

IRON MINERALS IN SEDIMENTARY PHOSPHORITES
OF THE SOUTHEASTERN UNITED STATES

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INTRODUCTION

Phosphorus is a vital nutrient for plants and animals and is now commonly made available in the food chain through the agricultural application of phosphate fertilizers. Of the marketable phosphate rock produced in the United States, about 64 % goes into fertilizer production, 9 % into industrial chemicals ranging from water conditioning to incendiary bombs (Figure 1), and 28 % into exports (Stowasser, 1977). With the continued worldwide decline in the quality of phosphate raw materials, nonpremium-grade phosphate rock has been recently introduced into commercial manufacturing of phosphate products. Non-premium-grade phosphate rock, which ranges from 23 to 31% P_2O_5 , contains significant amounts of iron, aluminum, magnesium and other mineral impurities. The rising level of these contaminants causes problems for current processing technology, which was originally developed for the once abundant premium-grade ores, which typically range from 34 to about 37 % P_2O_5 . Iron is a particularly troublesome impurity which adversely affects phosphate processing and products (Table 1); however, the iron mineral species in sedimentary phosphorites are diverse and their identities and distribution in the ores are only poorly known (McClellan and Gremillion, 1980).

The purpose of this paper is to describe the authigenic and diagenetic iron minerals associated with sedimentary phosphorites of the southeastern United States. This region contains three economically important phosphorite deposits (Figure 2), which account for 90 % of the marketable phosphate production in the United States (U. S. Bureau of Mines, 1986). The clastic phosphorites of the upper portion of the Hawthorn Group in central Florida are used in all facets of fertilizer production. The primary phosphorites of the Pungo River Formation in North Carolina are used in the manufacture of phosphoric acid and ammonium phosphates. The brown rock phosphorites of the Bigby-Cannon

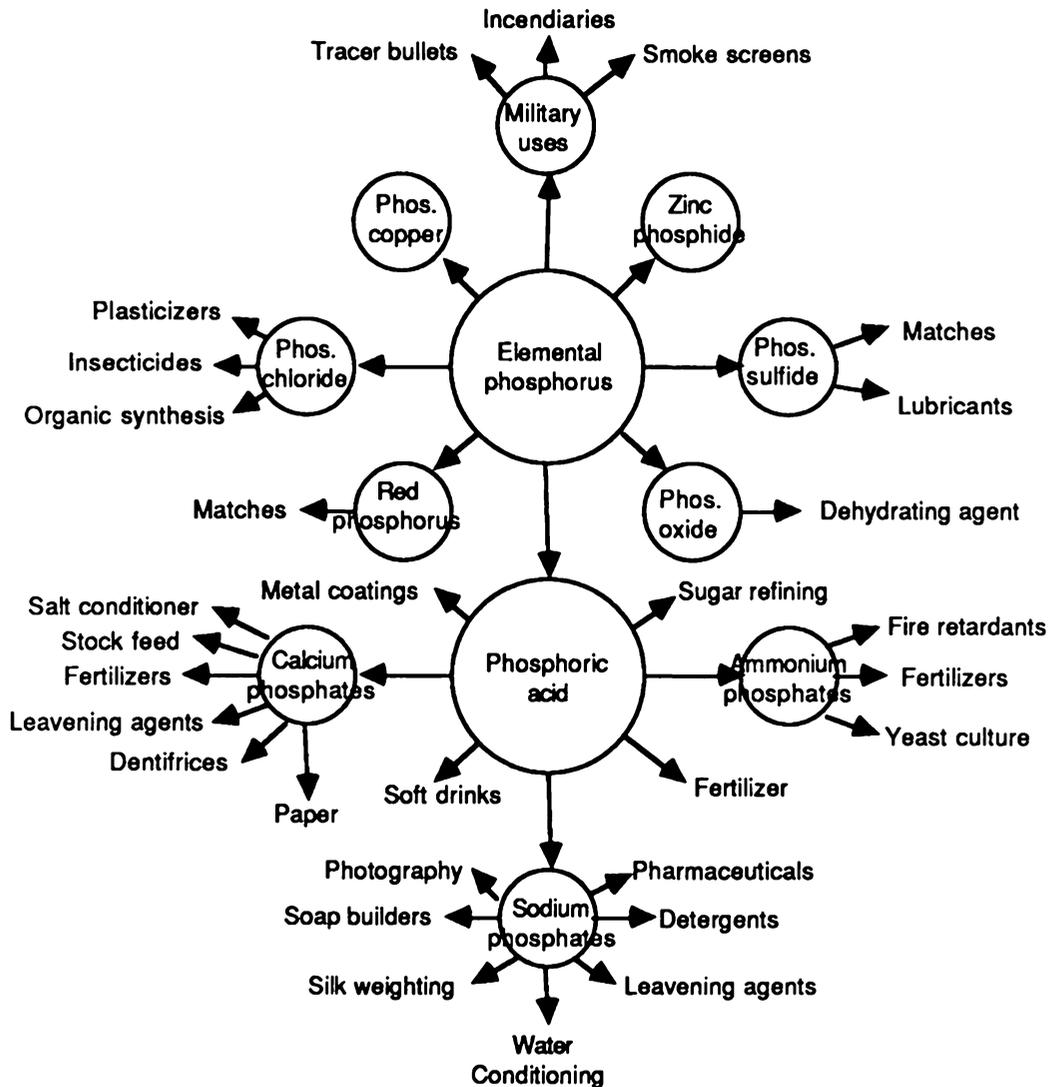


Figure 1. Intermediate and end products derived from phosphate rock (Waggaman and Ruhlman, 1960).

Table 1. Some effects of iron on the most common phosphate products
(after Lehr, 1980; McClellan and Gremillion, 1980; and McClellan and Lehr, 1982).

PROCESS	PRODUCT (% P ₂ O ₅)	EFFECT OF IRON CONTAMINATION
DH WPA by acidulation	FG H ₃ PO ₄ (28-40)	Precipitation of Fe orthophosphates in acid when concentration ≥ 35 % P ₂ O ₅
	SWP H ₃ PO ₄ (40-50)	Precipitation of Fe orthophosphates
	MG H ₃ PO ₄ (50-54)	Precipitation of acidic, insoluble Fe orthophosphate sludges
	CMG H ₃ PO ₄ (54-70)	Precipitation of acid ferrous phosphate
	Super H ₃ PO ₄ (> 70)	Precipitation of insoluble pyro-, tripoly-, and metaphosphate salts
Ammoniation of WPA	MAP (56-61) or DAP (46-72)	(1) Precipitation of highly reactive, water-insoluble Fe and Al phosphate gels (2) Precipitation of water-insoluble, low citrate-soluble Fe and Al phosphate salts ("Haseman compounds")
	APP (57)	(1) Precipitation of Fe or Fe-NH ₄ pyro-, tripoly-, or metaphosphate salts (2) Precipitation of Fe pyrophosphate salt, which forms scale on production equipment
Phosphate rock + H ₂ SO ₄	OSP (16-21)	(1) Precipitation of insoluble Fe and Al phosphate gels (2) Unreacted phosphate rock
Phosphate rock + H ₃ PO ₄	CSP (43-48)	Byproduct WPA "sludge acids" contain large amounts of K, Al, Fe phosphate salts, which partially dissolve and react with Fe and Al released from phosphate rock to form similar insoluble phosphates
Phosphate rock + HNO ₃	NP (15-30)	(1) As in ammoniation of WPA (2) Substitution in composition of ammoniation products upon ammoniation
Electric furnace (Phos. rock + coke + silica)	Elemental P	(1) Byproduct ferrophosphorus lowers the elemental phosphorus yield and has a 0.4 % market value, increases power requirements, and reacts with furnace carbon electrodes to decrease their current efficiency and service life (2) Difficulties in tapping byproduct slag due to increased viscosity

Abbreviations: DH - dihydrate process; WPA - wet process acid; FG - filter grade; SWP - strong wet process; MG - merchant grade; CMG - concentrated merchant grade; MAP - monoammonium phosphate; DAP - diammonium phosphate; APP - ammonium polyphosphate; OSP - ordinary superphosphate; CSP - concentrated superphosphate; NP - nitric phosphates.

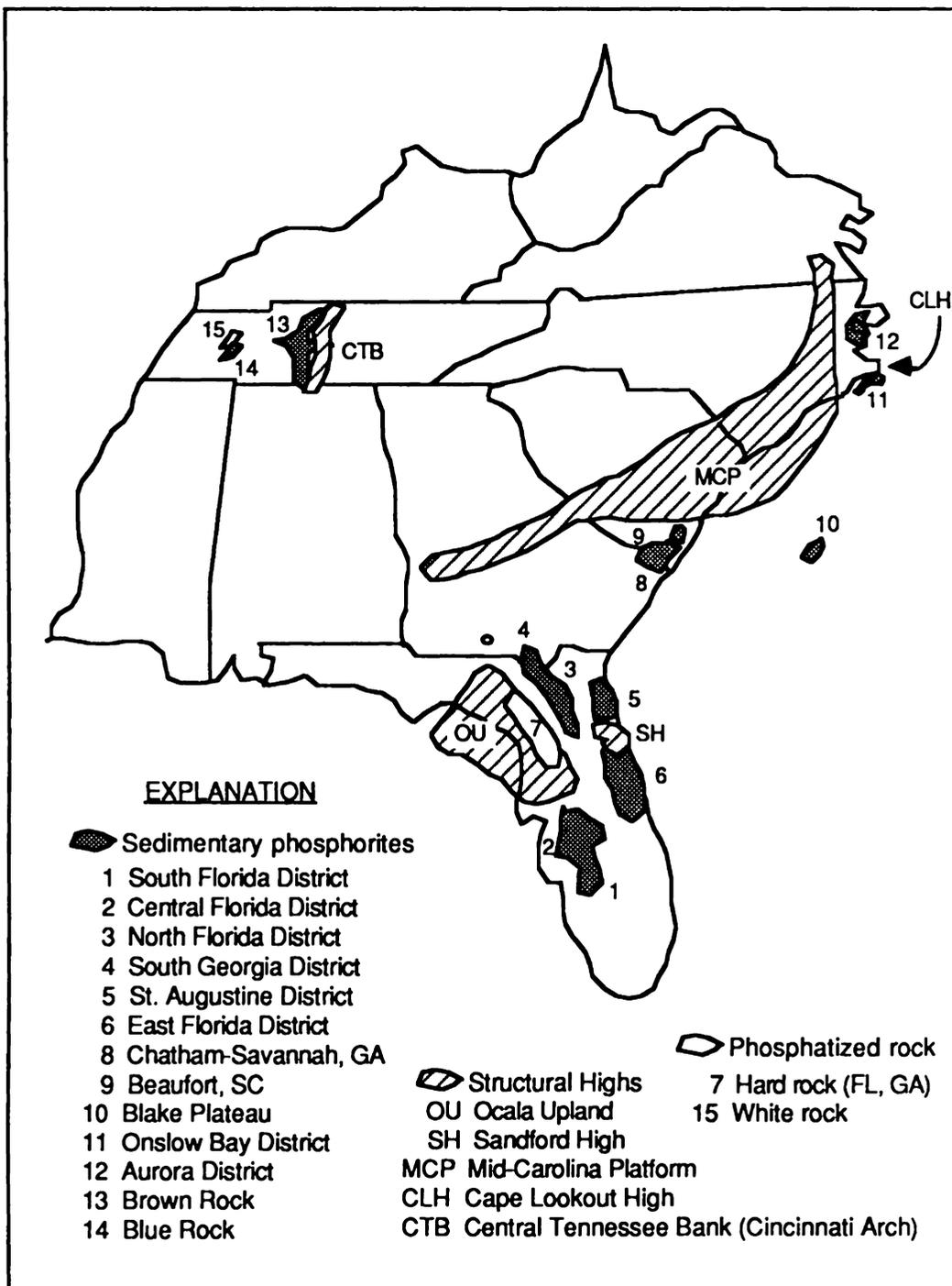
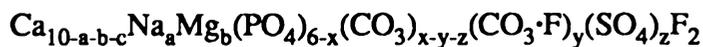


Figure 2. Location of sedimentary phosphorite deposits in the southeastern United States (after Cathcart, 1980 and Riggs, et al., 1985).

Formation in the Central Basin of Tennessee are used exclusively in electric furnace production of elemental phosphorus.

These three phosphorite deposits differ in geologic setting and degree of weathering. The North Carolina Pungo River and Florida Hawthorn phosphorites are contemporaneous and part of the Atlantic Miocene coastal plain-continental shelf phosphorite deposits, which extend from southeastern Virginia to Florida. Whereas the Pungo River phosphorites are relatively unweathered, the Hawthorn phosphorites exhibit extensive and variable degrees of weathering. The Tennessee brown phosphorites are the residual products of middle to late Pleistocene weathering of Ordovician phosphatic limestones.

Sedimentary phosphorites are authigenic minerals precipitated biochemically or inorganically in a shallow, reducing marine environment. A sediment or rock is called a phosphorite when it contains 10 % or more (volumetrically) individual phosphate grains mixed with any other mineral component (Riggs, 1979a). The fundamental component (10-100 %) of a sedimentary phosphate macrograin is the matrix (Riggs, 1979a), which consists of microcrystalline (0.02- to 0.2 μm) francolite, or carbonate fluorapatite, (Lehr, et al., 1967). To avoid confusion, this matrix shall henceforth be referred to as the "apatite matrix." Crystallite chemical composition is heterogeneous primarily due to the systematic isomorphous substitutions for both cations and anions exhibited by francolite (Nathan, 1984). Table 2 summarizes some possible substitutions in the apatite structure. The general structural formula for francolite can be idealized as:



where a, b, c = moles of Na, moles of Mg, and number of Ca vacancies respectively
 y and z = moles of $(\text{CO}_3\cdot\text{F})^{3-}$ and SO_4^{2-} substitution respectively
 $x = y + a + 2c$ (Nathan, 1984).

Micrograined components constitute the remainder of a phosphate macrograin and occur as discrete free inclusions of invertebrate fossils, carbonates, clastic phosphorite pellets, and/

Table 2. Some possible substitutions in the apatite structure (Nathan, 1984).

Constituent ion	Substituting ion
Ca^{2+}	Na^+ , K^+ , Ag^+ Sr^{2+} , Mn^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , Ba^{2+} Sc^{3+} , Y^{3+} , R.E. ³⁺ (rare earths), Bi^{3+} U^{4+}
PO_4^{3-}	CO_3^{2-} , SO_4^{2-} , CrO_4^{2-} AsO_4^{3-} , VO_4^{3-} , $(\text{CO}_3 \cdot \text{F})^{3-}$, $(\text{CO}_3 \cdot \text{OH})^{3-}$ SiO_4^{4-}
F^-	OH^- , Cl^- , Br^- O^{2-}

or terrigenous materials (Riggs, 1979a). Previous works which include discussions concerning the presence of iron minerals in phosphorites of the southeastern United States include Hill, et al., (1931), Riggs (1979a), Smith and Whitlatch (1940), Stow (1968, 1969, 1976), Swanson and Legal (1967), and Weaver and Wampler (1972).

A modified version of Riggs' (1979a) classification scheme will be used to describe the various components of sedimentary phosphorites. Appendix 1 is a review of terminology and a discussion of the modifications. Table 3 is a translation of industrial to scientific language.

Table 3. Translation of phosphatic terms.

mining term	locality	geological term
land pebble	Florida	predominantly intraclastic phosphorite
river pebble	Florida	lithochemical phosphorite
hard rock	Florida	phosphatized limestone (metachemical phosphorite)
leached zone	Florida	stage I or II metachemical phosphorite
gossan	Florida	stage II metachemical phosphorite
pebble	North Carolina	predominantly intraclastic phosphorite
phosphatic sand	Tennessee	pelletal and skeletal phosphorite
muck	Tennessee	pelletal and skeletal phosphorite and clays
plate rock	Tennessee	phosphatized limestone (metachemical phosphorite)

MATERIALS AND METHODS

The study area included the Central and South Florida Phosphate Districts, the North Carolina Aurora Phosphate District, and the Tennessee Brown Rock Phosphate District. Vertical profiles were obtained in the Agrico Payne Creek, Grace Four Corners, and IMC Noralyn mines of central Florida (Figure 3) and in the Stauffer Spring Hill, Columbia, and Giles County mines of central Tennessee (Figure 4). Extremely hazardous conditions accompanying a wet pit in the TGS Lee Creek mine of North Carolina prevented sampling a vertical profile; however, several pebbles were collected from spoil piles near the dragline.

Iron is generally present in phosphorites of the southeastern United States as very fine grain mineral inclusions (Hill, et al., 1931 and Weaver and Wampler, 1972), which necessitated the use of scanning electron microscopy to identify the iron-bearing phases. Selected phosphorite grains of deslimed separates of each profile were embedded in *EpoFix* resin, cross-sectioned, polished to 0.05 μm , and then examined with scanning electron and reflected light microscopy. The mineral inclusions in the apatite matrix were readily detected using backscattered electrons and then analyzed with energy dispersive X-ray (EDX). Clay mineralogy was determined using X-ray diffraction and differential scanning calorimetry (DuPont 1090 scanning calorimeter) after Mg^{2+} -glycerol or K^+ saturation and heat treatment. Appendix 2 gives a detailed description of the various methods used in sample preparation.

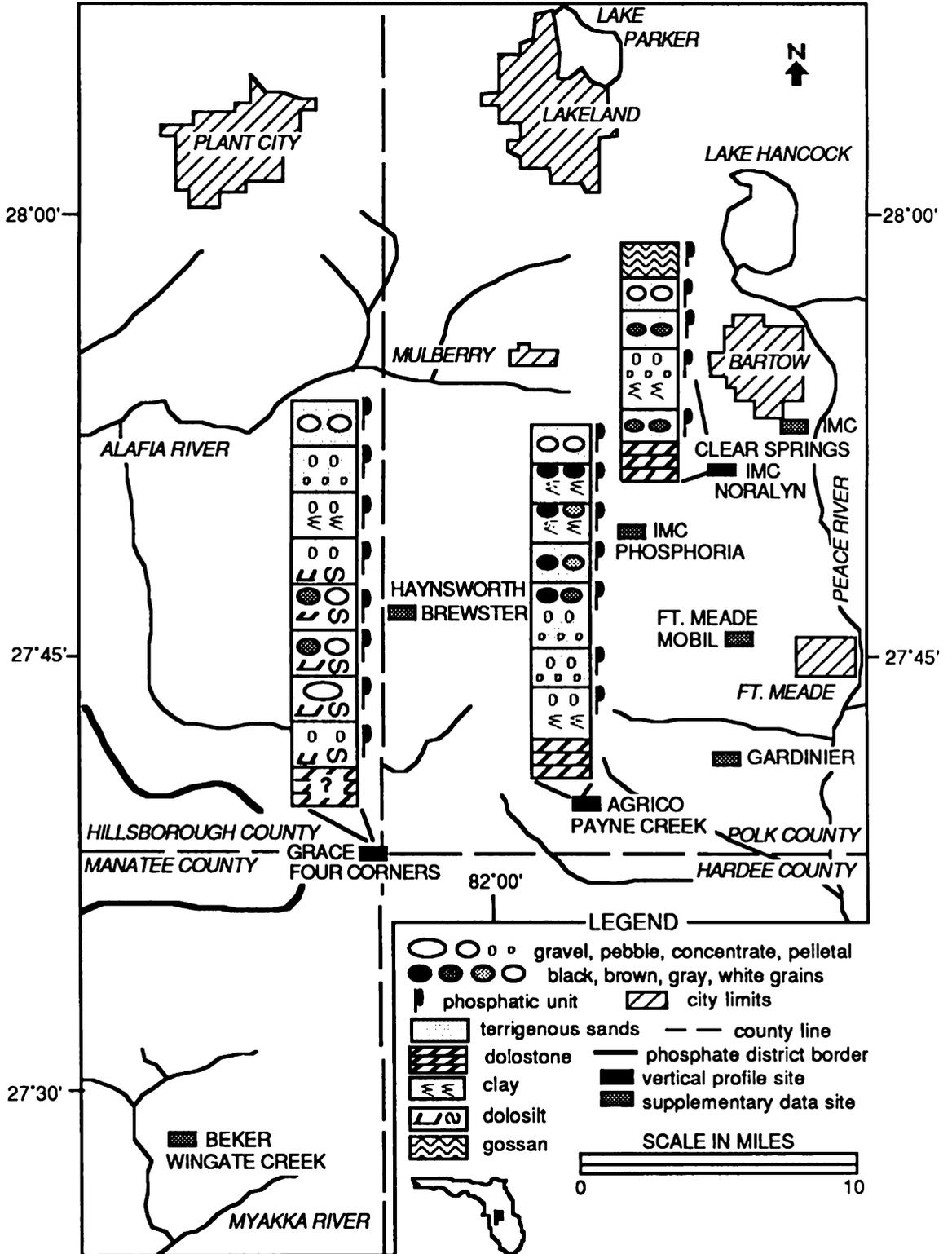


Figure 3. Sample location map in the Central and South Florida Phosphate Districts (after Altschuler, et al., 1964 and IMC, 1980).

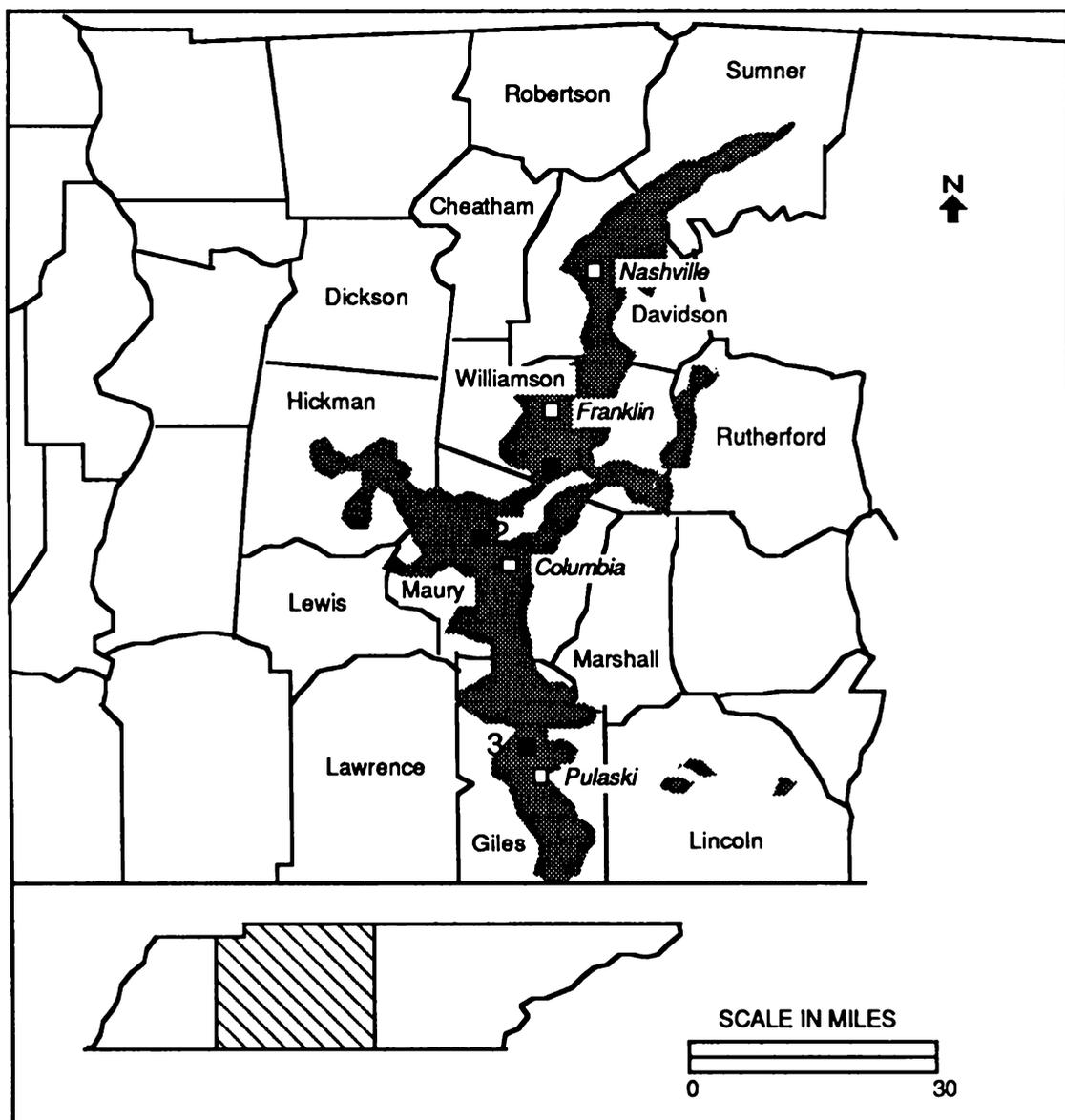


Figure 4. Sample location map of some cutter deposits in the Tennessee Brown Rock District (after Smith and Whitlatch, 1940).

PHOSPHORITE SEDIMENTATION

Atlantic Coastal Plain - Continental Shelf

The structural framework which controlled the episodic formation and deposition of phosphorite throughout the Florida and North Carolina Miocene-Pliocene consisted of a series of arches or topographic highs associated with the Ocala Upland and Mid-Carolina Platform High (Figure 2) (Riggs, 1979b and Riggs, et al., 1985). A broad shallow-water coastal and shelf marine environment existed around the topographic highs and resulted in an inner perimeter of orthochemical and intraclastic phosphorites (Riggs, 1979b).

Florida

Intraclastic phosphorites were deposited during the early active stages of the phosphogenic system in carbonates and later in terrigenous sands and clays. Some of these early Miocene phosphorite deposits were exposed to subaerial weathering and subsequently reworked and redeposited with primary phosphorites during an ensuing phosphogenic transgression. Phosphogenesis continued intermittently probably to the late middle Miocene and resulted in considerable phosphorite sedimentation in adjacent major entrapment basins (Riggs, 1979b). During the Pliocene, some of the Miocene deposits in the upslope areas adjacent to the Ocala Upland were reworked by fluvial processes and redeposited in complex estuarine or open-bay facies (Riggs, 1984). In the downdip areas, primary allochemical phosphorites accumulated in shallow marine environments. Collectively, these Miocene and Pliocene phosphorites constitute the "land pebble phosphate" districts of north, central, and south Florida. Some of the fluviually reworked phosphorites were concentrated in river bars and channel fillings as "river pebble phosphate."

The outer perimeter deeper basinal marine environments and offshore areas around the Sandford High accumulated phosphorite pellets (Riggs, 1979b), which dominate the St. Augustine, East, and portions of the South Florida Districts (Riggs, 1979a). Phosphorite sands and clays were deposited locally over a long, narrow belt of Eocene and Oligocene limestones on the Ocala Upland area during a series of maximum transgressions sometime during the Miocene. With subsequent subaerial exposure, phosphate was removed from these marine phosphorite beds by intense groundwater leaching and reprecipitated at depth as secondary apatite mostly replacing limestone (Espenshade and Spencer, 1963). Two types of secondary apatite are present in the Ocala Hard Rock District: "hard rock phosphate," which is a hard massive apatite forming irregular botryoidal masses, and "soft rock phosphate," which is a soft apatite with clay-like appearance and consistency (Sellards, 1913).

North Carolina

A series of environmental migrations in response to marine onlap resulted in cyclic phosphorite and carbonate depositional sequences. The sites of maximum phosphorite accumulation occurred in two regional embayments, defined by the Cape Lookout High: the Aurora embayment to the north and the Onslow embayment to the south (Riggs, et al., 1985). The Aurora embayment contains producing phosphate mines in the Aurora Phosphate District, and the offshore Onslow embayment contains two recently discovered phosphate districts: the northeast Onslow Bay Phosphate District and the southwest Frying Pan Phosphate District (Riggs, et al., 1985).

Tennessee

The structural framework which controlled sedimentation throughout the Central Tennessee late middle to middle late Ordovician was the Central Tennessee Bank topographic high (Figure 2) associated with the Cincinnati arch and its local swelling, the Nashville Dome (Wilson, 1962). A shallow-water coastal reef environment existed along the western part of the broad, relatively north-south trending Central Tennessee Bank (Wilson, 1962). Phosphogenesis probably resulted in orthochemical and intraclastic phosphorite sedimentation and phosphate replacement of reef detritus on or near the reef front. Low-energy and periodic high-energy physical reworking by normal and storm wave action respectively, ground the intraclasts into subangular to subrounded pellets and the skeletal phosphorites into rounded sands. The pelletal and skeletal phosphorites accumulated with reef detritus mainly on the fore reef slope to form a phosphatic limestone facies, which graded west into deeper marine carbonate environments and east into a tide-level shelf lagoon facies (Wilson, 1962). Intermittant uplift of the limestone plateau during the late Pliocene to middle or late Pleistocene resulted in fluvial removal of rocks, which had been subsequently deposited over the phosphatic limestones, leaving them exposed to the weathering processes which mechanically reworked the phosphorites into residual "rim," "blanket," and "cutter" deposits (Smith and Whitlatch, 1940). The outcropping edges of phosphatic limestones that remain covered by overlying rocks weather to form rim, or "collar" deposits. Phosphatic limestones that have been exposed at the surface to weathering may form very extensive blanket deposits, which may cover gently sloping terraces or crown low hills. Preferential dissolution of phosphatic limestones by acid groundwater along joint planes produces cutter deposits.

MINING HISTORY AND TECHNOLOGY

Florida

Low-grade phosphate rock was discovered near Hawthorn in Alachua County by Dr. C. A. Simmons in 1880 (Blakey, 1973). The subsequent discoveries of the river pebble, land pebble, and hard rock deposits led to the development of the Florida phosphate mining industry (Figure 5). Both the river pebble and hard rock industries enjoyed early success; however, exploiting these irregular, localized deposits incurred high production costs and the mining operations over the broad, relatively uniform land pebble deposits quickly dominated. While soft rock, which is used mainly as a soil-builder, has been mined continuously since 1931, it has never assumed major importance because of its low phosphorus content (23 to 30 % P_2O_5) and high percentage of iron and aluminum oxides (Blakey, 1973).

A schematic of modern mining operations is represented in Figure 6. The greatest technological impact on the mining of phosphate rock has been the introduction of electrically powered draglines and the application of flotation to the recovery of phosphatic materials which resulted in much cheaper production and recovery of a considerably higher percentage of phosphate (Blakey, 1973). Until modern mining practices were fully entrenched about 1946, "matrix," which consists predominantly of phosphate ore and terrigenous sediments and ranges in grade from 12 % to 20 % P_2O_5 , was mined *in situ* using primarily hydraulic methods following the removal of overburden; draglines now handle both overburden and matrix. To avoid confusion with the "apatite matrix," this matrix shall henceforth be referred to as the "ore matrix." The ore matrix is dumped into a sump where it is fluidized using high-pressure water jets and then pumped as a slurry to

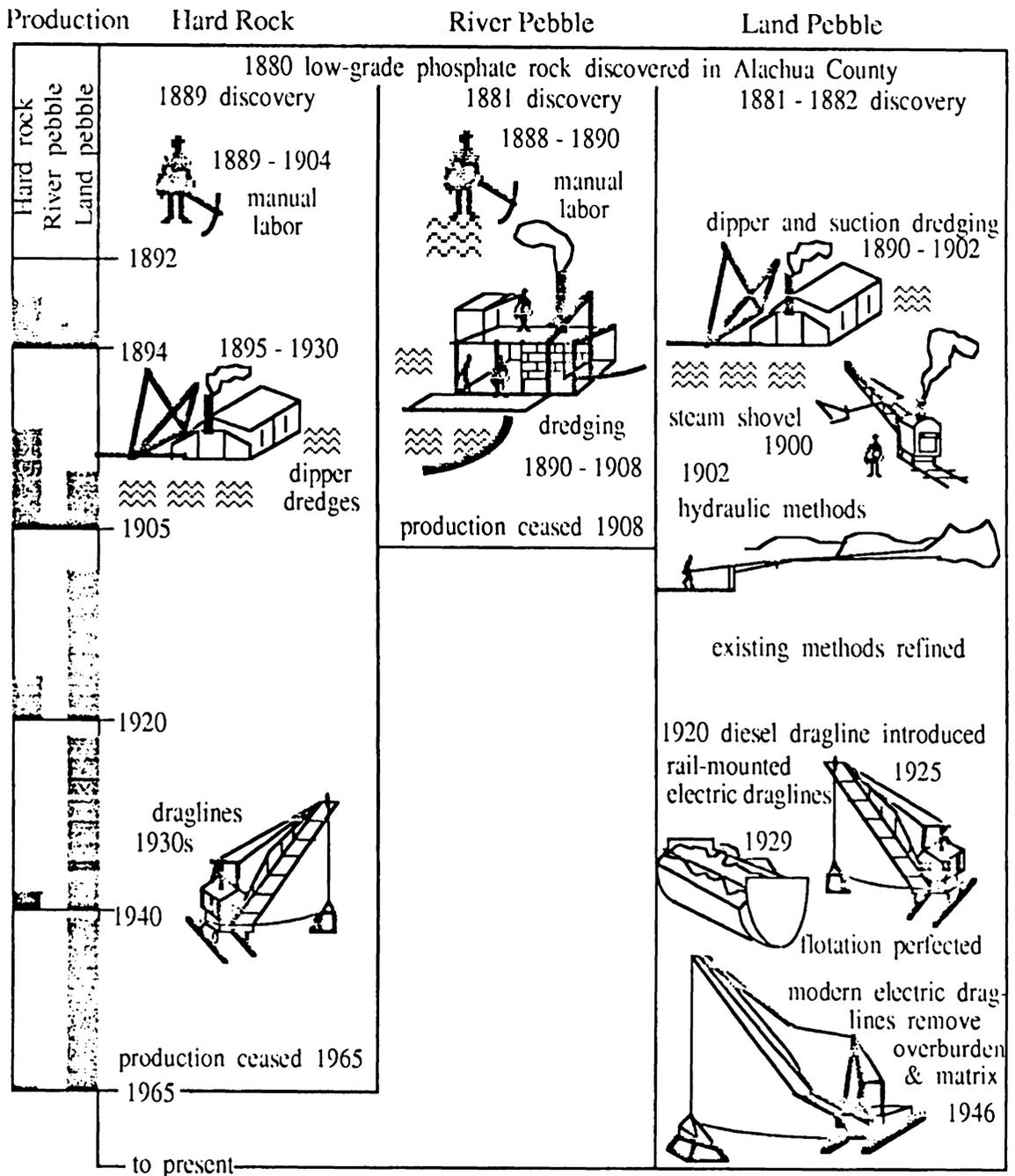


Figure 5. Major developments in the mining of Florida phosphate rock (after Blakey, 1973).

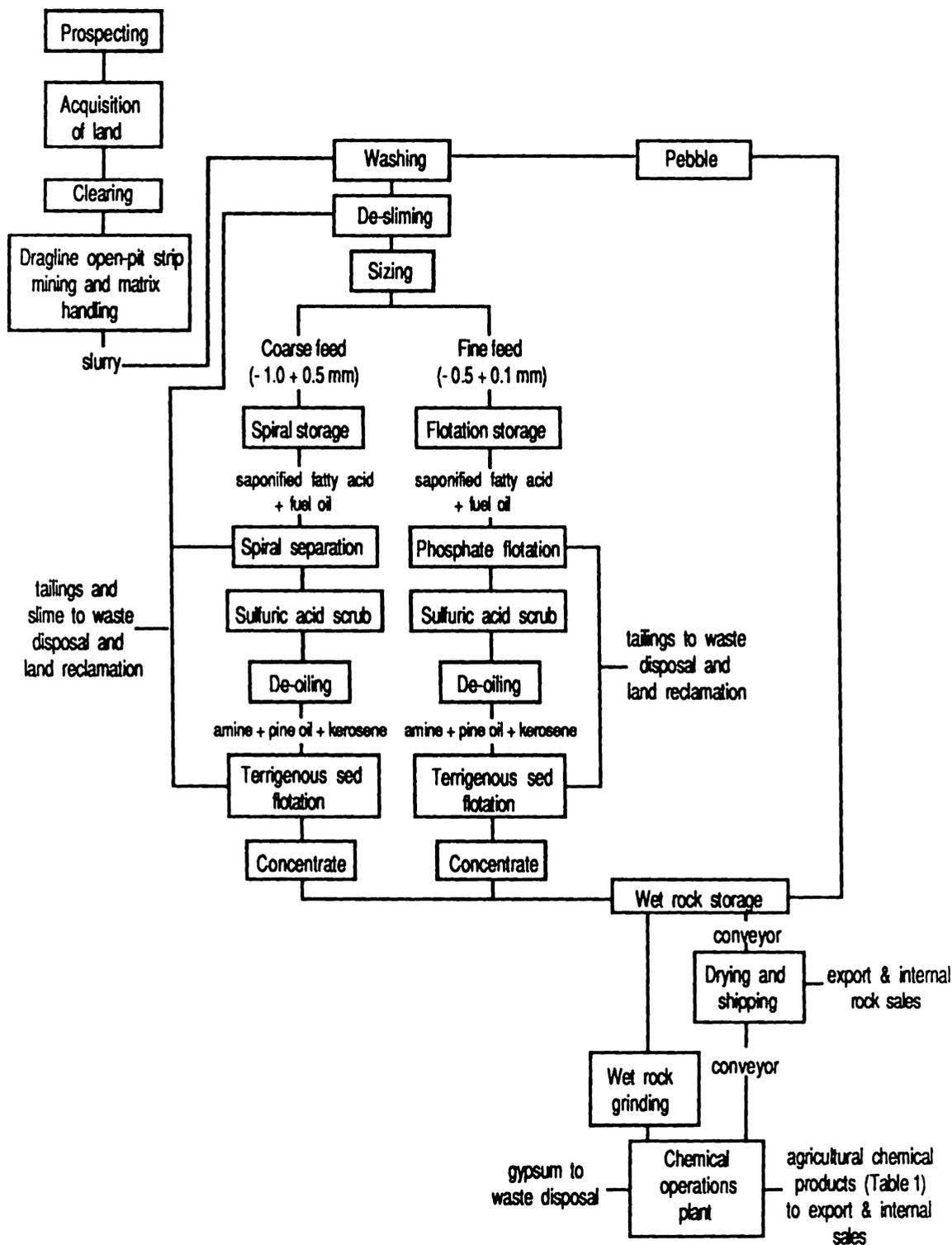


Figure 6. Simplified schematic of a modern Florida phosphate mining operation (after Blakey, 1973 and Brami, 1977).

the processing plant for beneficiation. Double flotation is applied to deslimed raw material finer than 1 mm and coarser than 0.1 mm in grain size ("flotation feed") to effect the separation of terrigenous sands ("tailings") from phosphate rock and render upgraded ore ("concentrate"), which ranges in grade from 32 to 34 % P_2O_5 . This is accomplished basically in an anionic circuit, where phosphate particles are preferentially conditioned with fatty acid reagent, enabling the hydrophobic phosphate grains to be floated; however, some gangue is incorporated with the phosphate in the froth and is subsequently removed in a cationic circuit, where quartz is preferentially rendered hydrophobic by amine treatment and floated away from phosphate. The greatest influence the flotation process has had in the Florida field is to create a longer life expectancy for the industry and for the known possible and probable reserves (Blakey, 1973).

North Carolina

Whereas the Florida phosphate industry experienced "boom years" of rapid development immediately following the discoveries of economic deposits, the North Carolina industry evolved in a more cautious and methodical manner following the 1956 discovery of the major phosphorite ore body (Figure 7).

A dry, open-pit mining and beneficiation method emulating the very economically profitable Florida mining operations was tailored for the North Carolina industry with minor adaptations to account for inherent variations in geography and geology (Table 4).

Otherwise, the Pungo River ore matrix, which averages 15 % P_2O_5 , is similarly slurried in a sump and pumped to the mill for beneficiation. Physical sizing and desliming rejects the coarse pebble phosphate and remaining carbonate gangue so that the [- 1.0 mm + 0.075 mm] flotation feed is upgraded to about 17 to 18 % P_2O_5 . Because coarse-grained phos-

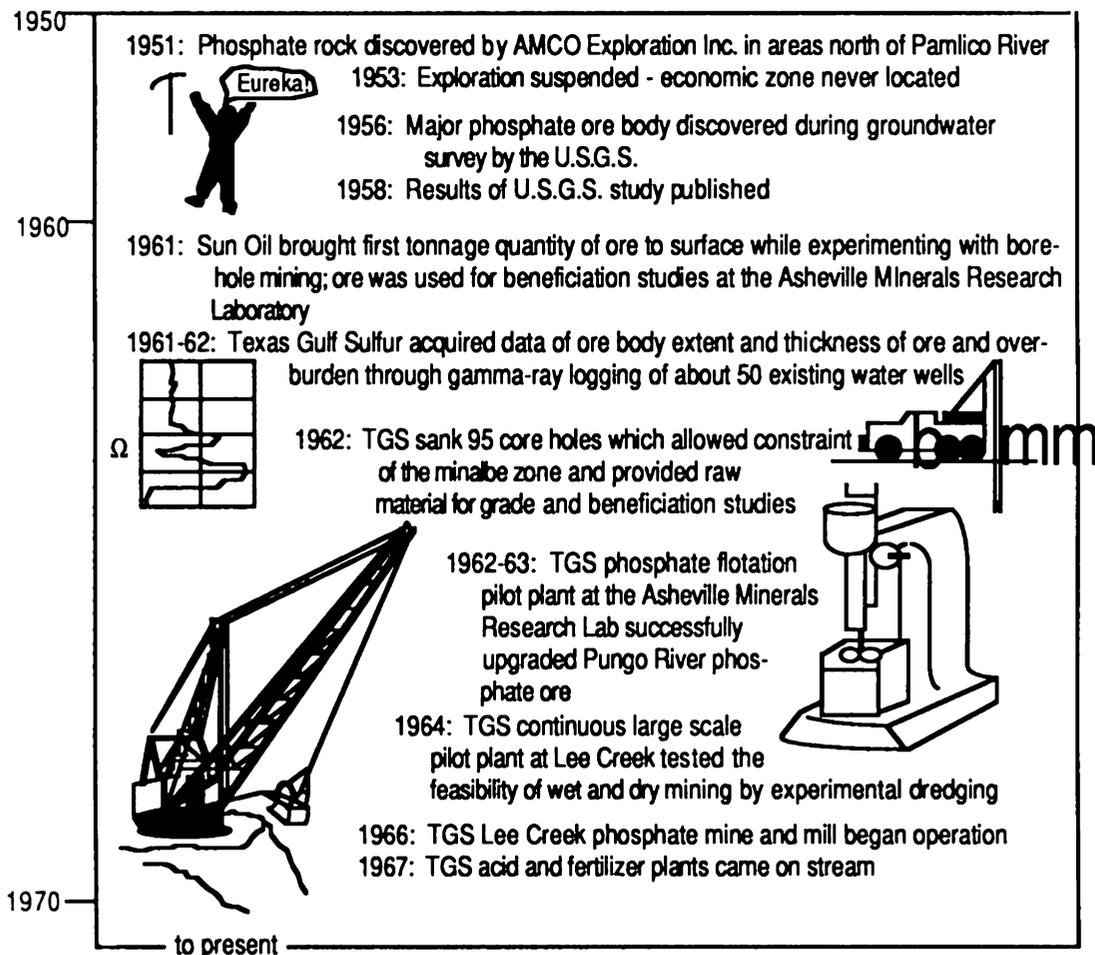


Figure 7. Major developments in the mining of North Carolina phosphate rock (after Redeker, 1971 and Trauffer, 1969).

Table 4. Variations between Florida and North Carolina mining techniques
(after Caldwell, 1968, Trauffer, 1969, and Redeker, 1971).

Variation	Florida	North Carolina	North Carolina Modification
deposit location	inland	below sea level and near an ocean-connected water body	plant site elevation raised to 10 ft above sea level with dredged overburden
overburden thickness	5 to 50 ft	70 to 105 ft	hydraulic dredging removes top 50 ft of overburden from a 60-acre tract during initial mine development; small dragline with 19 yd ³ bucket strips next 30 ft of overburden
ore zone thickness	5 to 25 ft	40 ft	large dragline with 72 yd ³ bucket strips remaining overburden and mines ore zone
hydrogeology	overlies aquifer	overlies a major artesian aquifer	water-impregnated surface sands drained over 3 months by 45 ft ditches; 14 of 24 pumps relieve aquifer pressure by continuously handling about 60 million gal of water per day so that the pit is dry
ore matrix	dominantly terrigenous	interbedded with dolosilt	ore body delineated into low-grade and high-grade sections for selective mining

phate represents only 3 to 5 % of the total ore, there is no pebble plant and the pebble "product" is used for fill and roads in the mine area (Trauffer, 1969). The feed is fed into three lines for the separation of terrigenous tailings from phosphate ore using flotation technology analogous to the Florida industry. Whereas the Florida feed must be divided into a coarse and fine fraction to achieve a successful separation, flotation of the North Carolina feed is so efficient that separate treatment is unnecessary. One line undergoes only the single fatty acid flotation circuit and yields a concentrate product of about 26 to 29 % P_2O_5 . The other two lines are provided with a second stage amine flotation circuit, which raises the rougher concentrate grade to about 30 to 32 % P_2O_5 .

Tennessee

Brown rock phosphate was discovered in 1895 by Judge S. Q. Weatherly and dragline mining began replacing crude pick and shovel, steam shovel, and hydraulicking methods as early as 1913 (Hook, 1914).

The brown rock phosphate residual deposits are presently located by prospecting over a predetermined 100 feet centers grid with a truck-mounted, power-driven auger. The mining potential is accessed according to the overburden to ore zone thickness ratio: a ratio of 1:1 or 2:1 is desirable, but a maximum of 6:1 is generally acceptable (Collete, 1968). On the average, overburden is about 6 feet thick and the ore matrix ranges from 4 to 10 feet in thickness (Van Wazer, 1961). Draglines are used to strip overburden and mine the ore matrix, which is loaded into trucks and hauled to the beneficiation plant. Brown rock does not respond well to flotation. Consequently, the low grade feed is upgraded from about 15 % to about 27 % P_2O_5 using an intricate washing system designed to separate clays from terrigenous and phosphatic sands based on settling rates (Figure 8).

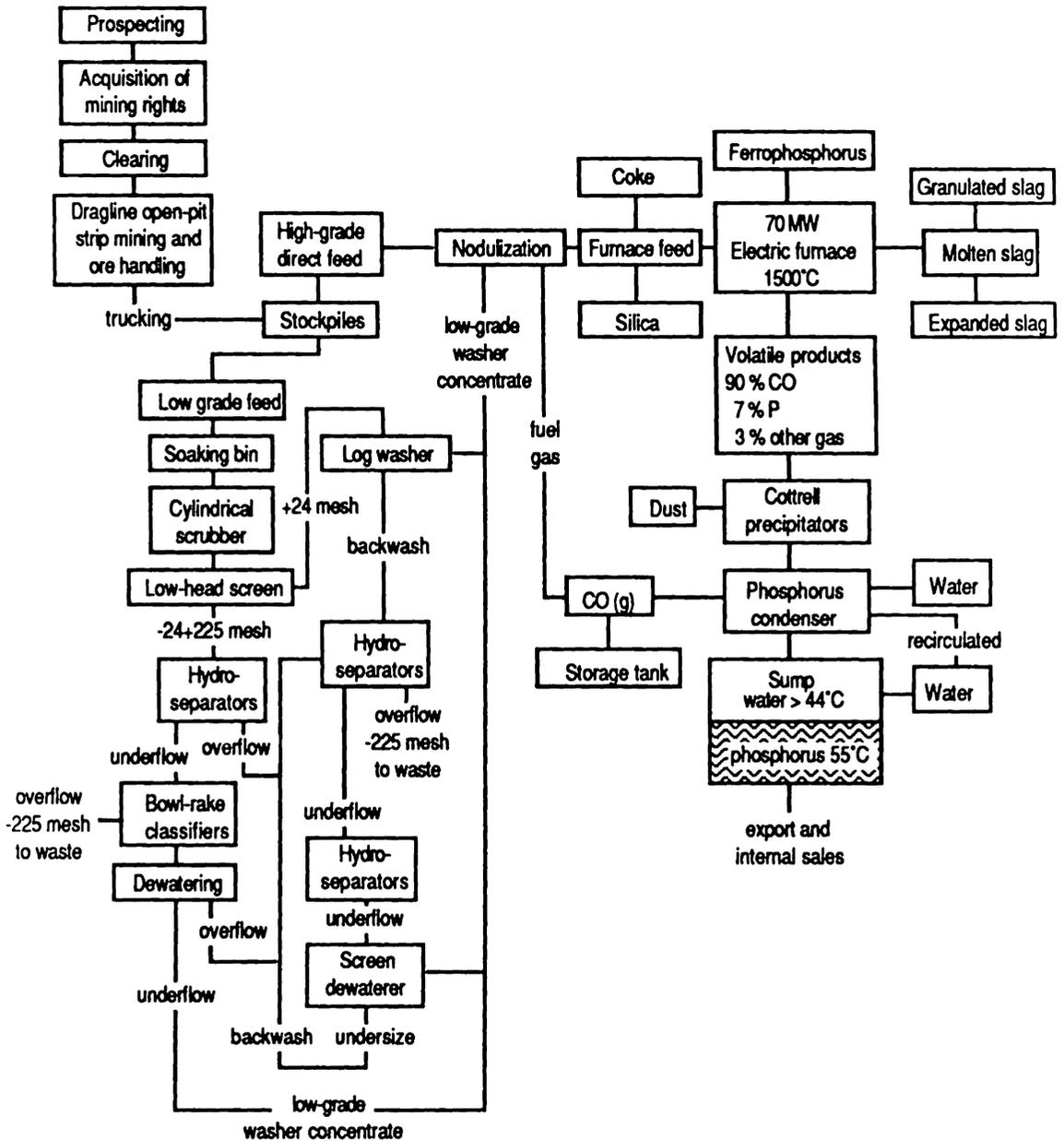
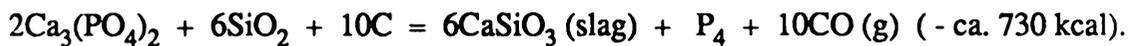
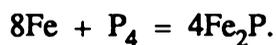
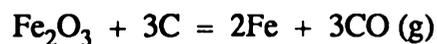


Figure 8. Simplified schematic of a modern Tennessee phosphate mining operation (after Ruhlman, 1958 and Waggaman and Ruhlman, 1960).

White phosphorus or elemental phosphorus, P_4 , is commercially produced by the electric furnace reduction of phosphate in the presence of silica and carbon. High energy costs associated with this highly endothermic reduction have decreased the attractiveness of the electric furnace process; however, it remains a popular method for utilizing ores of lower grade than those required in acidulation processes (McClellan and Gremillion, 1980). The mechanism of reduction is complex, but the overall reaction, which may be simplified by expressing francolite in terms of tricalcium phosphate, is represented by Hurst (1961):



In addition, oxides and sulfides of iron, with other metal oxide contaminants, are reduced to form an unwanted metallic, mixed phosphide byproduct called ferrophosphorus, which may contain from 46 % to 64 % P_2O_5 (Hurst, 1961):



Losses of 8 % P in total yield due to ferrophosphorus are common (McClellan and Gremillion, 1980).

STRATIGRAPHY AND ECONOMIC GEOLOGY

Florida

The phosphatic portion of the Florida section is the Hawthorn Group, which is lithologically subdivided into the Miocene Arcadia and Noralyn Formations and the Pliocene Bone Valley Formation (Table 5). The Arcadia Formation or "bedrock" is presently not economical due to the presence of the phosphorite in a dolostone substrate, which precludes conventional beneficiation techniques to upgrade the phosphate. The Noralyn Formation (Figure 9a) is the main economic unit in the Central Florida District and consists predominantly of intraclastic phosphorites and terrigenous sands and clays throughout the section (Figure 9b) with minor to major basal or "transition zone" lithochemical phosphorite concentrations. The Bone Valley Formation contains abundant terrestrial and marine fossils, for which the district is so famous, and low-grade lithochemical phosphorites; however, only locally does it constitute a major portion of the mined phosphate (Riggs, 1979a).

North Carolina

The phosphatic portions of the North Carolina section are the Miocene Pungo River Formation, which is subdivided into four major sediment units reflecting cyclical patterns of deposition, and the Pliocene Lower Yorktown Formation (Table 6). The Pungo River Formation is the only known primary phosphorite unit on the Atlantic coast with good stratigraphic and environmental control (Gibson, 1967). The section is economically delineated on the basis of lime and P_2O_5 content into low-grade zones and a high-grade

Table 5. Phosphate stratigraphy of the Florida peninsula (modified after Riggs, 1979b).

Age	Group	Formation	Depositional environment	Sediment structures	Nonphosphate lithology	Phosphate lithology	Fossil Assemblage	Stratigraphic relationships
Pliocene	P O R N	Bone Valley	Complex fluvial facies (upslope)	Linear geometries, abundant cut and fill channels, well-bedded and often cross-bedded	Rapidly changing terrigenous clays and sands; common quartz and chert granules and pebbles	Lithochemical sands and gravels, often black-stained, low-grade, and local deposits	Mixed assemblages of (1) reworked marine vertebrates and (2) articulated and disarticulated terrestrial vertebrates	Unconformably cut into the Noralyn Fm., unconformably overlain by various nonphosphatic Pliocene and Pleistocene units, grades downslope into the estuarine facies
			Estuarine and open-bay facies (downslope)	Blanket geometry, well-bedded to highly burrowed and homogenous	Interbedded to homogenous sands and clays, minor quartz and chert granules	Lithochemical sands and minor gravels, black-stained, and very low grade	As above with increasing abundance of calcite invertebrate shell material	Unconformably overlies the Arcadia or Noralyn Fm, unconformably overlain by various nonphosphatic Pliocene and Pleistocene units
Miocene	H A W T H O R N	Noralyn	Complex coastal marine facies grading downslope to uniform nearshore shelf facies	Well-bedded and cross-bedded coastal facies grading to poorly bedded and highly burrowed nearshore shelf facies	Dominantly intermixed terrigenous sands and clays with minor dolomite	Dominantly orthochemical microspherite and allochemical intraclasts in middle and upper sections; about equal distribution of primary intraclasts and secondary lithochems in the transition zone; grain size grades from gravels and coarse sands in coastal facies to sands and fine gravels in the nearshore shelf facies	Limited marine vertebrates consisting of scattered nekton teeth and bones with an occasional articulated serinian and cetacean; invertebrates very limited with some molds in microspherite beds; abundant trace fossils	Conformably overlies and grades downslope and southward into Arcadia Fm.; in the upslope portion it unconformably overlies either the Oligocene Suwanee Limestone or the Eocene Ocala Limestone Group
			Arcadia	Uniform marine continental shelf facies	Poorly bedded to mottled and homogenous, highly burrowed	Dominantly a dolosilt with subordinant amounts of terrigenous quartz sand and clay, interbedded with facies of the reverse lithologies	Dominantly allochemical fine sand pellets with subordinant amounts of sand intraclasts and fossil skeletal material	Locally fossiliferous with abundant invertebrate molds, limited marine vertebrates consisting of scattered teeth and bones of various nekton, abundant trace fossils



Figure 9a. Photograph of the Noralyn Formation exposed in an open pit mine in central Florida.



Figure 9b. Photograph of the ore matrix in the Noralyn Formation.

Table 6. Phosphate stratigraphy of the North Carolina Aurora District (modified after Riggs, et al., 1982 and Scarborough, et al., 1982).

Age	Formation	Av. Thickness (m)	Depositional environment	Sediment structures	Nonphosphate lithology	Phosphate lithology	Stratigraphic relationships
Pliocene	Lower Yorktown	2-4	Open-marine continental shelf	Interbedded in upper section	Clayey and shelly, fine to medium quartz sand	Sparse intraclastic sands in upper section grading to more abundant coarse intraclastic pebbles and gravels in basal section	Minor unconformable contact with nonphosphatic Pliocene Upper Yorktown; Lower Yorktown may be locally absent due to Pleistocene channel erosion; major unconformable contact with Pungo River units D and C

Miocene	Pungo River	Unit D	Regressing open-marine continental shelf	Highly burrowed and bored upper surface	Shelly and slightly quartz sandy dolosilt	Thin and minor upper orthochemical microsporite beds; negligible phosphorite throughout section	Generally present only in the eastern portion of the district; minor unconformable contact with unit C
		Unit C	Open-marine	Interbedded	Nonindurated to indurated calcareous mud or limestone interbedded with slightly shelly, quartz sand	Dominantly intraclastic fine to medium sands; minor pelletal phosphorite	
		Unit B	Middle or outer continental shelf	Highly burrowed and mottled	Clayey quartz sand	Dominantly intraclastic fine to medium sands	Minor unconformable contact with unit B
		Unit B	Open-marine	Highly burrowed grading downward to mottled	Semi-indurated to indurated sandy quartz dolosilt grading downward to dolosilt and clayey quartz sand	Carbonates often contain significant concentrations of well-sorted sands infilling burrows	
		Unit A	Inner or middle continental shelf	Massive and mottled	Clayey quartz sand	Dominantly intraclastic fine to medium sands; minor pellets; gravels at base	Minor unconformable contact with unit A
		Unit A	Open marine	Highly burrowed	Nonindurated to indurated dolosilt	-	
		3-5	Inner or middle continental shelf	Burrowed to mottled	Clayey quartz sand	Dominantly intraclastic fine to medium sands; abundant pellets; minor basal pebbles	Generally east-dipping, regional major unconformable contact with nonphosphatic Eocene Castle Hayne Fm

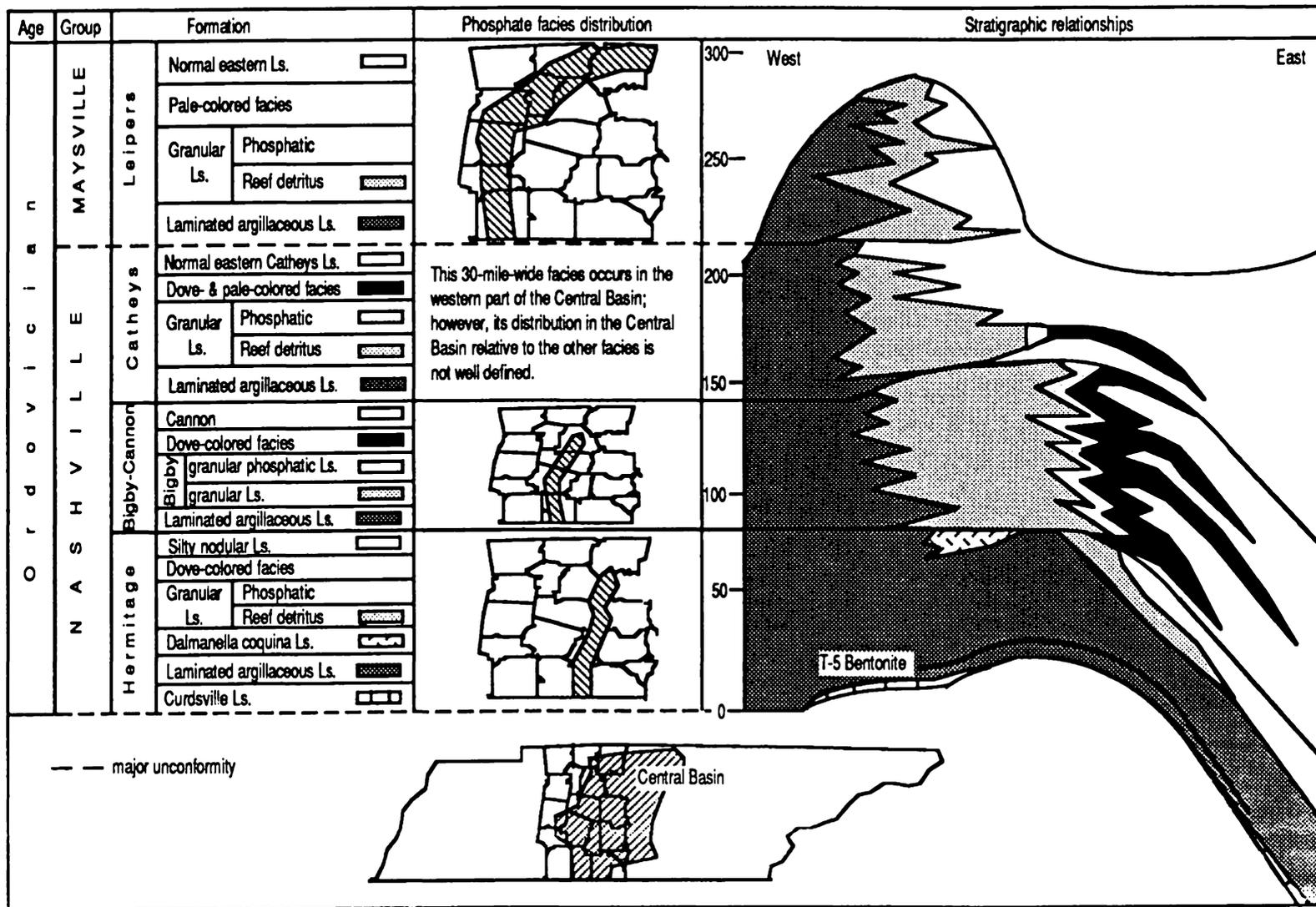
----- minor unconformity or hiatus - - - - major unconformity

zone for selective mining (Redeker, 1971). The Lower Yorktown and the Pungo River unit D constitute the rejected upper low-grade section. Units C and B contain 90 % of the total P_2O_5 in the phosphate section (Redeker, 1971) and constitute the economic high-grade section. They consist predominantly of intraclastic phosphorite sands and terrigenous sands and clays, which grade upward generally into carbonate caprocks. The contact is easily distinguished by the shelly dolosilt nature of unit D. Unit A is the lower low-grade section and is left in place as a barrier against the adjacent Castle Hayne Aquifer.

Tennessee

The phosphatic portions of the Ordovician section in central Tennessee are the Nashville Group, which is lithologically subdivided into the Hermitage, Bigby-Cannon, and Catheys Formations, and the Leipers Formation (Table 7). All of these units form local, residual deposits; however, the residual deposits associated with the Bigby facies of the Bigby-Cannon Limestone constitute the major economic resource. Whereas rims are the most common of the residual deposits, but are of very limited extent, and blankets formerly furnished the majority of the phosphate mined in central Tennessee, cutters are the current deposits of economic interest. Cutters may be relatively large (generally 15 m diameter) "sinkhole-like" structures or long, narrow (generally 3 by 6 m) trenches in the limestone. The ore matrix in cutter deposits mostly consists of plate rock and muck phosphate, silica sand, and terrigenous clays.

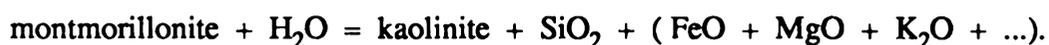
Table 7. Ordovician phosphate stratigraphy of the Tennessee Central Basin (after Wilson, 1962).



GEOCHEMISTRY OF WEATHERED PHOSPHORITE DEPOSITS

Florida

The central Florida deposits exhibit extensive and variable degrees of weathering. The regional weathering pattern is expressed in the alteration of montmorillonite to kaolinite (Altschuler, et al., 1963):



The liberated Fe^{2+} may be transported in groundwater and be subsequently immobilized as Fe^{3+} oxyhydroxides upon contact with an oxidizing environment. In the river drainage basins, a more restricted and more intense variety of weathering is displayed most commonly through the development of supergene Ca-Al and Al phosphates in discontinuous upper "leached" zones. The processes which form this leached zone have been thoroughly described by Altschuler, et al. (1955, 1964). The Agrico Payne Creek and the Grace Four Corners mines are examples of slightly weathered sections with a relatively thin leached zone (Figure 3). Less commonly, iron may be leached from iron-rich montmorillonite in the overburden during weathering and precipitated from downward-moving humate-rich groundwaters, which are neutralized by the basic calcium phosphates in the upper phosphate zone, as concretions and hardpans of goethite and limonite (Altschuler, et al., 1964). Due to interaction with phosphatic solutions, these hardpans may be partly replaced by iron phosphates to form secondary iron gossans (Moore, 1970 and Altschuler, 1973). The IMC Noralyn mine is an example of a section capped by such a gossan. The gossans range in thickness from centimeters to one meter and are of limited aerial extent.

North Carolina

The Pungo River Formation is relatively unaltered by subaerial weathering as determined from selected trace element analysis of constituent whole and separated grains (Tobiassen, 1981) and groundwater geochemistry and hydrogeologic reconstruction (Brown, 1958). Consequently, the iron-bearing mineral inclusions in these primary phosphorites are preserved in their authigenic state of formation.

Tennessee

The Tennessee brown rock deposits are primarily the residual concentrates of differential weathering of less soluble phosphate from more soluble calcareous rocks. However, a more restricted and intense type of weathering is most strikingly displayed in the cutter deposits, where plate rock is disseminated with muck and pelletal phosphorite sands throughout the ore matrix. Plate rock, which is appropriately named for its platy morphology, is an example of the solution of apatite in the upper soil horizon and the supergene transportation and fixation of phosphate at depth by replacement of limestone (Altschuler, 1973). The following sequence of events are inferred by Altschuler (1973) to produce plate rock.

1. Progressive decalcification results in the accumulation of apatite-rich mantles in the upper soil zone.
2. Meteoric water is no longer significantly buffered by calcite and groundwater may be slightly acid to slightly alkaline (pH 6.5 to 7.5).
3. Meteoric and groundwaters dissolve apatite and become enriched in phosphate.
4. Downward-moving phosphate-rich groundwater comes in contact with limestone

at depth; the limestone dissolves releasing Ca^{2+} and HCO_3^- , which consequently raises the pH to probably 7.5 to 8.5.

5. Due to the increased concentration of Ca^{2+} and the increase in pH, apatite replaces limestone.

Apatite may also precipitate from the ambient solutions to form banded coatings. The underground solution of limestone throughout this process enhances collapse and brecciation, causing an intermingling of plate rock with the infiltrating overlying clastic residues (Altschuler, 1973).

IRON-BEARING MINERALS IN THE CENTRAL AND SOUTH FLORIDA DISTRICTS

A formidable number of iron-bearing minerals occur in the phosphorite deposits of the Central and South Florida Phosphate Districts (Table 8); however, their spatial distribution greatly simplifies the mineralogy. The major iron-bearing mineral (> 10 %) inclusions in the black and brown phosphorite grains of the ore zone are pyrite and goethite respectively. The principal minor iron-containing phase (1-10 %) inclusion in the phosphorites is ilmenite. These results are consistent with the high iron and moderate titanium and sulfur concentrations obtained with EDX analysis of acid insoluble residues of numerous phosphate samples (Riggs, 1979a). The supergene iron phosphates, which account for one third of the iron-bearing minerals listed, are located only in the gossans of the overburden.

Major iron-bearing mineral phases in intraclastic phosphorites

Terrigenous diluted intraclastic phosphorites

Throughout the Miocene, the inner perimeter of the Ocala Upland received fluviially transported terrigenous sediments, which were derived from the Appalachian Mountains (Riggs, 1979b). Consequently, terrigenous sediments constitute the major diluents in the intraclastic phosphorites formed in this area. Terrigenous diluted intraclastic phosphorites are typically black or brown in color, or various shades thereof, and are admixed together throughout the ore matrix.

Table 8. Summary of the iron-bearing minerals in the Central and South Florida District phosphorite deposits.

Mineral	Chemical composition	Occurrence	Origin	References
Almandine	$\text{Fe}_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$	PI	TgS	Pirkel, et al., 1965
Ankerite	$\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$	ore matrix bedrock	TgS ?	Stow, 1968 ‡
Barbosalite	$\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$	gossan	2°	Swanson & Legal, 1967
Beraunite	$\text{Fe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_5 \cdot 6\text{H}_2\text{O}$	gossan	2°	Blanchard & Denahan, 1968
Cacoxenite	$\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_3 \cdot 12\text{H}_2\text{O}$	gossan	2°	Blanchard & Denahan, 1968
Chalcopyrite	$\text{CuFe}^{2+}\text{S}_2$	PI	1°	†
Chromite	$\text{Fe}^{2+}\text{Cr}_2\text{O}_4$	PI	1°	†
Cyrlivite	$\text{NaFe}_3^{3+}(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	gossan	2°	Barwood, et al., 1983
Dufrenite	$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$	gossan	2°	Swanson & Legal, 1967
Epidote	$\text{Ca}_2(\text{Al}, \text{Fe}^{3+}, \text{Mn})_3\text{O}(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})$	PI	1°	Pirkel, et al., 1965
Ferrian-millisite	$\text{Ca}_3(\text{Al}, \text{Fe}^{3+})_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$	ore matrix L zone	TgS 2°	Stow, 1968 †
Ferroan-variscite	$(\text{Al}, \text{Fe}^{3+})\text{PO}_4 \cdot 2\text{H}_2\text{O}$	gossan	2°	Barwood, et al., 1983
Glaucconite	$(\text{K}, \text{Na}, \text{Ca})_{<1.8}(\text{Al}, \text{Mg}, \text{Fe}^{3+}, \text{Fe}^{2+})_4(\text{Si}_7\text{Al})\text{O}_{20}(\text{OH}, \text{F})_4$	PI	1°	Weaver & Wampler, 1972
Goethite	$\text{Fe}^{3+}\text{O}(\text{OH})$	ore matrix PI gossan	1° 2° 2°	‡ † †
Hematite	$\text{Fe}_2^{3+}\text{O}_3$	ore matrix PI	2° 2°	† †
Illite	$(\text{Na}_{0.07}\text{K}_{1.34})(\text{Al}_{3.06}\text{Fe}_{0.45}^{3+}\text{Mg}_{0.56}\text{Fe}_{0.07}^{2+})(\text{Si}_{6.8}\text{Al}_{1.2})\text{O}_{20}(\text{OH})_4$	ore matrix PI ore matrix	2° 1°, 2° TgS	Barwood, et al., 1983 Weaver & Wampler, 1972 †, Bromwell, 1982

PI = phosphorite inclusion; TgS = terrigenous sediment; 1° = primary; 2° = secondary; D = diagenetic; L zone = leached zone; OB = overburden; † = this study; ‡ = personal communication. H. Barwood

Table 8 (con't). Summary of the iron-bearing minerals in the Central and South Florida District phosphorite deposits.

Mineral	Chemical composition	Occurrence	Origin	References
Ilmenite	$\text{Fe}^{2+}\text{TiO}_3$	PI	TgS	†
Leucoxene	$\text{Fe}_{1-x}^{2+}\text{TiO}_{3-x}$ (where $0 < x < 1$)	PI	2°	†
		ore matrix	2°	Stow, 1968
Limonite	$\text{Fe}^{3+}\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$	PI	2°	†, Swanson & Legal, 1967
Marcasite	Fe^{2+}S_2	PI	1°	†, Stow, 1976
		OB	D	†
Montmorillonite	$(\text{Al}_{3.35}\text{Fe}_{0.2}^{3+}\text{Mg}_{0.35}\text{Fe}_{0.1}^{2+})(\text{Si}_{7.7}\text{Al}_{0.3})\text{O}_{20}(\text{OH})_4$	ore matrix	TgS	†, Altschuler, et al., 1963
Palygorskite	$(\text{Mg}_{1.96}\text{Fe}_{0.03}^{2+}\text{Al}_{1.61}\text{Fe}_{0.37}^{3+})(\text{Si}_{7.79}\text{Al}_{0.21})\text{O}_{20}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	ore matrix	?	†, Barwood, et al., 1983
Phosphosiderite	$\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$	gossan	2°	Barwood, et al., 1983
Pyrite	Fe^{2+}S_2	PI	1°	†, Stow, 1976
		OB	D	†
		ore matrix	1°	†, Stow, 1968
Rockbridgeite	$(\text{Fe}^{2+}, \text{Mn})\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$	gossan	2°	Swanson & Legal, 1967
Staurolite	$(\text{Fe}^{2+}, \text{Mg})_2(\text{Al}, \text{Fe}^{3+})_9\text{O}_6(\text{SiO}_4)_4(\text{O}, \text{OH})_2$	ore matrix	TgS	Stow, 1968
Strengite	$\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$	gossan	2°	Barwood, et al., 1983
Strunzite	$\text{MnFe}^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	gossan	2°	Barwood, et al., 1983
Tourmaline	$(\text{Na}, \text{Ca})(\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{Al}, \text{Fe}^{3+}, \text{Mn})_6(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})_4$	ore matrix	TgS	Stow, 1968
Turgite	$\text{Fe}_2^{3+}\text{O}_3 \cdot n\text{H}_2\text{O}$?	?	Swanson & Legal, 1967
Unknown 1	Iron-potassium-silicate	PI	?	†
Vivianite	$\text{Fe}^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	gossan	2°	†, Swanson & Legal, 1967
		bedrock	2°	†, Barwood, et al., 1983

PI = phosphorite inclusion; TgS = terrigenous sediment; 1° = primary; 2° = secondary; D = diagenetic; L zone = leached zone; OB = overburden; † = this study; ‡ = personal communication, H. Barwood

Slightly weathered sections in the Payne Creek and Four Corners mines

Organic carbon is responsible for the color of black and gray phosphorites (Swanson and Legal, 1967 and Stow, 1969), which represent particles that have undergone minimal weathering (Stow, 1976). The EDX analysis of black and gray intraclastic phosphorite pebbles indicate that iron occurs predominantly as iron sulfide. X-ray diffraction of the acid insoluble residues of black phosphorites revealed the presence of pyrite and marcasite (Stow, 1976). The polymorphs are compositionally equivalent (FeS_2) and consequently are indistinguishable using EDX analysis. However, marcasite is easily differentiated optically from pyrite by its diagnostic strong blue to yellowish anisotropism with slightly offset crossed nichols. The present study found that pyrite is the dominant iron sulfide and that it occurs in a broad range of textures. Stow (1976), however, reported that the finely crystalline masses in acid insoluble residues are marcasite.

A ubiquitous texture in black pebbles is the randomly disseminated, discrete iron sulfide microcrysts, which frequently are so densely packed that they interlink to form complex, irregularly shaped aggregates ranging in grain size from 10 to 20 μm . Another common texture is the roughly linear 5 to 20 μm strands of pyrite which often branch to form crude dendritic patterns. Under crossed-nichols, the brownish-gray to black color of these pyrite "dendrites" allows them to be traced as continuous structures. However, they may appear discontinuous in plain polarized light. The ambiguity is the result of surface exposure; when dendrite segments, or any other iron sulfide texture, penetrate into the translucent apatite matrix, they do not reflect light and consequently deceptively appear discontinuous. Other common textures are pyrite as 1 to 10 μm subhedral to euhedral cubes and as 5 μm framboids. Framboids are spheroids or modifications of spheroids consisting entirely of randomly or non-randomly distributed discrete equant microcrysts (Rickard, 1970). The black phosphorite pebbles in Gardinier-Hardee-County and Beker-Wingate Creek-Manatee

County ores of the South Florida District are also terrigenous-diluted intraclasts. These grains are relatively pyrite-rich, similar to the North Carolina phosphorites, and contain two additional textures which are not readily observed in black pebble of the Payne Creek and Four Corners ore. Irregular meandering void areas created by bioturbation and interstitial pore spaces, which partially or completely surround terrigenous and pelletal phosphorite inclusions, are commonly filled with equigranular, simple interlocking pyrite with rectilinear and cusped margins. The grain size of the individual pyrite crystals varies from microcrysts to 4 μm depending on the pore space thickness, which ranges from 5 to 60 μm .

X-ray diffraction revealed the presence of goethite in brown phosphorites (Stow, 1976). Goethite occurs predominantly as randomly disseminated inclusions, which are identical in morphology to the pyrite inclusions in black phosphorites, and to a lesser extent with limonite as minute botryoidal stains on the apatite matrix. Their identical morphologies suggest that the goethite inclusions are pseudomorphs after pyrite and marcasite (Stow, 1976). Because there is no significant decrease in molar volume during the transition from pyrite to goethite, it is likely that the extremely fine-grained goethite and limonite stains, which impart the color to brown phosphorites (Swanson and Legal, 1967 and Stow, 1969), are secondary. The presence of goethite indicates that brown phosphorites once experienced oxidizing conditions (Altschuler, 1965 and Stow, 1976), perhaps similar to the weathering process exhibited in a section of the Noralyn mine.

An intensely weathered section in the Noralyn mine

The profile examined in the Noralyn mine is a typical example of a phosphorite section enriched in iron by weathering. The most intense weathering occurs in the overburden, where gossans form. The gossans consist of residual quartz and complex assemblages of

cryptocrystalline, supergene iron phosphates and iron oxyhydroxides (Table 9). Because iron is immobilized in the gossans capping the ore zone, this process does not appear to significantly affect the overall phosphorite section.

However, weathering extends to the middle of the ore body as evidenced by the distribution of kaolinite, which is the weathering product of montmorillonite. The EDX and reflected light analysis of the phosphorite pebbles, which are all brown or shades thereof in color, indicates the iron-bearing inclusions (excluding the terrigenous minerals) are exclusively goethite. Apparently, the geochemical conditions within phosphorites in weathered terrigenous sand and clay environments favor the oxidation of pyrite and marcasite to goethite. The brown color is imparted by secondary stains of goethite and limonite, which are introduced by the percolation of meteoric waters rich in iron leached from montmorillonite during weathering.

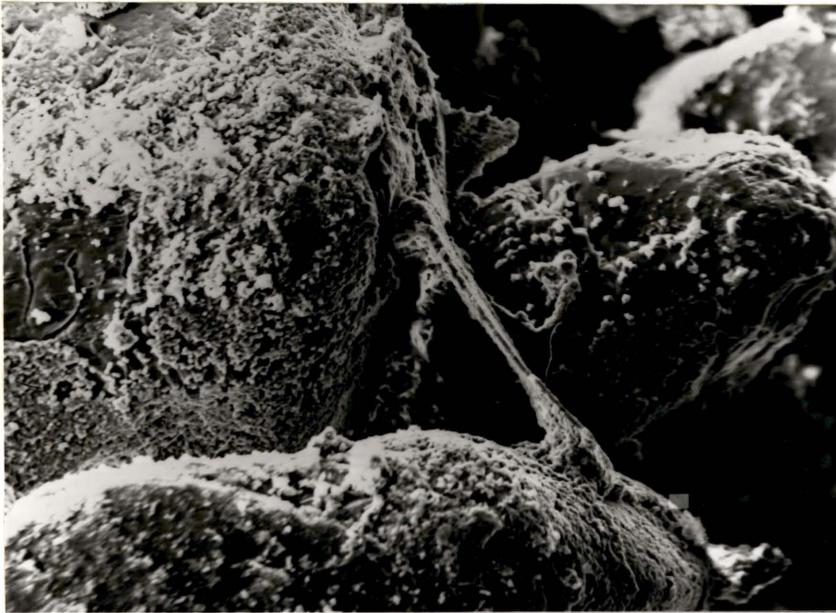
The intraclastic pebbles in the leached zone under the gossan have undergone intense weathering resulting in either simple or complex exterior, iron-bearing textural assemblages, which are evident macroscopically as "bleached" or "scaly" surfaces respectively. The relatively smooth bleached pebbles contain thin, discontinuous rims of goethite. The scaly pebbles contain irregular, coarsely-aggregated crusts. The crust is essentially an outer "fortress" of quartz grains, which are covered by a myriad of 5 μm , anhedral, supergene crystals of ferrian-millisite, $\text{Ca}_3(\text{Al,Fe}^{3+})_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$ (Figure 10a, 10b). The differential leaching of more soluble phosphate has produced the less soluble silica barricade and a plethora of pockets and microchasms. These pits invariably contain accumulations of clay-sized goethite (also derived from montmorillonite weathering) and iron oxyhydroxide-stained, clay-sized phosphate and kaolinite.

Table 9. Iron-bearing minerals occurring in central Florida iron gossans.

Iron Minerals	Composition	Description	Reference
Barbosalite	$\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$	Appears as black "coal veins;" admixed with rockbridgeite and dufrenite.	Swanson & Legal, 1967
Beraunite	$\text{Fe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_5 \cdot 6\text{H}_2\text{O}$	Commonly occurs as blades arranged in spherulite aggregates; cryptocrystalline variety imparts greenish or bluish colors to rock; red oxidized variety also recognized; associated with cacoxenite.	Blanchard & Denahan, 1968
Cacoxenite	$\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_3 \cdot 12\text{H}_2\text{O}$	Commonly occurs as small yellow "specks," which are actually spherulites of radiating acicular crystals lining the walls of small cavities; associated with beraunite and as nearly pure masses within porous red iron oxides.	Blanchard & Denahan, 1968
Cyrilovite	$\text{NaFe}_3^{3+}(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	Occurs as fine grained yellow coatings on rockbridgeite.	Barwood, et al., 1983
Dufrenite	$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$	Greenish alteration product of barbosalite.	Swanson & Legal, 1967
Ferroan-variscite	$(\text{Al},\text{Fe}^{3+})\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Minute green crystals in a mass of altering rockbridgeite.	Barwood, et al., 1983
Goethite	$\text{Fe}^{3+}\text{O}(\text{OH})$	Commonly as discontinuous masses and nodules.	Barwood, et al., 1983
Hematite	$\text{Fe}_2^{3+}\text{O}_3$	Commonly as discontinuous masses and nodules.	Barwood, et al., 1983
Limonite	$\text{Fe}^{3+}\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$	Commonly as discontinuous masses and nodules with goethite.	Altschuler, 1973
Phosphosiderite	$\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$	White to pale pink crystals; associated with rockbridgeite, beraunite, and cacoxenite.	Barwood, et al., 1983
Rockbridgeite	$(\text{Fe}^{2+},\text{Mn})\text{Fe}_4^{3+}(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$	Nodules of greenish to black microcrystalline mixtures with goethite, beraunite, cacoxenite, ferroan-variscite, wavellite, cyrilovite, strengite, phosphosiderite, strunzite, and vivianite.	Swanson & Legal, 1967 Blanchard, 1969
Strengite	$\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$	White to pale pink crystals; associated with rockbridgeite, beraunite, and cacoxenite.	Barwood, et al., 1983
Strunzite	$\text{MnFe}^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	Minute yellow crystals resembling cocoxenite; associated with rockbridgeite.	Barwood, et al., 1983

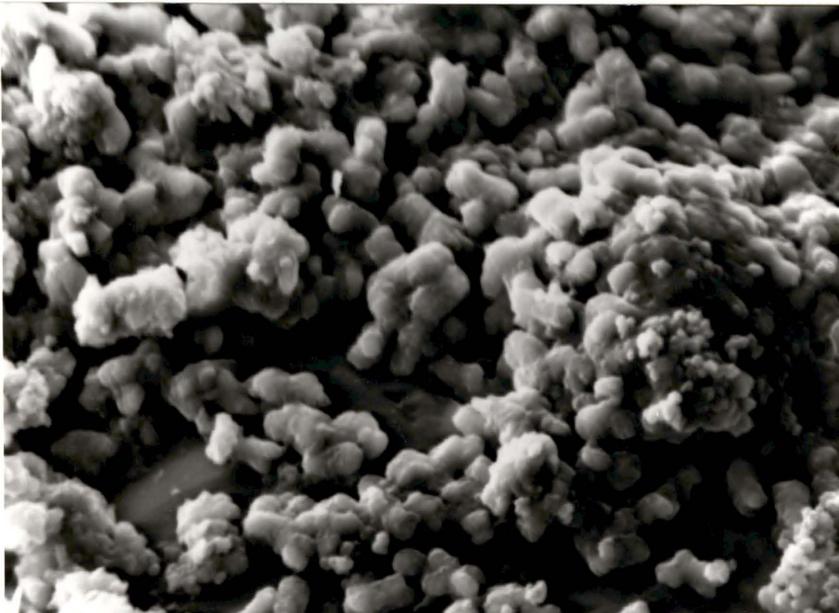
Table 9 (con't). Iron-bearing minerals occurring in central Florida iron gossans.

Iron mineral	Composition	Description	Reference
Vivianite	$\text{Fe}^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Alteration product of iron phosphates occurring as small deep blue to black crystals; rarely bright green crystals found in open pockets.	This study; Swanson & Legal, 1967



200 μm

Figure 10a. SEM photomicrograph of ferrian-millsite coating residual quartz "barricade" in a phosphorite pebble.



20 μm

Figure 10b. SEM photomicrograph of ferrian-millsite crystals.

Carbonate diluted intraclastic phosphorites

Sedimentation from the south and southeast provided a major source of carbonate diluents, which were subsequently incorporated into the apatite matrix during intraclast genesis (Riggs, 1979b). Many of the pebbles in the Payne Creek and Four Corners profile contain abundant randomly disseminated inclusions of microscopic "ghost" or relic dolomite rhombs. These ghost rhombs are distinct in reflected light and are present generally only in gray to brownish-gray pebbles. The Four Corners mine also contains pebbles with rhombic dolosilt inclusions. There are virtually no iron-bearing minerals associated with either the ghost or dolosilt rhombs nor the apatite matrix. However, these pebbles often contain inclusions of goethite-bearing brown phosphorite pellets or pyrite-bearing black phosphorite pellets. Pyrite is also present in thin, second generation, black phosphorite rims, which often encase carbonate diluted intraclasts.

Major iron-bearing mineral phases in lithochemical phosphorites

Minor to major concentrations of brown lithochemical phosphorite pebbles are present in the transition zone of the Noralyn, Payne Creek, and Four Corners mines. Goethite is the iron-bearing inclusion in these lithochemical phosphorites (excluding the terrigenous minerals) and occurs as pyrite pseudomorphs and as secondary stains. However, hematite, which is easily distinguished optically from goethite by its deep red internal reflections, is the pyrite pseudomorph in a lithochem of the Noralyn transition zone. Because the transition zone has not undergone post-Miocene weathering, the iron oxides in the lithochems must be the result of paleo-weathering. Miocene weathering is implicit in the irregular and solution-pitted surface of the carbonate bedrock and the presence of residual phosphorite accumulations in some of the post-depositional surface depressions

(Altschuler, et al., 1964). In the Tennessee brown rock phosphorites, which are modern examples of phosphorites residually concentrated by weathering of phosphatic limestones, hematite is the iron-bearing inclusion (refer to Iron-bearing minerals in the Tennessee Brown Rock District). The lithochems which contain hematite inclusions are, therefore, reworked phosphorites derived from weathered phosphatic Arcadia limestone. The lithochems which contain inclusions of goethite, however, are reworked phosphorites derived from a weathered phosphatic terrigenous sand and clay environment. Miocene weathering of a phosphatic terrigenous sand and clay environment may be illustrated in the Noralyn mine, where the transition zone is overlain by a bed of goethite-containing phosphorite sands, clay-sized goethite, smectite, and palygorskite.

The Pliocene lithochems are mostly reworked allochemical and orthochemical phosphorite sediments and consequently possess the same internal features as their primary equivalents except where they have been modified by erosion and weathering during their subsequent transport and depositional history (Riggs, 1979a).

Major iron-bearing mineral phases in pelletal phosphorites

Pelletal phosphorites constitute an average of 5 to 15 % of the total phosphorite grains in the inner perimeter of the Ocala Upland; however, 80 to 90 % of the phosphorite sediments down the depositional slope and in the outer belt are pellets (Riggs, 1979a). The most commonly observed iron mineral textures in primary pellets are pyrite cubes, generally ranging from 3 to 4 μm but to 20 μm , microcrysts and microcryst aggregates, and dendrite strands varying from 3 to 10 μm . Brown pellets are similar, except goethite is the iron phase.

Iron-bearing mineral phases in skeletal phosphorites

Skeletal phosphorites generally constitute about 2 to 3 % of the phosphorite macrograins in the Central Florida District; however, locally skeletal material may increase to 10 to 15 % of the phosphorite (Riggs, 1979a). Shark teeth are the overwhelmingly dominant component of skeletal phosphorites because teeth are produced continuously throughout the life of a shark and are initially composed of enamel, which is readily fossilized. It has been estimated that a single tiger shark may produce 24,000 teeth during a ten-year period (Tessman, 1966). Pyrite and marcasite are present as a multitude of 3 to 20 μm simple sinuous strands in the teeth of *Carcharodon megalodon* (mackerel shark), *Hemipristis serra* and *Galeocerdo aduncus* (requiem sharks), *Odontaspis* (sand shark), and other shark species. These features have also been noted in vertebrate bone fragments, ray tail spines, serinian ribs, and alligator teeth and are probably present in other fossils. This texture is unique to skeletal phosphorites and is the result of iron sulfide filling nerve canals. The shark teeth of the pyrite-rich Beker Wingate Creek mine additionally contain pyrite filling the central nerve canal. Goethite may also infill the nerve network through pseudomorphism and/or migration-precipitation under oxidizing conditions.

Minor and trace iron-bearing mineral phases in phosphorites

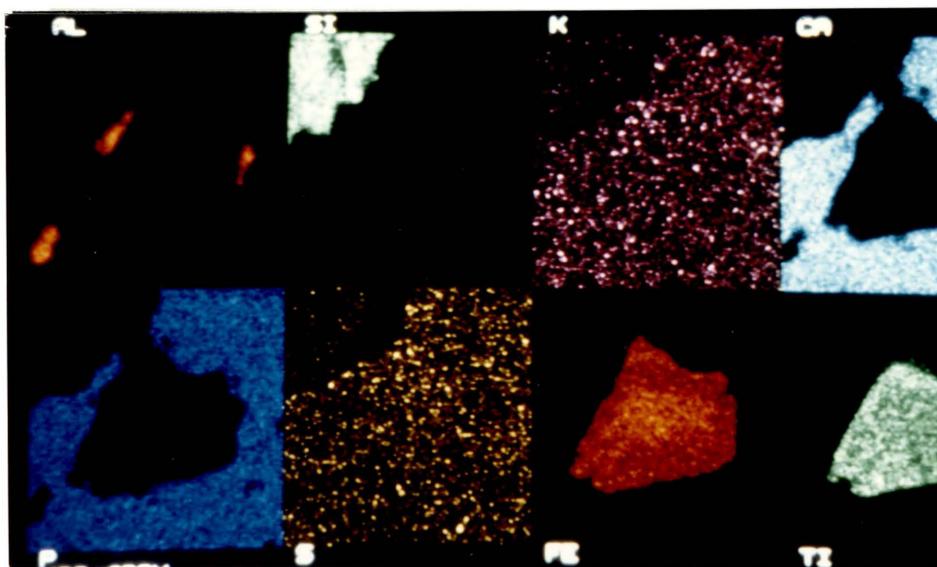
The most significant concentrations of minor (1-10 %) and trace (< 1 %) iron-bearing mineral phases occur in the intraclastic phosphorites and in the Pliocene and Miocene lithochemical phosphorites. They are practically nonexistent in pellets, and totally absent in skeletal phosphorites.

Ilmenite, FeTiO_3 , is the only minor iron-bearing mineral phase consistently present in unweathered and weathered terrigenous diluted intraclasts. Its relatively large 25 to 75 μm

grain size and brownish-black color easily distinguishes it from the iron oxides or sulfides in reflected light. Semiquantitative EDX analysis of different iron-titanium-bearing grains in Noralyn mine pebbles indicated abnormally large variations in the concentration of these two elements. Progressive weathering results in iron removal (Figure 11a) and mineral alteration (Figure 11b). The alteration product may have a variety of intermediate compositions, ranging from 70 to 95 % TiO₂ (5 to 30 % FeO) (Pirkle and Yoho, 1970), and colors, varying from reddish-brown to yellowish to white (Temple, 1966), during its transition to the final weathering product, leucoxene, Fe_{1-x}TiO_{3-x} (where 0 < x < 1).

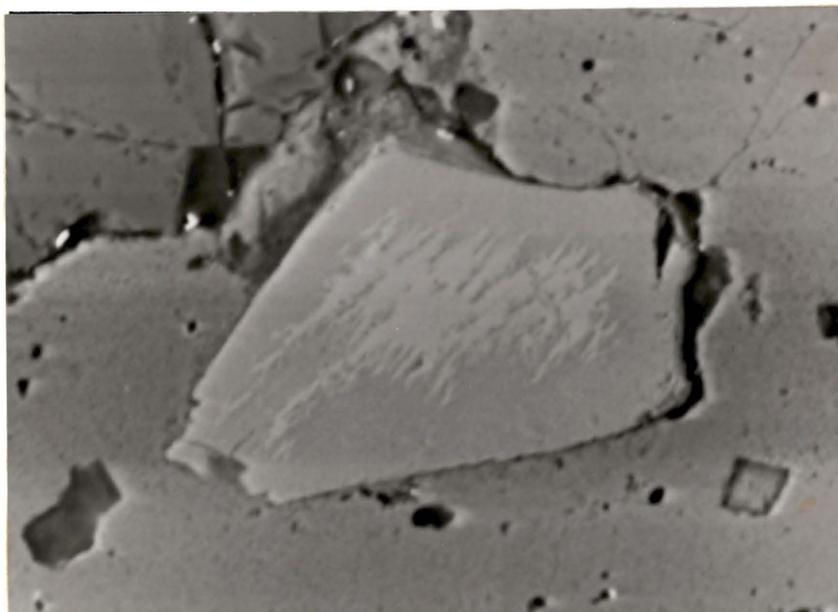
EDX examination revealed the presence of two heretofore undetected metallic iron-bearing minerals in central Florida phosphorites and consequently their overall distribution is not known. Iron occurs with copper and sulfur as chalcopyrite, CuFeS₂, (Figure 12) and with chromium as chromite, FeCr₂O₄ (Figure 13). Chalcopyrite is a trace iron phase throughout the Payne Creek pebbles occurring as a few scattered 5 μm anhedral grains and is similarly present in one Noralyn mine pebble. Two separate, approximately equigranular, 50 μm, anhedral chromite inclusions occur in a single Noralyn mine pebble.

Some of the iron sulfide and oxide inclusions in the black phosphorites of the Payne Creek and Four Corners mines are completely or partially encased with an irregular sheath, which consists of iron, potassium, and silicon (Figure 14a, 14b). There are three clay minerals which satisfy the chemistry of this alumina deficient iron-potassium-silicate: celadonite, K₂X₄Si₈O₂₀(OH,F)₄, glauconite, Y_{<1.8}X₄(Si₇Al)O₂₀(OH,F)₄, and ferroan nontronite, (Y_{0.66},OH₂)X₄(Si_{7.34}Z_{0.66})O₂₀(OH)₄, where X = Fe²⁺ and Fe³⁺ in the octahedral layer, Y = K⁺ in the interlayer, and Z = Fe³⁺ in the tetrahedral layer. These sheaths were observed and tentatively identified as amorphous silica by Riggs (1979a). Apparently, the iron-potassium-silicate alters to amorphous silica when exposed to acid.



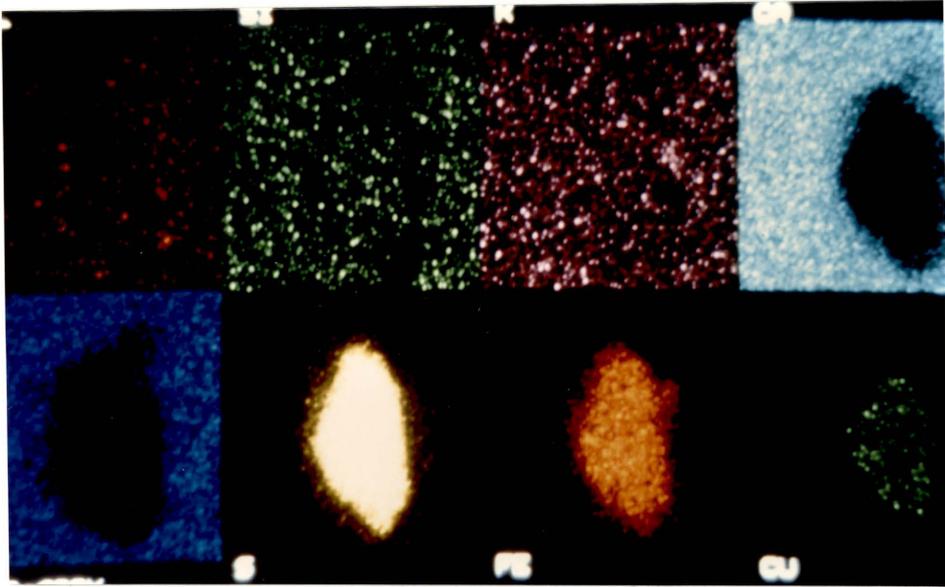
— 50 μm

Figure 11a. Cu-K α electron dot map of a weathered ilmenite inclusion. (weathered areas are red; unweathered areas are orange)



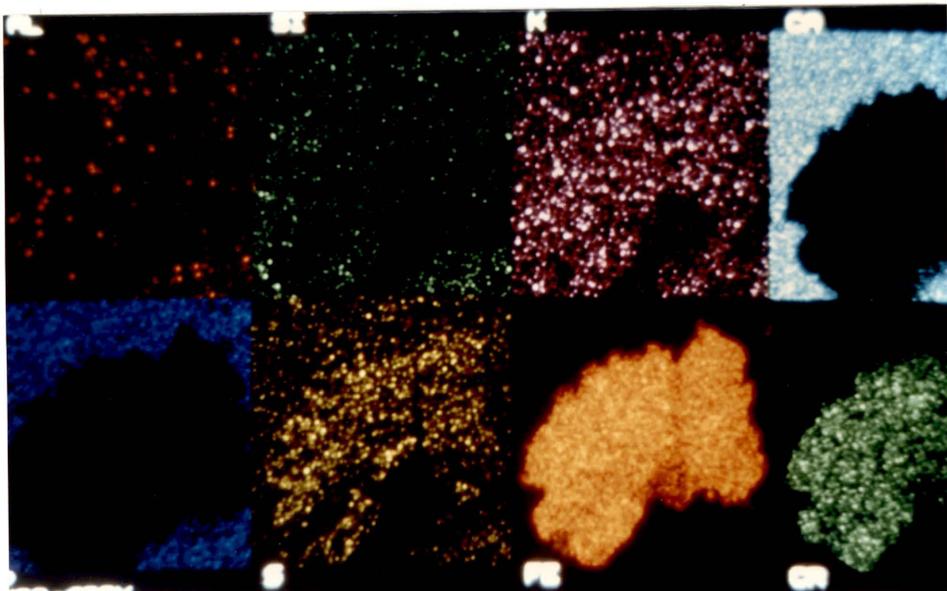
— 50 μm

Figure 11b. SEM backscattered electron photomicrograph of ilmenite inclusion (light gray) altering to leucoxene (dark gray).



— 5 μm

Figure 12. Cu-K α electron dot map of chalcopyrite inclusion.



— 20 μm

Figure 13. Cu-K α electron dot map of chromite inclusion.

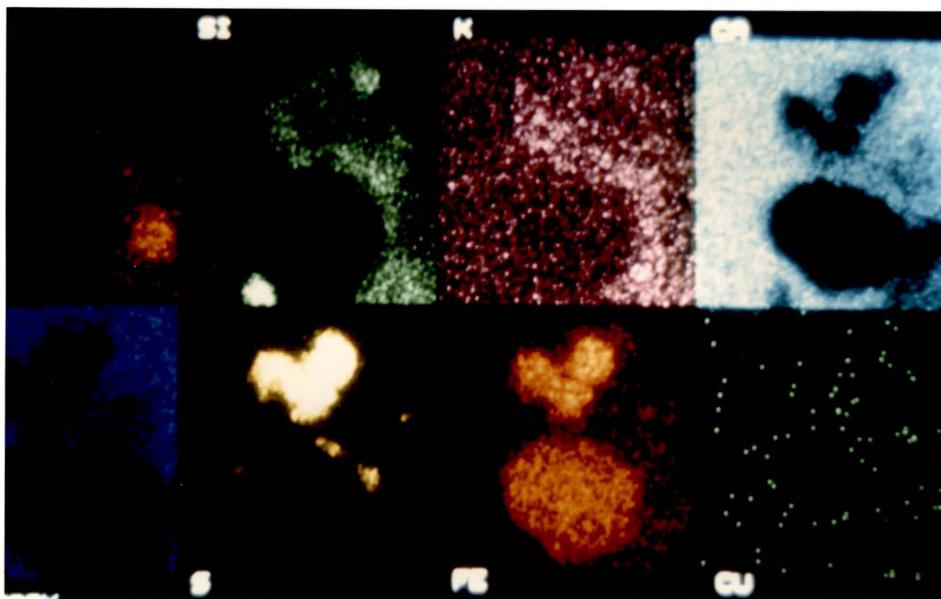


Figure 14a. Cu-K α electron dot map of iron-potassium-silicate sheath.

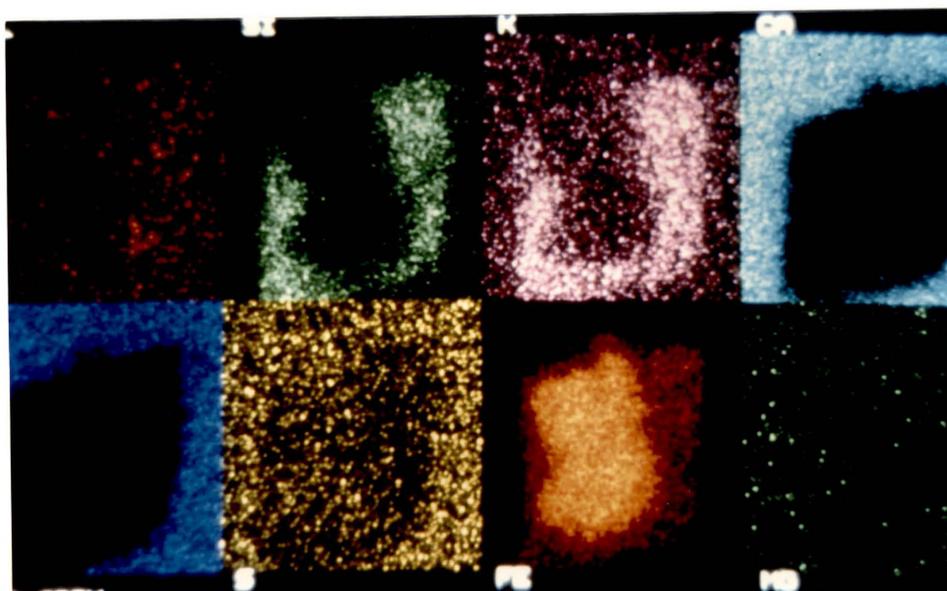


Figure 14b. Cu-K α electron dot map of iron-potassium-silicate sheath.

Glauconite and celadonite are readily attacked by acids. However, montmorillonite treated with 1 N HCl in the same manner used to obtain acid insoluble phosphorite residue is not significantly affected (Weaver and Wampler, 1972). Therefore, ferroan nontronite is the least likely of the three possible clay minerals. When present, the sheaths may act as impermeable barriers to meteoric fluids and thereby prevent the iron sulfide from oxidizing during weathering. An incompletely developed or breached rim permits oxidizing fluids to penetrate to the grain and alter the iron sulfide to iron oxide. It may be possible to subject a large quantity of finely ground powder of phosphorite pebbles to magnetic separation and thereby obtain a concentrated mass of these particles suitable for X-ray diffraction.

The present study found that iron oxide, detected using EDX analysis, is distributed as a trace phase in black and gray intraclasts. Weaver and Wampler (1972), however, reported goethite aggregates to be common constituents in gray and black grains. An infrequent texture of complex origin is represented by iron-potassium-silicate and iron oxide zoned rhombs, which are probably relics of dolomite dissolution (Figure 14b). Because glauconite has been reported in only one Florida phosphorite grain (Weaver and Wampler, 1972), it is presumed to be rare in Florida phosphorites. Illite is the only clay mineral present in phosphorite grains (Weaver and Wampler, 1972). Some of the octahedral cation positions in illite may be filled with Fe^{3+} , although Fe^{2+} may also substitute to a lesser degree. Garnet and epidote, both iron-bearing silicates, have also been reported as common phosphorite inclusions (Pirkel, et al., 1965). They were not observed in this study and, consequently, their distribution is unknown, but probably rare.

Accessory iron-bearing minerals in the phosphorite deposits

The principal accessory iron-bearing phases in the ore matrix are the heavy minerals (Table 10) and the clay minerals. The most common phyllosilicates in the ore matrix are

Table 10. Composition of the acid insoluble heavy mineral suites of the amine flotation waste products (after Stow, 1968).

Iron-bearing mineral	Chemical composition	Phase	% FeO	% Fe ₂ O ₃
Leucoxene	Fe _{1-x} TiO _{3-x} (where 0 < x < 1)	M	34.7	-
Staurolite	(Fe,Mg) ₂ (Al,Fe) ₉ O ₆ (SiO ₄) ₄ (O,OH) ₂	m	10.8	2.95
Almandine garnet	Fe ₃ Al ₂ Si ₃ O ₁₂	m	28.5	-
Tourmaline	(Na,Ca)(Al,Fe ²⁺ ,Fe ³⁺) ₃ (Al,Fe ³⁺ ,Mn) ₆ (BO ₃) ₃ (Si ₆ O ₁₈)(OH) ₄	m	nr	nr
Epidote	Ca ₂ (Al,Fe,Mn) ₃ O(SiO ₄)(Si ₂ O ₇)(OH)	m	-	nr
Pyrite	FeS ₂	t	nr	-

M = major phase (> 10 %); m = minor phase (1-10 %); t = trace phase (< 1 %); nr = not reported.

montmorillonite, illite, kaolinite, and palygorskite and all contain iron in their structure. However, the distribution of these clay minerals throughout the ore zone is ambiguous (Table 11). Montmorillonite or smectite, $(Al_{3.35}Fe_{0.2}^{3+}Mg_{0.35}Fe_{0.1}^{2+}) \cdot (Si_{7.7}Al_{0.3})O_{20}(OH)_4$ (Bromwell, 1982) is iron-rich, containing 6.24 % Fe_2O_3 and 0.11 % FeO (Altschuler, et al., 1963). Fe^{2+} and Fe^{3+} may be structurally present in palygorskite, $(Mg_{1.96}Fe_{0.03}^{2+}Al_{1.61}Fe_{0.37}^{3+}) \cdot (Si_{7.79}Al_{0.21})O_{20}(OH)_2(OH_2)_4$, and illite, $(Na_{0.07}K_{1.34}) \cdot (Al_{3.06}Fe_{0.45}^{3+}Mg_{0.56}Fe_{0.07}^{2+}) \cdot (Si_{6.8}Al_{1.2})O_{20}(OH)_4$ (Bromwell, 1982). Clayballs are the clays, derived from a stratum in the ore matrix, which remain relatively consolidated after water treatment. Swanson and Legal (1967) report two varieties of clayballs in the ore matrix: one is a yellow, "iron-rich" (11.52 % Fe_2O_3), "magnesium-poor" (4.09 % MgO) variety and the other is a white, "iron-poor" (4.34 % Fe_2O_3), "magnesium-rich" (7.12 % MgO) variety; X-ray spectrograph results gave a distinct pattern similar to the mica minerals, but not comparable to any of the clay minerals other than illite or palygorskite.

Phosphorite deposits are sometimes capped by iron sulfide bodies, which range in thickness from centimeters to one meter. The iron sulfide bodies consist predominantly of pyrite and marcasite, which form diagenetically from sediments deposited in a mangrove swamp facies (personal communication, H. Barwood). Pyrite is always present and is most common as nongranular masses or simple interlocking equigranular grains with straight, rectilinear, cusped margins. Less frequently, distorted hexagons and trapezoids of pyrite exhibit multiple zonation. Marcasite is most abundant as clusters in the nongranular masses of pyrite. The individual marcasite crystals are typically twinned and equigranular with simple interlocking, straight, rectilinear, cusped margins. Wavellite or vivianite frequently fill the numerous pore spaces associated with these textures.

Table 11. Description of clay mineral distribution throughout the Central Florida Phosphate District.

Altschuler, et al., 1965		Barwood, et al., 1983		Norilyn mine section	
		<u>Depth</u>	<u>Clay Mineralogy*</u>	<u>Profile</u>	<u>Clay Mineralogy*</u>
K, Sm	OB	0 - 2	-	OB	-
		2 - 10	K, IS	gossan	-
<u>unleached</u>	<u>leached</u>	10 - 11	K, IS, W	leached zone	I, S, K, M, Go, IS, Ap
K, Sm, Ap	C, W, M, Ap, K, G, Pa	11 - 19	Sm, IS, K, W, I	upper matrix	I, IS, S, Ap, K
		19 - 20	Sm, W, I, K	middle matrix	Go, Pa, Sm, Ap
	NF	20.0 - 20.5	Sm, I, W	transition zone	I, IS, S, Ap
<u>matrix zone</u>		20.5 - 23.5	Sm, I, W		
Sm		23.5 - 25.5	Pa, Ap, Sm		
<u>bedclay zone</u>					
Sm, Pa	AF	25.5 - 30.5	Pa, Ap		
<u>bedrock zone</u>		30.5 - 32	Pa, Ap		
Sm		32 - 37	Pa, Ap		
		37+	-		

* In order of relative abundance

OB = overburden; NF = Norilyn Formation; AF = Arcadia Formation;

Ap = apatite (francolite); C = crandallite; G = gibbsite; Go = goethite; IS = interstratified; K = kaolinite;

M = millisite; Pa = palygorskite; Sm = smectite (montmorillonite); W = wavellite.

Glauconite and ankerite may be locally important. A portion of the section in the IMC Phosphoria mine, which is normally dolomitic bedrock, contained interbedded sands and clays. A phosphatic clayey quartz sand bed near the base of this sequence contained glauconite pellets. Glauconite may represent 30 % of the pellets in basal cross-bedded phosphatic quartz sands (personal communication, H. Barwood). Ankerite, $\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$, is usually located in the bedrock (personal communication, H. Barwood).

IRON-BEARING MINERALS IN THE NORTH CAROLINA AURORA DISTRICT

There is a less imposing number of iron-bearing minerals in the Aurora District than in the Central and South Florida Districts (Table 12). Pyrite is the overwhelmingly dominant iron-bearing mineral inclusion in the phosphorites of the Aurora District, although, ilmenite and glauconite are minor iron-containing phase (1-10 %) inclusions.

Fine to medium sand-sized, terrigenous-diluted intraclastic phosphorites comprise approximately 80 % of the phosphorite grains in the Pungo River Formation (Scarborough, et al., 1982). The intraclast pebbles collected for the present study are externally black in color, but internally they are dark to light gray. The EDX and reflected light analysis of these intraclasts indicated iron is almost exclusively present as pyrite, which exhibits textures identical to those observed in their Florida intraclast equivalents. Myriads of < 1 to 2 μm discrete microcrysts are disseminated throughout the apatite matrix and may be so densely packed that they form irregularly shaped aggregates. Framboids are very common and generally reach 10 μm in diameter with approximately 0.5 μm diameter microcrysts. They are often present as "allochems" in a pyrite matrix infilling relatively large void spaces. Irregular, meandering bioturbation structures may be completely or partially filled with pyrite. The relatively thin, 2 to 4 μm -wide segments are usually completely filled. Equigranular, 5 μm , simple interlocking grains with rectilinear and cusped margins form pyrite "clots" in the wider, 30 μm segments. Thin seams of pyrite may partially or completely fill the interstitial pore spaces between pelletal phosphorite and terrigenous grain inclusions.

Pelletal allochems comprise the second major group of phosphorite grain types, accounting for 20 % of the phosphorites in the Pungo River Formation (Scarborough, et al., 1982). Distribution varies, as pyrite may be quite abundant in one pellet and virtually

Table 12. Summary of the iron-bearing minerals in the North Carolina Aurora District phosphorite deposits.

Mineral	Chemical composition	Occurrence	Origin	References
"Black opaques" (hm)	mostly iron and titanium oxide (minor alumina and silica)	ore matrix	?	Lewis, 1974
"Brown miscellaneous" (hm)	iron-titanium-alumina-silica	ore matrix	?	Lewis, 1974
Chlorite [†] (hm)	(Al,Fe ²⁺ ,Fe ³⁺ ,Li,Mg,Mn) ₅₋₆ (Al,Fe ³⁺ ,Si) ₄ O ₁₀ (OH) ₈	ore matrix [‡]	TgS	Rooney & Kerr, 1967
Garnet* (hm)	Fe ²⁺ ₃ Al ₂ Si ₃ O ₁₂	ore matrix	TgS	Lewis, 1974
Glauconite	(K,Na,Ca) _{<1.8} (Al,Mg,Fe ³⁺ ,Fe ²⁺) ₄ (Si ₇ Al)O ₂₀ (OH,F) ₄	PI	1°	Scarborough, et al., 1982
Goethite	Fe ³⁺ O(OH)	PI	2°	This study
Illite	K _{1.5} Al _{3.5} (Mg,Fe ²⁺) _{0.5} (Si ₇ Al)O ₂₀ (OH,F) ₄	PI	1°,2°	Weaver & Wampler, 1972
Ilmenite	Fe ²⁺ TiO ₃	ore matrix	TgS	Rooney & Kerr, 1967
		PI	TgS	This study
Marcasite	Fe ²⁺ S ₂	ore matrix	TgS	Lewis, 1974
		PI	1°	This study
Montmorillonite	(Na,Ca) _{0.66} Al _{3.34} (Fe ²⁺ ,Mg) _{0.66} Si ₈ O ₂₀ (OH) ₄	ore matrix	TgS	Rooney & Kerr, 1967
Palygorskite	(Mg,Fe ²⁺ ,Al,Fe ³⁺) ₄ Si ₈ O ₂₀ (OH) ₂ · 4H ₂ O	ore matrix	?	Weaver & Wampler, 1972
Pyrite	Fe ²⁺ S ₂	PI	1°	This study
		ore matrix	1°	Weaver & Wampler, 1972

hm = heavy mineral

[†]The chlorite group consists of a variety of minerals; the specific chlorite mineral was not specified.

[‡]Chlorite is present only in the Lower Yorktown and Pungo River unit D sections.

*The garnet is probably almandine based on the high iron chemical analysis obtained by Lewis (1974).

PI = phosphorite inclusion

1° = primary

2° = secondary

absent in another. Although microcrysts and microcryst aggregates are the most commonly observed pyrite texture in pelletal phosphorites, any of the previously defined textures may be the dominant form in any given phosphorite pellet.

Invertebrate and vertebrate skeletal material generally constitute less than 15 % of the phosphorite macrograins in any given sample, but may range locally from 5 to 20 % (Scarborough, et al., 1982). A shark tooth exhibited pyrite fillings in the microscopic nerve network and in the central nerve areas (Figure 15). Similar nerve canal filling is probably present in marine vertebrate fossils.

A layer of indurated orthochemical phosphorite mud occurs between the Lower Yorktown and Pungo River unit D. Although this orthochem layer is economically unimportant because it is in the rejected upper low-grade section, it is of interest geologically because it represents the parent material from which intraclastic phosphorites are derived (Riggs, 1979a). This phosphorite genetic relationship is consistent with pyrite morphology, as the pyrite textures observed in the intraclasts are identical to those in the orthochems. However, orthochems exhibit lamination, rod, and ellipsoid textures which were not observed in intraclasts during the present study. Lamellae are distinct, varying in color from light brown to black and in size from 20 μm to 3 mm. Whereas pyrite framboids and microcrysts are intimately associated with black lamellae, the relationship is not absolute. That is, black lamellae may be traced throughout an orthochem macrograin, whereas pyrite is discontinuous or concentrated in segments of the lamellae. Rods and ellipsoids of pyrite, typically 5 x 20 μm and 10 x 30 μm in grain size respectively, are abundant. Subhedral pyrite cubes are much larger than those observed in intraclasts and commonly reach a maximum size of 60 μm . The lamellae and relatively larger pyrite grains may act as cleavage planes during subsequent boring and fragmentation and be destroyed during transportation, thus accounting for their relative absence in intraclasts.

The most significant concentrations of minor iron-containing phases (1-10 %) occur in

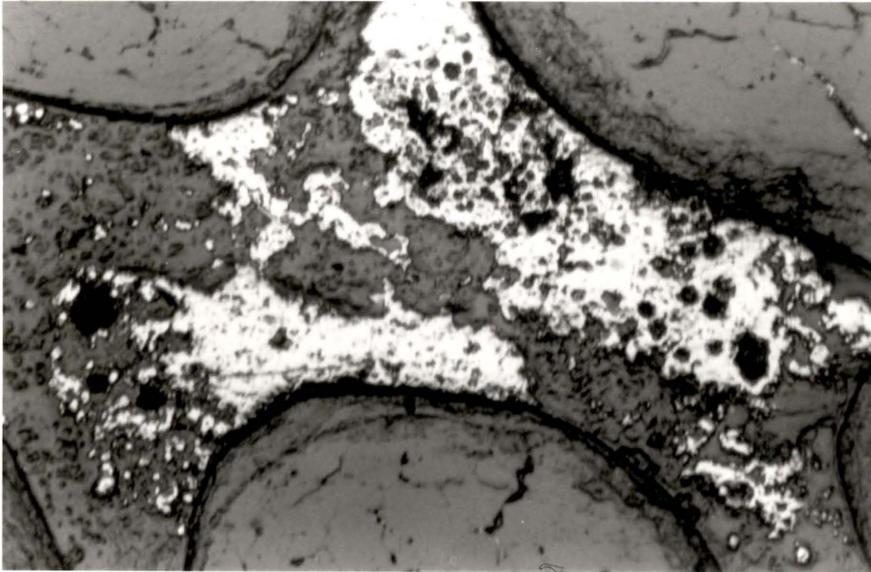


Figure 15. Plain-polarized-reflected-light photomicrograph of pyrite filling the central nerve canal of a shark tooth.

the intraclastic and orthochemical phosphorites. Ilmenite is the only minor iron-bearing phase detected in the present study and typically occurs as discrete 25 μm anhedral grains. However, glauconite grains have also been reported as common minor phase inclusions (Rooney and Kerr, 1967 and Scarborough, et al., 1982). Trace iron mineral phases (< 1 %) of marcasite and goethite are present in segments of some burrows in orthochemical phosphorites.

The principal accessory iron-bearing minerals in the ore matrix are the heavy minerals (Table 12) and, perhaps, the clay minerals. Rooney and Kerr (1967) report that the clay minerals often constitute up to 40 % of the ore matrix and are relatively uniform in distribution as opposed to the Florida deposits. The predominant clay minerals throughout the ore matrix are montmorillonite and illite, which both may contain Fe^{2+} and Fe^{3+} structurally. Kaolinite and chlorite appear at all depths to 90 feet, but neither are present in the economic zone.

IRON-BEARING MINERALS IN THE CENTRAL TENNESSEE BROWN ROCK DISTRICT

Goethite and hematite are the dominant iron-bearing minerals in the residual deposits of the Tennessee Brown Rock Phosphate District and occur as very fine-grained phosphorite inclusions and as accessory minerals in the ore matrix (Table 13). The only minor iron-containing phase (1-10 %) phosphorite inclusion identified in this study is ilmenite, which occurs only in the pelletal phosphorites.

The parent phosphatic limestone is gray in color when unweathered and contains, in addition to pelletal and skeletal phosphorites, inclusions of anhedral, 50 μm marcasite crystals, which commonly exhibit twinning. Pyrite is abundant in the black pelletal phosphorites and occurs as inclusions of randomly disseminated cubes, microcrysts, and irregularly shaped microcryst aggregates in the apatite matrix. The skeletal phosphorites in the limestone predominantly consist of white to gray-colored fragments of bryozoan colonies. Pyrite often fills many of the approximately 5 μm diameter bryozoan zooecium. The parent phosphatic limestone weathers brown as a result of minute goethite and limonite staining. The oxidizing environment accompanying weathering has altered the pyrite inclusions in the phosphorites and the marcasite inclusions in the limestone to iron oxides. The end product of pyrite alteration optically appears to be hematite; marcasite, however, optically appears to be altering to a complex assemblage of very fine grained goethite, hematite, and lepidocrocite.

Pelletal, skeletal, and plate rock phosphorites constitute the major phosphate component in the residual deposits. The EDX examination of polished cross-sections of these phosphorites reveals that iron oxides are the only major iron-bearing inclusions. All of the disseminated cubes, microcrysts, and irregularly shaped microcryst aggregates in the pelletal phosphorites (Figure 16) and the zooecium fillings in the skeletal phosphorites

Table 13. Summary of the iron-bearing minerals in the Tennessee brown rock phosphorite deposits.

Mineral	Chemical composition	Occurrence	Origin
Ferromanganese oxide	presently not known	ore matrix	2°
Goethite	$\alpha\text{-Fe}^{3+}\text{O(OH)}$	phosphorite stain	2°
Hematite	$\text{Fe}_2^{3+}\text{O}_3$	ore matrix	2°
		clayball stain	2°
		limestone stain	2°
		phosphorite inclusion	2°
		ore matrix	2°
Illite	$\text{K}_{1.5}\text{Al}_{3.5}(\text{Mg}, \text{Fe}^{2+})_{0.5}(\text{Si}_7\text{Al})\text{O}_{20}(\text{OH}, \text{F})_4$	clayball inclusion	2°
		ore matrix	†
Ilmenite	$\text{Fe}^{2+}\text{TiO}_3$	phosphorite inclusion	TgS
Lepidocrocite	$\gamma\text{-Fe}^{3+}\text{O(OH)}$	ore matrix	2°
		limestone inclusion	2°
		clayball inclusion	2°
		phosphorite stain	2°
Limonite	$\text{Fe}^{3+}\text{O(OH)} \cdot n\text{H}_2\text{O}$	clayball stain	2°
		limestone stain	2°
		limestone inclusion	1°
		ore matrix	TgS
		phosphorite inclusion	1°
Marcasite	Fe^{2+}S_2	phosphorite inclusion	1°
Montmorillonite	$(\text{Na}, \text{Ca})_{0.66}\text{Al}_{3.34}(\text{Fe}^{2+}, \text{Mg})_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4$	ore matrix	TgS
Pyrite	Fe^{2+}S_2	phosphorite inclusion	1°

† illite could be authigenic, terrigenous, or a weathering product

1° = primary

2° = secondary

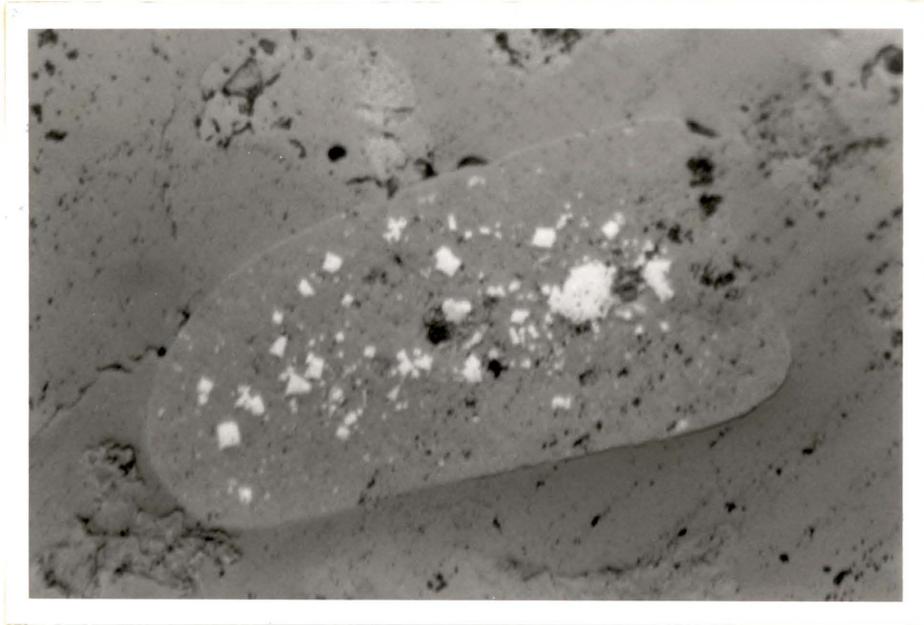
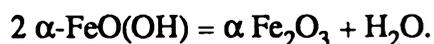


Figure 16. Plain-polarized-reflected-light photomicrograph of hematite microcryst and cube inclusions in a phosphorite pellet.

optically appear to be hematite pseudomorphs after pyrite. Confirmation using X-ray diffraction of ground phosphorite pellets is inconclusive, because the 2.72 Å peak of francolite interferes with the most intense hematite peak, 2.69 Å. It may be possible to subject a large quantity of finely ground powder of phosphorite pellets to magnetic separation and thereby obtain a concentrated mass of hematite suitable for X-ray diffraction. Because there is an approximately 37 % reduction in molar volume during the transition from pyrite to hematite, the altered inclusions should theoretically exhibit a significant increase in porosity. However, the hematite pseudomorphs are non-porous, which indicates that iron was mobile during recrystallization. It also suggests that some iron may have escaped during the alteration process and subsequently precipitated as the minute iron oxyhydroxide stains on the apatite matrix. Another possible source of the secondary goethite and limonite stains is from percolation of meteoric waters enriched in iron leached from montmorillonite during weathering. Since plate rock phosphate is parent phosphatic limestone that has undergone weathering and supergene phosphatization, the iron-bearing inclusions are hematite, as iron sulfide pseudomorphs, and goethite, as secondary stains. The internal molds and casts of the tiny gastropod *Cyclora minuta* constitute a minor phosphate component in the residual deposits. These microphorite mud-filled molds and casts contain abundant inclusions of hematite as spherical microcrysts and up to 10 µm rods.

The geochemistry of hematite formation is complex. Hematite can be formed as a dehydration product of goethite:



However, the rate of goethite to hematite transformation at earth surface temperature and pressure is very slow (Berner, 1969) and, consequently, requires a geologically long period of time. At one atmosphere of water pressure, a temperature of about 80°C is

required for coarse-grained ($> 1 \mu\text{m}$) goethite to convert to coarse-grained hematite (Langmuir, 1971). It is unlikely that the hematite inclusions in the phosphorites proceed through a goethite intermediate, because the Tennessee brown residual deposits are geologically recent, being middle to late Pleistocene in age, and have not undergone any heating. Fischer and Schwertmann (1975) suggest that hematite does not form exclusively from goethite by a simple dehydration reaction, but can form by a separate pathway from a source common to goethite. Environmental conditions play a decisive role in determining whether goethite or hematite is produced, probably because of their influence on the kinetics of the alternative reactions (Fischer and Schwertmann, 1975). Apparently, the geochemical conditions within phosphorites in weathered carbonate environments inhibit the oxidation of pyrite to goethite and favor the formation of hematite.

The phyllosilicates in the clay separate of the Williamson County sample are illite, kaolinite, montmorillonite, and interstratified kaolinite-smectite. Kaolinite and montmorillonite are present throughout the vertical section as minor phases (1-10 %) in the clay fraction. Illite is dominant in the lower section and kaolinite-smectite in the middle and upper sections. The presence of interstratified kaolinite-smectite indicates that smectite alteration to kaolinite, similar to that observed by Altschuler, et al. (1963) in Florida, may also occur in the Tennessee brown rock residual deposits. This weathering mechanism provides a source of iron leached from montmorillonite in the secondary enrichment process. However, the iron chemistry of the phyllosilicates needs to be investigated before this process can be confirmed. Illite is also commonly present in the ore matrix as irregularly shaped clayballs, which are partially surrounded by thin, 1 to 5 μm rims of supergene apatite. These goethite- and limonite-stained illite clayballs invariably contain goethite microfracture fillings, randomly disseminated inclusions of 1 to 5 μm hematite, and 15 to 50 μm iron oxide particles, which consist of a complex assemblage of very fine grained goethite, hematite, and lepidocrocite.

Secondary ferromanganese oxide spherulites (Figure 17), referred to as "buckshot" by local miners, are present in the ore matrix with 20 to 50 μm anhedral to subhedral iron oxide grains as minor iron-containing phases (1-10%). Optically the iron oxide grains appear to be a complex assemblage of very fine grained goethite, hematite, and lepidocrocite. Terrigenous quartz contains no iron, but 3 to 5 μm particles of hematite are sometimes lodged in the minute crevices of the grains. Secondary, irregularly-shaped chalcedony nodules often contain inclusions of hematite.

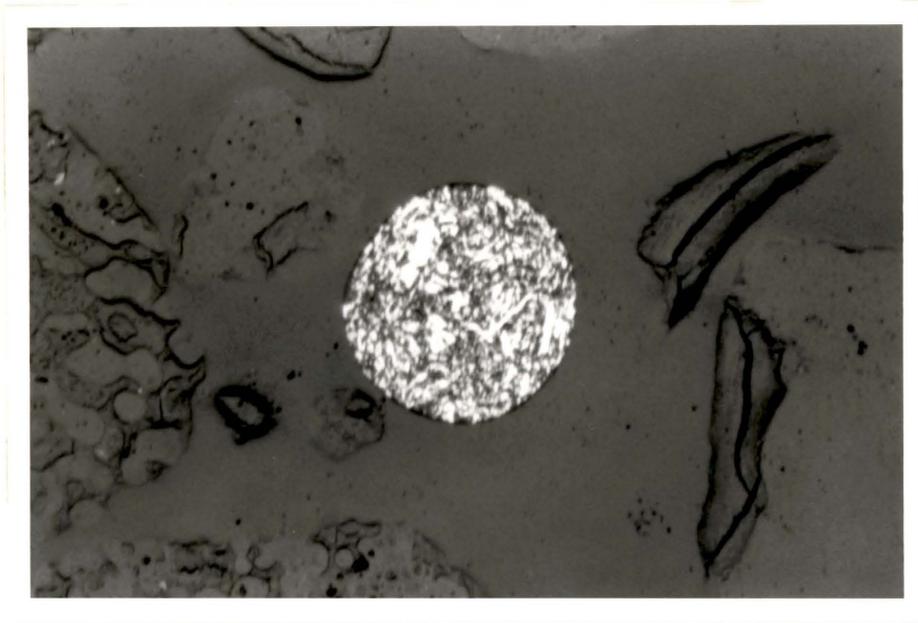


Figure 17. Plain-polarized-reflected-light photomicrograph of a ferromanganese oxide spherulite.

THE IRON BUDGET IN SEDIMENTARY PHOSPHORITES OF THE SOUTHEASTERN UNITED STATES

Iron is incorporated into the apatite matrix during phosphorite formation principally as inclusions of authigenic pyrite and marcasite, FeS_2 , and to a lesser extent as terrigenous heavy mineral inclusions (Figure 18). The pyrite inclusions occur as discrete, randomly disseminated microcrysts, 10 to 20 μm irregularly shaped microcryst aggregates, 5 to 10 μm dendrites, 4 to 20 μm cubes, 5 to 10 μm framboids, and interstitial and bioturbation void-fillings. Ilmenite, FeTiO_3 , is the most common iron-bearing heavy mineral inclusion. Pyrite and marcasite commonly fill the microscopic nerve canals of shark teeth and other marine and terrestrial vertebrate hard parts in Atlantic coastal plain skeletal phosphorites and bryozoan zooecium in Tennessee skeletal phosphorites.

The primary phosphorites of the Pungo River Formation in the North Carolina Aurora District have generally not been subjected to subaerial weathering. Consequently, the iron-bearing mineral inclusions are preserved in their authigenic state of formation as described above. However, subaerial weathering processes have dramatically affected the iron mineralogy of the phosphorites in central Florida and Tennessee.

The clastic phosphorites of the Hawthorn Group in the Central Florida District exhibit extensive and variable degrees of weathering. The oxidizing environment accompanying weathering has altered the iron sulfide inclusions in phosphorites to goethite, $\text{FeO}(\text{OH})$. Because this oxidation apparently involves no loss of iron, it is likely that the minute goethite and limonite stains on the apatite matrix, which are responsible for the color of brown phosphorites, are secondary and have been introduced by the percolation of meteoric waters enriched in iron leached from montmorillonite during weathering. The iron leached during weathering of iron-rich montmorillonites in the upper overburden form

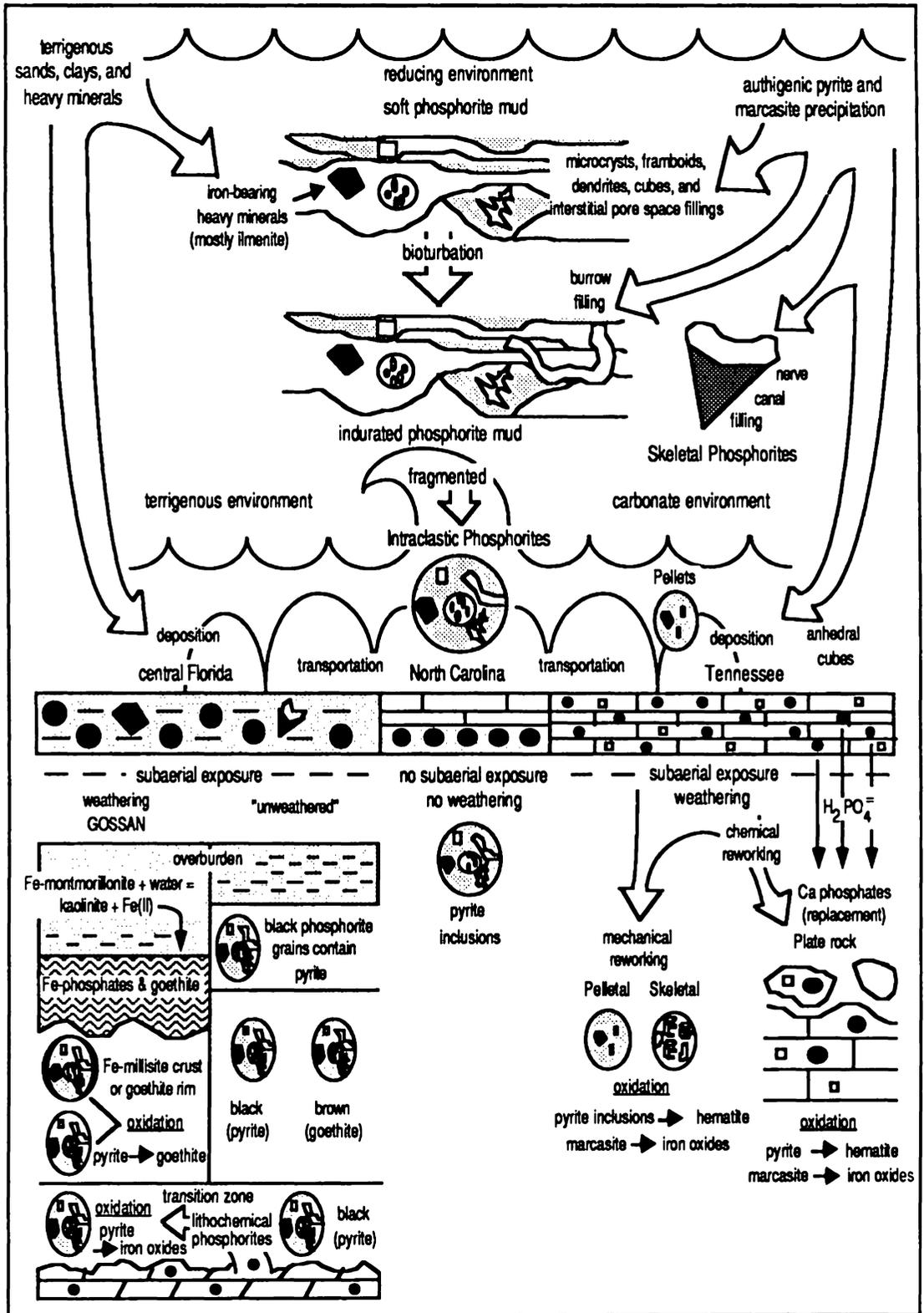


Figure 18. The iron budget in sedimentary phosphorites of the southeastern U. S.

goethite hardpans at the lower overburden-ore body contact. These hardpans react with phosphatic solutions to form iron gossans, which are localized zones of iron phosphate and iron oxyhydroxides. The phosphorites in the leached zone directly under the iron gossan are partially coated with either supergene goethite rims or Ca-Fe-Al phosphate crusts. The phosphorites in the transition zone between the basal bedrock and the main ore body of both weathered and "unweathered" deposits are richer than average in iron oxide inclusions, which suggests that they underwent weathering during the early Miocene and were subsequently reworked and redeposited during an ensuing phosphogenic transgression with pyrite-containing black phosphorites.

The Tennessee brown rock phosphorites are residually concentrated by the weathering of the phosphatic Bigby-Cannon Limestone. During weathering, the cube, microcryst, and irregular aggregate inclusions in phosphorites oxidize to hematite, Fe_2O_3 . The inclusions of marcasite in the parent limestone oxidize to a complex assemblage of very fine grained goethite, hematite, and lepidocrocite. The deep brown color of the residual phosphorites is imparted by secondary goethite stains, which may be the result of iron mobilized during pyrite oxidation to hematite or by percolation of meteoric waters enriched in iron leached from smectite during weathering.

THE RELATIONSHIP OF IRON-BEARING MINERALS TO THE IRON PROBLEM IN THE PHOSPHATE INDUSTRY

The iron-bearing minerals in sedimentary phosphorites of the southeastern United States principally occur as disseminated inclusions in the apatite matrix which precludes their liberation using conventional beneficiation methods. The iron-containing minerals that adversely affect wet-process acid processes used by the Florida and North Carolina industries to manufacture fertilizer products are primarily the acid-soluble Fe^{3+} oxyhydroxides and oxides such as goethite and hematite. Any of the iron-bearing minerals identified in this study which enter the electric furnace, used by the Tennessee industry to manufacture elemental phosphorus, adversely affect the process by forming byproduct ferrophosphorus.

Florida

The economic Noralyn Formation contains abundant black and brown phosphorite grains throughout the unit. The predominant iron-bearing mineral inclusions in black phosphorites are pyrite and in brown phosphorites are goethite. It is not economically or technologically possible to prevent these Fe^{3+} oxyhydroxide-containing brown phosphorites from entering the acidulation process. However, some sections of the Noralyn Formation are unusually rich in Fe^{3+} due to weathering processes and their detrimental effects can be reduced by selective mining. The phosphorites in the leached zone under the iron gossans, in addition to containing abundant goethite inclusions, are coated with supergene rims of goethite or crusts of ferrian-millsite, a Ca-Fe-Al phosphate. The secondary lithochemical phosphorites in the transition zone between the Noralyn and the basal bedrock limestone contain abundant inclusions of goethite or hematite. The leached zone

should be stripped with the iron gossan and the transition zone left in place. However, the loss of phosphate associated with this procedure needs to be examined before the worth of selective mining can be assessed. The Florida ore matrix generally consists of terrigenous sands and clay minerals. The terrigenous iron-bearing heavy minerals are acid-insoluble and mostly removed during flotation, and therefore do not contribute to the iron problem. However, some washer circuits are not designed to handle high-slime ore matrix and, consequently, iron-containing clays enter into the beneficiation and acidulation process. This usually results in the solubilization of a large fraction of the impurity constituents along with the phosphate (McClellan and Lehr, 1982). As mining progresses southward into the lower-grade dolosilt- and pyrite-diluted phosphorite ores of the South Florida District, the effects of iron contamination in acidulation processes should decline.

North Carolina

The Pungo River Formation in the Aurora District is basically unweathered and iron has consequently remained in its authigenic pyrite state. Because pyrite is acid-insoluble, the North Carolina phosphate industry does not experience the iron problems encountered by the Florida industry. However, Fe^{2+} may present significant corrosion problems with some types of construction materials and create problems in filtrations or ion-exchange operations by forming solids with undesirable physical properties (McClellan and Gremillion, 1980).

Tennessee

Only the clays which are dispersed by hydraulicking and washing are removed during beneficiation. The principal contributors to the ferrophosphorus problem are goethite and

hematite, which occur as phosphorite and clayball inclusions and as accessory minerals. Accessory secondary ferromanganese oxide spherulites might be removed by magnetic separation; however, the economics associated with this separation currently make this relatively insignificant iron reduction impractical. Davenport and Haseman (1947) report significant losses of P_2O_5 during mechanical conditioning experiments which prohibits the use of agitation methods to disaggregate clayballs. Iron contamination is a problem the Tennessee industry will probably have to endure.

CONCLUSIONS

- (1) The principal syngenetic iron-bearing mineral in sedimentary phosphorites of the southeastern United States is authigenic pyrite, FeS_2 , which occurs as microcrysts, 10 to 20 μm irregularly shaped microcryst aggregates, 5 to 20 μm dendrites, 4 to 20 μm cubes, and 5 to 10 μm framboids, and interstitial and bioturbation void-filling inclusions in the apatite matrix.
- (2) Two subaerial weathering processes have been identified in this study which are responsible for the alteration of iron sulfide inclusions in phosphorites to iron oxide pseudomorphs. The geochemical conditions within phosphorites in the weathered terrigenous sand and clay environment of central Florida favor the oxidation of pyrite to goethite, $\text{FeO}(\text{OH})$. The geochemical conditions within phosphorites in the weathered carbonate environment of central Tennessee inhibit the oxidation of pyrite to goethite and favor the formation of hematite, Fe_2O_3 .
- (3) Goethite-containing brown phosphorite grains, which are admixed throughout the Florida ore matrix with pyrite-containing black phosphorite grains, may be reworked phosphorites derived from a paleo-weathered terrigenous sand and clay environment.
- (4) The lithochemical phosphorites in the transition zone of central Florida deposits which contain inclusions of hematite are reworked phosphorites derived from early Miocene weathering of the phosphatic Arcadia Formation .
- (5) The pyrite and goethite inclusions in the central Florida phosphorites are sometimes surrounded by an alumina deficient iron-potassium-silicate clay mineral, which may be celadonite, $\text{K}_2\text{X}_4\text{Si}_8\text{O}_{20}(\text{OH},\text{F})_4$, or glauconite, $\text{Y}_{<1.8}\text{X}_4(\text{Si}_7\text{Al})\text{O}_{20}(\text{OH},\text{F})_4$, where $\text{X} = \text{Fe}^{2+}$ and Fe^{3+} in the octahedral layer and $\text{Y} = \text{K}^+$ in the interlayer.
- (6) Ilmenite, FeTiO_3 , is the most commonly occurring minor iron-containing phase (1-10 %) inclusion in sedimentary phosphorites of the southeastern United States.

- (7) Chalcopyrite, CuFeS_2 , and chromite, FeCr_2O_4 , are two heretofore undetected minerals in phosphorites and were identified in this study in central Florida intraclastic phosphorites.
- (8) Phosphorite deposits in central Florida are sometimes capped by either gossans or iron sulfide bodies. Gossans consist of residual quartz, complex assemblages of cryptocrystalline iron phosphates, and iron oxyhydroxides, and are formed by the interaction of phosphatic solutions with secondary hardpans during weathering. The iron sulfide bodies consist of pyrite and marcasite and are the result of diagenesis of sediments deposited in a mangrove swamp facies. The gossans and iron sulfide bodies are localized zones ranging in thickness from centimeters to one meter.
- (9) Supergene ferrian-millisite, $\text{Ca}_3(\text{Al,Fe}^{3+})_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$, occurs as myriads of 5 μm anhedral crystals in crusts coating phosphorites in the leached zone under the Noralyn mine gossan in central Florida.
- (10) Secondary ferromanganese oxide spherulites occur as accessory minerals in the Tennessee brown rock cutter deposits.

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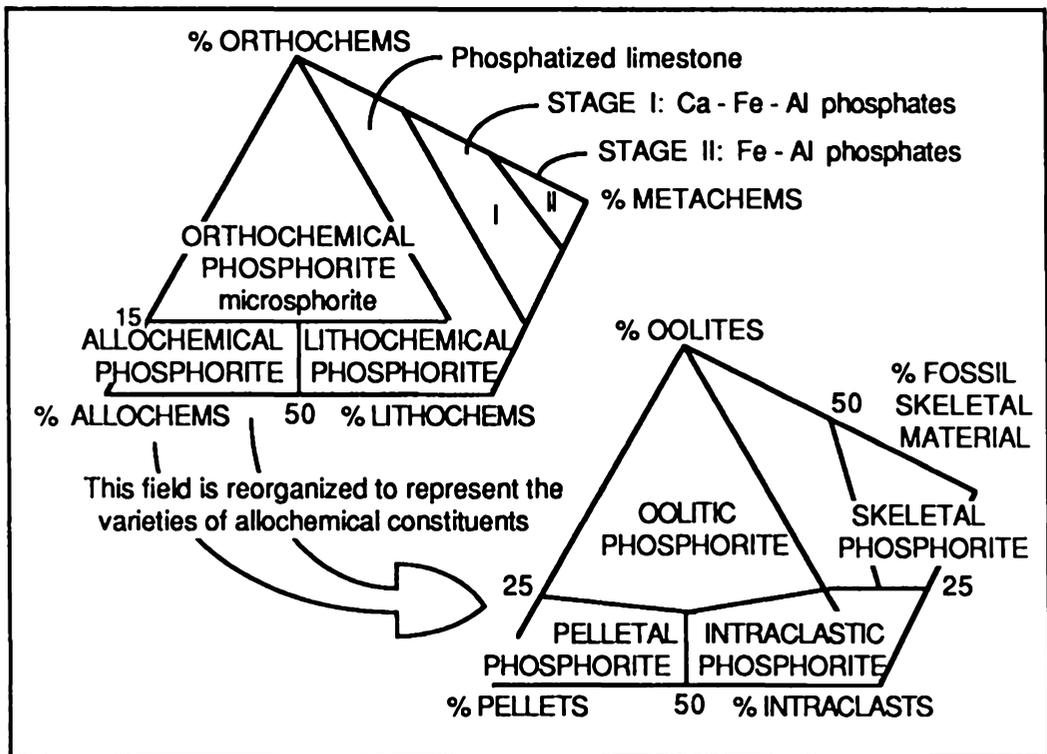
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APPENDIX 1



Classification of the macroscopic components of sedimentary phosphorites
(modified after Riggs, 1979a)

Appendix 1 is a review of the sedimentary phosphorite classification scheme introduced by Riggs (1979a). Only the pelletal and metachemical phosphorite components have been modified.

- I. **PRIMARY SEDIMENTARY PHOSPHORITES** are authigenic phosphorite minerals formed on the sea floor and may be classified as either orthochems or allochems.
 - A. *Orthochemical Phosphorites (orthochems)* are clay-sized phosphate minerals formed physicochemically or biochemically *in situ* in the marine environment and show little or no evidence of transportation (microcrystalline phosphorite = microsphorite).
 - B. *Allochemical Phosphorites (allochems)* are larger than clay-sized, clastic phos-

phate sediments that have been precipitated physicochemically or biochemically within the area of deposition and organized into discrete aggregated bodies that have, for the most part, suffered some transportation within the area of deposition.

1. *Intraclastic Phosphorites (intraclasts)* are fragments of penecontemporaneous phosphorite sediments that have been torn up from adjoining parts of the sea bottom and redeposited by currents to form a new sediment.
 2. *Pelletal Phosphorites (pellets)* are ovoid, semispherical, or rod-shaped phosphorite grains which range in size from 0.177 to 0.062 mm. Riggs defined pelletal phosphorites to be of fecal origin. They are often very difficult to distinguish from highly abraded and fine-grained intraclasts, but are readily recognized when occurring as clusters or aggregates filling internal fossil molds, infilling burrows, and in clusters on microsporite surfaces. This study found that the iron-bearing mineral inclusions in fine-grained intraclasts and a Riggs pelletal phosphorite are essentially equivalent. Therefore, all fine sand- to very fine sand-sized phosphorites shall be regarded as pelletal phosphorites in this study.
 3. *Skeletal Phosphorites* are grains of fossil skeletal material such as vertebrate bones and teeth and invertebrate shell material. This category does not include the internal molds and casts which are actually phosphorite mud.
 4. *Oolitic Phosphorites* are microsporite accretions symmetrically and concentrically laminated around a major nucleus. *Pseudo-oolitic phosphorites* are oolitic phosphorites which generally lack sphericity and well-defined concentric laminations.
- II. *SECONDARY SEDIMENTARY PHOSPHORITES* are primary phosphorites which have been modified by secondary processes and may be classified as either lithochems or metachems.

- A. *Lithochemical Phosphorites (lithochems)* are phosphorite fragments that have been eroded from older phosphorite rocks or sediments either off an emergent land area or submarine outcrops, transported, and redeposited in younger sediments.
- B. *Metachemical Phosphorites (metachems)* are phosphorites which have been formed by alteration or precipitation as a result of weathering. The term metachemical phosphorite was first introduced to describe the progressive mineralogical and chemical modification of orthochemical, allochemical, and/or lithochemical phosphorites by the processes of supergene alteration and weathering. As weathering processes in phosphorite deposits continue to be better understood, it has become necessary to update the metachemical term. The metachemical phosphorites may be classified according to their mineral assemblages, which reflect a natural weathering sequence.
1. Phosphatized limestones are carbonates which have been replaced by calcium phosphate, typically francolite or apatite. Since limestones are authigenic and phosphatization involves the replacement of calcium carbonate with calcium phosphate, these metachems are often very difficult to distinguish from their primary phosphorite counterparts using internal textures. The principal distinguishing features are their increased hardness and external morphology, which often resembles chewed chewing gum.
 2. Stage I metachemical phosphorites are the transitional supergene phosphates, such as millisite, $(\text{Na,K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}$, and crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$.
 3. Stage II metachemical phosphorites represent the final stage of weathering and are the stable Fe-Al phosphates, such as wavellite, $\text{Al}_3(\text{PO}_4)_2(\text{OH})_5 \cdot 5\text{H}_2\text{O}$, and the iron phosphates in gossans.

APPENDIX 2

The ore matrix of each profile was diluted with deionized water, as necessary to achieve a non-viscous slurry, and then mixed in a *Hamilton Beach Drink Master* milkshake machine from 5 to 10 minutes, as necessary to disaggregate slimes from the phosphorite grains. No dispersant was added so that the desliming processes used by industry could be simulated in this study. The Florida ore matrix was wet-sieved into +10, -10+60, -60+270, and -270 mesh (U. S. Standard Sieve) separates and the Tennessee ore matrix into -60+270 and -270 mesh separates. The coarse grained separates were dried overnight under room conditions and the fine grain separates by acetone evaporation in a filtration apparatus. The -270 mesh slimes were stored in transparent plastic bottles and shaded from sunlight.

Preliminary attempts to examine the iron-bearing inclusions in central Florida phosphorites involved SEM and EDX analysis of grains exposed at the surface of cracked phosphorite pebbles. Because the iron-bearing minerals were not completely exposed during cracking (cleavage left thin apatite sheaths covering the iron-containing inclusions), it was necessary to cross-section and polish the phosphorite grains. Selected phosphorite grains from the +10 mesh separate and bulk samples from the other separates were embedded in *Epofix* resin, cross-sectioned, and polished according to the methods described by Craig and Vaughan (1981). Preliminary investigation also revealed that iron sulfide is present as very fine grained inclusions in black phosphorites. Because phosphorites require about three days of vibropolishing with 0.05 μm alumina oxide to attain an acceptable polished surface, it was necessary to maintain anaerobic conditions during vibropolishing to prevent possible iron sulfide alteration. The first attempt used an immiscible solution of glycerol and distilled water as the liquid medium and was successful in obtaining polished surfaces and controlling reducing conditions. However, it was

abandoned after a bacteria culture grew within a few days. The next attempt used an immiscible mixture of *Johnson's Baby Oil* and distilled water. This solution formed a thin paste with the alumina oxide on the phosphorite surface which was only detectable using SEM analysis and required subsequent removal by polishing with a 0.05 μm diamond lap. However, this technique was indirectly successful in obtaining polished surfaces with unaffected iron-bearing inclusions. Later experiments found that fine grained iron sulfide inclusions are not altered under aerobic conditions during vibropolishing (that is, distilled water is the best liquid medium). The polished cross-sections were stored in a desiccator.

The free iron oxides, which are mainly responsible for high background in XRD analysis, were removed from the IMC Noralyn mine and Stauffer Spring Hill mine -270 mesh slimes following the methods described by Mehra and Jackson (1960). The clay-sized minerals were separated from the silt-sized minerals in these slimes following the procedures described by Jackson, et al. (1950), with an *International Equipment Company* Model 2K centrifuge. The clay separates were then flocculated using the methods described by Kunze (1965) and, when necessary, by freeze-drying. Duplicates of the clay concentrates from each profile were then impregnated on ceramic tile by vacuum suction. One tile mount was saturated with Mg^{2+} , solvated with glycerol, and analyzed with XRD at room temperature and 110°C. The other tile mount was saturated with K^+ and analyzed with XRD at room temperature, 110°C, 300°C, and 550°C and with DSC.

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IRON MINERALS IN SEDIMENTARY PHOSPHORITES OF THE SOUTHEASTERN UNITED STATES

by

James Louis Lemine

(ABSTRACT)

The central Florida, North Carolina, and central Tennessee phosphorite deposits account for 90 % of the marketable phosphate produced in the United States. Scanning electron and reflected light microscopy reveals that the iron-bearing minerals associated with these sedimentary phosphorites are related to the geologic setting and degree of weathering of the deposit.

Pyrite and marcasite (FeS_2) are the principal iron mineral inclusions in unweathered phosphorites of Florida, North Carolina, and Tennessee, and occur as discrete, randomly disseminated microcrysts, irregularly shaped microcryst aggregates, cubes, dendrites, framboids, or bioturbation and interstitial pore space fillings. Pyrite and marcasite also fill the void spaces in skeletal phosphorites such as nerve canals in shark teeth of Florida and North Carolina and in bryozoan zoecium of Tennessee. The oxidizing conditions accompanying weathering in the terrigenous sand and clay environments of central Florida alter these inclusions to goethite (FeOOH), which occurs as pseudomorphs after the iron sulfides. However, hematite (Fe_2O_3) optically appears to be the iron sulfide pseudomorph in the phosphorites of the weathered carbonate environments in central Tennessee.

The first reported occurrences of chalcopyrite (CuFeS_2), chromite (FeCr_2O_4), and an iron-potassium-silicate sheath surrounding some iron sulfide and iron oxides as inclusions in phosphorites, supergene ferrian-millisite [$\text{Ca}_3(\text{Al,Fe}^{3+})_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$] as coatings on phosphorites in the leached zone under a central Florida gossan, and secondary

ferromanganese oxide spherulites as accessory minerals in Tennessee deposits are made in this study.