

Michael S. Indorf. URANIUM-PHOSPHORUS DETERMINATIONS FOR SELECTED PHOSPHATE GRAINS FROM THE MIOCENE PUNGO RIVER FORMATION, NORTH CAROLINA. (Under the direction of Dr. Stanley R. Riggs) Department of Geology, April 1982.

The Aurora Phosphate District is located in the Central Coastal Plain of North Carolina. Phosphate production in the area is derived from the mining of the phosphorite sediments of the Pungo River Formation. This thesis evaluates the relationship between uranium content and phosphorus content within the central facies phosphorite of the Formation in terms of regional location, stratigraphic position, grain size, and grain type.

A total of 154 subsamples representing five core hole locations were examined for this study. They were obtained from 19 sediment samples representing units A, B, C, and D/DD of the Pungo River Formation and 3 sediment samples representing the Yorktown Formation. Subsamples consisted of phosphate grains selected from the 0 ϕ , 2 ϕ , and 4 ϕ size ranges. Grains in the 0 ϕ and 2 ϕ size ranges were further separated into intraclast, skeletal fragment, pellet, and disc grain type groups.

Uranium and phosphorus contents have been determined by fluorometric and spectrophotometric methods, respectively. Uranium contents ranged from 5.1 to 285.9 ppm U.

QE
390.2
U7
I5x

Phosphorus contents ranged from 23.25 to 38.22 % P_2O_5 . The combined mean uranium content was calculated to be 92.5 ± 27.4 ppm U. The combined mean phosphorus content was calculated to be $30.64 \pm 0.84\%$ P_2O_5 .

There are no significant trends in the regional distribution of uranium and phosphorus in the study area. Phosphate grains from unit D/DD may be slightly depleted in uranium and phosphorus relative to underlying and overlying units. There is an apparent inverse relationship between grain size and mean uranium content. The mean uranium content was 71.6 ppm U for 0 ϕ size phosphate grains; 82.3 ppm U for 2 ϕ size phosphate grains; and 123.5 ppm U for 4 ϕ size phosphate grains. The mean phosphorus and uranium contents of skeletal grains were slightly higher than those of the intraclast, pellet, and disc grains.

The apparent differences which have been identified among the data as grouped by core hole, unit, grain size, and grain type are very slight. The differences exist within an overall context of extreme variance. Statistical comparisons show that the mean values for the particular subgroups are essentially the same.

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FOR SELECTED PHOSPHATE GRAINS
FROM THE MIOCENE PUNGO RIVER FORMATION,
NORTH CAROLINA

A Thesis
Presented to
the Faculty of the Department of Geology
East Carolina University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Geology

by
Michael S. Indorf

April 1982

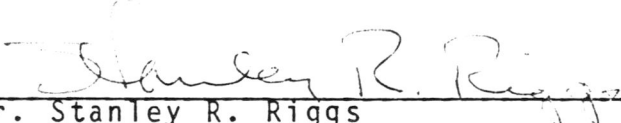
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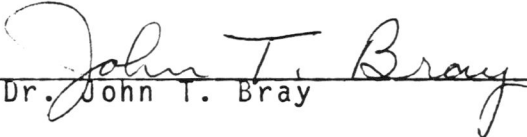
Michael S. Indorf

APPROVED BY:

Committee



Dr. Stanley R. Riggs



Dr. John T. Bray

Dr. Richard L. Mauger


Dr. Richard K. Spruill

CHAIRMAN OF THE DEPARTMENT OF GEOLOGY



Dr. Charles Q. Brown

DEAN OF THE GRADUATE SCHOOL



Dr. Joseph G. Boyette

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INTRODUCTION

GLOBAL SIGNIFICANCE OF PHOSPHATE

The current world population explosion is demanding tremendously increased food supplies. More than ever before, there is an urgent need for greater agricultural production on a global scale. Therefore, concern has focused on the need for phosphorus. Phosphorus is one of the three basic plant nutrients found in the chemical fertilizers used to enhance quality and quantity in agricultural production. U.S. General Accounting Office reports (GAO, 1979) indicate that agriculture consumes roughly 90% of the 120 million metric tons of annual world phosphate production. A large proportion of this phosphate product is derived from the strip mining and processing of marine sedimentary phosphate.

The United States accounts for 41% (GAO, 1979) of worldwide phosphate production. The major producing districts of the Southeast Atlantic Coastal Plain include Florida and North Carolina (Figure 1) which contribute 86% of domestic phosphate, and therefore an impressive 35% of total global production of phosphate (GAO, 1979). Table 1 summarizes current estimates of the phosphate resource base for the southeastern United States. Considering the importance of these Coastal Plain deposits, and the fact that

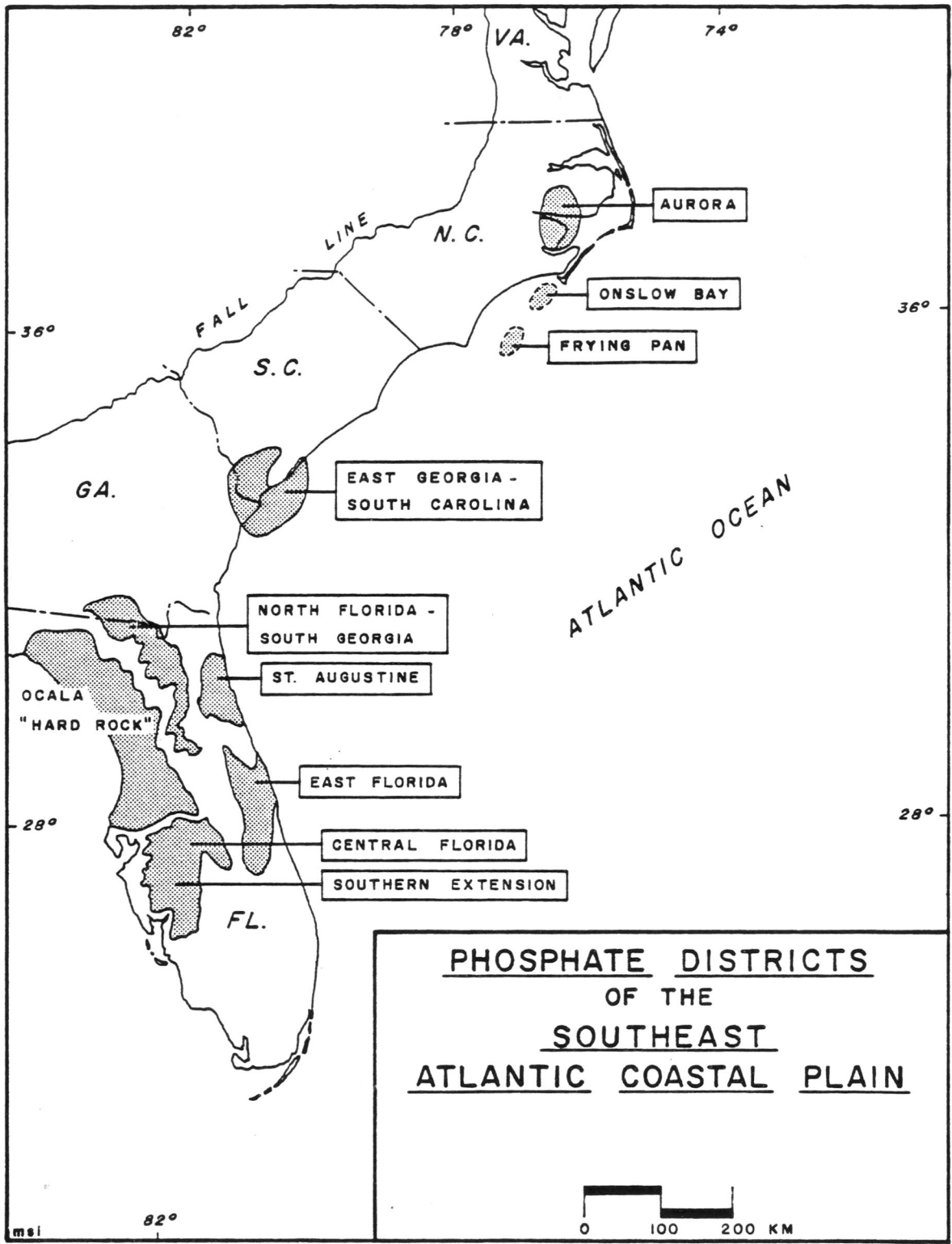


Figure 1. Phosphate districts of the Southeast Atlantic Coastal Plain (adapted from Riggs, 1979a)

Characteristic	Phosphate District							
	Central Florida	Southern Extension of Central Florida	North Florida-South Georgia	East Florida	Ocala "Hard Rock"	East Georgia-South Carolina	Aurora (North Carolina)	Central Tennessee
Geologic Type								
1	m	m	m	m	m, k	m	m	r, k
Average Overburden Thickness	20-30'	20-30'	30-40'	70-100'	20-90'	20-90'	80-110'	10-20'
Average Phosphorite Thickness	15-25'	20-30'	15-30'	30-45'	5-15'	15-35'	35-60'	5-20'
Average P ₂ O ₅ Content of Phosphorite	15-18%	10-15%	8-10%	8-16%	20-23%	4-15%	8-18%	16-20%
Average U Content of Phosphorite	65 ppm	36 ppm	55-82 ppm	47-57 ppm	50-55 ppm	30-60 ppm	20-40 ppm	20 ppm
Total Phosphate Resource (millions of tons)	9,760	25,854	19,110	25,590	114	18,179	71,761	158
Estimated Recoverable Phosphate Product (millions of tons)	1,129	3,050	1,764	2,662	9	1,787	9,429	60
Estimated Recoverable Uranium (tons)	124,000	336,000	123,000	272,000	500	142,000	566,000	1,200

1 m = marine phosphorite, with marine and fluvial reworking in some cases
r = weathered residual material
k = karst-filling aspect

Table 1. Summary of general characteristics of uraniferous phosphate resources, Southeastern United States (Based on an assumed mineable grade of 4.0 percent P₂O₅ and thickness of 5 feet; Fountain and Hayes, 1979.)

they represent a depleting resource, it is not surprising that they are the subject of intense governmental interest, industrial exploitation, and academic research.

OBJECTIVE OF THIS THESIS

The intent of this study is to add to the present understanding of the detailed geochemical relationships between uranium, phosphorus and the phosphate sediments within the economically important Aurora Phosphate District in the Central Coastal Plain of North Carolina. Specifically, the objective of this thesis is to evaluate the relationship between uranium content and phosphorus content within the central facies phosphorite of the Pungo River Formation (Figure 2). The evaluation of this relationship will include the consideration of the following controls:

1. regional location;
2. stratigraphic position;
3. grain size; and
4. grain type.

Placing this study in its proper context requires a brief review of the geologic nature of 1) uranium in phosphate deposits; 2) uranium in the phosphate mineral; and 3) the Pungo River phosphorite of North Carolina.

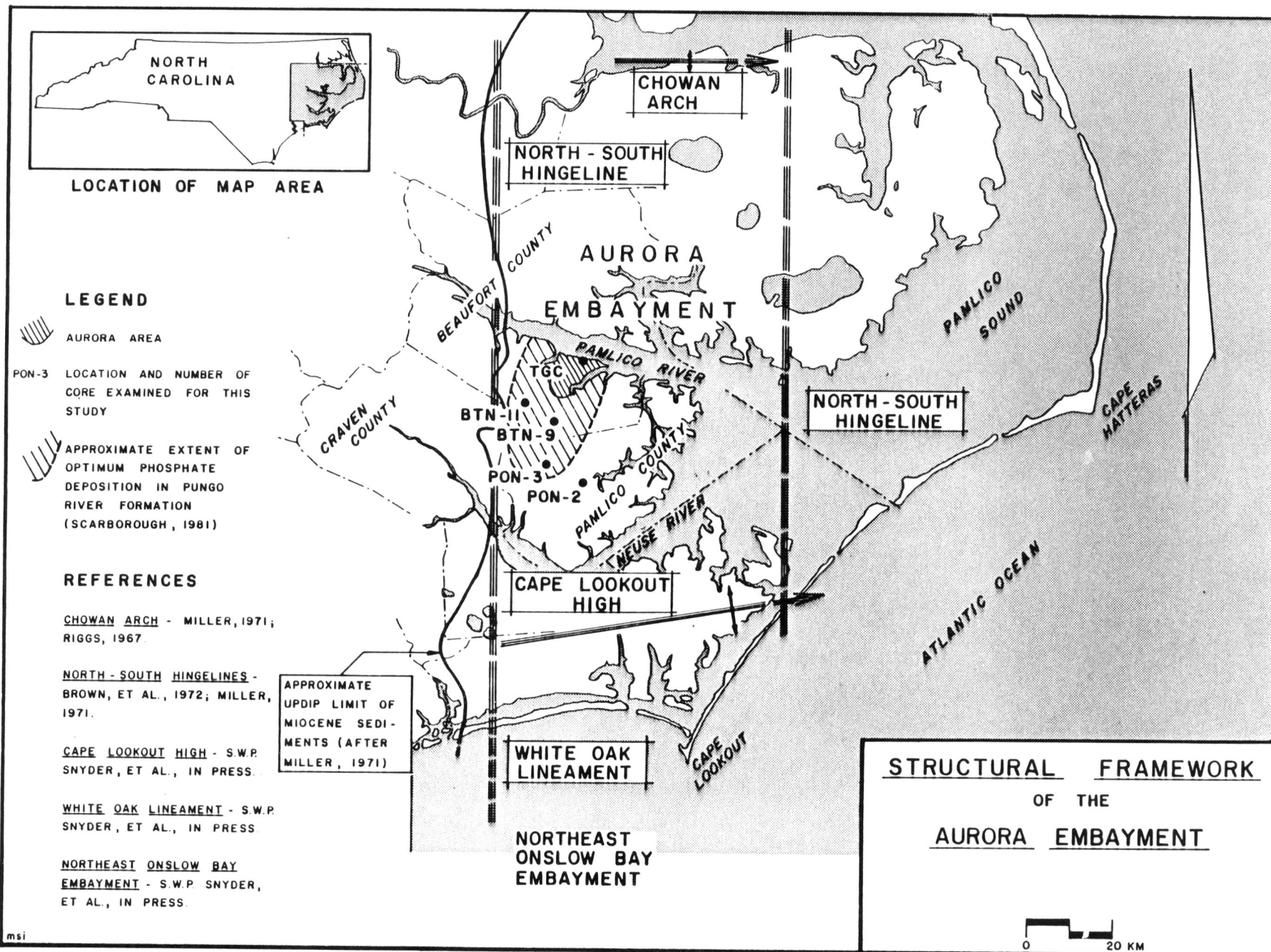


Figure 2. Structural framework of the Aurora Embayment (adapted from Scarborough, 1981)

PREVIOUS WORK

URANIUM IN PHOSPHATE DEPOSITS

a. Sedimentary Marine Phosphorite Nomenclature

Reports on phosphate deposits often present nomenclature which is not consistent from one author to the next. The terminology used by Riggs (1979a) to describe material containing phosphate as a mineralogic component has been adopted for this report:

Phosphorite - a rock term applied to all sediments or rocks containing at least 10 percent (volumetrically) individual phosphate grains;

Phosphatic - a rock term applied to all sediments or rocks containing at least 1 percent but less than 10 percent (volumetrically) individual phosphate grains; and

Phosphate - a general term applied to a class of chemical compounds, a group of minerals, a type of mineral deposit or a type of sedimentary grain or particle.

b. Uranium as a Phosphorite Component

Cathcart (1978) stated that marine phosphorites worldwide normally contain 50 to 300 ppm U. He has tabulated uranium contents along with phosphate reserve and

production volumes, for the major producing countries. Altschuler (1980) has tabulated the regional or formational average trace element abundances for rich phosphorites from around the world. He cited an average concentration of 120 ppm U in phosphorite, based on the analysis of seven phosphorites. The overall range of 30-260 ppm U reported by Altschuler compares favorably with that of Cathcart noted above. A more extensive review of the free world's uraniumiferous phosphate resources is found in DeVoto and Stevens (1979). Slansky (1977) has compiled the published data on the U and P_2O_5 contents of prominent phosphate deposits in the African and Asian areas; his findings are condensed in Tables 2-4.

There are several important observations concerning these data.

1. Syrian phosphorite does not indicate a consistent relationship between high U content and high P_2O_5 content (Table 2).
2. Israeli phosphorite does indicate a variation in samples from two different areas (Table 2).
3. Moroccan phosphorite does indicate that U content varies with the age of the unit. Also U content is independent of P_2O_5 content (Table 2).

Source	Number of Samples	Uranium (in ppm)			(P ₂ O ₅ (in %))		ppm U:%P ₂ O ₅
		Average Conc.	Range: Min-Max	Misc. Values	Average Conc.	Range Min-Max	
Egypt (upper Cret.)	---	---	30-100	---	---	---	---
Red Sea	---	---	98-190	---	---	---	---
Upper Nile	---	---	---	82, 97, 68, 150, 130	---	---	---
Jordan (upper Cret.)	26	---	14-156	---	---	5.0-34.3	3 ⁺
Syria (upper Cret.)	---	---	---	130, 60	35.0 35.0	---	3.7 1.7
Israel: Zefa : Saraf	254	---	115-126 67-132	---	---	20-36 21.2-29.4	6.0 3.5
Tunisia			50-75		---	27-32	---
Morocco							
1. Ypresien		130			highest		
2. Thanetien		160					
3. Maestrichtien		190					
4. Maestrichtien		250			lowest		

Table 2. Uranium and P₂O₅ concentrations of phosphorites from Africa and Middle East (compiled from Slansky, 1977)

Sample Type	Average Values			Number of Specimens
	% P ₂ O ₅	ppm U	Ratio ppm U:%P ₂ O ₅	
Phosphate/Diatom Mud	8.32	5	0.5	3
Concretions				
- soft	25.20	14	0.6	3
- compact	29.37	35	1.4	6
- hard	33.09	53	1.6	5
Coprolites				
- soft	25.85	28	1.0	2
- compact	31.64	68	2.2	1
- hard	32.06	77	2.4	1

Table 3. P₂O₅ and U concentrations for samples taken from sea floor phosphate accumulations off the western margin of South Africa (from Slansky, 1977)

Source	Number of Samples	Uranium (in ppm)			P2O5 (in %)		Ratio ppm U/%P ₂ O ₅
		Average Conc.	Range: Min-Max	Misc. Values	Average Conc.	Range: Min-Max	
Eocene-Bakouma (central Africa)	15		1660-5600		20.37	8.75-32.58	155.7 (81.7-392.9)
Jurassic-Mussouri (India)	24	408	25-831		15.34	9.19-23.62	29.0 (2.2 - 50.5)
Paleozoic (Siberia)			100-4000			1-24	
Eocene Lacustrine deposits (Wyoming-Utah)				1200			
Phosphatic Limestone (north England)				700			

Table 4. Miscellaneous occurrences of high U contents in phosphate deposits (compiled from Slansky, 1977)

4. Sea floor samples from the western margin of South Africa do indicate an increase in U content with progressive lithification (Table 3).
5. Samples from certain phosphorites do indicate extremely high and variable concentrations of U (Table 4).

Data such as those presented by Slansky (1977), Cathcart (1978), and DeVoto and Stevens (1979) must be evaluated with caution and a number of assumptions made if the data are to be used in making comparisons. For example, the authors seldom indicate the following information:

1. The type of the sample analyzed (e.g. concentrated mine products vs. total sediment; weathered vs. unweathered).
2. The amount or size of sample analyzed.
3. The number of samples analyzed (if reported, the number is often low).
4. The method and reliability of the analysis.
5. The relationships between analytical values and basic geological parameters such as the petrology, associated lithologies, or the structural-stratigraphic framework (if reported, the degree of control for these parameters is poor).

For the most part, the data published to date is intended to show economic potential, with grand tonnage estimates given for U and P_2O_5 production based upon assumed values of concentration. Such broad generalizations can be misinterpreted, due to the factors mentioned, when applied at a more detailed or specific level.

c. U/P₂O₅ Relationships

It is generally accepted that uranium is associated with the apatite component of phosphate deposits. The relationship between uranium and apatite is usually reported as a linear correlation value for U vs. P_2O_5 or as a ratio of U/P₂O₅. However, the analysis of U/P₂O₅ ratios demonstrates conflicting trends. Altschuler et al. (1958) analyzed 18 samples from various beds and locations within the Moroccan Oulad-Abdoun phosphorites. They noted an overall positive U vs. P_2O_5 correlation, in spite of a marked scatter (100 to 160 ppm U) among the higher grade (20 to 25% P_2O_5) samples. Slansky (1977) referred to a study of Jordanian phosphorite in which U/P₂O₅ ratios were found to stay between 2 and 3 when the uranium concentration was less than 50 ppm. U/P₂O₅ ratios appeared to vary randomly, from 3.6 to 12, when uranium concentrations were greater than 50 ppm. In contrast, an analysis of 123 phosphate samples from 5 locations within the Phosphoria

Formation of Idaho (Thompson, 1953, 1954) indicated that when the uranium content was higher (average U = 310 ppm for 12 samples), the U vs. P_2O_5 correlation was the strongest (+0.9). Altschuler et al. (1958) postulated that this strong correlation could be associated with a relative lack of post-depositional change. McKelvey and Carswell (1956) also showed that on a regional scale, uranium concentrations were highest in the portions of the Phosphoria Formation having the richest and thickest phosphorite accumulation. Samples from the Bone Valley Formation of Florida (Cathcart, 1956) exhibited an increase in uranium content with a corresponding increase from 10 to 20% P_2O_5 .

Cathcart (1956) has also linked grain size to U/ P_2O_5 ratios. He reported a -0.64 correlation coefficient for U vs. P_2O_5 in samples of +150 mesh "pellets and pebbles" from the Bone Valley Formation. However, testing of the Moroccan Khouribga pelletal phosphorites (Altschuler et al., 1958) indicated the same basic uranium content in all grain sizes. Likewise, Thompson (1953, 1954) concluded that, in her analysis of samples from the Phosphoria Formation, there was "little reason for believing that pellet size has an influence upon, or reflects [the uranium concentration]..."

Further observational notes pertaining to the phosphate deposits of the southeast Atlantic Coastal Plain

have been made by various authors. McKelvey (1956) stated that U content increased with P_2O_5 content in Florida pellets. Concentrations above 100 ppm U were associated with P_2O_5 contents above 30%.

Cathcart (1956) explained an inverse relationship between grain size and U content in the Central Florida Phosphate District as proof of the syngenetic marine origin (rather than groundwater percolation emplacement) of the uranium in the Miocene Hawthorn Formation. Marine reworking caused U enrichment of the Pliocene Bone Valley Formation of the same district.

Olson (1966) noted that in South Georgia the white phosphate pebbles had the highest P_2O_5 content (34.1%) and U content (90 ppm). The black phosphate pebbles had the lowest P_2O_5 content (26.0%) and U content (60 ppm).

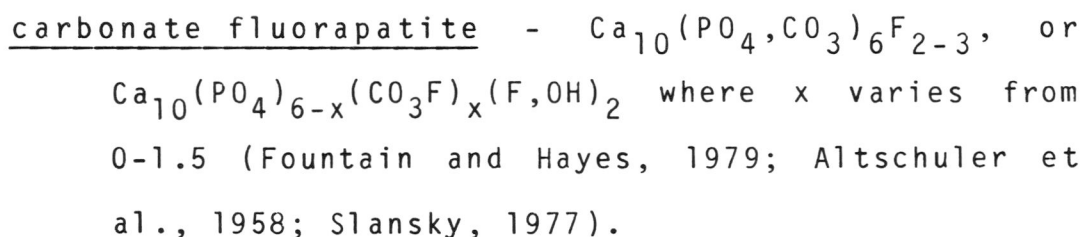
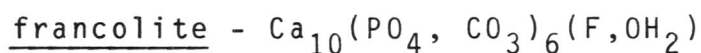
Cathcart (1978) reported 1) an overall range of 30 to 300 ppm U for Central Florida Bone Valley phosphates; 2) an average of 110 ppm U for the high P_2O_5 sand size pellets; 3) an average of 150 ppm U for the low P_2O_5 pebbles; and 4) an overall range of 40 to 110 ppm U (average 60 ppm) for the North Florida-South Georgia District.

Altschuler (1980) cited a concentration of 140 ppm U for chemically analyzed pebbly and pelletal phosphorites in the Bone Valley Formation. He specified that the reported value was based on the average of "eight composites: four

pebble and four pellet concentrates composited from one week's production at each of four mining localities in [the] Land Pebble Field, representative of approximately 100,000 tons, P_2O_5 :20-35%" (Altschuler, 1980).

URANIUM IN THE PHOSPHATE MINERAL

The minerals which make up sedimentary phosphorites are related to the theoretical fluorapatite: $Ca_{10}(PO_4)_6F_2$. Due to substitutions, especially of PO_4 by CO_3 , the chemistry is actually more complex:



Other notable substitutions include: SO_4 , SiO_4 , or H_4O_4 for PO_4 ; H_2O , OH or Cl for F; and Sr, U, Th, or rare earths for Ca.

Altschuler et al. (1958) made a detailed examination of evidence supporting two modes of occurrence of uranium within the apatite mineral. The first mode involves the substitution of U^{+4} for Ca^{+2} within the apatite structure. They suggested four major lines of support for this lattice replacement:

1. U and Ca contents are parallel through sections of leached and altered phosphorite.
2. Ionic radii of Ca^{+2} (0.99A) and U^{+4} (0.97A) are comparable.
3. Uranium in apatite has a cosmopolitan, rather than a provincial nature. This was demonstrated by the petrographic fluorescence analysis of phosphate, as well as by chemical and nuclear emulsion analyses.
4. Uranium minerals are generally scarce in phosphatic sediments.

The second mode involves the adsorption onto the crystal surface of U^{+6} as $(\text{UO}_2)^{+2}$, which is too large to replace Ca^{+2} within the lattice.

According to Altschuler et al. (1958) both U^{+4} and U^{+6} occur as primary constituents of the apatite. U^{+4} is the dominant form, although it oxidizes easily to the U^{+6} form in weathered phosphate deposits, thereby increasing the relative abundance of hexavalent uranium in some phosphorites.

Through "regenerative capture" the marine apatite removes "the small amounts of U^{+4} produced in sea water by the reduction of $(\text{UO}_2)^{+2}$ [and] causes more U^{+4} to be produced for its own uptake... it thus interferes with the attainment of equilibrium while fixing an unusual quantity

of U^{+4} (Altschuler et al., 1958, p. 45). According to Gony (1971), this uptake of uranium by phosphate is limited mainly by the significance of substitution of $(PO_4)^{-3}$ and Ca^{+2} by $(CO_3)^{-2}$ and Na^+ .

Thus, the ultimate quantity of primary uranium in a given depositional environment, as pointed out by Slansky (1977), is a function of:

1. the minute amount of uranium initially present in the sea water [1 to 2 ppb, according to Altschuler, et al. (1958); approximately 3 ppb, according to Ku, et al. (1977)];
2. the amount of organic matter accumulation;
3. the abundance of particulate surface area available; and
4. the rate and duration of actual phosphate sedimentation [which is in turn a function of structural limitations, physicochemical conditions and regional tectonic influences (Riggs, 1979b, 1980, 1981)].

The effect of these limiting factors upon the concentration of primary uranium is such that levels in unmodified marine apatite seldom exceed 300 ppm (Cathcart, 1978).

According to Altschuler, et al. (1958), secondary concentration or removal of uranium in phosphate sediments can also be quite significant. They described a number of

the uraniferous phosphorites in the southeast Atlantic Coastal Plain (Fig. 1; Table 1) which have been affected by secondary processes. Postdepositional enrichment of uranium in residual phosphates characterizes the Central Tennessee District phosphates. Uranium enrichment by ground water has influenced phosphate deposits in South Carolina. Enrichment in the Bone Valley aluminum phosphate mineral grains has resulted from extreme lateritic weathering processes. More moderate weathering has produced surficial enrichment in South Carolina's Cooper Marl.

GEOLOGY OF THE PUNGO RIVER FORMATION

The Miocene Pungo River Formation is a sedimentary phosphorite which underlies the northeastern half of the Atlantic Coastal Plain in North Carolina (Figure 2), and forms part of a southeast dipping sedimentary sequence. According to Miller (1971) the unit increases in thickness from its feather-edged western limit to over 35 meters in eastern Beaufort County, beneath 12 to 70 meters of overburden. The extremely fossiliferous, unconsolidated, interbedded sands and clays of the Pliocene Yorktown Formation unconformably overlie the phosphorite. The phosphorite is unconformably underlain by sandy and fossiliferous moldic carbonates of pre-Miocene age.

Brown (1958) first noted the occurrence of a phosphorite unit in Beaufort County in water well cuttings. He recognized the unit as Miocene on the basis of a foraminiferal correlation with the Middle Miocene Calvert Formation in Maryland. Kimrey (1964) named this unit the Pungo River Formation, and later described the unit and its distribution (Kimrey, 1965). Gibson (1967) subdivided the section at the Lee Creek Mine into zones, based upon lithology and microfossils. Rooney and Kerr (1967) identified the phosphate at the Texasgulf mine as a carbonate fluorapatite ($\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6\text{F}_{2-3}$). Regional stratigraphic evaluations of the unit have been made by Riggs (1967), Miller (1971) and Brown et al. (1972). A suite of papers is presently in press which synthesizes the regional structural, stratigraphic, petrologic, seismic and paleontologic aspects of the Pungo River Formation within the Aurora Embayment and off the North Carolina coast in Onslow Bay (Riggs et al., in press; Scarborough et al., in press; Katrosh and Snyder, in press; Lewis et al., in press; Snyder, S.W. et al., in press; Snyder, S.W.P. et al., in press).

a. Structural-Stratigraphic Framework

Variations in the volume and P_2O_5 content of a given district's resources are linked to the relative position of

the individual district within the regional structural and stratigraphic framework (Riggs, 1979b, 1980, 1981). In North Carolina (Figure 2), maximum development of the phosphates occurred during the Miocene in the southwestern portion of the Aurora Embayment (Riggs, et al., in press; Scarborough et al., in press), which is separated from the equivalent stratigraphic sequence in the Chesapeake Bay region to the north by the Norfolk Arch (Gibson, 1967). The Aurora Embayment is bounded on the south by the Cape Lookout High (Snyder, S.W.P., et al., in press), a pre-Miocene positive topographic structure upon which the Pungo River sediments thin to approximately 15 meters. The depositional basin is outlined on the west by a north-south trending structural hingeline (Brown, et al., 1972), which defines the updip erosional truncation of the phosphorite. The Chowan Arch, an east-west trending structure, marks the northern limit of the basin.

Scarborough (1981) has identified seven major lithologic units within the Pungo River Formation: units A, B, C, D, BB, CC, and DD (Figure 3). He recognized three regional facies among these units in the southwestern Aurora Embayment. The central facies is characterized by the following well defined phosphorite units: A, a dolomitic, muddy phosphorite quartz sand; B, a muddy phosphorite quartz sand with a dolomitic cap rock; and C, a quartz

CENTRAL FACIES: COMPOSITE SECTION AURORA EMBAYMENT			SOUTHERN FACIES:			EASTERN FACIES:		
UNIT	THICKNESS	LITHOLOGY	UNIT	THICKNESS	LITHOLOGY	UNIT	THICKNESS	LITHOLOGY
P U N G O R I V E R F M	D/ DD	0-7m White, slightly phosphatic and quartz sandy, calcareous, bioclastic shell hash (barnacles, bryozoans) with <20% calcite mud Yellowish-green, slightly phosphatic and quartz sandy, dolosilty bioclastic shell hash (bryozoans, barnacles, annelid tubes) to shelly dolomite muds			ABSENT	D	0-7m	Yellowish-green, slightly phosphatic and quartz sandy, dolosilty bioclastic shell hash (bryozoans, barnacles, annelid tubes) to shelly dolomite muds
	C	0-9m 0-5m Cream colored, nonindurated to indurated, fossiliferous and moldic, phosphatic and quartz sandy calcareous mud or limestone interbeds which decrease downward Interbedded, very dark greenish gray, slightly shelly, quartz phosphorite sand which becomes more massive downward 0-6m Very dark greenish gray, massive, burrowed to mottled, moderately muddy quartz phosphorite sand with minor shell material	CC	0-17m	White to light gray to light olive green, calcareous silty muds to very shelly, calcareous muddy, sometimes gravelly, slightly phosphatic (<10%) quartz sands	BB	0-11m	Light grayish-green, slightly calcareous, slightly phosphatic and quartz sandy, diatomaceous mud; diatom fragments compose up to 70% of the sediment
	B	0-12m 0-7m Light olive green, indurated to semi-indurated, highly burrowed and locally silicified, slightly fossiliferous and moldic, phosphatic and quartz sandy dolomite mud Moderate olive green, burrowed to mottled, dolomite muddy, phosphorite quartz sand Dark olive green, massive and mottled, muddy phosphorite quartz sand which is locally gravelly (phosphorite granules) near base				B	0-12m	Dark green, gravelly (phosphorite granules), muddy, phosphorite quartz sand
	A	0-6m 0-1m 0-5m Light olive green, indurated to nonindurated, highly burrowed and locally silicified, slightly fossiliferous and moldic, phosphatic and quartz sandy dolomite mud Moderate olive green, burrowed to mottled, dolomitic, muddy phosphorite quartz sand which is locally gravelly (phosphorite and quartz gravels) near base				A		?

Figure 3. Summary description and correlation of major lithologies (after Scarborough, 1981)

phosphorite sand with a calcareous cap rock. These three units are overlain by unit DD, a bioclastic hash in a calcite matrix. Unit D, a bioclastic hash in a dolosilt matrix, occurs in place of unit DD in the Aurora Area. The eastern facies is distinguished by the presence of unit BB, a slightly phosphatic and quartz-bearing diatomaceous mud. This 11 meter thick unit is the downdip equivalent of units B and C. Also present in the eastern facies is the dolomitic unit D. The southern facies is associated with the "shoaling environment" of the Cape Lookout High. Units D and DD are absent in the southern facies; units A, B, and C grade into unit CC, a slightly phosphatic, calcareous, shelly quartz sand.

b. Petrology

Sedimentary phosphate grains have been classed by Riggs (1979a) into four basic groups on the basis of their petrology. These are the intraclastic, pelletal, oolitic, and skeletal grain types (see Figure 4). Figure 5 shows grains typical of those used in this thesis.

Scarborough (1981) has examined phosphate grain types as they occur in the Pungo River Formation. He stated that phosphate intraclasts (Fig. 5a) are the dominant grain type within the formation. Granule size intraclasts are usually dark brown to black; those of sand size are usually light

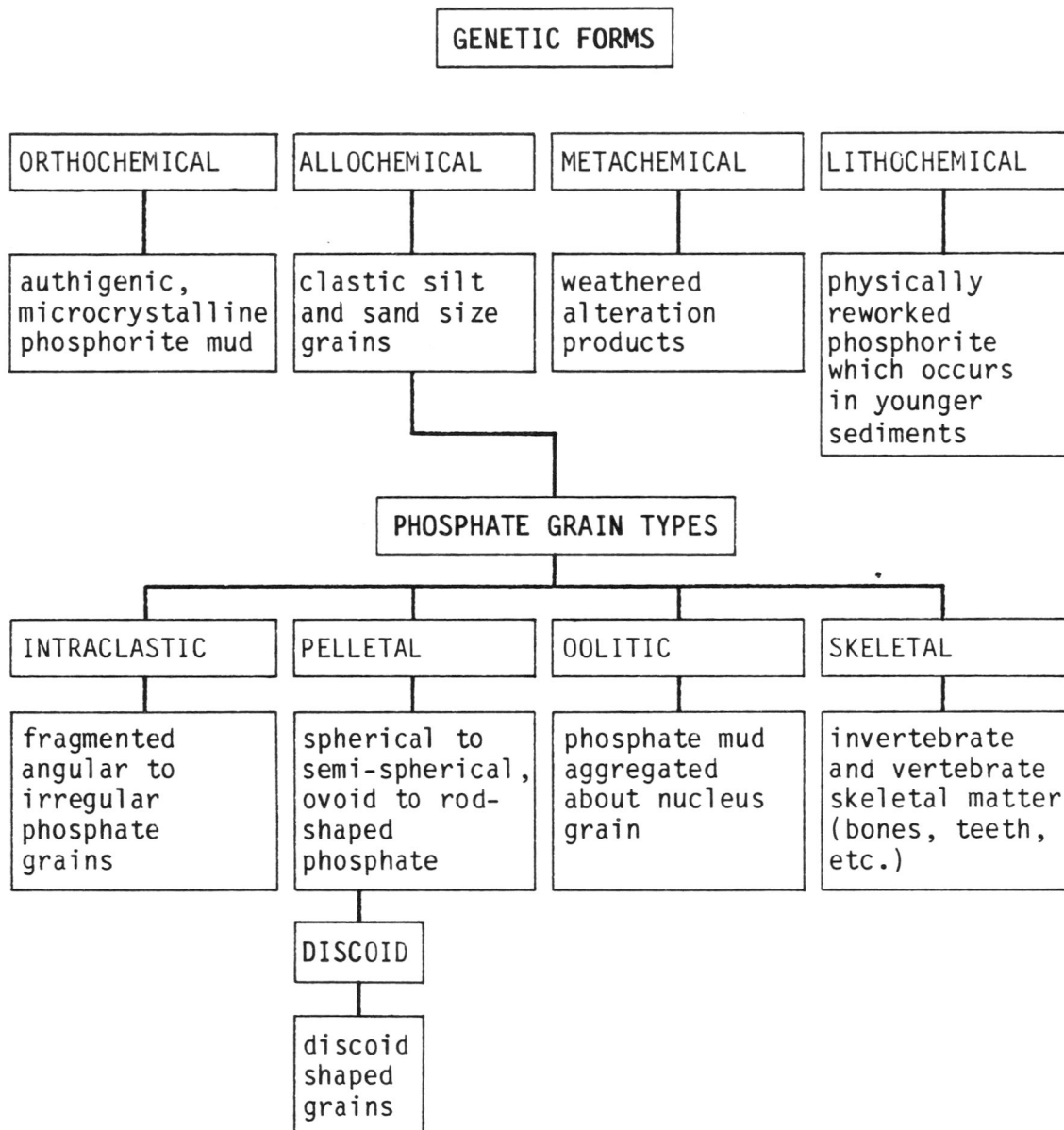


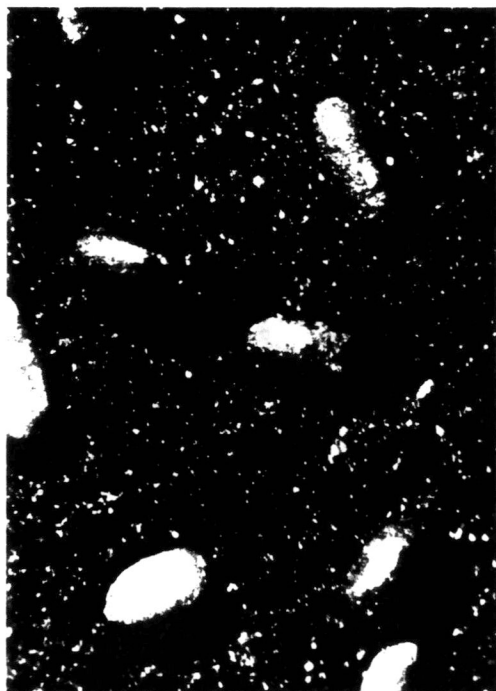
FIGURE 4. Forms of occurrence of macroscopic phosphorites (adapted from Riggs, 1979a)



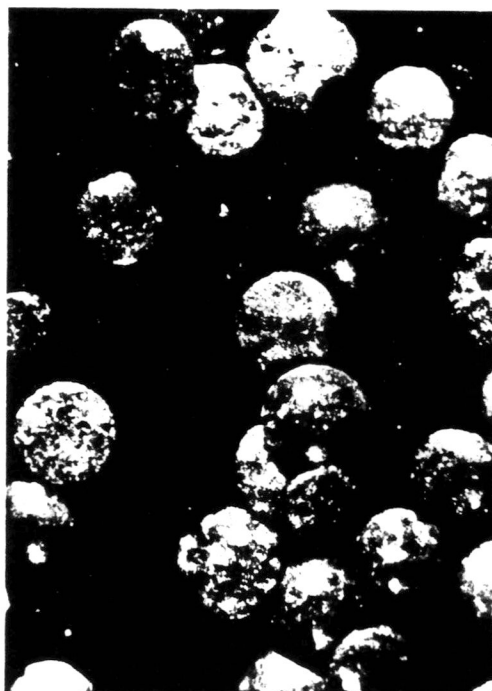
a. Intraclasts 0.5 mm



b. Skeletal fragments 0.5 mm



c. Pellets 0.5 mm



d. Discs 0.5 mm

Figure 5. Typical phosphate grains

to dark brown. Abundant phosphate pellets (Fig. 5c) distinguish the very fine to fine sand size fraction of unit A. Pellets within the formation are moderate to dark brown in color. Phosphatic skeletal fragments (Fig. 5b) are plentiful within the formation and phosphate discs (Fig. 5d) are also present. The overall proportion of phosphate grains to terrigenous or carbonate sediments according to Scarborough (1981), is the highest in the mid-slope region within the central facies. He suggested that the relative volume of phosphate sediments decreases updip to the west of the mid-slope. A decrease in the volume of phosphatic sediments also reflects the downdip transition from the central facies to the southern and eastern facies.

Scarborough (1981) defines four significant sedimentological trends with respect to the Pungo River Formation:

1. The phosphate content of the total sediment increases upsection from unit A through unit C.
2. Mean grain size decreases from unit A through unit C (a "fining upward" trend).
3. The phosphate content of the total sediment increases from the southern embayment margin to the Aurora Area (central facies).

4. Periods of increased carbonate sedimentation and decreased phosphate deposition separate successive phosphorite units in the Aurora Area (central facies).

Interpretation of the Pungo River lithologies by Scarborough (1981) suggests the following depositional scenario. Marine transgression first led to the accumulation of units A, B, and C. Phosphogenic conditions prevailed throughout most of this transgression; intermittent carbonate sedimentation, non-deposition, and perhaps erosion also took place. Deposition of the unit C phosphorite, the unit BB diatomite, and the unit CC quartz sands marked the maximum transgression. Subsequent regression produced units D and DD. Finally, erosion caused truncation of Pungo River sediments across the western and southern margins of the Aurora Embayment. As a result of this truncation, the Pungo River sediments appear to represent a regressive (offlap) episode; however, he concluded on the basis of the lithologic interpretation that the phosphate units of the formation actually indicate a predominantly transgressive sequence.

c. Uranium as a Phosphorite Component

The estimated composite P_2O_5 content for the entire vertical section (units A through D/DD) of the Pungo River

Formation is from 2 to 12+%, according to Fountain and Hayes (1979). They reported 8.8 to 18.5% P_2O_5 in the "middle member" [interpreted to be the unit B phosphorite] currently being mined in the Aurora area. Average concentrations have been variously reported as 10.3% P_2O_5 for the entire Pungo River section (Gibson, 1967); and 13.9% P_2O_5 (Fountain and Hayes, 1979) or 15.3% P_2O_5 (Redeker, 1966) for the [unit B] phosphorite ore of Texasgulf, Inc. Sand size grains (concentrate) make up 90-95% of the phosphate in the beneficiated product; only a small fraction of the total available P_2O_5 is discarded in mud and clay wastes.

The uranium concentration of the [unit B] phosphorite ore has been estimated at 20-40 ppm U (Fountain and Hayes, 1979). Cathcart (1978) has indicated an average content of 60 ppm U, with a range of 40-110 ppm U for the North Carolina phosphate concentrate. Average contents of 70 ppm U for the beneficiated product have recently been reported for two analyses by the Tennessee Valley Authority (TVA, 1979). According to Fountain and Hayes (1979) the Texasgulf phosphoric acid product has a concentration of 80 ug/ml U_3O_8 (or approximately 60 ppm U for the beneficiated product); the clay waste has a concentration of 17 ppm U_3O_8 (based on one sample). Altschuler (1980) cited a 65 ppm U content for "pelletal phosphorites" from the Pungo River

Formation. This uranium value was based on the chemical analysis of two samples which were "concentrates from prospecting composites of the entire mined zone in two areas" (Altschuler, 1980). Estimates of the uraniumiferous resources of the Aurora phosphate district are summarized in Table 5.

d. U/P₂O₅ Relationships

Although there have been a number of reports citing P₂O₅ contents and even U contents for the Pungo River Formation, there have been virtually no attempts to relate the two chemical components to one another in terms of petrologic, stratigraphic, and regional structural controls. Rooney and Kerr (1967) did distinguish between phosphate grains in the Aurora Area on the basis of color. Their "dark" grains were dark green to black in color, hard, and polished. Their "light" grains were brown to white in color, soft, and somewhat dull (pitted). The results of chemical analyses performed on samples of their "light" and "dark" grains indicated concentrations of: 1) 28.65% P₂O₅ and 0.0002% U₃O₈ (1.7 ppm U) for "dark" grains; and 2) 30.97% P₂O₅ and 0.0002% U₃O₈ (1.7 ppm U) for "light" grains. These values seem to indicate variation in phosphorus content. The uranium concentrations suggest uniformity, but at a level much lower than reported by Cathcart (1978), Fountain and Hayes (1979) and the TVA

 Phosphate

Total Phosphate Resource	71,761 x 10 ⁶ tons
Typical P ₂ O ₅ Content of Phosphorite	8-18%
Total Potential Phosphate Product ¹	20,876 x 10 ⁶ tons
Excluded Phosphate Resource ²	19,902 x 10 ⁶ tons
Potentially Mineable Phosphate Resource	51,859 x 10 ⁶ tons
Potentially Mineable Phosphate Product ¹	15,086 x 10 ⁶ tons
Estimated Recoverable Phosphate Product ³	9,429 x 10 ⁶ tons
Typical P ₂ O ₅ Content of Phosphate Product	29-32%

Uranium

Average Uranium Content of Phosphorite	30 ppm
Uranium in Total Phosphate Resource	2,153,000 tons
Uranium in Potentially Mineable Phosphate Resource	1,556,000 tons
Average Uranium Content of Phosphate Product	60 ppm
Estimated Recoverable Uranium ⁴	566,000 tons

¹Includes 100 percent of in-place phosphate pebble (+14 mesh) and phosphate sand (-14 to 200 mesh) of the phosphorite.

²Excluded phosphate resource includes that underlying municipalities, principal roads, areas of high population density, large lakes, and other environmentally sensitive areas.

³A district-wide average recovery factor of 62.5 percent has been applied to the "Potentially Mineable Phosphate Product" to determine this estimated recoverable phosphate product.

⁴The total uranium contained in the estimated recoverable phosphate product.

Table 5. Uraniferous phosphate resources of the Aurora Phosphate District (Fountain and Hayes, 1979)

(1979). It may be significant that the distinction between light and dark grains which formed the basis for the Rooney and Kerr analysis has not been substantiated by the detailed petrologic work of Scarborough (1981).

Tobiassen (1981) recently completed a trace element analysis of "whole rock" and grain type (skeletal fragment, intraclast, and pellet) subsamples obtained from sediment samples of units A, B, and C in a single core from the Aurora Area. He distinguished between light and dark grains, after the manner of Rooney and Kerr (1967), in the selection of his samples. Tobiassen measured phosphorus by spectrophotometry and uranium by alpha spectrometry. His analysis of three sediment samples indicated 1) 6.78% P_2O_5 and 18.2 ppm U for unit A; 2) 13.04% P_2O_5 and 23.4 ppm U for unit B; and 3) 19.21% P_2O_5 and 45.0 ppm U for unit C. He concluded that both phosphorus and uranium content increase upsection from unit A to unit C. Tobiassen's analysis of eleven subsamples (separated by grain type and color) indicated that 1) phosphorus content ranged from 28.15 to 31.49% P_2O_5 ; 2) uranium content ranged from 44.3 to 63.3 ppm U; 3) the skeletal fragments contained slightly higher concentrations of U and P_2O_5 ; 4) the intraclast and pellet subsamples were not consistently different from each other; and 5) the light and dark subsamples were not consistently different from each other.

PROCEDURES

SAMPLING

The samples analyzed in this study were obtained from five cores from the central facies (Scarborough, 1981) of the Pungo River Formation (Fig. 2). Four of these cores (BTN-9, BTN-11, PON-3, and PON-2) were drilled by the International Minerals and Chemical Corporation (IMC) in 1966. The fifth core (TGC) was drilled by Texasgulf, Inc. in the active mine area in 1979. These five cores are in storage at the Department of Geology, East Carolina University. The lithostratigraphic framework set up by Scarborough (1981) provided the basis for sample selection in this study. He included core holes BTN-11, BTN-9 and PON-3 in his petrologic and lithostratigraphic study of the Pungo River Formation. He also evaluated the petrology and lithostratigraphy of the remaining two cores used in this study (holes PON-2 and TGC), although they were not included in his report (Scarborough, pers. comm., 1980).

Samples were selected from at least three distinct stratigraphic positions (i.e. from units A, B, C, D or DD or the Pungo River Formation) within each of the five drill holes. Comparison samples of the Yorktown overburden sediments were also used in three cores.

The 0 ϕ (-2.0 mm, +1.0 mm), 2 ϕ (-0.52 mm, +0.25 mm), and 4 ϕ (-0.13 mm, +0.063 mm) grain size fractions of each core sample were provided by Scarborough. Each of these fractions was examined through a binocular microscope. A subsample of the skeletal, intraclast, pellet, or disc grains was hand picked if the type comprised at least 5% by volume of the size fraction being examined. Where possible, 1 to 2 mg subsamples of each grain type were hand picked from the 0 ϕ and 2 ϕ size fractions. Samples of this quantity were estimated by trial and error to contain adequate concentrations for the uranium analytical procedures. Composite subsamples of phosphate grains were picked from the 4 ϕ grain size fraction. Each size/type subsample was then photographed and stored in a labelled grain-mount microscope slide prior to chemical analysis.

Subsamples were labelled using a name having three parts (separated by slashes). The first part consisted of the letters and numbers from the original drillers log, locating the particular sediment sample by core hole and depth. The second part of the name represented the grain size of the subsample; either 0 ϕ , 2 ϕ or 4 ϕ . The third part of the name identified the grain type of the subsamples of the 0 ϕ and 2 ϕ grain sizes. The four grain categories that were used were abbreviated by the letter "C" (intraclast),

"S" (skeletal fragment), "P" (pellet), or "D" (disc). The subsample of intraclasts in the 2 ϕ size range from sample 7 of hole BTN-11 would be identified, using this scheme, as BTN 11-7/2 ϕ /C.

A total of 154 subsamples were examined for this study. They were obtained from 19 sediment samples representing units A, B, C, and D/DD of the Pungo River Formation and from 3 sediment samples representing the Yorktown Formation.

FLUOROMETRIC DETERMINATION OF URANIUM

a. Summary of Method

Low level uranium concentrations in geological samples have been determined fluorometrically for over thirty years. The method is based on the measurement of the fluorescence of a fused tablet (of mixed fluoride flux and uranium compound) exposed to ultraviolet light. The uranium concentration is proportional to the fluorescence intensity; sample fluorescence is compared to that of known standards. Two primary variations of this method are currently in use: 1) the "direct" method; and 2) the "extraction" method. They are so named because of differences in sample preparation.

Price et al. (1953), in a comprehensive review of fluorometric technique, proposed the direct method as the

solution to interference problems in uranium analysis. Certain ions were shown to quench or enhance the fluorescence of a fused uranium-fluoride tablet. These authors pointed out that interference effects could be reduced or eliminated by diluting the sample and withdrawing extremely small aliquots for analysis. They found that the effect of sample impurities was a function of their concentration in the fused flux tablet; the proportion of impurities to uranium in the tablet was not a factor.

The range of concentrations tested by Price et al. (1953) was from 0.0001 to 10 ug U per flux tablet (0.3 g NaF). They reported a 21+% coefficient of variation in their analyses at the 0.0001 ug U (per flux tablet) level; this value incorporated variation in both the blanks and samples. For the 0.001 to 10 ug U (per flux tablet) range, they indicated a 5+% coefficient of variation.

The advantage of the direct method is that it eliminates time consuming chemical preparation of the samples. The two main problems associated with this (and other) fluorometric analyses are: 1) fluorescence ("noise") in the blanks; and 2) variation in the optical properties of the fused flux tablet. Sample spiking and tight control of the procedure can lessen the impact of these sources of error (Price et al., 1953).

The extraction method was developed by Grimaldi and Levine (1950). This technique involved the mixing of the sample digestate with aluminum nitrate. The "salted" uranium was then extracted into ethyl acetate. An aliquot of the extracted uranium was fused with a flux tablet for analysis.

Grimaldi et al. (1954) reviewed several techniques of uranium analysis, including direct and extraction fluorometry. They stated that with routine analysis using these methods, errors usually amounted to 8-15% of the uranium content being measured. "When errors occur, the results are generally low (Grimaldi et al., 1954)." In other words, the uranium fluorescence is generally quenched rather than enhanced.

Grimaldi and Guttag (1954) described a direct fluorometric method for measuring the uranium content of phosphate rock. They digested 150 mg of sample in 50 ml (18+82) HNO_3 , and fused a 0.6 ml aliquot (=1.8 mg of sample) with 3 g of flux. A 2 minute digestion was reported to give excellent dissolution.

In an effort to reduce interference and quenching errors, Centanni et al., (1956) employed a combination of sample dilution and extraction techniques. Previously, Price et al. (1953), had pipetted each aliquot of solution onto the fusion dish, evaporated the solution, and then

added the NaF flux tablet. However, Centanni et al. (1956) transferred each solution aliquot directly onto the flux tablet in the fusion dish prior to evaporation. In this revised method, the 0.4 g flux tablets consisted of a 98% NaF-2% LiF mixture. Fusion was accomplished by using a propane-air burner assembly monitored by a thermocouple to heat the flux tablets to 900°C for 2 minutes, then at 850°C for 1 minute. The fluorescence of the flux tablets was measured after a 30 minute cooling at room temperature. This cooling step allowed for an initial increase in the fluorescence intensity, after which the fluorescence was stable for about one hour. Centanni et al. (1956) analyzed solutions containing approximately 0.01 mg (10 ug) U₃O₈ per ml of 5% HNO₃. They reported a 0.7% coefficient of variation in their results.

A brief fluorometric analytical note by Jaroszeski and Gregg (1965) stressed the need for a "uniform" flux mixture having a low blank. They mixed the 98% NaF-2% LiF flux for 8 hours at 32 rpm using a modified Patterson-Kelley blender. Jaroszeski (pers. comm., 1980) pointed out that the NaF-LiF flux was generally accepted as superior to other mixtures. Their procedure involved pipetting the aliquot into the fusion dish, evaporating the liquid, and then adding the flux tablet. Samples were fused over a propane burner at 950°C for 1 minute after the flux was

completely melted. The fused tablets were cooled in a dessicator for 30 minutes prior to being analyzed.

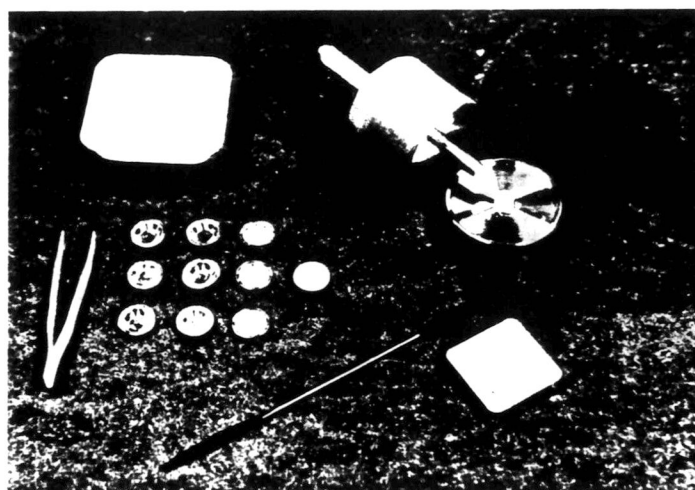
The ASTM (American Society for Testing and Materials, 1978) and the Bendix Field Engineering Corporation (Korte, pers. comm., 1980) use fluorometric routines derived from those mentioned above, particularly from that of Centanni et al. (1956).

The method used for uranium analysis in this thesis was based on the direct method of Price et al. (1953) as modified by ASTM (1978). Extensive testing of other techniques and variations proved the following adaptation to be the most effective.

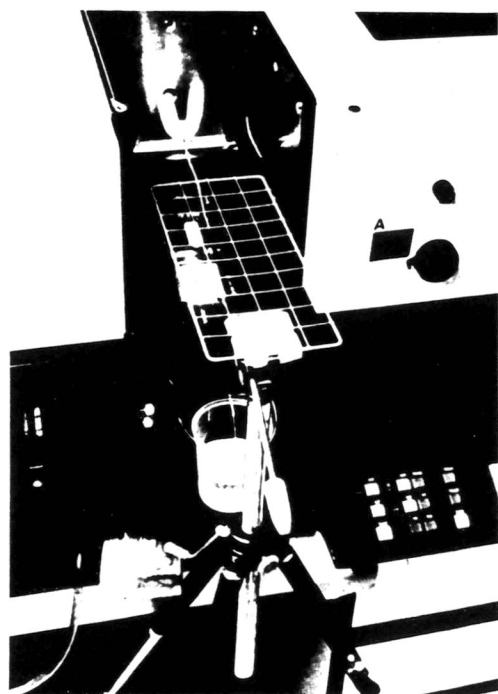
b. Apparatus

Air/acetylene burner (Figure 6b). The torch assembly in an atomic absorption spectrometer was chosen as the heat source because of its controlled flame, protection from drafts, and proximity to a ventilation hood.

Fluorometer (Figure 6c). Turner Model 111 equipped with a Uranium Pellet Holder Door, 7-60 optical filter (primary, 360 nm), and 2A-12 optical filter (secondary, above 510 nm), measured uranium fluorescence in the flux tablets.



a. Flux tablet maker



b. Tablet fusion



c. Fluorometer

Figure 6. Apparatus for uranium analysis

Glasses (didymium). These facilitated observation of molten flux.

Platinum fusion dishes (Figure 6a). Ten dishes were made to order by Engelhard Industries Division, Iselin, NJ to the specifications of the Turner 110-804 Uranium Fusion Dish. The interior diameter of each dish was 14 mm at the top and 9 mm at the bottom. Each dish was 3 mm deep, and had a 0.5 g flux capacity. Dishes were cleaned with 20% HNO_3 wash acid and rinsed thoroughly after every use.

Tablet maker (Figure 6a). This simple press was made to order locally for compatibility with platinum fusion dishes. The base was machined from a 15 mm section of 63 mm diameter stainless steel rod. The top was machined from a 50 mm section of 57 mm diameter aluminum rod. The top was compatible with a 2 mm deep recess machined into the base. A 9 mm diameter hole through the center of the aluminum top accepted a 130 mm long stainless steel plunger.

c. Reagents

Flux Mixture. 98% by weight reagent grade sodium fluoride (NaF) and 2% by weight reagent grade

lithium fluoride (LiF) were tumbled for 48 hrs at 20 rpm on a modified tube rotator to ensure homogeneity.

Nitric Acid. 18 volumes of double distilled concentrated nitric acid (HNO_3) were mixed with 82 volumes of water.

Water. Deionized distilled water was used throughout.

d. Uranium Standard

Primary. Alfa product number 88115, AAS Standard Solution had a concentration of 1000 ug U/ml at 20⁰C when packaged by Alfa Products, Danvers, MA.

Secondary. A 0.5 ml portion of the 1000 U/ml stock solution was pipetted into a 50 ml volumetric flask, and diluted to mark with nitric acid. This made a 10 ug U/ml solution.

e. Working Standards

0.01, 0.05, 0.1, and 0.2 ml volumes of the 10 ug U/ml solution were pipetted into 10 ml volumetric flasks, and diluted to mark with nitric acid. These made 0.01, 0.05, 0.1 and 0.2 ug U/ml solutions, respectively.

f. Control Samples

A control sample of either National Bureau of Standards (NBS) Standard Reference Material 120b or Association of Florida Phosphate Chemists (AFPC) Standard Check Sample No. 20 was run in each set of 10 samples. One duplicate sample was also run in each of 3 consecutive sets of 10 samples. The order of analysis was thus (B = blank; S = sample; C = control; D = duplicate; and standards are indicated by concentration of U in ug/ml):

Position:	1	2	3	4	5	6	7	8	9	10
Set 1	B	.01	C	.05	S	S	S	S	S	D
Set 2	B	.10	C	.20	S	S	S	S	S	D
Set 3	B	.05	C	.20	S	S	S	S	S	D

g. Protocol

- Control samples and grain size/grain type subsamples were weighed, with an estimated error of ± 0.001 mg, on a Cahn Model 26 Electrobalance. Subsamples of 0 ϕ grain size were ground to a fine powder with a mortar and pestle prior to weighing; those of 2 ϕ and 4 ϕ size were weighed as grains. Weighed subsamples and control samples were placed into 16 x 150 mm glass culture tubes.
- Two ml of nitric acid were added and the solutions were then heated for 2 hours at 140 $^{\circ}$ C on a block digester. After cooling, the solutions were

brought back to volume with nitric acid and transferred to 14.5 x 45 mm (1 dram) stoppered glass vials.

3. A 0.4 g flux tablet was added to each of the 10 platinum fusion dishes. NOTE: The fusion dishes were cleaned, rinsed with water and dried under an infrared heating lamp before addition of flux tablets.
4. A 0.04 ml aliquot of nitric acid blank, standard, control, or sample solution was pipetted onto each flux tablet following the order of analysis previously set forth.
5. The solution aliquots were evaporated by placing the fusion dishes and flux tablets under the heating lamp for 5 minutes.
6. The flux tablets were fused using the air/acetylene burner in the following manner:
 - preheated, at a level 20 cm above flame head, for 15 seconds
 - heated, at a level 10 cm above flame head, for 15 seconds
 - heated at melting point, predetermined by trial and error to be at a level 5 cm above flame head, for 15 seconds

- heated above melting point, at a level 3 cm above flame head, until the flux had completely melted (average time = 1 min. 15 sec.), then the sample was heated for an additional 30 seconds to ensure thorough mixing
 - cooled at 5 cm level for 15 seconds
 - cooled at 10 cm level for 15 seconds
 - cooled at 20 cm level for 30 seconds
 - removed from burner and cooled on an asbestos pad for an additional 30 minutes
7. After cooling, the relative fluorescence of each tablet was measured with the fluorometer.

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS

a. Summary of Method

Phosphorus analysis in this study was by the single solution, phospho-molybdenum blue method as modified by Strickland and Parsons (1972). An aliquot of sample digestate was diluted and allowed to react with a mixed reagent. The absorbance of the resulting blue solution was measured at 885 nm.

b. Apparatus

Absorbance measurements were made using the Beckman Model 35 Spectrophotometer. Readings were recorded using the Beckman Model 39 printer.

c. Reagents

Ammonium molybdate solution. 15 g of ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (reagent grade) was dissolved in 500 ml deionized distilled water.

Ascorbic acid solution. 27 g of ascorbic acid was dissolved in 500 ml deionized distilled water.

Potassium antimonyl-tartrate solution. 0.34 g of potassium antimonyl-tartrate was dissolved in 250 ml deionized distilled water.

Sulfuric acid solution. 140 ml of sulfuric acid (reagent grade) was added to 900 ml of deionized distilled water.

Water. Deionized distilled water was used throughout.

d. Mixed Reagent

The reagents were mixed as follows:

5 parts potassium antimonyl-tartrate

10 parts ammonium molybdate

10 parts ascorbic acid

25 parts sulfuric acid

e. Phosphorus Standard

Spex Industries ICP Standard had a concentration of 1000 ug/ml phosphorus in 2% HNO₃. The standard was obtained from Spex Industries, Inc., Metuchen, NJ.

f. Working Standards

0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 ml volumes of the 1000 ug P/ml stock solution were pipetted into 25 ml volumetric flasks, and diluted to mark with water. These made 10, 20, 30, 40, 50, and 60 ug P/ml solutions, respectively.

g. Control Samples

Three control samples of either NBS 120b or AFPC No. 20 were run with each set of 30 samples. The order of analysis for sets of 40 tubes was: 1 water blank; 6 working standards; 3 control samples; and 30 samples. The instrument baseline was checked with water after every 10 analyses.

h. Protocol

1. A 0.02 ml aliquot of each control sample and sample digestate (g-2, Uranium Protocol) was pipetted into a test tube and diluted with 10 ml of water.

2. A 0.1 ml aliquot of each phosphorus working standard was pipetted into a test tube and diluted with 9.9 ml of water.
3. A 1.0 ml aliquot of mixed reagent was added to each tube and mixed by inversion immediately.
4. After a minimum 5 minute period of color development, the absorbance of each solution was measured at 885 nm, in a 1 cm cell. The cell was rinsed once with each new solution prior to filling.

CALCULATIONS

URANIUM ANALYSIS

a. Working Standards

A working (calibration) curve of fluorometer reading vs. concentration was prepared using the four standards and the blanks (Fig. 7). The correlation coefficient for 66 analyses of the standards and blanks (Table A-1) was 0.944. Uranium concentration (in ppm U) was determined for the samples and control samples as follows:

$$\text{ppm U} = \left(\text{conc from regression, } \frac{\text{ug U}}{\text{ml}} \right) \times \frac{2 \text{ ml (digest.)}}{(\text{wt. of sample, g})}$$

b. Control Samples

Recovery of the control samples (in %) was determined as follows:

$$\% \text{ recovery} = \frac{\text{ppm U (by calculation)}}{\text{ppm U (by certificate)}} \times 100$$

where NBS = 128.4 ppm U (by certificate)

and AFPC = 121 ppm U (by certificate)

A total of 18 NBS and 7 AFPC control samples were analyzed (Table A-2). The mean percent recovery of these 25

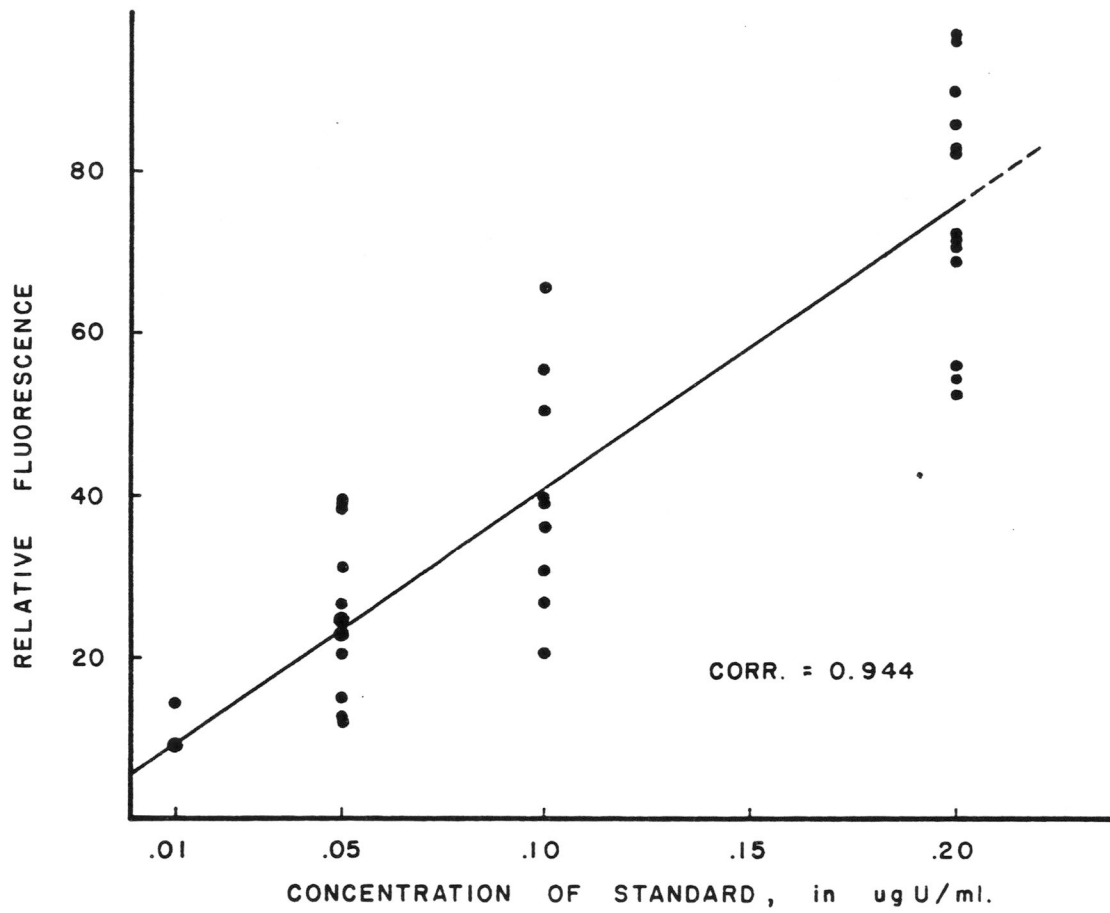


Figure 7. Uranium calibration curve

controls was $81.9 \pm 32.5\%$. All samples were corrected by a factor of 1.22 based on this recovery.

The effect of initial sample size on the percent recovery of uranium was analyzed by linear regression. The correlation coefficient for mass vs. percent recovery was -0.063 for the 25 control samples, indicating no significant mass effects for the 1 to 4 mg range which was tested.

c. Duplicate Samples

Seven duplicate samples (Table A-3) were run through the fluxing and fluorometric procedures. A ± 18.1 ppm pooled estimate of sample variance (Crow et al., 1960) was determined for these seven sets.

PHOSPHORUS ANALYSIS

a. Working Standards

A working (calibration) curve of solution absorbance vs. concentration was prepared from the six concentration standards and the blanks (Fig. 8). The correlation coefficient for 35 standards and blanks (Table A-4) was 1.000. Phosphorus concentration (in % P_2O_5) was determined for the samples and control samples as follows:

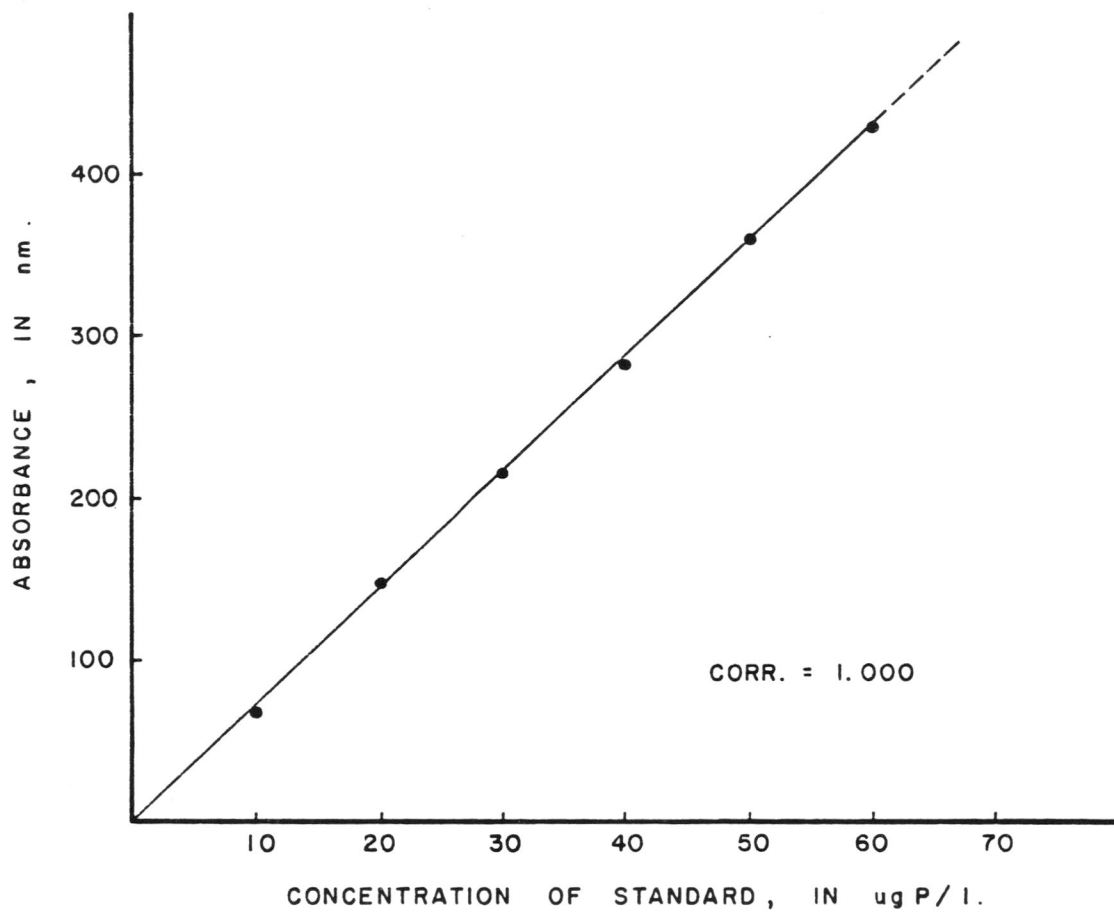


Figure 8. Phosphorus calibration curve

$$\% P_2O_5 = \frac{(\text{conc from regression, ugP/ml})}{(\text{weight of sample, mg})} \times \text{Factor, where}$$

$$\begin{aligned} \text{Factor} &= \frac{2 \text{ ml (digestate)}}{0.02 \text{ ml (aliquot)}} \times 10 \text{ (dilution factor)} \\ &\times \frac{141.9 \text{ g P}_2\text{O}_5}{61.9 \text{ g P}} \times \frac{1}{1000} \\ &= 2.292 \end{aligned}$$

b. Control Samples

Recovery of the control samples (in %) was determined as follows:

$$\% \text{ recovery} = \frac{\% P_2O_5 \text{ (by calculation)}}{\% P_2O_5 \text{ (by certificate)}} \times 100, \text{ where}$$

NBS = 34.57% P_2O_5 (by certificate), and

AFPC = 32.93 % P_2O_5 (by certificate)

A total of 16 NBS and 6 AFPC control samples were analyzed (Table A-5). The mean percent recovery of these 22 controls was $78.2 \pm 4.6\%$, a value consistent with the recovery of uranium. All samples were corrected by a factor of 1.28 based on this recovery.

The effect of initial sample size on the percent recovery was analyzed by linear regression. The correlation coefficient for mass vs. percent recovery was -0.353 for the 22 control samples, indicating no significant mass effects for the 1 to 4 mg range.

RESULTS

A total of 154 phosphate subsamples obtained from 22 sediment samples representing the five core locations shown in Figure 2 were examined in this study. Table 6 summarizes the results of the uranium and phosphorus determinations for the 134 subsamples which were analyzed. Uranium was measured in 110 subsamples; phosphorus was measured in all 134 subsamples.

Uranium contents ranged from 5.1 ppm U in subsample BTN 11-9/0 ϕ /skel. to 285.9 ppm U in subsample BTN 11-7/4 ϕ . The mean uranium content for 110 samples was 92.5 ± 27.4 ppm U. Tables 7 and 8 summarize the mean uranium contents for all samples when grouped by unit vs. grain size and core hole vs. grain size, respectively. Tables 11 and 12 summarize the mean uranium contents for all samples when grouped by unit vs. grain type and core hole vs. grain type, respectively.

Phosphorus contents ranged from 23.25% P_2O_5 in subsample PON 3-11/4 ϕ to 38.22% P_2O_5 in subsample PON 2-10/2 ϕ /pellet. The mean phosphorus content for 134 samples was $30.64 \pm 0.84\%$ P_2O_5 . Tables 9 and 10 summarize the mean phosphorus contents for all samples when grouped by unit vs. grain size and core hole vs. grain size, respectively. Tables 13 and 14 summarize the mean

Core	Strat.	0 ϕ Size						2 ϕ Size						4 ϕ Size														
		C (intraclast)			S (skeletal)			C (intraclast)			S (skeletal)			P (pellet)			D (disc)			(composite)								
		mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅	mass	U	P ₂ O ₅			
(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)	(mg)	(ppm)	(%)		
BTN 9																												
9.10	Yorktown	2.664	60.6	28.80	3.298	100.6	34.09	4.010	108.0	31.91	3.017	132.9	35.91	2.323	112.5	32.16	1.169	104.8	32.34	0.698	---	31.06	0.698	---	31.06	0.698	---	31.06
9.11	DD	---	---	---	---	---	---	7.552	54.1	29.97	1.144	56.1	31.15	0.140	---	31.65	0.473	---	28.47	0.657	18.3	26.74	0.657	18.3	26.74	0.657	18.3	26.74
9.14	C	1.251	76.3	30.46	2.321	75.6	31.98	3.843	42.9	30.12	3.609	78.8	32.97	1.799	56.9	31.00	1.423	---	33.70	2.656	88.3	32.90	2.656	88.3	32.90	2.656	88.3	32.90
9.16	B	2.803	51.4	30.15	2.830	50.9	31.16	1.494	166.2	31.28	2.179	69.3	43.63	0.259	---	31.38	1.414	50.3	32.17	0.137	---	32.35	0.137	---	32.35	0.137	---	32.35
9.18	A	6.012	69.1	27.38	3.211	64.4	36.16	2.330	142.4	29.92	2.048	66.4	31.43	---	---	---	---	---	---	0.158	76.1	28.04	0.158	76.1	28.04	0.158	76.1	28.04
BTN 11																												
11.7	C	3.326	55.1	31.09	3.020	138.6	30.29	5.625	71.3	30.79	3.328	125.0	33.20	0.487	24.7	33.55	---	---	---	0.115	285.9	34.96	0.115	285.9	34.96	0.115	285.9	34.96
11.9	B	3.135	44.9	29.58	2.354	5.1	32.24	6.873	67.3	29.73	5.364	94.9	33.36	---	---	---	4.905	51.3	33.80	---	---	---	---	---	---	---	---	---
11.10	B	5.524	89.8	28.98	4.737	116.2	31.79	6.509	---	28.57	6.679	---	31.06	---	---	---	3.233	47.3	32.49	0.322	58.9	26.52	0.322	58.9	26.52	0.322	58.9	26.52
11.13	A	2.199	84.5	26.48	3.087	92.8	33.63	1.796	47.3	29.90	3.994	108.3	31.96	---	---	---	---	---	---	0.189	---	29.96	0.189	---	29.96	0.189	---	29.96
PON 3																												
2.10	Yorktown	3.624	92.5	27.39	---	---	---	2.255	67.0	29.64	1.276	145.6	35.97	0.326	---	33.75	1.111	104.7	32.44	0.824	162.2	24.81	0.824	162.2	24.81	0.824	162.2	24.81
3.11	DD	---	---	---	---	---	---	0.731	78.3	30.22	0.818	108.2	32.02	0.301	16.9	31.10	0.391	---	28.13	0.067	179.5	23.25	0.067	179.5	23.25	0.067	179.5	23.25
3.15	C	3.006	14.4	24.42	2.061	117.1	32.63	6.439	55.1	32.62	2.794	21.7	32.44	---	---	---	1.087	---	32.40	1.458	79.8	32.89	1.458	79.8	32.89	1.458	79.8	32.89
3.16	B	5.001	10.7	29.37	6.734	54.4	23.39	2.895	160.6	30.75	4.026	101.4	33.53	1.722	67.5	31.43	1.038	---	28.40	0.653	---	27.53	0.653	---	27.53	0.653	---	27.53
3.17	A	3.526	65.5	26.52	2.092	45.6	35.49	4.383	129.6	30.81	5.045	100.2	31.48	1.029	---	30.24	0.518	9.8	29.96	0.460	116.8	30.17	0.460	116.8	30.17	0.460	116.8	30.17
PON 2																												
2.10	Yorktown	3.032	68.1	28.53	3.876	99.9	31.76	2.422	88.2	31.33	3.564	114.5	30.97	0.030	---	38.22	0.362	62.0	31.52	0.390	173.9	27.63	0.390	173.9	27.63	0.390	173.9	27.63
2.12	?	2.466	56.1	30.52	1.523	94.6	32.30	3.418	58.4	32.17	2.236	31.8	33.39	---	---	---	---	---	---	0.173	---	30.36	0.173	---	30.36	0.173	---	30.36
2.16	B	3.280	57.3	26.01	2.140	41.3	30.66	2.209	41.6	29.14	1.906	126.6	32.38	0.303	108.5	29.54	1.012	121.8	27.92	0.554	46.8	32.46	0.554	46.8	32.46	0.554	46.8	32.46
2.17	A	3.233	19.8	27.66	1.847	63.0	30.41	2.764	113.7	30.42	2.031	112.0	31.29	0.930	27.9	31.70	0.982	---	28.44	0.2793	---	29.10	0.2793	---	29.10	0.2793	---	29.10
TGC																												
34.1	C	2.495	99.5	32.71	2.188	138.9	33.55	5.932	79.4	31.64	4.401	142.5	32.92	---	---	---	1.716	---	32.97	0.091	---	30.65	0.091	---	30.65	0.091	---	30.65
34.2	C	3.332	61.0	29.68	2.569	66.9	28.41	3.819	45.0	30.83	3.012	111.3	33.91	---	---	---	1.624	71.6	30.54	0.452	---	31.61	0.452	---	31.61	0.452	---	31.61
40.1	B	3.513	82.6	29.44	2.350	93.8	30.54	3.618	39.3	30.09	1.874	87.1	31.94	---	---	---	---	---	---	0.159	---	35.63	0.159	---	35.63	0.159	---	35.63
41.3	A	4.802	82.8	26.75	5.121	89.2	31.82	4.470	88.2	27.81	3.908	83.1	33.29	0.317	---	30.82	0.429	137.4	34.26	0.168	195.7	31.27	0.168	195.7	31.27	0.168	195.7	31.27

Table 6. Summary of sample mass, U content, and P O content, based on analysis of 134 samples from the Pungo River Formation, North Carolina

Unit	Grain Size						Summary	n
	0 ϕ	n	2 ϕ	n	4 ϕ	n		
Yorktown	84.3	5	104.0	10	168.1	2	118.8	5
D/DD	--	0	62.7	5	98.9	2	80.8	2
C	84.3	10	71.2	13	151.3	3	102.3	3
B	49.9	12	87.5	16	52.9	2	63.4	3
A	67.7	10	89.3	13	129.5	3	95.5	3
Summary	71.6	39	82.3	59	123.5	12		
		<u>Combined Mean</u>		<u>n</u>		<u>S.D.</u>		
		92.5		3		27.4		

Table 7. Summary of mean ppm U, by unit and grain size

Core Hole	Grain Size						Summary	n
	0 ϕ	n	2 ϕ	n	4 ϕ	n		
BTN 9	68.6	8	88.7	14	60.9	3	72.7	3
BTN 11	78.4	8	70.2	9	172.4	2	107.0	3
PON 3	57.2	7	83.3	14	134.6	4	91.7	3
PON 2	62.5	8	83.9	12	110.4	2	85.6	3
TGC	89.3	8	88.5	10	195.7	1	124.5	3
Summary	71.6	39	82.3	59	123.5	12		
		<u>Combined Mean</u>		<u>n</u>		<u>S.D.</u>		
		92.5		3		27.4		

Table 8. Summary of mean ppm U, by core hole and grain size

Unit	Grain Size						Summary	n
	0 ϕ	n	2 ϕ	n	4 ϕ	n		
Yorktown	30.11	5	33.01	12	27.83	3	30.32	3
D/DD	---	0	30.34	8	25.00	2	27.67	2
C	30.52	10	32.23	16	32.60	5	31.78	3
B	30.19	12	31.17	20	30.90	6	30.75	3
A	30.23	10	30.86	16	29.71	5	30.27	3
Summary	30.34	39	31.58	74	29.99	21		
		<u>Combined Mean</u>		<u>n</u>	<u>S.D.</u>			
		30.64		3	+0.84			

Table 9. Summary of mean % P_2O_5 , by unit and grain size

Core Hole	Grain Size						Summary	n
	0 ϕ	n	2 ϕ	n	4 ϕ	n		
BTN 9	31.27	8	31.79	18	30.22	5	31.09	3
BTN 11	30.51	8	31.67	11	30.48	3	30.89	3
PON 3	29.74	7	31.44	19	27.73	5	29.64	3
PON 2	29.73	8	31.31	14	29.89	4	30.31	3
TGC	30.36	8	31.75	12	32.29	4	31.47	3
Summary	30.34	39	31.58	74	29.99	21		
		<u>Combined Mean</u>		<u>n</u>	<u>S.D.</u>			
		30.64		3	+0.84			

Table 10. summary of mean % P_2O_5 , by core hole and grain size

Unit	0 ϕ		2 ϕ				4 ϕ	Summary
	C	S	C	S	P	D		
Yorktown	73.7	100.3	87.7	131.0	112.5	90.5	168.1	109.1
D/DD	--	--	66.2	82.2	16.9	--	98.9	66.1
C	61.3	107.4	58.7	95.9	40.8	71.6	151.3	83.9
B	56.1	60.3	95.0	95.7	88.0	67.7	52.9	73.7
A	64.3	71.0	104.2	93.0	27.9	73.6	129.5	80.5
Summary	62.1	81.5	83.0	96.1	59.3	76.1	123.5	

Table 11. Summary of mean ppm U, by unit and grain type

Core Hole	0 ϕ		2 ϕ				4 ϕ	Summary
	C	S	C	S	P	D		
BTN 9	64.4	72.9	102.7	80.7	84.7	77.6	60.9	77.7
BTN 11	68.6	88.2	62.0	109.4	24.7	49.3	172.4	82.1
PON 3	45.8	72.4	98.1	95.4	42.2	57.3	134.6	80.0
PON 2	50.3	74.7	75.5	96.2	68.2	91.9	110.4	81.0
TGC	81.5	97.2	63.0	106.1	--	104.5	195.7	108.0
Summary	62.1	81.5	83.0	96.1	59.3	76.1	123.5	

Table 12. Summary of mean ppm U, by core hole and grain type

Unit	0 ϕ		2 ϕ				4 ϕ	Summary
	C	S	C	S	P	D		
Yorktown	28.24	32.93	30.96	34.28	34.71	32.10	27.83	31.58
D/DD	--	--	30.10	31.59	31.38	28.30	25.00	29.27
C	29.67	31.37	31.20	33.09	32.28	32.40	32.60	31.80
B	28.92	31.46	29.93	32.80	30.78	30.96	30.90	30.82
A	26.96	33.50	29.77	31.89	30.92	30.89	29.71	30.52
Summary	28.60	32.17	30.44	32.78	32.04	31.17	29.99	

Table 13. Summary of mean % P_2O_5 , by unit and grain type

Core Hole	0 ϕ		2 ϕ				4 ϕ	Summary
	C	S	C	S	P	D		
BTN 9	29.20	33.35	30.64	33.22	31.55	31.67	30.22	31.41
BTN 11	29.03	31.99	29.75	32.40	33.55	33.15	30.48	31.48
PON 3	26.93	33.50	30.81	33.09	31.63	30.27	27.73	30.57
PON 2	28.18	31.28	30.77	31.98	33.15	29.29	29.89	30.65
TGC	29.65	31.08	30.09	33.02	30.82	32.59	32.29	31.36
Summary	28.60	32.17	30.44	32.78	32.04	31.17	29.99	

Table 14. Summary of % P_2O_5 , by core hole and grain type

phosphorus contents for all samples when grouped by unit vs. grain type and core hole vs. grain type, respectively.

A variety of statistical procedures were applied to the data using the SAS computer system (Helwig and Council, 1979) which is centered at the SAS Institute, Inc., Box 10066, Raleigh, NC 27605. The GLM (General Linear Models) procedure carried out a multiple regression analysis. Uranium and phosphate concentrations within each grain size/grain type subgroup were modeled against each other. The uranium and phosphate concentrations of each size/type subgroup were modeled against those of the other grain size/grain type subgroups. The PLOT procedure generated scatter diagrams for visual inspection of each model. The CORR and RANK procedures listed in order from highest to lowest the correlation coefficient for uranium vs. phosphate concentration within each size/type subgroup, as well as those for uranium vs. uranium and phosphate vs. phosphate between all subgroups. The MEANS procedure tabulated simple univariate descriptive statistics for the entire data set.

DISCUSSION

Figure 9 is a scatter diagram relating P_2O_5 content to U content for 110 subsamples of the Pungo River Formation from the Aurora Embayment in the Central Coastal Plain of North Carolina. U/P_2O_5 ratios within this sample group exhibit an apparently random distribution. However, as Altschuler et al. (1958) have pointed out, "assemblies of [uranium-phosphorus] data from different parts of the same formation may represent a variety of different [physico-chemical conditions] and an average of such varied groups of data may have the effect of masking, rather than demonstrating, a universal relation." On the basis of this reasoning, the variance in the U/P_2O_5 values plotted in Figure 9 does not necessarily reflect a simple, homogeneous distribution of uranium and phosphorus throughout the formation.

Recent and ongoing studies of the Miocene Aurora Embayment and Onslow Bay phosphorites actually point to an increasingly complex geological scenario for the region. It follows that any valid interpretation of the U/P_2O_5 data (Tables 6-14) must be made in terms of the complexities characterizing the unit from which the data came. In an effort to "unmask" the potential relationships between uranium, phosphorus and the Pungo River phosphorite,

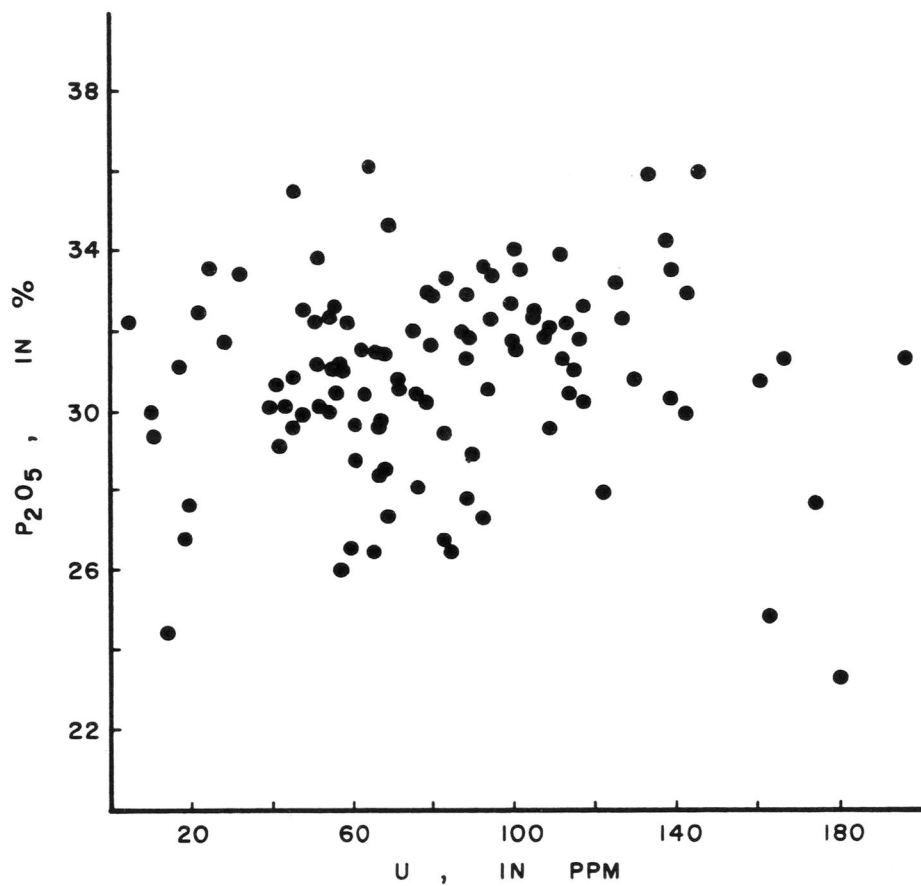


Figure 9. Scatter diagram of % P₂O₅ vs. ppm U, for all samples (excluding sample BTN 11-7/40)

interpretations have been made on the basis of the controls set forth in the Objectives.

1. Regional Location

Samples analyzed in this thesis were taken from five different core locations (Figure 2). Scatter diagrams relating P_2O_5 content to U content for samples from these cores are shown in Figure 10. Distinct differences in U/P_2O_5 values between the different cores would appear as tight clusters on such plots. Because of the high degree of variance in the data for each core, there is in fact no significant difference between the mean U/P_2O_5 values. This suggests that uranium and phosphorus are evenly distributed laterally within the central facies area of the Aurora Embayment.

2. Stratigraphic Position

Analyzing samples from different units of the Pungo River Formation in each core hole provided additional control. Figure 11 shows scatter diagrams of P_2O_5 vs. U, by stratigraphic unit (compare to Tables 6, 7 and 9). Although there is still a high degree of variance in the values when grouped in this manner, several observations can be made. Uranium and phosphorus concentrations in the Pliocene Yorktown phosphate grains tend to be slightly

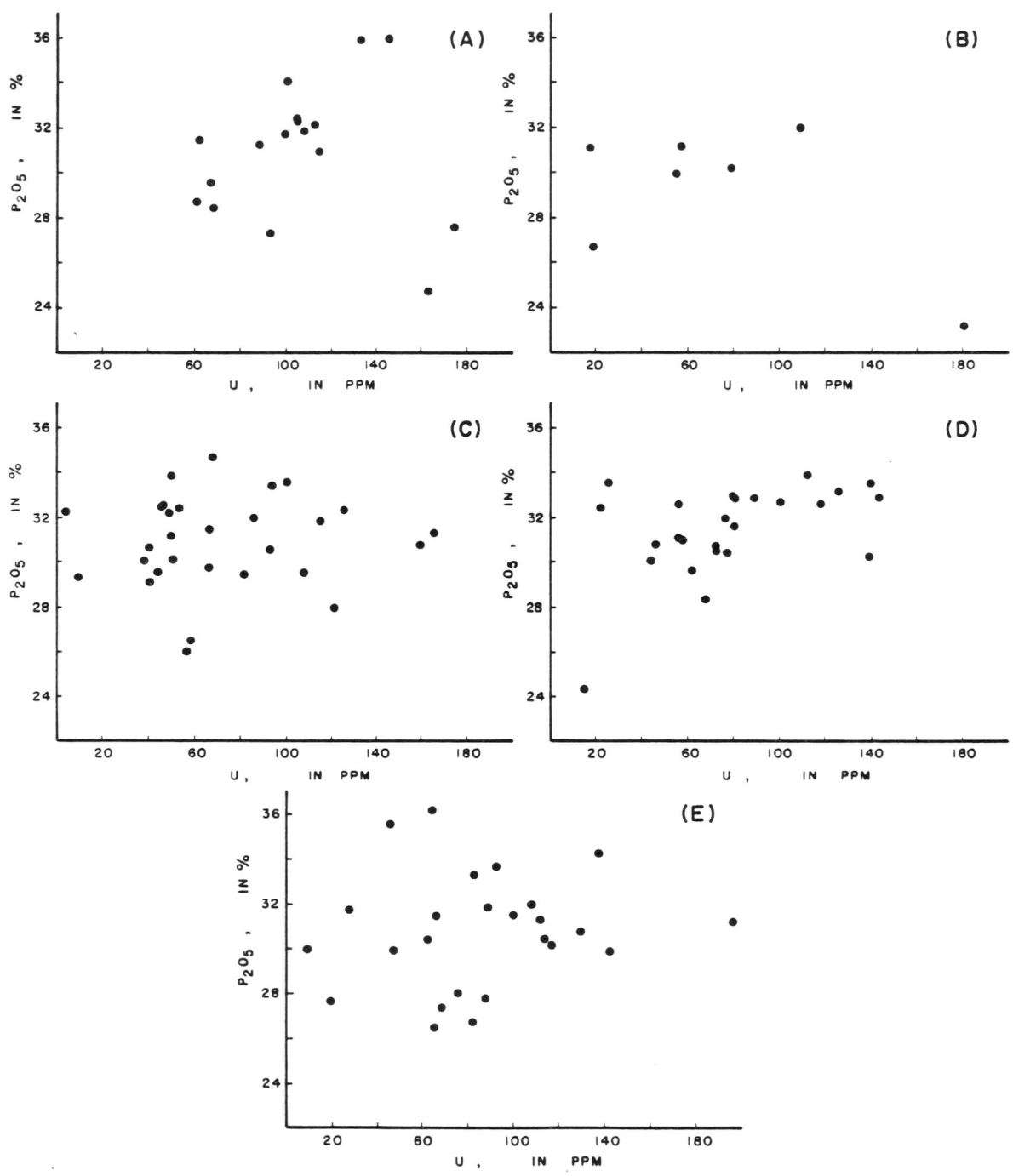


Figure 11. Scatter diagrams of % P_2O_5 vs. ppm U, by unit.
 A) Yorktown; B) unit D/DD; C) unit B; D) unit C;
 E) unit A

higher than those in the underlying carbonate unit D/DD. It is possible that the Miocene phosphate was enriched if it was reworked into the Yorktown. Sedimentary evidence contradicts this possibility. It is more likely that the minor relative enrichment reflects different phosphogenic conditions within the Yorktown. Bachelet et al. (1952) noted that carbonate tends to complex $(\text{UO}_2)^{+2}$ and make it more soluble; the generally low uranium content of unit D/DD may be a result of such a process. Because unit D/DD represents a non-phosphogenic regressive period distinctly different from the phosphogenic transgression that culminated with the deposition of unit C (Scarborough, 1981), one would expect to see lower phosphorus concentrations in unit D/DD. Since the $\text{U}/\text{P}_2\text{O}_5$ values for the phosphorite unit C also tend to be slightly higher than those of unit D/DD, it appears that the comparison of $\text{U}/\text{P}_2\text{O}_5$ values for units C, D/DD, and the Yorktown agrees with the lithostratigraphic distinctions made by Scarborough. The samples from units A, B and C do not exhibit any statistically significant differences or trends, due to the high degree of variance in their $\text{U}/\text{P}_2\text{O}_5$ values. The results presented here do not support the suggestion of Tobiassen (1981) that P_2O_5 content increases from unit A through unit C.

3. Grain Size

Figure 12 demonstrates the relationship of P_2O_5 vs. U by grain size for 110 samples. Examination of this scatter diagram in conjunction with Tables 6-10 suggests that grains of 2 ϕ size tend to have slightly higher uranium and phosphorus contents than the grains of 0 ϕ size. Grains of 4 ϕ size appear to have the highest uranium contents and the lowest phosphorus contents. These phosphorus values do not support the suggestion of Riggs (1979a) that the finest grain sizes have the highest P_2O_5 content (due to less included matter). These minor variations do not appear to be related to differences in regional and/or stratigraphic position. The large variance and low "n" values are such that tests of significance indicate that the grain size groups are statistically the same.

4. Grain Type

Due to the widely varying U and P_2O_5 concentrations within the grain type subsamples (Tables 6; 11-14), no statistically significant differences have been determined for grain types when grouped by unit or core hole. Comparison of the 0 ϕ intraclast to the 0 ϕ skeletal grain analytical values indicates that there is a slight tendency for skeletal grains to have higher P_2O_5 and U

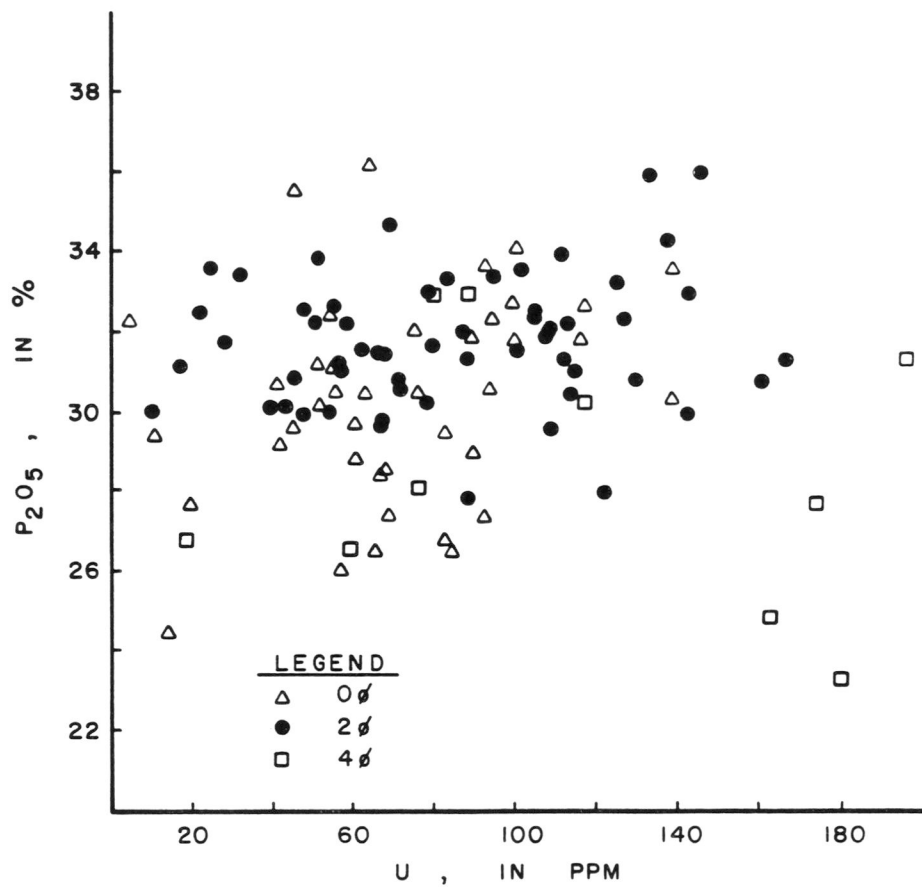


Figure 12. Scatter diagram of % P_2O_5 vs. ppm U, for all samples (excluding sample BTN 11-7/4φ), by grain size

concentrations. Skeletal grains in the 2 ϕ size range also appear to have a slightly higher average concentration of U and P₂O₅. This relative enrichment of skeletal grains has also been observed by Tobiassen (1981). The 0 ϕ intraclast and skeletal grains have a lower average P₂O₅ and U content than the corresponding grains in the 2 ϕ size range. Because of the general paucity of pellet and disc grain data, these two types are not very useful in making direct comparisons at this time.

CONCLUSIONS

Uranium and phosphorus contents have been determined by fluorometric and spectrophotometric methods for 134 selected phosphate grain samples from the Pungo River Formation. Interpretation of the results of these analyses allows for several observations. It must be stressed that the apparent differences which have been identified among the data groups are very slight, and that the differences exist within an overall context of extreme variance. When compared statistically the mean values of the particular subgroups are therefore essentially the same. In summary then,

1. Uranium contents ranged from 5.1 to 285.9 ppm U. Phosphorus contents ranged from 23.25 to 38.22 % P_2O_5 .
2. Based upon the evaluation of samples from five different core holes there appear to be no statistically significant lateral trends in the distribution of uranium and phosphorus in the central facies area of the Aurora Embayment.
3. Phosphate grains from units A, B, C, and D/DD do not exhibit any statistically significant or consistent stratigraphic trends with respect to their phosphorus and uranium contents. Grains from unit

D/DD may be slightly depleted in phosphorus and uranium relative to underlying and overlying sediments.

4. Although it is not statistically significant, there is an apparent inverse relationship between grain size and mean uranium content. The mean uranium content was 71.6 ppm U for the 0 ϕ size phosphate grains; 82.3 ppm U for 2 ϕ size grains; and 123.5 ppm U for 4 ϕ size grains.
5. The mean phosphorus and uranium contents of skeletal phosphate grains were slightly higher than those of the intraclast, pellet, and disc grains.

Further research at the grain level is recommended. It is possible that trends do exist in the distribution of uranium and phosphorus within the Pungo River Formation. The results presented here neither confirm nor deny the presence of such trends. Trace element studies of phosphate grains must be more tightly controlled with respect to the complexities of the phosphate environment. It is recommended that more expedient and precise analytical methods be used in conjunction with more comprehensive sampling schemes. In addition, studies of other trace elements in the phosphate grains may be of help in identifying and understanding not only the Pungo River Formation but also the phosphogenic system in general.

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APPENDIX A

PRECISION AND ACCURACY DETERMINATIONS

Table A-1. Fluorometer readings for uranium standards and blanks.

Table A-2. Summary of control sample recovery (U).

Table A-3. Summary of duplicate sample analyses.

Table A-4. Absorbance measurements for phosphorus standards and blanks.

Table A-5. Summary of control sample recovery

	Concentration of Standard, in ug U/ml						
	Blank	.01	.05	.10	.20		
Fluorometer Reading	5.0	14.5	21.0	21.0	56.5		
	n=23	9.5	23.5	40.0	97.0		
		9.5	12.5	31.0	55.0		
			23.5	27.0	53.0		
			26.0	51.0	73.0		
			23.5	66.0	76.0		
			31.5	56.0	83.5		
			39.5	36.5	86.5		
			13.0	39.5	97.5		
			39.0		90.5		
			27.0		69.5		
			25.0		83.0		
			15.5		71.5		
			25.0		72.0		
			31.5				
			25.0				
			40.0				
		Mean	5.0	11.2	26.0	40.9	76.0
		S.D.	0	2.9	8.4	14.5	14.6
		n	23	3	17	9	14

Table A-1. Fluorometer readings for uranium standards and blanks

Standard	Mass (mg)	Theory U (ppm)	Found U (ppm)	% Recovery
NBS 1206	0.812	128.4	148.8	115.9
	0.915		132.1	102.9
			29.4	22.9
			157.0	122.2
	2.032		88.9	69.2
	2.094		124.3	96.8
	2.130		71.4	55.6
	2.338		169.8	132.2
	2.358		73.0	56.8
			51.3	39.9
	2.385		67.4	52.5
			67.4	52.5
	2.518		72.9	56.7
			111.3	86.7
	3.372		98.3	76.6
	3.580		112.5	87.6
	3.674		119.7	93.2
	122.8	95.6		
AFPC #20	1.388	121.0	99.4	82.1
			177.3	146.5
	1.669		94.6	78.7
			144.0	119.0
			26.4	21.8
	3.435		123.8	102.3
	98.1	81.1		
Combined (n=25) Mean Recovery				81.9+32.3
Correction Factor				1.22
Correlation Coefficient, Mass vs. % Recovery = -0.063				

Table A-2. Summary of Control Sample Recovery (U)

Sample	Uranium Concentration, in ppm					
				n	Mean	S.D.
BTN 9-14/2 ϕ	54.4	87.1	94.8	3	78.8	<u>+21.5</u>
BTN 9-18/2 ϕ	67.0	43.2	89.0	3	66.4	<u>+22.9</u>
BTN 11-9/2 ϕ	63.9	62.4	75.6	3	67.3	<u>+ 7.2</u>
BTN 11-10/0 ϕ	77.7	102.8	89.0	3	89.8	<u>+12.6</u>
PON 3-15/2 ϕ	49.9	59.6	55.8	3	55.1	<u>+ 4.9</u>
PON 3-16/2 ϕ	155.4	178.2	148.2	3	160.6	<u>+15.7</u>
PON 2-16/0 ϕ	56.6	29.1	86.3	3	57.3	<u>+28.6</u>

Table A-3. Summary of duplicate sample analyses

	Concentration of Standard, in ug P/ml						
	Blank	10	20	30	40	50	60
	0	76	148	217	284	362	429
	1	78	148	216	284	360	431
	1	76	147	217	284	361	434
Absorbance, in nm	1	78	149	218	285	361	431
	3	76	149	217	285	365	435
Mean	1.2	76.8	148.2	217.0	284.4	361.8	432.0
S.D.	1.1	1.1	0.8	0.7	0.5	1.9	2.4
n	5	5	5	5	5	5	5

Table A-4. Absorbance measurements for phosphorus standards and blanks

Standard	Mass (mg)	Theory % P ₂ O ₅	Found % P ₂ O ₅	% Recovery
NBS 120b	3.580	34.57	25.83	74.7
	3.372		26.94	77.9
	2.094		27.28	78.9
	0.915		27.68	80.1
	2.338		28.28	81.8
	3.674		27.35	79.1
	4.293		26.93	77.9
	4.408		27.61	79.9
	5.146		28.13	81.4
	8.421		21.92	63.4
	3.934		28.14	81.4
	2.032		28.73	83.1
	2.518		29.30	84.8
	2.130		27.58	79.8
	2.385		26.24	75.9
2.358	27.36	79.1		
AFPC #20	1.388	32.93	22.88	69.5
	3.523		26.79	81.4
	1.669		25.57	77.6
	0.520		24.62	74.8
	3.435		26.62	80.8
	5.334		25.69	78.0
Combined Mean Recovery	(n=22)			78.2 _± 4.6
Correction Factor				1.28
Correlation Coefficient, Mass vs. % Recovery = -0.353				

Table A-5. Summary of control sample recovery (P)