Stratigraphic Modeling for Concealed Phosphate Deposits in Virginia's Coastal Plain

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"Opportunities for new discoveries are good, and the increasing knowledge about the origin and occurrence of phosphate deposits should aid prospecting."
V. E. McKelvey, 1967

Abstract

A study to outline an exploration program for phosphates beneath Virginia's Coastal Plain was undertaken by the Virginia Division of Geology and Mineral Resources with funding support from the U.S. Geological Survey. An in-depth literature review highlighted the importance of two primary stages in the development of phosphate deposits in the geologic setting of the mid-Atlantic Coastal Plain. During stage one, primary phosphatic material was precipitated in the early Paleogene marine environment from nutrient-rich, oxygen-poor seawater. During stage two, primary phosphate deposits were exposed to weathering, reworked, and concentrated. The model presented here, at its simplest, advocates the concept of a genesis unit, the Paleocene-Eocene Pamunkey Group, bounded on top by an unconformity, which is overlain by the host unit, the Miocene Calvert Formation, whose base contains a lag deposit of phosphatic sand and gravel.

Using geologic data derived from geologic maps and water wells completed in Virginia's Coastal Plain, the depth to the base of the Calvert Formation was mapped and a target zone was defined based upon a maximum overburden thickness of one hundred feet. Reconnaissance-scale field investigations included sampling of selected outcrops along the Rappahannock, Mattaponi, and Pamunkey rivers, together with borehole drilling in the interfluvial regions. Laboratory analytical results of sediment samples indicate P_2O_5 concentrations up to 3.96%, and good correlation between phosphate, uranium, thallium, and yttrium. Field observations, geochemical results from laboratory analyses, and analysis of the structural morphology of the basal Calvert Formation support the concept of phosphate enrichment in the basal lag deposits and within other defined structural lows. Several areas were identified for the next phase of investigations that would include evaluations of gamma activity from existing well logs and additional borehole drill testing and sample collection.

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1.0 Introduction

1.1 Statement of Problem

As the primary source of phosphorous contained in commercial phosphate fertilizers and animal feed additives, the demand for phosphate rock is expected to increase in proportion to the steady increase in world population and food demand. Driven by increased world demand for phosphate products coupled with tight supplies of raw materials in 2007, the price of marketable phosphate rock increased dramatically (nearly fourfold), spawning new interest in geologic resources around the globe. Formerly the world's leading producer of phosphate rock, production in the United States is now overshadowed by the combination of increased production in China and North Africa, new mines in planning or development in Australia, the Middle East, South Africa, and South America, and the depletion of higher yield domestic reserves.

Domestic production of phosphate rock has long been dominated by mines located in central Florida, although other important deposits are currently mined in North Carolina, Idaho, and Utah. The Florida and North Carolina deposits occur as sedimentary marine phosphorites that were deposited along the continental shelf and are recognized as part of a larger potential geologic resource along the Atlantic Coastal Plain. In North Carolina, phosphate rock is mined from sedimentary units within the Pungo River Formation, which was deposited in early to middle Miocene time (Miller, 1982). In Virginia, this formation is equivalent to marine and marginal marine strata of the Chesapeake Group, including the Calvert Formation (Ward and Blackwelder, 1980).

The Virginia Division of Geology and Mineral Resources (VDGMR) is aware of past exploration interest in phosphate rock resources in the Calvert Formation and other Tertiary strata in Virginia's Coastal Plain, yet there has never been a comprehensive assessment of the mineral potential. In addition, Neogene sedimentary formations in Virginia's Coastal Plain are known to host deposits of potash in glauconite, as well as rare earth elements and commercial heavy mineral deposits. The regional distribution and specific depositional environments of these mineral deposits remains poorly constrained and consequently under-explored due to the lack of an adequate understanding of the stratigraphic framework.

1.2 Statement of Purpose

This study addresses two primary goals that are consistent with the Mineral Resources External Research Program (MRERP) of the U.S. Geological Survey (USGS), specifically: 1) to ensure the availability of reliable geologic, geochemical, geophysical, and mineral locality data; and 2) to ensure the availability of up-to-date quantitative assessments of the potential for undiscovered mineral deposits.

In Virginia, there is a substantial need to organize and re-evaluate existing data, identify and address critical information gaps, and revise current models of phosphate deposition in the Atlantic Coastal Plain environment. In the past, phosphate rock has been frequently overlooked in mineral exploration, largely because sources have been sufficient and prices remained flat, and also, in part, because of difficulties recognizing deposits in the field. The results of this study are intended to provide the basis for new exploration interest by mineral producers in Virginia. Other elements that might be identified and recovered as byproducts of phosphate mining include fluorine, vanadium, boron, uranium, scandium, and the increasingly valuable rare earth elements.

1.3 Value and Economics of Phosphate

Phosphorus is a vital component of every cell of every organism that ever lived; it is a necessary constituent of nucleic acids and is instrumental in organic metabolism as adenosine triphosphate, or ATP, the energy currency of all living things. Phosphorus is essential to photosynthesis, entering the food chain through plants that acquire it from soils. Although it occurs naturally in most soils, it is not particularly abundant and is only slowly released by insoluble phosphate compounds. Because of its low concentrations and its high demand by plants and microorganisms, phosphate is usually the ultimate limiting factor in soil fertility. For sustained crop yields additional regular applications are necessary, particularly in tropical soils, which are often highly deficient due to leaching. There are no known substitutes and recycling efforts are insignificant, thus it is clear that the demand for phosphate will continue to expand in lock step with global population growth and food consumption.

The importance of phosphate resources cannot be overstated. Together with nitrogen and potassium, phosphorous is one of the three cornerstones of modern agriculture and is crucial for sustaining food production for the world's human population. Other commercial and industrial products such as detergents, toothpaste, dyes, flame-retardants, insecticides, and incendiary bombs also depend upon phosphate as a raw material.

Phosphate market conditions have become increasingly volatile in the last decade. From 2002 to 2008, global production of phosphate rock jumped from 125 million metric tons to 167 million metric tons, an increase of 34 percent (Jasinski, 2009, 2007a). Despite this upturn in supply, beginning in late 2007 and continuing into 2008, burgeoning agricultural demand caused the price of phosphate to escalate dramatically worldwide. The average U.S. price more than doubled while spot prices from North Africa and other exporting regions approached $500 per ton, more than *five times* the average price in 2007 (Jasinski, 2009). Based on the present installed global production capacity Rosemarin *et al.* (2009) predicted that phosphate extraction will peak around the year 2030, "after which time global economic development could be constrained not only by supplies of oil, but the availability of phosphorus."

The United States was formerly the world's leading producer of phosphate, but its contribution has steadily dwindled, dropping from nearly half of the global output in the mid-1950s to just over 18 percent in 2008 (Gurr, 2009; Jasinski, 2009, 2007a). Domestic output has been in a steady decline, from 42.6 million metric tons in 1999 to 27.9 million metric tons in 2009, largely due to the depletion of higher yield reserves (Jasinski, 2000, 2010). In central Florida, which historically has been the country's leading phosphate-producing region, plans to develop new mines to replace existing operations have encountered stiff opposition from local governments concerned about environmental issues, and the future of phosphate mining in the United States remains uncertain.

1.4 Types of Phosphate Resources

1.4.1 Guano

Commercial phosphate deposits occur in two basic forms, animal excrement (guano) and phosphate rock. Guano is the accumulation of excrement from seabirds and is especially well preserved in dry climate regions. The term also applies to accumulations of bat excrement in cave environments. The word "guano" is derived from an Incan word meaning the "droppings of sea birds," and formerly vast deposits occurred along the Pacific Coast of South America where upwelling ocean currents provide abundant food for immense colonies of seabirds. The huge number of birds, in conjunction with an arid climate that prevents the leaching of their waste,

creates an ideal circumstance for the formation of guano. These deposits were the focus of rampant commercial harvesting during the 19th century, and from 1845 to 1880 Peru shipped 11 million tons of bird manure while creating an oligarchic class based upon feces. The Chincha Islands War from 1864 to 1866, which involved the first use of iron warships in the Pacific, resulted when Peru denied Spain access to their guano islands (Gootenberg, 1993). This resource is now almost entirely depleted.

1.4.2 Phosphate Rock and Mineral Apatite

Phosphate rock is a general term for any rock that contains phosphatic minerals in sufficient purity and quantity to permit commercial extraction. The most common phosphate mineral is apatite, or more specifically the calcium-phosphate mineral group that includes fluorapatite ($Ca_5(PO_4)_3F$), chlorapatite ($Ca_5(PO_4)_3Cl$), or hydroxyl-apatite ($Ca_5(PO_4)_3OH$). Distinguishing between these varieties is difficult, but fluorapatite is by far the most common. Apatite is found in both igneous and metamorphic settings, but its chief occurrence is in marine sedimentary deposits.

The word "apatite" comes from a Greek root for "deceit," because apatite can look like many other minerals. The crystals are hexagonal, but may be elongate or stubby, may occur as flat tabular plates or as acicular or globular earthy masses, and may assume many colors. A microcrystalline form known as cellophane ($Ca_3P_2O_8{\cdot}2H_2O$) frequently constitutes the bulk of phosphate rock. The chemical formulas given here are approximations since the structure of apatite favors a wide variety of substitutions. The chemical composition changes on exposure to different fluids and numerous impurities can completely alter the formula. Small amounts of VO_4, As_2O_4, SO_4, or CO_3 readily replace the phosphate (PO_4) tetrahedra and the calcium position may be occupied by minor amounts of magnesium, manganese, strontium, lead, sodium, uranium, yttrium, or rare earth elements. All these elements can become concentrated in significantly higher than normal values (McConnell, 1938; McKelvey, 1967).

Compounds of phosphate, such as apatite, contain trace quantities of uranium and thorium that are radioactive. Cathcart and Gulbrandsen (1972) reported the uranium content in marine phosphorite to range from 50 to 500 parts per million, averaging about 100 ppm. Marine phosphorites can be radioactive enough to be identified in gamma-ray well logging and under favorable circumstances by aerial radiometric reconnaissance (McKelvey, 1967). Some uranium enrichment is attributable to remobilization or re-precipitation of uranium in the ground water zone (Altschuler *et al*., 1958).

Much like calcium carbonate compounds, calcium phosphate compounds are intimately associated with organisms. Many skeletal components are composed of apatite, including brachiopod shells, gastropod radulae, conodont elements, and crustacean exoskeletons, as well as the bones and teeth of vertebrate animals, including humans.

1.4.3 Apatite in Igneous Rocks

Apatite occurs as an accessory mineral in almost all igneous rocks, particularly in hydrothermal veins, disseminated replacements, marginal differentiations near the boundaries of intrusions, and pegmatites. The most heavily concentrated hard-rock phosphate deposits are intrusive masses associated with carbonatite, nepheline-syenite, and other alkalic rocks related to rifting (McKelvey, 1967).

Igneous phosphate deposits have provided between 10 and 20 percent of the world's production during the last decade, and such deposits have been or are currently being exploited

in Russia (Kola Peninsula), the Republic of South Africa (Palabora), Uganda, Brazil, Canada (Quebec and Ontario), Finland, Zimbabwe, Malawi, and Sri Lanka among other locations. In Virginia, igneous phosphate deposits are known to occur in a hydrothermal apatite-ilmentite rock named nelsonite, after the type locality in Nelson County. The nelsonite occurrences, however, are generally uneconomic with respect to phosphate resource potential (Ross, 1941). Igneous phosphate deposits usually contain varieties of apatite that are relatively un-reactive and therefore are the least suitable for fertilizer (AGI, 1987).

1.4.4 Marine Sedimentary Apatite Deposits (Phosphorites)

The great majority (80 to 90 percent) of the world production of phosphate comes from marine sedimentary deposits known as phosphorites, informally referred to as brown rock, bone phosphate, or pebble phosphate. Phosphorite, according to the American Geological Institute definition, is "a sedimentary rock with a high enough content of phosphate minerals to be of economic interest. Most commonly it is a bedded primary or reworked secondary marine rock composed of microcrystalline carbonate fluorapatite in the form of laminae, pellets, oolites, nodules, and shell and bone fragments."

Modern marine sedimentary phosphate deposits have been identified on the seafloor of the continental shelves in both the Atlantic Ocean and the Pacific Ocean. Significant deposits are found off the coasts of southwestern Africa, the southeastern United States, southern California, northern South America, Mexico, Australia, and New Zealand (Friedman *et al*., 1992). These deposits occur at depths both shallow and very deep, but economic recovery using current marine mining technology is considered limited.

Phosphorite also occurs in ancient marine deposits, now terrestrial, that span a vast spectrum of the geological time scale. Notable ancient phosphogenic provinces include:

1) The Upper Precambrian and Cambrian of Southeast Asia, extending from China to northern Australia;
2) Ordovician limestones in Tennessee;
3) Mississippian deposits in Utah;
4) Mississippian and Triassic deposits in Northern Alaska;
5) Permian beds in western U.S., particularly the Phosphoria Formation extending through Wyoming, Utah, Colorado, Idaho, Montana, and Nevada;
6) Jurassic La Caja and La Casita Formations in north-central Mexico;
7) Jurassic strata in Peru;
8) Jurassic-Lower Cretaceous deposits in Eastern Europe;
9) Cretaceous deposits in Columbia and England;
10) Upper Cretaceous-Eocene strata in the Middle East and North Africa extending into West Africa and the northern part of South America;
11) Miocene Monterrey Formation in California;
12) Miocene deposits in the Sechura Desert of Peru;
13) Miocene deposits in Venezuela;
14) The Miocene and Pliocene deposits in the southeastern U.S. Atlantic Coastal Plain (focus of this study).

Marine sedimentary phosphorites originate through a chemical process that is still poorly understood. Phosphate is usually concentrated in rounded nodular grains, granules, pebbles, and

cobbles ranging in diameter from a few millimeters to more than 20 centimeters. Some nodules assay as high as 96 percent phosphate (Friedman *et al*., 1992), but most contain significant impurities.

Most phosphate macrograins are aggregated amalgamations of mineralogical and biological components, a mixture of whatever materials that were in the environment at the time of the precipitation of the orthochemical mud. Nodules often occur in the form of coprolites, or may contain fragments of bones, calcareous shells, corals, organic matter, sand-sized pellets of possible fecal origin, ooids, pisoids, partially phosphatized shark teeth, siliceous radiolarian tests, quartz sand grains, mica flakes, and sponge spicules, all more or less enveloped in collophane.

Riggs (1979a) performed detailed microscopic petrology of Florida phosphorites and adopted a descriptive/analytical scheme for phosphate similar to Folk's (1959) classification of carbonates.

<u>Primary phosphate</u>

Orthochemical

- authigenic microcrystalline phosphorite mud (microsphorite)

Allochemical

- mud torn up by biological or physical processes to produce clastic allochems
- sediments ingested and excreted by organisms to form pelletal phosphorites
- sediments modified into discrete particles, e.g. aggregated into pseudo-oolites
- fossil skeletal material which accumulates in the sediment

<u>Secondary phosphate</u>

Metachemical

- grains altered from subaerial weathering

Lithochemical

- grains reworked into younger deposits

Primary apatite is likely precipitated in the interstitial fluid microenvironment, where phosphate is concentrated in the pores, sometimes as much as twenty times the levels found in ambient waters (Baturin, 1978; Manheim and Gulbrandsen, 1979). Such supersaturated conditions readily permit the replacement of calcium carbonate with calcium phosphate. This replacement has been demonstrated experimentally, and Ames (1959) suggested it might be the main process by which marine phosphorite is deposited. Many authors dispute this as a significant process based on the lack of evidence, suggesting that interstitial accretion is probably a quantitatively more important diagenetic process in the formation of primary apatite (Sheldon, 1957; Cressman and Swanson, 1964; D'Anglejan, 1967; McKelvey, 1967).

Regardless of the specific processes involved in primary phosphate deposition, most researchers accept that these deposits originate in offshore marine conditions where deep, cold, phosphate-rich, oxygen-poor waters up-well to a shallow shelf, often in association with diatomaceous sedimentation (Manheim and Gulbrandsen, 1979). The solubility of apatite

decreases with increasing water temperature[1], and, since the ocean is nearly saturated with respect to phosphorus, in such circumstances both organic and inorganic processes can readily precipitate apatite. Manheim and Gulbrandsen (1979) point out the remarkable coincidence between some of the world's most prominent upwelling zones and submarine phosphate deposits, particularly off the west coasts of North America, South America, and Africa, where the tradewinds drive surface currents away from the coast and cold water rises from deep basin levels to replace the ocean-ward moving surface water. Upwelling can also occur along the eastern margins of continents where warm, pole-ward-moving currents create cool, coastal countercurrents. Less common scenarios of upwelling are areas where two strong currents meet and produce turbulence, areas where pronounced seasonal variation in temperature causes density mixing, and the mouths of deep estuaries.

Upwelling alone may not be sufficient to produce large-scale phosphate precipitation. Paleo-latitude studies indicate that phosphorites have typically formed in lower latitudes (Cook and McElhinny, 1979). Upwelling within the lower latitudes characteristically produces the "lushest gardens of the sea", with immense plankton blooms that are swallowed by swarming schools of fish that in turn provide a smorgasbord for seals, whales, and colonies of seabirds. Blooms of dinoflagelates ("red tides") are commonplace, along with mass mortalities of marine animals (Brongersma-Sanders, 1957). A rain of excrement and dead organisms constantly contributes concentrated phosphate to the seafloor. Manheim and Gulbrandsen (1979) state: "Thus, the requirement for phosphate generation may not be so much phosphate-rich bottom water as organic production, whose debris accumulates in bottom sediment and sustains high phosphate concentrations in pore fluid."

A closely related factor is the oxygen content of the water. Modern phosphorite deposits are often associated with oxygen minimum zones (Friedman *et al*., 1992), and such zones of oxygen-depleted water allow high concentrations of organic material to accumulate. An additional requirement for phosphate enrichment is a lack of diluting terrigenous material (Manheim and Gulbrandsen, 1979). Phosphorite deposits are typically found where the rate of deposition of clastic material is minimal; therefore the phosphorite beds tend to be thin compared with sedimentary sequences deposited elsewhere at the same time (Cathcart and Gulbrandsen, 1972; Friedman *et al*., 1992).

Phosphate deposition may be influenced by the configuration of the seafloor. Youssef (1965) postulated that sheltered depressions of the seabed create conditions favorable for accumulation of phosphate material. Miller (1982) studied the stratigraphy of the Atlantic Coastal Plain from New Jersey to North Carolina and concluded that structural lineaments are closely associated with the distribution and composition of Coastal Plain sediments. These lineaments trend roughly parallel to the coastline and are believed to be either flexures or deeply seated faults in the basement rocks. Areas of thickening or thinning strata and the presence of phosphate were determined by these lineaments; higher concentrations of phosphate are favored where the strata attain maximum extent and thickness.

Episodes of phosphorite formation also may have been controlled by major climatic variations (Burnet, 1980). Phosphorites seem to accumulate during stratigraphic breaks (Friedman *et al*., 1992), and secondary processes such as subaerial weathering and erosional reworking, along with phosphatization of limestone, assume a prominent role in forming economic deposits. Goldman (1922) long ago noted the frequent occurrence of phosphorite at

[1] Apatite is soluble in cold acidic waters, but this solubility decreases with increasing temperature, alkalinity, and hardness (Kazakov, 1937; Kramer, 1964; Roberson, 1966; McKelvey, 1967).

unconformities, reflecting the combined effects of weathering and submarine reworking. The highest-grade beds in the Phosphoria Formation appear to have been extensively washed by submarine currents (McKelvey, 1967). Indeed, secondary processes are afoot today — the Tennessee "brown rock" deposit consists of residuum recently formed from the decomposition of Ordovician phosphatic limestones (Smith and Whitlatch, 1940), and the well-known "river pebble" deposits of Florida are modern placers.

In summary, ideal depositional conditions exist where cold, oxygen-poor, phosphorus-rich, organic-rich water rises up into a shallow, low-latitude basin with a minimal clastic input, presumably on a topographic high where shoreward-moving waters are progressively warmed. Phosphorus from the seawater becomes concentrated in a multitude of organisms, which die and drift down to accumulate in the bottom sediments, where elevated interstitial concentrations of phosphorus lead to precipitation of apatite. Much later, the apatite is residually concentrated during erosion, and re-deposited during an ensuing sedimentary cycle. This last step is perhaps the most important factor in generating an economic deposit.

2.0 Atlantic Coastal Plain Phosphate Deposits

Known phosphate occurrences and economic deposits along the Atlantic Coastal Plain provide valuable insight and serve as the basis for developing a depositional model for phosphate in Virginia. Phosphate is currently mined in Florida and North Carolina, was formerly mined in South Carolina, and was prospected in Georgia (Figure 1). These deposits occur in coastal plain sediments ranging in age from Eocene to early Pleistocene. Figure 2 shows a stratigraphic correlation chart for formations discussed in the following sections.

2.1 Phosphate Deposits of Florida

2.1.1 Economic Interest

Phosphate was discovered in Polk County, Florida in 1881. The discovery attracted little attention at the time, but a few years later two men on a hunting trip recognized the potential value of phosphate pebbles along the Peace River. They began to acquire land along a forty-mile stretch of the river in Bone Valley, and in early 1888 the Arcadia Phosphate Company began mining placer phosphate pebbles in the river, while the Peace River Phosphate Company worked the shoreline. The central Florida pebble deposits were soon overshadowed by events further north, where the discovery of high-grade consolidated phosphatic rock near Dunnellon in Marion County created a land rush. Production began in 1889 by the Marion Phosphate Company followed by the Dunnellon Phosphate Company the ensuing year. The news spread and the boom was on; prospectors and investors descended on Florida in droves and by 1894 there were 215 mining companies operating statewide (Florida Institute of Phosphate Research).

There are three types of phosphate deposits in Florida including river pebble, land pebble, and consolidated rock deposits. River pebble mining, a form of placer mining primarily located along the Peace River, peaked in 1893, but because of high production costs ceased in 1908 as it could not compete with production from land pebble and consolidated rock deposits. Consolidated rock mining, which was centered in Marion County and dominated the early years of the industry, also had high production costs relative to land pebble mining, and eventually shut down in 1965. Land pebble mining continues to this day in central and northern Florida, and phosphate remains the state's third largest industry, trailing only the vast tourism and agriculture sectors.

Technological advances have extended the resources and expected mine life, but already more than 300,000 acres of land have been mined in Polk and Hillsborough counties. With the recent closing of the Clear Springs and Noralyn operations, active mining in the heart of the district has ceased. As the dragline operations shift southward, the quality of the ore decreases, bringing greater challenges. Nevertheless, the phosphate industry has a multi-billion dollar capital investment in Florida and controls mineral rights to about 440,000 acres of land while currently seeking permits to open new mines in Manatee, DeSoto, and Hardee counties (Florida Institute of Phosphate Research).

The phosphate industry faces considerable public opposition to new mining. For every ton of phosphoric acid produced, about 5 tons of phosphogypsum byproduct is generated. A very small amount is used for wallboard or Portland cement, but most is left in waste piles that create significant environmental problems. The waste typically contains radioactive material and high levels of fluorine, and runoff water is extremely acidic with pH values as low as 1.0.

2.1.2 Stratigraphy

All of the Florida phosphate deposits are closely associated with the Miocene-age Hawthorn Group, which underlies much of the Atlantic Coastal Plain of Florida, Georgia, and South Carolina. This was one of the first geological units described in the region, yet unraveling the associated stratigraphic nomenclature remains a complicated problem fraught with stratigraphic equivocation.

The "Hawthorne beds" were originally named by Dall and Harris (1892) for strata of phosphatic rock broken up and enclosed in a younger matrix, found near Hawthorne in Alachua County in north-central Florida. Matson and Clapp (1909), in a preliminary report on Florida's stratigraphy for the newly-formed state geological survey, raised the Hawthorne to formation status using a type section where it occurs as a soft porous limestone overlying the Oligocene-age Ocala Limestone and underlying the Miocene-age Alum Bluff Formation. They believed that the Hawthorne was in part contemporaneous with the Tampa Formation. Matson (1915) later changed his position on the matter when he determined that the Hawthorne beds were continuous with the Alum Bluff Formation, a more established name, so he abandoned the term. For the Florida state geologic map, Cooke and Mossom (1929) reinstated the Hawthorn (sans the "e") as a lithologic unit placing it as a formation within their Alum Bluff Group. Cooke *et al*. (1943), in their correlation of Cenozoic formations of the Atlantic and Gulf coastal plains, identified the Hawthorn Formation as a time equivalent to the Alum Bluff Group, sitting directly on top of the Tampa Limestone and unconformably overlain by the "Bone Valley gravel."

Cathcart (1963), in a USGS Bulletin characterized the Miocene as divided into three main units, in ascending order: early Miocene Tampa Limestone, middle Miocene Hawthorn Formation, and Pliocene Bone Valley Formation. Cathcart's Tampa Limestone contains a trace of low-grade phosphate along with chert fragments. His Hawthorn Formation is composed of lenticular beds of marine sand, clay, limestone, and dolomite, all containing phosphate nodules, although the phosphatic material rarely constitutes more than 10 percent of the mass. He divided the unit into a very impure sandy and clayey limestone at the base grading upward to clayey, silty sand, and calcareous clay, all containing minor phosphate. The top may be a "bedclay," a massive, structureless residuum containing more quartz and phosphate and less carbonate than the underlying bedrock. Cathcart's Hawthorn Formation disconformably overlies the Bone Valley Formation, which, like Matson and Clapp (1909), he divided into a lower unit of clayey

quartz sand containing abundant phosphate and a basal, phosphatic conglomerate, overlain conformably with an upper unit of clayey sand containing leached phosphate.[2]

Riggs (1979a) raised the Hawthorn to "Group" status in central Florida and subdivided it into the Miocene-age Arcadia Formation on the bottom, the Miocene-age Noralyn Formation in the middle, and the Pliocene-age Bone Valley Formation on top. Riggs's Arcadia Formation is characterized as dolomite mixed with primary allochemical phosphorite and subordinate amounts of terrigenous material, deposited in extensive, open marine conditions. The Noralyn Formation (new name) is composed of shallow water coastal marine terrigenous sands and clays mixed with primary orthochemical and transported allochemical phosphate. This unit provides for most of the phosphate mining in central Florida. Riggs characterized the Bone Valley Formation as a thin and localized unit, limited in distribution, composed of fluvial, estuarine, and coastal marine terrigenous sands and clays. Even though the Bone Valley contains abundant phosphatized fossil material and reworked lithochemical phosphate, because of its limited extent it rarely constitutes a major part of the mining activity.

Scott (1988), in describing the lithostratigraphy of the Hawthorn Group significantly rearranged the nomenclature, dividing the group into two formations: the Arcadia on the bottom and the Peace River (new name) on the top. He recognized two members in the Arcadia, the Nocatee Member (new name), and the overlying Tampa Member (rank reduced). He also reduced the Bone Valley Formation to a member of his new Peace River Formation.

Because the Arcadia usage introduced by Riggs was never formalized, Scott officially proposed the name and designated a type section from a core in DeSoto County.[3] With the exception of the Nocatee Member, Scott's Arcadia Formation consists primarily of limestone and dolostone with varying amounts of quartz sand, clay and phosphate grains. The limestones and dolostones are sandy, moldic and phosphatic. Scattered, thin beds of sand and clay are generally calcareous and phosphatic. Phosphate content ranges up to 25 percent, but is usually about 10 percent. The Nocatee Member is a complexly interbedded unit of quartz sands, clays, and carbonates containing varying percentages of phosphate, and previously referred to as the "sand and clay unit" of the Tampa Limestone by Wilson (1977). Scott's Tampa Member consists of sediments formerly assigned to the Tampa Limestone by King and Wright (1979), a package of sandy clay with chert, carbonate, and some phosphate pebbles, all conformably overlying the Nocatee member where present, otherwise lying unconformably atop the Suwannee Limestone. Scott based the change in status on the Tampa's limited areal extent and

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[2] Matson and Clapp (1909) had originally described the Pliocene-age Bone Valley gravel using a type section from the phosphate mines in Polk County in central Florida, where a 30-foot-thick unit is distinguished by a basal gravel containing phosphatic pebbles and bone fragments in a fine-grained sand and marly clay matrix, grading upward into a leached, less phosphatic quartz sand. Bone Valley is aptly named: no other region in North America can claim a more varied or richer fossil fauna of middle Miocene to early Pliocene vertebrate animals.

[3] Dall and Harris (1892) originally proposed the name "Arcadia marl" for a nine-foot thickness of yellowish, sandy marl composed of a putty-like mixture of lime and sand, with "minute" phosphatic pebbles, a few small shark's teeth, and obscure casts of oysters and other bivalves. Assigned to the Pliocene, the Arcadia strata were overlain by the "Peace Creek bone bed." Matson and Clapp (1909) subsequently abandoned the name; they considered the marl to be a facies of the Caloosahatchee, but Riggs (1967), in a Ph.D. Dissertation, choose to name the Arcadia Formation as the bottom of the Hawthorn carbonate section in south Florida, and the following year Freas and Riggs (1968) defined their Arcadia Formation as very pale orange dolomite, phosphatic, clayey and sandy, poorly sorted and massive, fossiliferous, with abundant sand-filled burrows and molds of mollusks, overlying, and in part, interfingering with the Tampa Formation, and underlying the Bone Valley Formation. Scott (1988) included the original "Arcadia Marl" within his new Peace River Formation.

its lithologic similarities and relationships with the remainder of his redefined Arcadia Formation. Scott's suggested age for the Tampa Member is "early early" Miocene to "late early" Miocene, and earliest Miocene for the Nocatee, though some authors (Morgan, 1993; McCartan *et al*., 1995) believe these units might be as old as late Oligocene.

The Peace River Formation is Scott's new name for the upper Hawthorn siliciclastic strata of Cathcart, combined with the former Bone Valley Formation, which Scott reduced to a member of the Peace River. The Peace River Formation everywhere disconformably overlies Scott's redefined Arcadia Formation, and rubble zones may mark the contact. The siliciclastic strata are composed of phosphatic and calcareous quartz sand and clay beds comprising two-thirds or more of the formation, and includes beds previously placed in the Tamiami Formation by Parker (1951) and Hunter (1968). Within the quartz sands, the phosphate content is greater toward the bottom of the section. Scott's Bone Valley Member consists of pebble or gravel-sized phosphate grains in a matrix of quartz and phosphate sand, occasionally strongly cross-bedded. The base of the Bone Valley contains beds of carbonate rubble overlain by "bedclay," possibly the residuum of argillaceous carbonate rock in the Hawthorn Formation (Altschuler, *et al*., 1964). Scott's reasons for dropping the Bone Valley in rank are its limited areal extent, the gradational nature of its boundaries, and its lithologic similarities to his Peace River Formation. The Peace River is thought to range in age from late Miocene to early Pliocene.

Popenoe (1990) partially rejected the revisions of Scott and followed the lead of Riggs (1979a), dividing the Hawthorn Group in central Florida into three formations: the Bone Valley, the Peace River (an equivalent of the defunct Noralyn), and the Arcadia. Popenoe's upper and lower formations represent sea level highstands, and the middle unit represents a period of lower sea level. Cathcart and Botinelly (1991) also used this tri-fold configuration, and they clearly refuted the Peace River usage as defined by Scott, restoring the Bone Valley Member to formation rank.

Perhaps the best way to look at the stratigraphy is in a simplified form, wherein a unit composed of beds of marine sand, clay, limestone, and dolomite containing scattered, sparse phosphate nodules (Cathcart's Hawthorn Formation, Scott's Arcadia Formation) is unconformably overlain by a unit whose base contains concentrations of phosphate (Cathcart's Bone Valley Formation, Scott's Peace River Formation).

2.1.3 Depositional Setting

Riggs and Freas (1965) and Pirkle (1967) divided Florida phosphate deposits into two types, each of different age and origin. One type is distinctly marine and associated with the remains of Miocene sharks, rays, teleost fish, porpoises, and sirenians, while the second type is post-Miocene, at least partly terrestrial, and contains reworked phosphorite accumulations along with the fossils of land vertebrates. Such terrestrial deposits frequently occupy channels, but can also occur as blanket deposits over older phosphatic sediments. Most are middle Pliocene, but some are Pleistocene in age. The Florida deposits occur as both primary phosphate accumulations and concentrations of phosphatic material by weathering and reworking.

From the Cretaceous through the middle Cenozoic, the Florida peninsula had been essentially a stable, isolated carbonate platform separated from the North American continent by the Gulf Trough. Sedimentary material was almost exclusively carbonate, with scarcely any terrigenous contribution. During the late Eocene an extremely pure fossiliferous carbonate, the Ocala Limestone, was deposited. Near the close of Eocene time, the Ocala Arch formed as a

gentle flexure about 200 miles long, with its axis trending north-northwest from Tampa Bay up the Gulf side of the Florida Peninsula.

Following an early Miocene regression, a major transgressive sea inundated Florida as well as most of the Atlantic Coastal Plain perhaps even encroaching on the foothills of the Appalachian Mountains. In central Florida, initial Miocene deposition is represented by fully marine, continental-shelf strata of the Tampa Limestone/Arcadia Formation, a deposit enriched in phosphate, which is disconformably overlain by the highly phosphatic Peace River (Noralyn) Formation, a coastal marine and nearshore shelf deposit (Riggs, 1979b). Phosphate precipitation took place as the cold, nutrient-rich upwellings moved across shallow platforms and into the coastal environment.

Riggs (1979b) believed that the structural framework dictated the circumstance of primary phosphate sedimentation in Florida. Two deep basins served as counterpoints to the Ocala Arch structural high, the Okeechobee Basin to the south and the Jacksonville Basin to the north. Two southern extensions off the Ocala Arch, the Central Florida Platform and the Ocala Platform may be the primary sites where most of the phosphate was generated (Riggs, 1979b). The magnitude of phosphorite deposition reflects the extent of the phosphogenic system, the duration of the system through geologic time, and the paucity of diluting terrigenous sedimentation.

Near the end of Miocene time, the sea retreated and the land surface was eroded. Cathcart (1963) describes this late Miocene topography as highly irregular with buried ridges showing karst erosion, suggesting an optimal environment for chemical weathering to remove $CaCO_3$ and create a residuum enriched in phosphate. Cathcart observed that several periods of weathering have influenced phosphate character and concentration. First, the regression after the deposition of the middle Miocene (his Hawthorn Formation) resulted in extensive karst, where chemical weathering removed the $CaCO_3$ and left a residuum enriched in calcium phosphate that was reworked into the base of the Bone Valley Formation, a complex association of fluvial, estuarine, and open bay facies. A second period of weathering followed the deposition of the Bone Valley Formation, and aluminum phosphate was formed at the same time that the limestone of the Hawthorn was altered to calcareous clay and dolomitized.[4] A third weathering period followed the deposition of the loose surficial sands on top of the Bone Valley Formation. Perhaps there is even another cycle, an older cycle. Cathcart noted that the Tampa Limestone when weathered is commonly covered with a thin residual mantle of calcareous clay that contains chert, limestone fragments, and phosphate nodules, and this could have provided phosphatic material for later sedimentary units. Cathcart and Botinelly (1991) believed that the abundant phosphate in the middle Miocene was at least partially derived from older, underlying carbonate rock.

Altschuler *et al*. (1964) determined that the Bone Valley deposits of Florida originated through reworking of phosphatic residuum developed during deep weathering of phosphatic marls in the Miocene Hawthorn Formation. In discussing the Pliocene Bone Valley Formation and the Pungo River Formation of North Carolina, McKelvey (1967) states: "In fact, only where these deposits have been extensively reworked by submarine currents and (or) subjected to weathering are they rich enough to be mined." McKelvey ultimately believed that the bulk of the world's production of phosphate comes from deposits that have been enriched by weathering.

[4] Cathcart (1963) pointed out that there are two zones of phosphates. On top is an irregular zone of leaching characterized by aluminum phosphate minerals such as wavelite, and high concentrations of uranium. This zone cuts across stratigraphic units. Beneath this is the calcium phosphate (francolite) zone.

Altschuler *et al*. (1964) believed that recent weathering has upgraded some of the Hawthorn deposits of Florida.

2.2 Phosphate Deposits of Georgia

2.2.1 Economic Interest

In the early 1960s the Georgia Department of Mines, Mining, and Geology initiated an exploration program to assess the state's potential for phosphate resources. Concurrent with the development of the Lee Creek Mine in North Carolina, several large mining companies had begun to explore for phosphate in Georgia, including Kerr-McGee Corporation, which started acquiring options in 1966 and went so far as to make an application for a state lease. However, when public hearings protracted the process the bid was withdrawn and interest waned. Cathcart and Gulbrandsen (1972) asserted that the material could not be mined at a profit using existing methods. Several concentrated deposits were identified in the coastal marshlands of eastern Chatham County, but are presently considered uneconomic.

2.2.2 Stratigraphy

Georgia's phosphate deposits occur within the Duplin Formation, a unit which was first described in North Carolina by Dall (1898) and Clark *et al*. (1912), referring to unconsolidated sands, arenaceous clays, and shell marls representing the final phase of Miocene deposition. Cooke and Munyan (1938) extended the Duplin into Georgia along the Savannah River. These sediments occupy the same stratigraphic position as the Yorktown Formation to the north, but contain different faunas, with the Neuse River forming the approximate boundary.

The Upper Miocene to lower Pliocene Duplin Formation is a time-transgressive unit that contains a distinctive marine fauna but shows little lithologic uniformity. In the Savannah area, the Duplin occurs as an olive-green sand, sandy clay, and clayey sand very similar to the underlying Hawthorn Formation. However, whereas the Hawthorn in this area averages 2 to 3 percent Bone Phosphate of Lime (BPL) and is never higher than 5 percent BPL, phosphate content increases abruptly to 13 to 30 percent BPL at the base of the Duplin, and high concentrations are common throughout the unit (Furlow, 1969). Ward, *et al*., (1991) characterize the base of the Duplin as a widespread unconformity, with the lower part regularly containing a phosphatic basal conglomerate.

The Duplin Formation rests unconformably on the Middle Miocene Hawthorn Formation, which Cooke (1936) had mapped in Georgia. The Hawthorn Formation rests on what Furlow (1969) referred to a "Tampa Limestone equivalent," largely because the limestone is scant and sandy, although it is probably time equivalent to the lower Miocene Tampa Limestone to the south. Phosphate occurrences have been identified at the base of the Miocene, which rests unconformably on undifferentiated Oligocene deposits of calcareous sand, sandy marl, sandy to clean limestone (Furlow, 1969). Oligocene deposits rest disconformably on the Eocene-age Ocala Limestone.

2.2.3 Depositional Setting

Furlow (1969) stated that the conventional theory of phosphate precipitation and deposition from upwelling cold water did not fit the characteristics of Georgia phosphate deposits, based on lithologic evidence, specifically the absence of black shale or chert deposits. Pevear (1967) observed that large concentrations of phosphorite are confined to relatively small areas on the Coastal Plain, suggesting that the phosphate was concentrated in small coastal

basins or estuaries. In addition, fossils of land vertebrates are intermixed with marine fossils and brackish water creatures such as the manatee, indicating a very nearshore, possibly estuarine environment. On a coastline of low relief during a warm climate, limey sediments accumulated in the estuaries, but cooling conditions increased CO_2 solubility, thereby stopping carbonate production while increasing organic activity, thus raising phosphorous concentrations and replacing the lime mud with phosphorite.

The estuaries may have served as nutrient traps. As out-flowing surface waters were replaced by a countercurrent of seawater, decaying organic material may have been trapped and deposited. In this model, as the surf zone transgressed and regressed at the edge of the estuary, phosphorite may have been broken up and redistributed. Pevear stated, "As this type of phosphorite is believed to form by replacement of limestone or lime mud, deposits should always occur adjacent to or above limestone or marl." Furlow (1969) recognized that a significant amount of the phosphate in the Duplin Formation might have come from the Hawthorn Formation.

2.3 Phosphate Deposits of South Carolina

2.3.1 Economic Interest

The first commercial mining of phosphate in the United States began in South Carolina in 1867 and by 1870 production in Beaufort, Colleton, and Charleston counties totaled 65,000 tons (Cathcart and Gulbrandsen, 1972). Operations peaked around 1880, but soon began a steep decline due to the lower costs associated with richer and more extensive deposits discovered in Florida. By 1920, phosphate mining in South Carolina had declined substantially and eventually ceased in 1938. Total production for the state is estimated to be about 13.4 million tons (Cathcart and Gulbrandsen, 1972).

2.3.2 Stratigraphy

South Carolina's phosphate deposits occur where the Oligocene-age Cooper Marl has been reworked and concentrated into the lower strata of the Ladson Formation, a Pleistocene-age fluvial/deltaic sand and gravel (Wehmiller *et al*., 1988). The Cooper Marl, which contains between 5 to 20 percent phosphate and likely was the source of the Ladson Formation phosphate, is a poorly indurated, impure, fine-grained, sandy marl with thin zones of limestone. The carbonate was largely derived from a rich fauna of foraminifera that are characteristic of moderately deep water, along with a minor fauna of free-swimming mollusks characteristic of cool water (Malde, 1959). In outcrop, calcite shells remain, while aragonite shells leave ghost molds.

The Ladson Formation, which was the target of mineral exploitation in the 19th Century, is a locally widespread Pleistocene deposit consisting of unconsolidated phosphatic gravel, sand, and clay, all rather poorly sorted into layers. The gravel, which is concentrated in the lower two feet, consists of reworked, irregular pieces of phosphate rock, rounded pebbles of phosphate and quartz, mixed sizes of phosphatic sand, and minor clay along with phosphatic bones, fish teeth, and shell fragments. Above this basal gravel the formation is better sorted with zones of pure sand and pure clay incorporated into layers of mixed sand and clay. This overlying strata rarely contains significant phosphate (Malde, 1959).

Within the South Carolina phosphate district, the section between Oligocene-age and Pleistocene-age strata is missing (Figure 2), yet some formations from this period have been mapped on the district periphery. Cooke (1936) mapped the middle Miocene Hawthorn

Formation from Georgia northward toward Charleston, but this unit has been removed by erosion to the north. The Upper Miocene/lower Pliocene Duplin Formation occurs in scattered outcrops on the South Carolina coastal plain, where it is represented by a variety of facies from massively bedded sandy limestone near the present coastline to coquina farther inland (Malde, 1959). The base of the Duplin is a widespread unconformity, and the lower part regularly contains abundant phosphatic pebbles and sand.

2.3.3 Depositional Setting

During the Oligocene, the Cooper Marl was deposited under alternately shallow (limestone) and moderately deep (marl) marine conditions (Malde, 1959). This scenario, with cool deep, water rising onto a shallow platform, is conducive to phosphate formation. Following deposition, the Cooper Marl was exposed and eroded subaerially. During the late Miocene, the Duplin Formation was deposited in near-shore environments across this broad eroded surface. During initial stages of deposition, the Duplin picked up phosphate from the eroded surface. Following a marine regression in the Pliocene, the Ladson Formation was deposited in fluvial/deltaic environments across a surface cut into residuum of the Cooper Marl. In areas where the Cooper Marl was directly supplying sediments to the Ladson Formation, there was a considerable amount of residual phosphate incorporated.

2.4 Phosphate Deposits of North Carolina

2.4.1 Economic Interest

Phosphate was first reported in North Carolina in 1883 from a deposit in Duplin County, and by 1888 at least two attempts had been made to exploit the resource, without success, and interest waned (Stuckey, 1970). In the early 1950s, cuttings from water wells in Beaufort County showed significant phosphate. American Metals Company acquired a lease, but test holes failed to find a commercial ore body. In 1956, another well in Beaufort County penetrated a considerable thickness of phosphate. A USGS geologist who was investigating groundwater in the area had a sample analyzed that assayed 60.2 percent BPL and concluded that a phosphate field of major economic importance lay beneath Beaufort County (Brown, 1958).

In 1961, Texas Gulf Sulfur Company began investigating the extent of phosphate resources by measuring gamma-ray activity in water wells (Stuckey, 1970). Meanwhile, the North Carolina Geological Survey, in a co-operative agreement with the USGS, began its own gamma ray study (Kimrey, 1965), and in 1962 the state solicited bids for leases along the Pamlico River. Texas Gulf, which had been acquiring land in the Lee Creek area, was successful in its bid, and in the fall of 1963 began a test mining operation, which was completed the following year. Full-scale operations began in 1965, and two years later the world's largest phosphoric acid plant went into production in tandem with the world's largest sulfuric acid plant. Currently owned and operated by Phosphate Corporation of Saskatchewan (PCS), it remains the largest vertically integrated phosphate operation in the world, annually mining up to 6 million metric tons of phosphate rock, and producing 1.3 million tons of phosphoric acid (Gilmore, 2006).

2.4.2 Stratigraphy

Brown (1958) first described phosphate in the subsurface of Beaufort County, and correlated these sediments with the middle Miocene Calvert Formation of Virginia on the basis of benthic forams. Kimrey (1964, 1965) proposed the name Pungo River Formation for these

deposits and provided lithologic descriptions and gamma-ray log patterns from a core-hole type section in Beaufort County. Kimrey's Pungo River formation is basically a package of interbedded phosphatic sands, silts, clays, diatomaceous clays, and phosphatic and non-phosphatic limestones that were deposited during the middle Miocene, and that unconformably overlie the Eocene Castle Hayne Limestone while unconformably underlying the Pliocene Yorktown Formation. Even though the Pungo River Formation exists only in the subsurface, it is extensive, stretching from Beaufort County eastward to the coastline and out beneath the continental shelf (Lewis *et al*., 1980). The thickness ranges from a featheredge beneath western Beaufort County to approximately 1000 feet near Cape Hatteras (Miller, 1982). The top of the formation dips generally to the east at a rate of about 10 feet per mile. Bedding is thick to very thick, often vertically consistent for 5 to 15 feet of section, and bedding planes and laminations are uncommon. Kimrey (1965) stated that individual lithologic horizons could be traced laterally and correlated based on grain size and phosphate content.

Miller (1982) further defined the type section in a detailed report for the North Carolina state geological survey. He placed the base of the unit just above the highest occurrence of either sandy limestone or glauconitic sand, or at the highest persistent occurrence of pre-Pungo River fossils. He defined the top of the formation as the highest occurrence of any of the following:

1) Primary phosphate, usually sand-sized, spheroidal to ovate, or oolitic in form.
2) Light-green diatomaceous clay.
3) The abundant occurrence of any of six specific foraminifera, which are considered to be restricted, in North Carolina at least, to the Pungo River Formation.[5]
4) Relatively high radioactivity, as recorded by natural gamma ray logs, which is nearly continuous throughout the formation.

Gibson (1983b) divided the Pungo River Formation into two members, the Belhaven on the bottom and the Bonnerton on top. The Belhaven Member (lower and middle Miocene) consists of greenish-brown phosphatic sand with gray-green clay and limestone and dolomite beds. It unconformably overlies the Castle Hayne Formation (upper Eocene) and it conformably grades upward into the Bonnerton Member (middle Miocene), which consists of white to light gray-green phosphatic limestone and sand, calcareous clay, and coquina.

Snyder and Riggs (1993) characterized the Pungo River Formation as composed of multi-cyclical deposits of phosphatic clays and sands and carbonates, and they subdivided the Lee Creek Mining District into four informal stratigraphic units. The lower three units show similar successions of sediment types, a predominantly terrigenous sand grading upward into phosphorite sand capped by variably indurated carbonates that are dolomitic in the lowest two units, calcitic in the third. All three are muddy throughout. The fourth unit, which caps the

[5] *Uvigerina calvertensis* and *Cibicides concentricus* are the most widespread species, both horizontally and vertically, and prefer an argillaceous substrate. *Siphogenerina lamellata* is associated with diatomaceous and calcareous clays and occurs in profusion where found. This is the only species known to occur abundantly in the phosphatic sands (Brown, 1958). *Spiroplectamina mississippiensis* is found only in carbonate rocks or in calcareous clays. *Robulus americanus* is restricted to deeper water argillaceous environments. *Fursenkoina miocenica*, along with *Bolivina calvertensis*, occurs immediately adjacent to phosphatic sands, either vertically or laterally. The most prolific foraminifera occurrences are just east of the area of high phosphate concentration in Beaufort and Pamlico counties.

Pungo River sequence, is only slightly phosphatic, and consists of sandy, bioclastic-rich dolosilt with fossil fragments mostly barnacles and bryozoans.

The base of the Pungo River Formation, across its full extent, rests on a variety of formations. It fills shallow channels carved into an eroded, weathered surface cut into the Paleocene Beaufort Formation (highly glauconitic clayey sand), the Eocene Castle Hayne Formation (massive, well indurated, shelly, sandy limestone), the Oligocene River Bend Formation (well indurated shell limestone), and the Oligocene Belgrade Formation (shelly sands, laminated with clay lenses) (Miller, 1982). Whereas the Pungo River Formation rests on several stratigraphic units of different ages, it is almost everywhere overlain by the Pliocene-age Yorktown Formation. The base of the Yorktown consists of a blanket deposit of well-rounded pebbles of quartz and phosphate mixed with coarse sand and abundant phosphatized fish and animal remains, frequently occupying small, shallow channels only a few feet deep, while the intervening high areas are covered with well-rounded pebbles of phosphate. This pervasive basal conglomerate is formed from reworked Pungo River sediments entrained by the transgressing Yorktown Sea (Miller, 1982).

2.4.3 The Lee Creek Ore Zone

Mine geologists at Lee Creek have subdivided the ore zone and the overburden into twenty-two distinct strata groupings (Ward, 2007). The lowest unit (#22) is the top of the Castle Hayne limestone, composed of moldic, vuggy, coquina limestone capped by an erosional surface of dense black phosphate replacing the vuggy carbonate. Overlying this is the base of the Pungo River Formation, a 5-foot-thick section of slightly dolomitic and phosphatic clay containing abundant phosphates pebbles (21). Above this is a pervasive 3-foot-thick section of fine-grained dolomitic sandstone that also contains abundant phosphatic pebbles interspersed with molds of pelecypods (20). Above this is the main ore body, starting with a substantial 18-foot-thick layer of highly phosphatic sand containing concentrated phosphatic pebbles and fossils at the base (19). Overlying this is a thin, indurated dolostone unit with phosphate pebbles and clam borings (18). On top of this are situated a fine-grained, clayey phosphatic sand (17), a semi-indurated phosphatic clay (16), and a clayey fine-grained phosphatic sand (15), altogether making up about 15 feet of section and the top of the ore body. Gilmore (2006) reports good, sharp contacts at the top and bottom of the ore body, which tends to be a higher grade at the top. The ore body is overlain by about 8 feet of coquina filled with rich black phosphatic sand and black vuggy phosphatic pebbles (14). This is capped by the “chartreuse bed,” a sparsely phosphatic bryozoan hash that makes up the top of the Pungo River Formation (13).

The bottom of the Yorktown Formation is composed of 10 feet of phosphatic sandy clay with copious reworked phosphatized pebbles and fossils, particularly in the base of the unit (12). This basal unit is buried by 2 feet of stiff marly clay containing conspicuous pecten shells, reworked phosphate pebbles, and phosphatic bones and teeth (11). This thin layer is overlain by 23 feet of marly clay with scattered echinoid spines and large black phosphatic pebbles at the base (10). The next three units (9, 8, 7) make up about 20 feet of marly, non-phosphatic clays of the upper Yorktown Formation. Unit 6 is a shell hash assigned to the Pliocene/Pleistocene Croatan Formation. Units 5 through 1 represent about 30 feet of Pleistocene sedimentary overburden. The approximate content of high-grade ore is reported to be: 40-50 % phosphate pebble, 30-35 % silica sand, 15-20 % clay and fine silt, 5-10 % calcite, dolomite, and other minerals. Yields approach 30,000 short tons of phosphate concentrate per acre.

2.4.4 Pungo River Formation Depositional Environments

Miller (1982) subdivided the Pungo River Formation according to facies. In his scheme the two principle units are diatomaceous clay and phosphatic sand, with minor dolomitic limestone, coquina, and chalk. They are summarized as follows:

1) Diatomaceous Clay. Light-yellowish green (5GY 7/2 on the NRC rock color chart), low density (due to diatom content), thickly to very thickly bedded, illitic to montmorillonitic clay containing diatoms, radiolarians, forams, pelletal phosphate, phosphatized fish scales and small vertebrae, as well as bituminous material in trace amounts as evidenced by the fetid odor from freshly broken samples. Some strata contain up to 90 percent diatom shells and fragments. Exposed surfaces can appear fissile. Locally contains rounded tubes and channels that appear to be burrows filled with phosphate sand, indicating shallow water deposition in a low energy environment where biological sedimentation (plankton) equaled or exceeded clastic deposition. Current ripples probably created the minor thin laminations and lenses of phosphate sand. This facies occurs primarily in the middle and upper strata of the Pungo River Formation, and comprises the bulk of the formation to the north and the east, being prominent in Beaufort, Hyde, and Pamlico counties. East of Beaufort County, in the deeper part of the basin, drilling data indicates that the formation is comprised mainly of clay. Occasionally diatomaceous clays are inter-bedded with coquinas and calcareous clays.

2) Phosphatic Sand. A mixture of fine to medium-grained, clear, angular to sub-rounded, flat-sided, polished quartz sand and varying amounts of fine- to medium-grained phosphate sand, along with minor silt, clay, phosphatized fossil fragments, and accessory minerals including garnet and ilmenite. There are few identifiable forams associated with this facies due to complete replacement of the calcareous tests with phosphate, while the siliceous tests of radiolarians remain recognizable. The more clayey phosphatic sand often contains weathered shell material. Phosphatic sand is usually very thickly bedded, and well to moderately well sorted. The color of the sand varies from dusky yellowish brown (10 YR 2/2) to olive gray (5 Y 3/2) depending on clay and phosphate content. Phosphate sand grains are typically smooth, glossy, spheroidal to ovate, and individual grains commonly show concentric rings or bandings. Phosphate usually accounts for less than 10 to 15 percent of the overall composition of the sands, but may reach 50 to 60 percent. Pebble-sized phosphate grains (+10 mesh) normally comprise less than 5 percent volume. Phosphatic sands are found at several levels in the Pungo River section, and are frequently interbedded with diatomaceous clays and dolomitic limestone. Within the area of highest concentration the sands tend to be more dominant in the upper part of the formation and show higher phosphate content than those in the lower part. Thicker sand accumulations seem to hold higher phosphate percentages. These sediments are interpreted to be deposited in an open marine, shallow shelf environment winnowed by active bottom currents.

3) Dolomitic Limestone. Thin intercalations (1 to 3 feet thick) of fine, crystalline, light olive green (10 Y 4/2) to light gray (N 7) dolomite and dolomitic limestone. Typically highly inter-bedded, dense, and vuggy, and containing varying amounts of marly phosphatic clay, quartz sand, and pebble phosphate. Locally, this rock is composed

entirely of cast-and-moldic limestone. Although beds are thin, they can be laterally continuous for several miles. This facies is more common in the middle and lower two-thirds of the formation, and is generally restricted to an area of high phosphate concentration in Beaufort and Pamlico counties. Miller (1982) includes two sheet-like accumulations of fossils within this depositional environment: 1) a well indurated mollusk biostrome extending from eastern Carteret County to Cape Hatteras in the lower one-third of the formation, and 2) a poorly indurated bryozoan biostrome in the uppermost part of the formation in Hyde, Dare, and the eastern part of Beaufort County. These deposits represent a high-energy environment with little clastic input. Minor calcareous clays occur on the margins of limestone areas and represent a transitional environment. Large species of the forams *Oolina*, *Marginulina*, and *Polymorphina* occur in these calcareous clays.

4) Coquina Limestone. Creamy white (5YR 8/1) to light gray (N 7) accumulations of shells and shell fragments impregnated with re-crystallized calcite and locally containing significant amounts of pebble- and cobble-sized phosphate. Deposits vary in degree of induration from highly competent to very poorly cemented. The coquinas are commonly interbedded with calcareous clays. Coquina limestone occurrences are confined to Beaufort County on the south side of the Pamlico River.

5) Chalk. Tan (5YR 6/4) to white (N 9), soft, highly friable chalk. Occurs in the central part of the Pungo River Formation in Hyde County. This facies reflects deposition in a low energy, deep-water environment.

Miller (1982) identified a regular facies progression from shallow water basinward:

1) carbonate rocks and coquina
2) interbedded carbonates and phosphatic sands
3) phosphatic sands
4) interbedded phosphatic sands and diatomaceous clays
5) diatomaceous clays and chalky to algal limestone.

2.4.5 Structure of the Pungo River Formation

Miller (1980, 1982) compared phosphorite occurrences in North Carolina and Florida and concluded that in both cases the structure of their basins during Miocene time was largely responsible for the initial deposition and concentration of primary phosphate. He identified a series of lineaments on the Atlantic coast that he believed had a significant effect on the lithology, distribution, and thickness of sedimentation. These lineaments represent either flexures in the basement surface or deep-seated faults that die out upward, and they are expressed in the coastal plain sedimentary blanket as areas of thickening, thinning, or absence of stratigraphic units.

The bulk of the Pungo River Formation sediments lie directly to the east of one of Miller's north-south lineaments, a persistent down-to-the-east basement flexure that also affected underlying older units. Running obliquely eastward of the flexure, oriented roughly east-northeast, are two parallel structural highs. The southern structural high, in the Carteret County area, was in place preceding, during, and after the deposition of the Pungo River Formation; the

northern structure was not operating until ongoing deposition of the Pungo River. Lying between these two ridges is the Albemarle Embayment, a relatively flat floored, shallow embayment that drops off steeply on the seaward side at a north-south, down-to-the-east flexure. According to Miller, this configuration, a confined, flat-floored basin with a steep slope on one side, is similar to other basins where phosphorite is found.

2.4.6 Depositional Setting

Interpretations of phosphate deposition in North Carolina rely heavily on Miller (1980, 1982), who believed that the great majority of the phosphate was primary and was generated during the middle-Miocene deposition of the Pungo River Formation. Snyder *et al.* (1980) thought the phosphate in the lower parts of the Pungo River was formed *in situ*, while that in the upper part was derived from reworking. Both of these ideas need to be revisited and re-evaluated.

Miller noted that the majority of the phosphate was associated with sandy units and believed that it was primary and "undisturbed," as opposed to reworked pebbles and gravel. Among his supporting reasons: 1) the fresh, unleached appearance of the majority of the pellets precludes extensive exposure to seawater during submarine reworking, which would have altered the montmorillonite into illite and leached the uranium content, neither of which have occurred; 2) no recognizable rock fragments or fauna from older units have been found in the Pungo River Formation; and 3) no known source for the phosphate exists in the older sedimentary strata in the area. However, the first statement only applies to submarine reworking, the second statement can be regarded as negative evidence, and the last statement is simply incorrect.

During the middle Eocene (Claibornian Stage), eastern North Carolina, like much of the mid-Atlantic Coastal Plain, experienced a major transgression, resulting in a shallow tropical sea and the deposition of the widespread Castle Hayne Formation. The basal unit of the Castle Hayne is the New Hanover Member, a lithocalcirudite containing clasts coated with phosphate, along with shark teeth and fossil mollusks, echinoids, and crabs (Ward *et al*., 1978). The Comfort Member, the middle and most extensive of the Castle Hayne units, is a cyclic, bryozoan-echinoid calcirudite containing detrital phosphate, with concentrations of phosphate pebbles marking breaks in deposition (Ward *et al*., 1978). The Spring Garden Member, the upper unit of the Castle Hayne Formation, is an arenaceous, fossiliferous, molluscan-mold biocalcirudite that contains fine detrital phosphate as a common accessory, occasionally in amounts as great as 10 percent (Ward *et al*., 1978).

In the late middle Eocene, the Castle Hayne Sea receded and the Cape Fear and Norfolk arches became active. Throughout the late Eocene (Jacksonian Stage) and early Oligocene (early Vicksburgian) the exposed carbonate rocks were eroded subaerially, creating an extremely uneven surface and entirely reducing the Castle Hayne in some places. During this time, calcium carbonate would have been dissolved away, leaving a lag of calcium phosphate. A minor middle Oligocene (late Vicksburgian) transgression centered in the Neuse River area persisted through the late Oligocene (Chickasawhayan), resulting in the deposition of the phosphatic barnacle/shell hash of the River Bend Formation, which rests directly on top of a bed of middle Oligocene oysters attached to the phosphate-coated surface of the Castle Hayne limestone (Ward *et al*., 1978). A late Oligocene regression once again exposed the Castle Hayne along with the River Bend Formation. Once again, calcium carbonate would have been dissolved away, leaving a lag of calcium phosphate.

During latest Oligocene or earliest Miocene a small marine embayment incurred into the area now occupied by Craven, Jones, Carteret, and Onslow counties. Marine currents swept the underlying limestone clear of sediment, while marine mollusks bored into the exposed substrate. Huge *Crassostrea* oysters are preserved in the Pollocksville Member of the Belgrade Formation, a somewhat leached, very sandy, shell bed. Also during this transgression, the Haywood Landing Member of the Belgrade Formation was deposited, composed of moderately phosphatic, slightly calcareous quartz sands — basically an offshore, open-marine, time-equivalent of the Pollocksville Member.

During the early to middle Miocene, a major transgression inundated the North Carolina coastal plain, and the Pungo River Formation was deposited. The Pungo River filled channels carved into an eroded, weathered surface cut into several phosphate-bearing formations that might have been significant contributors, and there may be a relationship to carbonate rocks. Pevear (1966) stated that estuarine-style phosphorite is believed to form by replacement of limestone or lime mud, and such phosphate deposits should always occur adjacent to or above limestone or marl. Limestone in the Pungo River Formation is generally restricted to an area of high phosphate concentrations, and coquinas locally contain significant amounts of pebble- and cobble-sized phosphate (Miller, 1982). Clearly at this time there was a significant amount of available phosphate in the sedimentary system, although it seems equally clear that considerable primary phosphate was precipitated during deposition of the Pungo River.

Miller (1982) rejected Pevear's estuarine deposition hypothesis, and suggested that the Pungo River sediments were deposited in a restricted marine basin that had open seaward access to a southward-flowing cool-water currents that were directed upward by a steeply sloping seafloor. Forams from bioturbated diatomaceous clays indicate relatively shallow water deposition, somewhere between 100 and 200 meters, a low energy environment where biological sedimentation (plankton rain) equaled or exceeded clastic deposition. Benthonic foraminifera suites suggest a cold water environment, i.e. few species but a large number of individuals. Miller conjectured that the observed fauna could have resulted from a nearshore, southward flowing cool current, similar to the present day Labrador Current, which perhaps extended as far south as North Carolina in middle Miocene time. According to Manheim and Gulbrandsen (1979) the Gulf Stream did not establish itself until the middle to late Miocene. Paleontological data indicate that deposition of the Pungo River began about 19 million years ago and continued for about 6 million years (Denison *et al*., 1993).

Scarborough and Riggs (1980) broke out four informal units in the Pungo River Formation and determined that the lower three were laid down during a major transgression, while the upper unit was deposited during a regressive phase. Miller (1982) ascribed the Pungo River's complex interbedding to fluctuations in water depth as a result of a series of minor transgressions and regressions. Detailed stratigraphic mapping (previously described) reveals numerous minor unconformities and diastems marked by pebble beds. To recapitulate: Bed 21, the basal bed of the Pungo River Formation contains abundant phosphates pebbles; Bed 20 contains fine-grained dolomitic sandstone with abundant phosphatic pebbles; Bed 19, a substantial layer of highly phosphatic sand contains concentrated phosphatic pebbles and fossils at the base; and Bed 18 also contains phosphate pebbles. Bed 14, at the top of the unit, is a thick bed of coquina filled with rich black phosphatic sand and black vuggy phosphatic pebbles.

The occurrence of pebble-sized phosphate grains (+10 mesh), which can comprise up to 5 percent of the volume, indicate lag deposits and reworking. Although Miller thought that most of the phosphate was primary, he conceded that current ripples, which are found throughout the

Pungo River Formation, along with the water-polished surfaces and oolitic to sub-oolitic form of the phosphate grains show that bottom currents were active throughout Pungo River deposition and are "in part responsible for the accumulation of high concentrations of phosphate in the formation" He also observed that interbedding is particularly complex in the area of high phosphate concentration. This also suggests that reworking was a factor.

After Pungo River deposition, the sea retreated and the deposits were subjected to acidic groundwater conditions, resulting in cast-and-moldic texture of the limestone beds.

Miller (1982) attributed the phosphate cap at the Castle Hayne/Pungo River interface to mineralized solutions from the overlying Pungo River migrating downward into the permeable limestone, but this may not be the case, considering that this surface had acted as an attachment site for Oligocene oysters. During this period of exposure, another phosphate-rich residuum was formed. The base of the Yorktown Formation, like the base of the Pungo River Formation, is also a series of strata with lags of cobble- to boulder-sized pieces of black phosphate and well-rounded quartz pebbles laid down across the broad unconformable surface (Kimrey, 1965). To recapitulate: Bed 12 is a phosphatic sandy clay with copious reworked phosphatized pebbles and fossils, particularly in the base of the unit; Bed 11 is a marly clay containing reworked phosphate pebbles, along with phosphatic bones and teeth; and Bed 10 is a marly clay with large black phosphatic pebbles at the base of the unit.

Although not as obvious as in the case of Florida phosphate deposits, it is clear that unconformities and basal lags play an important part in the concentration of phosphate deposits in North Carolina.

3.0 Stratigraphic Setting for Phosphate in Virginia's Coastal Plain

In Virginia's Coastal Plain, significant phosphate occurrences have been reported in stratigraphic units ranging in age from Late Cretaceous to Neogene. Occurrences noted in the Cretaceous Patuxent Formation, the Paleocene Brightseat Formation, and the Eocene Nanjemoy Formation appear to offer limited commercial potential due to low grade, limited extent, and relatively thick overburden. However, these units may be important sources of phosphate re-mobilized and deposited during Neogene time. Based upon the review of significant deposits in other regions of the Atlantic Coastal Plain (Section 2.0), this study has targeted formations of the Chesapeake Group, particularly the Miocene-age Calvert Formation, which is correlative with the highly phosphatic Pungo River Formation in North Carolina (Figure 2).

The following sections include descriptions of the relevant stratigraphic units, from oldest to youngest, including those that may represent targets for exploration of phosphate ore reserves as well as those stratigraphic units that may have been the primary depositional sites for phosphate. Figure 3 shows a stratigraphic column for the formations in Virginia that will be discussed in the following sections.

3.1 Pamunkey Group

Darton (1891) named the Pamunkey Formation for extensive exposures on the Pamunkey River in Virginia. The Pamunkey Formation consists of a homogeneous, 150-foot-thick sheet of fine-grained sedimentary material, mainly glauconitic sands, usually profusely fossiliferous, and locally including a few beds of clay, secondary limestones, and some gravels at the base. The Pamunkey, as originally defined, unconformably overlies the Cretaceous section. Darton considered the Pamunkey to be representative of the Eocene.

Subsequently, the Pamunkey has been subdivided and its age extended. Clark and Martin (1901) raised the Pamunkey to "Group" status and divided it into the upper Nanjemoy Formation and the lower Aquia Formation. Bennett and Collins (1952) cut the Paleocene Brightseat Formation from the bottom of the Aquia; Glaser (1971) separated the Marlboro clay beds from the base of the Nanjemoy and raised this unit to formation status; Otton (1955) added the Piney Point Formation to the top of the Nanjemoy; and Ward (1985) added the Chickahominy Formation on top of the Piney Point.

Although superficially similar, Pamunkey Group units can vary considerably from those of the Chesapeake Group, which overlie the Pamunkey. Most notably, Pamunkey units are characteristically rich in glauconite. The Brightseat, Aquia, Nanjemoy, and Piney Point Formations all increase in glauconite content in a seaward direction (Ward, 1984b). In addition, the Pamunkey Group hosts a molluscan fauna with little in common with the Chesapeake Group.

The formations in the Pamunkey Group represent a lithologically intermediate zone on the Atlantic Coast during early Cenozoic time, lying between carbonate-dominated deposition to the south and clastic-dominated deposition to the north. Figure 3 provides a stratigraphic column for the formations, described from oldest to youngest, in the following sections.

3.1.1 Brightseat Formation

The lower Paleocene Brightseat Formation was separated from the bottom of the Aquia Formation by Bennett and Collins (1952) and named for an exposure southwest of Brightseat, Maryland. Their motive was largely biostratigraphic, rather than lithostratigraphic, and the Brightseat was originally intended to encompass all of the Paleocene deposits lying unconformably beneath the Eocene Aquia formation and overlying unconformably the Cretaceous Potomac Group. Hazel (1968) considered the Brightseat to be the basal formation of the Pamunkey Group.

The Brightseat is composed of discontinuous lenses of olive-gray to olive-black (5 Y 2/1), fine- to very fine grained quartz sand, clayey and silty, micaceous, variably glauconitic, up to 20 feet thick (Rader and Evans, 1993). The upper and lower contacts are locally burrowed. Pyrite is abundant and phosphate clasts are common (McCartan, 1989). Adams *et al*. (1961) described phosphate pebbles from the upper part of the Brightseat close to the contact with the overlying Aquia Formation.

The Brightseat was deposited on a shallow marine shelf (McCartan, 1989), and forams and ostracodes give it an earliest Paleocene age (Hazel, 1968; McCartan, 1989).

The Brightseat crops out on the Virginia side of the Potomac River in the vicinity of Aquia Creek, but is not found south of the Rappahannock River, either in outcrop or in the subsurface (Ward, 1984b).

3.1.2 Aquia Formation

Clark (1895, 1896) first formally described the Aquia beds at Aquia Creek in Stafford County, Virginia. His Aquia beds consist largely of greensand and greensand marl that Clark considered Eocene-age because they contain "middle Lignitic" fossils and overlie Cretaceous rocks. Clark assigned the Aquia beds to Darton's Pamunkey Formation.

Clark and Martin (1901) raised the status of the Aquia beds, placing the Aquia Formation into the Pamunkey Group. They distinguished their Aquia Formation from the overlying Nanjemoy Formation by it being more arenaceous and calcareous, and characterized by a well-

marked fauna representing a clearly defined paleontological stage. They divided the Aquia into two members, the upper Piscataway and lower Paspotansa members.

The Aquia Formation is composed of light- to dark olive-grey, thick-bedded to massive, medium- to very fine grained greensand and greensand marl that is clayey and silty (Rader and Evans, 1993). The Aquia can be extremely fossiliferous, with some interbedded layers consisting almost entirely of shells. Minor amounts of phosphate have been reported from water well cuttings into the Aquia in Hanover, Henrico, and King George counties (Virginia Division of Geology and Mineral Resources well records 1613, 1769, 1770, and 1852).

The unit, up to 130 feet thick, unconformably overlies the Lower Cretaceous Potomac Group and disconformably underlies the Nanjemoy Formation where present. Elsewhere the Aquia unconformably underlies younger formations.

Aquia Formation sediments were deposited during a major marine transgression and they are broadly distributed. The Aquia creates conspicuous bluffs along the Potomac, Rappahannock, and Pamunkey rivers, and lesser outcrops along the James. The best exposures occur near the mouth of Aquia Creek and along the south bank of the Potomac River between Bull Bluff and Fairview Beach. The Aquia also crops out on the Rappahannock River from the mouth of Massaponax Creek to Hopyard Landing opposite Skinners Neck; on the Mattaponi River from above Milford to near Kidds Fork; on the Pamunkey River from Wickham Crossing to near the Caroline-King William County line; and on the James River from the Turkey Island Cutoff to below Hopewell (Clark and Miller, 1912; Ward, 1984b; Ward, 2008). The Aquia is also well exposed along Shockoe Creek in Richmond, and occurs in outcrops as far south as Petersburg. There is an isolated Aquia locality along the Nottoway River in Sussex County (Clark and Miller, 1912).

The Aquia's basal Piscataway Member, named for Piscataway Creek on the Maryland side of the Potomac River, consists of fossiliferous, light greenish-gray, poorly sorted greensand and greensand marls. The lower beds are very argillaceous; the upper beds contain persistent layers of indurated marl. The Piscataway is calcareous, and contains a few thin to medium beds of olive-gray, white, and pale greenish-yellow limestone that form ledges. Large bivalves dominate the Piscataway, particularly *Cucullaea gigantica*, *Ostrea alepidota*, *Dosiniopsis lenticularis*, and *Crassatellites capricranium* (Ward, 1984b). Originally considered of Eocene age, the Piscataway molluscan taxa indicate a late Paleocene age, probably late Landenian (Hazel, 1969; Ward, 1984b).

Piscataway sediments were deposited in the Salisbury Embayment, a marine basin bordered on the south by the Norfolk Arch and on the west by the Piedmont, with access to the Atlantic to the northeast. During the Paleocene, the Norfolk Arch acted as a barrier between the Piscataway sea in the Salisbury Embayment to the north, and the Beaufort sea in the Albemarle Embayment to the south (Ward, 1984b).

The Paspotansa Member, named for Passapatanzy Creek, was deposited on an undulating disconformity atop the Piscataway Member. Ward (1984b) states, "No phosphate accumulations or burrows are present, indicating, at most, only a brief period of non-deposition." The Paspotansa contrasts to the Piscataway in that it is well-sorted, massive to thick-bedded, commonly contains concretions, is micaceous, and is characterized by thin layers packed with the large, high-spired gastropod *Turritella mortoni* (Rader and Evans, 1993). Many of the smaller fossils have been partially or entirely leached, leaving internal casts and molds. When fresh, the Paspotansa is dark olive black; when weathered it is yellowish orange due to oxidation

of iron in the glauconite. Like the Piscataway, it was originally assigned to Eocene, but is now considered Paleocene (Hazel, 1969).

3.1.3 Marlboro Clay

The late Paleocene Marlboro Clay was first described by Clark and Martin (1901) for exposures of red clay beds at the base of the Nanjemoy Formation near the town of Upper Marlboro, Prince Georges County, Maryland. They considered it to be Eocene in age and the basal unit of the Nanjemoy Formation, the "pink clay member" as they called it. Clark and Miller (1906) geographically extended the Marlboro clay beds into Virginia, Darton (1948) formally revised the clay beds as the lower member of the Nanjemoy Formation, and Glaser (1971) raised the Marlboro Clay to formation rank.

The Marlboro Clay is a thin but persistent unit consisting of tough, plastic, compact, uniform kaolinitic clay, the aluminum silicate derived from the crystalline rocks of the Piedmont (Darton, 1948). Its thickness ranges from a feather edge to 30 feet with an average of 20 feet. The clay is usually massively bedded, generally pure or with minor glauconite, interbedded with subordinate yellowish-gray to reddish, laminated and ripple cross-laminated silt and very fine-grained sand. The color ranges from a silvery-gray to pinkish-gray to pale-red, often with the lower part pink and upper part white. The clay contains rare molds of small mollusks and arenaceous foraminifers. Foraminifer and dinoflagellate assemblies suggest a brackish-water, estuarine environment (Nogan, 1964, Gibson et al., 1980).

The contact of the Marlboro Clay with the underlying Aquia Formation is abrupt with little or no mixing of materials (though there are some burrows into the Aquia that are filled with Marlboro clay) and this contact is probably an unconformity (Ward, 1984b). Darby (1984) reported phosphorite grains concentrated along this contact.

The age of the Marlboro Clay is still controversial. Gibson *et al*. (1980) used pollen and dinoflagellate data to determine a latest Paleocene to earliest Eocene age, while essentially the same authors (Bybell and Gibson, 1991) used calcareous nanofossil data to determine that the Marlboro Clay is entirely of late Paleocene age.

The Marlboro Clay has a widespread but spotty distribution. It is well developed between Potomac Creek and the Rappahannock River, but only occurs in two places along the Pamunkey River: about a mile above the Route 301 bridge and a half mile below Sturgeon Hole (Ward, 1984b). An outcrop occurs on the south bank of the James River below the mouth of Baileys Creek in Prince George County.

3.1.4 Nanjemoy Formation

The Nanjemoy Formation was named by Clark and Martin (1901) for exposures along Nanjemoy Creek in Charles County, Maryland. They subdivided it into the Woodstock greensand member (substage) above and the Potapaco clay member (substage) below. Cooke (1952) placed the Nanjemoy in the Pamunkey Group.

The Nanjemoy Formation exhibits marked lateral variations in lithology but it can be generally described as dark-olive-gray, greenish-gray, and olive-black glauconitic quartz sand, fine- to coarse-grained, very clayey and silty, intensely burrowed, sparsely to abundantly shelly, interbedded with sandy clay-silt (Rader and Evans, 1993). The sand in the upper part of the unit is less clayey, very micaceous, and contains scattered quartz pebbles. Large concretions are common and gypsum crystals occur at intersections of joints and bedding planes in the clay,

sometimes as rosettes. Somewhat indurated, fossiliferous, calcitic intervals are present, and the formation may be capped with a thin limestone. The Nanjemoy thickens to the north.

The Nanjemoy Formation is characterized by a well-marked fauna representing a clearly defined paleontological stage. The unit is very fossiliferous and shell beds are common. Typical lower Eocene mollusks include *Venericardia potapacoensis*, *Venericardia ascia*, and *Macrocallista subimpressa* (Rader and Evans, 1993). The fauna indicates deposition on a shallow, marine shelf (Reed and Obmeier, 1982: McCartan, 1989).

Gibson and Bybell (1995) used biostratigraphic dating (calcareous nannofossils) to determine that the Nanjemoy Formation in Virginia and Maryland is of early Eocene age, and that the Paleocene-Eocene boundary occurs within the hiatus between the Nanjemoy and the Marlboro Clay. Ward (1985) later changed the age of the Woodstock from early and middle Eocene to early Eocene, only, based principally on dinoflagellate and calcareous nannofossil assemblages.

The Nanjemoy Formation is frequently exposed in the western reaches of Virginia's Coastal Plain rivers. Throughout most of its distribution, the Nanjemoy unconformably overlies the Marlboro Clay and unconformably underlies the Chesapeake Group. Both unconformable contacts are burrowed and marked by abrupt lithologic changes (Glasser, 1971; McCartan, 1989). Near Hopewell, Virginia, the Nanjemoy unconformably underlies the St. Marys Formation (Dischinger, 1987). At the type section at Woodstock, the Nanjemoy unconformably underlies either the Piney Point Formation or younger beds (Ward, 1985). There is less relief on the Nanjemoy than underlying units.

Clark and Martin (1901) named the Potapaco Member, originally known as the Potapaco clay member, for the early name of Port Tobacco Creek, or a corruption of the word Potapaco found on early maps. The Potapaco consists of greensand, often very argillaceous and at times gypsifferous, forming the basal member of the Nanjemoy Formation. The Potapaco overlies the Aquia Formation and underlies the Woodstock Member of the Nanjemoy Formation. It is 60-65 feet thick. Small phosphate pebbles are common in the Potapaco (Ward, 1984b). The Potapaco truncates the Aquia Formation.

An unconformity separates the Potapaco from the Woodstock Member, originally known as the Woodstock greensand marl member. The Woodstock was named for an old estate a short distance above Mathias Point on the Virginia side of the Potomac River in King George County, and assigned to the top of the Nanjemoy Formation (Clark and Martin, 1901). The Woodstock Member is characterized by olive-black, fine to very fine, well sorted, silty, fossiliferous greensands and greensand marls, with a fine-textured, micaceous, massive appearance, less argillaceous than the Potapaco Member (Clark, 1896; Clark and Martin, 1901; Ward, 1985). The lower Woodstock boundary contains a lag deposit of phosphate, bone, and pebbles (Ward, 1984b).

Downdip, the Aquia Formation, the Marlboro Clay, and the Potapaco member of the Nanjemoy have been truncated by transgressive sea of middle Eocene time during which the Woodstock Member of the Nanjemoy was deposited (Cederstrom, 1957).

3.1.5 Piney Point Formation

The Piney Point Formation was named by Otton (1955) for glauconitic sands and interspersed shell beds that lie above the Nanjemoy Formation and below the Calvert Formation with conformable contacts. The type section (subsurface) is a well drilled near the tip of Piney

Point Peninsula, St. Marys County, Maryland. Ward (1985) assigned the Piney River to the Pamunkey Group.

The Piney Point Formation is generally described as up to 60 feet of olive-gray and grayish-olive-green, very glauconitic quartz sand, medium- to coarse-grained, and poorly sorted, containing scattered quartz pebbles interbedded with carbonate-cemented sand and moldic limestone (Rader and Evans, 1993). The unit is highly fossiliferous, characterized by large, calcitic shells of the oyster *Cubitostrea sellaeformis*, a middle Eocene marker. Aragonitic mollusks are generally leached, leaving only molds and casts. Based upon foraminifera and ostracodes, the Piney Point was deposited under normal marine conditions, in a slow clastic sedimentation regime, with quiet conditions and clear warm waters (Deck, 1985).

The Piney Point is recognizable in Northumberland and Westmoreland counties in Virginia, and there are many small exposures along the Pamunkey River from above the US Route 360 bridge to below the locale of Retreat. A reference section is located in an exposure along right bank of Pamunkey River at Horseshoe, Hanover County, Virginia (Ward, 1984b, 1985).

3.1.6 Chickahominy Formation

The Chickahominy Formation was first recognized in subsurface of Virginia by Cushman and Cederstrom (1945), who proposed the name in their report for beds in wells at the Navy Mine Depot, Yorktown, Virginia, where it is overlain by the Miocene Chesapeake Group and underlain by lower and middle Eocene strata. Their correlation chart shows it as late Eocene (Jacksonian) age and correlative with the Cooper Group in South Carolina, and part of the Ocala Limestone in Florida. Ward (1985) assigned the Chickahominy Formation as the youngest member of Pamunkey Group.

The Chickahominy consists of blue, gray, olive-gray, and dull-brown clays, clayey silt and silty clay, very compact, glauconitic, and micaceous with abundant finely crystalline iron sulfide (Rader and Evans, 1993). Chickahominy sediments coarsen downward to very fine- to fine-grained sand with pebbles at the base. This unit contains rare shell fragments, but microfossils are very abundant.

3.2 Chesapeake Group

The Chesapeake Group is an outgrowth of the Chesapeake Formation of Darton (1891) who described a three-tiered stratigraphy consisting of: 1) a basal unit of dark-colored clay and fine marly sand containing extensive diatomaceous deposits, 2) a middle unit of lighter-colored clays and sands, and 3) an upper, coarse-grained, white beach sand containing shells and shell fragments. Dall and Harris (1892) quickly raised the Chesapeake to group status and applied the name to all similar Miocene strata from Delaware to Florida, including Darton's Chesapeake Formation and any other beds belonging to same horizon and having the same general fauna, thereby forming a stratigraphic equivalent of the chronologic "Yorktown epoch" of Dana. Shattuck (1902) divided the Chesapeake Group in Maryland into a lower Calvert Formation, a middle Choptank Formation, and an upper St. Marys Formation. A short while later, Clark and Miller (1906) added the Yorktown Formation to the top of the group. Much later, Ward and Blackwelder (1980) broke out the Eastover Formation directly beneath the Yorktown while Blackwelder (1981) added the Chowan River Formation on top of the Yorktown in far southeastern Virginia and northeastern North Carolina. Ward (1985) then added the Old Church Formation as the basal piece of the Chesapeake Group. The formations that comprise the

Chesapeake Group are discussed in the following sections, from oldest to youngest, and are shown in the stratigraphic column in Figure 3.

3.2.1 Old Church Formation

The Old Church Formation was named by Ward (1985) for a village a few miles southwest of his type section on the south bank of the Pamunkey River at Horseshoe, Virginia, in Hanover County. Ward described a thin unit consisting of grayish-olive (10 Y 4/2), clayey and poorly sorted quartz sand, very calcareous due to shell fragments as well as large numbers of foraminifera and ostracodes (Ward and Blackwelder, 1979; Ward, 1985). Oyster and small pecten fragments are common, but aragonitic shells are usually leached, leaving molds and casts. Common fossils are *Anomia ruffini*, *Lucina sp*., and *Mercenaria capax*. Large boulder-sized concretions occur in the middle of the formation. Some sparse glauconite is present, probably reworked from underlying formations. The Old Church unconformably overlies the Piney Point Formation and unconformably underlies the Calvert Formation. Ward (1985) correlated this unit with the River Bend and Belgrade Formations in North Carolina, and determined the age to be late Oligocene and early Miocene.[6]

At the type section the formation is rather thin, no more than 5 feet, but it thickens seaward, becoming less calcareous and more glauconitic with increasing phosphatic sand. Powars *et al*., (1992) recognized 40 feet of deposits equivalent to the Old Church Formation in the Exmore corehole on the Eastern Shore of Virginia.

During Old Church time, the Norfolk Arch was again a high area separating the Salisbury Embayment from the Albemarle Embayment. This barrier probably served to divert the tropical currents that dominated North Carolina during this time, resulting in a temperate, low diversity molluscan fauna (Ward, 1984b). This was a time of widespread climatic changes accompanied by abrupt, short-term, small-scale marine pulses (Ward, 1984b).

Known outcrops of the Old Church Formation are rare, occurring in limited exposures along the Pamunkey River from near Horseshoe to below the mouth of Matadequin Creek, and at the bottom of the Warren Brothers sand and gravel borrow pit, now inundated on the Chickahominy floodplain below Bottoms Bridge. The Old Church is found in the subsurface elsewhere in Virginia and Maryland, perhaps even in Delaware and New Jersey (Ward, 1985). At Gravatt's Mill in King William County, Virginia, Ward (1984b) described beds "probably equivalent to Old Church" composed of large indurated blocks of conglomeratic sandstone containing phosphate pebbles and cobbles, along with worn bone and teeth. These beds directly overlie the Eocene-age Nanjemoy Formation, and are overlain by the basal Calvert. Among the bone fragments found that Ward found on this horizon was a periotic from an odontocete whale that was "certainly pre-Calvert and probably early Miocene or very late Oligocene in age."

3.2.2 Calvert Formation

The Calvert Formation was named by Shattuck (1902) for exposures along the Calvert Cliffs in southern Maryland, and it represented the basal unit of his original Chesapeake Group.

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[6] Ward (1985) placed the Old Church at the base of the Chesapeake Group because he believed these beds represent "Zone 1" in the original definition of the Calvert Formation by Shattuck (1904). However, Mixon *et al*. (1989a) excluded the Old Church Formation from Chesapeake Group in their map of the Virginia Coastal Plain, where the Calvert Formation was considered the base of the Chesapeake. Instead, they mapped the Old Church with other lower Tertiary formations. Rader and Evans (1993) lumped the Old Church Formation with some unnamed glauconitic sands as "undifferentiated lower Tertiary deposits."

Darton (1911) later extended the Calvert into Virginia, and Picket and Spoljaric (1971) much later brought it to Delaware. Siple (1960) extended it into North Carolina, but subsequently Gibson (1982, 1983b) replaced the Calvert in North Carolina with the Pungo River Formation. The Calvert and Pungo River formations were correlated by Brown (1958) on the basis of benthonic forams, and by Gibson (1967, 1980) on the basis of mollusks and forams.

Rader and Evans (1993) described the Calvert Formation as consisting of anywhere between two to seven fining-upward sequences, each sequence beginning with an olive-gray basal unit of very fine to fine sand with clay and silt, very sparsely to abundantly shelly, grading upward to a clay-silt diatomite. Typical mollusks include the scallop *Chesapecten coccymelus*, the clam *Crassatella melinus*, and the gastropod *Ecphora tricosta*.

The Calvert Formation is the thickest and most widespread of the Miocene sedimentary packages on the Coastal Plain, up to 600 feet thick. These sediments were deposited during the maximum Tertiary marine transgression, which reached 240 feet above current sea level (Daniels and Onuschak, 1974). Magnificent cliffs occur along the Potomac River, particularly at Nomini Cliffs and Westmoreland State Park. Exposures on the Rappahannock River occur from Wilmont Wharf to past Fones Cliffs to Bowlers Wharf, on the Mattaponi River from Bowling Green to West Point, and on the Pamunkey River from Wickham Crossing to below Elsing Green. The southwestern-most exposures of the Calvert are in Shockoe Valley in Richmond; it is the only formation of the Chesapeake Group present in the Richmond area (Darton, 1911). The Calvert dips into the subsurface just north of the James River and there are no outcrops of the Calvert along the James River.

The Calvert progressively overlaps older strata westward and at many places along the Fall Line it rests directly on the Paleozoic basement. The Calvert also overlaps progressively older formations southwestward, overlying the Nanjemoy Formation north of the James River and the Aquia Formation in Richmond. Due south of Petersburg, the Calvert is absent in the subsurface, and the Yorktown Formation rests directly on pre-Chesapeake Group units.

The Calvert Formation was originally divided by Shattuck (1904) into two members: the Fairhaven diatomaceous earth member on the bottom and the Plum Point marl on top. Gernant (1970) later identified the Calvert Beach Member as the uppermost of three members.

3.2.2.1 Fairhaven Member

The bottom unit of the Calvert Formation was named by Shattuck (1904) for Fairhaven, Anne Arundel County, Maryland. He did not designate a type section, but used the term "Fairhaven diatomaceous earth member" for brown to white to greenish beds characterized by the presence of a large proportion of diatoms embedded in a very fine quartz sand/silt matrix, containing only a small amount of calcareous material at the base of the member. It also contains casts of Miocene fossils and remains of reworked Eocene fossils. His section consists of three zones:

- Zone 1. A bed about two to six feet thick of brownish sand containing *Phacoides contractus* (a clam) and lying unconformably on Eocene deposits.
- Zone 2. A thin stratum of white sand about 1 foot thick, locally indurated to sandstone, and containing a large number and variety of fossils. According to Ward (1984b), Zone 2 contains two distinctive marine pulses involving basal transgressive lags and fining upward sequences. The two are "separated by a phosphate pebble lag indicating an unconformity or at least a diastem." Beds of the first pulse are found as far south as the Rappahannock River, beds of the second pulse as far south as the Mattaponi River.

- Zone 3. A greenish-colored diatomaceous earth that on weathering bleaches to a white or buff-colored deposit breaking into columnar sections with perpendicular surfaces. This zone, which is up to 20 feet thick and includes most of the Fairhaven, is frequently composed of more than 50 percent diatoms, and hosts large numbers of *Phacoides contractus*.

Reinhardt and others (1980) extended the Fairhaven Member into Virginia using data from the Oak Grove Core. Gibson (1983b) revised the Fairhaven Member to remove some lower muddy, glauconitic sand beds, with a basal layer of quartz and phosphate pebbles and phosphatized mollusk shells, which he placed in a newly named Popes Creek Sand Member of the Calvert. However, Ward and Powars (1991) discarded the name Popes Creek Sand Member and reassigned the strata to the Fairhaven Member. Their reasoning was that although a phosphate pebble lag indicates an unconformity, the diatomaceous clays on either side of that contact are so similar that they cannot be separated lithologically.

According to Honkala (unpublished manuscript, VDGMR), the base of the Fairhaven is a thin pavement of quartz, pebbles and phosphatized mollusk shells, echinoid plates and phosphatized sand and gravel. Honkala's Fairhaven member consists of two parts; a lower sand, 4 to 6 feet thick, and an upper fine muddy sand and silt, the two parts separated by a diatomaceous silt or clay. The basal sand member, absent to the west and thicker to the south, contains medium to very coarse, well-sorted quartzo-phosphatic sand, sub-rounded, with (unlike the underlying unit) only minor traces of glauconite, locally fossiliferous.

The diatomaceous member is prominent (100–180 feet thick) in the counties of Westmoreland, Northumberland, Lancaster, Richmond, and Middlesex. According to Ward (1984b), the Calvert Formation along the Pamunkey River should be assigned to the Fairhaven Member, based upon lithology.

3.2.2.2 Plum Point Marl Member

The middle unit of the Calvert Formation was named by Shattuck (1904) for Plum Point in Calvert County, Maryland, and consists of dense bluish-green, greenish, grayish-brown silty clays, and buff sandy clays and marls. Plant fragments are common, as are lignitic masses, organic remains, and diatoms. Authigenic gypsum and vivianite are locally prominent. Vivianite is a hydrated iron phosphate found in sedimentary rocks associated with fossil remains of bones and shells.

Ward and Powars (1991) contend that the Plum Point Marl Member, as a lithic entity, is recognizable only as far south as Westmoreland Bluffs along the Potomac River. Further to the south and east, beds equivalent to the Plum Point grade into silty, diatomaceous clays, although by correlating diatoms, equivalent beds have been identified on the Mattaponi River from Reedy Mill down to White Oak Landing and on the Pamunkey River from Horseshoe to Elsing Green (Ward, 1984b).

3.2.2.3 Calvert Beach Member

The type section for the Calvert Beach Member, the uppermost unit of the Calvert Formation, is at Calvert Beach, Calvert County, Maryland. Originally named by Gernant (1970) as a member of Choptank Formation, this unit occurs in southern Maryland and Virginia, and consists of green to blue, muddy, fine-grained sand. It gradationally underlies the Choptank Formation.

Ward (1984b, 1985) revised the Calvert Beach Member from the lowest member of the Choptank Formation to the uppermost member of the Calvert Formation, based on what he believed to be a correction of miscorrelation of lithologically similar beds in the upper part of the Calvert and the lower part of the Choptank Formation.

3.2.3 Choptank Formation

The Choptank was named for exposures along the Choptank River below the Dover Bridge in Talbot County, on the Eastern Shore of Maryland (Shattuck, 1902). Sanford (1913) tentatively extended the Choptank into Virginia along the Potomac River.

The Choptank is generally described as olive-gray sand, fine to very fine, clayey and silty, shelly, and diatomaceous, commonly forming fining-upward sequences (Rader and Evans, 1993). Bedding in many places has been destroyed by bioturbation, giving a mottled appearance, and sand-filled burrows are common. Middle Miocene mollusks include *Chesapecten nefrens, Mercenaria cuneata,* and *Ecphora meganae.* Ramsey (1993) gives the age of the Choptank as middle to late Miocene. McCartan (1989) interpreted the depositional environment as an open shelf with an eroded shore facies.

Ward (1984b) reports that at White Oak Landing on the Mattaponi River the Choptank is absent and the St. Marys Formation rests directly on the Calvert. Also, on the Pamunkey River at Wickham Crossing, Elsing Green, and in the vicinity of Horseshoe, the Eastover rests on the Calvert. Some authors (Powars and Bruce, 1999; McFarland and Bruce, 2006) contend that the Choptank is not present in Virginia.

3.2.4 St. Marys Formation

The St. Marys was named by Shattuck (1902) for exposures along the St. Marys River in Maryland, and is the uppermost of the three original formations in the Chesapeake Group. Cooke *et al*. (1943) extended the formation into Virginia, North Carolina, and Delaware.

The St. Marys Formation is generally described as up to 40 feet of bluish- to pinkish gray, muddy, very fine sand and sandy clay-silt and blue-grey clay, dense and sticky, similar to the Calvert without the profusion of diatoms. The St. Marys is locally abundantly shelly, with well-preserved and diverse upper and middle Miocene marine faunas including *Chesapecten santamaria*, *Buccinofusus parilis*, *Ecphora gardnerae*, *Turritella plebeian*, *Spisula rappahannockensis*, the scaphopod *Dentalium attenuatum*, and the barnacle *Balanus concavus* (Rader and Evans, 1993). A phosphatic horizon is located above the lower contact in Maryland (Hansen, 1981).

Cooke *et al*. (1943) correlated the St. Marys Formation in North Carolina, Virginia, Maryland, and Delaware, and placed the age as middle and late Miocene. Groot *et al*. (1990) put the age as late Miocene. Rader and Evans (1993) placed the age as middle and late Miocene.

Known outcrops of the St. Marys in Virginia are limited to thin exposures in the area of Piscataway Creek on the Rappahannock River, and White Oak Landing and Corbin Creek on the Mattaponi River. At Rickahock, just upstream from White Oak Landing, the St. Marys is absent and the Eastover rests directly on the Calvert. The St. Marys does not occur in any of the outcrops along the Pamunkey River and probably was not deposited that far south, although it may have been removed by erosion (Ward, 1984b).

3.2.5 Eastover Formation

Ward and Blackwelder (1980) named this unit for exposures above Mount Pleasant on the south bank of the James River, east of Eastover, in Surry County, Virginia. The Eastover Formation is described as up to 270 feet of dark-gray to bluish gray, muddy, very fine to fine-grained, micaceous sand that is interbedded with laminated silt and clay (Rader and Evans, 1993). *Isognomon maxillata*, the "purse-oyster," is the index fossil of the Eastover Formation.[7] Other upper Miocene mollusks include the scallop *Chesapecten middlesexensis*, and the clams *Marvacrassatella surrlensis* and *Glossus fraterna.*

The Eastover unconformably overlies the St. Marys Formation, or to the south, progressively older sedimentary formations. It is everywhere unconformably buried by the Yorktown Formation. Ward and Blackwelder (1980) divided the Eastover into two members, the lower Claremont Manor Member and the upper Cobham Bay Member. Ward (1992) shows the Claremont Manor Member in Virginia, North Carolina, and southeastern Maryland, while the Cobham Bay Member is shown only in Virginia and North Carolina.

3.2.6 Yorktown Formation

The Yorktown Formation was named by Clark and Miller (1906) to describe sands and clays crowded with the remains of calcareous shells, chiefly marine mollusks. They assigned this unit to the top of the Chesapeake Group. Stephenson and MacNeil (1954) extended the Yorktown into eastern Maryland and the Calvert Cliffs, where it overlies the St. Marys Formation. LeGrand and Brown (1955) brought the Yorktown into North Carolina (they considered the Duplin Marl to be a shallow-water facies of the Yorktown), while Blackwelder and Ward (1979) introduced the Yorktown to South Carolina, replacing the Duplin Marl.

The Yorktown Formation is generally described as bluish-gray to brownish-yellow sand, fine- to coarse-grained, commonly very shelly, interbedded with blue-gray, sandy and silty clay that is partly glauconitic and phosphatic (Rader and Evans, 1993). The sand tends to be quartzitic to the north, bioclastic to the south. In the lower York River and James River basins, the Yorktown is composed of cross-bedded shell hash and coquina; mollusks include *Glycymeris subovata*, *Mercenaria tridacnoides*, *Panopea reflexa*, and various pectens. A coarse-grained sand and gravel facies occurs in updip areas. Yorktown sediments were deposited during a major marine transgression and show the influence of shoaling and the influx of coarse-grained terrigenous sediments. The age is early Pliocene to late Pliocene (Gibson, 1983a; Cronin, 1991; Dowsett and Wiggs, 1992).

The Yorktown constitutes the present land surface over much of the Coastal Plain, with the nearshore, coarse-grained sand and gravel facies extending to the Fall Zone. To the south of the James River, in western Prince George, Sussex, and Southampton counties, the Calvert and Nanjemoy are absent and the Yorktown rests directly on the Aquia. The Yorktown is thickest near the mouth of the James River. Outcrops occur in Gloucester, York, James City, Isle of Wight, and Nansemond counties, and along Smith Creek in Suffolk. Coquina facies occur below Yorktown at Fergussons Wharf, at Benns Church near Smithfield, and near Reids Ferry at Suffolk.

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[7] *Isognomon maxillata* is a distinctive species easily recognizable by its thick shell, pearly luster, and flaky, chalky appearance and texture. Shells are almost never found whole, but most preserve the rather pointed beak and characteristic ridged "teeth."

Ward and Blackwelder (1980) divided the Yorktown in Virginia into four members (ascending): the Sunken Meadow, Rushmere, Morgarts Beach, and Moore House. However, Campbell (1993) contends that these members need revision because they are difficult to map.

3.2.6.1 Sunken Meadow Member

The type section for the Sunken Meadow Member is a cliff below Sunken Meadow Creek, on the south bank of James River in Surry County. This unit consists of a transgressive, coarse- to medium-grained, poorly sorted, very shelly quartz sand. *Chesapecten jeffersonii*, "Jefferson's Chesapeake Scallop," occurs in the Sunken Meadow Member, and is the index fossil for the Lower Yorktown Formation.[8] Calcite-cemented lumps are locally abundant. The Sunken Meadow contains a phosphatic bone and shark-tooth lag deposit common in middle and upper Miocene beds from Florida to Maryland (Ward, Bailey, and Carter, 1991). This lag deposit marks the lower contact to the west; to the east the basal deposits are finer and dominated by glauconitic and phosphatic sand (Ward and Blackwelder, 1980; Ward, 2008).

The Sunken Meadow Member unconformably overlies the Eastover Formation in much of Virginia, and overlies older sediments farther south. The unit is present in the subsurface at least as far as the Lee Creek Mine, but is unknown beyond the Neuse River (Ward, Bailey, and Carter, 1991).

The Sunken Meadow Member was deposited as an initial transgressive unit during the early Pliocene highstand of the sea, and it occurs widely across the Salisbury Embayment and extends southward into the Albemarle Embayment. It is exposed at Claremont, Cobham Wharf, and Kingsmill on the James River (Ward, 2008).

3.2.6.2 Rushmore Member

The type section for the Rushmere Member is east of the community of Rushmere, on the south bank of the James River at Burwell Bay, Isle of Wight County. This unit consists of blue-gray, fine, well sorted, shelly sand. Phosphatic sand and glauconite are common in amounts up to 10 percent (Ward, 2008). Coarse sand and pebbles are present near the lower contact.

The Rushmere represents the greatest extent of the Pliocene transgression, and it crops out from the Rappahannock River in Virginia to the Tar River in North Carolina. The Rushmere buried the Sunken Meadow Member wherever the older unit was deposited, apparently conformably, with the notable exception of an area north of the Rappahannock River in Lancaster County. Some evidence exists of a diastem between the Sunken Meadow and the Rushmere (Ward and Blackwelder, 1980). Elsewhere, the Rushmere overlaps a variety of older formations. To the south it covers the upper Miocene Eastover Formation in the Albemarle Embayment; farther south it covers the lower and middle Miocene Pungo River Formation, then Oligocene limestone or the Eocene Castle Hayne Formation where solution and erosion has removed the Oligocene, and then the lower Paleocene Beaufort Formation. Moving along the Norfolk arch westward, the Rushmere overlies Cretaceous deltaic sands (Ward, Bailey, and

[8] *Chesapecten* is a lineage of scallops that flourished in the Chesapeake Bay area from Eastover to Yorktown time (about 8 to 3 million years ago). Different species dominated during different intervals of time: *C. middlesexensis* during deposition of the Miocene Eastover Formation; *C. jeffersonius*, a species distinguished by the number of ribs (9 to 12) and the rounded shell edge, during the Early Pliocene (Lower Yorktown Formation, about 4.5 to 4.3 million years ago); and *C. madisonii* during Late Pliocene time (Upper Yorktown Formation, about 4 to 3 million years ago). Other scallops lived at the same time, but these were the most abundant.

Carter, 1991), then saprolitized granite in Greensville County (Ward and Blackwelder, 1980). All along the western margin of its outcrop belt, the Rushmere directly overlies crystalline rocks. The Rushmere sea was an open-marine, shallow shelf environment conducive to large, diverse populations of marine mollusks (Ward, 2008).

3.2.6.3 Morgarts Beach Member

The Morgarts Beach Member is named for Morgarts Beach, on the south bank of the James River in Isle of Wight County. This unit consists of gray, very fine, sandy to silty clay with a few silty, very fine sand beds. The Morgarts Beach shares the same molluscan assemblage with the underlying Rushmere Member and the overlying Moore House Member, although not as profusely as the sandier Rushmere, and in places exclusively populated by small bivalves such as *Mulina congesta*. However, in the east-central part of the Albemarle Embayment and in downdip areas, the unit can be very shelly. *Turritella alticosta*, the "high-ridged Turritella," is the index fossil for the upper members of the Yorktown Formation.[9]

The Morgarts Beach Member represents the regressive stages following the extensive Pliocene transgression. The Morgarts Beach conformably overlies the Rushmere; they share a similar geographic extent and the two grade into each other in places, elsewhere the contact is marked by a change in lithology (Ward, 2008). South of the Neuse River the Rushmere and Morgarts Beach are indistinguishable and the coeval strata are considered part of the Duplin Formation (Ward, Bailey, and Carter, 1991). In southeastern Virginia, the Morgarts Beach was probably deposited in broad sounds or lagoons behind barrier bars or shoals (Ward, Bailey, and Carter, 1991).

3.2.6.4 Moore House Member

The Moore House Member is named for the bluffs at Moore House on the south bank of the York River in Colonial National Historical Park, York County. This unit consists of orange and tan, sandy shell beds and cross-bedded shell hash, locally cemented into well indurated coquina. Mollusks such as oysters and pectens are abundant, as are planktonic foraminifer and ostracodes. The sands are highly calcareous, glauconitic, and locally phosphatic. Heavy minerals are locally abundant. The Moore House Member, which is geographically confined to the southeastern part of the Virginia Coastal Plain, conformably overlies the Morgarts Beach Member and the two grade into each other in places. The coquina indicates deposition in very shallow water with wave action, similar to the modern beach shell deposits of the West Indies.

3.3 Pliocene/Pleistocene Gravels

On the Coastal Plain west of the Surry Scarp, the Chesapeake Group is unconformably overlain by the Bacon's Castle Formation, a late Pliocene prograding fluvial-deltaic-estuarine deposit. This blanket of sediment consists of well-rounded gravels in a matrix of sand and clay. Seaward (east of the Surry Scarp), the Chesapeake Group is unconformably overlain by several Pleistocene deposits representing reworked material from the Bacons Castle Formation in a fining upward sequence with a basal pebbly sand grading upward into cross-bedded, quartzose sand and massive, clayey silt and silty clay. In inset terraces along the major rivers west of the Surry scarp, fluvial-estuarine deposits are comprised of muddy, coarse, trough cross-bedded sand

[9] This is one of many types of turritellids in the Yorktown and the underlying Eastover Formation. All turritellids have a distinctive corkscrew shape and a high pointed spire resembling turrets on castles. These snails are scavengers and are common in muddy marine environments.

and gravel grading upward to sandy silt and clay. Where these terraces are inset against Chesapeake Group formations, they have re-incorporated phosphate from the eroded material.

Recent drilling in the Chickahominy River terraces in the eastern half of Roxbury Quadrangle at surface elevations slightly above 40 feet showed abundances of heavy minerals and phosphate ranging up to 10 percent in places. An explanation for these occurrences in the pebbly coarse sands of the Shirley Alloformation is that the basal parts of the Calvert Formation were eroded by fluvial action during Shirley sediment deposition (C. R. Berquist, Jr., personal communication). Borings in this area typically show Shirley over 3 to 5 feet of basal Calvert. The Calvert lies above 5 to 8 feet of the Old Church Formation, which overlies the Piney Point Formation.

3.4 Summary of Stratigraphy

In summary, among the pre-Calvert sedimentary formations, phosphate has been found in the Paleocene Brightseat Formation, the Paleocene Aquia Formation, the Paleocene Marlboro Clay, the Eocene Nanjemoy Formation, and the Oligocene/Miocene Old Church Formation. Phosphate has not been reported from the Piney Point or Chickahominy Formations, but might have been overlooked.

The Calvert Formation contains a conspicuous phosphate pebble lag at the base, there is a phosphatic horizon located above the lower contact of the St. Marys Formation, and the lower contact of the Eastover Formation is sharp in most places and contains phosphatic nodules, pebbles, bone, and teeth. The Sunken Meadow Member of the Yorktown contains a phosphatic bone and shark-tooth lag deposit common in middle and upper Miocene beds from Florida to Maryland. This lag deposit marks the lower contact to the west; to the east the basal deposits are finer and dominated by glauconitic and phosphatic sand. The Rushmere Member of the Yorktown contains phosphatic sand and glauconite in amounts up to 10 percent. Coarse sand and pebbles are present near the lower contact. The Moore House Member sands are locally phosphatic.

Pre-Calvert formations were deposited on a shallow marine shelf in an embayment on the Atlantic Coast. Aquia sediments were deposited during a major marine transgression in this basin, which was bordered on the south by the Norfolk Arch and on the west by the Piedmont, with access to the Atlantic to the northeast. During the Paleocene, the Norfolk Arch acted as a barrier between the Salisbury Embayment to the north, and the Albemarle Embayment to the south. The Marlboro Clay was laid down in a brackish-water, estuarine environment. Nanjemoy deposition occurred on a shallow, marine shelf in the Salisbury Embayment. The Piney Point was deposited under normal marine conditions, in a slow clastic sedimentation regime, with quiet conditions and clear warm waters. During Old Church time, the Norfolk Arch was again a high area separating the Salisbury Embayment from the Albemarle Embayment. This barrier probably served to divert the tropical currents that dominated North Carolina during this time. This was a period of widespread climatic changes accompanied by abrupt, short-term, small-scale marine pulses.

The Calvert Formation is the thickest and most widespread of the Miocene sedimentary packages on the Coastal Plain. The Choptank was deposited in an open shelf with an eroded shore facies. The Eastover is a transgressive unit, grading upward from sandy, sheltered beach deposits to shallow water deposits with structural or depositional barriers. The lowest Yorktown Formation was deposited as an initial transgressive unit during the early Pliocene highstand of the sea, and it occurs widely across the Salisbury Embayment and extends southward into the

Albemarle Embayment. During the greatest extent of the Pliocene transgression, the Yorktown sea was an open-marine, shallow shelf environment conducive to large, diverse populations of marine mollusks. In southeastern Virginia, the Yorktown was deposited in broad sounds or lagoons behind barrier bars or shoals. The Yorktown coquina, which is geographically confined to the southeastern part of the Virginia Coastal Plain, was deposited in very shallow water with wave action.

4.0 Depositional Model for Phosphate in Virginia's Coastal Plain

One of the primary goals of this study is to develop a model for characterizing concealed phosphate deposits beneath Virginia's Coastal Plain. Field examinations, together with evidence gathered as part of a comprehensive review of published and unpublished data sources indicate two key criteria:

1) Phosphate occurs in trace amounts in most of the Cenozoic formations on the Atlantic Coastal Plain, and the highest concentrations are hosted in sediments of primarily Neogene age.
2) Higher phosphate concentrations occur primarily at the base of stratigraphic units.

Furthermore, these occurrences point to a two-stage process that involves accumulation of primary phosphate and secondary concentration. These stages are described in detail in the following sections.

4.1 Stage One: Phosphogenesis

In the Neogene marine environment, phosphatic material was likely precipitated from nutrient-rich, oxygen-poor waters as a consequence of dynamic upwelling or a cool countercurrent associated with warm density currents (McKelvey, 1967). It is also possible that primary phosphate was deposited as a result of processes of estuarine circulation and nutrient enrichment as suggested by Redfield et al. (1963), Pevear (1966, 1967), and McKelvey (1967). In this scenario, phosphorus is concentrated near the mouths of large rivers or estuaries where an outflow of surface river water is replaced by an inflow of deeper seawater. Decaying remains of organisms on the outward current fall into the inflowing current, where organic material is concentrated. Such estuaries often contain higher phosphate content than adjacent river or seawater.

Miller (1982) contends that the hypothesis of an estuarine depositional environment is not supported by field evidence. Miller notes that benthonic foraminifera suites from North Carolina suggest a cold water environment, i.e. few species but a large number of individuals, and he states, "The observed fauna could have resulted from a nearshore, southward flowing cool current, similar to the present day Labrador Current, that apparently extended as far south as North Carolina in middle Miocene time." The Gulf Stream established itself in middle-late Miocene time (Manheim and Gulbrandsen, 1979), and such an event would shut down this system.

Whatever the exact environment, it is clear that dispersed primary phosphate was deposited during the marine incursions of the Paleocene, Eocene, and Oligocene, and perhaps in the Miocene and Pliocene as well.

4.2 Stage Two: Reworking and Concentration

As the primary phosphate deposits are weathered and broken down, concentrations are exposed and reworked. The amount of phosphate material concentrated in a lag deposit is controlled by several factors, principally:

- The nature of the underlying bedrock
- The extent/duration of weathering
- Sediment distribution during reincorporation
- Post-depositional weathering

First and foremost, the amount of phosphate within the underlying bedrock coupled with the lithological nature of that bedrock will greatly influence the amount of phosphate concentrated in a lag. Carbonaceous bedrock is more favorable for phosphate lag formation than silicate-rich bedrock. The carbonate can be dissolved and mobilized away, leaving behind phosphate to be reworked into ensuing deposits. Carbonate material is common in the Pamunkey Group: the Aquia Formation has a significant marl component with the Piscataway Member containing indurated limestone, the Nanjemoy Formation contains marls and limestone, and the Piney Point Formation contains limestone and carbonate-cemented sands.

The extent and duration of exposure to weathering is also a significant factor in the formation of a phosphate lag. Longer periods of weathering result in greater concentrations of phosphate.

Sediment distribution during reincorporation is also a critical factor in phosphate concentration. Seafloor currents can winnow away lighter sediments such as fine sand and clay, resulting in reduced sections with concentrations of phosphatic sand, gravel, and fossils. Sediment distribution is largely structurally controlled, and Miller (1982) identified lineaments on the Atlantic Coast that he believed had a significant effect on the distribution, thickness, and lithology of Coastal Plain sediments. These lineaments are thought to represent either flexures in the basement or deep-seated faults that die out upward, and they are expressed as areas of thickening, thinning, or absence of stratigraphic units. Phosphorite is frequently deposited in structural basins on the flanks of domes or anticlines that were rising at time of deposition (Cathcart and Gulbrandsen, 1972).

Additional post-depositional weathering also contributes to the distribution of phosphorus, which can be mobilized by groundwater. Apatite may survive weathering for a while, but it eventually breaks down under prolonged exposure. Some of it may be re-deposited locally.

4.3 Key Stratigraphic Controls

The model presented here, at its simplest, advocates the concept of a *genesis unit*, bounded on top by an unconformity, which is overlain by a *host unit* whose base contains a lag deposit of phosphatic sand and gravel.

In this interpretation, potential genesis units belong to the Pamunkey Group, the Paleocene Brightseat Formation, the Paleocene Aquia Formation, the Paleocene Marlboro Clay, and the Eocene Nanjemoy Formation, as well as the Oligocene/Miocene Old Church Formation. In these units, primary phosphate was originally deposited in an open shelf or estuarine environment. Later, subaerial exposure removed clay and carbonate material but retained the

phosphate, which was incorporated in the base of host units deposited during ensuing marine transgressions.

The host units belong to the Chesapeake Group and are represented by the Calvert Formation and to a lesser degree the St. Marys, Eastover, and Yorktown Formations. These units were laid down during a series of Miocene and Pliocene marine incursions, and may have also acted as genesis units during the intervening lowstands of the sea.

Krumbein (1942) listed phosphate accumulations as one of the criteria for identifying an unconformity. Indeed, these phosphate horizons may be highly informative with regard to transgressions on the Atlantic Coastal Plain, both on the regional and local scale. It may be that major transgressions can be characterized as a series of minor incursions, baby steps.

5.0 Data Collection and Results

5.1 Sampling Strategy

Geologic map data in the project area indicates that the Chesapeake Group units generally dip to the east at about ten feet per mile (Mixon *et al*., 1989; unpublished VDGMR geologic mapping). The economic implication of this eastward dip is that there is an easternmost boundary where overburden thickness precludes the economic viability of phosphate deposits that can be recovered by surface mining methods. For the purposes of this assessment, it was assumed that overburden thickness in excess of 100 feet is not economic to mine. Using this criteria, it was determined that the target zone is a corridor bounded on the west by the Fall Line, where the edge of the Coastal Plain laps up onto the Piedmont, to a parallel line about thirty-five miles to the east, where the Chesapeake Group units are buried at a depth considered too deep to be economical with current extraction technology and market prices.

Within the target zone, two types of samples were acquired for laboratory testing. These included outcrop samples, which were gathered primarily along rivers, and samples from borehole cuttings (Figure 4). In addition, stratigraphic and lithologic data from pre-existing well logs were examined. Using the predictive aspect of our model, the focus was on basal lag deposits.

Reconnaissance mapping, outcrop sampling, and borehole drilling commenced in early June 2010 and field data collection was completed in mid-December 2010. A total of 63 samples were collected, and of these 44 were submitted to the USGS for laboratory geochemical analysis. Each sample consisted of approximately one-half kilogram or more of rock/sediment material sealed in a one-gallon zip-lock bag. Laboratory analyses were performed at the USGS lab located in Lakewood, CO, and included analysis for major oxides by XRF, 55 trace elements by ICP-AES-MS, and total organic carbon by carbon analyzer methods.

5.2 Outcrop Sampling Sites

The Coastal Plain is largely a broad, flat, low-lying accumulation of poorly consolidated sediments making good outcrop very scarce. Outcrops are available, however, along the major river corridors where meanders routinely carve out cut banks and cliffs. Such sites were investigated along the Rappahannock, Mattaponi, and Pamunkey rivers using VDGMR's 14-foot Boston Whaler (Photo 1). At selected sample sites, geologic materials were generally collected as 3-ft to 7-ft vertical channel samples in river cut banks. The coordinates of each sample site were recorded as latitude N and longitude W (NAD 83) using a hand-held Magellan GPS unit. Lithologic descriptions were also recorded, together with notation of any visible phosphate material. At most of the outcrop locations, total gamma activity was measured using a Scintrex

GRS-500 portable differential gamma ray spectrometer/scintillometer. Selected samples were submitted to the USGS and analyzed for phosphate and other major elements, as well as uranium, rare earth elements, and trace elements.

Along the Rappahannock River, Chesapeake Group deposits occur in cliffs from Wilmont Wharf downstream to Fones Cliffs and Pea Ridge. Channel samples were taken from the Calvert Formation below Wilmont Wharf (38.15410N, -77.07146W) and immediately upstream from the mouth of Bristol Mine Run (38.16189N, -77.06779W). Visual inspection revealed little phosphate and these samples were not submitted for analysis.

Along the Mattaponi River, Chesapeake Group deposits are found from Walkerton downstream to Sandy Point opposite Mantapike Creek. Four samples were submitted for analysis from the Eastover Formation at Scotland Landing (37.69033N, -76.96922W; samples R-09211 to R-09214, Photo 2), three from the Eastover near Madison Creek (37.68721N, -76.95132W; samples R-09215 to R-09217), and one from the Calvert just below the Eastover at Rickahock (37.70911N, -76.97583W; sample R-09210). Two samples taken from the millpond spillway in Walkerton (37.72798N, -77.02011W; R-09202, R-09203) were also submitted for analysis.

Along the Pamunkey River, Chesapeake Group deposits are found from the confluence of the North Anna and South Anna rivers downstream to just above White House Railroad Bridge. However, the narrowness of the river and downed trees preclude the use of the Boston Whaler upstream from the mouth of Matadequin Creek. Downstream from there, the Eastover/Calvert contact is exposed as the Calvert dips below sea level. Four samples (3 Eastover, 1 Calvert) were submitted from Elsing Green (37.59426N, -77.04480W; 37.59894N, -77.05153W; R-09195 to R-09198), two Calvert samples were submitted from Putney's Mill (37.60293N, -77.09132W; R-09199, R-09200, Photo 3), and one Calvert sample from Montague Landing (37.61741N, -77.08923W; R-09201).

Two samples were taken from the Calvert/Nanjemoy contact at the Carmel Church quarry (37.90773N, -77.48153W; R-09192, R-09193), located in Caroline County. At this location, phosphate nodules were noted in the thin (<1-ft) basal bone-lag zone of the Calvert Formation (Photo 5).

5.3 Borehole Sampling Sites

The limited amount of exposure on the Coastal Plain necessitates drilling to acquire adequate geological information. Boreholes were completed using VDGMR's diesel-powered, truck-mounted auger rig (Photo 4) capable of drilling to 110 feet below ground surface (bgs). Samples were taken directly from the auger flight as composites of 3- to 5-ft drill intervals. The samples were collected in plastic zip-lock bags.

Initial reconnaissance drilling was conducted near the Potomac and Rappahannock rivers. Boreholes were completed at Moss Neck on the Rappahannock Academy quadrangle in Caroline County (38.21109N, -77.32095W), at Belle Plains on the Passapatanzy quadrangle in Stafford County (38.33221N, -77.35376W), and near New Post on the Guinea quadrangle in Caroline County (38.20982N, -77.40552W). These sites were chosen in hopes of finding the base of the Calvert at a relatively shallow depth. The Moss Neck borehole encountered the Calvert at 11 feet bgs, with the top of the Nanjemoy at 49 feet bgs. A sample (R-09242) was taken from the bottom of the Calvert for laboratory analysis. The Belle Plains borehole penetrated a thin section of the Yorktown(?) Formation before encountering the Nanjemoy Formation and the Marlboro Clay. No laboratory sample was taken. The borehole completed at New Post encountered the

Calvert near the surface extending down to 43 feet bgs to the top of the Marlboro Clay. The hole encountered the Aquia Formation at 55 feet bgs. Phosphate was observed in the interval from 40 to 43 feet bgs. Six samples (R-09236 to R-09241) were taken for laboratory analysis.

Drilling was conducted in the vicinity of the Mattaponi and Pamunkey rivers. Drilling on the Bennett Mining Company's diatomite site west of Walkerton on the King William quadrangle in King and Queen County (37.74109N, -77.04566W) encountered Calvert at 13 feet bgs, extending down to the top of the Nanjemoy at 79 feet bgs. Five samples (R-10327 to R-10331) were sent to the USGS from the 73- to 80-foot depths. At Gravatts Mill Pond (37.76897N, -77.28430W) drilling encountered the Calvert Formation beneath one foot of alluvial cover, extending down to the top of the Nanjemoy at 18 feet bgs. The Calvert showed evidence of phosphate enrichment throughout and seven samples (R-10335 to R-10341) were sent to the USGS laboratory. In Photo 6, wet-sieved fractions from sample R-10339 show the abundance of sand- and gravel-size phosphate nodules, together with bone and shell fragments and fossilized shark teeth in the Calvert Formation.

In New Kent County, samples were taken from six boreholes drilled in the Quinton area, near the Chickahominy River, in conjunction with ongoing geologic mapping activities (R-09165, R-09167, R-09169, R-09170, R-09171, R-09173).

5.4 Results of Laboratory Analysis

A total of 44 samples were submitted to the USGS laboratory for geochemical analysis. Sample IDs and location information are summarized in Table 1. The statistical parameters shown in Table 2 include the calculated mean, standard deviation (SD), minimum and maximum values, and the correlation coefficient (with P_2O_5) for each constituent. The values were calculated using standard functions in Microsoft Excel. For laboratory values that were reported as below the detection limit, values equal to one-half of the detection limit were assigned. The USGS laboratory reports are provided in Appendix A1.

Values for P_2O_5 for 46 samples (44 plus 2 lab duplicates) ranged from 0.04% to 3.96%, with the overall mean value of 1.12% (Table 2). The highest concentration of phosphate was reported in sample R-09165, which was collected in a borehole at a depth of about 45 feet bgs, located near Providence Forge in New Kent County (Figure 5, Chickahominy sites). The sample consisted of silty clay from the lower Yorktown Formation. In a second borehole nearby, sample R-09167 contained 2.73% P_2O_5, also from an interval in the Yorktown Formation.

At Gravatts Mill Pond (Figure 5), samples of the Calvert Formation taken from a borehole show phosphate enrichment averaging 2.68% P_2O_5 over a 5-foot interval between 13 and 18 feet bgs. The contact with the underlying Nanjemoy Formation was encountered at 18 feet bgs, and the phosphate content decreased sharply to 0.37%.

Samples from the Calvert Formation at the upper contact with the Eastover Formation at Rickahock and at the spillway in Walkerton along the Mattaponi showed low levels of phosphate enrichment (<0.5% P_2O_5). Samples of the Calvert Formation taken along the Pamunkey River showed minor to moderate enrichment (0.74% to 1.77% P_2O_5). The borehole at Moss Neck yielded a Calvert sample with appreciable P_2O_5 at 2.65 %, while the nearby New Post samples showed negligible P_2O_5 (0.48 %) in the lower Calvert Formation, and less in the underlying Aquia (0.21 to 0.08 % P_2O_5).

The analytical results support the concept of phosphate enrichment in the basal lag deposits. The basal Calvert sample from the Carmel Church quarry was relatively enriched in P_2O_5 (1.33%) compared to the immediately underlying Nanjemoy (0.23%). In the borehole

completed at the Bennett Mining Company property, the five lower Calvert samples showed concentrations ranging from 1.51% to 2.17% P_2O_5, in sharp contrast to the lower concentration of 0.9% in the underlying Nanjemoy Formation.

For all (21) samples collected from the Calvert Formation, the mean value for P_2O_5 was 1.60%. The mean value for 4 samples collected from the Yorktown Formation was 2.29% P_2O_5. Elsewhere, none of the seven samples taken from the Eastover Formation along the Mattaponi River showed greater than 0.38% P_2O_5, and in general, the Eastover showed very low phosphate content averaging 0.43% P_2O_5 overall. Similarly, samples from the Nanjemoy Formation showed very low phosphate content, also averaging 0.43% P_2O_5.

For all samples, the concentration of P_2O_5 was positively correlated (correlation coefficient >0.50, Table 2) with thallium, uranium, yttrium and zinc. Generally, this reflects the close association of these constituents, excluding zinc, in samples collected from the Calvert Formation, which make up the majority of the total samples collected (21 out of 44). The correlation of uranium and yttrium with higher phosphate content is likely due to isomorphous substitution for calcium, while the correlation with thallium may be explained by the association of phosphate with clay-rich strata in which thallium is enriched by adsorption. Although the small number of samples collected precludes a rigorous statistical analysis, it is interesting to note that the average thorium to uranium ratio (Th:U) calculated from all samples of the phosphate-enriched Calvert Formation (0.81) and for the Yorktown Formation (0.36) are lower than the average Th:U calculated for the phosphate-poor Nanjemoy Formation (1.92) and Eastover Formation (1.60). These ratios may provide further evidence of the relative co-enrichment of uranium with phosphate when compared to other uranium- and thorium-bearing mineral forms in these marine sediments.

The close association of uranium with phosphate must be considered a key guide in the search for significant accumulations of phosphate. Well records containing gamma logs on file with the VDGMR are sparse, but several of those that were examined showed a good correlation between high gamma activity and phosphate reported at the base of the Calvert, particularly in New Kent County (W-4432, W-4443, and W-4495). Gamma logs for the Haynesville core in Richmond County also show a good correlation. The gamma activity readings taken with the VDGMR portable scintillometer during field sampling revealed no identifiable pattern, but this may have been partly as a result of weathering effects in the outcrops visited.

5.5 Structure Map for the Base of the Calvert Formation

Geologic logs contained in the VDGMR water well files were the primary source of information used for building the structure contour map of the base of the Calvert Formation (Figure 6). The quality of the geologic data was uneven and ran the gamut from barely-completed driller's reports to those few well logs with detailed lithological descriptions, geophysics, and repository samples. Geologic logs with higher than average assessments of phosphate are listed below, although it is important to note that these are based upon visual estimates by the driller (or attending geologist) and not upon laboratory results. The following well records were used to construct the three-dimensional computer model:

W-2478. Hanover County, Yellow Tavern quadrangle. The Calvert from 30 to 109 feet has 15% black phosphatic material. Here the Calvert rests directly on granite.

W-1368. Caroline County, Rappahannock Academy quadrangle. Abundant plates and rounded grains of brown and gray phosphorite from 70 to 80 feet; blocky, columnar, platy, and rounded grain and shell fragments of gray and yellowish brown phosphorite, about 15%, from 80 to 100 feet.

W-2791. King William County, West Point quadrangle. There are 10% fine phosphatic fragments throughout the Calvert, from 50 to 210 feet.

W-237. King and Queen County, Truhart quadrangle. Calvert contains 3% phosphate from 60 to 80 feet, 5% black phosphatic material and 3% bone fragments from 80 to 100 feet, 3% from 100 to 120 feet.

W-1635. King William County, West Point quadrangle. In the Yorktown Formation, carbono-phosphatic material from 25 to 39 feet, nodular black phosphorite from 30 to 103 feet.

W-1367. King George County, Port Royal quadrangle. The Calvert contains abundant phosphate (+10%) and shark teeth from 120 to 140 feet, 2-5% from 110 to 120 feet. Phosphate extends down into the Nanjemoy to 260 feet.

W-1851. King George County, King George Courthouse quadrangle. Phosphate occurs throughout the section down to 167 feet.

W-2500. Hanover County, Yellow Tavern quadrangle. The Eastover contains 2-5% phosphate from 40 feet to 110 feet.

W-1860. King George County, Dahlgren quadrangle. Near the base of the Calvert, phosphatic nodules and bone fragments common, but not abundant from 94 to 105 feet.

W-191. New Kent County, Walkers quadrangle. Calvert contains 7% bone fragments, 7% phosphate from 125 to 137 feet, contains 5% phosphatic material from 137 to 142 feet.

W-193. New Kent County, Walkers quadrangle. Calvert contains 7% black phosphatic material from 80 to 85 feet, 3% from 15 to 80 feet, and 5% from 85 to 90 feet.

W-2245. King George County, King George Courthouse quadrangle. Calvert base at 136 feet contains 15% brown and black fragmental phosphorite.

W-2246. King George County, King George Courthouse quadrangle. Base of the Calvert at 136 feet is 15% bone, shell, and pelletal phosphorite.

W-2349. Hanover County, Studley quadrangle. Base of Calvert (at 110 feet) contains 5-10% phosphate.

W-2158. Caroline County, Hanover quadrangle. Angular fragments of bone phosphorite common at base of Calvert, 120 130 feet down.

W-2238. Caroline County, Bowling Green quadrangle. Base of Calvert contains 5% fine-grained gravel, mainly phosphate nodules.

W-2329. New Kent County, Quinton quadrangle. Pelletal and fragmental phosphorite is common in lower Calvert, 50 to 60 feet deep.

W-1842. Hanover County, Seven Pines quadrangle. Nodular phosphorite in the Calvert from 30 to 70 feet; from 70 to 80 feet numerous phosphatic nodules and fragments, pelecypods shell fragments, bone fragments, and teeth. Phosphate continues downward in the Pamunkey group to 150 feet.

W-1851. King George County, King George Courthouse quadrangle. Phosphate through Calvert section from 63 feet to the base at 168 feet.

W-1183. Essex County, Tappahannock quadrangle. Abundant phosphate granules at the base of the Calvert, 210 to 225 feet.

W-1613. Hanover County, Hanover quadrangle. Calvert contains phosphatic material from 10 to 60 feet.

W-1694. Caroline County, Rappahannock Academy quadrangle. Calvert contains scattered grains and fragments of phosphorite from 90 to 140 feet; Pamunkey contains small amount of phosphorite throughout, down to 310 feet.

Well data was compiled in an Excel spreadsheet and imported into ESRI ArcMap where well head elevations were determined using a digital elevation model (DEM). The DEM, in turn, is based upon 2002 orthophotography acquired by the Virginia Base Mapping Program. The wellhead elevations were then used to determine the elevation of the base of the Calvert Formation at each location. This geodatabase was imported into ESRI ArcScene, which was used to construct a three-dimensional surface for the base of the Calvert Formation (Figure 6).

Analysis of the 3-D model indicates a saddle-like structure in the northern part of the study area. A central low area is located beneath the Rappahannock River near Skinners Neck, with a high to the southwest near Liberty, and an opposite corresponding high to the northeast under King George Courthouse. Maximum flexural displacement is estimated to be about 200 feet. This feature may be related to the Skinners Neck Anticline and Port Royal Fault as indentified by Mixon and Powars (1984) and Mixon *et al*. (1988). McFarland and Bruce (2006) mapped two sets of faults that roughly correspond to the margins of this feature. Youssef (1965) postulated that sheltered depressions on the seabed create conditions favorable for accumulation of phosphate material, and Cathcart and Gulbrandsen (1972) noted that phosphorite is frequently found in structural basins on the flanks of blocks that were rising at the time of deposition. If this is the case, this feature would be an excellent target for further exploratory drilling. The sample taken at Moss Neck within this feature was considerably enriched (2.65% P_2O_5) compared to the samples from New Post (maximum 0.48%), just east and outside of this feature.

Cross sectional profiles (Figure 7) show a slight trough on the west side of the depositional basin. This area, although presently untested, may also prove to be a viable drilling target for significant phosphate accumulations.

6.0 Recommendations for Future Work

The results of this study provide the basis for future work in the exploration for phosphate, and for refining our understanding of stratigraphic relationships in Virginia's Coastal Plain. Recommendations for the next phase of investigations include:

1) Continue to populate the GIS database. Additional well data may be available from files maintained by the Virginia Department of Environmental Quality (DEQ) and the USGS.

2) Continue the sampling program. This study was limited to analyses for 44 samples, but additional project samples taken by VDGMR should also be processed, as well as selected VDGMR rock repository samples. Samples continue to be provided from ongoing geologic mapping activities in the Coastal Plain. Targeted drilling along the base of the Calvert Formation near known structures could prove valuable.

3) Further investigate the usefulness of gamma logs in phosphate exploration. Gamma logs were highly effective in locating the Lee Creek deposits in North Carolina, but such logs are extremely scarce in the VDGMR records. Better coverage might be available at DEQ and USGS. A systematic down-hole data collection effort similar to a program conducted in North Carolina could prove valuable.

McFarland and Bruce (2006) report that potassium-containing clays, common to Coastal Plain sediments, produce relatively intense radiation, and intervals containing purer phosphatic sands exhibit among the highest radiation intensities observed. Powars and Bruce (2006) note that the coarse-grained phosphate and glauconite in the shelly, sandy facies at the base of the Calvert are responsible for giving this unit one of the most elevated gamma-log signatures of all the stratigraphic units in the study area.

4) Initiate an investigation of surface water and groundwater geochemistry with particular attention given to anomalies relating to phosphorus, uranium, fluorine, or rare earth elements. Cathcart and Gulbrandsen (1972) stated: "Anomalous amounts of uranium show up in acid streams draining phosphatic terranes, and in the Coastal Plain the presence of uranium in streams may be a clue to the presence of a phosphate deposit." They also estimated that marine phosphorites contain about 3% fluorine and up to 0.1% REE. Brown (1958) suggests that bromide and to a lesser extent iodide may be of value in determining the presence of buried phosphorites.

5) Further attempt to reconstruct paleoenvironments by linking sequence stratigraphy with depositional environments. This would involve a multidisciplinary interpretation of past environments, 4-dimensional mapping (including time), and spatially quantifying measurable variables tied to specific environments such as diatoms and foraminifera.

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8.0 References

Adams, John K., Groot, Johan J., and Hiller, N. William Jr., 1961, Phosphatic pebbles from the Brightseat Formation of Maryland, Journal of Sedimentary Petrology, Vol. 31, no. 4.

Abbott, W.H., and Huddlestun, P.F., 1980, The Miocene of South Carolina; Field trip no. 9, *in* Frey, R.W., and Neathery, T.L., eds., Excursions in southeastern geology; [Field trip nos. 1-3, 5, 7-13]; Volume 1: Geological Society of America Guidebook for Field Trips, [93rd] Annual Meeting, Atlanta, GA, p. 208–210.

Altschuler, Z. S., Clarke, R. S., and Young, E. J., 1958, Geochemistry of uranium in apatite and phosphorite, US Geological Survey Professional Paper 314-D, 45-90.

Altschuler, Z. S., Cathcart, J. B., and Young, E. J., 1964, Geology and geochemistry of the Bone Valley Formation and its phosphate deposits: Geological Society of America Annual Meeting, Miami Beach, 1964, Guidebook field trip 6, 68 p.

Ames, L.L., Jr., 1959, The genesis of carbonate apatites: Economic Geology, v. 54, no. 5, p. 829-840.

Baturin, G. N., 1969, Authigenic Phosphate concretions in recent sediments of the southwest African shelf, Dokl. Akad. Nau, Earth Science Sedimentology, English translation, 189, 227-230.

Baturin, G. N., 1971, Stages of phosphorite formation on the ocean floor, Nature Phys. Sci., 232, 61-62.

Baturin, G. N., 1978, *Fosfority na dna ikeanov* [Phosphorites on the ocean floor] Izdat. Nakua, Moscow, 231 p.

Baturin, G. N., Merkulova, K. I., and Chalov, P. I., 1972, Radiometric evidence for recent formation of phosphatic nodules in marine shelf sediments, Marine Geology, 13, 37-41.

Bennett, R.R., and Collins, G.G., 1952, Brightseat formation, a new name for sediments of Paleocene age in Maryland: Washington Academy of Sciences Journal, v. 42, no. 4, p. 114-116.

Bentor, Y. K., 1980, Phosphorites-the unsolved problems, p. 3-18 *in* Bentor, Y. K., editor, Marine phosphorites-geochemistry, occurrence, genesis: Society of Economic Paleontologists and Mineralogist Special Publication 29, 249 p.

Berquist, C. R. ed., 1990, Heavy-mineral studies — Virginia inner continental shelf; Virginia Division of Mineral Resources Publication 103, 124 p.

Blackwelder, B.W., and Ward, L.W., 1976, Stratigraphy of the Chesapeake Group of Maryland and Virginia: Geological Society of America, Southeastern Section, Guidebook for Field Trips, [25th] Annual Meeting, Arlington, Virginia, 55 p.

Blackwelder, B.W., and Ward, L.W., 1979, Stratigraphic revision of the Pliocene deposits of North and South Carolina: South Carolina Division of Geology, Geologic Notes, v. 23, no. 1, p. 33-43.

Bromley, R. G., 1967, Marine phosphorites as depth indicators, Marine Geology, 5, 5-3-509

Brongersma,-Sanders, Margretha, 1957, Mass mortality in the sea, *in* Hedgepeth, J. W., ed., Treatise on marine ecology and paleoecology, v. 1, Ecology, Geological Society of America Memoir 67, p. 941-1010.

Brown, P.M., 1958, The relation of phosphorites to ground water in Beaufort County, North Carolina: Economic Geology, v. 53, p. 85-101.

Brown, P.M., Miller, J.A., and Swain, F.M., 1972, Structural and stratigraphic framework, and spatial distribution of permeability of the Atlantic Coastal Plain, North Carolina to New York: U.S. Geological Survey Professional Paper 796, 79 p.

Burnett, W. C., and Gomberg, D. N., 1977, Uranium oxidization and probable subaerial weathering of phosphatized limestone from the Pourtales Terrace, Sedimentology, 21, 291-302.

Burnett, William C., 1980, Apatite-glauconite associations off Peru and Chile: paleo-oceanographic implications: Journal of the Geological Society, v. 137, issue 6, p. 757–764.

Bushinski, G.I., 1964, On shallow water origin of phosphorite sediments, *in* van Stratten, L.M.J.U., ed. Deltaic and shallow marine deposits — Proceedings of the Sixth International Sedimentological Congress, The Netherlands and Belgium 1963; Amsterdam, Elsevier Publishing Company, Developments in Sedimentology, vol. 1, p. 62-70.

Bybell, L.M., and Gibson, T.G., 1991, Calcareous nannofossils and foraminifers from Paleocene and Eocene strata in Maryland and Virginia, *in* Gibson, T.G., and Bybell, L.M., leaders, Paleocene-Eocene boundary; sedimentation in the Potomac River Valley, Virginia and Maryland; field trip guidebook: International Geological Correlation Programme Field Trip Guidebook, October 31, 1991, p. 15-19, International Geological Correlation Programme (IGCP) Project No. 308, Paleocene Eocene Boundary.

Campbell, L.D., 1993, Pliocene mollusks from the Yorktown and Chowan River Formations in Virginia: Virginia Division of Mineral Resources Publication, no. 127, 259 p.

Cathcart, J. B., 1963, Economic geology of the Keysville quadrangle, Florida; U.S. Geological Survey Bulletin 1128, 28 p.

Cathcart, J. B., and Gulbrandsen, R. A., 1972, Phosphate deposits, U.S. Geological Survey Professional Paper 820, 515-525.

Cathcart, J.B., and Botinelly, Theodore, 1991, Mineralogy and chemistry of samples from a drill hole in the southern extension of the Land-Pebble phosphate district, Florida: U.S. Geological Survey Bulletin, 1978, 25 p.

Cederstrom, D.J., 1957, Geology and ground-water resources of the York-James Peninsula, Virginia: U.S. Geological Survey Water-Supply Paper, 1361, 237 p.

Cisse, L., and Mrabet T., 2004: World phosphate production: overview and prospects, Phosphorus Research Bulletin Vol. 15, p. 21-25

Clark, W.B., 1895, Contributions to the Eocene fauna of the middle Atlantic slope: Johns Hopkins University Circular v. 15, no. 121, p. 3-6.

Clark, W.B., 1896, The Potomac River section of the middle Atlantic Coast Eocene: American Journal of Science, 4th series, v. 1, no. 5, p. 363-374.

Clark, W.B., and Martin, G.C., 1901, The Eocene deposits of Maryland, *in* Clark, W.B., and others, Eocene: Maryland Geological Survey Systematic Report, 331 p.

Clark, W.B., and Miller, B.L., 1906, Clay deposits of the Virginia coastal plain: Virginia Geological Survey Bulletin no. 2, pt. 1.

Clark, W.B., and Miller, B.L., 1912, The physiography and geology of the Coastal Plain Province of Virginia: Virginia Geological Survey Bulletin no. 4.

Clark, W.B., Miller, B.L., and Stephenson, L.W., 1912, The stratigraphy of the coastal plain of North Carolina; The geological history of the coastal plain of North Carolina, *in* The coastal plain of North Carolina; Part 1, The physiography and geology of the coastal plain of North Carolina: North Carolina Geological and Economic Survey [Report], v. 3, p. 34-44, 291-303., Prepared in cooperation with the U.S. Geological Survey.

Coch, N.K., 1968, Geology of the Benns Church, Smithfield, Windsor, and Chuckatuck quadrangles, Virginia: Virginia Division of Mineral Resources Report of Investigations, no. 17, p. 1-39.

Cook, Peter J., and McElhinny, Michael W., 1979, A reevaluation of the spatial and temporal distribution of sedimentary phosphate deposits in the light of plate tectonics; Economic Geology, vol. 74, pp. 315-330.

Cooke, C.W., 1936, Geology of the coastal plain of South Carolina: U.S. Geological Survey Bulletin, 867, 196 p.

Cooke, C.W., 1952, Sedimentary deposits of Prince Georges County and the District of Columbia, *in* Cooke, C.W., Martin, R.O.R., and Meyer, Gerald, Geology and water resources of Prince Georges County: Maryland Geological Survey Bulletin, no. 10, p. 1-52.

Cooke, C.W., and Mossom, D.S., 1929, Geology of Florida, with geologic map: Florida Geological Survey Annual Report, no.20, pt. 2, p. 29-228, (incl. geologic map, scale 1:1,000,000), Geologic map prepared in cooperation with the U.S. Geological Survey.

Cooke, C.W., and Munyan, A.C., 1938, Stratigraphy of Georgia's Coastal Plain: American Association of Petroleum Geologists Bulletin, v. 22, no. 7.

Cooke, C.W., Gardner, Julia, and Woodring, W.P., 1943, Correlation of the Cenozoic formations of the Atlantic and Gulf Coastal Plains and the Caribbean region: Geological Society of America Bulletin, v. 54, no. 11, p. 1713-1722.

Counts, H. B., and Donsky, Ellis, 1963, Salt-water encroachment geology and ground-water resources of the Savannah area, Georgia and South Carolina, USGS Water-Supply Paper 1611, 101 p.

Cressman, E.R., and Swanson, R.W., 1964, Stratigraphy and petrology of the Permian rocks of southwestern Montana: USGS Professional Paper 313-C, p. 275-569.

Cullen, D. J., 1978, The uranium content of submarine phosphorite and glauconite deposits on Chatham Rise, East of New Zealand, Marine Geology, 28, 67-76.

Cushman, J.A., and Cederstrom, D.J., 1945, An upper Eocene foraminiferal fauna from deep wells in York County, Virginia: Virginia Geological Survey Bulletin, no. 67, p. 2-3.

Dall, W.H., and Harris, G.D., 1892, Correlation papers; Neocene: U.S. Geological Survey Bulletin, 84, 349 p.

Dall, W.H., 1898, A table of North American Tertiary horizons, correlated with one another and with those of western Europe, with annotations, IN Walcott, C.D., Eighteenth annual report of the United States Geological Survey to the Secretary of the Interior, 1896-1897; Part II, Papers chiefly of a theoretical nature: U.S. Geological Survey Annual Report, 18, pt. 2, p. 323-348.

D'Anglejan, B.F., 1967, Origin of marine phosphorites off Baja California, Mexico, Marine Geology, v. 5, no. 1, p. 15-44.

Darby, Dennis A., 1984, Origin and deposition of transgressive coarse sediments marking unconformities in the Tertiary section exposed along the Pamunkey River, Virginia, *in* Ward, L.W., and Krafft, Kathleen, eds., Stratigraphy and paleontology of the outcropping Tertiary beds in the Pamunkey River region: Atlantic Coastal Plain Geological Association Field Trip Guidebook, [19th] Annual Field Conference, October 6-7, 1984, [no. 19], 280 p.

Darton, N.H., 1891, Mesozoic and Cenozoic formations of eastern Virginia and Maryland: Geological Society of America Bulletin, v. 2, p. 431-450.

Darton, N.H., 1911, Economic geology of Richmond, Virginia: U.S. Geological Survey Bulletin, 483, 47 p.

Darton, N.H., 1948, The Marlboro clay [Maryland-Virginia]; discussion and communications: Economic Geology, v. 43, no. 2, p. 154-155.

Deck, Linda T., 1985, The Piney Point Formation along the Pamunkey River, Virginia Coastal Plain; Virginia Minerals, Vol. 31, no. 2.

Denison, R.E., Hetherington, E.A., Bishop, B.A., Dahl, D.A., and Koepnick, R.B., 1993, The use of strontium isotopes in stratigraphic studies; an example from North Carolina: Southeastern Geology, v. 33, no. 2, p. 53-69.

Dowsett, H.J., and Wiggs, L.B., 1992, Planktonic foraminiferal assemblage of the Yorktown Formation, Virginia, USA: Micropaleontology, v. 38, no. 1, p. 75-86.

DMR, 1993, Geologic map of Virginia, scale 1:500,000: Virginia Division of Geology and Mineral Resources, Charlottesville, VA.

DuBar, J.R., 1991, Florida Peninsula, *in* DuBar, J.R., and others, Quaternary geology of the Gulf of Mexico coastal plain, Chapter 19, OF Morrison, R.B., ed., Quaternary nonglacial geology; conterminous United States: Geological Society of America, The Geology of North America, The Decade of North American Geology (DNAG), v. K-2, p. 595-604.

Dryden, A.L., and Overbeck, R.M., 1948, Detailed geology [Charles County, Maryland]: Maryland Geological Survey County Report, p. 29-127.

Florida Institute of Phosphate Research, 2005; http://www1.fipr.state.fl.us/

Folk, R.L., 1959, Practical petrographic classification of limestones: American Association of Petroleum Geologists Bulletin, v. 43, p. 1-38.

Force, E., Gregory, R., Gohn, S., Lucey, M., and Higgins, B., 1978, Uranium and phosphate resources in the Cooper Formation of the Chatham region, South Carolina, US Geological Survey Open-File Report 78-586, 22 p.

Freas, D.H., 1968, Exploration for Florida phosphate deposits, *in* Proceeding of the seminar on sources of mineral raw materials for the fertilizer industry in Asia and the far East: Economic Commission for Asia and the Far East, Bangkok, Thailand, Mineral Resources Development Ser. 32, New York, United Nations, 28 p.

Freas, D.H., and Riggs, S.R., 1968, Environments of phosphorite deposition in the central Florida phosphate district, *in* Forum on geology of industrial minerals: University of Texas-

Austin, Bureau of Economic Geology Proceedings, Austin, Texas, March, 1968, no. 4, p. 117-128.

Friedman, Gerald M., Sanders, John E., and Kopaska-Merkel, David C., 1992, Principles of sedimentary Deposits, Macmillan Publishing Company, New York

Furlow, J. W., 1969, Stratigraphy and economic geology of the eastern Chatham County phosphate deposits; Georgia Geological Survey Bulletin 82, 40 p.

Gernant, R.E., 1970, Paleoecology of the Choptank Formation (Miocene) of Maryland and Virginia: Maryland Geological Survey Report of Investigations, no. 12, 90 p.

Gibson, T.G., 1967, Stratigraphy and paleoenvironment of the phosphatic Miocene strata of North Carolina: Geological Society of America Bulletin v. 78, p. 631–650.

Gibson, T.G., 1980, Depositional framework and paleoenvironment of Miocene strata from North Carolina to Maryland: Miocene Symposium of the southeastern United States, schedule and abstracts, p 11 (abstract).

Gibson, T.G., 1982, Depositional framework and paleoenvironments of Miocene strata from North Carolina to Maryland, *in* Scott, T.M., and Upchurch, S.B., eds., Miocene of the southeastern United States; proceedings of a symposium: Florida Geological Survey Special Publication, Tallahassee, FL, December 4-5, 1980, no. 25, p. 1-22.

Gibson, T.G., 1983a, Key Foraminifera from upper Oligocene to lower Pleistocene strata of the U.S. central Atlantic Coastal Plain, *in* Ray, C.E., ed., Geology and paleontology of the Lee Creek Mine, North Carolina, I: Smithsonian Contributions to Paleobiology, no. 53, p. 355-454.

Gibson, T.G., 1983b, Stratigraphy of Miocene through lower Pleistocene strata of the United States central Atlantic Coastal Plain, *in* Ray, C.E., ed., Geology and paleontology of the Lee Creek Mine, North Carolina, I: Smithsonian Contributions to Paleobiology, no. 53, p. 35-80.

Gibson, T.G., Andrews, G.W., Bybell, L.M., Frederiksen, N.O., Hansen, Thor, Hazel, J.E., McLean, D.M., Witmer, R.J., and Van Nieuwenhuise, D.S., 1980, Biostratigraphy of the Tertiary strata of the core, *in* Geology of the Oak Grove core: Virginia Division of Mineral Resources Publication, no. 20, pt. 2, p. 14-30.

Gildersleeve, B., 1942, Eocene of Virginia: Virginia Geological Survey Bulletin, no. 57, 43 p.

Gilmore, I. K., 2006, Controlling Groundwater at PCS Phosphate-Aurora Mining Operations, [PowerPoint presentation]

Gilmore, I.K, 2007, Forty years of mining at PCS Phosphate mining operations — Aurora, North Carolina, *in* Ward, L.W., ed., Lee Creek Mine, Aurora, North Carolina, history,

mining operations, geology, stratigraphy, and paleontology: Carolina Geological Society annual field trip, Virginia Museum of Natural History Guidebook Number 8.

Glaser, J.D., 1971, Geology and mineral resources of southern Maryland: Maryland Geological Survey Report of Investigations, no. 15, 85 p.

Goldman, Marcus I., 1922, Basal glauconite and phosphate beds, Science, V. 56, Issue 1441, p. 171-173.

Goodman, D.K., 1991, Dinoflagellate biostratigraphy of the Nanjemoy Formation at Popes Creek, southeastern Maryland, *in* Gibson, T.G., and Bybell, L.M., leaders, Paleocene-Eocene boundary; sedimentation in the Potomac River Valley.

Gootenberg, Paul, 1993, Imagining Development: Economic Ideas in Peru's "Fictitious Prosperity" of Guano, 1840-1880, University of California Press, Berkeley.

Gurr, T.M., 2009, Phosphate Rock, *in* Industrial Minerals Review, Mining Engineering, Vol 61, No. 6, p. 63-65.

Hazel, J.E., 1968, Ostracodes from the Brightseat Formation (Danian) of Maryland: Journal of Paleontology, v. 42, no. 1, p. 100-142.

Hoppe, M.K., 2005, Phosphate at the Crossroads, special report for Bay Soundings, http://www.baysoundings.com/sum05/phosphate23.html (accessed February 22, 2011).

Hunter, M.E., 1968, Molluscan guide fossils in late Miocene sediments of southern Florida: Gulf Coast Association of Geological Societies Transactions, v. 18, p. 439-450.

Jasinski, Stephen M., 2000, Marketable phosphate rock — crop year 2000; 2000 Mineral Industry Surveys, U. S. Geological Survey.

Jasinski, Stephen M., 2007a, Phosphate rock; 2006 Minerals Yearbook, U. S. Geological Survey, p 56.1–56.10.

Jasinski, Stephen M., 2007b; Phosphate Rock, U. S. Geological Survey, Mineral Commodity Summaries, January 2007, p 120–121.

Jasinski, Stephen M., 2009; Phosphate Rock, U. S. Geological Survey, Mineral Commodity Summaries, January 2009, p 120–121.

Jasinski, Stephen M., 2010, Marketable phosphate rock — crop year 2009; 2010 Mineral Industry Surveys, U. S. Geological Survey.

Johnson, G.H., and Ramsey, K.W., 1987, Geology and geomorphology of the York-James peninsula, Virginia; 1987 meeting of the Atlantic Coastal Plain Geological Association, College of William and Mary.

Kazakov, A.V., 1937, The phosphorite facies and the genesis of phosphorites: U.S.S.R., Sci. Inst. Fertilizers and Insectofungicides Trans., no 142, p. 95-113.

Kidwell, S.M., 1984, Outcrop features and origin of basin margin unconformities in the lower Chesapeake Group (Miocene), Atlantic Coastal Plain, *in* Schlee, J.S., ed., Interregional unconformities and hydrocarbon accumulations: American Association of Petroleum Geologists Memoir, 36, p. 37-58.

Kimrey, J. O., 1964, The Pungo River Formation, a new name for middle Miocene phosphorites in Beaufort County, North Carolina, Southeastern Geology, v. 5, p. 195-205.

Kimrey, J. O., 1965, Description of the Pungo River Formation in Beaufort County, North Carolina, North Carolina Department of Conservation and Development, Division of Mineral Resources Bulletin no. 79, 131 p.

King, K.C., and Wright, R., 1979, Revision of the Tamp Formation, west central Florida: Transactions, Gulf Coast Association of Geological Societies, v. 29, p 257-262.

Kolodny, Y., 1969, Are marine phosphorites forming today? Nature, 224, 1017-1019.

Kramer, J. R., 1964, Sedimentary phosphate facies [abs.]: Geological Society of America Special Paper 76, p. 95.

Krumbein, W.C., 1942, Criteria for subsurface recognition of unconformities: Bulletin of the American Association of Petroleum geologists, v. 26, no.1.

LeGrand, H.E., and Brown, P.M., 1955, Guidebook of excursions in the coastal plain of North Carolina: Carolina Geological Society Field Trip Guidebook, October 8-9, 1955, 43 p.

Lewis, D. W., Riggs, S. R., Snyder, S. W., and Waters, V. J., 1980, Preliminary report on the Pungo River Formation in Onslow Bay, continental shelf, North Carolina, Miocene Symposium of the southeastern United States, Schedule and Abstracts, p. 10 (abstract).

Loeblich, A.R., Jr., and Tappan, H.N., 1957, Planktonic Foraminifera of Paleocene and early Eocene age from the Gulf and Atlantic Coastal Plains: U.S. National Museum Bulletin, no. 215, p. 173-198.

Malde, Harold E., 1959, Geology of the Charleston phosphate area, South Carolina: U.S. Geological Survey Bulletin 1079.

Manheim, F. T., and Gulbrandsen, R. A., 1979, Marine Phosphorites *in* Burns, Roger G., ed., Reviews in Mineralogy, Mineralogical Society of America.

Mansfield, W. C., 1926, Note on the occurrence of the Choptank Formation in the Nomini Cliffs, Virginia: Journal of the Washington Academy of Sciences, v. 16, no. 7, p. 175-177.

Matson, G.C., 1915, The phosphate deposits of Florida: U. S. Geological Survey Bulletin, 604, 101 p.

Matson, G.C., and Clapp, F.G., 1909, A preliminary report on the geology of Florida with special reference to the stratigraphy: Florida Geological Survey Annual Report, no. 2, p. 13-173.

McCartan, Lucy, 1989, Geologic map of Charles County: Maryland Geological Survey County Geologic Map, 1 sheet, scale 1:62,500

McCartan, Lucy, Weedman, S.D., Wingard, G.L., Edwards, L.E., Sugarman, P.J., Feigenson, M.D., Buursink, M.L., and Libarkin, J.C., 1995, Age and diagenesis of the Upper Floridan aquifer and the intermediate aquifer system in southwestern Florida: U.S. Geological Survey Bulletin, 2122, 26 p.

McConnell, Duncan, 1938, A structural investigation of isomorphism of the apatite group, American Mineralogist, v. 23, no. 1, p. 1-19.

McFarland, E. Randolph, and Bruce, T. Scott, 2006, The Virginia Coastal Plain hydrolgeologic framework: U.S. Geological Survey Professional Paper 1731, 118 p.

McKelvey, V. E., Williams, J. Steele, Sheldon, R. P., Cressman, E. R., Cheney, T. M., and Swanson, R. S., 1959, The Phosphoria, Park City, and Shedhorn formations in the western phosphate field, US Geological Survey Professional Paper 313-A, p. 1-47.

McKelvey, V. E., 1967, Phosphate deposits, U.S. Geological Survey Bulletin 1252-D, pp 21.

Miller, James A., 1980, Structural and sedimentary setting of phosphorite deposits in north Florida and North Carolina: Miocene Symposium of the Southeastern United States, Schedule and Abstracts (abstract).

Miller, James A., 1982; Stratigraphy, structure, and phosphate deposits of the Pungo River Formation of North Carolina: North Carolina Department of Natural Resources and Community Development, Division of Land Resources, Geological Survey Section Bulletin 87, 32 p.

Missimer, T.M., 1993, Pliocene stratigraphy of southern Florida; unresolved issues of facies correlation in time, *in* Zullo, V.A., and others, The Neogene of Florida and adjacent regions; Proceedings of the third Bald Head Island conference on coastal plains geology: Florida Geological Survey Special Publication, Hilton Head Island, SC, November 4-8, 1992, no. 37, p. 33-42.

Mixon, R.B. and Powars, D.S., 1984, Folds and faults in the inner coastal plain of Virginia and Maryland: their effect on distribution and thickness of Tertiary rock units and local geomorphic history; *in* Frederiksen, N.O. and Krafft, Kathleen, eds., Cretaceous and Tertiary stratigraphy, paleontology, and structure, southwestern Maryland and northeastern Virginia; Field trip guidebook, American Association of Stratigraphic Palynologists, Inc.

Mixon, R.B, Powars, D.S., and Daniels, D.L., 1988, Nature and timing of deformation of Upper Mesozoic and Cenozoic deposits in the inner Atlantic Coastal Plain, Virginia and Maryland: U.S. Geological Survey Circular 1059.

Mixon, R.B., Berquist, C.R., Jr., Newell, W.L., Johnson, G.H., Powars, D.S., Schindler, J.S., and Rader, E.K., 1989a, Geologic map and generalized cross sections of the coastal plain and adjacent parts of the Piedmont, Virginia: U.S. Geological Survey Miscellaneous Investigations Series Map, I-2033, 2 sheets, scale 1:250,000

Mixon, R.B., Powars, D.S., Ward, L.W., and Andrews, G.W., 1989b, Lithostratigraphy and molluscan and diatom biostratigraphy of the Haynesville cores; outer coastal plain of Virginia, *in* Mixon, R.B., ed., Geology and paleontology of the Haynesville cores; northeastern Virginia coastal plain: U.S. Geological Survey Professional Paper, 1489-A, 48 p., (incl. geologic maps, scale 1:125,000 and 1:400,000)

Morgan, G.S., 1993, Mammalian biochronology and marine-nonmarine correlations in the Neogene of Florida, *in* Zullo, V.A., and others, The Neogene of Florida and adjacent regions; proceedings of the Third Bald Head Island conference on coastal plains geology: Florida Geological Survey Special Publication, Hilton Head Island, SC, November 4-8, 1992, no. 37, p. 55-66.

Nogan, D.S., 1964, Foraminifera, stratigraphy, and paleoecology of the Aquia Formation of Maryland and Virginia: Cushman Foundation for Foraminiferal Research Special Publication, no. 7, 50 p.

O'Brien, G.W., Milnes, A.R., Veeh, H.H., Heggie, D.T., Riggs, S.R., Cullen, D.J., Marshall, J.F., and Cook, P J., 1990; Sedimentation dynamics and redox iron-cycling: controlling factors for the apatite-glauconite association on the East Australian continental margin, London Geological Society Special Publications; v. 52; p. 61–86.

Otton, E.G., 1955, Ground-water resources of the southern Maryland coastal plain: Maryland Geological Survey Bulletin, no. 15, 347 p.

Parker, G.G., 1951, Geologic and hydrologic factors in the perennial yield of the Biscayne aquifer: American Water Works Association Journal, v. 43, no. 10, p. 817-835.

Petuch, E.J., 1988, Field Guide to the Ecphoras: Charlottesville, Virginia, The Coastal Education and Research Foundation (CERF), 140 p.

Pevear, D.R., 1966, The estuarine formation of the United States Coastal Plain phosphate, Economic Geology v. 61, no. 2, p. 251-255.

Pevear, D.R., 1967, Shallow water phosphorites, Economic Geology v. 62, p. 562-575.

Pickett, T.E., and Spoljaric, N., 1971, Geology of the Middletown-Odessa area, Delaware: Delaware Geological Survey Geologic Map Series, 2, 1 sheet, scale 1:24,000

Pirkle, E.C., Yoho, W.H., and Webb, S.D., 1967, Sediments of the Bone Valley Phosphate District of Florida: Economic Geology, Vol. 62, pp. 237-261.

Popenoe, Peter, 1990, Paleoceanography and paleogeography of the Miocene of the southeastern United States, *in* Burnett, W.C. and Riggs, S.R., Phosphate deposits of the world: New York, Cambridge University Press, p. 352-380.

PotashCorp, http://www.potashcorp.com/about_potashcorp/operations_map/aurora/; accessed September 24, 2009.

Powars, D.S., Mixon, R.B., and Bruce, Scott, 1992, Uppermost Mesozoic and Cenozoic geologic cross section, outer coastal plain of Virginia, *in* Gohn, G.S., ed., Proceedings of the 1988 U.S. Geological Survey workshop on the geology and geohydrology of the Atlantic Coastal Plain: U.S. Geological Survey Circular, 1059, p. 85-101.

Powars, D.S., and Bruce, T.S., 2000, The effects of the Chesapeake Bay impact crater on the geological framework and correlation of hydrogeologic units of the lower York-James peninsula, Virginia: U.S. Geological Survey Professional /Paper 1612.

Puri, H.S., and Vernon R.O., 1964, Summary of the geology of Florida and a guidebook to classic exposures: Florida Geological Survey Special Publication 5, 312 p.

Rader, E.K., and Evans, N.H., 1993, Geologic map of Virginia; expanded explanation: Virginia Division of Mineral Resources, 80 p.

Redfield, A. C., Ketchum, B., H., and Richards, F. A, 1963, The influence of organisms on the composition of sea-water, *in* M. N. Hill, ed., The Sea v. 2, New York, Interscience.

Reed, J.C., Jr., and Obermeier, S.F., 1982, The geology beneath Washington, D.C.; the foundations of a nation's capitol, *in* Legget, R.F., ed., Geology under cities: Reviews in Engineering Geology, v. 5, p. 1-24.

Reinhardt, Juergen, Newell, W.L., and Mixon, R.B., 1980, Tertiary lithostratigraphy of the core, *in* Geology of the Oak Grove core: Virginia Division of Mineral Resources Publication, no. 20, pt. 1, p. 1-13.

Riggs, S. R., 1979a, Petrology of the Tertiary Phosphorite System of Florida, Economic Geology, v. 74, no. 2, p. 195-220.

Riggs, S.R., 1979b, Phosphorite sedimentation in Florida; a model phosphogenic system: Economic Geology, v. 74, no. 2, p. 285-314.

Riggs, S. R., 1984, Paleo-oceanographic model of Neogene phosphoritic deposition. US Atlantic continental margin, Science, Feb 13, 1984, v. 223, no 4632.

Riggs, S.R., and Freas, D.H., 1965, Stratigraphy and sedimentation of phosphorite in the central Florida phosphate district: New York, N.Y., Society of Mining Engineers of AIME, Paper No. 65H84, preprint.

Riggs, S.R., Snyder, S.W.P., Hine, A.C., Snyder, S.W., Ellington, M.D., and Mallette, P.M., 1985, Geologic framework of phosphate resources in Onslow Bay, North Carolina continental shelf: Economic Geology, v. 80, p. 716–738.

Roberson, C. E., 1966, Solubility implications of apatite in sea water, in Geological Survey research 1966: USGS Professional Paper 550-D, p. 178-185.

Rosemarin, Arno, de Bruijne, Gert, and Caldwell, Ian, 2009, The next inconvenient truth: peak phosphorus; The Broker, Issue 15, August 2009, p 6–9.

Ross, C. S., 1941, Occurrence and origin of the titanium deposits of Nelson and Amherst Counties, Virginia: US Geological Survey Professional Paper 198, 59 p.

Sanford, Samuel, 1913, The underground-water resources of the Coastal Plain province of Virginia, Virginia Geol. Survey Bulletin no. 5, 361 p., 1913

Scarborough, A.K., and Riggs, S.R., 1980, Stratigraphy and petrology of the Pungo River Formation, central Coastal Plain, North Carolina: Miocene Symposium of the Southeastern United States, Schedule and Abstracts, addenda (abstract).

Scott, T.M., 1985, The geology of the Florida Peninsula and its relationship to economic phosphate deposits, *in* Snyder, S.W., ed., International Geological Correlation Project No. 156, Phosphorites; Guidebook of the eighth international field workshop and symposium (southeastern United States): International Geological Correlation Programme Field Trip Guidebook, May, 1985, p. 97-113., International Geological Correlation Programme (IGCP) Project No. 156, Phosphorites.

Scott, T.M., 1988, The lithostratigraphy of the Hawthorn Group (Miocene) of Florida: Florida Geological Survey Bulletin, no. 59, 148 p.

Shattuck, G.B., 1902, The Miocene problem of Maryland [abs.]: Science, new series, v. 15, p. 906.

Shattuck, G.B., 1904, Geological and paleontological relations, with a review of earlier investigations; the Miocene deposits of Maryland, *in* Clark, W.B., and others, Miocene: Maryland Geological Survey Systematic Report, p. xxxiii-cxxxvii.

Sheldon, R.P., 1957, Physical stratigraphy of the Phosphoria formation in northwestern Wyoming: USGS Bulletin 1042-E, p. 105-185.

Sheldon, R.P., 1964, Exploration for phosphorite in Turkey— a case history: Economic Geology, v. 59, p. 1159-1175.

Sheldon, R. P., 1980, Episodicity of phosphate deposition and deep ocean circulation-a hypothesis, p. 239-247 *in* Bentor, Y. K., editor, Marine phosphorites-geochemistry, occurrence, genesis: Society of Economic Paleontologists and Mineralogist Special Publication 29, 249 p.

Siple, G.E., 1960, Some geologic and hydrologic factors affecting limestone terranes of Tertiary age in South Carolina: Southeastern Geology, v. 2, no. 1, p. 1-11.

Smith, R.W., and Whitlatch, G.I., 1940, The phosphate resources of Tennessee, Tennessee Division of Geology Bulletin 48, 444 p.

Snyder, S.W., Riggs, S.R., Katrosh, M.R., Lewis, D.W., and Scarborough, A.K., 1980, Synthesis of phosphatic sediment-faunal relationships within the Pungo River Formation: paleoenvironmental implications: Miocene Symposium of the Southeastern United States, Schedule and Abstracts (abstract).

Snyder, S.W., and Riggs, S.R., 1993, Geological overview of Lee Creek Mine and vicinity, North Carolina coastal plain: The Compass, Sigma Gamma Epsilon Journal of Earth Sciences, v. 70, no.1, p. 13-35.

Stephenson, L.W., and MacNeil, F.S., 1954, Extension of Yorktown formation (Miocene) of Virginia into Maryland: Geological Society of America Bulletin, v. 65, no. 8, p. 733-738.

Stuckey, Jasper L., 1970, Mineral Industry of North Carolina from 1960 through 1967: North Carolina Department of Conservation and Development Economic Paper 68, Raleigh.

Sverdrup, H.U, Johnson, M.W., and Fleming, R.H., 1942, The Oceans: New York, Prentice-Hall, 1087 p.

Virginia Division of Mineral Resources, 1962, Guidebook to the Coastal Plain of Virginia above the James River, information Circular # 6, Charlottesville, Virginia.

Ward, L.W., 1984a, Stratigraphy and molluscan assemblages of the Pamunkey and Chesapeake Groups, upper Potomac River, *in* Frederiksen, N.O. and Krafft, Kathleen, eds., Cretaceous and Tertiary stratigraphy, paleontology, and structure, southwestern Maryland and northeastern Virginia; Field trip guidebook, American Association of Stratigraphic Palynologists, Inc.

Ward, L.W., 1984b, Stratigraphy of outcropping Tertiary beds along the Pamunkey River, central Virginia coastal plain, *in* Ward, L.W., and Krafft, Kathleen, eds., Stratigraphy and paleontology of the outcropping Tertiary beds in the Pamunkey River region: Atlantic Coastal Plain Geological Association Field Trip Guidebook, [19th] Annual Field Conference, October 6-7, 1984, [no. 19], 280 p.

Ward, L.W., 1985, Stratigraphy and characteristic mollusks of the Pamunkey Group (lower Tertiary) and the Old Church Formation of the Chesapeake Group; Virginia coastal plain: U.S. Geological Survey Professional Paper, 1346, 78 p.

Ward, L.W., 1992, Molluscan biostratigraphy of the Miocene, middle Atlantic Coastal Plain of North America: Virginia Museum of Natural History Memoir, no. 2, 145 p.

Ward, L.W, 2007, editor, Lee Creek Mine, Aurora, North Carolina, history, mining operations, geology, stratigraphy, and paleontology: Carolina Geological Society annual field trip, Virginia Museum of Natural History Guidebook Number 8.

Ward, L.W., 2008a, Stratigraphy of the Calvert, Choptank, and St. Marys Formations (Miocene) in the Chesapeake Bay area, Maryland and Virginia: Virginia Museum of Natural History Memoir, no. 9, 169 p.

Ward, L.W., 2008b, Geology and paleontology of the James River; Richmond to Hampton Roads: Virginia Museum of Natural History Guidebook no. 7, 75 p.

Ward, L.W., Lawrence, D.R., and Blackwelder, B.W., 1978, Stratigraphic revision of middle Eocene, Oligocene and lower Miocene, Atlantic Coastal Plain of North Carolina, *in* Contributions to Stratigraphy, U.S. Geological Survey Bulletin 1457-F, 23 p.

Ward, L.W., and Blackwelder, B.W., 1980, Stratigraphic revision of upper Miocene and lower Pliocene beds of the Chesapeake Group, middle Atlantic Coastal Plain, *in* Contributions to Stratigraphy, U.S. Geological Survey Bulletin 1482-D 61 p.

Ward, L. W., and Krafft, Kathleen, editors, 1984, Stratigraphy and Paleontology of the outcropping Tertiary Beds in the Pamunkey River Region, central Virginia Coastal Plain, Guidebook for the 1984 field trip Atlantic Coastal Plain Geological Association.

Ward, L.W., and Powars, D.S., 1991, Tertiary lithology and paleontology, Chesapeake Bay region, *in* Schultz, Art, and Compton-Gooding, Ellen, eds., Geologic evolution of the eastern United States; Field trip guidebook NE-SE GSA 1991: Virginia Museum of Natural History Guidebook, Joint meeting of Geological Society of America, Northeastern Section and Southeastern Section, no. 2, p. 161-193.

Ward, L.W., Bailey, R.H., and Carter, J.G., 1991, Pliocene and early Pleistocene stratigraphy, depositional history, and molluscan paleobiogeography of the coastal plain, *in*

Horton, J.W., Jr., and Zullo, V.A., eds., The geology of the Carolinas: Carolina Geological Society, 50th Anniversary Volume, p. 274-289.

Wehmiller, J.F., Belknap, D.F., Boutin, B.S., Mirecki, J.E., Rahamin, S.D., and York, L.L., 1988, A review of the aminostratigraphy of Quaternary mollusks from United States Atlantic Coastal Plain sites, *in* Esterbrook, D.J., ed., Dating Quaternary sediments: Geological Society of America Special Paper, 227, p. 69-110.

Wilson, W. E., 1977, Ground water resources of DeSoto and Hardee Counties, Florida: Florida Bureau of geology, Report of Investigation 83, 102 p.

Youssef, Mourad I., 1965, Genesis of bedded phosphates; Economic Geology, v 60, no. 3 p. 590–600.