteristics of some of the above types of deposits are reviewed by McKelvey and colleagues (1953).



Table 1.-- Summary of stratigraphy and lithology, land-pebble phosphate district, Florida.

Age	Formation or deposit	Lithology: "Normal" Section	Lithology: Intensely weathered Section	
Pleistocene or Recent	Pleistocene (?) sand or Residual sand mantle	Unconsolidated quartz sand, massive. Some organic material at surface. May have ground-water podsol.  Overburden	Unconsolidated quartz sand, massive. Some organic material at surface. May have ground-water podsol.  Overburden	
Pliocene	Bone Valley Formation	CONTACT LOWERED OR A WEATHERING BOUNDARY		
		Upper Unit	Green clayey sand, minor apatite particles that are more abundant at base. Finely bedded, graded bedded, and crossbedded. Clay mineral, montmorillonite, weathered to kaolinite at top of unit.  Overburden	White clayey sand, leached and indurated. Secondary aluminum phosphate minerals replacing clay and apatite. Clay is kaolinite. Basal layers may be vesicular, where the lower unit is altered. Aluminum phosphate alteration extends only partly into lower unit, but may replace parts of Hawthorn and Tampa Formations where they are close to the surface.
		Lower Unit	Phosphorite. Sand, clay, and gravel containing very abundant phosphate particles. Bedded, graded bedded, and crossbedded. Green, brown, and black.  Matrix	Leached or Aluminum Phosphate Zone  WEATHERING BOUNDARY
			CONTACT GRADATIONAL	Phosphorite, as in unweathered section.  Matrix
Miocene	Hawthorn Formation	Sandy, clayey, phosphate-bearing limestone. Dolomitic near surface. Buff, white, or cream. Contains interbedded sand, clay, or sandy clay.  Bedrock	Residual calcareous, sandy clay, containing abundant phosphate particles; lower part grades into carbonate rock. Possible development of aluminum phosphate minerals, particularly in the northern part of the district, where the overlying formations are thin or absent.  Bedclay	
	Tampa Limestone	CONTACT RELATIONS UNCERTAIN (CONFORMABLE TO SOUTH, DISCONFORMABLE TO NORTH)		
		Sandy and clayey limestone, contains chert nodules and trace amounts of phosphate. May form the bedrock in northern part of district. Tampa fossils reported from the Tenoroc mine.	Calcareous clay and sandy clay containing chert and phosphate. Aluminum phosphate minerals present when the formation is very close to the surface.	
Oligocene	Suwannee Limestone	CONTACT UNCONFORMABLE		
		Limestone, contains minor sand and clay, but no phosphate. Chert present.	Secondary chert replacing limestone near the surface.	
Eocene	Ocala Limestone	CONTACT UNCONFORMABLE		
		Very pure limestone.	Known only in subsurface.	

The formations exposed in the land-pebble phosphate district (table 1) are the Suwannee Limestone of late Oligocene age (Cooke and Mansfield, 1936; MacNeil, 1947); the Tampa Limestone of early Miocene age (Cooke, 1945; MacNeil, 1947); the Hawthorn Formation of early and middle Miocene age (Cooke, 1945; MacNeil, 1947); the Bone Valley Formation of middle Pliocene age (Simpson, 1929; Brodkorb, 1955; Cathcart and others, 1953), and surficial sands mapped as Pleistocene and Recent by Cooke (1945) and MacNeil (1950). More recently the surface sands in most areas above 100 feet have been portrayed as residual sand plains and their age is considered related to that of the underlying formations (Altschuler and Young, 1960). It should be noted that only the youngest and lowest of these sand plains, the Silver Bluff, at 8 - 10 feet (MacNeil, 1950), and the Pamlico, at 25 - 30 feet (Cooke, 1945) are parallel to the present coast and contain marine fossils (figure 3); an analogous situation exists along the entire eastern seaboard. Thus, the concept of residual origin for higher sand mantles in Florida may have widespread consequence. It would explain the general absence of marine fossils above the Pamlico as an effect of leaching, and indicate that the latest extensive marine transgression was limited to the Neogene.

The post-Eocene strata generally occur in offlap relation on the flanks of the Ocala uplift. East of the uplift, the Eocene Ocala Limestone is unconformably succeeded eastward by the lower and middle Miocene phosphatic dolomites of the Hawthorn, and farther east the Hawthorn beds are overlain by upper Miocene phosphatic sediments (Espenshade, and Spenser, 1963). Within the land-pebble district the Suwannee Limestone crops out at the Hillsborough River in the northern part of the section, the Tampa Limestone is exposed in Blackwater Creek to the south, and still farther south, the Hawthorn Formation is exposed along the Alafia and Peace Rivers (figure 2). This offlap relation could be due:

1. to uplift continuous with deposition,
2. to uplift alternating with deposition, but positive in net effect, or
3. to post-depositional doming and erosion.

It should be noted that the Ocala and Suwannee Limestones have karst and highly eroded surfaces, marking extensive weathering intervals prior to Oligocene and Miocene deposition. The Tampa-Hawthorn contact is irregular and disconformable in the northern part of the area. To the south, however, the contact is more regular, and drilling indicates that the contact is gradational. The contact between the Hawthorn Formation and the overlying Pliocene is unconformable and very irregular, except where it has been obliterated

by post-depositional leaching through the Bone Valley Formation.

The preceding data indicate a history of uplift and major subaerial exposure at the end of Eocene and Oligocene times, alternating with marine transgression and deposition during Oligocene and Miocene time. The regressions and transgressions appear to have become successively less extensive to judge by the conformity between the Tampa and Hawthorn Formations to the south, the relatively limited outcrop area of the Bone Valley Formation (fig. 2 and 3), and the restriction of the Caloosahatchie Formation to southern low-lying areas of the Florida peninsula (Puri and Vernon, 1959). In effect, all of post-Miocene time may represent the latest major cycle of uplift and weathering, except for restricted periods and areas of transgression.

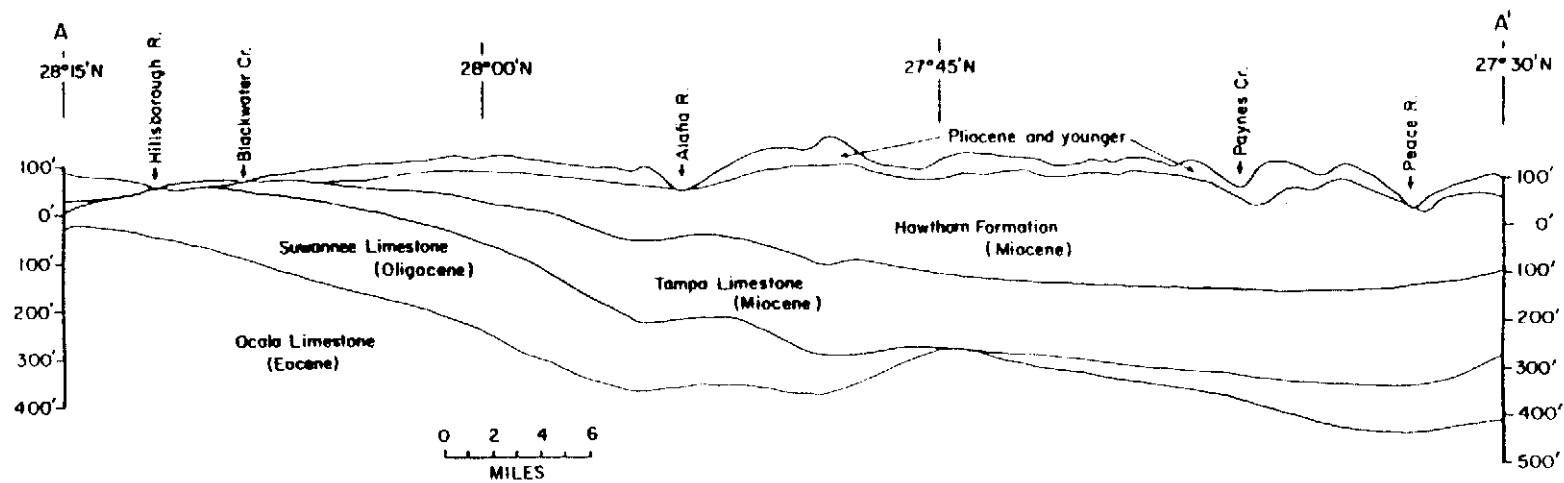


Figure 2. Cross-section A-A' through land-pebble phosphate district showing general structure and stratigraphy. Location of this section is shown in figures 3 and 12.

## GEOMORPHOLOGY

The surface of most of peninsular Florida is remarkably flat in consequence of its relative youth, the blanket of highly porous and permeable sands which underlie it, and the extensive solution networks in the subjacent limestone and dolomite. As Vernon (1951) noted, much of the 50 to 70 inches of annual rainfall is dissipated in seepage and subterranean flow; dissection and sculpturing by surface streams are minimized.

This near lack of surface erosion is reflected in the simplicity with which various synoptic works have treated the geomorphology of Florida. Thus, Cooke (1939, 1945) subdivides peninsular Florida into but 2 major regions, Coastal Lowlands and Central Highlands. The Coastal Lowlands are defined as the flat plains, less than 100 feet in altitude, which cover most of the southern half of the state and extend north along the two coastal belts. Cooke's Central Highlands, which extends through the center of the peninsula from the Georgia line, comprises a diversified area ranging in altitude from 40 to 325 feet, and includes extensive swamps, hills, thousands of lakes, and all the higher terraces recognized by Cooke (1945, p. 8). Vernon's (1951) terms Terraced Coastal Lowlands, and Tertiary Highlands are partly equivalent to Cooke's subdivisions but differ in that all terraces recognized by Vernon are included in his Coastal subdivision. In addition, Vernon separated the major river valleys into a distinct category, River Valley Lowlands.

The land surface of west-central Florida rises very monotonously inland from the Gulf of Mexico to form, in effect, a continuous marine plain, with few conspicuous interruptions, in the form of small elongate ridges and bars of low relief, or moderate discontinuous scarps. In low-altitude areas two sets of scarps occur more regularly and define two belts of plains parallel with the coast and underlain by marine shell beds. These are the Pamlico (25-30 feet) and Silver Bluff (8-10 feet) shorelines. "The Pamlico terrace .....is the most extensive plain in Florida. It covers most of Florida south of latitude 27° as well as broad strips along both coasts north of that line" (Cooke, 1945, p. 11). The Silver Bluff is a narrow littoral bench in the Pamlico terrace thought to record a still stand of the waning Pamlico sea. It is not well preserved in the Tampa Bay region.

Above 25 feet, however, the marine plain is not notably differentiated in the area east of Tampa Bay and the flights of terraces depicted in the region by Cooke (1945) and MacNeil (1950) before the area was fully mapped topographically cannot be identified with any assurance (Altschuler and Young, 1960; Espenshade and Spenser, 1963).

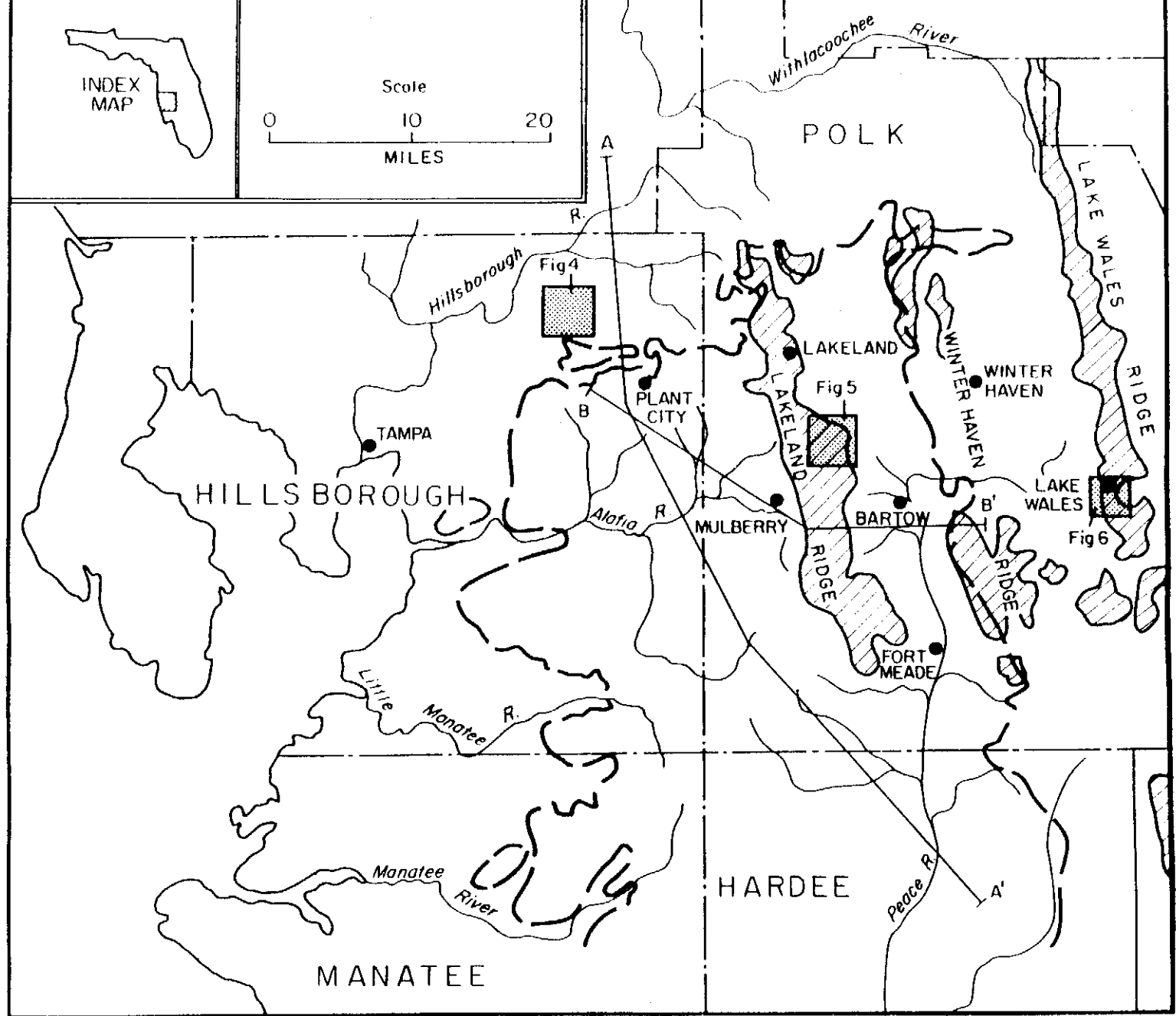


Figure 3. Map of west-central peninsular Florida showing limit of land-pebble phosphate district (dashed line) and major topographic features. Shading indicates ridge areas above 150 feet in elevation. Sections A-A' and B-B' are shown on figures 2 and 13.

The area of the land-pebble phosphate district is composed essentially of three principal types of terrain (fig. 3); poorly drained and virtually undissected sand plains and "hammocks"; long, narrow ridges rising 50 to 200 feet above the surrounding plains and trending approximately N.N.W.; and the slightly rolling alluvial plains and shallow valleys of the Peace, Alafia and Hillsborough rivers.

The sand plains are coextensive with the coastal lowlands, above the Pamlico terrace and rise progressively from these to altitudes of 130 feet in the plains north of Plant City and Lakeland. They are spattered with shallow irregular ponds and cypress swamps (fig. 4), which lose water only downward or by evapo-transpiration, as seepage is too high and the land is too flat for surface stream development. The plains are extensively colonized by saw-grass and clumps of palmetto-palm, and, in drier areas, by stands of pine. In tracts distant from ridges or major stream valleys, the surface gradients are as low as 1 - 3 feet per mile and stream development is limited to poorly defined, swampy interconnections between lakes; virtually no extended consequent flow exists (see particularly the eastern half of figure 4; and also the Bay Lake, Rock Ridge, and Branchborough topographic quadrangles, U. S. Geol. Survey). These tracts probably are juvenile and undissected parts of a regionally uplifted marine plain.

Near the river valleys surface gradients are 5 - 20 feet per mile and the topography is somewhat rolling and hilly owing to gully and interfluvial development. The valley floors, however, are highly alluviated throughout the region and commonly are occupied by extensive belts of dense cypress swamp. The combination of rolling valley sides, moderately incised channels, and flat-floored valley bottoms with extensive strips of swamp, creates a distinctive topography called River Valley Lowlands by Vernon (1951). This topography is clearly displayed at highway crossings of the Peace River near Bartow and Ft. Meade.

A number of well-defined long and narrow ridges rise abruptly above the sandy palmetto flats in central Florida (fig. 3). They range in altitude from 90 to more than 250 feet within the land-pebble district, and they contrast markedly with the lowlands as areas in which sharp relief ranges locally from 50 to 100 feet. The ridges are realms of karst (figs. 5 and 6), and contain chains and clusters of round sink-hole lakes. Whereas lakes of the lowland are shallow, swampy, and often interconnecting, the lake basins and dry sinkholes in the ridges are deep, steepwalled, and generally connected to an underground drainage network which itself has caverns up to 40 feet in diameter (Stewart, 1959). The luxuriant vegetation over the ridges may obscure karst features in areas where the basins are not filled with lakes. However, a careful observer can easily see (fig. 5) the large number of shallow, undrained, bowl-shaped depressions that dominate the topo-

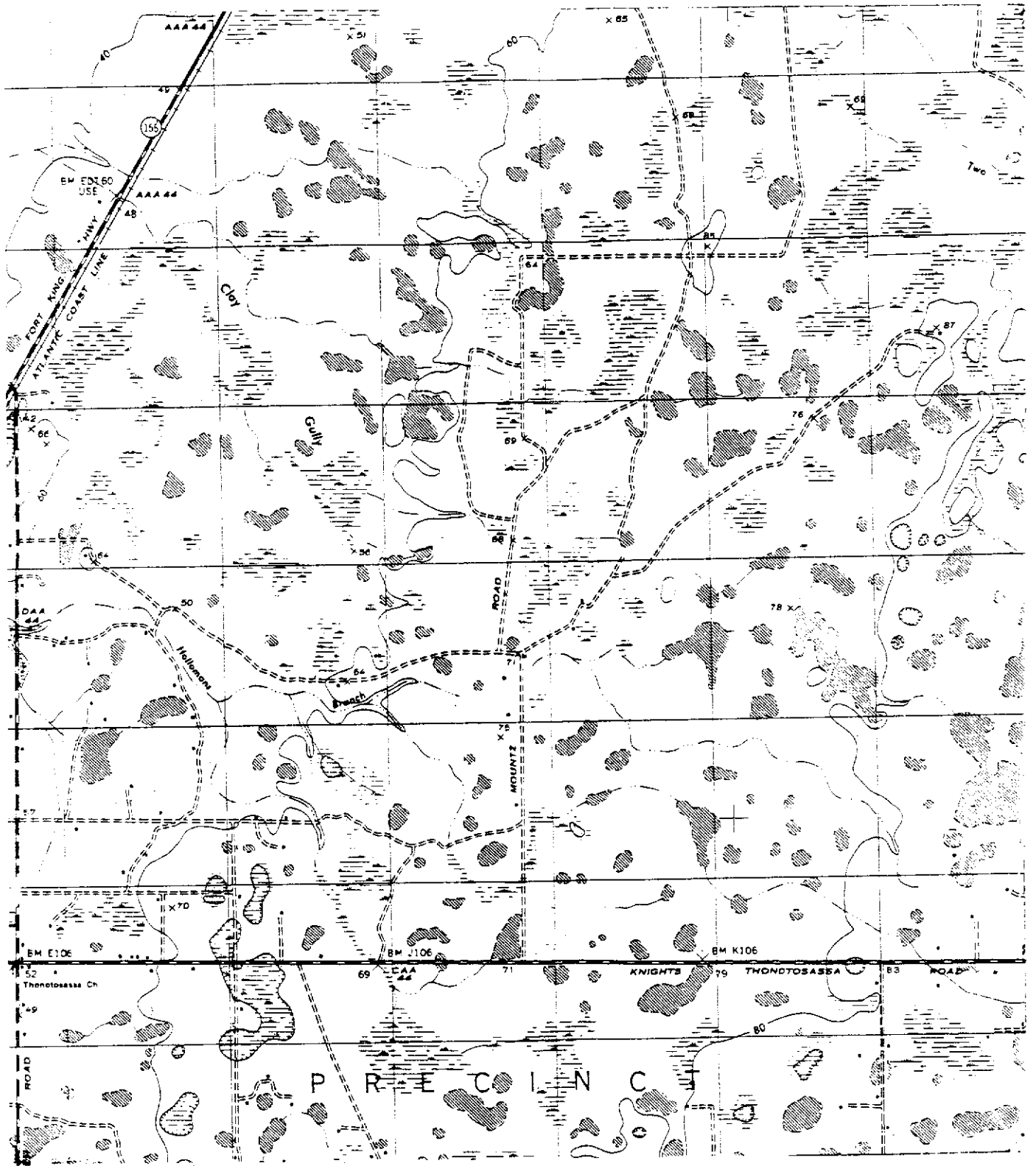


Figure 4.--Map of northwest part of Antioch quadrangle, showing typical area of poorly drained, undissected lowland (sand plain).



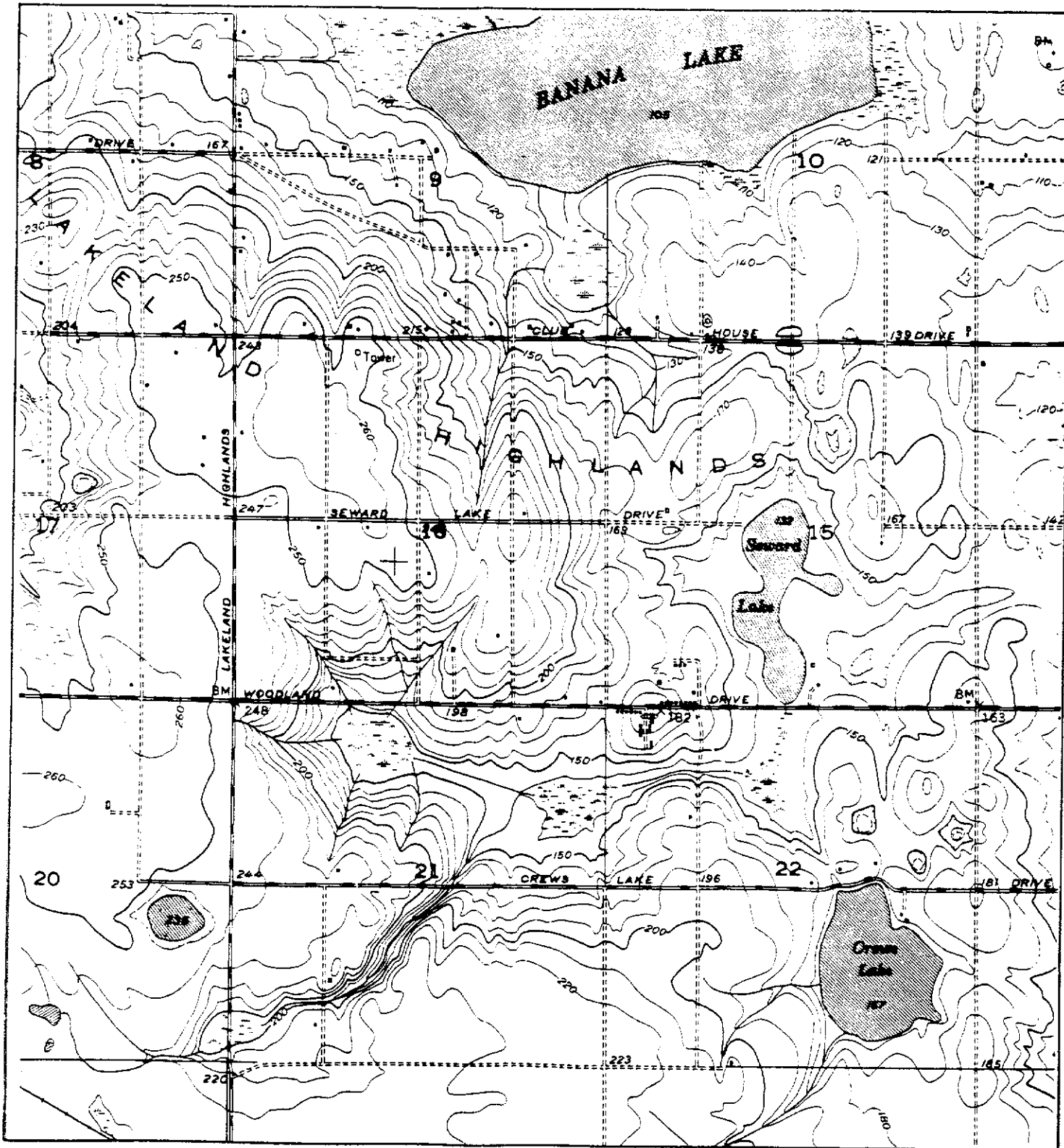


Figure 5.--Map of east-central part of Mulberry quadrangle, showing well-developed karst topography on Lakeland ridge.

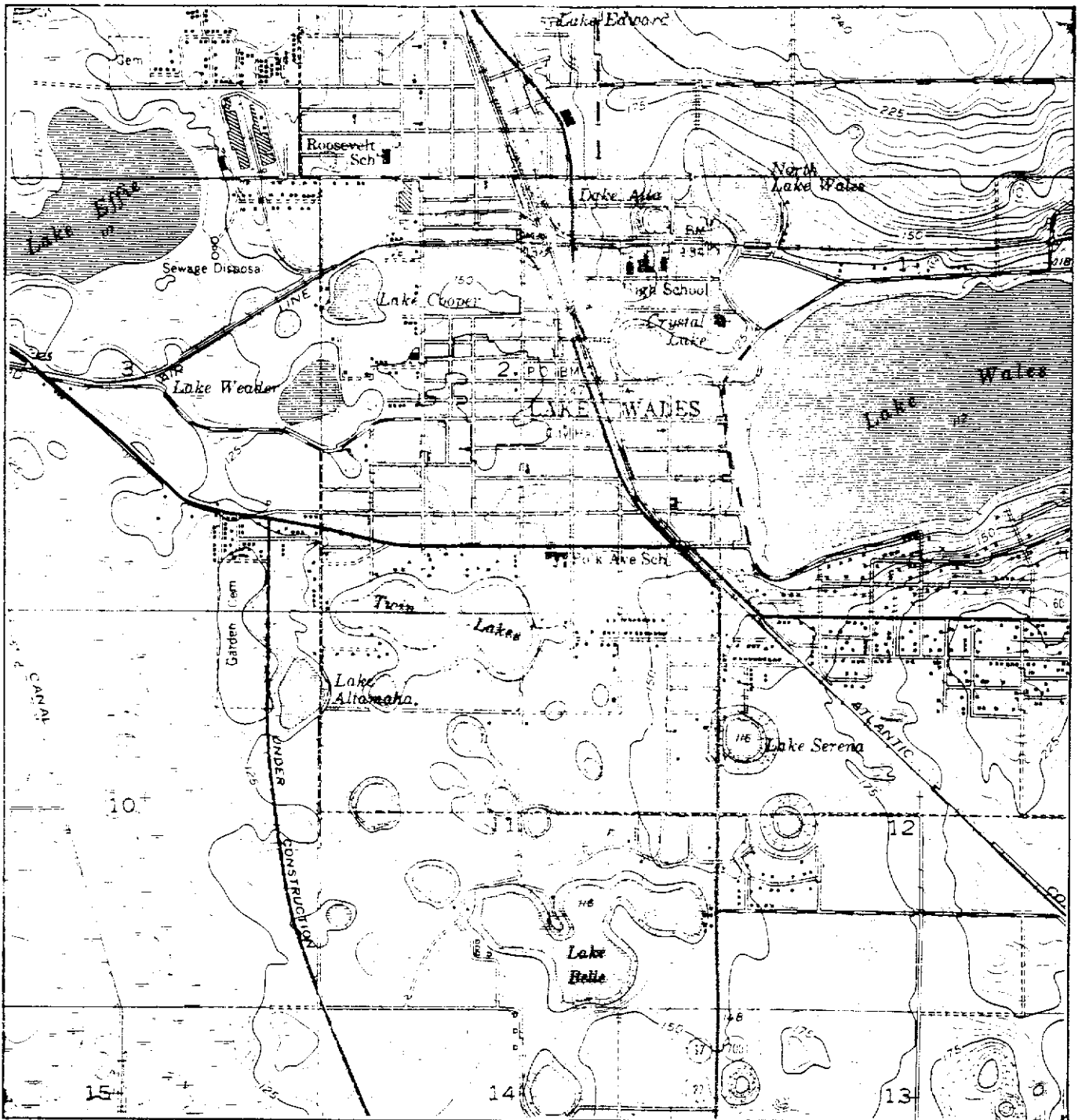


Figure 6. Map of southwest part of Lake Wales quadrangle, showing complex of sinkhole lakes in karst topography of Lake Wales ridge.

graphy in the lower flanks of the ridges, the general alignment of many of these basins, and theatre-like enlargements, "uvalas", of many headwater streams.

### Relations of Topography to Facies and Pleistocene History

The differentiation of central Florida into ridgeland and lowlands, is genetically related to regional differences of lithology, sedimentology, and paleontology, and has influenced the economic development of the region. It is thus of considerable interest to discuss the origins of the ridges.

The ridges have been considered Tertiary erosional remnants by most writers. Cooke (1945), Vernon (1951), and MacNeil (1950) believed that they became islands during the Pleistocene interglacial submergences, at which time they presumably were terraced, and bodies of littoral and marine sands were deposited upon them. This view is endorsed by White (1958) and Bishop (1956) in their discussions of the ridges, and has been widely accepted among geologists working in Florida. The proponents of high terraces differ both in the number and the altitudes of the shorelines recognized. All cite the indistinctness of the higher and older terraces, which may have been modified by stream dissection and local terrestrial deposition. MacNeil (1950) and Vernon (1951) have each modified Cooke's (1945) proposal of 7 terraces to 4 terraces. Nevertheless, as recently noted, these theories all share certain implicit assumptions.

1. As the presumed terraces are mapped by altitude accordance, post-depositional uplift is not permissible.
2. As they represent interglacial deposits, they must be transgressive, and unconformable or disconformable.
3. They must be Pleistocene in age.
4. Their materials "must be differentiated in a pattern and at altitudes consistent with the terrace hypothesis" (Altschuler and Young, 1960).

A number of the above assumptions have been tested in sedimentological studies of the so-called Pleistocene terrace sands. Field descriptions of the contact between the sand mantle and the underlying clayey sands by Sellards (1915), Ketner and McGreevy (1959), and Altschuler and Young (1960) have all noted its irregular and gradational nature, its hummocky surface determined by concretionary development, and the irregular patches of clayey sand above the "contact", and the eluviated nests of quartz sand in the clayey sand below. The loose sands are totally devoid of visible structures. Furthermore, size analyses and heavy-mineral analyses of paired samples across the contact, in an

TABLE 2. COMPARISON OF "PLEISTOCENE MARINE TERRACE" and "RESIDUAL" HYPOTHESES, FLORIDA.  
(Shoreline altitudes in feet)

Proposed Ages of Terraces		Florida Cooke, 1945	Florida McNeil, 1950	Citrus and Levy Counties, Vernon, 1951	West-Central Florida Altschuler and Young, 1960	
Early Nebraskan and possibly Pre-Nebraskan		Citronelle fm. Brandywine, 270			Regional and differential uplift, weathering, and formation of residual sand plains	
Nebraskan (glacial)		SUBAERIAL EROSION				
Aftonian (interglacial)		Coharie 215		Deposit of Coharie, 220		
Kansan (glacial)		SUBAERIAL EROSION				
Yarmouth (interglacial)		Sunderland, 170	Okefenokee, 150	Deposit of Okefenokee, 150		
Illinoian (glacial)		SUBAERIAL EROSION				
Sangamon (interglacial)		Wicomico, 100 Penholoway, 70 Talbot, 42	Wicomico, 100	Wicomico, 100		
Wisconsin	Glacial stade	SUBAERIAL EROSION				
	Interstade	Pamlico, 25 Silver Bluff, 8	Pamlico, 25-35	Pamlico, 25		Pamlico, 15-35
	Glacial stade	SUBAERIAL EROSION				
Recent	Altithermal	Modern littoral, Sea level	Silver Bluff, 8-10	Modern littoral, Sea level	Modern littoral, Sea level	
	Present		Modern littoral Sea level			

area in which the underlying clayey sand is differentiated into graded beds, show the sand blanket to be virtually identical to the sand fraction of the underlying Bone Valley Formation (Altschuler and Young, 1960, fig. B-93). Thus, the sand blanket appears to be eluvial, an insoluble weathering residue of the Pliocene Bone Valley Formation, and neither transgressive nor Pleistocene (Sellards, 1915; Ketner and McGreevy, 1959; Altschuler and Young, 1960). Pleistocene and Recent deposits are restricted in most higher areas (above 100') of the land-pebble field to a few channel and dune deposits and to the topmost veneer (about 6") of wind reworked material (Altschuler and Young, 1960). The relationship of this view to the various terrace proposals is given in table 2.

#### Variation of particle size with topography

The size differentiation of the sand blanket in relation to topography is another, and independent, means of testing the terrace origins of the surface sands. The reconstructions of Cooke (1945), MacNeil (1950), and Vernon (1951) portray the larger ridges as islands in the interglacial seas. We may thus expect their subaerially weathered surface and stream deposits (Vernon, 1951) to be reworked with the sands of coastal currents into the bars and beaches and dunes that are stated to characterize the marine interglacial terraces (see Flint, 1940, for 100 foot "Suffolk" scarp in Virginia; Cooke, 1945, for the Talbot terrace; and MacNeil, 1950, for the Okefenokee shoreline).

In studies of particle size distribution in the land-pebble district an accord between particle coarseness and surface elevation has been detected for the clastic phosphate of Bone Valley Formation (Davidson, 1952a; Cathcart and others, 1953) and for the surface sands (Davidson, 1952b). This relation of size to topography was studied in detail by Altschuler and Young (1960). They examined the size distribution of 100 samples from 9 townships straddling the Lakeland ridge, the dominant feature in the land-pebble field, and the surrounding lowlands. By contouring areal plots of size data they found (see fig. 7) a relation between size and present-day topography in which "coarser sands mantle the ridge, and the coarsest deposits form barlike accumulations on the ridge flanks. The finer sands are lowland deposits, flooring the valleys and straddling the lower parts of the ridge. Transitions between fine and coarse deposits are gradual except near the 'bars'. Despite this general relation of median size to topography (exhibited also by quartile, skewness, and sorting data) the sand differentiation is discordant to any of the proposed Pleistocene shorelines and to absolute altitudes. Note that the 160-foot contour outlining the

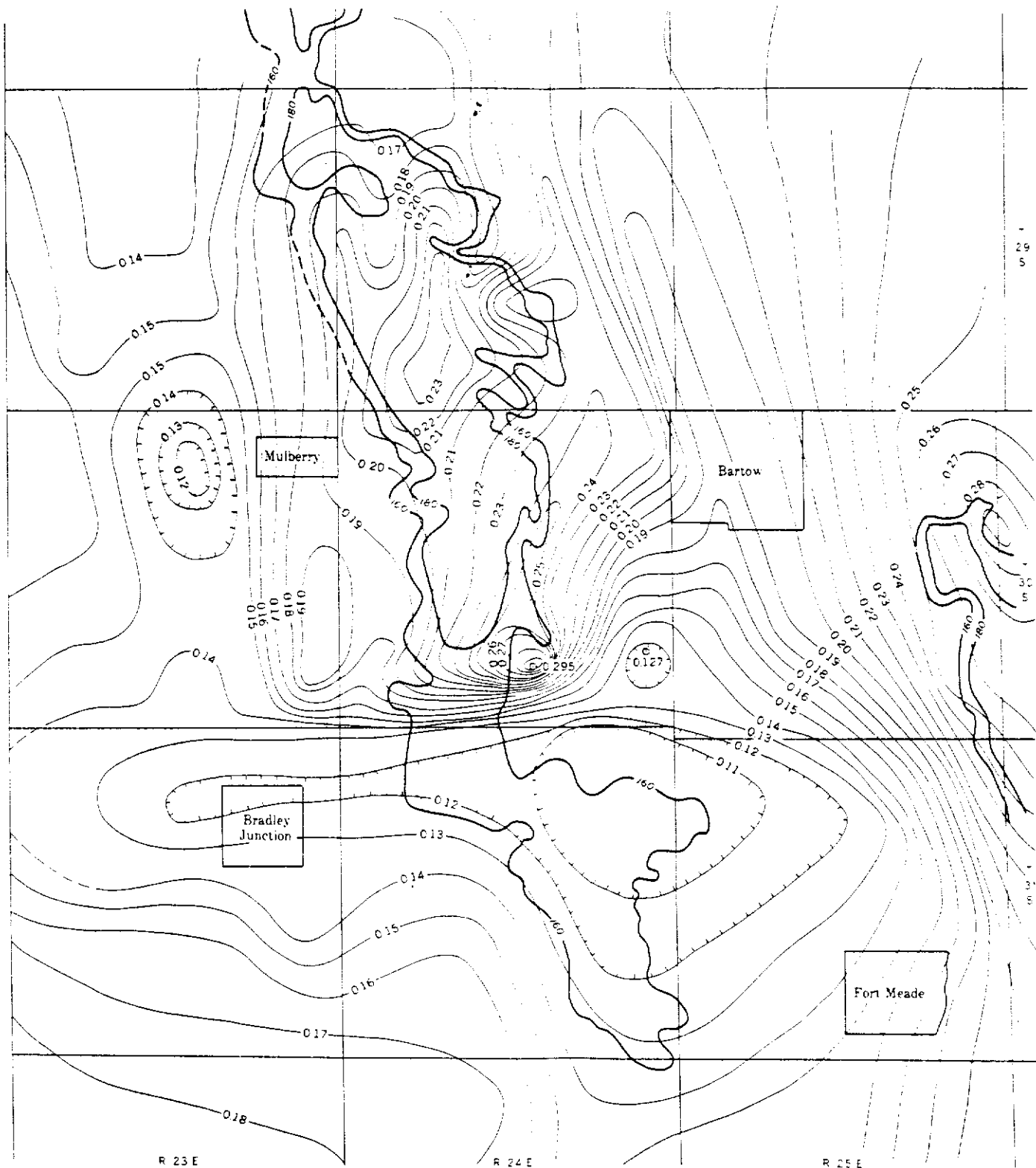


Figure 7.--Map showing median size distribution of sand in surface mantle in parts of Polk and Hillsborough Counties, Fla. Data obtained from cumulative frequency curves. Iso-grade contour interval = 0.01 mm. Heavy lines are the 160- and 180-foot topographic contours. From Altschuler and Young (1960, fig. 89.2).

ridge cuts directly across both the coarsest and finest deposits. In other words, the grade-size distribution of the body of sand is completely independent of the previously proposed Coharie (215 feet), Sunderland (170 feet), or Okefenokee (150 feet) terraces. It reflects the size differentiation of Bone Valley time and suggests that the modern ridge existed as a shallow submerged ridge during Bone Valley time." Figure 7 shows these relations.

The lower Bone Valley is also much coarser and more conglomeratic in the ridge than in the surrounding lowlands (fig. 13). We may thus infer that the ridge existed as an area of shoaling, and locus of winnowing, throughout Bone Valley time. This fact is further reflected in the paleoecology, and even in the name of the formation. The region of the ridge from Mulberry to Bartow and south throughout the general area of Range 24E, is the part of the land-pebble field in which, during the early days of mining, an abundant estuarine vertebrate fauna was found. The fauna included pelagic forms such as sharks, whales, and dolphins; estuarine species, such as crocodiles and manatees; and terrestrial animals, of which elephant, mammoth, camel, horse, tortoise, and many others have been found (Kellogg, 1929; Simpson, 1930; Case, 1934; Cooke, 1945).

These very coarse deposits of phosphate and abundant bones on the crest and flanks of the ridge were originally named the Bone Valley "gravel". With the development of phosphate flotation in the mid-thirties, finer grained deposits could be mined and the exploitation shifted to tracts off the ridge. Only a small number of previously found fossils have been reported from these mines in the lowlands; and terrestrial species are not important in the total assemblage. It seems clear from faunal and textural data that the Bone Valley Formation is differentiated into a ridge facies of coarse, shallow, possibly estuarine deposits, and a lowland facies of finer and deeper deposits and a more characteristically aquatic faunal assemblage. The probable paleogeographic setting for this complex of deposits is that of a large south-facing coastal embayment.

#### Origin of ridges

Insight into the structure of the ridges is obtained from drilling data which show the Bone Valley Formation to be continuous across the central part of the land-pebble field. As shown in cross sections of Cathcart and coworkers (1953) and Altschuler and Young (1960) the altitude of the Bone Valley Formation parallels the surface topography. Although the formation is only 30 to 40 feet thick, the maximum altitude of its base in the Lakeland ridge

exceeds its altitude in the Peace Valley by more than 80 feet (fig. 13). These facts have been interpreted to indicate that the ridges are linear uplifts in which the Bone Valley Formation was bowed up after deposition (Altschuler and Young, 1960). In this view, the ridges were initiated as subdued and submerged uplifts and caused a localization of coarse phosphatic gravels by winnowing in early Bone Valley time and continued to influence the deposition in late Bone Valley time, localizing coarser clayey sands. Subsequent renewal or continuation of uplift enlarged the ridges and accounts for the fact that the present-day sedimentation pattern is discordant to contemporary altitudes or presumed Pleistocene shorelines, as the residual sand plain over the region preserves the original sediment differentiation. The concentration of sinkhole lakes on the ridges and their relative absence in the surrounding lowlands has been ascribed to the fact that the uplift in the ridges increases the "head" in the underground drainage system and intensifies solutional downcutting and collapse. (Altschuler and Young, 1960). The relationship of the sinkholes to structural uplift in the ridges is also indicated in the linearity and alignment of the ridges and of the sinkhole chains within them, as though on joint and fault traces.



## STRATIGRAPHY AND PETROLOGY

The unconsolidated nature and near-surface occurrence of the Bone Valley Formation, coupled with its exposure to a warm climate of high, seasonal rainfall, have caused it to be pervasively altered at several stages of its development. This alteration has obliterated or transformed primary stratigraphic contacts in most areas of good percolation to an extent that, in many localities, originally unconformable contacts now appear gradational, and in other localities, irregular weathering boundaries create apparent unconformities.

One consequence of this post-depositional history on geologic studies has been the necessity of interpreting stratigraphy through petrologic information, and conversely, of distinguishing secondary from primary lithologies through stratigraphic control. Accordingly, stratigraphy and petrology will be discussed together, first in terms of the primary zonation and its minerals, and second in terms of the changes in zonation and mineralogy imposed by weathering.

The lithology and zonation that can be observed in the mines of the land-pebble district are shown in figure 8, and table 1. It should be noted that three kinds of subdivision are depicted. First, the stratigraphic subdivision, is simply that of the Pliocene Bone Valley Formation overlying the Miocene Hawthorn Formation, and being overlain by a deposit of loose quartz sand. The second category of subdivision is related to post-depositional alteration, and has arisen from the need to distinguish obvious secondary deposits produced, in situ, by leaching and alteration. The types of deposit so distinguished include "bedclay", "residuum", and "leached zone" or "aluminum phosphate zone". The third category of subdivision is economic, and utilizes the terms "matrix" and "overburden".

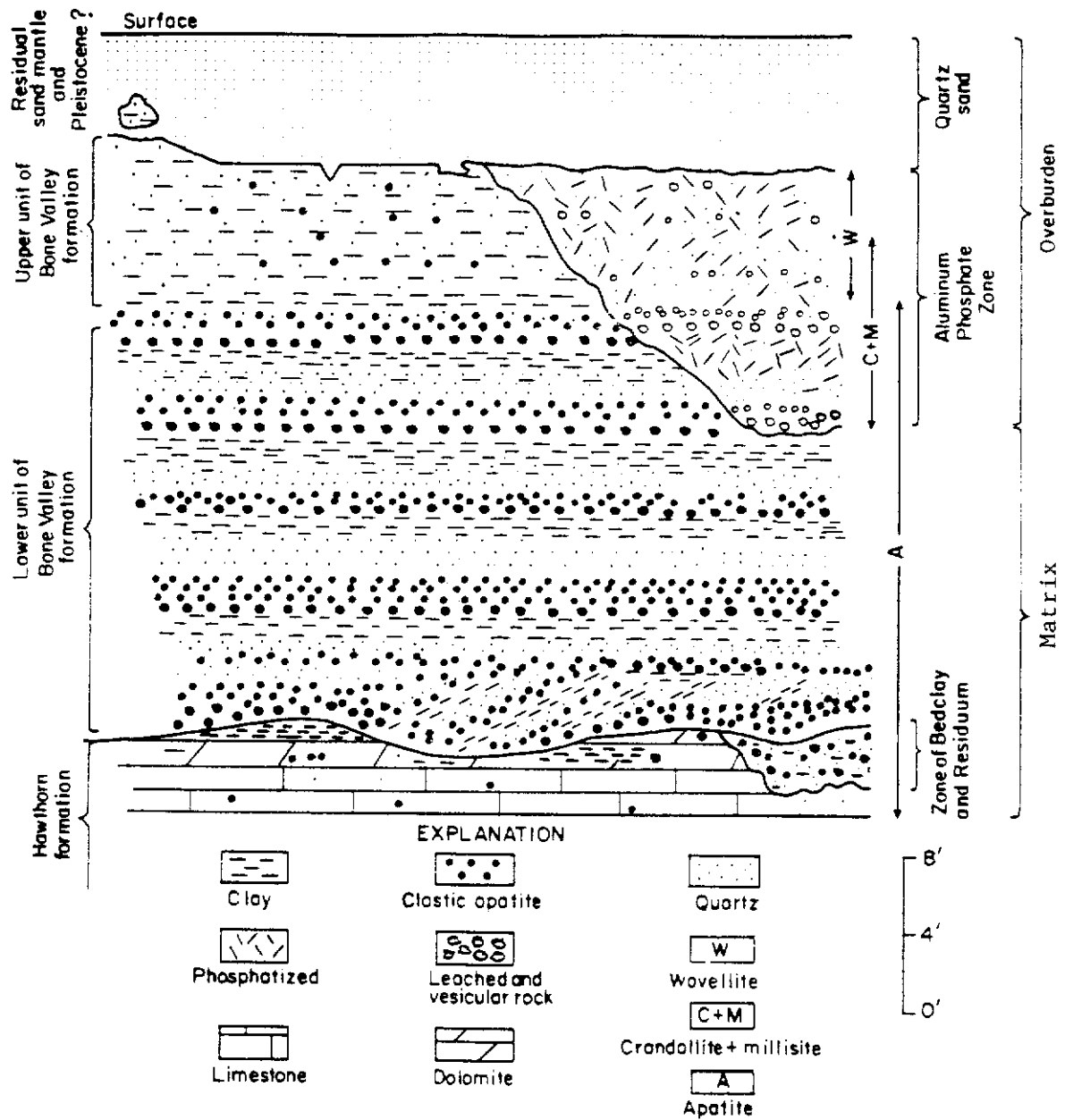


Figure 8. Lithology and stratigraphic relations in the land-pebble phosphate district.

## Definitions

A number of terms used in this report are peculiar to the land-  
pebble district, or vary from accepted terminology. These terms  
are defined below. (For more details see Altschuler, Clarke, and  
Young, 1958, and Cathcart, 1963a).

- BPL:** Bone phosphate of lime ( $\text{Ca}_3(\text{PO}_4)_2$ ). Equals percent  $\text{P}_2\text{O}_5 \times 2.185$ .
- Matrix:** That part of the calcium phosphate zone from which phosphate particles can be economically recovered. Equal to "ore".
- Overburden:** All rock overlying the matrix.
- Pebble:** Coarse phosphate product, +1 mm in size. Where used in this sense in this report will be in quotes--i.e.--"pebble".
- Concentrate:** Fine phosphate product, - 1 mm + 0.1 mm in size. Separated from quartz by flotation.
- Tailings:** Quartz sand, - 1 mm + 0.1 mm in size. Separated from phosphate particles by flotation.
- Slime:** -0.1 mm material. Includes clay minerals, quartz, and phosphate minerals (apatite, crandallite, and wavellite).
- Calcium phosphate zone:** That portion of the Bone Valley and the underlying Hawthorn Formations enriched in apatite pellets.
- Aluminum phosphate zone:** Zone of supergene leaching and alteration, characterized by white color, high porosity, and aluminum phosphate minerals.
- Leached zone:** Synonymous with aluminum phosphate zone; sometimes used by the mining companies for the lower, possibly economic, part of the aluminum phosphate zone.
- Bedclay:** Plastic, water-saturated calcareous clay containing phosphate particles. Residuum of argillaceous carbonate rock of the Hawthorn Formation.

- Bedrock: Hard, calcareous substrate of the matrix, usually of the Hawthorn Formation except at a few localities in the northern part of the district where bedrock is the Tampa Limestone.
- Phosphorite: Rock name, called phosphate rock in the land-pebble district. Used in this report to denote a rock or specimen containing substantial amounts of sedimentary apatite.
- Nodule: Rounded, irregular mass of any size. The term may apply to rock fragments, as well as apatite particles.
- Pellet: General term for rounded, oviform sedimentary apatite particles, commonly sand to granule in size.
- Apatite: Used in this report to mean the mineral carbonate-fluorapatite.

## Primary Zonation

### The Hawthorn Formation - bedrock

The Hawthorn Formation is known as "bedrock" in the land-pebble district, and it underlies most of the Bone Valley Formation. Very little of the Hawthorn Formation is exposed during mining, and information on the formation is restricted to samples from its upper few feet in mine exposures, and to well cuttings from deep drilling. The uppermost Hawthorn is composed of fine-grained, sandy and marly dolomite, and dolomitic sands and marls, all sparsely phosphatic.

The clay in the uppermost Hawthorn is generally a mixture of attapulgite and montmorillonite (Altschuler, 1952; Carr and Alverson, 1959; Espenshade and Spenser, 1963). At moderate depth the clay is principally montmorillonite, and the carbonate is entirely calcitic (Berman, 1953). It is not known whether the dolomite in the upper zone is post-depositional or primary. However, the association of attapulgite and dolomite in bed clay and equivalent bedrock over a wide area, despite the regional dip of the Hawthorn, suggests a replacement of montmorillonite by attapulgite, and of calcite by dolomite.

### The Hawthorn-Bone Valley Contact

The undulating surface of hard, yellow or tan dolomite exposed in ditches or floors of the mining pits is generally equivalent to the natural boundary between the Hawthorn and Bone Valley Formations. Its upper surface is irregular in detail, marked by solution features, and was an eroded karst surface at the time of Bone Valley deposition (Cathcart, 1963b). The top few feet of the Hawthorn Formation often is found to consist of recemented solution breccia, rich in residual sand, pebbles, and internal molds of fossils. Some of the pebbles and fossils are corroded. Where the Hawthorn is not decalcified, the Bone Valley Formation rests unconformably or nonconformably upon it. In some localities the bedded Bone Valley Formation is draped over the irregularities of the underlying dolomite surface at angles as large as 15°. These dips are mainly post-depositional, caused by later periods of solution and subsequent slumping of the Hawthorn Formation.

## The Bone Valley Formation

Name and definition - The name Bone Valley Formation stems from the "Bone Valley gravel" used by Matson and Clapp (1909) to describe the commercially mined phosphorite in what is now the center of the land-pebble district. Sellards (1910, p. 33) first used the name Bone Valley Formation, and Cooke (1945) formally applied the term "formation" to the clastic phosphate deposits that overlie the Hawthorn and are mantled by loose white sands of presumed Pleistocene age. Thus defined, the Bone Valley is typically between 30 and 40 feet thick through the center of the district, although it thickens considerably in many of the karst depressions surmounting the Hawthorn formation.

The Bone Valley is considered Pliocene on the basis of mammalian fauna described by Simpson (1929) and Cooke (1945), the avifauna recently described by Brodkorb (1955), and a number of horseteeth of the genera Neohipparion and Nannippus found during recent investigations of the U. S. Geological Survey (Cathcart and others, 1953), and observed to occur in bedded phosphorite above the Hawthorn.

Bedding and primary structures - The unaltered lower Bone Valley is characterized by green color, by pebbly and clayey textures, and by crude graded bedding (fig. 8). The upper Bone Valley, approximately the upper third of the formation, is a massive bedded or finely graded-bedded clayey sand. In the individual graded sets, the lower clastic layers are made up of apatite and quartz sand and apatite pebbles which grade upward to clayey quartz and phosphate sands, or quartzose clays. Although locally the lithology and thicknesses of beds vary greatly, the sequence of coarse phosphorite grading upward to sandy clay within each bed persists throughout the land-pebble area. The upper and lower Bone Valley are further differentiated in that graded sets are both thicker and coarser, and cross-bedding is more common, in the lower strata (fig. 8).

Composition - The composition of single beds of the lower Bone Valley ranges from almost pure montmorillonite clay to almost pure apatite conglomerate or sand, but the average composition of the deposit falls within the following ranges:

Apatite (carbonate-fluorapatite)	35 - 40 percent
Clay (montmorillonite)	20 - 25 percent
Quartz and minor chert	35 - 40 percent

## Nature of the apatite

(The following discussion is taken from

Altschuler, Clarke, and Young, 1958).

"Apatite [ commonly -  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  ] is host to many substitutions by cations, anions, and anionic radicals that resemble its normal constituents in size and charge (McConnell, 1938). As a result it may depart significantly from the composition of simple igneous fluorapatite, depending on its environment of genesis. The fluorine position may be occupied wholly or in part by hydroxyl. (Chlorine may also substitute for fluorine; however, as their size difference is appreciable, a structural rearrangement occurs in chlorapatite and it has only limited miscibility with fluorapatite). In fossil bone, hydroxyl is eventually replaced by fluorine through ion exchange. Minor to major amounts of Sr, Mn, Mg, and Pb are known to replace calcium in apatite, and  $\text{VO}_4$  and  $\text{AsO}_4$  occur as traces substituting for  $\text{PO}_4$  in apatite and form analogues of normal apatite in the pyromorphite series (Palache and others, 1951).

"Additional variety is effected by the opportunity for coupled diadochy in which cationic or anionic replacements causing loss or gain in valence are balanced by replacements of opposite kind. Thus, in apatites containing rare earths, an imbalance created by the substitution of trivalent cerium for calcium is quantitatively compensated by substitution of tetravalent silicate for phosphate, or by the monovalent sodium for calcium (Borneman-Starynkevitch, 1938; Volodchenkova and Melentiev, 1943).

"Composition of the Sedimentary Carbonate-Apatites. The fine-grained microcrystalline carbonate-apatites of the insular and marine phosphorites are best understood in terms of such coupled substitutions. This apatite is generally characterized relative to fluorapatite by a deficit in  $\text{P}_2\text{O}_5$  content of 3 to 6 percent, an excess of F, OH (or both) of 0.5 to 1.0 percent, and by the presence of 2 to 3 percent of carbonate. The exact mode of occurrence of carbonate in apatite is a controversial question. Hendricks and Hill (1950) have proposed that the carbonate is adsorbed on the surfaces of discontinuities within the apatite crystals. It is significant, however, that carbonate fluorapatite is demonstrably smaller in unit-cell dimensions than fluorapatite (Altschuler and others, 1953). It is felt therefore that the structural difference revealed by the characteristically smaller cell must reflect the major and equally characteristic chemical deviations, and that carbonate-fluorapatite is a structurally distinct species as proposed by Gruner and McConnell (1937). Lacking a precise determination of the position of carbonate in the structure

Table 3.--Chemical analyses of sedimentary apatite, Bone Valley Formation.

(from Altschuler, Clarke, and Young, 1958.  
Analyst, R. S. Clarke, Jr.)

	B. L.-3, Fine Pebble Bonny Lake Mine Ridgewood, Florida			Wa.-10, Pellets Watson Mine Fort Meade, Florida		
	1	2	3	1	2	3
Acid Inso.	-	6.6	-	-	2.4	-
CaO	49.5	-	52.9	51.5	-	52.7
P <sub>2</sub> O <sub>5</sub>	34.9	-	37.3	36.6	-	37.5
CO <sub>2</sub>	2.1	2.0	2.2	1.9	1.7	1.9
SiO <sub>2</sub> (total)	6.7	-	-	2.9	-	-
SiO <sub>2</sub> (soluble)	-	0.8	0.9	-	1.1	1.1
SO <sub>2</sub>	.3	-	.3	.1	-	.1
Al <sub>2</sub> O <sub>3</sub>	1.4	-	1.5	1.1	-	1.1
Fe <sub>2</sub> O <sub>3</sub>	.4	-	.4	.9	-	.9
Na <sub>2</sub> O	.1	-	.1	.2	-	.2
K <sub>2</sub> O	.1	-	.1	.2	-	.2
H <sub>2</sub> O (+)	1.6	-	1.7	1.8	-	1.8
H <sub>2</sub> O (-)	1.0	.6	1.1	.7	.5	.7
U	.016	-	.017	.0075	-	.0077
F	3.8	-	4.1	3.8	-	3.9
Total	101.9	-	102.6	101.7	-	102.1
F = 0	1.6	-	1.7	1.6	-	1.6
Corrected total	100.3	-	100.9	100.1	-	100.5

1. Analysis by complete decomposition of sample by solution in HNO<sub>3</sub> and fusion of insoluble residue with Na<sub>2</sub>CO<sub>3</sub>.
2. Partial analyses of same material. Acid insoluble determined after boiling sample for 20 minutes with 1 + 3 HCl. Nonleachable carbonate determined after treatment in 0.5 M tri-ammonium citrate (Silverman, Fuyat, and Weiser, 1952).
3. Corrected analyses, free of insoluble residue. Microscopic examination and the two sets of SiO<sub>2</sub> figures establish that acid insoluble is essentially quartz.



we shall adopt provisionally the structural formula which best rationalizes the chemical composition, as follows:  $\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_8\text{F}_{2-3}$ . Thus excess fluorine (or hydroxyl) serves to balance the charge difference created by the substitution of  $(\text{CO}_3)^{-2}$  for  $(\text{PO}_4)^{-3}$ .

"The chemical and spectrographic analyses in tables 2 and 3 (see tables 3 and 4) illustrate the chemical nature of the sedimentary carbonate-fluoroapatites. Theoretical fluorapatite has the following composition:

CaO = 55.5 (includes F for O = 1.6)

P<sub>2</sub>O<sub>5</sub> = 42.3

F = 3.8

The analyses portray the deficiency of P<sub>2</sub>O<sub>5</sub> relative to CaO (augmented by Na, Mg, Sr and other divalent metals shown in table 3 & table 4 here), and the excess of F plus (OH). It should be noted in table 2 (table 3 here) that the carbonate is substantially all nonleached and therefore assignable to apatite."

There are three essential varieties of clastic apatite in the Bone Valley Formation although a great number of intermediate textural varieties may be seen throughout the district.

1. Simple, structureless, ovoidal pellets, inherited from the Hawthorn Formation and reworked into the bedded sand deposits of the Bone Valley;
2. Simple relatively monomineralic pebbles of apatite, which probably originated as metasomatic replacements of relatively pure Hawthorn rock;
3. Complex and impure pebbles containing fragments of other pebbles and illustrative of several cycles of reworking of leached Hawthorn rock.

The important distinctions in composition which are reflected in the regional facies differentiation, and which greatly influence the patterns of mining, beneficiation, and the economics of recovery, are essentially related to nature and amount of impurity. Thus, the coarser materials, being dominantly of replacement origin, contain relatively high amounts of the more insoluble Hawthorn components-- quartz, clay, and chert. In addition, the coarsest pebbles, and the basal conglomeratic material, are less likely to be completely phosphatized, and therefore may contain calcite and dolomite as relict inclusions (table 5 and fig. 9).

Table 4.--Semi-quantitative spectrographic analyses of sedimentary  
apatite from the Bone Valley Formation.

(from Altschuler, Clarke, and Young, 1958)  
[Analyst, Katherine V. Hazel, U.S. Geological Survey]

Weight percent	B.L.-3, Fine Pebble, Bonny Lake mine, Ridgewood, Florida	Wa,-10, Pellets, Watson Min Fort Meade, Florida
Over 10.0	Ca, P	Ca, P
10.0-5.0	Si	-
5.0-1.0	Al	-
1.0-0.5	-	Si, Al, Fe
0.5-0.1	Mg, Fe, Na	Na, Mg
0.1-0.05	Sr, Ti	Ti, V, Sr
0.05-0.01	Pb, Mn, Cr	Mn, B, Y, Cr
0.01-0.005	Ba	Ba, La, Ni
0.005-0.001	Cu, V, Y	Zr, Yb, Cu
0.001-0.0005	Zr	} Ag, Be
0.0005-0.0001	Yb	

Table 5.--Mineral distribution in the land-pebble phosphate district

(s = secondary, m = minor, tr = trace)

Quartz Accessories			} Surface sands	
Residual patches of clay and apatite (m)				
<u>Upper Bone Valley</u>				
<u>Unleached</u>	<u>Leached and altered</u>		} Bone Valley Formation	
Quartz	Quartz	Kaolinite		
Kaolinite (s)	Crandallite	Gibbsite (tr)		
Montmorillonite	Wavellite	Attapulgate (tr)		
Apatite	Millisite	Manganese oxides (tr)		
Accessories (m)	Apatite	Accessories (m)		
Vivianite (m, s)				
<u>Matrix zone</u>				
Apatite				
Montmorillonite				
Quartz				
Chert (m)				
Accessories (m)				
Calcite (as constituent of pebbles at base)				
<u>Bedclay zone</u>				
Attapulgate (s ?)	Quartz	Apatite	} Hawthorn Formation	
Montmorillonite	Chert (s)	Dolomite (s ?)		
	Opal (s)	Calcite (m)		
<u>Bedrock zone</u>				
Montmorillonite	Quartz	Dolomite (s?)		
	Chert	Calcite (m)		
	Opal (s)	Apatite (m)		
		Attapulgate (s?)		
<u>Deeper bedrock</u>				
Montmorillonite	Quartz	Calcite		
	Chert	Dolomite (m, s ?)		
		Apatite (m)		

Table 6.--Chemical analyses of commercial "pebble" and concentrate, land-pebble phosphate district.

(Average of 10 "pebble" and 9 concentrate samples.  
Analyses by company chemists, Cathcart, 1963a  
and unpublished data)

Element	"Pebble"	Concentrate
CaO	46.98	49.76
MgO	.19	.29
MnO	.048	.044
K <sub>2</sub> O	.13	.10
Na <sub>2</sub> O	.21	.24
P <sub>2</sub> O <sub>5</sub>	32.07	34.21
V <sub>2</sub> O <sub>3</sub>	.014	.010
As <sub>2</sub> O <sub>3</sub>	.0011	.0014
CO <sub>2</sub>	3.07	2.59
SO <sub>3</sub>	.59	.52
SiO <sub>2</sub>	9.31	5.68
Al <sub>2</sub> O <sub>3</sub>	1.29	.95
Fe <sub>2</sub> O <sub>3</sub>	1.57	1.31
TiO <sub>2</sub>	.076	.105
Cr <sub>2</sub> O <sub>3</sub>	.007	.007
U <sub>3</sub> O <sub>8</sub>	.018	.010
F	3.68	3.81
Cl	.013	.014
H <sub>2</sub> O	1.88	1.52
Organic	.053	-
CaO/P <sub>2</sub> O <sub>5</sub>	1.465	1.455
F/P <sub>2</sub> O <sub>5</sub>	.115	.111

The analyses in table 3 illustrate the above distinctions. BL-3 is a composite sample of fine pebble material. It contrasts markedly with sample Wa-10, composed entirely of sand-size pelletal apatite, in having low  $P_2O_5$  and appreciable silica. The correction of the analyses, after determination of the acid insoluble portions, and of the acid soluble silica, reveals that the apatite of each of these materials is virtually identical.

Thus, the following very important economic and petrologic characteristics of the phosphate of the land-pebble district are determined by the petrography of the replaced material. (See section on Economic Geology and table 6).

1. The "pebble" fraction is lower grade than the concentrate fraction.
2.  $P_2O_5$  and size vary inversely among the various size fractions of the land-pebble deposits (Cathcart, 1956).
3. The quartzose nature of the "pebble" fraction makes it suitable as elemental phosphorus furnace feed, inasmuch as quartz must normally be added to electrolytic smelters for sequestration of lime in pseudowollastonite. The quartzose pebbles are also suitable for wet-process acid treatment, inasmuch as the quartz remains insoluble.

#### Nature and Composition of the Clay

The clay in the Bone Valley Formation occurs as intergranular matrix and cement throughout the Formation, and as the clayey upper member of each graded bed. The color zonation of the formation is conferred principally by the clay, and hence of interest as a field indication of mineral transformation during weathering.

The clay in the base of the formation and throughout the unaltered Bone Valley is generally monominerallic iron-rich, dioctahedral montmorillonite. It is blue-green or bright green on fresh surfaces, but alters rapidly to dull green and becomes rust stained on exposure to air and particularly on exposure to percolating meteoric water. Graded bedding controls the intimate ground-water circulation and hence the initial stages of clay alteration. Thus, as the clay becomes iron-stained and mottled by oxidation, the beds become varicolored in accordance with their texture, and solutions percolating through pebble layers paint the subjacent clays with vivid orange stain caused by the precipitation of goethite.

The composition of the primary clay is given in table 7. In the upper part of the Bone Valley Formation the green montmorillonite yields irregularly or gradually to a light green to gray or white kaolinite. The color and mineralogical changes transgress the bedding and are therefore post-depositional in origin. These changes, and other aspects of alteration, are discussed under "Weathering" below. In terms of the mineralogy and chemical zonation of the Bone Valley Formation, it is important to stress that the clay sequence from the base to the top of the formation is pure montmorillonite, montmorillonite plus kaolinite, and pure kaolinite. Laterally these zones shift downward, with weathering.

## Weathering and Secondary Zonation

Weathering of several different kinds and epochs is manifested in a variety of ways in the mines of the land-pebble district. Sub-aerial leaching and reworking of limestones is inferred from the deposits overlying the solution-pitted limestones of the Hawthorn. This weathering is mostly pre-Bone Valley in age, although its effects have been extended by Quaternary groundwater activity. Post-Bone Valley weathering of a regional nature is expressed in clay alteration in the upper part of the section, by color zonation, mottling, and merging contacts with the overlying surface sands. A more restricted and more intense variety of post-Bone Valley weathering is seen in the discontinuous white zones of leaching and alteration which occur within the color-zoned and "normally" weathered clayey sands. This latter variety creates zones of secondary aluminum phosphate minerals which are best developed in the river valleys.

The characteristics and products of the above types of weathering are discussed in the following sections. Additional details and discussions have been presented by Altschuler, Jaffe and Cuttitta, 1956; Carr and Alverson, 1959; Ketner and McGreevy, 1959; Espenshade and Spenser, 1963; and Altschuler, Dwornik and Kramer, 1963.

Pre-Pliocene, or post-Hawthorn and pre-Bone Valley weathering

Post-Hawthorn weathering is implicit in:

1. The irregular and solution-pitted surface of the Hawthorn Formation;
2. The nature of the clastic material of the Bone Valley Formation;
3. Residual accumulations of less-soluble Hawthorn clastic material in post-depositional surface depressions.

The pebble fraction of the Bone Valley Formation is chiefly composed of rounded and phosphatized fragments of Hawthorn limestone. Incompletely phosphatized pebbles in the coarse, poorly sorted basal conglomeratic zone still contain calcareous matter internally. In addition, the pebbles display compressed textures resulting from the differential leaching of calcite from the normally slightly phosphatic Hawthorn (see fig. 9). Evidence of the process may be

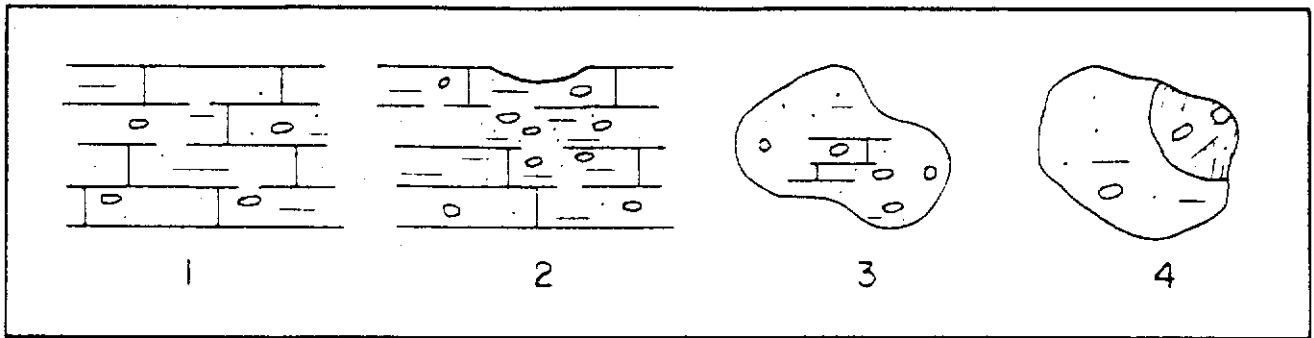


Figure 9. Diagram of stages in genesis of clastic phosphate from slightly phosphatic limestone.

1. Slightly phosphatic marine limestone, containing primary pellets of apatite (open circles).
2. Enrichment by leaching and phosphatization in weathering; showing residual enrichment of relatively less soluble apatite, and secondary development of apatite by replacement of limestone (fine shading).
3. Erosion of phosphatized and leached limestone, yields first-cycle pebble.
4. Reworking, fluvial or marine, yields multigeneration pebble of phosphatized limestone.



seen in the Hawthorn rocks exposed at the base of the mines in the land-pebble field. Such rock often is bleached and mottled by secondary leaching and the bleached parts are softer and contain relatively high concentrations of sand-size primary apatite pellets. In areas of accelerated drainage such differential solution has created extensive pockets of non-bedded highly phosphatic residuum in karst depressions on Hawthorn surfaces. Thus, from the textures in the basal conglomerate of the Bone Valley Formation, we infer that the Hawthorn was "exposed and weathered during late Miocene time, forming an irregular karst topography and accumulations of phosphatic residuum consisting of primary apatite nodules and secondary phosphatized limestone pebbles. Marine transgression during the Pliocene dolomitized the weathered limestone and reworked the clastic residuum and phosphatized limestone into the Bone Valley Formation, at the same time adding unknown amounts of quartz, clay, and phosphate." (Altschuler, Jaffe and Cuttitta, 1956). In places, pockets of residuum were trapped in surface depressions in the Hawthorn and overlain by well-bedded Bone Valley strata. Where the overlying bedded material does not slump into the residuum, the residuum clearly derives from pre-Bone Valley weathering.

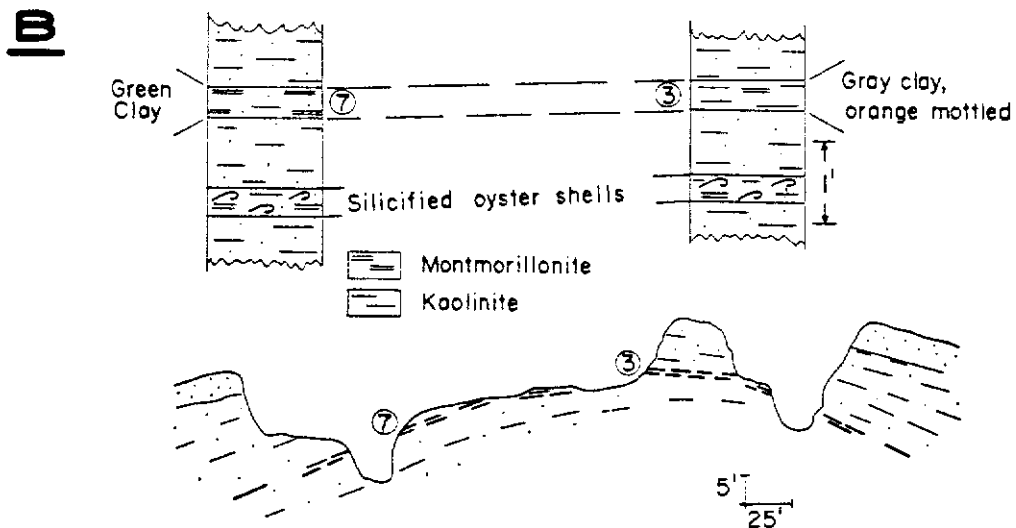
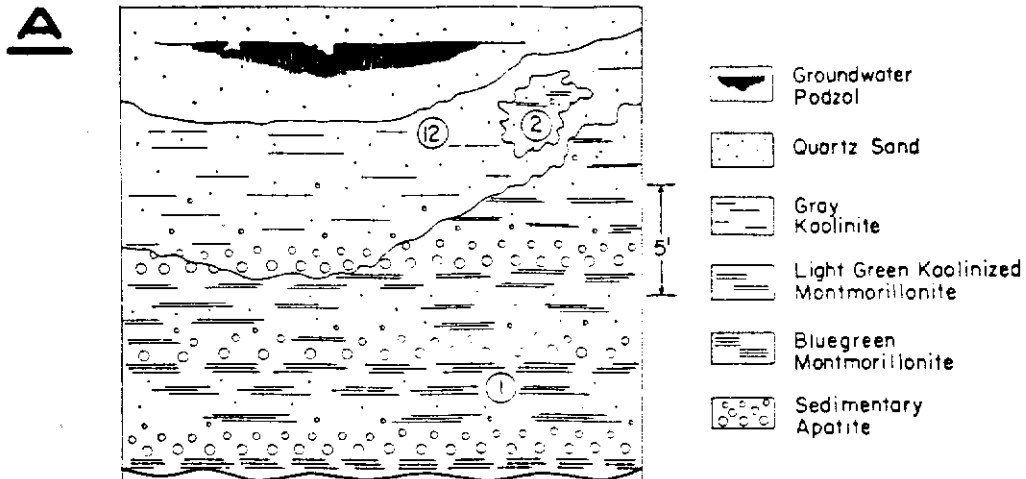


Figure 10.--Sections illustrating field relations of fresh and weathered clay. A - Bone Valley Formation, Saddle Creek area. B - Citronelle Formation, in borrow pit west of Mascotte, Florida. Circled numbers are sample locations for analyzed clays (table 7). From Altschuler, Dwornik, and Kramer (1963, fig. 1).



Table 7.--Chemical analyses of clays, Bone Valley  
Formation, Saddle Creek, Florida <sup>1/</sup>

(From Altschuler, Dwornik and Kramer, 1963)  
[Analyst, H. Kramer, U. S. Geological Survey]

Constituent	SC 1	SC 2	SC 12
SiO <sub>2</sub>	56.91	51.99	47.38
TiO <sub>2</sub>	.65	1.03	2.01
Al <sub>2</sub> O <sub>3</sub>	22.65	30.78	35.19
Fe <sub>2</sub> O <sub>3</sub>	6.29	2.55	1.56
FeO	.11	.21	.20
MgO	3.62	2.19	.86
CaO	1.47	.32	.26
Na <sub>2</sub> O	.18	.12	.06
K <sub>2</sub> O	.74	.92	.52
Li <sub>2</sub> O	.03	.01	.01
H <sub>2</sub> O +	7.34	9.89	11.94
Total	99.99	100.01	99.99

<sup>1/</sup> Analyses were made of clay fractions (-2 $\mu$ ) settled from clays containing quartz, apatite, and accessory minerals. Analyses have been corrected for identified apatite and crandallite after chemical determination of leachable P<sub>2</sub>O<sub>5</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub>.

Samples: SC 1, montmorillonite, basal part of the formation;  
SC 2, kaolinized montmorillonite, upper part of formation;  
SC12, kaolinite, completely transformed, stratigraphic equivalent of sample SC 2.

The conversion process has widespread geochemical and economic consequences. In the Citronelle Formation the absence of fossils has been taken to indicate terrestrial deposition. However, silicified oysters found at Mascotte, in strata immediately underlying transforming clay reveal that some, and possibly much of the Citronelle or Unnamed Coarse Clastics originated as a fossiliferous marine sequence (Altschuler, Dwornik, and Kramer, 1963). The silica released during alteration enriches the ground water, or precipitates as opal or chert, by replacement of subjacent limestones or of any calcareous fossils that have escaped prior leaching. Ledges of chert in the uppermost parts of the Hawthorn Formation, and the Tampa and Suwannee Limestones, are usually of this derivation. The development of major deposits of kaolinite throughout peninsular Florida may be attributed to the conversion process.

The development of the residual sand mantle in the land-pebble field and probably elsewhere in peninsular Florida may be the most striking geomorphic and stratigraphic consequence of the supergene groundwater alteration. The clayey sands are made much more porous and friable by the volume losses incident to clay transformation and leaching, and by loss of swelling property. More voids are then created by clay translocation or downward physical removal. This process is evident in secondary clay cements called cutans, (Brewer, 1960) which floor cavities, coat fractures, and build up minor clay hardpans throughout the weathered zone in the region (Altschuler, Jaffe, and Cuttitta, 1956). The combined effects of clay degradation and clay translocation ultimately create a completely eluviated quartz sand blanket over the region. Where weathering has not grossly altered the montmorillonite, the overlying sands are thin (Altschuler, Dwornik, and Kramer, 1963).

Many aspects of the weathering process can be observed in the soil profiles of the ground-water podzols which are extensively developed on poorly drained plains in the area. The profiles exhibit eluviated quartz sand zones, 1-2 feet thick, immediately underlying the topmost (6 inch to 1 foot) zone of soil and grass. Under the eluviated, or pallid zone, a zone heavily impregnated with translocated organic matter extends for another 1 to 2 feet. Beneath this zone the clayey sands are being actively degraded by drainage through the overlying organic-rich layer. Total clay content is minimal just under the organic layer, and a foot or so below it is found a zone in which clay pans and secondary iron concretions are deposited in previously weathered and iron-stained clayey sand. As the zonation is extended downward with continued degradation, the thickness of surmounting loose sands increases.

Table 8.--Chemical analyses of seven samples from  
a profile through the aluminum phosphate zone.

(see fig. 11 for stratigraphic relations)

(from Altschuler, Jaffe, and Cuttitta, 1956)  
[Analyst, F. Cuttitta]

Constituent	Ho-20	Ho-20A	Ho-21	Ho-22	Ho-23	Ho-24	Ho-25
SiO <sub>2</sub>	51.48	62.60	40.92	57.24	69.46	68.08	51.32
Al <sub>2</sub> O <sub>3</sub>	8.26	5.98	12.48	14.17	8.16	9.40	14.91
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	2.76	2.86	2.61	2.17	1.32	1.33	2.19
MnO	0.70	0.53	2.14	0.16	0.16	0.14	0.13
MgO	0.01	0.01	0.01	0.01	0.01	0.01	0.01
CaO	8.98	8.25	8.00	3.10	0.90	0.20	1.20
Na <sub>2</sub> O	0.23	0.13	0.12	0.15	0.06	0.04	0.03
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO <sub>2</sub>	0.37	0.40	0.63	0.63	0.31	0.42	0.65
P <sub>2</sub> O <sub>5</sub>	19.72	13.60	20.79	12.79	11.61	11.32	16.35
Loss on ignition <sup>b</sup>	6.76	6.09	11.72	9.96	7.91	9.18	13.24
CO <sub>2</sub>	0.80	0.24	0.26	0.05	0.02	0.02	0.05
F	1.15	0.52	0.63	0.59	0.51	0.70	0.53
Cl	0.03	0.02	0.04	0.01	0.03	0.02	0.01
SO <sub>3</sub> <sup>c</sup>	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.01	0.01	0.01	0.01	0.01
V <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
U <sup>d</sup>	0.01	0.03	0.02	0.01	0.01	0.01	0.01
Total	101.28	101.28	100.39	101.06	100.49	100.89	100.65
Less F = 0	0.48	0.22	0.27	0.25	0.22	0.30	0.22
Less Cl = 0	0.01	0.01	0.01	0.00	0.01	0.01	0.00
Corrected total	100.79	101.05	100.11	100.81	100.26	100.58	100.43
H <sub>2</sub> O (110°C)	0.35	0.49	1.13	0.64	0.73	0.39	0.88

(a) This represents total iron, some of which may be present as ferrous iron.

(b) The figures for loss on ignition include adsorbed water (H<sub>2</sub>O) and exclude CO<sub>2</sub>.

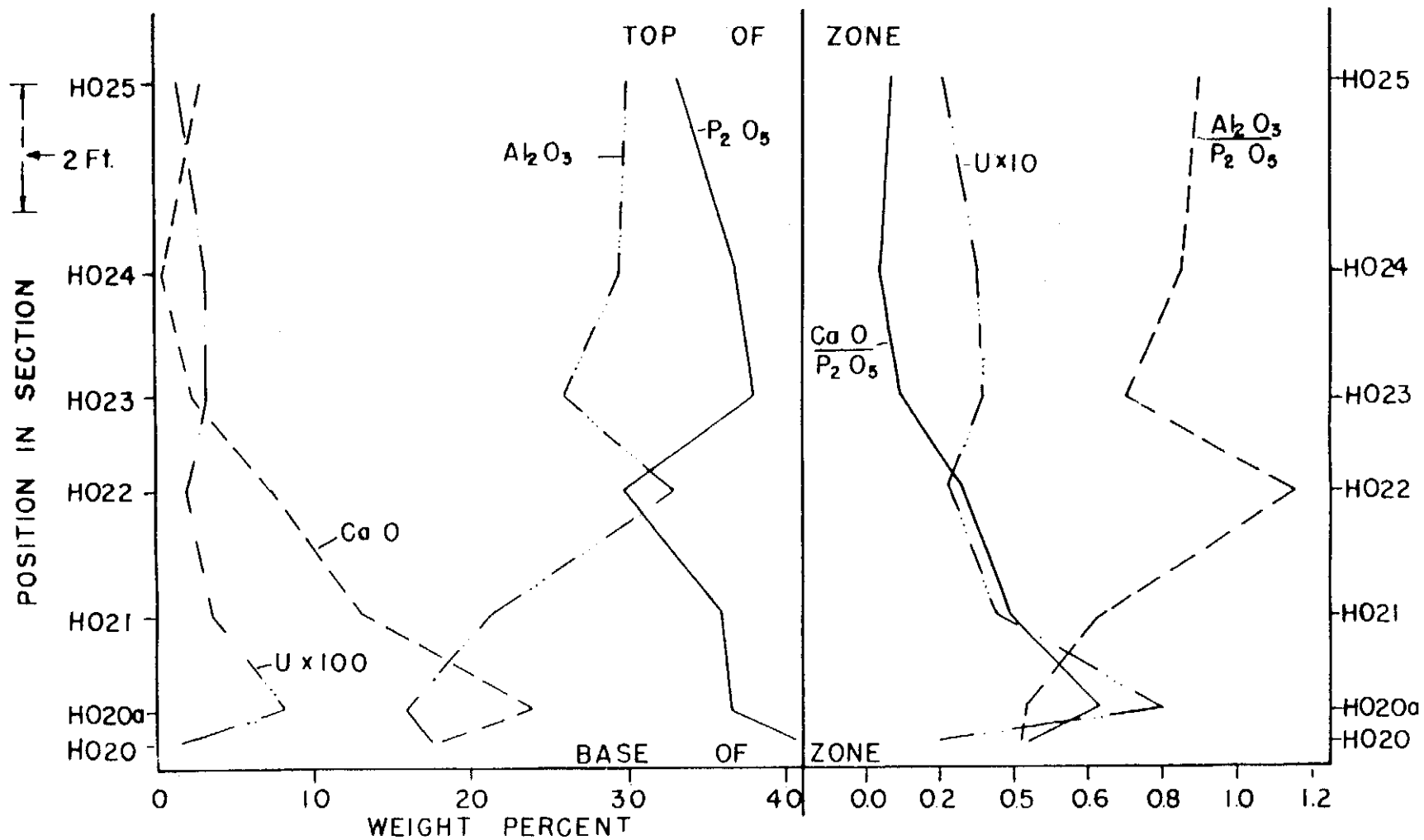
(c) This represents total sulfur; no sulfides were found.

(d) Uranium is reported as a metal, as its valence state was not determined.

Lateritic weathering - the aluminum phosphate zone - The upper Bone Valley commonly is compact, but unindurated, and light gray or greenish gray, owing to the secondary development of kaolinite throughout the area. In many areas red or orange coloration is irregularly superimposed on the clayey sands. However, in the mines of the Peace and Alafia drainage basins the upper part of the section is irregularly transgressed by a white zone of leaching and alteration in which the rock has become vesicular, friable, or indurated, and very light in weight. This is the aluminum phosphate zone. It is composed of quartz sand, cemented and indurated by the secondary minerals wavellite, crandallite and, locally, millisite (fig. 8) (Altschuler, Jaffe, and Cuttitta, 1956).

The aluminum phosphate zone is the product of more intense leaching and alteration than normally prevails in the southeast. The zone is essentially lateritic. This is evident chemically in the appreciable vertical changes from a calcic and silicate-rich rock to one in which all bases and silicates other than quartz have been leached. It is seen texturally in the extremely porous and vesicular rock whose open spongelike texture is indurated, and maintained, by secondary minerals and cements, as in the classic laterite of India. At the same time the character of the aluminum phosphate zone is greatly influenced by the primary Bone Valley texture and petrography. Where graded-bedded pebbly rock of the lower Bone Valley is altered, coarse vesicularity, with relic graded texture results, and as these layers were rich in apatite, they become rich in calcium aluminum phosphates. Where the alteration is restricted to the upper, more clayey unit of the Bone Valley Formation, the pure aluminum phosphate, wavellite, dominates, and the rock is finely vesicular.

At the base of the zone, carbonate-fluorapatite and clay still occur, though both are incipiently leached and altered. Higher in the section pebbles are gone and large cavities display the original pebbly texture. In the middle of the zone, bases and silicates are substantially diminished and the calcium aluminum phosphates crandallite [  $\text{CaAl}_3(\text{PO}_4)_2(\text{OH}_5 \cdot \text{H}_2\text{O})$  ] and millisite [  $(\text{Na}, \text{K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}$  ] prevail. The crandallite and millisite in the middle of the zone generally occur as a microcrystalline intergrowth within the clay bands they replace (Owens, Altschuler, and Berman, 1959). At the top of the zone the rock is essentially quartz sand cemented by intergranular wavellite [  $\text{Al}_3(\text{PO}_4)_2(\text{OH}_3 \cdot 5\text{H}_2\text{O})$  ]. The wavellite has therefore replaced the former intergranular clay, as well as the secondary calcium phosphates which represented an earlier stage in the replacement process. The wavellite of this origin occurs as bands of cryptocrystalline fibrous material (Altschuler, Jaffe, and Cuttitta, 1956). Wavellite also occurs as euhedral druses, vein fillings and large spherulites (Bergendahl, 1955). Microscopic seams of chert occur discontinuously in layers of replaced and wavellitized clays, but the quantity of such chert is small.



A. Oxides recalculated on silica free basis

B. Ratios of oxides on silica free basis

Figure 11.--Variations of chemical composition with stratigraphy in a profile through the aluminum phosphate zone. From Altschuler, Jaffe, and Cuttitta (1956, fig. 173). For analyses, see table 8.



The chemical changes in the aluminum phosphate zone further portray the phosphatization of clay, and aluminum phosphate metasomatism of apatite. It can be seen from the analyses in table 8 and from figure 11, which is a plot of these analyses according to stratigraphic position, that  $\text{Al}_2\text{O}_3$ , on the whole, varies inversely with  $\text{CaO}$ .

Trends through a vertical section correspond very closely to replacement of apatite ( $3.3\text{CaO}:1\text{P}_2\text{O}_5$ ) by wavellite ( $3\text{Al}_2\text{O}_3:2\text{P}_2\text{O}_5$ ). Thus,  $\text{Al}_2\text{O}_3$  increases half as rapidly as  $\text{CaO}$  falls!

Secondary precipitates are important products of the lateritic modification, and provide an insight into the nature of the process. Secondary precipitates of chert, apatite, limonite, and goethite underlie the aluminum phosphate zone in the form of discontinuous seams of hardpan, cementing porous sands, and encrusting the upper surfaces of clay (Altschuler, Jaffe, and Cuttitta, 1956). The hardpans are a sample of the labile materials removed from the overlying leached zone by acid groundwaters and deposited in the unleached zone below, where groundwater is neutralized by the basic calcium phosphates still present in the section.

An additional variety of fine-grained secondary cement occurs within the leached zone. It is composed of kaolinite and the aluminum phosphate minerals. It visibly coats fractures and builds layered accumulations on the floors of most large cavities. Its habit indicates deposition from descending solutions from which phosphate minerals were precipitating, and kaolinite was reforming from solution or redepositing from suspension. Cement composition changes throughout the zone in the same manner as the enclosing rock. Microscopic examination reveals wavellite needles growing discordantly across accumulations in floors of cavities and replacing the calcium aluminum phosphates of previously deposited mixtures. This demonstrates the progressively more aluminous replacement with continuation of alteration.

## ECONOMIC GEOLOGY

### History of Mining and Production

The first discovery of phosphate rock in Florida was made near Hawthorn, Alachua County, apparently in 1879 (Day, 1886; Wright, 1893). The initial find was a low-grade, phosphatic limestone or marl, probably of the Hawthorn Formation. A quarrying operation was started in 1883 and abandoned sometime before 1886.

In 1881, Captain J. Francis LeBaron of the Army Engineers discovered phosphate pebble placers along the Peace River (Davidson, 1892). These deposits were not exploited until 1888, when the Arcadia Phosphate Co. shipped the first phosphate rock from Florida. Production that year was about 3000 tons. The river-pebble discovery did not cause much excitement, but in 1888, high-grade phosphatized limestone (hardrock deposits) was discovered near Dunnellon, and production of this material began in 1889. This discovery set off a mining and prospecting boom in Florida and, by 1892, 18 river-pebble mines and 88 hardrock and land-pebble mines were operating. Most of these mines were in the hardrock field. The discovery of land-pebble phosphate followed the river-pebble discovery, as the companies engaged in the mining began to move from the river bars, first into the floodplains and, later, completely away from the rivers. The first prospecting for land-pebble deposits probably took place in 1890, as the first recorded production was in 1891.

The phosphate discoveries attracted foreign as well as domestic companies, and from the time of the discovery of phosphate until World War I, French, Belgian, and English companies mined phosphate in Florida. Day (1891), for example, reported that in 1890, the largest mine in the land-pebble area was that of the "English company", situated on the Peace River about 7 miles south of Bartow. French companies mined extensively in the area south of Lakeland near Medulla and Christina and in the valley of the Peace River, and a tract of land in the Peace River valley area is still known as the French property. Belgian companies operated in the hardrock field and one mine continued operation until World War II.

Exploitation gravitated from the low-grade placer bars along the rivers (river-pebble) to the hardrock district, where the ore deposits consist of karst-controlled residuum and replaced limestone. These deposits are small (50 to 100,000 tons), but of very high grade. As the demand for phosphate fertilizer increased, mining shifted to the much larger and more continuous ores of the land-pebble district. Today there are no river-pebble mines, and only one hardrock mine; 8 companies are mining in the land-pebble district, and 3 companies are removing old tailings and washer debris mounds in the land-pebble district.

River-pebble material was mined from 1888 to 1908. Production reached a maximum of 120,000 tons in 1893, and total production was about 1.25 million long tons. Mining ceased, owing to competition with the higher grade land-pebble material, and because of the tax levied on the river-pebble by the State of Florida (Wyatt, 1894, p. 78).

Land-pebble phosphate mining began in 1891. The first separate production figures are for 1892, when about 22,000 tons was produced. Production has increased steadily and is accelerating. In 1963, an estimated 15 million long tons of beneficiated phosphate was produced, valued approximately at 7 dollars per ton. Phosphate is the third most important industry in Florida, and the land-pebble district is the world's major producer of phosphate rock. Total production from the land-pebble district amounts to 268 million long tons.

The first recorded production of phosphate rock in the United States was in South Carolina in 1867. Only a few tons, valued at \$6.00 per ton, were produced. It is a tribute to the efficiency of the phosphate mining industry that the average value of the 15 million tons produced in Florida almost 100 years later was not much greater -- about 7 dollars per ton (far less in "constant" dollars) despite the continuous rise of land and mining costs.

#### Recovery and Beneficiation

The economic zone or "matrix" of the land-pebble district includes the lower, unweathered unit of the Bone Valley Formation and the underlying residual phosphorite of the Hawthorn Formation. The thickness of the matrix ranges from 0 to 50 feet and averages about 12 feet; the thickest deposits commonly are in depressions in the Hawthorn surface (Cathcart, 1963b, compare figs. 11 and 12).

The matrix is an unconsolidated mixture of phosphate pellets and granules, cobbles, and boulders of phosphatized limestone, quartz sand and silt, and clay. The matrix mined consists, on the average, of about equal parts of recoverable phosphate particles ("pebble" and "concentrate"), quartz sand (tailings), and slime (-0.1 mm material, including clay). Dependent on the thickness of the matrix and the relative abundance of phosphate particles, the content of recoverable phosphate ( $P_2O_5$ ) ranges from about 500 tons to about 35,000 tons per acre, and averages about 5000 tons per acre.

The phosphate particles are beneficiated by washing, screening, and flotation into "pebble" (+ 1 mm) and - "concentrate" (- 1 mm + 0.1 mm) products. Because there is little or no quartz coarser than 1 mm, the "pebble" fraction becomes a beneficiated product merely by screening. The fine fraction (- 1 mm) must be deslimed for removal of the -0.1 mm material. It is then treated by flotation methods to separate the sand-sized phosphate ("concentrate") from the quartz particles. (See simplified flow sheet in road log.)

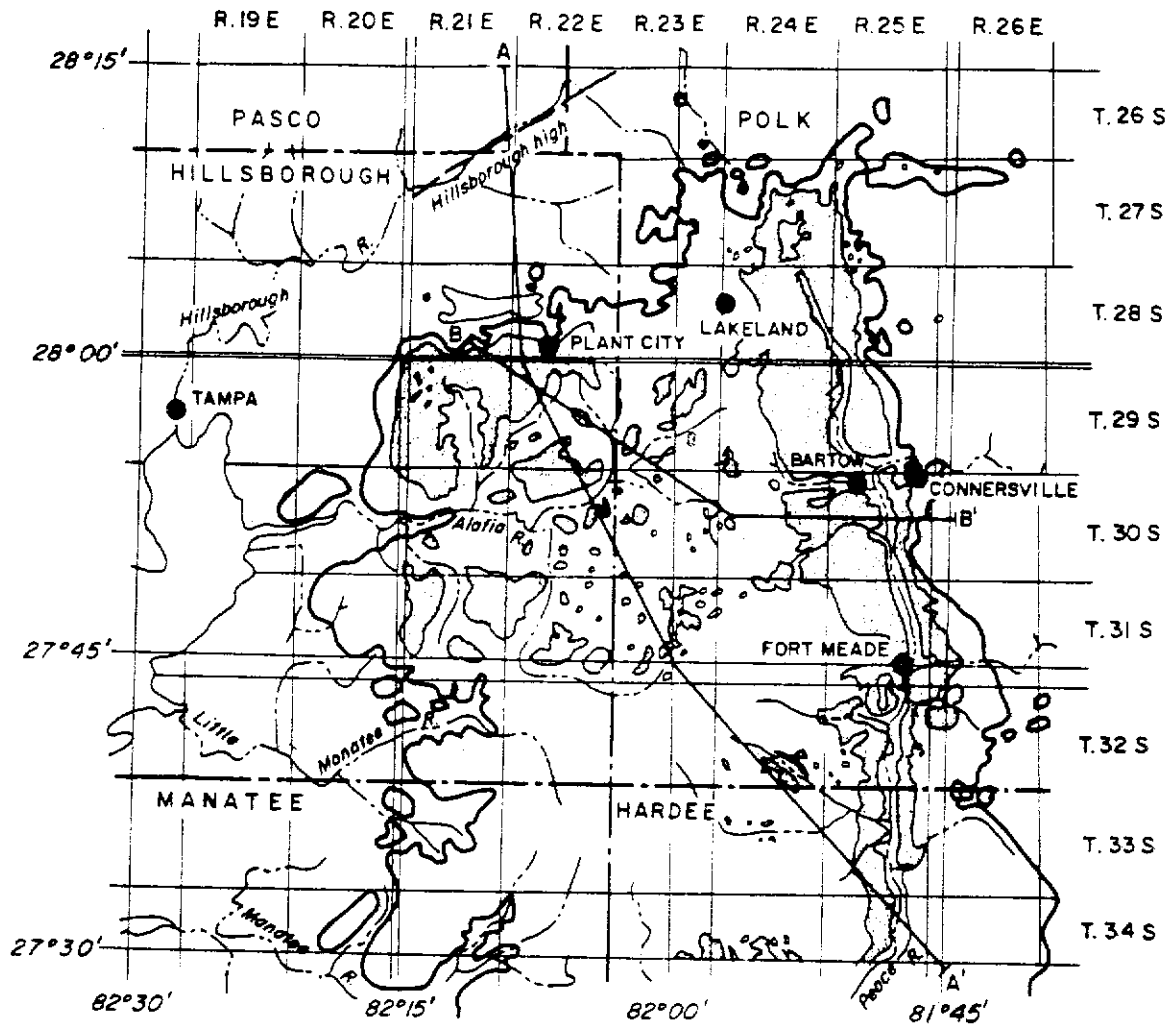
#### Economic Factors

The factors determining the economic value of phosphate deposits are not absolute, and vary in detail with different companies (Cathcart and McGreevy, 1959; Cathcart, 1963a). But in general terms they are as follows:


1. Phosphate particles should contain more than 66 percent BPL (=30 percent  $P_2O_5$ ) and less than about 5 percent of combined  $Fe_2O_3$  and  $Al_2O_3$ ;
2. The recoverable phosphate, as a particulate product, should exceed 400 tons per acre-foot, and the thickness of the matrix must exceed 3 feet -- the minimum thickness minable by large dragline;
3. The volume of material mined per ton of product recovered -- expressed as cubic yards per ton of product -- should be less than 25;
4. The maximum thickness mined -- overburden plus matrix -- is a function of the digging depth of the draglines, and if it exceeds the digging depth, the area can be mined only by putting the dragline on a previously mined bench -- a generally prohibitive requirement.

These are discussed in detail, below.

The economics of grade and recovery are controlled by the geology and mineralogy of the deposits in an interesting manner. As noted elsewhere, particle size and grade are inversely related. However, as the coarsest materials can be beneficiated solely by screening, "pebble" deposits of lower grade than sand size deposits may be profitably mined. This is not always true for "pebble" deposits in residuum or bed clay. These latter have not been reworked, are therefore not as extensively phosphatized, and hence contain calcite diluent which is deleterious in the acid production of superphosphates.



EXPLANATION

 Approximate limit of land-pebble phosphate district

 Area where the ratio of coarse to fine phosphate is greater than 1.

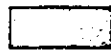
 Area where the ratio of coarse to fine phosphate is less than 1.

Figure 12.--Map showing extent and distribution of coarse and fine phosphate, land-pebble phosphate district, Florida. Section A-A' and B-B' are shown in figures 3 and 13.

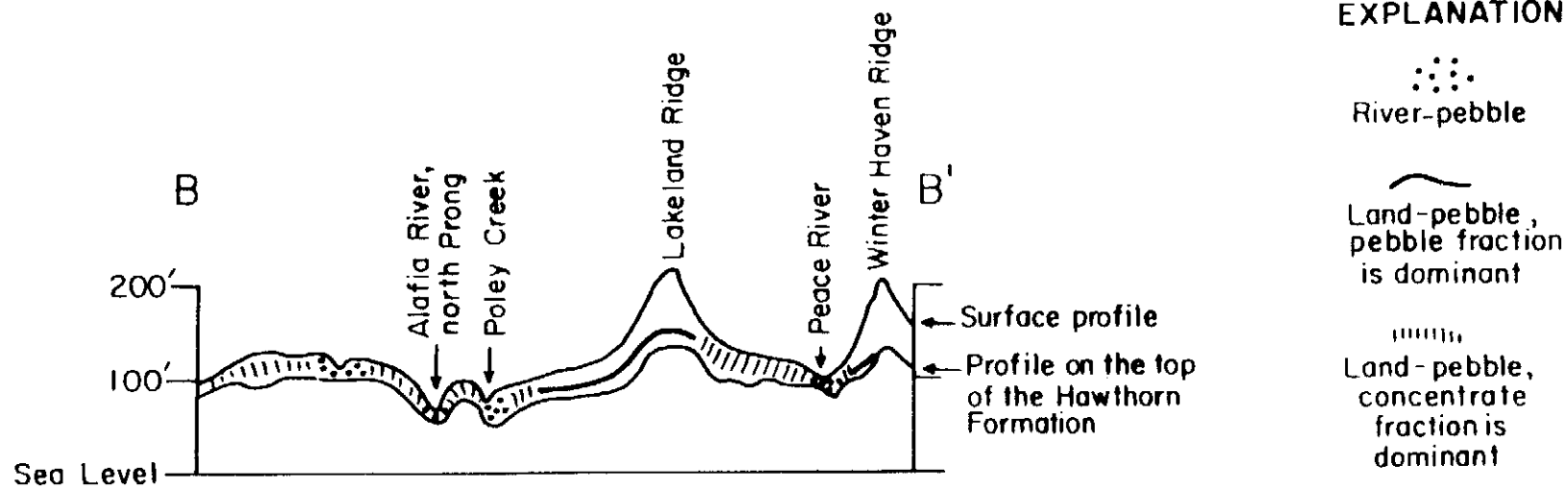


Figure 13. Profile (B-B' fig. 12) showing interrelations of coarse and fine phosphate, topography, and surface of the Hawthorn Formation. Dotted pattern at stream valleys is river-pebble of Pleistocene and Recent age. Heavy solid line - land-pebble phosphate, pebble fraction dominant, cross notched line - land-pebble phosphate, concentrate fraction dominant.

The contents of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the phosphate particles are generally low and uniform (table 4), except at the top of the matrix or the base of the aluminum phosphate zone (fig. 8). Here the phosphate particles are softened and rimmed by bleached borders of wavellite and crandallite (Altschuler, Jaffe, and Cuttitta, 1956). This material is referred to as "soft white phosphate" or "transition zone" by the companies. The zone may or may not be minable, depending on the amount of alumina, the flotation characteristics, and whether or not the replacement rims slime in processing.

Iron content is prohibitively high only locally, where secondary iron oxide cement impregnates the matrix. The secondary goethite is a byproduct of clay transformation, resulting from meteoric water percolation. Its effects are therefore more intense in the upper part of the section.

Recoverable particulate phosphate varies considerably in total amount and in its relative proportions of "pebble" and concentrate. On the ridge, "pebble" tonnages are far higher than concentrate tonnages, and in the lowlands the reverse is true. Both fractions are present in each area. The total tonnage varies with thickness of the matrix, and is somewhat higher in the lowlands area than in the ridge area.

The ratio of cubic yards mined to ton of product depends on the total thickness of the overburden and the relative amounts of waste products (sand tailings and slime) and recoverable product in the matrix. This ratio is somewhat higher on the ridge than on the lowlands, because of the generally greater overburden thickness, and the poorer sorting of the more pebbly facies on the ridge.

#### Size Distribution of Phosphate Particles

The areal distribution of coarse and fine phosphate can be shown most conveniently by plotting the ratio, in tons per acre, of pebble to concentrate (fig. 12). The shaded area on the figure is underlain by phosphorite that has a ratio of pebble to concentrate of less than 1; the unshaded area is underlain by phosphorite that has a ratio of pebble to concentrate of more than 1. The figure clearly shows the predominance of concentrate in the lowlands adjacent to both the Peace and Alafia Rivers and the predominance of coarse phosphate in the Lakeland ridge.

These relations of phosphate product distribution to topography are shown in a profile across the land-pebble district (fig. 13). The valley floors of the major rivers are additional locales for deposits of low-grade pebble phosphate. These "river-pebble" deposits are placers, winnowed of clay and fine phosphate particles by current action. The profile also shows the limit of phosphate deposition on the western flank of the Winter Haven ridge.

## Chemical Composition of the Phosphate Particles

Only a few samples of commercially beneficiated products have been completely analyzed. They are of great interest as guides to potential recovery and also as indications of effectiveness of processing. The average compositions for 10 pebble and 9 concentrate samples are listed on table 6.

The compositional differences between "pebble" and "concentrate" (table 6) are significant in the mining, processing, and sale of phosphate. Most important economically is the fact that the pebble fraction is consistently lower in  $P_2O_5$ . This chemical variation is due principally to differences in content and nature of diluting inclusions. In the pebble from residually enriched Hawthorn deposits calcite is also an important diluent. In the Bone Valley Formation the principal diluent is silt-size quartz (table 2). Figure 9 illustrates development of a coarse phosphate pebble from limestone of the Hawthorn Formation. As shown, much calcite may be present in the nodule prior to reworking. As phosphatization continues, all of the calcite is eventually replaced by phosphate, and pebbles reworked into the Bone Valley in the ridge area generally are completely phosphatized, and quartz becomes the principal diluent. Thus, industrial analyses of Bone Valley beneficiation products show high negative correlation between acid insoluble content and grade of  $P_2O_5$  (Cathcart, 1963a, fig. 13).

The content of  $Fe_2O_3$  and  $Al_2O_3$  (reported together as percent "I and A" in production analysis) is consistently between 2 and 4 percent, in both the pebble and concentrate fractions, except in the weathered upper part of the section where the  $Al_2O_3$  content may be very high -- as much as about 10 percent.

The abundances of most of the minor elements in phosphorites (tables 3 and 6) are not known to differ greatly in pebble or concentrate fractions, but some small differences may be significant. One notable example is the consistently higher uranium content of the pebble fraction in any single deposit. Uranium is discussed in detail below. Other minor element data are given in Jacob, Hill, and others (1933); McKelvey, Cathcart, and Worthing (1951); and Waring and Mela (1953).

The  $P_2O_5$  content of the phosphate particles ranges from 30 to a maximum of about 37 percent (table 2), and is higher in the northern part of the district, in Polk and Hillsborough Counties, and lower in the southern part of the district, in Hardee and Manatee Counties. In the northern part of the district a further division on the basis of  $P_2O_5$  content can be made. Here there is a central area where the phosphate particles contain from 30 to 33 percent  $P_2O_5$ , and peripheral areas where the  $P_2O_5$  content of the particles ranges from 31 to 36 percent (Cathcart, 1956, fig. 170). This is yet another economic effect of the previously discussed facies differentiation in relation to topography during Bone Valley time.



Uranium. The relation between  $U_3O_8$  and  $P_2O_5$  content in the phosphate particles of the land-pebble phosphate district has been examined in some detail by Cathcart (1956) and Altschuler, Clarke, and Young (1958), and reviewed by Davidson and Atkin (1953), and McKelvey, Everhart, and Garrels (1955). In general, the  $U_3O_8$  content of coarse particles is higher than the  $U_3O_8$  content of finer particles, and there is a definite areal distribution -- the highest  $U_3O_8$  content of the phosphate particles is in the area of the Lakeland ridge (Cathcart, 1956, fig. 169). The relation between  $P_2O_5$  and  $U_3O_8$  is inverse when all phosphate particles are considered, though for individual samples the relation is not consistent. For example, when sized samples of phosphate particles were compared in local areas, coefficients of correlation ranged from direct and strong to inverse and weak, and when nodules of a restricted size from many areas are compared, the correlation is direct, but weak. The inverse correlation between uranium and phosphate content is demonstrated, however, in summary data, which irons out local and individual tendencies. In a low-grade deposit of about 10 million tons, the weighted average  $P_2O_5$  content of its products is 31 percent, the  $U_3O_8$  content is 0.019 percent. In a medium-grade deposit of 36 million tons, the average  $P_2O_5$  content of its products is 35 percent and the  $U_3O_8$  content is 0.014 percent, and in a high-grade deposit of 42 million tons, the average  $P_2O_5$  content of total product is 34.5 percent and the average  $U_3O_8$  content is 0.012 percent (Cathcart, 1956).

Altschuler, Clarke, and Young (1958) have shown that uranium is more abundant in the reworked and texturally complex pebbles of the Bone Valley Formation. These pebbles are coarser than simple nodules, and have gone through several cycles of deposition and accretion, during each of which new uranium was acquired by older parts or inclusions in the pebbles. Autoradiographs of such pebbles reveal their uranium distribution and thereby demonstrate the reexposure to marine sources of uranium by reworking (Altschuler, Clarke, and Young, 1958).

#### Gamma-ray Logs

Characteristic gamma-ray logs in the land-pebble district of Florida reflect much of the petrographic history of the deposits. Some of these are compared in figure 14.

At hole A, the highest radioactivity (equivalent to uranium content) is at the base of the aluminum phosphate zone, in the zone of soft white phosphate. Radioactivity is very low in the surficial sand and the calcareous clay at the base of the hole, and is medium to low in the matrix, just below the zone of soft white phosphate. This is a characteristic log of a thoroughly leached section.

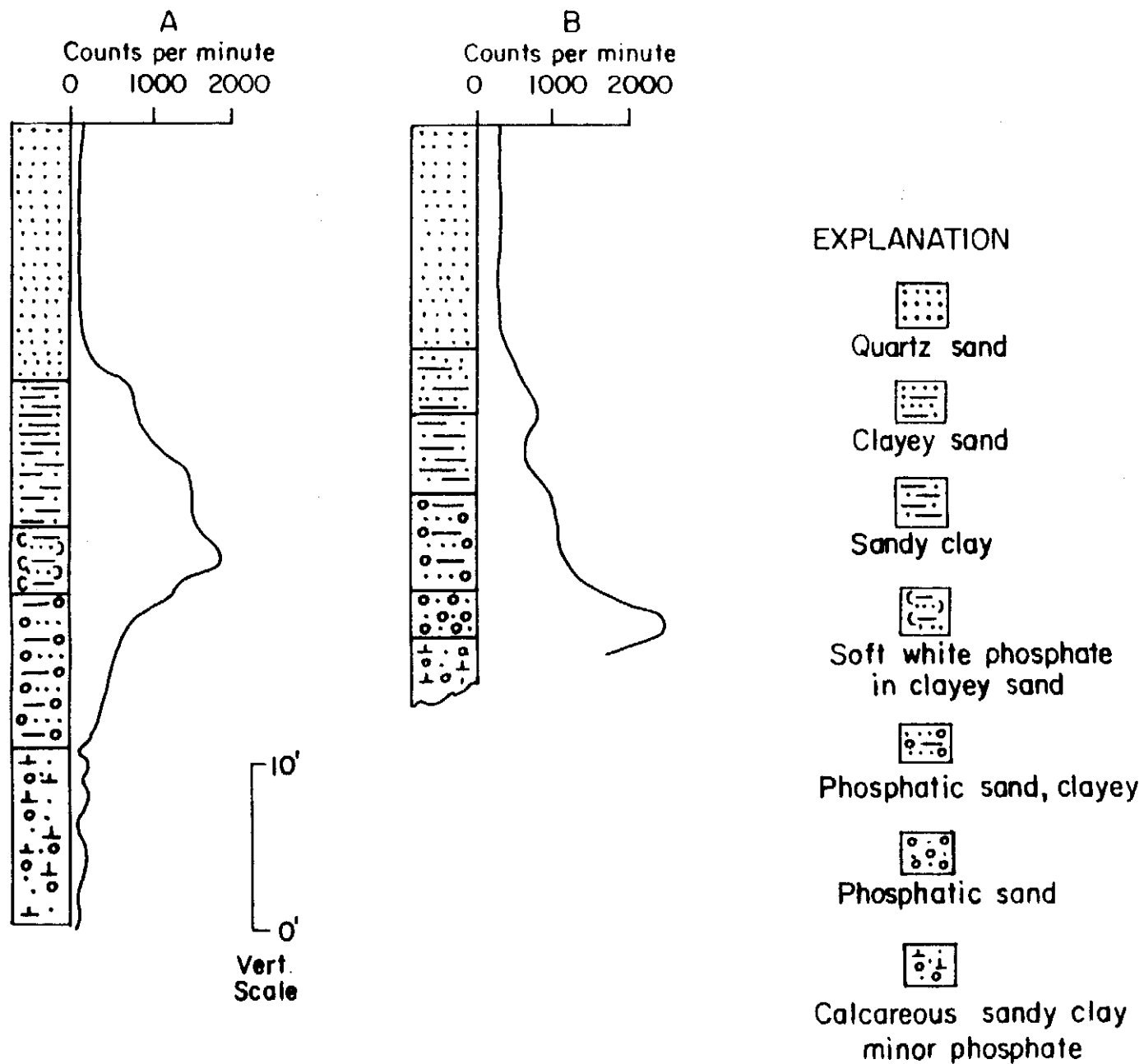


Figure 14. Comparison of gamma ray logs of weathered and unweathered sections, land-pebble phosphate district, Florida. After Cathcart, (1963a, fig. 17).

By contrast, log B represents a hole at a location where the deposit has not been leached. The highest radioactivity is at the base of the matrix in a sand of phosphate and quartz, and the radioactivity drops off sharply in the underlying calcareous clay. The unconsolidated sand at the surface is very low in radioactivity, the clayey sand beds above the matrix are low in radioactivity, and the matrix above the basal bed is fairly high in radioactivity.

The very high radioactivity in the aluminum phosphate zone is characteristic of the land-pebble phosphate district, where uranium has been concentrated in the base of the aluminum phosphate zone, by secondary enrichment from solutions which have leached apatite and uranium from above. The uranium is emplaced by ion exchange in the partly altered and highly porous apatite, in early stages of alteration at the base of the aluminum phosphate zone (Altschuler, Jaffe, and Cuttitta, 1956).

#### Potential Byproducts of the Land-Pebble Phosphate District

Aluminum phosphate zone:- The aluminum phosphate zone is a potential resource of phosphate, and possibly of uranium and alumina. Much research work has been done on recovery of  $P_2O_5$  from the aluminum phosphate zone by the Tennessee Valley Authority, but rock from the zone is being discarded with the overburden at the present time. The following brief description of a process to make fertilizer from the aluminum phosphate zone is based on Hignett, Siegel, Kelso, and Meline (1957).

The raw aluminum phosphate zone material is calcined and uranium and  $P_2O_5$  are extracted with a mixture of nitric and sulfuric acid. After filtration, the extract is concentrated by evaporation and made into fertilizer by continuous ammoniation and granulation. Potash is added to make a three component fertilizer. Uranium can be recovered from the extract prior to the ammoniation step.

Aluminum: - Alumina is not recovered in the above process; about half of the total alumina goes into the fertilizer and the rest to waste. However, alumina is being recovered from aluminum phosphate minerals in Senegal, and is a potential byproduct in the aluminum phosphate zone which is an easily beneficiated resource of hundreds of millions of tons of the element (Altschuler, Jaffe, and Cuttitta, 1956).

Fluorine:- A large tonnage of phosphate rock is treated to make phosphoric acid in the land-pebble phosphate district, and in the wet process the 3 to 4 percent fluorine in the phosphate rock is liberated. Fluorine must be eliminated from the stack gases to reduce air pollution and a part of this fluorine is being recovered as fluosilicic acid by Virginia-Carolina Chemical Corp. The product is sold to Kaiser Aluminum Company and is treated further at their

plant near Mulberry. Additional fluorine is recovered as sodium fluosilicate by Swift and Company and U. S. Phosphoric Products Company.

Uranium: - Uranium was recovered experimentally from phosphoric acid at several plants in the land-pebble district. The process of recovery was too costly to compete with the high-grade uranium ores of the western United States, and no uranium is now being recovered.

## ORIGIN OF THE PHOSPHATE DEPOSITS

The phosphate deposits of the land-pebble district are of complex derivation: partly residual, partly reworked, and substantially altered by post-depositional lateritic weathering to aluminum phosphates.

The Hawthorn Formation, an extensive body of open shelf carbonate deposits underlying vast areas of the southeast coastal plain, is the immediate source of secondary phosphate deposits of Florida. The primary precipitation of marine phosphorite such as that in the Hawthorn has been related by Kazakov (1937) to the upwelling of deep phosphate-rich ocean waters along steeply inclined continental slopes onto the relatively shallow areas of the continental shelves. This theory is a cogent synthesis of oceanographic data. It is known that aqueous phosphate solubility varies inversely with pH. Dissolved phosphate in ocean water therefore varies directly with dissolved CO<sub>2</sub>, and is high in the cold waters of deep ocean basins (Atkins, 1923; Sverdrup, Johnson and Fleming, 1942). The upwelling of such deep water to shallow, more agitated and warmer zones causes loss of dissolved CO<sub>2</sub>, increase in pH, and supersaturation of phosphate, and would further the precipitation of apatite.

Too little is known of the stratigraphy and phosphate distribution within the Hawthorn Formation to warrant an interpretation of its lithology in terms of Kazakov's theory. However, as a number of other phosphate deposits in the eastern United States are of economic interest largely because of second-cycle enrichment or reworking, or both, these processes of secondary concentration merit careful study. The phosphate deposits of Tennessee, Arkansas, North Carolina, and South Carolina are all examples of such multistage concentration.

The Hawthorn Formation in the land-pebble district was deposited in shallow water on the flanks of the Ocala uplift. In this area the formation contains minor amounts (2 - 10%) of low-grade, silt- and sand-size phosphate pellets dispersed in a matrix of fine-grained and partly bio-clastic limestone and dolomite. Exposed parts of the Hawthorn Formation were leached of carbonates during an erosional interval preceding Bone Valley time. The insoluble residue, further enriched in phosphate cements and pellets, quartz, and clay, accumulated on the surface, particularly in solution depressions. Such deposits are mined today from trapped pockets underlying the Bone Valley Formation, if their tonnage and grade are adequate.

Most of phosphatized and residually enriched weathering debris on the Hawthorn surface was reworked during marine transgression, into the crossbedded and graded-bedded, pebbly and clayey sands of the Bone Valley Formation. The phosphate is differentiated into low-grade coarse material on the central basement ridge and high-grade, fine-grained material in the lowlands adjacent to the ridge. This ridge, which underlies the contemporary Lakeland ridge, existed as part of the submerged topography at the time of phosphate reworking, and coarse pebbly phosphate is a lag deposit of the submarine winnowing of fines from this shallow ridge area. The ridge influenced deposition throughout Bone Valley time and has been uplifted considerably since then.

The phosphorite fills low areas on the Hawthorn surface. It was not deposited east of the Winter Haven Ridge, just east of the Peace River, and was restricted on the north by the Hillsborough high, a positive element during lower Bone Valley time. It was partly restricted on the west by the ridge near Valrico. To the south, the paleogeography is not known. However, the regional slopes of both the Hawthorn and the present land surfaces, and the lack of known structural or topographic uplifts to the South, make plausible the assumption of open-water marine conditions. The general paleogeography at the time of deposition of the Bone Valley was that of a wide, south-facing, marine embayment, or estuary, or both -- a shallow-water near-shore environment.

Lateritic weathering altered the phosphorite and formed the aluminum phosphate zone, a secondary feature. The economic phosphate deposit is also a second-stage deposit, and the origin of the phosphate in the Bone Valley can be accounted for by (1) weathering of the source limestone to remove carbonate, concentrate the phosphate particles, and phosphatize surfaces and fragments of limestone and dolomite.

(2) reworking in a marine environment to further concentrate the phosphate particles and to enrich them in  $P_2O_5$  and uranium; and (3) post-depositional alteration to form the aluminum phosphate zone.

Ketner and McGreevy (1959) have suggested that the sequence of lithology in central Florida, descending as follows,

quartz sand  
clayey quartz sand  
clayey quartzose phosphorite  
quartzose and clayey phosphatic limestone (or dolomite)

may be the expression of a single weathering profile developed continuously or discontinuously over the area.

There is appreciable evidence that the upper sand mantle is residual (Altschuler and Young, 1960), and that pockets of phosphorite of entirely residual origin fill large and small solution depressions in the surface of the Hawthorn. However, a residual origin for the entire Bone Valley, or a large part of it, seems untenable in view of its content of Pliocene vertebrates (Simpson, 1929; Cathcart and others, 1953; Brodkorb, 1955); the evidence of appreciable increase in primary stratigraphic structures in the Bone Valley Formation overlying leached accumulated Hawthorn (fig. 7); the evidence of unconformity; and the changes in mineralogy concurrent with unconformity (see section on Primary lithology).

### The Search for New Deposits

The search for other deposits of similar type must take into consideration favorable source areas and favorable conditions for secondary enrichment.

1. Phosphatic limestones and marls like those of the Hawthorn Formation and the Duplin Marl are generally open shelf deposits adjoining or inland from steep continental slopes, and thus auspiciously situated for the precipitation of phosphate from upwelling currents, as suggested by Kazakov (1937). McKelvey (1964) has discussed the geologic and meteorologic consequences of upwelling of cold nutrient-rich waters.
2. The geologic opportunities for enrichment by subaerial weathering, and by marine reworking, may be delineated through appraisal of epochs, and extent and location of both weathering and marine transgression. Locales of residual concentration may be anticipated through understanding of groundwater drainage, joint systems and stratigraphic or geochemical evidence of subaerial exposure. Locales of mechanical enrichment may be anticipated through study of sedimentary structures which reflect wave and current activity.
3. The search for deposits of favorable grade and tonnage should take cognizance of the influence of structural position and paleogeography on the amount of clastic diluent, and the thickness of the deposits.
4. The nature and paleogeography of younger deposits must also be studied as a means of predicting areas of tolerable overburden thickness.

## Prospecting Methods

As large areas of the southeastern United States might contain sedimentary phosphorite deposits, the possible dimensions of the search efforts, in terms of time, area, and cost become a significant problem. The extensive use of gamma-ray equipment to detect phosphorite by its radioactivity greatly minimizes the problem. Marine phosphorite has much more uranium (generally ranging from 0.005 to 0.015%<sup>u</sup>) than the closely associated limestone, sand, and shale (0.001 to 0.005%<sup>u</sup>). This is particularly true of reworked deposits in which new increments of marine uranium may be secondarily emplaced in the apatite by ion exchange (Altschuler, Clarke, and Young, 1958). Thus gamma-ray logging of water and oil wells can generally provide cheap but reliable information on the occurrence of phosphate. Airborne radioactivity logging is another quick means of discovering or extending phosphate deposits under shallow burial (Moxham, 1954). Radioactivity measurements by Geiger Counter may be used to monitor stream placers and thereby to quickly assay naturally integrated samples of broad areas through a watershed.

Chemical determinations for phosphate and uranium should be made a part of any radioactivity prospecting program as a means of establishing the quantitative relationships among equivalent uranium, actual uranium present, and  $P_2O_5$ . Such analyses also provide a safeguard against misleading measurements due to disequilibrium induced by leaching or post-depositional enrichments. A convenient semiquantitative field test for phosphate has been devised by Leonard Shapiro of the U. S. Geological Survey (Shapiro, 1952).



## PATTERN OF THE FIELD TRIP

The land-pebble phosphate district of Florida covers about 2000 square miles in Polk, Hillsborough, Hardee, and Manatee Counties. The surface in this area is blanketed by quartz sand; exposures of the phosphorite are confined almost entirely to the mine pits. The major rivers--the Peace and Alafia--flow, in part of their courses, on the Hawthorn Formation, but slumping of the banks has covered the overlying Bone Valley Formation, and sand bars along the rivers cover most exposures of the Hawthorn Formation. Road cuts in the district seldom expose even the top of the Bone Valley Formation. We therefore, depend on mine exposures for the exposition of stratigraphy and economic geology, and we wish to thank the phosphate companies for their cooperation in allowing access to their mines. All mining companies in the district--The American Agricultural Chemical Co., Armour Agricultural Chemical Co., American Cyanamid Co., Davidson Chemical Division of W. R. Grace and Co., International Minerals and Chemical Corp., Smith-Douglass Co., Inc., Swift and Company, and Virginia-Carolina Chemical Corp., have cooperated to the fullest extent.

During the course of the field trip, we will cross the central Lakeland ridge several times, and observe features of the regional geomorphology. The ridge area has karst topography, controlled by joints and faults. It abounds in round sinkhole lakes, which are particularly evident in the city of Lakeland. The contrast with the lowlands will be evident. The lowland area between the ridges and the valleys of the present streams is a flat to gently rolling sand plain, dotted with irregularly shaped, shallow ponds, called "bayheads." Cypress ponds, one form of "bayheads," are well developed in the area northeast of Lakeland, and we will be able to observe several of these so-called "cypress domes."

The visits to the mining pits in the area will be based in part, at least, on logistics. Driving from Tampa, for example, makes it logical to visit the westernmost mine first, and to proceed in an orderly manner from that mine toward our overnight destination--Lakeland. For this reason, the last stop of the first day will be at the mine closest to Lakeland, the Orange Park mine.

We will be able to contrast the overall features--the similarities and the differences--of the mines on the ridge and the mines in the lowlands as follows:

1. Ridge mines contain very abundant "pebble", lowlands mines contain abundant concentrate, but individual beds in each area may be "pebble" or concentrate beds or a mixture.

2. The phosphate particles tend to be dark-colored in the ridge mines and light-colored in the lowlands mines, although all colors are present at all mines.

3. Crossbedding and graded bedding are present at all mines, but these features are much more prominent and easily seen in the mines in the ridge.

4. The ridge mines are sandier than the lowlands mines, and the lowlands mines at the west and north fringes of the district tend to have more clay than those in the Peace River Valley.

5. Ridge mines are deeper than lowlands mines; the overburden in the ridge mines is thicker, and in many places the matrix is thicker.

6. Quartz sand of the overburden tends to be coarser grained in the mines in the ridge than in the mines in the lowlands.

Mining with large draglines in unconsolidated material is extremely rapid, and land rehabilitation is carried on concurrently with the mining, so the mined-out pits are rapidly back-filled and are not available for examination. For this reason, the guidebook does not contain a road log, which will be made just before the trip is taken, mimeographed, and passed out to the participants at the start of the trip. Even using this method, stratigraphic sections, taken about a week prior to the trip, may be covered, but should represent the sections to be seen at the mines. The road log will show directions and distances to the mine offices only, not to the actual exposure at the mines. For anyone desiring to repeat this trip at a later date, inquiries must be made at the mine office for permission to enter the mining area, and for directions to the mining area. Hard hats and safety glasses are required for visits to the mines. These will be provided for the field trip through the courtesy of the mining companies.

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